



(51) International Patent Classification:

C09K 9/02 (2006.01) C07D 409/14 (2006.01)

C07D 407/14 (2006.01) C07D 495/04 (2006.01)

C07D 409/04 (2006.01) C07D 519/00 (2006.01)

(21) International Application Number:

PCT/EP2024/065737

(22) International Filing Date:

07 June 2024 (07.06.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

23305920.3 09 June 2023 (09.06.2023) EP

(71) Applicant: **ESSILOR INTERNATIONAL** [FR/FR]; 147 rue de Paris, 94220 CHARENTON-LE-PONT (FR).

(72) Inventors: **GABBUTT, Christopher David**; C/O Essilor International, 147 rue de Paris, 94220 CHARENTON-LE-PONT (FR). **ARMITAGE, Georgina Kate**; C/O Essilor International, 147 rue de Paris, 94220 CHARENTON-LE-PONT (FR). **HERON, Bernard Mark**; C/O Essilor International, 147 rue de Paris, 94220 CHARENTON-LE-PONT (FR). **BIVIER, Claudine**; C/O Essilor International, 147 rue de Paris, 94220 CHARENTON-LE-PONT (FR). **BERIT-DEBAT, Fabien**; C/O Essilor International, 147 rue de Paris, 94220 CHARENTON-LE-PONT (FR). **AR-CHAMBEAU, Samuel**; C/O Essilor International, 147 rue de Paris, 94220 CHARENTON-LE-PONT (FR). **CROSS-LEY, Daniel**; C/O Essilor International, 147 rue de Paris, 94220 CHARENTON-LE-PONT (FR). **AIKEN, Stuart**; C/O Essilor International, 147 rue de Paris, 94220 CHARENTON-LE-PONT (FR).

(74) Agent: **PLASSERAUD IP**, 104 rue de Richelieu CS92104, 75080 PARIS CEDEX 02 (FR).

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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, 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, ME, 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))
- in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE

(54) Title: ELECTROCHROMIC COMPOUNDS, COMPOSITIONS AND DEVICES COMPRISING THE SAME

(57) Abstract: A family of electrochromic compounds of formula (I) comprising a thiophene, selenophene or furan ring is herein disclosed, as well as electrochromic compositions and devices comprising at least one of said electrochromic compounds of formula (I).

Description**ELECTROCHROMIC COMPOUNDS, COMPOSITIONS AND DEVICES
COMPRISING THE SAME**

5 **[001]** This disclosure relates to a family of electrochromic compounds. More specifically, it relates to a group of electrochromic compounds comprising a 5-membered heterocycle containing sulfur, selenium or oxygen atoms. The present disclosure also refers to compositions and optical articles comprising said electrochromic compounds.

10 **[002]** Electrochromism is a well-known physical phenomenon which is observed with certain classes of chemical compounds that reversibly change color when a voltage is applied to them. The material undergoes reversible changes in optical properties by oxidation and reduction. Advantageously, the electrochromic material is colorless when an electric field is not applied and becomes colored when an electric field is applied.

15 **[003]** An electrochromic device, i.e. a device containing electrochromic compounds (for instance electrochromic dyes), the absorbance of which depends only on the presence of an electric field, can thus have two states, i.e. a colored state (when electrically activated) and a bleached state (in the inactive state). The optical transmission properties of the device depend on the nature of the electrochromic compounds.

20 **[004]** Electrochromic compositions having a desired color can be obtained by mixing different electrochromic compounds. These different electrochromic compounds can be oxidizing electrochromic compounds (compounds undergoing a reduction when activated) as well as reducing electrochromic compounds (compounds undergoing an oxidation when activated). However, obtaining the desired color for an electrochromic composition is an exercise much more complex than simply mixing colors. Indeed, in addition to the numerous requirements that the electrochromic compounds should meet, the challenge of using a combination of different electrochromic compounds lays in the compatibility of said electrochromic compounds with each other.

30 **[005]** For example, when preparing an electrochromic composition to be used as transparent media for forming high quality optical articles, in particular high quality ophthalmic lenses and electrochromic eyewear devices, the choice of electrochromic compounds is an important factor. Indeed, electrochromic compounds need not only to show good electrochromic properties such as high absorption of the visible light in the colored state, low absorption of visible radiations in the bleached state, fast coloring and fading rates, but should also have long-term stability, in particular in the presence of oxygen, and good solubility in conventional solvents. In addition, compounds with a narrow absorption band advantageously allow absorbing specific wavelengths in order to provide specific eye protection, visual aid and contrast enhancement.

35 **[006]** Gathering all the required properties in one single compound is a real challenge. Several studies have already been conducted for providing electrochromic compounds having the best

compromise. For example, viologen compounds have been identified as oxidizing electrochromic compounds of particular interest due to their high molar absorption coefficient.

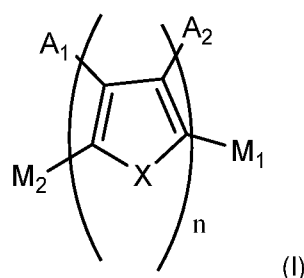
[007] On the other hand, the use of a combination of several electrochromic compounds in a single composition further requires that the electrochromic compounds have oxido-reducing potentials close enough so that they can change color simultaneously when a potential is applied to the composition and avoid producing the so-called chameleon effect during the activation of the formulation.

[008] Another difficulty to face when using electrochromic composition in ophthalmic applications is to meet the consumer demand, which requires a wide range of colors available, and in particular neutral colors (i.e. brown, grey, grey-green...). In this context, blue viologens are well-known. Green, orange, yellow or red viologens have also been described. These molecules are oxidizing electrochromic compounds which are colored under their reduced state and are usually associated with reducing electrochromic molecules that are colored under oxidation; however some of those are weakly colored.

[009] There remains therefore a need for new electrochromic compounds which would allow the expansion of the range of colors, avoiding the so-called chameleon effect, while at the same time providing increased molar absorptivity. This would allow minimizing the concentration of those dyes in the formulation while providing the desired tint with the desired intensity when those are activated and the manufacturing of optical devices providing superior eye protection, visual aid and contrast enhancement.

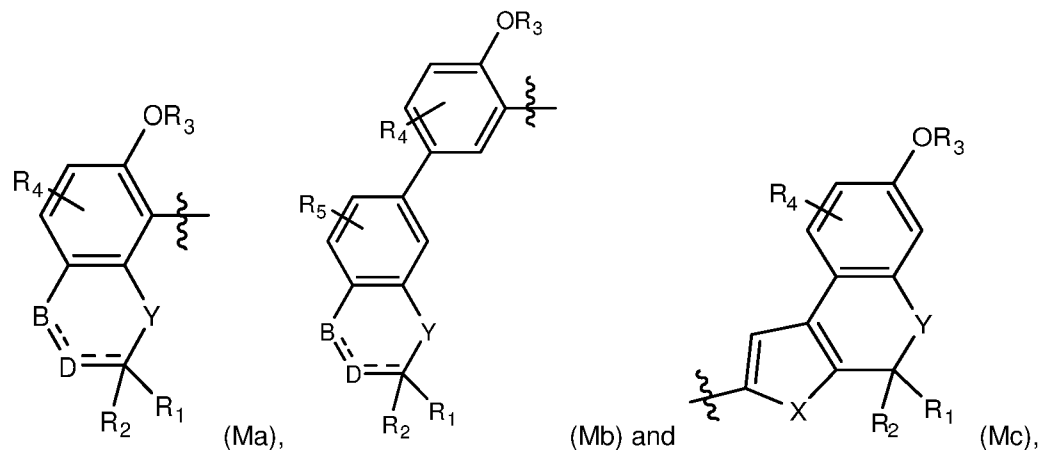
[0010] After conducting extensive research, the present inventors provide a family of electrochromic compounds of formula (I), comprising an aromatic ring thiophene, selenophene or furan, which solve some of the issues encountered in the prior art.

[0011] The present disclosure refers, therefore, to an electrochromic compound represented by formula (I):



wherein

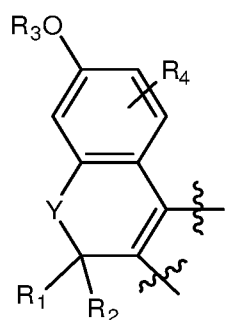
- (i) **A₁** and **A₂** are both H; **n** is 1, 2 or 3; and **M₁** and **M₂** are each independently selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc:



and wherein **at least one** of M_1 and M_2 is selected from the group consisting of Ma, Mb and Mc;

or

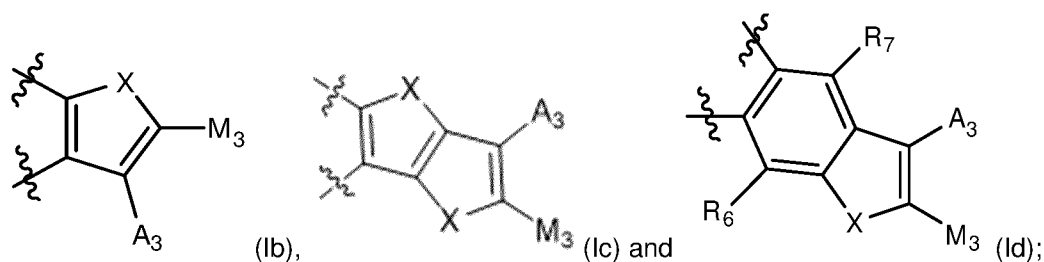
- 5 (ii) n is 1; A_2 is H; A_1 and M_2 form together a heterocyclic group fused to the central 5-membered heterocyclic ring they are attached to; wherein said heterocyclic group formed is a group Ia:



(Ia); and M_1 is selected from the group consisting of H, 2,6-di- C_{1-12} alkoxyphenyl, Ma, Mb and Mc;

or

- 10 (iii) n is 1; A_1 is H; M_2 is selected from the group consisting of H, 2,6-di- C_{1-12} alkoxyphenyl, Ma, Mb and Mc; and A_2 and M_1 form together a heterocyclic group fused to the central 5-membered heteroaromatic ring they are attached to; wherein said heterocyclic group is selected from the group consisting of Ib, Ic and Id:



- 15 and wherein A_3 is H and M_3 is selected from the group consisting of H, 2,6-di- C_{1-12} alkoxyphenyl, Ma, Mb and Mc, wherein **at least one** of M_2 and M_3 is selected from the group consisting of Ma, Mb and Mc;

and wherein

----- is a single bond or a double bond;

each **X** is an atom independently selected from the group consisting of S, Se and O;

each **Y** is an atom independently selected from the group consisting of O, S, -NR₈, N-C(O)R₈ and N-S(O)₂R₈ ;

B is present or not, and, if present is CH or CH₂;

D is C-R₁₀, CH or (CH₂)_m, wherein m is 1, 2 or 3;

R₁ is present or not;

when **R**₁ is present, each **R**₁ is independently selected from the group consisting of H, C₃₋₁₂ cycloalkyl, linear C₁₋₁₂ alkyl and branched C₃₋₁₂ alkyl; and each **R**₂ is independently selected from the group consisting of H, C₃₋₁₂ cycloalkyl, linear C₁₋₁₂ alkyl and branched C₃₋₁₂ alkyl; or **R**₁ and **R**₂ form together with the carbon atom to which they are attached, a C₄₋₁₂ spiro-cycloalkyl group;

when **R**₁ is not present, **D** is C-R₁₀, wherein **R**₂ and **R**₁₀ form together with the carbon atom to which they are attached a C₆₋₁₀ aryl group fused to the ring to which **R**₁₀ and **R**₂ are attached to;

each **R**₃ is independently selected from the group consisting of linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl, C₁₋₁₂ haloalkyl, C₃₋₁₂ cycloalkyl, -C(O)NR₈R₉, and a 6-membered heteroaromatic ring including at least 1 oxygen atom; and each **R**₄ is independently selected from the group consisting of H, C₁₋₁₂ alkoxy, C₁₋₁₂ alkyl and -NR₈R₉; or when **R**₄ and **OR**₃ are substituents of two adjacent carbon atoms of the benzene ring they are attached to, said **R**₄ and **OR**₃ form together with the carbon atom to which they are attached, a 5 to 7-membered oxygen-containing ring fused to the benzene ring to which **R**₄ and **OR**₃ are attached; wherein said 5 to 7-membered oxygen-containing ring is optionally substituted with one or more C₁₋₆ alkyl groups;

each **R**₅ is independently selected from the group consisting of H, C₁₋₁₂ alkoxy, C₁₋₁₂ alkyl and -NR₈R₉

R₆ and **R**₇ are each independently selected from the group consisting of H, linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl, C₆₋₁₀ aryl, C₁₋₁₂ alkoxy; and

R₈ and **R**₉ are each independently selected from the group consisting of H, linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl and C₆₋₁₀ aryl.

[0012] In particular, the compounds of formula (I) herein disclosed provide an intense, , absorption in the visible range and are strongly colored when oxidized, allowing reducing the concentration of said dyes in the compositions and devices comprising those. Advantageously, some of the compounds of formula (I) herein disclosed also present a narrow absorption band which makes them particularly useful in the manufacturing of optical devices providing superior eye protection, visual aid and contrast enhancement.

[0013] Advantageously, some of the electrochromic compounds of formula (I) herein disclosed also feature increased molar absorptivity on the derived radical cation species compared to other compounds of the prior art.

5 [0014] Indeed, the side groups **M**₁ and **M**₂, may efficiently conjugate with and act as an electron donor to the central aromatic ring thiophene, selenophene or furan, due to their highly restricted conformational mobility. Without wishing to be bound by theory, it appears that the structural characteristics of the groups **M**₁ and **M**₂ exert a very significant increase in the molar absorptivity of the compounds compared to other structurally similar compounds.

10 [0015] For all of the above, the present invention also relates to an electrochromic composition comprising at least one compound of formula (I).

[0016] Finally, the present invention relates to an electrochromic device, such as an ophthalmic lens, comprising an electrochromic compound of formula (I) or an electrochromic composition according to the invention.

15 [0017] The expression “alkyl” or “C₁-C₁₈ alkyl” represents any monovalent radical of a linear or branched hydrocarbon chain comprising 1 to 18 carbon atoms. The expression “C₁₋₆ alkyl” represents an alkyl group having 1 to 6 carbon atoms. Examples of C₁₋₁₈ alkyl groups include, among others, C₁₋₄ alkyl groups such as methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *s*-butyl or *t*-butyl, C₆₋₈ alkyl groups such as *n*-hexyl, *n*-heptyl or *n*-octyl, as well as *n*-pentyl, 2-ethylhexyl, 3,5,5-trimethylhexyl, *n*-nonyl, *n*-decyl, *n*-undecyl, *n*-dodecyl or *n*-octadecyl.

20 [0018] The expression “alkoxy” means an alkyl-O- group, wherein said alkyl is as defined herein. Examples of alkoxy groups notably include, among others, methoxy, ethoxy and isopropoxy. The expression “haloalkyl” refers to an alkyl group as defined herein comprising one or more halogen atom (F, Cl, Br or I) substitution, among which (per)fluoroalkyl groups refer to alkyl groups as defined herein, having one to three fluorine atom substitutions.

25 [0019] As used herein, the expression “aromatic group” or “aromatic ring” or “heteroaromatic ring” refer to unsaturated chemical groups characterized by one or more planar rings of atoms joined by covalent bonds. The expressions “heteroaromatic group” or “heteroaromatic ring” refers to aromatic groups or rings comprising at least one heteroatom, i.e., contain at least one sulfur, selenium, nitrogen, oxygen, or other non-carbon atoms.

30 [0020] The expression “aryl” represents any monovalent radical of an aromatic group comprising 6 to 18 carbon atoms, notably 6 to 10 carbon atoms, either monocyclic or polycyclic. Examples of C₆₋₁₈ aryl groups include, among others, phenyl, naphthyl, anthracenyl and phenanthrenyl. The expressions “aryl” and “aromatic group” refer to the same chemical group, but while “aryl” refers to a monovalent radical, “aromatic group” may refer indistinctively to a monovalent radical or to a bivalent or a trivalent radical of the corresponding aromatic group.

35

[0021] The expression “heteroaryl” represents any monovalent radical of a monocyclic or polycyclic 5 to 10 membered aromatic group (such as a bicyclic group) comprising from 1 to 3 heteroatoms independently selected from oxygen, nitrogen and sulfur. Thus, the expression “heteroaryl” includes

heteroatom-containing aromatic rings or heteroatom-containing polycyclic aromatic groups. The expressions “heteroaryl” and “hetero aromatic group” refer to the same chemical group, but while “heteroaryl” refers to a monovalent radical, “hetero aromatic group” may refer indistinctively to a monovalent radical or to a bivalent or a trivalent radical of the corresponding chemical group.

- 5 Examples of heteroaryl or hetero aromatic groups include, among others, furyl, thienyl (or thiophen-2-yl or thiophen-3-yl), selenophenyl, pyrrolyl, pyrazoyl, imidazolyl, isoxazolyl, isothiazoyl, thiazolyl, oxazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, pyridinyl, pyridazinyl, pyrimidinyl and pyrazinyl, as well as their respective bivalent and trivalent radicals.

- [0022]** The expression “heterocycle” refers to a chemical group featuring a closed ring of atoms, aromatic or non-aromatic comprises one or more heteroatoms. Accordingly, a heterocyclic cycle may refer to a heteroaryl, but also to non-aromatic rings containing heteroatoms. Examples of heterocycles include, among others, furan, dihydro and tetrahydrofuran, thiophene, dihydro and tetrahydrothiophene, selenophene, dihydro and tetrahydroselenophene, pyrrole, pyrrolidine, pyrazole, pyrazolidine, imidazole, imidazoline, imidazolidine, oxazole, isoxazole, thiazole, isothiazole, 15 pyridine, pyridazine, pyrimidine, piperidine, piperazine, pyran, tetrahydropyran, thiane, dithiane, thiopyran, as well as their respective monovalent, bivalent and trivalent radicals. In an analogous manner, the expression “heterocyclic group” refers to chemical groups featuring one or more closed rings of atoms, aromatic or non-aromatic, wherein at least one ring comprises one or more heteroatoms. Accordingly, a heterocyclic group may contain an aromatic group, a hetero aromatic group, but also non-aromatic heterocycles. Examples of heterocyclic groups include, among others, 20 furyl, thienyl (or thiophen-2-yl or thiophen-3-yl), selenophenyl, pyrrolyl, pyrazoyl, imidazolyl, isoxazolyl, isothiazoyl, thiazolyl, oxazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1-benzofuryl, 1-benzothienyl, indolyl, benzimidazolyl, benzimidazolium, benzimidazoliumyl, indazolyl, 1,2-benzisoxazolyl, 2,1-benzisoxazolyl, 1,2-benzisothiazolyl, 2,1-benzisothiazolyl, benzothiazolyl, benzoxazolyl, 25 benzoxazoliumyl, benzoselenazoliumyl, benzotriazolyl, 2H-chromenyl, 4H-chromenyl, 1H-isochromenyl, 3H-isochromenyl, chromanyl (dihydrobenzopyranyl), benzothianyl, dihydrobenzothianyl, benzofuranyl, 2,3-dihydrobenzofuranyl, dibenzofuranyl, pyridinyl, pyridiniumyl, N-alkylpyridiniumyl, N-arylpyridiniumyl, quinoliny, quinolinium, quinoliniumyl, isoquinoliny, isoquinolinium, isoquinoliniumyl, pyridazinyl, cinnoliny, phthalazinyl, pyrimidinyl, quinazolinyl, 30 pyrazinyl and quinoxalinyl, as well as their respective bivalent and trivalent radicals.

[0023] In some embodiments the compound of formula (I) comprises more than one atom **X** and:

- each **X** is the same type of atom and is selected from the group consisting of S, Se and O; or
- each **X** is a different type of atom, and each **X** is independently selected from the group consisting of S, Se and O.

- 35 **[0024]** In some embodiments the compound of formula (I) comprises more than one atom **X** and at least one **X** is S, or all **X** are S. In other embodiments the compound of formula (I) comprises more than one atom **X** and at least one **X** is Se or all **X** are Se. In yet other embodiments the compound of formula (I) comprises more than one atom **X** and at least one at least one **X** is O or all **X** are O. In

some embodiments, the compound of formula (I) comprises more than one atom **X** and each **X** is **S** or **Se**, or each **X** is **S** or **O**, or each **X** is **Se** or **O**.

[0025] In some embodiments one or more of **X** is **S**. In other embodiments one or more of **X** is **Se**. In yet other embodiments one or more of **X** is **O**.

- 5 [0026] In some embodiments **A**₁ and **A**₂ are both **H**; **n** is 1, 2 or 3, preferably **n** is 1 or 2, also preferably **n** is 1.

[0027] In some embodiments each **Y** is independently **O** or **S**. In some embodiments **Y** is **O**. In some other embodiments **Y** is **S**. In some embodiments one or more of **Y** is **S**. In other embodiments one or more of **Y** is **O**.

- 10 [0028] In some preferred embodiments **B** is present, both **B** and **D** are **CH**₂ and **-----** is a single bond. In other embodiments **B** is present, both **B** and **D** are **CH** and **=====** is a double bond. In some embodiments **B** is not present.

[0029] In some embodiments **R**₁ is present and:

- 15 each **R**₁ is independently selected from the group consisting of **H**, **C**₃₋₁₂ cycloalkyl, linear **C**₁₋₁₂ alkyl and branched **C**₃₋₁₂ alkyl; and each **R**₂ is independently selected from the group consisting of **H**, **C**₃₋₁₂ cycloalkyl, linear **C**₁₋₁₂ alkyl and branched **C**₃₋₁₂ alkyl; preferably each **R**₁ is independently a linear **C**₁₋₆ alkyl or branched **C**₃₋₆ alkyl; and each **R**₂ is independently a linear **C**₁₋₆ alkyl or a branched **C**₃₋₆ alkyl; more preferably each **R**₁ and **R**₂ are independently methyl, ethyl, propyl or isopropyl; or

- 20 **R**₁ and **R**₂ form together with the carbon atom to which they are attached, a **C**₄₋₁₂ spiro-cycloalkyl, preferably a **C**₅₋₆ spiro-cycloalkyl; more preferably a **C**₆ spiro-cycloalkyl group.

[0030] In some embodiments **R**₁ is present and both **R**₁ and **R**₂ are a same moiety, being said moiety selected from the group consisting of **H**, **C**₃₋₁₂ cycloalkyl, linear **C**₁₋₁₂ alkyl and branched **C**₃₋₁₂ alkyl, preferably a linear **C**₁₋₆ alkyl or branched **C**₃₋₆ alkyl; more preferably methyl, ethyl, propyl or isopropyl.

- 25 [0031] In other embodiments **R**₁ is present and both **R**₁ and **R**₂ are a different moiety, being each **R**₁ and **R**₂ independently selected from the group consisting of **H**, **C**₃₋₁₂ cycloalkyl, linear **C**₁₋₁₂ alkyl and branched **C**₃₋₁₂ alkyl, preferably a linear **C**₁₋₆ alkyl or branched **C**₃₋₆ alkyl; more preferably methyl, ethyl, propyl or isopropyl.

- [0032] In some embodiments **R**₁ is present and both **R**₁ and **R**₂ are methyl, ethyl, propyl or isopropyl; or **R**₁ and **R**₂ form together with the carbon atom to which they are attached a **C**₅₋₆ spiro-cycloalkyl; more preferably a **C**₆ spiro-cycloalkyl group.

- [0033] In some embodiments **R**₁ is not present and **D** is **C-R**₁₀, wherein **R**₂ and **R**₁₀ form together with the carbon atom to which they are attached a **C**₆₋₁₀ aryl group, preferably a benzene ring, fused to the ring to which **R**₁₀ and **R**₂ are attached to.

[0034] In some embodiments, **B** and **R₁** are not present and **D** is C-**R₁₀**, wherein **R₂** and **R₁₀** form together with the carbon atom to which they are attached a C₆₋₁₀ aryl group, preferably a benzene ring, fused to the ring to which **R₁₀** and **R₂** are attached to.

[0035] In some embodiments each **R₃** is independently selected from the group consisting of linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl, C₁₋₁₂ haloalkyl, C₃₋₁₂ cycloalkyl, -C(O)NR₈R₉, and a 6-membered heteroaromatic ring including at least 1 oxygen atom, such as pyran or dioxine; preferably each **R₃** is independently a linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl, or C₁₋₁₂ (per)fluoroalkyl, more preferably a linear C₁₋₆ alkyl, a branched C₃₋₆ alkyl or C₁₋₆ (per)fluoroalkyl, even more preferably methyl, ethyl, propyl or isopropyl.

10 [0036] In some embodiments **R₁** and **R₂** are each independently a linear C₁₋₆ alkyl group or a branched C₃₋₆ alkyl group; **R₃** is independently a linear C₁₋₆ alkyl group, a branched C₃₋₆ alkyl group or C₁₋₆ (per)fluoroalkyl group; and **R₄**, **R₅**, **R₆** and **R₇** are all H.

[0037] In some embodiments **R₁**, **R₂** and **R₃** are all a same moiety, being said moiety selected from the group consisting of H, C₃₋₁₂ cycloalkyl, linear C₁₋₁₂ alkyl and branched C₃₋₁₂ alkyl, preferably a linear C₁₋₆ alkyl or branched C₃₋₆ alkyl; more preferably methyl, ethyl, propyl or isopropyl.

[0038] In other embodiments **R₁**, **R₂** and **R₃** may be each a different moiety, being each **R₁**, **R₂** and **R₃** independently selected from the group consisting of H, C₃₋₁₂ cycloalkyl, linear C₁₋₁₂ alkyl and branched C₃₋₁₂ alkyl, preferably a linear C₁₋₆ alkyl or branched C₃₋₆ alkyl; more preferably methyl, ethyl, propyl or isopropyl.

20 [0039] In some embodiments **R₁**, **R₂** and **R₃** are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl.

[0040] In some embodiments, each **R₄** is independently selected from the group consisting of H, C₁₋₁₂ alkoxy, C₁₋₁₂ alkyl and -NR₈R₉; wherein **R₈** and **R₉** are each independently selected from the group consisting of H, linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl and C₆₋₁₀ aryl, preferably each independently selected from the group consisting of H, linear C₁₋₆ alkyl, branched C₃₋₆ alkyl and C₆ aryl. In some preferred embodiments **R₄** is H.

[0041] In some other embodiments, when **R₄** and **OR₃** are substituents of two adjacent carbon atoms of the benzene ring they are attached to, said **R₄** and **OR₃** form together with the carbon atom to which they are attached, a 5 to 7-membered oxygen-containing ring, preferably dihydropyran, fused to the benzene ring to which **R₄** and **OR₃** are attached; wherein said 5 to 7-membered oxygen-containing ring is optionally substituted with one or more C₁₋₆ alkyl groups. In some embodiments, when **R₄** and **OR₃** are substituents of two adjacent carbon atoms of the benzene ring they are attached to, said **R₄** and **OR₃** form together with the carbon atom to which they are attached, a dihydropyran substituted with one or more C₁₋₆ alkyl groups.

35 [0042] In some embodiments each **R₅** is independently selected from the group consisting of H, C₁₋₁₂ alkoxy, C₁₋₁₂ alkyl and -NR₈R₉, preferably selected from the group consisting of H, linear C₁₋₆ alkyl, branched C₃₋₆ alkyl and C₆ aryl. In some preferred embodiments **R₅** is H.

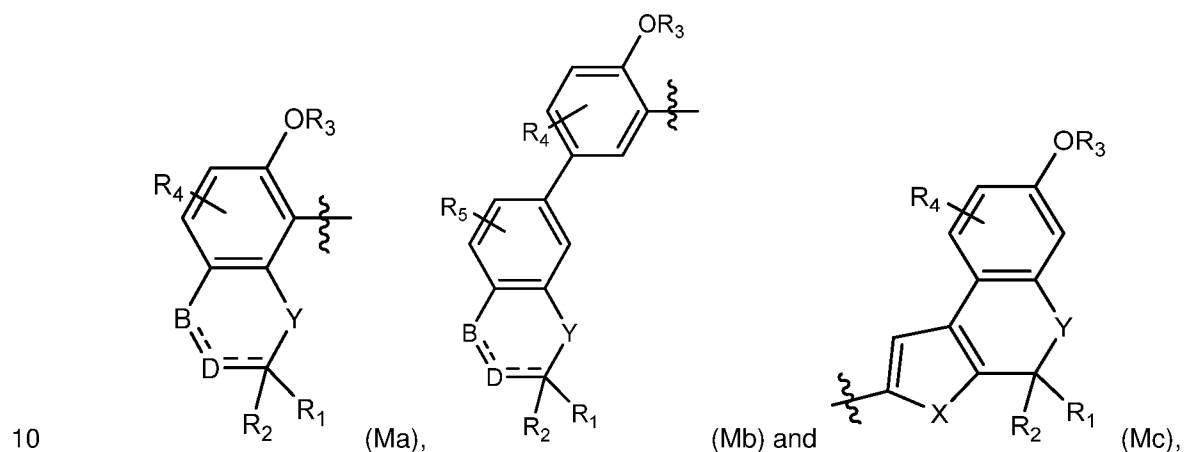
[0043] In some embodiments **R**₄ and **R**₅ are both H.

[0044] In some embodiments **R**₆ and **R**₇ are each independently selected from the group consisting of H, linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl, C₆₋₁₀ aryl, C₁₋₁₂ alkoxy; preferably each independently selected from the group consisting of H, linear C₁₋₆ alkyl, branched C₃₋₆ alkyl, C₆ aryl and C₁₋₆ alkoxy.

5 [0045] In some embodiments **R**₆ and **R**₇ are both H.

[0046] In some embodiments, **R**₁, **R**₂ and **R**₃ are each independently a C₁₋₆ alkyl group and **R**₄, **R**₅, **R**₆ and **R**₇ are all H.

[0047] In some embodiments, **A**₁ and **A**₂ are both H; **n** is 1, 2 or 3; and **M**₁ and **M**₂ are each independently selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc:



wherein **at least one** of **M**₁ and **M**₂ is selected from the group consisting of Ma, Mb and Mc; and wherein **R**₁, **R**₂, **R**₃, **R**₄, **R**₅, -----, **X**, **Y**, **B** and **D** are each independently as described in the claims and the present description.

15 [0048] In some embodiments, **A**₁ and **A**₂ are both H; **n** is 1, and **M**₁ and **M**₂ are each independently selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc as described in the claims and the present description; wherein **at least one** of **M**₁ and **M**₂ is selected from the group consisting of Ma, Mb and Mc.

[0049] In some embodiments, **M**₁ is Ma and **M**₂ is Mb. In other embodiments **M**₁ is Ma and **M**₂ is Mc. In yet other embodiments **M**₁ is Mb and **M**₂ is Mc.

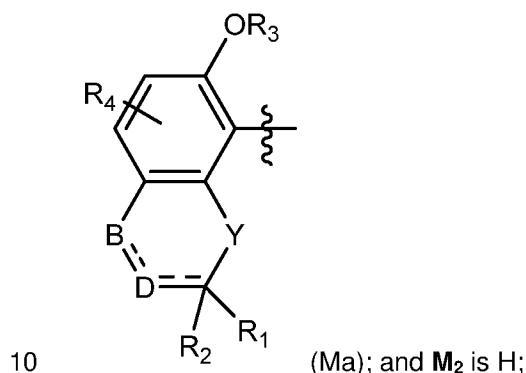
20 [0050] In some embodiments, **M**₁ and **M**₂ are the same moiety, wherein said moiety is selected from the group consisting of Ma, Mb and Mc as described in the claims and the present description, preferably **M**₁ and **M**₂ are the same moiety, wherein said moiety is Ma or Mb.

25 [0051] In some embodiments **M**₁ and **M**₂ are different and are each independently selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc as described in the claims and the present description, wherein at least one of **M**₁ and **M**₂ is selected from the group consisting of Ma, Mb and Mc.

[0052] In some embodiments M_1 and M_2 are different, wherein one of M_1 and M_2 is H or 2,6-di- C_{1-12} alkoxyphenyl and another one of M_1 and M_2 is selected from the group consisting of Ma, Mb and Mc as described in the claims and the present description.

[0053] In some embodiments, at least one of M_1 and M_2 is Ma as described in the claims and the present description. In some embodiments both M_1 and M_2 are a group Ma as described in the claims and the present description. In some embodiments one or both of M_1 and M_2 is Ma as described in the claims and the present description.

[0054] In some embodiments one of M_1 is Ma and M_2 is H. In some embodiments, X is S; A_1 and A_2 are both H; n is 1; M_1 is Ma:



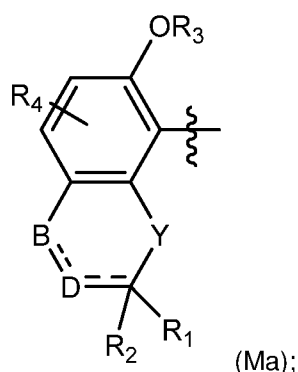
wherein R_1 , R_2 , R_3 , R_4 , -----, Y , B and D are each independently as described in the claims and the present description; preferably R_1 is a linear C_{1-6} alkyl or branched C_{3-6} alkyl; R_2 is a linear C_{1-6} alkyl or a branched C_{3-6} alkyl; R_3 is a linear C_{1-6} alkyl, a branched C_{3-6} alkyl, or C_{1-6} (per)fluoroalkyl; R_4 is H; Y is S; B is present, and both B and D are CH_2 and ----- is a single bond; more preferably

15 R_1 , R_2 and R_3 are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl; R_4 is H; Y is S; B is present, and both B and D are CH_2 and ----- is a single bond.

[0055] In some embodiments, A_1 and A_2 are both H; n is 2, and M_1 and M_2 are each independently selected from the group consisting of H, 2,6-di- C_{1-12} alkoxyphenyl, Ma, Mb and Mc, as described in the claims and the present description; wherein at least one of M_1 and M_2 is selected from the group

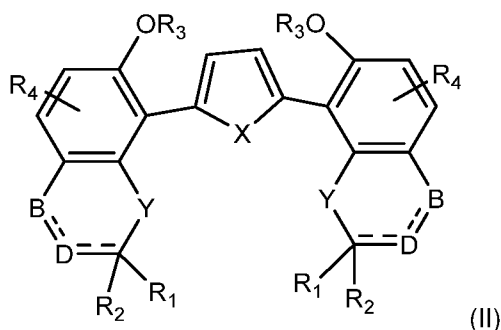
20 consisting of Ma, Mb and Mc.

[0056] In some embodiments, X is S, A_1 and A_2 are both H; n is 2, and M_1 and M_2 are both Ma:



wherein **R**₁, **R**₂, **R**₃, **R**₄, -----, **Y**, **B** and **D** are each independently as described in the claims and the present description, preferably, each **R**₁ is independently a linear C₁₋₆ alkyl or branched C₃₋₆ alkyl; each **R**₂ is independently a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl; each **R**₃ is independently a linear C₁₋₆ alkyl, a branched C₃₋₆ alkyl, or C₁₋₆ (per)fluoroalkyl; **R**₄ is H; **Y** is O; **B** is present, and both **B** and **D** are CH₂ and ----- is a single bond; more preferably **R**₁, **R**₂ and **R**₃ are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl; **R**₄ is H; **Y** is O; **B** is present, and both **B** and **D** are CH₂ and ----- is a single bond.

[0057] In some embodiments **A**₁ and **A**₂ are both H; **n** is 1, both **M**₁ and **M**₂ are Ma, and the electrochromic compound disclosed is represented by Formula (II):



wherein **R**₁, **R**₂, **R**₃, **R**₄, -----, **Y**, **B** and **D** are each independently as described in the claims and the present description.

[0058] In some embodiments, when one or both of **M**₁ and **M**₂ is Ma:

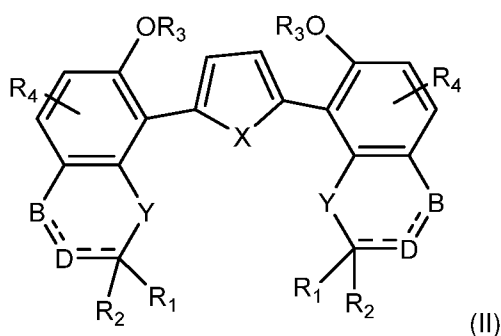
each **R**₁ is independently selected from the group consisting of H, C₃₋₁₂ cycloalkyl, linear C₁₋₁₂ alkyl and branched C₃₋₁₂ alkyl; and each **R**₂ is independently selected from the group consisting of H, C₃₋₁₂ cycloalkyl, linear C₁₋₁₂ alkyl and branched C₃₋₁₂ alkyl; preferably each **R**₁ is independently a linear C₁₋₆ alkyl or branched C₃₋₆ alkyl; and each **R**₂ is independently a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl; more preferably **R**₁ and **R**₂ are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl; or **R**₁ and **R**₂ form together with the carbon atom to which they are attached, a C₄₋₁₂ spiro-cycloalkyl, preferably a C₅₋₆ spiro-cycloalkyl, more preferably a C₆ spiro-cycloalkyl;

each **R**₃ is independently selected from the group consisting of linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl, C₃₋₁₂ cycloalkyl, C₁₋₁₂ haloalkyl -C(O)NR₈R₉, and a 6-membered heteroaromatic ring including at least 1 oxygen atom; such as pyran or dioxine; preferably each **R**₃ is independently a linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl or C₁₋₁₂ (per)fluoroalkyl, more preferably linear C₁₋₆ alkyl, a branched C₃₋₆ alkyl or C₁₋₆ (per)fluoroalkyl; even more preferably methyl, ethyl, propyl or isopropyl; and

each **R**₄ is independently selected from the group consisting of H, C₁₋₁₂ alkoxy, C₁₋₁₂ alkyl and -NR₈R₉; **R**₄ preferably is H; or when **R**₄ and **OR**₃ are substituents of two adjacent carbon atoms of the benzene ring they are attached to, said **R**₄ and **OR**₃ form together with the carbon atom to which they are attached, a 5 to 7-membered oxygen-containing ring fused to the benzene ring to which **R**₄ and **OR**₃ are attached; wherein said 5 to 7-membered

oxygen-containing ring is optionally substituted with one or more C₁₋₆ alkyl groups; preferably a pyran or a dihydropyran ring, more preferably a dihydropyran ring, fused to the benzene ring to which **R**₄ and **OR**₃ are attached; wherein said pyran or dihydropyran ring, more preferably said dihydropyran ring, is substituted with one or more C₁₋₆ alkyl groups.

- 5 [0059] In some embodiments, **X** is S, O or Se, more preferably S; **A**₁ and **A**₂ are both H; **n** is 1, both **M**₁ and **M**₂ are Ma, and the electrochromic compound disclosed is represented by Formula (II):



wherein

each **Y** is independently O or S;

- 10 each **R**₁ is independently a linear C₁₋₆ alkyl or branched C₃₋₆ alkyl, preferably methyl, ethyl, propyl or isopropyl; and each **R**₂ is independently a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl, preferably methyl, ethyl, propyl or isopropyl; or **R**₁ and **R**₂ form together with the carbon atom to which they are attached, a C₆ cycloalkyl;

- each **R**₃ is independently a linear C₁₋₆ alkyl, a branched C₃₋₆ alkyl or C₁₋₆ (per)fluoroalkyl, preferably methyl, ethyl, propyl or isopropyl; and **R**₄ is H; or when **R**₄ and **OR**₃ are substituents of two adjacent carbon atoms of the benzene ring they are attached to, said **R**₄ and **OR**₃ form together dihydropyran ring fused to the benzene ring to which **R**₄ and **OR**₃ are attached, wherein said dihydropyran ring, is substituted with one or more C₁₋₆ alkyl groups; and

- 15 **B** is present, and both **B** and **D** are CH₂ and ----- is a single bond or both **B** and **D** are CH and ----- is a double bond;

or wherein

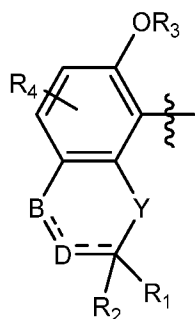
each **Y** is independently O or S, preferably O;

- R**₁ is not present and **D** is C-**R**₁₀, wherein **R**₂ and **R**₁₀ form together with the carbon atom to which they are attached a C₆₋₁₀ aryl group, preferably a benzene ring, fused to the ring to which **R**₁₀ and **R**₂ are attached to;

each **R**₃ is independently a linear C₁₋₆ alkyl, a branched C₃₋₆ alkyl or C₁₋₆ (per)fluoroalkyl; and **R**₄ is H.

[0060] In some embodiments one of **M**₁ or **M**₂ is a group 2,6-di-C₁₋₁₂ alkoxyphenyl, preferably a group 2,6-di-C₁₋₆ alkoxyphenyl.

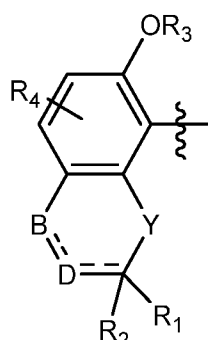
[0061] In some embodiments **M**₁ is Ma:



(Ma) and **M**₂ is a group 2,6-di-C₁₋₁₂ alkoxyphenyl;

wherein **R**₁, **R**₂, **R**₃, **R**₄, -----, **Y**, **B** and **D** are each independently as described in the claims and the present description.

[0062] In some embodiments **X** is S; **A**₁ and **A**₂ are both H; **n** is 1; **M**₁ is Ma:

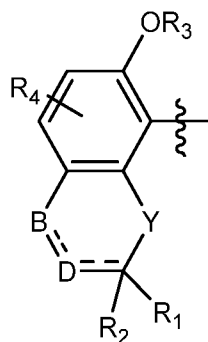


5 (Ma) and **M**₂ is a group 2,6-di-C₁₋₁₂ alkoxyphenyl, preferably a group 2,6-di-C₁₋₆ alkoxyphenyl;

wherein **R**₁, **R**₂, **R**₃, **R**₄, -----, **Y**, **B** and **D** are each independently as described in the claims and the present description, preferably **R**₁ is a linear C₁₋₆ alkyl or branched C₃₋₆ alkyl; **R**₂ is a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl; **R**₃ is a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl; **R**₄ is H; **Y** is O; **B** is present, and both **B** and **D** are CH₂ and ----- is a single bond or both **B** and **D** are CH and ----- is a double bond; more preferably **R**₁, **R**₂ and **R**₃ are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl; **R**₄ is H; **Y** is O; **B** is present, and both **B** and **D** are CH₂ and ----- is a single bond or both **B** and **D** are CH and ----- is a double bond.

10 [0063] In some embodiments **M**₁ is Ma, wherein Ma is as described in the claims and the present description, and **M**₂ is H.

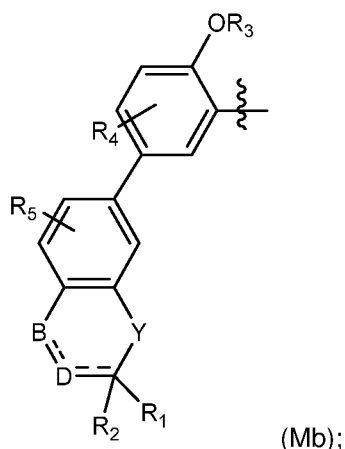
[0064] In some embodiments, **X** is S; **A**₁ and **A**₂ are both H; **n** is 1; **M**₁ is Ma:



(Ma) and **M**₂ is H;

- wherein **R**₁, **R**₂, **R**₃, **R**₄, -----, **Y**, **B** and **D** are each independently as described in the claims and the present description, preferably **R**₁ is a linear C₁₋₆ alkyl or branched C₃₋₆ alkyl; **R**₂ is a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl; **R**₃ is a linear C₁₋₆ alkyl, a branched C₃₋₆ alkyl or C₁₋₆ (per)fluoroalkyl; **R**₄ is H, **Y** is O; **B** is present, and both **B** and **D** are CH₂ and ----- is a single bond; more preferably
- 5 **R**₁, **R**₂ and **R**₃ are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl; **R**₄ is H, **Y** is O; **B** is present, and both **B** and **D** are CH₂ and ----- is a single bond.

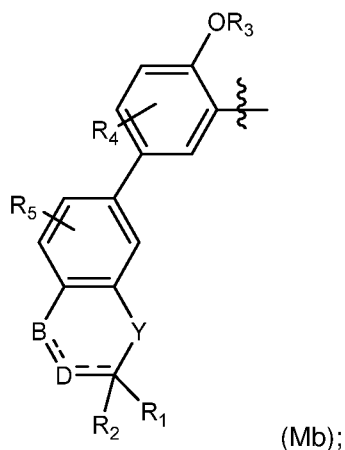
[0065] In some embodiments one or both **M**₁ and **M**₂ is Mb:



- wherein **R**₁, **R**₂, **R**₃, **R**₄, **R**₅, -----, **Y**, **B** and **D** are each independently as described in the claims and the present description.
- 10

[0066] In some embodiments both **M**₁ and **M**₂ are Mb, wherein Mb is as described in the claims and the present description.

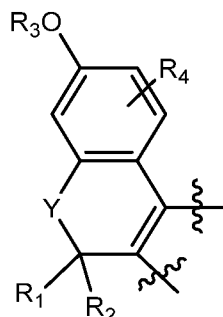
[0067] In some embodiments **X** is S; **A**₁ and **A**₂ are both H; **n** is 1; **M**₁ and **M**₂ are both Mb:



- 15 wherein **R**₁, **R**₂, **R**₃, **R**₄, **R**₅, -----, **Y**, **B** and **D** are each independently as described in the claims and the present description, preferably each **R**₁ is independently a linear C₁₋₆ alkyl or branched C₃₋₆ alkyl; each **R**₂ is independently a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl; each **R**₃ is independently a linear C₁₋₆ alkyl, a branched C₃₋₆ alkyl or C₁₋₆ (per)fluoroalkyl; **R**₄ and **R**₅ are H; **Y** is O; **B** is present, and both **B** and **D** are CH₂ and ----- is a single bond; more preferably **R**₁, **R**₂ and **R**₃ are each

independently selected from the group consisting of methyl, ethyl, propyl and isopropyl; **R**₄ is H, **Y** is O; **B** is present, and both **B** and **D** are CH₂ and ----- is a single bond.

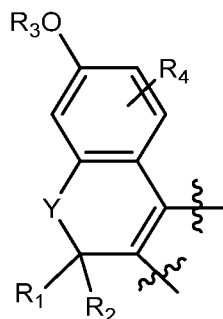
- [0068] In some embodiments **n** is 1; **A**₂ is H; **A**₁ and **M**₂ form together a heterocyclic group fused to the central 5-membered heterocyclic ring they are attached to; wherein said heterocyclic group formed is a group **la**:



(**la**); and **M**₁ is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc;

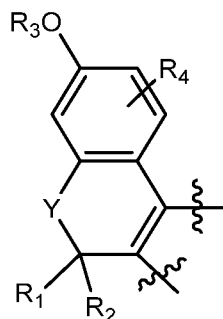
wherein **R**₁, **R**₂, **R**₃, **R**₄, **Y**, Ma, Mb and Mc are each independently as described in the claims and the present description.

- 10 [0069] In some embodiments **X** is S, **A**₂ is H; **A**₁ and **M**₂ form together a heterocyclic group fused to the central 5-membered heterocyclic ring they are attached to; wherein said heterocyclic group formed is a group **la**:



(**la**);

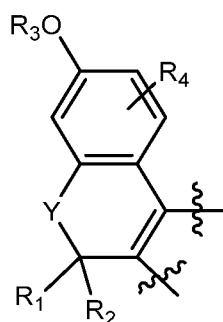
- and **M**₁ is 2,6-di-C₁₋₁₂ alkoxyphenyl or Mc, wherein **Mc**, **R**₁, **R**₂, **R**₃, **R**₄, and **Y** are each independently as described in the claims and the present description; preferably each **R**₁ is independently a linear C₁₋₆ alkyl or branched C₃₋₆ alkyl; each **R**₂ is independently a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl; each **R**₃ is independently a linear C₁₋₆ alkyl, a branched C₃₋₆ alkyl or C₁₋₆ (per)fluoroalkyl; **R**₄ is H and **Y** is O; more preferably **R**₁, **R**₂ and **R**₃ are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl; **R**₄ is H and **Y** is O.
- 20 [0070] In one embodiment **X** is S, **A**₂ is H; **A**₁ and **M**₂ form together a heterocyclic group fused to the central 5-membered heterocyclic ring they are attached to; wherein said heterocyclic group formed is a group **la**



(Ia); and **M**₁ is 2,6-di-C₁₋₁₂ alkoxyphenyl, preferably 2,6-di-C₁₋₆ alkoxyphenyl;

wherein **R**₁, **R**₂, **R**₃, **R**₄ and **Y** are each independently as described in the claims and the present description; preferably **R**₁ is a linear C₁₋₆ alkyl or branched C₃₋₆ alkyl; **R**₂ is a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl; **R**₃ is a linear C₁₋₆ alkyl, a branched C₃₋₆ alkyl or C₁₋₆ (per)fluoroalkyl; **R**₄ is H and **Y** is O; more preferably **R**₁, **R**₂ and **R**₃ are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl; **R**₄ is H and **Y** is O.

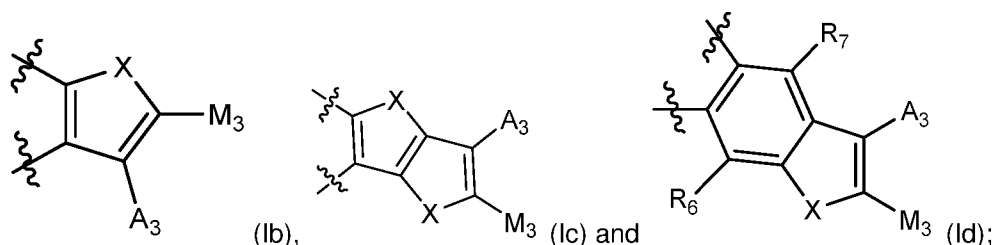
[0071] In another embodiment **X** is S, **A**₂ is H; **A**₁ and **M**₂ form together a heterocyclic group fused to the central 5-membered heterocyclic ring they are attached to; wherein said heterocyclic group formed is a group **Ia**:



(Ia);

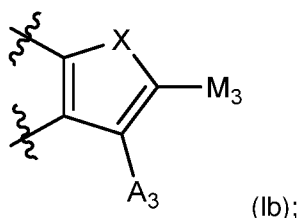
and **M**₁ is Mc, wherein **Mc**, **R**₁, **R**₂, **R**₃, **R**₄, **Y** and **Mc** are each independently as described in the claims and the present description; preferably each **R**₁ is independently a linear C₁₋₆ alkyl or branched C₃₋₆ alkyl; each **R**₂ is independently a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl; each **R**₃ is independently a linear C₁₋₆ alkyl, a branched C₃₋₆ alkyl or C₁₋₆ (per)fluoroalkyl; **R**₄ is H and **Y** is O; more preferably **R**₁, **R**₂ and **R**₃ are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl; **R**₄ is H and **Y** is O.

[0072] In some embodiments, **n** is 1; **A**₁ is H; **M**₂ is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc; and **A**₂ and **M**₁ form together a heterocyclic group fused to the central 5-membered heteroaromatic ring they are attached to; wherein said heterocyclic group is selected from the group consisting of Ib, Ic and Id:



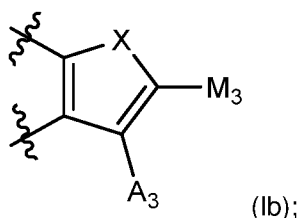
wherein **A₃** is H and **M₃** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc, and wherein **at least one** of **M₂** and **M₃** is selected from the group consisting of Ma, Mb and Mc; and wherein **R₆**, **R₇**, **X**, Ma, Mb and Mc are each independently as described in the claims and the present description.

- 5 **[0073]** In some embodiments **n** is 1; **A₁** is H; **M₂** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc; and **A₂** and **M₁** form together a heterocyclic group fused to the central 5-membered heteroaromatic ring they are attached to; wherein said heterocyclic group is **lb**:



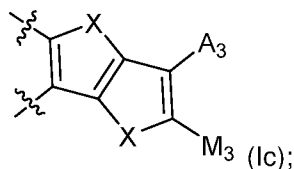
- wherein **A₃** is H and **M₃** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc, and wherein **at least one** of **M₂** and **M₃** is selected from the group consisting of Ma, Mb and Mc; and wherein **X**, Ma, Mb and Mc are each independently as described in the claims and the present description.
- 10

- [0074]** In some embodiments **X** is S, **n** is 1; **A₁** is H; **M₂** is Ma and **A₂** and **M₁** form together a heterocyclic group fused to the central 5-membered heteroaromatic ring they are attached to; wherein said heterocyclic group is **lb**;
- 15



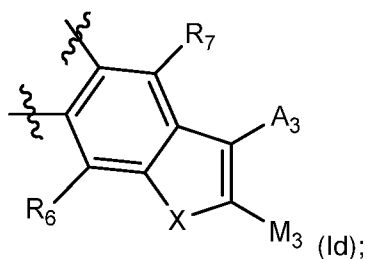
- wherein **A₃** is H and **M₃** is Ma, and wherein Ma, **R₁**, **R₂**, **R₃**, **R₄**, -----, **Y**, **B** and **D** are each independently as described in the claims and the present description, preferably wherein each **R₁** is independently a linear C₁₋₆ alkyl or branched C₃₋₆ alkyl; each **R₂** is independently a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl; each **R₃** is independently a linear C₁₋₆ alkyl, a branched C₃₋₆ alkyl or C₁₋₆ (per)fluoroalkyl; **R₄** is H, **Y** is O; **B** is present, and both **B** and **D** are CH₂ and ----- is a single bond; more preferably wherein **R₁**, **R₂** and **R₃** are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl; **R₄** is H, **Y** is O; **B** is present, and both **B** and **D** are CH₂ and ----- is a single bond.
- 20

- [0075]** In some embodiments **n** is 1; **A₁** is H; **M₂** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc; and **A₂** and **M₁** form together a heterocyclic group fused to the central 5-membered heteroaromatic ring they are attached to; wherein said heterocyclic group is **lc**:
- 25



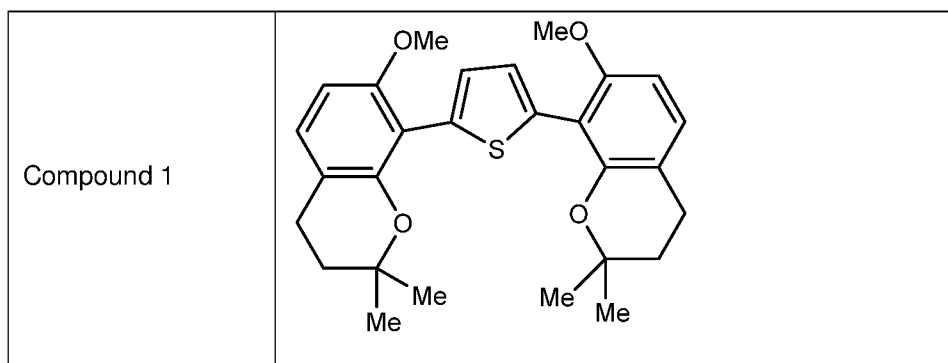
- and wherein **A₃** is H and **M₃** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc, wherein **at least one** of **M₂** and **M₃** is selected from the group consisting of Ma, Mb and Mc; and wherein **X**, Ma, Mb and Mc are each independently as described in the claims and the present description.

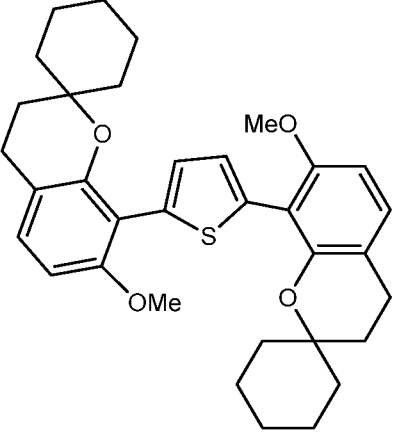
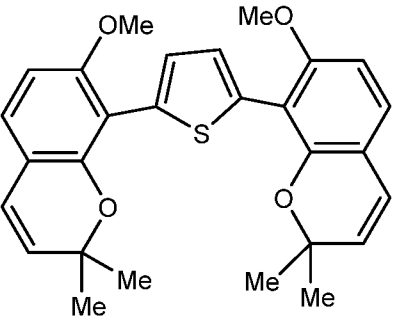
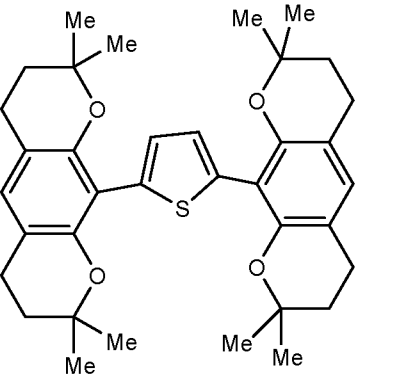
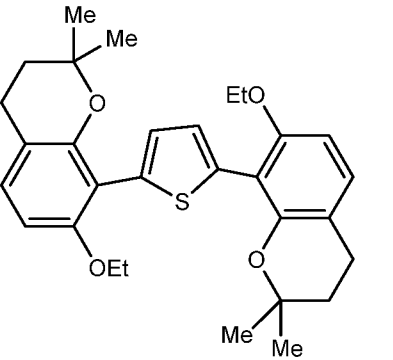
[0076] In some embodiments **n** is 1; **A₁** is H; **M₂** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc; and **A₂** and **M₁** form together a heterocyclic group fused to the central 5-membered heteroaromatic ring they are attached to; wherein said heterocyclic group is **Id**:



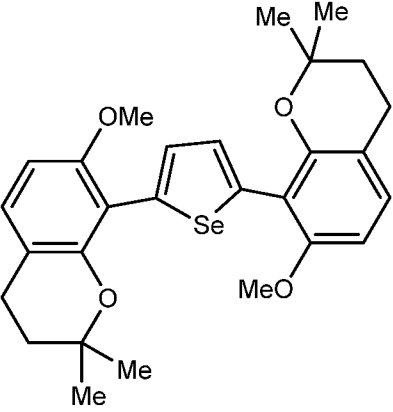
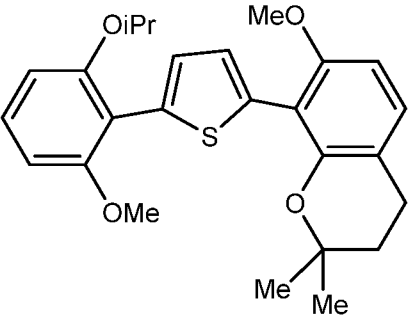
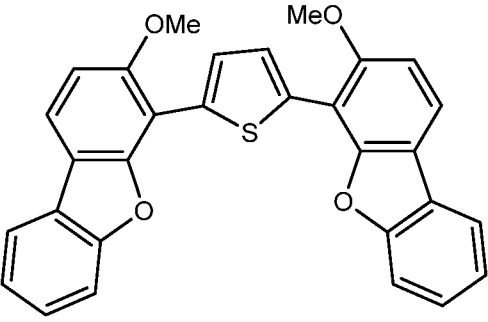
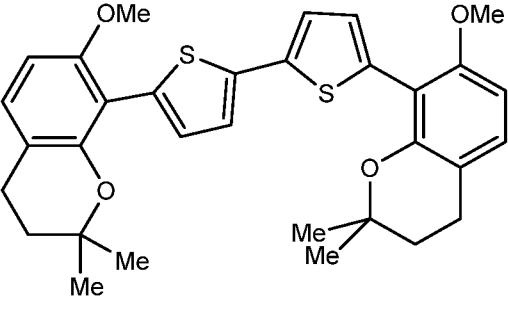
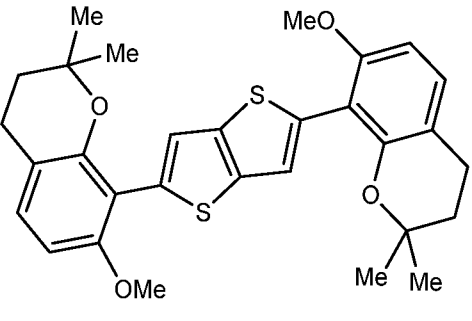
- and wherein **A₃** is H and **M₃** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc, wherein **at least one** of **M₂** and **M₃** is selected from the group consisting of Ma, Mb and Mc; and wherein **R₆**, **R₇**, **X**, Ma, Mb and Mc are each independently as described in the claims and the present description.

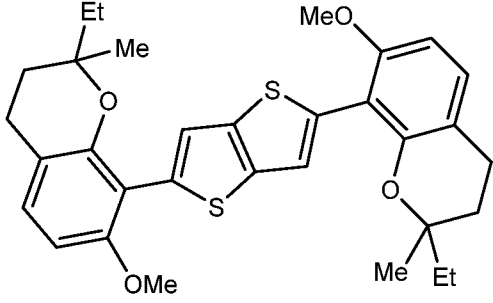
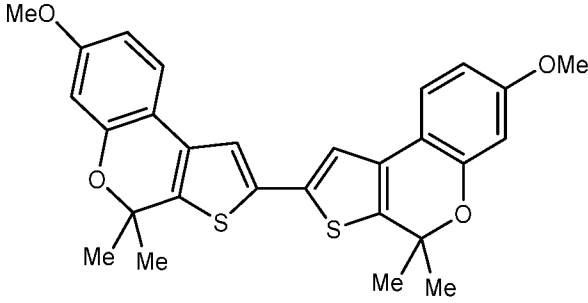
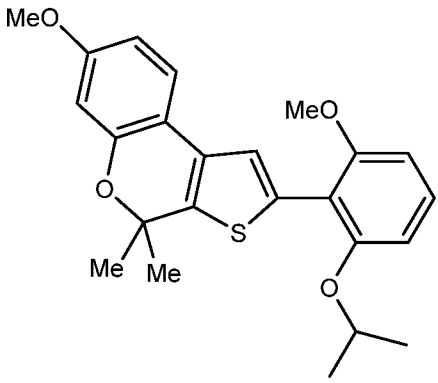
- [0077]** Some preferred embodiments refer to a compound of formula (I) as defined in the claims and the present description, selected from the group consisting of compound 1, compound 2, compound 3, compound 4, compound 5, compound 6, compound 7, compound 8, compound 9, compound 10, compound 11, compound 12, compound 13, compound 14, compound 15, compound 16 and compound 17, herein disclosed:



Compound 2	
Compound 3	
Compound 4	
Compound 5	

Compound 6	
Compound 7	
Compound 8	
Compound 9	

Compound 10	
Compound 11	
Compound 12	
Compound 13	
Compound 14	

Compound 15	
Compound 16	
Compound 17	

Electrochromic composition

[0078] The present invention also relates to electrochromic compositions comprising at least one compound of formula (I) as described in the claims and the present description and a host medium.

- 5 **[0079]** The composition may also comprise at least one or more additional reducing electrochromic compound. The reducing compound may also be an electrochromic compound. Example of reducing compounds include 5,10-dihydrophenazine, phenothiazine, phenoxazine, N,N,N',N'-tetramethyl-p-phenylenediamine, thioanthrene, tetrathiafulvalene, ferrocene and their derivatives.

- 10 **[0080]** Preferably, the additional compound has a redox potential close to the compound of formula (I).

[0081] One or more oxidizing electrochromic compounds can be added to the composition of the invention. For example, the additional electrochromic compound can be selected from anthraquinones, alkylviologens, arylviologens, alkylarylviologens and cationic derivatives of the nitrogen containing heterocyclic systems including benzazoles, condensed azoles, benzoxazoles,

benzoxisoxazoles, imidazo[1,2- α]pyridines, benzothiazoles, 2,1,3-benzothiadiazoles, benzisothiazoles, imidazoles, benzimidazoles, imidazole pyridines, phenantroimidazoles, benzoselenadiazoles, benzoselenazoles pyridopyrazines, dihydropyridopyrazines, dipyridopyrazines, pyridopyrazinoquinoline, dihydropyridopyrazinoquinoline, benzimidazolepyridopyrazine, dipyridinylpyrazines, triazines, dipyridinyltriazines, thienopyrazines, and derivatives. In particular derivatives thereof comprising pyridine, N-alkyl or N-aryl pyridinium, quinoline, or N-alkyl or N-aryl quinolinium, isoquinoline, N-alkyl or N-aryl isoquinolinium substitutions.

[0082] The composition of the invention may comprise a host medium that may be a fluid, a mesomorphous medium or a gel. The host medium is introduced in the composition of the invention to dissolve the electrochromic compounds. The host medium is preferably selected from the group consisting of organic solvents, liquid crystals, polymers, liquid crystal polymers and mixtures thereof.

[0083] Examples of suitable organic solvents that can be used as host medium are redox-compatible solvents which cannot react with the electrochromic compounds of the composition, such as ethylene carbonate, propylene carbonate, γ -butyrolactone, γ -valerolactone, acetonitrile, propionitrile, benzonitrile, glutaronitrile, methylglutaronitrile, dimethylformamide, N-methylpyrrolidone, sulfolane, 3-methyl sulfolane, benzene, toluene, methyl ethyl ketone, acetone, ethanol, tetrahydrofurfuryl alcohol, 2-methoxyethyl ether, xylene, cyclohexane, 3-methylcyclohexanone, ethyl acetate, ethyl phenylacetate, tetrahydrofuran, methanol, methyl propionate, ethylene glycol, ethylene carbonate, ionic liquids, and mixtures thereof. Preference is given to carbonates and particularly propylene carbonate.

[0084] Examples of suitable liquid crystals that can be used as host medium are nematic or chiral nematic media.

[0085] Examples of suitable polymers that can be used as host medium are polymers which are soluble with the solvent, in particular PMMA or other acrylate polymers, polyurethane, polyethylene oxide, polypropylene oxide, polyvinyl acetate, poly(N-vinyl pyrrolidone), and polyvinylidene fluoride.

[0086] Examples of suitable liquid crystal polymers that may be used as host medium are Merck RM257 (Merck), LC242 (BASF) or SLM 90519 (Wacker). These liquid crystal polymers are generally used in combination with an organic solvent, for example one of the organic solvents mentioned above.

30 **Electrochromic device**

[0087] The present invention also relates to an electrochromic device comprising a compound of formula (I) or a composition according to the invention. Said device may be selected from an optical article, preferably an optical lens, or an optical filter, a window, preferably an aircraft window, a visor, a mirror, a variable transmission device and a display element or device, in particular a segmented or matrix display. Preferably, the device of the invention is an optical article, more preferably an optical lens, and even more preferably an ophthalmic lens.

[0088] Non-limiting examples of ophthalmic lens include corrective and non-corrective lenses, including single vision or multi-vision lenses, which may be either segmented or non-segmented, as well as other elements used to correct, protect, or enhance vision, including without limitation contact lenses, intra-ocular lenses, sunglasses, ski goggles, sport lenses, augmented reality and virtual reality lenses, magnifying lenses, protective lenses and visors, for example motorcycle visors and helmets. Non-limiting examples of display elements and devices include screens and monitors. Non-limiting examples of windows include automotive, marine, aircraft or building windows. Non limiting examples of variable transmission devices include filters, shutters, and optical switches. Variable transmission devices (lenses, goggles, visors, etc.) refer in general to a device which can quickly change between a high-transmission (or "clear") state and a low-transmission (or "dark") state.

[0089] Preferably, the device of the invention comprises a mechanism for holding the compound or composition of the invention in a mechanically stable environment. More preferably, said device may comprise a pair of opposed substrates having a gap there between for receiving the mixture of the host medium and said compound or said composition of the present invention, and a frame for holding said pair of substrates adjacent one another.

[0090] The device of the present invention may thus comprise an optical component provided with at least one transparent cell arrangement juxtaposed in a parallel direction to the surface thereof, as disclosed in WO 2006/013250, each cell being tightly closed and containing at least one compound or composition of the present invention.

[0091] Other devices according to the invention can be devices as described in FR 2937154 or FR2950710 comprising at least one compound or composition of the invention.

[0092] This invention will be further illustrated by the following non-limiting examples which are given for illustrative purposes only and should not restrict the scope of the appended claims.

Examples

Example 1: Synthesis of exemplary compounds of formula (I)

[0093] The synthesis of chroman-4-ones by either the Kabbe base-catalysed condensation protocol between 2'-hydroxyacetophenones and ketones (H. J. Kabbe, *Synthesis*, 1978, 886-887) or by the acid-catalysed condensation of phenols with substituted acrylic acids (K. Meraz *et al.*, *Tetrahedron Letters*, 2016, 57, 5057-5061; R. Chaturvedi *et al.*, *Indian Journal of Chemistry, Section B*: 1992, 31B, 338-339) are well established protocols. The latter reaction, when applied to thiophenols, readily affords thiochroman-4-ones (S. E. Clayton *et al.*, *Tetrahedron*, 1993, 49, 939-946). The subsequent transformation of the carbonyl function of the chroman-4-ones and thiochroman-4-ones by reduction to the (thio)chroman-4-ol and subsequent acid-catalysed dehydration enables the synthesis of chromenes (P. J. Brogden *et al.*, *Journal of the Chemical Society, Perkin Transactions 1*, 1983, 827-830) and thiochromenes (J. Tercio *et al.*, *Synthesis*, 1987, 2, 149-153). Alternatively, complete reduction of the carbonyl function can be accomplished leading to the chroman system (B. M. Trost *et al.*, *Journal of the American Chemical Society*, 1998, 120, 9074-9075; A. Bermejo *et al.*, *Bioorganic & Medicinal Chemistry*, 2019, 27, 115162) and thiochroman system (B. Robillard *et al.*,

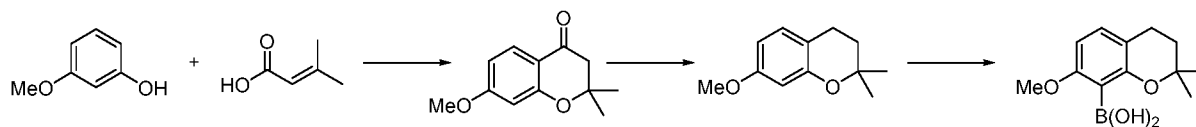
Journal of Organic Chemistry, 1986, 51, 1700-1704). Catalytic hydrogenation of chromenes and thiochromenes can be accomplished and provides an alternative route to chromans and thiochromans (S. R. Fletcher *et al.*, *Journal of Medicinal Chemistry*, 2002, 45, 492-503).

[0094] The concept of *ortho*-metalation or heteroatom directed metalation is a well-established synthetic chemistry protocol for the introduction of substituents adjacent to heteroatoms such as O or S, or functional groups, for example, ethers, amides, thioethers, alcohols, on aromatic rings wherein such functional groups have the ability to coordinate to an organolithium reagent and enable reaction with an electrophile such that the electrophile is introduced into a site adjacent to the coordinating group (V. Snieckus, *Chemical Reviews*, 1990, 90, 879-933; V. Snieckus *et al.*, in 'Modern Arene Chemistry', Ed. D. Astruc, 2002, 330-367; V. Snieckus, *Pure and Applied Chemistry*, 1990, 62, 2047-2056; V. Snieckus, *Bulletin de la Societe Chimique de France*, 1988, 67-78; V. Snieckus *et al.*, in 'Handbook of C-H Transformations', Ed. G. Dyker, 2005, 1, 106-118, 262-264).

[0095] The ability of the oxygen heteroatom of a benzopyran ring to introduce a substituent into the peri position (C-8) has been described (M. Hallet *et al.*, *Bulletin des Societes Chimiques Belges*, 1952, 61, 33-43; L. A. Paquette *et al.*, *Tetrahedron Letters*, 1993, 34, 3235-3238; R. J. Bethune *et al.*, *Journal of the Chemical Society, Perkin Transactions 1*, 1994, 1925-1933).

[0096] Employing the foregoing published strategies readily provided access to a range of substituted chromans, thiochromans and chromenes. Their subsequent heteroatom directed metalation was accomplished and quenching the generated organolithium with, for example, trimethyl borate afforded the substituted chroman, thiochroman and chromene substituted 8-boronic acids. The coupling of the foregoing substituted chroman, thiochroman and chromene substituted 8-boronic acids with a range of dibromo substituted thiophenes, selenophenes and dibromo substituted bithiophenes proceeded smoothly using the widely established Suzuki cross-coupling methodology (N. Miyaura *et al.*, *Chemical Reviews*, 1995, 95, 2457-2483) to afford the new electrochromic compounds as depicted by the following reaction schemes (reaction schemes A and A.1 to A.4, and reaction schemes B and B.1 to B.15). The compounds of formula (I) and their intermediates had spectroscopic data in full accord with their proposed structures.

A. Synthesis of (7-Methoxy-2,2-dimethylchroman-8-yl)boronic acid



Reaction scheme A

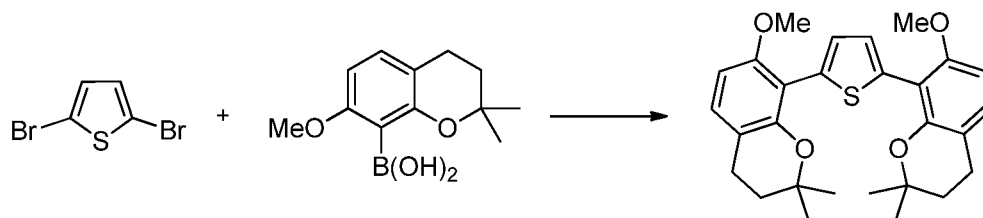
[0097] 3-Methoxyphenol (5.5 mL, 50.1 mmol) and 3,3-dimethylacrylic acid (5.51 g, 55.1 mmol, 1.1 equiv.) were dissolved in MeSO₃H (50 mL) and stirred at 70 °C for 4 hours. The reaction was allowed to cool, poured onto 200 mL ice-water and stirred for 30 min. The product was extracted with Et₂O (3 × 100 mL) and the combined organic portions were washed with 5 % NaOH solution (2 × 50 mL), water (100 mL) and brine (100 mL). The organic portion was dried (Na₂SO₄) and the solvent removed *in vacuo* to afford an orange oil which solidified. The solid was recrystallised from EtOH to afford 7-

methoxy-2,2-dimethylchroman-4-one as colourless crystals (8.47g, 82 %). m.p. 76–77 °C (lit. m.p. 79–81 °C [K. Meraz *et al.*, *Tetrahedron Letters*, 2016, 57, 5057 - 5061]). $\nu_{\max}$ 3004, 2985, 2962, 2907, 1665, 1600, 1574, 1261, 1022, 839 cm^{-1} . δ_{H} (400 MHz, CDCl_3) 1.45 [6H, s, $\text{C}(\text{CH}_3)_2$], 2.66 (2H, s, CH_2), 3.82 (3H, s, OCH_3), 6.37 (1H, d, $J = 2.4$ Hz, 8-*H*), 6.53 (1H, dd, $J = 2.4, 8.8$ Hz, 6-*H*), 7.89 (1H, d, $J = 8.8$ Hz, 5-*H*). δ_{C} (100 MHz, CDCl_3) 26.7 ($2 \times \text{CH}_3$), 48.6 (CH_2), 55.6 (CH_3), 79.6 (C), 101.1 (CH), 109.3 (CH), 114.1 (C), 128.3 (CH), 162.0 (C), 166.2 (C), 191.1 (C). HRMS (ESI-TOF) found $[\text{M}+\text{H}]^+ = 207.1019$ $\text{C}_{12}\text{H}_{15}\text{O}_3$ requires $[\text{M}+\text{H}]^+ = 207.1016$.

[0098] 7-Methoxy-2,2-dimethylchroman-4-one (1.00 g, 4.8 mmol) was added to Zn dust (7.93 g, 121 mmol, 25 equiv.) in AcOH (30 mL) and stirred at reflux overnight. The reaction was allowed to cool to r.t. and filtered through Celite. The reaction mixture was diluted with EtOAc (200 mL) and PhMe (200 mL). The solvent was removed under reduced pressure. The residue was dissolved in DCM and the solvent removed, the insoluble material was discarded. The product was purified by flash column chromatography [10 % EtOAc in hexane] to afford 7-methoxy-2,2-dimethylchroman as a colourless oil (0.81 g, 86.9 %). $\nu_{\max}$ 2973, 2932, 1619, 1580, 1504, 1147, 1119 cm^{-1} . δ_{H} (400 MHz, CDCl_3) 1.33 [6H, s, $\text{C}(\text{CH}_3)_2$], 1.79 [2H, t, $J = 6.7$ Hz, $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2$], 2.71 [2H, t, $J = 6.7$ Hz, $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2$], 3.75 (3H, s, OCH_3), 6.36 (1H, d, $J = 2.6$ Hz, 8-*H*), 6.43 (1H, dd, $J = 2.6, 8.3$ Hz, 6-*H*), 6.95 (1H, d, $J = 8.3$ Hz, 5-*H*). δ_{C} (100 MHz, CDCl_3) 21.7 (CH_2), 26.9 ($2 \times \text{CH}_3$), 33.0 (CH_2), 55.2 (CH_3), 74.3 (C), 101.7 (CH), 106.9 (CH), 113.0 (C), 129.9 (CH), 154.7 (C), 159.1 (C). HRMS (ESI-TOF) found $[\text{M}+\text{H}]^+ = 193.1230$ $\text{C}_{12}\text{H}_{17}\text{O}_2$ requires $[\text{M}+\text{H}]^+ = 193.1223$.

[0099] To a solution of 7-methoxy-2,2-dimethylchroman (1.94 g, 10.1 mmol) in anhydrous THF (35 mL) at -20 °C under N_2 was added *n*-BuLi [2.5 M in hexanes, 4.9 mL, 12.2 mmol, 1.2 equiv.] dropwise over 5 min followed by the addition of TMEDA (1.84 mL, 12.2 mmol, 1.2 equiv.) in one portion. The reaction mixture was stirred at -20 °C for 30 min and allowed to warm to r.t., the reaction was stirred for a further 3.5 h. The reaction mixture was cooled to -78 °C and $\text{B}(\text{OMe})_3$ (2.2 mL, 20.0 mmol, 2 equiv.) was added. The mixture was allowed to warm to r.t. and stirred for 16 h. The reaction was quenched with 2 M HCl at 0 °C and stirred for 30 min. The product was extracted with EtOAc (3×50 mL) and washed with water and brine. The organic layer was dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was triturated with hexane and the solid isolated by vacuum filtration to afford (7-methoxy-2,2-dimethylchroman-8-yl)boronic acid as a white crystalline solid (1.24 g, 52 %). m.p. 100–101 °C. $\nu_{\max}$ 3513, 3473, 2971, 2943, 2924, 1599, 1582, 1313, 1085, 798, 690 cm^{-1} . δ_{H} (400 MHz, CDCl_3) 1.40 [6H, s, $\text{C}(\text{CH}_3)_2$], 1.83 [2H, t, $J = 6.8$ Hz, $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2$], 2.76 [2H, t, $J = 6.8$ Hz, $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2$], 3.88 (3H, s, OCH_3), 6.52 (1H, d, $J = 8.4$ Hz, 6-*H*), 7.12 (1H, d, $J = 8.4$ Hz, 5-*H*), 7.39 [2H, s, $\text{B}(\text{OH})_2$]. δ_{C} (100 MHz, CDCl_3) 22.0 (CH_2), 27.0 ($2 \times \text{CH}_3$), 32.3 (CH_3), 55.9 (CH_2), 76.4 (C), 103.4 (CH), 106.0 (C)*, 114.4 (C), 133.0 (CH), 159.5 (C), 163.9 (C). HRMS (ESI-TOF) found $[\text{M}+\text{NH}_4]^+ = 253.1596$ $\text{C}_{12}\text{H}_{21}\text{BNO}_4$ requires $[\text{M}+\text{NH}_4]^+ = 253.1594$. (*by HMBC)

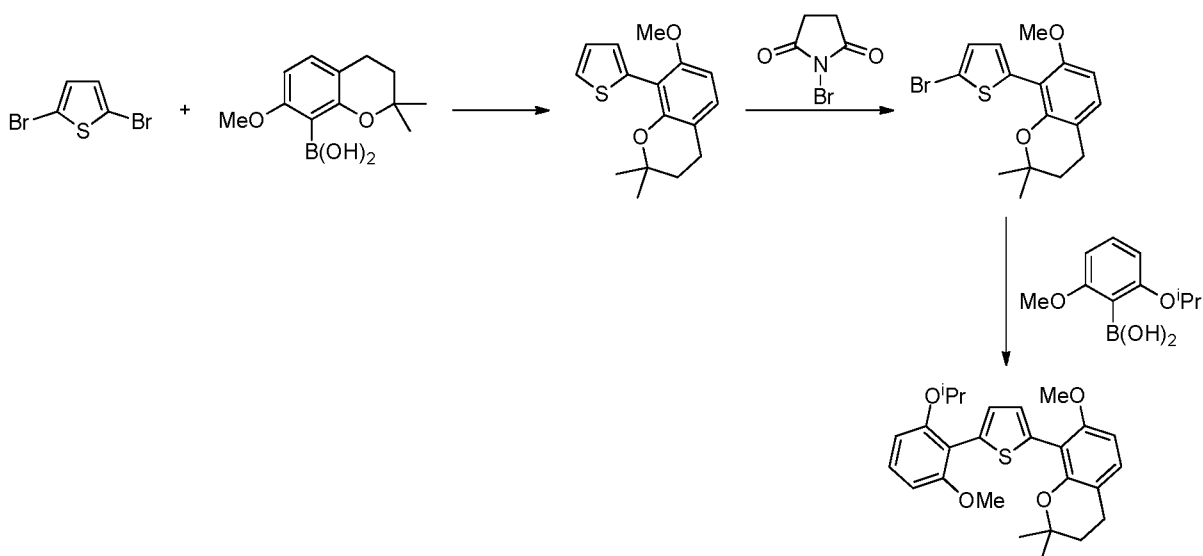
A.1. Synthesis of 2,5-bis(7-methoxy-2,2-dimethylchroman-8-yl)thiophene – Compound 1



Reaction scheme A.1

[00100] 2,5-Dibromothiophene (0.28 mL, 2.5 mmol), (7-methoxy-2,2-dimethylchroman-8-yl)boronic acid (1.48 g, 6.3 mmol, 2.5 equiv.), potassium carbonate (2.07 g, 15 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (0.29 g, 0.3 mmol, 10 mol%) were added to degassed PhMe (20 mL) and EtOH (20 mL), the reaction mixture was stirred at reflux under N₂ for 3 h. The reaction was allowed to cool to r.t., poured onto water (80 mL) and extracted with DCM (3 × 20 mL). The combined organic portions were dried (Na₂SO₄) and the solvent removed. The product was purified by flash column chromatography [10 % EtOAc in hexane] to afford 2,5-bis(7-methoxy-2,2-dimethylchroman-8-yl)thiophene as a yellow oil which was crystallised from pentane (1.16 g, 100%). m.p. 118 – 120 °C. $\nu_{\max}$ 2973, 2930, 2831, 1481, 1417, 1154, 1122, 1104, 1082, 804 cm⁻¹. δ_{H} (400 MHz, CDCl₃) 1.40 [12H, s, 2 × C(CH₃)₂], 1.82 [4H, t, J = 6.8 Hz, 2 × CH₂C(CH₃)₂], 2.80 [4H, t, J = 6.8 Hz, 2 × CH₂CH₂C(CH₃)₂], 3.84 (6H, s, 2 × OCH₃), 6.54 (2H, d, J = 8.4 Hz, 2 × 6-*H*), 6.94 (2H, d, J = 8.4 Hz, 2 × 5-*H*), 7.62 (2H, s, 3-*H*, 4-*H*). δ_{C} (100 MHz, CDCl₃) 22.5 (2 × CH₂), 27.0 (4 × CH₃), 32.8 (2 × CH₂), 56.0 (2 × CH₃), 74.9 (2 × C), 103.5 (2 × CH), 112.9 (2 × C), 113.9 (2 × C), 127.7 (2 × CH), 127.8 (2 × CH), 133.9 (2 × C), 151.1 (2 × C), 156.0 (2 × C). HRMS (ESI-TOF) found [M+K]⁺ = 503.1650 C₂₈H₃₂KO₄S requires [M+K]⁺ = 503.1653.

A.2. Synthesis of 8-[5-(2-isopropoxy-6-methoxyphenyl)thiophenyl]-7-methoxy-2,2-dimethylchromane – Compound 11



Reaction scheme A.2

[00101] 2,5-Dibromothiophene (0.43 mL, 3.9 mmol), (7-methoxy-2,2-dimethylchroman-8-yl)boronic acid (1.00 g, 4.2 mmol, 1.1 equiv.), potassium carbonate (3.19 g, 23.1 mmol, 6 equiv.) and

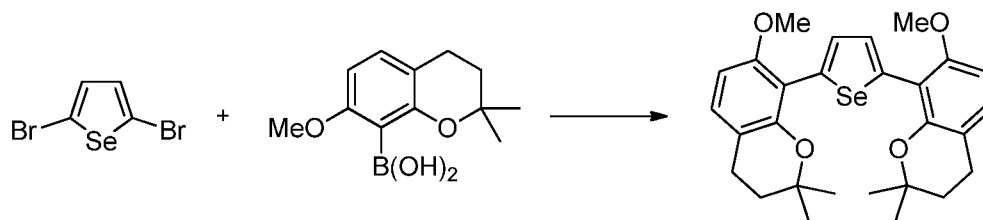
tetrakis(triphenylphosphine)palladium(0) (0.44 g, 0.4 mmol, 10 mol%) were added to degassed PhMe (30 mL) and EtOH (30 mL), the reaction mixture was stirred at reflux under N₂ for 3 h. The reaction was allowed to cool to r.t., poured onto water (80 mL) and extracted with DCM (3 × 20 mL). The combined organic portions were dried (Na₂SO₄) and the solvent removed. The product was purified by flash column chromatography [5 % EtOAc in hexane] to afford 7-methoxy-2,2-dimethyl-8-(thiophen-2-yl)chromane as a fluorescent yellow oil (0.76 g, 72%). $\nu_{\max}$ 2972, 2930, 2835, 1601, 1480, 1102, 689 cm⁻¹. δ_{H} (400 MHz, CDCl₃) 1.37 [6H, s, C(CH₃)₂], 1.81 [2H, t, *J* = 6.8 Hz, CH₂CH₂C(CH₃)₂], 2.79 [2H, t, *J* = 6.8 Hz, CH₂CH₂C(CH₃)₂], 3.82 (3H, s, OCH₃), 6.53 (1H, d, *J* = 8.4 Hz, 6-Ch-*H*), 6.97 (1H, d, *J* = 8.4 Hz, 5-Ch-*H*), 7.08 (1H, dd, *J* = 3.7, 5.2 Hz, 4-Th-*H*), 7.34 (1H, dd, *J* = 1.1, 5.2 Hz, 5-Th-*H*), 7.58 (1H, dd, *J* = 1.1, 3.7 Hz, 3-Th-*H*). δ_{C} (100 MHz, CDCl₃) 22.3 (CH₂), 26.9 (2 × CH₃), 32.7 (CH₂), 55.9 (CH₃), 75.1 (C), 103.2 (CH), 112.0 (C), 114.0 (C), 124.8 (CH), 125.6 (CH), 128.3 (CH), 128.6 (CH), 134.5 (C), 151.6 (C), 155.8 (C).

[00102] 7-Methoxy-2,2-dimethyl-8-(thiophen-2-yl)chromane (0.70 g, 2.5 mmol) was dissolved in anhydrous THF (10 mL) followed by the addition of a solution of NBS (0.45 g, 2.5 mmol, 1 equiv.) in anhyd. THF (15 mL). The reaction was stirred at 35 °C under N₂ for 6 h and allowed to cool to r.t. The reaction was poured onto water (100 mL) and the product extracted with DCM (3 × 50 mL), the combined organic layers were dried (Na₂SO₄) and the solvent removed *in vacuo* to afford 8-(5-bromothiophen-2-yl)-7-methoxy-2,2-dimethylchromane as a yellow oil which slowly solidified (0.86 g, 95%). m.p. 90–92 °C. $\nu_{\max}$ 3077, 2972, 2910, 1688, 1429, 1105, 811, 796 cm⁻¹. δ_{H} (400 MHz, CDCl₃) 1.41 [6H, s, C(CH₃)₂], 1.82 [2H, t, *J* = 6.8 Hz, CH₂CH₂C(CH₃)₂], 2.79 [2H, t, *J* = 6.8 Hz, CH₂CH₂C(CH₃)₂], 3.85 (3H, s, OCH₃), 6.53 (1H, d, *J* = 8.3 Hz, 6-Ch-*H*), 6.97 (1H, d, *J* = 8.3 Hz, 5-Ch-*H*), 7.03 (1H, d, *J* = 4.0 Hz, 4-Th-*H*), 7.49 (1H, d, *J* = 4.0 Hz, 3-Th-*H*). δ_{C} (100 MHz, CDCl₃) 22.3 (CH₂), 26.9 (2 × CH₃), 32.6 (CH₂), 55.9 (CH₃), 75.6 (C), 103.3 (CH), 111.3 (C), 112.0 (C), 114.0 (C), 128.4 (CH), 128.6 (CH), 128.9 (CH), 136.5 (C), 151.4 (C), 155.7 (C).

[00103] 8-(5-Bromothiophen-2-yl)-7-methoxy-2,2-dimethylchromane (0.25 g, 0.7 mmol), (2-isopropoxy-6-methoxyphenyl)boronic acid (0.27 g, 1.3 mmol, 1.8 equiv.), potassium carbonate (0.59 g, 4.2 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (0.09 g, 0.1 mmol, 10 mol%) were added to degassed PhMe (20 mL) and EtOH (20 mL), the reaction mixture was stirred at reflux under N₂ for 16 h. The reaction was allowed to cool to r.t., poured onto water (50 mL) and extracted with DCM (3 × 20 mL). The combined organic portions were dried (Na₂SO₄) and the solvent removed. The product was purified by flash column chromatography [5 % EtOAc in hexane] to afford 8-[5-(2-isopropoxy-6-methoxyphenyl)thiophenyl]-7-methoxy-2,2-dimethylchromane as a yellow glass (0.22 g, 71%). $\nu_{\max}$ 2973, 2931, 2834, 1582, 1463, 1248, 1102, 1073, 805 cm⁻¹. δ_{H} (400 MHz, CDCl₃) 1.37 [6H, d, *J* = 6.0 Hz, CH(CH₃)₂], 1.42 [6H, s, C(CH₃)₂], 1.85 [2H, t, *J* = 6.8 Hz, CH₂CH₂C(CH₃)₂], 2.82 [2H, t, *J* = 6.8 Hz, CH₂CH₂C(CH₃)₂], 3.87 (6H, m, 2 × OCH₃), 4.58 [1H, sep, *J* = 6.0 Hz, CH(CH₃)₂], 6.57 (1H, d, *J* = 8.4 Hz, 6-Ch-*H*), 6.66 (1H, d, *J* = 8.3 Hz, 5-Ar-*H*), 6.69 (1H, d, *J* = 8.3 Hz, 3-Ar-*H*), 6.97 (1H, d, *J* = 8.4 Hz, 5-Ch-*H*), 7.20 (1H, t, *J* = 8.3 Hz, 4-Ar-*H*), 7.55 (1H, d, *J* = 4.0 Hz, 4-Th-*H*), 7.67 (1H, d, *J* = 4.0 Hz, 3-Th-*H*). δ_{C} (100 MHz, CDCl₃) 22.2 (2 × CH₃), 22.4 (CH₂), 27.0 (2 × CH₃), 32.7 (CH₂), 55.9 (CH₃), 56.0 (CH₃), 71.4 (CH), 75.0 (C), 103.5 (CH), 104.4 (CH), 108.0 (CH), 112.8 (C), 113.9 (C), 115.0 (C), 127.6 (CH), 127.8 (3 × CH), 133.5 (C), 134.3 (C), 151.6 (C), 155.9 (C),

156.0 (C), 158.0 (C). HRMS (Jetstream) found $[M+H]^+ = 439.1938$ $C_{26}H_{31}O_4S$ requires $[M+H]^+ = 439.1938$.

A.3. Synthesis of 2,5-bis(7-methoxy-2,2-dimethylchroman-8-yl)selenophene – Compound 10

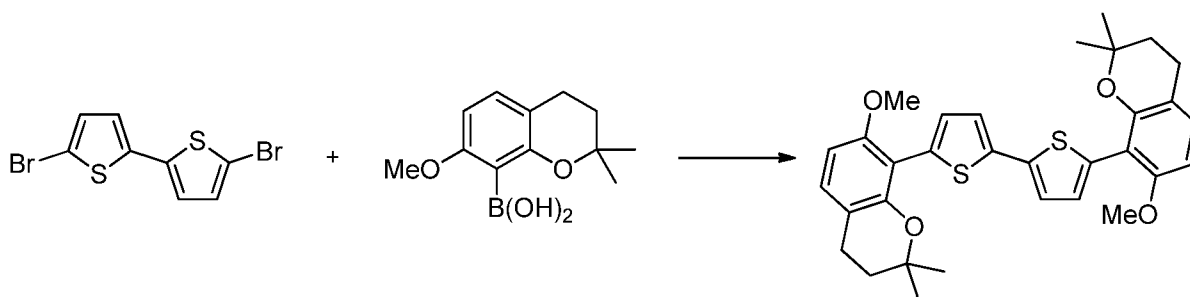


5

Reaction scheme A.3

[00104] 2,5-Dibromoselenophene (0.4 mL, 3.5 mmol), (7-methoxy-2,2-dimethylchroman-8-yl)boronic acid (1.72 g, 7.3 mmol, 2.1 equiv.), potassium carbonate (2.88 g, 21 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (0.40 g, 0.3 mmol, 10 mol%) were added to degassed PhMe (25 mL) and EtOH (25 mL), the reaction mixture was stirred at reflux under N_2 for 3 h. The reaction was allowed to cool to r.t., poured onto water (80 mL) and extracted with DCM (3×20 mL). The combined organic portions were dried (Na_2SO_4) and the solvent removed. The product was purified by flash column chromatography [5 % EtOAc in hexane] to afford 2,5-bis(7-methoxy-2,2-dimethylchroman-8-yl)selenophene as an orange glass (0.20 g, 11%). ν_{max} 2970, 2930, 1477, 1415, 1152, 1101, 810, 787 cm^{-1} . δ_H (400 MHz, $CDCl_3$) 1.43 [12H, s, $2 \times C(CH_3)_2$], 1.83 [4H, t, $J = 6.8$ Hz, $2 \times CH_2C(CH_3)_2$], 2.80 [4H, t, $J = 6.8$ Hz, $2 \times CH_2CH_2C(CH_3)_2$], 3.86 (6H, s, $2 \times OCH_3$), 6.54 (2H, d, $J = 8.4$ Hz, $2 \times 6-H$), 6.91 (2H, d, $J = 8.4$ Hz, $2 \times 5-H$), 8.07 (2H, s, 3-H, 4-H). δ_C (100 MHz, $CDCl_3$) 22.5 ($2 \times CH_2$), 27.1 ($4 \times CH_3$), 32.8 ($2 \times CH_2$), 55.9 ($2 \times CH_3$), 75.2 ($2 \times C$), 103.7 ($2 \times CH$), 113.9 ($2 \times C$), 115.0 ($2 \times C$), 127.2 ($2 \times CH$), 130.2 ($2 \times CH$), 138.6 ($2 \times C$), 150.9 ($2 \times C$), 155.5 ($2 \times C$). HRMS (Jetstream) found $[M+H]^+ = 513.1539$ $C_{28}H_{33}O_4Se$ requires $[M+H]^+ = 513.1539$.

20 A.4. Synthesis of 5,5'-bis(7-methoxy-2,2-dimethylchroman-8-yl)-2,2'-bithiophene – Compound 13

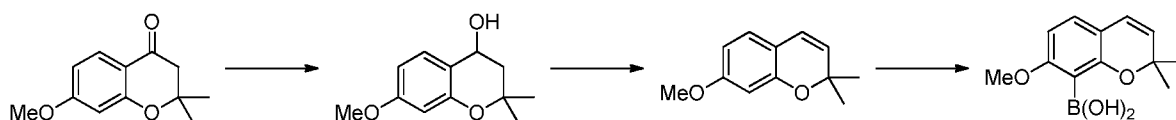


Reaction scheme A.4

[00105] 5,5'-Dibromo-2,2'-bithiophene (1.12 g, 3.5 mmol), (7-methoxy-2,2-dimethylchroman-8-yl)boronic acid (1.72 g, 7.3 mmol, 2.1 equiv.), potassium carbonate (2.88 g, 20.8 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (0.4 g, 0.3 mmol, 10 mol%) were added to degassed PhMe (25 mL) and EtOH (25 mL), the reaction mixture was stirred at reflux under N_2 for 28 h. The reaction was allowed to cool to r.t., poured onto water (50 mL) and extracted with DCM (3×20 mL). The

combined organic portions were dried (Na_2SO_4) and the solvent removed. The product was purified by flash column chromatography [5 % EtOAc in hexane] to afford 5,5'-bis(7-methoxy-2,2-dimethylchroman-8-yl)-2,2'-bithiophene as a pale yellow powder which was crystallised from pentane (0.26 g, 14%). m.p. 206 – 208 °C. ν_{max} 2973, 2923, 2829, 1485, 1464, 1453, 1420, 1158, 1122, 1105, 794 cm^{-1} . δ_{H} (400 MHz, CDCl_3) 1.40 [12H, s, $2 \times \text{C}(\text{CH}_3)_2$], 1.82 [4H, t, $J = 6.8 \text{ Hz}$, $2 \times \text{CH}_2\text{C}(\text{CH}_3)_2$], 2.79 [4H, t, $J = 6.8 \text{ Hz}$, $2 \times \text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2$], 3.85 (6H, s, $2 \times \text{OCH}_3$), 6.53 (2H, d, $J = 8.4 \text{ Hz}$, $2 \times 6\text{-H}$), 6.95 (2H, d, $J = 8.4 \text{ Hz}$, $2 \times 5\text{-H}$), 7.16 (2H, d, $J = 3.7 \text{ Hz}$, 4-H , $4'\text{-H}$) 7.57 (2H, d, $J = 3.7 \text{ Hz}$, 3-H , $3'\text{-H}$). δ_{C} (100 MHz, CDCl_3) 22.4 ($2 \times \text{CH}_2$), 26.9 ($4 \times \text{CH}_3$), 32.7 ($2 \times \text{CH}_2$), 56.0 ($2 \times \text{CH}_3$), 75.3 ($2 \times \text{C}$), 103.4 ($2 \times \text{CH}$), 114.0 ($2 \times \text{C}$), 122.1 ($2 \times \text{C}$, $2 \times \text{CH}$), 128.1 ($2 \times \text{CH}$), 129.5 ($2 \times \text{C}$, $2 \times \text{CH}$), 137.2 ($2 \times \text{C}$), 151.5 ($2 \times \text{C}$), 155.8 ($2 \times \text{C}$). HRMS (Jetstream) found $[\text{M}+\text{H}]^+ = 547.1972$ $\text{C}_{32}\text{H}_{35}\text{O}_4\text{S}_2$ requires $[\text{M}+\text{H}]^+ = 547.1973$.

B. Synthesis of (7-methoxy-2,2-dimethyl-2H-chromen-8-yl)boronic acid



Reaction scheme B

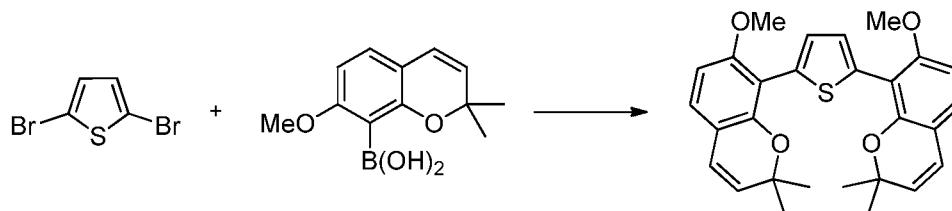
[00106] 7-Methoxy-2,2-dimethylchroman-4-one (1.99 g, 9.6 mmol) and NaBH_4 (0.44 g, 11.6 mmol, 1.2 equiv.) were stirred at reflux in EtOH (35 mL, anhyd.) for 2 hours under N_2 . The reaction was allowed to cool to r.t. and poured onto 150 mL ice-water containing salt and stirred. The product was extracted with EtOAc ($3 \times 75 \text{ mL}$). The combined organic portions were dried (Na_2SO_4) and the solvent removed under reduced pressure to afford 7-methoxy-2,2-dimethylchroman-4-ol as a colourless oil (1.97 g, 98 %). δ_{H} (400 MHz, CDCl_3) 1.32 [3H, s, $\text{C}(\text{CH}_3)_a(\text{CH}_3)_b$], 1.44 [3H, s, $\text{C}(\text{CH}_3)_a(\text{CH}_3)_b$], 1.65 (1H, d, $J = 7.5 \text{ Hz}$, OH), 1.85 (1H, dd, $J = 8.2, 13.5 \text{ Hz}$, CH_aH_b), 2.15 (1H, dd, $J = 6.0, 13.5 \text{ Hz}$, CH_aH_b), 3.76 (3H, s, OCH_3), 4.78–4.83 (1H, m, CHOH), 6.34 (1H, d, $J = 2.5 \text{ Hz}$, 8-H), 6.52 (1H, dd, $J = 2.5, 8.5 \text{ Hz}$, 6-H), 7.33 (1H, d, $J = 8.5 \text{ Hz}$, 5-H). δ_{C} (100 MHz, CDCl_3) 26.1 (CH_3), 28.7 (CH_3), 42.8 (CH_2), 55.3 (CH_3), 63.4 (CH), 75.6 (C), 101.4 (CH), 107.7 (CH), 116.7 (C), 128.6 (CH), 154.3 (C), 160.6 (C). HRMS (ESI-TOF) found $[\text{M}+\text{Na}]^+ = 231.0983$ $\text{C}_{12}\text{H}_{16}\text{NaO}_3$ requires $[\text{M}+\text{Na}]^+ = 231.0992$.

[00107] To 7-methoxy-2,2-dimethylchroman-4-ol (2.24 g, 10.8 mmol) in dry THF (50 mL) was added *p*-TsOH (0.03 g, 0.2 mmol, 2 mol%) and the reaction was stirred at reflux for 2 hours. The reaction was allowed to cool and 10 % NaOH solution was added (25 mL). The product was extracted with DCM ($2 \times 50 \text{ mL}$). The combined organic portions were washed with 10 % NaOH ($3 \times 25 \text{ mL}$), brine and water and dried (Na_2SO_4). The solvent was removed under reduced pressure to afford 7-methoxy-2,2-dimethyl-2H-chromene as an orange oil (1.84 g, 90 %). ν_{max} 2973, 2835, 1613, 1501, 1156, 1128 cm^{-1} . δ_{H} (400 MHz, CDCl_3) 1.42 [6H, s, $\text{C}(\text{CH}_3)_2$], 3.77 (3H, s, OCH_3), 5.47 [1H, d, $J = 9.8 \text{ Hz}$, $\text{CHCHC}(\text{CH}_3)_2$], 6.28 [1H, d, $J = 9.8 \text{ Hz}$, $\text{CHCHC}(\text{CH}_3)_2$], 6.37–6.42 (2H, m, 6-H, 8-H), 6.88 (1H, d, $J = 8.2 \text{ Hz}$, 5-H). δ_{C} (100 MHz, CDCl_3) 28.0 ($2 \times \text{CH}_3$), 55.3 (CH_3), 76.4 (C), 102.0 (CH), 106.6

(CH), 114.6 (C), 121.9 (CH), 126.9 (CH), 127.9 (CH), 154.2 (C), 160.6 (C). HRMS (ESI-TOF) found $[M+H]^+ = 191.1067$ $C_{12}H_{15}O_2$ requires $[M+H]^+ = 191.1067$.

[00108] To a solution of 7-methoxy-2,2-dimethyl-2*H*-chromene (1.91 g, 10.0 mmol) in anhyd. THF (35 mL) at -20 °C under N_2 was added *n*-BuLi [2.5 M in hexanes, 4.9 mL, 12.2 mmol, 1.2 equiv.] dropwise over 5 min followed by the addition of TMEDA (1.84 mL, 12.2 mmol, 1.2 equiv.) in one portion. The reaction mixture was stirred at -20 °C for 30 min and allowed to warm to r.t., the reaction was stirred for a further 3.5 h. The reaction mixture was cooled to -78 °C and $B(OMe)_3$ (2.2 mL, 20.0 mmol, 2 equiv.) was added. The mixture was allowed to warm to r.t. and stirred for 16 h. The reaction was quenched with 2M HCl (30 mL) at 0 °C and stirred for 30 min. The product was extracted with EtOAc and washed with water and brine. The organic layer was dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was triturated with hexane and the solid isolated by vacuum filtration to afford (7-methoxy-2,2-dimethyl-2*H*-chromen-8-yl)boronic acid as an orange solid (1.20 g, 51 %). m.p. 91–94 °C. ν_{max} 3508, 2976, 1595, 1575, 1318, 1081, 735 cm^{-1} . δ_H (400 MHz, $CDCl_3$) 1.49 [6H, s, $C(CH_3)_2$], 3.90 (3H, s, $OCCH_3$), 5.57 [1H, d, $J = 9.8$ Hz, $CHCHC(CH_3)_2$], 6.30 [1H, d, $J = 9.8$ Hz, $CHCHC(CH_3)_2$], 6.50 (1H, d, $J = 8.4$ Hz, 6-*H*), 7.05 (1H, d, $J = 8.4$ Hz, 5-*H*), 7.26** [2H, s, $B(OH)_2$]. δ_C (100 MHz, $CDCl_3$) 28.0 (2 × CH_3), 55.9 (CH_3), 78.2 (C), 103.6 (CH), 106.8 (C)*, 115.6 (C), 121.9 (CH), 128.3 (CH), 130.0 (CH), 159.0 (C), 164.9 (C). HRMS (ESI-TOF) found $[M+NH_4]^+ = 251.1434$ $C_{12}H_{19}BNO_4$ requires $[M+NH_4]^+ = 251.1438$. (**overlaps with residual $CHCl_3$, *by HMBC)

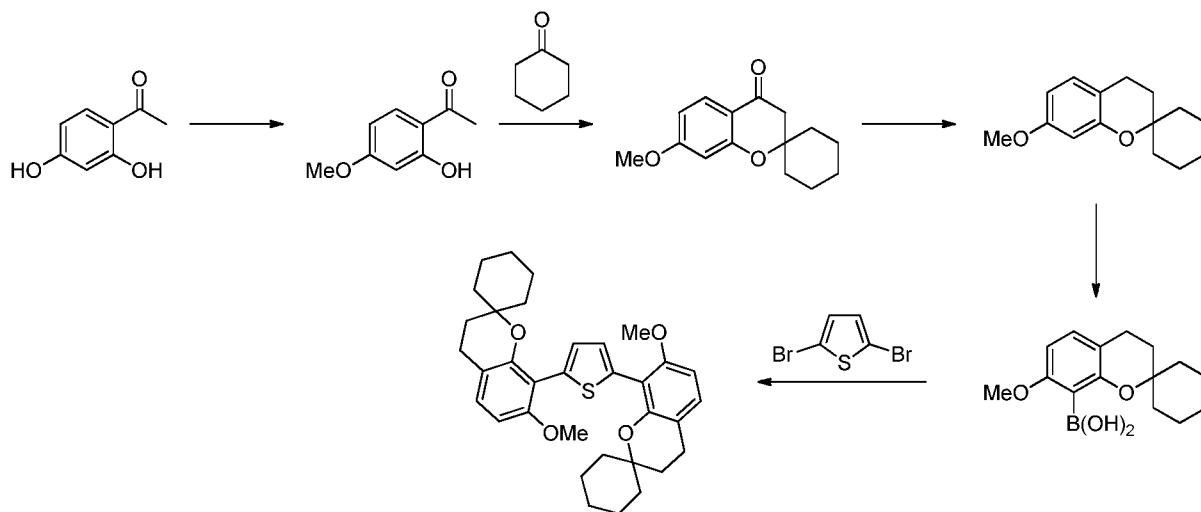
B.1. Synthesis of 2,5-Bis(7-methoxy-2,2-dimethyl-2*H*-chromen-8-yl)thiophene – Compound 3



Reaction scheme B.1

[00109] 2,5-Dibromothiophene (0.22 mL, 1.9 mmol), (7-methoxy-2,2-dimethyl-2*H*-chromen-8-yl)boronic acid (1.14 g, 4.9 mmol, 2.5 equiv.), potassium carbonate (1.61 g, 11.7 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (0.22 g, 0.2 mmol, 10 mol%) were added to degassed PhMe (20 mL) and EtOH (20 mL), the reaction mixture was stirred at reflux under N_2 for 4 h. The reaction was allowed to cool to r.t., poured onto water (80 mL) and extracted with DCM (3 × 20 mL). The combined organic portions were dried (Na_2SO_4) and the solvent removed. The product was purified by flash column chromatography [10 % EtOAc in hexane] to afford 2,5-bis(7-methoxy-2,2-dimethyl-2*H*-chromen-8-yl)thiophene as a yellow oil (0.91 g, 100 %). ν_{max} 2971, 2935, 2835, 1594, 1121, 1099, 799 cm^{-1} . δ_H (400 MHz, $CDCl_3$) 1.50 [12H, s, 2 × $C(CH_3)_2$], 3.87 (6H, s, 2 × $OCCH_3$), 5.55 [2H, d, $J = 9.7$ Hz, 2 × $CHCHC(CH_3)_2$], 6.33 [2H, d, $J = 9.7$ Hz, 2 × $CHCHC(CH_3)_2$], 6.52 (2H, d, $J = 8.3$ Hz, 2 × 6-*H*), 6.88 (2H, d, $J = 8.3$ Hz, 2 × 5-*H*), 7.64 (2H, s, 3-*H*, 4-*H*). δ_C (100 MHz, $CDCl_3$) 27.9 (4 × CH_3), 55.8 (2 × CH_3), 76.9 (2 × C), 103.5 (2 × CH), 112.9 (2 × C), 115.5 (2 × C), 122.4 (2 × CH), 125.0 (2 × CH), 128.0 (2 × CH), 128.4 (2 × CH), 133.5 (2 × C), 150.8 (2 × C), 157.5 (2 × C). HRMS (JS) found $[M+H]^+ = 461.1777$ $C_{28}H_{28}O_4S$ requires $[M+H]^+ = 461.1777$.

B.2. Synthesis of 2,5-Bis(7-methoxyspiro[chromane-2,1'-cyclohexan]-8-yl)thiophene – Compound 2



Reaction scheme B.2

- 5 **[00110]** To a solution of 2,4-dihydroxyacetophenone (5.00 g, 32.9 mmol) in acetone (30 mL) was added K_2CO_3 (2.27 g, 16.4 mmol, 0.5 equiv.) followed by iodomethane (2.25 mL, 36.1 mmol, 1.1 equiv.) at r.t. The reaction was then stirred at reflux for 8 h. The reaction mixture was allowed to cool and filtered. The filtrate was concentrated *in vacuo* and the product purified by flash column chromatography [10 % EtOAc in hexane] to afford 2-hydroxy-4-methoxyacetophenone as a colourless solid (3.98 g, 73 %). m.p. 48 – 49 °C (lit. m.p. 52–53 °C [M. V. B. Reddy *et al.*, *Bioorganic and Medicinal Chemistry*, 2008, 16, 7358 - 7370]). ν_{max} 2974, 2846, 1616, 1574, 1365, 1247, 1206, 808, 570 cm^{-1} . δ_H (400 MHz, $CDCl_3$) 2.56 (3H, s, $COCH_3$), 3.84 (3H, s, OCH_3), 6.42–6.46 (2H, m, 3-H, 5-H), 7.64 (1H, d, $J = 8.7$ Hz, 6-H), 12.77 (1H, s, OH). δ_C (100 MHz, $CDCl_3$) 26.3 (CH_3), 55.6 (CH_3), 100.8 (CH), 107.7 (CH), 113.9 (C), 132.3 (CH), 165.3 (C), 166.1 (C), 202.6 (C). HRMS (ESI-TOF) found $[M+H]^+ = 167.0702$ $C_9H_{11}O_3$ requires $[M+H]^+ = 167.0703$.

- 20 **[00111]** To a solution of 2-hydroxy-4-methoxyacetophenone (3.74 g, 22.5 mmol) in EtOH (40 mL) was added cyclohexanone (23.3 mL, 225 mmol, 10 equiv.) and pyrrolidine (5.6 mL, 67.5 mmol, 3 equiv.). The reaction was stirred at reflux for 6 hours and the solvent was removed under reduced pressure. The residue was diluted with EtOAc (50 mL), washed with saturated NH_4Cl (100 mL) and brine (100 mL). The product was extracted from the aqueous layer with EtOAc (2 × 75 mL) and the combined organic layers dried (Na_2SO_4) and the solvent removed under reduced pressure. The product was purified by flash column chromatography [10% EtOAc in hexane] to afford 7-methoxyspiro[chromane-2,1'-cyclohexan]-4-one as a yellow oil which slowly crystallised (4.84 g, 87 %). m.p. 69 – 70 °C (lit. m.p. 68 °C [Y. Jacquot *et al.*, *Medicinal Chemistry Research*, 2013, 22, 681 - 691]). ν_{max} 3656, 2980, 2928, 2889, 1670, 1601, 1123 cm^{-1} . δ_H (400 MHz, $CDCl_3$) 1.28–1.99 (10H, m, Cy-H), 2.64 (2H, s, $COCH_2$), 3.83 (3H, s, OCH_3), 6.41 (1H, d, $J = 2.3$ Hz, 8-H), 6.52 (1H, dd, $J = 2.3, 8.8$ Hz, 6-H), 7.78 (1H, d, $J = 8.8$ Hz, 5-H). δ_C (100 MHz, $CDCl_3$) 21.5 (2 × CH_2), 25.2 (CH_2), 34.9 (2 × CH_2), 47.9 ($COCH_2$), 55.6 (CH_3), 80.4 (C), 101.2 (CH), 109.2 (CH), 114.7 (C), 128.2

(CH), 161.6 (C), 166.2 (C), 191.2 (C). HRMS (ESI) found $[M+H]^+ = 247.1326$ $C_{15}H_{18}O_3$ requires $[M+H]^+ = 247.1329$.

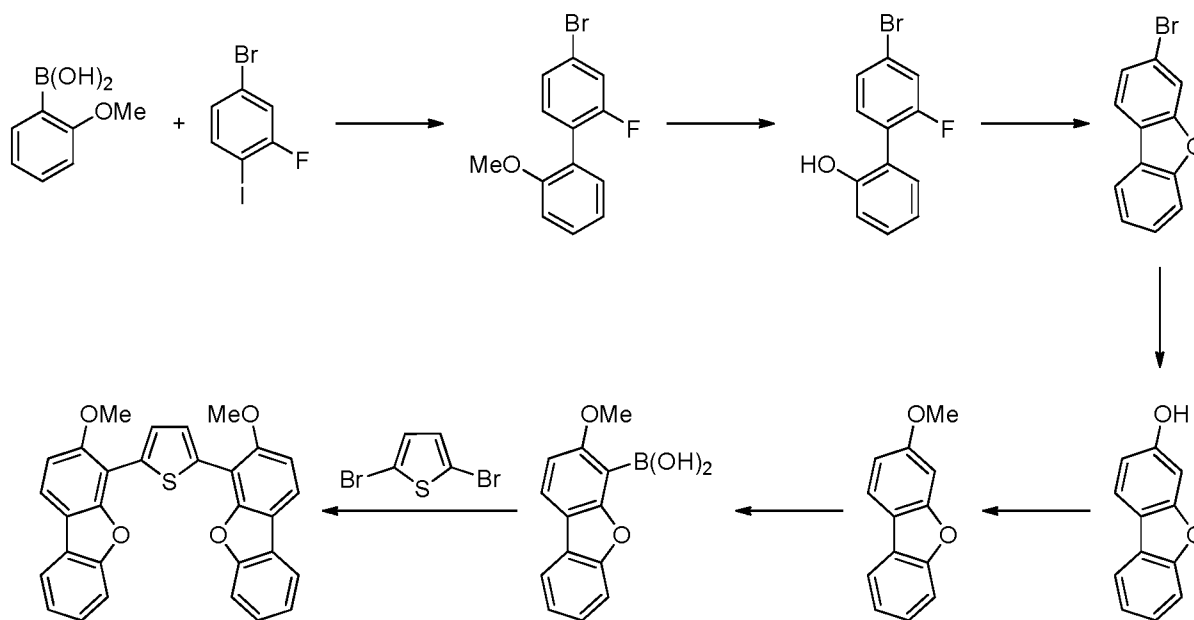
[00112] 7-Methoxyspiro[chromane-2,1'-cyclohexan]-4-one (4.00 g, 16.2 mmol) was added to Zn dust (26.55 g, 406 mmol, 25 equiv.) in AcOH (100 mL) and stirred at reflux overnight. The reaction was allowed to cool to r.t. and filtered through Celite. The reaction mixture was diluted with EtOAc (100 mL) and PhMe (100 mL). The solvent was removed under reduced pressure. The residue was dissolved in DCM and the solvent removed to afford 7-methoxyspiro[chromane-2,1'-cyclohexane] as an orange oil (3.79 g, 100 %). $\nu_{\max}$ 2928, 2855, 1618, 1582, 1503, 1441, 1156, 1145, 985 cm^{-1} . δ_H (400 MHz, $CDCl_3$) 1.31–1.79 (12H, m, Cy-H, CH_2CCy), 2.68 (2H, t, $J = 6.8$ Hz, CH_2CH_2CCy), 3.76 (3H, s, OCH_3), 6.40 (1H, d, $J = 2.6$ Hz, 8-H), 6.42 (2H, dd, $J = 2.6, 8.3$ Hz, 6-H), 6.93 (1H, d, $J = 8.3$ Hz, 5-H). δ_C (100 MHz, $CDCl_3$) 20.9 (CH_2), 21.8 ($2 \times CH_2$), 26.0 (CH_2), 31.6 (CH_2), 35.1 ($2 \times CH_2$), 55.3 (CH_3), 74.9 (C), 101.8 (CH), 106.7 (CH), 113.7 (C), 129.9 (CH), 154.6 (C), 159.0 (C). HRMS (ESI-TOF) found $[M+H]^+ = 233.1538$ $C_{15}H_{21}O_2$ requires $[M+H]^+ = 233.1536$.

[00113] To a solution of 7-methoxyspiro[chromane-2,1'-cyclohexane] (3.50 g, 15.1 mmol) in anhydrous THF (50 mL) at $-20^\circ C$ under N_2 was added n -BuLi [2.5 M in hexanes, 7.4 mL, 18.4 mmol, 1.2 equiv.] dropwise over 5 min followed by the addition of TMEDA (2.8 mL, 18.4 mmol, 1.2 equiv.) in one portion. The reaction mixture was stirred at $-20^\circ C$ for 30 min and allowed to warm to r.t., the reaction was stirred for a further 3.5 h. The reaction mixture was cooled to $-78^\circ C$ and $B(OMe)_3$ (3.4 mL, 30.1 mmol, 2 equiv.) was added. The mixture was allowed to warm to r.t. and stirred for 16 h. The reaction was quenched with 2M HCl (30 mL) at $0^\circ C$ and stirred for 30 min. The product was extracted with EtOAc and washed with water and brine. The organic layer was dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was triturated with hexane and the solid isolated by vacuum filtration to afford 7-(methoxyspiro[chromane-2,1'-cyclohexan]-8-yl)boronic acid as a pale orange solid (2.10 g, 51 %). m.p. $86 - 87^\circ C$. $\nu_{\max}$ 3459, 3217, 2935, 2857, 1309, 1295, 1082, 797 cm^{-1} . δ_H (400 MHz, $CDCl_3$) 1.29–1.73 (8H, m, Cy-H), 1.80–1.86 (4H, m, Cy-H, CH_2Cy), 2.73 (2H, t, $J = 6.7$ Hz, CH_2CH_2Cy), 3.87 (3H, s, CH_3), 6.51 (1H, d, $J = 8.4$ Hz, 6-H), 7.11 (1H, d, $J = 8.4$ Hz, 5-H), 7.48 [2H, s, $B(OH)_2$]. δ_C (100 MHz, $CDCl_3$) 21.2 (CH_2), 21.9 ($2 \times CH_2$), 25.5 (CH_2), 31.3 (CH_2), 34.9 ($2 \times CH_2$), 55.9 (CH_3), 77.4** (C), 103.4 (CH), 106.1 (C), 115.0 (C), 133.1 (CH), 159.4 (C), 163.9 (C). HRMS (ESI-TOF) found $[M+Na]^+ = 298.1463$ $C_{15}H_{21}BNaO_4$ requires $[M+Na]^+ = 298.1461$. (**Overlaps with residual $CHCl_3$)

[00114] 2,5-Dibromothiophene (0.33 mL, 2.9 mmol), 7-(methoxyspiro[chromane-2,1'-cyclohexan]-8-yl)boronic acid (2.00 g, 7.2 mmol, 2.5 equiv.), potassium carbonate (2.40 g, 17.4 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (0.33 g, 0.3 mmol, 10 mol%) were added to degassed PhMe (20 mL) and EtOH (20 mL), the reaction mixture was stirred at reflux under N_2 for 3 h. The reaction was allowed to cool to r.t., poured onto water (80 mL) and extracted with DCM (3×30 mL). The combined organic portions were dried (Na_2SO_4) and the solvent removed. The product was purified by flash column chromatography [10 % EtOAc in hexane $\rightarrow$ 50 % DCM in hexane] to afford 2,5-bis(7-methoxyspiro[chromane-2,1'-cyclohexan]-8-yl)thiophene as a yellow solid (1.36 g, 86 %). m.p. $167 - 169^\circ C$. $\nu_{\max}$ 2920, 2881, 2836, 1457, 1418, 1115, 1097, 787 cm^{-1} . δ_H (400 MHz, $CDCl_3$)

1.21–1.43 (10H, m, Cy-*H*), 1.52–1.59 (92H, m, Cy-*H*), 1.66–1.70 (4H, m, Cy-*H*), 1.78 (4H, t, $J = 6.8$ Hz, $2 \times \text{CH}_2\text{CH}_2\text{Cy}$), 1.82–1.87 (4H, m, Cy-*H*), 2.76 (4H, t, $J = 6.8$ Hz, $2 \times \text{CH}_2\text{CH}_2\text{Cy}$), 3.80 (6H, s, $2 \times \text{OCH}_3$), 6.52 (2H, d, $J = 8.4$ Hz, $2 \times 6\text{-H}$), 6.94 (2H, d, $J = 8.4$ Hz, $2 \times 5\text{-H}$), 7.46 (2H, s, 3-H , 4-H). δ_{C} (100 MHz, CDCl_3) 21.6 ($2 \times \text{CH}_2$), 21.8 ($4 \times \text{CH}_2$), 26.1 ($2 \times \text{CH}_2$), 31.8 ($2 \times \text{CH}_2$), 35.3 ($4 \times \text{CH}_2$), 56.0 ($2 \times \text{CH}_3$), 75.7 ($2 \times \text{C}$), 103.4 ($2 \times \text{CH}$), 113.1 ($2 \times \text{C}$), 114.6 ($2 \times \text{C}$), 127.8 ($2 \times \text{CH}$), 128.1 ($2 \times \text{CH}$), 133.7 ($2 \times \text{C}$), 151.8 ($2 \times \text{C}$), 156.2 ($2 \times \text{C}$). HRMS (JS) found $[\text{M}+\text{H}]^+ = 545.2720$. $\text{C}_{34}\text{H}_{40}\text{O}_4\text{S}$ requires $[\text{M}+\text{H}]^+ = 545.2720$.

B.3. Synthesis of 2,5-Bis(3-methoxydibenzo[*b,d*]furan-4-yl)thiophene – Compound 12



Reaction scheme B.3

10

[00115] 3-Fluoro-4-iodobromobenzene (12.04 g, 40 mmol), 2-methoxybenzeneboronic acid (7.29 g, 48 mmol, 1.2 equiv.), potassium carbonate (33.17 g, 240 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (4.62 g, 4 mmol, 10 mol%) were added to degassed PhMe (150 mL) and EtOH (150 mL), the reaction mixture was stirred at reflux under N_2 for 4 h. The reaction was allowed to cool to r.t., poured onto water (400 mL) and extracted with DCM (3×100 mL). The combined organic portions were dried (Na_2SO_4) and the solvent removed. The product was purified by flash column chromatography [10% EtOAc in hexane] to afford 4-bromo-2-fluoro-2'-methoxybiphenyl as a colourless oil (9.59 g, 85 %). ν_{max} 3069, 2954, 2835, 1477, 1244, 746 cm^{-1} . δ_{H} (400 MHz, CDCl_3) 3.84 (3H, s, OCH_3), 7.00 (1H, d, $J = 8.3$ Hz, 3-H), 7.03 (1H, dt, $J = 0.9, 7.5$ Hz, 5-H), 7.22 – 7.26 (1H, m, 6-H), 7.30 – 7.41 (4H, m, 4-H , $6'\text{-H}$, $3'\text{-H}$, $5'\text{-H}$). δ_{C} (100 MHz, CDCl_3) 55.7 (CH_3), 111.1 (CH), 119.1 (d, $J_{\text{C-F}} = 27.0$ Hz, CH), 120.6 (CH), 121.5 (d, $J_{\text{C-F}} = 9.4$ Hz, C), 123.9 (C), 125.4 (d, $J_{\text{C-F}} = 16.2$ Hz, C), 127.1 (d, $J_{\text{C-F}} = 3.7$ Hz, CH), 129.8 (CH), 131.1 (d, $J_{\text{C-F}} = 3.0$ Hz, CH), 132.9 (d, $J_{\text{C-F}} = 5.6$ Hz, CH), 156.8 (C), 160.0 (d, $J_{\text{C-F}} = 251$ Hz, C).

[00116] To a solution of 4-bromo-2-fluoro-2'-methoxybiphenyl (8.36 g, 29.7 mmol) in anhyd. DCM (50 mL) was added a solution of BBr_3 (5.7 mL, 59.5 mmol, 2 equiv.) in anhyd. DCM (35 mL) dropwise at 0 °C over 20 min. The reaction was stirred for 3 h at r.t. The reaction was cooled and quenched

25

with ice-water (100 mL) and the product extracted with DCM (2 × 50 mL). The combined organic portions were dried (Na₂SO₄) and the solvent removed under reduced pressure. The residue was purified by flash column chromatography [10 % EtOAc in hexane] to afford 4'-bromo-2'-fluoro-[1,1'-biphenyl]-2-ol as an oil which crystallised (6.96 g, 88 %). m.p. 80 – 81 °C. $\nu_{\max}$ 3243, 1470, 1213, 1195, 817, 754 cm⁻¹. δ_{H} (400 MHz, CDCl₃) 4.87 (1H, s, OH), 6.97 (1H, d, J = 8.1 Hz, 3-*H*), 7.00–7.04 (1H, m, 5-*H*), 7.22 (1H, d, J = 7.4 Hz, 6-*H*), 7.28–7.33 (2H, m, 4-*H*, 6'-*H*), 7.38–7.42 (2H, m, 3'-*H*, 5'-*H*). δ_{C} (100 MHz, CDCl₃) 116.2 (CH), 119.8 (d, $J_{\text{C-F}}$ = 25.5 Hz, CH), 121.0 (CH), 121.5 (C), 122.3 (d, $J_{\text{C-F}}$ = 9.3 Hz, C), 123.9 (d, $J_{\text{C-F}}$ = 15.9 Hz, C), 127.9 (d, $J_{\text{C-F}}$ = 3.6 Hz, CH), 130.1 (CH), 131.1 (d, $J_{\text{C-F}}$ = 1.2 Hz, CH), 132.9 (d, $J_{\text{C-F}}$ = 4.0 Hz, CH), 152.7 (C), 159.7 (d, $J_{\text{C-F}}$ = 250 Hz, C). HRMS (ESI) found $[\text{M}+\text{H}]^+ = 266.9810$ C₁₂H₈BrFO requires $[\text{M}+\text{H}]^+ = 266.9815$.

[00117] To 4'-bromo-2'-fluoro-[1,1'-biphenyl]-2-ol (6.21 g, 23.2 mmol) in NMP (60 mL) was added K₂CO₃ (2.76 g, 20 mmol, 2 equiv.) and the reaction was stirred under N₂ at 180 °C for 3 h. The reaction was allowed to cool to r.t., poured onto water (500 mL) and stirred for 1 h. The colourless precipitate was isolated by vacuum filtration to afford 3-bromodibenzo[*b,d*]furan (5.20 g, 91 %). m.p. 119 – 121 °C (lit. m.p. 118 – 119 °C [Y Wei *et al.*, *Organic Letters*, 2011, 13, 5504 - 5507]). $\nu_{\max}$ 3062, 1588, 1455, 1412, 812, 742, 718, 687 cm⁻¹. δ_{H} (400 MHz, CDCl₃) 7.34–7.38 (1H, m, 8-*H*), 7.45–7.51 (2H, m, 2-*H*, 7-*H*), 7.57 (1H, d, J = 8.2 Hz, 6-*H*), 7.75 (1H, d, J = 1.6 Hz, 4-*H*), 7.81 (1H, d, J = 8.2 Hz, 1-*H*), 7.92–7.94 (1H, m, 9-*H*). δ_{C} (100 MHz, CDCl₃) 111.8 (CH), 115.2 (CH), 120.2 (C), 120.7 (CH), 121.6 (CH), 123.1 (CH), 123.4 (C), 123.5 (C), 126.1 (CH), 127.6 (CH), 156.3 (C), 156.5 (C). HRMS (APCI) found $[\text{M}]^+ = 245.9677$ C₁₂H₇BrO requires $[\text{M}]^+ = 245.9675$.

[00118] To 3-bromodibenzo[*b,d*]furan (1.48 g, 6 mmol) in anhyd. THF (50 mL) was added *n*-BuLi (2.5 M in hexanes, 2.6 mL, 6.6 mmol, 1.1 equiv.) followed by TMEDA (1 mL, 6.6 mmol, 1.1 equiv.) at -78 °C under N₂, the reaction was stirred at -78 °C for 1.5 h. B(OMe)₃ (3.3 mL, 29.9 mmol, 5 equiv.) was added dropwise and the reaction stirred at -78 °C for a further 3 h. The reaction was allowed to warm to r.t. and stirred for a further 30 min. The reaction was cooled to 0 °C and H₂O₂ (30 %, 6.8 mL) and sat. aqueous Na₂CO₃ (6.8 mL) were added slowly and the reaction was stirred for 1 h at r.t. The reaction was cooled to 0 °C before the addition of sat. aqueous Na₂S₂O₃ (50 mL) and sat. aqueous NH₄Cl (80 mL) and the product extracted with EtOAc (3 × 75 mL) and the combined organic portions were washed with water (2 × 100 mL) and brine (100 mL), dried (Na₂SO₄) and the solvent removed under reduced pressure. The residue was purified by flash column chromatography [10 % EtOAc in hexane] to afford dibenzo[*b,d*]furan-3-ol as a colourless solid (0.70 g, 63 %). m.p. 145 – 147 °C (lit. m.p. 141 – 141.5 °C [H. Erdtman *et al.*, *Acta Chemica Scandinavica*, 1961, 15, 1761-1764]). $\nu_{\max}$ 3253, 3044, 1596, 1437, 1270, 846, 761, 740 cm⁻¹. δ_{H} (400 MHz, CDCl₃) 6.86 (1H, dd, J = 2.2, 8.3 Hz, 2-*H*), 7.05 (1H, d, J = 2.2 Hz, 4-*H*), 7.31 (1H, m, 7-*H*), 7.38 (1H, m, 8-*H*), 7.52 (1H, d, J = 8.1 Hz, 6-*H*), 7.78 (1H, d, 1-*H*), 7.85 (1H, m, 9-*H*). δ_{C} (100 MHz, CDCl₃) 98.8 (CH), 111.3 (CH), 111.4 (CH), 117.7 (C), 119.8 (CH), 121.2 (CH), 122.8 (CH), 124.3 (C), 125.9 (CH), 155.6 (C), 156.3 (C), 157.4 (C). HRMS (APCI) found $[\text{M}]^+ = 184.0520$ C₁₂H₈O₂ requires $[\text{M}]^+ = 184.0519$.

[00119] To dibenzo[*b,d*]furan-3-ol (1.66 g, 9 mmol) in 2-butanone (50 mL) was added iodomethane (4.4 mL, 72 mmol, 8 equiv.) followed by K₂CO₃ (3.74 g, 27 mmol, 3 equiv.) at room temperature

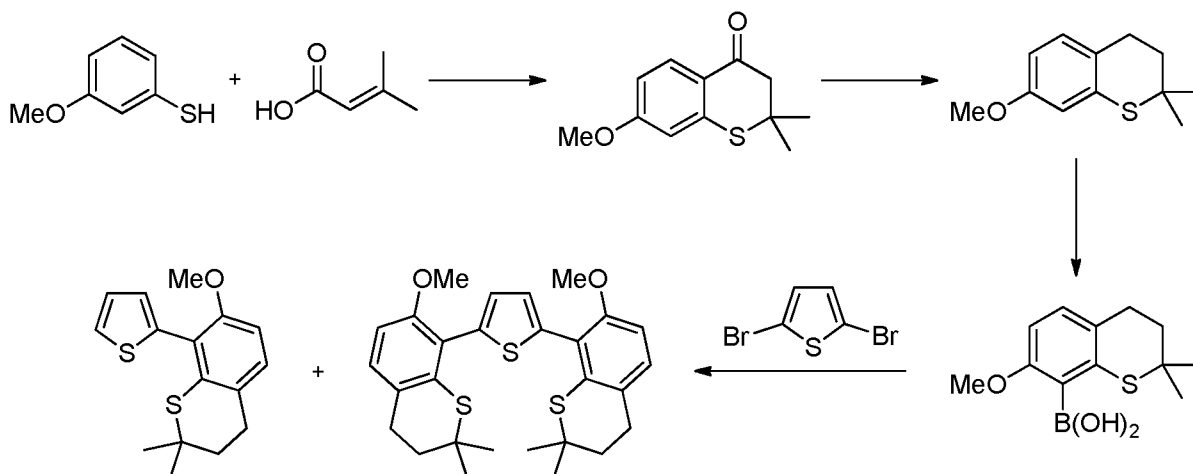
under N₂ before stirring at reflux for 72 h. The reaction was allowed to cool to r.t. and quenched with water (100 mL). The product was extracted with EtOAc (3 × 50 mL), and the combined organic portions were dried (Na₂SO₄) and the solvent removed under reduced pressure. The product was purified by flash column chromatography [10 % EtOAc in hexane] to afford 3-methoxydibenzo[*b,d*]furan as a colourless solid (1.26 g, 71 %). (0.44 g, 63 %). m.p. 98 – 100 °C. $\nu_{\max}$ 3044, 2845, 1633, 1595, 1455, 1423, 1275, 032, 815, 761, 748 cm⁻¹. δ_{H} (400 MHz, CDCl₃) 3.91 (3H, s, OCH₃), 6.95 (1H, dd, *J* = 2.2, 8.5 Hz, 2-*H*), 7.10 (1H, d, *J* = 2.2 Hz, 4-*H*), 7.29–7.33 (1H, m, 7-*H*), 7.36–7.40 (1H, m, 8-*H*), 7.53 (1H, d, *J* = 8.1 Hz, 6-*H*), 7.82 (1H, d, *J* = 8.5 Hz, 1-*H*), 7.86 (1H, m, 9-*H*). δ_{C} (100 MHz, CDCl₃) 55.8 (CH₃), 96.5 (CH), 111.0 (CH), 111.4 (CH), 117.3 (C), 119.8 (CH), 121.0 (CH), 122.7 (CH), 124.4 (C), 125.7 (CH), 156.3 (C), 157.5 (C), 159.9 (C). HRMS (APCI) found [M]⁺ = 198.0676 C₁₃H₁₀O₂ requires [M]⁺ = 198.0675.

[00120] To a stirred solution of TMEDA (2.4 mL, 15.8 mmol, 2 equiv.) in anhyd. THF (75 mL) at -20 °C under N₂ was added *n*-BuLi (6.3 mL, 15.8 mmol, 2 equiv.) slowly and the mixture stirred for 5 minutes before the dropwise addition of 3-methoxydibenzo[*b,d*]furan (1.57 g, 7.9 mmol, 1 equiv.). in THF (25 mL). The reaction was stirred for 30 min at -20 °C then 3.5 h at r.t. The reaction was cooled to -78 °C and B(OMe)₃ (1.8 mL, 15.8 mmol, 2 equiv.) was added, the reaction was allowed to warm to r.t. overnight. The reaction was cooled to -20 °C and quenched with dil. HCl (2M) and stirred for 30 min at r.t. The product was extracted with EtOAc (3 × 50 mL) and the combined organic extracts were washed with water (100 mL) and brine (100 mL), dried (Na₂SO₄) and the solvent removed under reduced pressure to afford (3-methoxydibenzo[*b,d*]furan-4-yl)boronic acid as a colourless solid (1.60 g, 84%). m.p. 150 – 151 °C. $\nu_{\max}$ 3285, 2933, 2836, 1599, 1457, 1341, 1081, 778 cm⁻¹. δ_{H} (400 MHz, CDCl₃) 4.04 (3H, s, OCH₃), 6.80 [2H, s, B(OH)₂], 7.01 (1H, d, *J* = 8.5 Hz, 2-*H*), 7.34–7.38 (1H, m, 8-*H*), 7.41–7.45 (1H, m, 7-*H*), 7.57 (1H, d, *J* = 8.1 Hz, 6-*H*), 7.88 (1H, d, *J* = 7.4 Hz, 9-*H*), 7.99 (1H, d, *J* = 8.5 Hz, 1-*H*). δ_{C} (100 MHz, CDCl₃) 56.6 (CH₃), 102.5 [CB(OH)₂]^{*}, 106.5 (CH), 111.5 (CH), 117.9 (C), 120.1 (CH), 123.4 (CH), 123.5 (C), 124.2 (CH), 126.6 (CH), 155.9 (C), 161.8 (C), 164.1 (C). HRMS (APCI) found [M+H]⁺ = 243.0825 C₁₃H₁₂BO₄ requires [M+H]⁺ = 243.0823. (*Only visible from HMBC.)

[00121] 2,5-Dibromothiophene (0.28 mL, 2.5 mmol), (3-methoxydibenzo[*b,d*]furan-4-yl)boronic acid (1.20 g, 5 mmol, 2 equiv.), potassium carbonate (2.06 g, 14.9 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (0.29 g, 0.2 mmol, 10 mol%) were added to degassed PhMe (30 mL) and EtOH (30 mL), the reaction mixture was stirred at reflux under N₂ for 4 h. The reaction was allowed to cool to r.t., poured onto water (80 mL) and extracted with DCM (3 × 30 mL). The combined organic portions were dried (Na₂SO₄) and the solvent removed. The product was purified by flash column chromatography [5 % EtOAc in hexane → 10 % EtOAc in hexane] to afford 2,5-bis(3-methoxydibenzo[*b,d*]furan-4-yl)thiophene as a yellow powder (0.23 g, 20 %). m.p. 235–237 °C (decomp. 230 °C). $\nu_{\max}$ 1592, 1456, 1185, 1069, 803, 732 cm⁻¹. δ_{H} (400 MHz, CDCl₃) 4.09 (6H, s, 2 × OCH₃), 7.09–7.11 (2H, m, 2 × 8-*H*), 7.34–7.37 (2H, m, 2 × 7-*H*), 7.63–7.65 (2H, m, 2 × 6-*H*), 7.81–7.83 (2H, m, 2 × 1-*H*), 7.91–7.93 (2H, m, 2 × 9-*H*), 8.29 (2H, s, 3-th-*H*, 4-th-*H*). δ_{C} (100 MHz, CDCl₃) 56.8 (2 × CH₃), 107.7 (2 × C), 110.0 (2 × C), 111.7 (2 × C), 118.5 (2 × C), 118.8 (2 × C), 119.9 (2 × C), 122.9 (2 × C), 124.3 (2 × C), 126.1 (2 × C), 128.5 (2 × C), 133.9 (2 × C), 154.2 (2 ×

C), 155.7 (2 × C), 156.4 (2 × C). HRMS (JS) found $[M+H]^+ = 477.1147$ $C_{30}H_{21}O_4S$ requires $[M+H]^+ = 477.1155$.

B.4. Synthesis of 7-Methoxy-2,2-dimethyl-8-(thiophen-2-yl)thiochromane – Compound 7 and of 2,5-bis(7-methoxy-2,2-dimethylthiochroman-8-yl)thiophene - Compound 8



5

Reaction scheme B.4

[00122] 3-Methoxythiophenol (4.4 mL, 36 mmol) and 3,3-dimethylacrylic acid (3.93 g, 39 mmol, 1.1 equiv.) were dissolved in $MeSO_3H$ (50 mL) and stirred at 70 °C for 4 hours. The reaction was allowed to cool, poured onto 200 mL ice-water and stirred for 30 min. The product was extracted with Et_2O (3 × 100 mL) and the combined organic portions were washed with 5 % NaOH solution (2 × 50 mL), water (100 mL) and brine (100 mL). The organic portion was dried (Na_2SO_4) and the solvent removed *in vacuo* to afford a viscous yellow oil. The product was purified by FCC [5% EtOAc in hexane] to afford 7-methoxy-2,2-dimethylthiochroman-4-one as a pale yellow solid (4.59 g, 58 %). m.p. 67–69 °C (lit. m.p. 67–68 °C [F. Camps *et al.*, *Journal of Heterocyclic Chemistry*, 1983, 20, 1115 - 1117]).

ν_{max} 3011, 2977, 2965, 1668, 1589, 1484, 1305, 1237, 1041, 839 cm^{-1} . δ_H (400 MHz, $CDCl_3$) 1.46 [6H, s, $C(CH_3)_2$], 2.83 (2H, s, CH_2), 3.84 (3H, s, OCH_3), 6.68 – 6.72 (2H, m, 6-*H*, 8-*H*), 8.07 (1H, d, $J = 8.5$ Hz, 5-*H*). δ_C (100 MHz, $CDCl_3$) 28.7 (2 × CH_3), 44.9 (C), 53.7 (CH_2), 55.5 (CH_3), 110.7 (CH), 112.3 (CH), 123.4 (C), 130.9 (CH), 143.6 (C), 163.6 (C), 193.7 (C).

[00123] 7-Methoxy-2,2-dimethylthiochroman-4-one (4.00 g, 18 mmol) was added to Zn dust (29.41 g, 450 mmol, 25 equiv.) in AcOH (75 mL) and stirred at reflux overnight. The reaction was allowed to cool to r.t. and filtered through Celite®. The reaction mixture was diluted with EtOAc (200 mL) and PhMe (200 mL). The solvent was removed under reduced pressure. The residue was dissolved in DCM and the solvent removed, the insoluble material was discarded. The product was purified by FCC [5 % EtOAc in hexane] to afford 7-methoxy-2,2-dimethylthiochromane as a colourless oil (2.60 g, 69 %). ν_{max} 2957, 2923, 2844, 1600, 1490, 1245, 1060, 1041, 804 cm^{-1} . δ_H (400 MHz, $CDCl_3$) 1.41 [6H, s, $C(CH_3)_2$], 1.90 [2H, t, $J = 6.5$ Hz, $CH_2CH_2C(CH_3)_2$], 2.86 [2H, t, $J = 6.5$ Hz, $CH_2CH_2C(CH_3)_2$], 3.75 (3H, s, OCH_3), 6.56 – 6.60 (2H, m, 6-*H*, 8-*H*), 7.00 (1H, d, $J = 8.2$ Hz, 5-*H*). δ_C (100 MHz, $CDCl_3$)

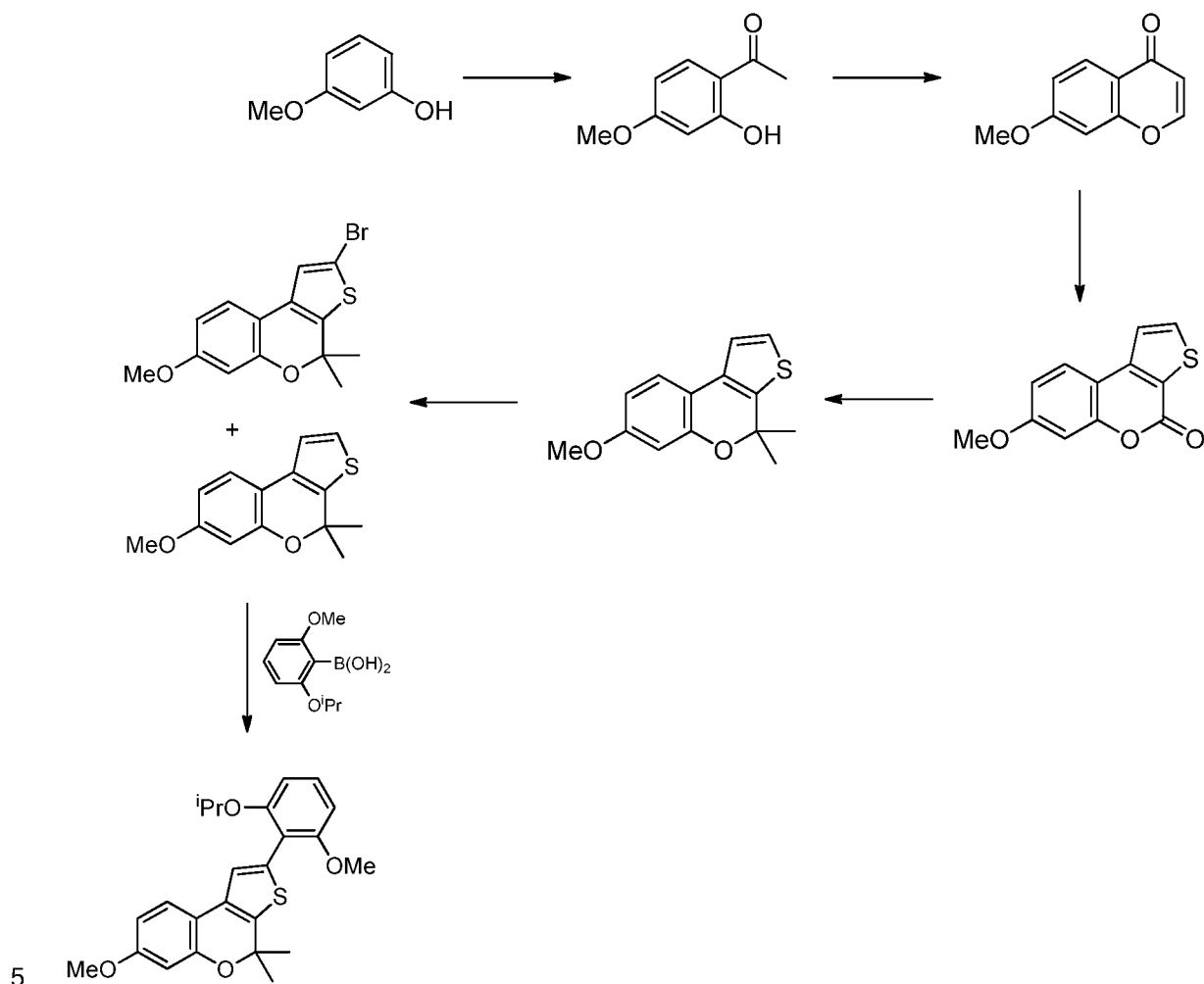
26.2 (CH₂), 30.2 (2 × CH₃), 37.9 (CH₂), 42.3 (C), 55.3 (CH₃), 110.7 (CH), 110.9 (CH), 124.3 (C), 130.5 (CH), 134.5 (C), 157.9 (C).

[00124] To TMEDA (2.9 mL, 19.2 mmol, 2 equiv.) in anhydrous THF (50 mL) at -20 °C under N₂ was added *n*-BuLi [2.5 M in hexanes, 7.7 mL, 19.2 mmol, 2 equiv.] dropwise over 5 min followed by the dropwise addition of a solution of 7-methoxy-2,2-dimethylthiochromane (2.00 g, 9.6 mmol) in THF (10 mL). The reaction mixture was stirred at -20 °C for 30 min and allowed to warm to r.t., the reaction was stirred for a further 3.5 h. The reaction mixture was cooled to -78 °C and B(OMe)₃ (2.1 mL, 19.2 mmol, 2 equiv.) was added. The mixture was allowed to warm to r.t. and stirred for 16 h. The reaction was quenched with 2 M HCl at 0 °C and stirred for 30 min. The product was extracted with EtOAc (3 × 50 mL) and washed with water and brine. The organic layer was dried (Na₂SO₄) and the solvent was removed under reduced pressure. The residue was triturated with hexane and the solid isolated by vacuum filtration to afford (7-methoxy-2,2-dimethylthiochroman-8-yl)boronic acid as an off-white powder (1.17 g, 48 %). m.p. 114–117 °C. ν_{max} 3210, 2980, 1579, 1566, 1463, 1386, 1193, 1033, 800, 779 cm⁻¹. δ_{H} (400 MHz, CDCl₃) 1.43 [6H, s, C(CH₃)₂], 1.83 [2H, t, *J* = 6.4 Hz, CH₂CH₂C(CH₃)₂], 2.80 [2H, t, *J* = 6.4 Hz, CH₂CH₂C(CH₃)₂], 3.87 (3H, s, OCH₃), 6.71 (1H, d, *J* = 8.4 Hz, 6-*H*), 6.86 [2H, s, B(OH)₂], 7.17 (1H, d, *J* = 8.4 Hz, 5-*H*). δ_{C} (100 MHz, CDCl₃)* 28.9 (CH₂), 31.2 (2 × CH₃), 38.8 (CH₂), 45.6 (C), 56.0 (CH₃), 107.9 (CH), 130.5 (C), 131.6 (CH), 141.4 (C), 163.1 (C). (*CB(OH)₂ not visible in ¹³C.)

[00125] 2,5-Dibromothiophene (0.21 mL, 1.9 mmol), (7-methoxy-2,2-dimethylthiochroman-8-yl)boronic acid (1.00 g, 4 mmol, 2.1 equiv.), potassium carbonate (1.57 g, 11.3 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (0.22 g, 0.2 mmol, 10 mol%) were added to degassed PhMe (20 mL) and EtOH (20 mL), the reaction mixture was stirred at reflux under N₂ for 24 h. The reaction was allowed to cool to r.t., poured onto water (50 mL) and extracted with DCM (3 × 25 mL). The combined organic portions were dried (Na₂SO₄) and the solvent removed. The product was purified by flash column chromatography [5 % EtOAc in hexane] to afford: Fraction 1: 7-methoxy-2,2-dimethyl-8-(thiophen-2-yl)thiochromane as a colourless oil which solidified (0.17 g, 36 %). m.p. 99 – 101 °C. ν_{max} 2960, 2926, 1581, 1459, 1260, 1045, 809, 700 cm⁻¹. (400 MHz, CDCl₃) 1.34 [6H, s, C(CH₃)₂], 1.86 [2H, t, *J* = 6.4 Hz, CH₂CH₂C(CH₃)₂], 2.94 [2H, t, *J* = 6.4 Hz, CH₂CH₂C(CH₃)₂], 3.73 (3H, s, OCH₃), 6.66 (1H, d, *J* = 8.4 Hz, 6-*Ch-H*), 6.99 (1H, dd, *J* = 1.1, 3.4 Hz, 3-*Th-H*), 7.10–7.14 (2H, m, 5-*Ch-H*, 4-*Th-H*), 7.44 (1H, dd, *J* = 1.1, 5.1 Hz, 5-*Th-H*). δ_{C} (100 MHz, CDCl₃) 27.0 (CH₂), 30.2 (2 × CH₃), 37.3 (CH₂), 42.4 (C), 56.0 (CH₃), 106.8 (CH), 120.1 (C), 125.0 (C), 126.3 (CH), 126.7 (CH), 128.5 (CH), 130.4 (CH), 136.5 (C), 137.3 (C), 156.5 (C). HRMS (Jetstream) found [M+H]⁺ = 291.0871 C₁₆H₁₉OS₂ requires [M+H]⁺ = 291.0872. Fraction 2: 2,5-bis(7-methoxy-2,2-dimethylthiochroman-8-yl)thiophene as an off-white solid (0.56 g, 60 %). m.p. 162 – 164 °C. ν_{max} 2960, 2924, 1735, 1582, 1435, 1260, 1234, 1042, 797 cm⁻¹. δ_{H} (400 MHz, CDCl₃) 1.37 [12H, s, 2 × C(CH₃)₂], 1.87 [4H, t, *J* = 6.5 Hz, 2 × CH₂C(CH₃)₂], 2.93 [4H, t, *J* = 6.5 Hz, 2 × CH₂CH₂C(CH₃)₂], 3.75 (6H, s, 2 × OCH₃), 6.66 (2H, d, *J* = 8.4 Hz, 2 × 6-*H*), 7.01 (2H, s, 3-*H*, 4-*H*), 7.08 (2H, d, *J* = 8.4 Hz, 2 × 5-*H*). δ_{C} (100 MHz, CDCl₃) 27.2 (2 × CH₂), 30.3 (4 × CH₃), 37.3 (2 × CH₂), 42.3 (2 × C), 56.1 (2 × CH₃), 106.9 (2 × CH), 120.6 (2 × C), 125.0 (2 × C), 128.0 (2 × CH), 130.2 (2 × CH), 137.3 (2 × C),

137.4 (2 × C), 156.4 (2 × C). HRMS (Jetstream) found $[M+H]^+ = 497.1638$ $C_{28}H_{33}O_2S_3$ requires $[M+H]^+ = 497.1637$.

B.5. Synthesis of 2-(2-Isopropoxy-6-methoxyphenyl)-7-methoxy-4,4-dimethyl-4H-thieno[2,3-c]chromene – Compound 17



Reaction scheme B.5

- [00126] 3-Methoxyphenol (30 g, 0.24 mol), $ZnCl_2$ (22.9 g, 0.24 mol) and acetic acid (60 mL) were stirred and heated at 120 °C for 6 hours. The reaction mixture was cooled to ambient temperature and poured into water (300 mL) and extracted with EtOAc (3 × 300 mL). The organic layers were combined, dried (Na_2SO_4) and the solvent was removed under reduced pressure. The resulting orange residue was chromatographed on silica gel [eluent = 7:93 EtOAc:Hexane] to give 2'-hydroxy-4'-methoxyacetophenone as a colourless solid, (10.3 g, 26 %). δ_H (400 MHz, $CDCl_3$) 12.76 (s, 1 H), 7.63 (d, $J = 8.8$ Hz, 1 H), 6.44 (dd, $J = 8.8, 1.2$ Hz, 1 H), 6.39 (d, $J = 1.4$ Hz, 1H), 3.83 (s, 3H), 2.56 (s, 3H). δ_C (101 MHz, $CDCl_3$) 202.8, 166.3, 165.4, 132.4, 114.0, 107.7, 100.9, 55.7, 26.3.
- 15 [00127] 2'-Hydroxy-4'-methoxyacetophenone (10.0 g, 56.8 mmol) and DMFDMA (22.7 mL, 170.4 mmol) dissolved toluene (300 mL). The reaction mixture was then stirred and heated at 90 °C for 16 hours. The reaction mixture was then cooled to 0 °C and $HCl_{(aq)}$ (37 %) (34 mL) was added. The reaction mixture was then stirred and heated at 60 °C for 1 hour. The reaction mixture was cooled to

ambient temperature and diluted with EtOAc (500 mL). The reaction mixture was washed with water (3 × 250 mL), brine (2 × 200 mL), dried (Na₂SO₄) and the solvent was removed under reduced pressure. The resulting residue was chromatographed on silica gel [eluent = 3:7 EtOAc:Hexane graduated to 1:1 EtOAc:Hex] to give the 7-methoxy-4*H*-chromen-4-one as a yellow solid, (7.8 g, 74 %). δ_{H} (300 MHz, CDCl₃) 8.09 (d, *J* = 8.8 Hz, 1 H), 7.77 (d, *J* = 6.1 Hz, 1 H), 6.96 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.82 (d, *J* = 2.4 Hz, 1 H), 6.26 (d, *J* = 6.1 Hz, 1 H), 3.90 (s, 3 H). δ_{C} (75 MHz, CDCl₃) 177.2, 164.3, 158.6, 155.1, 127.5, 119.1, 114.9, 113.2, 100.8, 56.1.

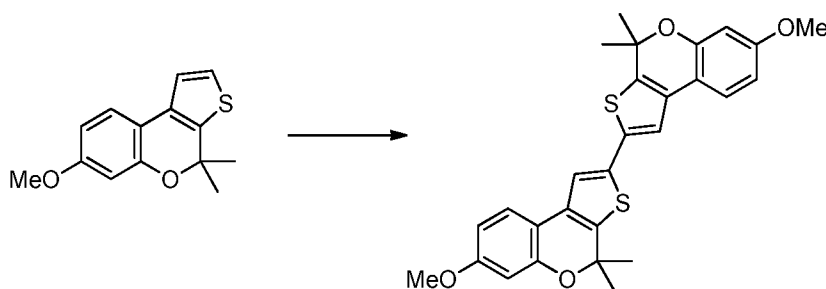
[00128] 7-Methoxy-4*H*-chromen-4-one (7.0 g, 40 mmol), ethyl mercaptoacetate (4.82 mL, 44 mmol), and DBU (11.94 mL, 80.0 mmol) were dissolved in 1,4-dioxane (200 mL). The reaction mixture was then heated and stirred at 60 °C for 12 hours under N₂. The reaction mixture was then cooled to ambient temperature and the reaction mixture was filtered to acquire a colourless precipitate. The precipitate was washed with 1,4-dioxane (30 mL) and dried under reduced pressure to give the 7-methoxy-4*H*-thieno[2,3-*c*]chromen-4-one as a colourless solid, (6.58g, 71 %). δ_{H} (300 MHz, CDCl₃) 7.90 (d, *J* = 5.2 Hz, 1 H), 7.73 (d, *J* = 5.2 Hz, 1 H), 7.56 (d, *J* = 5.2 Hz, 1 H), 6.98 – 6.87 (m, 2 H), 3.89 (s, 3 H). δ_{C} (75 MHz, CDCl₃) 158.1, 157.0, 147.8, 145.6, 137.4, 125.6, 123.0, 119.3, 118.5, 117.9, 107.7, 56.7.

[00129] 7-Methoxy-4*H*-thieno[2,3-*c*]chromen-4-one (2.0 g, 8.6 mmol) was stirred in THF (30 mL) at 0 °C under N₂. A solution of MeMgBr (3.0 M in diethyl ether, 7.2 mL, 21.6 mmol) was added dropwise and the reaction mixture was stirred at 0 °C for 2 hours. The reaction mixture was then warmed to ambient temperature and stirred for 1 hour. Brine (50 mL) was added and the reaction mixture as extracted with EtOAc (3 × 50 mL). The organic layers were combined, dried (Na₂SO₄) and the solvent was removed under reduced pressure. The resulting residue was dissolved in toluene (10 mL) and molecular sieves 3 Å (2 g) added and the reaction mixture was heated at 100 °C for 6 hours. The reaction mixture was filtered and the solids were washed with toluene (10 mL). The solvent was removed under reduced pressure and the resulting residue was chromatographed on silica gel [eluent = 1.5:98.5 EtOAc:Hexane] to give 7-methoxy-4,4-dimethyl-4*H*-thieno[2,3-*c*]chromene as a colourless oil, (1.76 g, 83 %). δ_{H} (400 MHz, CDCl₃) 7.35 (dd, *J* = 6.4, 2.4 Hz, 1 H), 7.73 (app. s, 2 H), 6.60 - 6.51 (m, 2 H), 3.81 (s, 3 H), 1.68 (s, 6 H). δ_{C} (101 MHz, CDCl₃) 160.1, 152.8, 137.2, 131.1, 123.8, 123.7, 123.2, 122.2, 114.2, 107.5, 103.0, 77.7, 55.4, 28.9.

[00130] 7-Methoxy-4,4-dimethyl-4*H*-thieno[2,3-*c*]chromene (0.50 g, 2.0 mmol) was dissolved in anhydrous THF (10 mL) and the reaction mixture was cooled to -78 °C under N₂. A solution of *n*-BuLi (2.5 M in hexanes, 0.84 mL, 2.1 mmol) was added dropwise and the reaction mixture was stirred at -78 °C under N₂ for 1 hour. Dibromoethane (DBE) (0.35 mL, 4.0 mmol) was added dropwise and the reaction mixture was warmed to ambient temperature. Brine (10 mL) was added and the reaction mixture was extracted with EtOAc (3 × 20 mL). The dried (anhyd. Na₂SO₄) solvent was removed under reduced pressure and the resulting residue was chromatographed on silica gel [eluent = 1:99 EtOAc:Hexane] to give an inseparable mixture of 7-methoxy-4,4-dimethyl-4*H*-thieno[2,3-*c*]chromene (45 %) and 2-bromo-7-methoxy-4,4-dimethyl-4*H*-thieno[2,3-*c*]chromene (55 %) (relative percentages determined by ¹H NMR spectroscopy). The foregoing mixture was used directly in the next step

without further purification. The aforementioned mixture was dissolved in a mixture of toluene and 1,4-dioxane (1:1) (8 mL) and (2-isopropoxy-6-methoxyphenyl)boronic acid (3.0 mmol) and K_3PO_4 (0.86, 4.0 mmol) was added. The reaction mixture was then degassed with argon and $Pd(OAc)_2$ (9 mg, 0.04 mmol) and X-Phos (38 mg, 0.08 mmol) was added. The reaction mixture was then stirred and heated at 105 °C for 16 hours under N_2 . The reaction mixture was then cooled to ambient temperature whereupon brine (30 mL) was added followed by extraction with EtOAc (3 × 30 mL). The organic layers were combined, dried (anhyd. Na_2SO_4) and the solvent was removed under reduced pressure. The resulting residue was chromatographed on silica gel [eluent = 1:19 EtOAc:Hexane] to give 2-(2-isopropoxy-6-methoxyphenyl)-7-methoxy-4,4-dimethyl-4*H*-thieno[2,3-*c*]chromene as a colourless oil, (0.28 g, 31 %, yield over two steps). δ_H (300 MHz, $CDCl_3$) 7.66 (s, 1 H), 7.34 (dd, $J = 5.4, 3.6$ Hz, 1 H), 7.19 (t, $J = 8.3$ Hz, 1 H), 6.64 (t, 8.3 Hz, 2 H), 6.58 - 6.49 (m, 2H), 4.56 (sept, $J = 5.9$ Hz, 1 H), 3.86 (s, 3H), 3.80 (s, 3 H) 1.70 (s, 6 H), 1.34 (d, $J = 6.1$ Hz, 6 H). δ_C (75 MHz, $CDCl_3$) 159.6, 157.7, 155.9, 152.9, 137.2, 132.9, 129.6, 128.3, 123.8, 123.5, 114.6, 113.6, 107.7, 107.4, 104.2, 102.9, 77.8, 71.6, 55.9, 55.4, 29.0, 22.1.

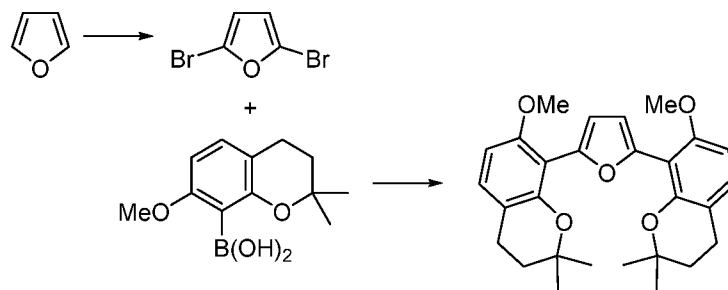
B.6. Synthesis of 7,7'-Dimethoxy-4,4,4',4'-tetramethyl-4*H*,4'*H*-2,2'-bithieno[2,3-*c*]chromene – Compound 16



Reaction scheme B.6

[00131] 7-Methoxy-4,4-dimethyl-4*H*-thieno[2,3-*c*]chromene (0.50 g, 2.0 mmol) was dissolved in anhydrous THF (10 mL) and the reaction mixture was cooled to -78 °C under N_2 . A solution of *n*-BuLi (2.5 M in hexanes, 1.0 mL, 2.5 mmol) was added dropwise and the reaction mixture was stirred at -78 °C under N_2 for 20 minutes then slowly warmed to -15 °C. The reaction mixture was then re-cooled to -78 °C and $CuCl_2$ (0.54 g, 4 mmol) was added. The reaction mixture was then slowly warmed to room temperature and then diluted with toluene (30 mL) followed by brine (30 mL). The reaction mixture was then extracted with EtOAc (3 × 30 mL). The organic layers were combined, dried (anhyd. Na_2SO_4) and the solvent was removed under reduced pressure. The resulting residue was chromatographed on silica gel [eluent = 1:19 EtOAc:Hexane graduated to 1:9 EtOAc:Hexane] to give 7,7'-dimethoxy-4,4,4',4'-tetramethyl-4*H*,4'*H*-2,2'-bithieno[2,3-*c*]chromene as a colourless solid, (0.35 g, 70 %). δ_H (300 MHz, $CDCl_3$) = 7.33 (dd, $J = 7.9, 0.6$ Hz, 2 H), 7.25 (app. s, 2 H), 6.60 - 6.51 (m, 4 H), 3.81 (s, 6 H), 1.68 (s, 12 H). δ_C (75 MHz, $CDCl_3$) 160.2, 153.0, 136.3, 135.7, 131.8, 123.6, 118.5, 113.7, 107.6, 103.0, 77.5, 55.4, 28.8.

B.7. Synthesis of 2,5-bis(7-Methoxy-2,2-dimethylchroman-8-yl)furan – Compound 6

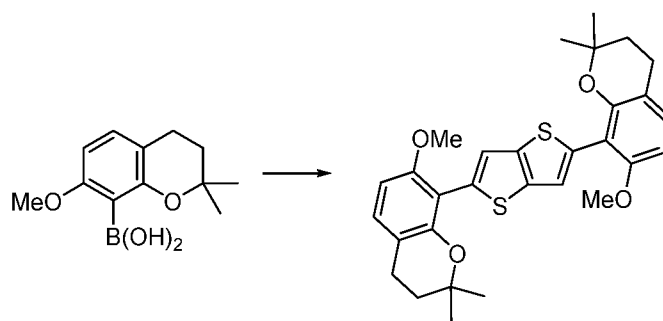


Reaction scheme B.7

[00132] A mixture of furan (20 g, 294 mmol) and NBS (104.71 g, 588.4 mmol) in DCM (600 ml) was sonicated for 5 min with occasional stirring, left to stand at rt for 12 h. The resulting mixture was washed with water (400 ml), dried (Na_2SO_4) and the solvent removed under reduced pressure. The residue was filtered through silica using pet ether (40-60) as eluent and the solvent removed under reduced pressure to give 2,5-dibromofuran as a pale-yellow oil, (15.65 g, 23 %) which was used without further purification in the next step.

[00133] 2,5-Dibromofuran (1.31 g, 5.8 mmol), (7-methoxy-2,2-dimethylchroman-8-yl)boronic acid (3.48 g, 14.5 mmol, 2.5 equiv.), potassium carbonate (4.82 g, 34.9 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (669 mg, 0.3 mmol, 10 mol%) were added to degassed PhMe (30 mL) and EtOH (30 mL), the reaction mixture was stirred at reflux under N_2 for 16 h. The reaction was allowed to cool to r.t., poured onto water (100 mL) and extracted with DCM (3 $\times$ 50 mL). The combined organic portions were dried (Na_2SO_4) and the solvent removed under reduced pressure. The product was purified by flash column chromatography [10 – 15 % gradient EtOAc in pet ether 40-60] to afford 2,5-bis(7-methoxy-2,2-dimethylchroman-8-yl)furan as a viscous pale-yellow oil which was crystallised from pentane (2.24 g, 79 %). δ_{H} (600 MHz, CDCl_3) 1.32 [12H, s, 2 $\times$ $\text{C}(\text{CH}_3)_2$], 1.78 [4H, t, $J = 6.8$ Hz, 2 $\times$ $\text{CH}_2\text{C}(\text{CH}_3)_2$], 2.75 [4H, dt, $J = 0.9, 6.8$ Hz, 2 $\times$ $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2$], 3.79 (6H, s, 2 $\times$ OCH_3), 6.49 (2H, d, $J = 8.4$ Hz, 2 $\times$ 6- H), 6.72 (2H, s, 3- H , 4- H), 6.94 (2H, dt, $J = 0.9, 8.4$ Hz, 2 $\times$ 5- H). δ_{C} (150 MHz, CDCl_3) 22.3 (2 $\times$ CH_2), 27.0 (4 $\times$ CH_3), 32.7 (2 $\times$ CH_2), 56.7 (2 $\times$ CH_3), 74.5 (2 $\times$ C), 104.3 (2 $\times$ CH), 1110.3 (2 $\times$ C), 112.3 (2 $\times$ C), 114.0 (2 $\times$ CH), 128.7 (2 $\times$ CH), 146.3 (2 $\times$ C), 152.4 (2 $\times$ C), 157.0 (2 $\times$ C).

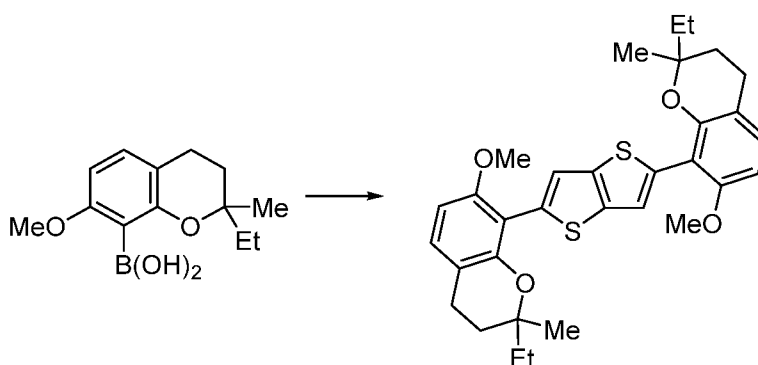
B.8. Synthesis of 2,5-bis(7-Methoxy-2,2-dimethylchroman-8-yl)thieno[3,2-*b*]thiophene – Compound 14



Reaction scheme B.8

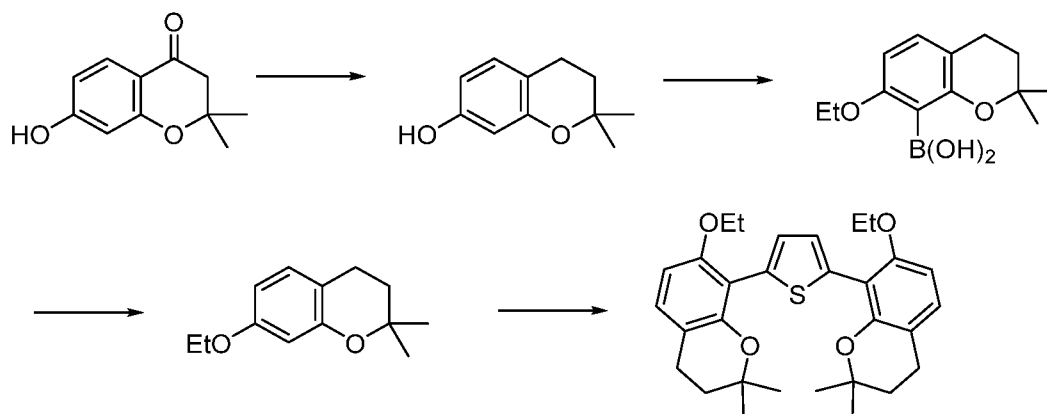
[00134] 2,5-Dibromothiopheno[3,2-*b*]thiophene (1.50 g, 5.0 mmol), (7-methoxy-2,2-dimethylchroman-8-yl)boronic acid (3.78 g, 11 mmol, 2.2 equiv.), potassium carbonate (3.05 g, 22.1 mmol, 4.4 equiv.) and tetrakis(triphenylphosphine)palladium(0) (500 mg, 0.43 mmol, 9 mol%) were added to degassed PhMe (30 mL) and EtOH (30 mL), the reaction mixture was stirred at reflux under N₂ for 16 h. The reaction was allowed to cool to r.t., poured onto water (100 mL) and extracted with DCM (3 × 50 mL). The combined organic portions were dried (Na₂SO₄) and the solvent removed under reduced pressure. The product was purified by flash column chromatography [10 % EtOAc in pet ether 40-60] to DCM [40 % in pet ether 40-60] gradient. The solvent was removed under reduced pressure and the residue crystallised twice from hot EtOAc/hexanes to afford 2,5-bis(7-methoxy-2,2-dimethylchroman-8-yl)thieno[3,2-*b*]thiophene as yellow needles (1.75 g, 47 %). δ_H (600 MHz, CDCl₃) 1.38 [12H, s, 2 × C(CH₃)₂], 1.81 [4H, t, *J* = 6.8 Hz, 2 × CH₂C(CH₃)₂], 2.78 [4H, dt, *J* = 1, 6.8 Hz, 2 × CH₂CH₂C(CH₃)₂], 3.83 (6H, s, 2 × OCH₃), 6.53 (2H, d, *J* = 8.4 Hz, 2 × 6-*H*), 6.97 (2H, dt, *J* = 1, 8.4 Hz, 2 × 5-*H*), 7.66 (2H, s, 3-*H*, 6-*H*). δ_C (150 MHz, CDCl₃) 22.4, 27.0, 32.7, 56.0, 75.2, 103.4, 112.8, 114.0, 121.0, 128.5, 135.6, 139.0, 151.9, 156.1.

B.9. Synthesis of 2,5-bis(2-Ethyl-7-methoxy-2-methylchroman-8-yl)thieno[3,2-*b*]thiophene – Compound 15



Reaction scheme B.9

[00135] 2,5-Dibromothiopheno[3,2-*b*]thiophene (1.50 g, 5.0 mmol), (2-ethyl-7-methoxy-2-methylchroman-8-yl)boronic acid (2.77 g, 11 mmol, 2.2 equiv.), potassium carbonate (2.29 g, 16.6 mmol, 3.32 equiv.) and tetrakis(triphenylphosphine)palladium(0) (290 mg, 0.25 mmol, 5 mol%) were added to degassed PhMe (30 mL) and EtOH (30 mL), the reaction mixture was stirred at reflux under N₂ for 16 h. The reaction was allowed to cool to r.t., poured onto water (100 mL) and extracted with DCM (3 × 50 mL). The combined organic portions were dried (Na₂SO₄) and the solvent removed under reduced pressure. The product was purified by flash column chromatography on silica using (DCM/EtOAc/pet ether [40-60]) (10/7/83) eluent. The fluorescent band was collected and the solvent was removed under reduced pressure. The residue crystallised hot PhMe/hexanes to give the *title compound* (2.16 g, 49 %) as yellow needles. δ_H (600 MHz, CDCl₃) 0.97 [6H, t, *J* = 7.5 Hz, CH₂CH₃], 1.31 [6H, s, 2 × C(CH₃)₂], 1.60 – 1.90 [8H, m], 2.73 – 2.85 [4H, m], 3.84 (6H, s), 6.54 (2H, d, *J* = 8.4 Hz, 2 × 6-*H*), 6.98 (2H, dt, *J* = 1, 8.4 Hz, 2 × 5-*H*), 7.66 (2H, s, 3-*H*, 6-*H*). δ_C (150 MHz, CDCl₃) 8.3, 22.0, 23.5, 30.3, 32.6, 56.0, 77.6, 103.3, 112.8, 114.3, 121.0, 128.5, 135.5, 139.0, 151.9, 156.2.

B.10. Synthesis of 2,5-bis(7-Ethoxy-2,2-dimethylchroman-8-yl)thiophene – Compound 5*Reaction scheme B.10*

[00136] To a vigorously stirred mixture of 7-hydroxy-2,2-dimethylchroman-4-one (10 g, 40.9 mmol) and Zn (33.34 g, 513 mmol) in MeOH (100 mL) was added c. HCl (100 mL) dropwise. After the addition stirring was continued for 2 h and the mixture poured into water (400 mL) and extracted with DCM (3 × 120 mL). The combined organic phase was washed with water (200 mL), dried (Na₂SO₄) and the solvent removed under reduced pressure to give 2,2-dimethylchroman-7-ol (9.03 g, 97 %) as a colourless oil which was used without further purification in the next step.

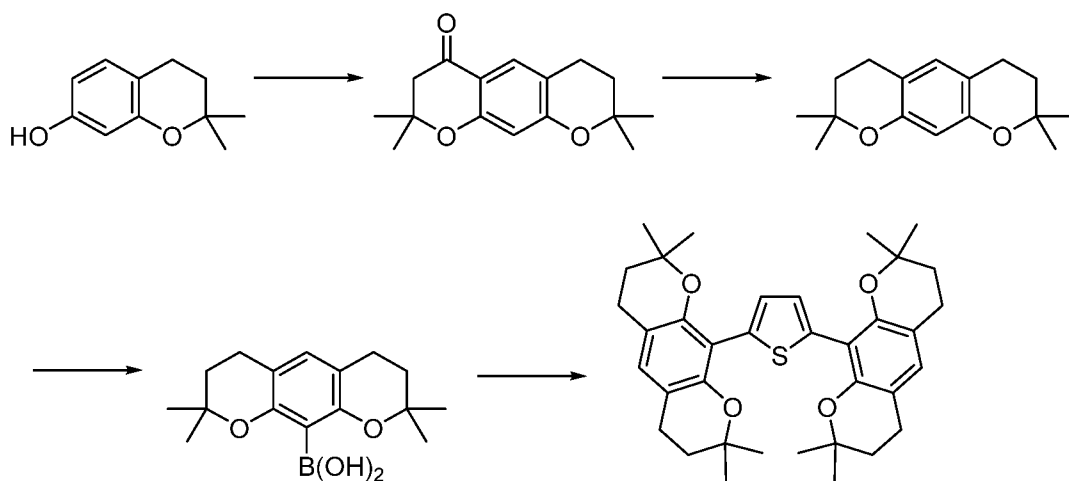
[00137] A mixture of 2,2-dimethylchroman-7-ol (5 g, 28.1 mmol), EtI (8.76 g, 56.2 mmol) and K₂CO₃ (9.69 g, 70.2 mmol) in AcMe (60 mL) was heated at reflux for 6 h, cooled, poured into water and extracted with DCM (3 × 50 mL). The combined organic phase was dried (Na₂SO₄) and the solvent removed under reduced pressure. The residue was filtered through silica using DCM (50 % in pet ether 40-60) as eluent. The solvent was removed under reduced pressure to give 7-ethoxy-2,2-dimethylchromane as a colourless oil, (4.46 g, 77 %). δ_H (600 MHz, CDCl₃) 6.83 (app. d, J = 8.3 Hz, 1 H), 6.32 (dd, J = 8.3, 2.5 Hz, 1 H), 6.24 (d, J = 2.5 Hz, 1 H), 3.87 (q, J = 7 Hz, 2 H), 2.60 (app. t, J = 6.7 Hz, 2 H), 1.68 (t, J = 6.8 Hz, 2 H), 1.28 (t, J = 6.7 Hz, 2 H), 1.23 (s, 6 H). δ_C (150 MHz, CDCl₃) 158.4, 154.6, 129.8, 112.9, 107.5, 102.3, 74.2, 63.3, 33.0, 26.8, 21.7, 14.9.

[00138] A solution of BuLi (10.5 mL, 2.5 M, 26.2 mmol) in hexanes was added dropwise to a solution of 7-ethoxy-2,2-dimethylchromane (4.50 g, 21.8 mmol) and TMEDA (4 mL, 26.8 mmol) in THF (50 mL) with stirring at -78 °C. Stirring was continued for 20 min B(OMe)₃ (4.7 mL, 42 mmol) was added in one portion with stirring. The resulting solution was warmed to rt, acidified with HCl (2 M, 50 mL) and the phases separated. The aqueous phase was extracted with Et₂O (2 × 50 mL) and the combined organic phase washed with water (100 mL), dried (Na₂SO₄). The solvent was removed under reduced pressure and the residue triturated with hexanes to give (7-ethoxy-2,2-dimethylchroman-8-yl)boronic acid as a colourless powder, (3.44 g, 63 %) which was used without further purification in the next step.

[00139] 2,5-Dibromothiophene (1.41 g, 5.8 mmol), (7-ethoxy-2,2-dimethylchroman-8-yl)boronic acid (3.00 g, 12.1 mmol, 2.5 equiv.), potassium carbonate (4.82 g, 34.9 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (336 mg, 0.15 mmol, 5 mol%) were added to degassed

PhMe (30 mL) and EtOH (30 mL), the reaction mixture was stirred at reflux under N₂ for 16 h. The reaction was allowed to cool to r.t., poured onto water (100 mL) and extracted with DCM (3 × 50 mL). The combined organic portions were dried (Na₂SO₄) and the solvent removed under reduced pressure. The product was purified by flash column chromatography [10 % EtOAc in pet ether 40-60]. The solvent was removed under reduced pressure and the residue crystallised from DCM/pet ether (40-60) to afford 2,5-bis(7-ethoxy-2,2-dimethylchroman-8-yl)thiophene (2.24 g, 79 %). δ_H (400 MHz, CDCl₃) 1.40 [12H, s, 2 × C(CH₃)₂], 1.43 [6H, t, J = 6.9 Hz, OCH₂CH₃] 1.81 [4H, t, J = 6.8 Hz, 2 × CH₂C(CH₃)₂], 2.89 [4H, dt, J = 1.0, 6.8 Hz, 2 × CH₂CH₂C(CH₃)₂], 4.06 (4H, q, J = 6.9 Hz, 2 × OCH₂), 6.53 (2H, d, J = 8.4 Hz, 2 × 6-*H*), 6.91 (2H, dt, J = 1, 8.4 Hz, 2 × 5-*H*), 7.68 (2H, s, 3-*H*, 4-*H*). δ_C (100 MHz, CDCl₃) 15.0 (2 × CH₂CH₂C(CH₃)₂), 22.5 (2 × CH₂CH₂C(CH₃)₂), 27.0 (4 × CH₃), 32.8 (2 × CH₂CH₂C(CH₃)₂), 64.8 (2 × OCH₂CH₃), 74.8 (2 × C), 105.0 (2 × CH), 113.4 (2 × C), 113.9 (2 × C), 127.6 (2 × CH), 127.9 (2 × CH), 133.9 (2 × C), 151.6 (2 × C), 155.2 (2 × C).

B.11. Synthesis of 2,5-bis(2,2,8,8-tetramethyl-3,4,7,8-tetrahydro-2*H*,6*H*-pyrano[3,2-*g*]chromen-10-yl)thiophene – Compound 4



Reaction scheme B.11

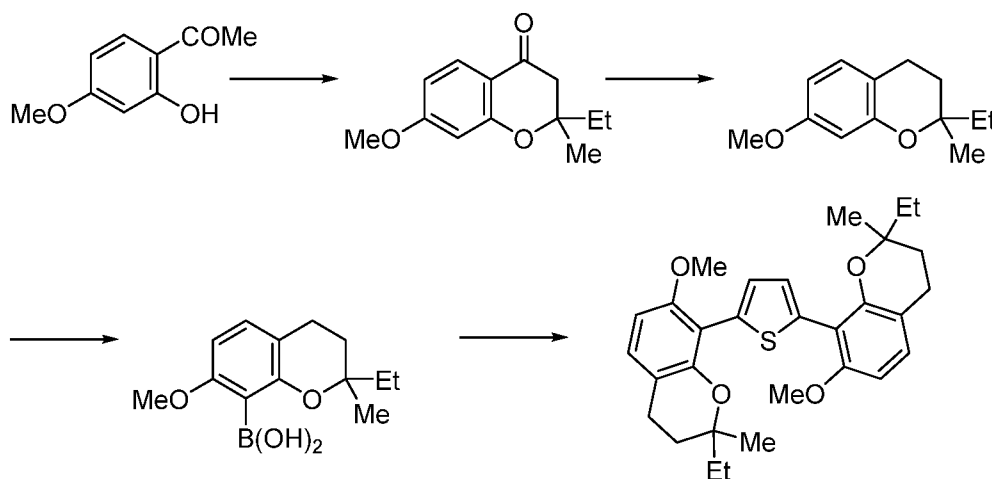
[00140] A mixture of 2,2-dimethylchroman-7-ol (10.71 g, 60.2 mmol) and 3,3-dimethylacrylic acid (6.62 g, 62 mmol) in methanesulfonic acid (50 ml) was heated at 50 °C for 2 h and poured into water (300 ml). The resulting mixture was basified with NaHCO₃ and extracted with EtOAc (3 × 100 ml). The combined organic phase was washed with aq. NaHCO₃ (100 ml), dried (Na₂SO₄) and the solvent removed under reduced pressure. The residue was filtered through silica using DCM as eluent and the solvent removed under reduced pressure to give 2,2,8,8-tetramethyl-3,4,7,8-tetrahydro-2*H*,6*H*-pyrano[3,2-*g*]chromen-6-one as a colourless powder, (12.34 g, 74 %). δ_H (400 MHz, CDCl₃) 1.34 (6H, s, 2 × CH₃), 1.42 (6 H, s, 2 × CH₃), 1.80 (2 H, t, J = 6.7 Hz, CH₂CH₂C(CH₃)), 2.63 (2 H, s, CH₂CO), 2.73 (2 H, dt, J = 1, 6.7 Hz, CH₂CH₂C(CH₃)), 6.26 (1H, s, CH), 6.60 (1H, t, J = 1 Hz, CH). δ_C (100 MHz, CDCl₃) 21.6, 26.8, 27.0, 32.7, 48.8, 75.8, 79.0, 104.8, 113.8, 114.9, 127.7, 159.9, 161.4, 191.5.

[00141] To a vigorously stirred mixture of 2,2,8,8-tetramethyl-3,4,7,8-tetrahydro-2*H*,6*H*-pyrano[3,2-*g*]chromen-6-one (12.31 g, 47.3 mmol) and Zn (38.47 g, 592 mmol) in MeOH (200 mL) was added c. HCl (120 mL) dropwise. After the addition stirring was continued for 2 h and the mixture poured

into water (500 mL) and extracted with DCM (3 × 150 mL). The combined organic phase was washed with water (200 mL), dried (Na₂SO₄) and the solvent removed under reduced pressure to give 2,2,8,8-tetramethyl-3,4,7,8-tetrahydro-2*H*,6*H*-pyrano[3,2-*g*]chromene (11.33 g, 97 %) as a colourless powder. δ_{H} (400 MHz, CDCl₃) 1.35 (12H, s, 4 × CH₃), 1.80 (4 H, t, *J* = 6.7 Hz, 2 × CH₂CH₂C(CH₃)), 2.71 (2 H, app. t, *J* = 6.7 Hz, 2 × CH₂CH₂C(CH₃)), 6.27 (1H, s, CH), 6.77 (1H, app. s, CH). δ_{C} (100 MHz, CDCl₃) 21.8, 26.9, 33.2, 73.8, 104.8, 112.6, 129.4, 153.1.

[00142] A solution of BuLi (21.5 ml, 2.5 M, 53.8 mmol) in hexanes was added dropwise to a solution of 2,2,8,8-tetramethyl-3,4,7,8-tetrahydro-2*H*,6*H*-pyrano[3,2-*g*]chromene (11.01 g, 44.8 mmol) and TMEDA (8.1 mL, 54.3 mmol) in THF (100 mL) with stirring at -78 °C. Stirring was continued for 20 min B(OMe)₃ (9.7 mL, 86.7 mmol) was added in one portion with stirring. The resulting solution was warmed to rt, acidified with HCl (2 M, 100 mL) and the phases separated. The aqueous phase was extracted with Et₂O (2 × 50 mL) and the combined organic phase washed with water (100 mL), dried (Na₂SO₄). The solvent was reduced under reduced pressure (~50 mL) and diluted with hexanes. The resultant precipitate was filtered, washed with hexanes and air dried to give (2,2,8,8-tetramethyl-3,4,7,8-tetrahydro-2*H*,6*H*-pyrano[3,2-*g*]chromen-10-yl)boronic acid as a colourless powder, (5.54 g, 43 %) which was used without further purification in the next step. δ_{H} (600 MHz, CDCl₃) 1.40 (12H, s, 4 × CH₃), 1.83 (4 H, t, *J* = 6.8 Hz, 2 × CH₂CH₂C(CH₃)), 2.73 (4 H, dt, *J* = 1.0, 6.8 Hz, 2 × CH₂CH₂C(CH₃)), 6.89 (1H, p, *J* = 1.0 Hz, CH), 7.56 (2H, s, B(OH)₂). δ_{C} (150 MHz, CDCl₃) 21.9, 26.9, 32.5, 76.0, 105.5, 113.2, 133.1, 157.9.

[00143] 2,5-Dibromothiophene (1.41 g, 5.8 mmol), (2,2,8,8-tetramethyl-3,4,7,8-tetrahydro-2*H*,6*H*-pyrano[3,2-*g*]chromen-10-yl)boronic acid (3.58 g, 12.5 mmol, 2.15 equiv.), potassium carbonate (4.82 g, 34.9 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (336 mg g, 0.15 mmol, 5 mol%) were added to degassed PhMe (30 mL) and EtOH (30 mL), the reaction mixture was stirred at reflux under N₂ for 16 h. The reaction was allowed to cool to r.t., poured onto water (100 mL) and extracted with DCM (3 × 50 mL). The combined organic portions were dried (Na₂SO₄) and the solvent removed under reduced pressure. The residue was filtered through silica using DCM/EtOAc/hex (30/5/65) and the solvent removed under reduced pressure. The residue was crystallised twice from hot DCM (40 ml) at -20 °C. The colourless plates were dried under vacuum (70 °C, 2 × 10⁻² mmHg) afford 2,5-bis(2,2,8,8-tetramethyl-3,4,7,8-tetrahydro-2*H*,6*H*-pyrano[3,2-*g*]chromen-10-yl)thiophene as a colourless powder (2.49 g, 76 %). δ_{H} (400 MHz, CDCl₃) 1.39 (24H, s, 8 × CH₃), 1.79 (8 H, t, *J* = 6.8 Hz, 4 × CH₂CH₂C(CH₃)), 2.75 (8 H, t, *J* = 6.8 Hz, 4 × CH₂CH₂C(CH₃)), 6.67 (2H, bs, 2 × CH), 7.74 (2H, bs, 2 × CH). δ_{C} (150 MHz, CDCl₃) 22.5, 27.1, 33.0, 53.4, 74.5, 112.2, 127.5, 126.6, 134.0, 149.8.

B.12. Synthesis of 2,5-bis(2-Ethyl-7-methoxy-2-methylchroman-8-yl)thiophene – Compound 9*Reaction scheme B.12*

[00144] A solution of 1-(2-hydroxy-4-methoxyphenyl)ethan-1-one (8 g, 48.2 mmol), butanone (5.20 g, 72.2 mmol) and pyrrolidine (5.13 g, 72.2 mmol) in MeOH (200 mL) was stood at rt overnight. The solvent was removed under reduced pressure and the residue chromatographed on silica using DCM 80 – 100 % gradient in pet ether 40-60) as eluent. The second band was collected and the solvent was removed under reduced pressure to give 2-ethyl-7-methoxy-2-methylchroman-4-one as pale brown viscous oil, (3.37 g, 34 %) which was used in the next step without further purification.

[00145] A mixture of 2-ethyl-7-methoxy-2-methylchroman-4-one (9.83 g, 44.7 mmol) and Zn (36.30 g, 558 mmol) in MeOH (100 mL) was added c. HCl (100 mL) dropwise. After the addition stirring was continued for 2 h and the mixture poured into water (300 mL) and extracted with DCM (3 × 80 mL). The combined organic phase was washed with water (100 mL), dried (Na₂SO₄) and the solvent removed under reduced pressure to give 2-ethyl-7-methoxy-2-methylchromane (8.64 g, 94 %) as a colourless oil which was used without further purification in the next step. δ_{H} (600 MHz, CDCl₃) = 6.84 (dt, J = 0.9, 8.3 Hz, 1 H), 6.33 (dd, J = 8.3, 2.6 Hz, 1 H), 6.27 (d, J = 2.6 Hz, 1 H), 3.66 (s, 3 H), 2.60 (dt, J = 0.9, 6.5 Hz, 2 H), 1.76 – 1.47 (m, 4 H), 1.17 (app. s, 3 H), 0.87 (app. t, J = 7.5 Hz, 3 H). δ_{C} (150 MHz, CDCl₃) 159.1, 154.8, 129.8, 113.3, 106.8, 101.8, 76.6, 55.2, 32.2, 30.6, 23.6, 21.4, 8.0.

[00146] A solution of BuLi (20.1 mL, 2.5 M, 52.5 mmol) in hexanes was added dropwise to a solution of 2-ethyl-7-methoxy-2-methylchromane (8.64 g, 41.9 mmol) and TMEDA (8.1 mL, 50.9 mmol) in THF (100 mL) with stirring at -78 °C. Stirring was continued for 20 min and B(OMe)₃ (9.1 mL, 81.3 mmol) was added in one portion with stirring. The resulting solution was warmed to rt, acidified with HCl (2 M, 100 mL) and the phases separated. The aqueous phase was extracted with Et₂O (2 × 50 mL) and the combined organic phase washed with water (100 mL), dried (Na₂SO₄) and the solvent was reduced under reduced pressure. The residue was chromatographed on silica using EtOAc (70 % in pet ether 40-60) as eluent. The second band was collected and the solvent removed under reduced pressure to give (2-ethyl-7-methoxy-2-methylchroman-8-yl)boronic acid as a pale yellow oil, (7.30 g, 70 %). δ_{H} (400 MHz, CDCl₃) 0.98 (3H, t, J = 7.5 Hz, CH₂CH₃), 1.33 (3 H, s, CH₂C(CH₃)Et), 1.60 – 1.93 (4 H, m), 2.74 (2H, app. t, J = 6.7 Hz, CH₂CH₂C(Me)Et), 3.87 (3H, s, OMe), 6.51 (1H, d,

$J = 8.5$ Hz, CH), 7.11 (1H, app. d, $J = 8.5$ Hz, CH), 7.39 (2H, s, $B(OH)_2$). δ_c (150 MHz, $CDCl_3$). 8.0, 21.6, 23.8, 30.0, 32.2, 55.9, 78.9, 103.3, 114.7, 133.0, 159.5, 163.9, (C8 not observed under applied NMR acquisition parameters)

- 5 [00147] 2,5-Dibromothiophene (1.41 g, 5.8 mmol), (2-ethyl-7-methoxy-2-methylchroman-8-yl)boronic acid (3.00 g, 12.1 mmol, 2.08 equiv.), potassium carbonate (4.82 g, 34.9 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium(0) (336 mg, 0.15 mmol, 5 mol%) were added to degassed PhMe (30 mL) and EtOH (30 mL), the reaction mixture was stirred at reflux under N_2 for 16 h. The reaction was allowed to cool to r.t., poured onto water (100 mL) and extracted with DCM (3 $\times$ 50 mL). The combined organic portions were dried (Na_2SO_4) and the solvent removed under reduced pressure. The residue was chromatographed on silica using EtOAc (12 % in pet ether 40-60) as eluent. The solvent was removed under reduced pressure and the residue chromatographed on silica using EtOAc (8 – 15 % in pet ether 40-60) as eluent to give 2,5-bis(2-ethyl-7-methoxy-2-methylchroman-8-yl)thiophene as a viscous yellow oil (1.82 g, 64 %). δ_H (400 MHz, $CDCl_3$) 0.92 – 0.99 (6H, m, 2 $\times$ CH_2CH_3), 1.29 (6H, s, CH_3), 1.59 – 1.90 (8 H, m), 2.70 – 2.85 (4 H, m), 6.52 (2H, $J = 8.4$ Hz, 2 $\times$ CH), 6.93 (2H, bd, $J = 8.4$ Hz, 2 $\times$ CH), 7.55 (2H, bs). δ_c (100 MHz, $CDCl_3$) 8.2, 22.1, 23.4, 23.5, 30.4, 32.5, 32.6, 56.077.3, 103.4, 113.0, 114.2, 127.7, 127.8, 133.9, 151.7, 156.0. (1 Mixture of diastereomers, all carbon resonances are listed)
- 10
- 15

Example 2: characterization and activity of exemplary compounds of formula (I)

- 20 [00148] The oxidation-reduction potentials of exemplary compounds of formula (I) were measured and compared to a compound of the prior art.

Procedure for the measurement of the oxidation-reduction potential: cyclic voltammetry method with 3 electrodes:

- [00149] The oxido-reduction potentials of the compounds are measured by cyclic voltammetry with 3 electrodes:
- 25

[00150] - 1 platinum working electrode

- 1 platinum counter electrode
- 1 platinum reference electrode immersed in a solution composed of 0.01M $AgNO_3$ + 0.1 TBAP (tetrabutylammonium perchlorate) in acetonitrile.

- 30 [00151] All redox potentials are given for scan rate of the potential fixed to 100mV/s.

[00152] $E_{1^{ox}}$ refers to the first oxidation peak of the analyzed molecule.

[00153] $E_{2^{ox}}$ refers to the second oxidation peak of the analyzed molecule.

[00154] $E_1^{1/2}$ corresponds to the oxido-reduction potential of an oxidant/reductor system as calculated below:

- 35 $E_1^{1/2} = (E_{1^{red}} + E_{1^{ox}})/2$; wherein $E_{1^{red}}$ corresponds to the first reduction peak of the analyzed compound.

ΔE^{ox} corresponds to the difference between E_1^{ox} and E_2^{ox} as calculated below:

$$\Delta E^{\text{ox}} = |E_2^{\text{ox}}| - |E_1^{\text{ox}}|.$$

[00155] The values of the indicated potentials correspond to the first oxidation/reduction potentials of the molecules compared to a standard reference electrode of hydrogen SHE.

- 5 The solution used for the analysis was prepared with 0.005 M of the electrochromic dye to be analyzed, 0.250 M of TBABF₄ salt in propylene carbonate as solvent.

Measurement of the absorption spectrum of the dyes by spectroelectrochemistry:

Principle of the measurement:

- 10 [00156] In a quartz cell, the dye of formula (I) is activated on a platinum grid using a scan of the potential close to the $E^{1/2}$ potential. The absorption spectrum is recorded in a continuous manner.

[00157] The solution of the dye to be analyzed is composed of :

0.005 M of the dye of formula (I) to be analyzed

0.250 M of TBA BF₄- in propylene carbonate as solvent

15

Method of measurement:

- [00158] The solution with the dye of formula (I) is introduced into a quartz cell where at least one working electrode in the form of a platinum grid is placed to color the analyzed compound of formula (I) on this electrode. The absorption spectrum of the analyzed compound as a function of time is
20 measured by uv-visible spectroscopy.

[00159] The counter electrode is a platinum wire and the reference electrode is a platinum wire immersed in a solution containing 0.01M AgNO₃ and 0.1 M TBAP in acetonitrile.

[00160] The activation potential falls within the scan of the potential as follows $E_{1/2} + 0.2V$ to $E_{1/2} - 0.1V$.

- 25 [00161] The results for each of the synthesized compounds are indicated in **Table 1** below. E_1^{ox} corresponds to the first oxidation potential. The color indicated in Table 1 is the visual colour perceived by emmetropic eyes under day light conditions.

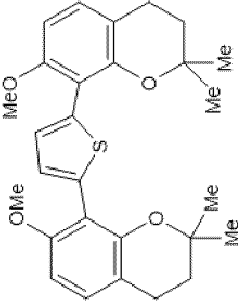
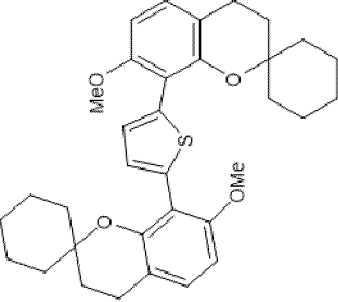
[00162] For comparison purposes, **Table 1** also includes the results obtained for a known compound, COMP.1 (a red methyl phenothiazine).

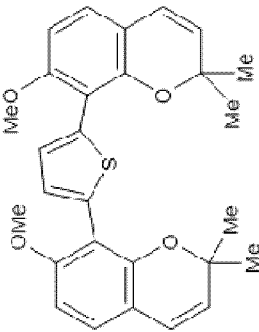
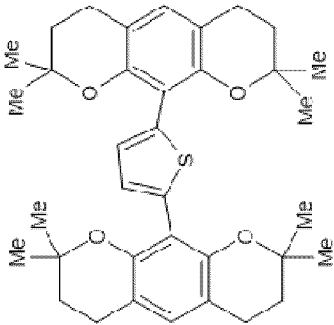
- 30 [00163] By comparing the known compound (comparative reducing electrochromic compound 1) COMP. 1 (red) to the exemplary compound of formula (I), Compound 11 (orange), we see that Compound 11 features a narrower absorption band than COMP. 1 and, in addition, the FWHM (full width at mid height) of compound 11 is about twice smaller than that of COMP. 1 as seen in **Table 2**. As previously indicated, narrow absorption bands are particularly interesting since it allows

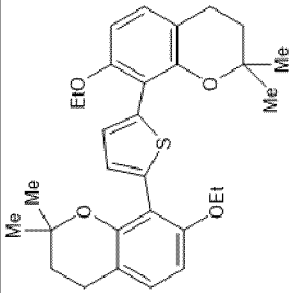
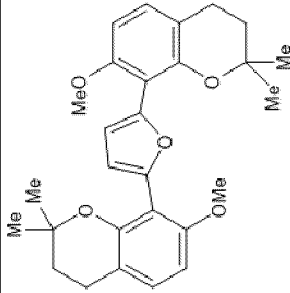
manufacturing optical devices which provide better eye protection, visual aid and contrast enhancement.

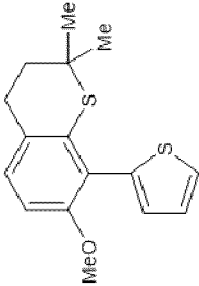
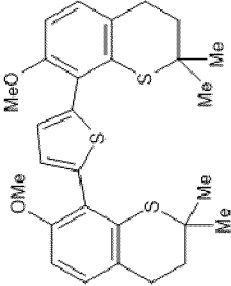
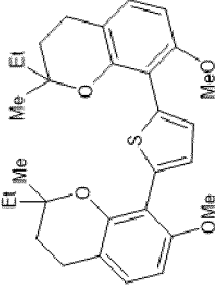
[00164] In addition, the molar absorptivity of the compounds of formula (I) is as seen in **Table 2** below, in many cases significantly higher when compared to that of other compounds of the prior art, such as for example COMP. 1. For example, the molar absorptivity of compound 11 is of ϵ_{503} of 32500 L/mol/cm, whereas COMP. 1 features a molar absorptivity ϵ_{520} of only 6130 L/mol/cm. Accordingly, the use of compounds of formula (I) herein disclosed having a high absorptivity is particularly interesting since it allows reducing the concentration of those dyes in the formulations and devices comprising those, while providing the desired tint with the desired intensity when activated.

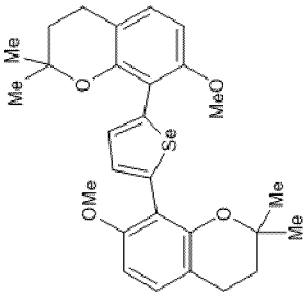
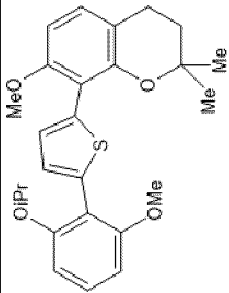
Table 1

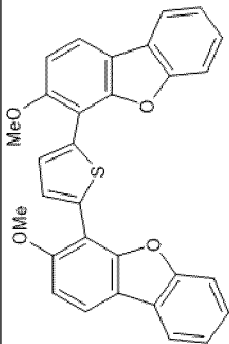
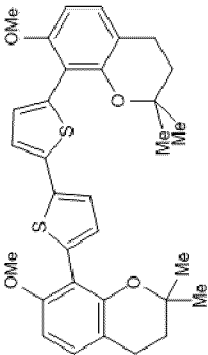
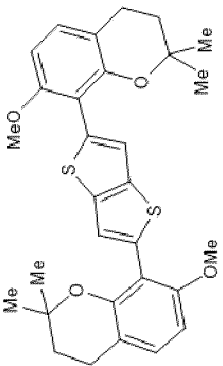
Compound	Structure	$E_{1/2}$ (V)	E_1 ^{1/2} (V) vs SHE	Color	$E_{1^{ox}}$ peak potential (V)	E1 peak potential vs SHE	$E_{2^{ox}}$ peak potential (V)	E2 peak potential vs SHE	ΔE^{ox}
1		0.52	1.062	Brown	0.57	1.112	0.93	1.472	0.36
2		0.53	1.072	Brown	0.55	1.092	0.98	1.522	0.43

Compound	Structure	$E_{1}^{1/2}$ (V) vs SHE	Color	E_1^{ox} peak potential (V)	E1 peak potential (V) vs SHE	E_2^{ox} peak potential (V)	E2 peak potential (V) vs SHE	ΔE^{ox}
3		n.a.	Grey	0.69	1.232	0.99	1.532	0.3
4		0.42	Orange	0.47	1.012	0.84	1.382	0.37

Compound	Structure	$E_{1/2}^{1/2}$ (V)	$E_1^{1/2}$ vs SHE	Color	$E_{1^{ox}}$ peak potential (V)	E1 peak potential (V) vs SHE	$E_{2^{ox}}$ peak potential (V)	E2 peak potential (V) vs SHE	ΔE^{ox}
5		0.51	1.05	Red	0.53	1.072	0.85	1.392	0.32
6		0.46	1	Orange	0.5	1.042	0.8	1.342	0.3

Compound	Structure	$E_{1/2}$ (V)	$E_1^{1/2}$ (V) vs SHE	Color	E_1^{ox} peak potential (V)	E1 peak potential (V) vs SHE	E_2^{ox} peak potential (V)	E2 peak potential (V) vs SHE	ΔE^{ox}
7		n.a	n.a	Pale pink	0.96	1.502	n.a.	n.a	n.a
8		n.a.	n.a	Green	0.83	1.372	1.02	1.562	0.19
9		n.a	n.a	Red	0.57	1.112	0.89	1.432	0.32

Compound	Structure	$E_{-1/2}$ (V)	$E_{-1}^{1/2}$ (V) vs SHE	Color	$E_{1^{ox}}$ peak potential (V)	$E_{1^{ox}}$ peak potential (V) vs SHE	$E_{2^{ox}}$ peak potential (V) vs SHE	ΔE_{ox}
10		0.46	1	Purple	0.5	1.042	1.392	0.35
11		0.55	1.092	Orange	0.57	1.112	1.462	0.35

Compound	Structure	$E_{1/2}$ (V)	$E_{1/2}$ (V) vs SHE	Color	$E_{1^{ox}}$ peak potential (V)	E1 peak potential (V) vs SHE	$E_{2^{ox}}$ peak potential (V)	E2 peak potential (V) vs SHE	ΔE^{ox}
12		n.a.	n.a.	Brown	0.63	1.172	n.a.	n.a.	n.a.
13		0.38	0.92	Purple	0.4	0.942	0.75	1.292	0.35
14		0.45	0.99	Red	0.48	1.022	0.76	1.302	0.28

Compound	Structure	$E_{1/2}$ (V)	E_1 $^{1/2}$ (V) vs SHE	Color	$E_{1^{ox}}$ peak potential (V)	$E_{2^{ox}}$ peak potential (V)	ΔE^{ox}
15		0.47	1.01	Red	0.5	1.322	0.28
16		n.a	n.a	Blue	0.7	n.a	n.a

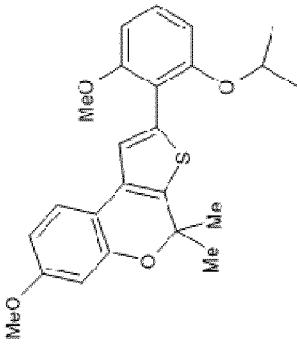
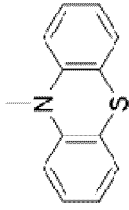
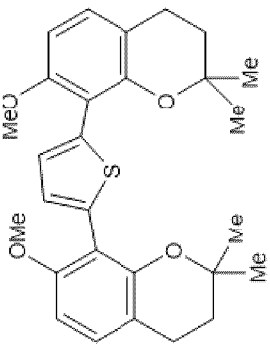
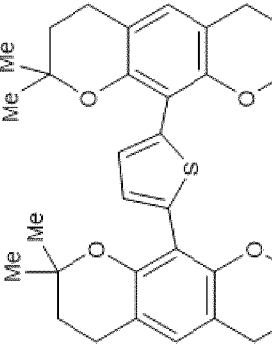
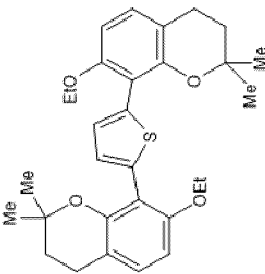
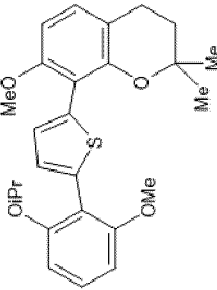
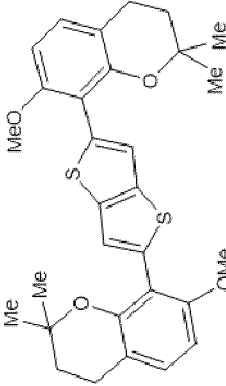
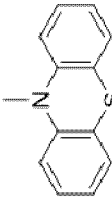
Compound	Structure	$E_{1/2}$ (V)	$E_{1/2}$ (V) vs SHE	Color	$E_{1^{ox}}$ peak potential (V)	E1 peak potential (V) vs SHE	$E_{2^{ox}}$ peak potential (V)	E2 peak potential (V) vs SHE	ΔE^{ox}
17		n.a.	n.a.	Purple	0.65	1.192	0.8	1.342	0.15
COMP. 1		0.4	0.942	Rad	0.45	0.992	1.01	1.552	0.56

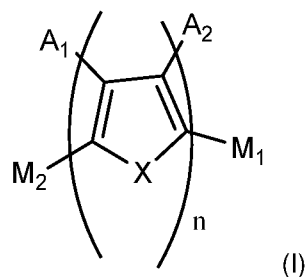
Table 2

Compound	Structure	ϵ_{max} (L/mol/cm)	FWMH (nm)
1		32000	20-30
4		38000	20-50

Compound	Structure	ϵ_{max} (L/mol/cm)	FWMH (nm)
5		44000	30-60
11		32500	20-50
14		52000	20-50
COMP. 1		6130	80-100

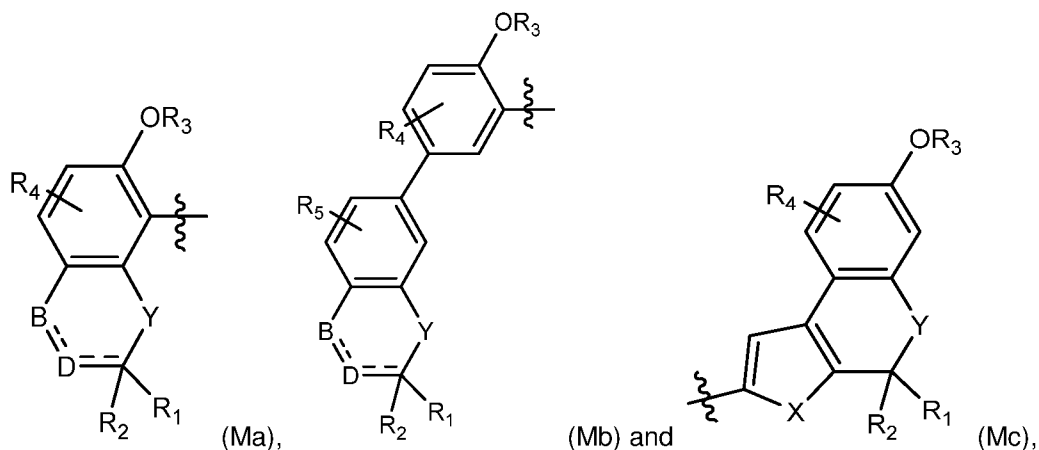
[00165] In addition, the present disclosure also refers to the present embodiments:

[00166] Embodiment 1: An electrochromic compound represented by formula (I):



wherein

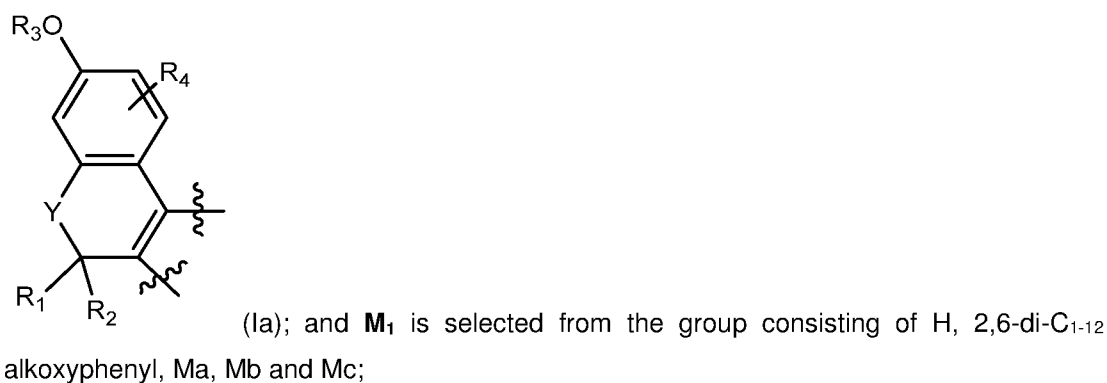
- 5 (i) **A₁** and **A₂** are both H; **n** is 1, 2 or 3; and **M₁** and **M₂** are each independently selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc:



and wherein **at least one** of **M₁** and **M₂** is selected from the group consisting of Ma, Mb and Mc;

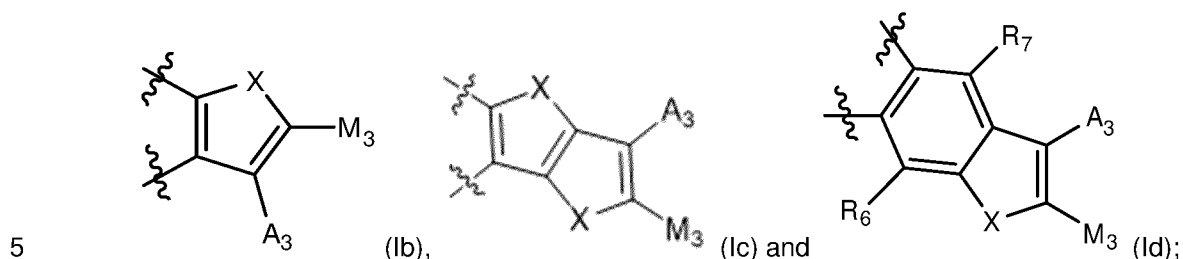
10 or

- (ii) **n** is 1; **A₂** is H; **A₁** and **M₂** form together a heterocyclic group fused to the central 5-membered heterocyclic ring they are attached to; wherein said heterocyclic group formed is a group Ia:



15 or

- (iii) **n** is 1; **A₁** is H; **M₂** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc; and **A₂** and **M₁** form together a heterocyclic group fused to the central 5-membered heteroaromatic ring they are attached to; wherein said heterocyclic group is selected from the group consisting of Ib, Ic and Id:



and wherein **A₃** is H and **M₃** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc, wherein **at least one** of **M₂** and **M₃** is selected from the group consisting of Ma, Mb and Mc;

and wherein

- 10 **-----** is a single bond or a double bond;

each **X** is independently selected from the group consisting of S, Se and O;

each **Y** is independently selected from the group consisting of O, S, -NR₈, N-C(O)R₈ and N-S(O)₂R₈;

B is present or not, and, if present is CH or CH₂;

D is C-R₁₀, CH or (CH₂)_m, wherein m is 1, 2 or 3;

- 15 **R₁** is present or not;

when **R₁** is present, each **R₁** is independently selected from the group consisting of H, C₃₋₁₂ cycloalkyl, linear C₁₋₁₂ alkyl and branched C₃₋₁₂ alkyl; and each **R₂** is independently selected from the group consisting of H, C₃₋₁₂ cycloalkyl, linear C₁₋₁₂ alkyl and branched C₃₋₁₂ alkyl; or **R₁** and **R₂** form together with the carbon atom to which they are attached, a C₄₋₁₂ spiro-cycloalkyl group;

20

when **R₁** is not present, **D** is C-R₁₀, wherein **R₂** and **R₁₀** form together with the carbon atom to which they are attached a C₆₋₁₀ aryl group fused to the ring to which **R₁₀** and **R₂** are attached to;

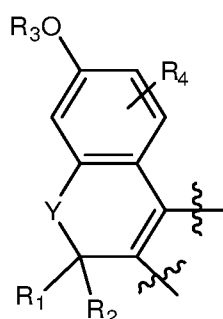
- each **R₃** is independently selected from the group consisting of linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl, C₃₋₁₂ cycloalkyl, C₁₋₁₂ haloalkyl, -C(O)NR₈R₉, and a 6-membered heteroaromatic ring including at least 1 oxygen atom; and each **R₄** is independently selected from the group consisting of H, C₁₋₁₂ alkoxy, C₁₋₁₂ alkyl and -NR₈R₉; or when **R₄** and **OR₃** are substituents of two adjacent carbon atoms of the benzene ring they are attached to, said **R₄** and **OR₃** form together with the carbon atom to which they are attached, a 5 to 7-membered oxygen-containing ring fused to the benzene ring to which **R₄** and **OR₃** are attached; wherein said 5 to 7-membered oxygen-containing ring is optionally substituted with one or more C₁₋₆ alkyl groups;
- 25
- 30

each **R**₅ is independently selected from the group consisting of H, C₁₋₁₂ alkoxy, C₁₋₁₂ alkyl and -NR₈R₉

R₆ and **R**₇ are each independently selected from the group consisting of H, linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl, C₆₋₁₀ aryl, C₁₋₁₂ alkoxy; and

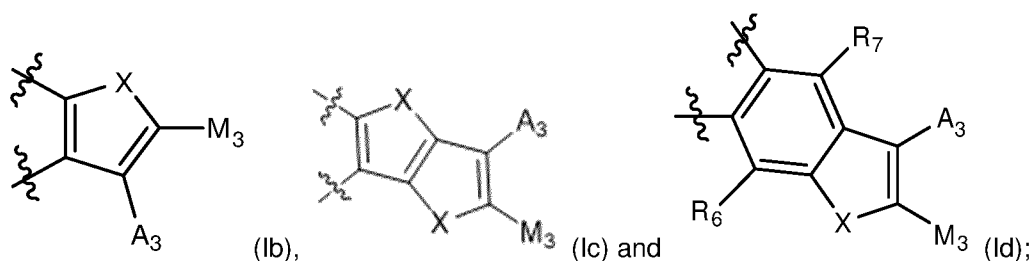
- 5 **R**₈ and **R**₉ are each independently selected from the group consisting of H, linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl and C₆₋₁₀ aryl.

[00167] Embodiment 2: The electrochromic compound according to the embodiment 1, wherein **n** is 1; **A**₂ is H; **A**₁ and **M**₂ form together a heterocyclic group fused to the central 5-membered heterocyclic ring they are attached to; wherein said heterocyclic group formed is a group Ia:



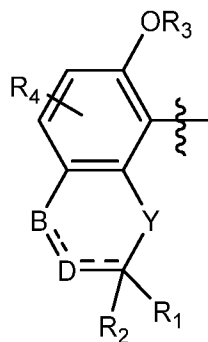
- 10 (Ia); and **M**₁ is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc; and wherein **R**₁, **R**₂, **R**₃, **R**₄, **Y**, Ma, Mb and Mc are each independently as defined in the embodiment 1.

- [00168] Embodiment 3: The electrochromic compound according to the embodiment 1, wherein **n** is 1; **A**₁ is H; **M**₂ is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc; and **A**₂ and **M**₁ form together a heterocyclic group fused to the central 5-membered heteroaromatic ring they are attached to; wherein said heterocyclic group is selected from the group consisting of Ib, Ic and Id:



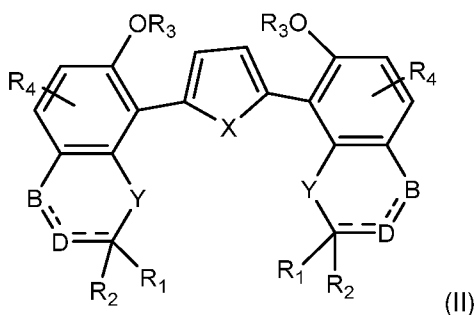
- and wherein **A**₃ is H and **M**₃ is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc, wherein **at least one** of **M**₂ and **M**₃ is selected from the group consisting of Ma, Mb and Mc; and wherein **R**₆, **R**₇, **X**, Ma, Mb and Mc are each independently as defined in the embodiment 1.

[00169] Embodiment 4: The electrochromic compound according to the embodiment 1, wherein **A**₁ and **A**₂ are both H; **n** is 1, 2 or 3; and at least one of **M**₁ and **M**₂ is Ma:



(Ma), wherein **R₁**, **R₂**, **R₃**, **R₄**, **-----**, **X**, **Y**, **B** and **D** are each independently as described in embodiment 1.

[00170] Embodiment 5: The electrochromic compound according to the embodiment 4, wherein both **M₁** and **M₂** are Ma and the electrochromic compound disclosed is represented by Formula (II):



wherein **R₁**, **R₂**, **R₃**, **R₄**, **-----**, **Y**, **B** and **D** are each independently according to the embodiment 1.

[00171] Embodiment 6: The electrochromic compound according to any of the embodiments 1 to 4, wherein one of **M₁** and **M₂** is H or 2,6-di-C₁₋₁₂ alkoxyphenyl.

[00172] Embodiment 7: The electrochromic compound according to the embodiment 6, wherein one of **M₁** and **M₂** is H or 2,6-di-C₁₋₆ alkoxyphenyl.

[00173] Embodiment 8: The electrochromic compound according to the embodiment 1, wherein **A₁** and **A₂** are both H; **n** is 1, 2 or 3; and at least one of **M₁** and **M₂** is Mb.

[00174] Embodiment 9: The electrochromic compound according to the embodiment 1, wherein **A₁** and **A₂** are both H; **n** is 1, 2 or 3; and at least one of **M₁** and **M₂** is Mc.

[00175] Embodiment 10: The electrochromic compound according to any of the embodiments 4 to 9, wherein **n** is 1 or 2.

[00176] Embodiment 11: The electrochromic compound according to any of the embodiments 1 to 10, wherein **R₁** and **R₂** are each independently selected from the group consisting of H, linear C₁₋₁₂ alkyl and branched C₃₋₁₂ alkyl.

[00177] Embodiment 12: The electrochromic compound according to any of the embodiments 1 to 11, wherein **R₁** and **R₂** are each independently a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl.

- [00178] Embodiment 13: The electrochromic compound according to any of the embodiments 1 to 12, wherein **R**₁ and **R**₂ are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl.
- 5 [00179] Embodiment 14: The electrochromic compound according to any of the embodiments 1 to 10, wherein **R**₁ and **R**₂ form together with the carbon atom to which they are attached a C₄-C₈ cycloalkyl.
- [00180] Embodiment 15: The electrochromic compound according to the embodiment 14, wherein **R**₁ and **R**₂ form together with the carbon atom to which they are attached a C₅-C₆ cycloalkyl.
- 10 [00181] Embodiment 16: The electrochromic compound according to any of the embodiments 14 or 15, wherein **R**₁ and **R**₂ form together with the carbon atom to which they are attached a C₆ cycloalkyl.
- [00182] Embodiment 17: The electrochromic compound according to any of the embodiments 1 to 10, wherein **B** and **R**₁ are not present and **D** is C-**R**₁₀, wherein **R**₂ and **R**₁₀ form together with the carbon atom to which they are attached a C₆₋₁₀ aryl group, preferably a benzene ring, fused to the ring to which **R**₁₀ and **R**₂ are attached to.
- 15 [00183] Embodiment 18: The electrochromic compound according to any of the embodiments 1 to 17, wherein **R**₃ is a linear C₁₋₆ alkyl, a branched C₃₋₆ alkyl or C₁₋₆ (per)fluoroalkyl.
- [00184] Embodiment 19: The electrochromic compound according to any of the embodiments 1 to 18, wherein **R**₃ is selected from the group consisting of methyl, ethyl, propyl and isopropyl.
- [00185] Embodiment 20: The electrochromic compound according to any of the embodiments 1 to 20 [00185] Embodiment 20: The electrochromic compound according to any of the embodiments 1 to 19, wherein **R**₄ is H.
- [00186] Embodiment 21: The electrochromic compound according to any of the embodiments 1 to 20, wherein **R**₅ is H.
- [00187] Embodiment 22: The electrochromic compound according to any of the embodiments 1 to 17, wherein when **R**₄ and **OR**₃ are substituents of two adjacent carbon atoms of the benzene ring 25 they are attached to, said **R**₄ and **OR**₃ form together with the carbon atom to which they are attached, a 5 to 7-membered oxygen-containing ring, preferably a dihydropyran, fused to the benzene ring to which **R**₄ and **OR**₃ are attached; wherein said 5 to 7-membered oxygen-containing ring is optionally substituted with one or more C₁₋₆ alkyl groups.
- [00188] Embodiment 23: The electrochromic compound according to any of the embodiments 1 or 30 3, wherein one or both of **R**₆ and **R**₇ are H.
- [00189] Embodiment 24: The electrochromic compound according to any of the embodiments 1 to 10, wherein **R**₁, **R**₂ and **R**₃ are each independently a linear C₁₋₆ alkyl or a branched C₃₋₆ alkyl group and **R**₄, **R**₅, **R**₆ and **R**₇ are all H.
- [00190] Embodiment 25: The electrochromic compound according to any of the embodiments 1 to 35 10, wherein **R**₁, **R**₂ and **R**₃ are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl and **R**₄, **R**₅, **R**₆ and **R**₇ are all H.

[00191] Embodiment 26: The electrochromic compound according to any of the embodiments 1 to 25, wherein one or more **X** is S.

[00192] Embodiment 27: The electrochromic compound according to any of the embodiments 1 to 25, wherein one or more **X** is Se.

5 [00193] Embodiment 28: The electrochromic compound according to any of the embodiments 1 to 25, wherein one or more **X** is O.

[00194] Embodiment 29: The electrochromic compound according to any of the embodiments 1 to 28, wherein one or more **Y** is O.

10 [00195] Embodiment 30: The electrochromic compound according to any of the embodiments 1 to 28, wherein one or more **Y** is S.

[00196] Embodiment 31: An electrochromic composition comprising at least one electrochromic compound as defined in any one of the embodiments 1 to 30, and a host medium.

15 [00197] Embodiment 32: The electrochromic composition according to the embodiment 31, wherein the host medium is selected from the group consisting of organic solvents, liquid crystals, polymers, liquid crystal polymers and mixtures thereof.

[00198] Embodiment 33: An electrochromic device comprising at least one electrochromic compound as defined in any one of the embodiments 1 to 30, or an electrochromic composition according to any of the embodiments 31 or 32.

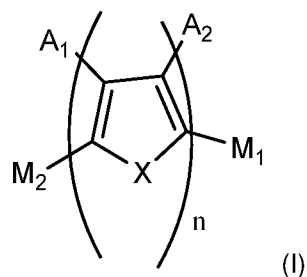
20 [00199] Embodiment 34: The electrochromic device according to the embodiment 33 selected from the group consisting of an optical article, preferably an optical lens or an optical filter, even more preferably an ophthalmic lens, a window, preferably an aircraft window, a visor, a mirror, a variable transmission device and a display element or device.

25 [00200] Embodiment 35: The electrochromic device according to any of the embodiments 33 or 34, wherein the electrochromic device is an ophthalmic lens selected from the group consisting of corrective lenses, non-corrective lenses, contact lenses, intra-ocular lenses, sunglasses, ski goggles, sport lenses, augmented reality and virtual reality lenses, magnifying lenses, protective lenses and visors.

30 [00201] The electrochromic device according to the embodiment 35, wherein the ophthalmic lenses are corrective lenses selected from the group consisting of single vision lenses and multi-vision lenses.

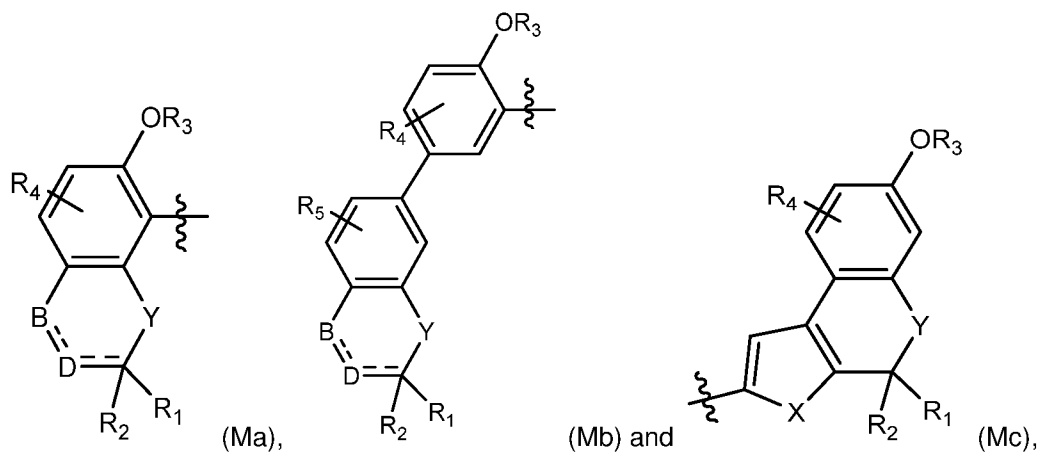
Claims

[Claim 1] An electrochromic compound represented by formula (I):



wherein

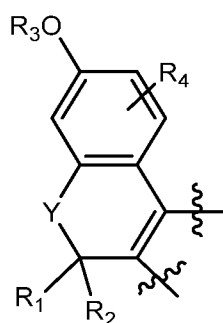
- 5 (i) **A₁** and **A₂** are both H; **n** is 1, 2 or 3; and **M₁** and **M₂** are each independently selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc:



and wherein **at least one** of **M₁** and **M₂** is selected from the group consisting of Ma, Mb and Mc;

10 or

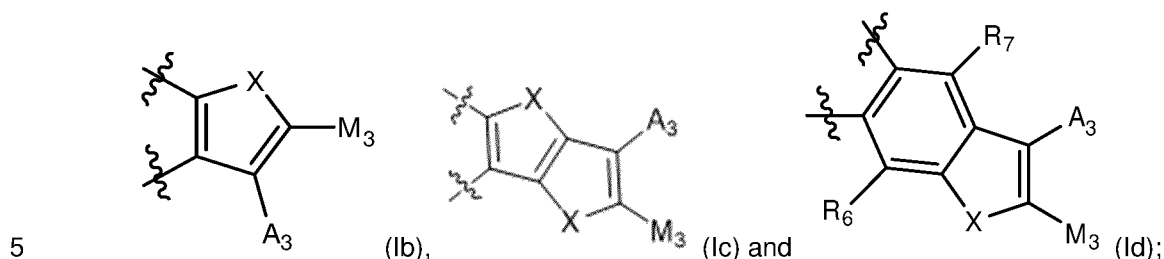
- (ii) **n** is 1; **A₂** is H; **A₁** and **M₂** form together a heterocyclic group fused to the central 5-membered heterocyclic ring they are attached to; wherein said heterocyclic group formed is a group Ia:



(Ia); and **M₁** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc;

15 or

- (iii) **n** is 1; **A₁** is H; **M₂** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc; and **A₂** and **M₁** form together a heterocyclic group fused to the central 5-membered heteroaromatic ring they are attached to; wherein said heterocyclic group is selected from the group consisting of Ib, Ic and Id:



and wherein **A₃** is H and **M₃** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc, wherein **at least one** of **M₂** and **M₃** is selected from the group consisting of Ma, Mb and Mc;

and wherein

- 10 **-----** is a single bond or a double bond;

each **X** is an atom independently selected from the group consisting of S, Se and O;

each **Y** is an atom independently selected from the group consisting of O, S, -NR₈, N-C(O)R₈ and N-S(O)₂R₈;

B is present or not, and, if present is CH or CH₂;

- 15 **D** is CR₁₀, CH or (CH₂)_m, wherein m is 1, 2 or 3;

R₁ is present or not; when **R₁** is present, each **R₁** is independently selected from the group consisting of H, C₃₋₁₂ cycloalkyl, linear C₁₋₁₂ alkyl and branched C₃₋₁₂ alkyl; and each **R₂** is independently selected from the group consisting of H, C₃₋₁₂ cycloalkyl, linear C₁₋₁₂ alkyl and branched C₃₋₁₂ alkyl; or **R₁** and **R₂** form together with the carbon atom to which they are attached, a C₄₋₁₂ spiro-cycloalkyl group; and when **R₁** is not present, **D** is CR₁₀, wherein **R₂** and **R₁₀** form together with the carbon atom to which they are attached a C₆₋₁₀ aryl group fused to the ring to which **R₁₀** and **R₂** are attached to;

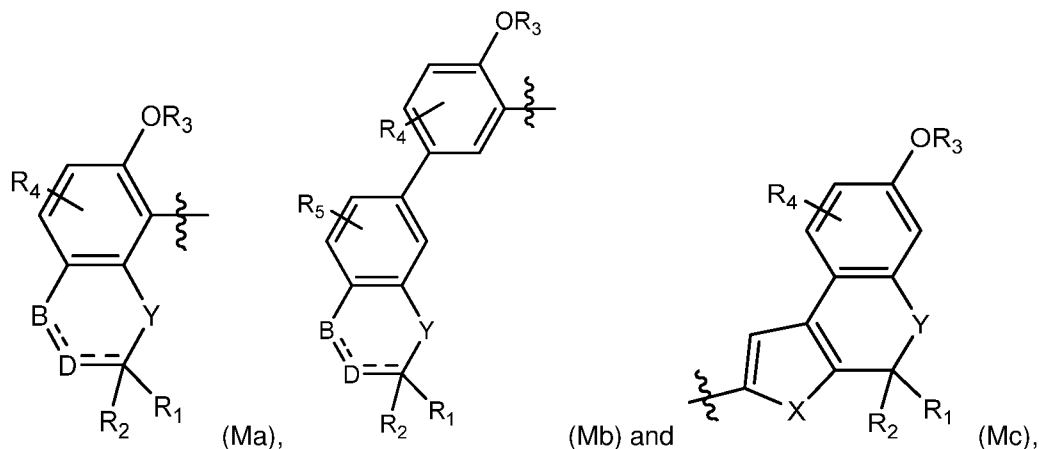
- 20 each **R₃** is independently selected from the group consisting of linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl, C₁₋₁₂ haloalkyl, C₃₋₁₂ cycloalkyl, -C(O)NR₈R₉, and a 6-membered heteroaromatic ring including at least 1 oxygen atom; and each **R₄** is independently selected from the group consisting of H, C₁₋₁₂ alkoxy, C₁₋₁₂ alkyl and -NR₈R₉; or when **R₄** and **OR₃** are substituents of two adjacent carbon atoms of the benzene ring they are attached to, said **R₄** and **OR₃** form together with the carbon atom to which they are attached, a 5 to 7-membered oxygen-containing ring fused to the benzene ring to which **R₄** and **OR₃** are attached; wherein said 5 to 7-membered oxygen-containing ring is optionally substituted with one or more C₁₋₆ alkyl groups;

- 25 each **R₅** is selected from the group consisting of H, C₁₋₁₂ alkoxy, C₁₋₁₂ alkyl and -NR₈R₉;

R₆ and **R₇** are each independently selected from the group consisting of H, linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl, C₆₋₁₀ aryl, C₁₋₁₂ alkoxy; and

R₈ and **R₉** are each independently selected from the group consisting of H, linear C₁₋₁₂ alkyl, branched C₃₋₁₂ alkyl and C₆₋₁₀ aryl.

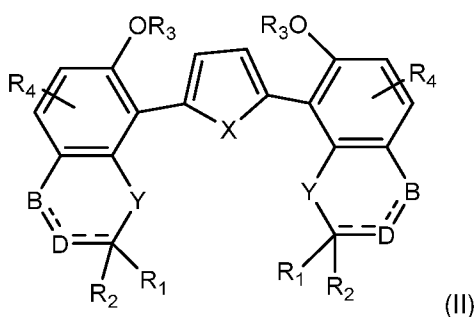
- 5 **[Claim 2]** The electrochromic compound according to claim 1, wherein **A₁** and **A₂** are both H; **n** is 1, 2 or 3; and **M₁** and **M₂** are each independently selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc:



- wherein **at least one** of **M₁** and **M₂** is selected from the group consisting of Ma, Mb and Mc; and
 10 wherein **R₁**, **R₂**, **R₃**, **R₄**, **-----**, **Y**, **B** and **D** are each independently defined according to claim 1.

[Claim 3] The electrochromic compound according to claim 2, wherein **A₁** and **A₂** are both H and **n** is 1.

[Claim 4] The electrochromic compound according to any of claims 1 to 3, wherein said compound is represented by Formula (II):

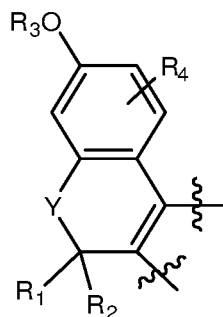


15

and wherein **R₁**, **R₂**, **R₃**, **R₄**, **-----**, **Y**, **B** and **D** are each independently defined according to claim 1.

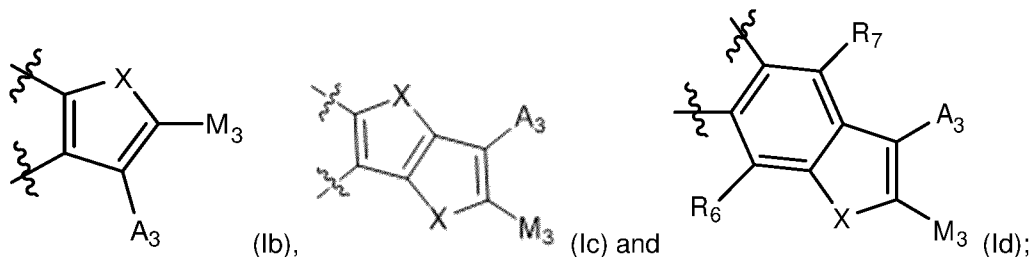
[Claim 5] The electrochromic compound according to claim 1, wherein one of **M₁** or **M₂** is a group 2,6-di-C₁₋₁₂ alkoxyphenyl.

- 20 **[Claim 6]** The electrochromic compound according to claim 1, wherein **n** is 1; **A₂** is H; and **A₁** and **M₂** form together a heterocyclic group fused to the central 5-membered heterocyclic ring they are attached to; wherein said heterocyclic group formed is a group Ia:



(Ia); and **M₁** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc; and wherein **R₁**, **R₂**, **R₃**, **R₄**, **Y**, Ma, Mb and Mc are each independently defined according to claim 1.

[Claim 7] The electrochromic compound according to claim 1, wherein **n** is 1; **A₁** is H; **M₂** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc; and **A₂** and **M₁** form together a heterocyclic group fused to the central 5-membered heteroaromatic ring they are attached to; wherein said heterocyclic group is selected from the group consisting of Ib, Ic and Id:



and wherein **A₃** is H and **M₃** is selected from the group consisting of H, 2,6-di-C₁₋₁₂ alkoxyphenyl, Ma, Mb and Mc, wherein **at least one** of **M₂** and **M₃** is selected from the group consisting of Ma, Mb and Mc; and wherein **R₆**, **R₇**, **X**, Ma, Mb and Mc are each independently defined according to claim 1.

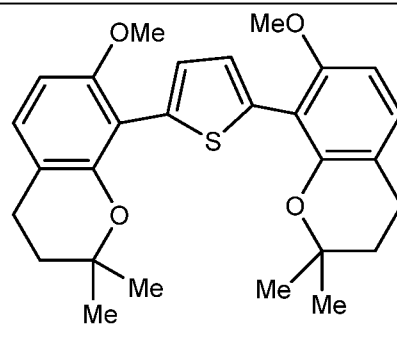
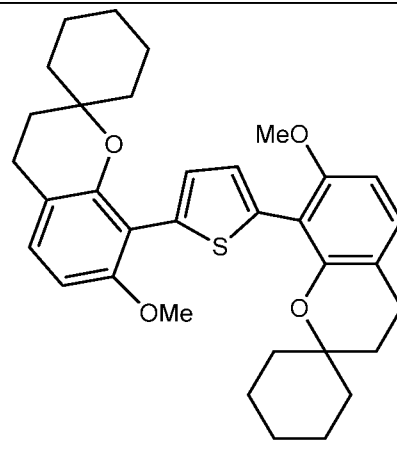
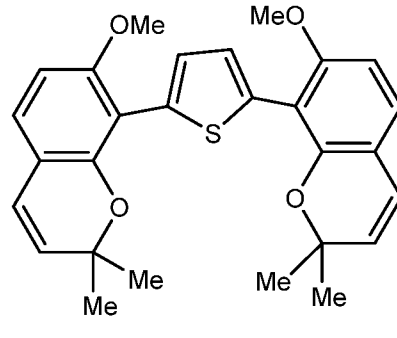
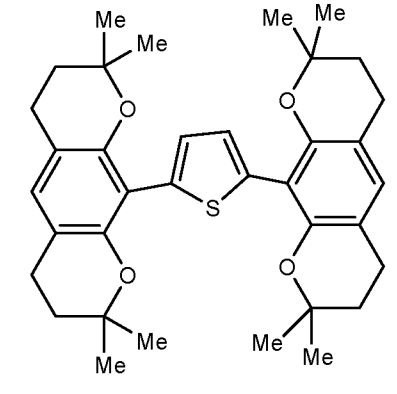
[Claim 8] The electrochromic compound according to any of claims 1 to 7, wherein one or more of X is S.

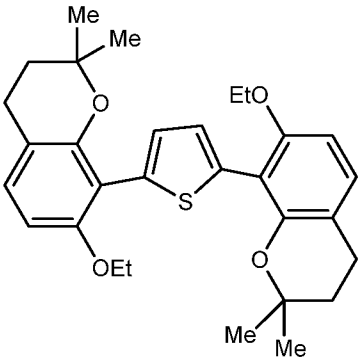
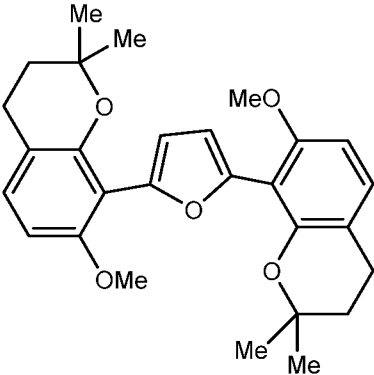
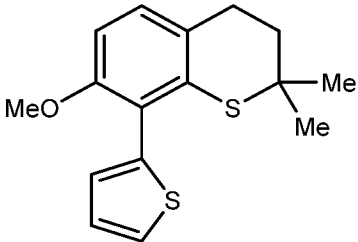
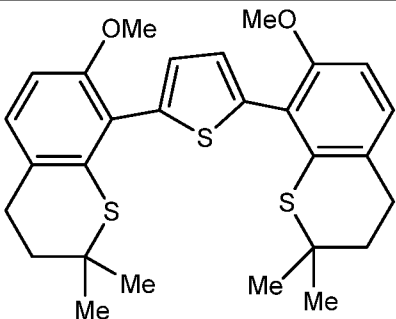
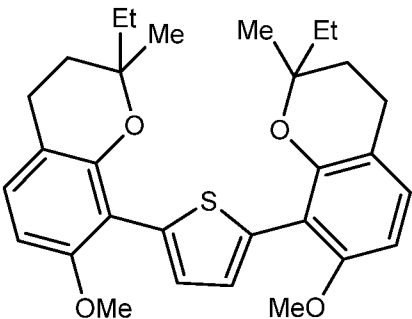
[Claim 9] The electrochromic compound according to any of claims 1 to 8, wherein one or more of Y is O.

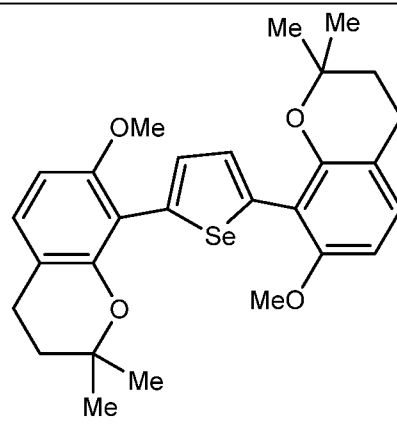
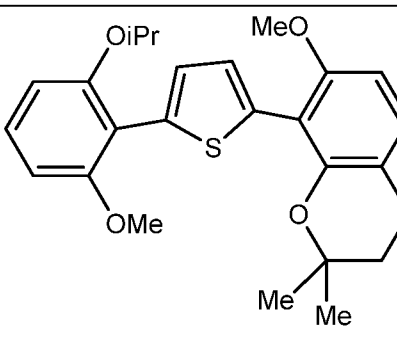
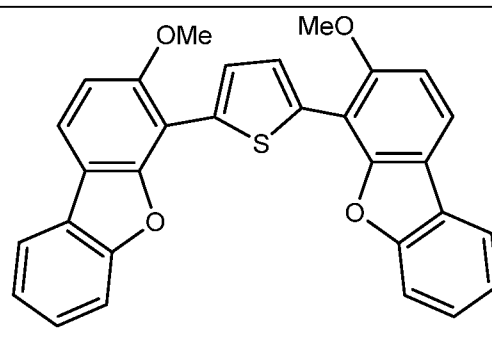
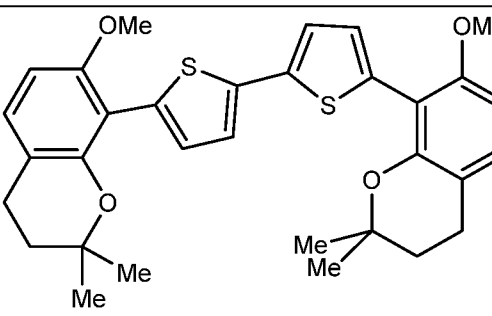
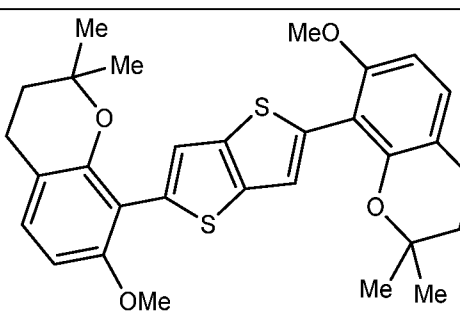
[Claim 10] The electrochromic compound according to any of claims 1 to 9, wherein ----- is a single bond and B and D are both CH₂.

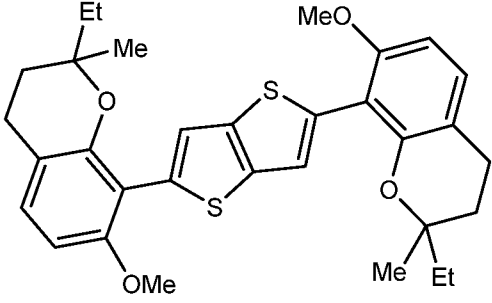
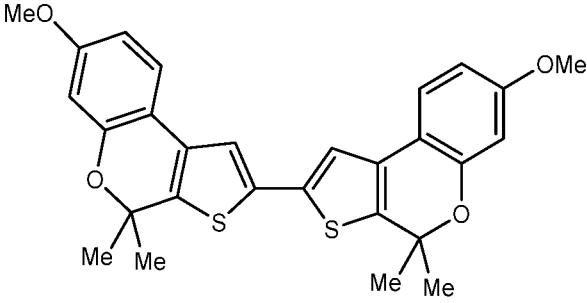
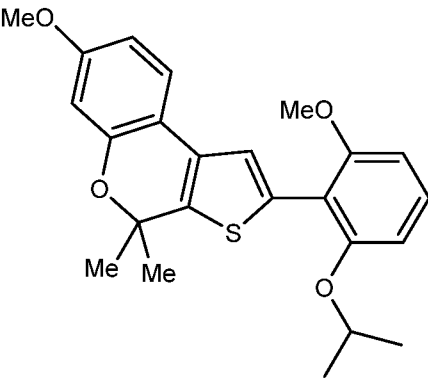
[Claim 11] The electrochromic compound according to any of claims 1 to 11, wherein **R₁** and **R₂** are each independently a linear C₁₋₆ alkyl group or a branched C₃₋₆ alkyl group; **R₃** is independently a linear C₁₋₆ alkyl group, a branched C₃₋₆ alkyl group or C₁₋₆ (per)fluoroalkyl group; and **R₄**, **R₅**, **R₆** and **R₇** are all H.

[Claim 12] The electrochromic compound according to claim 1, wherein said compound is selected from the group consisting of:

Compound 1	
Compound 2	
Compound 3	
Compound 4	

Compound 5	
Compound 6	
Compound 7	
Compound 8	
Compound 9	

Compound 10	
Compound 11	
Compound 12	
Compound 13	
Compound 14	

Compound 15	
Compound 16	
Compound 17	

[Claim 13] An electrochromic composition comprising at least one electrochromic compound as defined in any one of claims 1 to 12, and a host medium.

[Claim 14] An electrochromic device comprising at least one electrochromic compound as defined in any of claims 1 to 12, or an electrochromic composition to claim 13, wherein said electrochromic device is selected from an optical article, a window, a visor, a mirror, a head mounted device, a variable transmission device and a display.

[Claim 15] The electrochromic device according to claim 14, wherein said optical article is an optical lens, preferably an ophthalmic lens, or an optical filter.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/065737

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C09K9/02	C07D407/14 C07D409/04 C07D409/14 C07D495/04
	C07D519/00	
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
C09K C07D G02F		
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, COMPENDEX, INSPEC, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2021/284902 A1 (LIM BOGYU [KR] ET AL) 16 September 2021 (2021-09-16) claims 1-20 -----	1 - 15
☐ 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	"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	
"E" earlier application or patent but published on or after the international filing date	"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	
"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)	"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	
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
15 July 2024	24/07/2024	
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 Mehdaoui, Imed	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/065737

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2021284902 A1	16-09-2021	CN 110603309 A	20-12-2019
		JP 6919140 B2	18-08-2021
		JP 2020519936 A	02-07-2020
		KR 20190037062 A	05-04-2019
		US 2021284902 A1	16-09-2021
