Photoswitched and Functionalized Oligothiophenes: Synthesis and Photochemical and Electrochemical Properties

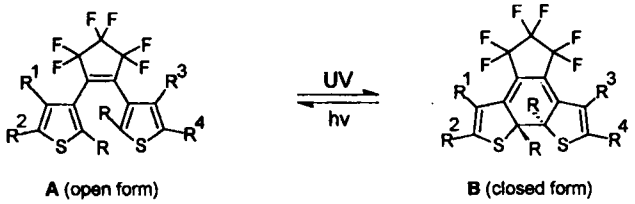
Gerasimos M. Tsivgoulis and Jean-Marie Lehn*

Abstract: The extended dithienylethene compounds **1**–**3** have been synthesized. They undergo photochromic and electrochemical changes by photoinduced interconversion between open and closed forms of type **A** and **B**. In addition, both forms of the *N*-methylated derivatives **1b** and **2b** have absorption bands in which excitation results in very large differences in fluorescence between the two forms with very little effect on the opening/closing state, a feature of interest for optical memory data systems. The compounds **2** and **3** contain six and eight conjugated thiophene units in the closed forms, respectively, and thus represent oligothiophenes endowed with a photoactivated switch; they are of special interest in this respect in view of the potential use of switched oligothiophenes in molecular electronic devices.

Keywords
electrochromes · fluorescence · molecular devices · oligothiophenes · photochromes

Introduction

Switching units represent basic components of molecular and supramolecular devices, since they allow the modulation of the function of such devices by external physical or chemical triggers.[1] Light-driven molecular switches[2] have been the subject of a considerable amount of work, since they may be of interest for optical data memory systems.[3] Numerous other uses have also been explored, such as photoresponsive macrocycles,[4] photoactivated enzymes[5] or switching of optical and electrical properties.[6] Diarylethenes, notably bisthien-3-yl systems of type **A** (Scheme 1), have been shown to exhibit such desirable properties as thermal and chemical stability, as well as remarkable fatigue resistance.[3, 7]



A (open form) **B** (closed form)

Scheme 1. Open and closed forms of the perfluorocyclopentenebisthien-3-yl system.

Conjugated oligomers provide insight into the more complex properties of the corresponding polymers. Investigations of the chemical stability and conductivity of modified or nonmodified oligothiophenes show that their properties have the potential for use as electronic materials as well as for the development of conducting polymers.[8] Recently, oligothiophenes containing up to 16 thiophene units have been synthesized and studied.[8, 9]

An important line of research aimed at the eventual construction of an advanced, multifunctional, high-density molecular electronic device is the attempt to build highly integrated interconversion modes into a single molecule.[10] The insertion into a polyenic path of a switching unit that interrupts or establishes electronic conjugation may be used to turn properties dependent on this conjugation "ON" or "OFF". Some models have already been described.[6, 11–13] Such systems possessing both photochromism and molecular wire type properties[6, 11–13] could achieve higher information storage density and multiple operations than molecules exhibiting each response individually.

Reports from our laboratory[6, 11–13] have described several switching devices based on the dithienylethene group, which undergoes the **A**/**B** photoinduced interconversion. They exhibit remarkable photochromism and can usually interconvert from one form to another in nearly quantitative yields (>98%). We describe in the present article the synthesis and some physicochemical properties of the functionalized oligothiophenes **1**–**3** incorporating a dithienylethene molecular switch unit. These systems represent a combination within the same entity of both the switching and the oligothiophene features and display a total conjugation corresponding to about eight connected thiophenes in the closed state **B**.

Results and Discussion

Synthesis: Attempts to condense the precursor **4a** with octafluorocyclopentene (C_5F_8) in hexane, THF, HMPT or their mixtures following the synthetic procedure first introduced by

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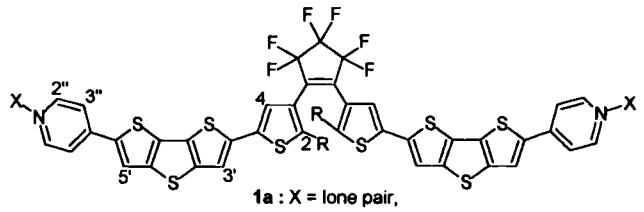
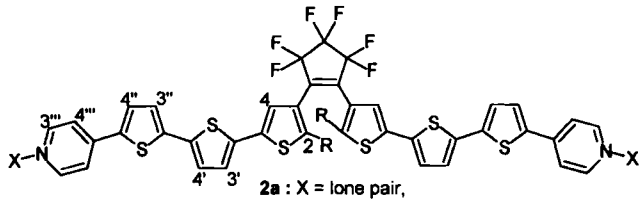
Irie et al.[14] failed because of solubility problems (hexane, THF) or side reactions (HMPT). These were overcome by replacing the two methyl groups of the bisthien-3-yl system **A** by longer *n*-hexyl chains. The corresponding compound **4b** was soluble enough (about 30 times more soluble than **4a** in THF) to permit the reaction with BuLi; however, the product was not that expected from halogen–lithium interchange. At least one of the side reactions was hydrogen–lithium exchange of the condensed thiophene protons. This result can be explained: a) the pyridine group increases the acidity of the thiophene protons and b) the condensed thiophenes show higher reactivity[15] than thiophene.

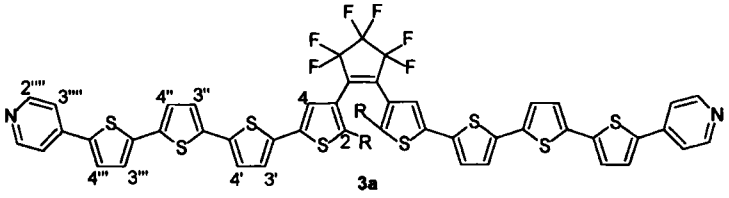
Finally, the synthesis of the target compounds **1–3** was carried out by a new synthetic approach,[13] shown in Scheme 2. This approach is a variation of a procedure that was reported after completion of the present synthesis.[12] It is of general application and has certain advantages over the previous one.[14] Firstly, the key compound **9** gives access to more complicated switch molecules with fewer steps and simultaneously allows the use of a well-known, usually high-yield reaction as final step, namely palladium-catalyzed carbon–carbon bond formation. This coupling reaction has already been applied with success in the synthesis of oligothiophenes.[16] Secondly, it is not necessary for the end groups that are to be attached to the central "switch" unit to be inert against carbanions or to bear the unstable boronic acid group (as in the case of refs. [12] and [14]); they need only to bear a halogen at the position of connection.



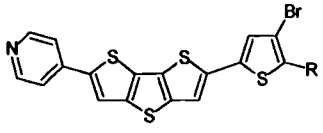
1a : X = lone pair,
1b : X = CH_3, counterion = $CF_3SO_3^-$



2a : X = lone pair,
2b : X = CH_3, counterion = $CF_3SO_3^-$



3a



4a : R = CH_3
4b : R = C_6H_{13}

Another problem was the instability of some of the intermediate boronic acids. It is known that some boronic acids show a tendency to lose boron[17, 18] or to form anhydrides[18] on isolation; dithieno[3,2-b:2',3'-d]thiophene-2-boronic acid **13** could thus only be isolated as a wet solid. Also, the bisboronic acid **9** could only be used in solution; any attempt to isolate it led to loss of the boronic acid group.

Physical properties: Although unsubstituted oligothiophenes generally have very low solubility,[9c, 19] compounds **1a–3a** were soluble in many common organic solvents such as $CHCl_3$, CH_2Cl_2, acetone, THF, higher alcohols and even, to some extent, in hexane. The solubility decreases in the order **2a** > **1a** ≫ **3a**. On the other hand, compounds **1b** and **2b**, carrying two positive charges, were insoluble in solvents of low or medium polarity like hexane, $CHCl_3$, CH_2Cl_2 and acetone, but moderately soluble in high polarity solvents like CH_3CN, DMSO, DMF and MeOH. Water was not a good solvent since a long hydrophobic group is present in the molecule. The counterion also plays an important role in solubility, iodides being less soluble than triflates.

In the ^{1}H NMR (200 MHz) spectrum the signals of the two methylene groups of the hexyl chains next to the diarylethene system appeared as one triplet at $\delta \approx 2.3$ in the open forms and as two double triplets at $\delta = 2.44$ and 2.91 (ABX_2 system) in the closed forms (Fig. 1). This reflects the significant structural

Abstract in French: *Les produits 1–3, dérivés du système dithienylethène, ont été synthétisés. Leurs propriétés photochromiques et électrochimiques peuvent être modifiées par interconversion sous l'action de la lumière entre une forme ouverte (A) et une forme fermée (B). De plus, les deux formes N-méthylées 1b et 2b présentent des bandes d'absorption qui n'affectent pratiquement pas le processus d'ouverture–fermeture. L'excitation de ces bandes met en évidence une très grande différence d'émission de fluorescence entre les deux formes, propriété intéressante pour les systèmes de mémoire optique. Les produits 2 et 3 sous forme fermée contiennent respectivement six et huit thiophènes conjugués et représentent ainsi des oligothiophènes associés à un interrupteur photoactivable. De tels oligothiophènes commutables sont très prometteurs en vue de l'élaboration de systèmes moléculaires électroniques.*

Abstract in Greek: Οι ενώσεις **1-3** αποτελούν επέκταση του διθειενυλαιθενιακού συστήματος με ομάδες συζυγιακών διπλών δεσμών. Κατά την φωτοχημική μετατροπή τους από τις ανοιχτές δομές (**A**) στις κλειστές δομές (**B**) και αντίθετα παρατηρούνται σημαντικές φωτοχρωμικές και ηλεκτροχημικές μεταβολές. Στην περίπτωση των N-μεθυλιωμένων παραγώγων **1b** και **2b**, τόσο οι κλειστές όσο και οι ανοιχτές δομές παρουσιάζουν επιπλέον απορροφήσεις στο υπεριώδες/ορατό φάσμα αδρανείς ως προς τη φωτοχημική διαδικασία. Ακτινοβόληση αυτών των απορροφήσεων συνοδεύεται από φθορισμό με θεαματικές διαφορές ως προς την ένταση του ανάμεσα στους δύο τύπους (**A** και **B**). Ενώσεις με τέτοιες ιδιότητες έχουν άμεσο ενδιαφέρον στα οπτικά συστήματα μνήμης. Οι ενώσεις **2** και **3** περιέχουν, αντίστοιχα, έξι και οχτώ ομάδες θειοφενίου (κλειστές δομές) συνδεδεμένες συζυγιακά και ως εκ' τούτου αποτελούν συνδυασμό ολιγοθειοφενίων με φωτοενεργοποιήσιμους "μοριακούς διακόπτες". Από αυτή την άποψη είναι ιδιαίτερα σημαντικές για πιθανή χρήση τους στο πεδίο των μοριακών ηλεκτρονικών συστημάτων.

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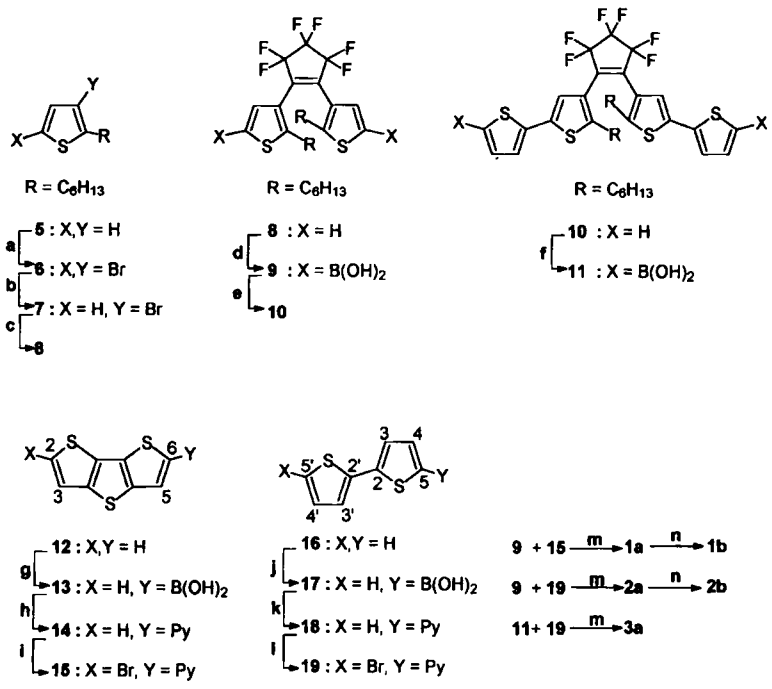

Scheme 2. Pathways for the synthesis of compounds **1a–b**, **2a–b**, **3a**. Reagents and conditions: a) Br_2 ($CHCl_3$/AcOH); b) 1. BuLi (Et_2O); 2. MeOH; c) 1. BuLi (pentane/THF); 2. C_5F_8; d) 1. BuLi/TMEDA (Et_2O); 2. $B(n\text{OBu})_3$; e) 2-bromothiophene/$Pd(PPh_3)_4$ (THF/aq. Na_2CO_3); f) 1. BuLi/TMEDA (Et_2O); 2. $B(n\text{OBu})_3$; g) 1. BuLi (Et_2O); 2. $B(n\text{OBu})_3$; h) 4-bromopyridine:HCl/$Pd(PPh_3)_4$ (THF/aq. Na_2CO_3); i) NBS ($CHCl_3$/AcOH); j) 1. BuLi (Et_2O); 2. $B(n\text{OBu})_3$; k) 4-bromopyridine:HCl/$Pd(PPh_3)_4$ (THF/aq. Na_2CO_3); l) NBS ($CHCl_3$/AcOH); m) $Pd(PPh_3)_4$ (THF/aq. Na_2CO_3); n) $CF_3SO_3CH_3$ (CH_2Cl_2).

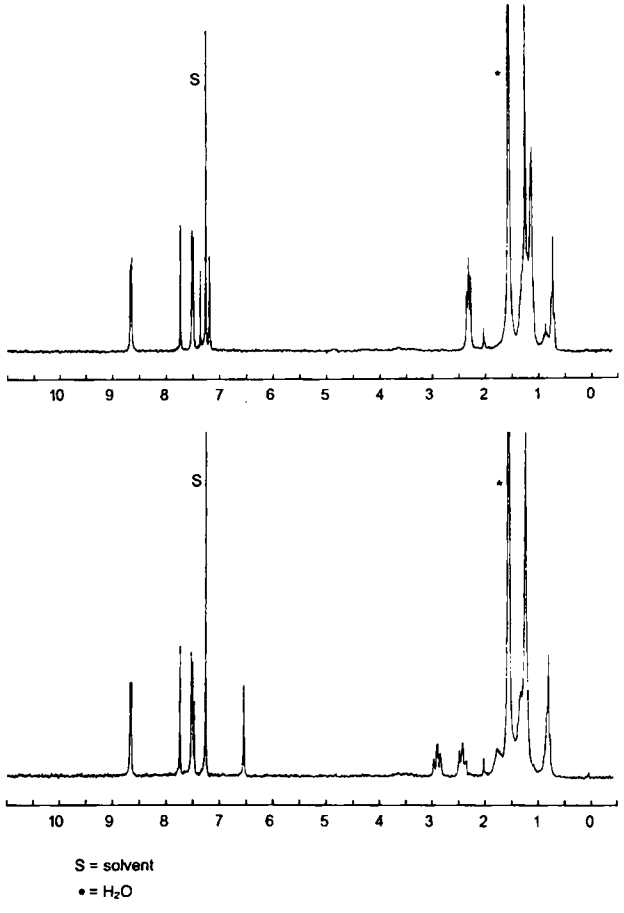

Fig. 1. 200 MHz ^{1}H NMR spectra ($CDCl_3$, 25 °C) of the open (top) and closed (bottom) forms of compound **1a**.

changes that take place between the two forms. Regarding the rest of the molecule, considerable differences were also observed related to the changes in the conjugation between the two forms (Figs. 1 and 2).

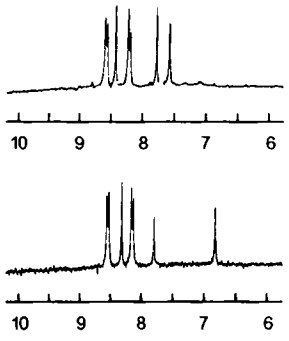

Fig. 2. Part of the aromatic region of the 200 MHz ^{1}H NMR spectra ([D_6]DMSO, 25 °C) of the open (top) and closed (bottom) forms of compound **1b**.

Photochromic properties: The replacement of the two methyl groups in the bisthien-3-yl system **A** by the longer *n*-hexyl chains not only improved the solubility greatly but also enhanced the switching properties. In particular, i) the absorption maxima were shifted to longer wavelengths (24–30 nm red shift for the closed form), ii) the separation between the peaks of open and closed forms was increased.[20] Also, the photostationary state for all compounds tested was not affected by this replacement.

Tables 1 and 2 list the most important absorption bands of the UV/vis spectra of the open and closed forms of compounds

Table 1. UV/vis electronic absorption λ_{max} values (nm) of compounds **1a**, **2a** and **3a** in benzene. Concentration of solution $\approx 1 \times 10^{-5}$ M.

Open forms			Closed forms		
1a	**2a**	**3a**	**1a**	**2a**	**3a**
395	398	420	426	417	440
			701	692	701

Table 2. UV/vis electronic absorption λ_{max} (nm) and ε ($M^{-1}cm^{-1}$, in parenthesis) values of the open and closed forms of compounds **1b** and **2b** in methanol. Concentration of solution $\approx 1 \times 10^{-5}$ M.

Open forms		Closed forms	
1b	**2b**	**1b**	**2b**
261 (25400)	261 (32700)	246 (23250)	253 (23000)
329 (21700)	333 (21500)	454 (78900)	440 (67600)
459 (92800)	451 (80500)	704 (41000)	698 (37500)

1a–3a and **1b–2b** respectively; the complete UV/vis spectra of the compounds **2a** and **2b** are shown in Figures 3–4.

The photochromic properties of compounds **2a** and **3a** were similar to **1a** and those of **2b** were similar to **1b**.[13] Notably, in the case of compounds **1a–3a** UV light was not necessary to obtain the closed forms: photoswitching between the two forms, open (**A**) and closed (**B**), could be achieved by irradiation with two different wavelengths of the visible region. In particular, the open forms could be generated by irradiation of the closed forms at a wavelength >600 nm[21] while subsequent irradia-

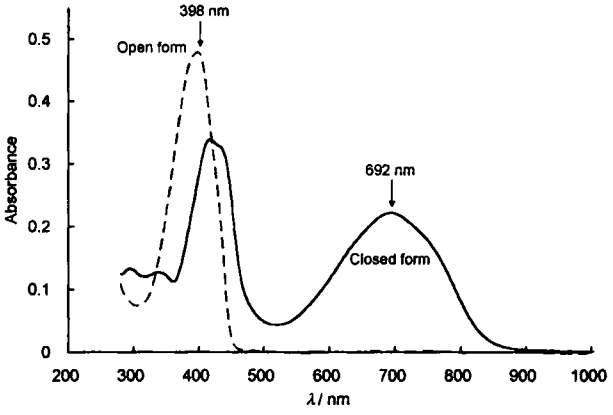

Fig. 3. UV/vis electronic absorption spectrum of the open and closed forms of compound **2a** in benzene solution.

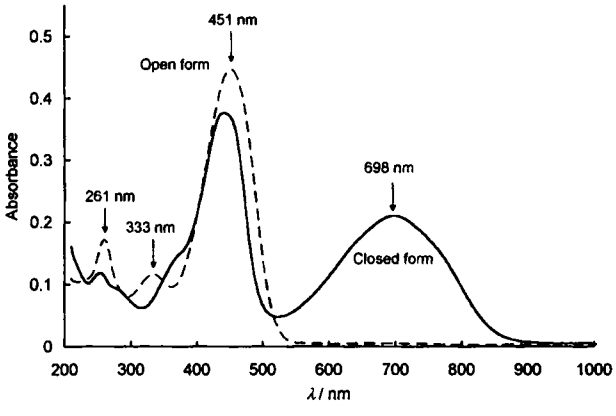

Fig. 4. UV/vis electronic absorption spectrum of the open and closed forms of compound **2b** in methanol solution.

tion of the open forms at a wavelength <450–500 nm returned the compounds quantitatively (according to ^{1}HNMR at 200 MHz) to the closed forms.

On the other hand, the methylated compounds **1b** and **2b** displayed remarkably different behaviour. Methylation affected mainly the absorption bands of the open forms, causing a 50–65 nm red shift of λ_{max}, while the λ_{max} of the closed forms were red-shifted only 4–6 nm (Tables 1 and 2). When the closed forms were irradiated at $\lambda > 600$ nm[21] they opened quantitatively, but even prolonged irradiation of the intense absorption bands of the open forms ($\lambda_{max} = 459$ nm, $\varepsilon = 92800\,M^{-1}cm^{-1}$ for **1b** and $\lambda_{max} = 451$ nm, $\varepsilon = 80500\,M^{-1}cm^{-1}$ for **2b**) at 400–500 nm[22] did not result in the closed forms. Conversion to the closed forms (in ≈92% yield in both cases) could only be achieved by irradiation of the relatively small absorption bands at $\lambda_{max} = 329$ nm and 333 nm for **1b** and **2b** respectively. To confirm that these correspond to photostationary states, solutions of the closed forms of **1b** and **2b** were irradiated at 365 nm and 312 nm respectively, resulting in a maximum conversion to the open forms of around 8%.

Compounds **1a–3a** exist in the closed form in the daylight while **1b–2b** are in the open form. The λ_{max} of the absorption bands of the closed forms of compounds **1a–3a** and **1b–2b** are in the range of 690–705 nm; this is important from the viewpoint of practical applications, since photochromic compounds should be sensitive in the range between 650–830 nm.[3]

Comparison between the rates of conversion to the closed forms for **1b** and **2b** by means of three commercial UV lamps[23] at 254 nm, 312 nm and 365 nm demonstrated that irradiation at 365 nm and 312 nm always gives significantly faster closing than irradiation at 254 nm. This shows that the absorption bands at $\lambda_{max} = 329$ nm and 333 nm for **1b** and **2b**, respectively, are the most (if not the only) active bands for conversion to the closed forms. In general, **1b** appeared to undergo somewhat faster opening–closing interconversions than **2b**, irradiated under similar conditions, at 312 nm, 365 nm, 400–500 nm[22] or >600 nm[21] (Table 3), while for the non-methylated compounds **1a–3a** the order is **1a** ≥ **2a** > **3a**.

Table 3. Interconversion between the open and closed forms. Proportion of final form (%) after 30 min of irradiation in MeOH.

Irradiation wavelength	Open → Closed		Closed → Open	
	1b	**2b**	**1b**	**2b**
312 nm UV [a]	91.5	91 [b]	–	7
365 nm UV [a]	92	85	7–8	–
400–500 nm [a]	<0.5	0	5	3
>610 nm [a]	0	0	98	95 [c]
459 nm (2.5 [d,e])	<0.5	–	2	–
459 nm (1.0 [d,e])	–	–	<0.5	–
451 nm (2.5 [d,e])	–	0	–	1.6

[a] Concentration of solution $\approx 1 \times 10^{-5}$ M. [b] At $t = 35$ min, conversion = 92–93%. [c] At $t = 40$ min, conversion >98%. [d] Irradiation width in nm. [e] Concentration of solution $\approx 1 \times 10^{-6}$ M.

The closed forms **B** of **1b** and **2b** also present strong absorption bands in the 400–500 nm domain. As in the case of the open forms these bands gave little conversion, so that after 30 min of irradiation at 400–500 nm[22] only 3–5% opening is observed (Table 3). Such absorption bands that affect the state of conversion only little or not at all are of great interest in optical data memory systems.[3, 13] Quantum yield measurements on opening and closing reactions are necessary for describing the present processes more quantitatively.

Fluorescence properties: The open and closed forms of compound **1b** were found to display a very large change in fluorescence when excited at 400–500 nm.[13] In particular, when the absorption bands of both forms were excited at about 455 nm, only the open form was strongly fluorescent, while the closed form emitted very weakly. The same behaviour is shown by compound **2b** (Fig. 5). The luminescence λ_{max} of the open and closed forms of **2b** are at 611 nm and 604 nm, respectively, while for **1b** they are at 589 nm and 586 nm. The non-methylated compounds seem to behave in a similar way, since at least in case

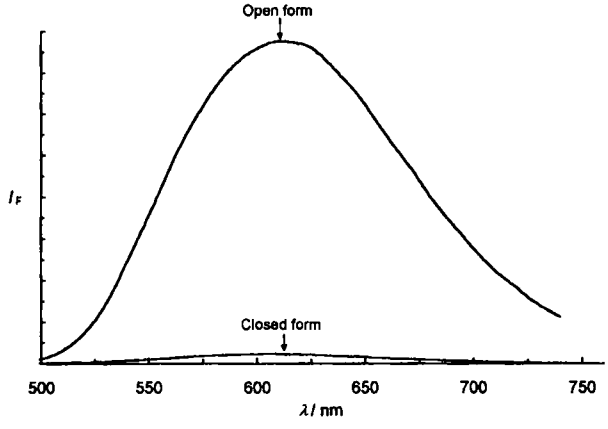

Fig. 5. Fluorescence spectra of the open and closed forms of compound **2b** in methanol solution (excitation at 451 nm).

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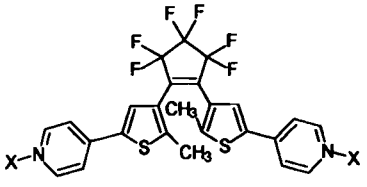
of compound **1a** a large change in fluorescence was observed between open and closed forms.[24] This fluorescence difference between the two forms by excitation of the inactive absorption bands (with respect to the opening–closing photoreactions) around 450 nm (Table 3) presents much potential for the sensitive nondestructive[3, 13, 25] "reading" of optically stored data.

With respect to photostability, compounds **1a**–**2a** and **1b**–**2b** showed no signs of decomposition when exposed to daylight or oxygen for 2–3 days, but an inert atmosphere (N_2) was always used during irradiation experiments. After 10 opening–closing photocycles no significant change was found in the UV spectra.[26] The open and closed forms were thermally stable at room temperature for periods of more than 10 days.

Electrochemical properties: Compounds **1b** and **2b** present the features of molecular wires, namely an extended conjugated polyenic chain for electron conduction (closed forms), fitted with terminal electroactive pyridinium groups for reversible electron exchange. It has already been demonstrated that a caroviologen composed of nine double bonds separating two pyridinium units facilitated electron transport across a phospholipid vesicle membrane.[27]

We performed cyclic voltammetry experiments in DMSO (0.1 M $Bu_4N^+PPh_6^-$) in order to study the electrochemical properties of these compounds. Both **1b** and **2b** gave similar voltammograms, which were different from those of the molecule **20b**,[6b] in which the two pyridinium units are directly connected to the diarylethene unit.[6] The results are summarized in Table 4 and the voltammograms of the open and closed form of **1b** and the closed form of **1a** are shown in Figures 6 and 7, respectively.



20a : X = lone pair,
20b : X = CH_3, counterion = $CF_3SO_3^-$

Table 4. Cyclic voltammetry data: redox potentials (vs SCE) for compounds **1b**, **2b**, **1a**, **20a** and **20b** in DMSO (0.1 M $nBu_4N^+PPh_6^-$).

Compound	Form	E_{ox1}	E_{red1}	E_{red2}
20a [a]	open	–	−1.78 [b]	–
	closed	1.13 [b]	−0.90 [b]	−1.25 [b]
20b	open	–	−1.01 [b]	−1.47 [b]
	closed	–	−0.27	−1.41 [b]
1b	open	–	−0.98	−1.43 [b]
	closed	0.79 [c]	−0.68 [b]	−0.83 [b]
2b	open	–	−1.01	−1.43 [b]
	closed	1.03 [c]	−0.68 [b]	−0.81 [b]
1a [a]	closed	0.78	−0.99 [b]	−1.34 [b]

[a] In CH_2Cl_2 (0.1 M $nBu_4N^+ClO_4^-$). [b] Irreversible. [c] Quasireversible.

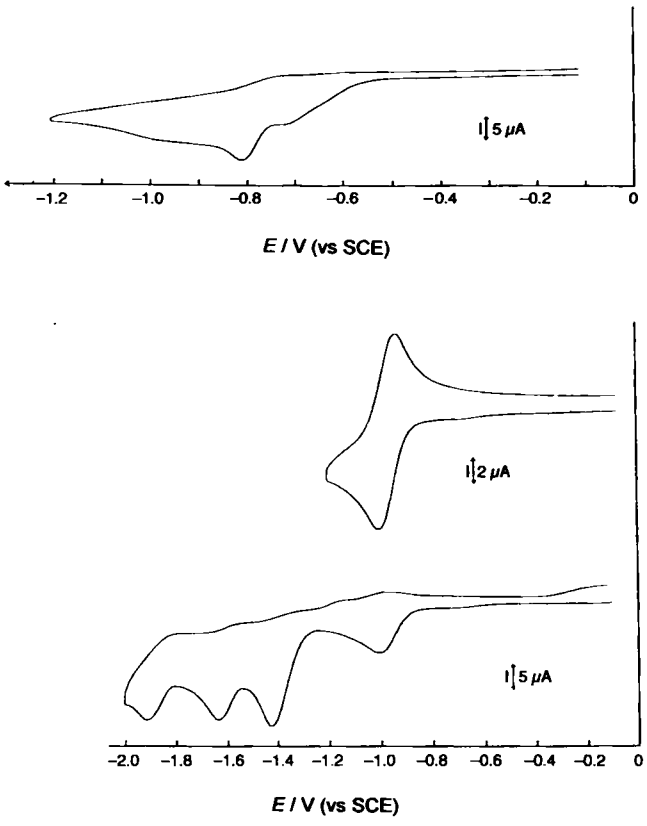


Fig. 6. Cyclic voltammograms for the reduction of the closed (top) and the open form (bottom) of compound **1b**; scanning rate = 100 mVs^{-1}.

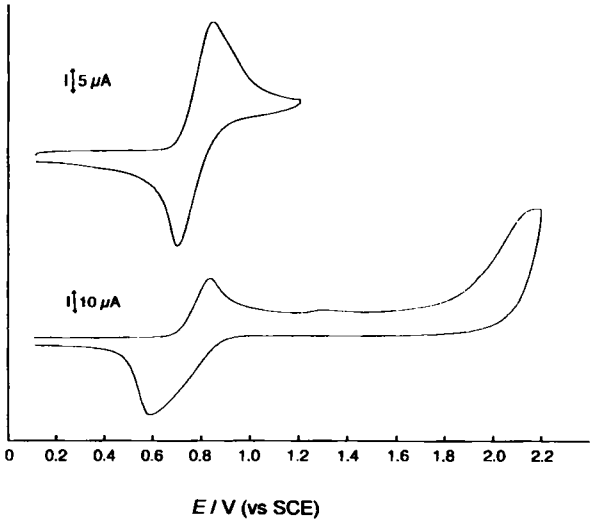


Fig. 7. Cyclic voltammogram for the oxidation of the closed form of compound **1a**; scanning rate = 100 mVs^{-1}.

Whereas the open form of compound **20b** was reduced irreversibly at −1.01 V, those of **1b** and **2b** were reduced reversibly at −0.98 and −1.01 V, respectively, probably owing to the stabilizing effect of the additional thiophene units on the radical formed. For the closed form of **20b** a reversible reduction wave at −0.27 V was observed,[6] whereas compounds **1b** and **2b** (closed forms) were irreversibly reduced at a potential around −0.68 V. The more negative value can be attributed to the donor properties of the additional thiophene groups. A possible explanation for the irreversibility is that in the closed forms the perfluorodithienylethene is reduced first and irreversibly, although it is apparently stable at even more negative potentials in the corresponding open forms. Replacement of the condensed thiophene rings in the closed form of compound **1b** by linearly connected ones in compound **2b** did not improve the electrochemical behaviour. This is also consistent with the irreversible reduction of the closed form of compound **20a**[6b] at −0.90 V in CH_2Cl_2 and at −0.78 V in MeCN. Finally, the closed form of the non-methylated compound **1a** could be reversibly oxidized at 0.78 V.[24]

Conclusion

The large differences between the voltammograms of the open and closed forms represent the different level of conjugation. Similar observations have been made in previous work.[6, 11, 12] Such changes represent photocontrol of electrochemical properties in the fashion of a photoswitched molecular wire. They are of special significance in the case of the elongated compounds **2** and **3**, whose closed forms correspond respectively to about six and eight conjugated thiophene units, in view of the interest in oligothiophenes as materials for molecular electronic devices.

Experimental Procedure

General: *n*BuLi (10 M, 1.6 M) hexane solutions, 3-bromothiophene 97%, sodium sulfinate 98%, 4-bromopyridine hydrochloride salt, tributyl borate 99%, 2,2′ bisthiophene 97% and methyl trifluoromethane sulfonate (Aldrich), 2-*n*-hexylthiophene 98%, 2-bromothiophene and 2-methylthiophene (Lancaster), sulfur dichloride (Fluka) and octafluorocyclopentene (PCR) were used as obtained.

UV/vis spectra were recorded on a Beckman DU-640 spectrophotometer with spectrograde solvents. ^{1}H NMR spectra were determined with a Bruker AM 200 SY spectrometer at 200.13 MHz. The chemical shifts are given with respect to the $CDCl_3$, [D$_6$]DMSO, CD_3OD, CD_3COCD_3 or CD_3CN signals assigned values of $\delta = 7.26$, 2.49, 3.30, 2.05 and 2.00, respectively. Microanalyses (for C, H and N) were performed by the Centre Nationale de le Recherche Scientifique à Vernaison. Mass spectra were supplied by the Centre Nationale de le Recherche Scientifique à Vernaison as well as the Université de Paris VI Centre de Spectrophotométrie.

Cyclic voltammetry was performed by means of a standard three-electrode configuration employing a glassy carbon working electrode (3 mm diameter disk) and a platinum-wire counterelectrode, the reference electrode being a saturated calomel electrode (SCE). A Princeton 362 scanning potentiostat was used and the results were recorded on an Ifalec 1 F-3802 recorder. All experiments were performed under nitrogen at 20 °C with solvents previously saturated with nitrogen. The surface of the working electrode was polished before each measurement. The electrolytes used were nBu$_4$NPPh$_6$ for experiments carried out in DMSO and nBu$_4$NClO$_4$ for experiments carried out in CH_2Cl_2. Solutions of 3 or 5 mL containing compounds **1** or **2** at 10^{-3} M concentration and 0.1 M in electrolyte were employed.

All reactions involving organolithium reagents were carried out under dry, oxygen-free nitrogen, and reagents and solvents were dried by standard procedures. Reagents were transferred with syringes through a rubber septum fitted to the reaction vessel. In some cases reactions with BuLi were performed in the presence of indicator. Particularly in the case of small-scale experiments or with compounds of low solubility, 1,10-phenanthroline was added prior to the solvent (≈1 mg per 10 mL for Et_2O and THF) then followed by addition of 1.6 M *n*BuLi until a pink-red colour was formed. The persistence of a constant pink-red colour for about a minute was taken as an indication that there were no more traces of water or compounds that can react with *n*BuLi in the system. 1,10-phenanthroline and 2,2′-biquinoline have already been used as indicators in titrations of metal alkyls [28]. It must be emphasized that even when no more *n*BuLi-sensitive compounds exist the pink colour turns yellow after a few minutes (at room temperature), since alkyllithium compounds react slowly at room temperature with THF or even Et_2O [29].

Dithieno[3,2-b:2′,3′-d]thiophene (12): This compound was synthesized according to the literature method [30] from commercially available 10 M *n*BuLi solution in hexane instead of ethereal solution. The intermediate bis(phenylsulfonyl) sulfide was prepared in CH_2Cl_2 as solvent instead of benzene. It was found that in CH_2Cl_2 the reaction proceeded faster and gave better yields.

Dithieno[3,2-b:2′,3′-d]thiophene-2-boronic acid (13): Under nitrogen, *n*-butyllithium (1.05 mmol, 0.66 mL of 1.58 M solution in hexane) was added dropwise over 35 min to dithieno[3,2-b:2′,3′-d]thiophene (0.196 g, 1 mmol) dissolved in freshly distilled (over $LiAlH_4$) Et_2O (12 mL). The yellow-orange suspension was stirred for an additional 1 h and then cooled in an acetone/dry-ice bath (−78 °C). B(*n*OBu)$_3$ (0.38 mL, 1.41 mmol) was added in one portion and the stirring at −78 °C continued for 3 h while the suspension turned clear orange. Then the solution was allowed to reach room temperature slowly and stirring was continued overnight. To the gray-black solution was added HCl (2.0 mL, 1 N). A light green-gray solid formed, which dissolved on stirring. The two phases were separated and the aqueous phase was extracted again with Et_2O (12 mL). The combined Et_2O phases were extracted with aqueous NaOH (3 × 12 mL, 1 N) while some product separated as a solid suspended in the aqueous phase. The combined aqueous phases were heated to ≈60 °C (to dissolve the solid product) and filtered (G4) to remove coloured impurities. Addition of concentrated HCl up to pH = 1–2 and cooling to 0 °C gives a dirty white suspension. Filtration (G4) of the solid gives wet product **13** [31] (> 75% yield based on the dry material). ^{1}H NMR (200 MHz, [D$_6$]DMSO): $\delta = 8.44$ (s, 2H; HO), 7.93 (s, 1H; 3-CH), 7.72 (d, ^3J(H6,H5) = 5.2 Hz, 1H; 6-CH), 7.52 (d, ^3J(H5,H6) = 5.2 Hz, 1H; 5-CH).

Dithieno[3,2-b:2′,3′-d]thiophene-2-(pyridin-4′-yl) (14): The wet dithieno[3,2-b:2′,3′-d]thiophene-2-boronic acid (**13**) of the previous reaction was dissolved in THF (14 mL). A clear, dark brown solution was formed, and 4-bromopyridine hydrochloride (0.270 g, 1.41 mmol), Pd(PPh$_3$)$_4$ (0.067 g, 0.06 mmol) and aqueous Na_2CO_3 (14 mL, 1.9 M) were added. The two-phase system was refluxed for 22 h. After cooling to room temperature and addition of $CHCl_3$ (37 mL) the phases were separated and the aqueous phase was extracted with $CHCl_3$ (2 × 18 mL). The combined organic phases were dried (Na_2SO_4), filtered (paper) and concentrated to about 3 mL. Chromatography through silica with CH_2Cl_2/MeOH (80:2 p.v.) gives 0.139 g (60%) of product. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.63$ (A of AA′BB′, J(app) = 6.2 Hz, 2H; 2′,6′-CH), 7.52 (B of AA′BB′, J(app) = 6.2 Hz, 2H; 3′,5′-CH), 7.72 (s, 1H; 3-CH), 7.45 (d, ^3J(H5,H6) = 5.3 Hz, 1H; 5-CH), 7.32 (d, ^3J(H6,H5) = 5.3 Hz, 1H; 6H); MS (CI, NH_3): *m/z* (%): 273 (100) [M^+]; $C_{13}H_7NS_3$ (273.4): calcd C 57.12, H 2.58, N 5.12; found C 57.42, H 2.82, N 4.72.

2′-Bromodithieno[3,2-b:2′,3′-d]thiophene-6-(pyridin-4′-yl) (15): Dithieno[3,2-b:2′,3′-d]thiophene-2-(pyridin-4′-yl) (**14**) (0.227 g, 0.831 mmol) was dissolved in $CHCl_3$/AcOH (30 mL, 1:1 p.v.). The opalescent yellow-orange solution was cooled to 0 °C and a clear colourless solution of NBS (0.148 g, 0.831 mmol in 13 mL $CHCl_3$/AcOH, 1:1 p.v.) was added dropwise over 35 min, during which a yellow solid appeared. Stirring was continued for 2 h at 0 °C and then for an additional 1.5 h at room temperature. The yellow suspension was evaporated (12 mmHg/60 °C) and then CH_2Cl_2 (20 mL), H_2O (15 mL) and aqueous Na_2CO_3 (1.9 M) were added to achieve a pH > 8. Evaporation of the CH_2Cl_2 gave a yellow solid suspended in the aqueous phase. Filtration (G4) and washing with H_2O and then Et_2O gave 0.235 g (80%) of product. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.63$ (A of AA′BB′, J(app) = 6.2 Hz, 2H; 2′,6′-CH), 7.49 (B of AA′BB′, J(app) = 6.2 Hz, 2H; 3′,5′-CH), 7.71 (s, 1H; 3-CH), 7.32 (s, 1H; 5-CH); MS (CI, NH_3): *m/z* (%): 351/353 (87/100) [M^+], 352/354 (52/55) [MH$^+$], 273 (50) [M^+ − Br], 274 (33) [MH$^+$ − Br]; $C_{13}H_6NS_3Br$ (352.3): calcd C 44.32, H 1.72, N 3.98; found C 44.00, H 1.71, N 3.81.

A second batch of product can be isolated from the filtrate as follows. The organic phase from the filtrate was evaporated on a rotary evaporator and the remaining aqueous phase was extracted with CH_2Cl_2. Separation and evaporation of the CH_2Cl_2 phase gave a yellow solid that, on treatment with H_2O/Et_2O (1:1 p.v.) and filtration (G4), gave another 0.03 g (10%) of product.

2,2′-Bisthiophene-5-boronic acid (17): 2,2′-Bisthiophene (**16**) (3.783 g, 22.7 mmol) was dissolved in freshly distilled (over $LiAlH_4$) Et_2O (80 mL). *n*-Butyllithium (22.7 mmol, 14.5 mL of 1.60 M solution in hexane) was added under nitrogen, dropwise, over 35 min. The orange-brown suspension was stirred for an additional 1 h and then cooled in an acetone/dry-ice bath (−78 °C). B(*n*OBu)$_3$ (8.63 mL, 31.2 mmol) was added in one portion and the stirring at −78 °C continued for 3 h while the suspension turned to a viscous clear orange solution. The cooling bath was removed and stirring was continued overnight. To the gray-black solution HCl (25 mL, 1 N) and Et_2O (160 mL) were added. The two phases were separated and the Et_2O phase was extracted with NaOH (3 × 160 mL, 1 N). Addition of concentrated HCl to attain pH = 1–2 and cooling to 0 °C gave a gray-white precipitate. Filtration (G4) of the solid gave the wet product **17** as a light green solid (> 70% yield based on the dry material). ^{1}H NMR (200 MHz, CD_3COCD_3): $\delta = 7.41$ (s, 2H; OH), 7.29 (m, 2H; 3,3′-CH), 7.59 (d, ^3J(H4′·H3′) = 3.6 Hz, 1H; 4-CH), 7.06 (dd, ^3J(H4′,H3′) = 3.6 Hz, ^3J(H4′,H5′) = 5.2 Hz, 1H; 4′-CH), 7.42 (dd, ^3J(H5′,H4′) = 5.2 Hz, ^4J(H5′,H3′) = 1.1 Hz, 1H; 5′-CH).

2,2′-Bisthiophene-5-(pyridin-4′-yl) (18): The wet 2,2′-bisthiophene-5-boronic acid (**17**) of the previous reaction (≈23 mmol) was dissolved in THF (350 mL). A clear blue-green solution was obtained and 4-bromopyridine hydrochloride (5.4 g, 27.7 mmol), Pd(PPh$_3$)$_4$ (0.375 g, 0.325 mmol), aqueous Na_2CO_3 (135 mL, 1.9 M) and ethylene glycol (1.2 mL) were added. The two-phase system was refluxed in the dark for 12 h. The organic phase was evaporated on the rotary evaporator and then CH_2Cl_2 (370 mL) and H_2O (100 mL) were added. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 120 mL). The combined organic phases were dried (Na_2SO_4), filtered (paper) and concentrated to about 15 mL. Chromatography through silica with CH_2Cl_2/AcOEt (2:1 p.v.) gave 3.563 g (64%) of product. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.59$ (A of AA′BB′, J(app) = 6.2 Hz, 2H; 2″,6″-CH), 7.46 (B of AA′BB′, J(app) = 6.2 Hz, 2H; 3″,5″-CH), 7.43 (d, ^3J(H4,H3) = 4.0 Hz, 1H; 4-CH), 7.19 (d, ^3J(H3,H4) = 4.0 Hz, 1H; 3-CH), 7.23–7.29 (m, 2H; 3′,5′-CH), 7.06 (dd, ^3J(H4′,H3′) = 3.7 Hz, ^3J(H4′,H5′) = 5.0 Hz, 1H; 4′-CH); MS (CI, NH_3): *m/z* (%): 244 (100) [MH$^+$], 243 (72) [M^+]; $C_{13}H_9NS_2$ (243.3): calcd C 64.17, H 3.73, N 5.76; found C 64.01, H 3.97, N 5.57.

5′-Bromo-2,2′-bisthiophene-5-(pyridin-4′-yl) (19): 2,2′-Bisthiophene-5-(pyridin-4′-yl), (**18**, 1.113 g, 4.57 mmol) was dissolved in $CHCl_3$/AcOH (75 mL 1:1 p.v.). The clear orange solution was cooled to 0 °C. A solution of NBS (0.855 g, 4.8 mmol in 55 mL $CHCl_3$/AcOH 1:1 p.v.) was added dropwise over 35 min. Stirring at 0 °C was

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continued for 2 h and then for an additional 1.5 h at room temperature, followed by evaporation of the yellow, opalescent and strongly fluorescent solution (12 mmHg/60 °C). CH_2Cl_2 (300 mL), H_2O (150 mL) and aqueous Na_2CO_3 (1.9 M) were added to achieve pH > 8. Evaporation of the CH_2Cl_2 phase gave a yellow solid suspended in the aqueous phase. Filtration (G4) and washing with H_2O then Et_2O/hexane (1:1 p.v.) yielded 1.298 g (88%) of pure product. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.59 (A of AA'BB', J(app) = 6.2 Hz, 2H; 2",6"-CH), 7.44 (B of AA'BB', J(app) = 6.2 Hz, 2H; 3",5"-CH), 7.41 (d, ^3J(H4,H3) = 3.9 Hz, 1H; 4-CH), 7.13 (d, ^3J(H3,H4) = 3.9 Hz, 1H; 3-CH), 7.00 (two doublets, ^3J(H3',H4') = 3.9 Hz, 2H; 3',4'-CH); MS (CI, NH_3): m/z (%): 321/323 (83/100) [M^+], 322/324 (91/96) [MH^+], 241/243 (4/17) [M^+ − Br], 242/244 (14/16) [MH^+ − Br]; $C_{13}H_8NS_2Br$ (322.2): calcd C 48.46, H 2.50, N 4.35; found C 48.49, H 2.49, N 4.24.

2-*n*-Hexyl-3,5-dibromothiophene (6): 2-*n*-Hexylthiophene (**5**, 10.0 g, 59.5 mmol) was dissolved in $CHCl_3$/AcOH (42 mL, 1:1 p.v.). The light orange solution was cooled at 0 °C and a solution of Br_2 (7.7 mL, 148.75 mmol, in 20 mL $CHCl_3$/AcOH 1:1 p.v.) was added dropwise over 5 h. Stirring was continued at 0 °C for 2 h and then overnight at room temperature. $CHCl_3$ (20 mL) and H_2O (70 mL) were added to the dark brown solution. The phases were separated and the aqueous phase was extracted with $CHCl_3$ (2 × 25 mL). The combined $CHCl_3$ phases were washed with aqueous Na_2CO_3 until the pH was > 9 and then dried ($MgSO_4$). Filtration (paper) and removal of the solvent gave a red oil which was chromatographed through silica with hexane as eluent. Clear colourless oil, 10.65 g (55%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.86 (s, 1H; 3-CH), 0.90 (t, ^3J(Hα,Hβ) = 6.4 Hz, 3H; α-CH_3), 1.33 (m, 6H; β,γ,δ-CH_2), 1.62 (m, 2H; ε-CH_2), 2.72 (t, ^3J(Hζ,Hε) = 7.3 Hz, 2H; ζ-CH_2); MS (70 eV, EI): m/z (%): 324/326/328 (27/46/28) [M^+], 253/255/257 (62/100/64) [$C_5H_3Br_2^+$], 175/177 (34) [$C_5H_3Br^+$].

2-*n*-Hexyl-3-bromothiophene (7): 2-*n*-Hexyl-3,5-dibromothiophene (**6**, 3.008 g, 9.23 mmol) was dissolved in dry Et_2O (45 mL) under nitrogen. The clear colourless solution was cooled in an acetone/dry-ice bath (−78 °C). *n*-Butyllithium (9.7 mmol, 5.94 mL of 1.63 M solution in hexane) was added dropwise over 20 min and stirred at −78 °C for a further 20 min. MeOH (3.7 mL, 92.3 mmol) was added. The system was permitted to reach room temperature and H_2O (10 mL) was added. The phases were separated; the aqueous phase was extracted with Et_2O (2 × 10 mL), and the combined Et_2O phases were dried ($MgSO_4$) and filtered (paper). The solvent was removed with a rotary evaporator and the remaining orange oil was chromatographed through silica with hexane as eluent. The product was isolated as a pale yellow oil, 2.136 g (94%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.11 (d, ^3J(H5,H4) = 5.3 Hz, 1H; 5-CH), 6.92 (d, ^3J(H4,H5) = 5.3 Hz, 1H; 4-CH), 0.93 (t, ^3J(Hα,Hβ) = 6.3 Hz, 3H; α-CH_3), 1.36 (m, 6H; β,γ,δ-CH_2), 1.68 (m, 2H; ε-CH_2), 2.80 (t, ^3J(Hζ,Hε) = 7.8 Hz, 2H; ζ-CH_2); MS (70 eV, EI): m/z (%): 246/248 (26) [M^+], 175/177 (95/93) [$C_5H_4BrS^+$], 97 (100) [$C_5H_4S^+$].

1,2-Bis-(2'-*n*-hexylthiophen-3'-yl)-perfluorocyclopentene (8): 2-*n*-Hexyl-3-bromothiophene (**7**, 1.449 g, 5.87 mmol) was dissolved in anhydrous THF/pentane (8 mL, 1:5 p.v.) and the clear colourless solution was cooled in an acetone/dry-ice bath (−78 °C). *n*-Butyllithium (6.16 mmol, 3.85 mL of 1.6 M in hexane) was added dropwise over 15 min and stirred at −78 °C for an additional 15 min. Anhydrous THF (3.2 mL) was added to the clear orange solution and the colour turned to red. After 5 min, THF (3.2 mL) and octafluorocyclopentene (0.395 mL, 2.935 mmol) were added; stirring was continued for 1 h at −78 °C. The green-black turbid solution was removed from the cooling bath and left to reach room temperature; the solvent was evaporated and then CH_2Cl_2 (30 mL) and H_2O (8 mL) were added. The organic layer was separated, dried ($MgSO_4$) and filtered (paper). Evaporation of the solvent gave a green-brown oil, which was chromatographed through silica with hexane as eluent. 1.11 g (75%) of crude product (yellow oil) was obtained. ^{1}H NMR (200 MHz, $CDCl_3$) showed that this liquid contained product **8** (≈70%); the main impurity was 2-*n*-hexylthiophene, which could be removed under vacuum (110 °C/1 mmHg). The crude product (after removal of 2-*n*-hexylthiophene) was used in the next step without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.21 (d, ^3J(H5,H4) = 5.3 Hz, 1H; 5-CH), 7.07 (d, ^3J(H4,H5) = 5.3 Hz, 1H; 4-CH), 0.88 (t, ^3J(Hα,Hβ) = 6.9 Hz, 3H; α-CH_3), 1.29–1.17 (m, 8H; $\beta,\gamma,\delta,\varepsilon$-$CH_2$), 2.19 (t, ^3J(Hζ,Hε) = 6.9 Hz, 2H; ζ-CH_2); MS (70 eV, EI): m/z (%): 508 (15) [M^+], 423 (33) [$C_{19}H_{17}F_6S_2^+$].

1,2-Bis(2'-*n*-hexyl-5'-boronylthiophen-3'-yl)perfluorocyclopentene (9): 1,2-Bis-(2'-*n*-hexylthiophen-3'-yl)-perfluorocyclopentene (**8**, 0.165 g, 0.325 mmol) was dissolved in anhydrous Et_2O (2.0 mL, containing 112 μL, 0.747 mmol of TMEDA). To the clear pale yellow solution *n*-butyllithium (0.747 mmol, 0.467 mL of 1.6 M solution in hexane) was added dropwise over 10 min under nitrogen. Stirring at room temperature was continued for 20 min and then B(*n*OBu)$_3$ (0.300 mL, 1.105 mmol) was added in one portion. The red-brown solution was stirred for 1 h and then diluted with anhydrous THF (4 mL). This solution was used in the next reaction without any workup because boronic acid **9** is deboronized during isolation. As a solution **9** can be stored at −20 °C for at least two days without significant deboronization.

1,2-Bis(2'-*n*-hexyl-5'-(thiophen-2-yl)-thiophen-3'-yl)perfluorocyclopentene (10): 2-Bromothiophene (0.300 g, 1.84 mmol) was diluted with THF (50 mL). $Pd(PPh_3)_4$ (0.012 g, 0.0103 mmol), a few drops of ethylene glycol and aqueous Na_2CO_3 (2.4 mL, 1.9 M) were added and the two-phase system (liquid + solid) was refluxed. During this time **9** (0.325 mmol), prepared as a solution in the previous reaction, was added dropwise over 1 h [32] and refluxing was continued overnight. The solvent was evaporated and Et_2O and H_2O were added. The organic layer was separated, dried (Na_2SO_4) and filtered (paper). The residue was dissolved in hexane (≈2.5 mL) and was chromatographed through silica with the same eluent. A light greenish liquid was collected (≈0.150 g, ≈68%) that turned dark blue in light. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.11 (s, 1H; 4-CH), 7.13 (dd, ^3J(H3',H4') = 3.6 Hz, ^4J(H3',H5') = 1.1 Hz, 1H; 3'-CH), 7.23 (dd, ^3J(H5',H4') = 5.1 Hz, ^4J(H5',H3') = 1.1 Hz, 1H; 5'-CH), 7.01 (dd, ^3J(H4',H5') = 5.1 Hz, ^3J(H4',H3') = 3.6 Hz 1H; 4'-CH), 0.88 (t, ^3J(Hα,Hβ) = 6.4 Hz, 3H; α-CH_3), 1.12–1.27 (m, 8H; $\beta,\gamma,\delta,\varepsilon$-$CH_2$), 2.27 (t, ^3J(Hζ,Hε) = 6.8 Hz, 2H; ζ-CH_2); MS (CI, CH_4): m/z (%): 673 (100) [MH^+], 701 (37.2) [$C_{35}H_{39}S_4F_6^+$].

Boronic acid derivative 11: 1,2-Bis(2'-*n*-hexyl-5'-(thiophen-2-yl)-thiophen-3'-yl)perfluorocyclopentene (**10**, 0.104 g, 0.155 mmol) was dissolved in dry Et_2O (2 mL, containing 2.5 equiv of TMEDA). *n*-Butyllithium (0.352 mmol, 0.220 mL, 1.6 M in hexane) was added dropwise over 10 min under nitrogen. Stirring at room temperature was continued for 20 min, B(*n*OBu)$_3$ (0.150 mL, 0.558 mmol) was added, the solution was stirred for 30 min at room temperature and then diluted to 5.0 mL with THF. This solution was used without any workup because boronic acid **11** (like boronic acid **9**) is deboronized during isolation.

Compounds 1a, 2a, 3a: 2'-Bromodithieno[3,2-b:2',3'-d]thiophene-6-(pyridin-4'-yl) (**15**, 0.120 g, 0.334 mmol) (or 5'-bromo-2,2'-bisthiophene-5-(pyridin-4'-yl), **19**, for **2a** and **3a**) was dissolved in anhydrous THF (30 mL) under nitrogen. To the yellow solution $Pd(PPh_3)_4$ (0.008 g, 0.0067 mmol), ethylene glycol (8 drops as phase transfer catalyst) and aqueous Na_2CO_3 (2.0 mL, 1.9 M) were added and the solution was refluxed for 30 min. While refluxing under nitrogen the solution of **9** from the earlier reaction (or boronic acid **11** for **3a**) was added dropwise over 1 h [32], and refluxing was continued for 10 h in the dark. The organic solvents were removed with a rotary evaporator and then CH_2Cl_2 (100 mL) and H_2O (20 mL) were added. The phases were separated and the organic phase was dried (Na_2SO_4) and filtered (paper).

Compound 1a: Evaporation of the solvent gave a green solid, which was dissolved in CH_2Cl_2 and chromatographed through silica with CH_2Cl_2/MeOH (20:2 p.v.) as eluent. ≈100 mg of crude product [33] was obtained after evaporation of the eluent, which, after recrystalization from heptane and preparative thin-layer chromatography (silica) with CH_2Cl_2/MeOH (20:2 p.v.) as eluent, gave ≈57 mg (32%) of the closed form of the product. A higher yield could be obtained with purer starting material. ^{1}H NMR (200 MHz, $CDCl_3$) of the closed form: δ = 8.65 (A of AA'BB', J(app) = 6.1 Hz, 2H; 2",6"-CH), 7.51 (B of AA'BB', J(app) = 6.1Hz, 2H; 3",5"-CH), 7.73 (s, 1H; 5'-CH), 7.47 (s, 1H; 3'-CH), 6.54 (s, 1H; 4-CH), 0.83 (t, ^3J(Hα,Hβ) = 6.1 Hz, 3H; α-CH_3), 1.1–1.4 (m, 8H; $\beta,\gamma,\delta,\varepsilon$-$CH_2$), 2.44 (A of ABX_2 system, $^2J_{app}(H_A,H_B)$ = 11.3 Hz, 1H; ζ_A-CH_2), 2.91 (B of ABX_2 system, $^2J_{app}(H_B,H_A)$ = 11.3 Hz, 1H; ζ_B-CH_2); MS (35 keV, LSIMS): m/z (%): 1051.6 (100) [MH^+]; $C_{51}H_{40}N_2S_8F_6$ (1051.4): calcd C 58.26, H 3.83, N 2.66; found C 58.39, H 4.02, N 2.51.

Compound 2a: Evaporation of the solvent gave a green solid, which was dissolved in CH_2Cl_2 and chromatographed through silica with CH_2Cl_2/MeOH (20:2 p.v.) as eluent. **2a** was too soluble in heptane to permit recrystallization, therefore successive preparative thin-layer chromatography (silica) with the same eluent was performed in order to purify it (≈23–27%). A higher yield could be obtained from purer starting material. ^{1}H NMR (200 MHz, $CDCl_3$) of the closed form: δ = 8.62 (A of AA'BB', J(app) = 6.0 Hz, 2H; 2"",6""-CH), 7.46 (m, 3H; 3"",5"",4"-CH), 7.17–7.30 (m, 3H; 3", 4', 3'-CH), 6.47 (s, 1H; 4-CH), 0.84 (t, ^3J(Hα,Hβ) = 6.1 Hz, 3H; α-CH_3), 1.0–1.5 (m, 8H; $\beta,\gamma,\delta,\varepsilon$-$CH_2$), 2.40 (A of ABX_2 system, $^2J_{app}(H_A,H_B)$ = 12.0 Hz, 1H; ζ_A-CH_2), 2.89 (B of ABX_2 system $^2J_{app}(H_B,H_A)$ = 12.0 Hz, 1H; ζ_B-CH_2); MS (35 keV, LSIMS): m/z (%): 992 (37) [MH^+]; $C_{51}H_{44}N_2S_6F_6$ (991.3): calcd C 61.80, H 4.47, N 2.83; found C 61.61, H 4.61, N 2.69.

Compound 3a: The solvent was evaporated and Et_2O was added. The green suspension was filtered (G4) and the yellow solid was washed with Et_2O and dried in the dark (20–30%). The compound (especially the open form) was much less soluble than **1a** and **2a**. ^{1}H NMR (200 MHz, $CDCl_3$) of the closed form: δ = 8.61 (A of AA'BB', J(app) = 6.1 Hz, 2H; 2"",6""-CH), 7.45 (m, 3H; 3"",5"",4""-CH), 7.15–7.30 (m, 5H; 3"", 4", 3",3',4'-CH), 6.46 (s, 1H; 4-CH), 0.84 (m, 3H; α-CH_3), 1.0–1.5 (m, 8H; $\beta,\gamma,\delta,\varepsilon$-$CH_2$), 2.40 (A of ABX_2 system, $^2J_{app}(H_A,H_B)$ = 12.3 Hz, 1H; ζ_A-CH_2), 2.88 (B of ABX_2 system, $^2J_{app}(H_B,H_A)$ = 12.3 Hz, 1H; ζ_B-CH_2); MS (35 keV, LSIMS): m/z (%): 1155 (100) [MH^+].

Compounds 1b and 2b: The product of the reaction described above, **1a** (0.020 g, 0.019 mmol) (or **2a** for **2b**), was dissolved in dry CH_2Cl_2 (7.5 mL). To the clear dark green solution $CF_3SO_3CH_3$ (6.0 μL, 0.0438 mmol) was added and the system was stirred in the dark and under nitrogen for 1 h while a green-black suspension formed. The suspension was filtered (G4) and the precipitate was washed many times with CH_2Cl_2 ($CHCl_3$ in the case of **2b**). The solid was dried at 0.1 mmHg over P_2O_5 for a few hours in the dark.

Compound 1b: 0.021 g (80%) of product. ^{1}H NMR (200 MHz, CD_3CN) of the closed form: δ = 8.53 (A of AA'BB', J(app) = 6.7 Hz, 2H; 2″,6″-CH), 8.12 (B of AA'BB', J(app) = 6.7 Hz, 2H; 3″,5″-CH), 8.30 (s, 1H; 5′-CH), 7.77 (s, 1H; 3′-CH), 6.80 (s, 1H; 4-CH), 4.27 (s, 3H; N-CH_3), 0.88 (m, 3H; α-CH_3), 1.2–1.7 (m, 8H; β,γ,δ,ε-CH_2), 2.58 (A of ABX_2 system, $^2J_{app}(H_A,H_B)$ = 9.8 Hz, 1H; ζ_A-CH_2), 3.05 (B of ABX_2 system, $^2J_{app}(H_B,H_A)$ = 9.8 Hz, 1H; ζ_B-CH_2); MS (35 keV, LSIMS): *m/z* (%): 1229 (5) $[C_{54}H_{46}N_2O_3S_9F_9^+]$, 1080 (15) $[C_{53}H_{46}N_2S_8F_9^+]$; $C_{55}H_{46}N_2S_{10}F_{12}O_6$ (1379.6): calcd C 47.9, H 3.4, N 2.0; found C 46.64, H 3.33, N 2.17.

Compound 2b: 0.0227 g (85%) of product. ^{1}H NMR (200 MHz, CD_3CN) of the closed form: δ = 8.52 (A of AA'BB', J(app) = 7.0 Hz, 2H; 2‴,6‴-CH), 8.11 (B of AA'BB', J(app) = 7.0 Hz, 2H; 3‴,5‴-CH), 8.02 (d, ^3J(H4″,H3″) = 4.1 Hz, 1H; 4″-CH), 7.4–7.7 (m, 3H; 3″,4′,3′-CH), 6.74 (s, 1H; 4-CH), 4.25 (s, 3H; N-CH_3), 0.89 (m, 3H; α-CH_3), 1.2–1.6 (m, 8H; β,γ,δ,ε-CH_2), 2.51 (A of ABX_2 system, $^2J_{app}(H_A,H_B)$ = 12.1 Hz, 1H; ζ_A-CH_2), 3.00 (B of ABX_2 system, $^2J_{app}(H_B,H_A)$ = 12.1 Hz, 1H; ζ_B-CH_2); MS (35 keV, LSIMS): *m/z* (%): 1169 (5) $[C_{54}H_{50}N_2O_3S_7F_9^+]$, 1021 (11) $[C_{53}H_{50}N_2S_6F_9^+]$; $C_{55}H_{50}N_2S_8F_{12}O_6$ (1319.5): calcd C 50.07, H 3.82, N 2.12; found C 48.25, H 3.77, N 2.07.
Although satisfactory microanalytical data were not obtained for **1b** and **2b**, these compounds were pure according to the ^{1}H NMR data.

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[20] Differences in UV/vis electronic absorption λ_{max} values (nm) between compounds bearing a methyl (Fig. 1, R = methyl, $R^1 = R^3$ = hydrogen) and a hexyl group (Fig. 1, R = hexyl, $R^1 = R^3$ = hydrogen) are shown in Table 5.

Table 5. Differences in UV/vis electronic absorption λ_{max} values (nm) between compounds bearing a methyl and a hexyl group.

Compound R^2, R^4	R	Solvent	λ_{max} open form (A)	λ_{max} closed form (B)	Separation (nm)
H	CH_3	nC_6H_{12}	230	510	280
H	C_6H_{13}	nC_6H_{12}	231	536	305
pyridine	CH_3	C_6H_6	300	592	292
pyridine	C_6H_{13}	C_6H_6	302	620	318
pyridinium	CH_3	CH_3CN	352	662	310
pyridinium	C_6H_{13}	CH_3CN	356	688	332

[21] A 300 W tungsten lamp with a cut-off filter was used. Characteristics of the cut-off filter: $\lambda > 620$ nm, transmittance = 83%; $\lambda < 585$ nm, transmittance < 1%.
[22] A 300 W tungsten lamp with a window filter was used. Characteristics of the window filter: 425–475 nm, transmittance = 68%; $\lambda < 400$ nm and $\lambda > 500$ nm, transmittance < 3%.
[23] Standard UV lamps of the same total power of 6 W were used for visualizing TLC plates. In the case of compound **1b** the monochromator of a fluorimeter was also used and irradiation at different wavelengths gave similar results (see ref. [13]).
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[31] Attempts to dry compound **13** led to loss of the boronic acid group.
[32] Since boronic acid **9** is very unstable, the addition of the solution must be carried out from the top of the condenser directly into the solution (to avoid warming the boronic acid before it reaches the reaction medium) and at a low addition rate (1–2 h).
[33] A compound containing phenyl groups seems to be the main impurity. This by-product may arise from the coupling between phenyl groups and the boronic derivative, since it is known that phenyl groups from PPh_3 can combine with boronic acids under these reaction conditions (E. M. Campi, W. R. Jackson, S. M. Marcuccio, C. G. M. Naeslund, *J. Chem. Soc. Chem. Commun.* **1994**, 2395–2395).