



(51) International Patent Classification:

C09B 23/01 (2006.01) *H01L 51/42* (2006.01)
C09B 57/00 (2006.01) *H01L 27/146* (2006.01)
H01L 51/00 (2006.01)

(21) International Application Number:

PCT/EP2016/051336

(22) International Filing Date:

22 January 2016 (22.01.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

15152662.1 27 January 2015 (27.01.2015) EP

(71) Applicant: SONY CORPORATION [JP/JP]; 1-7-1 Konan, Minato-ku, Tokyo 108-0075 (JP).

(71) Applicant (for JP only): SONY DEUTSCHLAND GMBH [DE/DE]; Hedelfinger Straße 61, 70327 Stuttgart (DE).

(72) Inventors: ROSSELLI, Silvia; Rheinaustrasse 6, 68163 Mannheim (DE). DANNER, David; Mirabellenstrasse 14, 70329 Stuttgart (DE). BAMEDI ZILAI, Ameneh; Steckfeldstrasse 27, 70599 Stuttgart (DE). NELLES, Gabriele; Duisburger Strasse 22, 70372 Stuttgart (DE). MITEVA, Tzenka; Rommelshauser Strasse 67, 70374 Stuttgart (DE). FUHRMANN, Gerda; Lisa-Scholl-Weg 2/5, 6170 Zirl (AT).

(74) Agent: BOEHMERT & BOEHMERT ANWALTS-PARTNERSCHAFT MBB; APPELT, Christian W., Hollerallee 32, 28209 Bremen (DE).

(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, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, 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, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, 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, 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))

(54) Title: SQUARINE-BASED MOLECULES AS MATERIAL FOR ORGANIC PHOTOELECTRIC CONVERSION LAYERS IN ORGANIC PHOTODIODES

(57) Abstract: The field of the DISCLOSURE lies in active materials for organic image sensors. The present disclosure relates to squaraine and thiophene-based active materials and their use in photoelectric conversion layer(s) and/or an organic image sensor and methods for their synthesis. The present disclosure also relates to photoelectric conversion layer(s) comprising an active material according to the present disclosure, to a device, comprising active material(s) according to the present disclosure or photoelectric conversion layer(s) according to the present disclosure. Moreover, the present disclosure relates to an organic image sensor comprising photoelectric conversion layer(s) according to the present disclosure.



SQUARAIN-BASED MOLECULES AS MATERIAL FOR ORGANIC PHOTOELECTRIC CONVERSION LAYERS IN ORGANIC PHOTODIODES

BACKGROUND

[0001] The field of the DISCLOSURE lies in active materials for organic image sensors.

[0002] The present disclosure relates to squaraine and thiophene-based active materials and their use in photoelectric conversion layer(s) and/or an organic image sensor and methods for their synthesis.

[0003] The present disclosure also relates to photoelectric conversion layer(s) comprising an active material according to the present disclosure, to a device, comprising active material(s) according to the present disclosure or photoelectric conversion layer(s) according to the present disclosure.

[0004] Moreover, the present disclosure relates to an organic image sensor comprising photoelectric conversion layer(s) according to the present disclosure.

DESCRIPTION OF THE RELATED ART

[0005] The “background” description provided herein is for the purpose of generally presenting the context of the disclosure. Work of the presently named inventors, to the extent it is described in this background section, as well as aspects of the description which may not otherwise qualify as prior art at the time of filing, are neither expressly or impliedly admitted as prior art against the present disclosure.

[0006] Image sensors, which are semiconductor devices for converting an optical image into an electric signal, include a light-sensing unit for sensing light and a logic circuit unit for processing the sensed light into an electrical signal to store data.

[0007] In the state of the art, the light-sensing unit includes a color filter and a photoelectric conversion film, a semiconductor p-n junction, such as silicon. The color filter separates light according to colors, but reduces the spatial resolution and light collection and utilization efficiency.

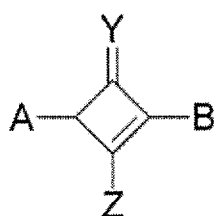
[0008] In order to overcome this problem geometries are reported where photoelectric conversion units capable of detecting light of different wavelengths are stacked in a longitudinal direction. In particular such photoelectrical conversion unit is an organic photoelectric conversion layer based on p-n junction or bulk heterojunction. The photoelectric

conversion efficiency of such a unit depends strongly on the type of material used in the layer. With the organic materials available so far, low conversion efficiencies and high dark currents are reported.

[0009] In another solution, an organic layer is used that is capable to absorb in the IR reagon but not in the visible reagon, that could be combined with a complementary metal oxide semiconductor (CMOS) based imager part for the visible range or with an organic based imager part that could absorb in the visible range. In both cases white ligth is collected and filter have to be used to get the BGR pixel resolution. In this case, as well as in the case of color filter, light is separated according to colors but the spatial resolution and light collection and utilization efficiency is reduced.

SUMMARY

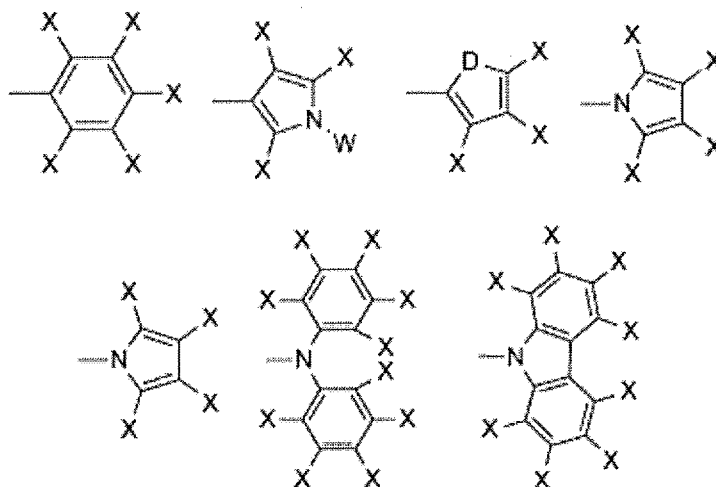
[0010] The present disclosure provides a (squaraine) molecule represented by formula I



(I)

wherein

A and B are the same or different and are, at each occurrence, independently selected from



pyrazole, thiazole, imidazole, indole, quinoline, benzothiophene, benzothiazole, benzothiadiazole, benzofuran, oxazole, benzoxazole, pyridine, diazine, triazine, selenophene, naphthalene, anthracene or pyrene, any of which can optionally be substituted,

D is S or O;

W is selected from H, alkyl, aryl;

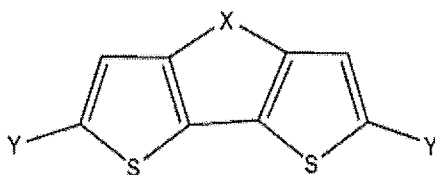
X is selected from the group comprising H, OH, SH, NH₂, NHR, NR₂, NO₂, alkyl, alkoxy, aryl, aryloxy, halogen, such as F, Cl, Br, I;

Y is selected from O, S, NH, NR, NC-CH₂-CN, NC-CH₂-COOH, HOOC-CH₂-COOH, indanedione, barbituric acid or thiobarbituric acid;

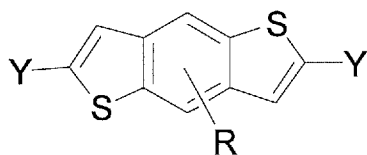
Z is selected from OH, SH, NH₂, NR₂;

R, at each occurrence, is independently selected from H or any straight or branched alkyl chain of general formula -C_nH_{2n+1}, or -COOR¹, -OR¹, -SR¹, -NR¹₂, or F, Cl, Br, I, O, N, NO₂, CN, CF₃, wherein **R**¹ is H or any straight or branched alkyl chain of general formula -C_nH_{2n+1}, or any substituted or non-substituted phenyl or biphenyl, heteroaryl, **n** = 0-12, preferably 0-6.

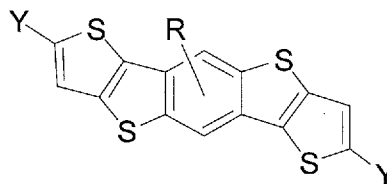
[0011] The present disclosure provides a (thiophene-based) molecule represented by a formula selected from formula II, III, IV, V and VI



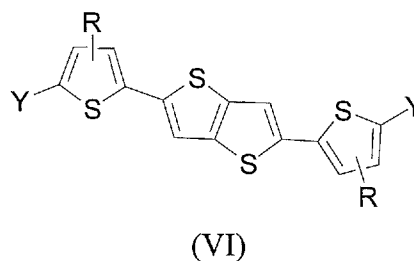
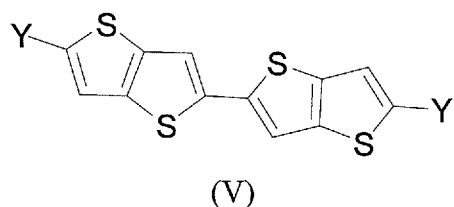
(II)



(III)



(IV)



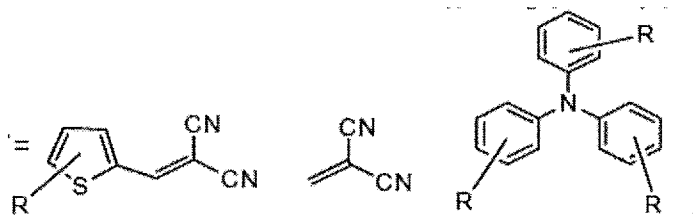
wherein

X is selected from the group comprising S, Se, N-R¹, SO₂, CR₂¹, cyclopentane, cyclohexane, SiR₂¹;

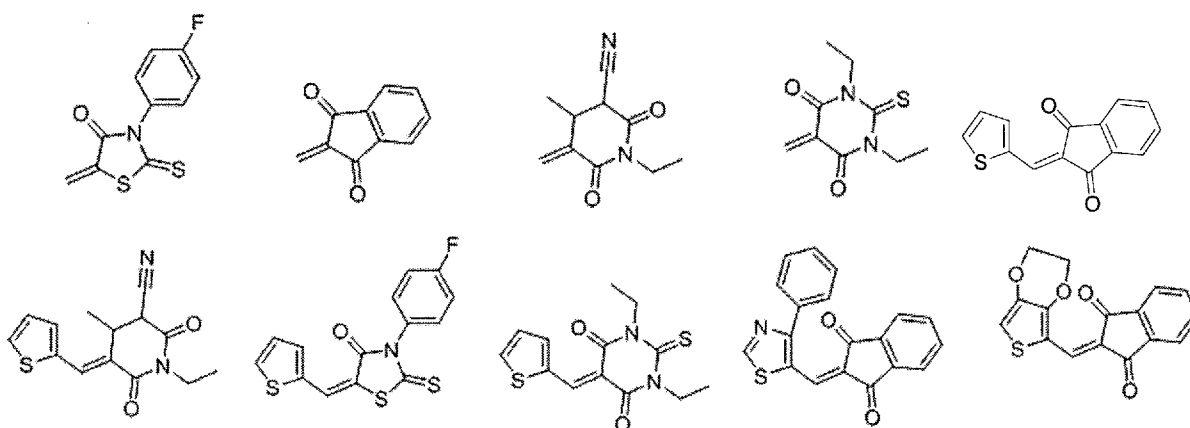
R¹ is selected from aryl, alkyl;

R is selected from H, aryl, substituted aryl, alkyl, thiophene, alkyl-substituted thiophene;

Y is selected from



carbazole, diarylamine, pyrrole, pyrazole, thieno[3,4-b]pyrazine, imidazole, thiazole, fluorine, tricyanovinyl, indole, quinolone, benzothiadiazole, indanedione, barbituric acid or thiobarbituric acid, rhodanine, thiazolinedione derivatives as for example:



[0012] The present disclosure provides the use of a molecule according to the present disclosure in an absorption layer, in a filter and/or in a photoelectric conversion layer and/or in an organic and/or hybrid module for optoelectronic application.

[0013] The present disclosure provides a photoelectric conversion layer comprising a molecule according to the present disclosure. The present disclosure provides an absorption layer comprising a molecule according to the present disclosure. The present disclosure provides a filter comprising a molecule according to the present disclosure.

[0014] The present disclosure provides a device comprising molecule(s) according to the present disclosure or a photoelectric conversion layer(s) according to the present disclosure.

[0015] The present disclosure provides an organic image sensor, comprising an organic photoelectric conversion unit comprising photoelectric conversion layer(s) according to the present disclosure.

[0016] The present disclosure provides a hybrid Silicon-organic image sensor, comprising an organic photoelectric conversion unit comprising photoelectric conversion layer(s) according to the present disclosure.

[0017] The present disclosure provides a method for synthesis of a (squaraine) molecule according to the present disclosure.

[0018] The present disclosure provides a method for synthesis of a (thiophene-based) molecule according to the present disclosure.

[0019] The foregoing paragraphs have been provided by way of general introduction, and are not intended to limit the scope of the following claims. The described embodiments, together with further advantages, will be best understood by reference to the following detailed description taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] A more complete appreciation of the disclosure and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

[0021] Figure 1 shows a CMOS image sensor.

[0022] Figure 2 shows a schematic representation of the hybrid silicon-organic image sensor.

[0023] Figure 3 shows a schematic representation of the organic based photoelectrical conversion unit with the different layers.

[0024] Figure 4 shows the squaraine molecule of Example 1 and its absorption in solution (left) and in the solid state (right).

[0025] Figure 5 shows the External Quantum Efficiency (EQE) of a photoelectric conversion layer wherein the squaraine molecule of Example 1 was used as donor material in combination with subphthalocyanine fluoride as acceptor.

[0026] Figure 6 shows the thiophene-based molecule of Example 2 and its absorption in solution (left) and in the solid state (right).

[0027] Figure 7 shows the squaraine molecule of Example 3 and its absorption in solution (left) and in the solid state (right).

[0028] Figure 8 shows the External Quantum Efficiency (EQE) of a photoelectric conversion layer wherein the squaraine molecule of Example 3 was used as donor material in combination with subphthalocyanine chloride as acceptor.

[0029] Figure 9 shows the thiophene-based molecule of Example 4 and its absorption in solution (left); and the External Quantum Efficiency (EQE) of a photoelectric conversion layer wherein the thiophene molecule of Example 4 was used as donor material in combination with subphthalocyanine chloride as acceptor (right).

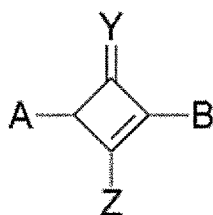
[0030] Figure 10 shows the thiophene-based molecule of Example 5 and its absorption in solution.

[0031] Figure 11 shows the thiophene-based molecule of Example 6 and its absorption in solution.

[0032] Figure 12 shows the thiophene-based molecule of Example 7 and its absorption in solution.

DETAILED DESCRIPTION OF THE EMBODIMENTS

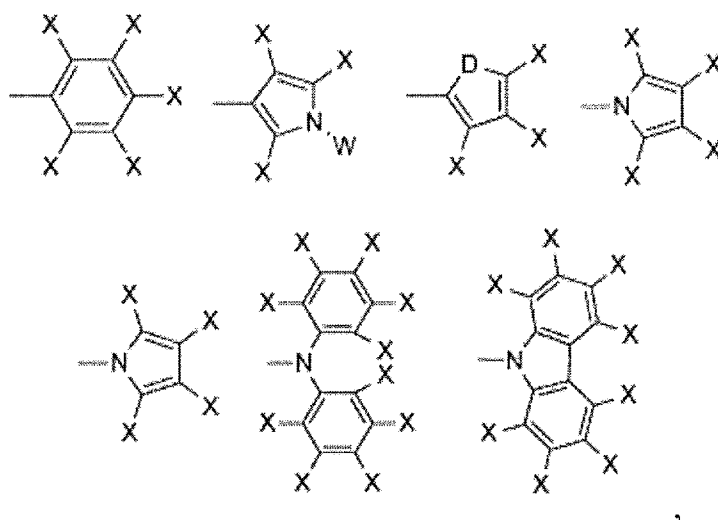
[0033] As discussed above, the present disclosure provides a *squaraine molecule* represented by formula I



formula I

wherein

A and **B** are the same or different and are, at each occurrence, independently selected from



pyrazole, thiazole, imidazole, indole, quinoline, benzothiophene, benzothiazole, benzothiadiazole, benzofuran, oxazole, benzoxazole, pyridine, diazine, triazine, selenophene, naphthalene, anthracene or pyrene, any of which can optionally be substituted,

D is S or O;

W is selected from H, alkyl, aryl;

X is selected from the group comprising H, OH, SH, NH₂, NHR, NR₂, NO₂, alkyl, alkoxy, aryl, aryloxy, halogen, such as F, Cl, Br, I;

Y is selected from O, S, NH, NR, NC-CH₂-CN, NC-CH₂-COOH, HOOC-CH₂-COOH, indanedione, barbituric acid or thiobarbituric acid;

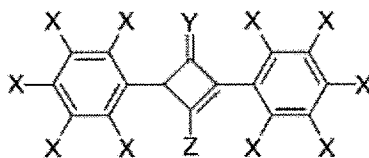
Z is selected from OH, SH, NH₂, NR₂;

R, at each occurrence, is independently selected from H or any straight or branched alkyl chain of general formula -C_nH_{2n+1}, or -COOR¹, -OR¹, -SR¹, -NR¹₂, or F, Cl, Br, I, O, N, NO₂, CN, CF₃, wherein **R**¹ is H or any straight or branched alkyl chain of general formula -C_nH_{2n+1}, or any substituted or non-substituted phenyl or biphenyl, heteroaryl, **n** = 0-12, preferably 0-6.

[0034] In one embodiment, the squaraine molecule comprises a spacer, such as a double bond, e.g. in an embodiment, where A and/or B is indole).

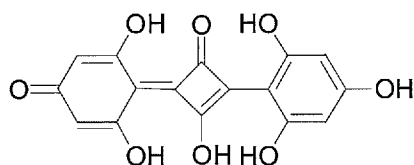
[0035] Mono-, di-, tri-, tetra- and penta-substitution with X is possible.

[0036] In a preferred embodiment, the squaraine molecule is represented by formula Ia

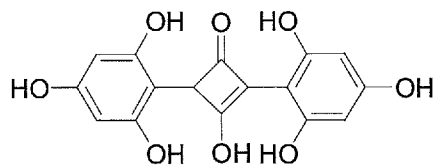


wherein X, Y and Z are as defined above.

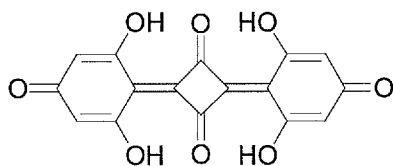
[0037] In one embodiment, the squaraine molecule is represented by any of structures



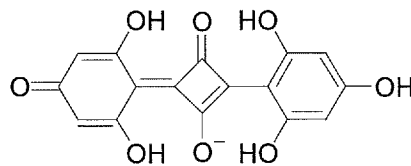
3,5-Dihydroxy-4-[2-hydroxy-4-oxo-3-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enylidene]-cyclohexa-2,5-dienone



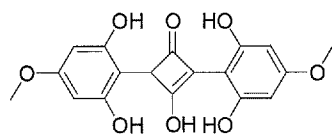
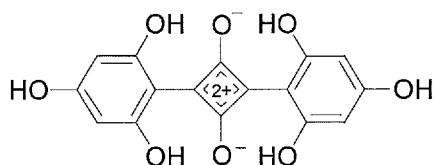
3-Hydroxy-2,4-bis-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enone



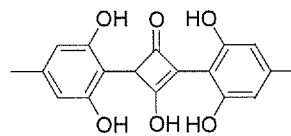
2,4-Bis-(2,6-dihydroxy-4-oxo-cyclohexa-2,5-dienylidene)-cyclobutane-1,3-dione



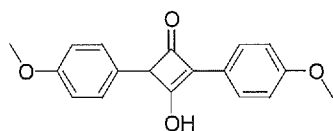
4-(2,6-Dihydroxy-4-oxo-cyclohexa-2,5-dienylidene)-3-oxo-2-(2,4,6-trihydroxy-phenyl)-cyclobut-1-enol anion



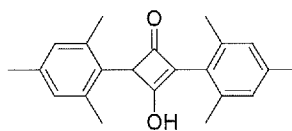
2,4-Bis-(2,6-dihydroxy-4-methoxy-phenyl)-3-hydroxy-cyclobut-2-enone



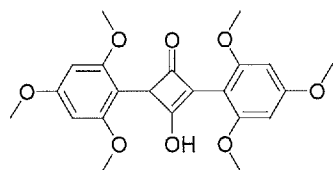
2,4-Bis-(2,6-dihydroxy-4-methyl-phenyl)-3-hydroxy-cyclobut-2-enone



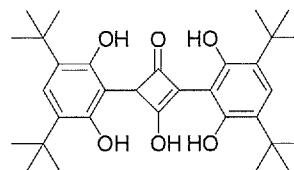
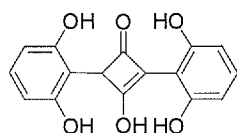
3-Hydroxy-2,4-bis-(4-methoxy-phenyl)-cyclobut-2-enone



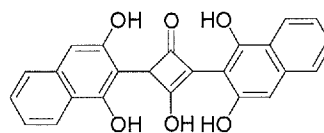
3-Hydroxy-2,4-bis-(2,4,6-trimethyl-phenyl)-cyclobut-2-enone



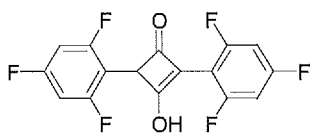
3-Hydroxy-2,4-bis-(2,4,6-trimethoxy-phenyl)-cyclobut-2-enone

2,4-Bis-(3,5-di-*tert*-butyl-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone

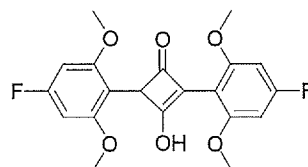
2,4-Bis-(2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



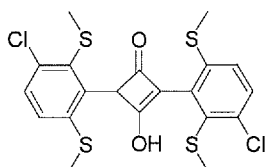
2,4-Bis-(1,3-dihydroxy-naphthalen-2-yl)-3-hydroxy-cyclobut-2-enone



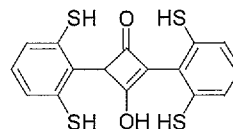
3-Hydroxy-2,4-bis-(2,4,6-trifluoro-phenyl)-cyclobut-2-enone



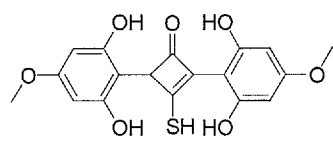
2,4-Bis-(4-fluoro-2,6-dimethoxy-phenyl)-3-hydroxy-cyclobut-2-enone



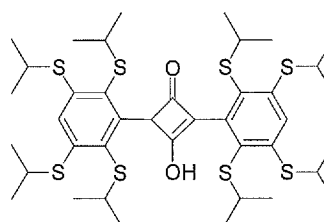
2,4-Bis-(3-chloro-2,6-bis-methylsulfanyl-phenyl)-3-hydroxy-cyclobut-2-enone



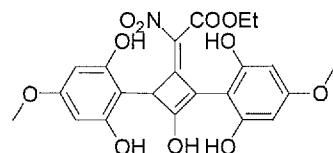
2,4-Bis-(2,6-dimercapto-phenyl)-3-hydroxy-cyclobut-2-enone



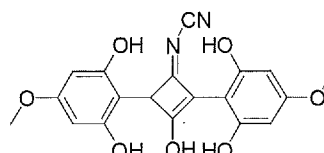
2,4-Bis-(2,6-dihydroxy-4-methoxy-phenyl)-3-mercapto-cyclobut-2-enone



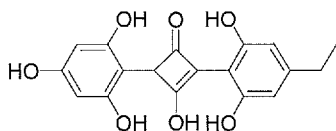
3-Hydroxy-2,4-bis-(2,3,5,6-tetrakis-isopropylsulfanyl-phenyl)-cyclobut-2-enone



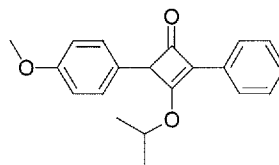
[2,4-Bis-(2,6-dihydroxy-4-methoxy-phenyl)-3-hydroxy-cyclobut-2-enylidene]-nitro-acetic acid ethyl ester



2,4-Bis-(2,6-dihydroxy-4-methoxy-phenyl)-3-hydroxy-cyclobut-2-enylidene-cyanamide



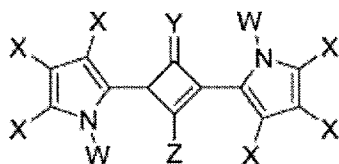
2-(4-Ethyl-2,6-dihydroxy-phenyl)-3-hydroxy-4-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enone



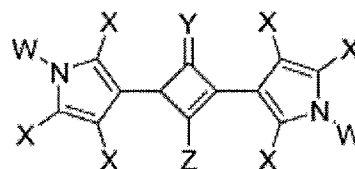
3-isopropoxy-4-(4-methoxy-phenyl)-2-phenyl-cyclobut-2-enone

[0038] In one embodiment, any of the above depicted substituents attached to the squaraine core can be used in combination with other substituent(s) in order to form asymmetric substituted squaraine molecules.

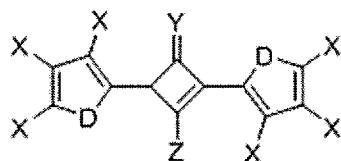
[0039] In a preferred embodiment, the squaraine molecule is represented by any one of



formula Ib,

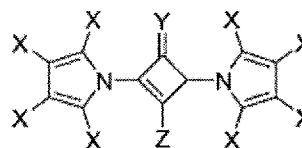


formula Ic,

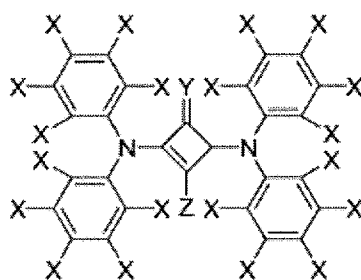


formula Id,

wherein D is S or O,

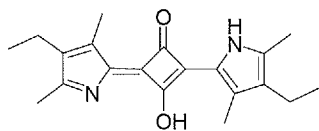


formula Ie, or

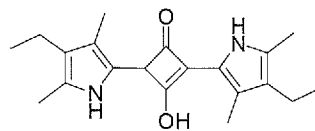


formula If.

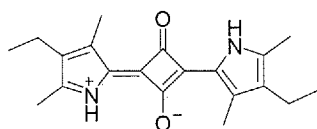
[0040] In one embodiment, the squaraine molecule is represented by any of structures



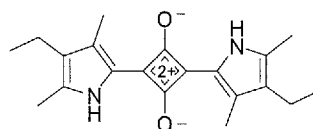
2-(4-Ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-4-(4-ethyl-3,5-dimethyl-pyrrol-2-ylidene)-3-hydroxy-cyclobut-2-enone



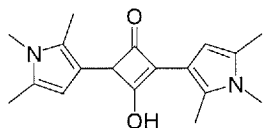
2,4-Bis-(4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-3-hydroxy-cyclobut-2-enone



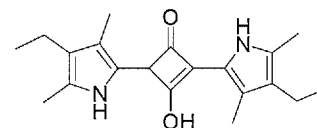
3-Oxo-2-(1,2,5-trimethyl-1H-pyrrol-3-yl)-4-(1,2,5-trimethyl-pyrrol-3-ylidene)-cyclobut-1-enol anion



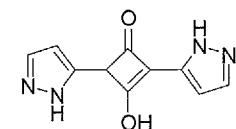
2,4-Bis-(4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-3-hydroxy-cyclobut-2-enone



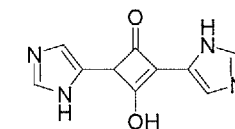
3-Hydroxy-2,4-bis-(2H-pyrazol-3-yl)-cyclobut-2-enone



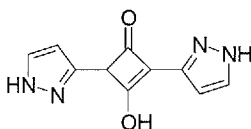
3-Hydroxy-2,4-bis-(3H-imidazol-4-yl)-cyclobut-2-enone



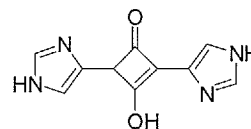
3-Hydroxy-2,4-bis-(1H-pyrazol-3-yl)-cyclobut-2-enone



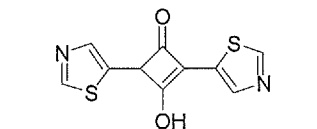
3-Hydroxy-2,4-bis-(1H-imidazol-4-yl)-cyclobut-2-enone



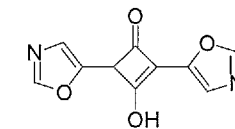
3-Hydroxy-2,4-bis-(thiazol-5-yl)-cyclobut-2-enone



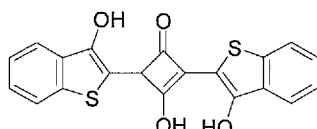
3-Hydroxy-2,4-bis-(oxazol-5-yl)-cyclobut-2-enone



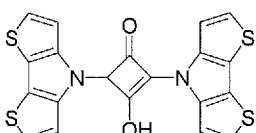
3-Hydroxy-2,4-bis-(3-hydroxy-benzo[b]thiophen-2-yl)-cyclobut-2-enone



3-Hydroxy-2,4-bis-indol-1-yl-cyclobut-2-enone

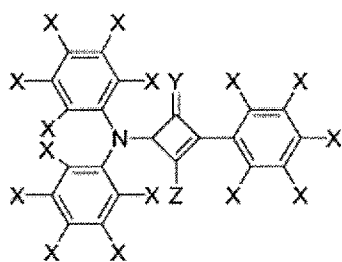


2,4-Bis-dithieno[3,2-b;2',3'-d]pyrrol-4-yl-3-hydroxy-cyclobut-2-enone

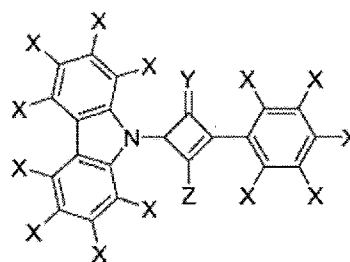


[0041] In one embodiment, any of the above depicted substituents attached to the squaraine core can be used in combination with other substituent(s) in order to form asymmetric substituted squaraine molecules.

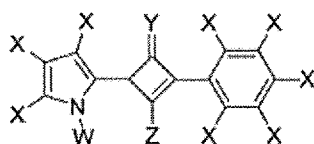
[0042] In a preferred embodiment, the squaraine molecule is represented by any one of



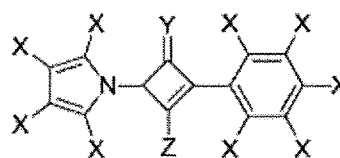
formula Ig,



formula Ih,

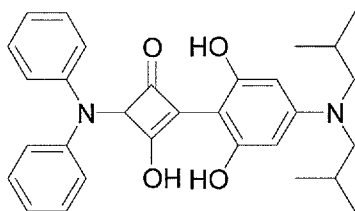


formula Ii, or

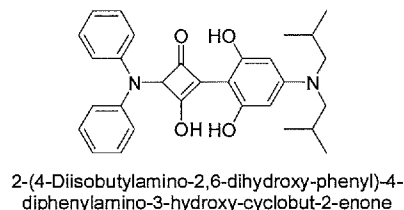
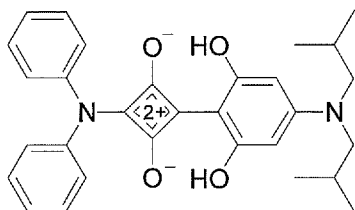
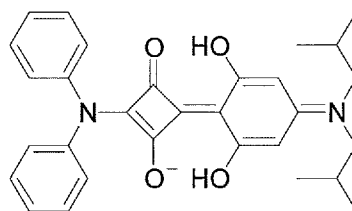


formula Ij.

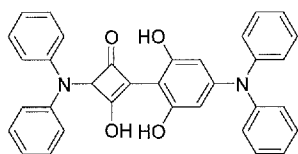
[0043] In one embodiment, the squaraine molecule is represented by any of structures



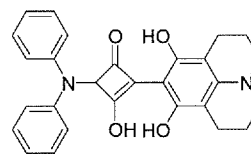
2-(4-Diisobutylamino-2,6-dihydroxy-phenyl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



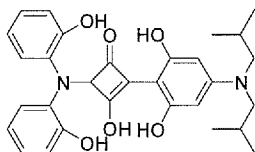
2-(4-Diisobutylamino-2,6-dihydroxy-phenyl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



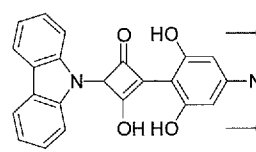
4-Diphenylamino-2-(4-diphenylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



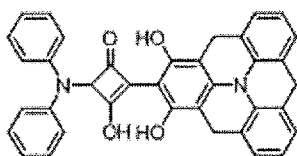
2-(8,10-Dihydroxy-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



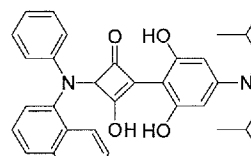
4-[Bis-(2-hydroxy-phenyl)-amino]-2-(4-diisobutylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



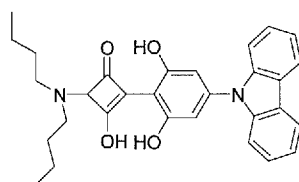
4-Carbazol-9-yl-2-(4-diisobutylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



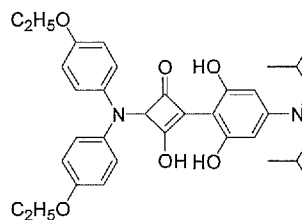
2-(1,3-Dihydroxy-4H,8H,12H-12c-aza-dibenzo[cd,mn]pyren-2-yl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



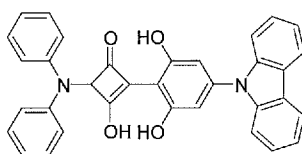
2-(4-Diisobutylamino-2,6-dihydroxy-phenyl)-3-hydroxy-4-(naphthalen-1-yl-phenyl-amino)-cyclobut-2-enone



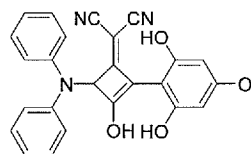
4-Dibutylamino-2-(4-diphenylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



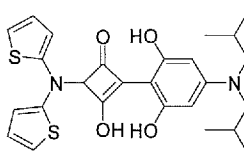
4-[Bis-(4-ethoxy-phenyl)-amino]-2-(4-diisobutylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



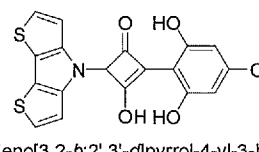
2-(4-Carbazol-9-yl-2,6-dihydroxy-phenyl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



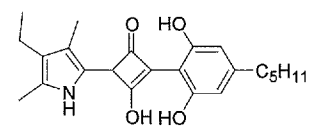
2-[4-Diphenylamino-3-hydroxy-2-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enylidene]-malononitrile



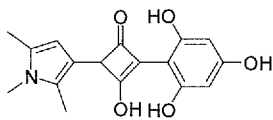
2-(4-Diisobutylamino-2,6-dihydroxy-phenyl)-4-(di-thiophen-2-yl-amino)-3-hydroxy-cyclobut-2-enone



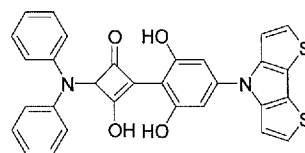
4-Dithieno[3,2-b;2',3'-d]pyrrol-4-yl-3-hydroxy-2-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enone



2-(2,6-Dihydroxy-4-pentyl-phenyl)-4-(4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-3-hydroxy-cyclobut-2-enone

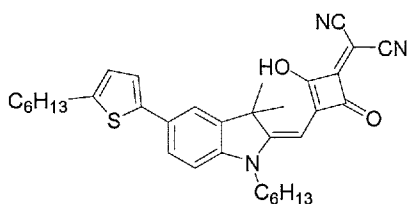
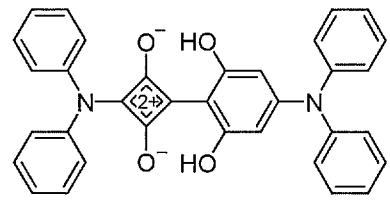
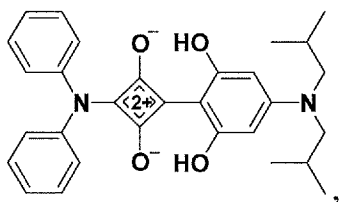


3-Hydroxy-2-(2,4,6-trihydroxy-phenyl)-4-(1,2,5-trimethyl-1H-pyrrol-3-yl)-cyclobut-2-enone

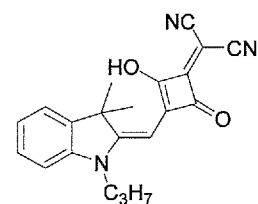


4-Diphenylamino-2-(4-dithieno[3,2-b;2',3'-d]pyrrol-4-yl)-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone

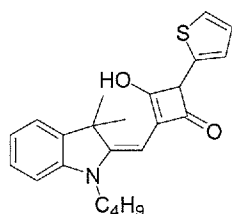
[0044] In one embodiment, the squaraine molecule is represented by any of structures



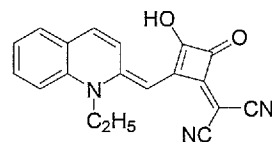
2-[3-[1-Hexyl-5-(5-hexylthiophen-2-yl)-3,3-dimethyl-1,3-dihydro-indol-2-ylidenemethyl]-2-hydroxy-4-oxo-cyclobut-2-enylidene]-malononitrile



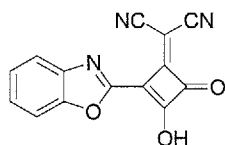
2-[3-(3,3-Dimethyl-1-propyl-1,3-dihydro-indol-2-ylidenemethyl)-2-hydroxy-4-oxo-cyclobut-2-enylidene]-malononitrile



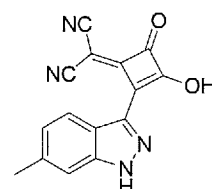
2-(1-Butyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidenemethyl)-3-hydroxy-4-thiophen-2-yl-cyclobut-2-enone



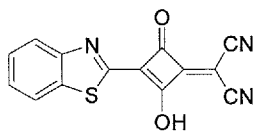
2-[2-(1-Ethyl-1H-quinolin-2-ylidenemethyl)-3-hydroxy-4-oxo-cyclobut-2-enylidene]-malononitrile



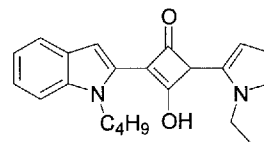
2-(2-Benzothiazol-2-yl-3-hydroxy-4-oxo-cyclobut-2-enylidene)-malononitrile



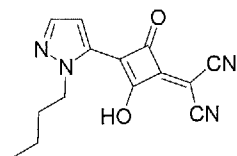
2-[3-Hydroxy-2-(6-methyl-1H-indazol-3-yl)-4-oxo-cyclobut-2-enylidene]-malononitrile



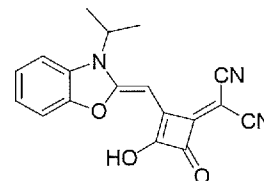
2-(3-Benzothiazol-2-yl-2-hydroxy-4-oxo-cyclobut-2-enylidene)-malononitrile



2-(1-Butyl-1H-indol-2-yl)-(1-ethyl-1H-pyrrol-2-yl)-3-hydroxy-cyclobut-2-enone



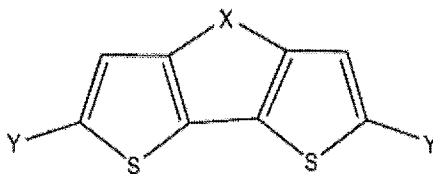
2-[3-(2-Butyl-2H-pyrazol-3-yl)-2-hydroxy-4-oxo-cyclobut-2-enylidene]-malononitrile



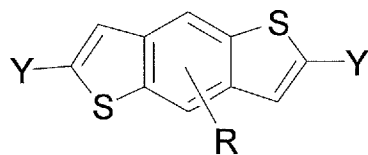
2-[3-Hydroxy-2-(3-isopropyl-3H-benzooxazol-2-ylidenemethyl)-4-oxo-cyclobut-2-enylidene]-malononitrile

[0045] In one embodiment, the squaraine molecule is an asymmetrical molecule, with any of the shown substituents attached to the squaraine core in combination with any other substituent.

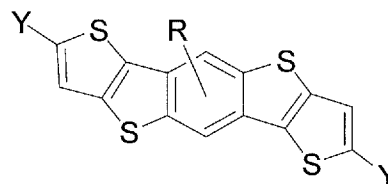
[0046] As discussed above, the present disclosure provides a *thiophene-based molecule* represented by a formula selected from formula II, III, IV, V and VI



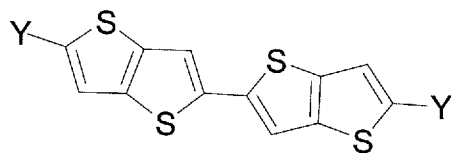
formula II



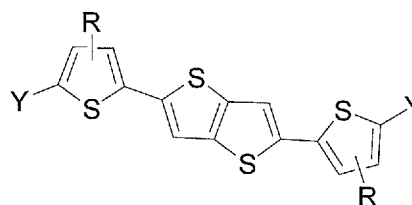
formula III



formula IV



formula V



formula VI

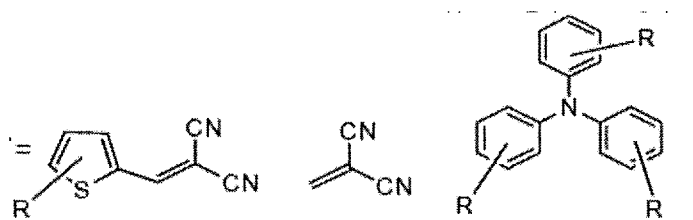
wherein

X is selected from the group comprising S, Se, N-R¹, SO₂, CR¹₂, cyclopentane, cyclohexane, SiR¹₂;

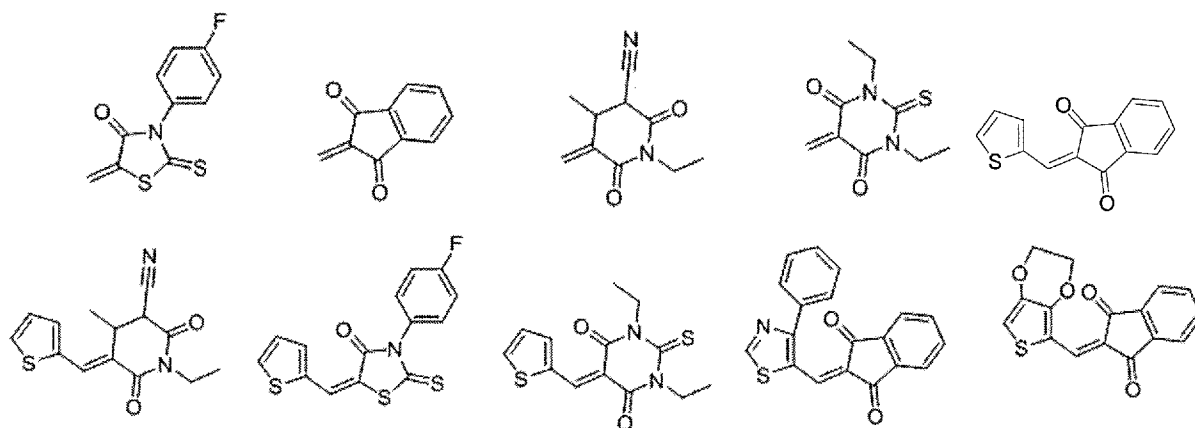
R¹ is selected from aryl, alkyl;

R is selected from H, aryl, substituted aryl, alkyl, thiophene, alkyl-substituted thiophene;

Y is selected from

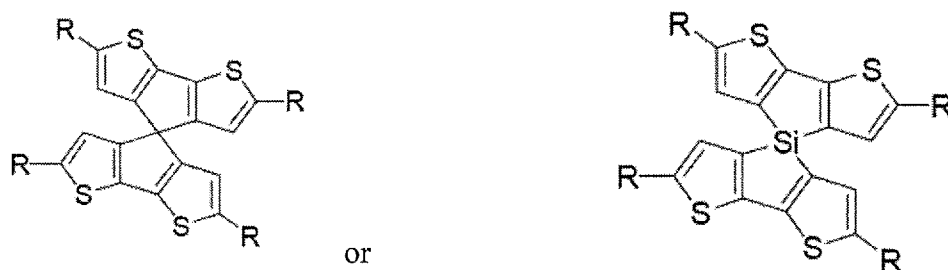


carbazole, diarylamine, pyrrole, pyrazole, thieno[3,4-b]pyrazine, imidazole, thiazole, fluorine, tricyanovinyl, indole, quinolone, benzothiadiazole, indanedione, barbituric acid or thiobarbituric acid, rhodanine, thiazolinedione derivatives as for example:



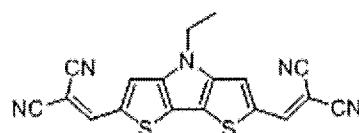
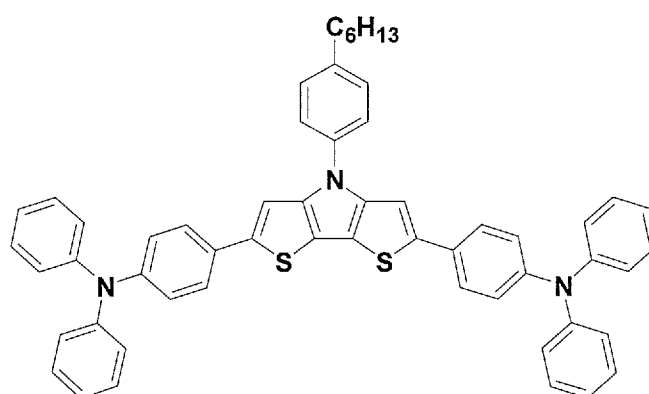
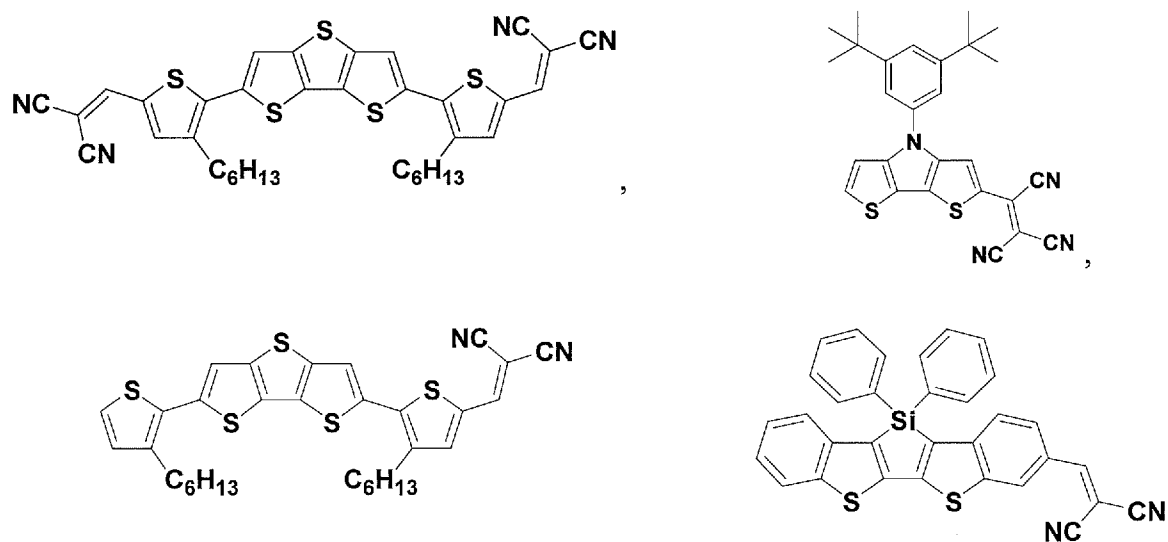
R is selected from H, aryl, substituted aryl, alkyl, thiophene, alkyl-substituted thiophene.

[0047] In a preferred embodiment, the thiophene-based molecule is a spiro-dimer selected from

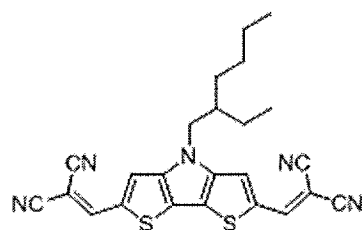


R is the same as the R defined above.

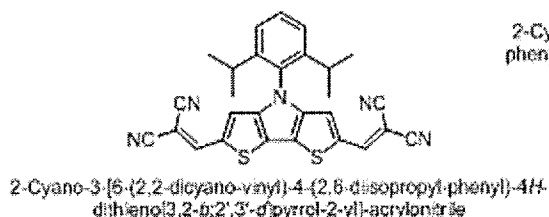
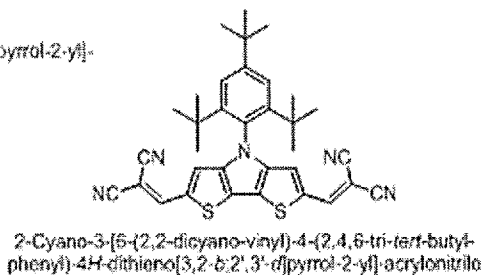
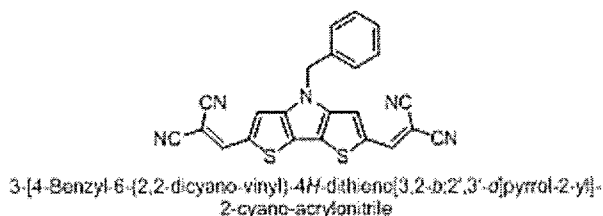
[0048] In a preferred embodiment, the thiophene-based molecule is represented by any of structures



2-Cyano-3-[6-(2,2-dicyano-vinyl)-4-ethyl-4H-dithieno[3,2-b;2',3'-d]pyrrol-2-yl]-acrylonitrile



2-Cyano-3-[6-(2,2-dicyano-vinyl)-4-(2-ethyl-hexyl)-4H-dithieno[3,2-b;2',3'-d]pyrrol-2-yl]-acrylonitrile



[0049] A molecule according to the present disclosure preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm), preferably in the range from 400 nm to 700 nm, or a sub-range thereof, preferably 400 nm to 500 nm, or 500 nm to 600 nm, or 600 nm to 700 nm.

[0050] A squaraine molecule represented by formula I according to the present invention preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and exhibits no absorption in the IR range (above 700 nm).

[0051] A thiophene molecule represented by formula II, III, IV, V or VI according to the present invention preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).

[0052] In one embodiment, the molecules of the present disclosure absorb in the blue absorption range.

[0053] In one embodiment, the molecules of the present disclosure absorb in the green absorption range.

[0054] In one embodiment, the molecules of the present disclosure absorb in the red absorption range.

[0055] Preferably, the molecules absorb less than 20% (more preferably less than 5%) of the maximum absorption outside of their main range of absorption, such as, at wavelengths shorter than 500 and longer than 600nm when absorption peak is between 500 and 600nm.

[0056] A molecule according to the present disclosure preferably shows an extinction coefficient of $> 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$, more preferably of $> 10^5 \text{ Lmol}^{-1}\text{cm}^{-1}$.

[0057] A molecule according to the present disclosure preferably allows furthermore:
[0058] easy alteration of HOMO and LUMO energies,
[0059] tuning of the absorption maximum (optical band gap) and shape over a broad range,
[0060] tuning of the molecular packing in films.
[0061] Films prepared from the molecules of the present disclosure preferably show
[0062] high electrons and holes mobilities,
[0063] high exciton diffusion efficiencies,
[0064] more preferably up to 99%.
[0065] Preferably those films are homogeneous (on the nm to μm scale) and even more preferably amorphous.

[0066] A molecule according to the present disclosure preferably exhibits a high photoelectric conversion efficiency of more than 15%, preferably of more than 50% and more preferably more than 80%.

[0067] As discussed above, the present disclosure provides the use of a molecule according to the present disclosure in an absorption layer.

[0068] In this embodiment, when the molecule according to the present invention is used in an absorption layer, the molecule (encompassing the squaraine molecules represented by formula I according to the present invention and the thiophene molecules represented by formula II, III, IV, V or VI according to the present invention) preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).

[0069] As discussed above, the present disclosure provides the use of a molecule according to the present disclosure in a filter.

[0070] In this embodiment, when the molecule according to the present invention is used as/in a filter, the molecule (encompassing the squaraine molecules represented by formula I according to the present invention and the thiophene molecules represented by formula II, III, IV, V or VI according to the present invention) preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).

[0071] As discussed above, the present disclosure provides the use of a molecule according to the present disclosure in a photoelectric conversion layer and/or in an organic and/or hybrid module for optoelectronic application, such as image sensor, photodiode, organic photovoltaics, comprising organic photoelectric conversion layer(s), OLED and OTFT organic modules.

[0072] As discussed above, the present disclosure provides a photoelectric conversion layer comprising at least one molecule according to the present disclosure.

[0073] In the embodiments, where the molecule according to the present invention is used or comprised in a photoelectric conversion layer,

- when the molecule of the present invention is the squaraine molecule represented by formula I according to the present invention, the molecule preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and exhibits no absorption in the IR range (above 700 nm).

- when the molecule of the present invention is the thiophene molecule represented by formula II, III, IV, V or VI according to the present invention, the molecule preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).

Here the application of the molecule(s) of the present disclosure is as active layer/component of a photoelectric conversion layer.

[0074] In one embodiment, the photoelectric conversion layer comprises further molecule(s).

[0075] As discussed above, the present disclosure provides an absorption layer or filter comprising at least one molecule according to the present disclosure.

[0076] As discussed above, the present disclosure provides a filter comprising at least one molecule according to the present disclosure.

[0077] In this embodiment, when the molecule according to the present invention is comprised in an absorption layer or filter, the molecule (encompassing the squaraine molecules represented by formula I according to the present invention and the thiophene molecules represented by formula II, III, IV, V or VI according to the present invention) preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).

Here the application of the molecule(s) of the present disclosure is as filter only, i.e. the films of molecules according to this disclosure are used only to absorb the light in the specific wavelength region (without to contribute to photoelectric conversion).

[0078] In one embodiment, the absorption layer or filter comprises further molecule(s).

[0079] Absorption layers (or filters) according to the present disclosure preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and possibly also absorption in the UV-Vis wavelength range (below 400 nm) and possibly also in the IR wavelength range (above 700 nm).

[0080] Absorption layers of the present disclosure absorb in the wavelength range of visible light, preferably in the range from 400 nm to 700 nm, or a sub-range thereof, preferably 400 nm to 500 nm, or 500 nm to 600 nm, or 600nm to 700 nm.

[0081] In one embodiment, the absorption layers of the present disclosure absorb in the blue absorption range.

[0082] In one embodiment, the absorption layers of the present disclosure absorb in the green absorption range.

[0083] In one embodiment, the absorption layers of the present disclosure absorb in the red absorption range.

[0084] Preferably, the the absorption layers absorb less than 20% (more preferably less than 5%) of the maximum absorption outside of their main range of absorption, such as, at wavelengths shorter than 500 and longer than 600 nm when absorption peak is between 500 and 600 nm.

[0085] In one embodiment, the photoelectric conversion layer comprises further molecules(s), wherein in one embodiment the molecule according to the present disclosure is the donor and the further molecule is the acceptor, wherein in another embodiment the molecule according to the present disclosure is the acceptor and one further molecule is the acceptor.

[0086] The photoelectric conversion layer can comprise different components (dyes) and combinations thereof.

[0087] In one embodiment, the photoelectric conversion layer and/or the absorption layer comprises further n and p type materials (molecules) that can be used together with the thiophene and or squaraine molecules(s) of the present disclosure, such as

phthalocyanine (Pc), subphthalocyanine (SubPc), merocyanine (MC), diketopyrrolopyrroles (DPP), borondipyrromethene (BODIPY), isoindigo (ID), perylene diimides (PDI), and quinacridone (QD), fused acenes, such as pentacene and tetracene and triphenylamine (TPA) as donor;

and/or

fullerenes, rylene diimides, phthalocyanines and subphthalocyanines and cyanopentacenes as acceptor.

[0088] In a preferred embodiment, said photoelectric (PE) conversion layer exhibits photo response in the visible absorption range.

[0089] The PE conversion layers according to the present disclosure preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and possibly also absorption in the UV-Vis wavelength range (below 400 nm) and in the IR wavelength range (above 700 nm).

[0090] The PE conversion layers of the present disclosure absorb in the wavelength range of visible light, preferably in the range from 400 nm to 700 nm, or a sub-range thereof, preferably 400 nm to 500 nm, or 500 nm to 600 nm, or 600nm to 700 nm.

[0091] In one embodiment, the PE layers of the present disclosure absorb in the blue absorption range (e.g.400-500nm).

[0092] In one embodiment, the molecules of the present disclosure absorb in the green absorption range (e.g. 500-600nm).

[0093] In one embodiment, the molecules of the present disclosure absorb in the red absorption range (e.g. 600-700nm).

[0094] Preferably, the PE layers absorb less than 20% (more preferably less than 5%) of the maximum absorption outside of their main range of absorption, such as, at wavelengths shorter than 500 and longer than 600nm when absorption peak is between 500 and 600nm.

[0095]

[0096] As discussed above, the present disclosure provides a device, comprising molecule(s) according to the present disclosure or photoelectric conversion layer(s) according to the present disclosure.

[0097] Said device of the present disclosure can be an organic image sensor, organic photovoltaics, organic photodiode, organic light-emitting diode (OLED), organic thin-film transistor (OTFT).

[0098] As discussed above, the present disclosure provides an organic image sensor, comprising photoelectric conversion layer(s) according to the present disclosure.

[0099] The organic image sensor of the present disclosure preferably comprises

- (a) an organic photoconversion unit comprising photoelectric conversion layer(s) according to the present disclosure,
- (b) at least one electrode,
- (c) a substrate,
- (d) optionally, a second electrode on top of said photoelectric conversion layer(s).

[00100] In a preferred embodiment, the organic image sensor does not comprise color filter(s).

[00101] The substrate can be silicon, quartz, glass, polymer, such as PMMA, PC, PS, COP, COP, PVA, PVP, PES, PET, PEN, mica, or combinations thereof.

[00102] The substrate can also be other photoelectric conversion unit(s) (e.g. blue 400-500nm and red 600-500nm conversion devices in case the organic conversion layer according to this disclosure is green 500-600nm conversion device).

[00103] This means, a device of this disclosure can comprise (i) two inorganic units with one organic unit, (ii) one inorganic unit with two organic units, or (iii) three organic units combined with each other in the organic image sensor. Any of the organic units can contain molecules/layers/devices according to this disclosure.

[00104] In a preferred embodiment, an organic image sensor consists of three organic conversion units containing molecules in layers as of this disclosure (in devices, each with transparent electrodes), combined with each other and operating each in one of the ranges 400nm to 500 nm, 500nm to 600 nm and 600 nm to 700nm.

[00105] Combined units can be realized either by vertical and/or horizontal stacking of the organic-organic or organic-inorganic units.

[00106] The electrode material can be

- transparent metal oxide, such as indium tin oxide (ITO), fluorine-doped indium oxide (IFO), tin oxide, fluorine-doped tin oxide (FTO), antimony-doped tin oxide (ATO), zinc oxide (including Al, B and Ga doped zinc Oxide), indium oxide-zinc oxide (IZO), TiO₂,
- non transparent or semitransparent metal or alloy or conductive polymer, such as Au, Ag, Cr, Ni, Pd, AlSiCu, or any metal or metal alloy or metal combination with suitable workfunction; PEDOT/PSS, PANI or PANI/PSS, graphene.

[00107] As discussed above, the present disclosure provides a hybrid Silicon-organic image sensor or organic image sensor, comprising

- (a) an organic photoelectric conversion unit or units comprising photoelectric conversion layer(s) according to the present disclosure (comprising the molecule(s) of the present disclosure),
- (b) optionally, a Si based photoelectric conversion unit,
- (c) metal wiring,
- (d) a (CMOS) substrate,
- (e) insulating layer(s), preferably oxide.

[00108] In one embodiment, said organic photoelectric conversion unit of the image sensors of the present disclosure comprises different layers within the organic based photoelectrical conversion unit(s), such as

- n-type material,
- p-type material,
- n-buffer layer,
- p-buffer layer,

or combinations and/or mixtures (e.g. n material and p material co-deposited in one layer) thereof.

[00109] For example, the organic image sensor of the present disclosure can have the structure:

- substrate/first electrode/n-buffer layer/n-material/p-material/p buffer layer/second electrode;

- substrate/first electrode/n-buffer layer/n-material/mixture of n- and p- material/ p-material/p buffer layer/second electrode;
- substrate/first electrode/n-buffer layer/n-material/mixture of n- and p- material/ p buffer layer/second electrode;
- substrate/first electrode/p-buffer layer/p-material/n-material/n buffer layer/second electrode.
- substrate/first electrode/p-buffer layer/p-material/ mixture of n- and p- material /n-material/n buffer layer/second electrode.
- substrate/first electrode/p-buffer layer/p-material/ mixture of n- and p- material /n buffer layer/second electrode.

[00110] The organic image sensor of the present disclosure can comprise different layer structures, in particular regarding the position of the n and p material with respect to the CMOS part.

[00111] The organic photoconversion unit can be used in combination with a Si based photoelectrical conversion unit where different layers absorb different color (BGR) in a hybrid silicon-organic image sensor (see Figure 2) or can be used without Si based photoelectrical conversion unit. In this case the organic photoconversion unit has the capability of absorbing different color (BGR) (see Figure 3).

[00112] The BGR ranges are 400-500 nm, 500-600 nm and 600-700nm and the absorption outside of the range is preferably less than 20%, more preferably less than 10 and 5%.

[00113] As discussed above, the substrate can also be other photoelectric conversion unit(s) (e.g. blue 400-500nm and red 600-500nm conversion devices in case the organic conversion layer according to this disclosure is green 500-600nm conversion device).

[00114] As discussed above, a device of this disclosure can comprise (i) two inorganic units with one organic unit, (ii) one inorganic unit with two organic units, or (iii) three organic units combined with each other in the organic image sensor. Any of the organic units can contain molecules/layers/devices according to this disclosure.

[00115] The deposition methods to produce the organic photoelectrical conversion layer are PVD, CVD, spin coating, dipping coating, casting process, inkjet printing, screen printing, spray coating, offset printing.

[00116] Different process temperatures for processing the layer are possible, namely from 150 to 245°Celsius.

[00117] As discussed above, the present disclosure provides a method for synthesis of a squaraine molecule according to the present disclosure.

[00118] Said method comprises the following step(s) (in embodiments wherein the squaraine molecule has a symmetric structure):

Attaching the donor group to the core by reacting the appropriate reagent with squaric acid in a refluxing azeotropic water removal mixture;

[00119] or said method comprises the following step(s) (in embodiments wherein the squaraine molecule has an asymmetric structure):

Attaching the first donor group to the core by reacting the appropriate reagent with diethyl squarate in the presence of alkylamine as catalyst, and

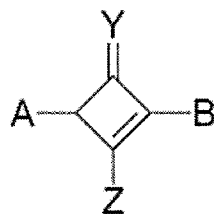
After deprotecting the ester with aqueous NaOH, reacting the semiquarate precursor with the second donor molecule in a refluxing azeotropic water removal mixture.

[00120] As discussed above, the present disclosure provides a method for synthesis of a thiophene-based molecule according to the present disclosure.

[00121] Said method comprises the following step(s): dithieno thiophenes, dithienopyrroles and dithienosiloles are reacted by condensation reaction or metal catalyzed with the desired group.

[00122] Note that the present technology can also be configured as described below.

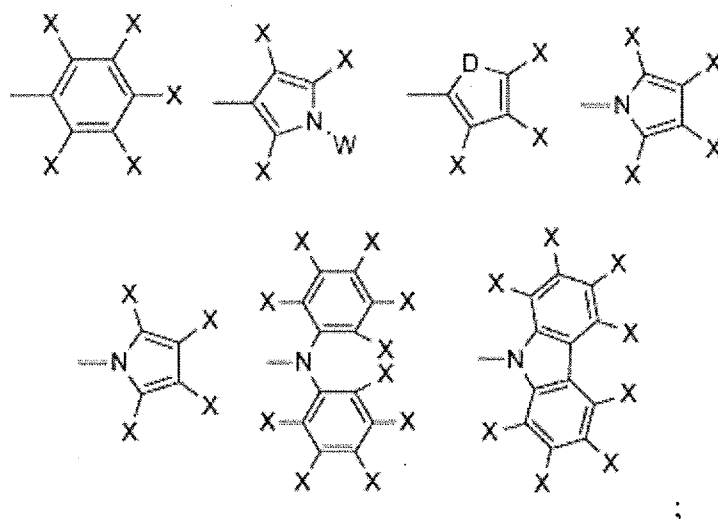
(1) A (squaraine) molecule represented by formula I



(I)

wherein

A and **B** are the same or different and are, at each occurrence, independently selected from



pyrazole, thiazole, imidazole, indole, quinoline, benzothiophene, benzothiazole, benzothiadiazole, benzofuran, oxazole, benzoxazole, pyridine, diazine, triazine, selenophene, naphthalene, anthracene or pyrene, any of which can optionally be substituted,

optionally comprising a spacer, such as a double bond (e.g. in an embodiment, where A and/or B is indole),

D is S or O;

W is selected from H, alkyl, aryl;

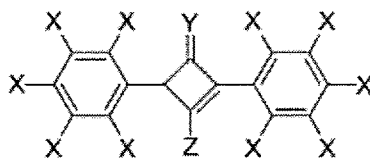
X is selected from the group including H, OH, SH, NH₂, NHR, NR₂, NO₂, alkyl, alkoxy, aryl, aryloxy, halogen, such as F, Cl, Br, I;

Y is selected from O, S, NH, NR, NC—CN, NC—COOH, HOOC—COOH, indanedione, barbituric acid or thiobarbituric acid;

Z is selected from OH, SH, NH₂, NR₂;

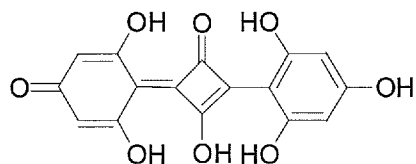
R, at each occurrence, is independently selected from H or any straight or branched alkyl chain of general formula —C_nH_{2n+1}, or —COOR¹, —OR¹, —SR¹, —NR¹₂, or F, Cl, Br, I, O, N, NO₂, CN, CF₃, wherein **R**¹ is H or any straight or branched alkyl chain of general formula —C_nH_{2n+1}, or any substituted or non-substituted phenyl or biphenyl, heteroaryl, **n** = 0-12, preferably 0-6.

(2) The molecule according to embodiment (1), wherein the molecule is represented by formula Ia

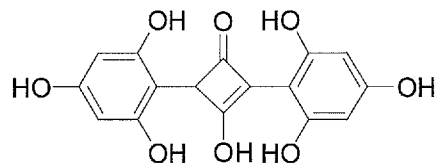


wherein X, Y and Z are as defined in embodiment (1).

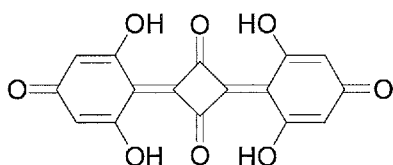
- (3) The molecule according to embodiment (1) represented by any of structures



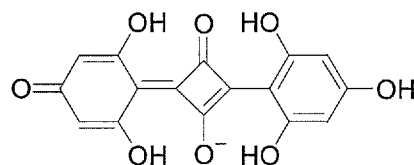
3,5-Dihydroxy-4-[2-hydroxy-4-oxo-3-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enylidene]-cyclohexa-2,5-dienone



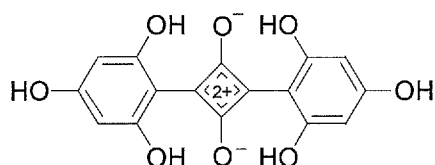
3-Hydroxy-2,4-bis-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enone



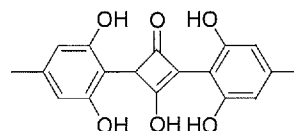
2,4-Bis-(2,6-dihydroxy-4-oxo-cyclohexa-2,5-dienylidene)-cyclobutane-1,3-dione



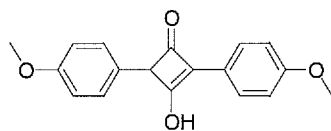
4-(2,6-Dihydroxy-4-oxo-cyclohexa-2,5-dienylidene)-3-oxo-2-(2,4,6-trihydroxy-phenyl)-cyclobut-1-enol anion



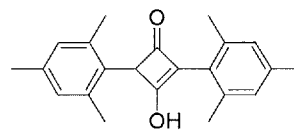
2,4-Bis-(2,6-dihydroxy-4-methoxy-phenyl)-3-hydroxy-cyclobut-2-enone



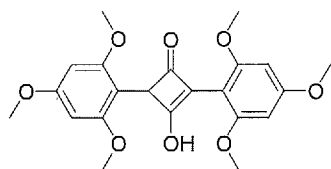
2,4-Bis-(2,6-dihydroxy-4-methyl-phenyl)-3-hydroxy-cyclobut-2-enone



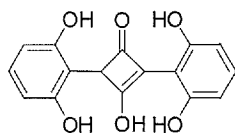
3-Hydroxy-2,4-bis-(4-methoxy-phenyl)-cyclobut-2-enone



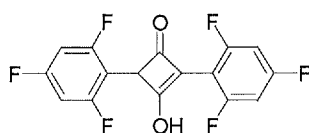
3-Hydroxy-2,4-bis-(2,4,6-trimethyl-phenyl)-cyclobut-2-enone



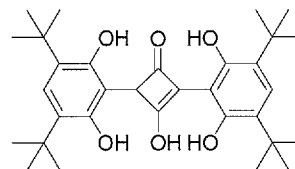
3-Hydroxy-2,4-bis-(2,4,6-trimethoxy-phenyl)-cyclobut-2-enone



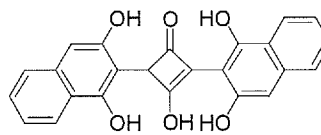
2,4-Bis-(2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



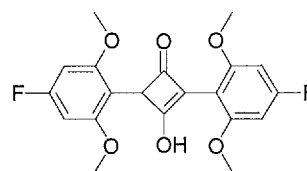
3-Hydroxy-2,4-bis-(2,4,6-trifluoro-phenyl)-cyclobut-2-enone



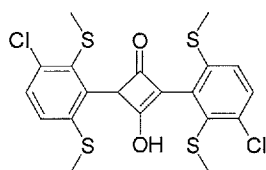
2,4-Bis-(3,5-di-tert-butyl-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



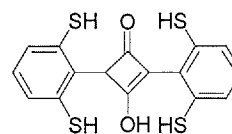
2,4-Bis-(1,3-dihydroxy-naphthalen-2-yl)-3-hydroxy-cyclobut-2-enone



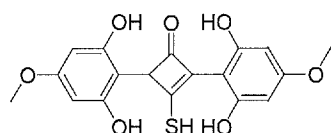
2,4-Bis-(4-fluoro-2,6-dimethoxy-phenyl)-3-hydroxy-cyclobut-2-enone



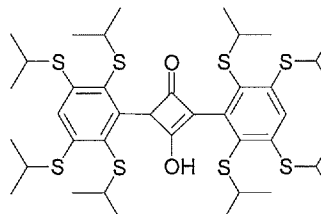
2,4-Bis-(3-chloro-2,6-bis-methylsulfanyl-phenyl)-3-hydroxy-cyclobut-2-enone



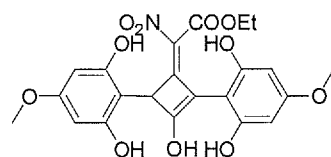
2,4-Bis-(2,6-dimercapto-phenyl)-3-hydroxy-cyclobut-2-enone



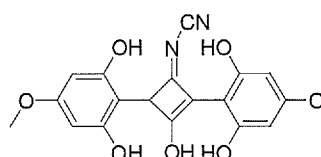
2,4-Bis-(2,6-dihydroxy-4-methoxy-phenyl)-3-mercapto-cyclobut-2-enone



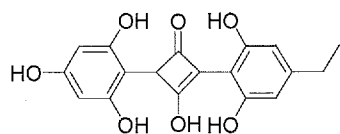
3-Hydroxy-2,4-bis-(2,3,5,6-tetrakis-isopropylsulfanyl-phenyl)-cyclobut-2-enone



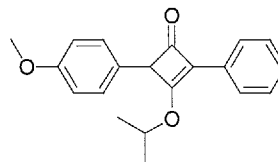
[2,4-Bis-(2,6-dihydroxy-4-methoxy-phenyl)-3-hydroxy-cyclobut-2-enylidene]-nitro-acetic acid ethyl ester



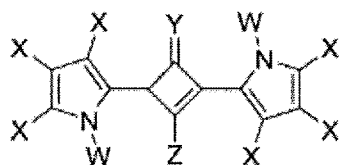
2,4-Bis-(2,6-dihydroxy-4-methoxy-phenyl)-3-hydroxy-cyclobut-2-enylidene-cyanamide



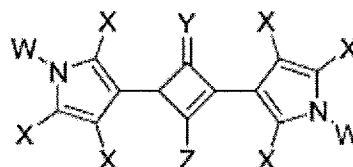
2-(4-Ethyl-2,6-dihydroxy-phenyl)-3-hydroxy-4-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enone

3-isopropoxy-4-(4-methoxy-phenyl)-
2-phenyl-cyclobut-2-enone

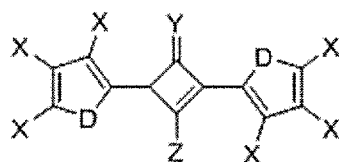
- (4) The molecule according to embodiment (1), wherein the molecule is represented by any one of



formula Ib,

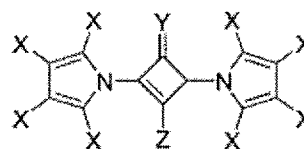


formula Ic,

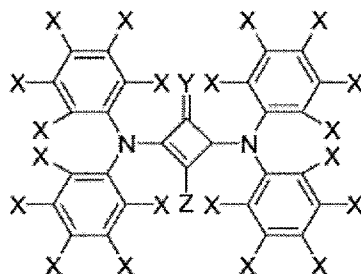


formula Id,

wherein D is S or O,

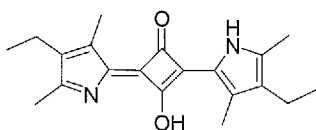
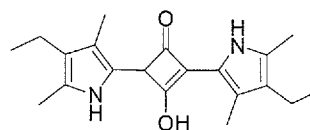
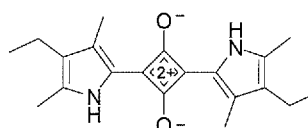
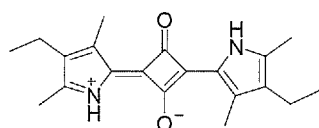


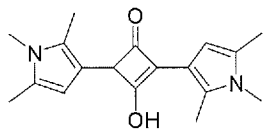
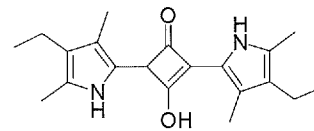
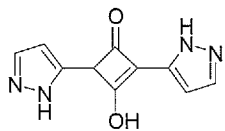
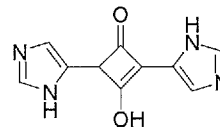
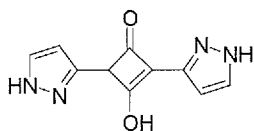
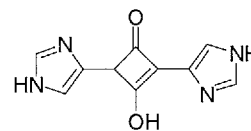
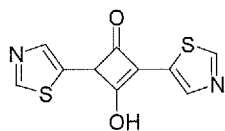
formula Ie, or



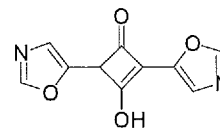
formula If.

- (5) The molecule according to embodiment (3) represented by any of structures

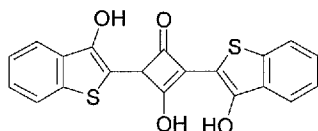
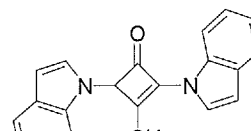
2-(4-Ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-4-(4-ethyl-3,5-
dimethyl-pyrrol-2-ylidene)-3-hydroxy-cyclobut-2-enone2,4-Bis-(4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-
3-hydroxy-cyclobut-2-enone

3-Oxo-2-(1,2,5-trimethyl-1*H*-pyrrol-3-yl)-4-(1,2,5-trimethylpyrrol-3-ylidene)-cyclobut-1-enol anion2,4-Bis-(4-ethyl-3,5-dimethyl-1*H*-pyrrol-2-yl)-3-hydroxy-cyclobut-2-enone3-Hydroxy-2,4-bis-(2*H*-pyrazol-3-yl)-cyclobut-2-enone3-Hydroxy-2,4-bis-(3*H*-imidazol-4-yl)-cyclobut-2-enone3-Hydroxy-2,4-bis-(1*H*-pyrazol-3-yl)-cyclobut-2-enone3-Hydroxy-2,4-bis-(1*H*-imidazol-4-yl)-cyclobut-2-enone

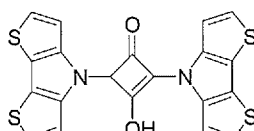
3-Hydroxy-2,4-bis-thiazol-5-yl-cyclobut-2-enone



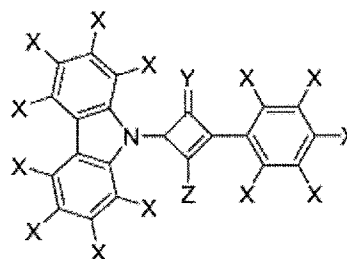
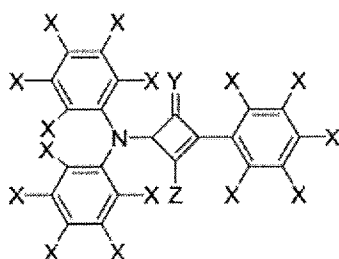
3-Hydroxy-2,4-bis-oxazol-5-yl-cyclobut-2-enone

3-Hydroxy-2,4-bis-(3-hydroxybenzo[*b*]thiophen-2-yl)-cyclobut-2-enone

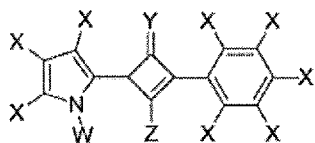
3-Hydroxy-2,4-bis-indol-1-yl-cyclobut-2-enone

2,4-Bis-dithieno[3,2-*b*;2',3'-*d*]pyrrol-4-yl-3-hydroxy-cyclobut-2-enone

(6) The molecule according to embodiment (1), wherein the molecule is represented by any one of

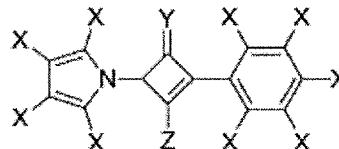


formula Ig,



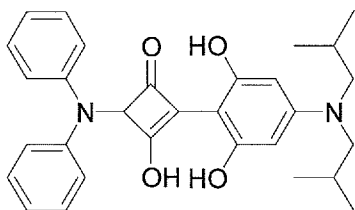
formula Ii, or

formula Ih,

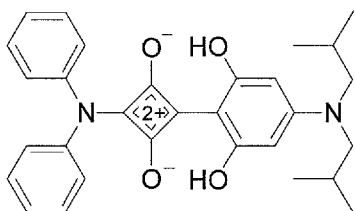
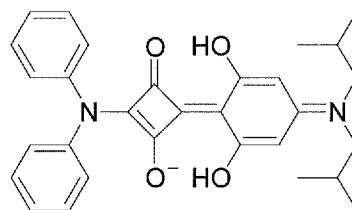


formula Ij.

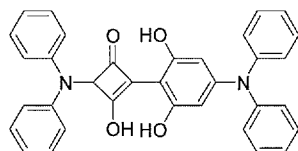
(7) The molecule according to embodiment (6) represented by any of structures



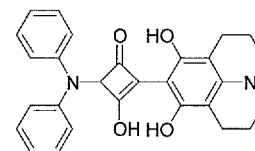
2-(4-Diisobutylamino-2,6-dihydroxy-phenyl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



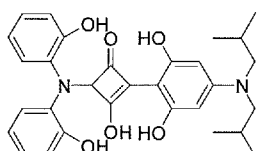
2-(4-Diisobutylamino-2,6-dihydroxy-phenyl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



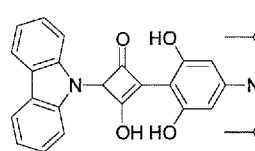
4-Diphenylamino-2-(4-diphenylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



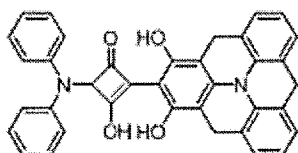
2-(8,10-Dihydroxy-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



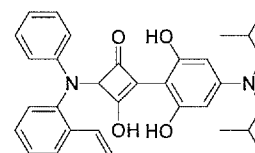
4-[Bis-(2-hydroxy-phenyl)-amino]-2-(4-diisobutylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



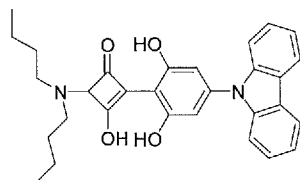
4-Carbazol-9-yl-2-(4-diisobutylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



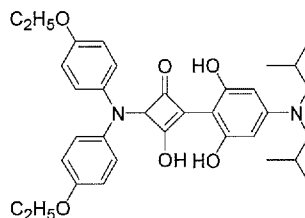
2-(1,3-Dihydroxy-4H,8H,12H-12c-aza-dibenzo[cd,mm]pyren-2-yl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



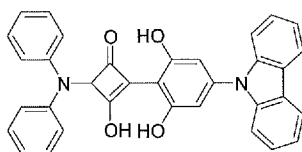
2-(4-Diisobutylamino-2,6-dihydroxy-phenyl)-3-hydroxy-4-(naphthalen-1-yl-phenyl-amino)-cyclobut-2-enone



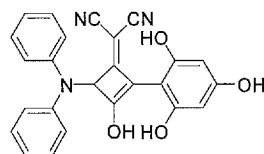
4-Dibutylamino-2-(4-diphenylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



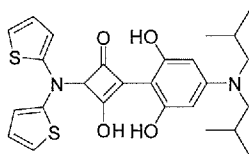
4-[Bis-(4-ethoxy-phenyl)-amino]-2-(4-diisobutylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



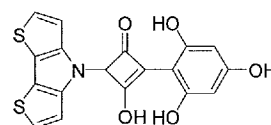
2-(4-Carbazol-9-yl-2,6-dihydroxy-phenyl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



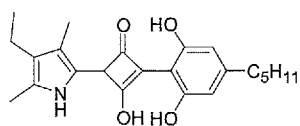
2-[4-Diphenylamino-3-hydroxy-2-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enylidene]-malononitrile



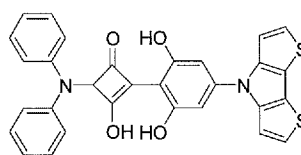
2-(4-Diisobutylamino-2,6-dihydroxy-phenyl)-4-(di-thiophen-2-yl-amino)-3-hydroxy-cyclobut-2-enone



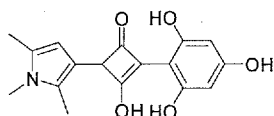
4-Dithieno[3,2-b;2',3'-d]pyrrol-4-yl-3-hydroxy-2-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enone



2-(2,6-Dihydroxy-4-pentyl-phenyl)-4-(4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-3-hydroxy-cyclobut-2-enone

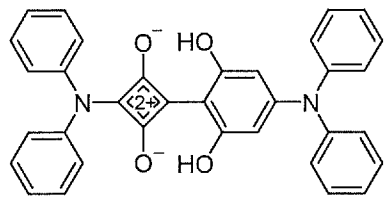
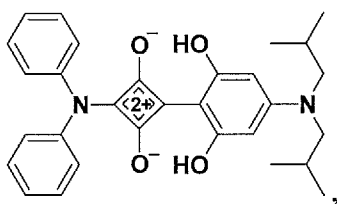


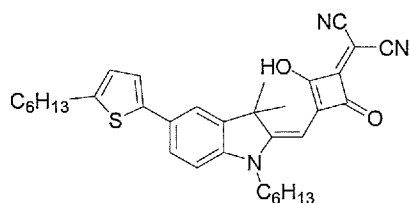
4-Diphenylamino-2-(4-dithieno[3,2-b;2',3'-d]pyrrol-4-yl)-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



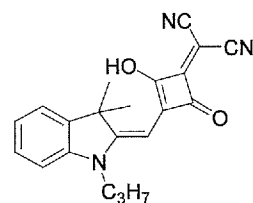
3-Hydroxy-2-(2,4,6-trihydroxy-phenyl)-4-(1,2,5-trimethyl-1H-pyrrol-3-yl)-cyclobut-2-enone

(8) The molecule according to embodiment (1) represented by any of structures

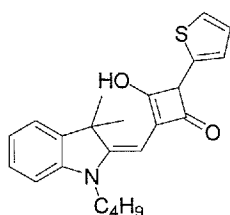




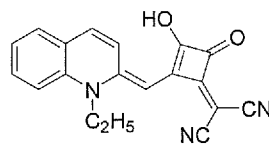
2-[3-[1-Hexyl-5-(5-hexyl-thiophen-2-yl)-3,3-dimethyl-1,3-dihydro-indol-2-ylidenemethyl]-2-hydroxy-4-oxo-cyclobut-2-enylidene]-malononitrile



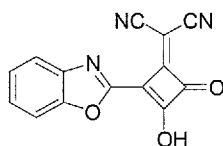
2-[3-(3,3-Dimethyl-1-propyl-1,3-dihydro-indol-2-ylidenemethyl)-2-hydroxy-4-oxo-cyclobut-2-enylidene]-malononitrile



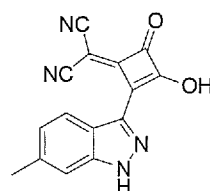
2-(1-Butyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidenemethyl)-3-hydroxy-4-thiophen-2-yl-cyclobut-2-enone



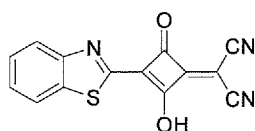
2-[2-(1-Ethyl-1H-quinolin-2-ylidenemethyl)-3-hydroxy-4-oxo-cyclobut-2-enylidene]-malononitrile



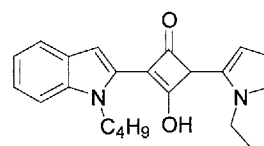
2-(2-Benzothiazol-2-yl-3-hydroxy-4-oxo-cyclobut-2-enylidene)-malononitrile



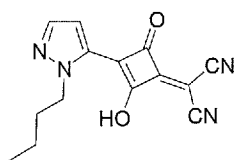
2-[3-Hydroxy-2-(6-methyl-1H-indazol-3-yl)-4-oxo-cyclobut-2-enylidene]-malononitrile



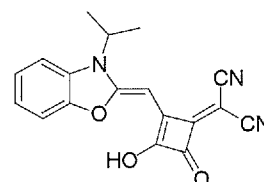
2-(3-Benzothiazol-2-yl-2-hydroxy-4-oxo-cyclobut-2-enylidene)-malononitrile



2-(1-Butyl-1H-indol-2-yl)-(1-ethyl-1H-pyrrol-2-yl)-3-hydroxy-cyclobut-2-enone

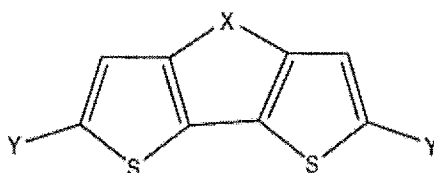


2-[3-(2-Butyl-2H-pyrazol-3-yl)-2-hydroxy-4-oxo-cyclobut-2-enylidene]-malononitrile

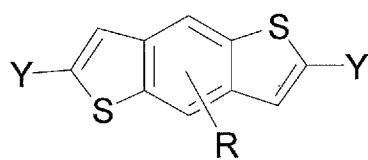


2-[3-Hydroxy-2-(3-isopropyl-3H-benzooxazol-2-ylidenemethyl)-4-oxo-cyclobut-2-enylidene]-malononitrile

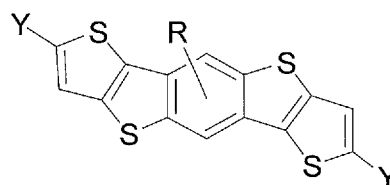
(9) A (thiophene-based) molecule represented by a formula selected from formula II, III, IV, V and VI



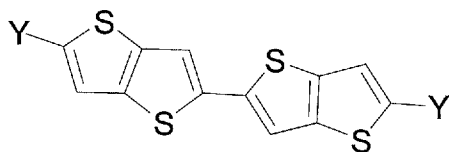
(II)



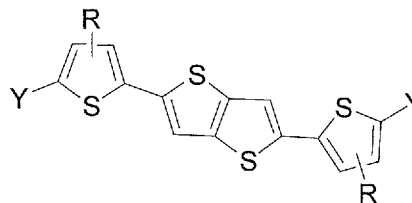
(III)



(IV)



(V)



(VI)

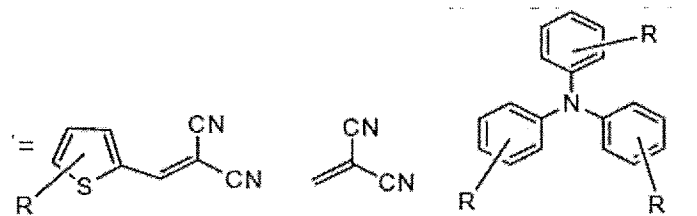
wherein

X is selected from the group including S, Se, N-R¹, SO₂, CR¹₂, cyclopentane, cyclohexane, SiR¹₂;

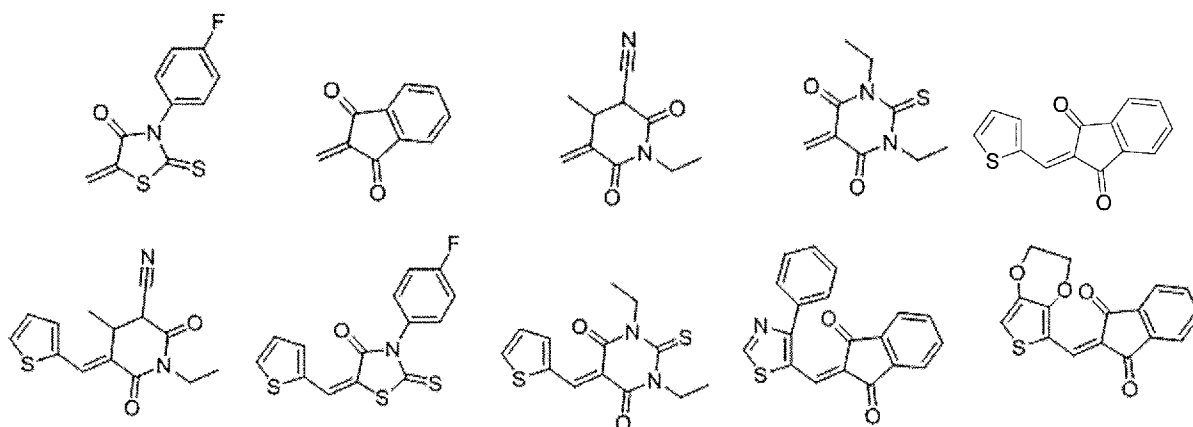
R¹ is selected from aryl, alkyl;

R is selected from H, aryl, substituted aryl, alkyl, thiophene, alkyl-substituted thiophene;

Y is selected from

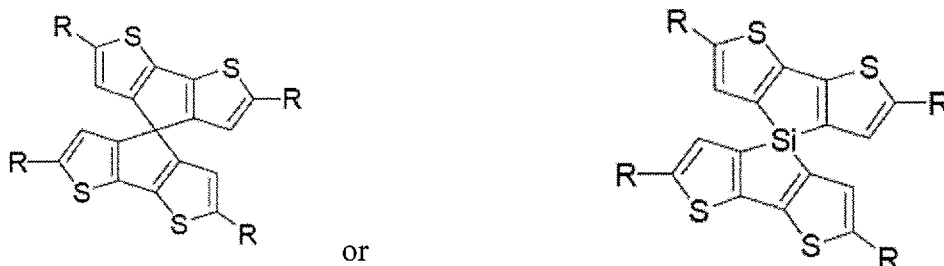


carbazole, diarylamine, pyrrole, pyrazole, thieno[3,4-b]pyrazine, imidazole, thiazole, fluorine, tricyanovinyl, indole, quinolone, benzothiadiazole, indanedione, barbituric acid or thiobarbituric acid, rhodanine, thiazolinedione derivatives as for example:



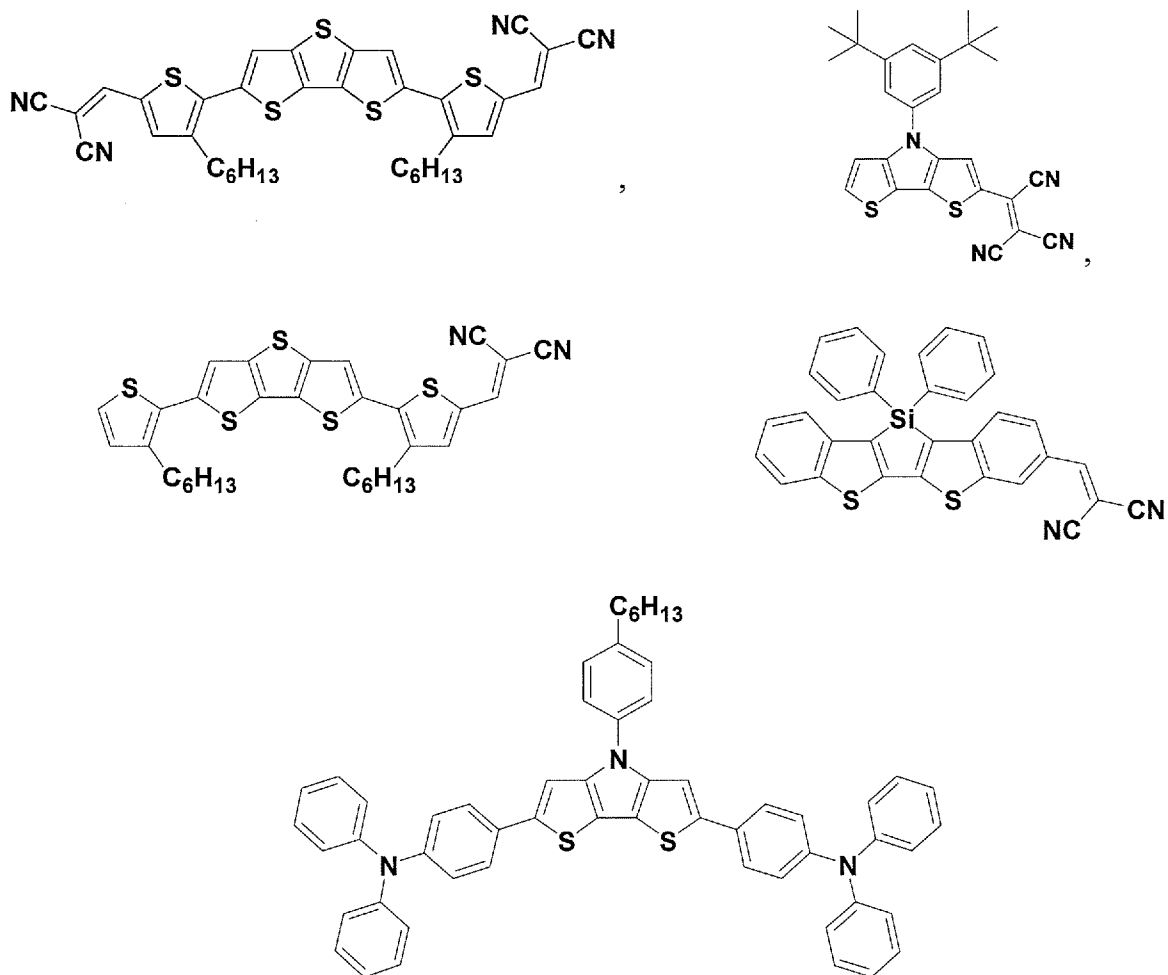
R is selected from H, aryl, substituted aryl, alkyl, thiophene, alkyl-substituted thiophene.

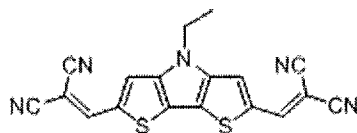
(10) The molecule according to embodiment (9) which is a spiro-dimer selected from



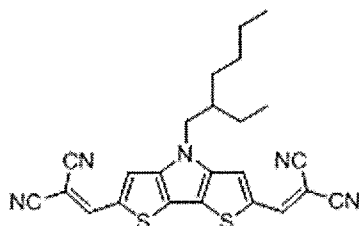
wherein R is the same as the R / as defined in embodiment (9).

(11) The molecule according to embodiment (9) represented by any of structures

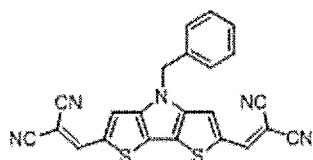




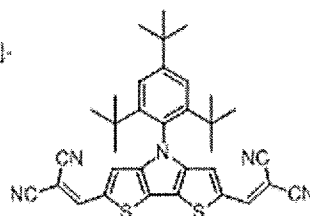
2-Cyano-3-[6-(2,2-dicyano-vinyl)-4-ethyl-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl]-acrylonitrile



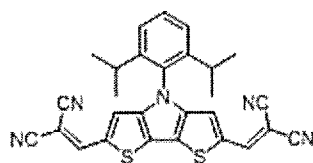
2-Cyano-3-[6-(2,2-dicyano-vinyl)-4-(2-ethyl-hexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl]-acrylonitrile



3-[4-Benzyl-6-(2,2-dicyano-vinyl)-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl]-2-cyano-acrylonitrile



2-Cyano-3-[6-(2,2-dicyano-vinyl)-4-(2,4,6-tri-tert-butyl-phenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl]-acrylonitrile



2-Cyano-3-[6-(2,2-dicyano-vinyl)-4-(2,6-diisopropyl-phenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl]-acrylonitrile

(12) The molecule according to any one of embodiments (1) to (8), wherein the molecule

- exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and exhibits no absorption in the IR range (above 700 nm).

(13) The molecule according to any one of embodiments (9) to (11), wherein the molecule

- exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and
- optionally, exhibits also absorption in the IR range (above 700 nm).

(14) The molecule according to any one of embodiments (1) to (13), wherein furthermore the molecule

- absorbs in the blue absorption range or absorbs in the green absorption range or absorbs in the red absorption range,
- preferably shows an extinction coefficient of $> 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$,
- absorbs less than 20% (more preferably less than 5%) of the maximum absorption outside of its main range of absorption.

and/or

- exhibits a high photoelectric conversion efficiency of more than 15%, preferably of more than 50% and more preferably more than 80%.

(15) Use of a molecule according to any of embodiments (1) to (14) in an absorption layer, wherein the molecule preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).

(16) Use of a molecule according to any of embodiments (1) to (14) in a filter, wherein the molecule preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).

(17) Use of a molecule according to any of embodiments (1) to (14) in a photoelectric conversion layer and/or in an organic and/or hybrid module for optoelectronic application, such as image sensor, photodiode, organic photovoltaics, including organic photoelectric conversion layer(s), OLED and OTFT organic modules.

(18) A photoelectric conversion layer including a molecule according to any one of embodiments (1) to (14), optionally including further molecule(s).

(19) An absorption layer including a molecule according to any one of embodiments (1) to (14), optionally including further molecule(s), wherein the molecule preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).

(20) A filter including a molecule according to any one of embodiments (1) to (14), optionally including further molecule(s), wherein the molecule preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).

(21) A device, including molecule(s) according to any one of embodiments (1) to (14) or photoelectric conversion layer(s) according to embodiment (18), wherein said device is preferably an organic image sensor, an hybrid image sensor, photodiode, organic photovoltaics, *organic light-emitting diode* (OLED), *organic thin-film transistor* (OTFT).

(22) The device according to embodiment (21), wherein said photoelectric conversion layer exhibits photo response in the visible absorption range.

(23) The device according embodiment (21) or (22), including molecule(s) according to any one of embodiments (1) to (14) or photoelectric conversion layer(s) according to embodiment (18),

and/or including further molecule(s).

(24) An organic image sensor, including

(a) an organic photoelectric conversion unit including photoelectric conversion layer(s) according to embodiment (18),

(b) at least one electrode,

(c) a substrate,

(d) optionally, a second electrode on top of said photoelectric conversion layer(s), preferably not including color filter(s).

(25) A hybrid Silicon-organic image sensor or organic image sensor, including

(a) an organic photoelectric conversion unit or units including photoelectric conversion layer(s) according to embodiment (18),

(b) optionally, a Si based photoelectric conversion unit,

(c) metal wiring,

(d) a (CMOS) substrate,

(e) insulating layer(s), preferably oxide.

(26) The organic image sensor according to embodiment (24) or embodiment (25), wherein said organic photoelectric conversion unit includes different layers, such as n-type material, p-type material, n-buffer layer and/or p-buffer layer or combinations or mixtures thereof.

(27) A method for synthesis of a molecule according to any one of embodiments (1) to (8), including the following step(s):

Attaching the donor group to the core by reacting the appropriate reagent with squaric acid in a refluxing azeotropic water removal mixture,

or including the following step(s):

Attaching the first donor group to the core by reacting the appropriate reagent with diethyl squarate in the presence of alkylamine as catalyst, and

After deprotecting the ester with aqueous NaOH, reacting the semiquarate precursor with the second donor molecule in a refluxing azeotropic water removal mixture.

(28) A method for synthesis of a molecule according to any one of embodiments (9) to (11), including the following step(s):

Reacting dithieno thiophenes, dithienopyrroles and dithienosiloles by condensation reaction or metal catalyzing with the desired group.

[00123] The term “squaraine molecule” or “squaraine-based molecule”, as used herein, refers to a molecule having one or several aromatic ring systems attached to a squaraine core, which aromatic ring systems, if there are several such ring systems, may be identical (symmetric dye) or different (asymmetric dye).

[00124] The term “thiophene molecule” or “thiophene-based molecule”, as used herein, refers to a molecule having at least two thiophene molecules directly connected to each other, and the term “spiro-thiophene molecule”, as used herein, refers to a molecule having at least three condensate ring in which at least two are thiophene rings

[00125] The term “absorption in the visible wavelength range” or “dye exhibiting absorption in the visible wavelength range”, as used herein, is meant to refer to a molecule/dye that is able to absorb light in only one or several parts of the entire range indicated or over the total range. For example a molecule may only absorb in the range of from 500 – 700 nm, whereas another molecule may absorb in the range of from 400 – 700 nm or 500 – 600 nm, whereas a third molecule may absorb over the range of from 400 – 500 nm (or the above described sub-ranges of preferably 400 nm to 500 nm, or 500 nm to 600 nm, or 600 nm to 700 nm). All these scenarios are meant to be encompassed by such wording.

[00126] The term “no absorption in the IR range” or “dye exhibiting no absorption in the IR range”, as used herein, is meant to refer to a molecule/dye that is able to absorb light in wavelength ranges until but not above 700 nm.

[00127] The term “narrow absorption band”, as used herein, is meant to refer to / means that the width of the absorption band at 0 intensity is 200 nm , more preferably 150 nm, more preferably 100 nm.

[00128] The term “intense absorption band”, as used herein, is meant to refer to / means that the extinction coefficient $\epsilon > 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$.

[00129] In accordance with the present disclosure, the term "electrode" refers to an electrical lead to apply voltage. An electrode may be "interdigitated", meaning that it has a comb-like

shape with two combs lying opposite each other and the respective figures of the combs engaging with each other. Alternatively, an electrode may be a non-interdigitated. An electrode may be transparent or non-transparent. A transparent electrode may, for example, be formed from indium tin oxide (ITO) or from fluorinated tin oxide (FTO). A non-transparent electrode may be reflective and may, for example, be formed from silver (Ag) or gold (Au).

[00130] The requirements of a photoelectric conversion layer to be used in image sensors are demanding and can be summarised as followed:

- (i) narrow absorption band;
- (ii) high extinction coefficient, $\epsilon > 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$ (for high sensitivity in thin film);
- (iii) heat resistant;
- (iv) high photoelectric conversion efficiency (EQE);
- (v) high-speed responsivity / high charge carrier mobility;
- (vi) low dark-current in device;
- (vii) thin film by thermal vapour deposition ($T_{vp} < T_{dec}$).

[00131] The present inventors have found novel squaraines and thiophene based dyes / molecules which are highly suitable as active materials for organic photoelectric conversion layers with improved conversion efficiency and response speed in organic photodiodes for vertically-integrated (VI) CMOS image sensors application. The advantages of those materials with respect to the requirements, the different type of possible molecular structures and example of molecules for use as photoelectrical conversion layer are reported herein.

[00132] The present disclosure relates to squaraine dyes / molecules and thiophene base dyes / molecules with specific molecular formulas that absorb in the visible range (400-700nm) and their use as active materials for use in bulk heterojunction or PN or PiN junction as photoelectric conversion layer.

[00133] The squaraine dyes / molecules of the present disclosure can be used as active materials for the organic photoconversion unit.

[00134] The organic photoconversion unit can be used in combination with a Si based photoelectrical conversion unit where different layer absorbed different colour (BGR) in a hybrid Silicon-organic image sensor or can be used without Si based photoelectrical

conversion unit. In this case the organic photoconversion unit having the capability of absorbing different colour (BGR).

[00135] The general structure of the resulting hybrid image sensor device as well as the details of the organic based photoelectrical conversion unit are schematic represented in the Figure 2 and 3.

[00136] The squaraine dyes / molecules of the present disclosure have a donor-acceptor-donor structure, wherein A and B are donor group (electron donating groups), while the central part (squaraine core) is the acceptor part (electron withdrawing group).

[00137] The main advantages of the squaraine dyes / molecules of the present disclosure for the application in photoelectrical conversion layers are as follows:

- (1) narrow and intense absorption bands (extinction coefficient $\epsilon > 10^5 \text{ Lmol}^{-1}\text{cm}^{-1}$);
- (2) high photoelectric conversion efficiencies (xerographic applications);
- (3) processability already proven for organic photovoltaics (OPV), photodetectors and organic imager as IR absorber (absorption $> 700 \text{ nm}$) (for this dye type)

[00138] The absorption and energy levels of the squaraine dyes / molecules of the present disclosure are tunable by the type of donor attached to the squaric acid/squaraine core.

Moreover, squaraine dyes are known to form aggregates in thin films that cause a broadening of the absorption peak. The molecular packing and the morphology of the solid state thin film can be tuned varying the substituent groups X in the donor moieties A and B. This makes the squaraine dyes / molecules of the present disclosure a very versatile dye / molecule to be used in the organic photoelectric conversion layer.

[00139] The main advantages of the thiophene-based dyes / molecules of the present disclosure for the application in photoelectrical conversion layer are as follow:

- (1) absorption range in the required wavelength range with intense absorption bands (extinction coefficient $\epsilon > 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$);
- (2) excellent charge transport properties;
- (3) thermally stable, thermal vapour deposition possible;
- (4) processability already proven for application in organic photovoltaics (OPV) (for this dye type).

[00140] The absorption, energy levels and morphology of the thiophene-based dyes / molecules of the present disclosure can be tuned by molecular structure variation. The spiro-unit narrows the absorption band width by reducing the degree of vibrational freedom in the thiophene conjugated chain.

[00141] In specific embodiments, different molecular dye / molecule structures, different components and combination of the photoelectric conversion layer (list of possible electrodes, list of other possible n and p type materials that could be used together with the thiophene and or squaraine, list of different n and p type buffer layer), different layer structures (position of the n and p material with respect to the electrodes) and different process temperature for processing the layer (from 150 to 245°Celsius) are described herein.

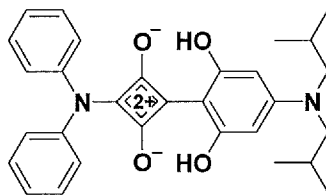
[00142] The dyes / molecules of the present disclosure and their use in photoelectric conversion layers have the following advantages:

- (1) no color filter(s) is/are needed and therefore no moiré and shading;
- (2) no color filter(s) is/are needed and therefore higher brightness;
- (3) less process steps and therefore cost reduction;
- (4) high color reproducibility (less false color);
- (5) high sensitivity and pixel resolution;
- (6) new IP and therefore less cost reduction;
- (7) dyes with high extinction coefficient - less material needed.

EXAMPLES

EXAMPLE 1: Squaraine molecule

[00143] The inventors used a specific asymmetrical N,N-diarylanilino squarylium molecule (DAASQ) (SQ3) as n-type material, green absorber as part of the organic photoelectric conversion unit.



[00144] The absorption of the molecule in solution and in the solid state fits perfectly with the requirements (see Figure 4).

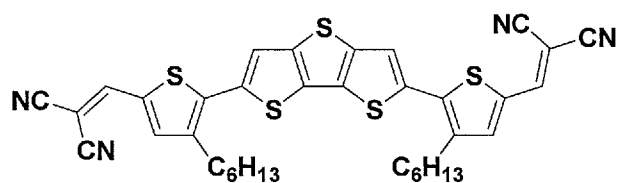
[00145] Furthermore, no broadening of the absorption peak occurred even after annealing at higher temperature (130°C for 1h, 180°C for 5min, 245°C for 5 min) , often needed during the processing of the image sensor device.

[00146] The thermal properties are also in line with the requirements, $T_{\text{evaporation}} = 210^{\circ}\text{C}$ ($3 \cdot 10^{-7}$ mbar) $< T_{\text{decomposition}} = 310^{\circ}\text{C}$.

[00147] The squaraine molecule SQ3 was used as donor material in combination with subphthalocyanine fluoride (SubPcF) as acceptor in the following configuration: ITO / SQ3 30nm / SubPcF 30nm / BPhen 3.5nm / AlSiCu 100nm / LiF 100nm. The layer gave an External Quantum Efficiency (EQE) of 5.6% at 585nm and at 0V (Figure 5).

EXAMPLE 2: Thiophene molecule

[00148] The inventors used of a specific spiro thiophene derivative (Spiro-4T) as p-type material, green absorber as part of the photoelectric conversion layer in an organic image sensor module.



[00149] The absorption of the molecule in solution and in the solid state fits perfectly with the requirements (see Figure 6).

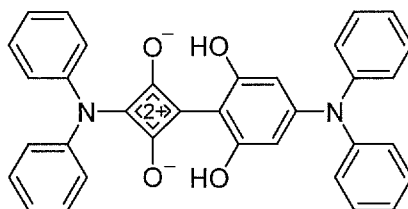
[00150] The absorption in thin film stays constant even after annealing at higher temperature (130°C for 1h, 180°C for 5min, 245°C for 5 min), often needed during the processing of the image sensor device.

[00151] The thermal properties are also in line with the requirements $T_{\text{evaporation}} = 210^{\circ}\text{C}$ ($3 \cdot 10^{-7}$ mbar) $< T_{\text{decomposition}} = 350^{\circ}\text{C}$.

[00152] The thiophene derivate Spiro-4T was used as donor material in combination with subphthalocyanine chloride (SubPc-Cl) as acceptor in the following configuration: ITO/10nm Spiro-4T/Spiro-4T & SubPc-Cl 120nm/10nm SubPc-Cl /AlSiCu 100nm/LiF 100nm. The device gave an EQE (535nm LED) of 0.5% at 0V and 2% at -1V.

EXAMPLE 3: Squaraine molecule

[00153] A further squaraine derivative was used, called 4-Diphenylamino-2-(4-diphenylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone (SQ8).

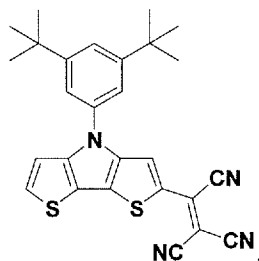


[00154] The absorption of the dye in solution and in the solid state fits perfectly with the requirements (see Figure 7).

[00155] The squaraine SQ8 was used as donor material in combination with subphthalocyanine chloride (SubPc-Cl) as acceptor in the following configuration: ITO /SQ8 50nm/ SubPc-Cl 50nm / NBPhen 3,5 nm /AlSiCu 100 nm /LiF 100nm. The device showed and EQE of 0.7 % at 0V and 2% at -1V (Figure 8).

EXAMPLE 4: Thiophene molecule

[00156] A further thiophene molecule derivative was used, called N-(di-tert-butylphenyl)-(tricyanovinyl)-dithienopyrrole (DTP3)

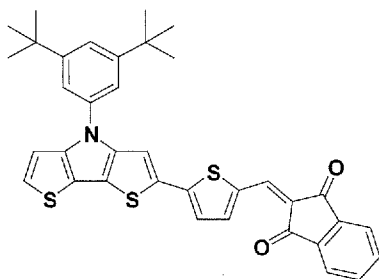


[00157] The absorption of the molecule in solution fits with the requirements (see Figure 9).

[00158] The thiophene molecule derivative was used as donor material in combination with subphthalocyanine chloride (SubPc-Cl) as acceptor in the following configuration: ITO/5nm MoO3/5nm HG01/10nm DTP-3/100nm DTP-3 &SubPc-Cl/10nm SubPc-Cl/3.5nm NBPhen /100nm AlSiCu /100nm LiF. The device showed and EQE of 6 % at 0V and 12% at -1V (Figure 9).

EXAMPLE 5: Thiophene molecule

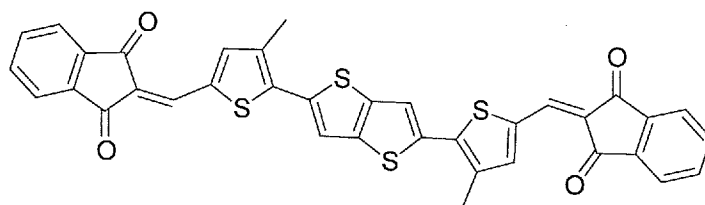
[00159] A further thiophene molecule derivative was used, called N-(di-tert-butylphenyl)-dithienopyrrole-thiophene indandione (DTP6)



[00160] The absorption of the molecule in solution fits with the requirements (see Figure 10).

EXAMPLE 6: Thiophene molecule

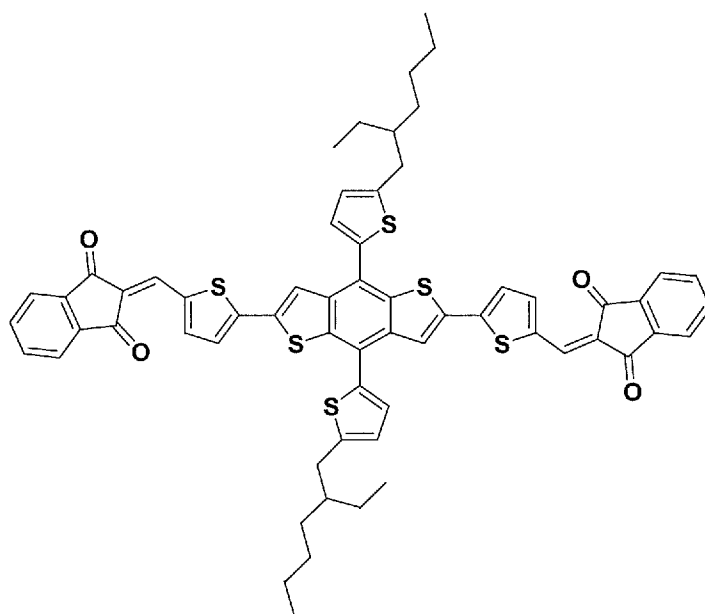
[00161] A further thiophene molecule derivative was used, called methyl bithieno-thienothiophene indandione (m-BT-TT)



[00162] The absorption of the molecule in solution fits with the requirements (see Figure 11).

EXAMPLE 7: Thiophene molecule

[00163] A further thiophene molecule derivative was used, called benzodithieno-thiophene – indandione (Th-1)

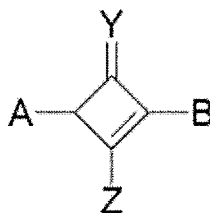


[00164] The absorption of the molecule in solution fits with the requirements (see Figure 12).

[00165] Thus, the foregoing discussion discloses and describes merely exemplary embodiments of the present disclosure. As will be understood by those skilled in the art, the present disclosure may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. Accordingly, the disclosure of the present disclosure is intended to be illustrative, but not limiting of the scope of the disclosure, as well as other claims. The disclosure, including any readily discernible variants of the teachings herein, define, in part, the scope of the foregoing claim terminology such that no inventive subject matter is dedicated to the public.

CLAIMS

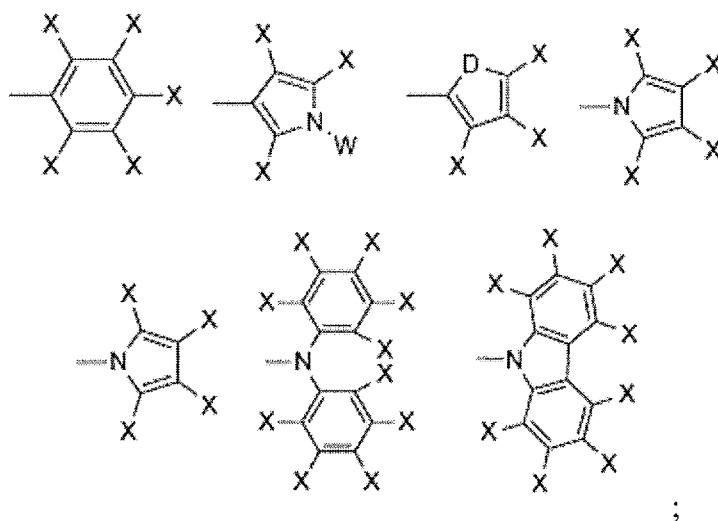
1. A (squaraine) molecule represented by formula I



(I)

wherein

A and B are the same or different and are, at each occurrence, independently selected from



pyrazole, thiazole, imidazole, indole, quinoline, benzothiophene, benzothiazole, benzothiadiazole, benzofuran, oxazole, benzoxazole, pyridine, diazine, triazine, selenophene, naphthalene, anthracene or pyrene, any of which can optionally be substituted,

D is S or O;

W is selected from H, alkyl, aryl;

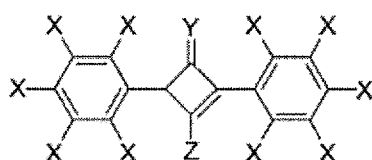
X is selected from the group comprising H, OH, SH, NH₂, NHR, NR₂, NO₂, alkyl, alkoxy, aryl, aryloxy, halogen, such as F, Cl, Br, I;

Y is selected from O, S, NH, NR, $\text{NC}-\text{CH}_2-\text{CN}$, $\text{NC}-\text{CH}_2-\text{COOH}$, $\text{HOOC}-\text{CH}_2-\text{COOH}$, indanedione, barbituric acid or thiobarbituric acid;

Z is selected from OH, SH, NH_2 , NR_2 ;

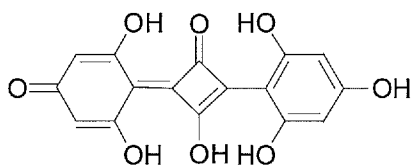
R, at each occurrence, is independently selected from H or any straight or branched alkyl chain of general formula $-\text{C}_n\text{H}_{2n+1}$, or $-\text{COOR}^1$, $-\text{OR}^1$, $-\text{SR}^1$, $-\text{NR}_2^1$, or F, Cl, Br, I, O, N, NO_2 , CN, CF_3 , wherein R^1 is H or any straight or branched alkyl chain of general formula $-\text{C}_n\text{H}_{2n+1}$, or any substituted or non-substituted phenyl or biphenyl, heteroaryl, $n = 0-12$, preferably 0-6.

2. The molecule according to claim 1, wherein the molecule is represented by formula Ia

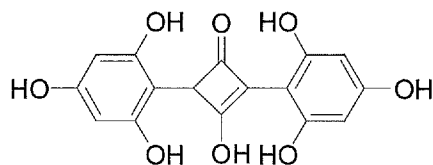


wherein X, Y and Z are as defined in claim 1.

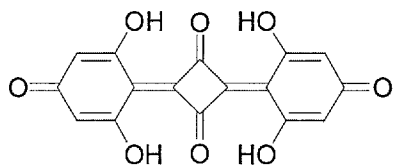
3. The molecule according to claim 1 represented by any of structures



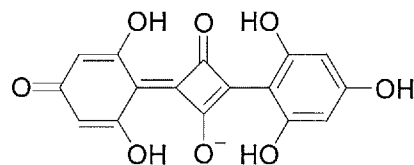
3,5-Dihydroxy-4-[2-hydroxy-4-oxo-3-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enylidene]-cyclohexa-2,5-dienone



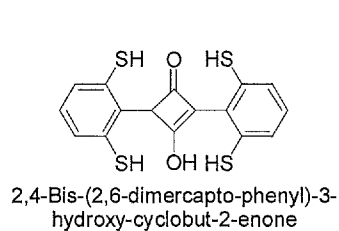
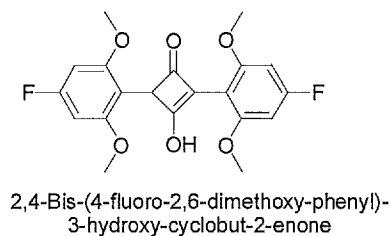
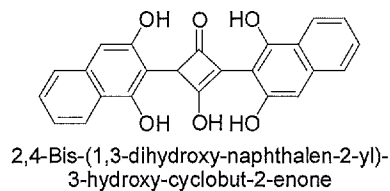
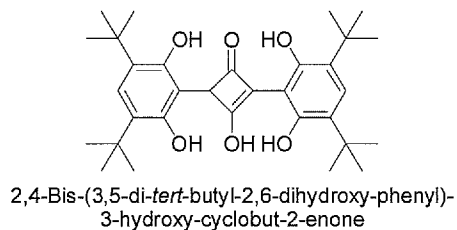
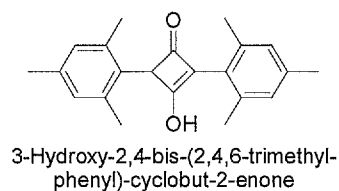
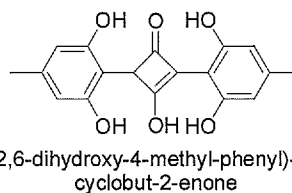
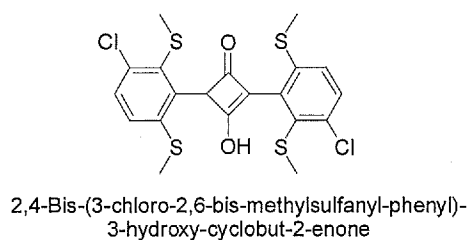
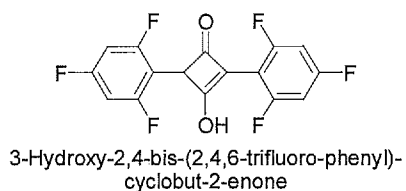
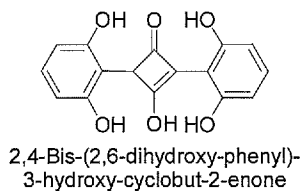
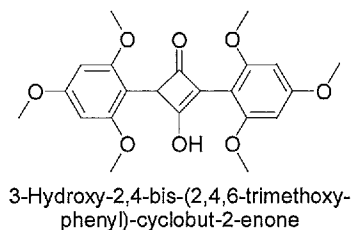
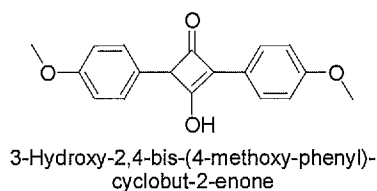
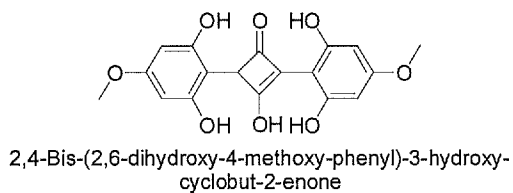
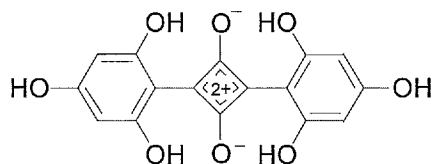
3-Hydroxy-2,4-bis-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enone

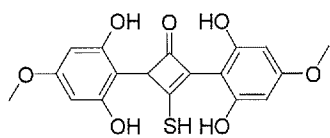
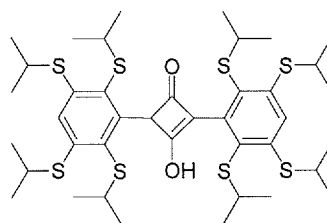
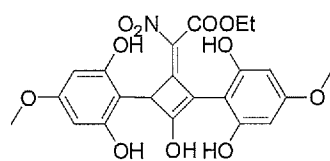
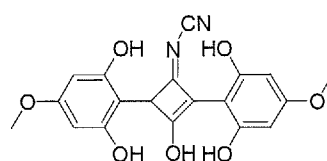
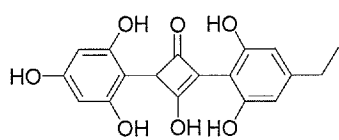
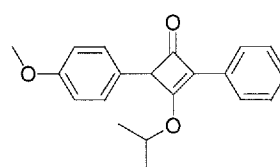


2,4-Bis-(2,6-dihydroxy-4-oxo-cyclohexa-2,5-dienylidene)-cyclobutane-1,3-dione

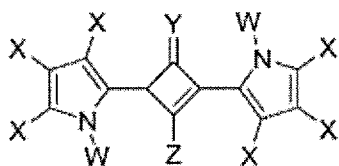


4-(2,6-Dihydroxy-4-oxo-cyclohexa-2,5-dienylidene)-3-oxo-2-(2,4,6-trihydroxy-phenyl)-cyclobut-1-enol anion

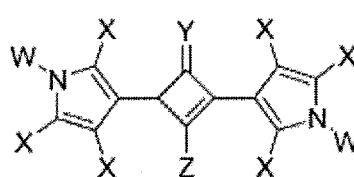


2,4-Bis-(2,6-dihydroxy-4-methoxy-phenyl)-
3-mercapto-cyclobut-2-enone3-Hydroxy-2,4-bis-(2,3,5,6-tetrakis-
isopropylsulfanyl-phenyl)-cyclobut-2-
enone[2,4-Bis-(2,6-dihydroxy-4-methoxy-phenyl)-
3-hydroxy-cyclobut-2-enylidene]-
nitro-acetic acid ethyl ester2,4-Bis-(2,6-dihydroxy-4-methoxy-phenyl)-
3-hydroxy-cyclobut-2-enylidene-cyanamide2-(4-Ethyl-2,6-dihydroxy-phenyl)-3-hydroxy-4-
(2,4,6-trihydroxy-phenyl)-cyclobut-2-enone3-Isopropoxy-4-(4-methoxy-phenyl)-
2-phenyl-cyclobut-2-enone

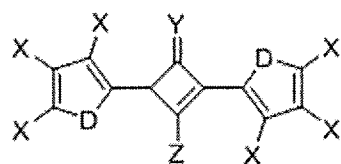
4. The molecule according to claim 1, wherein the molecule is represented by any one of



formula Ib,

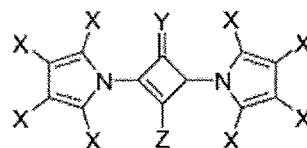


formula Ic,

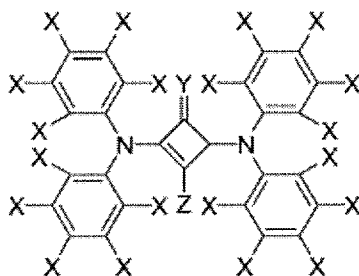


formula Id,

wherein D is S or O,

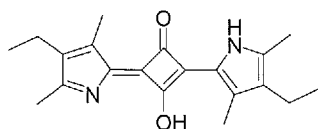


formula Ie, or

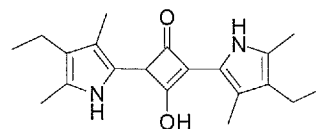


formula If.

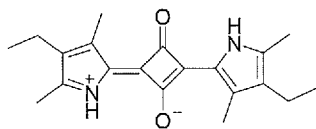
5. The molecule according to claim 3 represented by any of structures



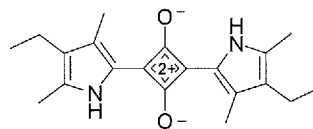
2-(4-Ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-4-(4-ethyl-3,5-dimethyl-pyrrol-2-ylidene)-3-hydroxy-cyclobut-2-enone



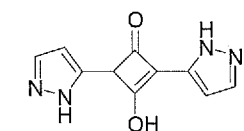
2,4-Bis-(4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-3-hydroxy-cyclobut-2-enone



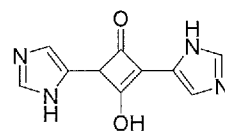
3-Oxo-2-(1,2,5-trimethyl-1H-pyrrol-3-yl)-4-(1,2,5-trimethyl-pyrrol-3-ylidene)-cyclobut-1-enol anion



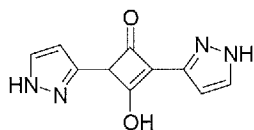
2,4-Bis-(4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-3-hydroxy-cyclobut-2-enone



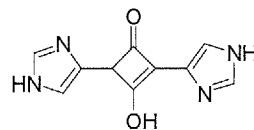
3-Hydroxy-2,4-bis-(2H-pyrazol-3-yl)-cyclobut-2-enone



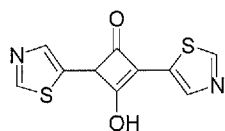
3-Hydroxy-2,4-bis-(3H-imidazol-4-yl)-cyclobut-2-enone



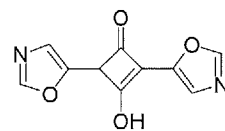
3-Hydroxy-2,4-bis-(1H-pyrazol-3-yl)-cyclobut-2-enone



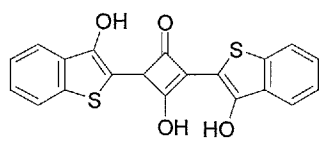
3-Hydroxy-2,4-bis-(1H-imidazol-4-yl)-cyclobut-2-enone



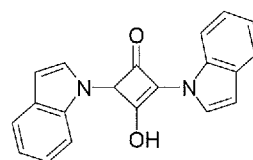
3-Hydroxy-2,4-bis-thiazol-5-yl-cyclobut-2-enone



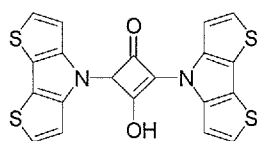
3-Hydroxy-2,4-bis-oxazol-5-yl-cyclobut-2-enone



3-Hydroxy-2,4-bis-(3-hydroxybenzo[b]thiophen-2-yl)-cyclobut-2-enone

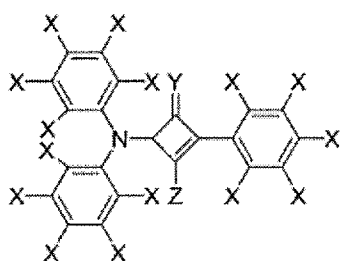


3-Hydroxy-2,4-bis-indol-1-yl-cyclobut-2-enone

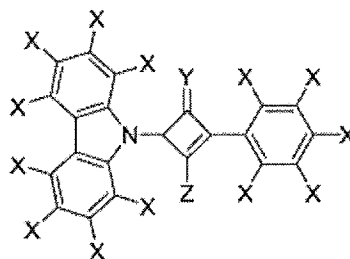


2,4-Bis-dithieno[3,2-b;2',3'-d]pyrrol-4-yl-3-hydroxy-cyclobut-2-enone

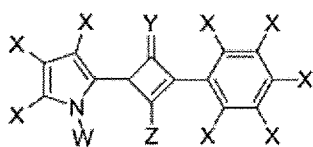
6. The molecule according to claim 1, wherein the molecule is represented by any one of



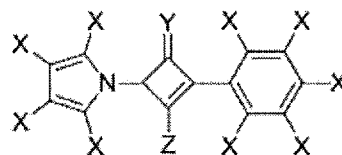
formula Ig,



formula Ih,

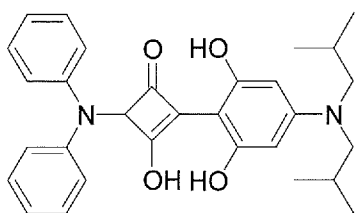


formula Ii, or

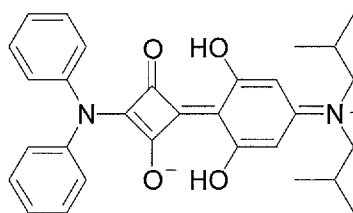


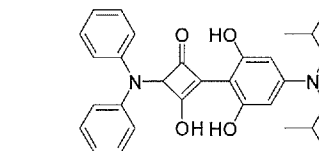
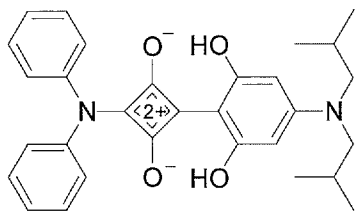
formula Ij.

7. The molecule according to claim 6 represented by any of structures

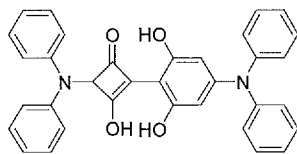


2-(4-Diisobutylamino-2,6-dihydroxy-phenyl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone

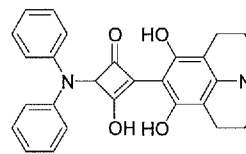




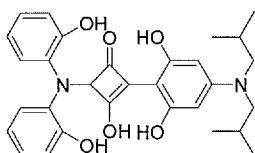
2-(4-Diisobutylamino-2,6-dihydroxy-phenyl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



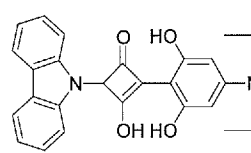
4-Diphenylamino-2-(4-diphenylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



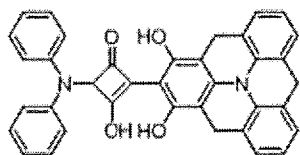
2-(8,10-Dihydroxy-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



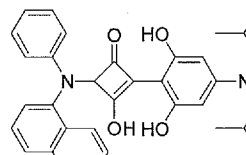
4-[Bis-(2-hydroxy-phenyl)-amino]-2-(4-diisobutylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



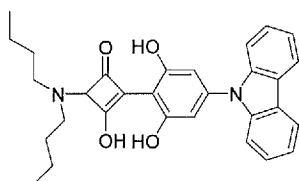
4-Carbazol-9-yl-2-(4-diisobutylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



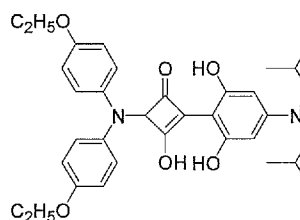
2-(1,3-Dihydroxy-4H,8H,12H-12a-aza-dibenzo[cd,mm]pyren-2-yl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



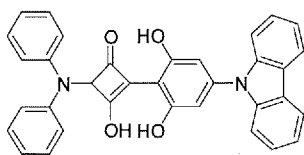
2-(4-Diisobutylamino-2,6-dihydroxy-phenyl)-3-hydroxy-4-(naphthalen-1-yl-phenyl-amino)-cyclobut-2-enone



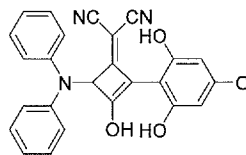
4-Dibutylamino-2-(4-diphenylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



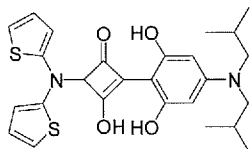
4-[Bis-(4-ethoxy-phenyl)-amino]-2-(4-diisobutylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone



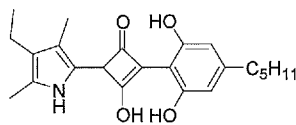
2-(4-Carbazol-9-yl-2,6-dihydroxy-phenyl)-4-diphenylamino-3-hydroxy-cyclobut-2-enone



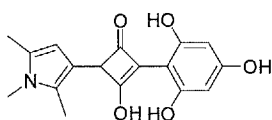
2-[4-Diphenylamino-3-hydroxy-2-(2,4,6-trihydroxy-phenyl)-cyclobut-2-enylidene]-malononitrile



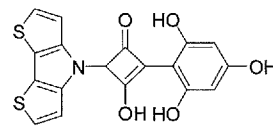
2-(4-Diisobutylamino-2,6-dihydroxy-phenyl)-
4-(di-thiophen-2-yl-amino)-3-hydroxy-cyclobut-2-enone



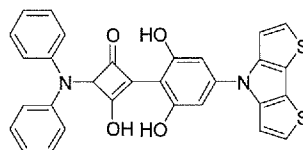
2-(2,6-Dihydroxy-4-pentyl-phenyl)-4-
(4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-
3-hydroxy-cyclobut-2-enone



3-Hydroxy-2-(2,4,6-trihydroxy-phenyl)-4-
(1,2,5-trimethyl-1H-pyrrol-3-yl)-cyclobut-2-enone

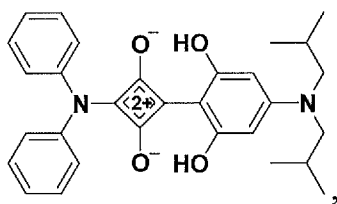


4-Dithieno[3,2-b;2',3'-d]pyrrol-4-yl-3-hydroxy-2-
(2,4,6-trihydroxy-phenyl)-cyclobut-2-enone

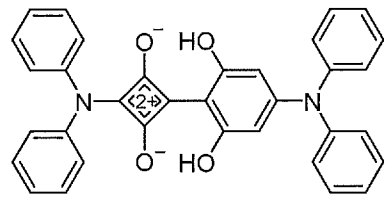


4-Diphenylamino-2-(4-dithieno[3,2-b;2',3'-d]pyrrol-4-yl)-
2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone

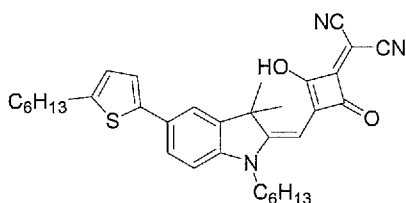
8. The molecule according to claim 1 represented by any of structures



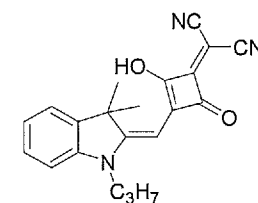
2-[3-[1-Hexyl-5-(5-hexyl-thiophen-2-yl)-3,3-dimethyl-
1,3-dihydro-indol-2-ylidenemethyl]-2-hydroxy-
4-oxo-cyclobut-2-enylidene]-malononitrile



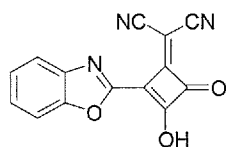
2-[3-(3,3-Dimethyl-1-propyl-1,3-dihydro-
indol-2-ylidenemethyl)-2-hydroxy-4-oxo-
cyclobut-2-enylidene]-malononitrile



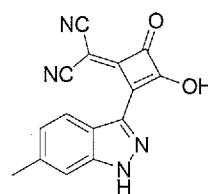
2-(1-Butyl-3,3-dimethyl-1,3-dihydro-indol-2-
ylidenemethyl)-3-hydroxy-4-thiophen-2-yl-
cyclobut-2-enone



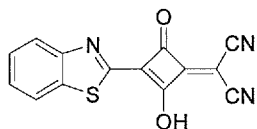
2-[2-(1-Ethyl-1H-quinolin-2-ylidenemethyl)-
3-hydroxy-4-oxo-cyclobut-
2-enylidene]-malononitrile



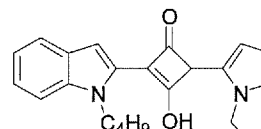
2-(2-Benzothiazol-2-yl-3-hydroxy-4-oxo-cyclobut-2-enylidene)-malononitrile



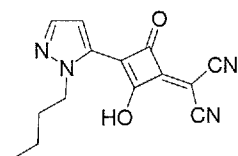
2-[3-Hydroxy-2-(6-methyl-1H-indazol-3-yl)-4-oxo-cyclobut-2-enylidene]-malononitrile



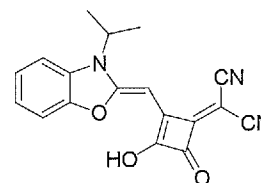
2-(3-Benzothiazol-2-yl-2-hydroxy-4-oxo-cyclobut-2-enylidene)-malononitrile



2-(1-Butyl-1H-indol-2-yl)-4-(1-ethyl-1H-pyrrol-2-yl)-3-hydroxy-cyclobut-2-enone

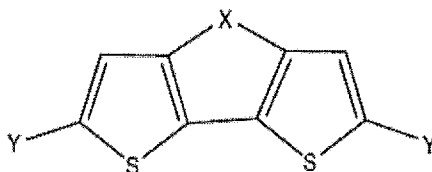


2-[3-(2-Butyl-2H-pyrazol-3-yl)-2-hydroxy-4-oxo-cyclobut-2-enylidene]-malononitrile

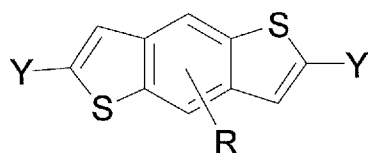


2-[3-Hydroxy-2-(3-isopropyl-3H-benzooxazol-2-ylidenemethyl)-4-oxo-cyclobut-2-enylidene]-malononitrile

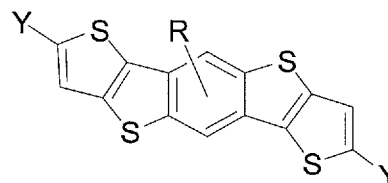
9. A (thiophene-based) molecule represented by a formula selected from formula II, III, IV, V and VI



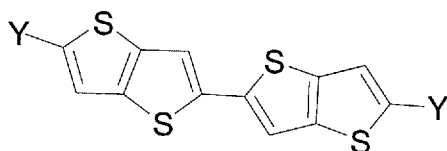
(II)



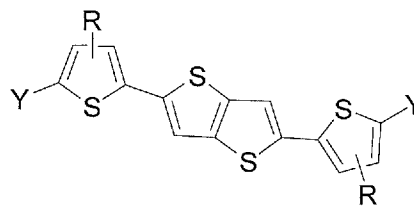
(III)



(IV)



(V)



(VI)

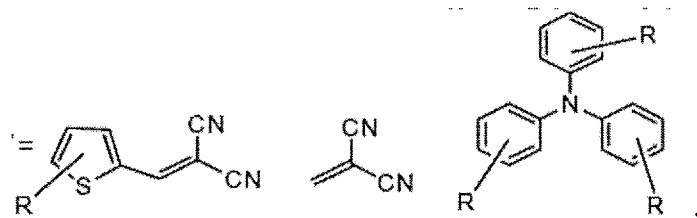
wherein

X is selected from the group comprising S, Se, N-R¹, SO₂, CR¹₂, cyclopentane, cyclohexane, SiR¹₂;

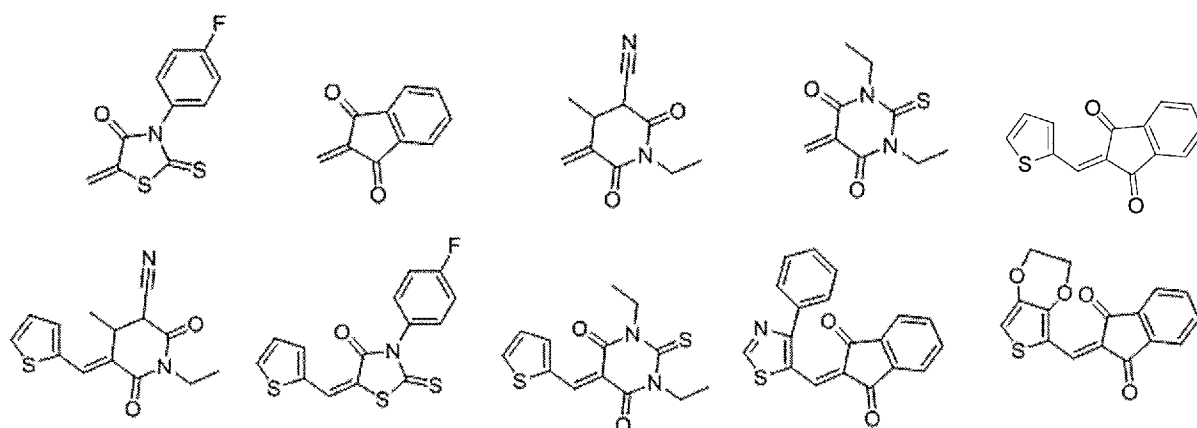
R¹ is selected from aryl, alkyl;

R is selected from H, aryl, substituted aryl, alkyl, thiophene, alkyl-substituted thiophene;

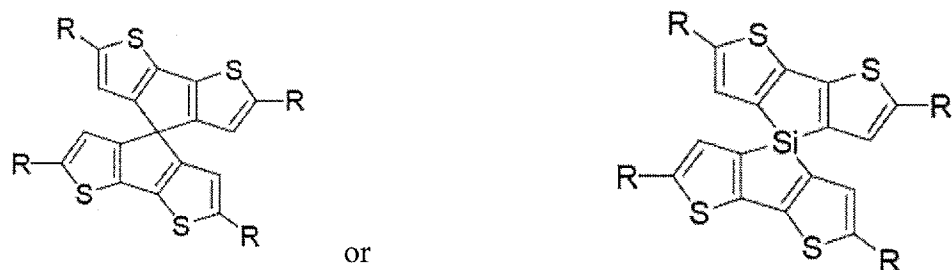
Y is selected from



carbazole, diarylamine, pyrrole, pyrazole, thieno[3,4-b]pyrazine, imidazole, thiazole, fluorine, tricyanovinyl, indole, quinolone, benzothiadiazole, indanedione, barbituric acid or thiobarbituric acid, rhodanine, thiazolinedione derivatives as for example:

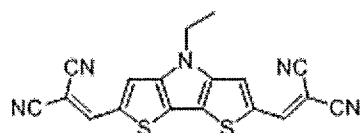
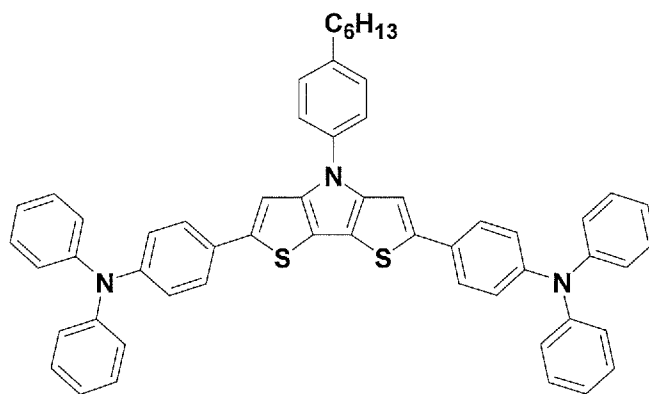
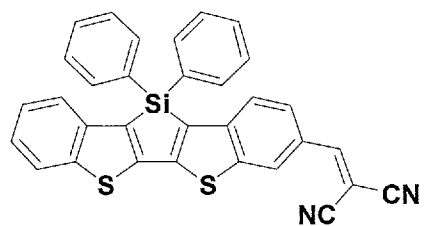
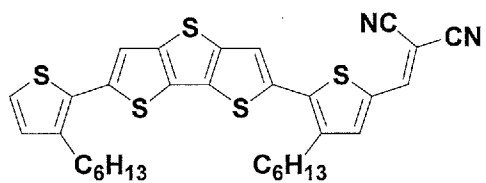
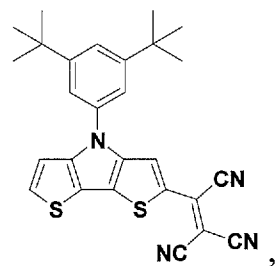
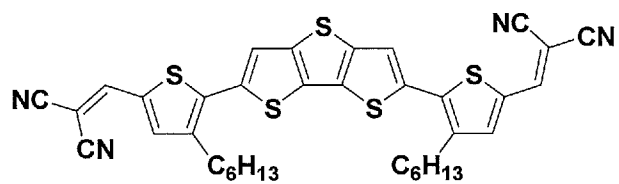


10. The molecule according to claim 9 which is a spiro-dimer selected from

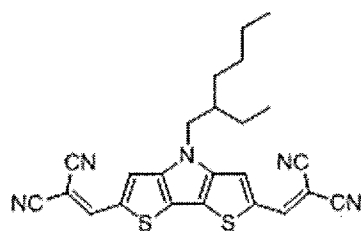


11. The molecule according to claim 9 represented by any of structures

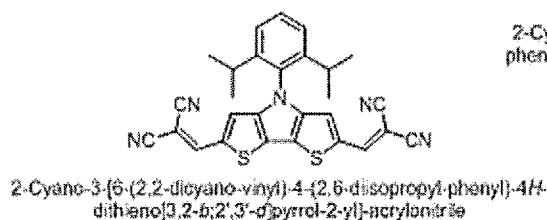
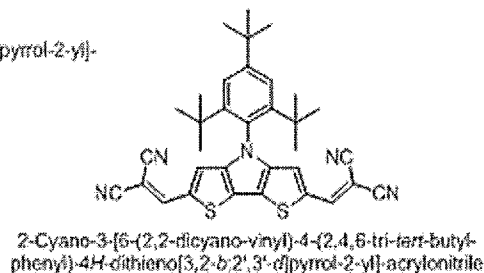
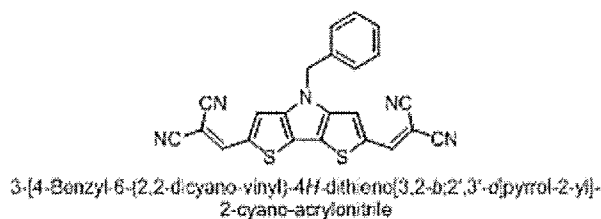
58



2-Cyano-3-[6-(2,2-dicyano-vinyl)-4-ethyl-4*H*-dithieno[3,2-*b*:2',3'-*d'*]pyrrol-2-yl]-acrylonitrile



2-Cyano-3-[6-(2,2-dicyano-vinyl)-4-(2-ethyl-hexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-yl]-acrylonitrile



12. The molecule according to any one of claims 1 to 8, wherein the molecule

- exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and exhibits no absorption in the IR range (above 700 nm).

13. The molecule according to any one of claims 9 to 11, wherein the molecule

- exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and
- optionally, exhibits also absorption in the IR range (above 700 nm).

14. The molecule according to any one of claims 1 to 13, wherein furthermore the molecule

- absorbs in the blue absorption range or absorbs in the green absorption range or absorbs in the red absorption range,
- preferably shows an extinction coefficient of $> 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$,
- absorbs less than 20% (more preferably less than 5%) of the maximum absorption outside of its main range of absorption.

and/or

- exhibits a high photoelectric conversion efficiency of more than 15%, preferably of more than 50% and more preferably more than 80%.

15. Use of a molecule according to any of claims 1 to 14 in an absorption layer, wherein the molecule preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).

16. Use of a molecule according to any of claims 1 to 14 in a filter, wherein the molecule preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).
17. Use of a molecule according to any of claims 1 to 14 in a photoelectric conversion layer and/or in an organic and/or hybrid module for optoelectronic application, such as image sensor, photodiode, organic photovoltaics, comprising organic photoelectric conversion layer(s), OLED and OTFT organic modules.
18. A photoelectric conversion layer comprising a molecule according to any one of claims 1 to 14, optionally comprising further molecule(s).
19. An absorption layer comprising a molecule according to any one of claims 1 to 14, optionally comprising further molecule(s), wherein the molecule preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).
20. A filter comprising a molecule according to any one of claims 1 to 14, optionally comprising further molecule(s), wherein the molecule preferably exhibits absorption in the visible wavelength range (about 400 to about 700 nm) and, optionally, exhibits also absorption in the IR range (above 700 nm).
21. A device, comprising molecule(s) according to any one of claims 1 to 14 or photoelectric conversion layer(s) according to claim 18, wherein said device is preferably an organic image sensor, an hybrid image sensor, photodiode, organic photovoltaics, *organic light-emitting diode* (OLED), *organic thin-film transistor* (OTFT).

22. The device according to claim 21, wherein said photoelectric conversion layer exhibits photo response in the visible absorption range.
23. The device according claim 21 or 22, comprising molecule(s) according to any one of claims 1 to 14 or photoelectric conversion layer(s) according to claim 18, and/or comprising further molecule(s).
24. An organic image sensor, comprising
- (a) an organic photoelectric conversion unit comprising photoelectric conversion layer(s) according to claim 18,
 - (b) at least one electrode,
 - (c) a substrate,
 - (d) optionally, a second electrode on top of said photoelectric conversion layer(s), preferably not comprising color filter(s).
25. A hybrid Silicon-organic image sensor or organic image sensor, comprising
- (a) an organic photoelectric conversion unit or units comprising photoelectric conversion layer(s) according to claim 18,
 - (b) optionally, a Si based photoelectric conversion unit,
 - (c) metal wiring,
 - (d) a (CMOS) substrate,
 - (e) insulating layer(s), preferably oxide.
26. The organic image sensor according to claim 24 or 25, wherein said organic photoelectric conversion unit comprises different layers, such as n-type material, p-type material, n-buffer layer and/or p-buffer layer or combinations or mixtures thereof.
27. A method for synthesis of a molecule according to any one of claims 1 to 8, comprising the following step(s):
- Attaching the donor group to the core by reacting the appropriate reagent with squaric acid in a refluxing azeotropic water removal mixture,
- or comprising the following step(s):

Attaching the first donor group to the core by reacting the appropriate reagent with diethyl squarate in the presence of alkylamine as catalyst, and

After deprotecting the ester with aqueous NaOH, reacting the semiquarate precursor with the second donor molecule in a refluxing azeotropic water removal mixture.

28. A method for synthesis of a molecule according to any one of claims 9 to 11, comprising the following step(s):

Reacting dithieno thiophenes, dithienopyrroles and dithienosiloles by condensation reaction or metal catalyzing with the desired group.

Figure 1

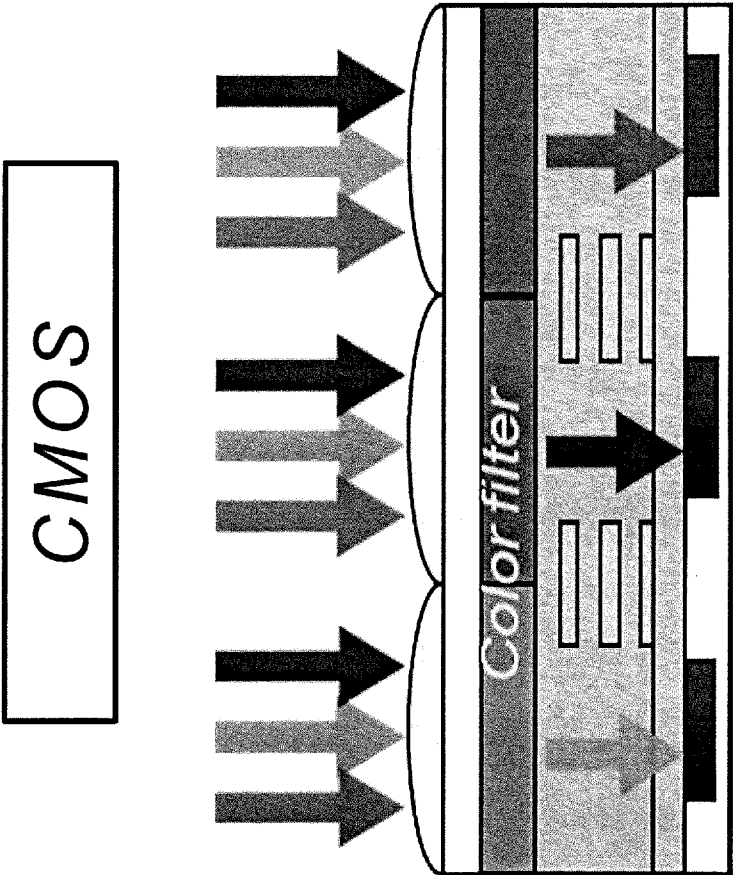


Figure 2

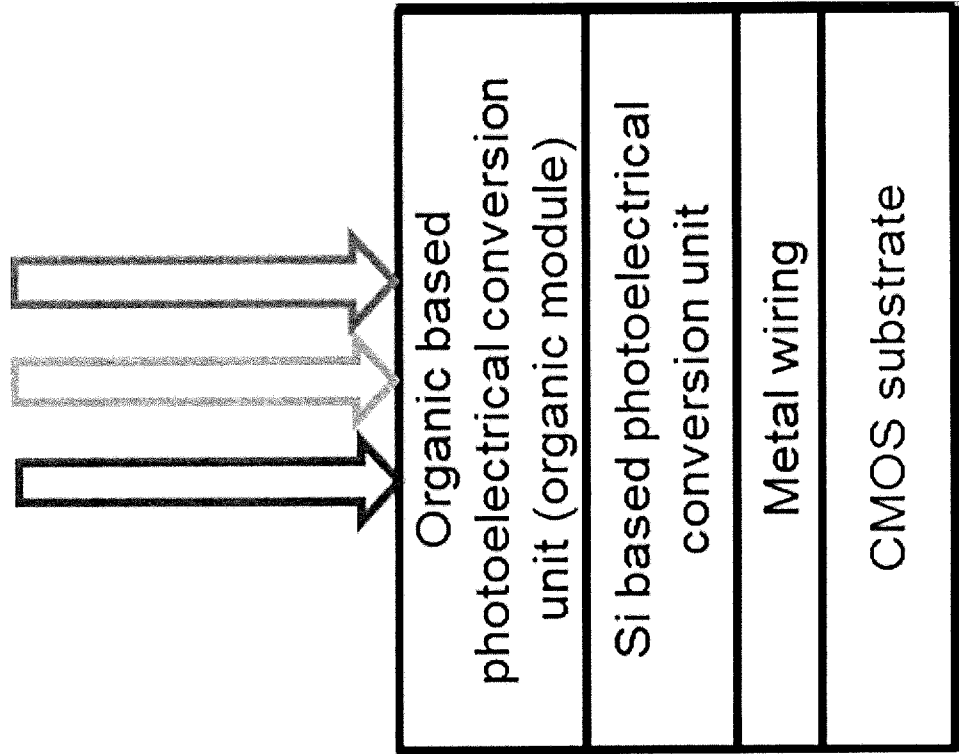


Figure 3

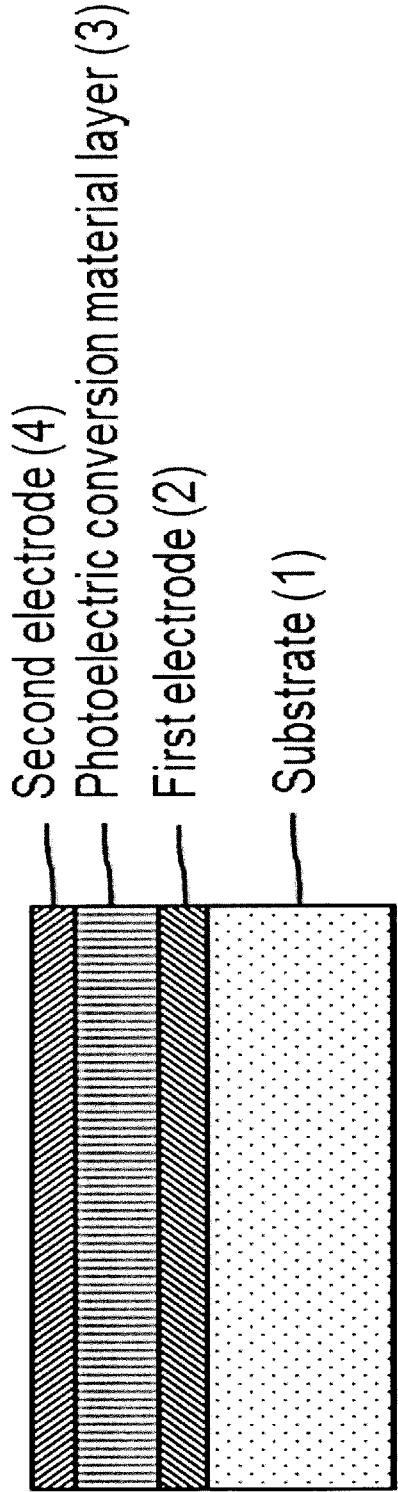
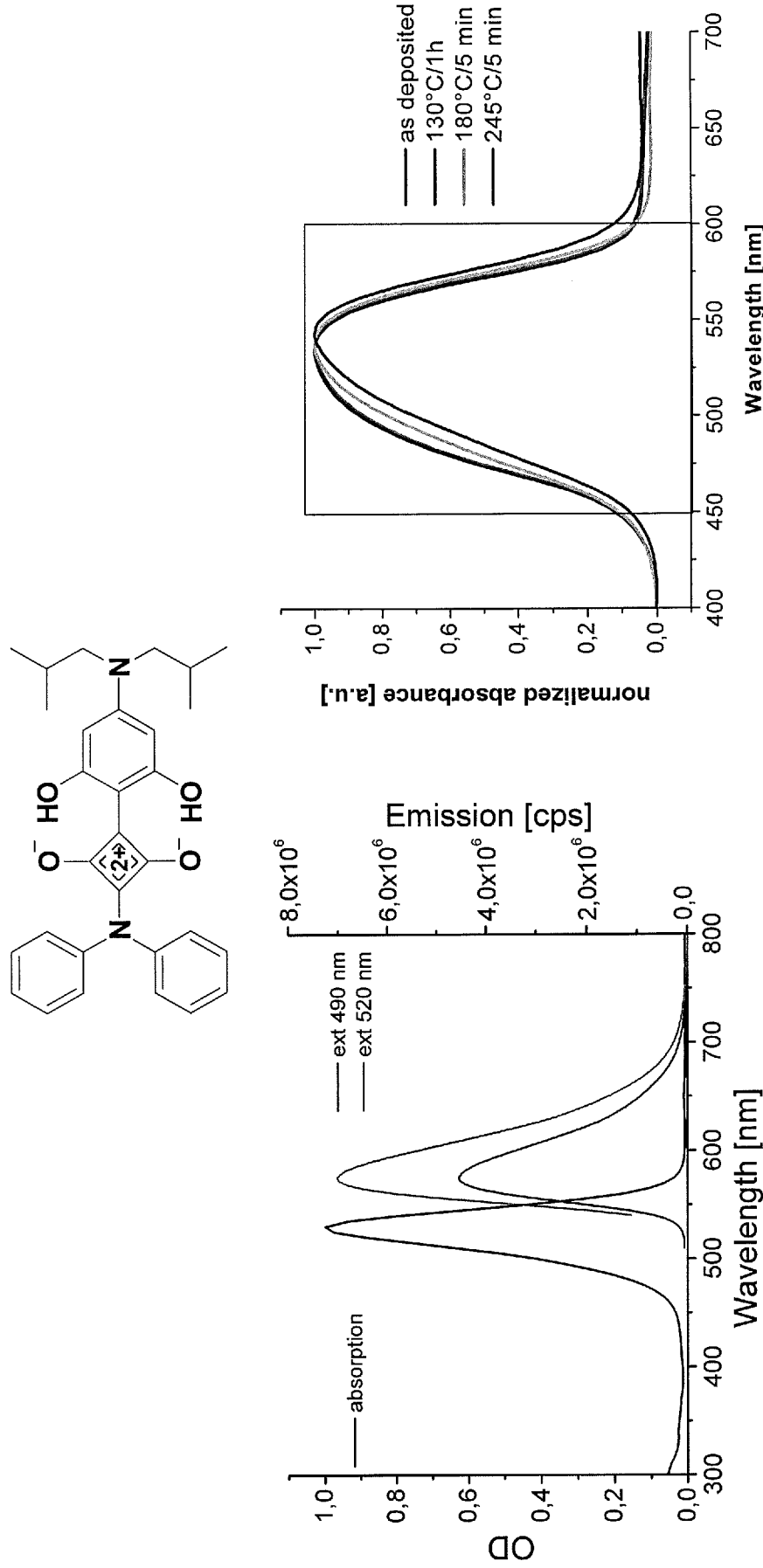


Figure 4



UV-Vis in solution

UV-Vis in thin film

Figure 5

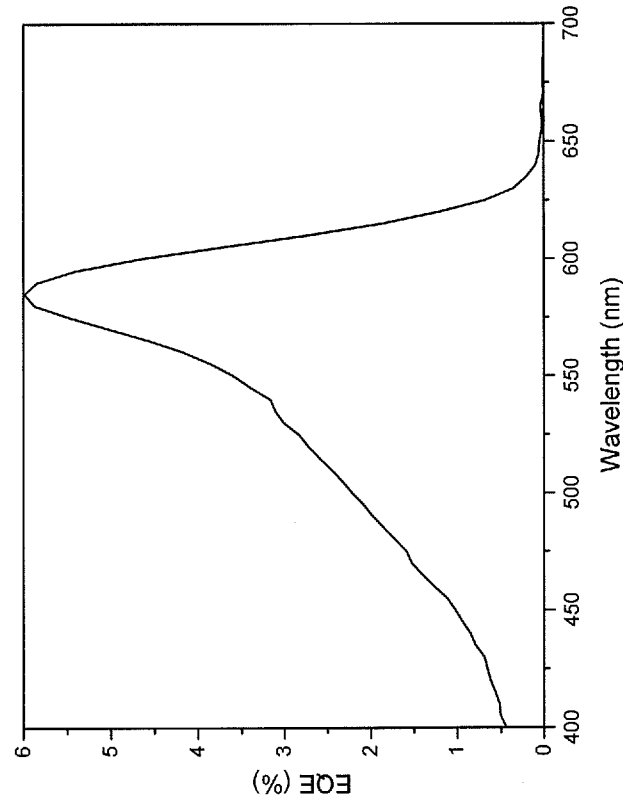
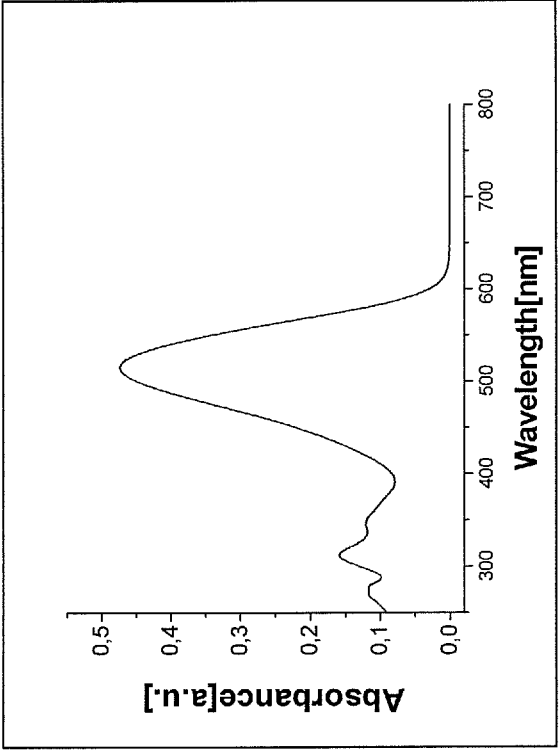
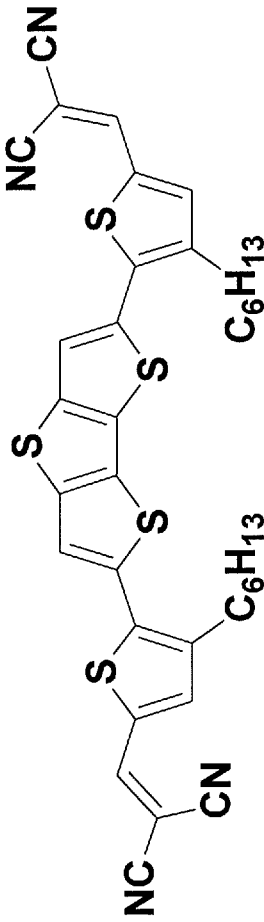
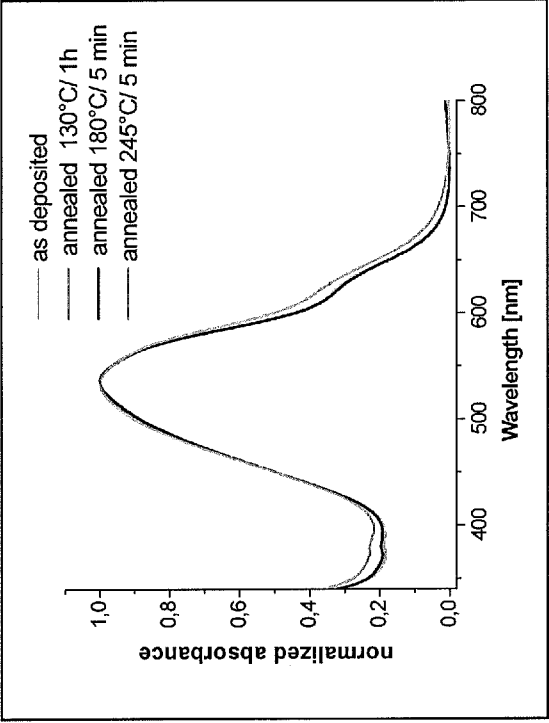


Figure 6

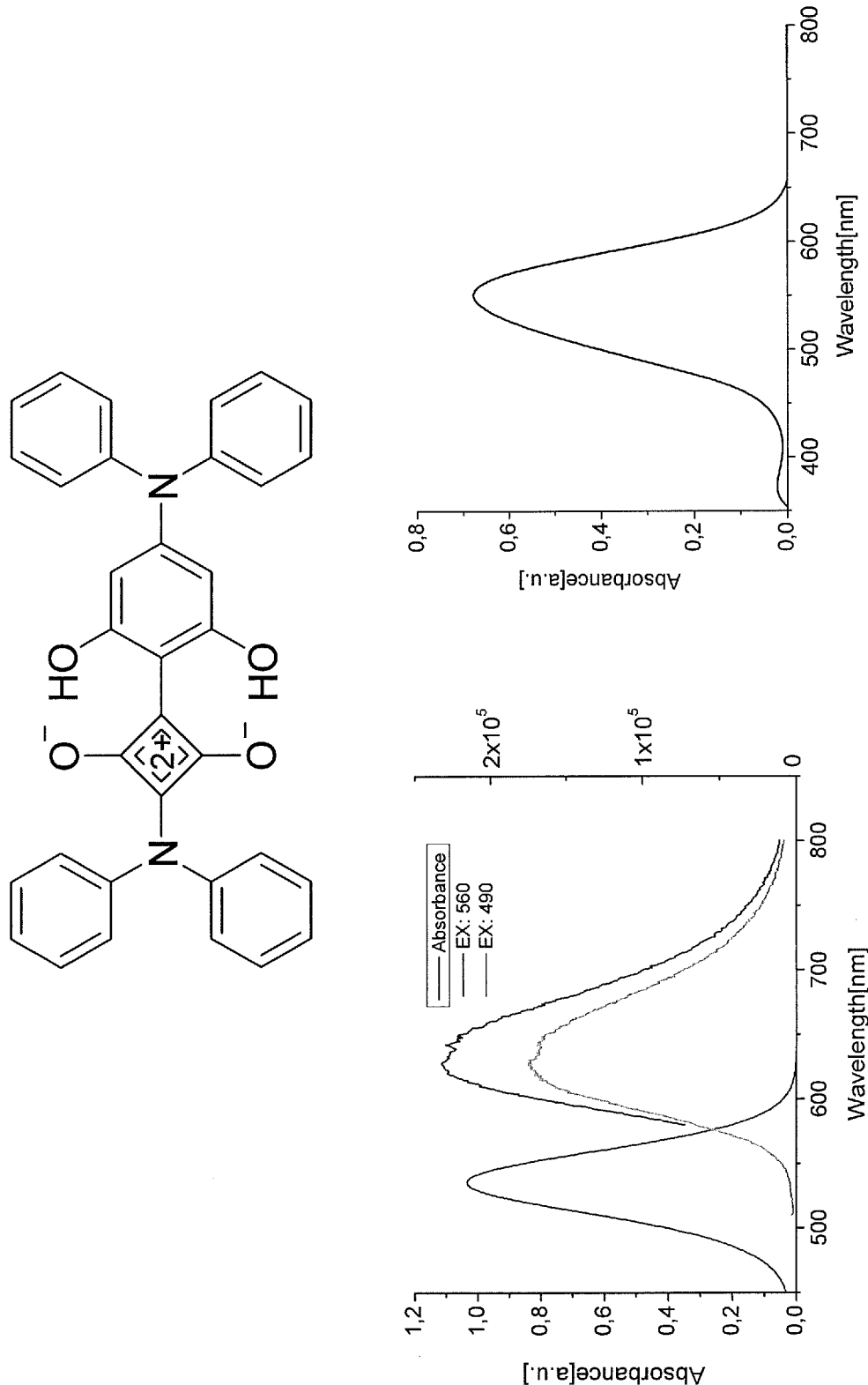


UV-Vis in solution



UV-Vis in thin film

Figure 7



UV-Vis in thin film

UV-Vis in solution

Figure 8

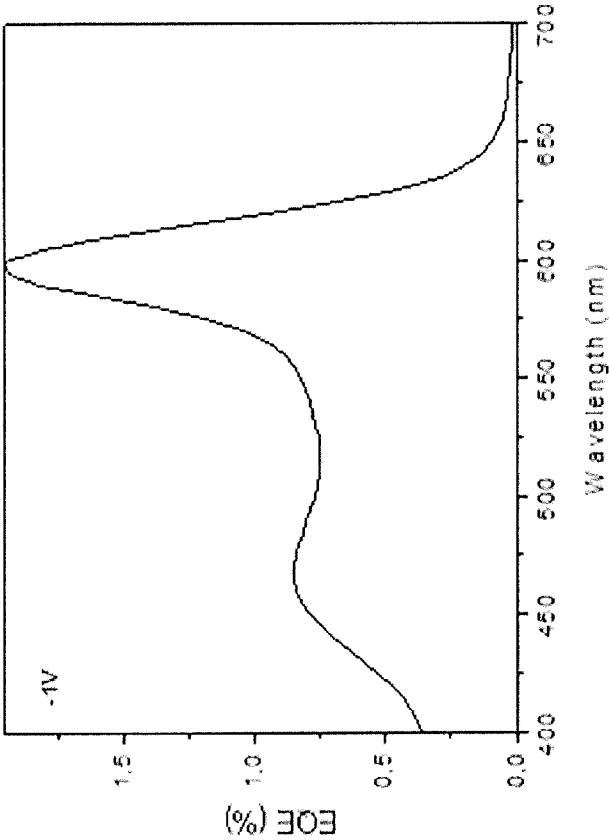


Figure 9

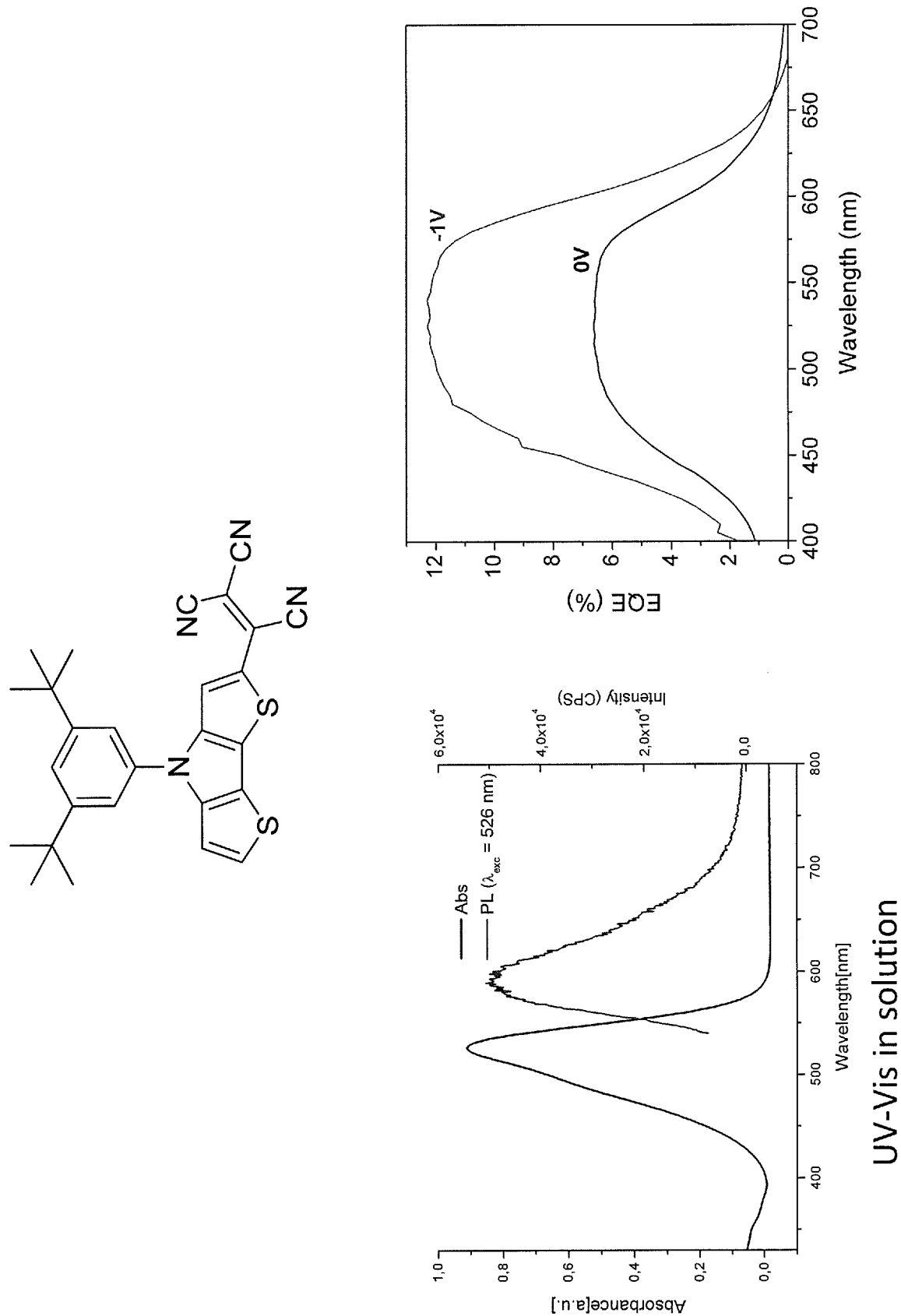
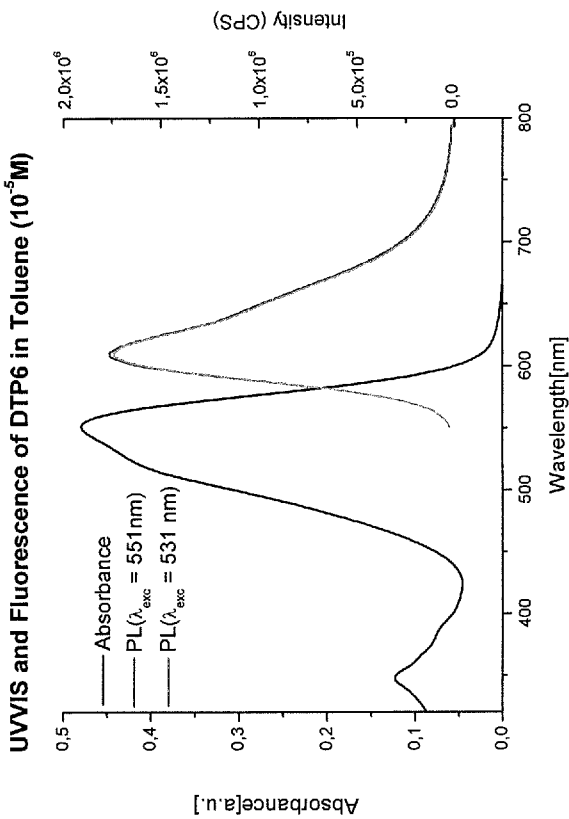
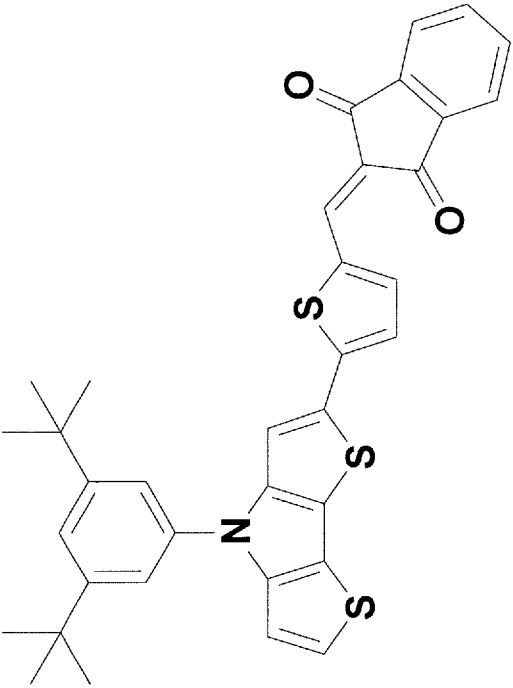
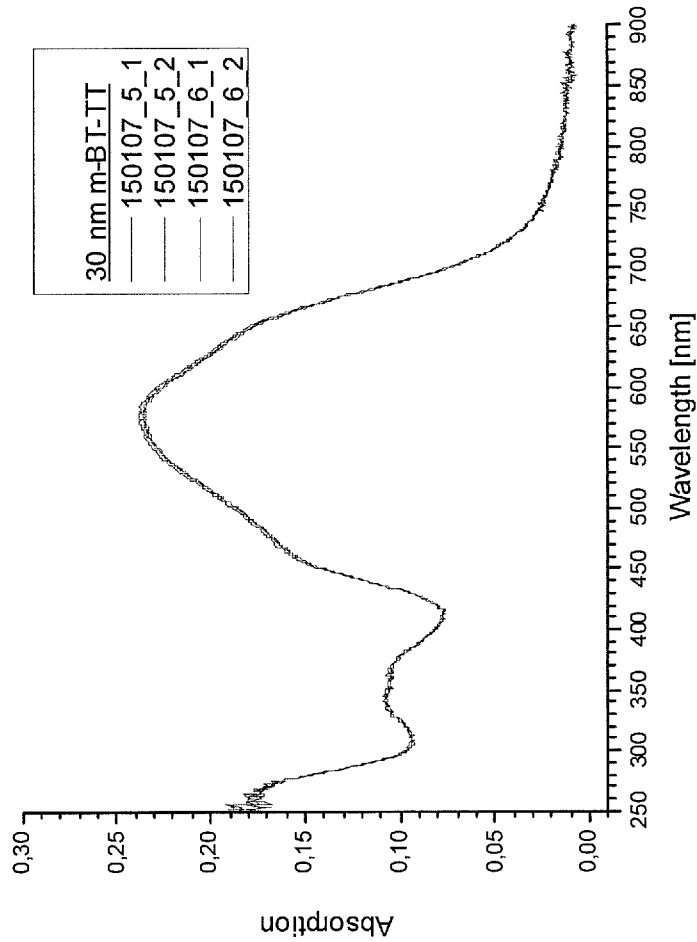
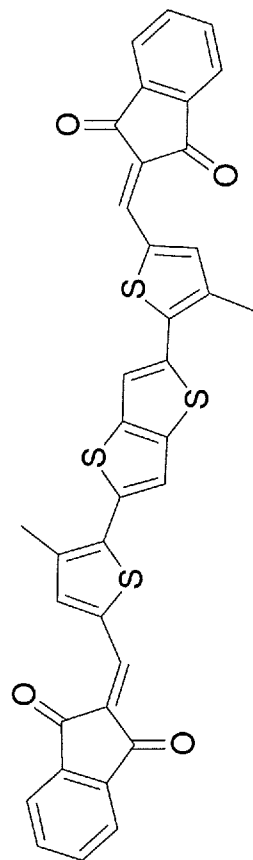


Figure 10



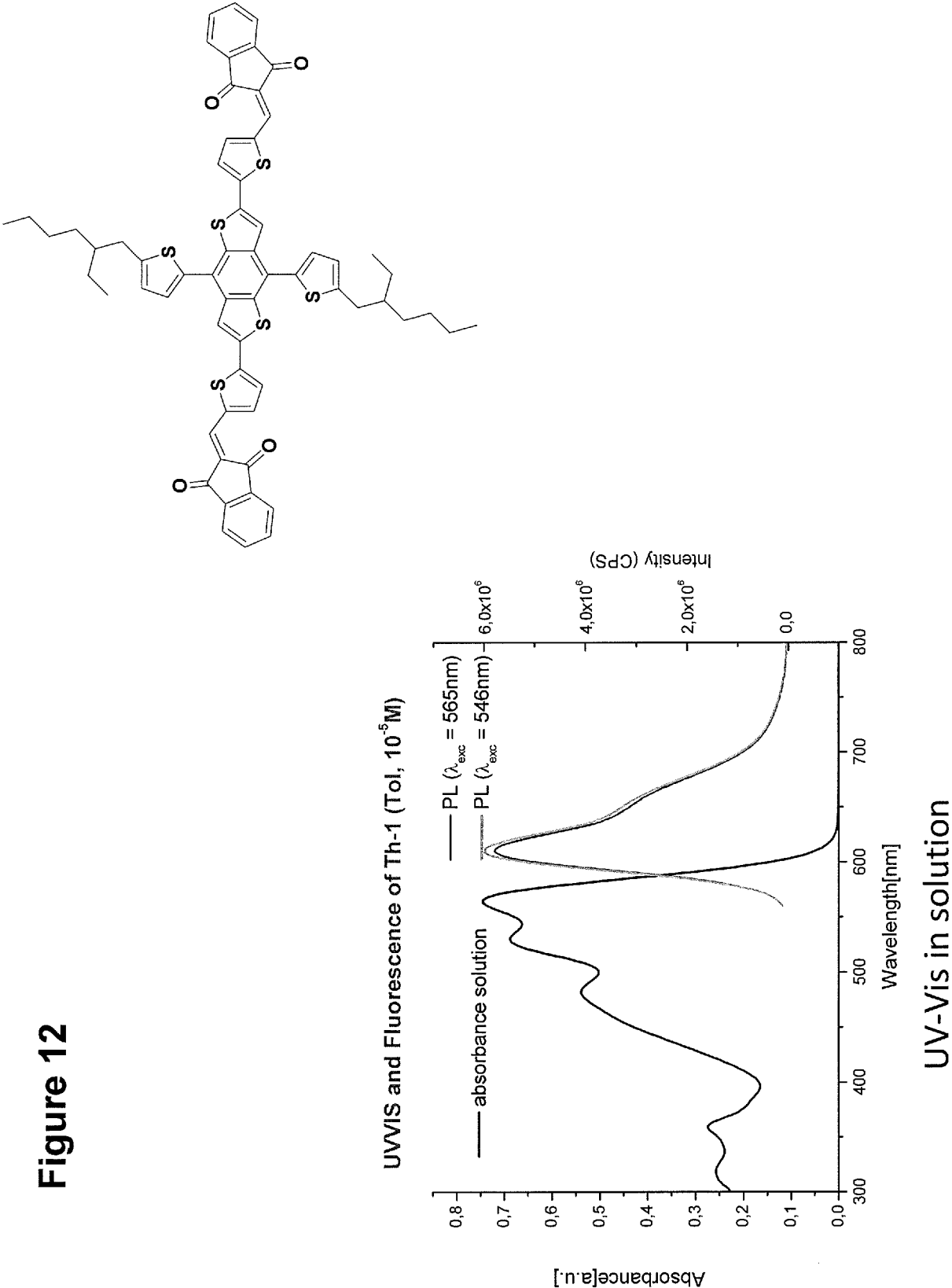
UV-Vis in solution

Figure 11



UV-Vis in film

Figure 12



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/051336

A. CLASSIFICATION OF SUBJECT MATTER INV. C09B23/01 C09B57/00 H01L51/00 H01L51/42 H01L27/146 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) C09B 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, CHEM ABS Data, WPI Data											
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>EP 1 970 959 A2 (FUJIFILM CORP [JP]) 17 September 2008 (2008-09-17) paragraphs [0001] - [0008], [0011] - [0123], [0173], [0174]; claims; examples; compound 5 -----</td> <td>1-8,12, 14-27</td> </tr> <tr> <td>X</td> <td>US 8 614 440 B2 (SRAMEK MARIA [DE] ET AL) 24 December 2013 (2013-12-24) column 2, line 6 - column 5, line 4; claims; table 1 ----- -/--</td> <td>1-8,12, 14-27</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	EP 1 970 959 A2 (FUJIFILM CORP [JP]) 17 September 2008 (2008-09-17) paragraphs [0001] - [0008], [0011] - [0123], [0173], [0174]; claims; examples; compound 5 -----	1-8,12, 14-27	X	US 8 614 440 B2 (SRAMEK MARIA [DE] ET AL) 24 December 2013 (2013-12-24) column 2, line 6 - column 5, line 4; claims; table 1 ----- -/--	1-8,12, 14-27
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.									
X	EP 1 970 959 A2 (FUJIFILM CORP [JP]) 17 September 2008 (2008-09-17) paragraphs [0001] - [0008], [0011] - [0123], [0173], [0174]; claims; examples; compound 5 -----	1-8,12, 14-27									
X	US 8 614 440 B2 (SRAMEK MARIA [DE] ET AL) 24 December 2013 (2013-12-24) column 2, line 6 - column 5, line 4; claims; table 1 ----- -/--	1-8,12, 14-27									
☒ Further documents are listed in the continuation of Box C. ☒ 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									
20 April 2016		21/07/2016									
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Butkowskyj-Walkiw, T									

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/051336

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JEREMIAH J. GASSENSMITH ET AL: "Self-Assembly of Fluorescent Inclusion Complexes in Competitive Media Including the Interior of Living Cells", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 129, no. 48, 1 December 2007 (2007-12-01), pages 15054-15059, XP055067880, ISSN: 0002-7863, DOI: 10.1021/ja075567v page 15055; compound 3a -----	1,2
X	GRIFFITHS J ET AL: "Facile preparative redox chemistry of bis(4-dialkylaminophenyl)squaraine dyes", TETRAHEDRON LETTERS, PERGAMON, GB, vol. 43, no. 43, 21 October 2002 (2002-10-21), pages 7669-7671, XP004385648, ISSN: 0040-4039, DOI: 10.1016/S0040-4039(02)01857-9 page 7670; compound 6 -----	1,2
X	US 3 511 879 A (FUKS ROBERT ET AL) 12 May 1970 (1970-05-12) column 7; compound q -----	1,2
X	G..J.ASHWELL ET AL: "Aggregation-induced linear and non-linear optical properties of four-substituted analogues of 2,4-bis[4-(dibutylamino)phenyl]squaraine", AUST.J.CHEM, vol. 51, 1998, pages 599-604, XP002756793, page 599 - page 600; compounds Sq0-Sq4 -----	1,2,12
X	HOUK R J T ET AL: "A colorimetric chemodosimeter for Pd(II): a method for detecting residual palladium in cross-coupling reactions", TETRAHEDRON, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 64, no. 36, 1 September 2008 (2008-09-01), pages 8271-8278, XP023315786, ISSN: 0040-4020, DOI: 10.1016/J.TET.2008.04.105 [retrieved on 2008-04-30] scheme 1 -----	1,2
X	R.FUKS: "Alkylation, protonation and bromination of ynamines", BULL.SOC.CHIM.BELG., vol. 86, no. 3, 1977, pages 219-235, XP002756794, compound 16 -----	1,2
	----- -/--	

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/051336

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	N.SCHULTE ET AL: "N,N-Bis(trimethylsilyl)ynamines: Cycloaddition Reactions with Dimethyl Acetylenedicarboxylate and Ketenes", CHEM.BER., vol. 127, 1994, pages 1287-1293, XP002756795, page 1289; table 1; compound 9e -----	1,2
X	J.E.BALDWIN ET AL: "Structure and Rearrangment of Neutral Phenylketene Dimer", J.AM.CHEM.SOC., vol. 85, 1963, pages 2444-2445, XP002756796, the whole document -----	1,2
X	WO 2005/122320 A1 (KYOWA HAKKO CHEMICAL CO LTD [JP]; SHIMIZU IKUO; IKUTA MASANORI; KATO S) 22 December 2005 (2005-12-22) paragraphs [0012] - [0045]; claims; examples -----	1-8,12, 14-27
X	ZHAO W ET AL: "Study on squarylium cyanine dyes for photoelectric conversion", SOLAR ENERGY MATERIALS AND SOLAR CELLS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 58, no. 2, 1 June 1999 (1999-06-01), pages 173-183, XP004177953, ISSN: 0927-0248, DOI: 10.1016/S0927-0248(98)00201-3 Experimental section; page 174 - page 183 -----	1-8,12, 14-27

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2016/051336

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-6(completely); 7, 8, 12, 14-27(partially)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-6(completely); 7, 8, 12, 14-27(partially)

Squaraine molecules represented by formula I and their use

2. claims: 7, 12, 14-27(all partially)

4-Dibutylamino-2-(4-diphenylamino-2,6-dihydroxy-phenyl)-3-hydroxy-cyclobut-2-enone and its use

3. claims: 8, 12, 14-27(all partially)

Malononitriles according to claim 8 and their use

4. claims: 9-11, 13, 28(completely); 14-26(partially)

Thiophene-based molecules and their use

5. claims: 7, 12, 14-27(all partially)

Pyrrol-derivatives according to claim 5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/051336

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1970959	A2	17-09-2008	EP 1970959 A2	17-09-2008
			EP 2750191 A1	02-07-2014
			US 2008230123 A1	25-09-2008
			US 2014054577 A1	27-02-2014

US 8614440	B2	24-12-2013	DE 102009043348 A1	07-04-2011
			EP 2486608 A1	15-08-2012
			JP 5487312 B2	07-05-2014
			JP 2013506282 A	21-02-2013
			KR 20120091020 A	17-08-2012
			US 2012181527 A1	19-07-2012
			WO 2011039182 A1	07-04-2011

US 3511879	A	12-05-1970	CA 938303 A	11-12-1973
			US 3511879 A	12-05-1970

WO 2005122320	A1	22-12-2005	NONE	
