(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 March 2023 (30.03.2023)

WIPO | PCT

(10) International Publication Number
WO 2023/049828 A1

(51) International Patent Classification:
C09K 11/06 (2006.01) *C08K 5/00* (2006.01)
C08K 5/55 (2006.01) *H01L 33/50* (2010.01)

(21) International Application Number:
PCT/US2022/076912

(22) International Filing Date:
23 September 2022 (23.09.2022)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/248,863 27 September 2021 (27.09.2021) US
63/278,944 12 November 2021 (12.11.2021) US

(71) Applicant: **NITTO DENKO CORPORATION** [US/US]; c/o Nitto Denko Technical Corporation, 501 Via Del Monte, Oceanside, California 92058 (US).

(72) Inventors: **ZHENG, Shijun**; 8390 Orange Haven Place, San Diego, California 92129 (US). **HAMMAKER, Jeffrey R.**; 7417 Keisha Terrace, San Diego, California 92126 (US). **DING, Xinliang**; 13567 Tiverton Rd, San Diego, California 92130 (US). **WANG, Peng**; 12062 Dapple Way, San Diego, California 92128 (US). **CAI, Jie**; 2325 Via Santos, Apt. T, Carlsbad, California 92008 (US). **LUU, Hiep**; 667 Edgewater Drive, San Marcos, California 92078 (US). **SAJOTO, Tissa**; 4824 Mesa Trail Pl., Carlsbad, California 92010 (US).

(74) Agent: **JOHNSON, Brent A.** et al.; 100 Spectrum Center Drive, Suite 1200, Irvine, California 92618 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: BORON-CONTAINING CYCLIC EMISSIVE COMPOUNDS AND COLOR CONVERSION FILM CONTAINING THE SAME

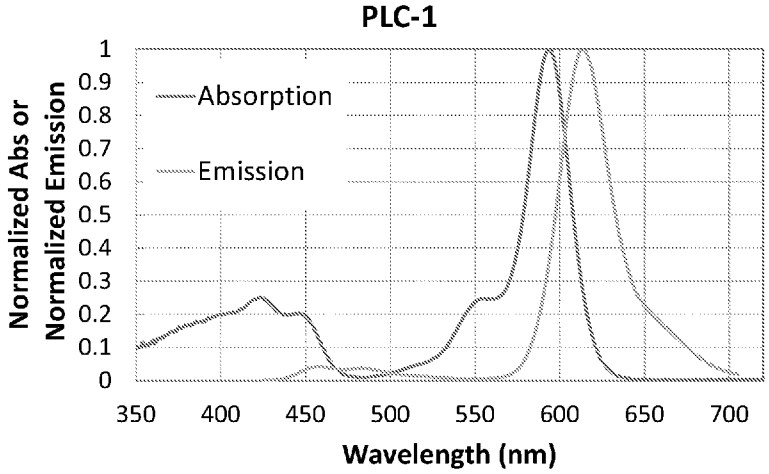


FIG. 1

(57) Abstract: The current disclosure relates to yeast cells that are genetically modified to reduce their propensity to degrade certain platform chemicals, such as acrylic acid, and to methods of preparing and using such yeast cells for the production of acrylic acid and other compounds.

[Continued on next page]

WO 2023/049828 A1

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

BORON-CONTAINING CYCLIC EMISSIVE COMPOUNDS AND COLOR CONVERSION FILM CONTAINING THE SAME

Inventors: Shijun Zheng, Jeffrey R. Hammaker, Xinliang Ding, Peng Wang, Jie Cai, Hiep Luu, and Tissa Sajoto

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application Nos. 63/248,863, filed September 27, 2021, and 63/278,944, filed November 12, 2021, both of which are incorporated by reference in their entirety.

BACKGROUND

Unless otherwise indicated in the present disclosure, the details described in the present disclosure are not prior art to the claims in the present application and are not admitted to be prior art by inclusion in this section.

In color reproduction the gamut, or color gamut, is a certain complete subset of colors available on a device such as a television or monitor. For example, Adobe™ Red Green Blue (RGB), a wide gamut color space achieved by using pure spectral primary colors, was developed to provide a broader color gamut and offer a more realistic representation of visible colors viewed through a display. It is believed that a device which could provide a wider gamut could enable the display to portray more vibrant colors.

As high-definition large screen displays become more common, the demand for higher performance, slimmer and highly functional displays have increased. Current light emitting diodes (LEDs) are obtained by a blue light source exciting a green phosphor, a red phosphor, or a yellow phosphor to obtain a white light source. However, the full width half maximum (FWHM) of the emission peak of the current green and red phosphors are quite large, usually greater than 40 nm, resulting in the green and red color spectrums overlapping and rendering colors that are not fully distinguishable from one another. This overlap leads to poor color rendition and the deterioration of the color gamut.

To correct the deterioration in the color gamut, methods have been developed using films containing quantum dots in combination with LEDs. However, quantum dots suffer from a variety of shortcomings including toxicity, low efficiency, expensive encapsulating processes and size uniformity.

Therefore, there exists a need for improving performance in color conversion films, backlight units, and display devices.

SUMMARY

Photoluminescent complexes described herein may be used to improve the contrast between distinguishable colors in televisions, computer monitors, smart devices, and any other device that utilize color displays. Photoluminescent complexes of the present disclosure include a color converting dye complex with good blue light absorbance and narrow emissions bandwidths, with the full width half maximum [FWHM] of emission band of less than 40 nm. In some embodiments, a photoluminescent complex absorbs light of a first wavelength and emits light of a second, longer wavelength than the first wavelength. The photoluminescent complexes disclosed herein can be utilized with a color conversion film for use in light emitting apparatuses. The color conversion film of the present disclosure reduced color deterioration by reducing overlap within the color spectrum, resulting in high quality color rendition.

Some embodiments include a photoluminescent complex, wherein the photoluminescent complex may comprise: a blue light absorbing naphthalimide derivative; a linker complex comprising an unsubstituted ester, substituted ester, unsubstituted ether, or substituted ether; and a ring-locked boron-dipyrromethene (BODIPY) moiety. In some embodiments, the linker complex may covalently link the naphthalimide derivative to the ring-locked BODIPY moiety. In many embodiments, the ring-locked BODIPY moiety absorbs the energy of a first excitation wavelength from the naphthalimide derivative and emits a light energy of a second higher wavelength. In various embodiments, the photoluminescent complex has an emission quantum yield greater than 80%.

In some embodiments, the photoluminescent complex can have an emission band with a full width half maximum [FWHM] of up to 40 nm.

In many embodiments, the photoluminescent complex can have a Stokes shift, the difference between the excitation peak of the blue light absorbing moiety and the emission peak of the BODIPY moiety, of equal to or greater than 45 nm.

Numerous embodiments include a color conversion film, wherein the color conversion film may comprise: a transparent substrate layer; a color conversion layer, wherein the color conversion layer includes a resin matrix; and at least one photoluminescent complex, as described herein, dispersed within the resin matrix. In some embodiments, the color

conversion film may have a thickness between 1 μm to about 200 μm. In many embodiments, the color conversion film of the present disclosure can absorb blue light in the 400 nm to about 480 nm range and emit light in the 510 nm to about 560 nm wavelength range. Another embodiment includes a color conversion film that can absorb blue light in the 400 nm to about 480 nm range and emit light in the 580 nm to about 670 nm wavelength range. In various embodiments, the color conversion film can further comprise a transparent substrate layer. In some embodiments, the transparent substrate layer may comprise of two opposing surfaces, wherein the color conversion layer is disposed on one of the opposing surfaces.

In some embodiments, the color conversion film may further comprise a singlet oxygen quencher. In some embodiments, the color conversion film may further comprise a radical scavenger.

Many embodiments include a method for preparing the color conversion film, the method comprising: dissolving a photoluminescent complex, as described herein, and a binder resin within a solvent; and applying the mixture on one of the opposing surfaces of the transparent substrate.

Some embodiments include a backlight unit including a color conversion film described herein.

Some embodiments include a display device including the backlight unit described herein.

The present application provides a photoluminescent complex having excellent color gamut and luminescent properties; a method for manufacturing color conversion films using photoluminescent complexes, and a backlight unit including the color conversion film. These and other embodiments are described in greater detail below.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph depicting the absorption and emission spectra of one embodiment of a photoluminescent complex (PLC-1).

FIG. 2 is a graph depicting the absorption and emission spectra of one embodiment of a photoluminescent complex (PLC-2).

FIG. 3 is a graph depicting the absorption and emission spectra of one embodiment of a photoluminescent complex (PLC-3).

DETAILED DESCRIPTION

The current disclosure is related to photoluminescent complexes for use in color conversion films, backlight units, and display devices including the same. The photoluminescent complex may be used to improve and enhance the transmission of one or more desired emissive bandwidths within a color conversion film. In some embodiments, the photoluminescent complex can both enhance the transmission of a desired first emissive bandwidth and decrease the transmission of a second emissive bandwidth. In some embodiments, the present disclosure describes a photoluminescent complex that can enhance the contrast or intensity between two colors, increasing their distinction from one another.

In some embodiments, boron-dipyrromethene (BODIPY) compounds are used as the emissive materials to replace the use of quantum dots. BODIPY complexes may have a narrow FWHM, high fluorescent efficiency, stability to both moisture and oxygen, and low production cost. Current BODPY strategies have some shortcomings, such as low absorption of blue LED light, e.g., 450 nm, resulting in inefficient conversion of blue LED light to green and red light, and broad FWHM when used in color converting films. In some embodiments, the BODIPY compounds disclosed herein overcome these limitations.

As used herein, when a compound or chemical structure is referred to as being "substituted", the compound or structure may include one or more substituents. A substituted group is derived from the unsubstituted parent structure wherein one or more hydrogen atoms on the parent structure have been independently replaced by one or more substituent groups. In some embodiments, the substituent groups may independently be F, Cl, Br, I, $C_{0-7}H_{1-15}O_{1-2}N_{0-2}$, $C_{0-7}H_{1-15}O_{0-2}N_{1-2}$, optionally substituted alkyl (including unsubstituted alkyl, such as methyl, ethyl, C_3 alkyl, C_4 alkyl, etc., fluoroalkyl, e.g. CF_3, etc.), alkenyl, or a C_{3-7} heteroalkyl.

The term "alkyl" group as used herein refers to a hydrocarbon group that is free of double or triple carbon-carbon bonds, and includes linear, branched, or cyclic alkyl.

An "alkene" moiety refers to a group that has at least one carbon-carbon double bond (-C=C-), and includes linear, branched, or cyclic alkene moieties.

An "alkyne" moiety refers to a group that has at least one carbon-carbon triple bond (-C≡C-), and includes linear, branched, or cyclic alkyne moieties.

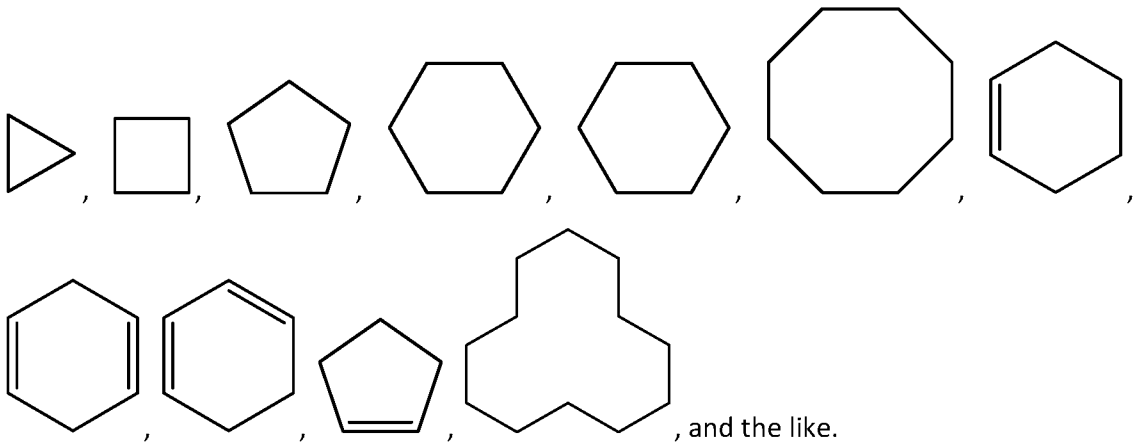
In some embodiments, the alkyl moiety may have 1 to 6 carbon atoms (whether it appears herein, a numerical range such as "1 to 6" refers to each integer in the given range: e.g., "1 to 6 carbon atoms" meaning that the alkyl group may have 1 carbon atom, 2 carbon atoms, 3 carbon atoms, etc., up to and including 6 carbon atoms, although the present definition also covers the occurrence of the term "alkyl" where no numerical range is designated. The alkyl group of the compound designated herein may be designated as "C_{1-6} alkyl" or similar designations. By way of example only, a "C_{1-6} alkyl" indicates that there are 1 to 6 carbon atoms in the alkyl chain, i.e., the alkyl chain is methyl, ethyl, propyl, isopropyl, n-butyl, iso-butyl, sec-butyl, or t-butyl, etc. Thus, C_{1-6} alkyl includes, for example, C_{1-2} alkyl, C_{3-4} alkyl, C_{4-5} alkyl, or C_{5-6} alkyl. Alkyl groups can be substituted or unsubstituted. Typical alkyl groups include, but are in no way limited to: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl, pentyl, hexyl, ethenyl, propenyl, butenyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and the like.

Typical alkene groups include, but are not limited to, ethenyl, propenyl, butenyl, etc.

The term "heteroalkyl" as used herein refers to an alkyl group, as defined herein, in which one or more of the constituent carbon and/or hydrogen atoms have been replaced by a nitrogen, oxygen, or sulfur. Examples include, but are not limited to, $-CH_2-O-CH_3$, $-CH_2-CH_2-O-CH_3$, $-CH_2-N(CH_3)-CH_3$, $-CH_2-CH_2-NH-CH_3$, $-CH_2-CH_2-N(CH_3)-CH_3$, $-CH_2-S-CH_2-CH_3$, $-CH_2-NH-O-CH_3$, etc.

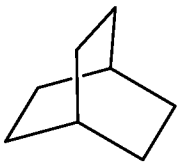
The term "aromatic" refers to a planar ring having a delocalized π-electron system containing $4n+2$ π electrons, where n is an integer. Aromatic rings can be formed from five, six, seven, eight, nine, or more than nine atoms. Aromatic rings can be optionally substituted. The term "aromatic" includes both carbocyclic aryl (e.g., phenyl) and heterocyclic aryl (or "heteroaryl" or "heteroaromatic") group (e.g., pyridine). The term includes monocyclic or fused-ring polycyclic (i.e., rings which share adjacent pairs of carbon atoms) groups.

The term "hydrocarbon ring" refers to a monocyclic or polycyclic ring system that contains only carbon and hydrogen and may be saturated. Monocyclic carbon rings include groups having from 3 to 12 carbon atoms. Illustrative examples of monocyclic groups include the following moieties:

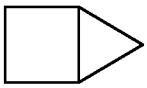


, and the like.

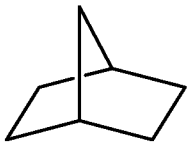
Illustrative examples of polycyclic groups include the following moieties:

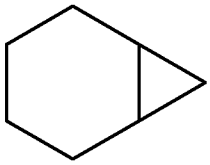


[bicyclooctane],

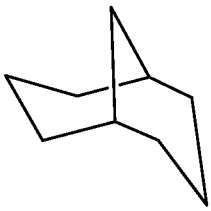


[bicyclopentane],



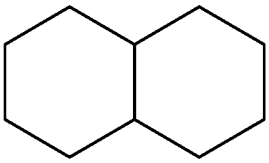


[bicycloheptane],

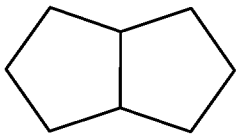


[bicycloheptane],

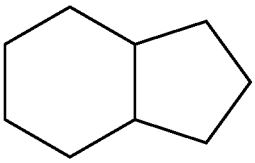
[bicyclodecane],



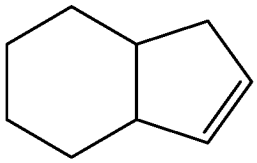
[decahydronaphthalene],



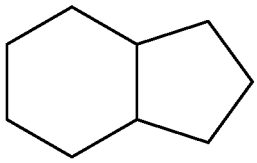
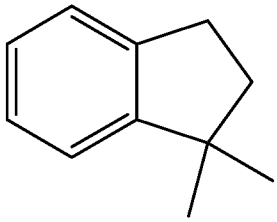
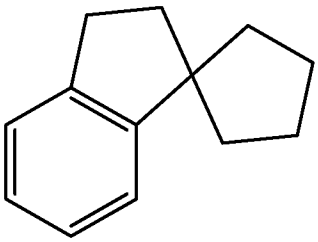
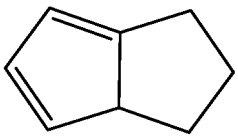
[octahydropentalene],



[octahydroindene],



[hexahydroindene],


[1,2,3,4-tetrahydronaphthalene],

[2,3-dihydro-1*H*-indene],

[2',3'-dihydrospiro[cyclopentane-1,1'-indene], or

[1,2,3,3a-tetrahydropentalene].

The term "aryl" as used herein means an aromatic ring wherein each of the atoms forming the ring is a carbon atom. Aryl rings can be formed by five, six, seven, eight, or more than eight carbon atoms. Aryl groups can be substituted or unsubstituted. Examples of aryl groups include, but are not limited to, phenyl, naphthalenyl, phenanthrenyl, etc.

The term "heteroaryl" refers to an aryl group that includes one or more ring heteroatoms selected from nitrogen, oxygen, sulfur, or a combination thereof, wherein the heteroaryl group has from 4 to 10 atoms in its ring system and with the proviso that the ring of the group does not contain two adjacent nitrogen, oxygen or sulfur atoms. It is understood that the heteroaryl ring can have additional heteroatoms in the ring. In heteroaryls that have two or more heteroatoms, those two or more heteroatoms can be the same or different from one another. Heteroaryls can be optionally substituted. An N-containing heteroaryl moiety refers to an aryl group in which at least one of the skeletal atoms of the ring is a nitrogen atom. Illustrative examples of heteroaryl groups include the following moieties: pyrrole, imidazole, etc.

The term "halogen" as used herein means fluorine, chlorine, bromine, and iodine.

The term "bond", "bonded", "direct bond" or "single bond" as used herein means a chemical bond between two atoms.

The term "moiety" as used herein refers to a specific segment or functional group of a molecule. Chemical moieties are often recognized chemical entities embedded in or appended to a molecule.

The term "cyano" or "nitrile" as used herein refers to any organic compound that contains a -CN functional group.

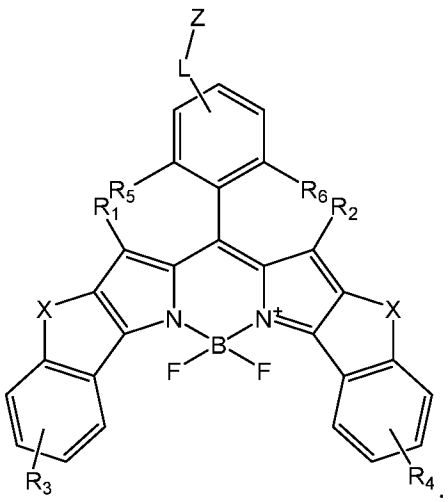
The term "ester" refers to a chemical moiety with the formula -COOR, where R is alkyl, cycloalkyl, aryl, heteroaryl (bonded through a ring carbon) or heterocyclic (bonded through a ring carbon). Any hydroxy, or carboxyl side chain on the compounds described herein can be esterified. The procedures and specific groups to make such ester may be any suitable method and can readily be found in reference sources.

As used herein the term "ether" refers to a chemical moiety that contains an oxygen atom connected to two alkyl or aryl groups with the general formula of R-O-R', where the term alkyl and aryl is as defined herein.

As used herein the term "ketone" refers to the chemical moiety that contains a carbonyl group (a carbon-oxygen double bond) connected to two alkyl or aryl groups with the general formula of RC(=O)R', wherein the terms alkyl and aryl are defined herein.

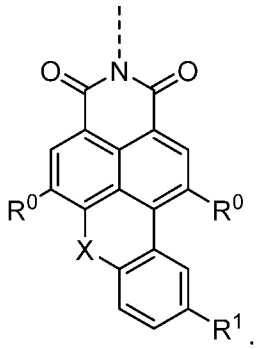
As used herein the term "ring-locked" refers to a chemical structure wherein one or more series of atoms in a compound are connected to form a ring. Rings may vary in size from three to many atoms (e.g., aromatic, carbocyclic rings).

The term "BODIPY" as used herein, refers to a chemical moiety with the formula:



The BODIPY may be composed of dipyrromethene complexed with a di-substituted boron atom, typically a BF_2 unit. The IUPAC name for the BODIPY is 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene.

The term "naphthalimide" or "naphthalimide derivative" as used herein, refers to a chemical moiety with the formula:



.

The present disclosure related to photoluminescent complexes that absorb light energy of first wavelength and emit light energy in a second higher wavelength. The photoluminescent complex of the present disclosure comprises an absorbing luminescent moiety and an emitting luminescent moiety that are coupled through a linker such that their distance is adjusted for the absorbing luminescent moiety to transfer its energy to the acceptor luminescent moiety, wherein the acceptor luminescent moiety then emits out at a second wavelength that is larger than the absorbing first wavelength.

Some embodiments include a photoluminescent complex. In some examples, the complex comprises: a blue light absorbing donor chromophore, wherein the donor chromophore comprises a naphthalimide derivative; a linker complex; and a ring-locked boron-dipyrromethene (BODIPY) moiety. In some embodiments, the linker complex can covalently link the naphthalimide derivative to the ring-locked BODIPY moiety. In some examples, the naphthalimide derivative absorbs light of a first excitation wavelength and transfers energy to the ring-locked BODIPY moiety, wherein the ring-locked BODIPY moiety then emits a light energy of a second wavelength. It is believed that energy transfer from the excited naphthalimide derivative to the ring-locked BODIPY moiety occurs through a Förster resonance energy transfer (FRET). This belief is due to the absorbance/emission spectra of the photoluminescent complexes where there are two major absorption bands, one at the blue light absorption band (naphthalimide derivative) and one at the ring-locked BODIPY

absorption band, and only one emission band located at the BODIPY moiety's emission wavelength (see **FIGs. 1** and **2**).

In one embodiment, the photoluminescent complex can have a high emission quantum yield. In some embodiments, the emission quantum yield can be greater than 50%, 60%, 70%, 80%, and/or 90%. In many embodiments, the emission quantum yield can be greater than 50%, or 55%, or 60%, or 65%, or 70%, or 75%, or 80%, or 85%, or 90%, or 95%. Emission quantum yield can be measured by dividing the number of photons emitted by the number of photons absorbed, which is equivalent to the emission efficiency of the luminescent moiety. In various embodiments, the absorbing luminescent moiety may have an emission quantum yield greater than 80%. In some embodiments, the quantum yield can be greater than 0.8 (80%), 0.81 (81%), 0.82 (82%), 0.83 (83%), 0.84 (84%), 0.85 (85%), 0.86 (86%), 0.87 (87%), 0.88 (88%), 0.89 (89%), 0.9 (90%), 0.91 (91%), 0.92 (92%), 0.93 (93%), 0.94 (94%), 0.95 (95%), 0.96 (96%), 0.97 (97%), 0.98 (98%), and may be up to nearly 100%. Quantum measurements in film can be made by spectrophotometer, e.g., Quantaurus-QY spectrophotometer (Hamamatsu, Inc., Campbell, CA, USA).

In some embodiments, the photoluminescent complex has an emission band, wherein the emission band may have a full width half maximum (FWHM) of less than 40 nm. The FWHM is the width of the emission band in nanometers at the emission intensity that is half of the maximum emission intensity for the band. In some embodiments, the photoluminescent complex has an emission band FWHM value that is less than or equal to about 35 nm, less than or equal to about 30 nm, less than or equal about 25 nm, or less than or equal to about 20 nm. In some embodiments, the FWHM is about 40 nm to about 35 nm, about 35 nm to about 30 nm, about 30 nm to about 25 nm, about 25 nm to about 20 nm, or less than about 20 nm.

In some embodiments, the photoluminescent complex can have a Stokes shift that is equal to or greater than 45 nm. As used herein, the term "Stokes shift" means the distance between the excitation peak of the blue light absorbing moiety and the emission peak of the BODIPY moiety. In some embodiments, the Stokes shift is at least 45 nm. In some embodiments, the Stokes shift of photoluminescent complex can be about 45-50 nm, about 50-55 nm, about 55-60 nm, about 60-65 nm, about 65-70 nm, about 70-75 nm, about 75-80

nm, about 80-85 nm, about 85-90 nm, about 90-95 nm, about 95-100 nm, or greater than about 100 nm, or any number in a range bounded by any of these values.

In some embodiments, the blue light absorbing moiety can have a peak absorption maximum between about 400 nm to about 480 nm wavelength. In some embodiments, the peak absorption wavelength may be between about 400 nm to about 405 nm, about 405-410 nm, about 410-415 nm, about 415-420 nm, about 420-425 nm, about 425-430 nm, about 430-435 nm, about 435-440 nm, about 440-445 nm, about 445-450 nm, about 450-455 nm, about 455-460 nm, about 460-465 nm, about 465-470 nm, about 470-475 nm, about 475-480 nm or any wavelength in a range bounded by any of these values.

In some embodiments, the blue light absorbing moiety can have red/orange absorption with a peak absorption maximum between about 580 nm to about 650 nm wavelength. In many embodiments, the peak absorption can be in the range of about 580 to about 585 nm, about 585-590 nm, about 590-595 nm, about 595-600 nm, about 600-605 nm, about 605-610 nm, about 610-615 nm, about 615-620 nm, about 620-625 nm, about 625-630 nm, about 630-635 nm, about 635-640 nm, about 640-645 nm, about 645-650 nm, or any wavelength in a range bounded by any of these values.

In some embodiments, the photoluminescent complex can have an emission peak between about 590 nm and about 660 nm. In many embodiments, the emission peak can be between about 590 nm to about 595 nm, about 595-600 nm, about 600-605 nm, about 605-610 nm, about 610-615 nm, about 615-620 nm, about 620-625 nm, about 625-630 nm, about 630-635 nm, about 635-640 nm, about 640-645 nm, about 645-650 nm, about 650-655 nm, about 655-660 nm, or any wavelength in a range bounded by any of these values.

Other embodiments include photoluminescent complexes wherein the blue light absorbing naphthalimide derivative and the BODIPY moiety's spatial distance is adjusted through the linker complex for improved transfer of the blue light absorbing naphthalimide derivative's energy to the BODIPY moiety.

The present disclosure describes a photoluminescent complex (PLC), comprising a blue light absorbing naphthalimide derivative, a linker complex, and a ring-locked BODIPY moiety. The linker complex covalently links the blue light absorbing naphthalimide derivative and the ring-locked BODIPY moiety. In some embodiments, the naphthalimide derivative absorbs light energy of a first excitation wavelength and transfers an energy to the ring-locked

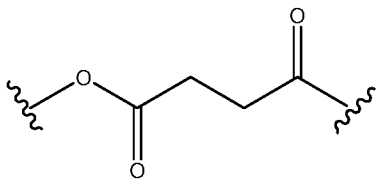
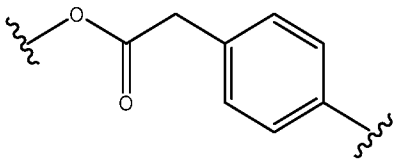
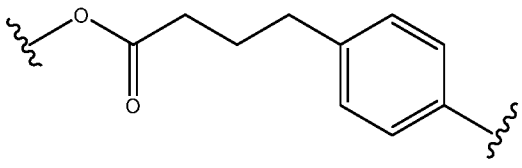
BODIPY moiety, wherein the ring-locked BODIPY moiety absorbs the energy from the naphthalimide derivative and emits a light energy of a second higher wavelength. In such embodiments, the photoluminescent complex has an emission quantum yield greater than 80%.

The linker complex covalently links the blue absorbing naphthalimide derivative with the ring-locked BODIPY moiety. The linker complex can be tuned to adjust the spatial distance between the blue light absorbing naphthalimide derivative and the ring-locked BODIPY moiety. By adjusting the spatial distance between the ring-locked naphthalimide derivative and the ring-locked BODIPY, the quantum yield may be tuned. In some embodiments, the distance separating the blue light absorbing naphthalimide derivative and the ring-locked BODIPY moiety can be about 8 Å or less. The linker complex can maintain a distance between the blue light absorbing naphthalimide derivative and the ring-locked BODIPY moiety.

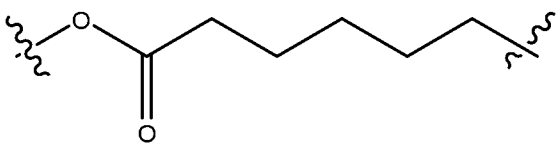
In some embodiments, the photoluminescent complex comprises a linker complex (L), wherein the linker complex covalently links the blue light absorbing naphthalimide derivative to the ring-locked BODIPY moiety. In some embodiments, the linker complex can comprise a single bond between the naphthalimide derivative and the ring-locked BODIPY moiety.

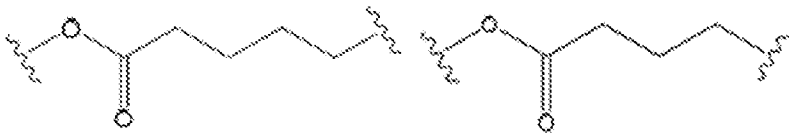
In some embodiments, the linker complex may comprise an unsubstituted ester, a substituted ester, an unsubstituted ether, or a substituted ether. In some embodiments, the linker complex can comprise an optically substituted C_{2-7} ester group.

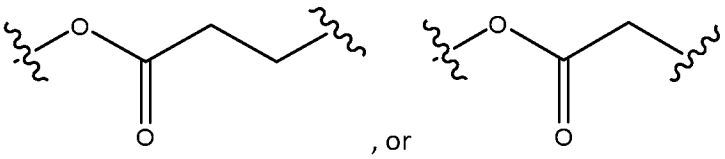
Some examples include a linker complex comprising a substituted ester group, wherein the linker complex can be selected from among one of the following structures:

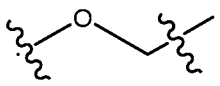

,

, or

.

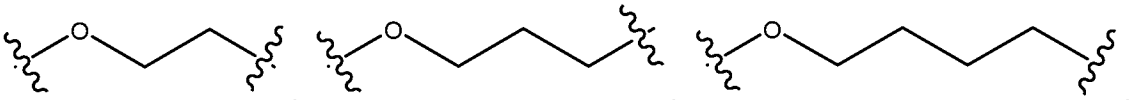
In some embodiments, the linker complex may comprise an unsubstituted ester group. When the linker complex comprises an unsubstituted ester group, the linker complex

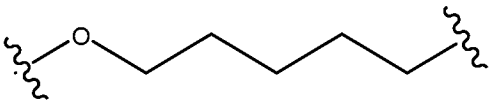
comprises one of the following structures:  ,

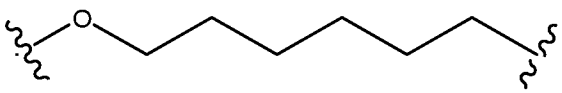
 ,

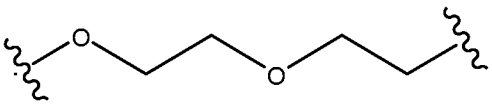
 , or .

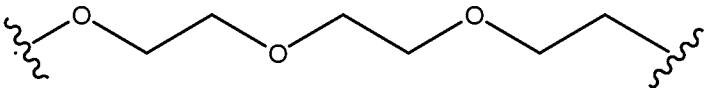
In some embodiments, the linker complex may comprise a unsubstituted and/or substituted ether. When the linker complex comprises a unsubstituted and/or substituted ether, the linker complex comprises one of the following structures:  ,

 ,

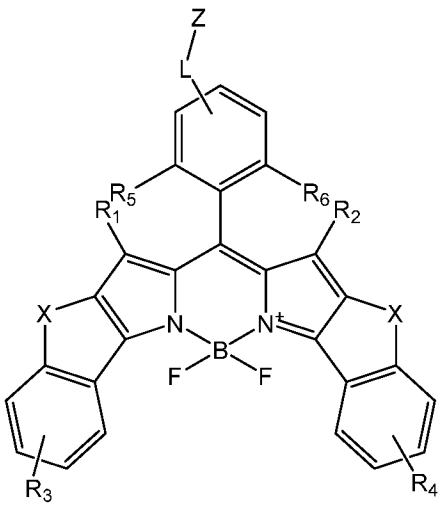
 ,

 ,

 , or

 .

The photoluminescent complex of the current disclosure can comprise a ring-locked BODIPY moiety. The ring-locked BODIPY moiety can have the following general formula:



. In some embodiments, R_1 and R_2 may be a H or a C_{1-3} alkyl. In some embodiments, R_1 and R_2 may be a substituted aryl moiety, wherein the substituents on the aryl moiety may be a C_{1-6} alkyl. In some embodiments, R_3 and R_4 may be a H, F, Br, or $-CF_3$. In some embodiments, R_5 and R_6 may be a H, halide, e.g., -F, -Cl and / or -Br, a C_1-C_3 alkyl group, e.g., $-CH_3$, a C_1-C_3 alkoxy, e.g., $-OCH_3$. In some embodiments, X may be an C_1-C_3 alkyl group, e.g., $-CH_2-$; $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, or a spiro-cycloalkane group.

In some embodiments, R_1 is H.

In some embodiments, R_1 is C_{1-3} alkyl.

In some embodiments, R_2 is H.

In some embodiments, R_2 is C_{1-3} alkyl.

In some embodiments, R_1 and R_2 are H.

In some embodiments, R_1 and R_2 are C_{1-3} alkyl.

In some embodiments, R_1 is a substituted aryl moiety, e.g., phenyl, wherein the substituents on the aryl moiety, e.g., phenyl, may be a C_{1-6} alkyl.

In some embodiments, R_2 is a substituted aryl moiety, e.g., phenyl, wherein the substituents on the aryl moiety, e.g., phenyl, may be a C_{1-6} alkyl.

In some embodiments, R_1 and R_2 are substituted aryl moieties, e.g., phenyl, wherein the substituents on the aryl moiety, e.g., phenyl, may be a C_{1-6} alkyl.

In some embodiments, R_3 is H.

In some embodiments, R_3 is F.

In some embodiments, R_3 is Br.

In some embodiments, R_3 is $-CF_3$.

In some embodiments, R_4 is H.

In some embodiments, R_4 is F.

In some embodiments, R_4 is Br.

In some embodiments, R_4 is $-CF_3$.

In some embodiments, R_3 and R_4 are H.

In some embodiments, R_3 and R_4 are F.

In some embodiments, R_3 and R_4 are Br.

In some embodiments, R_3 and R_4 are $-CF_3$.

In some embodiments, R_5 is H.

In some embodiments, R_5 is -F.

In some embodiments, R_5 is -Cl.

In some embodiments, R_5 is -Br.

In some embodiments, R_5 is a C_1-C_3 alkyl group.

In some embodiments, R_5 is $-CH_3$.

In some embodiments, R_5 is a C_1-C_3 alkoxy.

In some embodiments, R_5 is $-OCH_3$.

In some embodiments, R_6 is H.

In some embodiments, R_6 is -F.

In some embodiments, R_6 is -Cl.

In some embodiments, R_6 is -Br.

In some embodiments, R_6 is a C_1-C_3 alkyl group.

In some embodiments, R_6 is $-CH_3$.

In some embodiments, R_6 is a C_1-C_3 alkoxy.

In some embodiments, R_6 is $-OCH_3$.

In some embodiments, R_5 and R_6 are H.

In some embodiments, R_5 and R_6 are -F.

In some embodiments, R_5 and R_6 are -Cl.

In some embodiments, R_5 and R_6 are -Br.

In some embodiments, R_5 and R_6 are a C_1-C_3 alkyl group.

In some embodiments, R_5 and R_6 are $-CH_3$.

In some embodiments, R_5 and R_6 are a C_1-C_3 alkoxy.

In some embodiments, R_5 and R_6 are $-OCH_3$.

In some embodiments, R_5 and R_6 may be a H, $-CH_3$, Cl, F, or OCH_3.

In some embodiments, X is a C_1-C_3 alkyl group.

In some embodiments, X is $-CH_2$.

In some embodiments, X is $-CH_2CH_2-$.

In some embodiments, X is $-CH_2CH_2CH_2-$.

In some embodiments, X is a spiro-cycloalkane group.

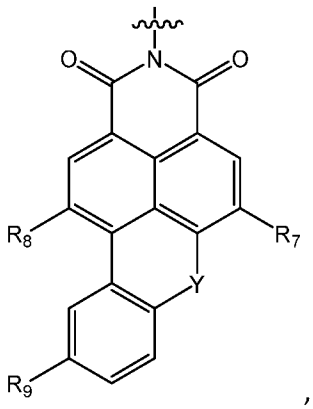
In some embodiments, L is an unsubstituted ester.

In some embodiments, L is a substituted ester.

In some embodiments, L is an unsubstituted ether.

In some embodiments, L is a substituted ether.

Many embodiments include a blue light absorbing naphthalimide derivative (Z), wherein the blue light absorbing naphthalimide derivative may be of the following general formula:



, wherein Y may be an oxygen (O) or a sulfur (S). In some embodiments, R_7 and/or R_8 may be a hydrogen (H), a substituted or unsubstituted aryl, or a $-CF_3$. In some embodiments, R_9 may be a H, a substituted or unsubstituted aryl, a C_{1-5} alkylaryl, a substituted or unsubstituted arylcarboxylic acid (such as p-CO_2-*t*-Bu-phenyl), or there is no substitution for R_9.

In some embodiments, Y is oxygen (O).

In some embodiments, Y is sulfur (S).

In some embodiments, R_7 is H.

In some embodiments, R_7 is a substituted aryl.

In some embodiments, R_7 is unsubstituted aryl.

In some embodiments, R_7 is $-CF_3$.

In some embodiments, R_8 is H.

In some embodiments, R_8 is a substituted aryl.

In some embodiments, R_8 is unsubstituted aryl.

In some embodiments, R_8 is $-CF_3$.

In some embodiments, R_7 and R_8 are H.

In some embodiments, R_7 and R_8 are substituted aryl.

In some embodiments, R_7 and R_8 are unsubstituted aryl.

In some embodiments, R_7 and R_8 are $-CF_3$.

In some embodiments, R_9 is H.

In some embodiments, R_9 is substituted aryl.

In some embodiments, R_9 is unsubstituted aryl.

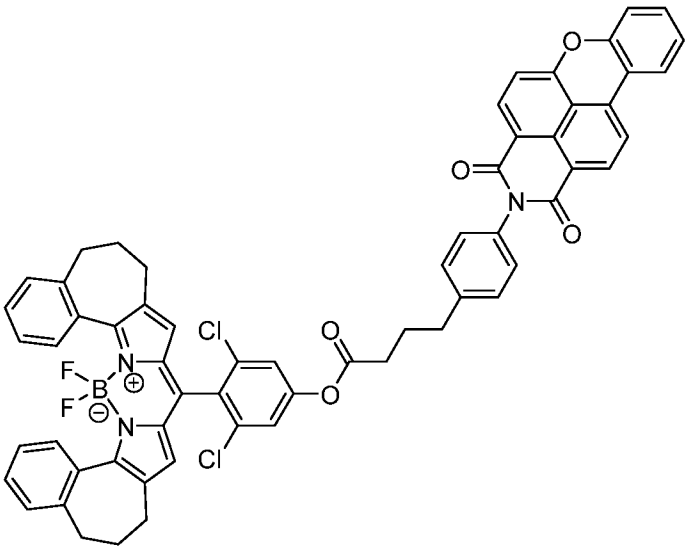
In some embodiments, R_9 is C_{1-5} alkylaryl.

In some embodiments, R_9 is a substituted arylcarboxylic acid.

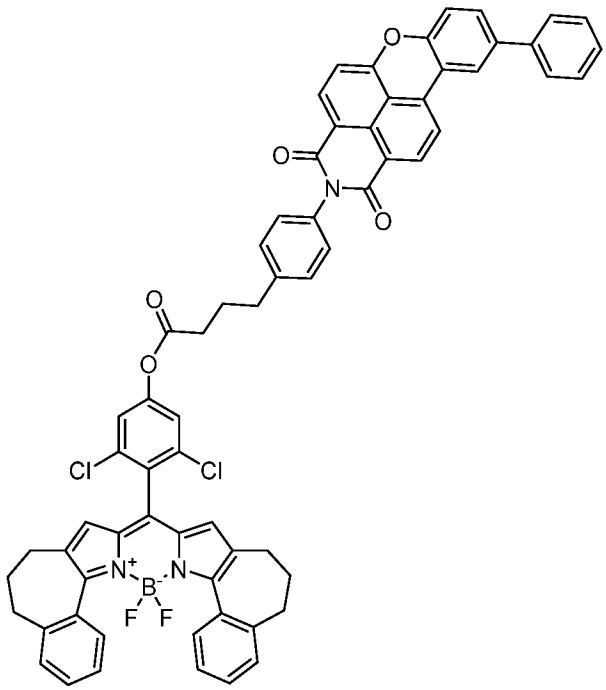
In some embodiments, R_9 is an unsubstituted arylcarboxylic acid.

In some embodiments, R_9 is p-CO_2-*t*-Bu-phenyl.

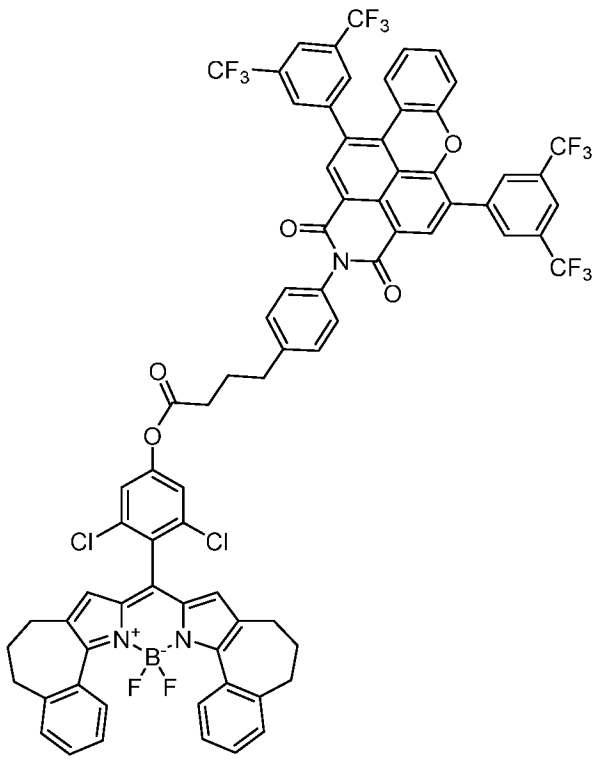
The photoluminescent complex of the present disclosure may be represented by the following structures which are provided for purpose of illustration only, and are in no way to be construed as limiting:



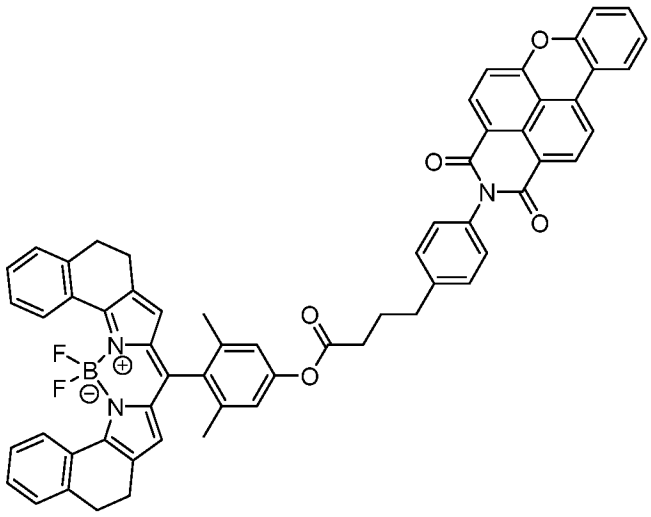
(PLC-1),



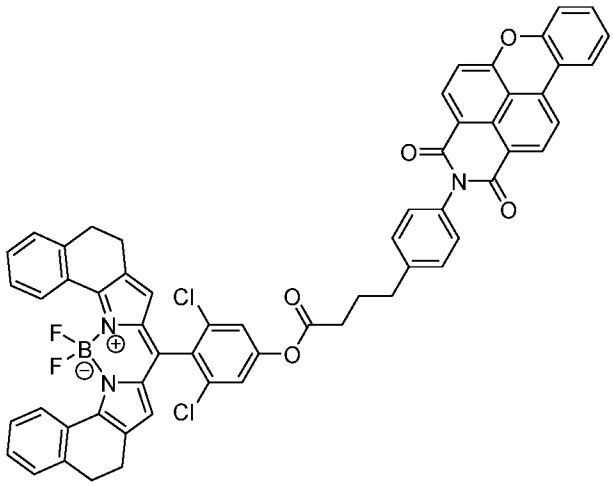
(PLC-2),



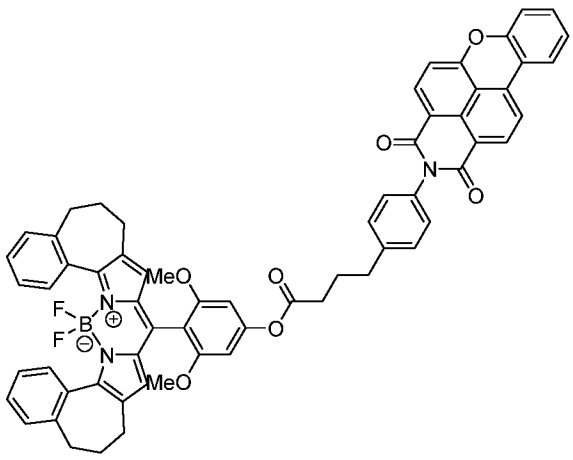
(PLC-3),



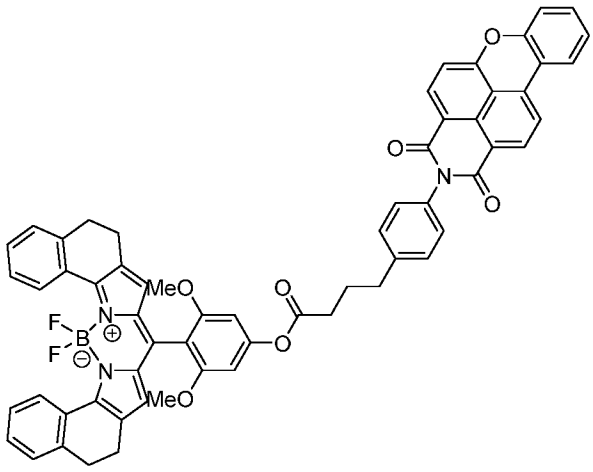
(PLC-4),



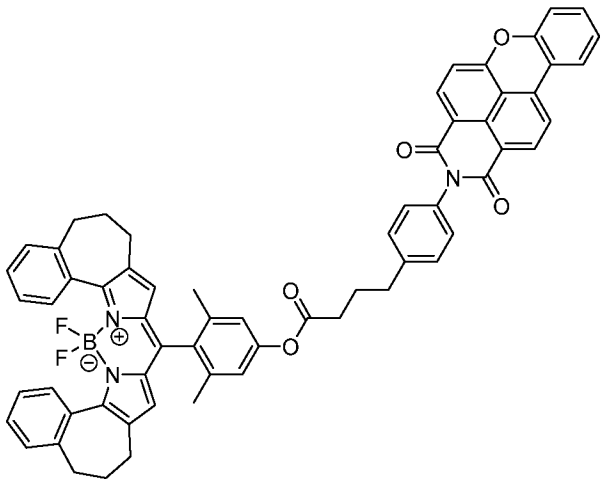
(PLC-5),



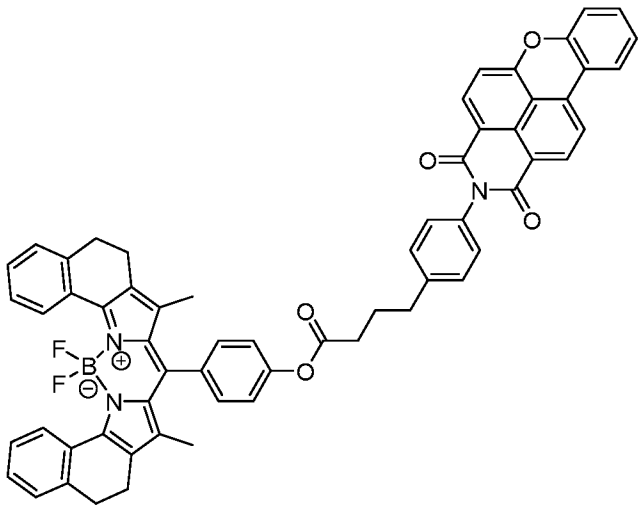
(PLC-6),



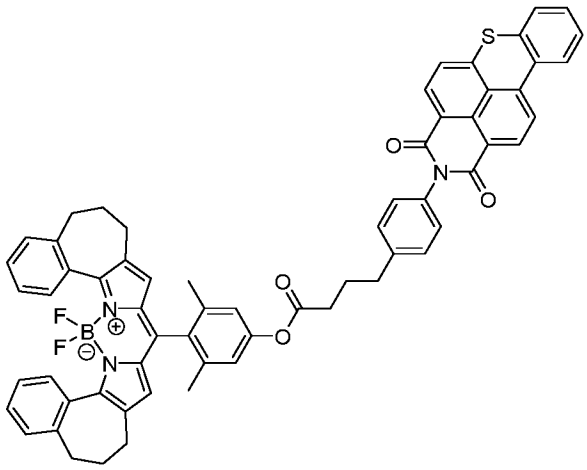
(PLC-7),



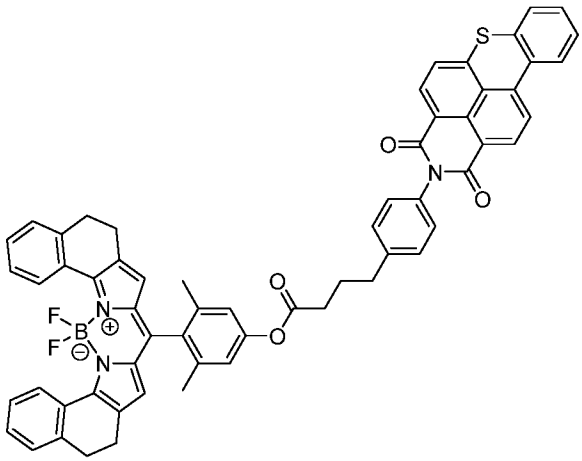
(PLC-8),



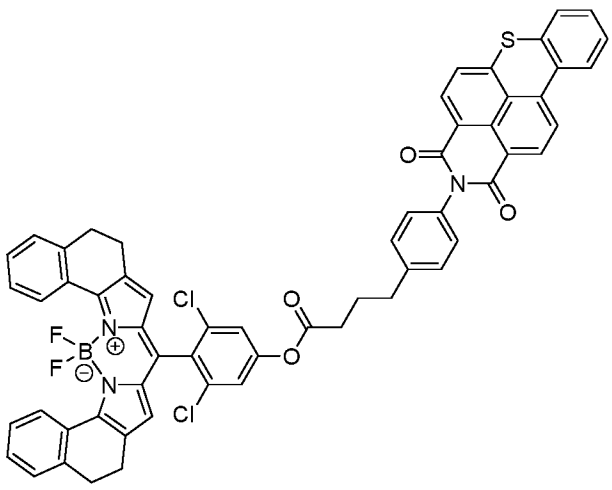
(PLC-9),



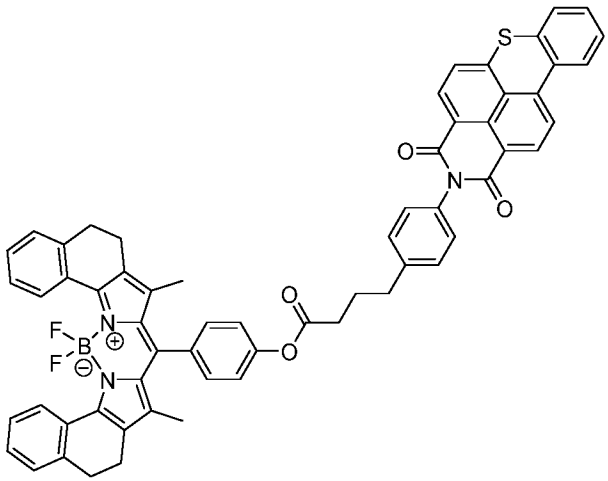
(PLC-10),



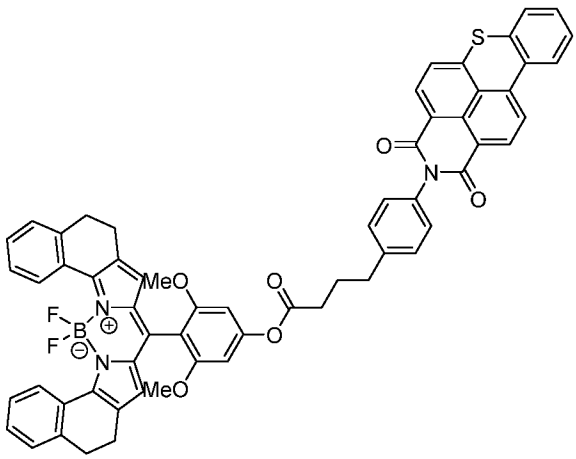
(PLC-11),



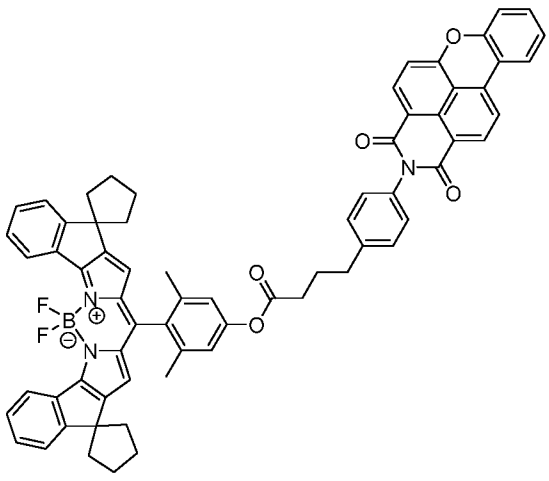
(PLC-12),



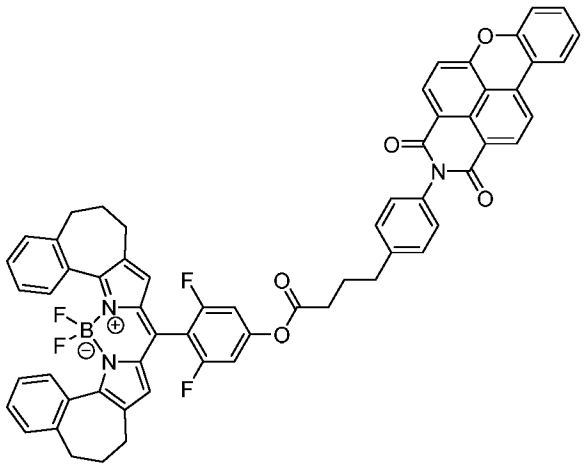
(PLC-13),



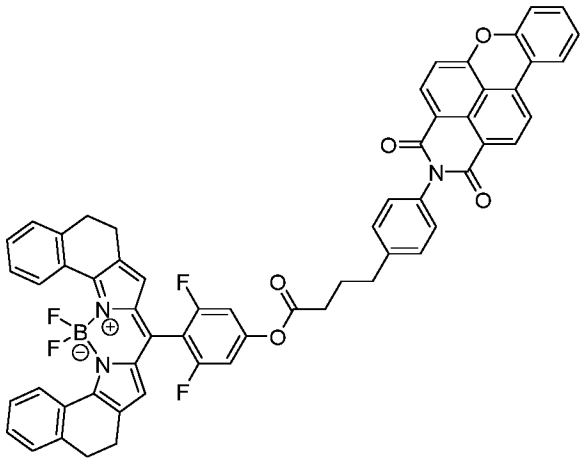
(PLC-14),



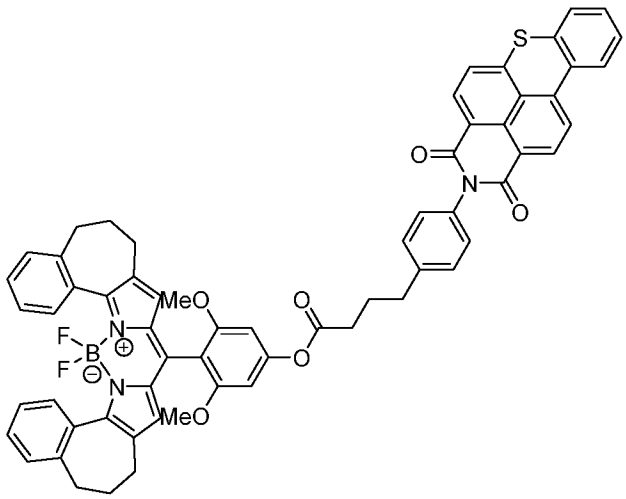
(PLC-15),



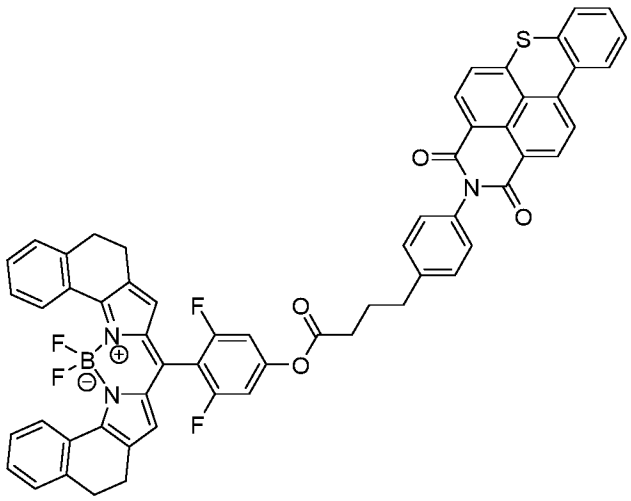
(PLC-16),



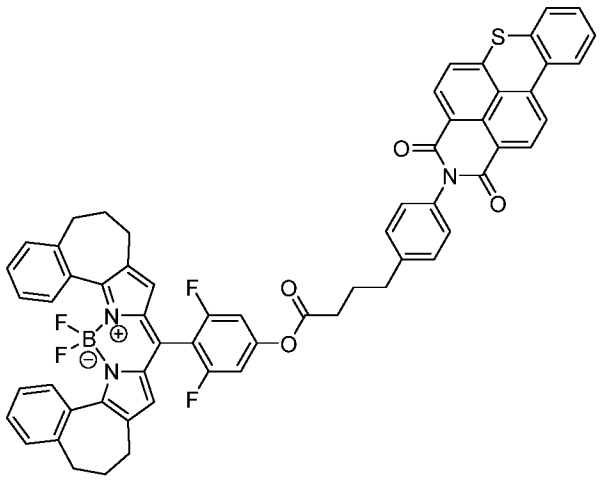
(PLC-17),



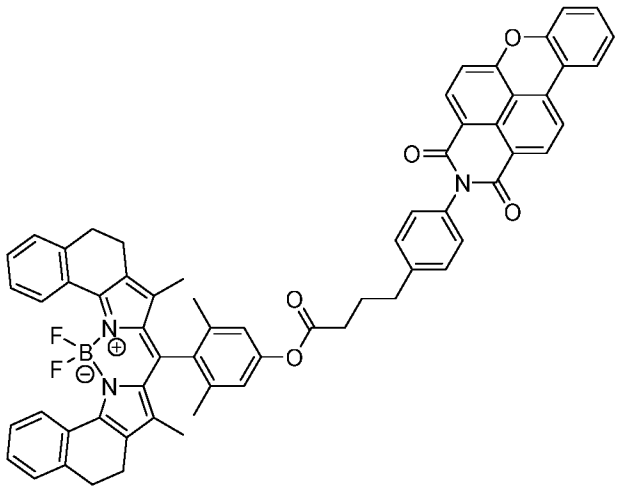
(PLC-18),



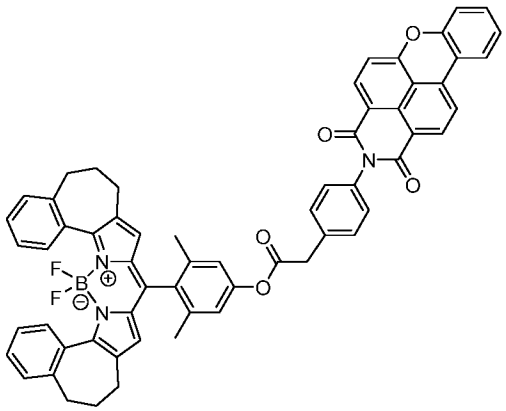
(PLC-19),



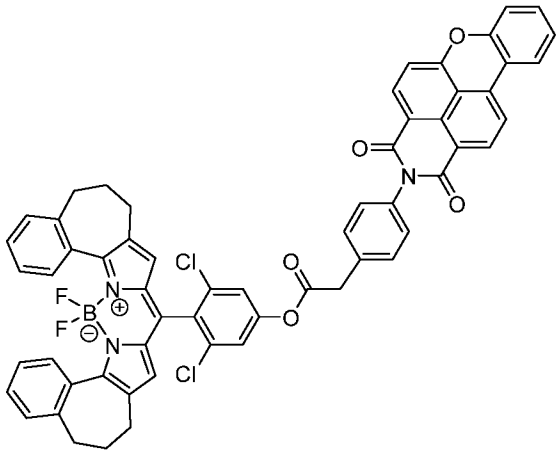
(PLC-20),



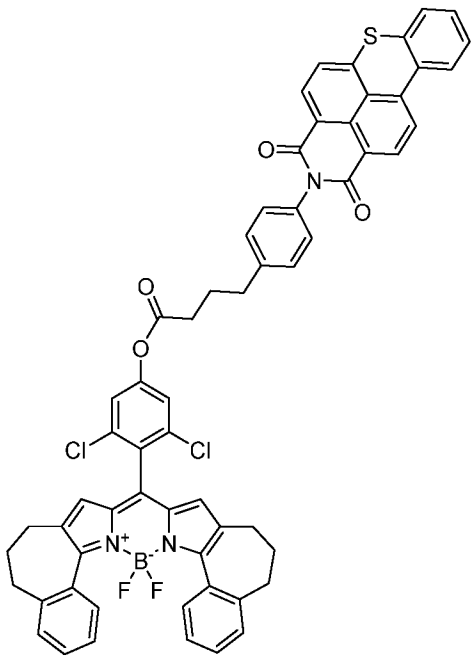
(PLC-21),



(PLC-22),

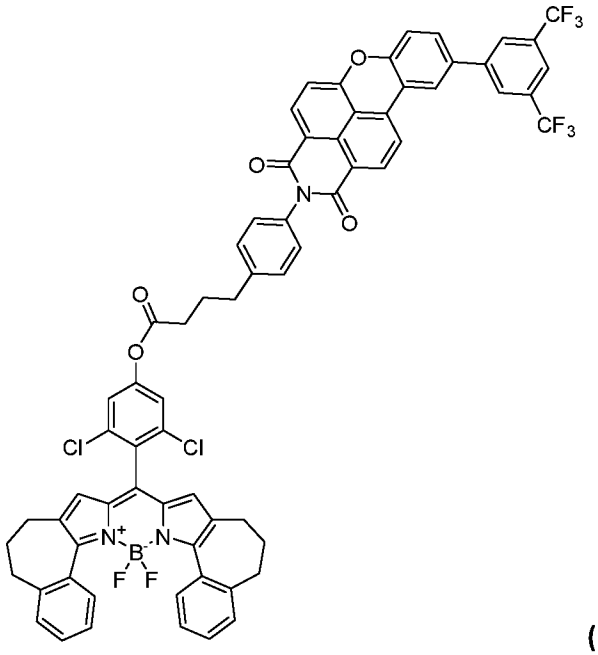


(PLC-23),

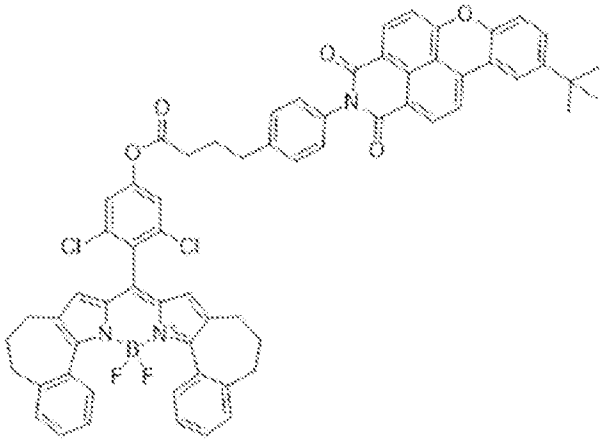


(PLC-24),

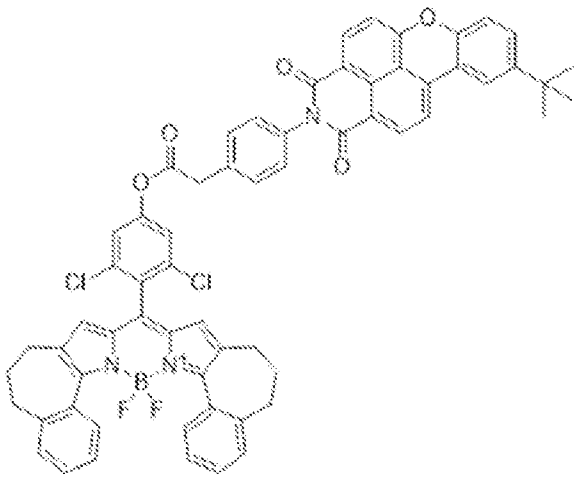
5



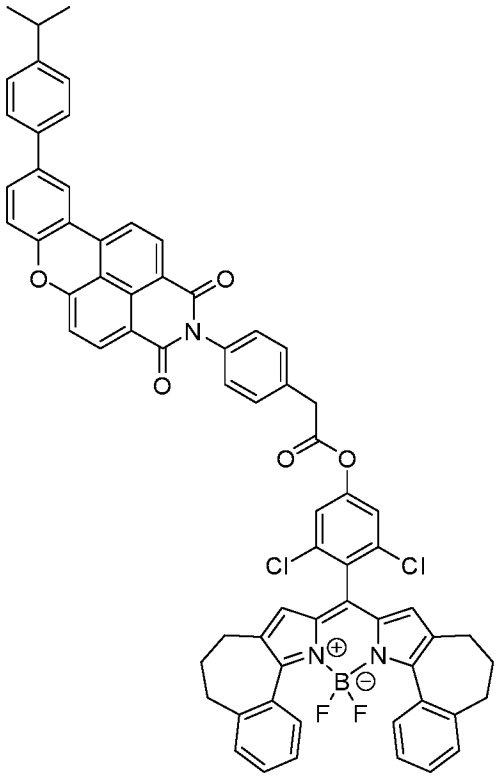
(PLC-25),



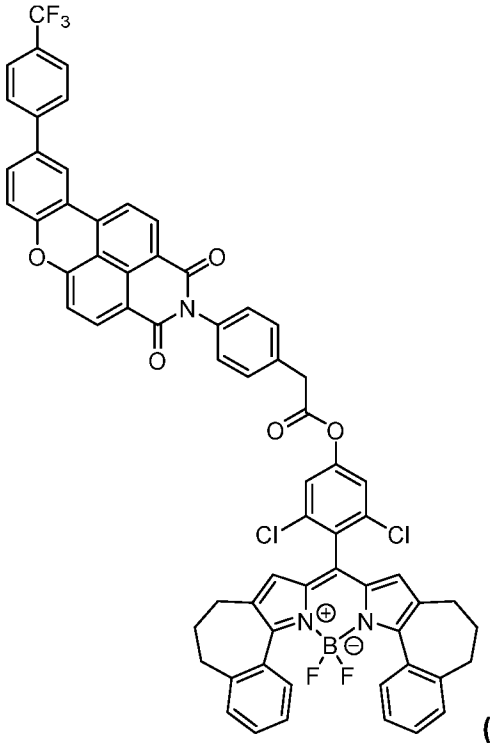
(PLC-26),



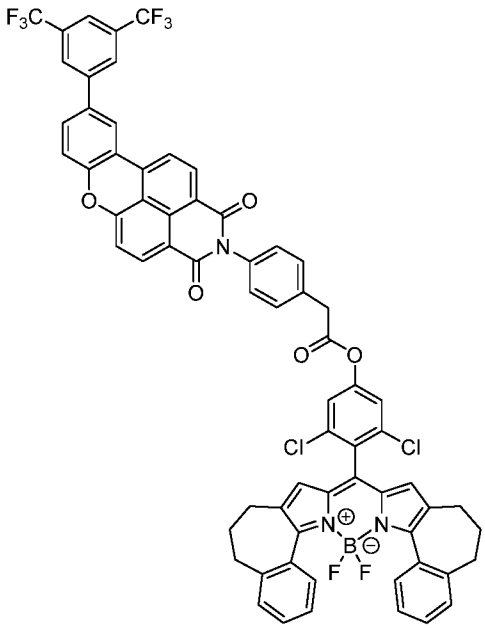
(PLC-27),



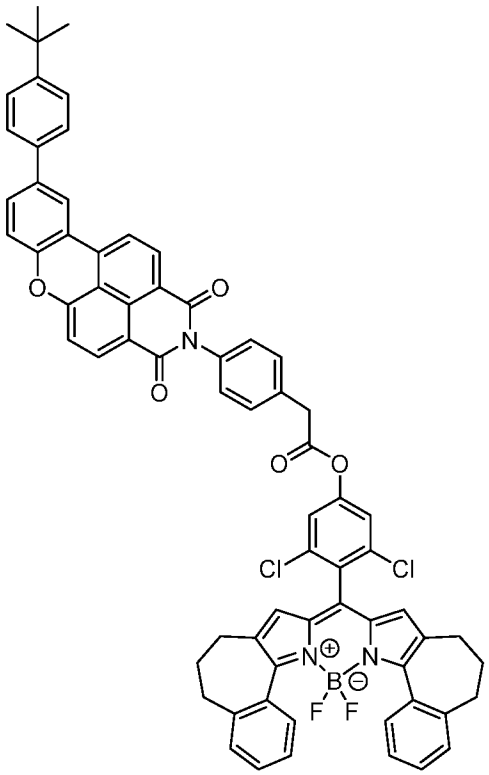
(PLC-28),



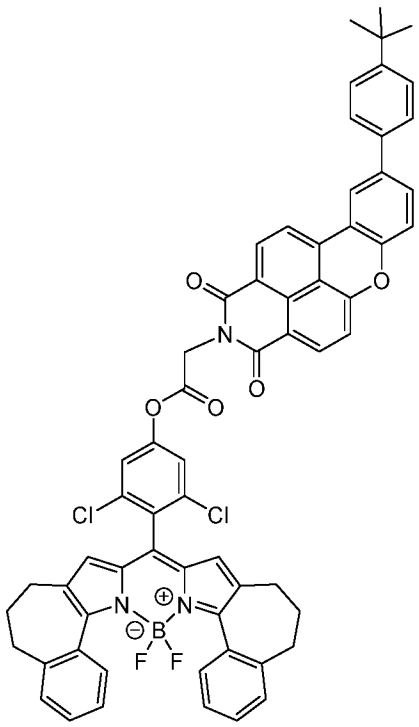
(PLC-29),



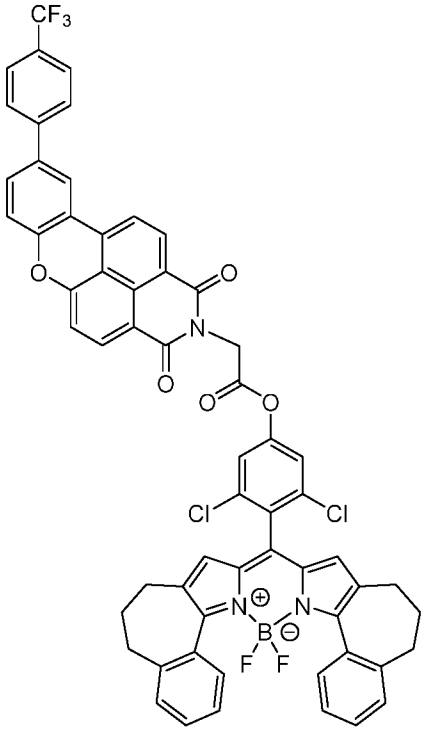
(PLC-30),



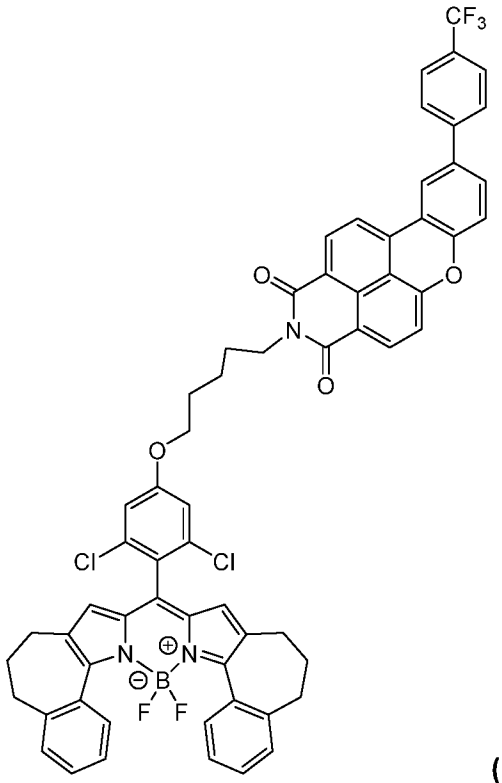
(PLC-31),



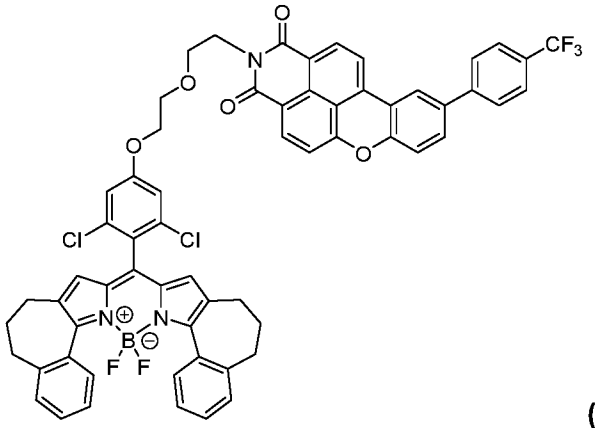
(PLC-32),



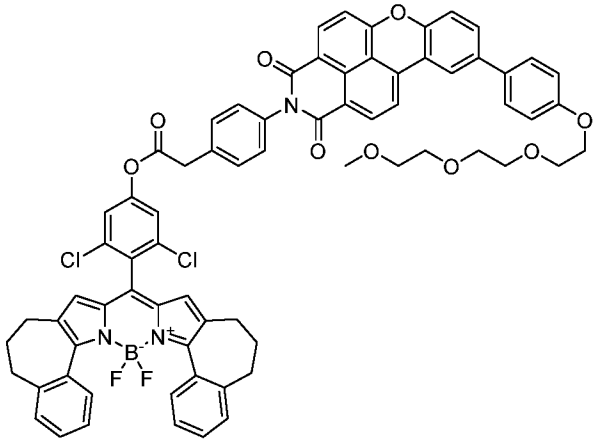
(PLC-33),



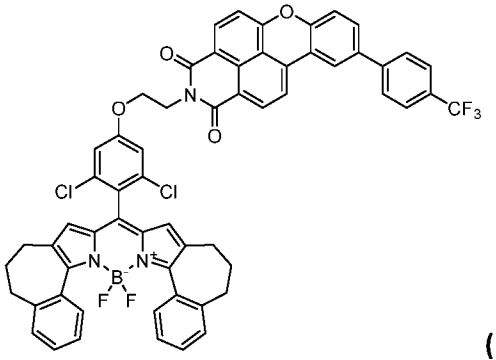
(PLC-34),



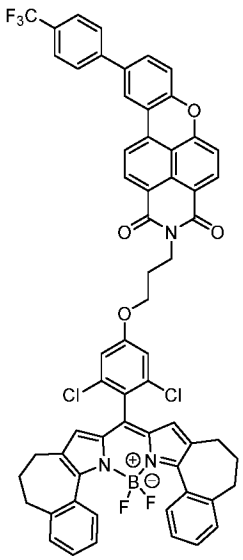
(PLC-35)



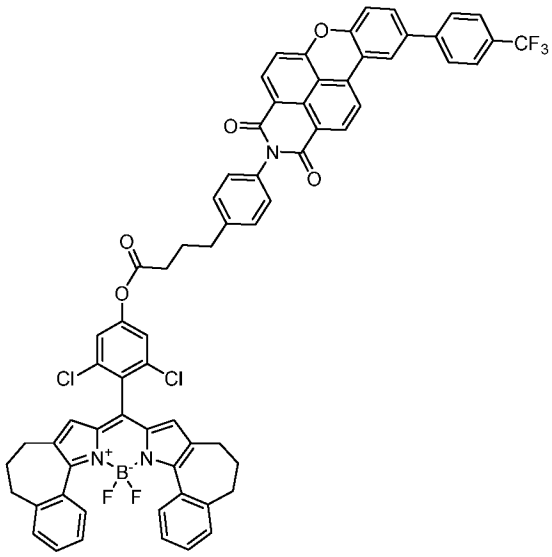
(PLC-36),



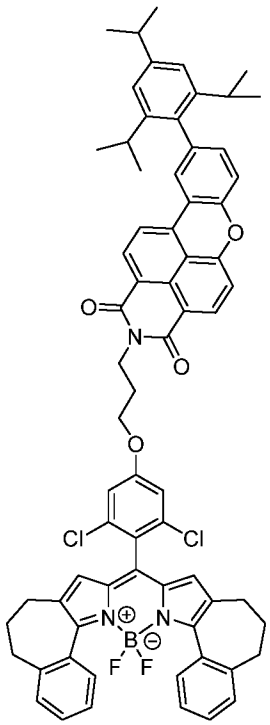
(PLC-37),



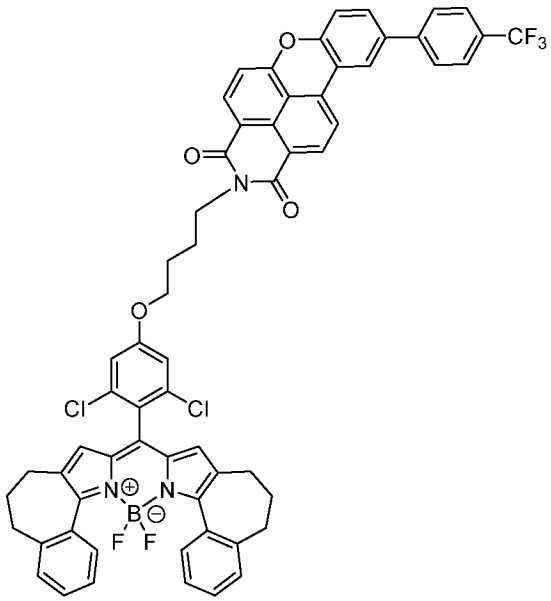
(PLC-38),



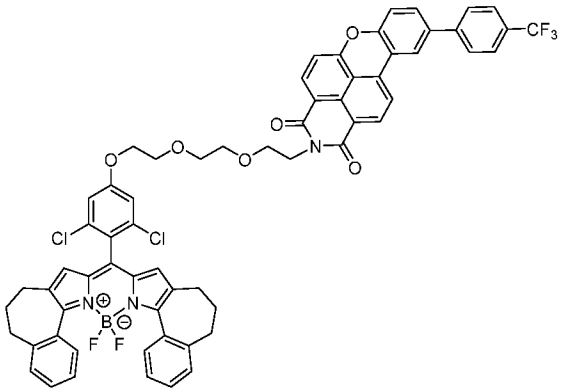
(PLC-39),



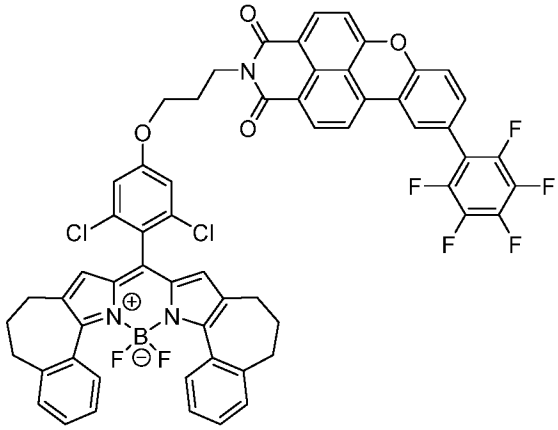
(PLC-40),



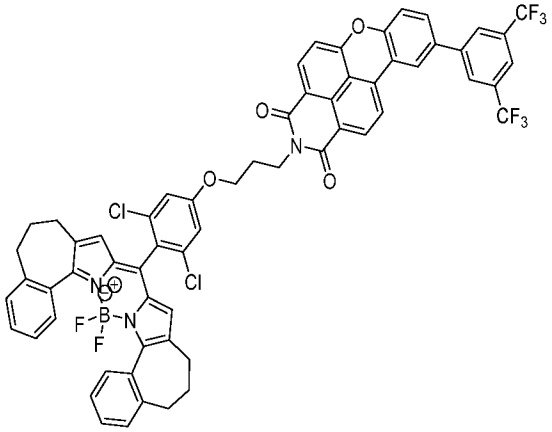
(PLC-41),



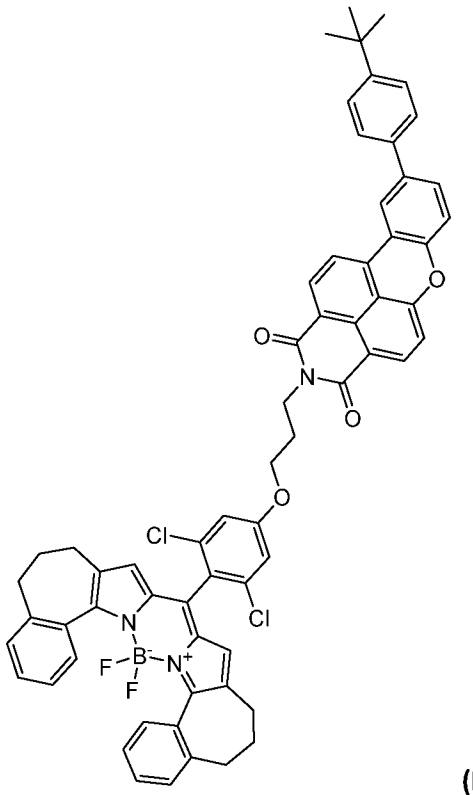
(PLC-42),



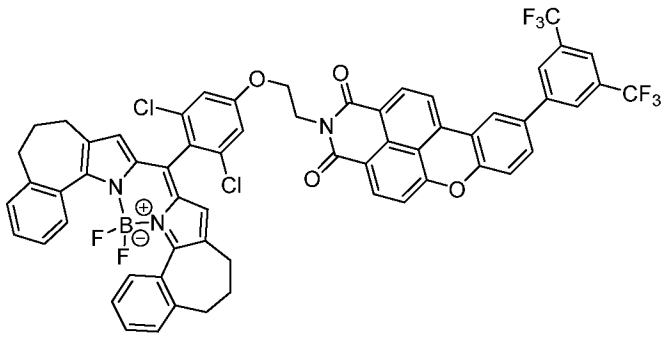
(PLC-43),



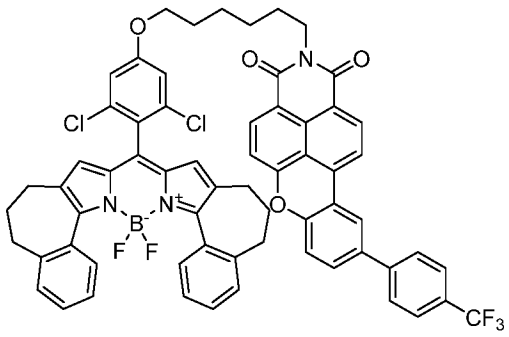
(PLC-44),



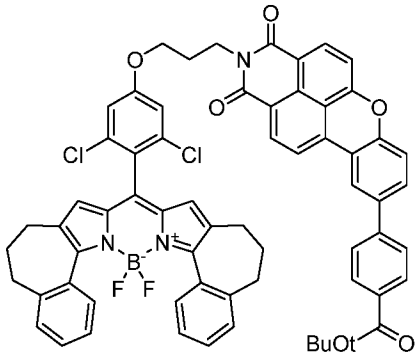
(PLC-45),



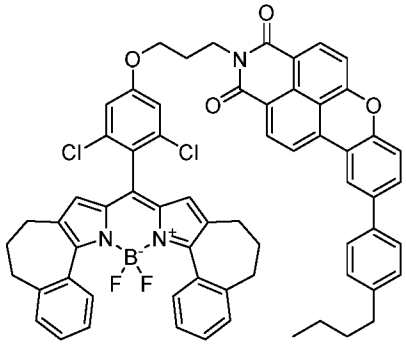
(PLC-46),



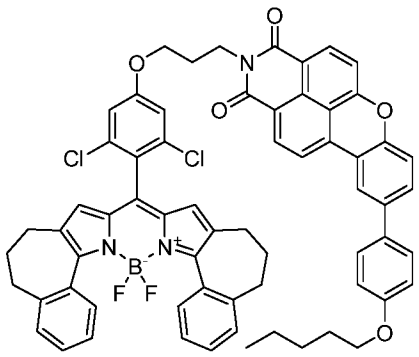
(PLC-47),



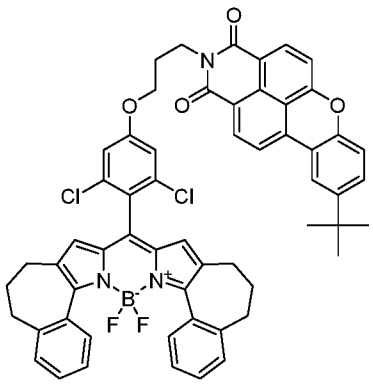
(PLC-48),



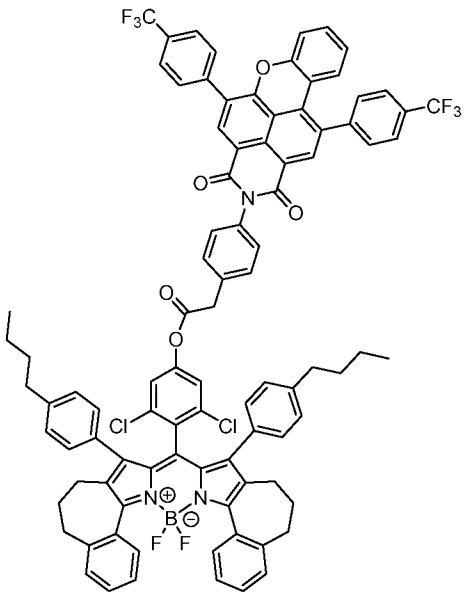
(PLC-49),



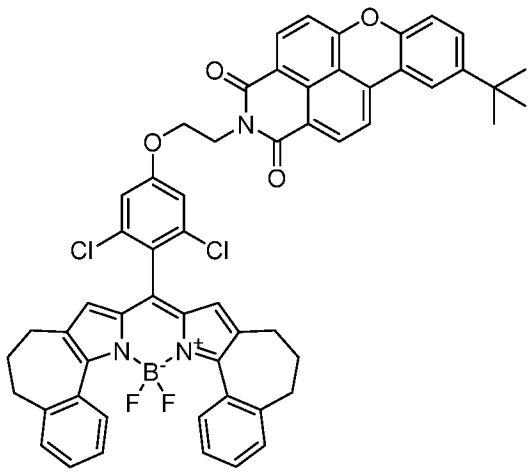
(PLC-50),



(PLC-51),



(PLC-52),



(PLC-53), or a combination thereof.

In some embodiments, the photoluminescent complex comprises a blue light absorbing naphthalimide derivative. In some examples, the blue light absorbing naphthalimide derivative can comprise an organic lumiphore. In many embodiments, the blue light absorbing moiety can have a peak absorption maximum between about 400 nm to about 480 nm wavelength. In some embodiments, the peak absorption can be at least about 400 nm, 410 nm, 420 nm, 430 nm, 440 nm, 450 nm, or 460 nm. In some embodiments, the peak absorption can be less than about 410 nm, 420 nm, 430 nm, 440 nm, 450 nm, and 460 nm, 470 nm, or 480 nm. In numerous embodiments, the photoluminescent complex can have an absorbance maximum peak of about 450 nm. In some embodiments, the blue light absorbing naphthalimide derivative can have a maximum peak absorbance of about 410 nm and a

lowest max absorbance peak of about 400 nm. Still, in many embodiments, the blue light absorbing naphthalimide derivative can have a maximum peak absorbance of about 480 nm.

Some embodiments include a color conversion film, wherein the color conversion film comprises: a color conversion layer wherein the color conversion layer includes a resin matrix and a photoluminescent complex described above, dispersed within the resin matrix. In many embodiments, the color conversion film can comprise one or more of the photoluminescent complexes described herein.

Some embodiments include the color conversion film which may be about 1 μm to about 200 μm thick. In many embodiments, the color conversion film can be described as being about 1 μm to about 5 μm thick, about 5 μm to about 10 μm thick, about 10 μm to about 15 μm thick, about 15 μm to about 20 μm thick, about 20 μm to about 40 μm thick, about 40 μm to about 80 μm thick, about 80 μm to about 120 μm thick, about 120 μm to about 160 μm thick, about 160 μm to about 200 μm thick, or any thickness bounded by the ranged above.

In some embodiments, the color conversion film can absorb light in the range of about 400 nm to about 480 nm wavelength and can emit light in the range of about 590 nm to about 660 nm.

In some embodiments, the color conversion film can further comprise a transparent substrate layer. The transparent substrate layer has two opposing surfaces, wherein the color conversion layer can be disposed on and in physical contact with the surfaces of the transparent layer that will be adjacent to a light emitting source. The transparent substrate is not particularly limited and one skilled in the art would be able to choose a transparent substrate from those used in the art. Some non-limiting examples of transparent substrates include PE (polyethylene), PP (polypropylene), PEN (polyethylene naphthalate), PC (polycarbonate), PMA (polymethylacrylate), PMMA (polymethylmethacrylate), CAB (cellulose acetate butyrate), PVC (polyvinylchloride), PET (polyethyleneterephthalate), PETG (glycol modified polyethylene terephthalate), PDMS (polydimethylsiloxane), COC (cyclo olefin copolymer), PGA (polyglycolide or polyglycolic acid), PLA (polyactic acid), PCL (polycaprolactone), PEA (polyethylene adipate), PHA (polyhydroxy alkanoate), PHBV (poly(3-hydroxybutyrate-co-3-hydroxyvalerate)), PBE (polybutylene terephthalate), PTT

(polytrimethylene terephthalate). Any of the aforementioned resins can be corresponding, respective monomers and/or polymers.

In some embodiments, the transparent substrate may have two opposing surfaces. In many embodiments, the color conversion film may be disposed on and in physical contact with one of the opposing surfaces. In some embodiments, the side of the transparent substrates without color conversion film disposed thereon, may be adjacent to a light source. The substrate may function as a support during the preparation of the material of the color conversion film. The type of substrates used are not particularly limited, and the material and/or thickness is not limited, as long as it is transparent and capable of functioning as a support. A person skilled in the art could determine which material and thickness to use as a supporting substrate.

Some embodiments include a method for preparing the color conversion film, wherein the method comprises: dissolving a photoluminescent compound described herein, and a binder resin within a solvent; and applying the mixture on to the surface of a transparent substrate.

The binder resin which may be used with the photoluminescent complex(es) includes resins, such as acrylic reins, polycarbonate resins, ethylene-vinyl alcohol copolymer resins, ethylene-vinyl acetate copolymer resins, and saponification products thereof, AS resins, polyester resins, vinyl chloride-vinyl acetate copolymer resins, polyvinyl butyral resins, polyvinylphosphonic acid (PVPA), polystyrene resins, phenolic resins, phenoxy resins, polysulfone, nylon, cellulosic resins, and cellulose acetate resins. In some embodiments, the binder resin can be a polyester resin and/or acrylic resin.

The solvent which may be used for dissolving or dispersing the complex and the resin may include an alkane, such as butane, pentane, hexane, heptane, and octane; cycloalkanes, such as cyclopentane, cyclohexane, cycloheptane, and cyclooctane; alcohols, such as ethanol, propanol, butanol, amyl alcohol, hexanol, heptanol, octanol, decanol, undecanol, diacetone alcohol, and furfuryl alcohol; Cellosolves™, such as Methyl Cellosolve™, Ethyl Cellosolve™, Butyl Cellosolve™, Methyl Cellosolve™ acetate, and Ethyl Cellosolve™ acetate; propylene glycol and its derivatives, such as propylene glycol monomethyl ether, propylene glycol monoethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monobutyl ether acetate, and dipropylene glycol dimethyl ether; ketones, such as acetone,

methyl amyl ketone, cyclohexanone, and acetophenone; ethers, such as dioxane and tetrahydrofuran; esters, such as butyl acetate, amyl acetate, ethyl butyrate, butyl butyrate, diethyl oxalate, ethyl pyruvate, ethyl 2-hydroxybutyrate, ethyl acetoacetate, methyl lactate, ethyl lactate, and methyl 3-methoxypropionate; halogenated hydrocarbons, such as chloroform, methyl chloride, and tetrachloroethane; aromatic hydrocarbons, such as benzene, toluene, xylene, and cresol; and highly polar solvents, such as dimethyl formamide, dimethyl acetamide, and N-methylpyrrolidone.

Some embodiments include a backlight unit. In some examples, the backlight unit may include the aforementioned color conversion film comprising the photoluminescent complex(es) described herein.

Other embodiments may include a display device, wherein the device may include the backlight unit described herein.

Unless otherwise indicated, all numbers expressing quantities of ingredients, properties, such as molecular weight, reaction conditions, and so forth used in the specifications and embodiments are to be understood as being modified in all instances by the term “about”. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached embodiments are approximations that may vary depending upon the desired properties sought to be obtained. At the very least, and not as an attempt to limit the application of the doctrine of equivalents, to the scope of the embodiments, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying conventional and ordinary rounding techniques.

For the processes and/or methods disclosed, the functions performed in the process and methods may be implemented in differing order, as may be indicated by context. Furthermore, the outlined steps and operations are only provided as examples and some of the steps and operations may be optional, combined into fewer steps and operations, or expanded into additional steps and operations.

This disclosure may sometimes illustrate different components contained within, or connected with, other different components. Such depicted architectures are merely examples, and many other architectures can be implemented to achieve the same or similar functionality.

The terms used in this disclosure and in the appended embodiment, (e.g., bodies of the appended embodiments) are generally intended as "open" terms (e.g., the term "including" should be interpreted as "including, but not limited to," the term "having" should be interpreted to "having at least", the term "includes" should be interpreted as "includes, but not limited to," etc.. in addition, if a specific number of elements is introduced, this may be interpreted to mean at least the recited number, as may be indicated by context (e.g., the bare recitation of "two recitations", without other modifiers, means at least two recitations or two or more recitations). As used in this disclosure, any disjunctive word and/or phrase presenting two or more alternative terms should be understood to contemplate the possibilities of including one of those terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B". Similarly, the phrase "A and/or B" will be understood to include the possibilities of "A" or "B" or "A and B".

The terms "a", "an", "the", and similar referents used in the context of describing the present disclosure (especially in the context of the following embodiments) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The use of any and all examples, or representative language (e.g., "such as" or "for instance") provided herein is intended merely to better illustrate the present disclosure and does not pose a limitation on the scope of any embodiments. No language in this specification herein shall be construed as indicating any non-embodied element essential to the practice of the present disclosure.

Groupings of alternative elements or embodiments disclosed herein are not to be construed as limitations. Each group member may be referred to and embodied individually or in any combination with other members of the group or other elements found herein. It is anticipated that one or more members of a group may be included in, or deleted from, a group for reasons of convenience and/or patentability. When any such inclusion or deletion occurs, the specification is deemed to contain the group as modified, thus fulfilling the written description of all Markush groups used in the appended embodiments.

Certain embodiments are described herein, including the best mode known to the inventors for carrying out the present disclosure. Of course, variations on these described embodiments, will become apparent to those of ordinary skill in the art upon reading the

foregoing description. The inventor expects skilled artisans to employ such variations as appropriate, and the inventors intend for the present disclosure to be practiced otherwise than specifically described herein. Accordingly, the embodiments are permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is contemplated unless otherwise indicated herein or otherwise clearly contradicted by context. In closing, it is to be understood that the embodiments disclosed herein are illustrative of the principles of the embodiments. Therefore, by way of example, but not of limitation, alternative embodiments may be utilized in accordance with the teachings herein. Henceforth, the embodiments are not limited to the embodiments precisely as shown and described herein.

EMBODIMENTS:

Embodiment 1.

A photoluminescent complex comprising:

a blue light absorbing donor chromophore, wherein the donor chromophore comprises a naphthalimide derivative;

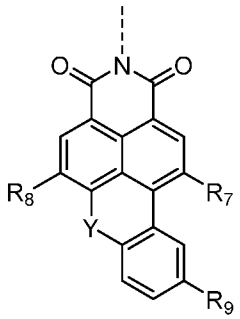
a linker complex; and

a ring-locked boron-dipyrromethene (BODIPY) moiety;

wherein the linker complex covalently links the donor chromophore with the naphthalimide derivative and the ring-locked BODIPY moiety, wherein the naphthalimide derivative absorbs blue light energy of a first excitation wavelength and transfers an energy to the ring-locked BODIPY moiety, wherein the ring-locked BODIPY moiety absorbs the energy from the naphthalimide derivative and emits a light energy of a second higher wavelength, and wherein the photoluminescent complex has an emission quantum yield greater than 80%.

Embodiment 2.

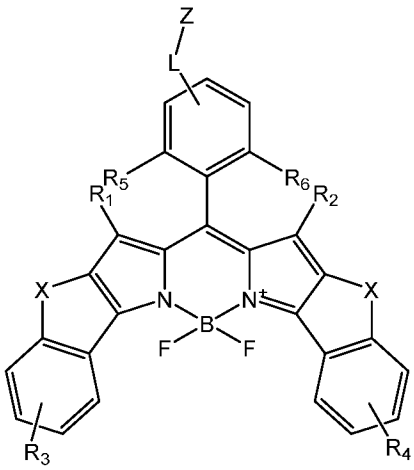
The photoluminescent complex of embodiment 1, wherein the naphthalimide derivative of the donor chromophore is of the general formula:



wherein Y is selected from a oxygen (O) or a sulfur (S); wherein R_7 and R_8 are independently selected from a hydrogen (H), a substituted or unsubstituted aryl, or a -CF_3; and wherein R_9 is independently selected from a hydrogen (H), a substituted or unsubstituted aryl, a C_1-C_5 alkyl, or there is no substitution for R_9.

Embodiment 3.

The photoluminescent complex of embodiment 1, wherein the ring-locked BODIPY moiety is of the general formula:



wherein R_1 and R_2 are independently selected from a H or a C_1-C_3 alkyl; wherein R_3 and R_4 are independently selected from a H, F, Br, -CF_3, or a bonding connecting to L—Z; wherein R_5 and R_6 are independently selected from a H, C_1-C_3 alkyl group, halide, or C_1-C_3 alkoxy; and wherein X is independently selected from a C_1-C_3 alkyl group, -CH_2CH_2-, -$CH_2CH_2CH_2$-, or a spiro-cychloalkane group.

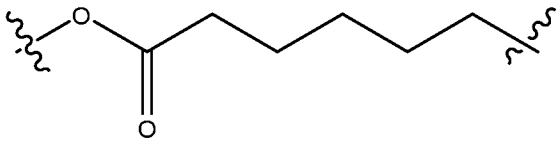
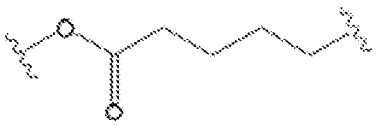
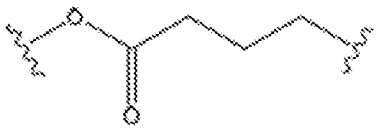
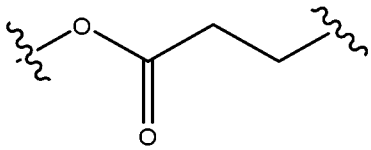
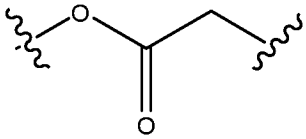
Embodiment 4.

The photoluminescent complex of embodiment 3, wherein L is a linker complex that can be a substituted ester, a unsubstituted ester, a substituted ether, or a unsubstituted ether.

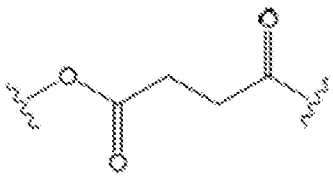
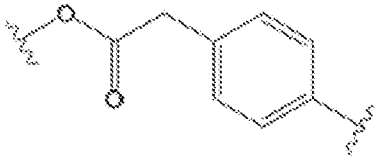
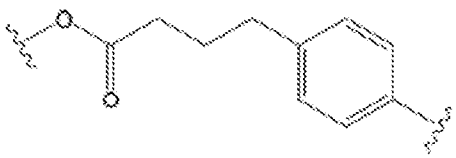
Embodiment 5.

The photoluminescent complex of embodiment 3, wherein Z is a donor chromophore comprising the naphthalimide derivative.

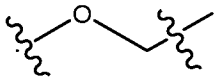
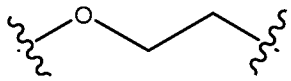
Embodiment 6.

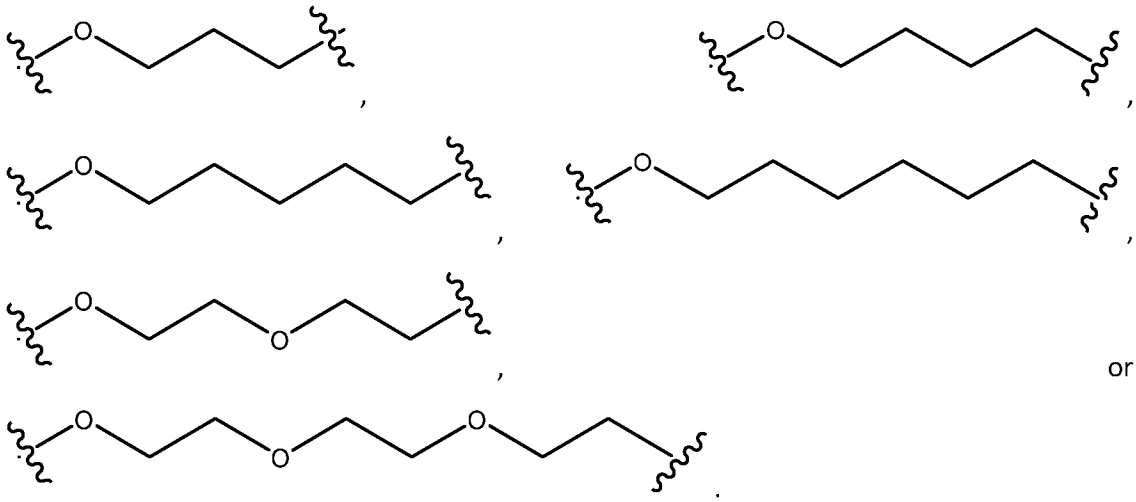
The photoluminescent complex as in embodiments 1 or 4, wherein the linker complex is a unsubstituted ester; wherein the unsubstituted ester comprises one of the following structures:  ,  ,  ,  , or  .

Embodiment 7.

The photoluminescent complex as in embodiments 1 or 4, wherein the linker complex is a substituted ester; wherein the substituted ester comprises one of the following structures:  ,  , or  .

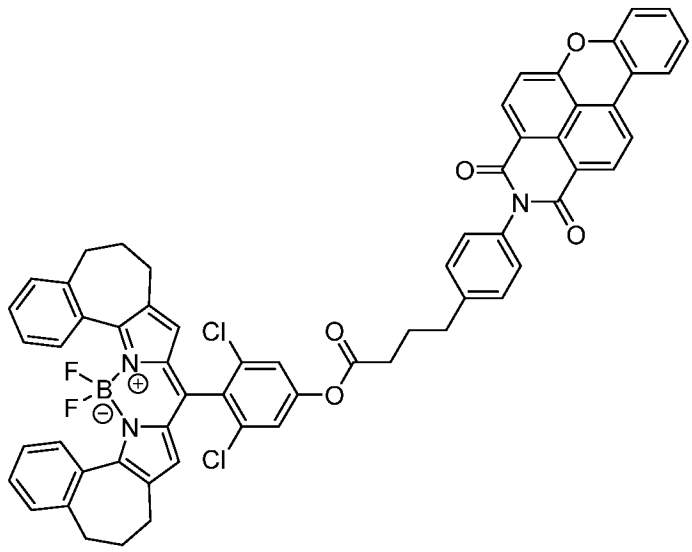
Embodiment 8.

The photoluminescent complex as in embodiments 1 or 4, wherein the linker complex is a unsubstituted and/or substituted ether; wherein the unsubstituted and/or substituted ether comprises one of the following structures:  ,  ,

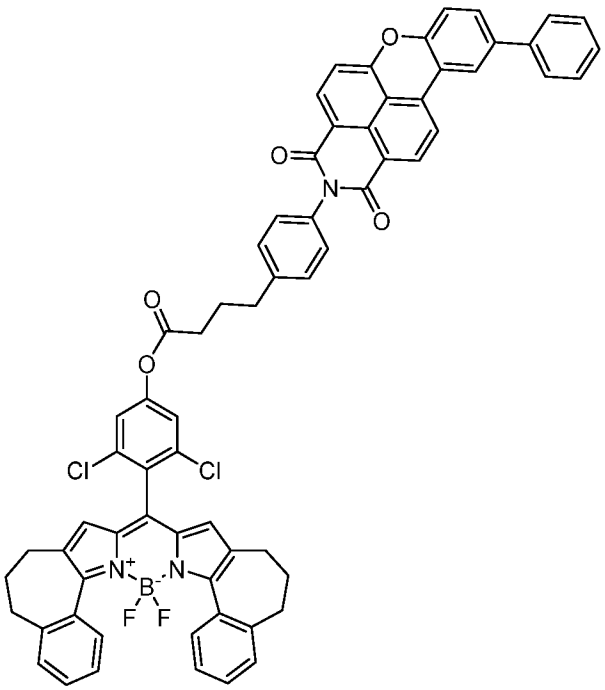


Embodiment 9.

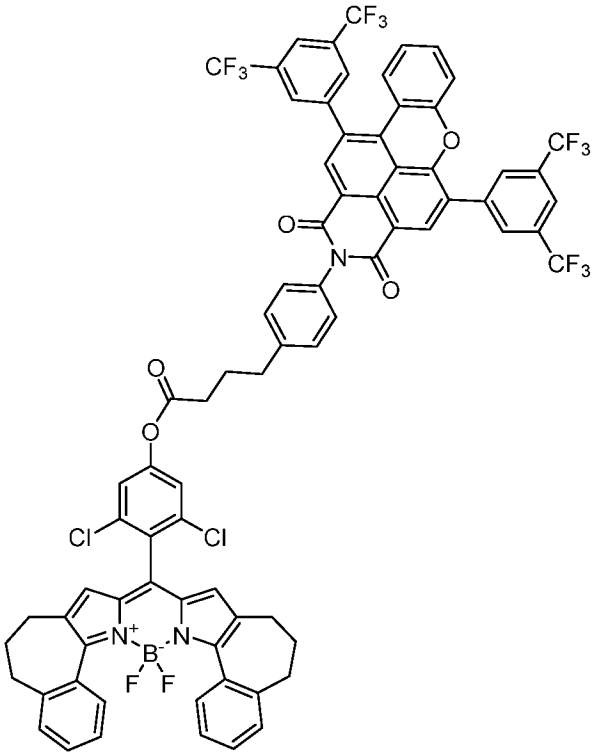
The photoluminescent complex as in embodiments 1, 2, 3, 4, 5, 6, 7, or 8 wherein the photoluminescent complex comprises one of the following structures:



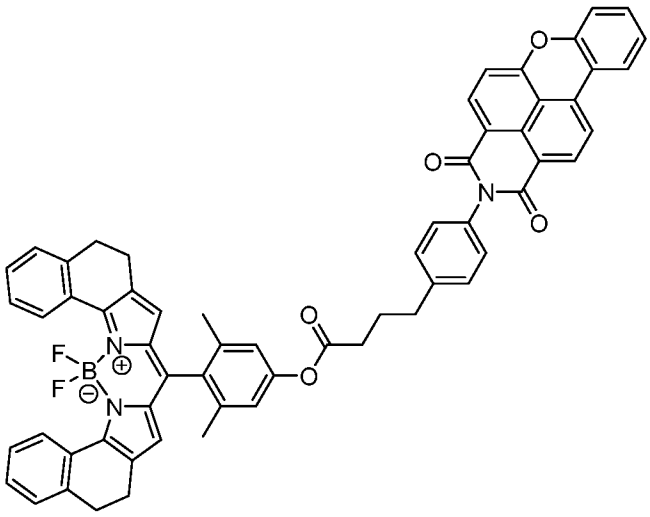
(PLC-1),



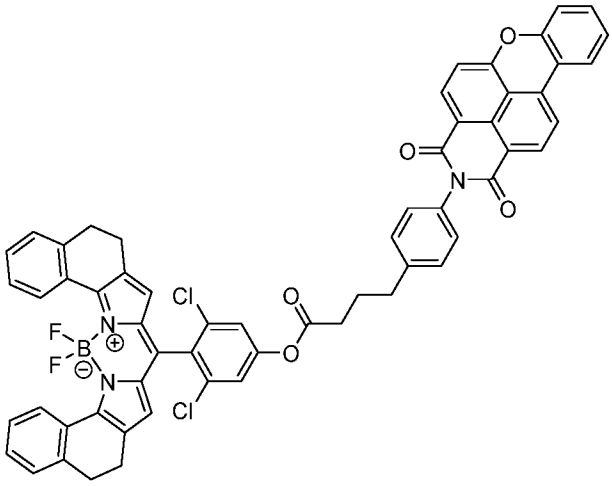
(PLC-2),



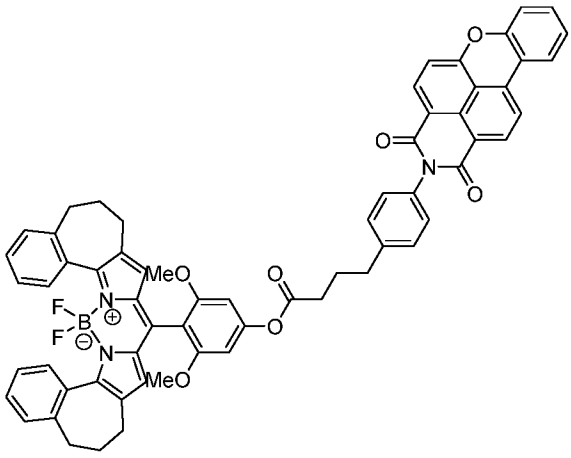
(PLC-3),



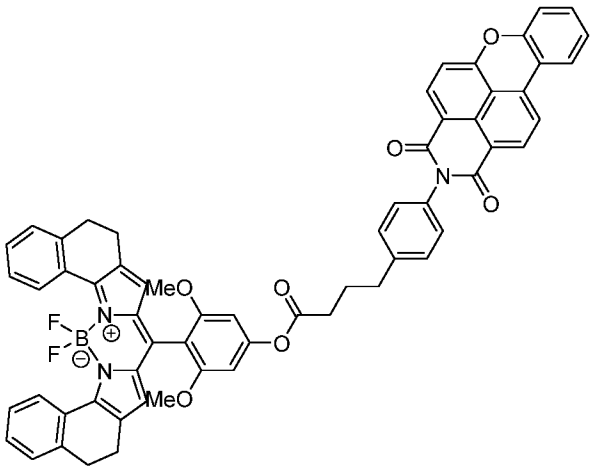
(PLC-4),



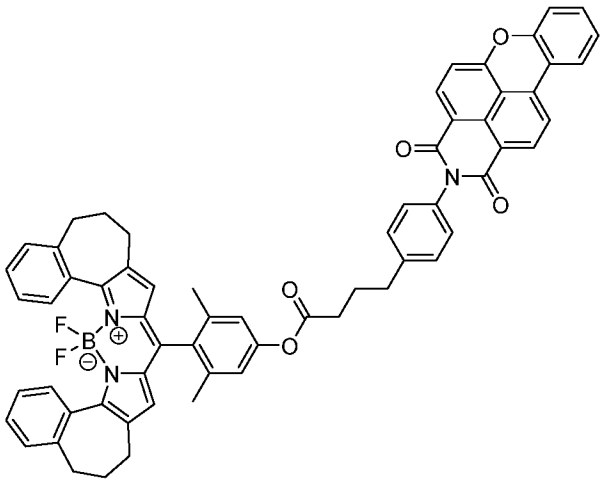
(PLC-5),



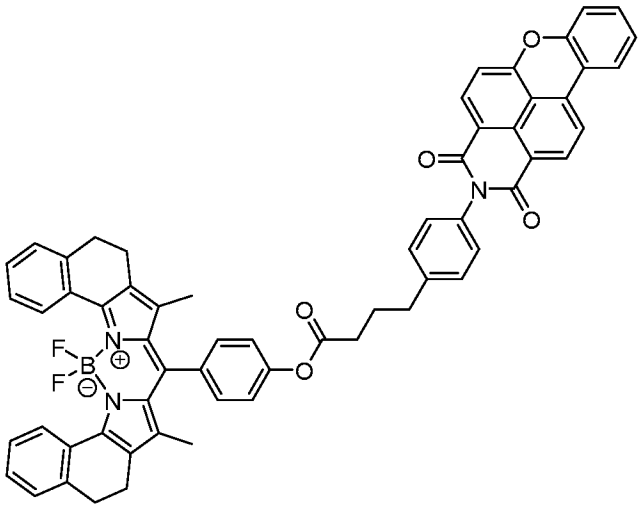
(PLC-6),



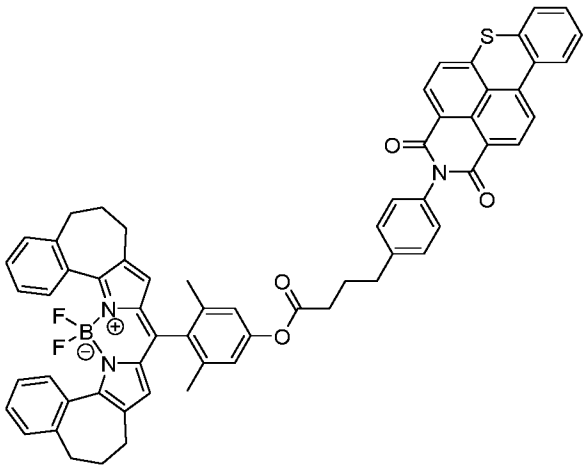
(PLC-7),



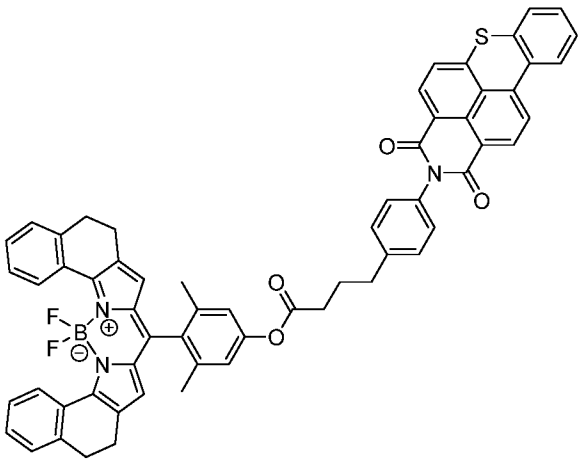
(PLC-8),



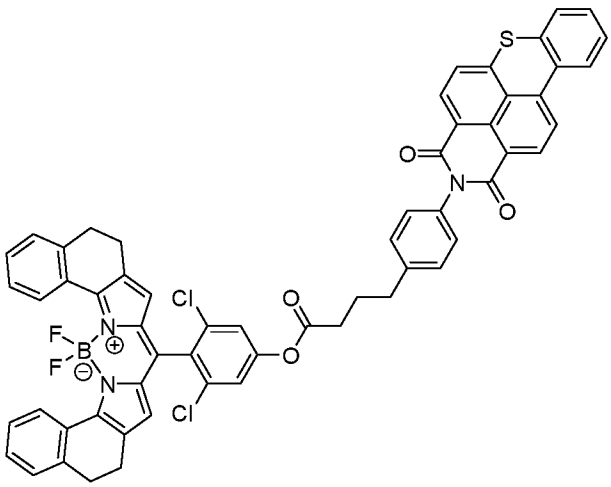
(PLC-9),



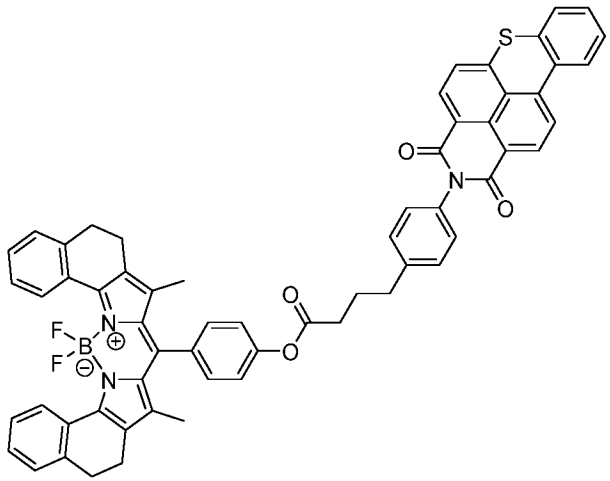
(PLC-10),



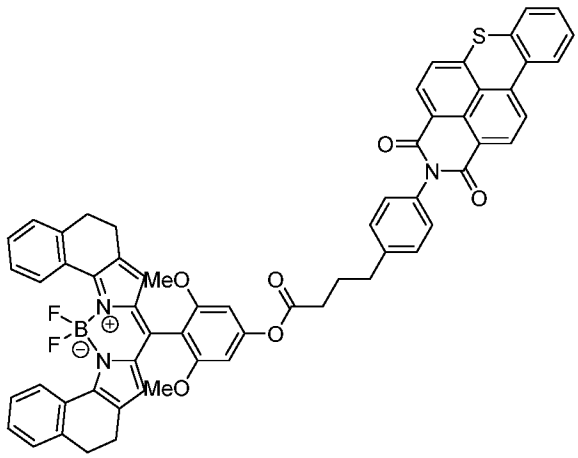
(PLC-11),



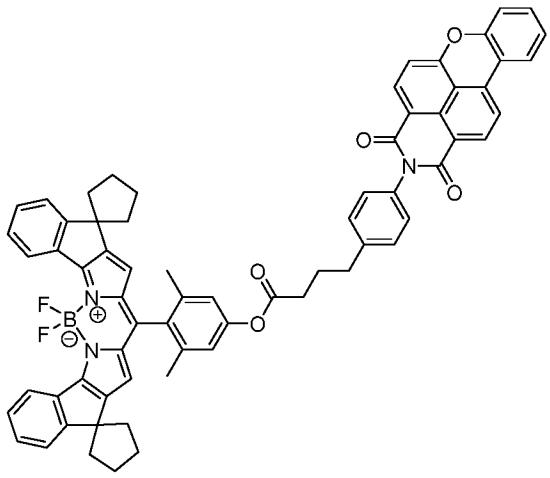
(PLC-12),



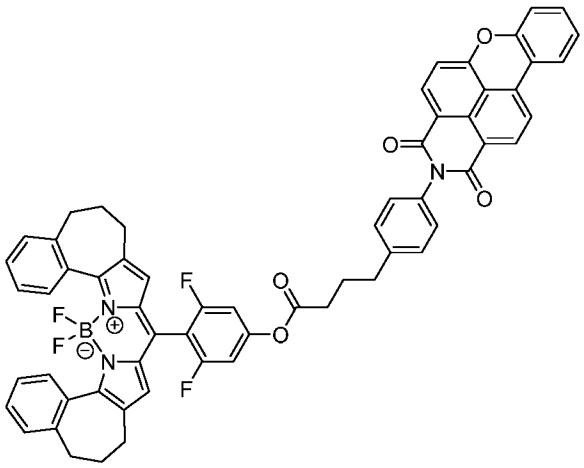
(PLC-13),



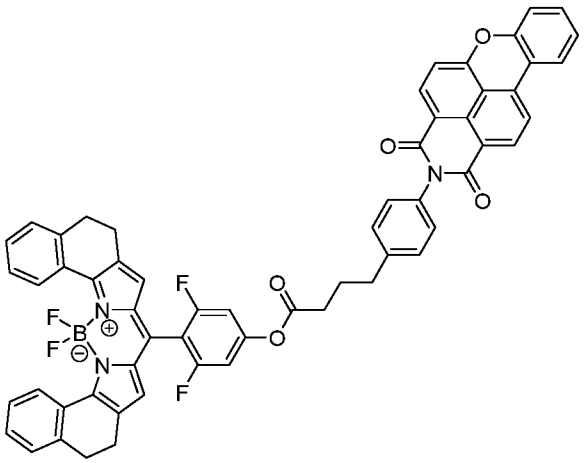
(PLC-14),



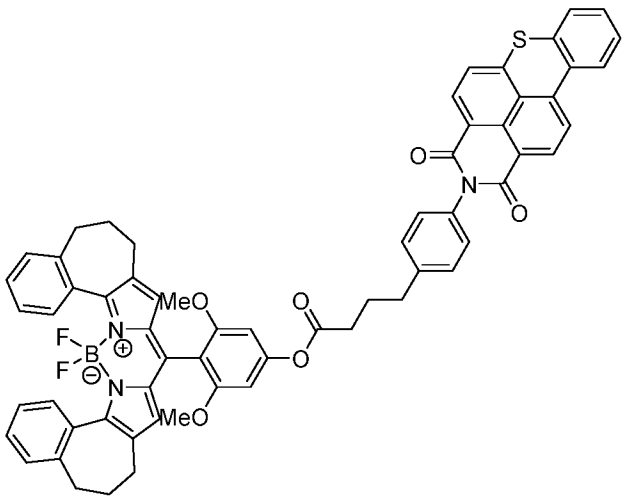
(PLC-15),



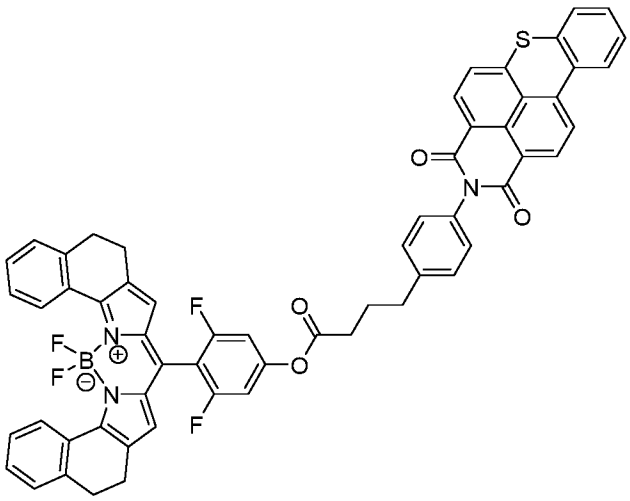
(PLC-16),



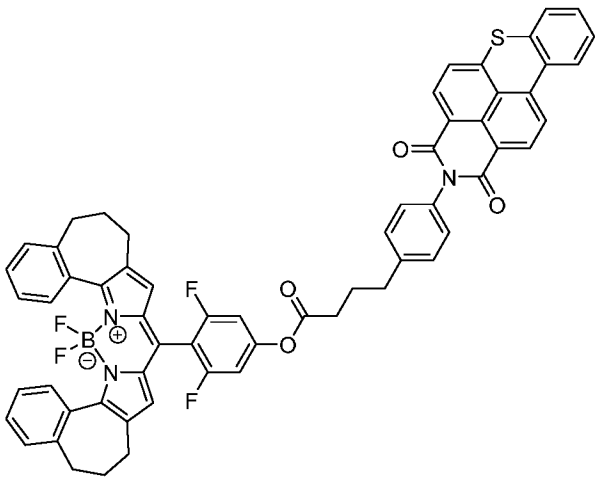
(PLC-17),



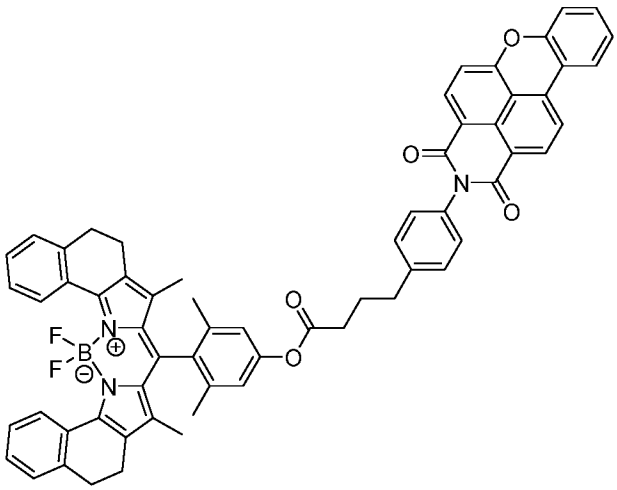
(PLC-18),



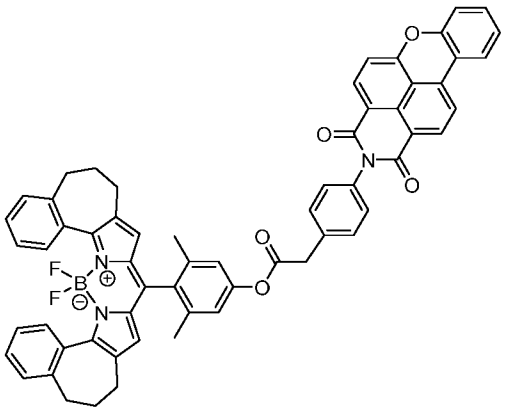
(PLC-19),



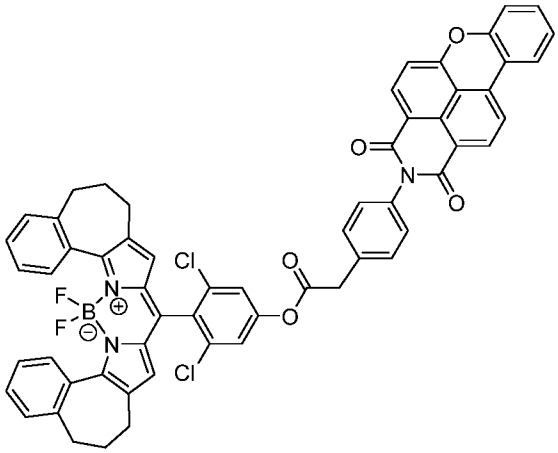
(PLC-20),



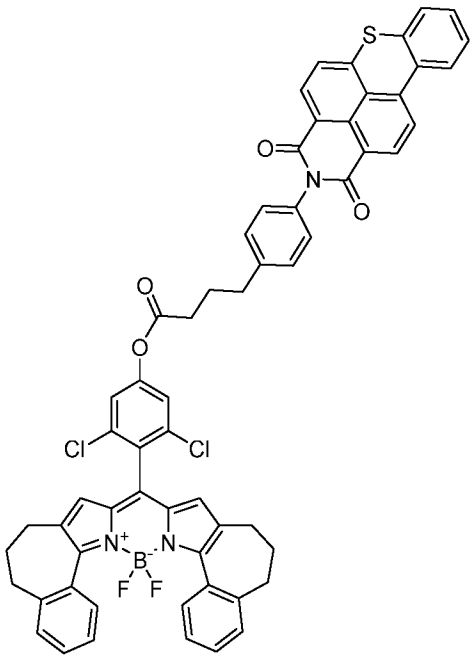
(PLC-21),



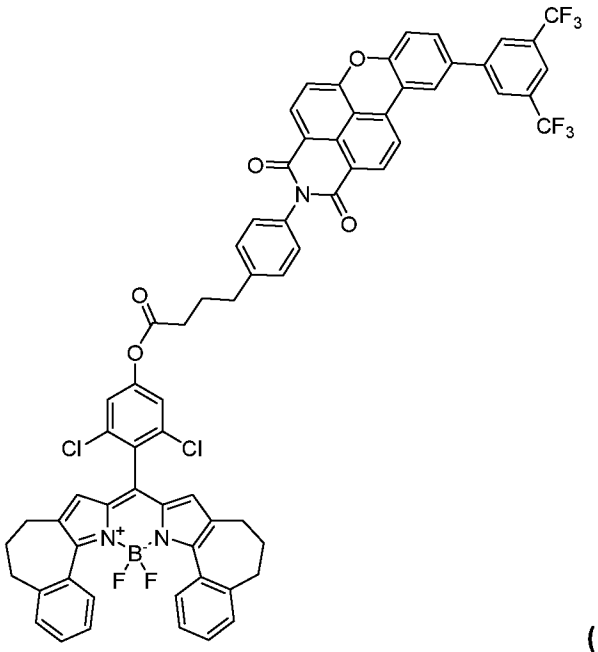
(PLC-22),



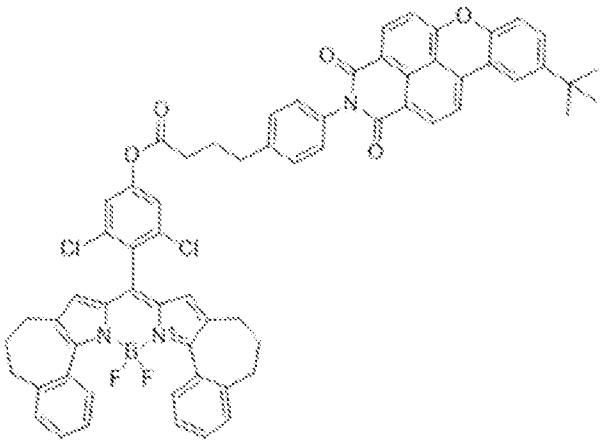
(PLC-23),



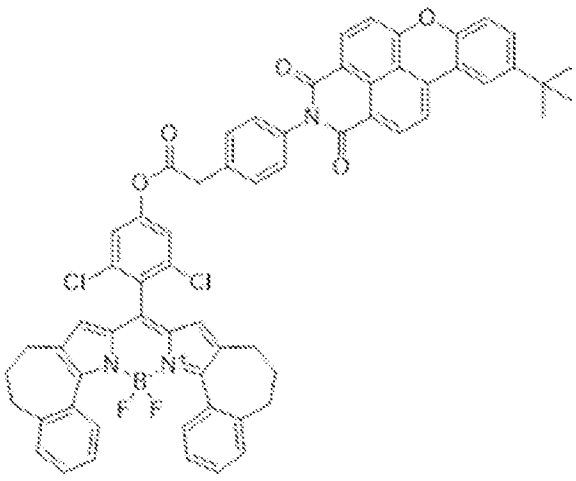
(PLC-24),



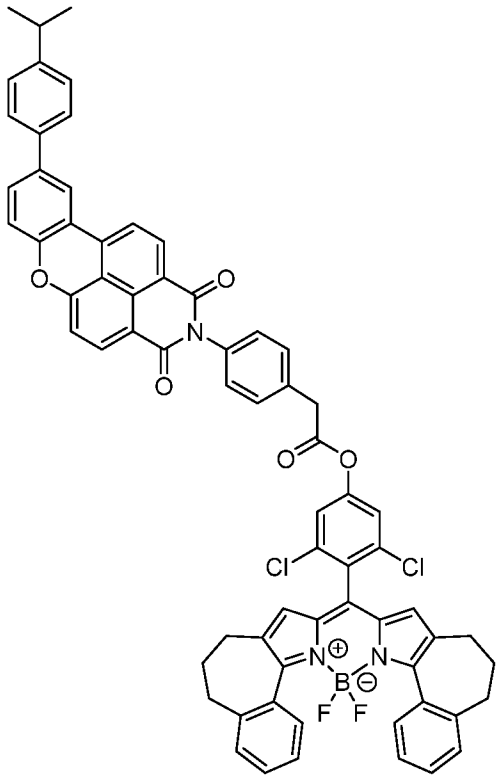
(PLC-25),



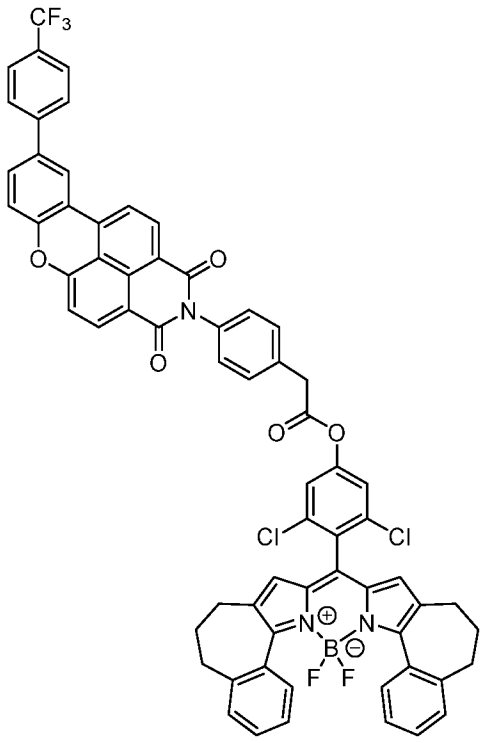
(PLC-26),



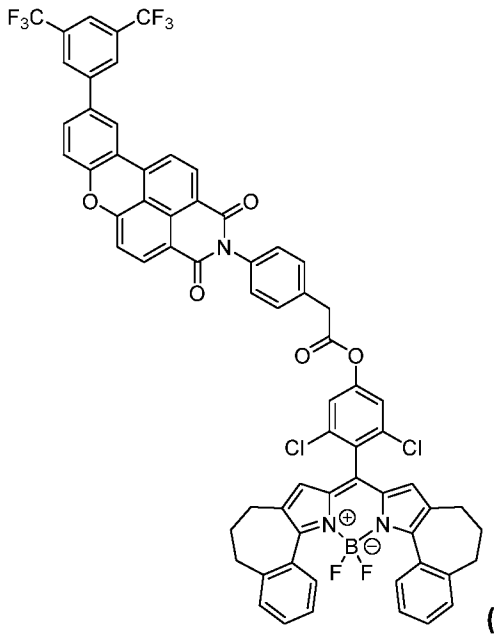
(PLC-27),



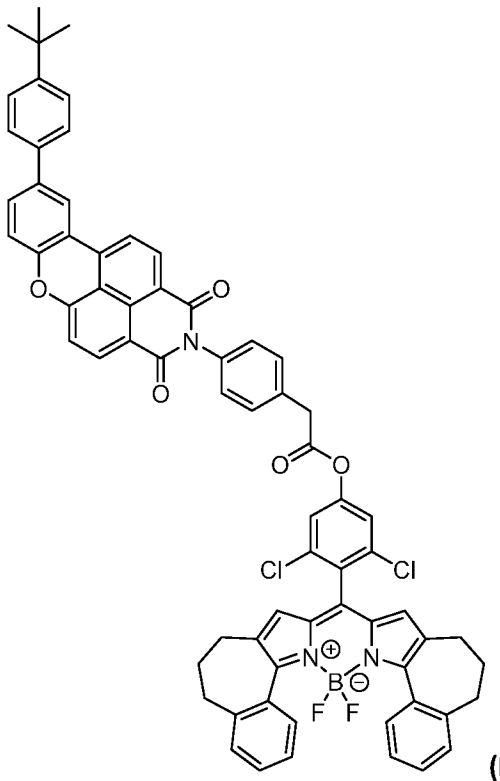
(PLC-28),



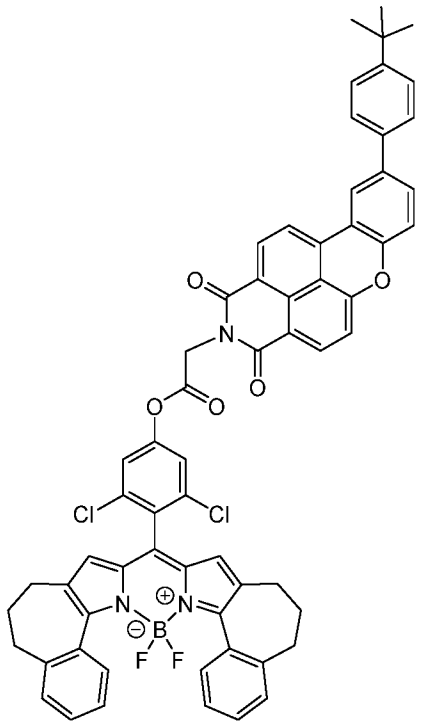
(PLC-29),



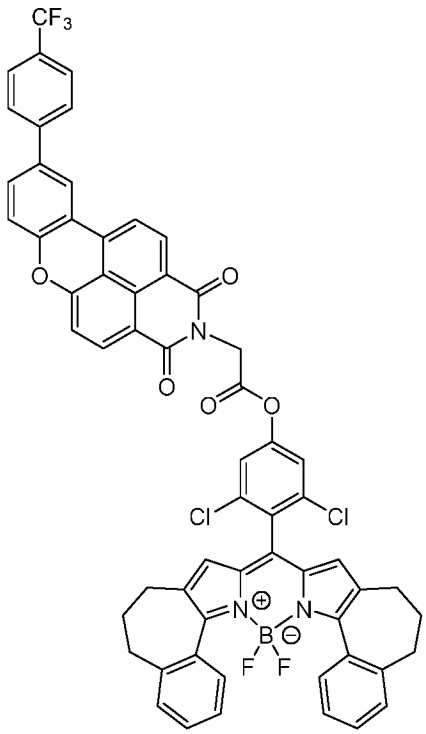
(PLC-30),



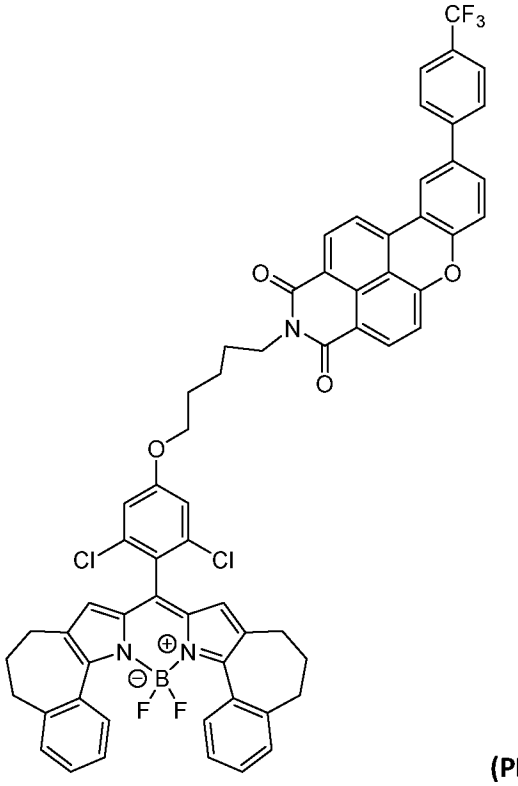
(PLC-31),



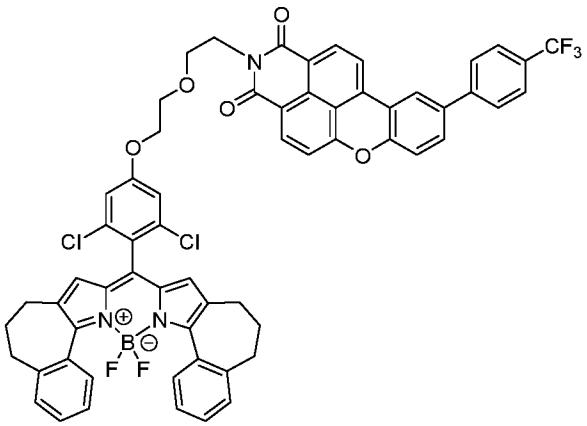
(PLC-32),



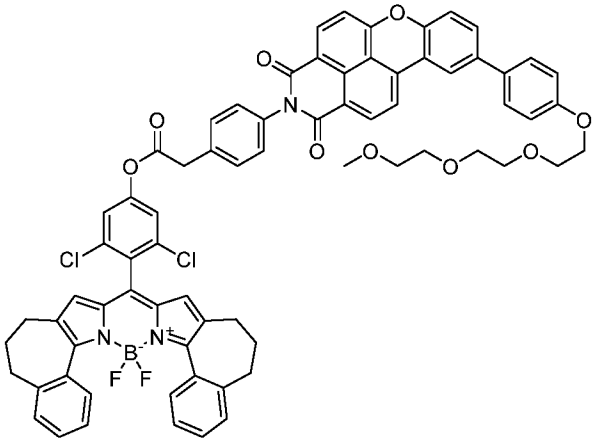
(PLC-33),



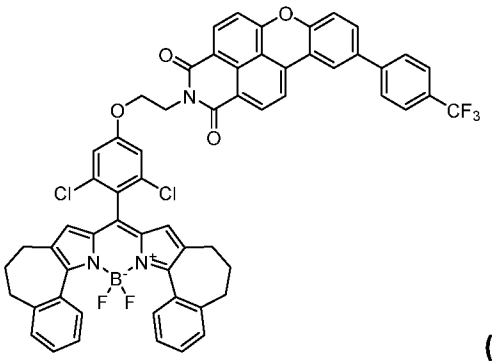
(PLC-34),



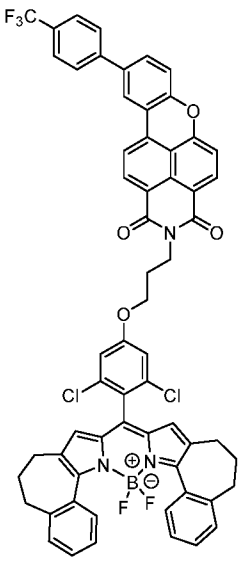
(PLC-35),



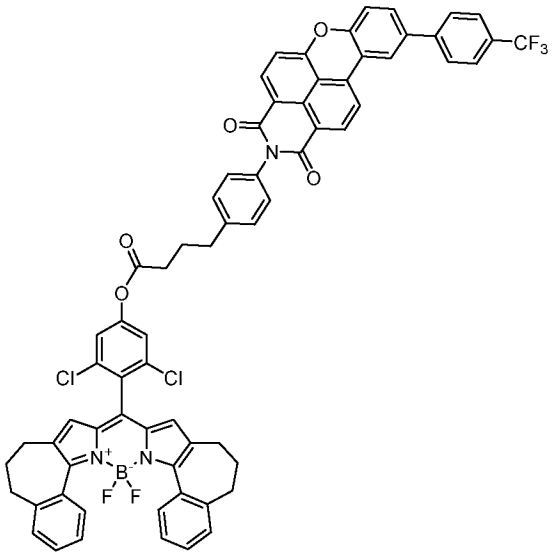
(PLC-36),



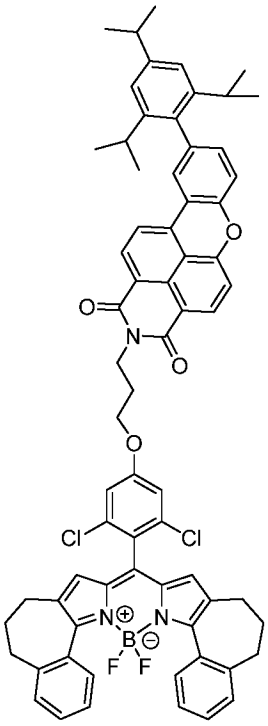
(PLC-37),



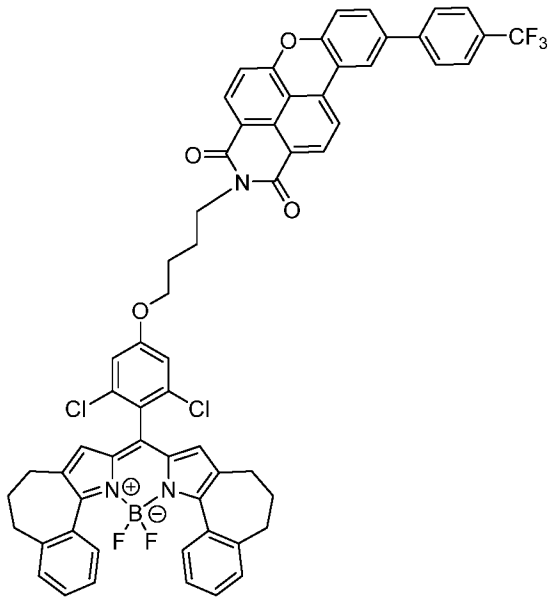
(PLC-38),



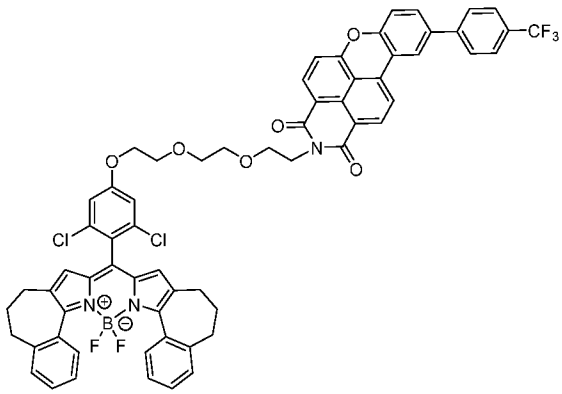
(PLC-39),



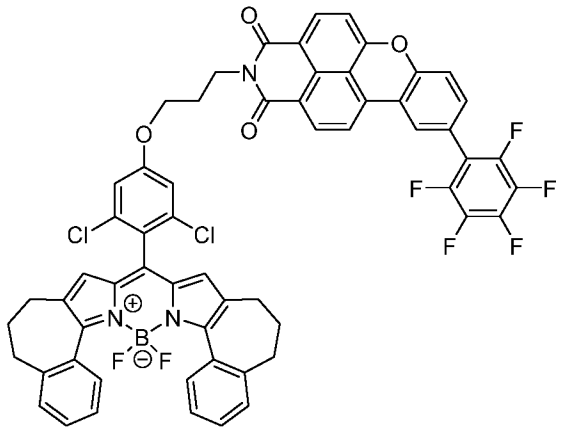
(PLC-40),



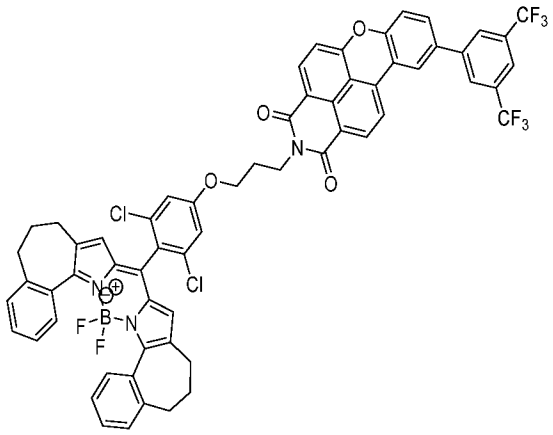
(PLC-41),



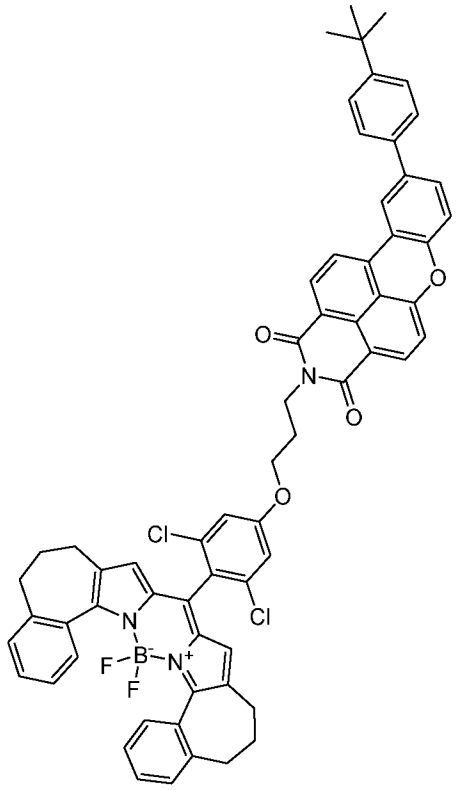
(PLC-42),



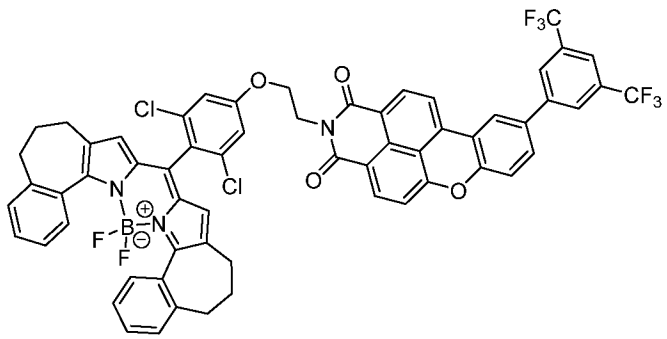
(PLC-43),



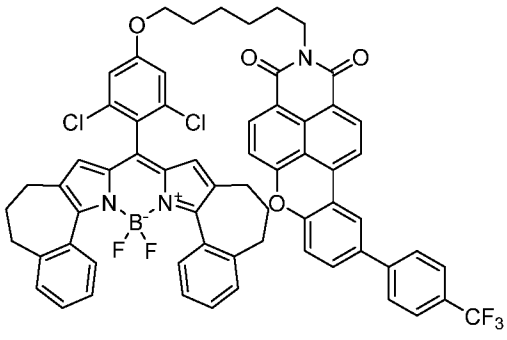
(PLC-44),



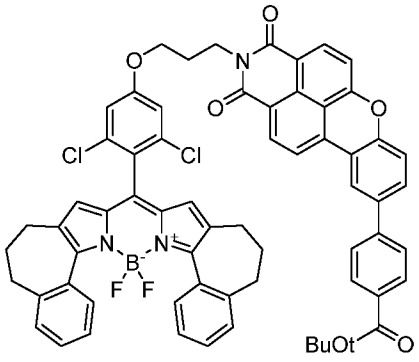
(PLC-45),



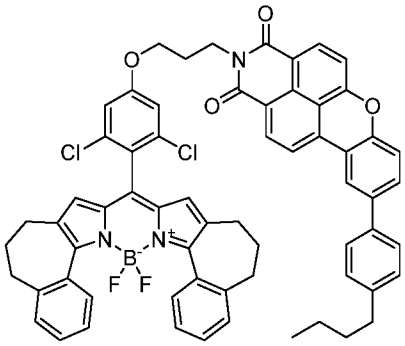
(PLC-46),



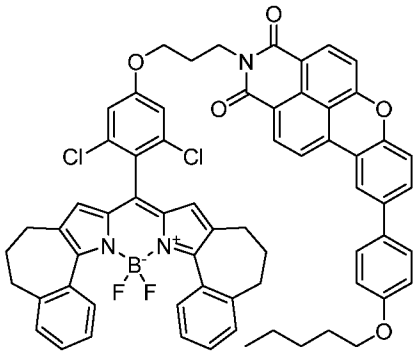
(PLC-47),



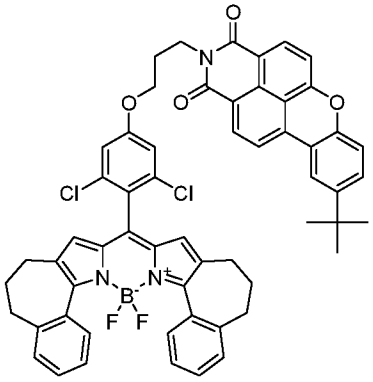
(PLC-48),



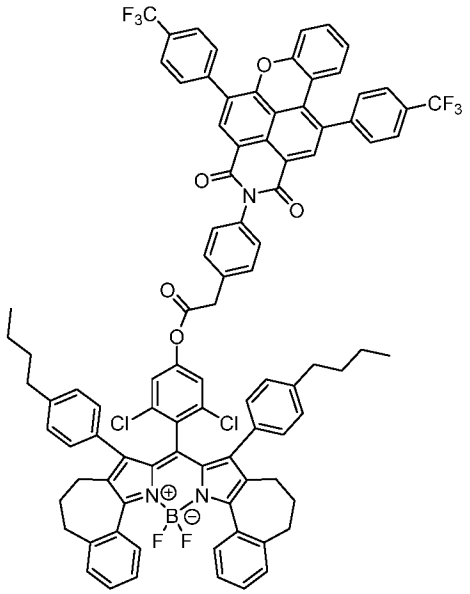
(PLC-49),



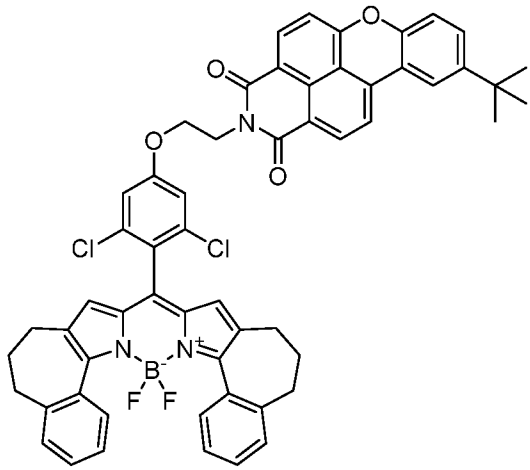
(PLC-50),



(PLC-51),



(PLC-52),



(PLC-53), or any combination thereof.

Embodiment 10.

A color conversion film comprising:

a transparent substrate layer;

a color conversion layer, wherein the color conversion layer includes a resin matrix; and

at least one photoluminescent complex, wherein the at least one photoluminescent complex is comprised of the photoluminescent complexes as in embodiments 1, 2, 3, 4, 5, 6, 7, 8, or 9 dispersed within the resin matrix.

Embodiment 11.

The color conversion film of embodiment 10, further comprising a singlet oxygen quencher.

Embodiment 12.

The color conversion film of embodiment 10, further comprising a radical scavenger.

Embodiment 13.

The color conversion film of embodiment 10, wherein the film has a thickness between 10 μm and 200 μm.

Embodiment 14.

The color conversion film of embodiment 10, wherein the film absorbs light in about 400 nm to about 480 nm wavelength range and emits light in about 590 nm to about 660 nm wavelength range.

Embodiment 15.

A method for preparing the color conversion film as in embodiments 10, 11, 12, 13, or 14, the method comprising:

dissolving the photoluminescent complexes as in embodiments 1, 2, 3, 4, 5, 6, 7, 8, or 9, and a binder resin within a solvent; and

applying the mixture to one of the transparent substrates opposing surfaces.

Embodiment 16.

A backlight unit including the color conversion film as in embodiments 10, 11, 12, 13, or 14.

Embodiment 17.

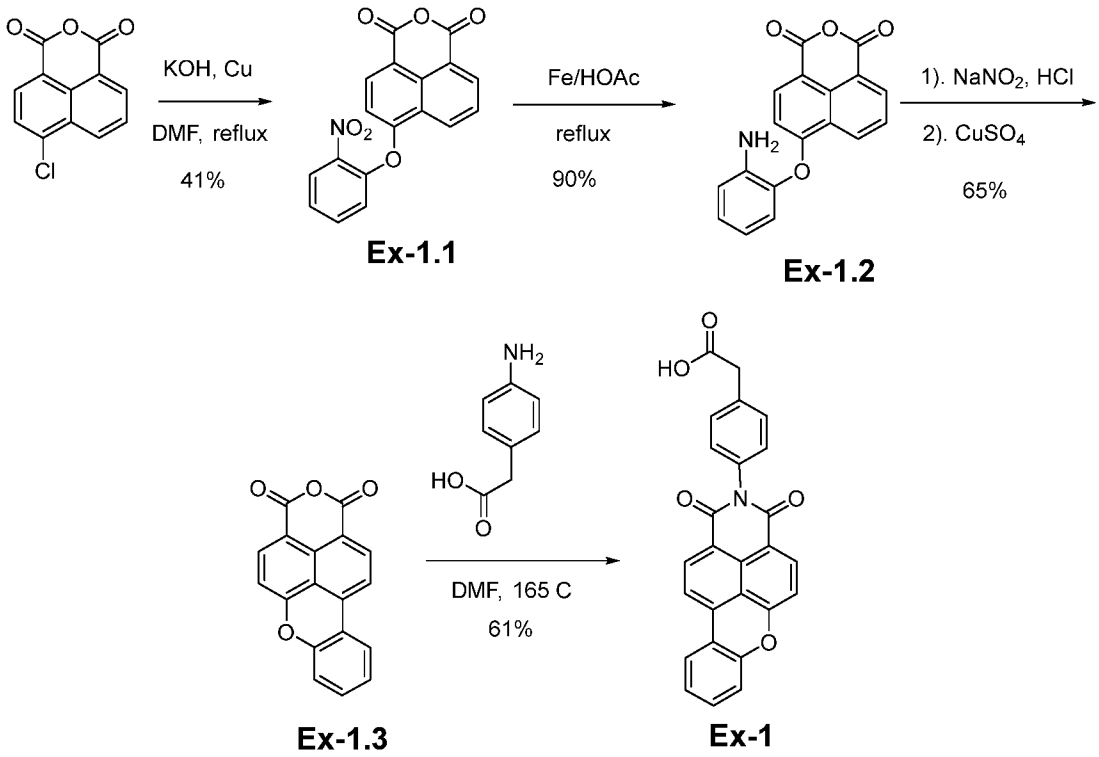
A display device including the backlight unit of embodiment 16.

EXAMPLES

It has been discovered that embodiments of the photoluminescent complexes described herein have improved performance as compared to other forms of dyes used in color conversion films. These benefits are further demonstrated by the following examples, which are intended to be illustrative of the disclosure but are not intended to limit the scope or underlying principles in anyway.

The following examples are synthesis procedures of many embodiments of the naphthalimide derivative (i.e., blue absorber intermediates) as described herein:

Example 1 (Ex-1):



Ex-1.1: A mixture of 2-nitrophenol (6.6 g, 48 mmol), KOH powder (2.4 g, 43 mmol) was mixed and stirred under vacuum for 30 min, then copper powder (0.4 g) was added, followed by 100 mL anhydrous DMF. The mixture was stirred for 5 min, then 4-chloronaphthalic anhydride (5.1g, 22 mmol) was added. The whole was degassed then heated at reflux for 1.5

hr. After cooled to room temperature, 100mL 20% hydrochloride acid was added dropwise into the resulted reaction mixture, which was allowed to sit for 2 hrs. The precipitate was collected by filtration, then was dried under vacuum overnight to give yellow brown solid (4.6 g). It was further purified by stirred in refluxed acetic acid (50 mL) for 1 hr, then cooled to room temperature. Filtration and dried in air gave a yellow solid (3.0 g, in 41% yield). Confirmed by LCMS (APCI): calculated for $C_{18}H_{10}NO_6$ (M+H): 336.0; Found: 336. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.72 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.50 (d, *J* = 8.2 Hz, 1H), 8.19 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.90 (dd, *J* = 8.5, 7.3 Hz, 1H), 7.79 (td, *J* = 7.9, 1.7 Hz, 1H), 7.54 (td, *J* = 8.0, 1.3 Hz, 1H), 7.39 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H).

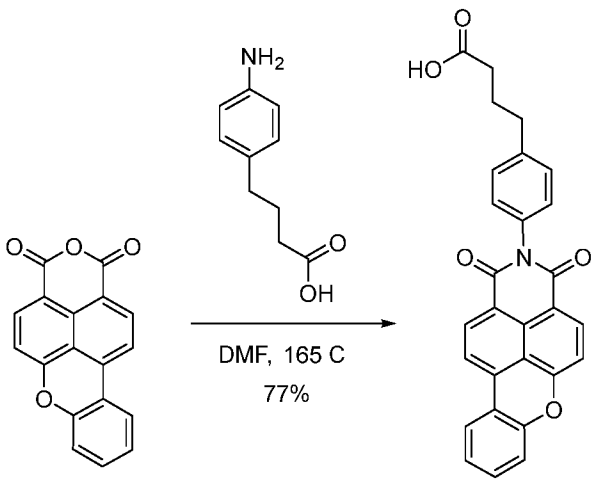
Ex-1.2: A mixture of 4-(2-nitrophenoxyl)-1,8-naphthalic anhydride (2.0 g, 6 mmol) and iron powder (<10 um, 0.9 1g, 16 mmol) in acetic acid (75 mL) was heated to reflux for 30 min. The resulting solution was poured into water (220 mL). The resulted precipitate was collected by filtration, then washed with water and dried thoroughly in air, then placed under vacuum to afford a yellow solid (1.65g, in 90% yield). Confirmed by LCMS (APCI): calculated for $C_{18}H_{12}NO_4$ (M+H): 306.1; Found: 306.

Ex-1.3: Compound 4-(2-aminophnoxy)-1,8-naphthalic anhydride (1.5 g, 4.9 mmol), was dispersed in acetic acid (35 mL) and cooled to 0 ºC. While being stirred, precooled hydrochloric acid (3 mL, 37 mmol) was added, then sodium nitrite solution (3.29 g, 46 mmol) in 12 mL water was added dropwise at 0 ºC. The whole was stirred for one hour at 0 ºC, then was transferred into additional funnel, and dropped into a refluxed copper sulfate solution (5.08 g, 20 mmol, in 50 mL water) over one hour period. After cooled to room temperature, the precipitate was collected by filtration, washed with water and acetone, then dried in air, then dried in vacuum to give a yellow solid (0.92 g, in 65% yield). Confirmed by LCMS (APCI): calculated for $C_{18}H_8O_4$ (M-): 288.0; Found: 288. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (dd, *J* = 17.1, 8.1 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H).

Ex-1: A mixture of 1H,3H-isochromeno[6,5,4-mna]xanthene-1,3-dione (100mg, 0.347 mmol), 2-(4-aminophenyl)acetic acid (135mg, 0.9 mmol) in 5mL DMF was heated at 165 ºC for 2 hrs in microwave reactor. After cooled to 50 ºC, to the resulted solution, 1.5 mL acetone was added dropwise to form yellow precipitate, which was collected by filtration and washed with acetone, dried in air to give a yellow solid (88mg, in 61% yield). Confirmed by LCMS

(APCI): calculated for $C_{26}H_{15}NO_5$ (M-): 421.1; Found: 421. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, J = 45.1 Hz, 4H), 7.67 – 7.00 (m, 8H), 3.58 (s, 2H).

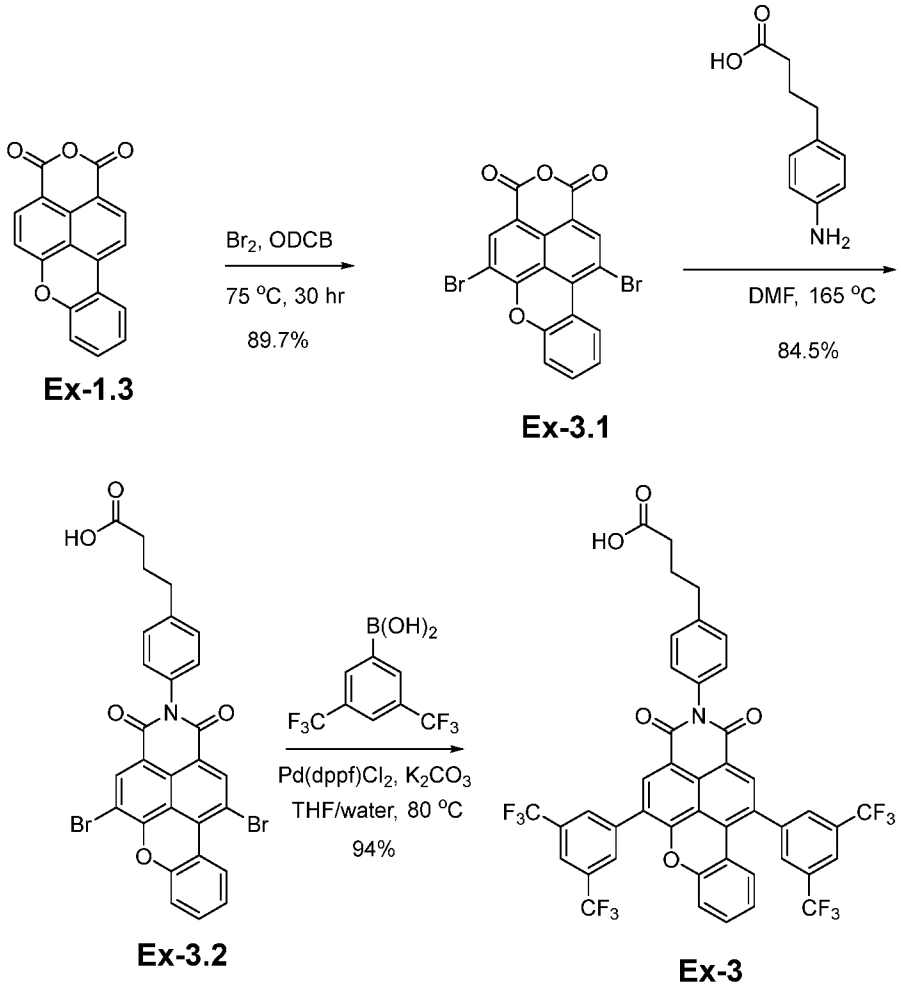
Example 2 (Ex-2):



Ex-1.3 **Ex-2**

Ex-2: A mixture of 1H,3H-isochromeno[6,5,4-mna]xanthene-1,3-dione (100 mg, 0.347 mmol), 4-(4-aminophenyl)butanoic acid (125 mg, 0.7 mmol) in 5 mL DMF was heated at 165 ºC for 2.5 hrs in microwave reactor. To the mixture, 15 mL acetone was added, the resulted precipitate was collected by filtration and dried in air, then dried in vacuum oven at 100 ºC for one hour to give a yellow solid (120 mg, in 77% yield). Confirmed by LCMS (APCI): calculated for $C_{28}H_{19}NO_5$ (M-): 449.1; Found: 449. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.38 (d, J = 41.6 Hz, 4H), 7.81 – 6.97 (m, 8H), 2.69 – 2.64 (m, 2H), 2.26 (t, J = 7.2 Hz, 2H), 1.87 (p, J = 7.2 Hz, 2H).

Example 3 (Ex-3):



Ex-1.3 Ex-3.1 Ex-3.2 Ex-3

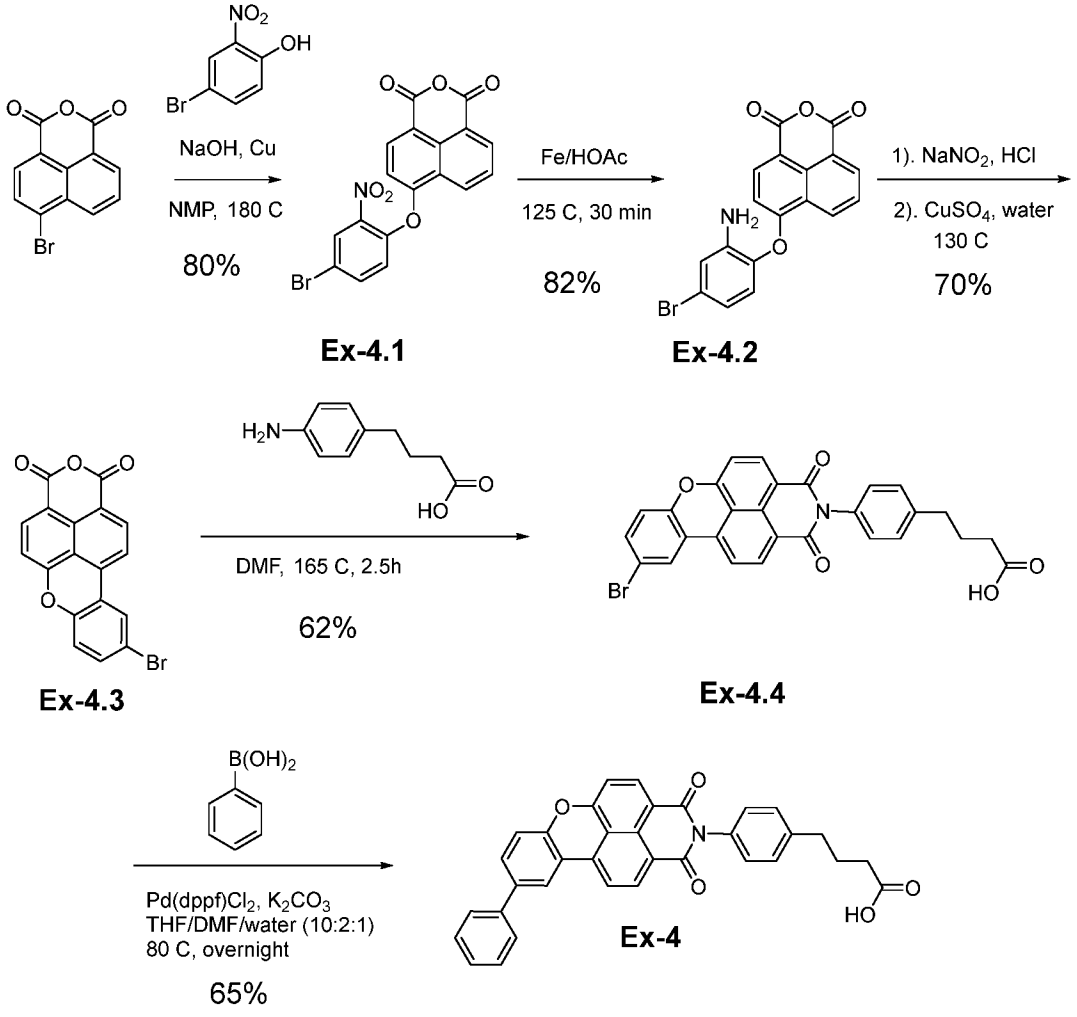
Ex-3.1: To a mixture of compound **Ex-1.3** (290mg, 1.0mmol) in ortho-dichlorobenzene (30mL), was added bromine (1.98g, 12 mmol). The mixture was heated at 75 ºC for 30 hrs. After cooled to room temperature, the solid was collected by filtration, dried in air to give 290mg yellow solid as desired product. The filtrate was loaded on silica gel and purified by flash chromatography using eluents of hexanes/dichloromethane (50% → 100% dichloromethane). The desired fraction was collected and removal of solvents to give 110mg yellow solid. Total product of 400 mg was obtained in 89.7% yield. LCMS (APCI-): calculated for $C_{18}H_6Br_2O_4$: 443.9; found 444. ^{1}H NMR (400 MHz, d_2-TCE) δ 9.40 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.71 (s, 1H), 8.67 (s, 1H), 7.60 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 1H), 7.48 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.38 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H).

Ex-3.2: A mixture of compound **Ex-3.1** (190mg, 0.426mmol), 4-(4-aminophenyl)butanoic acid (180 mg, 0.64 mmol), 4-(N,N-dimethylamino)-pyridine (4 mg) in

anhydrous N,N-dimethylformamide (DMF) (4mL) was heated at 165 ºC for 2.5 hrs. After the mixture was cooled to room temperature and let stand overnight, the solid was collected by filtration, which was washed with acetone and dried in vacuum oven at 90 ºC for 1hr to give a yellow solid (220mg, in 84.5% yield). LCMS (APCI-): calculated for $C_{28}H_{17}Br_2NO_5$: 604.95; found: 605. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.42 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.57 (d, *J* = 4.6 Hz, 2H), 7.83 – 7.68 (m, 1H), 7.63 – 7.44 (m, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.16 (m, 2H), 2.67 (dd, *J* = 4.8, 2.8 Hz, 2H), 2.28 (t, *J* = 7.4 Hz, 2H), 1.95 – 1.80 (m, 2H).

Ex-3: A mixture of compound **Ex-3.2** (100 mg, 0.165 mmol), (3,5-bis(trifluoromethyl)phenyl)boronic acid (170 mg, 0.66 mmol), Pd(dppf)Cl2 (20 mg, 0.027 mmol) and potassium carbonate (138 mg, 1 mmol) in THF/water (5 mL/0.5 mL) was degassed then heated at 80 ºC for 2hrs. After cooled to room temperature, the precipitate was collected by filtration, washed with acetone, then dried in vacuum oven at 90 ºC for 2hrs. A yellow solid was obtained (142mg, in 94% yield). LCMS (APCI-): calculated for $C_{44}H_{23}F_{12}NO_5$: 873.14; found: 873. ^{1}H NMR (400 MHz, d_2-TCE) δ 8.65 (s, 1H), 8.40 (s, 1H), 8.17 (s, 2H), 7.96 (d, *J* = 19.3 Hz, 4H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 3H), 6.90 (d, *J* = 6.3 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.38 (t, *J* = 7.4 Hz, 2H), 2.03 – 1.93 (m, 2H).

Example 4 (Ex-4):



Ex-4.1: A mixture of 4-bromo-1,8-naphthalic anhydride (2.77 g, 10 mmol), 4-bromo-2-nitrophenol (3.27 g, 15 mmol) was degassed under vacuum for 30 min, then anhydrous NMP (50 mL) was added, followed by addition of sodium hydroxide (0.2 g, 5 mmol) and copper powder (0.318 g, 5 mmol). The mixture was sparged with argon for 20 min, then heated at 180 ºC overnight under argon atmosphere. After the mixture is cooled down to room temperature, to the solution, 50 mL 20% hydrochloride acid aqueous solution was added dropwise, then added 50 mL water. The resulted mixture was allowed to stand for 3 hrs, then filtered to collect the precipitate, which was dried in vacuum to afford 4.6 g crude product. The crude product was dispersed in 30 mL acetone and stirred overnight at room temperature to dissolve the impurities. Filtration and dried in vacuum gave a brown yellow solid as desired product (3.3 g, in 80% yield). LCMS (APCI+): calculated for $C_{18}H_9BrNO_6$ (M+H) = 413.95; Found: 414. ^{1}H NMR (400 MHz, TCE-d2) δ 8.70 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.63 (dd, *J* = 7.3, 1.2 Hz, 1H),

8.41 (d, *J* = 8.3 Hz, 1H), 8.24 (d, *J* = 2.4 Hz, 1H), 7.89 – 7.79 (m, 2H), 7.20 (d, *J* = 8.7 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H).

Ex-4.2: A mixture of compound **Ex-4.1** (1.5 g, 3.6 mmol), iron powder (0.60 g, 10.8 mmol) in acetic acid (50 mL) was heated at 125 ºC for 30 min. After cooled to room temperature, to the mixture, 100 mL water was added while stirring. The resulted mixture was filtered and washed with water, dried in air and vacuum to give a solid (1.35 g, in 82% yield). LCMS (APCI-): calculated for $C_{18}H_{10}BrNO_4$ = 382.98; Found: 383. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 – 8.26 (m, 3H), 7.96 (s, 1H), 6.93 (dd, *J* = 85.2, 36.5 Hz, 4H), 5.54 (s, 2H).

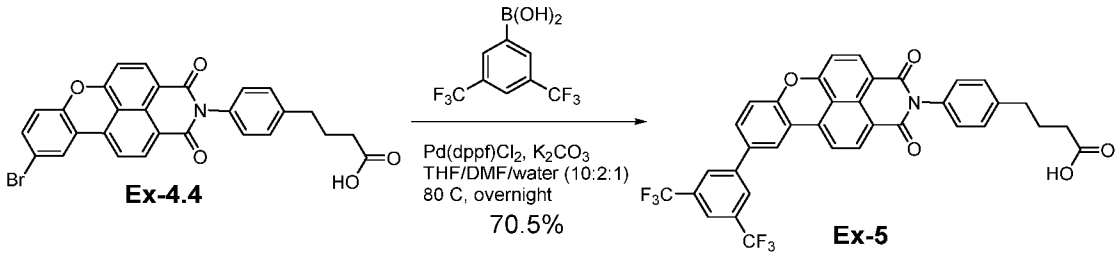
Ex-4.3: Compound **Ex-4.2** (2.65 g, 6. 9mmol), was dispersed in acetic acid (50 mL)/water (10 mL) and cooled to 0 ºC. While being stirred, precooled hydrochloric acid (2.8 mL, 34.5 mmol) was added, then sodium nitrite solution (3.57g, 52 mmol) in 15 mL water was added dropwise at 0 ºC. The whole was stirred for one hour at 0 ºC, then was transferred into additional funnel, and dropped into a copper sulfate solution (12g, 47 mmol, in 140 mL water) over one hour period at 130 ºC. After cooled to room temperature, the precipitate was collected by filtration, washed with water (100 mL × 3), then stirred in 50 mL acetone at 40 ºC for 30 min. Filtration, dried in air then in vacuum gave a brown yellow solid (1.76 g, in 70% yield). LCMS (APCI+): calculated for $C_{18}H_8BrO_4$ (M+H) = 366.95; Found: 367. ^{1}H NMR (400 MHz, d2-TCE) δ 8.51 (dd, *J* = 12.3, 8.1 Hz, 2H), 8.12 (d, *J* = 2.3 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.60 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H).

Ex-4.4: A mixture of compound **Ex-4.3** (550 mg, 1.5 mmol), 4-(4-aminophenyl)butanoic acid (537 mg, 3 mmol) and DMAP (12.2 mg, 0.1 mmol) in 10 mL DMF was heated at 165 ºC for 2.5 hrs in microwave reactor. The resulted solution was dropped into 50 mL acetone while stirring. Precipitate formed and was filtered and dried in vacuum oven at 60 ºC for overnight to afford the desired product as brown yellow solid (0.49 g, in 62% yield). LCMS (APCI-): calculated for $C_{28}H_{18}BrNO_5$ = 527.04; Found: 527. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.54 (d, *J* = 2.3 Hz, 1H), 8.41 (dd, *J* = 9.9, 8.0 Hz, 2H), 8.33 (d, *J* = 7.9 Hz, 1H), 7.71 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.39 (dd, *J* = 8.6, 4.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 2.63 – 2.55 (m, 2H), 2.27 – 2.15 (m, 2H), 1.87 – 1.73 (m, 2H).

Ex-4: A mixture of compound **Ex-4.4** (385 mg, 0.729 mmol), phenylboronic acid (178 mg, 1.45 mmol), Pd(dppf)Cl_2 (36 mg, 0.05 mmol), potassium carbonate (276 mg, 2 mmol) in

cosolvents of THF/DMF/water (20L/4mL/2mL) was degassed, then heated at 80 ºC for overnight. The mixture was worked up with 200 mL ethyl acetate and 50 mL 0.6 N hydrochloric acid aqueous solution. The aqueous phase was extracted with ethyl acetate (100 mL x 2). The organic phase was collected and washed with brine (100 mL x 2), dried over sodium sulfate, then dry loaded on silica gel and purified by flash chromatography using eluents of DCM/EA (0% to 40% EA with 0.1% TFA). The main desired fraction was collected, removal of solvents under reduced pressure gave a yellow solid (250 mg, in 65% yield). LCMS (APCI-): calculated for $C_{34}H_{23}NO_5$ = 525.16; Found: 525. ^{1}H NMR (400 MHz, TCE-d_2) δ 8.55 (dd, *J* = 19.5, 8.1 Hz, 2H), 8.20 (d, *J* = 2.1 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.72 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.51 – 7.28 (m, 7H), 7.17 (d, *J* = 8.2 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 1.99 (q, *J* = 7.2 Hz, 2H).

Example 5 (Ex-5)

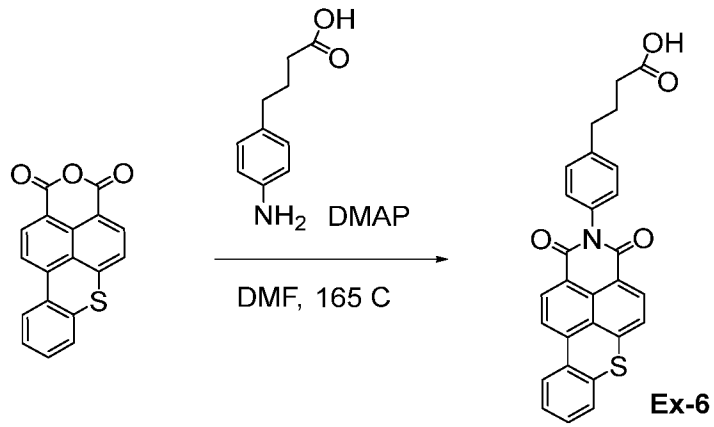


Ex-4.4 **Ex-5**

Ex-5: A mixture of compound **Ex-4.4** (385 mg, 0.729 mmol), 3,5-bis-(trifluoromethyl)phenylboronic acid (374 mg, 1.45 mmol), Pd(dppf)Cl_2 (36 mg, 0.05 mmol), potassium carbonate (276 mg, 2 mmol) in cosolvents of THF/DMF/water (20L/4mL/2mL) was degassed, then heated at 80 ºC for overnight. The mixture was worked up with 200 mL ethyl acetate and 50 mL 0.6 N hydrochloric acid aqueous solution. The aqueous phase was extracted with ethyl acetate (100 mL x 2). The organic phase was collected and washed with brine (100 mL x 2), dried over sodium sulfate, then dry loaded on silica gel and purified by flash chromatography using eluents of DCM/EA (0% to 40% EA with 0.1% TFA). The main desired fraction was collected, removal of solvents under reduced pressure gave a yellow solid (340 mg, in 70.5% yield). LCMS (APCI-): calculated for $C_{36}H_{21}F_6NO_5$ = 661.13; Found: 661. ^{1}H NMR (400 MHz, d_2-TCE) δ 8.57 (dd, *J* = 19.2, 8.1 Hz, 2H), 8.18 (d, *J* = 2.2 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.03 – 7.98 (m, 2H), 7.87 (s, 1H), 7.72 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.48 (d, *J* = 8.6 Hz,

1H), 7.33 (d, *J* = 8.3 Hz, 3H), 7.21 – 7.12 (m, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 2.04 – 1.97 (m, 2H).

Example 6 (Ex-6)

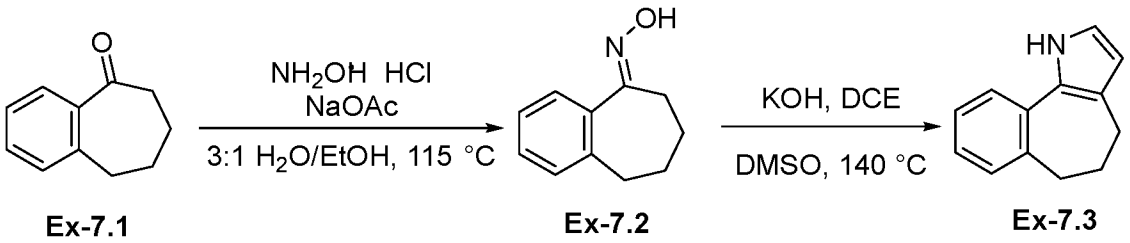


Ex-6

Ex-6: A mixture of 1H,3H-thioxantheno[2,1,9-def]isochromene-1,3-dione (458 mg, 1.5 mmol), 4-(4-aminophenyl)butanoic acid (537 mg, 3 mmol) and DMAP (14mg, 0.11 mmol) in 10 mL DMF was heated at 165 ºC for 2.5 hrs in microwave reactor. The resulted solution was dropped into 60 mL acetone while stirring. Orange precipitate formed, and was filtered and washed with diethyl ether, dried in air to give an orange solid (546 mg), which was further dried in vacuum oven at 100 ºC for 3 hrs to afford the desired product as orange solid (500 mg, in 71.7% yield). Confirmed by LCMS (APCI-): calculated for $C_{28}H_{19}NO_4S$ = 465.10; Found: 465. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.55 (d, *J* = 8.4 Hz, 1H), 8.52 – 8.46 (m, 2H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.52 (tt, *J* = 7.2, 5.5 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.30 – 7.23 (m, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.29 (t, *J* = 7.3 Hz, 2H), 1.88 (p, *J* = 7.5 Hz, 2H).

The following examples are synthesis procedures of many embodiments of pyrrole intermediates as described herein:

Example 7 (Ex-7.3):



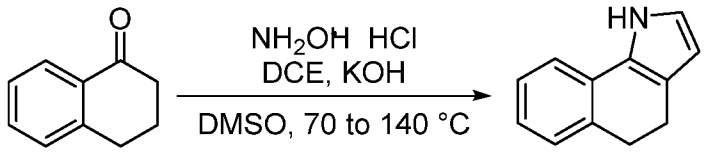
Ex-7.1 Ex-7.2 Ex-7.3

Ex-7.2 – General Synthesis Procedure of compound Ex-7.2, (E)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one oxime: A mixture of compound **Ex-7.1** (10.0 g, 62.0 mmol), $NH_2OH•HCl$ (6.50 g, 93.0 mmol) and NaOAc (12.7 g, 155.0 mmol) in EtOH/H_2O (45 mL/150 mL) was placed into a 500 mL two-neck round-bottom flask with a reflux condenser. The solution was heated up to 115 ºC to reflux and was kept at this temperature for 1 hour. TLC (50% EtOAc in Hexane) showed the reaction was completed. After cooling down to 0 ºC and filtration, compound **Ex-7.2** was obtained as a pale white solid for next step without further purification, quantitative yield. MS (APCI): calculated for $C_{11}H_{14}NO$ ($[M+H]^+$) = 176 found: 176. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (bs, 1H), 7.39 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.30 (td, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.23 (td, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 2.74 (m, 4H), 1.78 (ddd, *J* = 13.2 Hz, 6.0 Hz, 6.0 Hz, 2H), 1.65 (ddd, *J* = 12.4 Hz, 6.0 Hz, 6.0 Hz, 2H).

Ex-7.3 – General Synthesis Procedure of compound Ex-7.3, 1,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-b]pyrrole: A solution of compound **Ex-7.2** (8.8 g, 50.0 mmol) and KOH (10.1 g, 180.0 mmol) in DMSO (50 mL) was placed into a 250 mL two-neck round-bottom flask with a reflux condenser. The solution was degassed at room temperature and heated up to 140 ºC. To this solution, another solution of DCE (12.4 g, 125 mmol) in DMSO (50 mL) was added dropwise through syringe pump over 5.5 hours. After the completion of addition of the DCE solution, the reaction was cooled down to room temperature, followed by poured into saturated NH_4Cl solution (500 mL). EtOAc (500 mL*3) was used to extract the desired product from the workup solution. The combined organic layers were dried by anhydrous Na_2SO_4, concentrated under vacuum and purified by silica gel flash chromatography to provide compound **Ex-7.3** as a pale white solid using DCM in hexane (0-30%) as an eluant, 4.6 g, 50% yield. MS (APCI): calculated for $C_{13}H_{14}N$ ($[M+H]^+$) = 184 found: 184. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (bs, 1H), 7.34 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.22 (td, *J* =

7.6 Hz, 1.6 Hz, 1H), 7.16 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.09 (td, *J* = 7.6 Hz, 1.6 Hz, 1H), 6.84 (t, *J* = 2.8 Hz, 1H), 6.16 (t, *J* = 2.8 Hz, 1H), 2.90 (t, *J* = 6.8 Hz, 2H), 2.83 (m, 2H), 2.02 (m, 2H).

Example 8 (Ex-8.2):



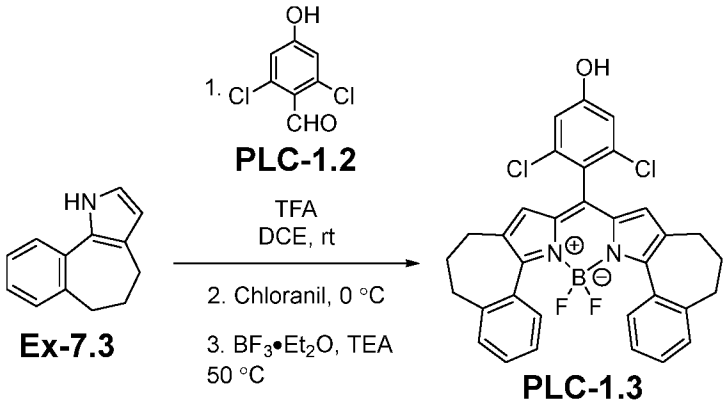
Ex-8.1 **Ex-8.2**

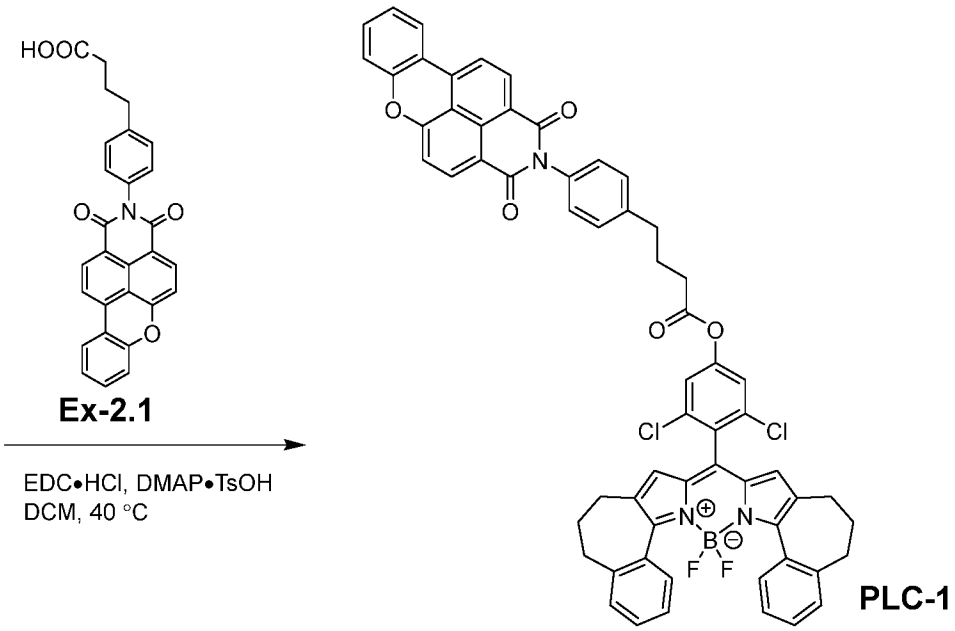
General Synthesis Procedure of compound Ex-8.2, 4,5-dihydro-1H-benzo[g]indole: A mixture of $NH_2OH•HCl$ (4.2 g, 60.0 mmol) and KOH (3.4 g, 60.0 mmol) in DMSO (50 mL) was placed into a 500 mL two-neck round-bottom flask with a reflux condenser. The solution was stirred at room temperature for 30 minutes. Then compound **Ex-8.1** (7.3 g, 50.0 mmol) in DMSO (25 mL) was added. The solution was heated up to 70 ºC and was kept at this temperature for 30 minutes. Then, another portion of KOH (8.4 g, 150.0 mmol) was added to the solution followed by heating up the solution to 140 ºC. To this solution, another solution of DCE (9.9 g, 100.0 mmol) in DMSO (25 mL) was added dropwise through syringe pump over 4 hours. After the completion of addition of the DCE solution, the reaction was cooled down to room temperature, followed by poured into saturated NH_4Cl solution (200 mL). EtOAc (200 mL*3) was used to extract the desired product from the workup solution. The combined organic layers were dried by anhydrous Na_2SO_4, concentrated under vacuum and purified by silica gel flash chromatography to provide compound **Ex-8.2** as a pale white solid using DCM in hexane (0-30%) as an eluant, 3.7 g, 43% yield. MS (APCI): calculated for $C_{12}H_{12}N$ ($[M+H]^+$) = 170 found: 170. ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (bs, 1H), 7.22 (ddd, *J* = 17.6 Hz, 10.4 Hz, 10.4 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.08 (td, *J* = 7.2, 1.6 Hz, 1H), 6.76 (m, 1H), 6.15 (m, 1H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.78 (t, *J* = 7.2 Hz, 2H).

Example 9 – Synthesis of Photoluminescent Complexes (PLC):

The following examples are synthesis procedures of many embodiments of the RL-naphthalimide-BODIPY, as described herein:

Synthesis of PLC-1:



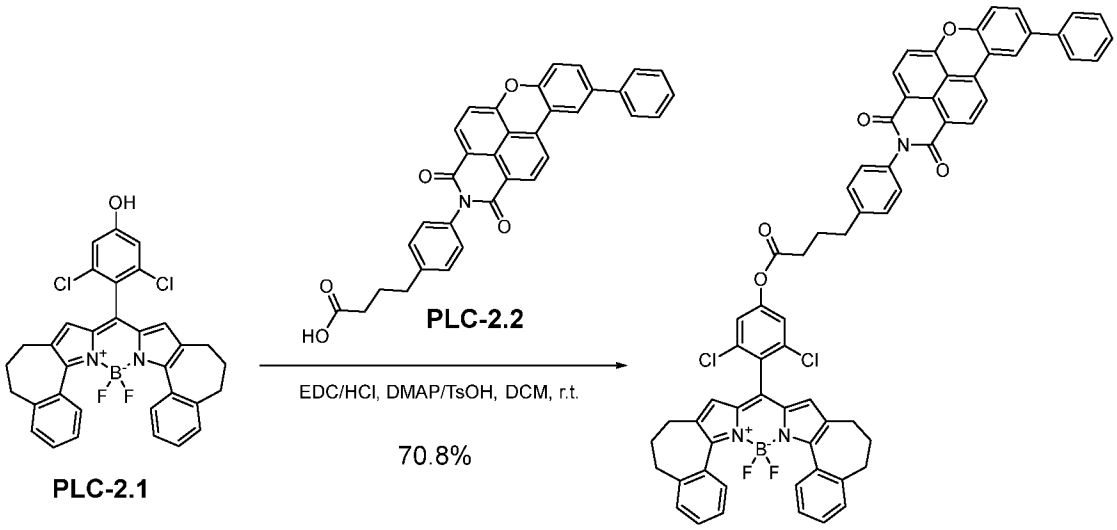


General Procedure of compound PLC-1.3: A 100 mL 2 neck round bottomed flask was fitted with an air condenser and a stir bar. To the flask, compound 1,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-b]pyrrole **PLC-1.1** (813.1 mg, 4.4 mmol) and 4-hydroxy-2,6-dichlorobenzaldehyde **PLC-1.2** (424.3 mg, 2.2 mmol) were added, followed by anhydrous dichloroethane (55 ml). The reaction mixture was sparged with Ar for 30 minutes, then TFA (4 drops) was added. The reaction solution was stirred at room temperature overnight. After the reaction was cooled down to 0 ºC in an ice-water bath, p-chloranil (731.8 mg, 2.98 mmol) was added. The reaction was kept at 0 ºC for 30 minutes. Then BF_3•OEt_2 (3.0 mL, 24.1 mmol) and Et_3N (1.9 mL, 13.3 mmol) were added at 0 ºC. The reaction mixture was heated up to 50

ºC for 3 hours. The reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in hexane (0-80-90%) as an eluant to provide the pure BODIPY **PLC-1.3** as a brown golden solid, 476.0 mg, 36% yield. MS (APCI): calculated for $C_{33}H_{24}BCl_2F_2N_2O$ ([M-H]$^-$) = 584 found: 584. ^{1}H NMR (400 MHz, $CDCl_3$) 8.09 (dd, *J* = 4.0 Hz, 2.0 Hz, 2H), 7.32 (dddd, *J* = 13.2 Hz, 7.2 Hz, 7.2 Hz, 2.0 Hz, 4H), 7.22 (dd, *J* = 6.4 Hz, 2.0 Hz, 2H), 6.99 (s, 2H), 6.43 (s, 2H), 5.77 (bs, 1H), 2.63 (dd, *J* = 6.8 Hz, 6.8 Hz, 4H), 2.32 (bs, 4H), 2.03 (ddd, *J* = 14.0 Hz, 6.8 Hz, 6.8 Hz, 4H).

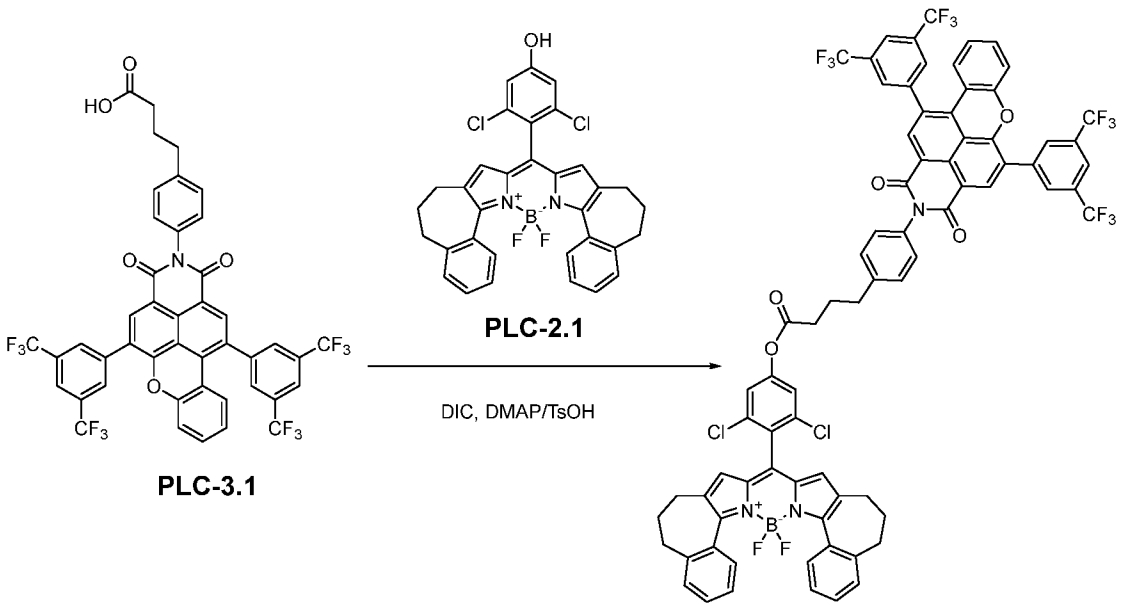
General Procedure of compound PLC-1: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-1.3** (25.0 mg, 0.043 mmol), **PLC-1.4** (24.0 mg, 0.053 mmol), EDC•HCl (40.9 mg, 0.21 mmol) and DMAP•TsOH (25.6 mg, 0.085 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-1** as a dark purple solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-1**, 21.0 mg, 48% yield. MS (APCI): calculated for $C_{61}H_{41}Cl_2F_2N_3O_5$ ([M-H]$^-$) = 1015 found: 1015. ^{1}H NMR (400 MHz, $CDCl_3$) 8.66 (dd, *J* = 18.4 Hz, 7.6 Hz, 2H), 8.10 (m, 3H), 7.99 (d, *J* =8.0 Hz, 1H), 7.56 (ddd, *J* = 8.0 Hz, 8.0 Hz, 1.6 Hz, 1H), 7.36 (m, 13H), 7.22 (dd, *J* = 6.8 Hz, 2.0 Hz, 2H), 6.45 (s, 2H) 2.88 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.63 (m, 4H), 2.20 (m, 6H), 2.04 (ddd, *J* = 6.8 Hz, 6.8 Hz, 6.8 Hz, 4H).

Synthesis of PLC-2:

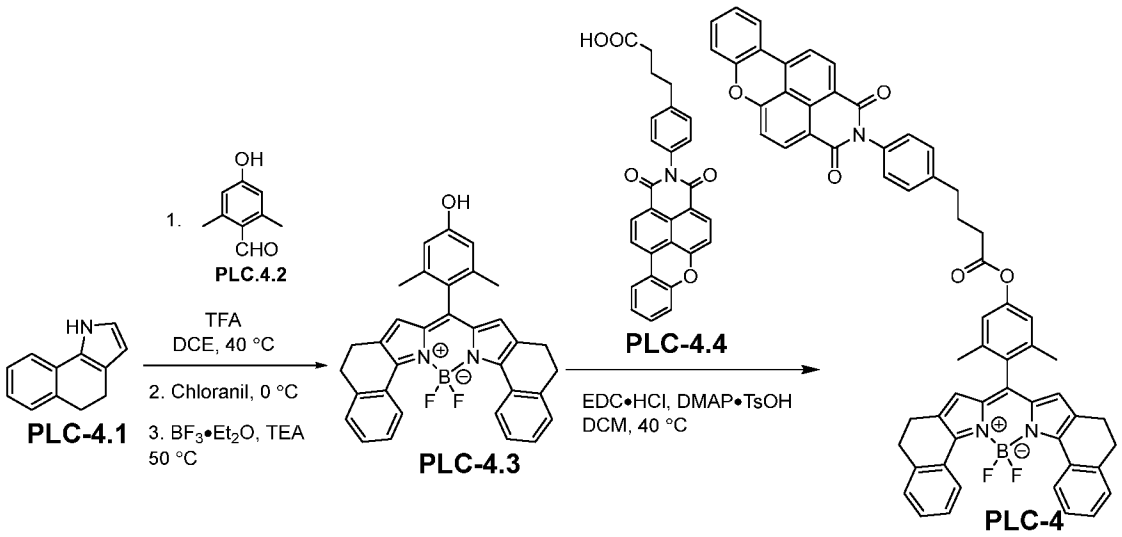


General Procedure of compound PLC-2: A mixture of compound **PLC-2.1** (31 mg, 0.053 mmol), compound **PLC-2.2** (43 mg, 0.082 mmol), EDC•HCl (100 mg, 0.52 mmol) and DMAP/p-TsOH (16 mg, 0.054 mmol) in DCM (8 mL) was stirred at room temperature overnight. The resulted mixture was then loaded on silica gel, purified by flash chromatography using eluents of DCM/ethyl acetate (0% → 5% ethyl acetate). The main red fraction was collected and concentrated to ~ 1 mL under reduced pressure, then 10 mL methanol was added. The resulted precipitate was filtered and dried in air to give a dark red solid (41 mg, in 70.8% yield). LCMS (APCI-): calculated for $C_{67}H_{46}BCl_2F_2N_3O_5$ (M-) = 1091.29; Found: 1091. ^{1}H NMR (400 MHz, d2-TCE) δ 8.56 (dd, *J* = 19.3, 8.1 Hz, 2H), 8.21 (d, *J* = 2.2 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.97 (t, *J* = 4.7 Hz, 2H), 7.73 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.63 (dd, *J* = 7.2, 1.7 Hz, 2H), 7.50 – 7.41 (m, 3H), 7.38 (dd, *J* = 8.0, 2.2 Hz, 3H), 7.34 – 7.25 (m, 7H), 7.25 – 7.18 (m, 4H), 6.40 (s, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.60 – 2.49 (m, 4H), 2.24 (s, 4H), 2.18 – 2.07 (m, 2H), 2.03 – 1.90 (m, 4H).

Synthesis of PLC-3:



General Procedure of compound PLC-3: A mixture of compound **PLC-3.1** (28 mg, 0.048 mmol), compound **PLC-2.1** (70 mg, 0.08 mmol), DIC (0.1 mL, 0.63 mmol), DMAP/TsOH salt (29 mg, 0.1 mmol) in anhydrous dichloromethane (5 mL) was stirred at room temperature for 40 hrs. The resulted mixture was loaded on silica gel and purified by flash chromatography using eluents of hexanes/dichloromethane (50% → 100% dichloromethane). The desired fraction was collected. After removal of solvents and washed with methanol, a dark red solid was obtained after filtration and dried in air (45 mg, in 65% yield). LCMS (APCI-): calculated for $C_{77}H_{46}BCl_2F_{14}N_3O_5$ (M-) = 1439.27; Found: 1439. ^{1}H NMR (400 MHz, d2-TCE) δ 8.66 (s, 1H), 8.41 (s, 1H), 8.18 (d, *J* = 1.5 Hz, 2H), 7.96 (d, *J* = 18.4 Hz, 6H), 7.39 (dd, *J* = 8.3, 2.4 Hz, 3H), 7.34 – 7.12 (m, 11H), 6.98 – 6.85 (m, 2H), 6.39 (s, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.54 (d, *J* = 6.1 Hz, 4H), 2.24 (m, 4H), 2.15 – 2.06 (m, 2H), 1.96 (m, 4H).



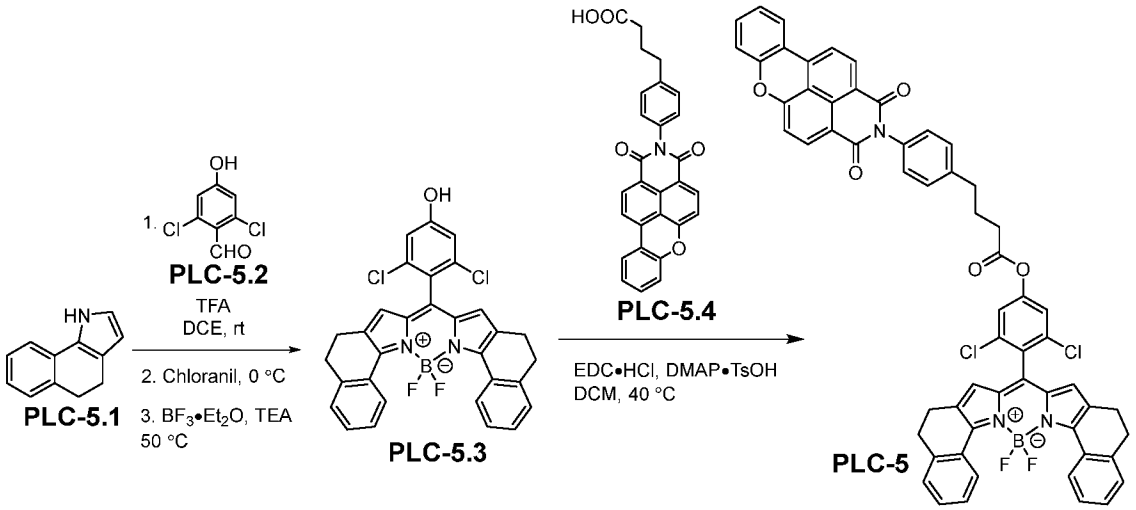
Synthesis of PLC-4:

General Procedure of compound PLC-4.3: A 100 mL 2 neck round bottomed flask was fitted with an air condenser and a stir bar. To the flask, compound 4,5-dihydro-1H-benzo[g]indole **PLC-4.1** (203.1 mg, 1.2 mmol) and 4-hydroxy-2,6-dimethylbenzaldehyde **PLC-4.2** (90.0 mg, 0.6 mmol) were added, followed by anhydrous dichloroethane (15 ml). The reaction mixture was sparged with Ar for 30 minutes., then TFA (3 drops) was added. The reaction solution was heated up to 40 ºC and stirred at 40 ºC overnight. After the reaction was cooled down to 0 ºC in an ice-water bath, p-chloranil (200.0 mg, 0.8 mmol) was added. The reaction was kept at 0 ºC for 30 minutes. Then $BF_3•OEt_2$ (0.8 mL, 6.5 mmol) and Et_3N (0.5 mL, 3.6 mmol) were added at 0 ºC. The reaction mixture was heated up to 50 ºC for 2 hours. The reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in hexane (0-80-90%) as an eluant to provide the pure BODIPY **PLC-4.3** as a dark purple golden solid, 242.2 mg, 78% yield. MS (APCI): calculated for $C_{33}H_{28}BF_2N_2O$ ($[M+H]^+$) = 517 found: 517. ^1H NMR (400 MHz, $CDCl_3$) 8.80 (d, *J* = 8.0 Hz, 2H), 7.44 (td, *J* = 7.2 Hz, 1.6 Hz, 2H), 7.31 (td, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.25 (m, 2H), 6.63 (s, 2H), 6.33 (s, 2H), 4.82 (s, 1H), 2.91 (t, *J* = 6.4 Hz, 4H), 2.65 (t, *J* = 6.4 Hz, 4H), 2.18 (s, 6H).

General Procedure of compound PLC-4: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-4.3** (25.0 mg, 0.048 mmol), **PLC-4.4** (27.2 mg, 0.061 mmol), EDC•HCl (46.4 mg, 0.24 mmol) and DMAP•TsOH (29.0 mg, 0.097 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and

purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-4** as a blue green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-4**, 20.1 mg, 44% yield. MS (APCI): calculated for $C_{61}H_{43}BF_2N_3O_5$ ([M-H]$^-$) = 947 found: 947. ^{1}H NMR (400 MHz, $CDCl_3$) 8.80 (d, *J* = 8.4 Hz, 2H), 8.66 (dd, *J* = 18.4 Hz, 8.0 Hz, 2H), 8.11 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.56 (ddd, *J* = 8.0 Hz, 8.0 Hz, 1.6 Hz, 1H), 7.37 (m, 11H), 7.25 (m, 2H), 6.93 (s, 2H), 6.35 (s, 2H), 2.90 (m, 6H), 2.68 (m, 6H), 2.24 (s, 6H), 2.20 (m, 2H).

Synthesis of PLC-5:

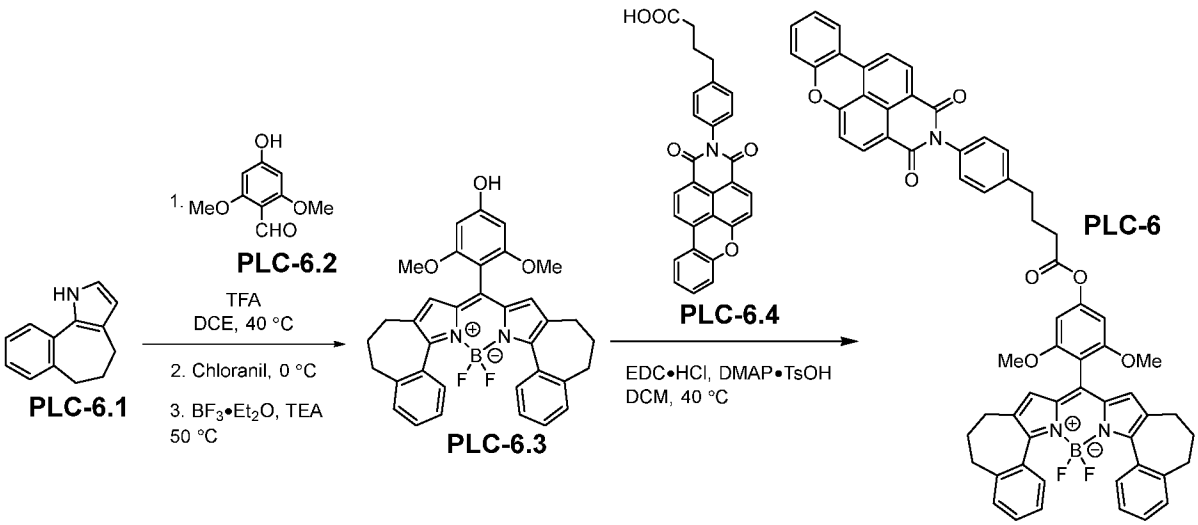


General Procedure of compound PLC-5.3: A 100 mL 2 neck round bottomed flask was fitted with an air condenser and a stir bar. To the flask, compound 4,5-dihydro-1H-benzo[g]indole **PLC-5.1** (203.1 mg, 1.2 mmol) and 4-hydroxy-2,6-dichlorobenzaldehyde **PLC-5.2** (114.6 mg, 0.6 mmol) were added, followed by anhydrous dichloroethane (15 ml). The reaction mixture was sparged with Ar for 30 minutes, then TFA (3 drops) was added. The reaction solution was stirred at room temperature overnight. After the reaction was cooled down to 0 ºC in an ice-water bath, p-chloranil (200.0 mg, 0.8 mmol) was added. The reaction was kept at 0 ºC for 30 minutes. Then BF_3•OEt_2 (0.8 mL, 6.5 mmol) and Et_3N (0.5 mL, 3.6 mmol) were added at 0 ºC. The reaction mixture was heated up to 50 ºC for 2 hours. The reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in hexane (0-80-90%) as an eluant to provide the pure BODIPY **PLC-5.3** as a dark purple golden solid, 200.3 mg, 57% yield. MS (APCI): calculated for $C_{31}H_{20}BCl_2F_2N_2O$ ([M-H]$^-$) = 556 found: 556. ^{1}H NMR (400 MHz, $CDCl_3$) 8.80 (d, *J* = 8.0 Hz, 2H), 7.44 (td, *J* = 7.6 Hz, 1.6 Hz, 2H), 7.32

(td, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.25 (m, 2H), 6.99 (s, 2H), 6.35 (s, 2H), 5.68 (bs, 1H), 2.93 (t, *J* = 7.6 Hz, 4H), 2.68 (t, *J* = 7.6 Hz, 4H).

General Procedure of compound PLC-5: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-5.3** (25.0 mg, 0.045 mmol), **PLC-5.4** (25.2 mg, 0.056 mmol), EDC•HCl (43.0 mg, 0.22 mmol) and DMAP•TsOH (26.9 mg, 0.089 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-5** as a green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-5**, 16.0 mg, 36% yield. MS (APCI): calculated for $C_{59}H_{37}BCl_2F_2N_3O_5$ ([M-H]$^-$) = 986 found: 986. ^{1}H NMR (400 MHz, $CDCl_3$) 8.80 (d, *J* = 8.4 Hz, 2H), 8.66 (dd, *J* = 18.0 Hz, 8.0 Hz, 2H), 8.11 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.56 (ddd, *J* = 8.0 Hz, 8.0 Hz, 1.6 Hz, 1H), 7.34 (m, 15H), 6.37 (s, 2H), 2.90 (m, 6H), 2.70 (dd, *J* = 14.8 Hz, 7.6 Hz, 6H), 2.24 (ddd, *J* = 7.6 Hz, 7.6 Hz, 7.6 Hz, 2H).

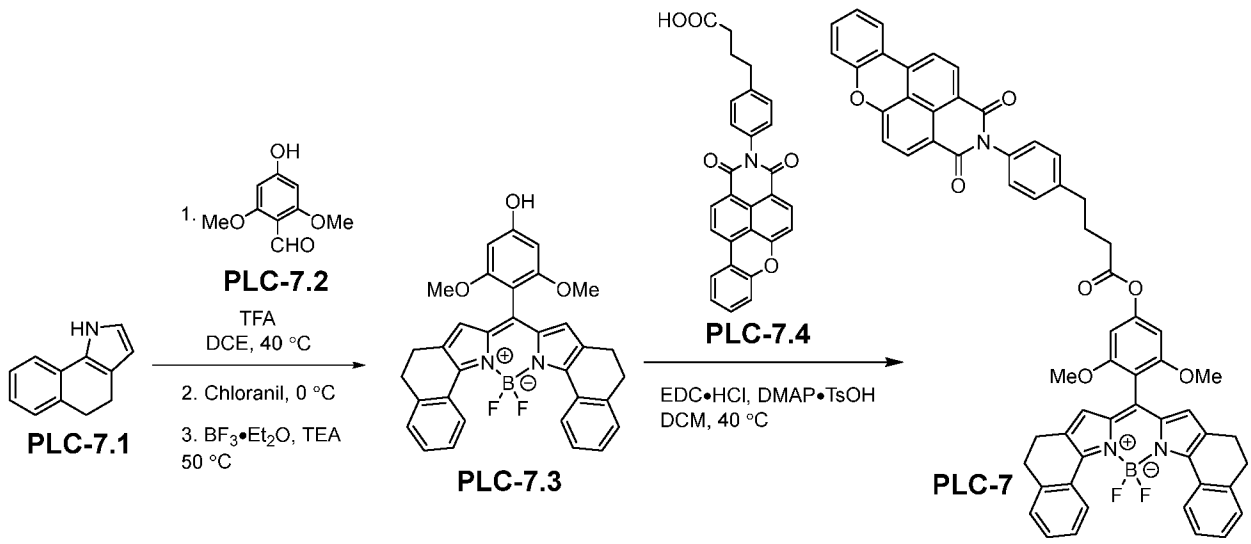
Synthesis of PLC-6:



General Procedure of PLC-6.3: A 100 mL 2 neck round bottomed flask was fitted with an air condenser and a stir bar. To the flask, compound 1,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-b]pyrrole **PLC-6.1** (220.0 mg, 1.2 mmol) and 4-hydroxy-2,6-dimethoxybenzaldehyde **PLC-6.2** (109.3 mg, 0.6 mmol) were added, followed by

anhydrous dichloroethane (15 ml). The reaction mixture was sparged with Ar for 30 minutes, then TFA (3 drops) was added. The reaction solution was heated up to 40 ºC and stirred at 40 ºC overnight. After the reaction was cooled down to 0 ºC in an ice-water bath, p-chloranil (200.0 mg, 0.8 mmol) was added. The reaction was kept at 0 ºC for 30 minutes. Then BF_3•OEt_2 (0.8 mL, 6.5 mmol) and Et_3N (0.5 mL, 3.6 mmol) were added at 0 ºC. The reaction mixture was heated up to 50 ºC for 2 hours. The reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in hexane (0-80-90%) as an eluant to provide the pure BODIPY **PLC-6.3** as a dark purple solid, 28.0 mg, 8% yield. MS (APCI): calculated for $C_{35}H_{30}BF_2N_2O_3$ ([M-H]-) = 576 found: 576. 1H NMR (400 MHz, CDCl3) 8.10 (d, J = 7.6 Hz, 2H), 7.29 (dddd, J = 17.2 Hz, 7.2 Hz, 7.2 Hz, 4H), 7.21 (dd, J = 7.2 Hz, 2H), 6.48 (s, 2H), 6.19 (s, 2H), 3.72 (s, 6H), 2.62 (dd, J = 6.8 Hz, 6.8 Hz, 4H), 2.29 (bs, 4H), 2.02 (ddd, J = 14.0 Hz, 7.2 Hz, 7.2 Hz, 4H).

General Procedure of PLC-6: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-6.3** (28.0 mg, 0.049 mmol), **PLC-6.4** (27.3 mg, 0.061 mmol), EDC•HCl (46.6 mg, 0.24 mmol) and DMAP•TsOH (29.2 mg, 0.097 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-6** as a dark red purple solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-6**, 4.0 mg, 8% yield. MS (APCI): calculated for $C_{63}H_{47}BF_2N_3O_7$ ([M-H]$^-$) = 1007 found: 1007. ^{1}H NMR (400 MHz, $CDCl_3$) 8.66 (dd, *J* = 18.4 Hz, 8.0 Hz, 2H), 8.11 (dd, *J* = 8.0 Hz, 1.6 Hz, 3H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.56 (ddd, *J* = 8.0 Hz, 8.0 Hz, 1.6 Hz, 1H), 7.41 (m, 4H), 7.32 (m, 7H), 7.21 (dd, *J* = 7.2 Hz, 1.6 Hz, 2H), 6.50 (s, 2H), 6.49 (s, 2H), 3.77 (s, 6H), 2.89 (t, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.62 (m, 4H), 2.30 (bs, 2H), 2.21 (ddd, *J* = 7.6 Hz, 7.6 Hz, 7.6 Hz, 4H), 2.02 (ddd, *J* = 6.8 Hz, 6.8 Hz, 6.8 Hz, 4H).



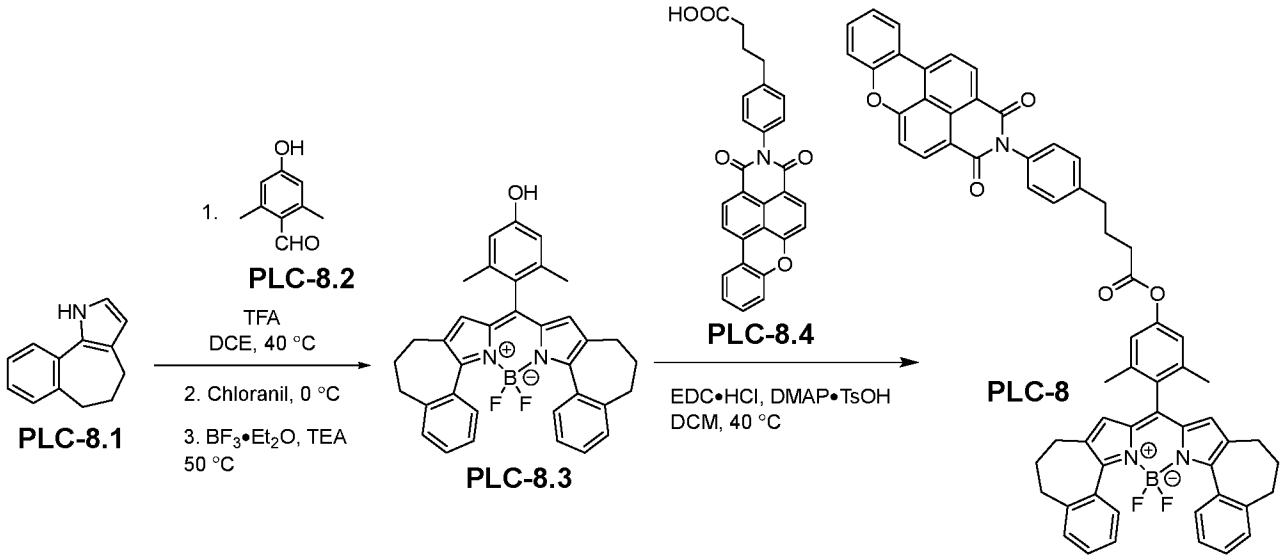
Synthesis of PLC-7:

General Procedure of PLC-7.3: A 100 mL 2 neck round bottomed flask was fitted with an air condenser and a stir bar. To the flask, compound 4,5-dihydro-1H-benzo[g]indole **PLC-7.1** (203.1 mg, 1.2 mmol) and 4-hydroxy-2,6-dimethoxybenzaldehyde **PLC-7.2** (109.3 mg, 0.6 mmol) were added, followed by anhydrous dichloroethane (15 ml). The reaction mixture was sparged with Ar for 30 minutes, then TFA (3 drops) was added. The reaction solution was heated up to 40 ºC and was stirred at 40 ºC overnight. After the reaction was cooled down to 0 ºC in an ice-water bath, p-chloranil (200.0 mg, 0.8 mmol) was added. The reaction was kept at 0 ºC for 30 minutes. Then BF_3•OEt_2 (0.8 mL, 6.5 mmol) and Et_3N (0.5 mL, 3.6 mmol) were added at 0 ºC. The reaction mixture was heated up to 50 ºC for 2 hours. The reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in hexane (0-80-90%) as an eluant to provide the pure BODIPY **PLC-7.3** as a brown golden solid, 78.4 mg, 24% yield. MS (APCI): calculated for $C_{33}H_{28}BF_2N_2O_3$ ([M+H]$^+$) = 549 found: 549. ^{1}H NMR (400 MHz, $CDCl_3$) 8.80 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.29 (m, 2H), 7.23 (d, *J* = 7.2 Hz, 2H), 6.41 (s, 2H), 6.17 (s, 2H), 5.05 (bs, 1H), 3.69 (s, 6H), 2.90 (t, *J* = 6.8 Hz, 4H), 2.65 (t, *J* = 6.8 Hz, 4H).

General Procedure of PLC-7: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-7.3** (25.0 mg, 0.045 mmol), **PLC-7.4** (25.6 mg, 0.057 mmol), EDC•HCl (43.7 mg, 0.23 mmol) and DMAP•TsOH (27.4 mg, 0.091 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and

purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-7** as a dark green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-7**, 23.0 mg, 51% yield. MS (APCI): calculated for $C_{61}H_{43}BF_2N_3O_7$ ([M-H]$^-$) = 979 found: 979. ^{1}H NMR (400 MHz, $CDCl_3$) 8.81 (d, *J* = 8.0 Hz, 2H), 8.67 (dd, *J* = 18.4 Hz, 7.6 Hz, 2H), 8.11 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.56 (ddd, *J* = 8.0 Hz, 8.0 Hz, 1.6 Hz, 1H), 7.34 (m, 11H), 7.23 (m, 2H), 6.46 (s, 2H), 6.43 (s, 2H), 3.73 (s, 6H), 2.89 (dd, *J* = 14.0 Hz, 6.4 Hz, 6H), 2.68 (m, 6H), 2.24 (ddd, *J* = 7.6 Hz, 7.6 Hz, 7.6 Hz, 2H).

Synthesis of PLC-8:

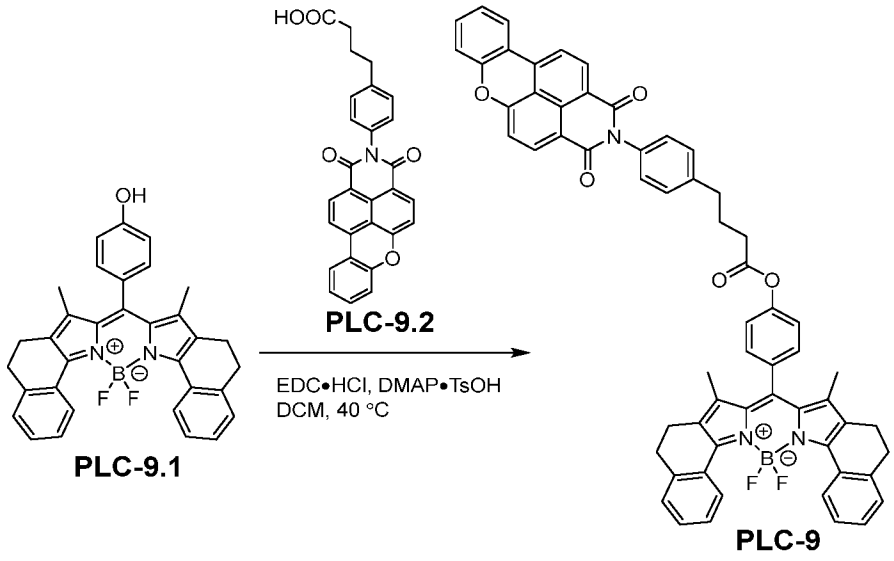


General Procedure of PCL-8.3: A 100 mL 2 neck round bottomed flask was fitted with an air condenser and a stir bar. To the flask, compound 1,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-b]pyrrole **PLC-8.1** (220.0 mg, 1.2 mmol) and 4-hydroxy-2,6-dimethylbenzaldehyde **PLC-8.2** (90.0 mg, 0.6 mmol) were added, followed by anhydrous dichloroethane (15 ml). The reaction mixture was sparged with Ar for 30 minutes, then TFA (3 drops) was added. The reaction solution was heated up to 40 ºC overnight. After the reaction was cooled down to 0 ºC in an ice-water bath, p-chloranil (200.0 mg, 0.8 mmol) was added. The reaction was kept at 0 ºC for 20 minutes. Then BF_3•OEt_2 (0.8 mL, 6.5 mmol) and Et_3N (0.5 mL, 3.6 mmol) were added at 0 ºC. The reaction mixture was heated up to 50 ºC for 2 hours. The reaction mixture was loaded with silica gel and purified by flash chromatography,

using DCM in hexane (0-80-90%) as an eluant to provide the pure BODIPY **PLC-8.3** as a dark purple solid, 162.5 mg, 48% yield. MS (APCI): calculated for $C_{35}H_{30}BF_2N_2O$ ([M-H]$^-$) = 543 found: 543. ^{1}H NMR (400 MHz, $CDCl_3$) 8.08 (d, *J* = 7.2 Hz, 2H), 8.02 (bs, 1H), 7.28 (m, 6H), 6.66 (bs, 2H), 6.41 (bs, 2H), 2.96 (bs, 4H), 2.89 (bs, 4H), 2.62 (m, 4H), 2.22 (s, 6H).

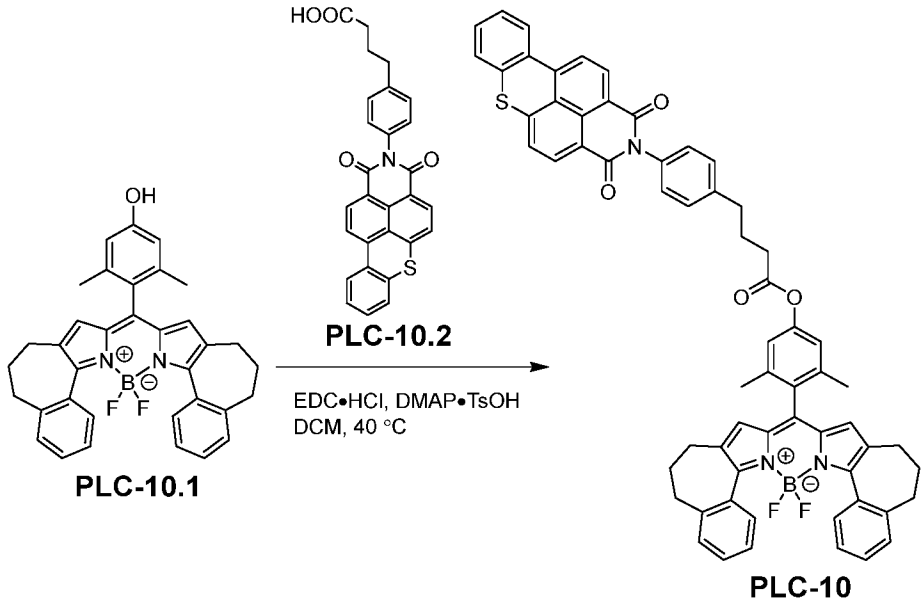
General Procedure of PLC-8: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-8.3** (25.0 mg, 0.046 mmol), **PLC-8.4** (25.8 mg, 0.057 mmol), EDC•HCl (44.1 mg, 0.23 mmol) and DMAP•TsOH (27.6 mg, 0.092 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-8** as a dark purple red solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-8**, 31.0 mg, 69% yield. MS (APCI): calculated for $C_{63}H_{47}BF_2N_3O_5$ ([M-H]$^-$) = 975 found: 975. ^{1}H NMR (400 MHz, $CDCl_3$) 8.66 (dd, *J* = 18.4 Hz, 7.6 Hz, 2H), 8.10 (td, *J* = 8.0 Hz, 1.6 Hz, 2H), 8.08 (bs, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.56 (ddd, *J* = 8.0 Hz, 8.0 Hz, 1.6 Hz, 1H), 7.36 (m, 11H), 7.22 (dd, *J* = 7.2 Hz, 2.0 Hz, 2H), 6.95 (s, 2H), 6.43 (s, 2H) 2.88 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.62 (m, 4H), 2.29 (s, 6H), 2.20 (m, 6H), 2.02 (ddd, *J* = 6.8 Hz, 6.8 Hz, 6.8 Hz, 4H).

Synthesis of PLC-9:



General Procedure of PLC-9: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-9.1** (25.0 mg, 0.048 mmol), **PLC-9.2** (27.2 mg, 0.061 mmol), EDC•HCl (46.4 mg, 0.24 mmol) and DMAP•TsOH (29.0 mg, 0.097 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-9** as a dark green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-9**, 25.0 mg, 54% yield. MS (APCI): calculated for $C_{61}H_{43}BF_2N_3O_5$ ([M-H]$^-$) = 947 found: 947. ^{1}H NMR (400 MHz, $CDCl_3$) 8.67 (dd, *J* = 18.4 Hz, 7.6 Hz, 2H), 8.10 (m, 3H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.56 (ddd, *J* = 8.0 Hz, 8.0 Hz, 1.6 Hz, 1H), 7.34 (m, 11H), 7.23 (m, 2H), 6.95 (m, 2H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.62 (m, 4H), 2.29 (s, 6H), 2.20 (ddd, *J* = 7.6 Hz, 7.6 Hz, 7.6 Hz, 6H), 2.24 (ddd, *J* = 7.6 Hz, 7.6 Hz, 7.6 Hz, 2H).

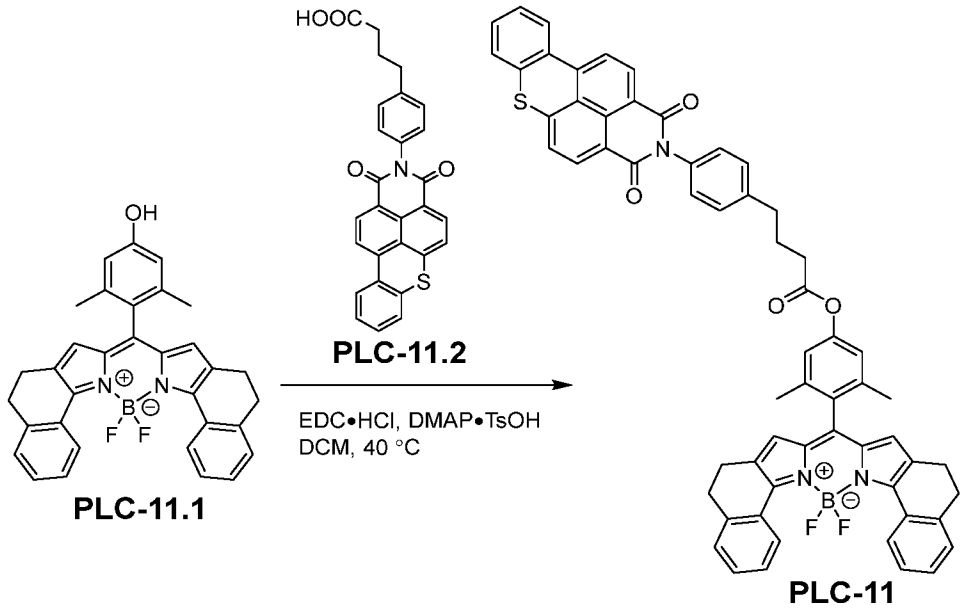
Synthesis of PLC-10:



General Procedure of PLC-10: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-10.1** (30.0 mg, 0.055 mmol), **PLC-10.2** (32.1 mg, 0.069 mmol), EDC•HCl (52.7 mg, 0.275 mmol) and DMAP•TsOH (33.0 mg, 0.110 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide

the pure RL-naphthalimide-BODIPY **PLC-10** as a dark purple solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-10**, 51.0 mg, 94% yield. MS (APCI): calculated for $C_{63}H_{48}BF_2N_3O_4S$ ([M-H]$^-$) = 991 found: 991. ^{1}H NMR (400 MHz, $CDCl_3$) 8.68 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.26 (m, 2H), 8.09 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.44 (m, 5H), 7.32 (m, 6H), 7.22 (m, 2H), 6.95 (s, 2H), 6.43 (s, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.62 (m, 4H), 2.29 (s, 6H), 2.20 (m, 6H), 2.24 (ddd, *J* = 6.8 Hz, 6.8 Hz, 6.8 Hz, 4H).

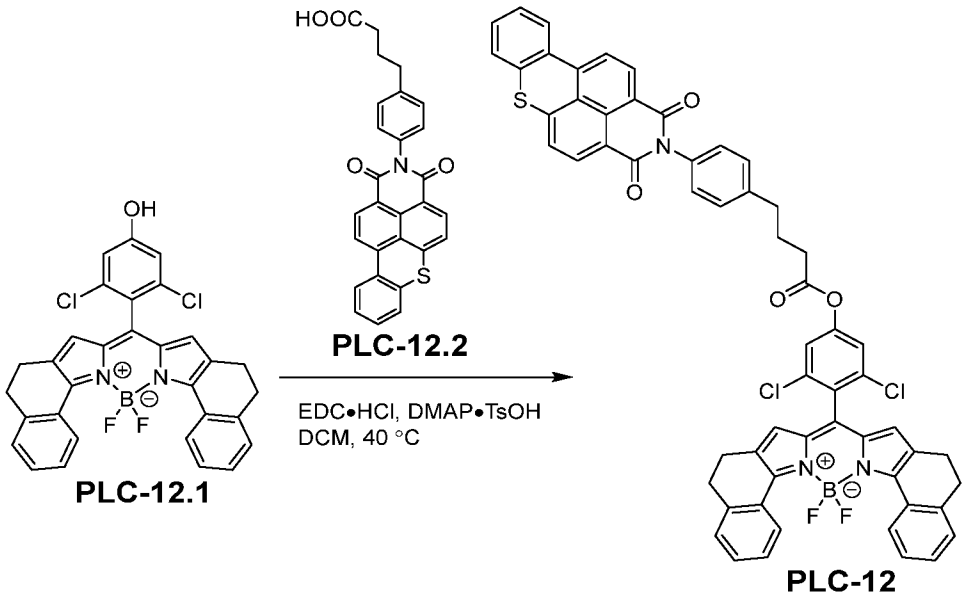
Synthesis of PLC-11:



General Procedure of PLC-11: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-11.1** (30.0 mg, 0.058 mmol), **PLC-11.2** (33.8 mg, 0.073 mmol), EDC•HCl (55.6 mg, 0.290 mmol) and DMAP•TsOH (34.8 mg, 0.116 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-11** as a dark green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-11**, 40.0 mg, 72% yield. MS (APCI): calculated for $C_{61}H_{44}BF_2N_3O_4S$ ([M-H]$^-$) = 963 found: 963. ^{1}H NMR (400 MHz, $CDCl_3$) 8.81 (d, *J* = 8.0 Hz, 2H), 8.68 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.26 (m, 2H), 7.56 (d, *J*

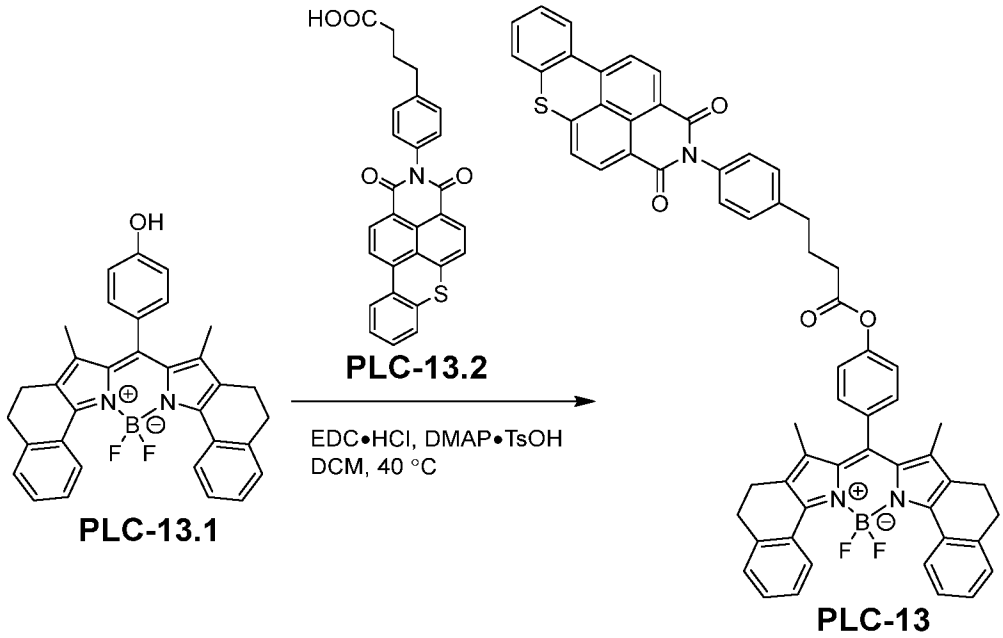
= 8.0 Hz, 1H), 7.44 (m, 7H), 7.29 (m, 6H), 6.93 (s, 2H), 6.35 (s, 2H), 2.90 (m, 6H), 2.68 (m, 6H), 2.24 (s, 6H), 2.19 (m, 2H).

Synthesis of PLC-12:



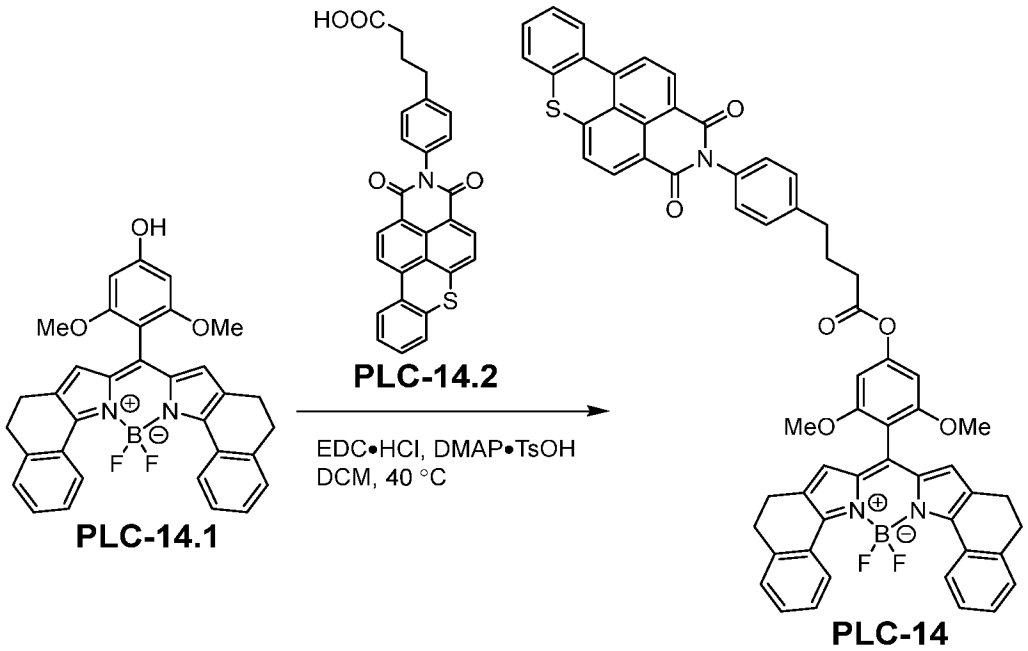
General Procedure of PLC-12: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-12.1** (30.0 mg, 0.051 mmol), **PLC-12.2** (29.8 mg, 0.064 mmol), EDC•HCl (48.9 mg, 0.255 mmol) and DMAP•TsOH (30.6 mg, 0.102 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-12** as a dark green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-12**, 31.0 mg, 61% yield. MS (APCI): calculated for $C_{59}H_{38}BCl_2F_2N_3O_4S$ ($[M+H]^+$) = 1005 found: 1005. ^1H NMR (400 MHz, $CDCl_3$) 8.81 (m, 2H), 8.68 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.26 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.43 (m, 7H), 7.31 (m, 6H), 7.25 (m, 2H), 6.37 (s, 2H), 2.93 (m, 4H), 2.87 (d, *J* = 7.6 Hz, 2H), 2.69 (m, 6H), 2.24 (s, 6H), 2.19 (ddd, *J* = 7.6 Hz, 7.6 Hz, 7.6 Hz, 2H).

Synthesis of PLC-13:



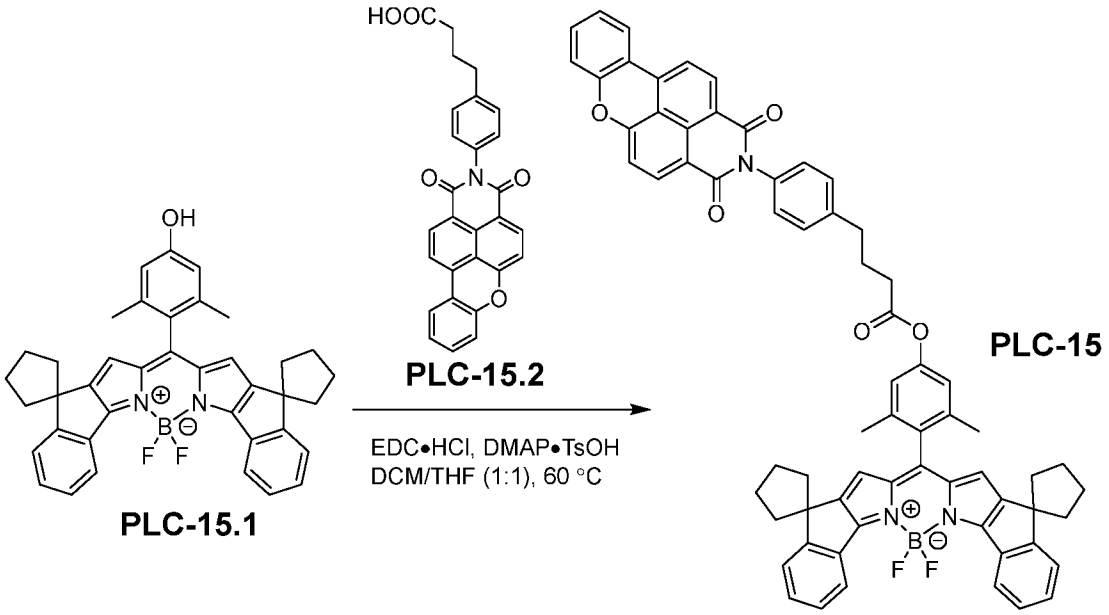
General Procedure of PLC-13: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-13.1** (30.0 mg, 0.058 mmol), **PLC-13.2** (33.8 mg, 0.073 mmol), EDC•HCl (55.6 mg, 0.290 mmol) and DMAP•TsOH (34.8 mg, 0.116 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-13** as a dark green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-13**, 29.0 mg, 52% yield. MS (APCI): calculated for $C_{61}H_{44}BF_2N_3O_4S$ ($[M-H]^-$) = 963 found: 963. ^1H NMR (400 MHz, $CDCl_3$) 8.81 (m, 2H), 8.68 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.26 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.43 (m, 9H), 7.29 (m, 6H), 7.24 (m, 2H), 2.88 (m, 6H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.54 (m, 4H), 2.21 (ddd, *J* = 7.2 Hz, 7.2 Hz, 7.2 Hz, 2H).

Synthesis of PLC-14:



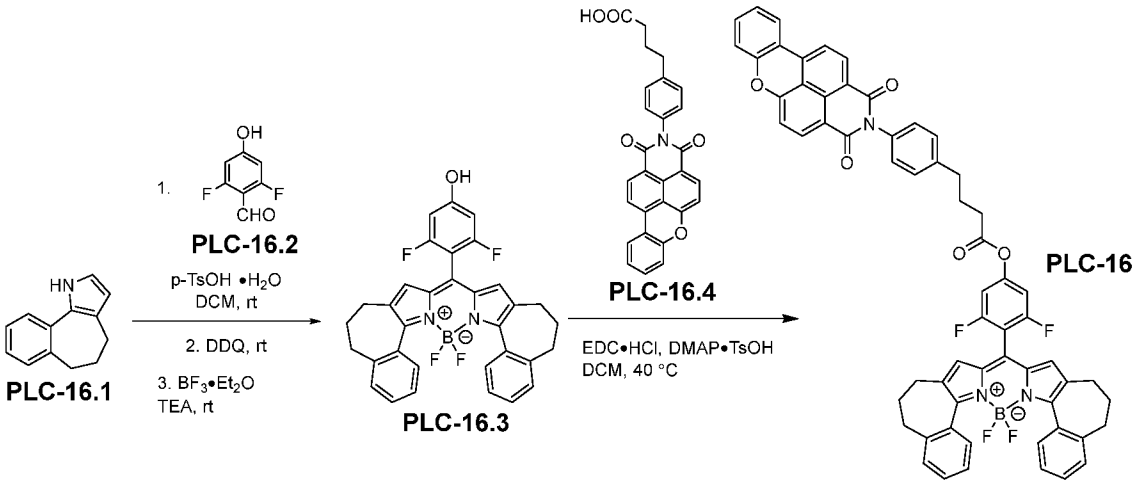
General Procedure of PLC-14: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-14.1** (30.0 mg, 0.055 mmol), **PLC-14.2** (31.8 mg, 0.068 mmol), EDC•HCl (52.7 mg, 0.275 mmol) and DMAP•TsOH (33.0 mg, 0.110 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-14** as a dark green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-14**, 44.0 mg, 80% yield. MS (APCI): calculated for $C_{61}H_{44}BF_2N_3O_6S$ ($[M-H]^-$) = 995 found: 995. ^1H NMR (400 MHz, $CDCl_3$) 8.81 (m, 2H), 8.68 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.26 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.44 (m, 7H), 7.29 (m, 4H), 7.23 (m, 2H), 6.46 (s, 2H), 6.42 (s, 2H), 3.73 (s, 6H), 2.89 (m, 6H), 2.68 (m, 6H), 2.21 (ddd, *J* = 7.6 Hz, 7.6 Hz, 7.6 Hz, 2H).

Synthesis of PLC-15:



General Procedure of PLC-15: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-15.1** (22.0 mg, 0.037 mmol), **PLC-15.2** (20.7 mg, 0.046 mmol), EDC•HCl (35.5 mg, 0.185 mmol) and DMAP•TsOH (22.2 mg, 0.074 mmol) were added, followed by anhydrous DCM (1.5 ml) and THF (1.5 ml). The reaction mixture was heated up to 60 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-15** as a dark green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-15**, 6.0 mg, 16% yield. MS (APCI): calculated for $C_{67}H_{52}BF_2N_3O_5$ ([M-H]$^-$) = 1027 found: 1027. ^{1}H NMR (400 MHz, $CDCl_3$) 8.68 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 8.0 Hz, 1H), 8.30 (m, 2H), 8.11 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.56 (td, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.41 (m, 10H), 7.31 (m, 3H), 7.00 (s, 2H), 6.19 (s, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.51 (s, 6H), 2.21 (m, 2H), 1.98 (m, 16H).

Synthesis of PLC-16:

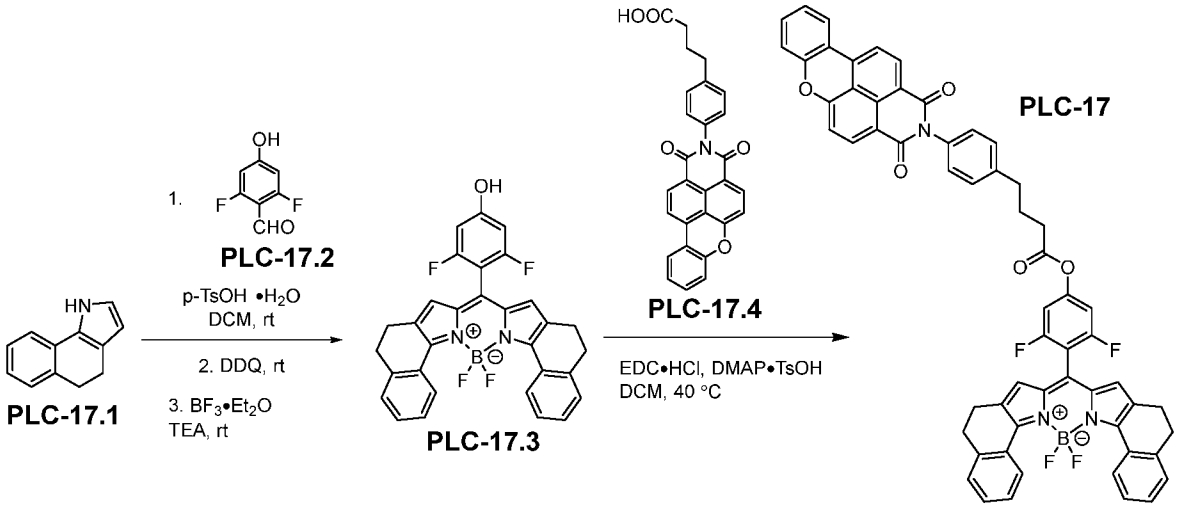


General Procedure of PLC-16.3: A 100 mL 2 neck round bottomed flask was fitted with an air condenser and a stir bar. To the flask, compound 1,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-b]pyrrole **PLC-16.1** (542.0 mg, 2.96 mmol) and 4-hydroxy-2,6-difluorobenzaldehyde **PLC-16.2** (222.6 mg, 1.4 mmol) were added, followed by anhydrous dichloromethane (20 ml). The reaction mixture was sparged with Ar for 30 minutes, then p-TsOH•H_2O (17.0 mg, 0.14 mmol) was added. The reaction solution was stirred at room temperature for 2 hours. DDQ (381.4 mg, 1.68 mmol) was added after the full consumption of the aldehyde starting material. The reaction was kept at room temperature for 1 hour. Then Et_3N (1.2 mL, 8.40 mmol) were added and the reaction was kept at room temperature for 30 minutes, followed by the addition of BF_3•OEt_2 (2.1 mL, 12.6 mmol) at room temperature. The reaction mixture was kept at room temperature for another hour. The reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in hexane (0-80-90%) as an eluant to provide the pure BODIPY **PLC-16.3** as a blue golden solid, 279.0 mg, 36% yield. MS (APCI): calculated for $C_{33}H_{25}BF_4N_2O$ ($[M-H]^-$) = 552 found: 552.

General Procedure of PLC-16: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-16.3** (30.0 mg, 0.054 mmol), **PLC-16.4** (30.5 mg, 0.068 mmol), EDC•HCl (51.8 mg, 0.270 mmol) and DMAP•TsOH (32.4 mg, 0.108 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-16** as a green purple solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-16**, 25.0 mg, 47% yield.

MS (APCI): calculated for $C_{61}H_{42}BF_4N_3O_5$ ([M-H]$^-$) = 983 found: 983. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) 8.65 (d, *J* = 8.0 Hz, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.13 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 8.02 (m, 3H), 7.60 (td, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.39 (m, 13H), 7.04 (m, 2H), 6.63 (s, 2H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.77 (t, *J* = 7.2 Hz, 2H), 2.64 (m, 4H), 2.70 (dd, *J* = 6.8 Hz, *J* = 6.8 Hz, 6H), 2.20 (m, 9H).

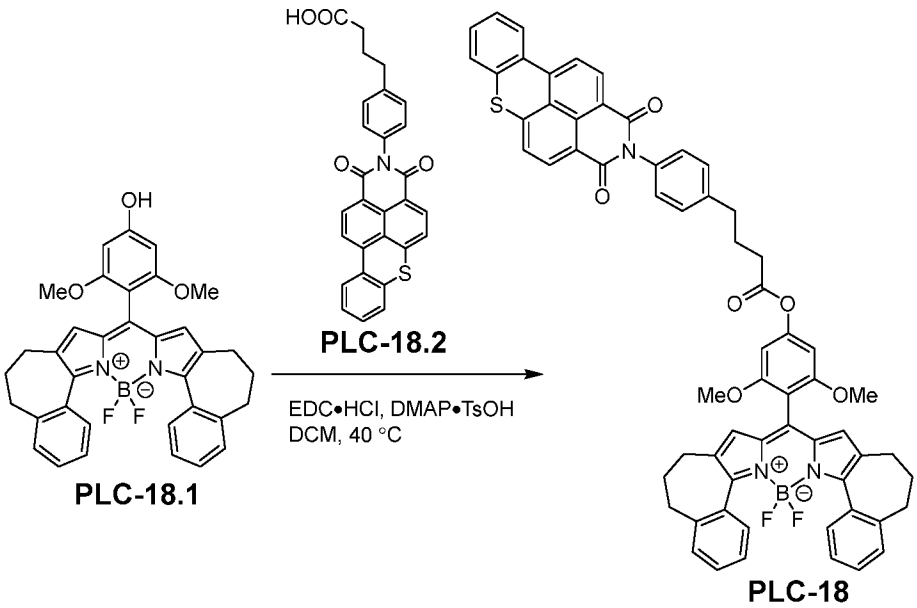
Synthesis of PLC-17:



General Procedure of PLC-17.3: A 100 mL 2 neck round bottomed flask was fitted with an air condenser and a stir bar. To the flask, compound 4,5-dihydro-1H-benzo[g]indole **PLC-17.1** (507.7 mg, 3.0 mmol) and 4-hydroxy-2,6-difluorobenzaldehyde **PLC-17.2**(225.9 mg, 1.43 mmol) were added, followed by anhydrous dichloromethane (20 ml). The reaction mixture was sparged with Ar for 30 minutes, then p-TsOH•H_2O (17.4 mg, 0.143 mmol) was added. The reaction solution was stirred at room temperature for 2 hours. DDQ (392.4 mg, 1.74 mmol) was added after the full consumption of the aldehyde starting material. The reaction was kept at room temperature for 1 hour. Then Et_3N (1.2 mL, 8.64 mmol) were added and the reaction was kept at room temperature for 30 minutes, followed by the addition of BF_3•OEt_2 (1.6 mL, 12.96 mmol) at room temperature. The reaction mixture was kept at room temperature for another hour. The reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in hexane (0-80-90%) as an eluant to provide the pure BODIPY **PLC-17.3** as a brown golden solid, 211.0 mg, 28% yield. MS (APCI): calculated for $C_{31}H_{21}BF_4N_2O$ ([M-H]$^-$) = 524 found: 524. ^{1}H NMR (400 MHz, $CDCl_3$) 8.80 (d, *J* = 8.0 Hz, 2H), 7.44 (m, 2H), 7.32 (m, 2H), 7.23 (m, 2H), 6.57 (m, 2H), 6.49 (s, 2H), 2.92 (m, 4H), 2.69 (m, 4H).

General Procedure of PLC-17: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-17.3** (30.0 mg, 0.057 mmol), **PLC-17.4** (32.1 mg, 0.072 mmol), EDC•HCl (54.6 mg, 0.285 mmol) and DMAP•TsOH (34.2 mg, 0.114 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-17** as a dark green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-17**, 38.0 mg, 70% yield. MS (APCI): calculated for $C_{59}H_{38}BF_4N_3O_5$ ([M-H]$^-$) = 955 found: 955. ^{1}H NMR (400 MHz, $CDCl_3$) 8.80 (m, 2H), 8.68 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 8.0 Hz, 1H), 8.11 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.56 (td, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.38 (m, 12H), 7.24 (m, 1H), 6.94 (m, 2H), 6.50 (s, 2H), 2.90 (m, 6H), 2.70 (dd, *J* = 6.8 Hz, *J* = 6.8 Hz, 6H), 2.19 (m, 2H).

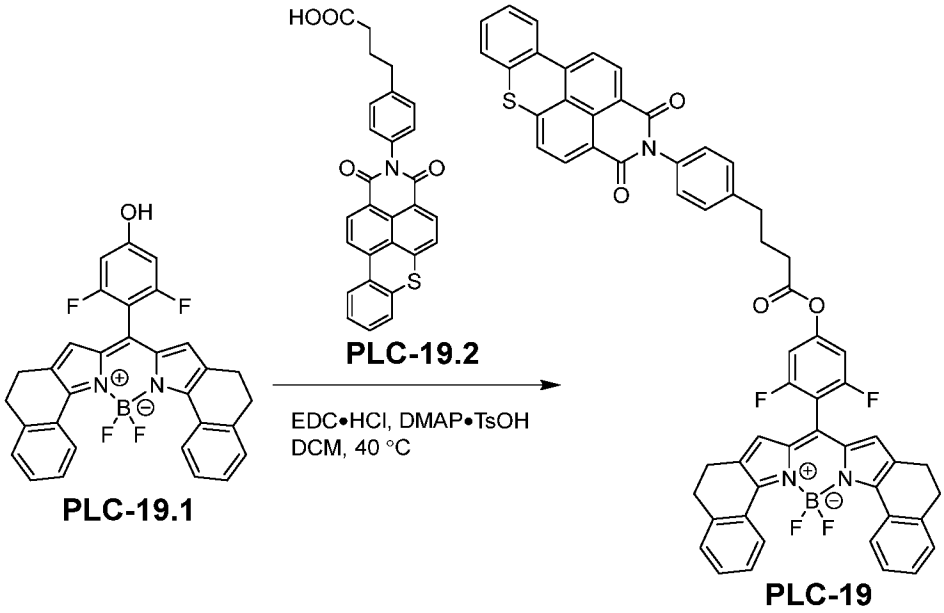
Synthesis of PLC-18:



General Procedure of PLC-18: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-18.1** (30.0 mg, 0.054 mmol), **PLC-18.2** (31.6 mg, 0.068 mmol), EDC•HCl (51.8 mg, 0.270 mmol) and DMAP•TsOH (32.4 mg, 0.108 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-18** as a dark purple solid. The solid was further

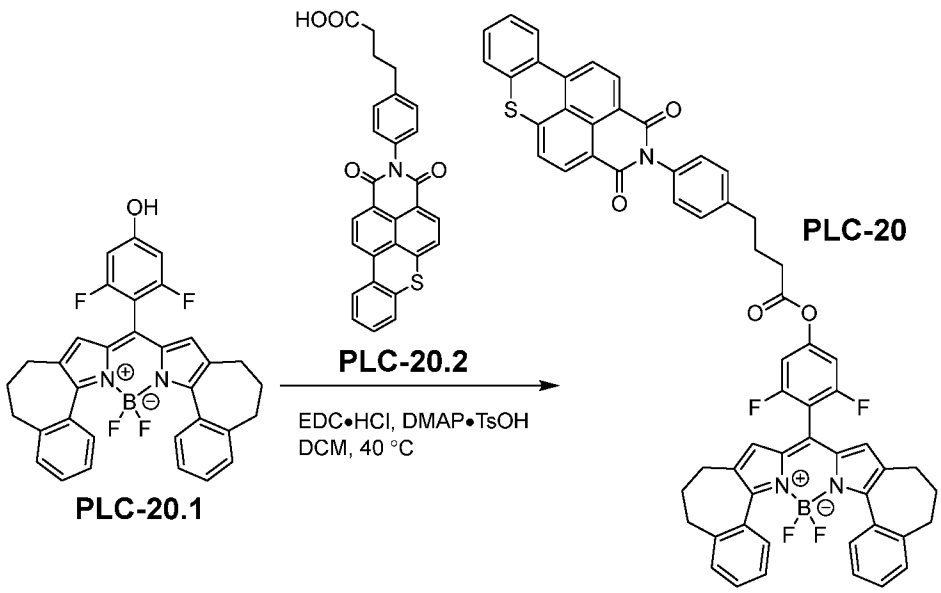
triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-18**, 43.0 mg, 78% yield. MS (APCI): calculated for $C_{63}H_{48}BF_2N_3O_6S$ ([M-H]$^-$) = 1023 found: 1023. ^{1}H NMR (400 MHz, $CDCl_3$) 8.68 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.26 (m, 2H), 8.11 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.44 (m, 5H), 7.31 (m, 6H), 7.21 (m, 2H), 6.50 (s, 2H), 6.49 (s, 2H), 3.77 (s, 6H), 2.89 (t, *J* = 7.2 Hz, 2H), 2.71 (t, *J* = 7.2 Hz, 2H), 2.62 (m, 4H), 2.28 (m, 6H), 2.02 (ddd, *J* = 7.2 Hz, *J* = 7.2 Hz, *J* = 7.2 Hz, 4H).

Synthesis of PLC-19:



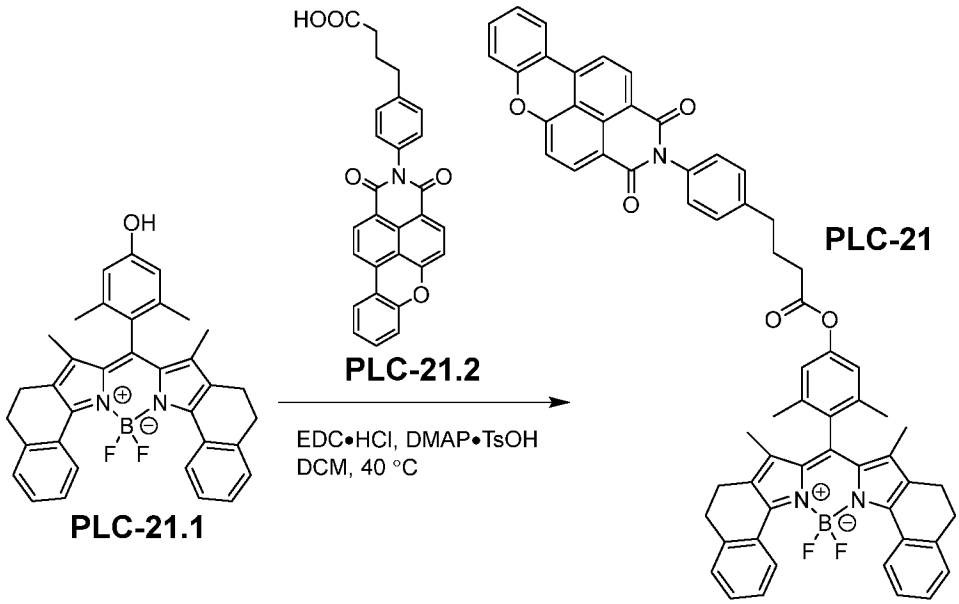
General Procedure of PLC-19: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-19.1** (30.0 mg, 0.057 mmol), **PLC-19.2** (33.3 mg, 0.072 mmol), EDC•HCl (54.6 mg, 0.285 mmol) and DMAP•TsOH (34.2 mg, 0.114 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-19** as a dark blue green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-19**, 43.0 mg, 78% yield. MS (APCI): calculated for $C_{59}H_{38}BF_4N_3O_4S$ ([M-H]$^-$) = 971 found: 971. ^{1}H NMR (400 MHz, $CDCl_3$) 8.80 (m, 2H), 8.67 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.25 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.44 (m, 7H), 7.31 (m, 5H), 7.24 (m, 1H), 6.94 (m, 2H), 6.50 (s, 2H), 2.91 (m, 6H), 2.70 (m, 6H), 2.20 (ddd, *J* = 7.6 Hz, *J* = 7.6 Hz, *J* = 7.6 Hz, 4H).

Synthesis of PLC-20:



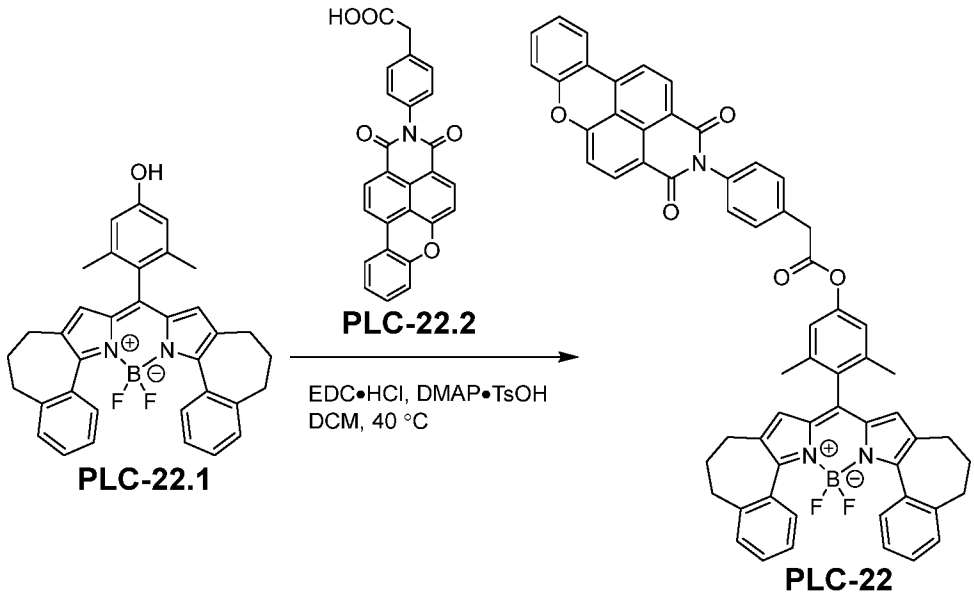
General Procedure of PLC-20: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-20.1** (30.0 mg, 0.054 mmol), **PLC-20.2** (31.6 mg, 0.068 mmol), EDC•HCl (51.8 mg, 0.270 mmol) and DMAP•TsOH (32.4 mg, 0.108 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-20** as a dark blue green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-20**, 30.0 mg, 56% yield. MS (APCI): calculated for $C_{61}H_{42}BF_4N_3O_4S$ ([M-H]$^-$) = 999 found: 999. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) 8.65 (d, *J* = 8.0 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.28 (m, 2H), 8.03 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.47 (m, 5H), 7.33 (m, 8H), 7.04 (m, 2H), 6.63 (s, 2H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.64 (m, 4H), 2.35 (bs, 3H), 2.13 (m, 6H).

Synthesis of PLC-21:



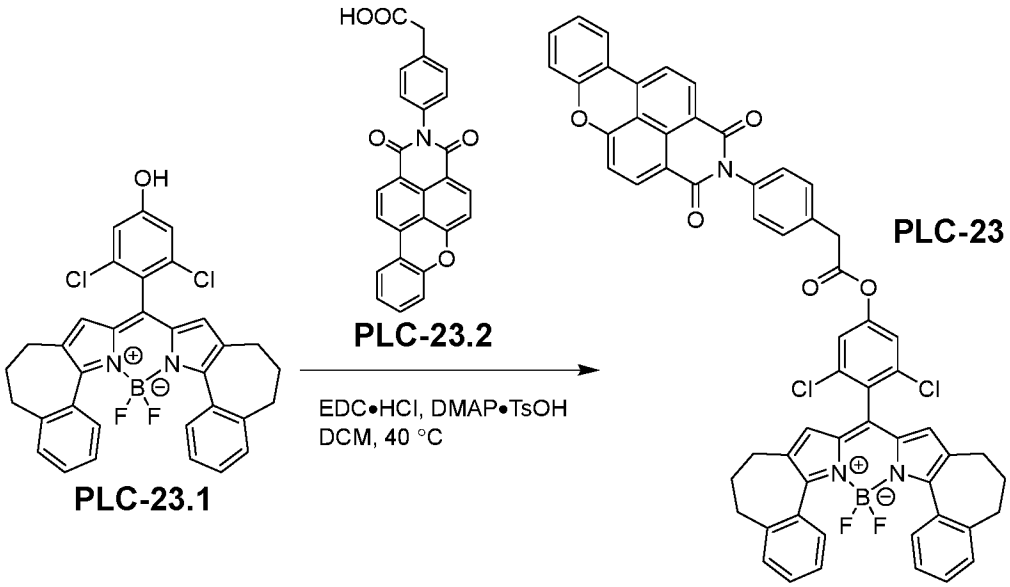
General Procedure of PLC-21: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-21.1** (30.0 mg, 0.055 mmol), **PLC-21.2** (31.0 mg, 0.069 mmol), EDC•HCl (52.7 mg, 0.275 mmol) and DMAP•TsOH (33.0 mg, 0.110 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-21** as a dark blue green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-21**, 39.0 mg, 72% yield. MS (APCI): calculated for $C_{63}H_{48}BF_2N_3O_5$ ([M-H]-) = 975 found: 975. 1H NMR (400 MHz, $CDCl_2CDCl_2$) 8.76 (m, 2H), 8.66 (d, J = 8.0 Hz, 1H), 8.61 (d, J = 8.0 Hz, 1H), 8.13 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.60 (td, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.38 (m, 13H), 7.01 (s, 2H), 2.91 (m, 6H), 2.72 (t, J = 7.2 Hz, 2H), 2.57 (m, 4H), 2.25 (s, 6H), 2.23 (m, 2H), 1.42 (s, 6H).

Synthesis of PLC-22:



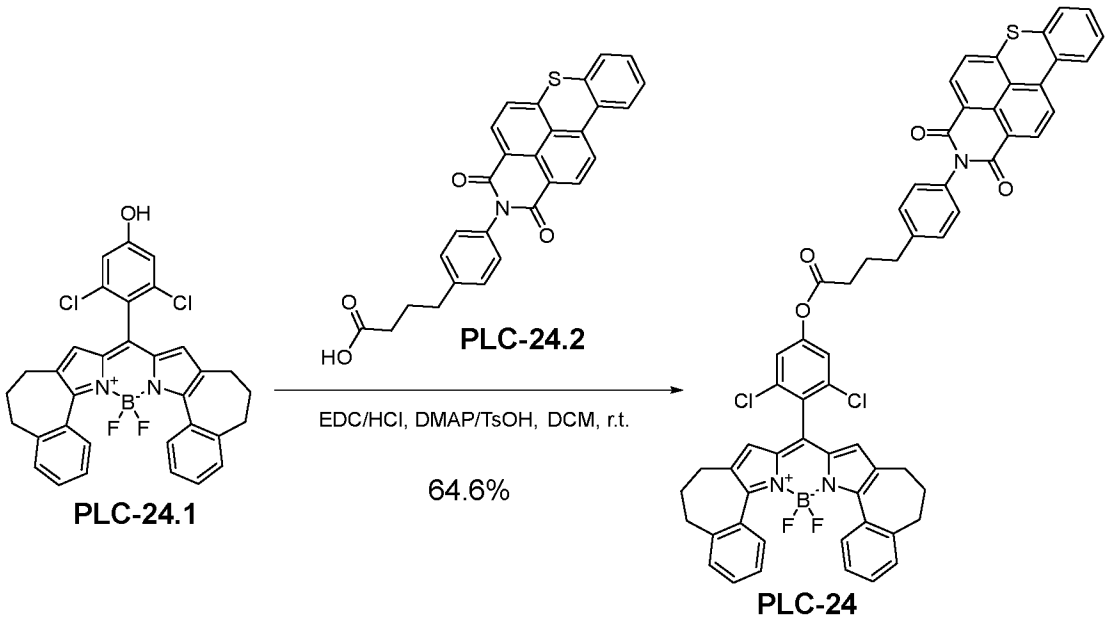
General Procedure of PLC-22: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-22.1** (30.0 mg, 0.055 mmol), **PLC-22.2** (29.0 mg, 0.069 mmol), EDC•HCl (52.7 mg, 0.275 mmol) and DMAP•TsOH (33.0 mg, 0.110 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-22** as a dark blue green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-22**, 33.0 mg, 63% yield. MS (APCI): calculated for $C_{61}H_{44}BF_2N_3O_5$ ($[M-H]^-$) = 947 found: 947. ^1H NMR (400 MHz, $CDCl_2CDCl_2$) 8.67 (d, *J* = 8.0 Hz, 1H), 8.62 (d, *J* = 8.0 Hz, 1H), 8.14 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 8.05 (m, 2H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.66 (m, 2H), 7.60 (td, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.37 (m, 11H), 7.01 (s, 2H), 6.46 (s, 2H), 4.04 (s, 2H), 2.63 (m, 4H), 2.30 (m, 9H), 2.04 (m, 4H).

Synthesis of PLC-23:



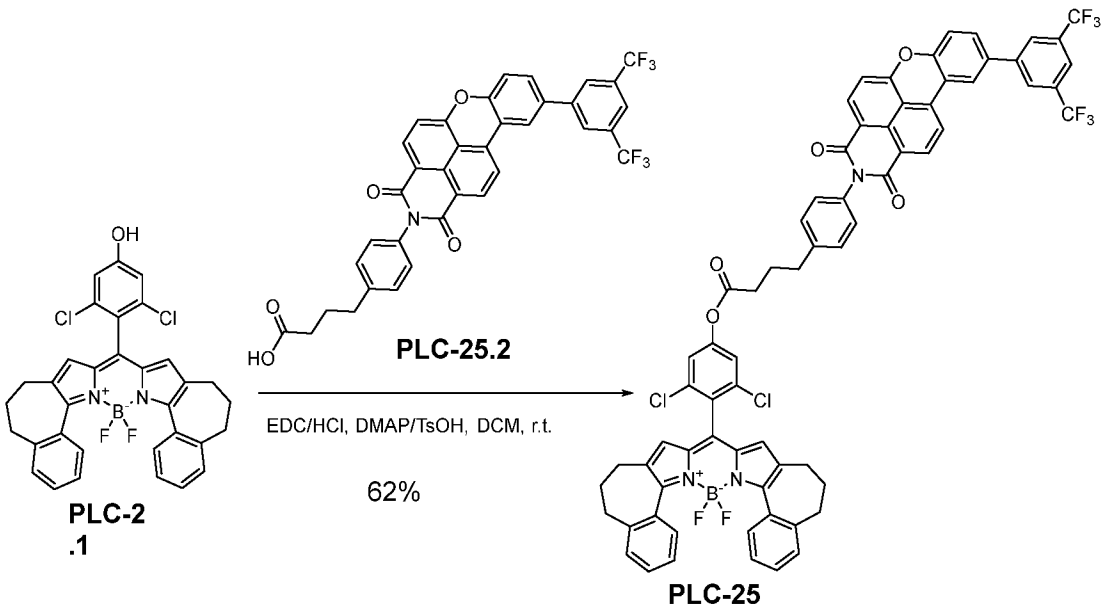
General Procedure of PLC-23: A 10 mL vial was fitted with a stir bar. To the vial, compound **PLC-23.1** (30.0 mg, 0.051 mmol), **PLC-23.2** (27.0 mg, 0.064 mmol), EDC•HCl (48.9 mg, 0.255 mmol) and DMAP•TsOH (30.6 mg, 0.102 mmol) were added, followed by anhydrous DCM (1.5 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down to room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-5%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-23** as a dark blue green solid. The solid was further triturated with MeOH (10 ml) to deliver RL-naphthalimide-BODIPY **PLC-23**, 17.0 mg, 34% yield. MS (APCI): calculated for $C_{59}H_{38}BCl_2F_2N_3O_5$ ([M-H]$^-$) = 988 found: 988. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) 8.67 (d, *J* = 8.0 Hz, 1H), 8.62 (d, *J* = 8.0 Hz, 1H), 8.14 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 8.05 (m, 2H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.65 (m, 2H), 7.60 (td, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.43 (s, 2H), 7.38 (m, 11H), 6.48 (s, 2H), 4.06 (s, 2H), 2.64 (m, 4H), 2.33 (bs, 3H), 2.05 (m, 4H).

Synthesis of PLC-24:



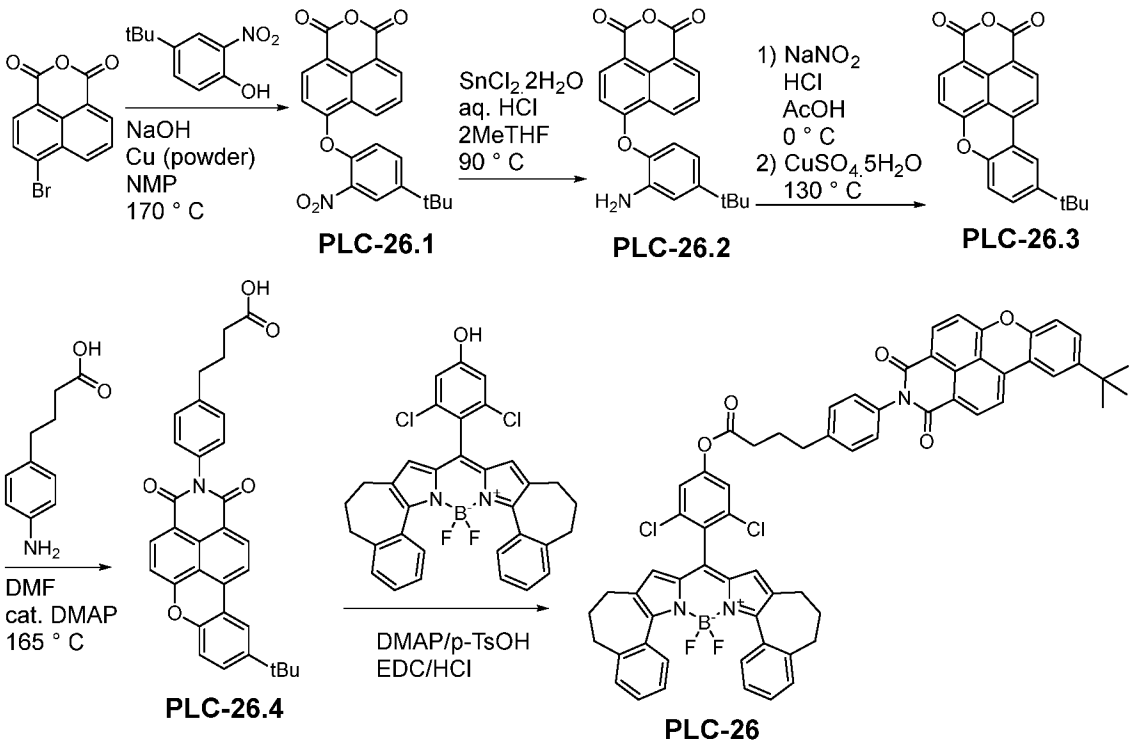
General Procedure of PLC-24: A mixture of compound **PLC-24.1** (16 mg, 0.027 mmol), compound **PLC-24.2** (19 mg, 0.04 mmol), EDC•HCl (52 mg, 0.27 mmol) and DMAP/p-TsOH (8 mg, 0.027 mmol) in DCM (5 mL) was stirred at room temperature overnight. The resulted mixture was then loaded on silica gel, purified by flash chromatography using eluents of hexanes/DCM (50% → 100% DCM), then DCM/ethyl acetate (0% → 5% ethyl acetate). The main red fraction was collected and concentrated under reduced pressure. The resulted solid was triturated with methanol, filtered and dried in air to give a dark red solid (18mg, in 64.6% yield). LCMS (APCI-): calculated for $C_{61}H_{42}BCl_2F_2N_3O_4S$ (M-) = 1031.23; Found: 1031. ^{1}H NMR (400 MHz, d2-TCE) δ 8.56 (d, *J* = 8.2 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.19 (dd, *J* = 8.8, 4.5 Hz, 2H), 7.97 (s, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.38 (dt, *J* = 7.3, 2.4 Hz, 5H), 7.29 (d, *J* = 9.3 Hz, 6H), 7.24 – 7.15 (m, 4H), 6.40 (s, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.54 (d, *J* = 6.8 Hz, 4H), 2.24 (s, 4H), 2.11 (td, *J* = 13.4, 11.8, 5.9 Hz, 2H), 2.04 – 1.89 (m, 4H).

Synthesis of PLC-25:



General Procedure of PLC-25: A mixture of compound **PLC-2.1** (20 mg, 0.034 mmol), compound **Ex-5** (27 mg, 0.051 mmol), EDC•HCl (60 mg, 0.31 mmol) and DMAP/p-TsOH (8.8 mg, 0.03 mmol) in DCM (4mL) was stirred at room temperature overnight. The resulted mixture was then loaded on silica gel, purified by flash chromatography using eluents of DCM/ethyl acetate (0% → 10% ethyl acetate). The main red fraction was collected and concentrated to 0.5mL under reduced pressure, then 10 mL methanol was added. The resulted precipitate was filtered and dried in air to give a dark red solid (23 mg, in 62% yield). LCMS (APCI-): calculated for $C_{69}H_{44}BCl_2F_8N_3O_5$ (M-) = 1227.26; Found: 1227. ^{1}H NMR (400 MHz, d2-TCE) δ 8.58 (dd, *J* = 19.5, 8.1 Hz, 2H), 8.18 (d, *J* = 2.2 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 1.5 Hz, 2H), 7.97 (t, *J* = 4.6 Hz, 2H), 7.87 (s, 1H), 7.72 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.32 – 7.25 (m, 6H), 7.25 – 7.18 (m, 4H), 6.40 (s, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.61 – 2.50 (m, 4H), 2.24 (s, 4H), 2.13 (q, *J* = 7.4 Hz, 2H), 2.04 – 1.90 (m, 4H).

Synthesis of PLC-26:



Compound PLC-26.1 (6-(4-(tert-butyl)-2-nitrophenoxy)-1H,3H-benzo[de]isochromene-1,3-dione): A 1L 2N round-bottom flask was charged with a stir bar and placed in an aluminum heat block. The flask was fitted with a finned condenser, gas adapter, and flow control. The flask was flushed with argon. To the flask was added 6-bromo-1H,3H-benzo[de]isochromene-1,3-dione (40.0 mmol, 11.084 g) and 4-(tert-butyl)-2-nitrophenol (60.0 mmol, 11.712 g), NaOH (20.0 mmol, 800 mg), copper powder (20.0 mmol, 1.271 g) and anhydrous NMP (150 mL). The flask was closed and stirred under argon. The heat block was set to 170 °C and the reaction mixture heated at this temperature overnight. LCMS indicated completion of the reaction. The reaction mixture was cooled to room temperature. To the flask was added 1N HCl (44 mL) and water (175 mL). After stirring for about 15 minutes, the resulting precipitate was filtered off, washing with water. The dried precipitate was dissolved in warm ethyl acetate and filtered warm to remove a small amount of insoluble material. The ethyl acetate was removed in vacuo. The resulting solid was triturated with hot methanol, then allowed to cool to room temperature. The resulting precipitate was filtered off, washing with methanol. The solid was dried in a vacuum oven at 100 °C. Gives 8.18 g (52% yield). MS (APCI): calculated for $C_{22}H_{17}NO_6$ (M+H) = 392; found: 392. 1H NMR (400 MHz, Tetrachloroethane-d_2) δ 8.82 (dd, J = 8.5, 1.2 Hz, 1H), 8.71 (dd, J = 7.3, 1.2 Hz, 1H), 8.49 (d, J =

8.3 Hz, 1H), 8.16 (d, J = 2.4 Hz, 1H), 7.91 (dd, J = 8.4, 7.3 Hz, 1H), 7.80 (dd, J = 8.6, 2.4 Hz, 1H), 7.34 (d, J = 8.6 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 1.43 (s, 9H).

Compound PLC-26.2 (6-(2-amino-4-(tert-butyl)phenoxy)-1H,3H-benzo[de]isochromene-1,3-dione): A 250 mL 2N round bottom flask was charged with a stir bar and fitted with a finned condenser, gas adapter, and flow control. The flask was placed in an aluminum heat block. The flask was flushed with argon. To the flask was added compound **PLC-26.1** (10.0 mmol, 3.914g), and $SnCl_2.2H_2O$ (40.0 mmol, 9.024 g), followed by 2-methylTHF (70 mL) and concentrated hydrochloric acid (4.0 M) (100 mmol, 25 mL). The flask was closed and heated to 90 °C under argon for 30 minutes, at which point TLC showed complete conversion to the product. The reaction mixture was cooled to room temperature, then the pH was adjusted to pH ~8 with 2N NaOH. The resulting precipitate was filtered off. The solids were extracted with 2-methylTHF (8X100mL). The layers were separated, the organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. The resulting solid was dried at 120 °C. Gives the product in quantitative yield. MS (APCI): calculated for $C_{22}H_{19}NO_4$ (M+H) = 362; found: 362. 1H NMR (400 MHz, Tetrachloroethane-d_2) δ 8.88 (dd, J = 8.4, 1.2 Hz, 1H), 8.69 (dd, J = 7.3, 1.2 Hz, 1H), 8.48 (d, J = 8.4 Hz, 1H), 7.89 (dd, J = 8.4, 7.3 Hz, 1H), 7.03 – 6.93 (m, 3H), 6.88 (dd, J = 8.4, 2.3 Hz, 1H), 1.35 (s, 9H).

Compound PLC-26.3 (9-(tert-butyl)-1H,3H-isochromeno[6,5,4-mna]xanthene-1,3-dione): A 40 mL vial was charged with $NaNO_2$ (30.0 mmol, 2.070 g), water (10 mL), and a stir bar. The vial was placed in an ice-water bath and stirred to dissolve. A 100 mL round bottom flask was charged with a stir bar and compound **PLC-26.2** (4.00 mmol, 1.446 g), hydrochloric acid (37%) (20.0 mmol, 12.1M, 1.65 mL), and glacial acetic acid (30 mL). The flask was lowered into an ice-water bath and stirred for about 1 minute, then the addition of the solution of sodium nitrite was begun in small portions over a period of 3 minutes. The solution was stirred in the ice-water bath for one hour. A 1 L 2N round bottom flask was clamped by of off-center neck at an angle, such that a dropping funnel inserted into the neck would drop into the top of the stirred vortex. The other neck was fitted with a finned condenser. To this flask was added a large stir bar, $CuSO_4.5H_2O$ (27.4 mmol, 6.842 g), and water (80 mL). Near the end of the one hour waiting period for the diazo salt, the copper (II) solution was placed in an aluminum heat block and the temperature set to 130 °C. When the copper (II) solution reached 130 °C, the diazo solution was transferred to the dropping funnel. The reaction was

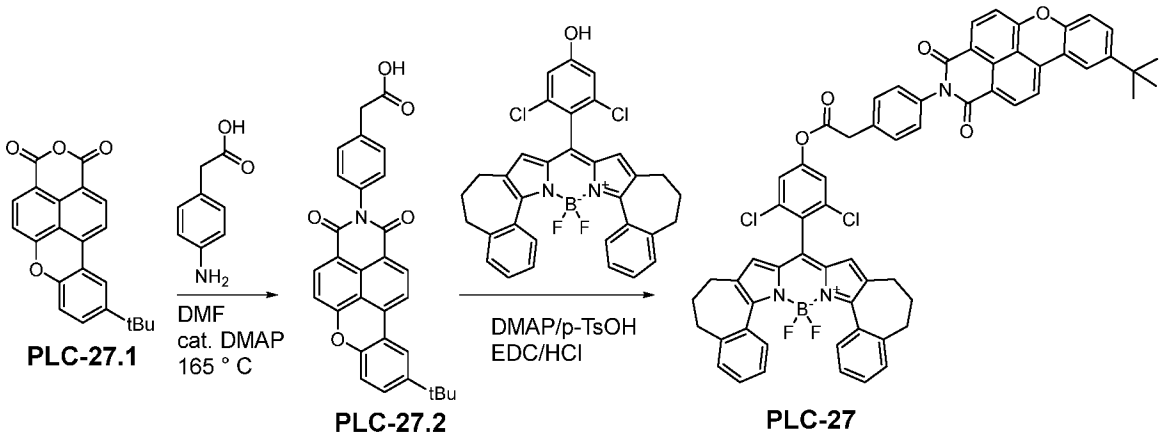
stirred at max RPM and the diazo solution was added dropwise over a period of about 20 minutes. The resulting solution was stirred at 130 °C for 2 minutes, then removed from the heat block and stirred at room temperature overnight. The precipitate was filtered off, washing with water. The crude precipitate was dried, then dissolved and evaporated in vacuo onto silica gel. Purified by column chromatography on silica gel (220 g, equilibrate 50% hexanes/DCM, eluting 50% (2 CV) → 100% DCM (20 CV), isocratic DCM (15 CV) → 0% EtOAc/DCM (0 CV) → 1% EtOAc/DCM (10 CV)). Product tails. Collected all fractions with product and evaporated to dryness in vacuo. Gives 528 mg (38% yield). MS (APCI): calculated for $C_{22}H_{16}O_4$ (M+H) = 345; found: 345. 1H NMR (400 MHz, Tetrachloroethane-d2) δ 8.61 (d, J = 7.9 Hz, 1H), 8.56 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 2.2 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.66 (dd, J = 8.8, 2.2 Hz, 1H), 7.38 (d, J = 8.7 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 1.44 (s, 9H).

Compound PLC-26.4 (4-(4-(9-(tert-butyl)-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)butanoic acid): A 100 mL 2N RBF was charged with a stir bar and fitted with a finned condenser, gas adapter, and flow control valve. The flask was flushed with argon and charged with compound **PLC-26.3** (1.525 mmol, 525 mg), 4-(4-aminophenyl) butanoic acid (3.05 mmol, 546 mg), and DMAP (0.1113 mmol, 14 mg). To the flask was added anhydrous DMF (10 mL). The flask was sealed and stirred under argon. The heat block was set to 175 °C and the reaction was heated and stirred for 6.5 hours, then stirred at room temperature overnight. To the reaction mixture was added acetone (25 mL) and water (25 mL). The precipitate was stirred for 5 minutes, then filtered off, washing with 1:1 water:acetone. The precipitate was dried under argon flow at 120 °C. Gives 738 mg (96% yield). MS (APCI): calculated for $C_{32}H_{27}NO_5$ (M+H) = 506; found: 506. 1H NMR (400 MHz, DMSO-d6) δ 12.12 (s, 1H), 8.48 – 8.29 (m, 3H), 8.23 (d, J = 2.3 Hz, 1H), 7.68 (dd, J = 8.8, 2.3 Hz, 1H), 7.43 – 7.30 (m, 4H), 7.25 (d, J = 7.9 Hz, 2H), 2.75 – 2.64 (m, 2H), 2.30 (t, J = 7.4 Hz, 2H), 1.88 (p, J = 7.5 Hz, 2H), 1.41 (s, 9H).

Compound PLC-26 (3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenyl 4-(4-(9-(tert-butyl)-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)butanoate): A 40 mL vial was charged with a stir bar, 3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-

c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenol (0.050 mmol, 29.3 mg), compound **PLC-26.4** (0.075 mmol, 37.9 mg), DMAP.pTsOH salt (0.100 mmol, 29.4 mg), and EDC.HCl (0.075 mmol, 14.4 mg), followed by anhydrous DCM (10 mL). The vial was capped and stirred at room temperature 4.5 hours. The reaction mixture was diluted with hexanes (to ~35 mL) and loaded onto a solid load cartridge (~20g SiO_2). The reaction mixture was purified by column chromatography on silica gel (120g, equilibrate 100% toluene, eluting 100% (5 CV) → 5% EtOAc/toluene (30 CV)). Fractions containing product were evaporated to dryness and re-purified by flash chromatography on silica gel (solid load, 120g column, equilibrate 40% DCM/hexanes, eluting 40% (2 CV) → 100% DCM (10 CV) → isocratic DCM until compound fully elutes)). Fractions containing product were evaporated to dryness in vacuo. Gives 19.8 mg (37% yield). MS (APCI): calculated for $C_{65}H_{50}BCl_2F_2N_3O_5$ (M-) = 1071; found: 1071. 1H NMR (400 MHz, Methylene Chloride-d2) δ 8.65 (d, J = 7.9 Hz, 1H), 8.58 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 2.3 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 6.8 Hz, 2H), 7.63 (dd, J = 8.7, 2.3 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.40 (s, 2H), 7.38 – 7.24 (m, 10H), 6.51 (s, 2H), 2.90 (t, J = 7.6 Hz, 2H), 2.75 (t, J = 7.4 Hz, 2H), 2.64 (t, J = 6.8 Hz, 4H), 2.43 – 2.26 (m, 4H), 2.21 (p, J = 7.5 Hz, 2H), 2.05 (p, J = 7.0 Hz, 4H), 1.44 (s, 9H).

Synthesis of PLC-27:

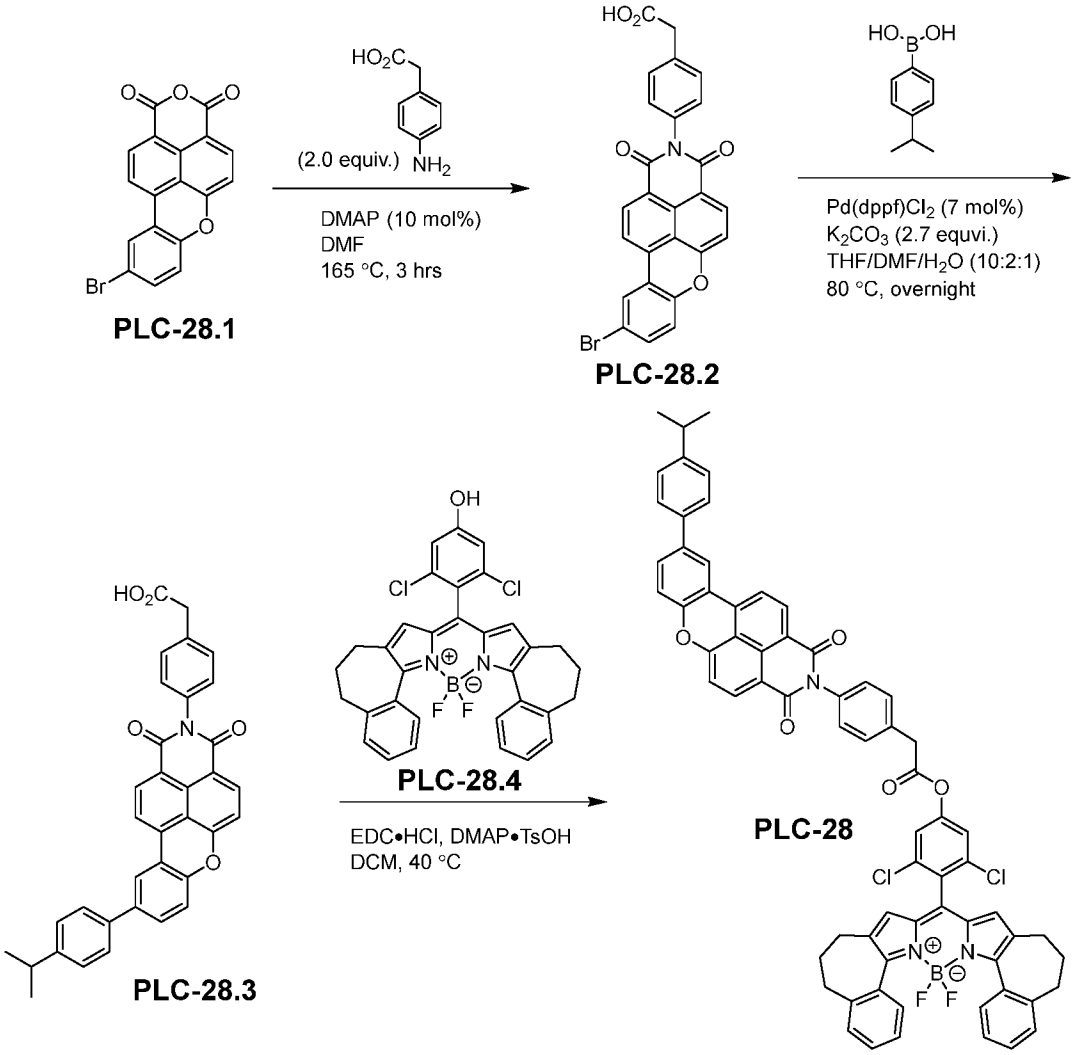


Compound PLC-27.2 (2-(4-(9-(tert-butyl)-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetic acid): Compound **PLC-27.2** was synthesized from compound **PLC-27.1** (1.191 mmol, 410 mg), 2-(4-aminophenyl)acetic acid (2.98 mmol, 450 mg), and DMAP (0.0869 mmol, 11 mg) in a manner similar to compound **PLC-26.4**. Gives the product in quantitative yield. MS (APCI): calculated for $C_{30}H_{23}NO_5$ (M+H) = 478; found: 478.

1H NMR (400 MHz, DMSO-d6) δ 8.48 (d, J = 7.9 Hz, 1H), 8.44 (d, J = 8.3 Hz, 1H), 8.38 (d, J = 8.1 Hz, 1H), 8.27 (d, J = 2.4 Hz, 1H), 7.69 (dd, J = 8.8, 2.3 Hz, 1H), 7.45 – 7.38 (m, 4H), 7.31 – 7.27 (m, 2H), 3.68 (s, 2H), 1.41 (s, 9H).

Compound PLC-27 (3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenyl 2-(4-(9-(tert-butyl)-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetate): Compound **PLC-27** was synthesized from 3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenol (0.100 mmol, 58.6 mg), compound **PLC-27.2** (0.150 mmol, 71.6 mg), DMAP/pTsOH salt (0.200 mmol, 58.8 mg), and EDC/HCl (0.150 mmol, 28.8 mg), followed by anhydrous DCM (10 mL). The vial was capped and stirred at room temperature overnight. The next morning, added more of compound EDC.HCl (0.200 mmol, 38.8 mg) and stirred at room temperature for 90 minutes. Added more EDC.HCl (0.200 mmol, 38.3 mg) and continued stirring at room temperature for 2 hours. Added compound **PLC-27.2** (0.075 mmol, 35.8 mg) and continued stirring at room temperature for 2 hours. The crude reaction mixture was purified by flash chromatography on silica gel (solid load, 120 g column, equilibrate 40% DCM/hexanes, eluting 40% (2 CV) → 100% DCM (10 CV) → isocratic DCM until compound fully elutes)). Fractions containing product were evaporated to dryness in vacuo. Gives 11.0 mg (11% yield). MS (APCI): calculated for $C_{63}H_{46}BCl_2F_2N_3O_5$ (M-) = 1043; found: 1043. 1H NMR (400 MHz, Methylene Chloride-d2) δ 8.67 (d, J = 7.9 Hz, 1H), 8.60 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 2.3 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 6.9 Hz, 2H), 7.64 (dd, J = 8.8, 2.3 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.44 (s, 2H), 7.40 – 7.27 (m, 10H), 6.51 (s, 2H), 4.07 (s, 2H), 2.70 – 2.58 (m, 4H), 2.33 (s, 4H), 2.05 (p, J = 7.1 Hz, 4H), 1.44 (s, 9H).

Synthesis of compound PLC-28



Compound PLC-28.2 2-(4-(9-bromo-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetic acid: A mixture of **PLC-28.1** (400.0 mg, 1.1 mmol), **4-aminophenylacetic acid** (329.4 mg, 2.2 mmol) and DMAP (9.3 mg, 0.080 mmol) in DMF (8 mL) was degassed at room temperature. Then the mixture was heated up to 165 ºC and has been kept at this temperature for 3 hrs. TLC and LCMS showed ~95% conversion without observable side-reaction. The mixture was cooled down to 50 ºC. Then it was poured into an acetone solution (40 mL), which has been pre-chilled by water-ice bath. The mixture has been kept at 0 ºC for 2 hrs and then has been kept stirring at room temperature overnight. The solid was collected through vacuum filtration and washed by acetone (4 mL). And it was dried by vacuum oven at 100 ºC for 3 hrs to provide the pure compound **PLC-28.2** as a yellow brown solid 395.0 mg, 73% yield. MS (APCI): calculated for $C_{26}H_{14}BrNO_5$ ($[M+H]^+$) = 500 found: 500. 1H NMR (400 MHz, CDCl2CDCl2) δ 8.65 (d, J = 8.0 Hz, 1H), 8.62 (d, J = 8.0 Hz, 1H), 8.21 (dd, J

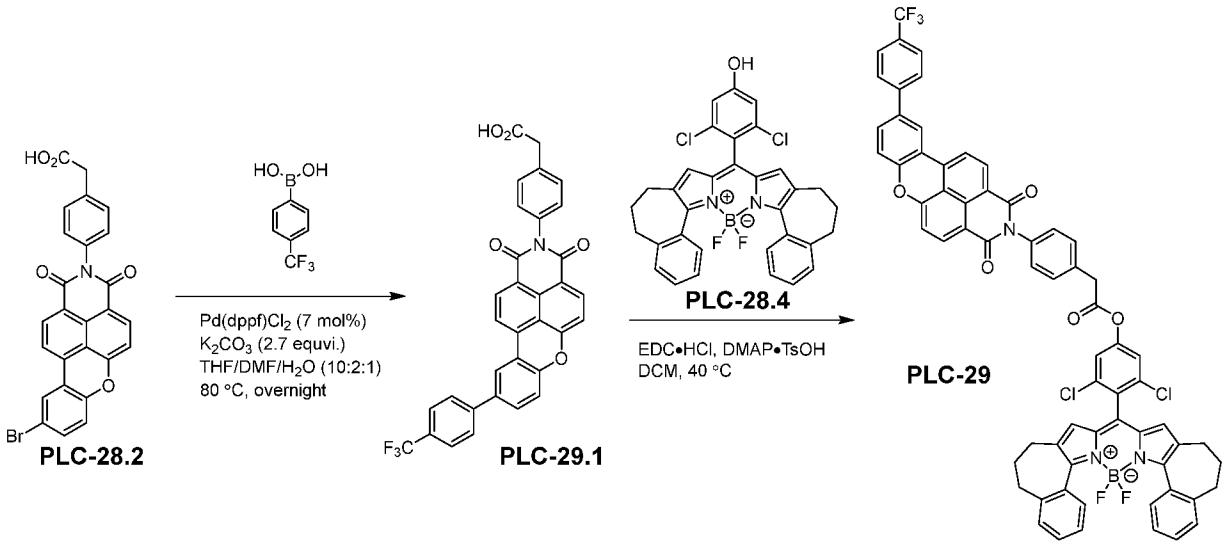
= 6.4 Hz, 2.4 Hz, 1H), 7.99 (bs, 1H), 7.95 (t, J = 7.6 Hz, 1H), 7.67 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.4 Hz, 1H), 7.32 (m, 3H), 2.94 (s, 2H).

Compound PLC-28.3 – 2-(4-(9-(4-isopropylphenyl)-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetic acid: A mixture of **PLC-28.2** (175.0 mg, 0.35 mmol), **4-isopropylphenylboronic acid** (114.8 mg, 0.70 mmol), $Pd(dppf)Cl_2$ (18.0 mg, 0.025 mmol) and K_2CO_3 (130.4 mg, 0.95 mmol) in THF-DMF-H_2O (10 mL/ 2 mL/ 1 mL) was degassed at room temperature. Then the mixture was heated up to 80 ºC and has been kept at this temperature overnight. TLC and LCMS showed the completion of the reaction. The mixture was cooled down to room temperature. Then it was added with 0.1 HCl (75 mL) and EtOAc (75 mL). Once separated by separation funnel, the aqueous solution was further extracted with THF (75 mL*3) after it was saturated with NaCl. The combined organic phase was dried over anhydrous Na_2SO_4, then it was filtered and concentrated under rotavapor, and purified by silica gel flash chromatography to provide **PLC-28.3** as a yellow solid using 0-40% EtOAc in DCM with 0.1% TFA as an eluant, 70.0 mg, 37% yield. MS (APCI): calculated for $C_{35}H_{25}NO_5$ ($[M-H]^-$) = 539 found: 539. ^1H NMR (400 MHz, $CDCl_2CDCl_2$) δ 8.66 (d, *J* = 7.6 Hz, 1H), 8.61 (d, *J* = 8.4 Hz, 1H), 8.26 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.79 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.45 (m, 11H), 3.81 (s, 2H), 3.01 (quintet, *J* = 7.2 Hz, 1H), 1.33 (d, *J* = 7.2 Hz, 6H).

Compound PLC-28 synthesis: A 25 mL vial was fitted with a stir bar. To the vial, compound **PLC-28.4** (44.0 mg, 0.075 mmol), **PLC-28.3** (81.0 mg, 0.15 mmol), EDC•HCl (71.9 mg, 0.38 mmol) and DMAP•TsOH (45.0 mg, 0.15 mmol) were added, followed by anhydrous DCM (4.4 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-4%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-28** as a dark blue solid. The solid was further triturated with MeOH (15 ml) to deliver RL-naphthalimide-BODIPY **PLC-28**, 46.0 mg, 55% yield. MS (APCI): calculated for $C_{68}H_{48}BCl_2F_2N_3O_5$ ($[M-H]^-$) = 1106 found: 1106. ^1H NMR (400 MHz, $CDCl_2CDCl_2$) 8.67 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 2.4 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.05 (m, 2H), 7.81 (dd, *J* = 8.0 Hz, *J* = 2.4 Hz, 1H), 7.65 (m, 4H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.39 (m,

11H), 7.30 (m, 2H), 6.49 (s, 2H), 4.07 (s, 2H), 3.01 (pentet, *J* = 6.8 Hz, 1H), 2.64 (m, 4H), 2.33 (bs, 3H), 2.06 (m, 4H), 1.33 (d, *J* = 6.8 Hz, 6H).

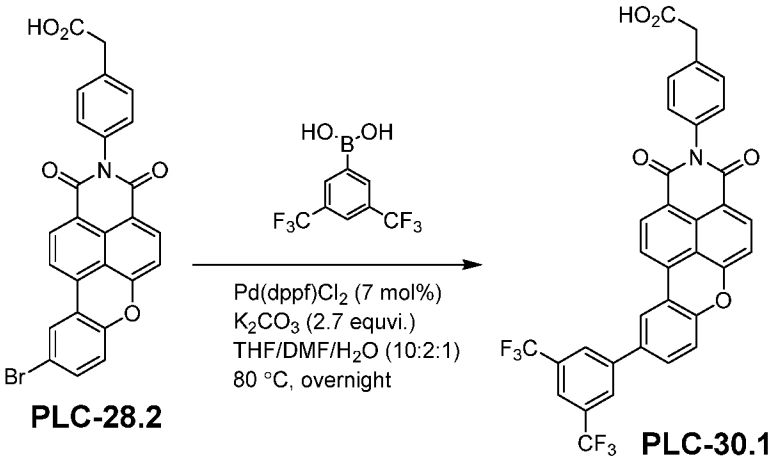
Synthesis of compound PLC-29



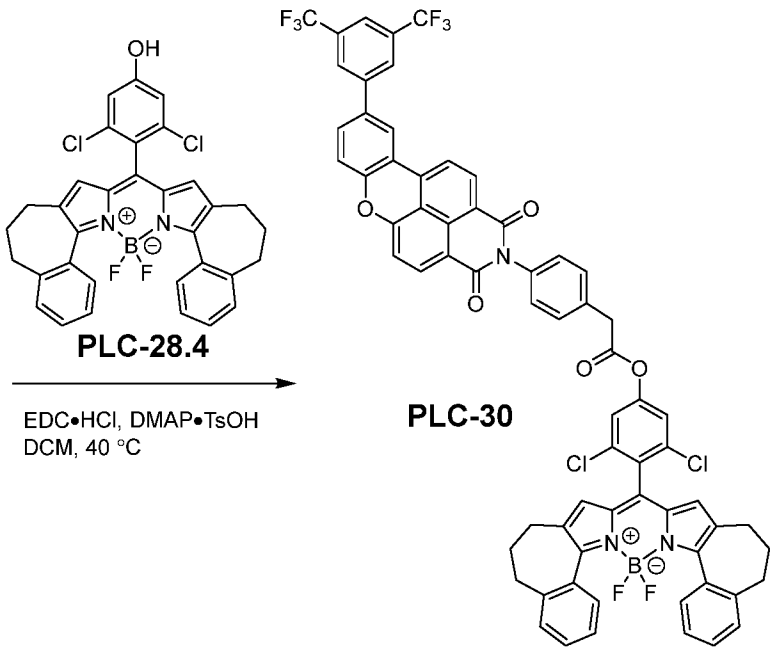
Compound 29.1 – 2-(4-(1,3-dioxo-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetic acid: A 100 mL vial was fitted with a stir bar. To the vial, compound **PLC-28.2** (400.0 mg, 0.80 mmol), **4-(trifluoromethyl)phenylboronic acid** (262.2 mg, 1.6 mmol), $Pd(dppf)Cl_2$ (41.0 mg, 0.056 mmol) and K_2CO_3 (298.0 mg, 2.2 mmol) in $THF/DMF/H_2O$ (22 ml/ 4.4 ml/ 2.2 ml) was degassed at room temperature. The reaction mixture was heated up to 80 ºC and the reaction has been kept at this temperature overnight. TLC was used to monitor the reaction. After the completion, the reaction was worked up by the addition of 0.1N HCl (150 ml) and EtOAc (150 ml). The aqueous phase was further extracted by THF (150 ml*3). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated under rotavapor and purified by flash chromatography, using DCM in EtOAc (0-40%, with 0.1% TFA) as an eluant to provide the pure RL-naphthalimide derivative **PLC-29.1** as a yellow/ yellow brown solid. 363.0 mg, 80% yield. MS (APCI): calculated for $C_{33}H_{18}F_3NO_5$ ($[M+H]^+$) = 566 found: 566. ^1H NMR (400 MHz, DMSO-d_6) 8.76 (m, 1H), 8.56 (m, 2H), 8.52 (dd, *J* = 8.0 Hz, *J* = 3.2 Hz, 1H), 8.15 (m, 2H), 8.06 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.66 (dd, *J* = 8.0 Hz, *J* = 4.0 Hz, 1H), 7.53 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 2H).

Compound PLC-29: A 25 mL vial was fitted with a stir bar. To the vial, compound **PLC-28.4** (40.0 mg, 0.068 mmol), **PLC-29.1** (77.5 mg, 0.137 mmol), EDC•HCl (65.2 mg, 0.340 mmol) and DMAP•TsOH (41.1 mg, 0.137 mmol) were added, followed by anhydrous DCM (4 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-4%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-29** as a dark blue solid. The solid was further triturated with MeOH (15 ml) to deliver RL-naphthalimide-BODIPY **PLC-29**, 46.0 mg, 60% yield. MS (APCI): calculated for $C_{66}H_{41}BCl_2F_5N_3O_5$ ($[M-H]^-$) = 1132 found: 1132. ^1H NMR (400 MHz, $CDCl_2CDCl_2$) 8.69 (d, *J* = 8.0 Hz, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 2.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.06 (m, 2H), 7.82 (m, 5H), 7.65 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.39 (m, 9H), 7.30 (m, 2H), 6.48 (s, 2H), 4.07 (s, 2H), 2.63 (m, 4H), 2.33 (bs, 3H), 2.06 (m, 4H).

Synthesis of compound PLC-30



PLC-28.2 PLC-30.1



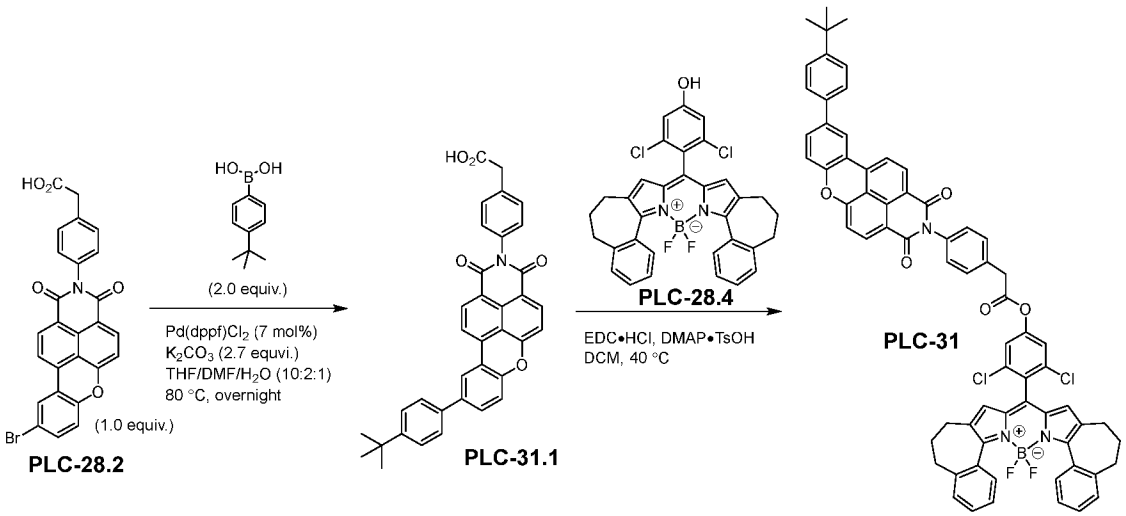
PLC-28.4 PLC-30

Compound PLC-30.1 —2-(4-(9-(3,5-bis(trifluoromethyl)phenyl)-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetic acid: A 100 mL vial was fitted with a stir bar. To the vial, compound **PLC-28.2** (400.0 mg, 0.80 mmol), **3,5-bis(trifluoromethyl)phenylboronic acid** (262.2 mg, 1.6 mmol), $Pd(dppf)Cl_2$ (41.0 mg, 0.056 mmol) and K_2CO_3 (412.6 mg, 2.2 mmol) in $THF/DMF/H_2O$ (22 ml/ 4.4 ml/ 2.2 ml) was degassed at room temperature. The reaction mixture was heated up to 80 ºC and the reaction has been kept at this temperature overnight. TLC was used to monitor the reaction. After the completion, the reaction was worked up by the addition of 0.1N HCl (150 ml) and EtOAc (150 ml). The aqueous phase was further extracted by THF (150 ml*3). The combined organic

phases were dried over anhydrous Na_2SO_4, concentrated under rotavapor and purified by flash chromatography, using DCM in EtOAc (0-40%, with 0.1% TFA) as an eluant to provide the pure RL-naphthalimide derivative **PLC-30.1** as a yellow/ yellow brown solid. 311.0 mg, 61% yield. MS (APCI): calculated for $C_{34}H_{17}F_6NO_5$ ([M+H]$^+$) = 634 found: 634. ^{1}H NMR (400 MHz, DMSO-d_6) 8.73 (m, 1H), 8.46 (m, 5H), 8.10 (m, 2H), 7.57 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.40 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 2H).

Compound PLC-30: A 25 mL vial was fitted with a stir bar. To the vial, compound **PLC-28.4** (40.0 mg, 0.068 mmol), **PLC-30.1** (86.8 mg, 0.137 mmol), EDC•HCl (65.2 mg, 0.340 mmol) and DMAP•TsOH (41.1 mg, 0.137 mmol) were added, followed by anhydrous DCM (4 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-4%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-30** as a dark blue solid. The solid was further triturated with MeOH (15 ml) to deliver RL-naphthalimide-BODIPY **PLC-30**, 76.0 mg, 93% yield. MS (APCI): calculated for $C_{67}H_{40}BCl_2F_8N_3O_5$ ([M-H]$^-$) = 1200 found: 1200. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) 8.70 (d, *J* = 8.0 Hz, 1H), 8.66 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 2.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.06 (m, 4H), 7.96 (m, 1H), 7.82 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.65 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.39 (m, 9H), 7.30 (m, 2H), 6.48 (s, 2H), 4.07 (s, 2H), 2.63 (m, 4H), 2.33 (bs, 3H), 2.05 (m, 4H).

Synthesis of compound PLC-31

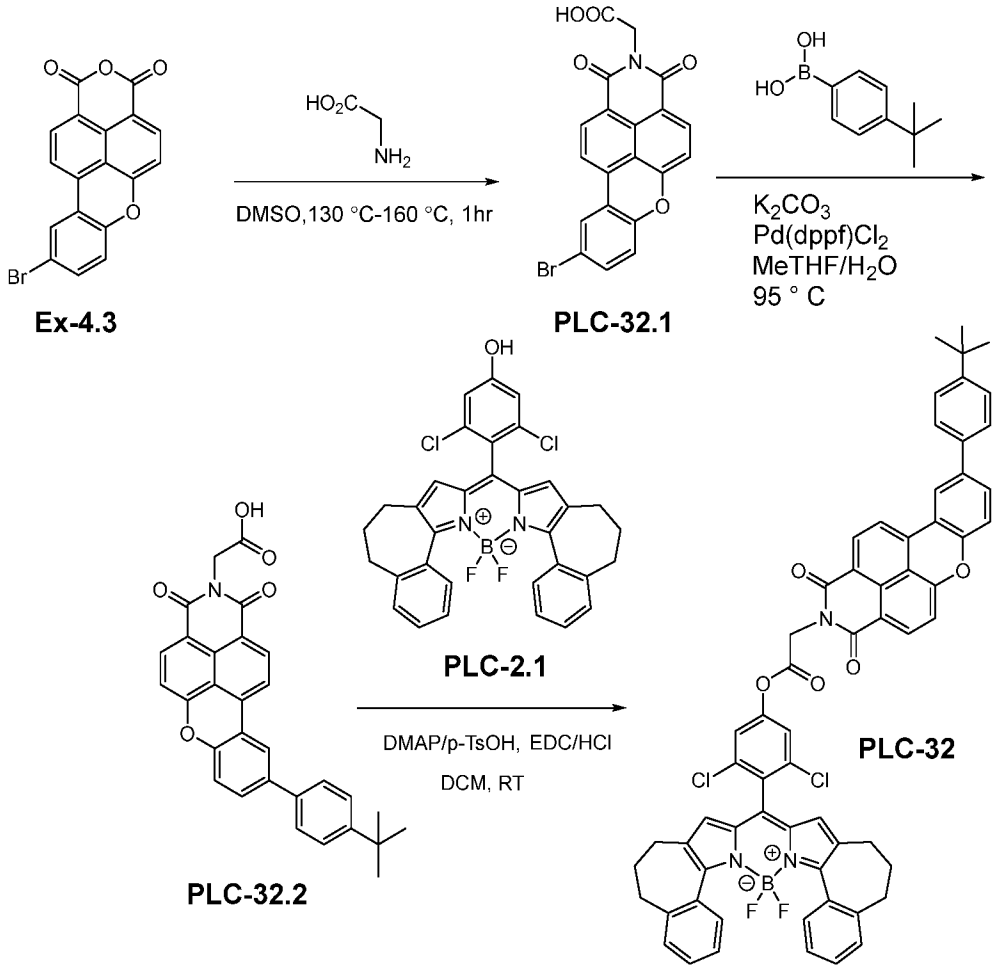


Compound PLC-31.1 – 2-(4-(9-(4-(tert-butyl)phenyl)-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetic acid: A mixture of **PLC-28.2** (175.0 mg, 0.35 mmol), **4-**

tert-butylphenylboronic acid (124.6 mg, 0.70 mmol), $Pd(dppf)Cl_2$ (18.0 mg, 0.025 mmol) and K_2CO_3 (130.4 mg, 0.95 mmol) in THF-DMF-H_2O (10 mL/ 2 mL/ 1 mL) was degassed at room temperature. Then the mixture was heated up to 80 ºC and has been kept at this temperature overnight. TLC and LCMS showed the completion of the reaction. The mixture was cooled down to room temperature. Then it was added with 0.1 HCl (75 mL) and EtOAc (75 mL). Once separated by separation funnel, the aqueous solution was further extracted with THF (75 mL*3) after it was saturated with NaCl. The combined organic phase was dried over anhydrous Na_2SO_4, then it was filtered and concentrated under rotavapor, and purified by silica gel flash chromatography to provide **PLC-31.1** as a yellow solid using 0-40% EtOAc in DCM with 0.1% TFA as an eluant, 76.0 mg, 39% yield. MS (APCI): calculated for $C_{36}H_{27}NO_5$ ($[M-H]^-$) = 553 found: 553. ^1H NMR (400 MHz, $CDCl_2CDCl_2$) δ 8.69 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.76 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.53 (m, 7H), 7.33 (m, 4H), 3.77 (s, 2H), 1.40 (s, 9H).

Compound PLC-31: A 25 mL vial was fitted with a stir bar. To the vial, compound **PLC-28.4** (40.0 mg, 0.068 mmol), **PLC-31.1** (75.8 mg, 0.137 mmol), EDC•HCl (65.2 mg, 0.340 mmol) and DMAP•TsOH (41.1 mg, 0.137 mmol) were added, followed by anhydrous DCM (4 ml). The reaction mixture was heated up to 40 ºC overnight. After the reaction was cooled down room temperature, the reaction mixture was loaded with silica gel and purified by flash chromatography, using DCM in EtOAc (0-4%) as an eluant to provide the pure RL-naphthalimide-BODIPY **PLC-31** as a dark blue solid. The solid was further triturated with MeOH (15 ml) to deliver RL-naphthalimide-BODIPY **PLC-31**, 40.0 mg, 52% yield. MS (APCI): calculated for $C_{69}H_{50}BCl_2F_2N_3O_5$ ($[M-H]^-$) = 1120 found: 1120. ^1H NMR (400 MHz, $CDCl_2CDCl_2$) 8.69 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 2.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.06 (m, 2H), 7.82 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.65 (m, 4H), 7.54 (m, 3H), 7.39 (m, 9H), 7.30 (m, 2H), 6.49 (s, 2H), 4.07 (s, 2H), 2.63 (m, 4H), 2.33 (bs, 3H), 2.06 (m, 4H), 1,40 (s, 9H).

Synthesis of compound PLC-32



Compound PLC-32.1

General Procedure of compound PLC-32.1: **Ex-4.3** (6.3 g, 17.159 mmol, 1 eq) was suspended in 35 mL DMSO anhydrous, glycine (2.31 g, 30.77 mmol, 1.8 eq) was added to the reaction mixture at RT. The resulting mixture was stirred at 130 °C for 1 hour (the mixture was not dissolved), it was then heated to 160 °C for 1hr, LMCMS shown reaction was completed. After cooling to room temperature, the solid product was filtered, washed with water (250 mL) then dried in vacuo-oven to gain 6.5g greenish yellow solid, yield 90%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.65 (s, 1H), 8.50 (s, 1H), 8.46 (d, J = 8.2 Hz, 2H), 8.09 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.7 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.6 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 4.71 (s, 2H).

Compound PLC-32.2

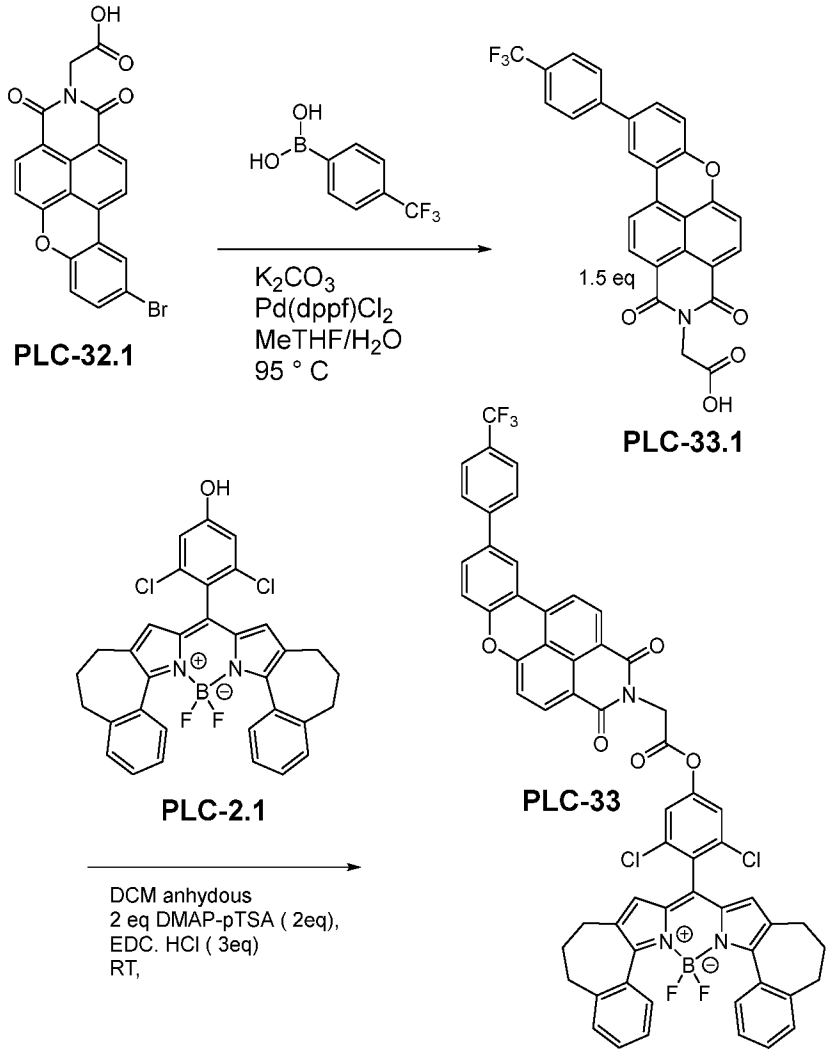
General Procedure of compound PLC-32.2: **PLC-32.1** (4.24 g, 10.0 mmol, 1eq) was suspended in 2-MeTHF (150 ml), H_2O (5.0 ml), added 4-(tert-butyl) benzeneboronic acid (3.56

g, 20 mmol, 2 eq), K_2CO_3 (2.76 g, 20 mmol, 2eq), Pd(dppf) Cl_2 DCM (163.3 mg, 0.2 mmol, 0.02eq). The reaction mixture was degassed by Vac- Fill Argon cycle 3 times, stirred & heated at 95 °C under Argon atmosphere 12 hours. After cooling to room temperature, added ethyl acetate (150 ml) acidified with 1N HCl to pH 4-5. Organic layer was washed with water, separated, concentrated. The residue was stirred in DMF (15 ml), filtered to obtain a solid which was washed with MeOH (50 mL) then dried in vacuo-oven to gain 4.1 g greenish yellow solid product, 85% yield. MS (APCI): calculated for $C_{20}H_{10}BrNO_5$ (M-H) = 423; found: 423. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 (d, J = 6.1 Hz, 3H), 8.24 (d, J = 7.9 Hz, 1H), 7.95 (s, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.70 (d, J = 7.9 Hz, 2H), 7.50 (d, J = 7.9 Hz, 2H), 7.39 (d, J = 8.3 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 4.52 (s, 2H), 2.89 (s, 3H), 2.73 (s, 3H), 2.54 – 2.47 (m, 21H), 1.34 (s, 10H).

Compound PLC-32

General Procedure of compound PLC-32: **PLC-32.2** (71.62 mg, 0.15 mmol, 1.5eq) was suspended in DCM anhydrous (10.0 ml). To the mixture, was added **PLC-2.1** (58.5 mg, 0.1 mmol, 1 eq), DMAP-pTSA (58.8 mg, 0.2 mmol, 2eq), EDC.HCl (57.5 mg, 0.3 mmol, 3 eq), then stirred at rt, under Argon atmosphere, 5 hours, diluted with DCM (150 ml), filtered, washed the solid with 50 ml DCM, collected the filtrate, loaded onto 80 g SiO_2 column, eluting with Hex-DCM (1/1) , DCM only then 0.5% EA in DCM. The good fractions were concentrated then washed with MeOH, gained 80 mg, yield 96%. MS (APCI): calculated for $C_{63}H_{46}BCl_2F_2N_3O_5$ (M-) = 1044; found: 1044. ^{1}H NMR (400 MHz, d_2-TCE) δ 8.63 (d, J = 7.9 Hz, 1H), 8.58 (d, J = 8.3 Hz, 1H), 8.20 (d, J = 2.1 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.98 – 7.91 (m, 2H), 7.73 (dd, J = 8.7, 2.1 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.49 – 7.44 (m, 2H), 7.42 (d, J = 8.6 Hz, 1H), 7.38 (s, 2H), 7.32 (d, J = 8.3 Hz, 1H), 7.27 (dt, J = 7.3, 3.7 Hz, 4H), 7.20 (dt, J = 5.1, 3.7 Hz, 2H), 6.35 (s, 2H), 5.18 (s, 2H), 2.54 (t, J = 6.7 Hz, 4H), 2.22 (s, 4H), 1.99 – 1.90 (m, 4H), 1.31 (s, 10H).

Synthesis Procedure of compound PLC-33



Compound PLC-33.1

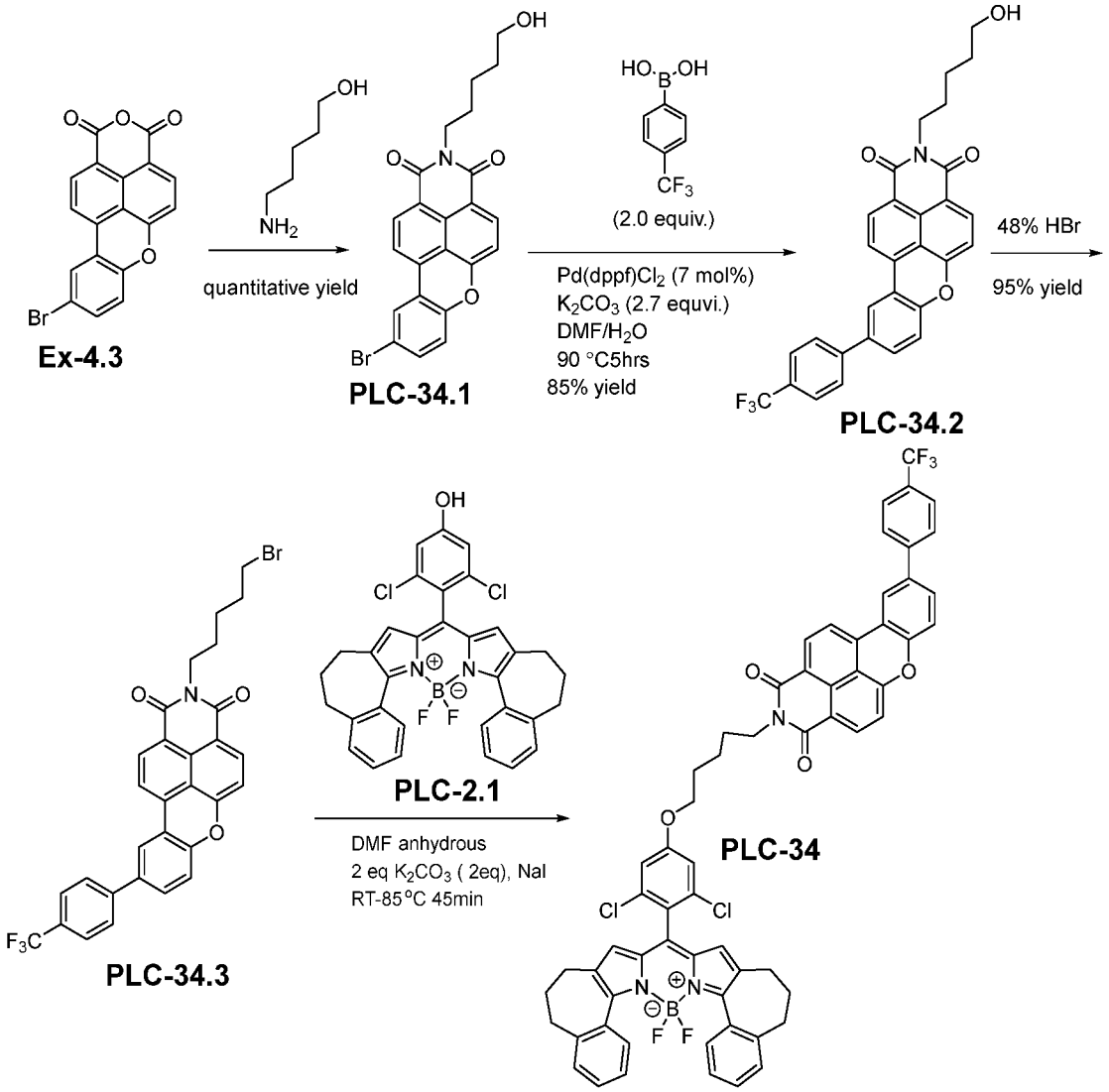
General Procedure of compound PLC-33.1: **PLC-32.1** (7.0g, 16.50 mmol, 1eq) was suspended in 2-MeTHF (150 mL), added 4-(trifluoromethyl)benzeneboronic acid (5.648 g, 29.7 mmol, 1.8 eq), K_2CO_3 (4.65 g, 33 mmol, 2eq), H2O (15 ml) $Pd(dppf)Cl_2$ DCM (269.5 mg, 0.33 mmol, 0.02eq).Vac- Fill Argon cycle 3 times, the resulting mixture was stirred & heated at 95 °C under Argon atmosphere 12 hours, the mixture was cooled to room temperature, added stirred with 1N HCl (20 ml) for 15 minutes then holding at RT 1 hours. The solid was filtered, stirred with DMF at room temperature 15 minutes then filtered, the greenish yellow solid was washed with MeOH, then dried in vacuo-oven to obtain 6.70 g greenish yellow solid which was used next step without further purification. 83% yield. MS (APCI): calculated for $C_{27}H_{14}F_3NO_5$ (M-) = 489; found: 489. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.52 (s, 1H), 8.37 (q, J =

8.1, 7.7 Hz, 3H), 8.04 (d, J = 7.9 Hz, 2H), 7.93 (d, J = 8.7 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.6 Hz, 1H), 7.34 (d, J = 8.3 Hz, 1H), 4.67 (s, 2H).

Compound PLC-33

General Procedure of compound PLC-33: **PLC-33.1** (73.4 mg, 0.15 mmol, 1.5eq) was suspended in DCM anhydrous (10.0 ml), added **PLC-2.1** (58.5 mg, 0.1 mmol, 1 eq), DMAP-pTSA (58.8 mg, 0.2 mmol, 2eq), EDC.HCl (57.5 mg, 0.3 mmol, 3 eq), stirred at room temperature, under Argon atmosphere, 5 hours, diluted with DCM (150 ml), filtered, washed the solid with 50 ml DCM, collected the filtrate , loaded onto 80 g SiO_2 column, eluting with Hex-DCM (1/1) , DCM only then 0.5% EA in DCM, the pure fractions were collected, concentrated, washed with hot MeOH to gain 82 mg, dark purple solid, yield 77%. MS (APCI): calculated for Chemical Formula: $C_{60}H_{37}BCl_2F_5N_3O_5$ (M-) = 1055; found: 1055. ^{1}H NMR (400 MHz, d_2-TCE) δ 8.66 (d, J = 7.9 Hz, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 2.2 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.96 (s, 2H), 7.73 (dd, J = 9.7, 1.8 Hz, H), 7.47 (d, J = 8.6 Hz, 1H), 7.38 (s, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.27 (dt, J = 7.3, 3.7 Hz, 3H), 7.23 – 7.16 (m, 2H), 6.35 (s, 2H), 5.19 (s, 2H), 2.53 (d, J = 7.4 Hz, 4H), 2.22 (s, 4H), 2.03 – 1.86 (m, 4H).

Synthesis Procedure of PLC-34



General Procedure of compound PLC-34.1: **Ex-4.3** (1.223 g, 3.33 mmol, 1 eq) was suspended in 35 mL DMSO anhydrous, 5-amino-1-pentanol (0.687 g, 6.66 mmol, 2 eq) was added to the reaction mixture at room temperature. The resulting mixture was stirred at 160 ºC for 45 minutes, LMCMS shown reaction was completed. After cooling to room temperature, the solid product was filtered, washed with water (250 mL) then MeOH (100 mL), dried in vacuo-oven to gain 1.2 g greenish yellow solid, yield 85%. MS (APCI): calculated for $C_{23}H_{18}BrNO_4$ (M-) = 453; found: 453. ^{1}H NMR (400 MHz, d_2-TCE) δ 8.52 (d, J = 7.8 Hz, 1H), 8.48 (d, J = 8.3 Hz, 1H), 8.09 (d, J = 2.3 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.54 (dd, J = 8.8, 2.3 Hz, 1H), 7.23 (d, J = 8.3 Hz, 1H), 7.19 (d, J = 8.8 Hz, 1H), 4.14 – 4.02 (m, 2H), 3.64 – 3.49 (m, 2H), 1.68 (p, J = 7.7 Hz, 2H), 1.60 – 1.54 (m, 2H), 1.41 (q, J = 8.0 Hz, 2H), 1.28 (s, 1H).

General Procedure of compound PLC-34.2: **PLC-34.1** (1.13 g, 2.5 mmol, 1eq) was suspended in DMF (10 ml), H_2O (5 ml), added 4-trifluoromethyl) benzene boronic acid (0.949 g, 5.0 mmol, 2 eq), K_2CO_3 (0.691 g, 5.0 mmol, 2eq), Pd(dppf) Cl_2 DCM (40.8 mg, 0.05 mmol, 0.02eq). The mixture was degassed by Vac- Fill Argon cycle 3 times, stirred & heated at 90 ºC for 5 hours. The reaction mixture was cooled to room temperature, water was added. The resulting mixture was held at room temperature 12 hours. The greenish yellow solid was filtered, washed with water then MeOH to obtain 1.24 g greenish yellow solid, yield 95%. MS (APCI): calculated for $C_{30}H_{22}F_3NO_4$ (M-) = 517; found: 517. ^{1}H NMR (400 MHz, d_2-TCE) δ 8.56 (d, J = 7.9 Hz, 1H), 8.51 (d, J = 8.3 Hz, 1H), 8.17 (d, J = 2.1 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.69 (dd, J = 10.3, 1.9 Hz, 4H), 7.42 (d, J = 8.6 Hz, 1H), 7.28 (d, J = 8.3 Hz, 1H), 4.09 (t, J = 7.5 Hz, 2H), 3.57 (q, J = 6.2 Hz, 2H), 1.69 (p, J = 7.8 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.42 (q, J = 8.0 Hz, 2H), 1.28 (t, J = 5.5 Hz, 1H).

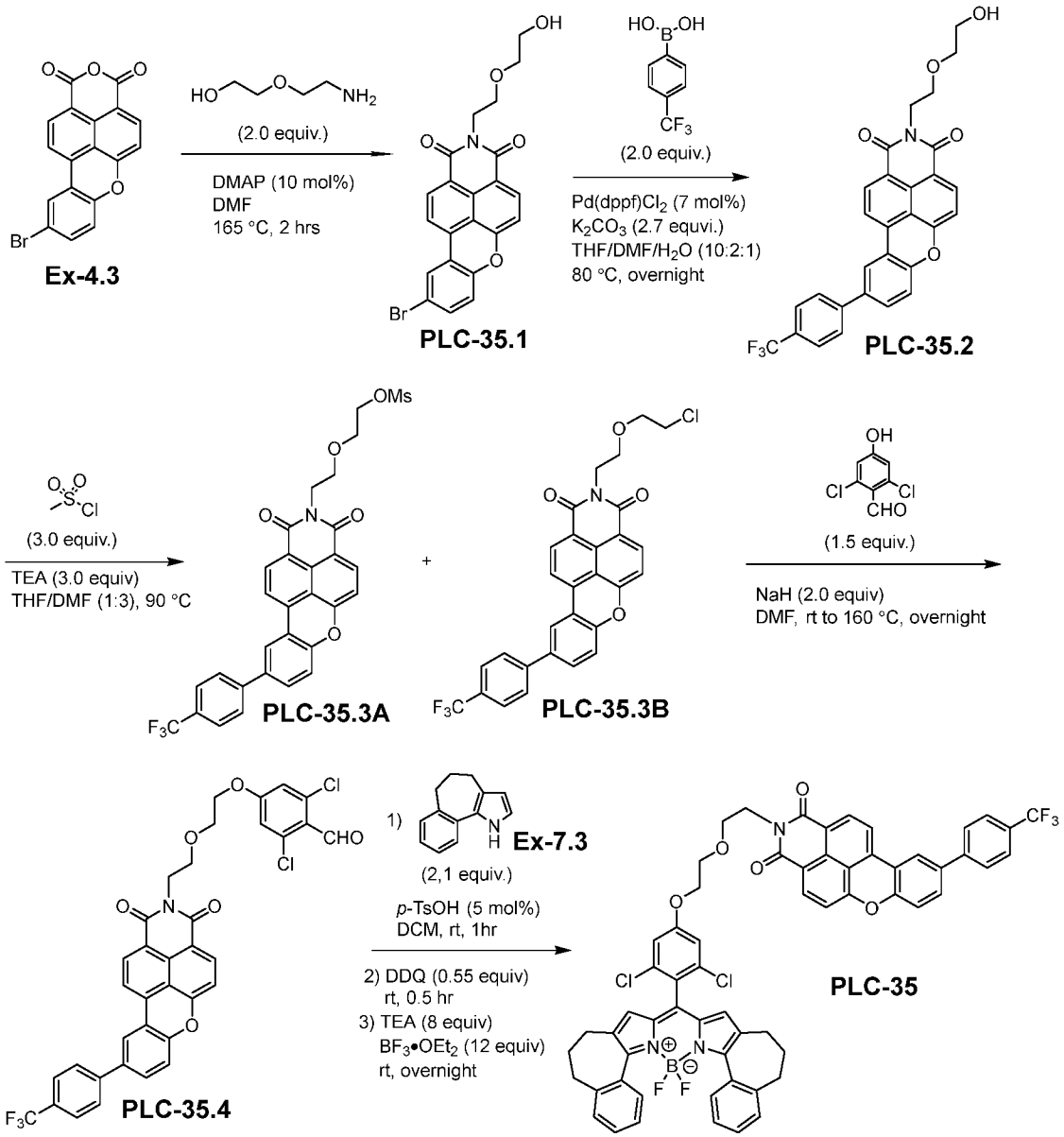
General Procedure of compound PLC-34.3: Reflux (HBr 48% bp:126 ºC) the mixture of **PLC-34.2** (0.66 g, 1.288 mmol) and 48% aqueous HBr (20.0 ml) by heating block at 120 ºC for 5 hours with stirring. After cooling to room temperature, the mixture was poured to ice water, the solid was filtered, washed with water, dried in vacuo-oven to obtain 82% desired compound containing with unreacted SM. Gained 0.7 g greenish yellow solid, yield 93%. Product was used next step without further purification. MS (APCI): calculated for $C_{30}H_{21}BrF_3NO_3$ (M-) = 581; found: 581. ^{1}H NMR (400 MHz, d_2-TCE) δ 8.57 (d, J = 7.9Hz, 1H), 8.51 (d, J = 8.3 Hz, 1H), 8.18 (d, J = 2.2 Hz, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.69 (dd, J = 9.6, 2.0 Hz, 4H), 7.43 (d, J = 8.6 Hz, 1H), 7.28 (d, J = 8.3 Hz,1H), 4.09 (t, J = 7.5 Hz, 3H), 3.38 (t, J = 6.7 Hz, 2H), 1.97 – 1.81 (m, 2H), 1.69 (t, J = 7.8 Hz, 2H).

Compound PLC-34

General Procedure of compound PLC-34: **PLC-34.3** (87.06 mg, 0.15 mmol, 1.5eq) was suspended in DMF anhydrous (10.0 ml), added **PLC-2.1** (63.65 mg, 0.10 mmol, 1 eq), K_2CO_3 (41.46 mg, 0.3 mmol, 2eq), NaI (8.3 mg, cat. amount). The resulting mixture was stirred at 65 ºC, under Argon atmosphere 15 hours, cooled to room temperature, the solid was filtered, washed with 50 ml water; crude product was loaded onto 40 g silica gel column, eluting with Hex: DCM (9:1) to DCM, gained 75 mg red brown solid, yield 69%. MS (APCI): calculated for $C_{63}H_{45}BCl_2F_5N_3O_4$ (M-) = 1083; found: 1083. ^{1}H NMR (400 MHz, d_2-TCE) δ 8.59 (d, J = 7.9 Hz,

1H), 8.54 (d, J = 8.3 Hz, 1H), 8.18 (d, J = 2.1 Hz, 1H),8.00 (d, J = 8.1 Hz, 1H), 7.96 (s, 1H), 7.70 (dd, J = 7.4, 2.2 Hz, 3H), 7.43 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 8.3 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.22 – 7.19 (m, 1H), 6.98 (s, 2H), 6.39 (s, 2H), 4.15 (t, J = 7.5 Hz, 2H), 3.99 (t, J = 6.2 Hz, 2H), 2.55 (t, J = 6.6 Hz, 2H), 2.23 (s, 2H), 1.98 – 1.92 (m, 2H), 1.86 (s, 1H), 1.77 (s, 1H), 1.58 (s, 2H).

Synthesis Procedure of PLC-35



General Procedure of compound PLC-35.1 – 9-bromo-2-(2-(2-hydroxyethoxy)ethyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: A 100 mL flask was fitted with a stir bar. To the flask, **Ex-4.3** (1.5 g, 4.1 mmol), 2-(2-aminoethoxy)ethan-1-ol (859.0 mg, 8.2 mmol) and DMAP (35.1 mg, 0.3 mmol) in DMF (30 ml) was degassed at room temperature. The reaction

mixture was heated up to 165 ºC and the reaction has been kept at this temperature for 2 hrs. TLC and LCMS showed the completion of the reaction. The reaction was cooled down to room temperature. H_2O (70 ml) was added to precipitate the product. The precipitate was collected by filtration. The solid was washed by H_2O (150 ml) and further dried in a vacuum oven at 100 ºC for 3 hours to provide **PLC-35.1** as a yellow solid for the next step without further purification. 1.45 g, 78% yield. MS (APCI): calculated for $C_{22}H_{16}BrNO_5$ ($[M-H]^-$) = 454 found: 454. ^1H NMR (400 MHz, $CDCl_2CDCl_2$) 8.62 (d, *J* = 8.0 Hz, 1H), 8.59 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 2.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 8.0 Hz, *J* = 2.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 4.42 (t, *J* = 5.6 Hz, 2H), 3.85 (t, *J* = 5.6 Hz, 2H), 3.67 (m, 4H).

General Procedure of compound PLC-35.2 – 2-(2-(2-hydroxyethoxy)ethyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: A 250 mL flask was fitted with a stir bar. To the flask, **PLC-35.1** (800.0 mg, 1.8 mmol), 4-(trifluoromethyl)phenylboronic acid (670.0 mg, 3.5 mmol), $Pd(dppf)Cl_2$ (90.6 mg, 0.1 mmol) and K_2CO_3 (659.5 mg, 4.8 mmol) in THF/DMF/H_2O (48 ml/ 9.6 ml/ 4.8 ml) was degassed at room temperature. The reaction mixture was heated up to 80 ºC and the reaction has been kept at this temperature overnight. TLC was used to monitor the reaction. After the completion, the reaction was worked up by the addition of H_2O (150 ml) added to precipitate the product. The precipitate was collected by filtration. The solid was washed by H_2O (200 ml) and MeOH (20 ml), and further dried in a vacuum oven at 100 ºC for 3 hours to provide **PLC-35.2** as a yellow green solid for the next step without further purification. Quantitative yield. MS (APCI): calculated for $C_{29}H_{20}F_3NO_5$ ($[M+H]^+$) = 520 found: 520. ^1H NMR (400 MHz, $CDCl_2CDCl_2$) 8.67 (d, *J* = 8.0 Hz, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 2.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.79 (m, 5H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 5.11 (bs, 1H), 4.44 (t, *J* = 1.6 Hz, 2H), 3.86 (t, *J* = 1.6 Hz, 2H), 3.68 (m, 4H).

General Procedure of compound PLC-35.3A and PLC-35.3B – 2-(2-(1,3-dioxo-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)ethoxy)ethyl methanesulfonate and 2-(2-(2-chloroethoxy)ethyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: A 100 mL flask was fitted with a stir bar. To the flask, **PLC-35.2** (900.0 mg, 1.7 mmol) and DMF/THF (18 ml/ 6 ml) were added. The solution was degassed at room temperature. Methanesulfonyl chloride (595.4 mg, 5.2 mmol) and TEA (526.2 mg, 5.2 mmol) were added. Then the solution heated up to 90 ºC and it has been kept

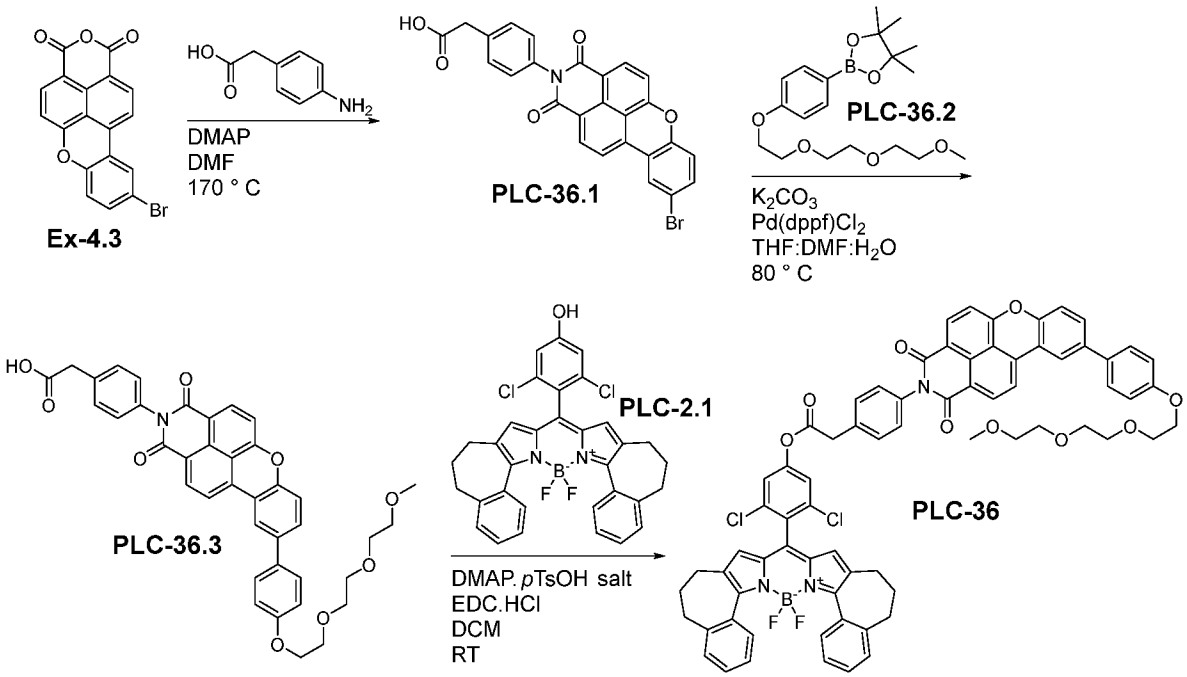
at this temperature for 20 minutes. TLC was used to monitor the reaction. After the completion, the reaction was worked up by the addition of H_2O (150 ml) added to precipitate the product. The precipitate was collected by filtration. The solid was washed by H_2O (100 ml) and MeOH (15 ml), and further dried in a vacuum oven at 100 ºC for 3 hours to provide a mixture of **PLC-35.3A** and **PLC-35.3B** (~ 1:1 molar ratio) as a yellow solid for the next step without further purification. Quantitative yield. For PLC-35.4A , MS (APCI): calculated for $C_{30}H_{22}F_3NO_7S$ ($[M+H]^+$) = 598 found: 598. ^1H NMR (400 MHz, $CDCl_2CDCl_2$) 8.65 (d, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 2.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.78 (m, 5H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 4.44 (t, *J* = 2.0 Hz, 2H), 4.35 (m, 2H), 3.86 (t, *J* = 2.0 Hz, 2H), 3.81 (m, 2H), 3.01 (s, 3H). For PLC-35.4B , MS (APCI): calculated for $C_{29}H_{19}ClF_3NO_4$ ($[M-H]^-$) = 537 found: 537. ^1H NMR (400 MHz, $CDCl_2CDCl_2$) 8.66 (d, *J* = 8.0 Hz, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 2.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.79 (m, 5H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 4.43 (t, *J* = 2.0 Hz, 2H), 3.86 (t, *J* = 2.0 Hz, 2H), 3.81 (t, *J* = 1.6 Hz, 2H), 3.63 (t, *J* = 1.6 Hz, 2H).

General Procedure of compound PLC-35.4 – 2,6-dichloro-4-(2-(2-(1,3-dioxo-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)ethoxy)ethoxy)benzaldehyde: To a 100 ml flask, NaH (69.1 mg, 2.9 mmol) and DMF (20 ml) was added, followed by the addition of 4-hydroxy-2,6-dichlorobenzaldehyde (413.3 mg, 2.2 mmol). The mixture has been kept stirring at room temperature for 10 minutes. The mixture of **PLC-35.3A** (0.7 mmol) and **PLC-35.3B** (0.7 mmol) (total of 862.0 mg, 1.4 mmol) was added. The reaction was heated up to 160 ºC and has been kept stirring at this temperature overnight. TLC (50% EtOAc in Hexane) showed the completion of the reaction. The reaction mixture was purified by silica gel flash chromatography using EtOAc in DCM (0-40%) as an eluant to provide pure compound **PLC-35.4** as a yellow solid, 580.0 mg, 60% yield. MS (APCI): calculated for $C_{36}H_{22}Cl_2F_3NO_6$ ($[M-H]^-$) = 691 found: 691. ^1H NMR (400 MHz, $CDCl_2CDCl_2$) δ 10.06 (s, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 2.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.81 (m, 5H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 6.56 (s, 2H), 4.44 (t, *J* = 2.0 Hz, 2H), 3.98 (m, 2H), 3.93 (t, *J* = 2.0 Hz, 2H), 3.86 (m, 2H).

General Procedure of compound PLC-35 – 2-(2-(2-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-

yl)phenoxy)ethoxy)ethyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: A 100 mL 2 neck round bottomed flask was fitted with an air condenser and a stir bar. To the flask, **PLC-35.4** (140.0 mg, 0.2 mmol) and **Ex-7.3** (77.7 mg, 0.4 mmol) were added, followed by anhydrous dichloromethane (4 ml). The reaction mixture was sparged with Ar for 30 minutes, then p-TsOH•H_2O (1.2 mg, 0.01 mmol) was added. The reaction solution has been kept at this temperature for 2 hrs. Then DDQ (25.0 mg, 0.1 mmol) was added. The reaction was kept at room temperature for 30 minutes. Then BF_3•OEt_2 (0.3 mL, 2.4 mmol) and Et_3N (0.2 mL, 1.6 mmol) were added at room temperature. The reaction mixture has been kept at room temperature overnight. The reaction mixture was loaded with silica gel and purified by flash chromatography, using EtOAc in DCM (0-5%) as an eluant to provide the pure **PLC-35** as a dark purple solid, 121.0 mg, 55% yield. MS (APCI): calculated for $C_{62}H_{43}BCl_2F_5N_3O_5$ ([M-H]$^-$) = 1086 found: 1086. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) 8.69 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 2.4 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.04 (m, 2H), 7.78 (m, 5H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.34 (m, 7H), 6.99 (s, 2H), 6.44 (s, 2H), 4.49 (t, *J* = 2.0 Hz, 2H), 4.18 (m, 2H), 3.96 (m, 4H), 2.63 (m, 4H), 2.31 (bs, 4H), 2.04 (m, 4H).

Synthesis Procedure of compound PLC-36



General Procedure of compound PLC-36.5 – (2-(4-(9-bromo-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetic acid): A 100 mL 2N round bottom flask was placed in an aluminum heat block and charged with a stir bar. The flask was fitted with a finned condenser/gas adapter and flow control valve. The system was flushed with argon. To the flask was added **Ex-4.3** (0.702 mmol, 250mg), 2-(4-aminophenyl)acetic acid (1.754 mmol, 265 mg), and DMAP (0.0512 mmol, 6.3 mg), followed by anhydrous DMF (10 mL). The reaction mixture was stirred under argon and the heat block set to 170 °C. The reaction mixture was stirred at 170 °C for 9 hours, then at room temperature. The crude reaction mixture was diluted with 75 mL of water. This mixture was stirred for 5 minutes, then the crude product was filtered off, drying by suction for 5 minutes. The wet precipitate was dried in a vacuum oven at ~110 °C overnight. Gives a yellowish powder, 366mg (107% yield). NMR shows about 10-15% dimethyl amide by-product. MS (APCI): calculated for $C_{26}H_{14}BrNO_5$ (M+H) = 500; found: 500. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.60 (d, J = 2.3 Hz, 1H), 8.49 – 8.45 (m, 2H), 8.39 (d, J = 8.1 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.48 – 7.43 (m, 2H), 7.43 – 7.38 (m, 2H), 7.31 – 7.27 (m, 2H), 3.67 (s, 2H).

General Procedure of compound PLC-36.2 – (2-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane): A 250 mL 2N round bottom flask was placed in an aluminum heat block and charged with a stir bar. The flask was fitted with a finned condenser/gas adapter and flow control valve. The system was flushed with argon. To the flask was added 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (11.0 mmol, 2.421 g), 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane (10.0 mmol, 2.48 mL), anhydrous DMF (25 mL), and K_2CO_3 (11.0 mmol, 1.520 g). The reaction mixture was stirred under argon atmosphere at room temperature for 5 minutes, then the heat block was set at 50 °C and the reaction mixture was stirred for 6 hours at 50 °C, then room temperature over the weekend. The reaction mixture was diluted with water (~200 mL), then extracted with ethyl ether (3 X 100 mL). The combined ether layers were washed with saturated aq. $NaHCO_3$ solution (50 mL), brine (50 mL), dried over $MgSO_4$, filtered and evaporated to dryness in vacuo. Gives a light yellow oil (4.166 g, 114% yield). NMR indicates it is a mixture of the desired product and the starting bromo-glycol, ~57% product estimated). Used without further purification in the next step. MS (APCI): calculated for $C_{19}H_{31}BO_6$ (M+H) = 367; found: 367. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.69 – 7.63 (m, 2H), 6.95 – 6.90 (m, 2H), 4.18 – 4.11

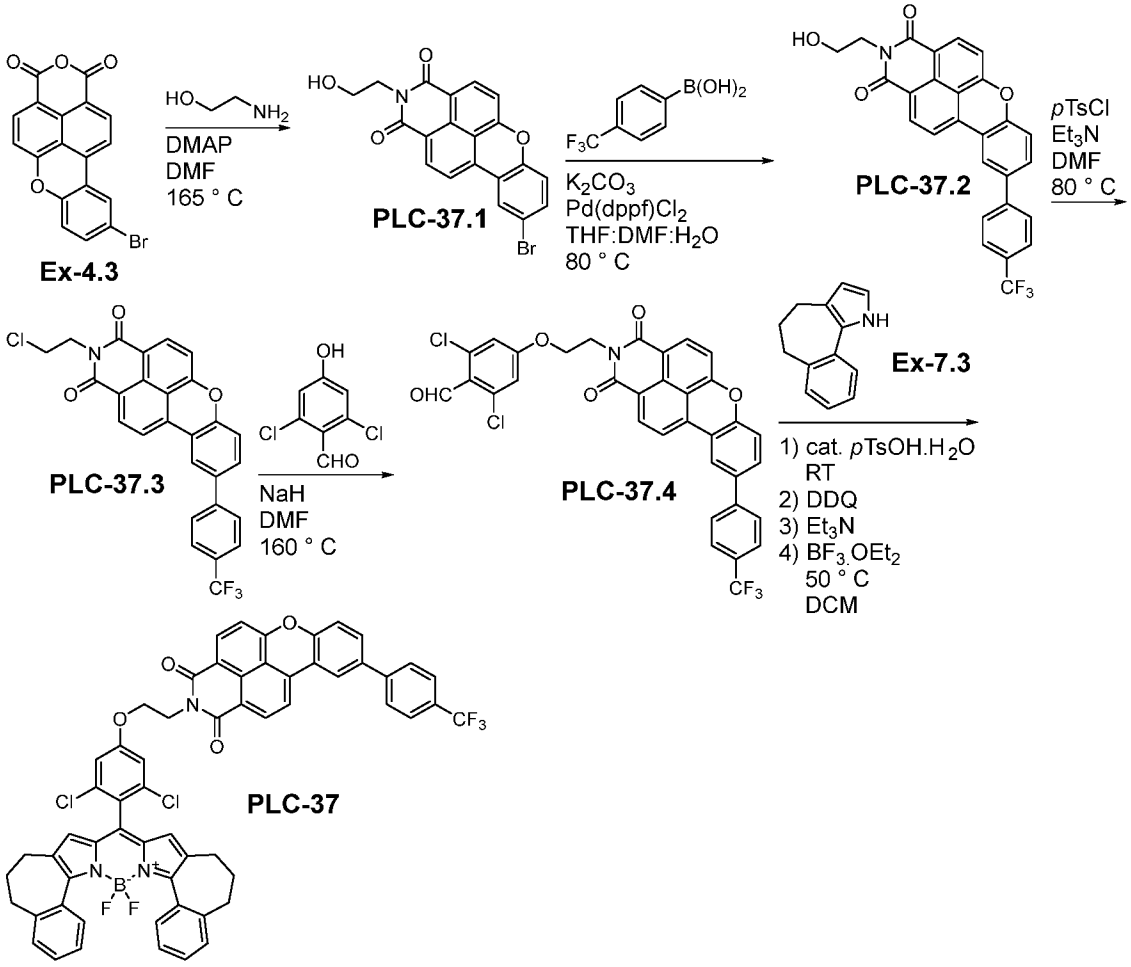
(m, 2H), 3.86 – 3.82 (m, 2H), 3.72 – 3.67 (m, 2H), 3.66 – 3.60 (m, 2H), 3.54 – 3.48 (m, 4H), 3.34 (s, 3H).

General Procedure of compound PLC-36.3 – (2-(4-(9-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetic acid): A 250 mL 2N round bottom flask was placed in an aluminum heat block and charged with a stir bar. The flask was fitted with a finned condenser/gas adapter and flow control valve. The system was flushed with argon. To the flask was added **PLC-36.1** (2.00 mmol, 1001 mg), **PLC-36.2** (4.00 mmol, 1465 mg), K_2CO_3 (5.50 mmol, 760 mg), and $Pd(dppf)Cl_2$ (0.140 mmol, 102 mg), followed by THF (60 mL), DMF (12 mL), and water (6 mL). The reaction mixture was stirred under argon and sparged with nitrogen for 10 minutes. The nitrogen sparge was stopped and stirring under argon was continued. The heat block was set at 80 °C for 2 hours. The reaction mixture was quenched with 6N HCl (5 mL) and diluted with water (50 mL) and THF (50 mL). Sodium chloride was added until the water layer was saturated, then the layers were separated, and the aqueous layer was extracted with THF (3X50 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered, and evaporated to dryness in vacuo (including DMF). The crude product was evaporated onto ~50g flash silica gel and placed in a loader. Purified by flash chromatography on silica gel (220g, solid load, equilibrate 100% DCM, eluting 100% DCM (2 CV) → 40% (EtOAc/0.1% TFA)/DCM (20CV) → 70% (EtOAc/0.1% TFA)/DCM (20 CV)). Fractions containing product were evaporated to dryness in vacuo. Gives a yellow solid, 722 mg (55% yield). MS (APCI): calculated for $C_{39}H_{33}NO_9$ (M+H) = 660; found: 660. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.57 (d, J = 2.2 Hz, 1H), 8.52 (s, 2H), 8.48 (d, J = 8.3 Hz, 1H), 7.90 (dd, J = 8.7, 2.2 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.55 (d, J = 8.7 Hz, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.41 (d, J = 8.1 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.12 – 7.07 (m, 2H), 4.22 – 4.14 (m, 2H), 3.82 – 3.76 (m, 2H), 3.68 (s, 2H), 3.65 – 3.59 (m, 2H), 3.58 – 3.51 (m, 4H), 3.48 – 3.41 (m, 2H), 3.25 (s, 3H).

General Procedure of compound PLC-36 – (3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenyl 2-(4-(9-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetate): A 40 mL vial was charged with a stir bar, followed by **PLC-2.1** – 3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-

benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenol (0.050 mmol, 29.3 mg), **PLC-36.3** (0.075 mmol, 49.5 mg), DMAP.*p*TsOH salt (0.100 mmol, 29.4 mg), and EDC.HCl (0.300 mmol, 29 mg), followed by anhydrous DCM. The vial was capped, and the reaction mixture stirred at room temperature overnight. The crude reaction was quenched with a few drops of TFA and loaded onto ~65 g flash silica gel in a loader. Purified by flash chromatography on silica gel (120 g, solid load, equilibrate 100% DCM, eluting 100% DCM (3 CV) → 5.8% EtOAc/DCM (11.6 CV) → 13.3% EtOAc/DCM (6.0 CV) → 50% EtOAc/DCM (10 CV)). Fractions containing product were evaporated to dryness in vacuo. The crude product was triturated with hot methanol. The product was filtered off, dried by suction, then dried in a vacuum oven at ~110 °C. Gives a dark red solid, 47.1 mg (77% yield). MS (APCI): calculated for $C_{72}H_{56}BCl_2F_2N_3O_9$ (M-) = 1225; found: 1225. ^{1}H NMR (400 MHz, Tetrachloroethane-d_2) δ 8.68 (d, *J* = 7.8 Hz, 1H), 8.63 (d, *J* = 8.3 Hz, 1H), 8.25 (d, *J* = 2.1 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 8.09 – 8.00 (m, 2H), 7.78 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.69 – 7.61 (m, 4H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.46 – 7.34 (m, 9H), 7.33 – 7.26 (m, 2H), 7.14 – 7.05 (m, 2H), 6.48 (s, 2H), 4.22 (t, *J* = 4.7 Hz, 2H), 4.07 (s, 2H), 3.94 – 3.88 (m, 2H), 3.78 – 3.72 (m, 2H), 3.72 – 3.62 (m, 4H), 3.59 – 3.53 (m, 2H), 3.38 (s, 3H), 2.64 (t, *J* = 6.8 Hz, 4H), 2.44 – 2.22 (m, 4H), 2.12 – 1.97 (m, 4H).

Synthesis Procedure of compound PLC-37



General Procedure of compound PLC-37.1 – (9-bromo-2-(2-hydroxyethyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): A 50 mL 2N round bottom flask was placed in an aluminum heat block and charged with a stir bar. The flask was fitted with a finned condenser/gas adapter, stopper and flow control valve. The system was flushed with argon. To the flask was added **Ex-4.3** (3.00 mmol, 1101 mg), ethanolamine (12.0 mmol, 0.725 mL), and DMAP (0.900 mmol, 110 mg), followed by anhydrous DMF (8 mL). The reaction mixture was stirred under argon and the heat block was set to 165 °C. The reaction mixture was stirred at this temperature for 3 hours, then the reaction mixture was cooled to room temperature. The solvent was evaporated to dryness in vacuo. The residue was triturated with water (50 mL) and 6N aqueous HCL (10 mL). The mixture was sonicated for a few minutes, then stirred at room temperature for 30 minutes, then the solid product was filtered off, washing with water. The crude filter cake was dried in a vacuum oven at ~110 °C overnight. Gives a dark

brownish solid, 1.038 g (84% yield). MS (APCI): calculated for $C_{20}H_{12}BrNO_4$ (M+H) = 410; found: 410.

General Procedure of compound PLC-37.2 – (2-(2-hydroxyethyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): **PLC-39.2** was synthesized from **PLC-37.1** (2.531 mmol, 1.038 g), (4-(trifluoromethyl)phenyl)boronic acid (5.062 mmol, 961 mg), K_2CO_3 (6.960 mmol, 962 mg), and $Pd(dppf)Cl_2$ (0.177 mmol, 130 mg) in THF/DMF/H_2O (60 mL/12 mL/6 mL) at 80 °C for 30 minutes in a manner similar to **PLC-36.7**. The crude product was precipitated by adding water (100 mL), then filtering off the resulting solid, washing with water. The crude product was triturated with methanol, then dried in a vacuum oven at ~110 °C overnight. Gives 1.017 g (84% yield). MS (APCI): calculated for $C_{27}H_{16}F_3NO_4$ (M+H) = 476; found: 476. ^{1}H NMR (400 MHz, TCE) δ 8.66 (d, J = 7.8 Hz, 1H), 8.61 (d, J = 8.3 Hz, 1H), 8.25 (d, J = 2.2 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.83 – 7.75 (m, 5H), 7.52 (d, J = 8.6 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 4.45 (t, J = 5.2 Hz, 2H), 3.98 (q, J = 5.3 Hz, 2H), 2.49 (t, J = 5.5 Hz, 1H).

General Procedure of compound PLC-37.3 – (2-(2-chloroethyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): A 250 mL 2N round bottom flask was placed in an aluminum heat block and charged with a stir bar. The flask was fitted with a finned condenser/gas adapter, stopper and flow control valve. The system was flushed with argon. To the flask was added **PLC-37.2** (2.124 mmol, 1.01 g), *p*TsCl (6.372 mmol, 1.215 g), anhydrous DMF (20 mL), and Et_3N (6.372 mmol, 0.888 mL). The reaction mixture was stirred under argon and heated to 80 °C for 2 hours. An unexpected reaction occurred when the tosylate was displaced in situ by chloride ion. The reaction mixture was cooled to room temperature and diluted with water (100 mL). The crude product was filtered off, washing with water. The crude product was triturated with MeOH. The product was dried in a vacuum oven at ~110 °C overnight. Gives 974 mg of an orange solid (93% yield). MS (APCI): calculated for $C_{27}H_{15}ClF_3NO_3$ (M+H) = 494; found: 494. ^{1}H NMR (400 MHz, TCE) δ 8.67 (d, J = 7.9 Hz, 1H), 8.62 (d, J = 8.3 Hz, 1H), 8.27 (d, J = 2.2 Hz, 1H), 8.08 (d, J = 7.9 Hz, 1H), 7.86 – 7.73 (m, 5H), 7.53 (d, J = 8.6 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 4.56 (t, J = 6.9 Hz, 2H), 3.87 (t, J = 6.8 Hz, 2H).

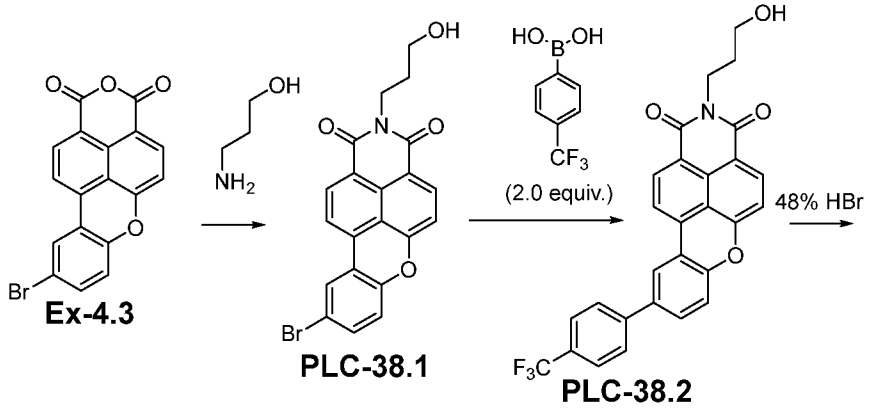
General Procedure of compound PLC-37.4 – (2,6-dichloro-4-(2-(1,3-dioxo-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)ethoxy)benzaldehyde): A 100 mL 2N round bottom flask was placed in an aluminum heat block and charged with a stir bar. The flask was fitted with a finned condenser/gas adapter, stopper and flow control valve. The system was flushed with argon. To the flask was added NaH (60% in mineral oil) (1.214 mmol, 29.1 mg, 60%, 49 mg), followed by anhydrous DMF (20 mL). To the flask was added 2,6-dichloro-4-hydroxybenzaldehyde (1.821 mmol, 348 mg). The reaction mixture was stirred under argon and the heat block set at 50 °C. The reaction was stirred for 5 minutes at 50 °C, then **PLC-37.3** (0.607 mmol, 300 mg) was added. The flask was stoppered and stirred under argon. The heatblock temperature was increased to 160 °C. The reaction mixture was stirred for 90 minutes at 160 °C, then at room temperature overnight. The crude product was crashed out by adding water (100 mL) and filtering off the product, washing with water. The crude product was dissolved in DCM and evaporated to dryness in vacuo. The crude product was evaporated onto flash silica gel (~20g) in vacuo. Purified by flash chromatography on silica gel (120g, solid load, equilibrate 100% DCM/hexanes, eluting 100% DCM/hexanes (7 CV) → 0% EtOAc/DCM (0 CV) → 0% EtOAc/DCM (5 CV) → 40% EtOAc/DCM (40 CV). Fractions containing product were evaporated to dryness in vacuo. Gives 152 mg (39% yield) of a yellow solid. MS (APCI): calculated for $C_{34}H_{18}Cl_2F_3NO_5$ (M-) = 647; found: 647. ^{1}H NMR (400 MHz, TCE) δ 10.36 (s, 1H), 8.68 (d, J = 7.9 Hz, 1H), 8.63 (d, J = 8.3 Hz, 1H), 8.26 (d, J = 2.1 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.85 – 7.72 (m, 5H), 7.52 (d, J = 8.6 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 6.99 (s, 2H), 6.93 (s, 1H), 4.65 (t, J = 6.1 Hz, 2H), 4.40 (t, J = 6.1 Hz, 2H).

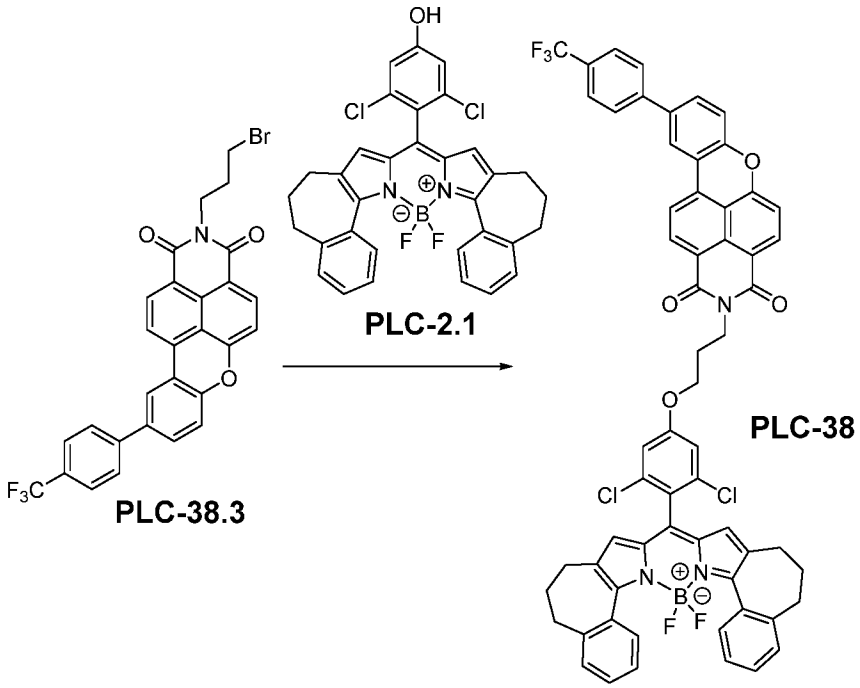
Compound PLC-37

General Procedure of compound PLC-37 – (2-(2-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)ethyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione):): A 100 mL 2N round bottom flask was placed in an aluminum heat block and charged with a stir bar. The flask was fitted with a finned condenser/gas adapter, stopper and flow control valve. The system was flushed with argon. To the flask was added **PLC-37.4** (0.075 mmol, 49 mg) and **Ex-7.3** – 1,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-b]pyrrole (0.1575 mmol, 29 mg), followed

by anhydrous DCM (20 mL). Under argon atmosphere, the reaction mixture was sparged with nitrogen for 10 minutes. A couple of small granules of *p*TsOH.H_2O were gathered onto the end of a spatula and these were dipped in the reaction mixture. Stirring and sparging with nitrogen were continued for another 5 minutes. The nitrogen sparge was stopped and the reaction mixture was stirred at room temperature for 1 hour, at which point TLC shows complete conversion to the desired dipyrromethane. To the flask was added DDQ (0.1275 mmol, 29 mg) and the reaction mixture was stirred at room temperature for 15 minutes. TLC indicates complete oxidation to dipyrromethene. To the flask was added Et_3N (0.600 mmol, 0.084 mL) and $BF_3.OEt_2$ (0.900 mmol, 0.111 mL). The addition of both reagents was repeated after 2 minutes, then the heat block was set to 50 °C and the reaction mixture stirred at this temperature for 2 hours under argon. The crude BODIPY was loaded onto flash silica gel directly (25 g). Purified by flash chromatography on silica gel (80g, solid load, equilibrate 80% DCM/hexanes, eluting 80% DCM/hexanes (2 CV) → 100 DCM/hexanes (5 CV) → isocratic 100% DCM/hexanes (~25 CV) → 100% DCM/hexanes/0.5% EtOAc modifier (~10 CV)). Product elutes as a broad peak. Fractions containing product were evaporated to dryness in vacuo. Gives a dark red solid, 89 mg (quantitative yield). MS (APCI): calculated for $C_{60}H_{39}BCl_2F_5N_3O_4$ (M-) = 1041; found: 1041. ^1H NMR (400 MHz, TCE) δ 8.72 (d, J = 7.9 Hz, 1H), 8.67 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 2.2 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 8.04 (dd, J = 5.8, 3.5 Hz, 2H), 7.84 – 7.75 (m, 5H), 7.53 (d, J = 8.6 Hz, 1H), 7.41 (d, J = 8.3 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.32 – 7.25 (m, 2H), 7.14 (s, 2H), 4.70 (t, J = 6.2 Hz, 2H), 4.42 (t, J = 6.2 Hz, 2H), 2.62 (t, J = 7.0 Hz, 4H), 2.41 – 2.18 (m, 4H), 2.11 – 1.93 (m, 4H).

Synthesis Procedure of PLC-38





Synthesis of PLC-38.1 (9-bromo-2-(3-hydroxypropyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): Ex-4.3 (1.223 g, 3.33 mmol, 1 eq) was suspended in 35 mL DMSO anhydrous, 3-amino-1-propanol (1.5 g, 20.0 mmol, 6 eq) was added to the reaction mixture at RT. The resulting mixture was stirred at 160 °C for 45 minutes, LCMS shown reaction was completed. After cooling to room temperature, the solid product was filtered, the solid was washed with water (250 mL) then MeOH (100 mL), dried in vacuo-oven to gain 1.2 g greenish yellow solid, yield 92%. MS (APCI): calculated for $C_{23}H_{18}BrNO_4$ (M-) = 425; found: 425. ^{1}H NMR (400 MHz) δ 8.56 (d, *J* = 7.9 Hz, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 2.3 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.57 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 4.24 (t, *J* = 6.1 Hz, 2H), 3.48 (q, *J* = 6.1 Hz, 2H), 3.06 (t, *J* = 6.9 Hz, 1H), 1.95 – 1.83 (m, 2H).

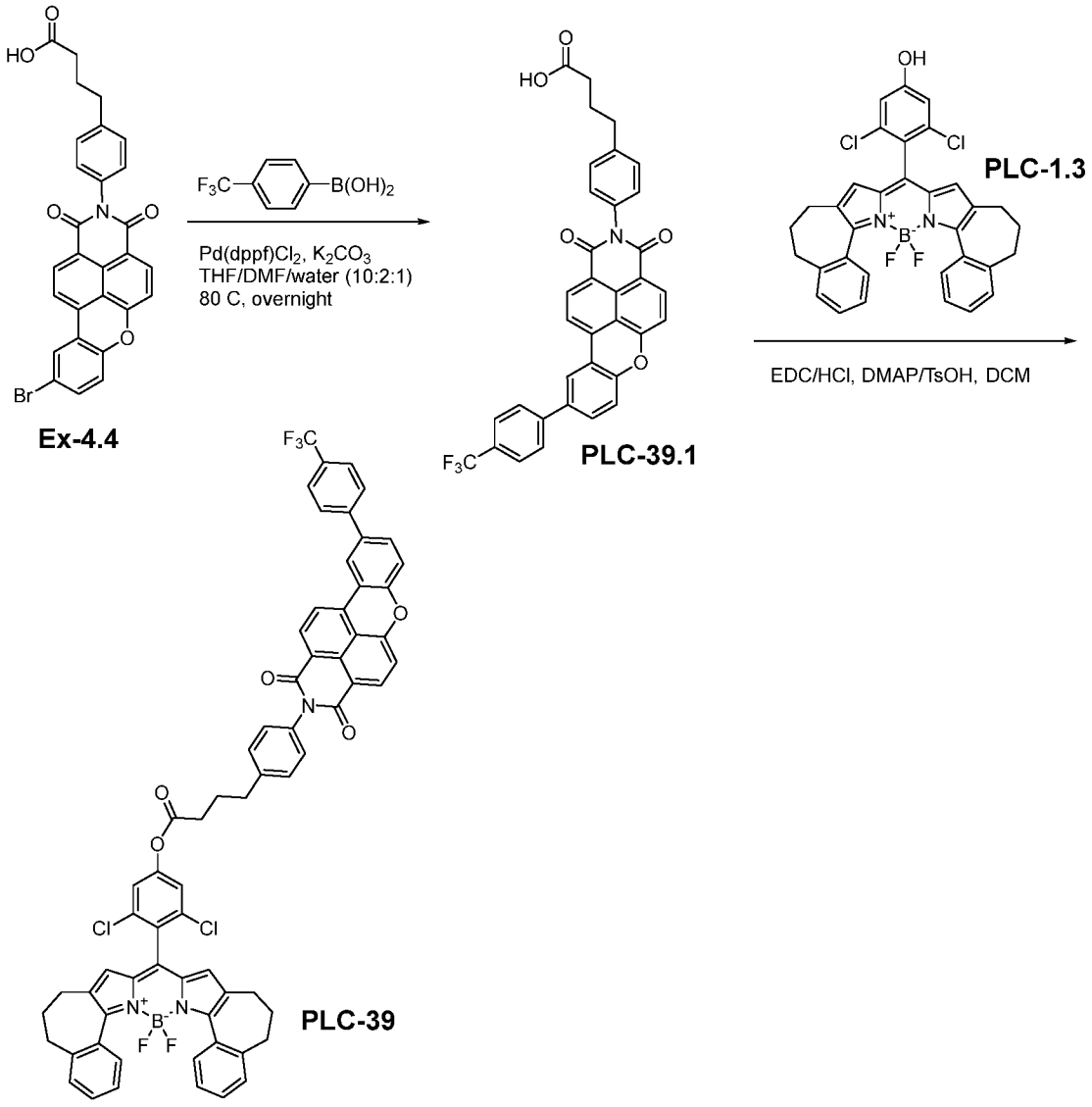
Synthesis of PLC-38.2 (2-(3-hydroxypropyl)-9-(4-(trifluoromethyl) phenyl)-1H-xantheno [2,1,9-def] isoquinoline-1,3(2H)-dione): PLC-38.1 (1.06 g, 2.5 mmol, 1eq) was suspended in DMF (10 ml), H_2O (5 ml), added 4-trifluoromethyl) benzene boronic acid (0.949 g, 5.0 mmol, 2 eq), K_2CO_3 (0.691 g, 5.0 mmol, 2eq), $Pd(dppf)Cl_2 \cdot DCM$ (40.8 mg, 0.05 mmol, 0.02eq). The mixture was degassed by Vac- Fill Argon cycle 3 times, stirred & heated at 90 ^{o}C 5 hours. The reaction mixture was cooled to room temperature, water was added. The resulting mixture was holding at room temperature 12 hours. The greenish yellow solid was filtered, washed with water then MeOH to obtain 1.04 g greenish yellow solid, yield 85%. MS (APCI): calculated for $C_{30}H_{22}F_3NO_4$ (M-) = 517; found: 517. ^{1}H NMR (400 MHz) δ 8.56 (d, *J* = 7.9 Hz, 1H), 8.51 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 2.1 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 10.3, 1.9 Hz, 4H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 4.09 (t, *J* = 7.5 Hz, 2H), 3.57 (q, *J* = 6.2 Hz, 2H), 1.69 (p, *J* = 7.8 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.42 (q, *J* = 8.0 Hz, 2H), 1.28 (t, *J* = 5.5 Hz, 1H).

Synthesis of PLC-38.3 (2-(3-bromopropyl)-9-(4-(trifluoromethyl) phenyl)-1H-xantheno [2,1,9-def] isoquinoline-1,3(2H)-dione): A mixture of **PLC-38.2** (1.6 g, 3.2 mmol) and 48% aqueous HBr (30.0 ml) heated to refluxed by heating block at 130 °C for 3 days with stirring. The same volume of 48% aq HBr was added for 2 more times in the next 2 days, total amount was 90 ml. After cooling to room temperature, the mixture was poured to ice water, the solid was filtered, washed with water, dried in vacuo-oven to obtain 82% desired compound containing with unreacted SM. Gained 1.7 g greenish yellow solid, yield 96%. Product was used next step without further purification. MS (APCI): calculated for $C_{30}H_{21}BrF_3NO_3$ (M-) = 551; found: 551. ^{1}H NMR (400 MHz) δ 8.55 (d, *J* = 7.9 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 2.2 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 5H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 4.22 (t, *J* = 7.1 Hz, 2H), 3.45 (t, *J* = 6.8 Hz, 2H), 2.25 (q, *J* = 6.9 Hz, 2H).

Synthesis of PLC-38 (2-(3-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)propyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): PLC-38.3 (41.425 mg, 0.075 mmol, 1.15eq)

was suspended in DMF anhydrous (2.0 ml), added **PLC-2.1** (38.04 mg, 0.065 mmol, 1 eq), K_2CO_3 (0.73 mg, 0.15 mmol, 2.3eq), NaI (4.15 mg). The resulting mixture was stirred at 85 °C, under Argon atmosphere 16 hours, cooled to room temperature, the solid was filtered, washed with 50 ml water; crude product was loaded onto 40 g silica gel column, eluting with Hex: DCM (9:1) to DCM, gained 49mg dark purple solid, yield 71%. MS (APCI): calculated for $C_{63}H_{45}BCl_2F_5N_3O_4$ (M-) = 1055; found: 1055. ^{1}H NMR (400 MHz,) δ 8.60 (d, *J* = 7.8 Hz, 1H), 8.55 (d, *J* = 8.3 Hz, 1H), 8.18 (d, *J* = 2.2 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 5.9 Hz, 2H), 7.74 – 7.65 (m, 4H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.34 – 7.24 (m, 4H), 7.24 – 7.14 (m, 2H), 6.91 (s, 2H), 6.38 (s, 2H), 4.36 (t, *J* = 6.9 Hz, 2H), 4.13 (t, *J* = 6.1 Hz, 2H), 2.54 (t, *J* = 6.7 Hz, 4H), 2.28 – 2.19 (m, 4H), 2.06 – 1.85 (m, 4H), 0.78 (d, *J* = 14.2 Hz, 2H).

Synthesis procedure of PLC-39

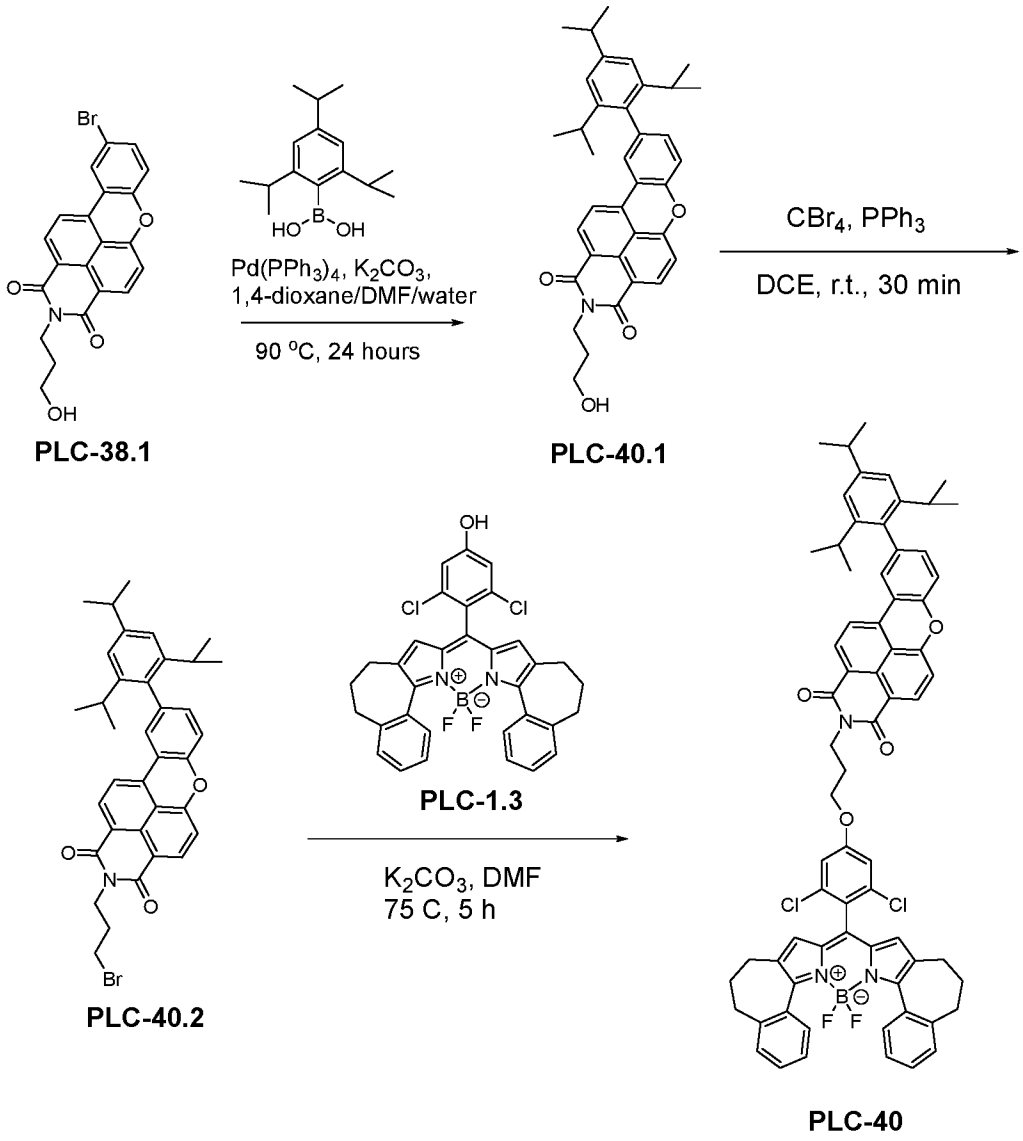


Compound 39.1: A mixture of compound **Ex-4.4** (649 mg, 1.23 mmol), 4-(trifluoromethyl)phenylboronic acid (467 mg, 2.46 mmol), Pd(dppf)Cl2 (45 mg, 0.06 mmol), potassium carbonate (345 mg, 2.5 mmol) in cosolvents of THF/DMF/water (30mL/6mL/3mL) was degassed, then heated at 80 ºC for overnight. The mixture was worked up with 300mL ethyl acetate and 50 mL 0.6 N hydrochloric acid aqueous solution. The aqueous phase was extracted with ethyl acetate (150 mL x 3). The organic phase was collected and washed with brine (100mL x 2), dried over sodium sulfate, then dry loaded on silica gel and purified by flash chromatography using eluents of DCM/EA (0% to 80% EA with 0.1% TFA). The main desired fraction was collected, removal of solvents under reduced pressure gave a yellow solid (414mg, in 57% yield). 1H NMR (400 MHz, d2-TCE) δ 8.55 (dd, J = 18.1, 8.1 Hz, 2H), 8.16 (d, J

= 2.2 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.68 (dd, J = 8.6, 2.1 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.43 (d, J = 8.6 Hz, 1H), 7.32 (tt, J = 8.2, 4.2 Hz, 5H), 7.20 – 7.13 (m, 2H), 2.72 (t, J = 7.6 Hz, 2H), 2.39 (t, J = 7.3 Hz, 2H), 1.99 (q, J = 7.4 Hz, 2H).

Compound PLC-39: A mixture of **PLC-1.3** (32mg, 0.0547mmol), **PLC-39.1** (48.7 mg, 0.082 mmol), EDC•HCl (60mg, 0.31 mmol) and DMAP/p-TsOH (15 mg, 0.05 mmol) in DCM (5mL) was stirred at room temperature overnight. The resulted mixture was then loaded on silica gel, purified by flash chromatography using eluents of DCM/ethyl acetate (0% → 10% ethyl acetate). The main red fraction was collected and concentrated to 0.5mL under reduced pressure, then 10 mL methanol was added. The resulted precipitate was filtered and dried in air to give a dark red solid (44mg, in 69% yield). 1H NMR (400 MHz, d2-TCE) δ 8.56 (dd, J = 17.8, 8.1 Hz, 2H), 8.16 (d, J = 2.2 Hz, 1H), 7.99 (dd, J = 19.8, 6.8 Hz, 3H), 7.68 (dd, J = 8.6, 2.1 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.44 (d, J = 8.6 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.35 – 7.25 (m, 9H), 7.22 (dd, J = 8.7, 4.2 Hz, 4H), 6.40 (s, 2H), 2.82 (t, J = 7.5 Hz, 2H), 2.67 (t, J = 7.4 Hz, 2H), 2.55 (t, J = 6.7 Hz, 4H), 2.24 (bs, 4H), 2.14 (q, J = 7.5 Hz, 2H), 1.96 (t, J = 7.1 Hz, 4H).

Synthesis procedure of PLC-40



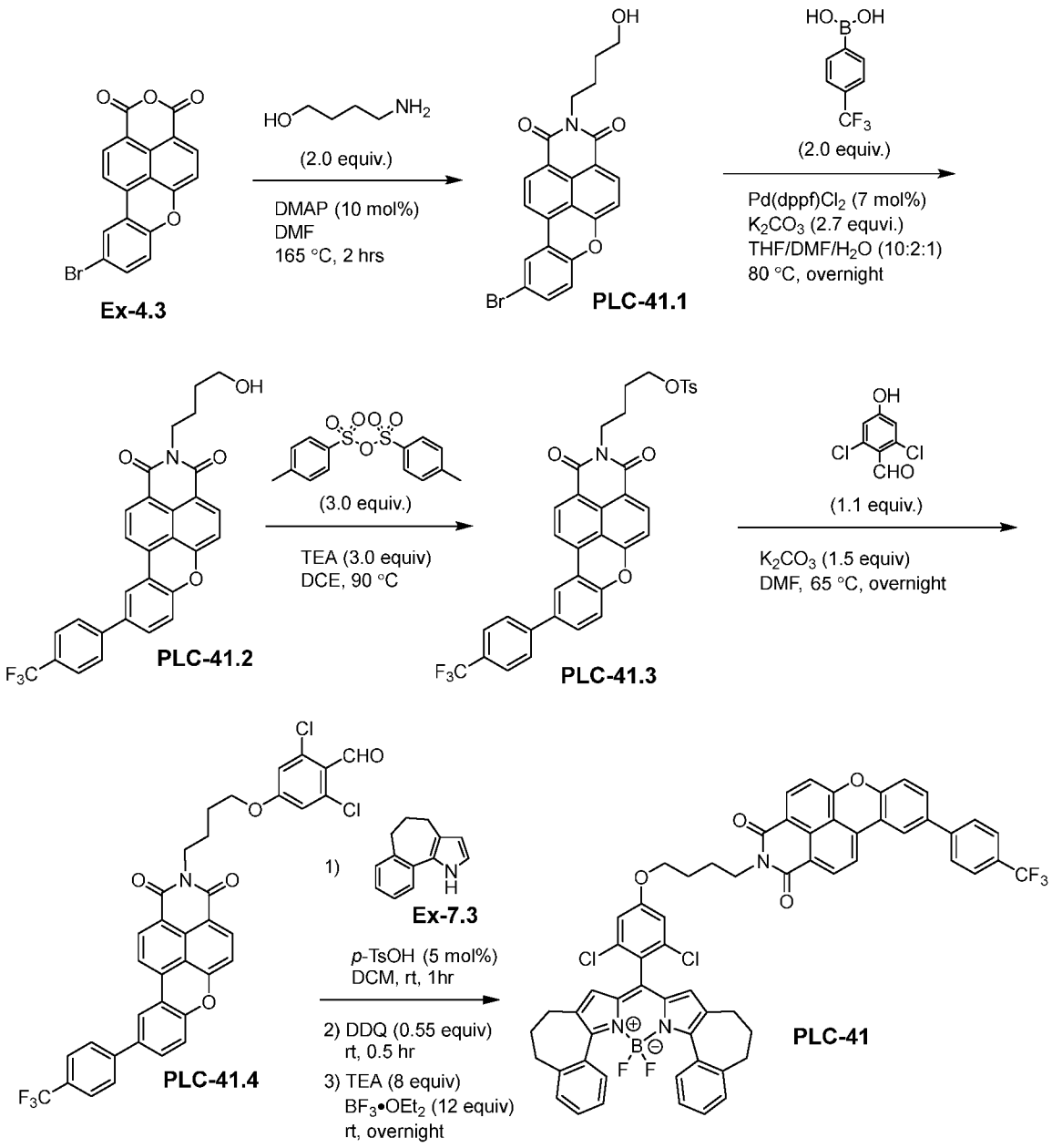
Compound 40.1: A mixture of 9-bromo-2-(3-hydroxypropyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione (**PLC-38.1**, 330 mg, 0.778 mmol), (2,4,6-triisopropylphenyl)boronic acid (290 mg, 1.17 mmol), Pd(PPh3)4 (80 mg, 0.069 mmol), K2CO3 (320 mg, 2.32 mmol) in 1,4-dioxane/DMF/water (15mL/3 mL/1.5 mL) was degassed and heated at 90 ºC for 24 hours. The resulted mixture was worked up with water and ethyl acetate. The organic phase was collected and loaded on silica gel, purified by flash chromatography using eluents of DCM/EA (0% to 40% EA). The desired fraction was collected, after removal of solvents under reduced pressure, a yellow solid was obtained (210mg, in 49% yield). LCMS (APCI-): Calcd for C36H37NO4: 547.27; Found: 547. 1H NMR (400 MHz, d2-TCE) δ 8.60 – 8.48 (m, 2H), 7.93 – 7.76 (m, 2H), 7.45 – 7.24 (m, 3H), 6.99 (s, 2H), 4.25 (t, J = 6.1 Hz,

2H), 4.01 (q, J = 7.2 Hz, 2H), 3.47 (t, J = 5.5 Hz, 2H), 2.88 (p, J = 6.8 Hz, 1H), 2.65 – 2.43 (m, 2H), 1.89 (d, J = 6.2 Hz, 2H), 1.24 (d, J = 6.9 Hz, 6H), 1.03 (t, J = 7.1 Hz, 12H).

Compound 40.2: To a solution of compound **PLC-40.1** (210 mg, 0.384 mmol) in 20 mL DCM was added carbon tetrabromide (CBr_4, 252mg, 0.76 mmol), triphenylphosphine (203 mg, 0.77 mmol) at room temperature. The whole was stirred for 30 min. TLC shows the reaction has completed. The mixture was loaded on silica gel and purified by flash chromatography using eluents of hexanes/DCM (0% to 100% DCM). The desired fraction was collected, concentrated under reduced pressure to give a yellow solid (100mg, in 43% yield). LCMS (APCI+): Calcd for C36H37BrNO3 (M+H): 610.19; Found: 610. 1H NMR (400 MHz, d2-TCE) δ 8.52 (dd, J = 8.1, 2.5 Hz, 2H), 8.00 – 7.72 (m, 2H), 7.45 – 7.19 (m, 3H), 6.98 (s, 2H), 4.23 (t, J = 7.0 Hz, 2H), 3.44 (t, J = 6.8 Hz, 2H), 3.01 – 2.80 (m, 1H), 2.69 – 2.45 (m, 2H), 2.26 (q, J = 6.9 Hz, 2H), 1.24 (d, J = 6.9 Hz, 6H), 1.03 (t, J = 6.9 Hz, 12H).

Compound 40: A mixture of compound **PLC-40.2** (50 mg, 0.082 mmol), **PLC-1.3** (58.5 mg, 0.10 mmol), K2CO3 (20.7 mg, 0.15 mmol) in anhydrous DMF, was sonicated for 3 minutes, then heated at 75 ºC for 5 hours under argon atmosphere. The resulted mixture was diluted with 100 mL DCM, washed with 0.1N HCl aqueous solution (50 mL x 2), dried over MgSO4, concentrated to 50 mL then loaded on silica gel, and purified by flash chromatography using eluents of DCM/EA (0% □ 5% EA). The main desired fraction was collected, concentrated and triturated with methanol followed by filtration to give a dark red solid (70 mg, in 76.6% yield). LCMS (APCI-): Calcd for C69H60BCl2F2N3O4: 1113.40; Found: 1113. 1H NMR (400 MHz, d2-TCE) δ 8.63 – 8.43 (m, 2H), 8.08 – 7.72 (m, 4H), 7.46 – 7.13 (m, 9H), 6.94 (d, J = 31.3 Hz, 4H), 6.38 (s, 2H), 4.35 (t, J = 6.8 Hz, 2H), 4.12 (t, J = 5.9 Hz, 2H), 2.98 – 2.77 (m, 1H), 2.54 (q, J = 6.8 Hz, 6H), 2.23 (d, J = 6.0 Hz, 6H), 2.04 – 1.89 (m, 4H), 1.23 (d, J = 6.9 Hz, 6H), 1.02 (dd, J = 6.9, 3.5 Hz, 12H).

Synthesis of compound PLC-41



General procedure of compound **PLC-41.1** synthesis— 9-bromo-2-(4-hydroxybutyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: A 100 mL flask was fitted with a stir bar. To the flask, compound **Ex-4.3** (1.0 g, 2.7 mmol), 4-aminobutan-1-ol (485.3 mg, 5.4 mmol) and DMAP (23.1 mg, 0.19 mmol) in DMF (20 ml) was degassed at room temperature. The reaction mixture was heated up to 165 ºC and the reaction has been kept at this temperature for 2.5 hrs. TLC and LCMS showed the completion of the reaction. The reaction was cooled down to

room temperature. H2O (80 ml) was added. The solid product was collected by vacuum filtration and washed with H2O (100 ml) and further dried in a vacuum oven at 100 ºC for 3 hours to provide **PLC-41.1** as a brown solid for the next step without further purification. 908.0 mg, 77% yield. MS (APCI): calculated for Chemical Formula: C22H16BrNO4 ([M-H]-) = 438 found: 438. 1H NMR (400 MHz, CDCl2CDCl2) 8.62 (d, J = 8.0 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 2.4 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.64 (dd, J = 8.0 Hz, J = 2.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 4.20 (t, J = 7.2 Hz, 2H), 3.83 (t, J = 6.0 Hz, 2H), 1.82 (m, 2H), 1.69 (m, 2H).

General procedure of compound **PLC-41.2** synthesis— 2-(4-hydroxybutyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: A 250 mL flask was fitted with a stir bar. To the flask, compound **PLC-41.1** (900.0 mg, 2.1 mmol), 4-(trifluoromethyl)phenylboronic acid (780.0 mg, 4.1 mmol), Pd(dppf)Cl2 (107.5 mg, 0.15 mmol) and K2CO3 (782.5 mg, 5.7 mmol) in THF/DMF/H2O (60 ml/ 12 ml/ 6 ml) was degassed at room temperature. The reaction mixture was heated up to 80 ºC and the reaction has been kept at this temperature overnight. TLC was used to monitor the reaction. After the completion, the reaction was worked up by the addition of H2O (150 ml) added to precipitate the product. The precipitate was collected by filtration. The solid was washed by H2O (200 ml) and MeOH (20 ml), and further dried in a vacuum oven at 100 ºC for 3 hours to provide **PLC-41.2** as a yellow solid for the next step without further purification. 990.0 mg, 94% yield. MS (APCI): calculated for Chemical Formula: C29H20F3NO4 ([M+H]+) = 504 found: 504. 1H NMR (400 MHz, CDCl2CDCl2) 8.67 (d, J = 8.0 Hz, 1H), 8.61 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 2.4 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.80 (m, 5H), 7.52 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 4.22 (t, J = 7.2 Hz, 2H), 3.73 (t, J = 6.0 Hz, 2H), 1.84 (m, 4H).

General procedure of compound **PLC-41.3** synthesis— 4-(1,3-dioxo-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)butyl 4-methylbenzenesulfonate: A 100 mL flask was fitted with a stir bar. To the flask, compound **PLC-41.2** (200.0 mg, 0.40 mmol) and DCE (20 ml) were added. The solution was degassed at room temperature. p-toluenesulfonic anhydride (519.0 mg, 1.6 mmol) and TEA (221.0 µL, 1.6 mmol) were added. Then the solution heated up to 90 ºC and it has been kept at this temperature for 4 hours. TLC and LCMS were used to monitor the reaction. More DCE (20 mL), p-toluenesulfonic anhydride (519.0 mg, 1.6 mmol) and was added. The reaction was cooled

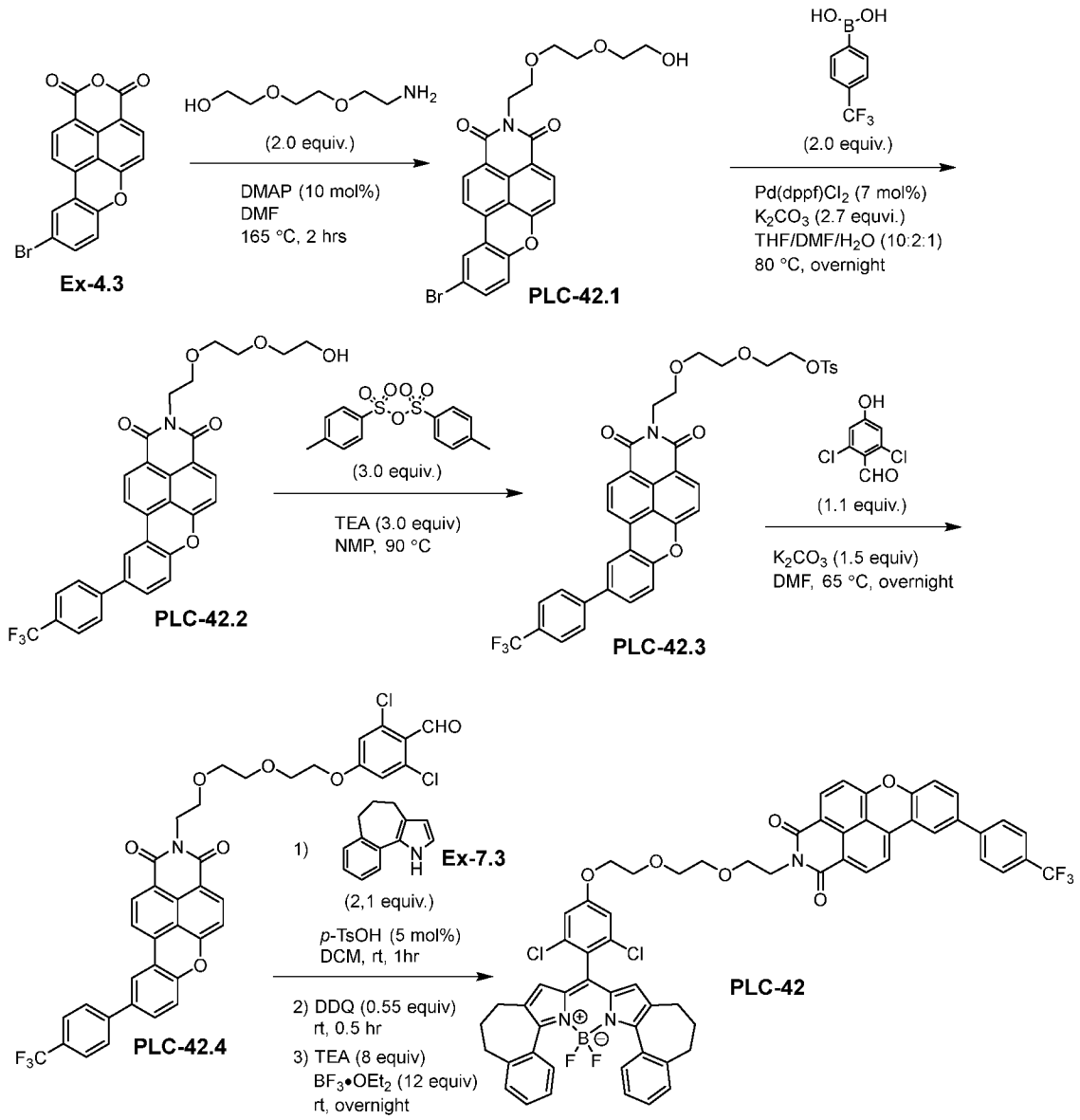
down to room temperature. H2O (100 ml), TEA (221.0 µL, 1.6 mmol) were added. The reaction has been kept at 90 ºC overnight. The mixture was extracted with DCM (150 ml *3) after H2O (150 ml) was added to stop the reaction. The combined organic phase was dried over anhydrous Na2SO4 and concentrated under vacuum rotavapor to provide **PLC-41.3** as a yellow solid, which was used for the next step without further purification. MS (APCI): calculated for Chemical Formula: C36H26F3NO6S ([M-H]-) = 657 found: 657. 1H NMR (400 MHz, CDCl3) 8.55 (d, J = 8.0 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 2.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.76 (m, 7H), 7.41 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 1H), 4.10 (m, 4H), 2.42 (s, 3H), 1.76 (m, 4H).

General procedure of compound **PLC-41.4** synthesis— 2,6-dichloro-4-(4-(1,3-dioxo-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)butoxy)benzaldehyde: A 25 ml vial was charged with **PLC-41.3** (131.5 mg, 0.20 mmol) and 4-hydroxy-2,6-dichlorobenzaldehyde (42.0 mg, 0.22 mmol) in DMF (5 mL). The solution was degassed at room temperature, K2CO3 (41.4 mg, 0.30 mmol) was added. The reaction was further degassed at room temperature. Then it was warmed up to 65 ºC and has been kept stirring at this temperature overnight. TLC (50% EtOAc in Hexane) showed the completion of the reaction. The reaction mixture was purified by silica gel flash chromatography using EtOAc in Hexane (5%-40%) as an eluant to provide pure compound **PLC-41.4** as a yield solid, 27.0 mg, 20% yield over two steps. MS (APCI): calculated for Chemical Formula: C36H22Cl2F3NO5 ([M-H]-) = 676 found: 676. 1H NMR (400 MHz, CDCl3) δ 10.37 (s, 1H), 8.67 (d, J = 8.0 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 2.4 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.78 (bs, 4H), 7.75 (m, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 6.88 (s, 2H), 4.26 (m, 2H), 4.09 (m, 2H), 1.96 (m, 4H).

General procedure of compound **PLC-41** synthesis— 2-(4-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)butyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: A 50 mL 2 neck round bottomed flask was fitted with an air condenser and a stir bar. To the flask, **PLC-41.4** (27.0 mg, 0.04 mmol) and **Ex-7.3** (15.3 mg, 0.084 mmol) were added, followed by anhydrous dichloromethane (5 ml). The reaction mixture was degassed at room temperature, then p-TsOH•H2O (0.2 mg, 0.002 mmol) was

added. The reaction solution has been kept at this temperature for 2 hrs. Then DDQ (5.0 mg, 0.02 mmol) was added. The reaction was kept at room temperature for 1 hour. Then BF3•OEt2 (59 μL, 0.48 mmol) and Et3N (44 μL, 0.32 mmol) were added at room temperature. The reaction mixture has been kept at room temperature overnight. The reaction mixture was loaded with silica gel and purified by flash chromatography, using EtOAc in DCM (0-3%) as an eluant to provide the pure **PLC-41** as a dark purple solid, 12.0 mg, 28% yield. MS (APCI): calculated for Chemical Formula: C62H43BCl2F5N3O4 ([M-H]-) = 1070 found: 1070. 1H NMR (400 MHz, CDCl2CDCl2) 8.69 (d, J = 8.0 Hz, 1H), 8.64 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 2.4 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.05 (m, 2H), 7.79 (m, 5H), 7.53 (d, J = 8.0 Hz, 1H), 7.38 (m, 5H), 7.30 (m, 2H), 7.08 (s, 2H), 6.48 (s, 2H), 4.30 (bs, 2H), 4.14 (bs, 2H), 2.64 (m, 4H), 2.32 (bs, 4H), 2.00 (m, 8H).

Synthesis of compound PLC-42



General procedure of compound **PLC-42.1** synthesis— 9-bromo-2-(2-(2-(2-hydroxyethoxy)ethoxy)ethyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: A 100 mL flask was fitted with a stir bar. To the flask, compound **Ex-4.3** (1.3 g, 3.4 mmol), 2-(2-(2-aminoethoxy)ethoxy)ethan-1-ol (1.0 g, 6.8 mmol) and DMAP (29.0 mg, 0.24 mmol) in DMF (25 ml) was degassed at room temperature. The reaction mixture was heated up to 165 ºC and the reaction has been kept at this temperature for 2 hrs. TLC and LCMS showed the completion of the reaction. The reaction was cooled down to 50 ºC. The solution was poured

into a pre-chilled acetone (100 ml) solution with ice-water batch. The mixture has been kept at this temperature for 2 hours and then has been kept at room temperature overnight. The precipitate was collected by filtration. The solid was washed by H2O (150 ml) and further dried in a vacuum oven at 100 ºC for 3 hours to provide **PLC-42.1** as a brown solid for the next step without further purification. 805.0 mg, 48% yield. MS (APCI): calculated for Chemical Formula: C24H20BrNO6 ([M-H]-) = 498 found: 498. 1H NMR (400 MHz, CDCl2CDCl2) 8.61 (d, J = 8.0 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 2.4 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.64 (dd, J = 8.0 Hz, J = 2.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 4.42 (t, J = 6.0 Hz, 2H), 3.83 (t, J = 6.0 Hz, 2H), 3.63 (m, 8H).

General procedure of compound **PLC-42.2** synthesis— 2-(2-(2-(2-hydroxyethoxy)ethoxy)ethyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: A 250 mL flask was fitted with a stir bar. To the flask, compound 1621-36 (800.0 mg, 1.6 mmol), 4-(trifluoromethyl)phenylboronic acid (609.8 mg, 3.2 mmol), Pd(dppf)Cl2 (82.4 mg, 0.1 mmol) and K2CO3 (600.0 mg, 4.4 mmol) in THF/DMF/H2O (44 ml/ 8.8 ml/ 4.4 ml) was degassed at room temperature. The reaction mixture was heated up to 80 ºC and the reaction has been kept at this temperature overnight. TLC was used to monitor the reaction. After the completion, the reaction was worked up by the addition of H2O (150 ml) added to precipitate the product. The precipitate was collected by filtration. The solid was washed by H2O (200 ml) and MeOH (20 ml), and further dried in a vacuum oven at 100 ºC for 3 hours to provide **PLC-42.2** as a yellow solid for the next step without further purification. Quantitative yield. MS (APCI): calculated for Chemical Formula: C31H24F3NO6 ([M+H]+) = 564 found: 564. 1H NMR (400 MHz, CDCl2CDCl2) 8.67 (d, J = 8.0 Hz, 1H), 8.61 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 2.0 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.96 (bs, 1H), 7.80 (m, 5H), 7.52 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 4.43 (t, J = 6.0 Hz, 2H), 3.84 (t, J = 6.0 Hz, 2H), 3.70 (m, 2H), 3.64 (m, 4H), 3.54 (m, 2H).

General procedure of compound **PLC-42.3** synthesis— 2-(2-(2-(1,3-dioxo-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate: A 100 mL flask was fitted with a stir bar. To the flask, compound 1621-41 (300.0 mg, 0.53 mmol) and NMP (8 ml) were added. The solution was degassed at room temperature. p-toluenesulfonic anhydride (522.2 mg, 1.6 mmol) and TEA (162.0 mg, 1.6 mmol) were added. Then the solution heated up to 90 ºC and it has been kept at this

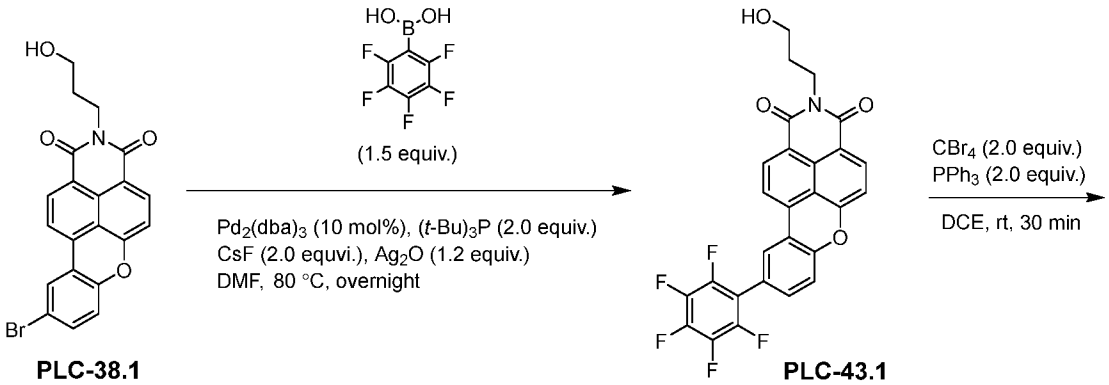
temperature overnight. TLC and LCMS were used to monitor the reaction. Even with extended time, the reaction stayed at 90 conversion. The conversion could be improved to 97% after more p-toluenesulfonic anhydride (130.0 mg) was added. The reaction was cooled down to room temperature. H2O (100 ml) was added. The mixture was extracted with DCM (150 ml *3). The combined organic phase was dried over anhydrous Na2SO4 and concentrated under vacuum rotavapor to provide **PLC-42.3** as a yellow solution (with NMP as the residue), which was used for the next step without further purification. MS (APCI): calculated for Chemical Formula: C38H30F3NO8S ([M-H]-) = 717 found: 717. 1H NMR (400 MHz, CDCl2CDCl2) 8.64 (d, J = 8.0 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 2.4 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.76 (m, 7H), 7.51 (d, J = 8.4 Hz, 1H), 7.34 (m, 3H), 4.38 (t, J = 6.0 Hz, 2H), 4.05 (m, 2H), 3.76 (t, J = 6.0 Hz, 2H), 3.61 (m, 4H), 3.54 (m, 2H), 2.42 (s, 3H).

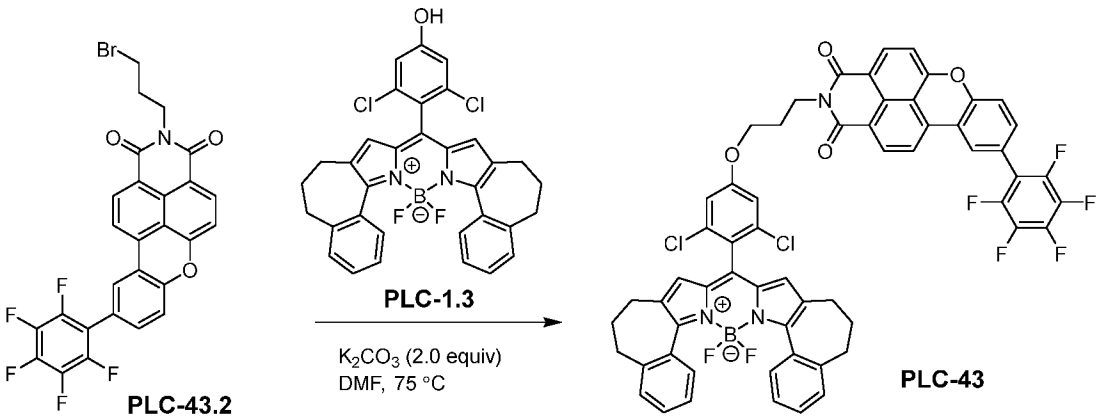
General procedure of compound **PLC-42.4** synthesis— 2,6-dichloro-4-(2-(2-(2-(1,3-dioxo-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)ethoxy)ethoxy)ethoxy)benzaldehyde: A 25 ml vial was charged with **PLC-42.3** (186.6 mg, 0.26 mmol) and 4-hydroxy-2,6-dichlorobenzaldehyde (54.6 mg, 0.29 mmol) in DMF (5 mL). The solution was degassed at room temperature, K2CO3 (53.8 mg, 0.39 mmol) was added. The reaction was further degassed at room temperature. Then it was warmed up to 65 ºC and has been kept stirring at this temperature overnight. TLC (50% EtOAc in Hexane) showed the completion of the reaction. The reaction mixture was purified by silica gel flash chromatography using EtOAc in Hexane (0-40%-60%) as an eluant to provide pure compound **PLC-42.4** as a yield solid, 37.0 mg, 19% yield over two steps. MS (APCI): calculated for Chemical Formula: C38H26Cl2F3NO7 ([M-H]-) = 736 found: 736. 1H NMR (400 MHz, CDCl2CDCl2) δ 10.20 (s, 1H), 8.62 (d, J = 8.0 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 2.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.80 (s, 4H), 7.76 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 6.69 (s, 2H), 4.45 (t, J = 6.0 Hz, 2H), 3.86 (m, 4H), 3.72 (m, 6H).

General procedure of compound **PLC-42** synthesis— 2-(2-(2-(2-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)ethoxy)ethoxy)ethyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: A 100 mL 2 neck round bottomed flask was fitted with an air condenser and a stir bar. To the flask, **PLC-42.4** (37.0 mg, 0.05 mmol) and

1605-44 (19.3 mg, 0.11 mmol) were added, followed by anhydrous dichloromethane (5 ml). The reaction mixture was degassed at room temperature, then p-TsOH•H2O (0.3 mg, 0.003 mmol) was added. The reaction solution has been kept at this temperature for 2 hrs. Then DDQ (6.2 mg, 0.03 mmol) was added. The reaction was kept at room temperature for 1 hour. Then BF3•OEt2 (74 µL, 0.6 mmol) and Et3N (56 µL, 0.4 mmol) were added at room temperature. The reaction mixture has been kept at room temperature overnight. The reaction mixture was loaded with silica gel and purified by flash chromatography, using EtOAc in DCM (0-6%) as an eluant to provide the pure **PLC-42** as a dark purple solid, 7.0 mg, 13% yield. MS (APCI): calculated for Chemical Formula: C64H47BCl2F5N3O6 ([M-H]-) = 1130 found: 1130. 1H NMR (400 MHz, CDCl2CDCl2) 8.68 (d, J = 8.0 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 2.4 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 8.04 (m, 2H), 7.78 (bs, 4H), 7.78 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.37 (m, 5H), 7.29 (m, 2H), 7.07 (s, 2H), 6.46 (s, 2H), 4.46 (t, J = 8.4 Hz, 2H), 4.13 (t, J = 4.4 Hz, 2H), 3.86 (m, 4H), 3.74 (m, 4H), 2.63 (m, 4H), 2.31 (bs, 4H), 2.04 (m, 4H).

Synthesis of compound PLC-43





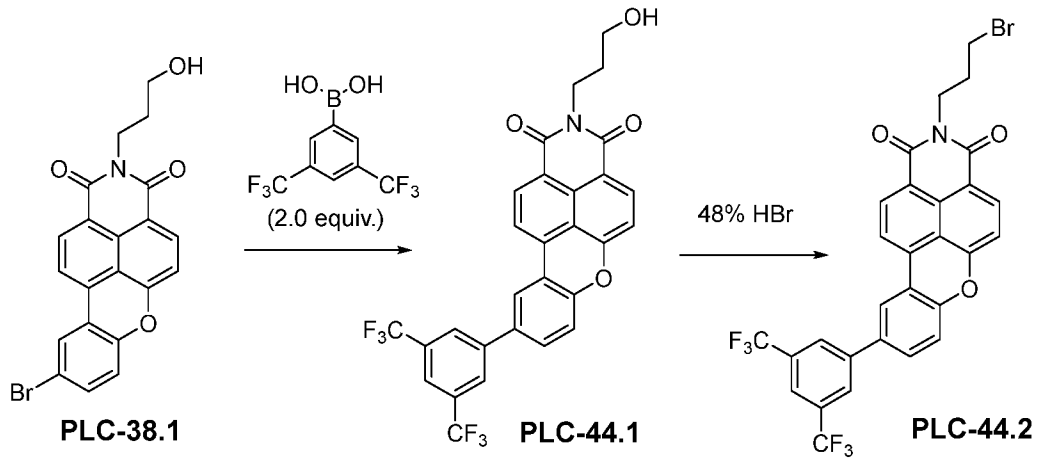
General procedure of compound **PLC-43.1** synthesis— 2-(3-hydroxypropyl)-9-(perfluorophenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: A 100 mL flask was fitted with a stir bar. To the flask, compound **PLC-38.1** (400.0 mg, 0.9 mmol), (perfluorophenyl)boronic acid (240.0 mg, 1.1 mmol), Pd2(dba)3 (43.0 mg, 0.05 mmol), CsF (285.6 mg, 1.9 mmol), Ag2O (259.4 mg, 1.1 mmol) and (t-Bu)3P (1.9 ml, 1.9 mmol) in DMF (30 ml) was degassed at room temperature. The reaction mixture was heated up to 80 ºC and the reaction has been kept at this temperature overnight. TLC was used to monitor the reaction. After the completion, the reaction was purified by silica gel flash chromatography using EtOAc in Hexane (5-10-50-70%) as an eluant to provide pure compound **PLC-43.1** as a yellow solid, 136.0 mg, 28% yield. MS (APCI): calculated for Chemical Formula: C27H14F5NO4 ([M-H]-) = 511 found: 511. 1H NMR (400 MHz, CDCl2CDCl2) 8.57 (d, J = 8.0 Hz, 1H), 8.55 (d, J = 8.0 Hz, 1H), 8.07 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 4.25 (t, J = 6.0 Hz, 2H), 3.48 (m, 2H), 3.07 (t, J = 6.8 Hz, 1H), 1.90 (m, 2H).

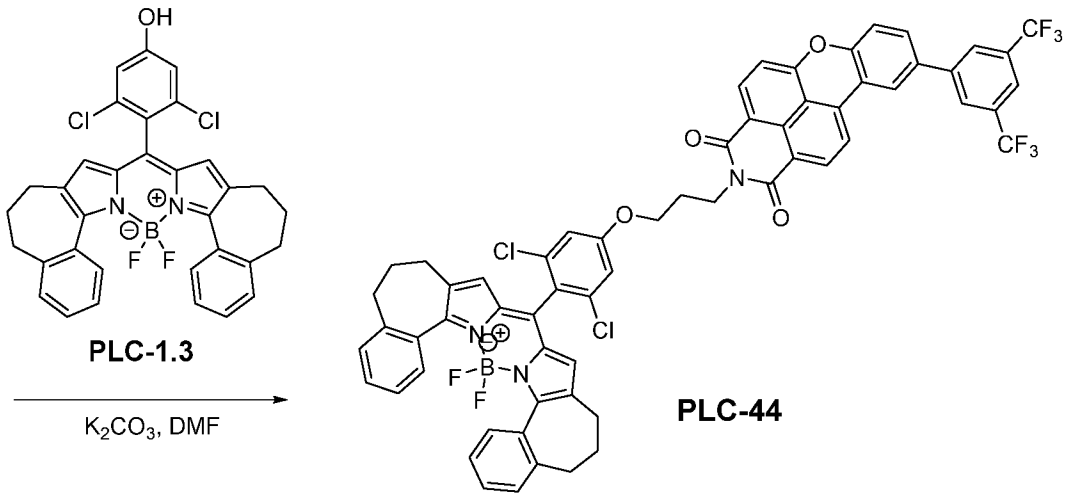
General procedure of compound **PLC-43.2** synthesis— 2-(3-bromopropyl)-9-(perfluorophenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: A 100 mL flask was fitted with a stir bar. To the flask, compound 1644-10 (136.0 mg, 0.3 mmol), CBr4 (176.3 mg, 0.5 mmol), PPh3 (140.2 mg, 0.5 mmol) and DCE (12 ml) were added. The solution was degassed at room temperature. The reaction has been kept at this temperature for 30 minutes. TLC and LCMS were used to monitor the reaction. After the completion, the reaction was purified by silica gel flash chromatography using EtOAc in Hexane (5-10-50-70%) as an eluant to provide pure compound **PLC-43.2** as a yellow solid, 116.0 mg, 76% yield. MS (APCI): calculated for Chemical Formula: C27H13BrF5NO3 ([M+H]+) = 573 found: 573. 1H NMR (400 MHz, CDCl2CDCl2) 8.64 (d, J = 8.0 Hz, 1H), 8.61 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 1.6 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.61 (m, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 4.32 (t, J = 6.8 Hz, 2H), 3.54 (t, J = 6.8 Hz, 2H), 2.34 (quintet, J = 6.8 Hz, 2H).

General procedure of compound **PLC-43** synthesis—2-(3-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)propyl)-9-(perfluorophenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: To a 25 ml vial, **PLC-1.3** (73.4 mg, 0.1 mmol), **PLC-43.2** (60.0 mg, 0.1 mmol), K2CO3 (28.7 mg, 0.2 mmol) and DMF (2 ml) were added. The mixture has been

sonicated at room temperature for 2 minutes. Then it was warmed up to 75 ºC and has been kept stirring at this temperature for 4 hours. TLC (50% EtOAc in Hexane) showed the completion of the reaction. The reaction mixture was purified by silica gel flash chromatography using EtOAc in DCM (0-3%) as an eluant to provide pure compound **PLC-43** as a dark purple solid, 91.0 mg, 81% yield. MS (APCI): calculated for Chemical Formula: C60H37BCl2F7N3O4 ([M-H]-) = 1077 found: 1077. 1H NMR (400 MHz, CDCl2CDCl2) 8.67 (d, J = 8.0 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.18 (bs, 1H), 8.05 (m, 2H), 8.01 (d, J = 8.0 Hz, 1H), 7.61 (m, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.38 (m, 5H), 7.30 (m, 2H), 7.02 (s, 2H), 6.47 (s, 2H), 4.44 (t, J = 6.0 Hz, 2H), 4.22 (t, J = 6.0 Hz, 2H), 2.64 (m, 4H), 2.32 (m, 6H), 2.05 (m, 4H).

Synthesis of Compound PLC-44





Compound **PLC-44.1**: 9-(3,5-bis(trifluoromethyl)phenyl)-2-(3-hydroxypropyl)-1H-xantheno[2,1,9-def] isoquinoline-1,3(2H)-dione: Compound **PLC-38.1** (0.4241 g, 1.0 mmol,

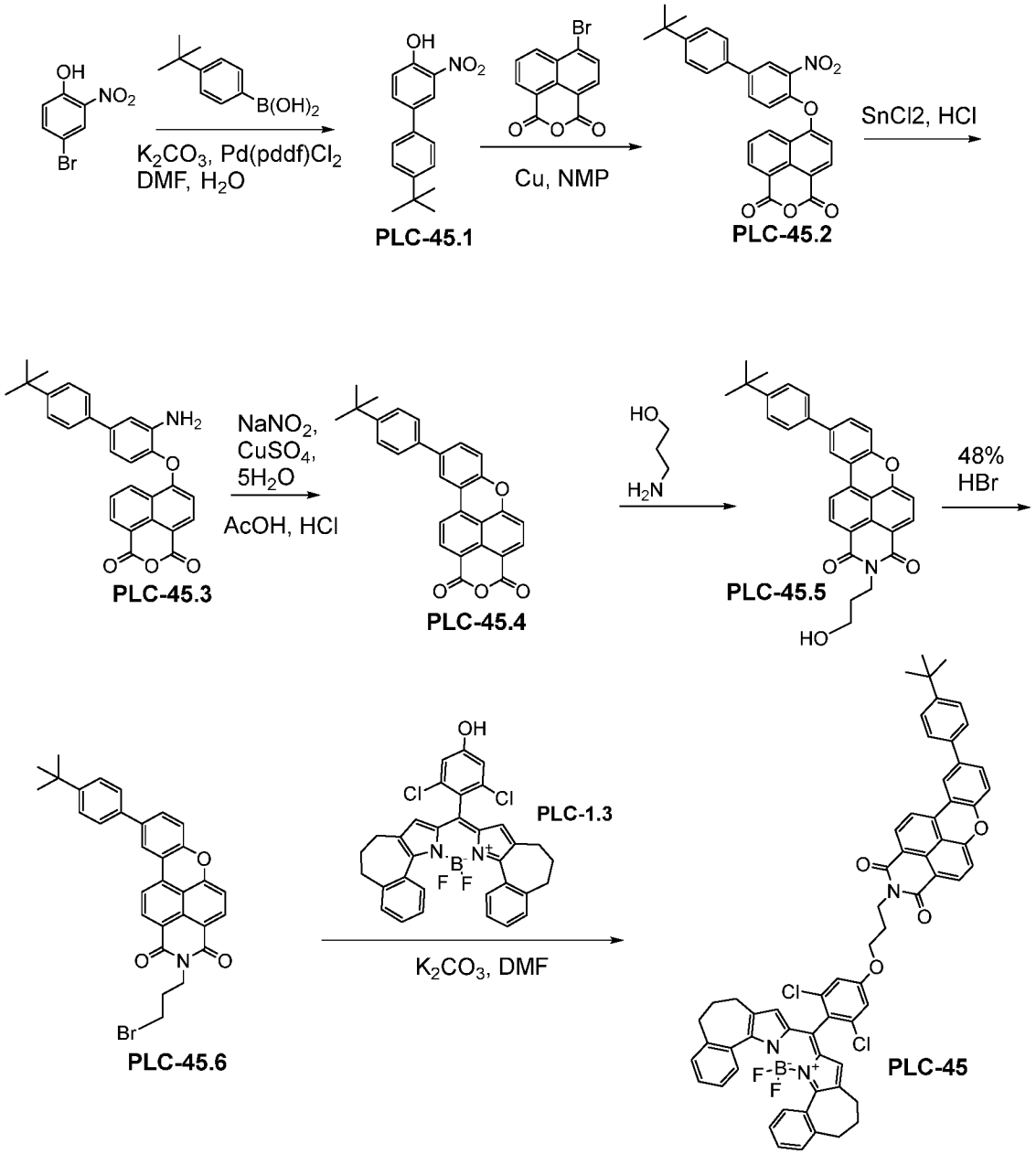
1eq) was suspended in DMF (5 ml), H2O (0.5 ml), added (bis-3,5 trifluoromethyl) benzeneboronic acid (0.51586 g, 2.0 mmol, 2 eq), K2CO3 (0.27642 g, 2.0 mmol, 2eq), Pd(dppf)Cl2 · DCM (16.33 mg, 0.02 mmol, 0.02eq). The resulting mixture was Vac- Fill Argon cycle 3 times, stirred & heated at 80 °C 45 minutes, the mixture became sticky, added 15 ml DMF, continued stirring at 80 °C further 15 minutes. Cooled the reaction mixture to room temperature, concentrated by rotavapor, added water to the residue mixture, holding at RT 1 hours. The precipitate was filtered, obtained 570 mg greenish yellow solid which was washed with MeOH to gain 270 mg pure product. Yield 48%. MS (APCI): calculated for Chemical Formula: C29H17F6NO4 (M-) = 557; found: 557. 1H NMR (400 MHz,) δ 8.60 (d, J = 7.9 Hz, 1H), 8.55 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 2.2 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 8.00 (s, 2H), 7.87 (s, 1H), 7.70 (dd, J = 8.7, 2.1 Hz, 1H), 7.47 (d, J = 8.6 Hz, 1H), 7.31 (d, J = 8.3 Hz, 1H), 4.25 (t, J = 6.2 Hz, 2H), 3.49 (d, J = 6.1 Hz, 3H), 3.08 (t, J = 6.8 Hz, 1H), 1.90 (t, J = 6.0 Hz, 2H).

Compound **PLC-44.2**: 9-(3,5-bis(trifluoromethyl)phenyl)-2-(3-bromopropyl)-1H-xantheno[2,1,9-def] isoquinoline-1,3(2H)-dione: A mixture of **PLC-44.1** (558 mg, 1.0 mmol) in 48% aqueous HBr (30.0 ml) was heated to reflux by heating block at 130 °C for 16 hours. LCMS shown >90 % conversion. After cooling to RT, the solid was filtered, washed with water, dried in vacuo-oven to obtain desired compound containing some unreacted SM. Gained 600 mg greenish yellow solid, yield 86 %. The product was used next step without further purification. MS (APCI): calculated for Chemical Formula: C29H16BrF6NO34 (M-) = 620; found: 620. 1H NMR (400 MHz) δ 8.58 (d, J = 7.8 Hz, 1H), 8.53 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 2.3 Hz, 1H), 8.04 – 7.97 (m, 2H), 7.86 (s, 1H), 7.70 (dd, J = 8.6, 2.2 Hz, 1H), 7.46 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 8.3 Hz, 1H), 4.23 (t, J = 7.1 Hz, 2H), 3.45 (t, J = 6.8 Hz, 2H), 2.34 – 2.16 (m, 2H).

Compound **PLC-44**: 9-(3,5-bis(trifluoromethyl)phenyl)-2-(3-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18□□4,19□□4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)propyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: Compound **PLC-44.2** (46.52 mg, 0.075 mmol, 1.15eq) was suspended in DMF anhydrous (2.0 ml), added **PLC-1.3** (38.04 mg, 0.065 mmol, 1 eq), K2CO3 (20.73 mg, 0.15 mmol, 2.3 eq), NaI (4.15 mg, cat. amount). The resulting was stirred at 85°C, under Argon atmosphere, 3 hours. The mixture was filtered, the solid was washed with 50 ml water then loaded onto 40 g column, eluting with Hex: DCM (9:1 to DCM only), the product from column was washed with EtOH gained 53 mg dark purple solid. Yield

62%. MS (APCI): calculated for Chemical Formula: C62H40BCl2F8N3O4 (M-) = 1124; found: 1124. 1H NMR (400 MHz) δ 8.61 (d, J = 7.8 Hz, 1H), 8.55 (d, J = 8.3 Hz, 1H), 8.16 (d, J = 2.2 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 8.00 (s, 2H), 7.95 (t, J = 4.7 Hz, 2H), 7.86 (s, 1H), 7.70 (dd, J = 8.6, 2.2 Hz, 1H), 7.47 (d, J = 8.6 Hz, 1H), 7.32 (d, J = 8.3 Hz, 1H), 7.27 (dt, J = 7.4, 3.7 Hz, 3H), 7.23 – 7.15 (m, 2H), 6.92 (s, 2H), 6.38 (s, 2H), 4.36 (t, J = 7.0 Hz, 2H), 4.13 (t, J = 6.0 Hz, 2H), 2.54 (t, J = 6.8 Hz, 4H), 2.24 (s, 4H), 1.96 (t, J = 7.2 Hz, 4H).

Synthesis of Compound **PLC-45**:



Compound **PLC-45.1**: 4'-(tert-butyl)-3-nitro-[1,1'-biphenyl]-4-ol: 4-bromo-2-nitro-phenol (5.45 g, 25.0 mmol) and 4-(t-butyl) benzene boronic acid (5.563 g, 31.25 mmol) were dissolved in dioxane (100 mL) at room temperature and stirred for 5 min. After a clear solution was formed, Pd (PPh3)2Cl2 (0.175 g, 0.25 mmol), and a solution of 4N aq. soln. K2CO3 (25.0 ml, 50 mmol, 2 eq) were added quickly; the mixture was degassed by Vac-Fil Nitrogen cycle 3 times before heating for 4 hrs at 80 °C. After reaction was cooled to RT, the pH was adjusted to 5-6 with 4N HCl aq. soln., extracted with ethyl acetate (250 mL), passed through a short pad of celite. The pad was washed with EA (150 ml x2). The organic layers were combined and washed with brine (25 mL), dried over anhydrous MgSO4, and concentrated under reduced pressure. The residue was dissolved into Hex: EA (95:5) (150 ml), the dark color solid was filtered off by filtering through short pad of celite, the filtrate was concentrated to obtain a yellow solid which was triturated with Hexanes to give 3.8 yellow solid, yield 56%. MS (APCI): calculated for Chemical Formula: C16H17NO3 (M-) = 271; found: 271. 1H NMR (400 MHz, Chloroform-d) δ 10.57 (s, 1H), 8.32 (d, J = 2.3 Hz, 1H), 7.83 (dd, J = 8.7, 2.4 Hz, 1H), 7.50 (d, J = 1.5 Hz, 4H), 7.23 (d, J = 8.7 Hz, 1H), 1.37 (s, 9H).

Compound **PLC-45.2**: . Mixing of 4-bromonaphthalic anhydride (10 g, 36 mmol, 1.15 eq), 4'-(tert-butyl)-3-nitro-[1,1'-biphenyl]-4-ol (**PLC-45.1**) (8.5 g, 31.32 mmol, 1eq), NaOH (0.864 g, 21.6 mmol, 0.6eq) in NMP anhydrous (65 mL), added copper powder (1.371 g, 21.6mmol, 0.6 eq) the resulting mixture was degassed by Vac-Fil Nitrogen cycle 3 times before heating and stirring at 145°C under N2 atmosphere for 5hrs, then RT overnight. The reaction mixture was worked up with HCl aq sol.; after standing at RT 12 hour, the brown solid was precipitated, filtered, washed with hot MeOH (250 ml x3) to obtain (10.8 g, 23.1 mmol) light brown solid, yield 73 %, purity 86%. MS (APCI): calculated for Chemical Formula: C28H21NO6 (M-) = 467; found: 467.

Compound **PLC-45.3**: 6-((3-amino-4'-(tert-butyl)-[1,1'-biphenyl]-4-yl) oxy)-1H,3H-benzo[de]isochromene-1,3-dione: To a mixture of **PLC-45.2** (4.885g, 10.45 mmol, 1.0 eq) in 2-MeTHF (70.0 mL) and HCl (4 M, 26.1 mL, 10 eq) was added SnCl2.2H2O (9.4 g, 41.75 mmol, 4.0 eq) in one portion. The mixture was stirred at 90 °C for 1/2 hr. TLC (Hexanes/Ethyl acetate = 7:3) and LCMS showed the reaction was completed. The white solid was filtered off, washed with EA/2-MeTHF (1:1) (100 mLx 2). The combined organic filtrates were washed with water, separated, concentrated under reduced pressure to give a sticky sold residue. The crude

product was washed with hot water 100 mL at 50 °C for 1/2 hour, filtered then drying under reduced pressure to gained **PLC-45.3** (4.5 g, 10.28 mmol) was obtained as a yellow brown solid. 98% yield. MS (APCI): calculated for Chemical Formula: C28H23NO4 (M-) = 437; found: 437

Compound **PLC-45.4:** 9-(4-(tert-butyl) phenyl)-1H,3H-isochromeno[6,5,4-mna] xanthene-1,3-dione: Compound **PLC-45.3** (1.844 g, 4.215 mmol, 1.0 eq) in AcOH (28.5 mL) and H2O (9.0 mL) was added dropwise HCl conc. (2.445 mL) and NaNO2 (2.9 g, 42.15 mmol, 10 eq) in H2O (9mL) at 0 °C and stirred at 0 °C for 1 hr. The above solution was added to CuSO4 5H2O (4.35 g, 17.42 mmol, 4.1 eq) in H2O (175 ml), AcOH (11 ml) via a dropping funnel at 130 °C over a period of 1/2 hr. After the addition was completed, the resulting was continued stirring at the same temperature 130 °C further 15 mins. The mixture was filtered and washed with H2O (3x100 mL) giving 0.445g crude product that was triturated EtOH to afford 0.42 g pure compound, yield 30%. MS (APCI): calculated for Chemical Formula: C28H20O4 (M-) = 420; found: 420

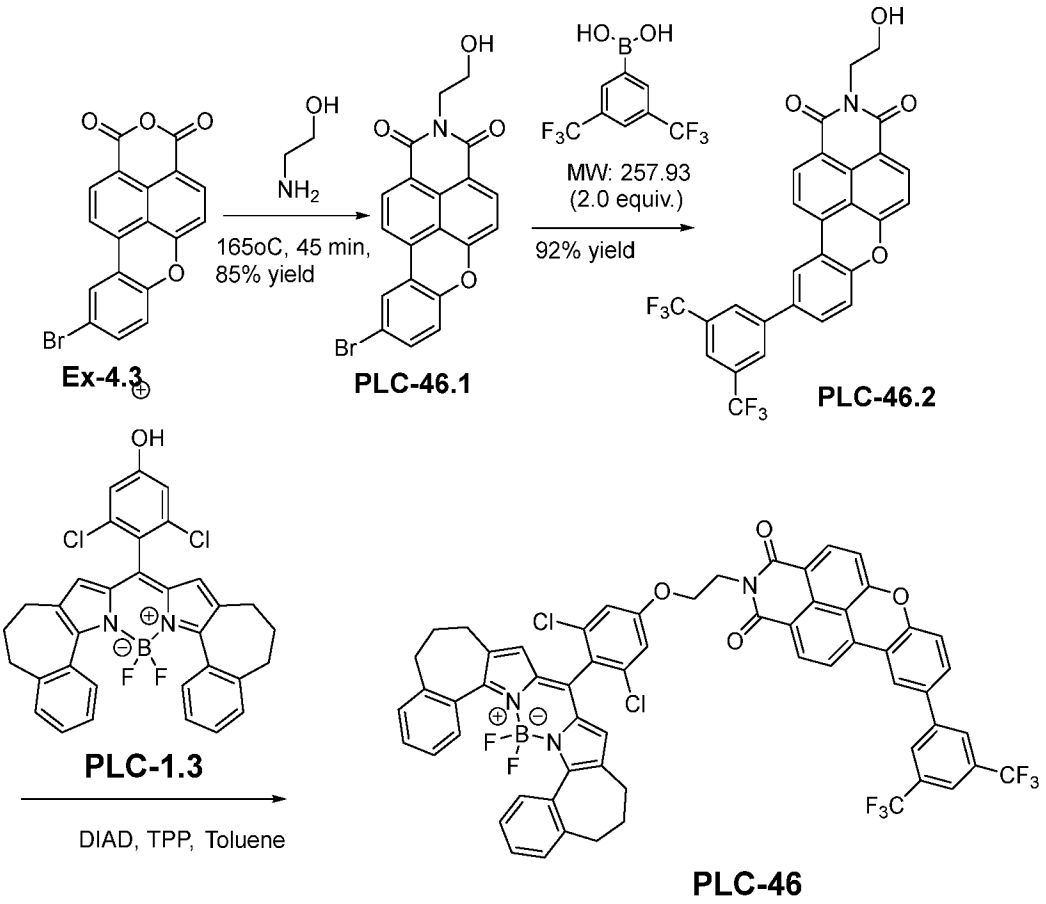
Compound **PLC-45.5**: 9-(4-(tert-butyl) phenyl)-2-(3-hydroxypropyl)-1H-xantheno[2,1,9-def] isoquinoline-1,3(2H)-dione: Compound **PLC-45.4** (0.420 g, 1.0 mmol, 1.0 eq) in DMSO anhydrous (4 mL) was added 3-amino-1-propanol (0.300 g, 4.0 mmol, 4.0 eq) at rt the resulting mixture was stirred over a period of 45 minutes at 130 °C. After the reaction was completed, DMSO were removed by filtering. The solid was washed with water (50 mlx3) and dried in vacuo- oven to achieve 0.45 g yellow solid; yield 94%. MS (APCI): calculated for Chemical Formula: C31H27NO4 (M-) = 477; found: 477. 1H NMR (400 MHz, Chloroform-d) δ 10.44 (s, 2H), 8.65 (d, J = 7.8 Hz, 1H), 8.60 (d, J = 8.3 Hz, 1H), 8.25 (d, J = 2.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.76 (dd, J = 8.6, 2.1 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.6 Hz, 1H), 7.32 (d, J = 8.3 Hz, 1H), 6.50 (s, 2H), 4.42 (t, J = 6.9 Hz, 2H), 4.17 (t, J = 6.2 Hz, 2H), 2.54 (s, 6H), 2.28 (s, 2H), 1.40 (s, 9H).

Compound **PLC-45.6**: 2-(3-bromopropyl)-9-(4-(tert-butyl) phenyl)-1H-xantheno[2,1,9-def] isoquinoline-1,3(2H)-dione: A mixture of 1643-002 (0.453g, 0.95 mmol) and 48% aqueous HBr (20 ml) was stirred and heated by heating block at 130oC for 8 h. LCMS shown the SM was completely consumed. The mixture was cooled to RT and standing at RT 16 hours. Yellow solid was filtered, washed with water several times, dried in vacuo oven to gain 0.275

g, yield 96%. Product was used next step without further purification. MS (APCI): calculated for Chemical Formula: C31H26BrNO3(M-) = 540; found: 540. 1H NMR (400 MHz) δ 8.59 (d, J = 7.8 Hz, 1H), 8.53 (d, J = 8.4 Hz, 1H), 8.19 (s, 1H), 7.99 (d, J= 8.0 Hz, 1H), 7.72 (d, J = 8.7 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.5 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 4.25 (s, 2H), 3.48 (d, J = 6.1 Hz, 2H), 3.16 (d, J = 6.8 Hz, 1H), 1.90 (s, 2H), 1.31 (s, 9H).

Compound **PLC-45**: 9-(4-(tert-butyl)phenyl)-2-(3-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18□□4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)propyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: Compound **PLC-45.6** (40.53 mg, 0.075 mmol, 1.15eq) was suspended in DMF anhydrous (2.0 ml), added **PLC-1.3** (38.04 mg, 0.065 mmol, 1 eq), K2CO3 (20.73 mg, 0.15 mmol, 2.3 eq), NaI (4.15 mg, cat. amount). The resulting mixture was stirred at 85oC, under Argon atmosphere, 4 hours. DMF and water were removed by rotavapor at 53oC; the residue was washed with 50 ml hot water then loaded onto 40 g column, eluting with Hex: DCM (9:1 to DCM only (4CV) then DCM/EtAco (99:1), the product from column chromatography purification was washed with hot water to gain 27 mg dark purple solid, yield 38.5 %. MS (APCI): calculated for Chemical Formula: C64H50BCl2F2N3O4 (M-) = 1044; found: 1044. 1H 1H NMR (400 MHz, Chloroform-d) δ 8.70 (d, J = 7.9 Hz, 1H), 8.64 (d, J = 8.4 Hz, 1H), 8.25 (d, J =2.2 Hz, 1H), 8.09 (d, J = 7.3 Hz, 2H), 8.05 (d, J = 8.0 Hz, 1H), 7.76 (dd, J = 8.6, 2.1 Hz, 1H), 7.60 (d,J = 8.4 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.33 –7.29 (m, 3H), 7.22 (d, J = 7.1 Hz, 2H), 6.95 (s, 2H), 6.42 (s, 2H), 4.47 (t, J = 6.8 Hz, 2H), 4.21 (t, J = 6.0 Hz, 2H), 2.62 (t, J = 6.8 Hz, 4H), 2.40 – 2.24 (m, 4H), 2.09 –1.97 (m, 4H), 1.39 (s, 9H).

Synthesis of Compound PLC-46:



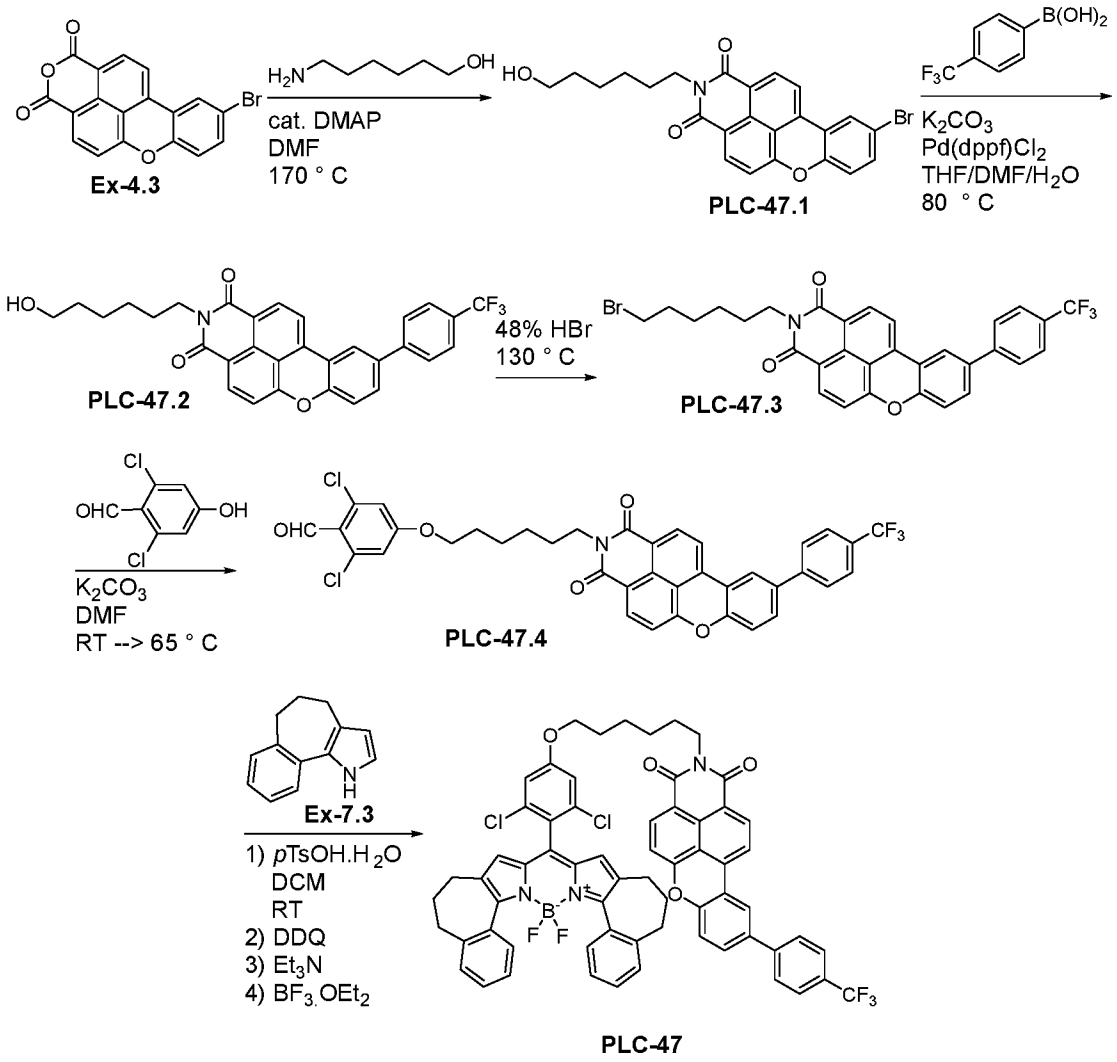
Compound **PLC-46.2**: 9-(3,5-bis(trifluoromethyl)phenyl)-2-(2-hydroxyethyl)-1H-xantheno[2,1,9-def] isoquinoline-1,3(2H)-dione: Step 1: A mixture of **Ex-4.3** (0.735 g, 2.0 mmol, 1.0 eq) and 3-amino-1-ethanol (0.732 g, 12.0 mmol, 6.0 eq) was placed in 20 mL vial with and sealed a septum cap. The resulting mixture was stirred over a period of 45 minutes at 160 °C. After cooling to RT, the reaction was stirred with MeOH (10 mL) at RT for 15 minutes then filtered. The crude product **PLC-46.1** was used next step without further purification. MS (APCI): calculated for Chemical Formula: C20H12BrNO4 (M-) = 410; found: 410. 1H NMR (400 MHz, Chloroform-d) δ 8.62 (d, J = 8.3 Hz, 1H), 8.20 (d, J = 2.3 Hz, 1H), 7.93 (d, J =7.9 Hz, 1H), 7.62 (dd, J = 8.8, 2.3 Hz, 1H), 7.32 (d, J = 8.3 Hz, 1H), 7.28 (s, 1H), 4.55 – 4.40 (m, 2H), 3.99 (s,

2H), 2.49 (s, 1H), 2.22 (t, J = 7.6 Hz, 1H). Step 2: At RT, the crude product of above step was mixed with DMF (5 ml), H2O (0.5 ml), (bis-3,5 trifluoromethyl) benzene boronic acid (1.031 g, 4.0 mmol, 2 eq), K2CO3 (0.553g, 4.0 mmol, 2eq), Pd(dppf)Cl2 · DCM (32.66 mg, 0.04 mmol, 0.02eq) was Vac- Fill Argon cycle 3 times, stirred & heated at 80 °C 45 minutes, the mixture became sticky, added 5 ml DMF, continued stirring at 80 °C further 15 minutes. Cooled the reaction mixture to room temperature, concentrated by rotavapor, added water to the residue mixture, holding at RT 1 hours, the precipitate was filtered, obtained 1.1 g greenish yellow solid which was washed with MeOH to gain 0.85 g desired product**, PLC-46.2**. Yield 80%. MS (APCI): calculated for Chemical Formula: C28H15F6NO4(M-)= 543; found 543. 1H NMR (400 MHz, Chloroform-d) δ 8.71 (d, J = 7.7 Hz, 1H), 8.65 (d, J = 8.2 Hz, 1H), 8.26 (s, 1H), 8.11 (s, 1H), 8.09 (s, 1H), 8.03 (s, 3H), 7.99 (s, 1H), 7.94 (s, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.53 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.4 Hz, 1H), 4.49 (d, J = 5.5 Hz, 2H), 4.01 (d, J = 5.4 Hz, 2H), 3.73 (s, 1H).

Compound **PLC-46**: 9-(3,5-bis(trifluoromethyl)phenyl)-2-(2-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18□□4,19□□4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)ethyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione: Triphenylphosphine (39.34 mg, 0.15 mmol), **PLC-1.3** (76.08 g, 0.13 mmol) and **PLC-46.2** (81.51 g, 0.15 mmol) were dissolved in anhydrous toluene (2 mL); a solution of 0.15 ml 1M DIAD/ toluene + 1 mL anhydrous toluene was added dropwise at room temperature over 15 minutes. The resulting mixture was stirred for 16 h under Argon atmosphere. An additional triphenylphosphine (19.73 mg, 0.075 mmol) and 0.075 ml 1M DIAD/ Toluene + 0.5mL Toluene anhydrous were consecutively added and the mixture was stirred for additional 8 h. Purification: The RX mixture was loaded onto 80 g SiO2 column, eluting with Hex: DCM (7:3) , (1:4), then DCM only, the fractions containing desired compounds were collected, concentrated. The dark purple solid was washed with water then MeOH, dried in vacuo oven to gain 43 mg dark brownish purple solid; yield 42%. MS (APCI): calculated for Chemical Formula: C61H38BCl2F8N3O4 (M-)= 1110, found 1110. 1H NMR (400 MHz, Chloroform-d) δ 8.74 (d, J = 7.9 Hz, 1H), 8.68 (d, J = 8.3 Hz, 1H), 8.26 (d, J = 2.2 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.09 – 8.03 (m, 4H), 7.95 (s,1H), 7.77 (dd, J = 8.6, 2.2 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 8.3 Hz,1H), 7.35 – 7.26 (m, 4H), 7.21 (dd, J = 6.8, 2.0 Hz, 2H), 7.11 (s, 2H), 6.39 (s, 2H), 4.72

(t, J = 6.2 Hz, 2H), 4.43 (t, J = 6.2 Hz, 2H), 2.61 (t, J = 6.8 Hz, 4H), 2.29 (s, 4H), 2.02 (q, J = 6.8 Hz, 4H).

Synthesis of compound PLC-47:



Compound **PLC-47.1**: (9-bromo-2-(6-hydroxyhexyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): Compound **Ex-4.3** (6.534 mmol, 2.401g), 6-aminohexan-1-ol (13.08 mmol, 1533 mg), and DMAP 1.962 mmol, 240 mg) and DMF were combined. The crude product was filtered off and washed with water, then the wet precipitate was used in the next step with no further purification. MS (APCI): calculated for Chemical Formula: C24H20BrNO4 (M+H) = 466; found: 466.

Compound **PLC-47.2**: (2-(6-hydroxyhexyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): Compound **PLC-47.1** (assume 100% yield, 6.534 mmol, 3.047 g), (4-(trifluoromethyl)phenyl)boronic acid (13.068 mmol, 2.482 g), K2CO3 (17.969 mmol, 2483 mg), and Pd(dppf)Cl2 (0.4574 mmol, 335 mg) in THF (120 mL)/DMF (24 mL)/H2O 12 mL) at 80 ° C were combined in a method similar to the above methods. After adding water and filtering, the resulting precipitate was washed with water, then methanol. The product was dried by suction, then dried in vacuo. Gives 1.191 g (34% yield, based on Compound 29.3, 2 steps). MS (APCI): calculated for Chemical Formula: C31H24F3NO4 (M+H) = 532; found: 532.

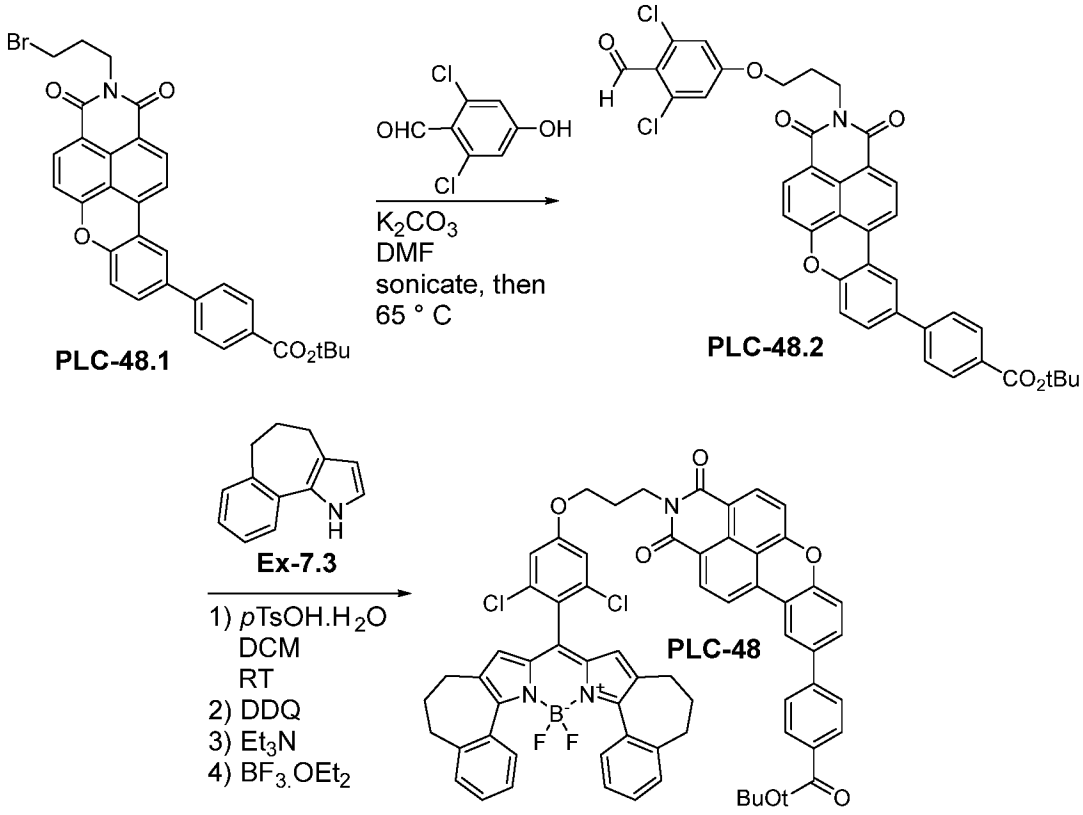
Compound **PLC-47.3**: (2-(6-bromohexyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): A 250 mL 2N RBF was charged with a stir bar and fitted with a gas adapter/finned condenser and a flow control. To the flask was added Compound **PLC-47.2** (2.239 mmol, 1.190 g), followed by 48% HBr/H2O (30 mL). The heat block was set to 130 ° C and the reaction mixture stirred at this temperature for 3 hours. Another portion of 48% HBr/H2O (30 mL) was added and the reaction mixture stirred at 130 °C overnight. The reaction mixture was cooled to room temperature and diluted with water (~100 mL), then the precipitate was filtered off, washing with water, then methanol. The product was loaded onto ~25g of silica gel in a loader. Purify by flash chromatography on silica gel (120g, solid load, equilibrate0% EtOAc/DCM, 0% (2 CV) to 10% EtOAc/DCM (20 CV)). Collect fractions with product and evaporate to dryness in vacuo. Gives material that is about 80% pure. Gives a yellow solid, 1.073 g (80% yield). MS (APCI): calculated for Chemical Formula: C31H23BrF3NO3 (M+H) = 594; found: 594. 1H NMR (400 MHz, TCE) δ 8.63 (d, J = 7.9 Hz, 1H), 8.58 (d, J = 8.3 Hz, 1H), 8.23 (d, J = 2.1 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.84 – 7.73 (m, 5H), 7.49 (d, J = 8.6 Hz, 1H), 7.34 (d, J = 8.3 Hz, 1H), 4.19 – 4.09 (m, 2H), 3.44 (td, J = 6.8, 1.9 Hz, 2H), 1.90 (p, J = 6.9 Hz, 2H), 1.75 (p, J = 7.8 Hz, 2H), 1.57 – 1.38 (m, 4H).

Compound **PLC-47.4**: (2,6-dichloro-4-((6-(1,3-dioxo-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)hexyl)oxy)benzaldehyde): Compound **PLC-47.4** was synthesized from Compound **PLC-47.3** (0.200 mmol, 119 mg), 2,6-dichloro-4-hydroxybenzaldehyde (0.300 mmol, 57 mg), and K2CO3 (0.260 mmol, 36 mg) in dry DMF (10 mL) in a manner similar to Compound 34.4. The crude compound was dissolved in DCM and loaded onto ~5g silica gel in a loader. Purified by flash chromatography on silica gel (80g, solid

load, equilibrate 70% DCM/hexanes, eluting 70% (2 CV) to 100% DCM/hexanes (5 CV) isocratic 100% DCM/hexanes (5 CV) to 0% EtOAc/DCM (0 CV) to isocratic 0% EtOAc/DCM (5 CV) 10% EtOAc/DCM (20 CV)). Fractions containing product were evaporated to dryness in vacuo. Gives a yellow solid, 113 mg, (60% yield). MS (APCI): calculated for Chemical Formula: C38H26Cl2F3NO5 (M+H) = 704; found: 704. 1H NMR (400 MHz, TCE) δ 10.37 (s, 1H), 8.64 (d, J = 7.9 Hz, 1H), 8.59 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 2.2 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.78 (dd, J = 11.2, 1.9 Hz, 5H), 7.50 (d, J = 8.6 Hz, 1H), 7.36 (d, J = 8.3 Hz, 1H), 6.92 (s, 2H), 4.23 – 4.11 (m, 2H), 4.02 (t, J = 6.4 Hz, 2H), 1.89 – 1.70 (m, 4H), 1.59 – 1.45 (m, 4H).

Compound **PLC-47**: (2-(6-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)hexyl)-9-(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): Compound **PLC-47** was synthesized from Compound **PLC-47.4** (0.1164 mmol, 82 mg), 1,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-b]pyrrole (0.2444 mmol, 45 mg (**Ex-7.3**), and pTsOH.H2O (0.0058 mmol, 1.1 mg), then DDQ (0.1989 mmol, 45 mg) and 2X Et3N (0.9312 mmol, 0.130 mL) and BF3.OEt2 (1.397 mmol, 0.172 mL) in dry DCM (20 mL) at room temperature, then 50 °C in a manner similar to the above methods. The crude reaction mixture was diluted with ~25% hexanes, then loaded onto ~15g silica gel in a loader. Purified by flash chromatography on silica gel (80g, solid load, equilibrate 70% DCM/hexanes, eluting 70% (2 CV) to 100% DCM/hexanes (5 CV) isocratic 100% DCM/hexanes (5 CV) 0.5% EtOAc modifier of 100% DCM/hexanes (isocratic). Fractions containing product were evaporated to dryness in vacuo. Gives a deep red solid, 79 mg (62% yield). MS (APCI): calculated for Chemical Formula: C64H47BCl2F5N3O4 (M+H) = 1098; found: 1098. 1H NMR (400 MHz, TCE) δ 8.66 (d, J = 7.9 Hz, 1H), 8.61 (d, J = 8.3 Hz, 1H), 8.26 (d, J = 2.1 Hz, 1H), 8.10 – 8.01 (m, 3H), 7.78 (dd, J = 9.4, 1.7 Hz, 5H), 7.55 – 7.46 (m, 5H), 7.43 – 7.32 (m, 5H), 7.33 – 7.25 (m, 2H), 7.07 (s, 2H), 6.48 (s, 2H), 4.20 (t, J = 7.7 Hz, 2H), 4.06 (t, J = 6.3 Hz, 2H), 2.63 (t, J = 6.9 Hz, 4H), 2.42 – 2.19 (m, 4H), 2.08 – 2.00 (m, 2H), 1.88 (q, J = 7.3 Hz, 2H), 1.85 – 1.73 (m, 2H), 1.67 – 1.49 (m, 4H).

Synthesis of Compound PLC-48

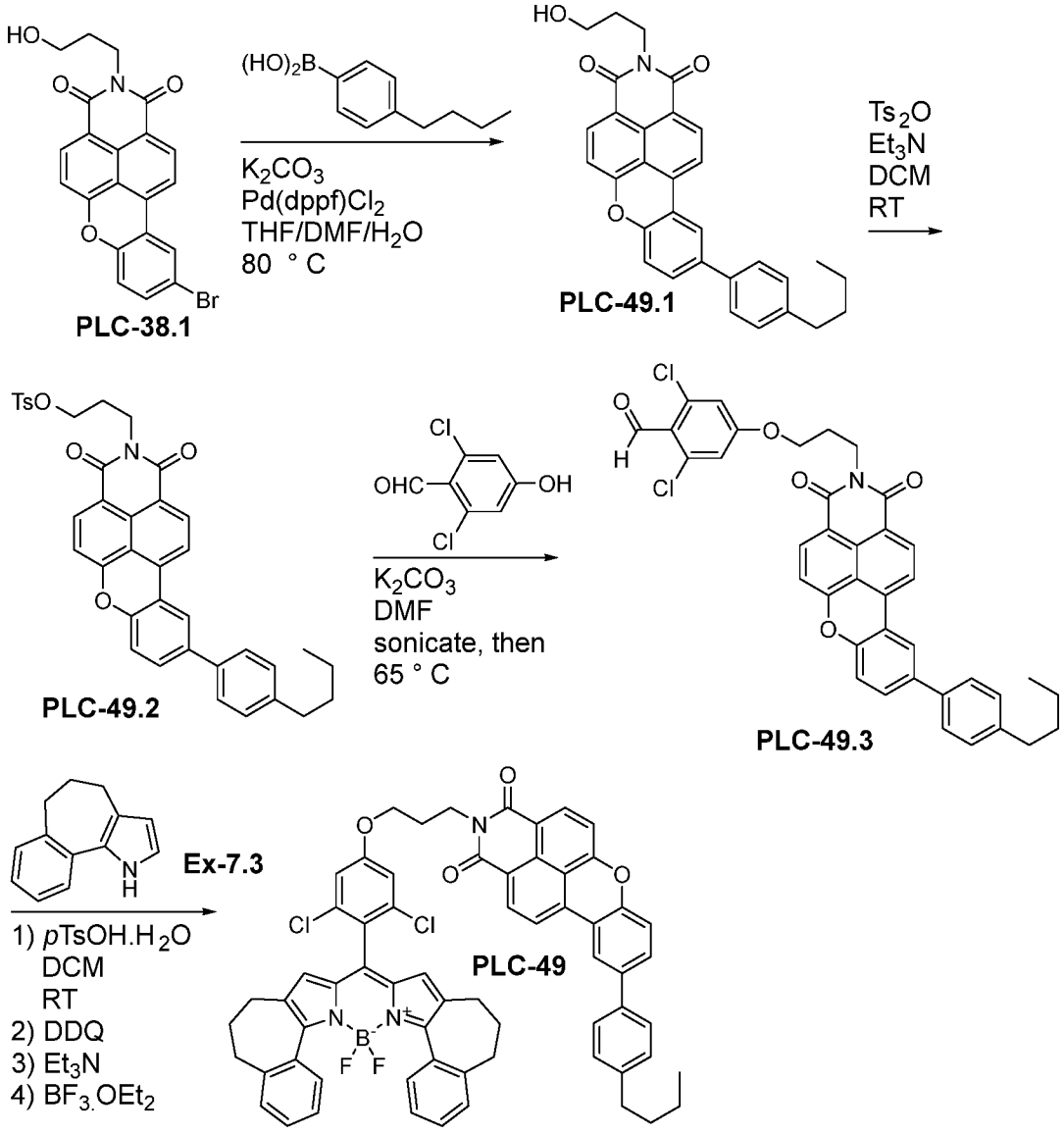


Compound **PLC-48.2** (tert-butyl 4-(2-(3-(3,5-dichloro-4-formylphenoxy)propyl)-1,3-dioxo-2,3-dihydro-1H-xantheno[2,1,9-def]isoquinolin-9-yl)benzoate): Compound **PLC-48.2** was synthesized from Compound **PLC-48.1** (0.1471 mmol), 2,6-dichloro-4-hydroxybenzaldehyde (0.441 mmol, 84 mg), and K2CO3 (0.4120 mmol, 57 mg) in dry DMF (10 mL) in a manner similar to the procedures above. The crude reaction was diluted with crushed ice (~50g). Once it had all melted, the crude product was isolated by centrifugation. The product dissolved in DCM and evaporated to dryness in vacuo. Gives a quantitative yield of a yellow solid. MS (APCI): calculated for Chemical Formula: C39H29Cl2NO7 (M+H) = 694; found: 694. 1H NMR (400 MHz, TCE) δ 10.37 (s, 1H), 8.64 (d, J = 7.9 Hz, 1H), 8.59 (d, J = 8.3 Hz, 1H), 8.28 (d, J = 2.2 Hz, 1H), 8.13 (d, J = 8.1 Hz, 2H), 8.07 (d, J = 8.0 Hz, 1H), 7.81 (dd, J = 8.6, 2.1 Hz, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 8.3 Hz, 1H), 6.85 (s, 2H), 4.39 (t, J = 6.7 Hz, 2H), 4.18 (t, J = 5.9 Hz, 2H), 2.28 (p, J = 5.9 Hz, 2H), 1.64 (s, 9H).

Compound **PLC-48** (tert-butyl 4-(2-(3-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)propyl)-1,3-dioxo-2,3-dihydro-1H-xantheno[2,1,9-def]isoquinolin-9-yl)benzoate): Compound **PLC-48** was

synthesized from Compound **PLC-48.2** (0.1471 mmol, 102 mg), 1,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-b]pyrrole (**Ex-7.3**, 0.3090 mmol, 57 mg, and TFA (1% v/v), then DDQ (0.2501 mmol, 57 mg) and 2X Et3N (1.177 mmol, 0.164 mL) and BF3.OEt2 (1.765 mmol, 0.218 mL) in dry DCM (20 mL) at room temperature, then 50 ° C in a manner similar to the procedures described above. The crude reaction mixture was diluted with hexanes and loaded onto ~20g of silica gel in a loader. Purified by flash chromatography on silica gel (220 g, solid load, equilibrate 10% EtOAc/hexanes, eluting 10% (2 CV) to 30% EtOAc/hexanes (40 CV)). Fractions containing pure product were evaporated to dryness in vacuo. Gives 80 mg (50% yield). MS (APCI): calculated for Chemical Formula: C65H50BCl2F2N3O6 (M+H) = 1088; found: 1088. 1H NMR (400 MHz, TCE) δ 8.69 (d, J = 7.8 Hz, 1H), 8.63 (d, J = 8.3 Hz, 1H), 8.28 (d, J = 2.2 Hz, 1H), 8.16 – 8.10 (m, 2H), 8.09 (d, J = 8.1 Hz, 1H), 8.05 (t, J = 4.7 Hz, 2H), 7.80 (dd, J = 8.6, 2.1 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.51 (d, J = 8.6 Hz, 1H), 7.42 – 7.33 (m, 5H), 7.33 – 7.25 (m, 2H), 7.01 (s, 2H), 6.47 (s, 2H), 4.44 (t, J = 6.9 Hz, 2H), 4.22 (t, J = 6.0 Hz, 2H), 2.63 (t, J = 6.9 Hz, 4H), 2.40 – 2.24 (m, 6H), 2.11 – 2.00 (m, 4H), 1.62 (s, 9H).

Synthesis of Compound PLC-49:



Compound **PLC-49.1** (9-(4-butylphenyl)-2-(3-hydroxypropyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): Compound **PLC-49.1** was synthesized from Compound **PLC-38.1** (1.500 mmol, 636 mg), (4-butylphenyl)boronic acid (3.00 mmol, 534 mg), K2CO3 (4.125 mmol, 570 mg), and Pd(dppf)Cl2 (0.105 mmol, 77 mg) in THF (30 mL)/DMF (6 mL)/water (3 mL) at 80 ° C in a manner similar to the procedures above. The precipitated compound was filtered off, washed with water, and dried in vacuo. Gives a brown-yellow solid, 655 mg (92% yield). MS (APCI): calculated for Chemical Formula: C31H27NO4 (M+H) = 478; found: 478. 1H NMR (400 MHz, TCE) δ 8.66 (d, J = 7.9 Hz, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.26 (d, J = 2.1 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.79 (dd, J = 8.6, 2.1 Hz, 1H), 7.61 (d, J = 7.9 Hz, 2H), 7.48 (d, J = 8.6 Hz, 1H), 7.41 – 7.30 (m, 3H), 4.34 (t, J = 6.1 Hz, 2H), 3.57 (q, J = 6.0 Hz, 2H), 3.24 (t, J = 6.9 Hz, 1H),

2.70 (t, J = 7.7 Hz, 2H), 2.06 – 1.92 (m, 2H), 1.75 – 1.64 (m, 2H), 1.42 (h, J = 7.4 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H).

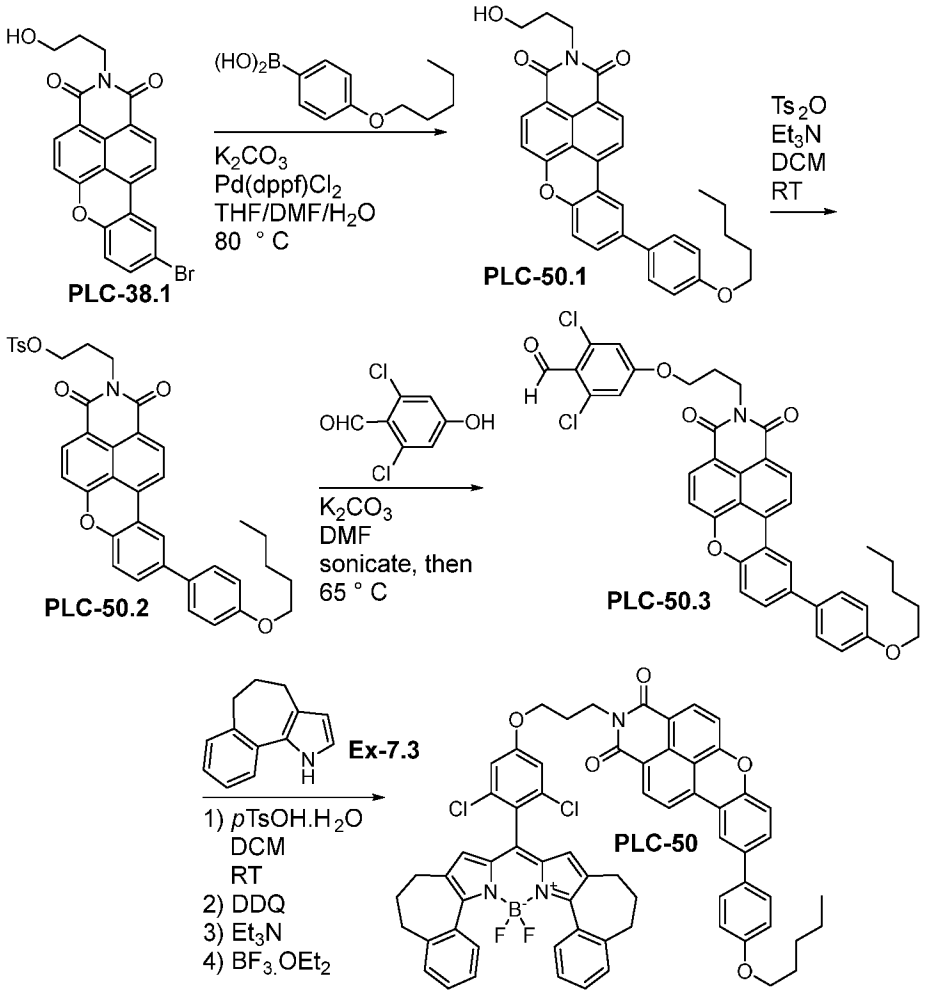
Compound **PLC-49.2** (3-(9-(4-butylphenyl)-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)propyl 4-methylbenzenesulfonate): A 100 mL 2N round bottom flask was placed in an aluminum heat block and charged with a stir bar. The flask was fitted with a finned condenser/gas adapter and flow control valve. The system was flushed with argon. To the flask was added **PLC-49.1** (0.325 mmol, 155 mg), 4-methylbenzenesulfonic anhydride (1.30 mmol, 424 mg), and dry DCE (20 mL). The reaction mixture was stirred under argon at room temperature and Et3N was added (1.463 mmol, 0.20 mL). The reaction mixture was stirred under argon and the heat block was set to 90 ° C and stirred at this temperature for one hour. The reaction was cooled to room temperature and loaded onto ~15 g silica gel in a loader. Purified by flash chromatography on silica gel (80g, solid load, equilibrate 0% EtOAc/DCM, eluting 0% (2 CV) to 10% EtOAc/DCM (10 CV)). Fractions containing product were evaporated to dryness in vacuo. Gives a yellow solid, 157 mg (77% yield). MS (APCI): calculated for Chemical Formula: C38H33NO6S (M+H) = 632; found: 632. 1H NMR (400 MHz, TCE) δ 8.61 (d, J = 7.9 Hz, 1H), 8.56 (d, J = 8.4 Hz, 1H), 8.24 (d, J = 2.2 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.81 – 7.72 (m, 3H), 7.61 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.6 Hz, 1H), 7.40 – 7.27 (m, 5H), 4.19 (dt, J = 11.9, 6.6 Hz, 4H), 2.70 (t, J = 7.8 Hz, 2H), 2.42 (s, 3H), 2.19 – 2.07 (m, 2H), 1.76 – 1.64 (m, 2H), 1.42 (h, J = 7.3 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H).

Compound **PLC-49.3** (4-(3-(9-(4-butylphenyl)-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)propoxy)-2,6-dichlorobenzaldehyde): Compound **PLC-49.3** was synthesized from **PLC-49.2** (0.122 mg, 77 mg),), 2,6-dichloro-4-hydroxybenzaldehyde (0.366 mmol, 70 mg), and K2CO3 (0.341 mmol, 47 mg) in dry DMF (10 mL) in a manner similar to the procedures described above. The crude product was loaded onto ~15g of silica gel in a loader. Purified by flash chromatography on silica gel (80g, solid load, equilibrate 0% EtOAc/DCM, eluting 0% (2 CV) to 10% EtOAc/DCM (10 CV)). Fractions containing product were evaporated to dryness in vacuo. Gives a yellow solid, 60 mg (76% yield). MS (APCI): calculated for Chemical Formula: C38H29Cl2NO5 (M+H) = 650; found: 650. 1H NMR (400 MHz, TCE) δ 10.37 (s, 1H), 8.63 (d, J = 7.9 Hz, 1H), 8.58 (d, J = 8.3 Hz, 1H), 8.26 (d, J = 2.1 Hz, 1H), 8.06 (d, J = 8.1 Hz, 1H), 7.79 (dd, J = 8.6, 2.1 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.48 (d, J = 8.6 Hz, 1H), 7.36 (d, J = 7.2 Hz, 1H), 7.34 (d, J = 7.1 Hz, 2H), 6.85 (s, 2H), 4.39 (t, J = 6.8 Hz, 2H), 4.18 (t, J = 6.0 Hz, 2H), 2.70 (t,

J = 7.8 Hz, 2H), 2.28 (p, J = 6.5 Hz, 2H), 1.73 – 1.62 (m, 2H), 1.42 (h, J = 7.4 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H).

Compound **PLC-49** (9-(4-butylphenyl)-2-(3-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)propyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): Compound **PLC-49** was synthesized from Compound **PLC-49.3** (0.0922 mmol, 60 mg),), 1,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-b]pyrrole (**Ex-7.3**, 0.194 mmol, 36 mg), and TFA (0.2% v/v) at room temperature, then DDQ (0.157 mmol, 36 mg) and 2X Et3N (0.738 mmol, 0..10 mL) and BF3.OEt2 (1.107 mmol, 0.14 mL) in dry DCM (20 mL) at room temperature, then 50 ° C, in a manner similar to Compound 32. The crude reaction mixture was loaded onto ~30g of silica gel in a loader. Purified by flash chromatography on silica gel (120g, solid load, equilibrate 0% EtOAc/hexanes, eluting 0% (2 CV) to 5% EtOAc/DCM (30 CV)). Fractions containing product were evaporated to dryness in vacuo. Gives 42 mg of a deep red solid, 44% yield. MS (APCI): calculated for Chemical Formula: C64H50BCl2F2N3O4 (M+H) = 1044; found: 1044. 1H NMR (400 MHz, TCE) δ 8.67 (d, J = 7.8 Hz, 1H), 8.62 (d, J = 8.3 Hz, 1H), 8.25 (d, J = 2.1 Hz, 1H), 8.12 – 8.01 (m, 3H), 7.78 (dd, J = 8.6, 2.1 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.48 (d, J = 8.6 Hz, 1H), 7.42 – 7.24 (m, 9H), 7.01 (s, 2H), 6.47 (s, 2H), 4.45 (s, 2H), 4.22 (t, J = 6.0 Hz, 6H), 2.70 (t, J = 7.8 Hz, 2H), 2.64 (t, J = 6.8 Hz, 4H), 2.42 – 2.23 (m, 6H), 2.11 – 1.97 (m, 4H), 1.73 – 1.62 (m, 2H), 1.42 (h, J = 7.3 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H).

Synthesis of Compound PLC-50:



Compound **PLC-50.1** (2-(3-hydroxypropyl)-9-(4-(pentyloxy)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): Compound **PLC-50.1** was synthesized from Compound **PLC-38.1** (1.500 mmol, 636 0mg), (4-(pentyloxy)phenyl)boronic acid (3.00 mmol, 624 mg), K2CO3 (4.125 mmol, 570 mg), and Pd(dppf)Cl2 (0.105 mmol, 77 mg) in THF (30 mL)/DMF (6 mL)/water (3 mL) at 80 ° C in a manner similar to the above procedures.. The precipitated compound was filtered off, washed with water, and dried in vacuo. Gives a brown-yellow solid, 730 mg (96% yield). MS (APCI): calculated for Chemical Formula: C32H29NO5 (M+H) = 508; found: 508. 1H NMR (400 MHz, TCE) δ 8.66 (d, J = 7.9 Hz, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 2.1 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.75 (dd, J = 8.6, 2.1 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.47 (d, J = 8.6 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.10 – 6.99 (m, 2H), 4.33 (t, J = 6.1 Hz, 2H), 4.03 (t, J = 6.6 Hz, 2H), 3.62 – 3.51 (m, 2H), 3.25 (t, J = 6.9 Hz, 1H), 2.08 – 1.91 (m, 2H), 1.84 (p, J = 6.7 Hz, 2H), 1.55 – 1.34 (m, 4H), 0.97 (t, J = 7.1 Hz, 3H).

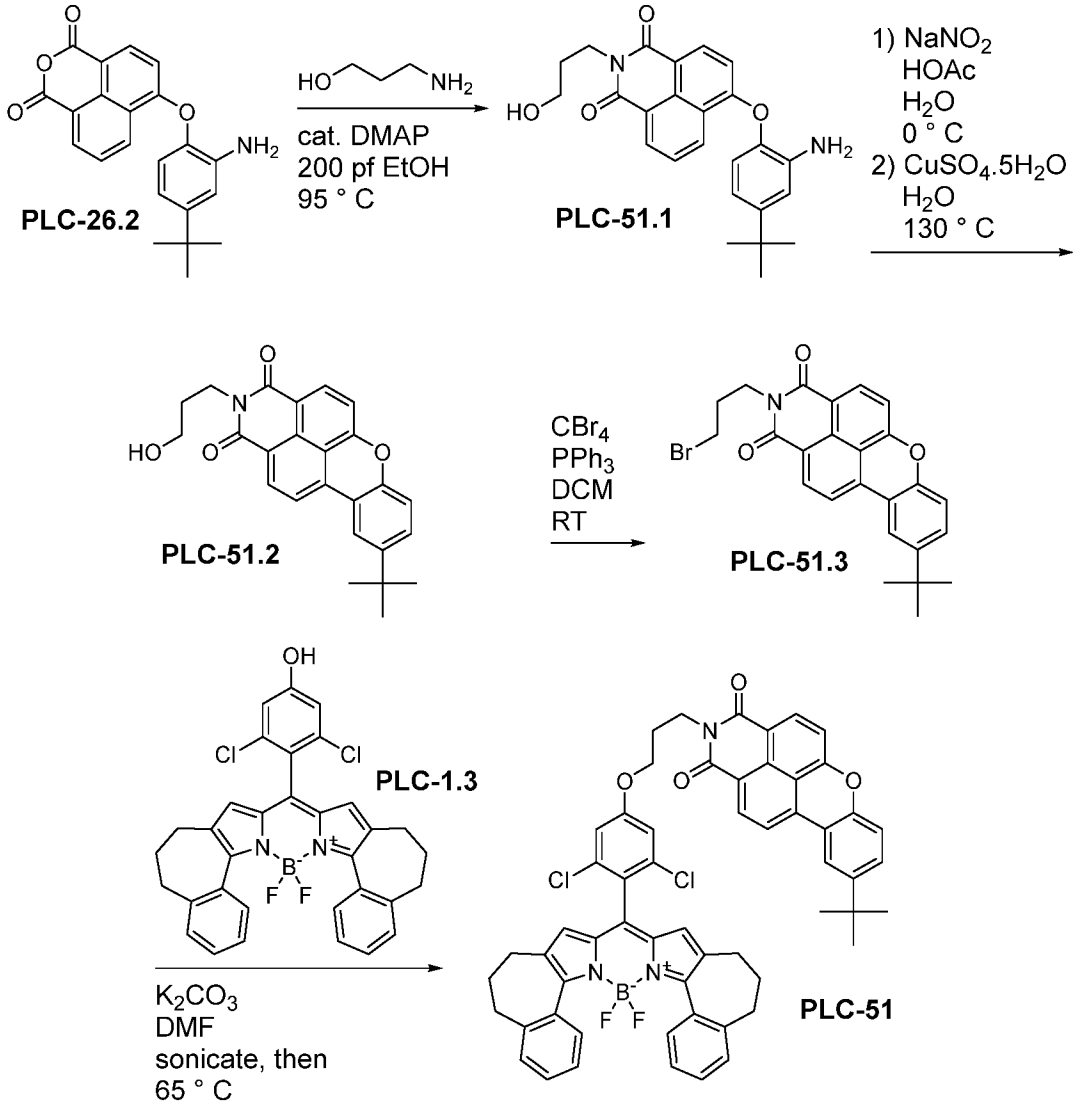
Compound **PLC-50.2** (3-(1,3-dioxo-9-(4-(pentyloxy)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)propyl 4-methylbenzenesulfonate): Compound **PLC-50.2** was synthesized from Compound **PLC-50.1** (1.550 mmol, 787 mg), 4-methylbenzenesulfonic anhydride (6.202 mmol, 2024 mg), and Et3N (6.977 mmol, 0.97 mL) in dry DCE (20 mL) at 90 ° C in a manner similar to Compound 46.2 The crude product was loaded onto ~65g of silica gel in a loader. Purified by flash chromatography on silica gel (120g, solid load, equilibrate 0% EtOAc/DCM, eluting 0% (2 CV) to 10% EtOAc/DCM (10 CV) to isocratic 10%). Fractions containing product were evaporated to dryness in vacuo to give a yellow solid, 528 mg (51% yield). MS (APCI): calculated for Chemical Formula: C39H35NO7S (M+H) = 662; found: 662. 1H NMR (400 MHz, TCE) δ 8.58 (d, J = 7.8 Hz, 1H), 8.53 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 2.2 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.79 – 7.75 (m, 2H), 7.73 (dd, J = 8.8, 2.3 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.43 (d, J = 8.6 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.08 – 7.01 (m, 2H), 4.25 – 4.13 (m, 4H), 4.03 (t, J = 6.6 Hz, 2H), 2.42 (s, 3H), 2.12 (p, J = 6.6 Hz, 2H), 1.90 – 1.77 (m, 2H), 1.55 – 1.34 (m, 4H), 0.97 (t, J = 7.1 Hz, 3H).

Compound **PLC-50.3** (2,6-dichloro-4-(3-(1,3-dioxo-9-(4-(pentyloxy)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)propoxy)benzaldehyde): Compound **PLC-50.3** was synthesized from Compound **PLC-50.2** (0.180 mmol, 119 mg), 2,6-dichloro-4-hydroxybenzaldehyde (0.539 mmol, 103 mg), and K2CO3 (0.503 mmol, 70 mg) in dry DMF (10 mL) in a manner similar to the procedures described above. The crude product was loaded onto ~15g of silica gel in a loader. Purified by flash chromatography on silica gel (80g, solid load, equilibrate 0% EtOAc/DCM, eluting 0% (2 CV) to 15% EtOAc/DCM (10 CV)). Fractions containing product were evaporated to dryness in vacuo. Gives a yellow solid, 103 mg (84% yield). MS (APCI): calculated for Chemical Formula: C39H31Cl2NO6 (M+H) = 680; found: 680. 1H NMR (400 MHz, TCE) δ 10.37 (s, 1H), 8.62 (d, J = 7.9 Hz, 1H), 8.57 (d, J = 8.3 Hz, 1H), 8.20 (d, J = 2.2 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.46 (d, J = 8.6 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.85 (s, 2H), 4.38 (t, J = 6.8 Hz, 2H), 4.18 (t, J = 6.0 Hz, 2H), 4.03 (t, J = 6.6 Hz, 2H), 2.28 (p, J = 6.5 Hz, 2H), 1.84 (p, J = 6.7 Hz, 2H), 1.55 – 1.35 (m, 4H), 0.97 (t, J = 7.1 Hz, 3H).

Compound **PLC-50** (2-(3-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)propyl)-9-

(4-(pentyloxy)phenyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): Compound 48 was synthesized from Compound **PLC-50.3** (0.150 mmol, 102 mg), 1,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-b]pyrrole (**Ex-7.3**, 0.315 mmol, 58 mg), and TFA (0.25% v/v) at room temperature, then DDQ (0.255 mmol, 58 mg) and 2X Et3N (1.199 mmol, 0.17 mL) and BF3.OEt2 (1.798 mmol, 0.22mL) in dry DCM (20 mL) at room temperature, then 50 ° C, in a manner similar to Compound 32. The crude reaction mixture was loaded onto ~30g of silica gel in a loader. Purified by flash chromatography on silica gel (120g, solid load, equilibrate and run 0% EtOAc/DCM isocratic). Fractions containing product were evaporated to dryness in vacuo. Gives a deep red solid, 127 mg (79% yield). MS (APCI): calculated for Chemical Formula: C65H52BCl2F2N3O5 (M+H) = 1074; found: 1074. 1H NMR (400 MHz, TCE) δ 8.67 (d, J = 7.9 Hz, 1H), 8.61 (d, J = 8.3 Hz, 1H), 8.20 (d, J = 2.2 Hz, 1H), 8.11 – 8.00 (m, 3H), 7.74 (dd, J = 8.6, 2.1 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.46 (d, J = 8.6 Hz, 1H), 7.41 – 7.33 (m, 5H), 7.33 – 7.26 (m, 2H), 7.04 (d, J = 8.9 Hz, 2H), 7.02 (s, 2H), 6.47 (s, 2H), 4.44 (t, J = 6.9 Hz, 2H), 4.22 (t, J = 6.0 Hz, 2H), 4.03 (t, J = 6.6 Hz, 2H), 2.64 (t, J = 6.7 Hz, 4H), 2.40 – 2.22 (m, 6H), 2.12 – 1.98 (m, 4H), 1.90 – 1.79 (m, 2H), 1.53 – 1.36 (m, 4H), 1.01 – 0.93 (m, 3H).

Synthesis of Compound PLC-51:



Compound **PLC-51.1** (6-(2-amino-4-(tert-butyl)phenoxy)-2-(3-hydroxypropyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione): A 100 mL 2N round bottom flask was placed in an aluminum heat block and charged with a stir bar. The flask was fitted with a finned condenser/gas adapter and flow control valve. The system was flushed with argon. To the flask was added **PLC-26.2** (2.559 mmol, 925 mg), 3-aminopropan-1-ol (5.119 mmol, 0.391 mL), and DMAP (0.768 mmol, 94 mg), followed by 200 proof ethanol (20 mL). The reaction was stirred under argon and the heat block set for 95 °C. The reaction mixture was stirred at this temperature for 2 hours, then cooled to room temperature. The reaction mixture was quenched with 6H HCl (3 mL) and diluted with water (~100 mL). The resulting precipitate was filtered off, washing with water. The precipitate was dried in vacuo to give a brown-yellow solid, quantitative yield. MS (APCI): calculated for Chemical Formula: C25H26N2O4 (M+H) =

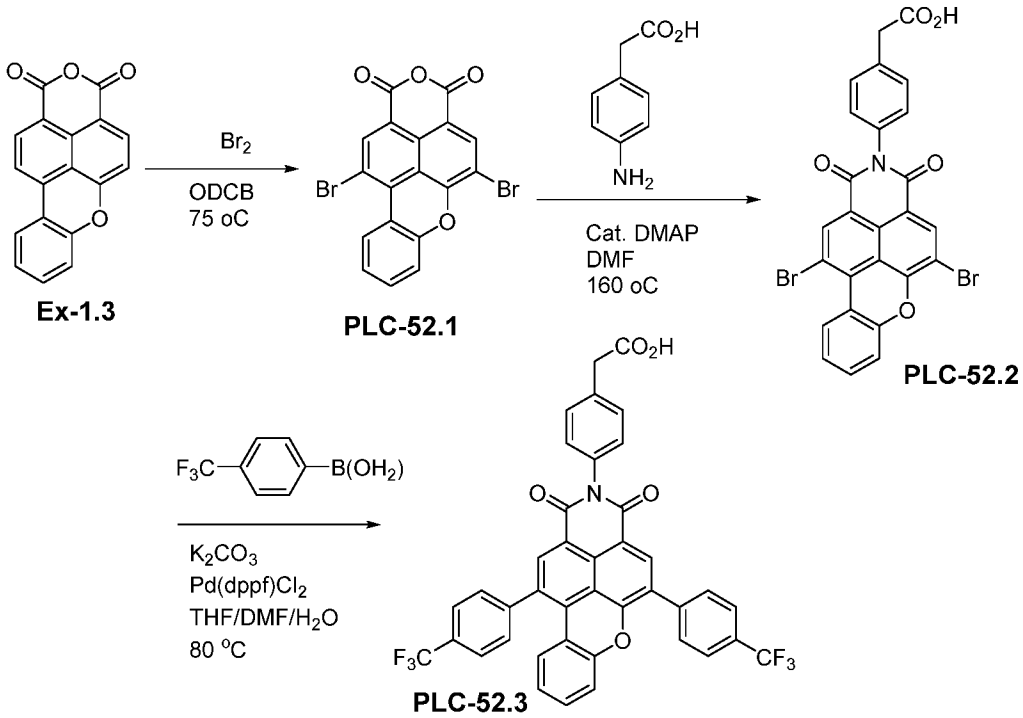
419; found: 419. 1H NMR (400 MHz, TCE) δ 8.80 (dd, J = 8.4, 1.2 Hz, 1H), 8.67 (dd, J = 7.3, 1.2 Hz, 1H), 8.46 (d, J = 8.3 Hz, 1H), 7.84 (dd, J = 8.4, 7.3 Hz, 1H), 7.02 – 6.92 (m, 3H), 6.87 (dd, J = 8.4, 2.2 Hz, 1H), 4.31 (t, J = 6.2 Hz, 2H), 3.56 (q, J = 5.0 Hz, 2H), 1.97 (p, J = 6.0 Hz, 2H), 1.35 (s, 9H).

Compound **PLC-51.2** (9-(tert-butyl)-2-(3-hydroxypropyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): A 40 mL vial was charged with a stir bar. To the vial was added NaNO2 (11.291 mmol, 779 mg) and water (4 mL). The vial was stirred in an ice-water bath at 0 ° C. A separate 40 mL vial was also charged with a stir bar. To this vial was added Compound **PLC-51.1** (1.505 mmol, 630 mg), acetic acid (12 mL), and con. HCl (7.527 mmol, mL). The vial was stirred at room temperature for a few minutes, then placed in a ice-water bath and stirred at 0 ° C for one minute. The aqueous solution of NaNO2 was added to this vial over a period of 10 minutes with stirring at 0 ° C. The diazo solution was stirred at 0 ° C for one hour. In the meantime, a 250 mL 2N round bottom flask was fitted with a finned condenser, and addition funnel, and a stir bar. To the flask was added CuSO4.5H2O (10.237 mmol, 2.556 g) and water (35 mL). The solution was stirred at room temperature. About 15 minutes before the one hour diazotization was expired, the copper sulfate solution was heated to 130 ° C (heat block temperature). The diazo solution was transferred to the addition funnel and added to the reaction mixture with high-speed stirring over a period of about 15 minutes. The reaction mixture was stirred for an additional minute, then placed in a room temperature water bath. Once the reaction had cooled to room temperature, the product was isolated by filtration. The crude product was a mixture of the desired alcohol and the acetate ester. The crude product was dispersed in methanol and treated with excess K2CO3 at 60 ° C to cleave the ester. The reaction was diluted with water, the product filtered off, washing with water. The crude product was dissolved in DCM and evaporated onto silica gel in vacuo. Purified by flash chromatography on silica gel (120g, solid load, equilibrate 0% EtOAc/DCM, eluting 0% (2 CV) → 75% EtOAc/DCM (20 CV). Fractions containing product were evaporated to dryness in vacuo. Gives a yellow solid, 379 mg (37% yield). MS (APCI): calculated for Chemical Formula: C25H23NO4 (M+H) = 419; found: 419. 1H NMR (400 MHz, TCE) δ 8.65 (d, J = 7.8 Hz, 1H), 8.60 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 2.3 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.63 (dd, J = 8.7, 2.2 Hz, 1H), 7.37 (d, J = 8.7 Hz, 1H), 7.34 (d, J = 8.3 Hz, 1H), 4.33 (t, J = 6.1 Hz, 2H), 3.57 (q, J = 6.1 Hz, 2H), 3.26 (t, J = 6.9 Hz, 1H), 1.98 (p, J = 5.9 Hz, 2H), 1.44 (s, 9H).

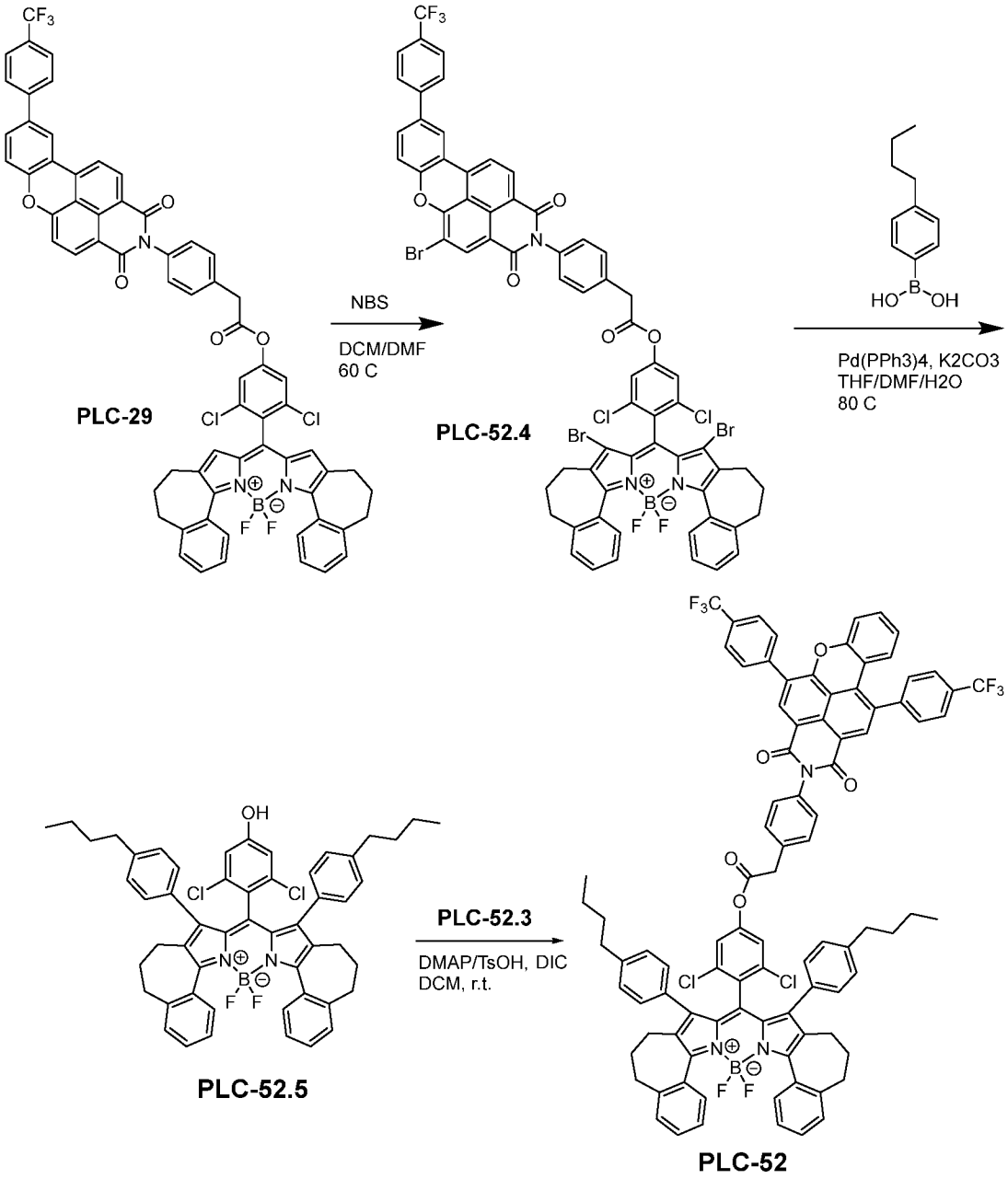
Compound **PLC-51.3** (2-(3-bromopropyl)-9-(tert-butyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione):): A 100 mL 2N round bottom flask was placed in an aluminum heat block and charged with a stir bar. The flask was fitted with a finned condenser/gas adapter and flow control valve. The system was flushed with argon. To the flask was added **PLC-51.2** (0.483 mmol, 194 mg and carbon tetrabromide (0.725 mmol, 240 mg), followed by dry DCE (20 mL). The reaction mixture was stirred under argon at room temperature and triphenylphosphine (0.725 mmol, 190 mg) was added. The reaction mixture was stirred at room temperature 30 minutes. The reaction mixture was loaded onto ~15g of silica gel in a loader. Purified by flash chromatography on silica gel (120g, solid load, equilibrate 0% EtOAc/DCM, eluting 0% (2 CV) to 10% EtOAc/DCM (20 CV)). Fractions containing product were evaporated to dryness in vacuo. Gives a yellow solid, 149 mg (66% yield). MS (APCI): calculated for Chemical Formula: C25H22BrNO3 (M+H) = 464; found: 464.

Compound **PLC-51** (9-(tert-butyl)-2-(3-(3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenoxy)propyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): Compound **PLC-51** was synthesized from Compound **PLC-51.3** (0.391 mmol, 148 mg), 3,5-dichloro-4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)phenol (**PLC-1.3**, 0.446 mmol, 261 mg), and K2CO3 (0.382 mmol, 53 mg) in dry DMF (10 mL) in a manner similar to the procedures described above. The crude reaction mixture was diluted with water and the product filtered off. The precipitate was dissolved in DCM and evaporated to dryness in vacuo. The product was dissolved in DCM, loaded onto ~20g silica gel in a loader, and purified by flash chromatography on silica gel (120g, solid load, equilibrate 0% EtOAc/DCM, eluting 0% (2 CV) to 5% EtOAc/DCM (50 CV)). Fractions containing product were evaporated to dryness in vacuo. Gives a deep red solid, 153 mg (50% yield). MS (APCI): calculated for Chemical Formula: C58H46BCl2F2N3O4 (M+H) = 968; found: 968. 1H NMR (400 MHz, TCE) δ 8.67 (d, J = 7.9 Hz, 1H), 8.60 (d, J = 8.3 Hz, 1H), 8.10 – 7.98 (m, 4H), 7.62 (dd, J = 8.8, 2.2 Hz, 1H), 7.40 – 7.25 (m, 8H), 7.02 (s, 2H), 6.48 (s, 2H), 4.43 (t, J = 7.0 Hz, 2H), 4.21 (t, J = 6.0 Hz, 2H), 2.70 – 2.59 (m, 4H), 2.33 (t, J = 6.7 Hz, 6H), 2.12 – 1.98 (m, 4H), 1.44 (s, 9H).

Synthesis of compound PLC-52:


Br2
ODCB
75 oC
Ex-1.3
PLC-52.1
CO2H
NH2
Cat. DMAP
DMF
160 oC
PLC-52.2
F3C
B(OH2)
K2CO3
Pd(dppf)Cl2
THF/DMF/H2O
80 °C
PLC-52.3

5



Compound **PLC-52.1** (5,11-dibromo-1H,3H-isochromeno[6,5,4-mna]xanthene-1,3-dione): A 2L 2N round bottom flask was charged with a stir bar and fitted with a long finned condenser. To the flask was added 1H,3H-isochromeno[6,5,4-mna]xanthene-1,3-dione (**Ex-1.3**, synthesized according to literature: RSC Adv., 2014, 4, 53072-53078) (34.688 mmol, 10.00 g), followed by ortho-dichlorobenzene (1000 mL). The reaction mixture was stirred at room temperature and Br2 (416.26 mmol, 21.3 mL) was added. The second neck was stoppered and the reaction mixture was heated with an aluminum heat block at 75 ° C open to air over the

weekend. The reaction mixture was cooled to room temperature and a solid was filtered off. The filtrate was diluted with hexanes (~20% of volume) and a second precipitate was filtered off. Both of these precipitates were dried in vacuo at 100 ° C. Orangish solids, 10.866 g total (69.9% yield). Both had similar LCMS and NMR. MS (APCI): calculated for Chemical Formula: C18H6Br2O4 (M+H) = 445; found: 445. 1H NMR (400 MHz, TCE) δ 9.47 (dd, J = 8.4, 1.5 Hz, 1H), 8.76 (d, J = 14.2 Hz, 2H), 7.72 – 7.63 (m, 1H), 7.56 (dd, J = 8.3, 1.4 Hz, 1H), 7.46 (ddd, J = 8.5, 6.7, 1.9 Hz, 1H).

Compound **PLC-52.2** (2-(4-(5,11-dibromo-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetic acid): Compound **PLC-52.2** was synthesized from **PLC-52.1** (7.000 mmol, 3.136 g), 2-(4-aminophenyl)acetic acid (14.00 mmol, 2.117 g), and DMAP (2.100 mmol, 257 mg) in anhydrous DMF (65 mL) at 160 ° C in a manner similar to the procedures described above. The crude reaction mixture was cooled to 0 °C and quenched with 6N HCl (~5 mL) and diluted with water (up to ~350 mL). The precipitate was filtered off, washing with water. The product was dried by suction and used without further purification in the next reactions. Assume 100% yield. MS (APCI): calculated for Chemical Formula: C26H13Br2NO5 (M+H) = 578; found: 578.

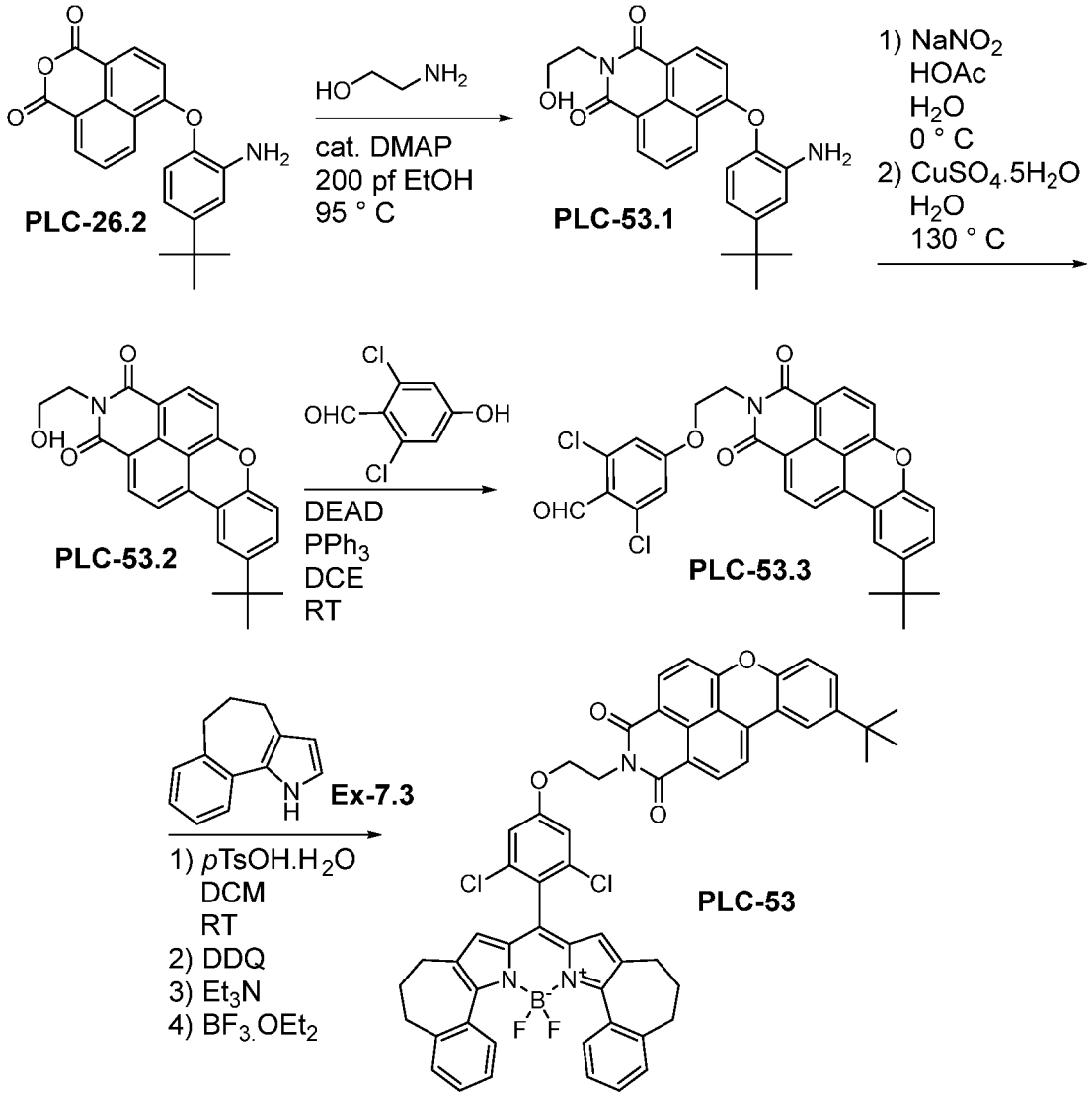
Compound **PLC-52.3** (2-(4-(1,3-dioxo-5,11-bis(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetic acid): Compound **PLC-52.3** was synthesized from Compound **PLC-52.2** (3.500 mmol, 2.034 g), (4-(trifluoromethyl)phenyl)boronic acid (14.00 mmol, 2.659 g), K2CO3 (19.25 mmol, 2.661 g), and Pd(dppf)Cl2 (0.0245 mmol, 179 mg) in THF (/60 mL), DMF (12 mL), and water (6 mL) with heating at 80 ° C under argon atmosphere overnight. The crude reaction mixture was evaporated to dryness in vacuo, taken up in DCM, and evaporated in vacuo onto ~35 g of flash silica gel. Purified by flash chromatography on silica gel (220g, equilibrate 0% EtOAc/DCM, eluting 0% (10 CV) to 15.3% EtOAc/DCM (15.3 CV) to 40% EtOAc/DCM (10 CV) to isocratic 40% EtOAc/DCM). EtOAc contains 0.1% v/v TFA. Fractions containing product were evaporated to dryness in vacuo. Gives a brown-yellow solid, 2.000 g (80.3% from Compound 80.1 (1655-11)). MS (APCI): calculated for Chemical Formula: C40H21F6NO5 (M+H) = 710; found: 710. 1H NMR (400 MHz, DMSO) δ 12.44 (s, 1H), 8.47 (s, 1H), 8.23 (s, 1H), 8.02 (d, J = 8.1 Hz, 2H), 7.97 – 7.88 (m, 4H), 7.75 (d, J = 8.0 Hz, 2H), 7.49 – 7.37 (m, 3H), 7.31 (d, J = 8.2 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.02 – 6.91 (m, 2H), 3.68 (s, 2H).

Compound **PLC-52.4**: To a solution of compound **PLC-29**(113 mg, 0.1 mmol) in 8 mL anhydrous DCM and 3 mL DMF was added NBS (106 mg, 0.6 mmol). The mixture was heated at 60 C overnight. The resulted mixture was diluted with 100 mL DCM, washed with water (2 x 50 mL), loaded on silica gel and purified by flash chromatography using eluents of DCM/EA (0% to 10% EA). The main peak was collected. After removal of solvent and triturated with methanol, a red-brown solid was obtained after filtration and drying in air (80 mg, in 58% yield). LCMS (APCI-): Calcd for C66H38BBr3Cl2F5N3O5: 1364.98 (M-); Found: 1365.

Compound **PLC-52.5**: A mixture of Compound **PLC-52.4** (54 mg, 0.039 mmol), 4-n-butylphenylbonoric acid (42 mg, 0.236 mmol), Pd(PPh3)4 (14 mg, 0.012 mmol) and potassium carbonate (32 mg, 0.236 mmol) in THF/DMF/water (10mL/2mL/1mL) was degassed and heated at 80 C for 6 hours. The resulted mixture was diluted with 100 mL DCM, dry loaded on silica gel and purified by flash chromatography using eluents of hexanes/DCM (0% to 50% DCM). The first main peak was collected, and removal of solvent gave the desired product as red solid (10 mg, in 30% yield). LCMS (APCI-): calcd for C53H49BCl2F2N2O: 848.33 (M-); Found: 848. 1H NMR (400 MHz, TCE) δ 8.02 (bs, 2H), 7.36 – 7.14 (m, 6H), 6.73 (m, 8H), , 4.42 (s, 1H),2.61 (bs, 4H), 2.39 – 2.31 (m, 4H), 1.86 (s, 8H), 1.37 (p, J = 7.6 Hz, 4H), 1.30 – 1.15 (m, 6H), 0.85 (t, J = 7.3 Hz, 6H).

Compound **PLC-52**: A mixture of Compound **PLC-52.5** (10 mg, 0.012 mmol), (2-(4-(1,3-dioxo-5,11-bis(4-(trifluoromethyl)phenyl)-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)phenyl)acetic acid) (16 mg, 0.022 mmol), DMAP/TsOH (5 mg, 0.017 mmol), DIC (0.05 mL, 0.31 mmol) in 5 mL anhydrous DCM was stirred at room temperature overnight. The resulted mixture was loaded on silica gel and purified by flash chromatography using eluents of hexanes/DCM (0% to 100% DCM). The main desired peak was collected, after removal of solvents and trituration with MeOH, a dark brown solid was obtained (10 mg, in 54% yield). LCMS (APCI-): Calcd for C93H68BCl2F8N3O5: 1539.45 (M-): Found: 1539. 1H NMR (400 MHz, TCE) δ 8.64 (s, 1H), 8.40 (s, 1H), 8.03 (s, 2H), 7.83 (d, J = 8.2 Hz, 2H), 7.81 – 7.74 (m, 4H), 7.59 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.39 – 7.17 (m, 11H), 7.02 (d, J = 8.0 Hz, 1H), 6.95 – 6.50 (m, 10H), 3.78 (s, 2H), 2.62 (s, 4H), 2.41 – 2.30 (m, 4H), 1.87 (s, 8H), 1.41 (p, J = 7.4 Hz, 4H), 1.32 – 1.21 (m, 4H), 0.87 (t, J = 7.3 Hz, 6H).

Synthesis of Compound **PLC-53**



Compound **PLC-53.1** (9-(6-(2-amino-4-(tert-butyl)phenoxy)-2-(2-hydroxyethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione): Compound **PLC-53.1** was synthesized from **PLC-26.2** (8.827 mmol, 3.190 g), ethanolamine (17.65 mmol, 1.066 mL), and DMAP (2.648 mmol, 324 mg), followed by 200 proof ethanol (70 mL) in a manner similar to the procedures described above. The crude precipitate was filtered off, dissolved in acetone, and evaporated to dryness in vacuo. Gives a brown-yellow solid, 2.777 g (78% yield). MS (APCI): calculated for Chemical Formula: C24H24N2O4 (M+H) = 405; found: 405. 1H NMR (400 MHz, TCE) δ 8.80 (dd, J = 8.4, 1.2 Hz, 1H), 8.67 (dd, J = 7.3, 1.2 Hz, 1H), 8.46 (d, J = 8.3 Hz, 1H), 7.84 (dd, J = 8.4, 7.3 Hz, 1H), 7.02 – 6.92 (m, 3H), 6.87 (dd, J = 8.4, 2.3 Hz, 1H), 4.42 (t, J = 5.2 Hz, 2H), 3.95 (t, J = 5.2 Hz, 2H), 3.74 (s, 2H), 2.39 (s, 1H), 1.35 (s, 9H).

Compound **PLC-53.2** (9-(tert-butyl)-2-(2-hydroxyethyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): Compound **PLC-53.2** was synthesized from Compound **PLC-53.1** (6.863 mmol, 2.776 g), $NaNO_2$ (51.475 mmol, 3.552 g), conc. HCl (34.317 mmol, 2.83 mL), and $CuSO_4 \cdot 5H_2O$ (46.67 mmol, 11.653 g) in a manner similar to the procedures described above. The crude product was ~10% acetate ester. It was cleaved with K_2CO_3 in the same manner as described above. The crude cleavage mixture was dissolved in acetone and evaporated onto ~20g of silica gel and placed in a loader. Purified by flash chromatography on silica gel (120g, solid load, equilibrate 0% EtOAc/DCM, eluting (2 CV) to 85% EtOAc/DCM (20 CV)). Fractions containing product were evaporated to dryness in vacuo. Gives a yellow solid, 732 mg (27% yield). MS (APCI): calculated for Chemical Formula: $C_{24}H_{21}NO_4$ (M+H) = 388; found: 388.

Compound **PLC-53.3** (4-(2-(9-(tert-butyl)-1,3-dioxo-1H-xantheno[2,1,9-def]isoquinolin-2(3H)-yl)ethoxy)-2,6-dichlorobenzaldehyde): Compound **PLC-53.2** (0.200 mmol, 78 mg) and 2,6-dichloro-4-hydroxybenzaldehyde (0.260 mmol, 50 mg) were added to a 40 mL screw-cap vial, followed by dry DCE (10 mL) and a stir bar. The reaction mixture was stirred at room temperature and DEAD (0.300 mmol, 0.137 mL) and PPh_3 (0.300 mmol, 79 mg) were added. The reaction mixture was stirred at room temperature for 60 minutes. Additional DEAD 0.100 mmol, 0.046 mL) and PPh_3 (0.100 mmol, 26 mg) were added and stirring continued at room temperature overnight. The crude reaction mixture was loaded onto ~20g of silica gel in a loader. Purified by flash chromatography on silica gel (80g, solid load, equilibrate 0% EtOAc/DCM, eluting 0% (2 CV) to 10% EtOAc/DCM (15 CV)). MS (APCI): calculated for Chemical Formula: $C_{31}H_{23}Cl_2NO_5$ (M+H) = 560; found: 560. 1H NMR (400 MHz, TCE) δ 10.36 (s, 1H), 8.66 (d, J = 7.9 Hz, 1H), 8.60 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 2.3 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.63 (dd, J = 8.7, 2.2 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 6.99 (s, 2H), 6.95 (d, J = 14.5 Hz, 1H), 4.64 (t, J = 6.2 Hz, 2H), 4.39 (t, J = 6.2 Hz, 2H), 1.44 (s, 9H).

Compound **PLC-53** (9-(tert-butyl)-2-(2-(4-(19,19-difluoro-6,7,11,12,13,19-hexahydro-5H-18l4,19l4-benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[1,2-c]benzo[3',4']cyclohepta[1',2':4,5]pyrrolo[2,1-f][1,3,2]diazaborinin-9-yl)-3,5-dimethylphenoxy)ethyl)-1H-xantheno[2,1,9-def]isoquinoline-1,3(2H)-dione): Compound **PLC-53** was synthesized from Compound 53.3 (0.186 mmol, 104 mg), 1,4,5,6-

tetrahydrobenzo[6,7]cyclohepta[1,2-b]pyrrole (**Ex-7.3**, 0.371 mmol, 68 mg), and pTsOH.H2O (0.0186 mmol, 3.5 mg), then DDQ (0.241 mmol, 55 mg) and 2X Et3N (1.485 mmol, 0.210 mL) and BF3.OEt2 (2.227 mmol, 0.280 mL) in dry DCM (20 mL) at room temperature, then 50 ° C, in a manner similar to Compound 32. The crude reaction mixture was diluted with hexanes, then loaded onto ~20g of silica gel in a loader. Purified by flash chromatography on silica gel (80g, solid load, equilibrate 0% EtOAc/hexanes, eluting 0% (2 CV) to 75% EtOAc/hexanes (30 CV)). Fractions containing product were evaporated to dryness in vacuo. The crude product was triturated and dried in vacuo. Gives a deep red solid, 138 mg (78% yield). MS (APCI): calculated for Chemical Formula: C59H50BF2N3O4 (M+H) = 954; found: 954. 1H NMR (400 MHz, TCE) δ 8.70 (d, J = 7.9 Hz, 1H), 8.64 (d, J = 8.4 Hz, 1H), 8.10 – 7.99 (m, 4H), 7.63 (dd, J = 8.7, 2.2 Hz, 1H), 7.42 – 7.32 (m, 6H), 7.32 – 7.24 (m, 2H), 7.14 (s, 2H), 6.43 (s, 2H), 4.70 (t, J = 6.2 Hz, 2H), 4.42 (t, J = 6.3 Hz, 2H), 2.62 (t, J = 6.6 Hz, 4H), 2.30 (s, 4H), 2.11 – 1.96 (m, 4H), 1.44 (s, 9H).

Example 10 – Fabrication of Filter Layer

A glass substrate was prepared in substantially the following manner. A 1.1 mm thick glass substrate measuring 1-inch X 1-inch was cut to size. The glass substrate was then washed with detergent and deionized (DI) water, rinsed with fresh DI water, and sonicated for about 1 hour. The glass was then soaked in isopropanol (IPA) and sonicated for about 1 hour. The glass substrate was then soaked in acetone and sonicated for about 1 hour. The glass was then removed from the acetone bath and dried with nitrogen gas at room temperature.

A 20 wt% solution of Poly(methylmethacrylate) (PMMA) (average M.W. 120,000 by GPC from MilliporeSigma, Burlington, MA, USA) copolymer in cyclopentanone (99.9% pure) was prepared. The prepared copolymer was stirred overnight at 40 °C. [PMMA] CAS: 9011-14-7; [Cyclopentanone] CAS: 120-92-3

The 20% PMMA solution prepared above (4g) was added to 3 mg of the photoluminescent complex made as described above in a sealed container and mixed for about 30 minutes. The PMMA/lumiphore solution was then spin coated onto a prepared glass substrate at 1000 RPM for 20 s and then 500 RPM for 5 s. The resulting wet coating had a thickness of about 10 μm. The samples were covered with aluminum foil before spin coating to protect them from exposure to light. Three samples each were prepared in this manner for

each for Emission/FWHM and quantum yield. The spin coated samples were baked in a vacuum oven at 80 °C for 3 hours to evaporate the remaining solvent.

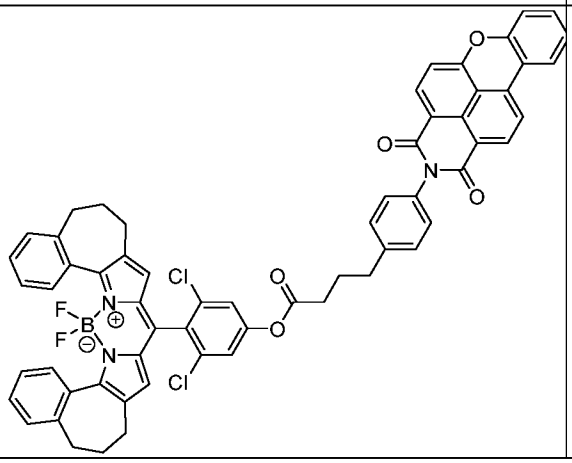
The 1-inch X 1-inch sample was inserted into a Shimadzu, UV-3600 UV-VIS- NIR spectrophotometer (Shimadzu Instruments, Inc., Columbia, MD, USA). All device operations were performed inside a nitrogen-filled glove-box. The resulting absorption/emission spectrum for PLC-1 is shown in **FIG.1**, the resulting absorption/emission spectrum for PLC-2 is shown in **FIG. 2**, and the resulting absorption/emission spectrum for PLC-3 is shown in **FIG. 3**.

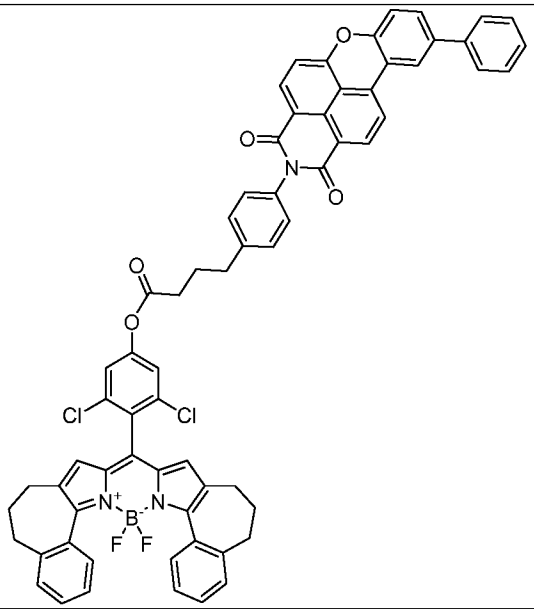
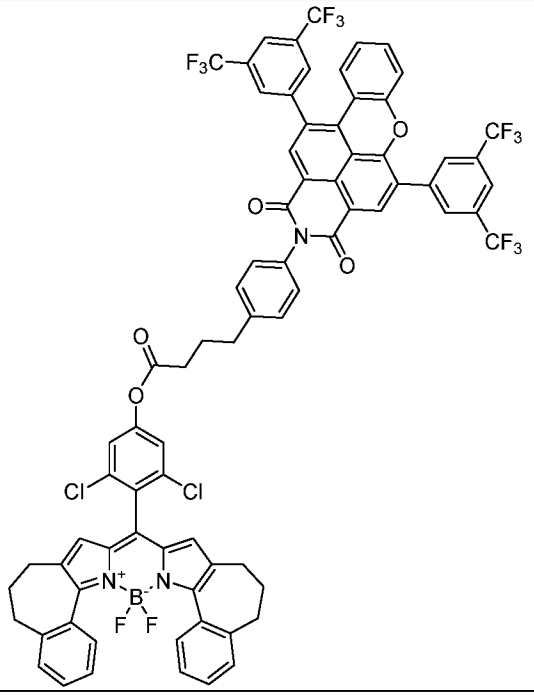
The fluorescence spectrum of a 1-inch X 1-inch film sample prepared as described above was determined using a Fluorolog spectrofluorometer (Horiba Scientific, Edison, NJ, USA) with the excitation wavelength set at the respective maximum absorbance wavelength. The maximum emission and FWHM are shown in Table 1.

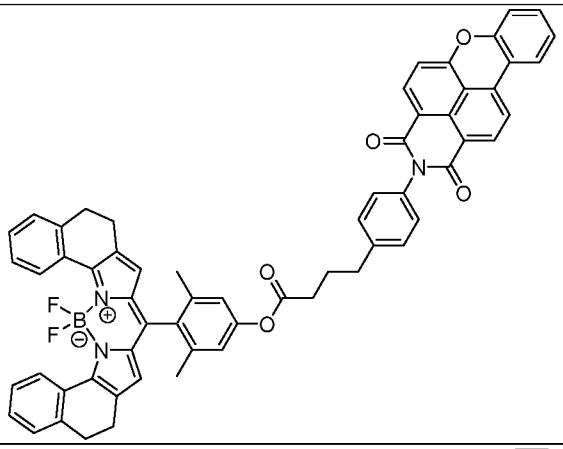
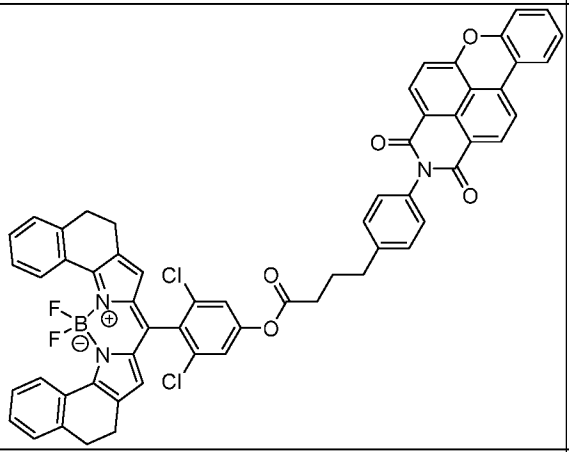
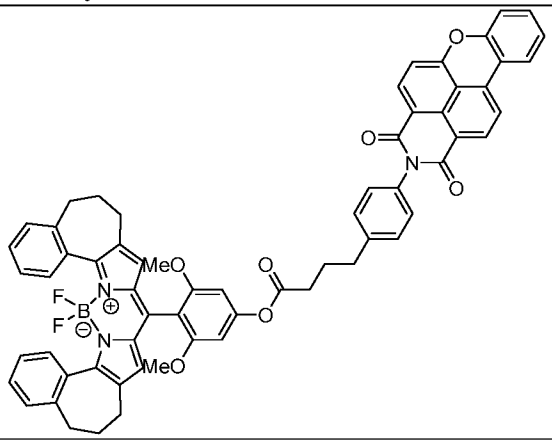
The quantum yield of a 1-inch X 1-inch sample prepared as described above were determined using a Quantarus-QY spectrophotometer (Hamamatsu Inc., Campbell CA, USA) was excited at the respective maximum absorbance wavelength. The results are reported in Table 1.

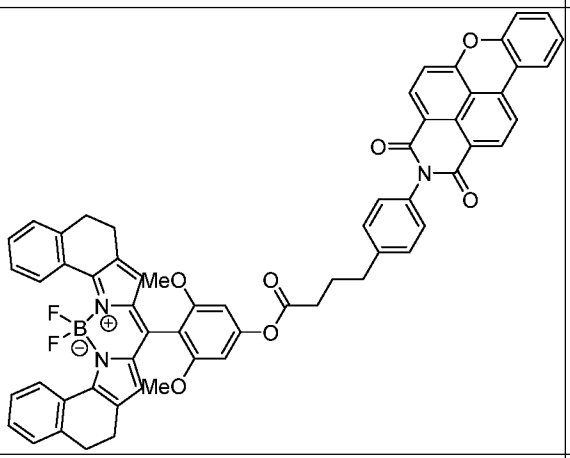
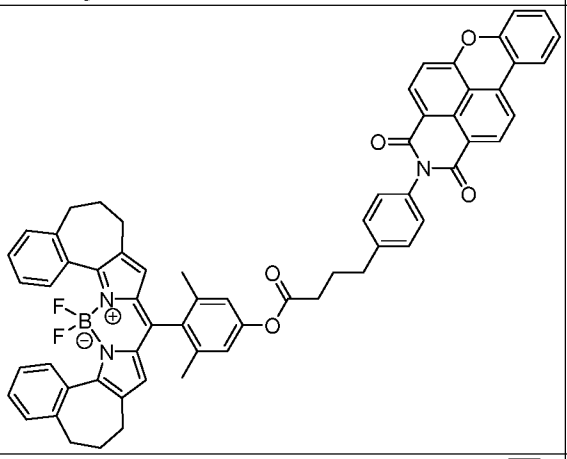
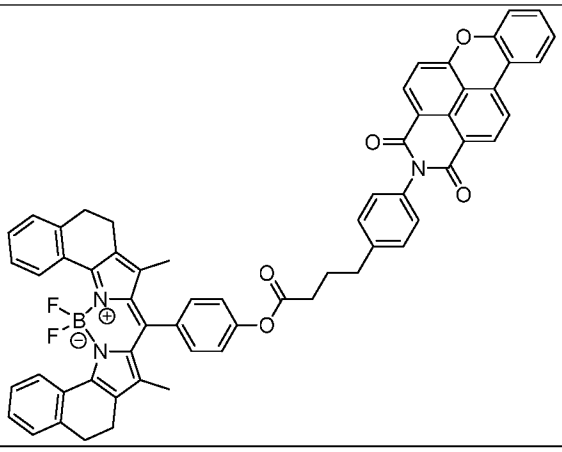
The results of the film characterization (absorbance peak wavelength, FWHM, and quantum yield) are shown in Table 1 below.

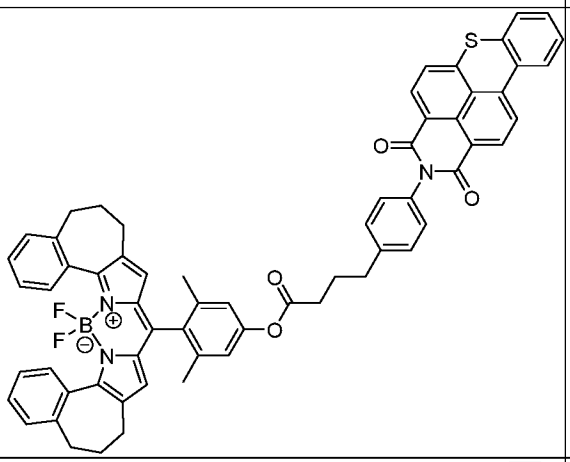
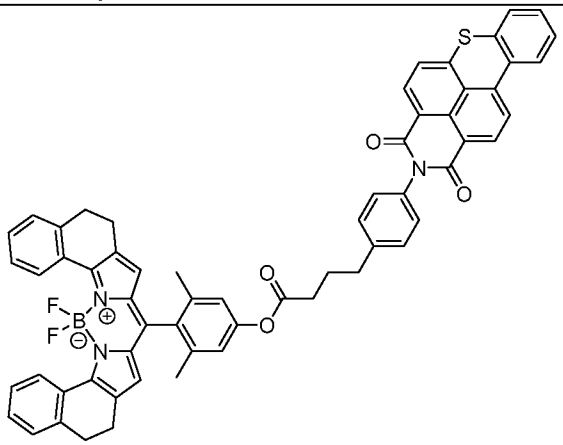
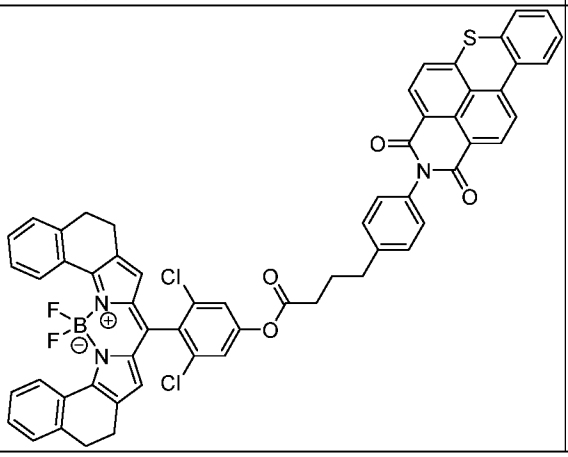
TABLE 1

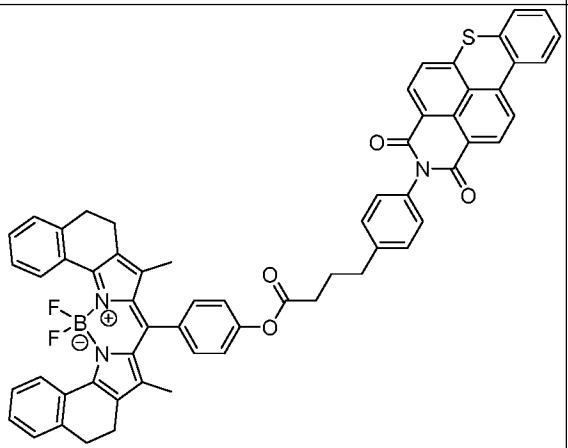
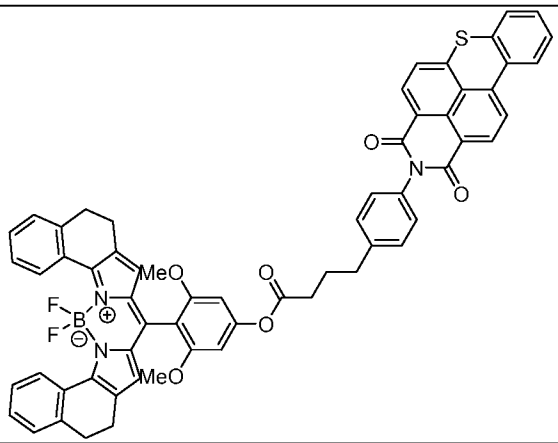
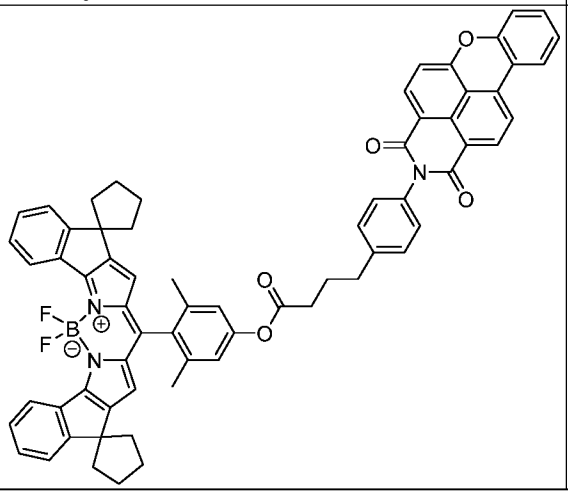
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-1		594	614	35	0.904

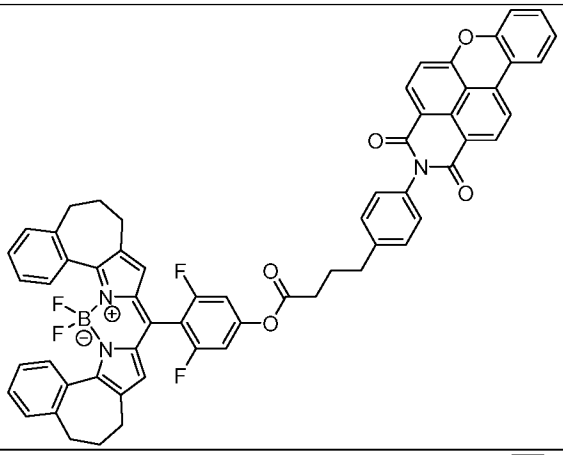
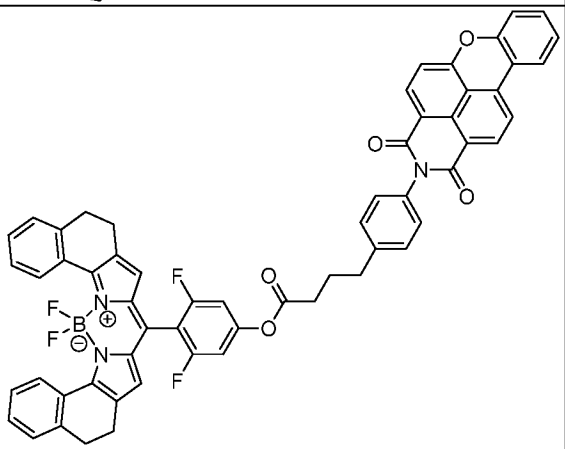
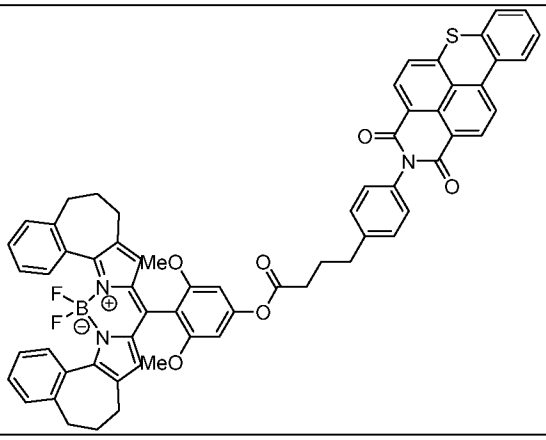
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-2		592	611	35	0.969
PLC-3		593	615	34	0.937

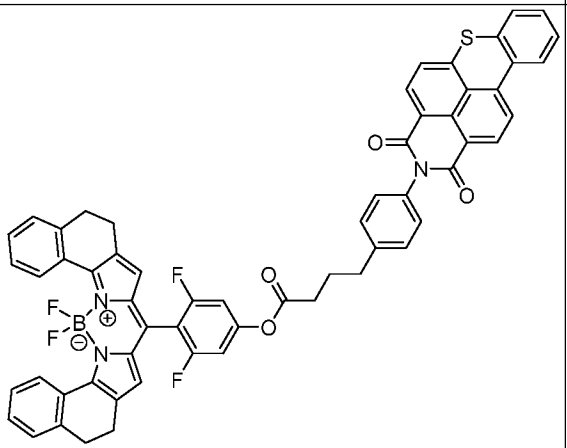
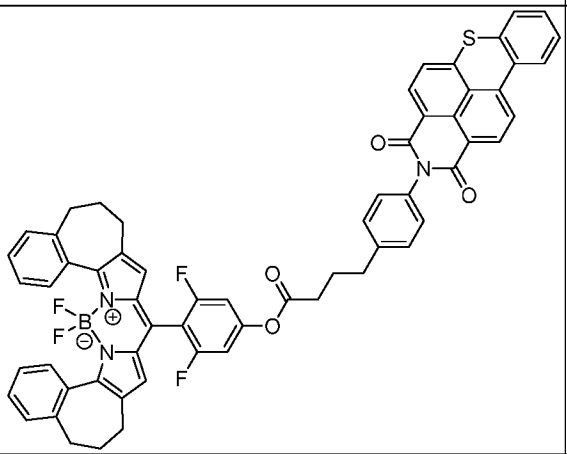
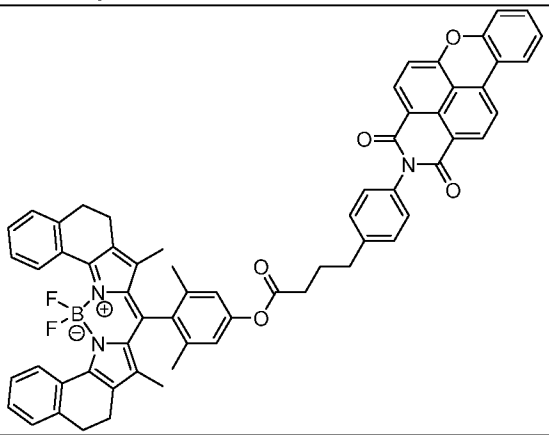
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-4		631	644	28	0.807
PLC-5		644	658	30	0.767
PLC-6		584	602	35	0.888

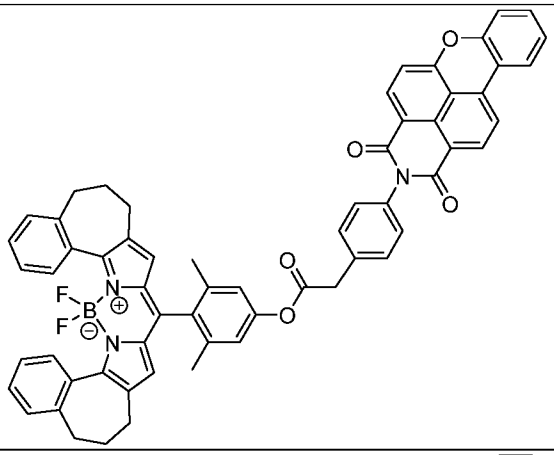
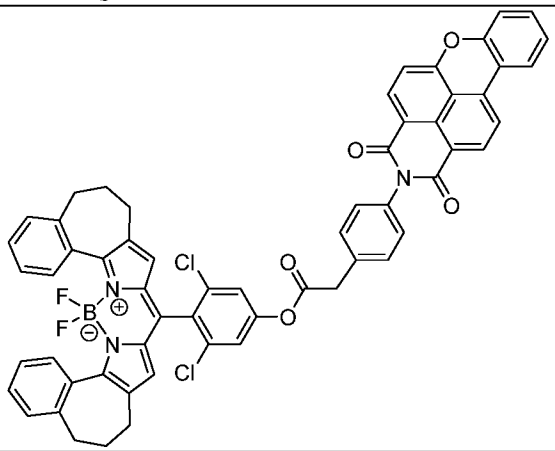
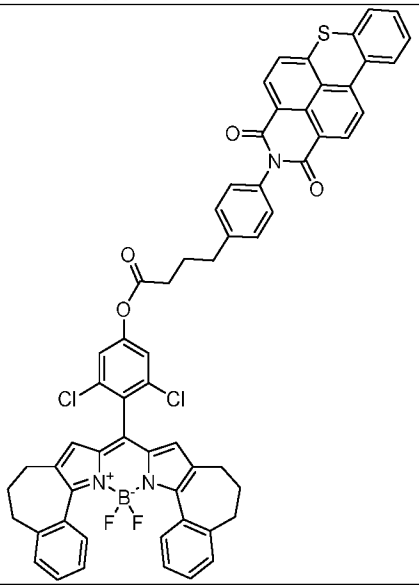
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-7		633	648	32	0.784
PLC-8		581	599	34	0.951
PLC-9		615	628	29	0.809

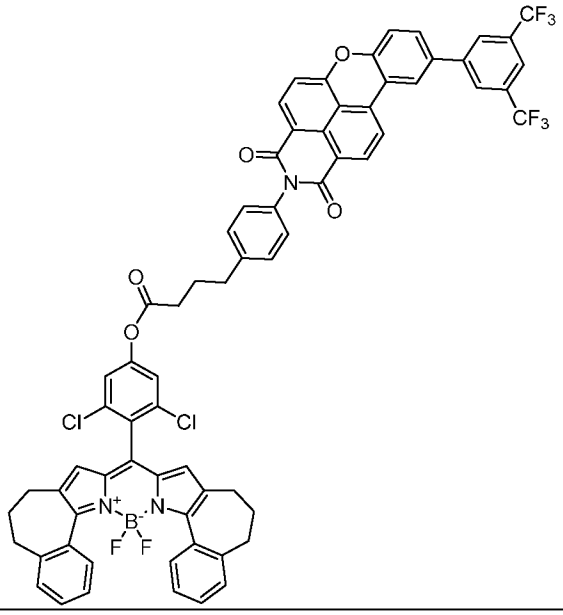
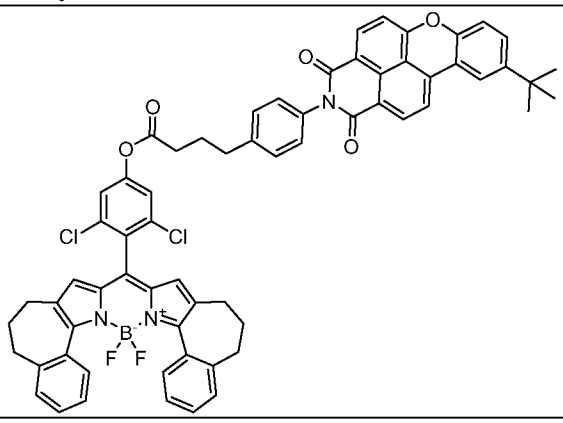
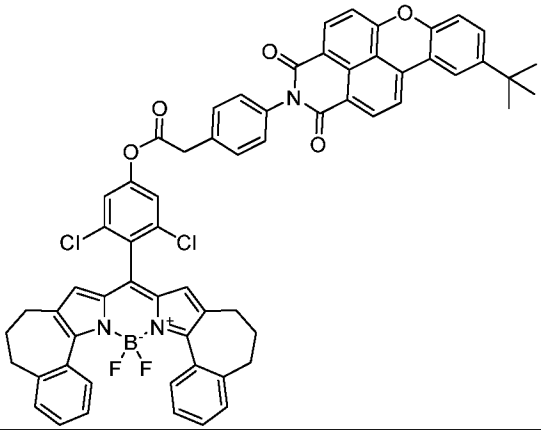
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-10		580	597	34	0.958
PLC-11		631	642	29	0.837
PLC-12		644	656	30	0.751

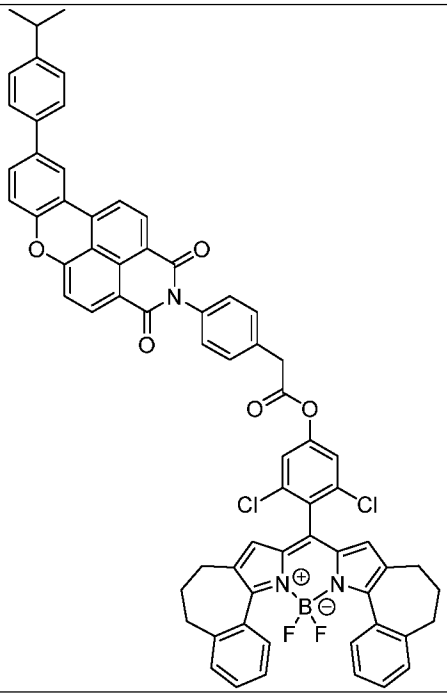
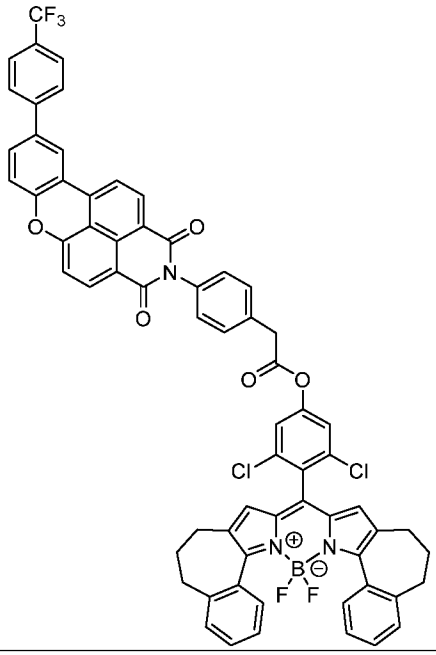
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-13		614	626	28	0.794
PLC-14		633	648	31	0.758
PLC-15		635	643	24	0.862

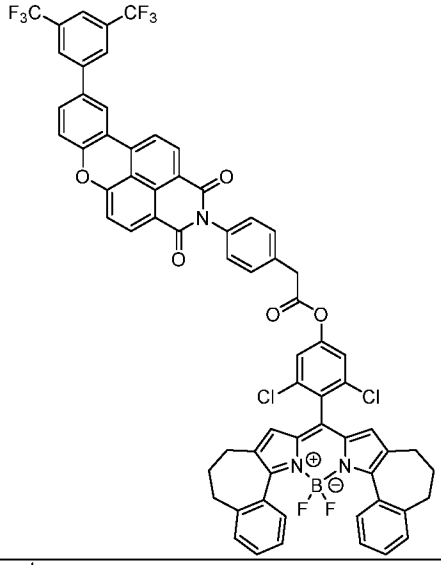
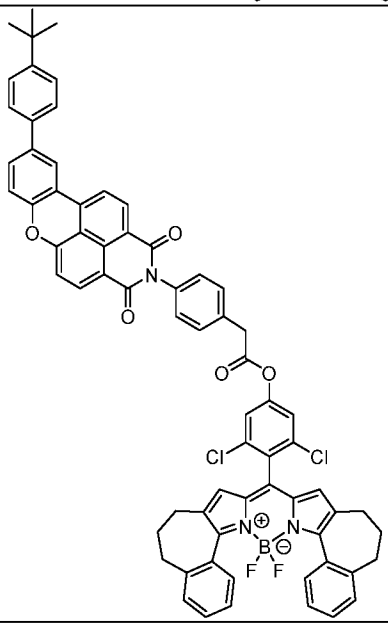
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-16		593	612	36	0.85
PLC-17		644	658	30	0.701
PLC-18		585	602	34	0.873

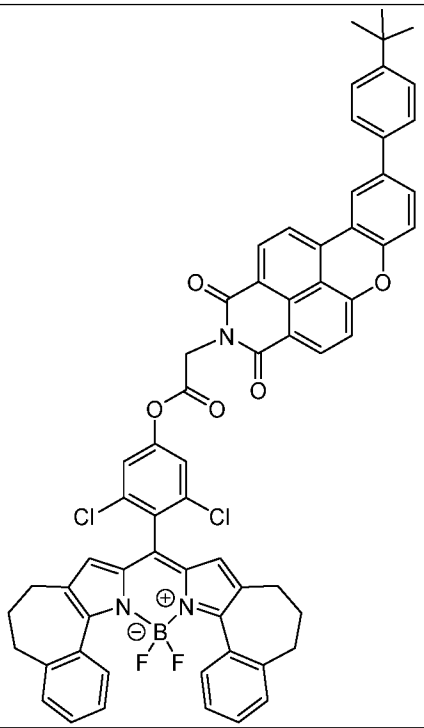
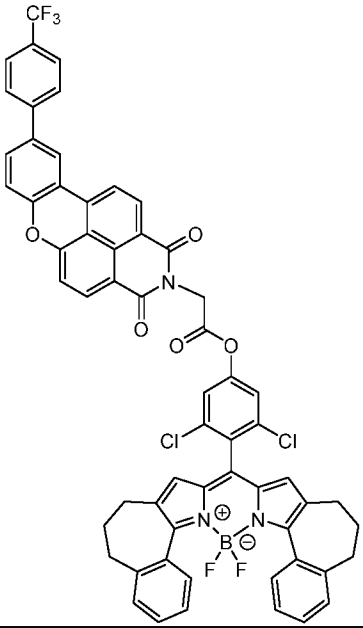
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-19		644	658	30	0.735
PLC-20		593	612	35	0.820
PLC-21		616	626	25	0.861

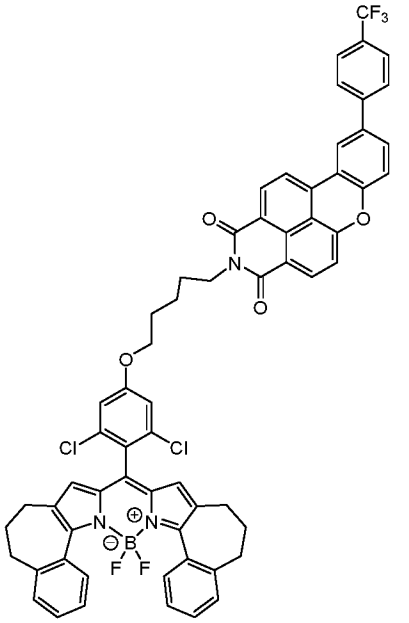
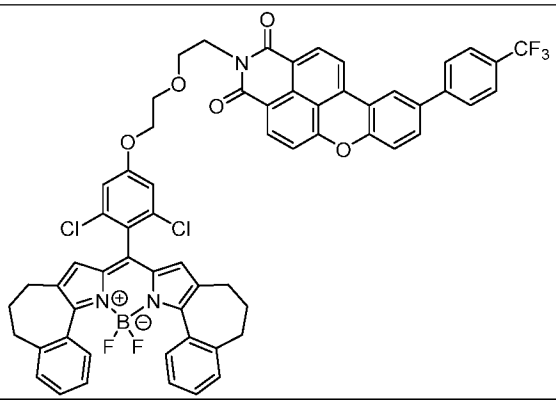
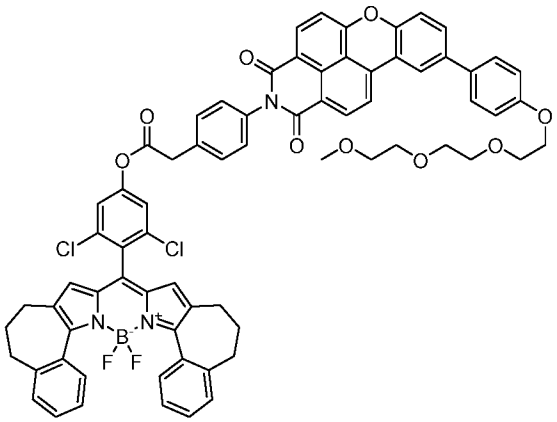
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-22		582	600	37	0.917
PLC-23		592	610	34	0.912
PLC-24		593	615	34	0.924

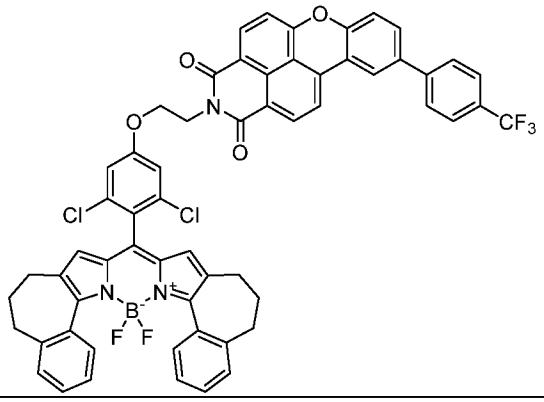
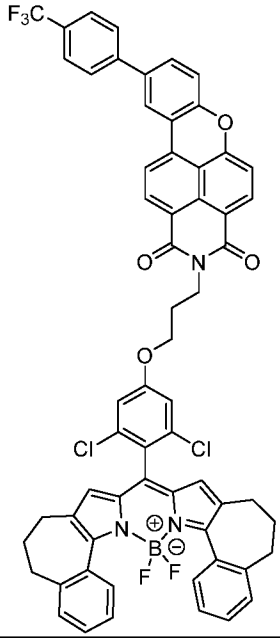
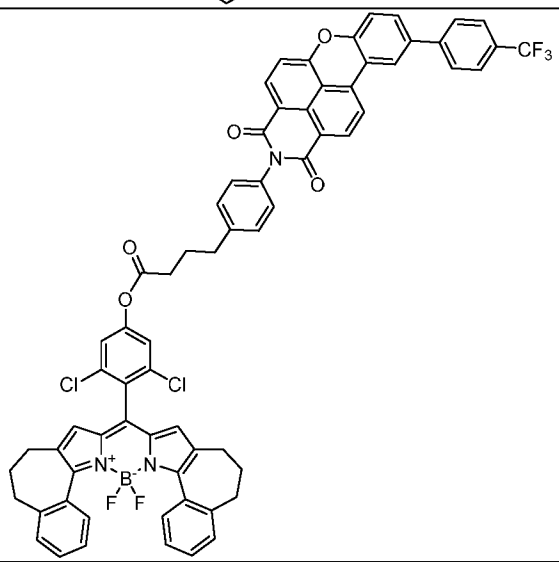
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-25		593	614	34	0.912
PLC-26		593	610	33	0.887
PLC-27		593	611	34	0.894

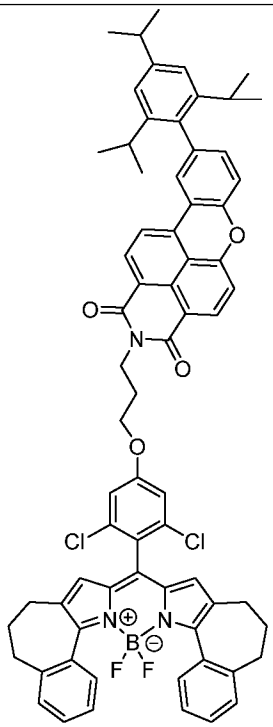
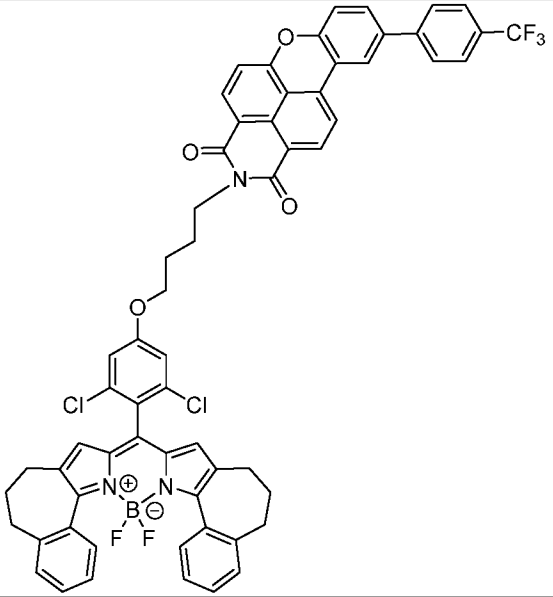
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-28		593	611	33	0.897
PLC-29		592	608	32	0.889

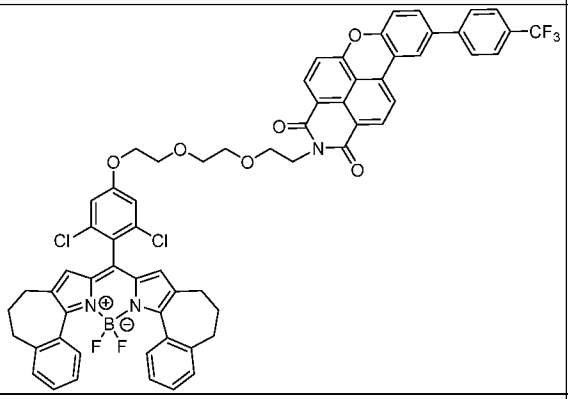
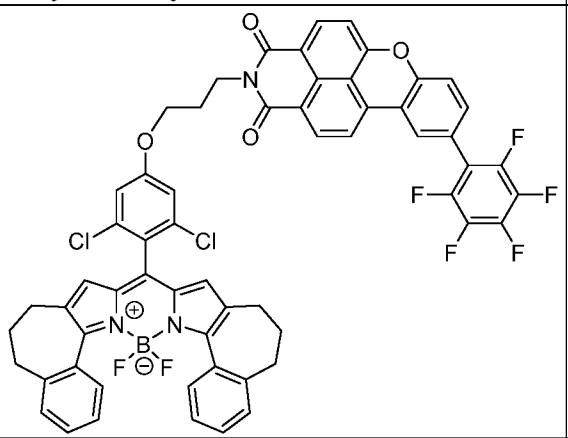
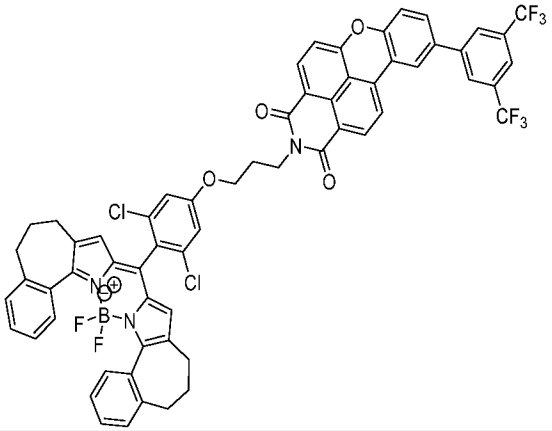
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-30		593	611	34	0.907
PLC-31		593	612	35	0.895

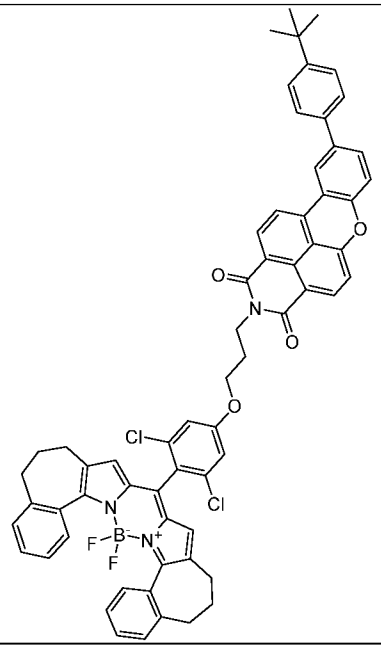
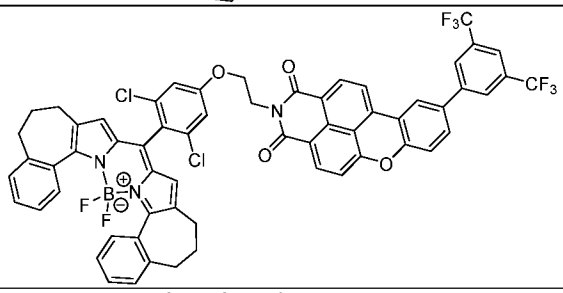
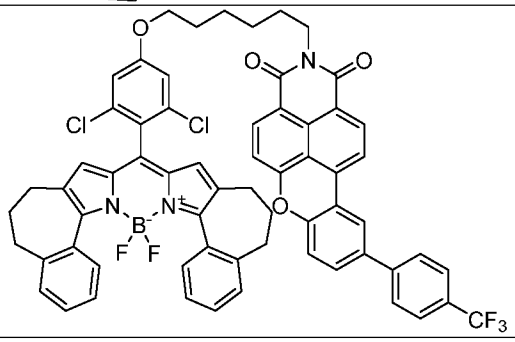
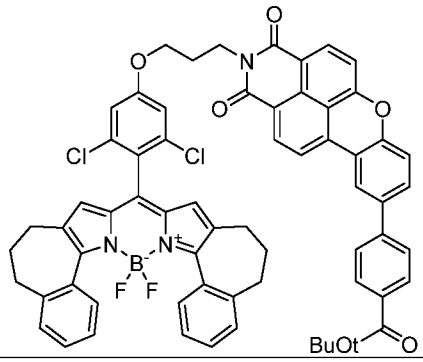
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-32		593	612	34	0.859
PLC-33		593	612	34	0.909

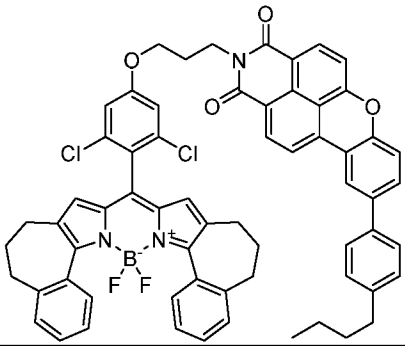
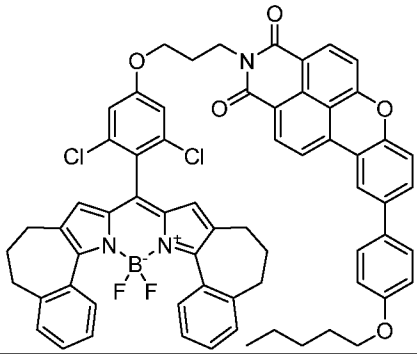
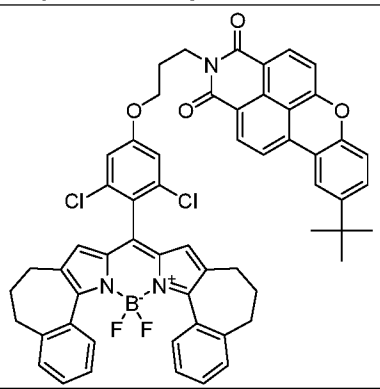
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-34		591	609	33	0.892
PLC-35		591	608	33	0.915
PLC-36		593	612	34	0.909

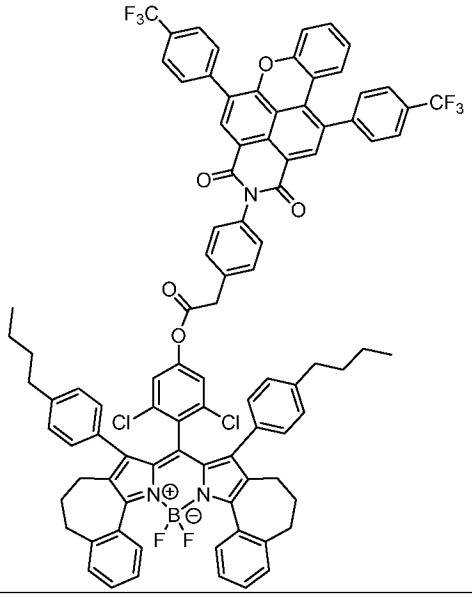
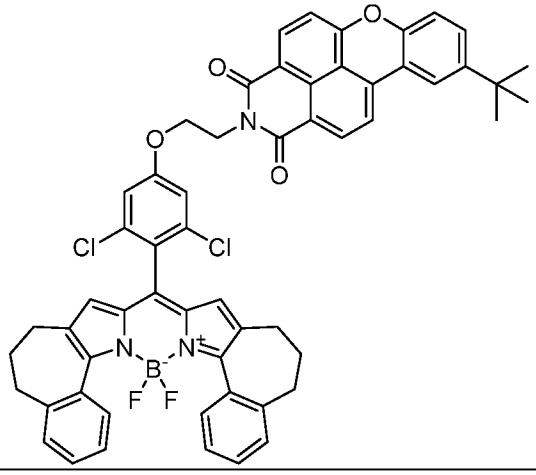
Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-37		592	608	33	0.890
PLC-38		591	607	33	0.867
PLC-39		593	610	33	0.903

Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-40		591	608	34	0.85
PLC-41		591	605	32	0.898

Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-42		592	610	34	0.869
PLC-43		591	608	34	0.869
PLC-44		592	609	34	0.911

Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-45		592	612	33	0.877
PLC-46		592	608	33	0.842
PLC-47		592	610	33	0.885
PLC-48		592	612	33	0.864

Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-49		591	607	36	0.867
PLC-50		591	607	35	0.859
PLC-51		591	606	34	0.857

Cmpd No.	Structure	Abs in PMMA (nm)	Emission in PMMA (nm)	FWHM (nm)	QY (@450 nm)
PLC-52		592	611	35	0.86
PLC-53		592	608	33	0.84

CLAIMS

What is claimed is:

1. A photoluminescent complex comprising:

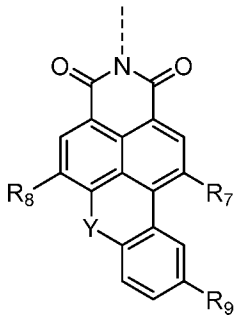
a blue light absorbing donor chromophore, wherein the donor chromophore comprises a naphthalimide derivative;

a linker complex; and

a ring-locked boron-dipyrromethene (BODIPY) moiety;

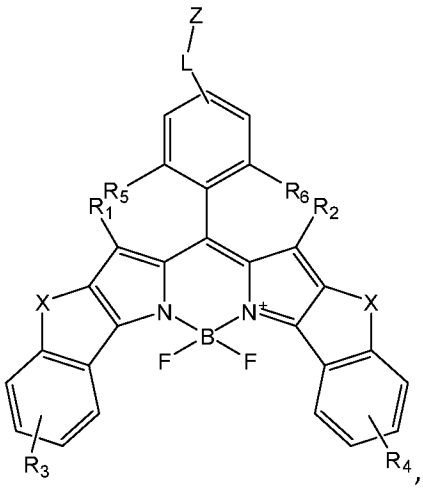
wherein the linker complex covalently links the donor chromophore with the naphthalimide derivative and the ring-locked BODIPY moiety, wherein the naphthalimide derivative absorbs blue light energy of a first excitation wavelength and transfers an energy to the ring-locked BODIPY moiety, wherein the ring-locked BODIPY moiety emits a light energy of a second longer wavelength, and wherein the photoluminescent complex has an emission quantum yield greater than 80%.

2. The photoluminescent complex of claim 1, wherein the naphthalimide derivative of the donor chromophore is of the general formula:



, wherein Y is O or S; wherein R_7 and R_8 are independently H, a substituted or unsubstituted aryl, or a $-CF_3$; and wherein R_9 is independently H, a substituted or unsubstituted aryl, or a C_1-C_5 alkyl.

3. The photoluminescent complex of claim 1, wherein the photoluminescent complex is of the general formula:

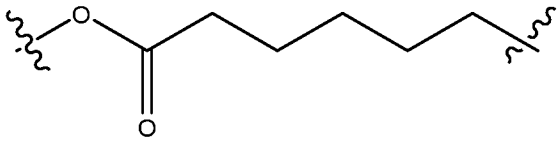


, wherein R_1 and R_2 are independently H, a C_1-C_3 alkyl, or a substituted aryl group; wherein R_3 and R_4 are independently H, F, Br, or -CF_3; wherein R_5 and R_6 are independently H, C_1-C_3 alkyl group, halide, or C_1-C_3 alkoxy; and wherein each X is independently a C_1-C_3 alkyl group or a spiro-cycloalkane group, wherein L is the linker complex and Z is the donor chromophore.

4. The photoluminescent complex of claim 3, wherein L is a substituted ester or an unsubstituted ester.

5. The photoluminescent complex of claim 3, wherein L is a substituted ether or an unsubstituted ether.

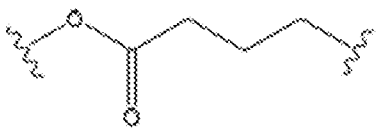
6. The photoluminescent complex of claim 1, 3, or 4, wherein the linker complex is a unsubstituted ester; wherein the unsubstituted ester comprises one of the following structures:



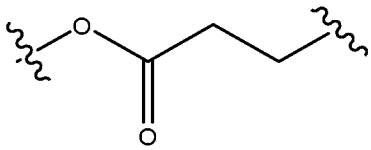
,



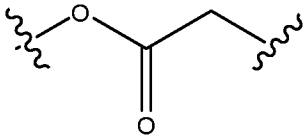
,



,

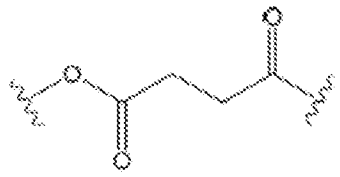
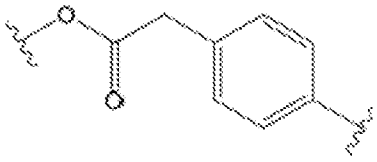
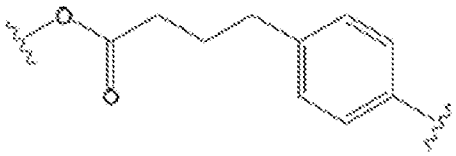


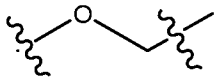
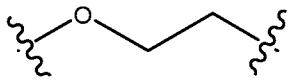
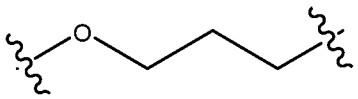
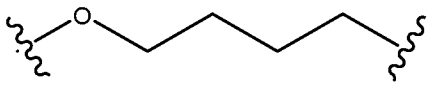
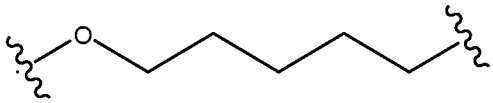
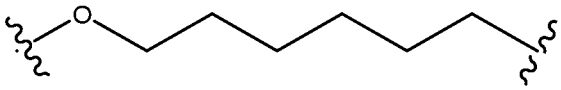
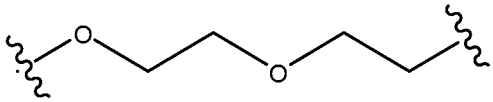
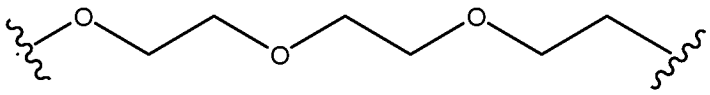
, or



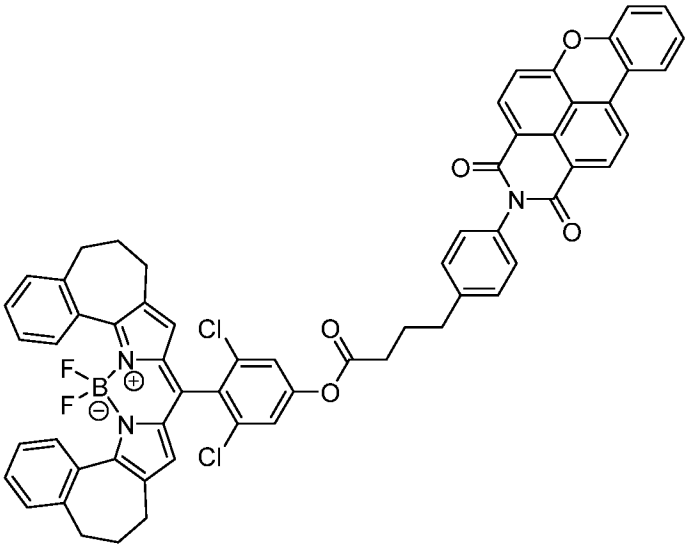
.

7. The photoluminescent complex of claim 1, 3, or 4, wherein the linker complex is a substituted ester; wherein the substituted ester comprises one of the following structures:

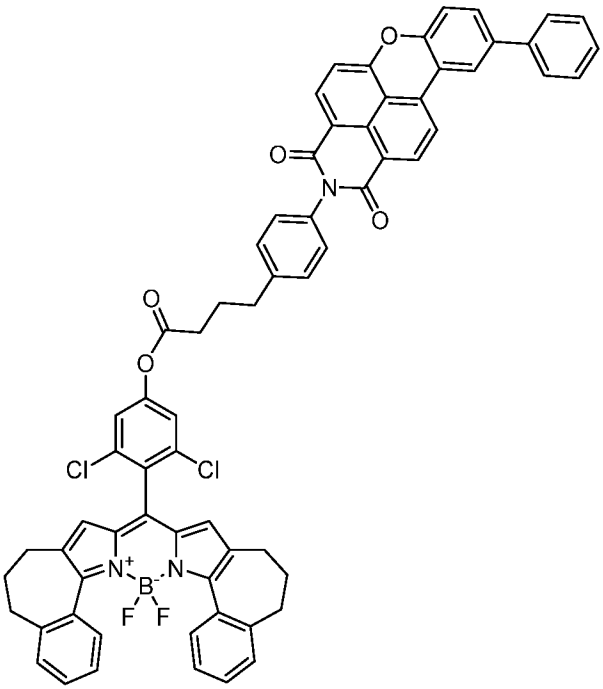

;

,
or

.

8. The photoluminescent complex of claims 1, 3, or 5, wherein the linker complex is a unsubstituted and/or substituted ether; wherein the unsubstituted and/or substituted ether comprises one of the following structures:

,

,

,

,

,

,

,
or

.

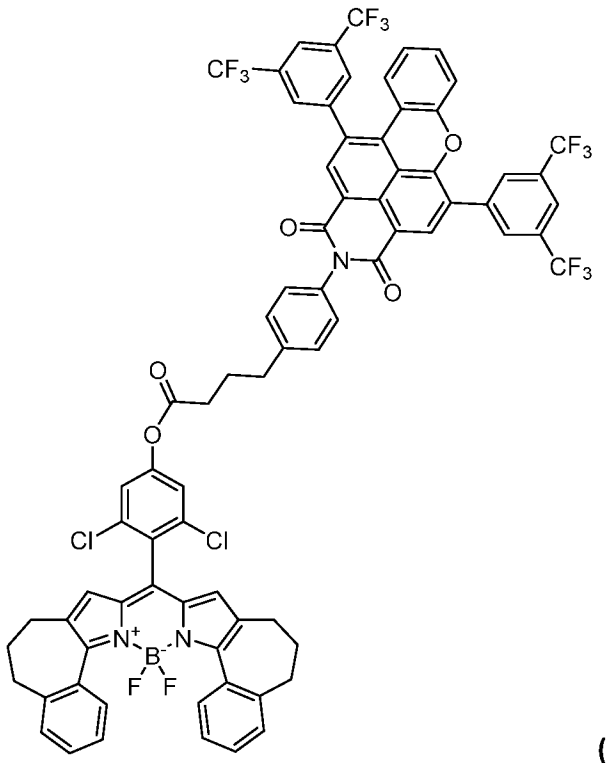
9. The photoluminescent complex as in claims 1, 2, 3, 4, 5, 6, 7, or 8 wherein the photoluminescent complex comprises one of the following structures:



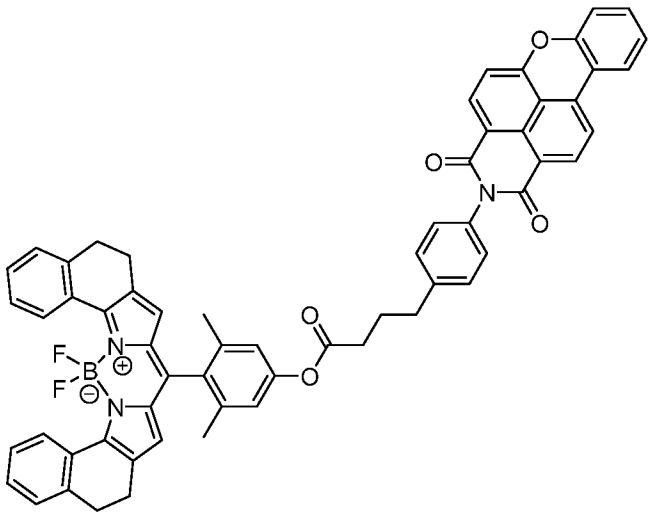
(PLC-1),



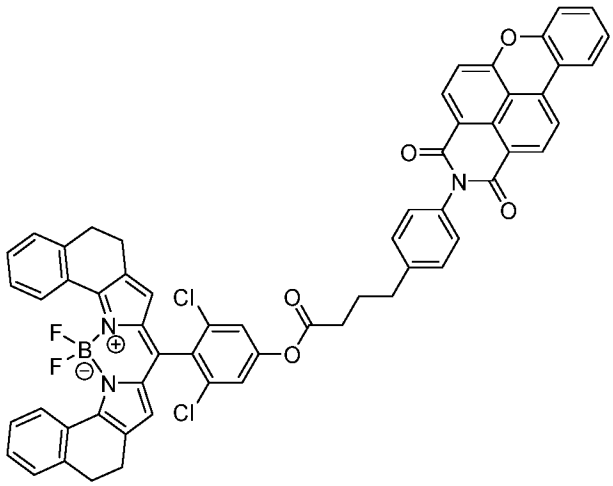
(PLC-2),



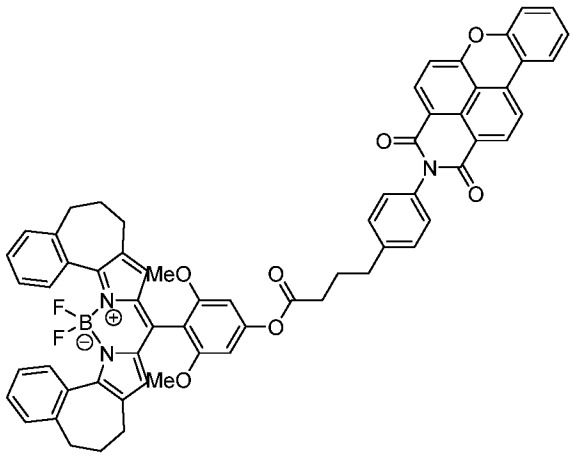
(PLC-3),



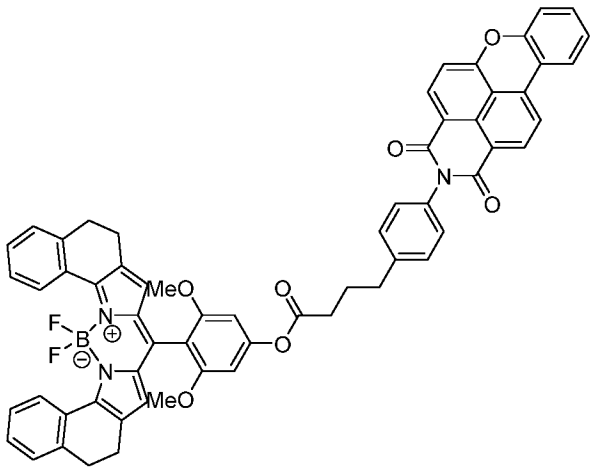
(PLC-4),



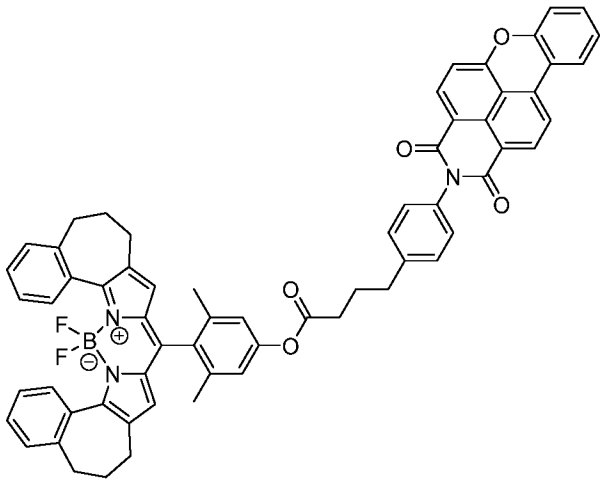
(PLC-5),



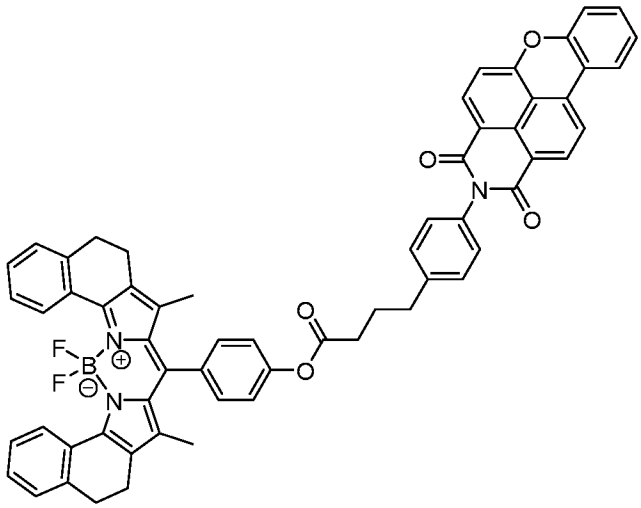
(PLC-6),



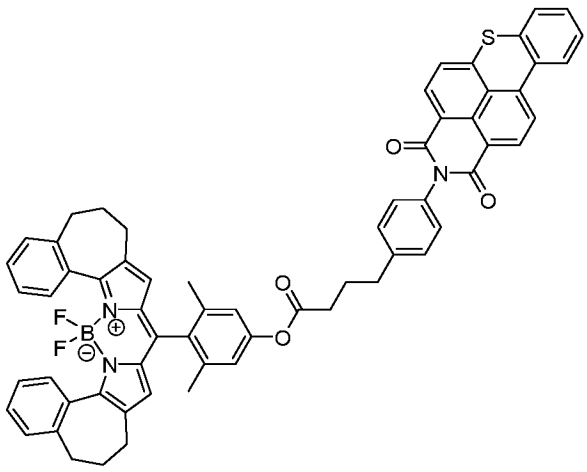
(PLC-7),



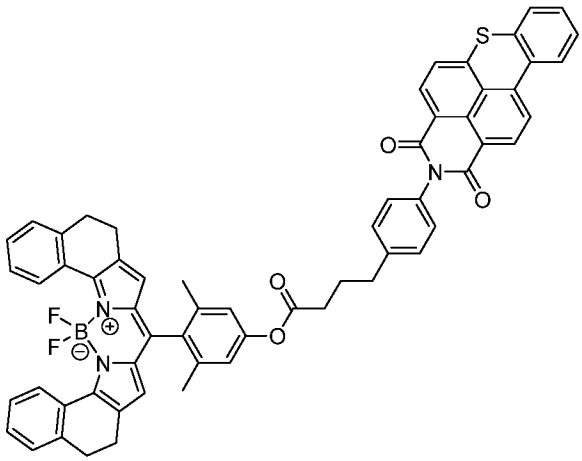
(PLC-8),



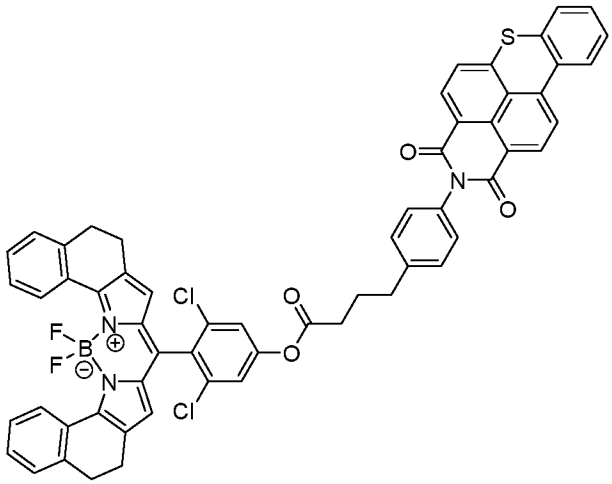
(PLC-9),



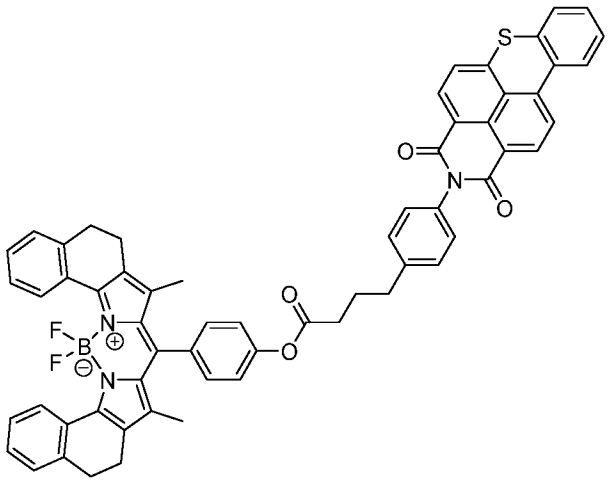
(PLC-10),



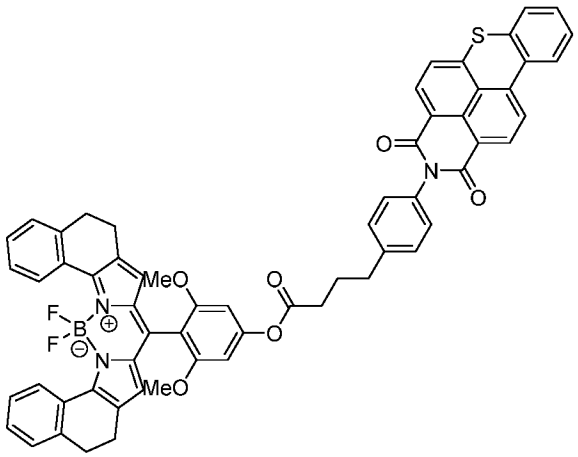
(PLC-11),



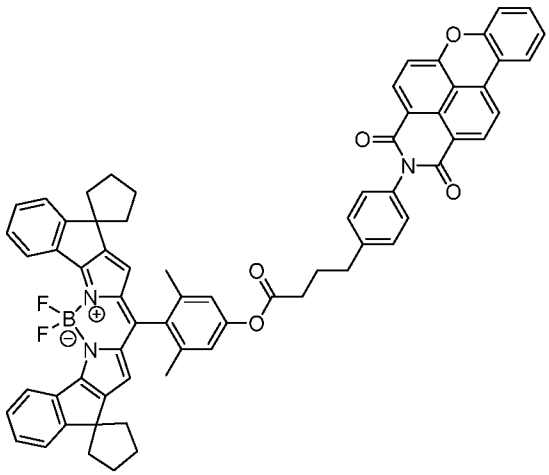
(PLC-12),



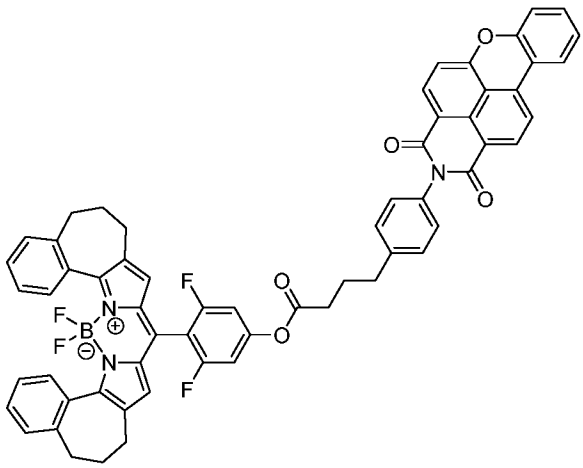
(PLC-13),



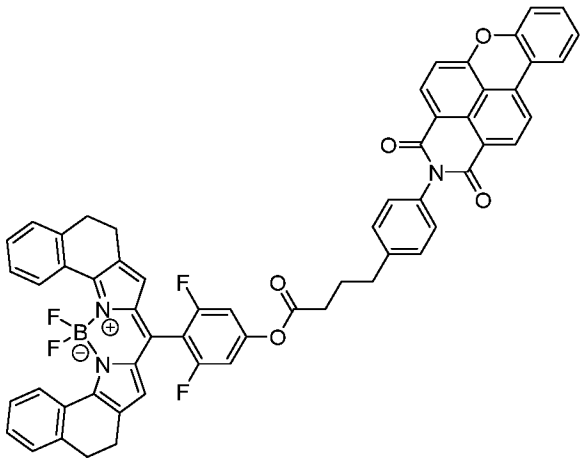
(PLC-14),



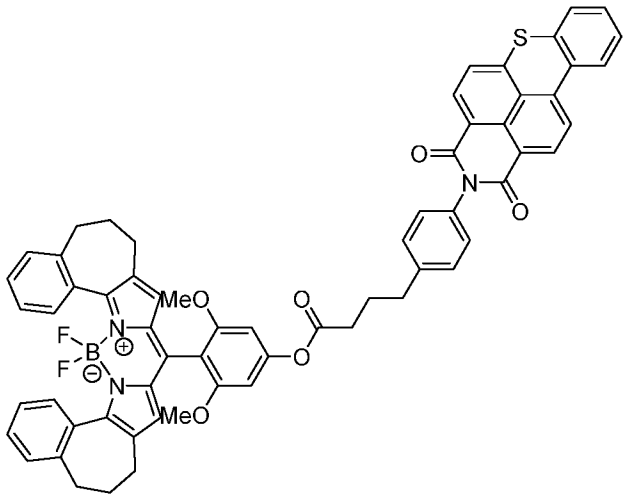
(PLC-15),



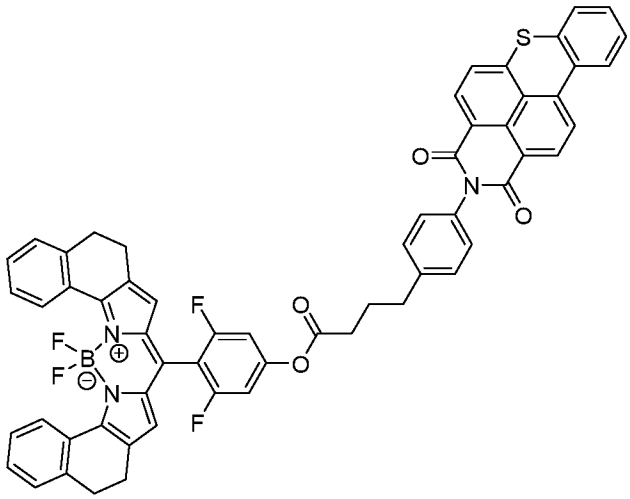
(PLC-16),



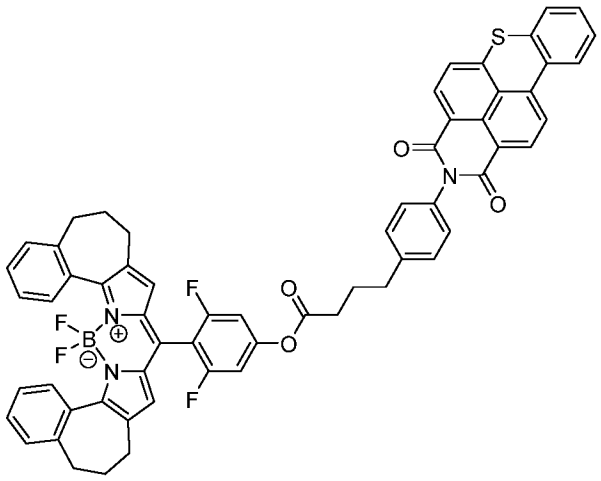
(PLC-17),



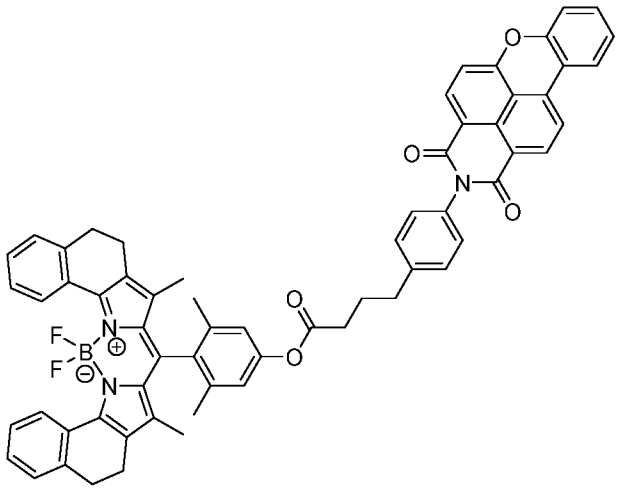
(PLC-18),



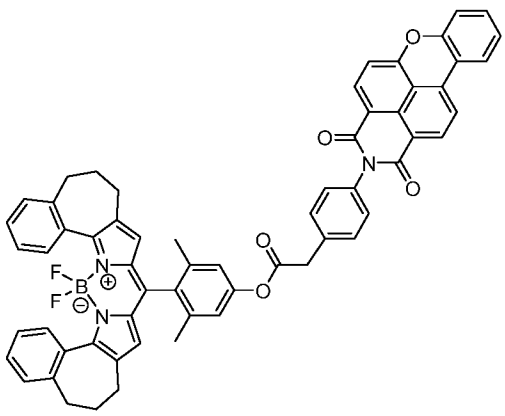
(PLC-19),



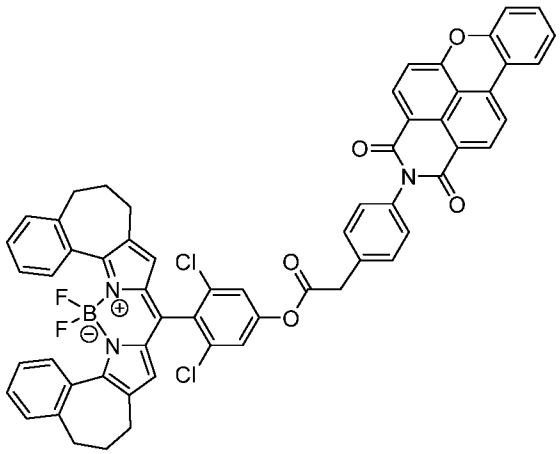
(PLC-20),



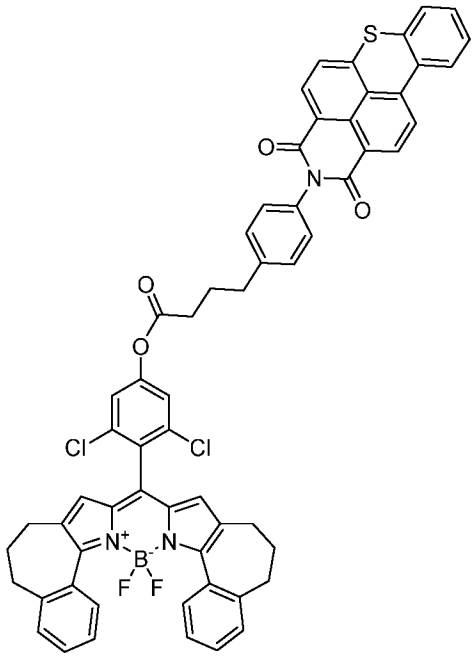
(PLC-21),



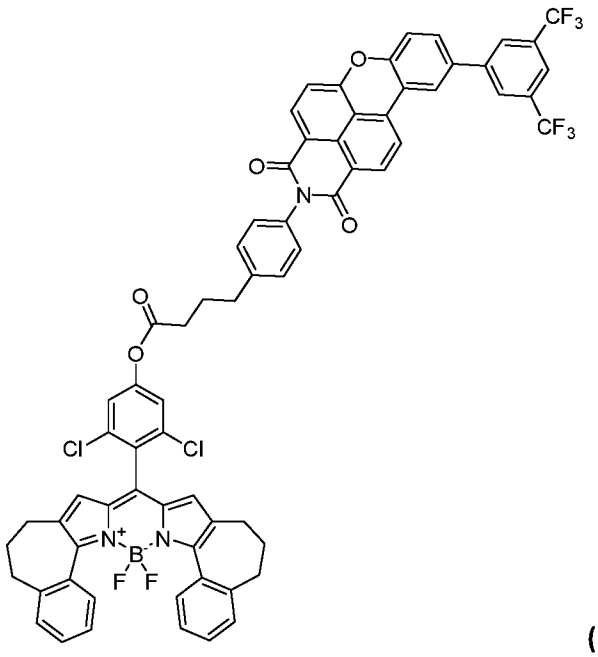
(PLC-22),



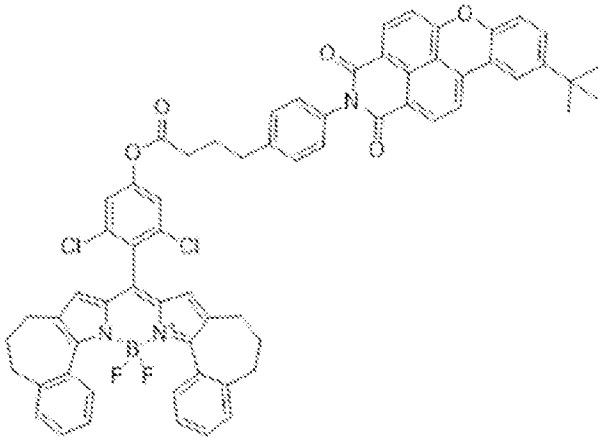
(PLC-23),



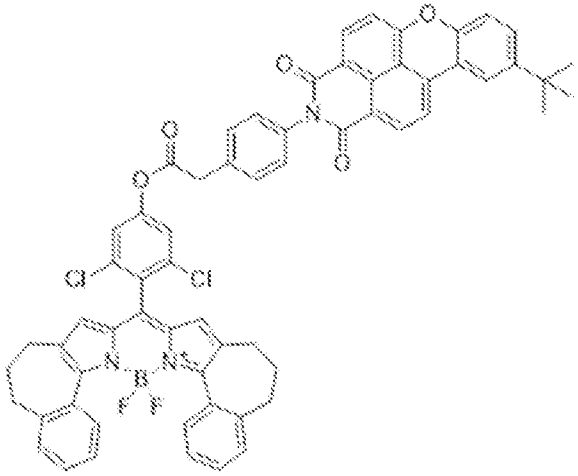
(PLC-24),



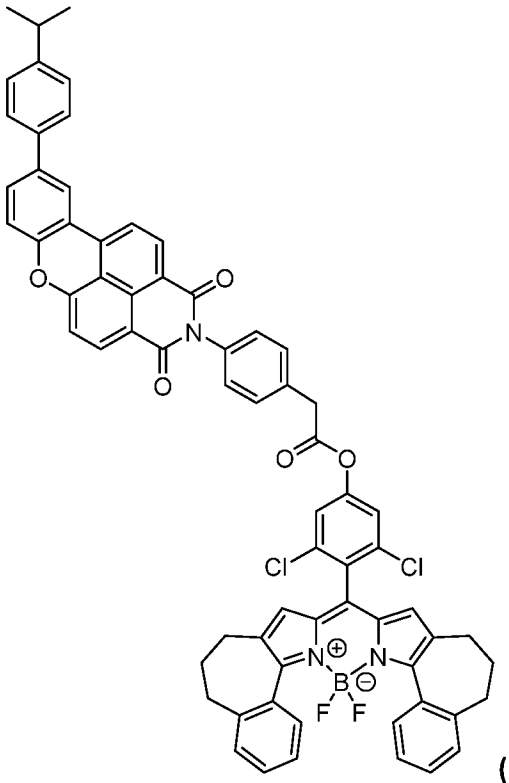
(PLC-25),



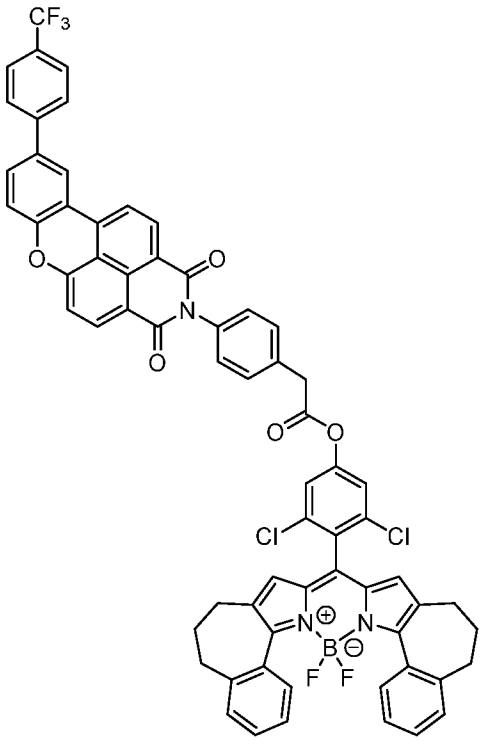
(PLC-26),



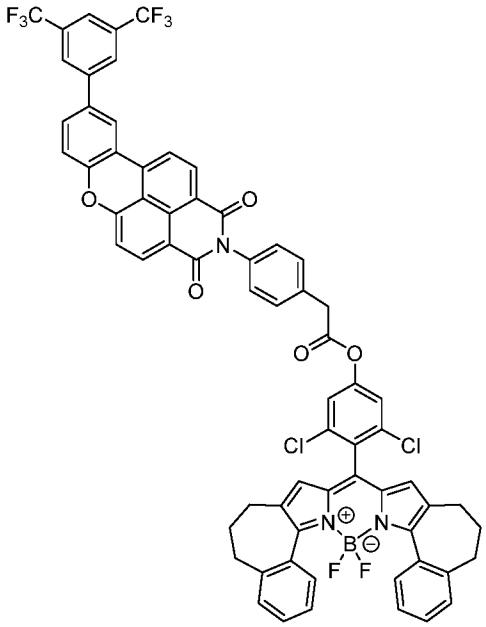
(PLC-27),



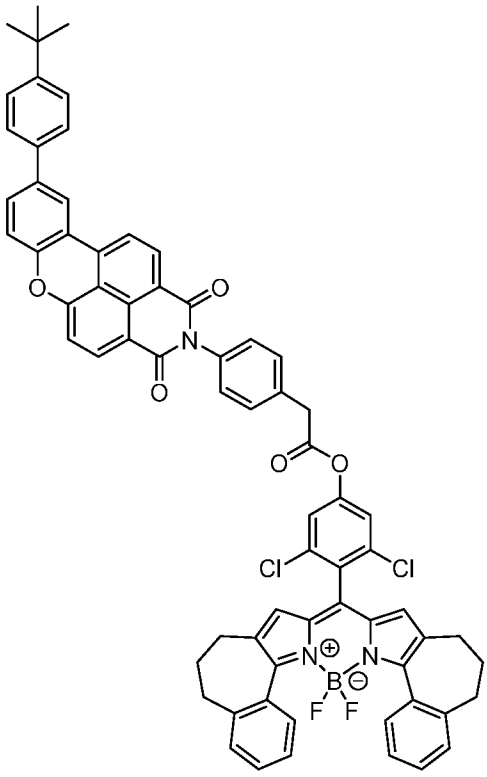
(PLC-28),



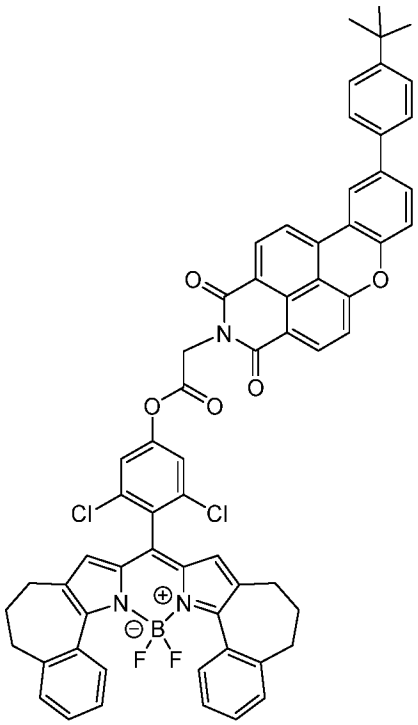
(PLC-29),



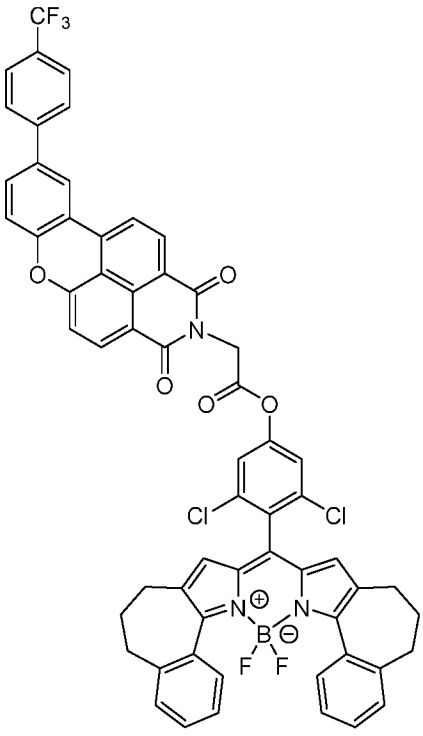
(PLC-30),



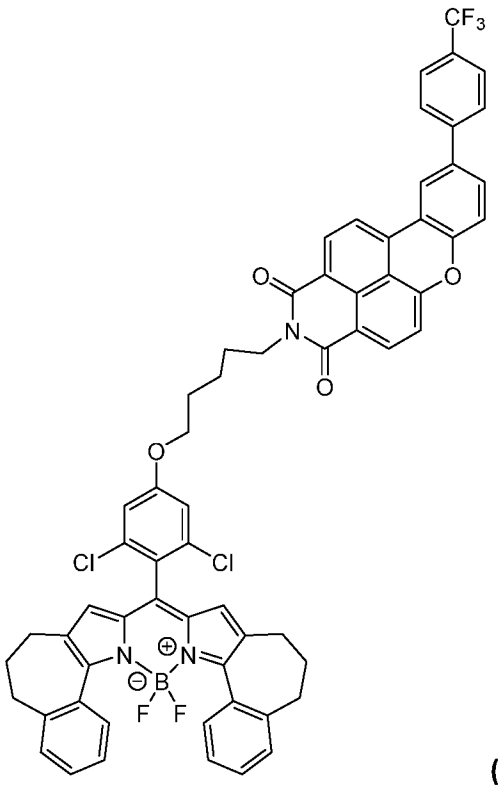
(PLC-31),



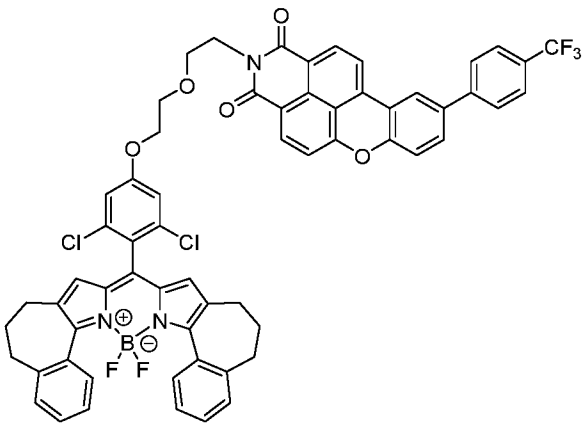
(PLC-32),



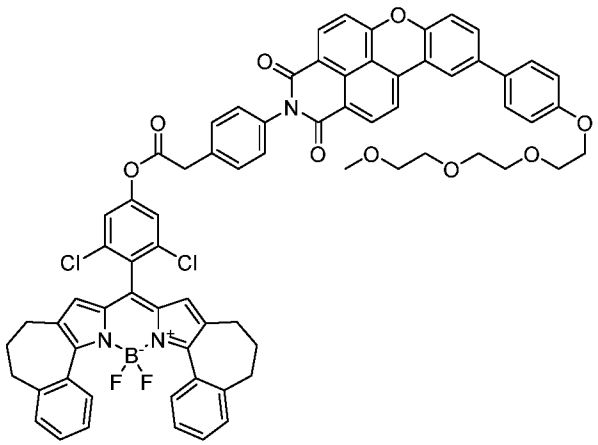
(PLC-33),



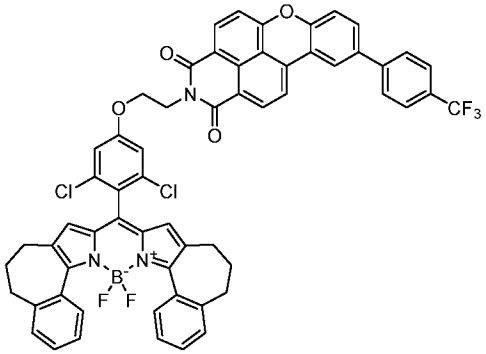
(PLC-34),



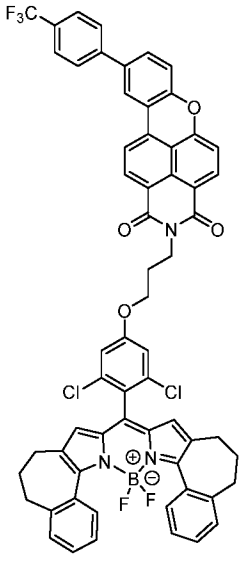
(PLC-35)



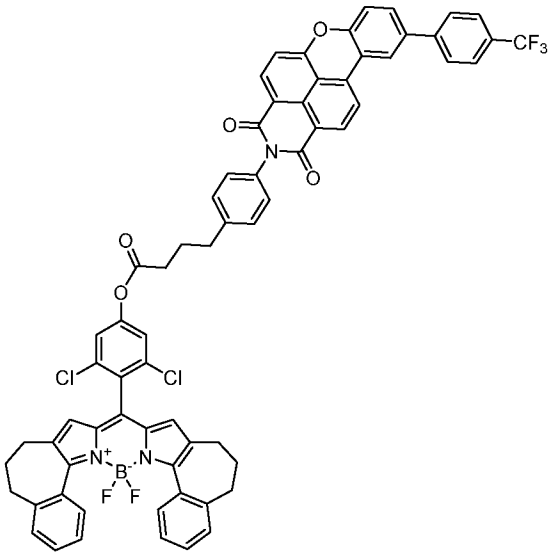
(PLC-36),



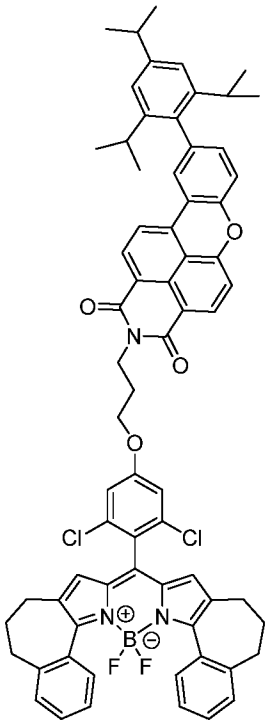
(PLC-37),



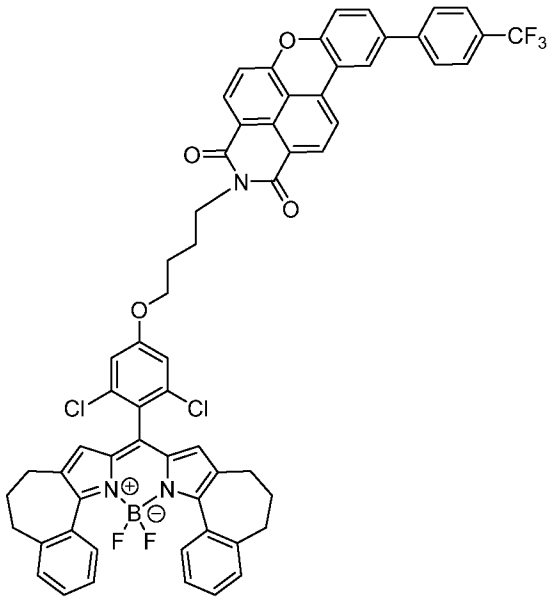
(PLC-38),



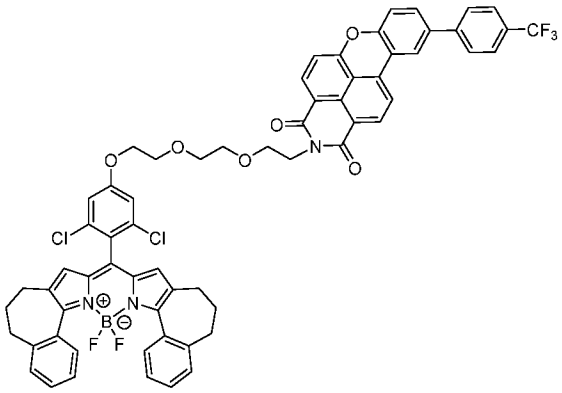
(PLC-39),



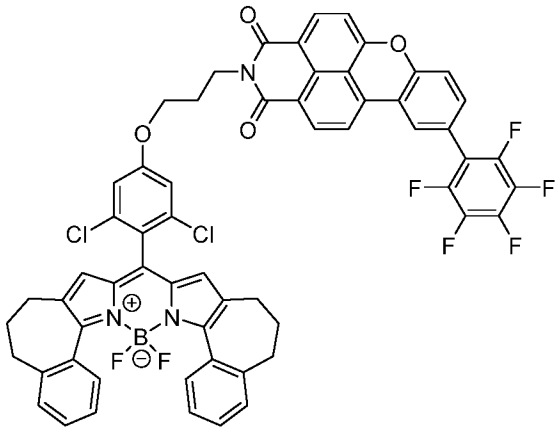
(PLC-40),



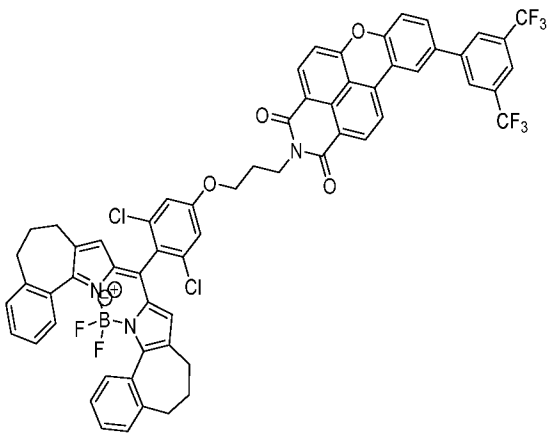
(PLC-41),



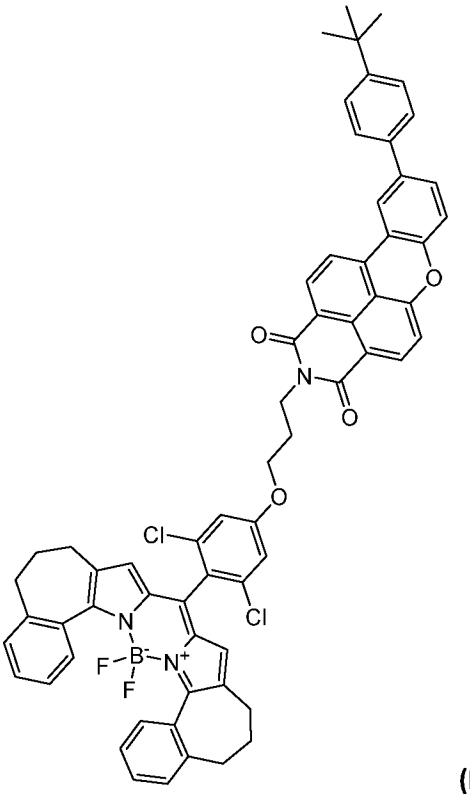
(PLC-42),



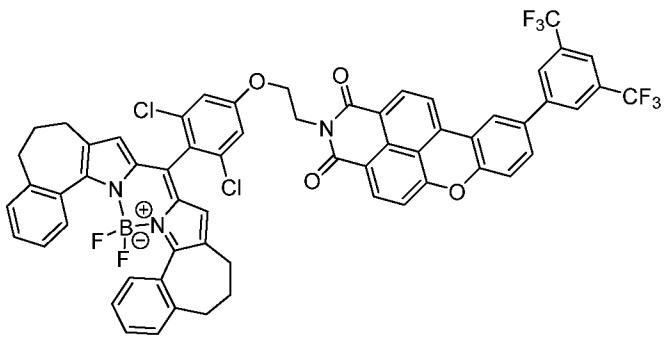
(PLC-43),



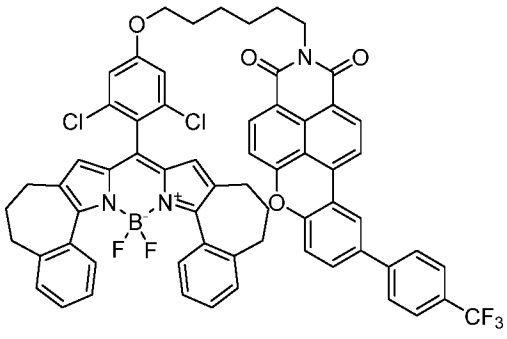
(PLC-44),



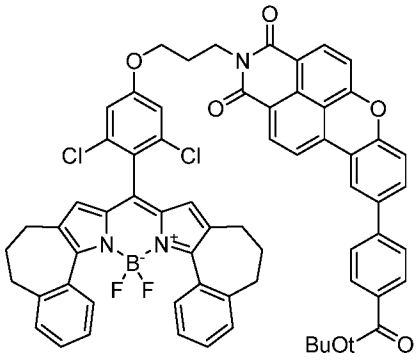
(PLC-45),



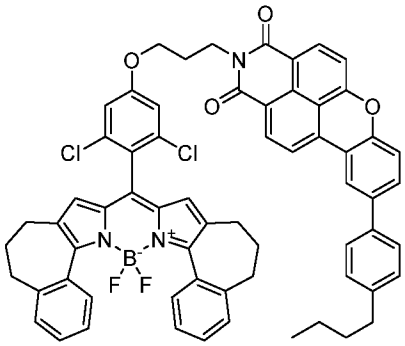
(PLC-46),



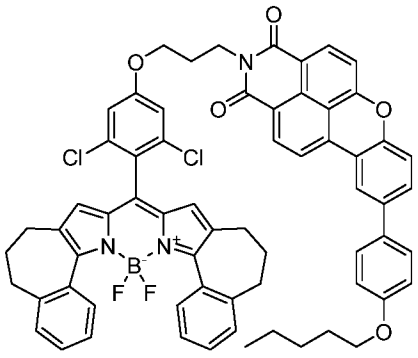
(PLC-47),



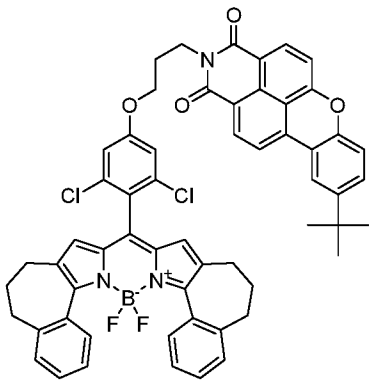
(PLC-48),



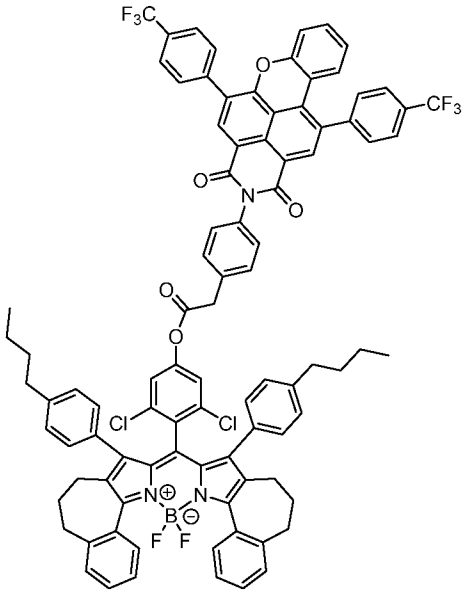
(PLC-49),



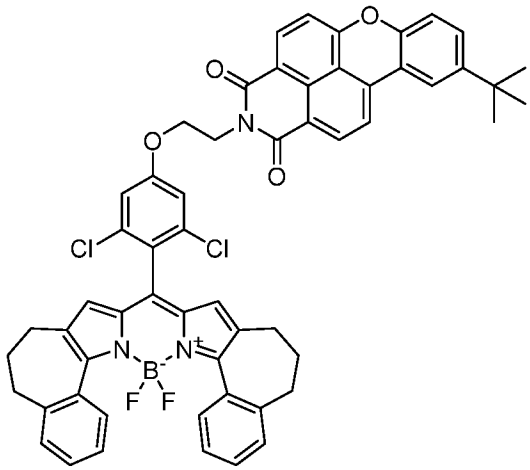
(PLC-50),



(PLC-51),



(PLC-52),



(PLC-53), or any combination thereof.

10. A color conversion film comprising:

a transparent substrate layer;

a color conversion layer, wherein the color conversion layer includes a resin matrix; and at least one photoluminescent complex according to claim 1, 2, 3, 4, 5, 6, 7, 8, or 9 dispersed within the resin matrix.

11. The color conversion film of claim 10, further comprising a singlet oxygen quencher.

12. The color conversion film of claim 10, further comprising a radical scavenger.

13. The color conversion film of claim 10, wherein the film has a thickness between 10 μm and 200 μm.

14. The color conversion film of claim 10, wherein the film absorbs light in a wavelength range of about 400 nm to about 480 nm and emits light in a wavelength range of about 590 nm to about 650 nm.

15. A method for preparing a color conversion film, the method comprising:

dissolving the photoluminescent complexes of claim 1, 2, 3, 4, 5, 6, 7, 8, or 9, and a binder resin within a solvent; and

applying the mixture to a transparent substrate layer.

16. A backlight unit including the color conversion film of claim 10, 11, 12, 13, or 14.

17. A display device including the backlight unit of claim 16.

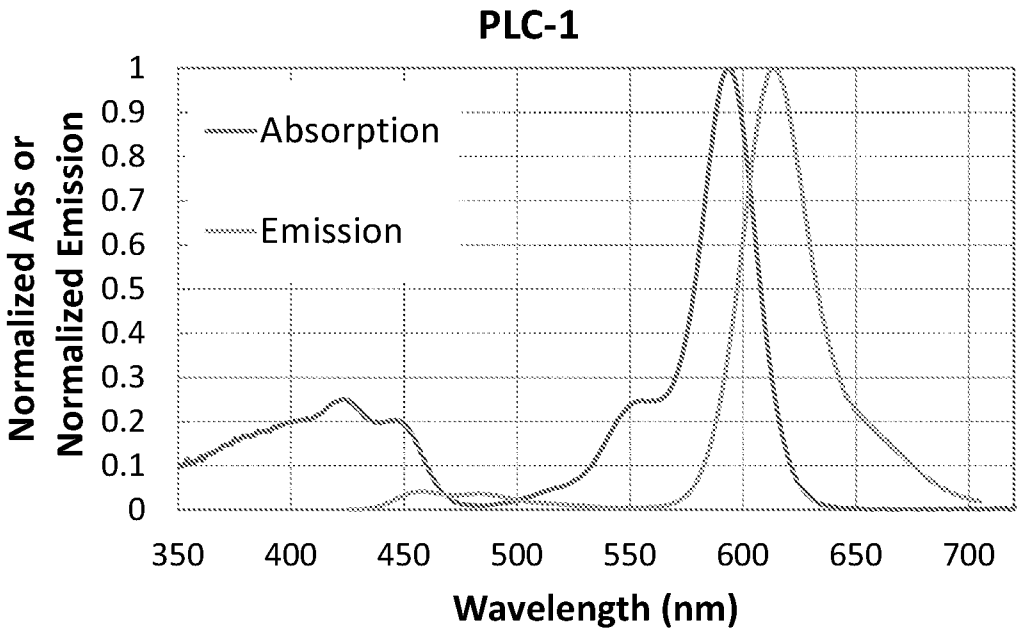

PLC-1
Normalized Abs or Normalized Emission
Absorption
Emission
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
350
400
450
500
550
600
650
700
Wavelength (nm)

FIG. 1

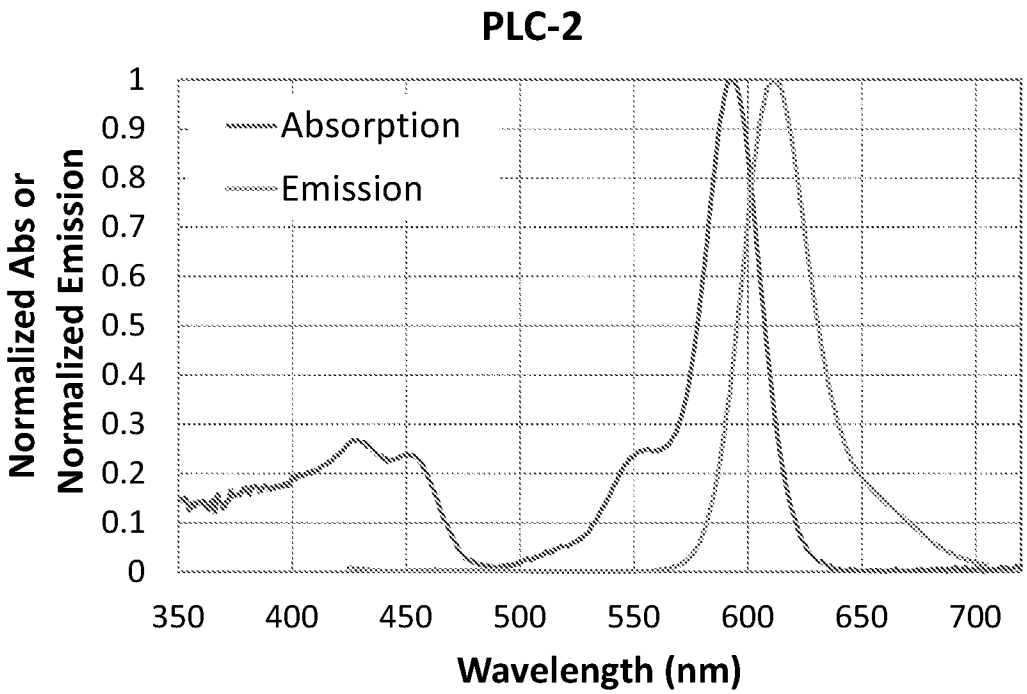

PLC-2
Absorption
Emission
Normalized Abs or Normalized Emission
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
350
400
450
500
550
600
650
700
Wavelength (nm)

FIG. 2

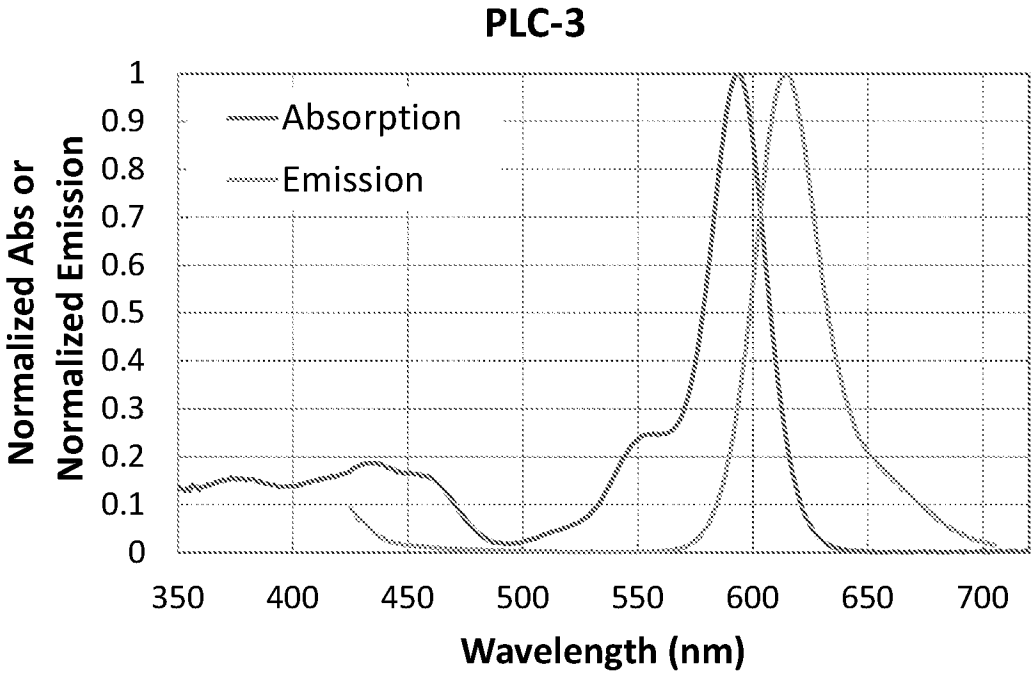

PLC-3
Absorption
Emission
Normalized Abs or Normalized Emission
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
350
400
450
500
550
600
650
700
Wavelength (nm)

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2022/076912

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/06 C08K5/55 C08K5/00 H01L33/50
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K C08K H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 3 505 592 A1 (FUJIFILM CORP [JP]) 3 July 2019 (2019-07-03) compounds F-4 the whole document	1-17
A	WO 2020/053124 A1 (BASF SE [DE]) 19 March 2020 (2020-03-19) page 90; compounds 26,27 claim 1 the whole document	1-17
A	US 2021/010051 A1 (WATANABE KENJI [JP] ET AL) 14 January 2021 (2021-01-14) probe 5, 57 the whole document	1-17

-/--

[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 January 2023	07/02/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Ziegler, Jan

2

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2022/076912

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2021/026402 A1 (ABBOTT LAB [US]) 11 February 2021 (2021-02-11) examples 52, 73 claims 16,17 the whole document -----	1-17
T	XIAONENG CUI ET AL: "Perylene-Derived Triplet Acceptors with Optimized Excited State Energy Levels for Triplet?Triplet Annihilation Assisted Upconversion", THE JOURNAL OF ORGANIC CHEMISTRY, vol. 79, no. 5, 21 February 2014 (2014-02-21), pages 2038-2048, XP055476678, ISSN: 0022-3263, DOI: 10.1021/jo402718e the whole document -----	

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2022/076912

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 3505592 A1	03-07-2019	CN 109642154 A	16-04-2019
		EP 3505592 A1	03-07-2019
		JP 6756839 B2	16-09-2020
		JP WO2018038138 A1	24-06-2019
		KR 20190031547 A	26-03-2019
		US 2019185745 A1	20-06-2019
		US 2021380881 A1	09-12-2021
		WO 2018038138 A1	01-03-2018
WO 2020053124 A1	19-03-2020	CN 112739794 A	30-04-2021
		EP 3850056 A1	21-07-2021
		JP 2022500707 A	04-01-2022
		KR 20210057037 A	20-05-2021
		TW 202020057 A	01-06-2020
		US 2022049158 A1	17-02-2022
		WO 2020053124 A1	19-03-2020
US 2021010051 A1	14-01-2021	JP WO2019044736 A1	29-10-2020
		US 2021010051 A1	14-01-2021
		WO 2019044736 A1	07-03-2019
WO 2021026402 A1	11-02-2021	EP 4010433 A1	15-06-2022
		JP 2022543618 A	13-10-2022
		US 2022291223 A1	15-09-2022
		WO 2021026402 A1	11-02-2021