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Synthesis and characterisation of 1,2-difluoro-1,2-bis(5-trimethylsilyl-2-thienyl)ethenes. A new family of conjugated monomers for oxidative polymerisation

Luca Albertin,[a] Chiara Bertarelli,[a] Maria C. Gallazzi,*[a] Stefano V. Meille[a] and Silvia C. Capelli[b]

[a] *Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy*
[b] *Swiss-Norvegian Beam Lines, European Synchrotron Radiation Facility - BP 220, 6 rue Jules Horowitz, 38043 Grenoble Cedex, France*

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The synthesis of a series of (E)-1,2-difluoro-1,2-bis(2-thienyl)ethenes (DFDTEs) by low temperature reaction of 2-lithiothiophenes with tetrafluoroethene (TFE) is described. A possible explanation of the mechanism leading to the formation of higher oligomers is also elucidated together with the use of TMS as protecting group to prevent it. All compounds are thoroughly characterised and their E – configuration proved by vibrational spectroscopy. The crystal structure at 120 K of a representative system evidences its essential planarity and suggests significant delocalisation of π-electrons. Fluorine atoms are involved both in short intra- and intermolecular interactions with sulfur atoms and hydrogen atoms, apparently stabilising the planar molecular arrangement.

Introduction

Poly[(E)-1,2-bis(2-thienyl)ethenes] (PDTEs) have been investigated by various authors because of their reduced energy gap (E_g) (*i.e.* the energy difference between the HOMO and LUMO), if compared to the parent polythiophenes, and because of the possibility of preparing them by facile oxidative polymerisation of (E)-1,2-bis(2-thienyl)ethene monomers by chemical or electrochemical means. Because low energy gap polymers are in demand for their intrinsic conductivity and third order non-linear optical properties, to further reduce the E_g value of the PDTEs obtained, up to now three main strategies have been followed:

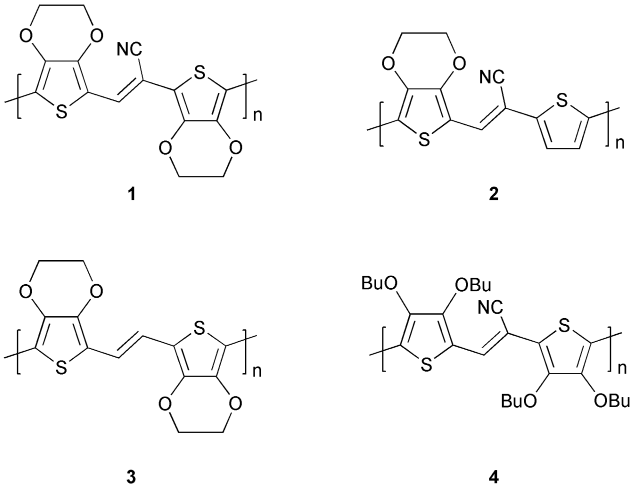
1 introduction of electron donating or electron withdrawing substituents on the polymer main chain;[1,2]

2 a regular alternation of electron donating and electron withdrawing substituents on the polymer main chain;[3]

3 stiffening of the monomer unit around the vinylene linkage.[4]

The second approach belongs to the general donor-acceptor strategy to low band gap polymers and, in the case of PDTEs, was implemented by Sotzing *et al.*[1] through the alternation of ethylenedioxy-substituted thiophene rings and cyano-substituted ethene units. Scheme 1 summarises the PDTEs, with the lowest band gaps reported in the literature: as shown, the cyano group is the only electron withdrawing substituent used up to now. In fact, this is one of the few groups that can be introduced on the ethene double bond of a poly[(arylene-2,5-diyl)ethene] system without producing a major distortion of its planar conformation; more sterically demanding substituents have been shown in some cases to dramatically decrease the conjugation degree[5] of the polymer distorting the macromolecular chain around the arylene–ethene single bond. Furthermore, cyanoethene units are readily obtained by the Knoevenagel condensation of an aryl-aldehyde with aryl-acetonitrile.

Searching new electron-withdrawing groups for PDTE systems, we addressed the possibility of introducing fluorine atoms on the vinylene linkage between two subsequent thiophene rings. The idea stemmed from the simple consideration that fluorine is the most electronegative element of the periodic table and its covalent radius (0.72 Å) is quite small, even compared to that of carbon atoms (0.77 Å), so that no steric drive to major distortions of the planar π-system is foreseen. In 1956, Dixon, a researcher at the Jackson Laboratory of the then E. I. du Pont de Nemours and Co., reported the preparation of a wide range of fluorinated olefin derivatives through low temperature reaction of aromatic and aliphatic lithium derivatives with fluoroolefins;[6] among others, three 1,2-difluoro-1,2-bis(2-aryl)-ethenes were described (Scheme 2). Unfortunately, the article provides scarce experimental details and only outlines a general synthetic procedure for all the compounds prepared. Moreover nothing is said about the *cis*- or *trans*- configuration of the 1,2-difluoro-1,2-bis(2-aryl)ethenes obtained.



Polymer	1	2	3	4
Energy Gap/eV	1.1	1.3	1.4	1.7

Scheme 1 Repeating units and E_g of the lowest band gap PDTEs reported in the literature.

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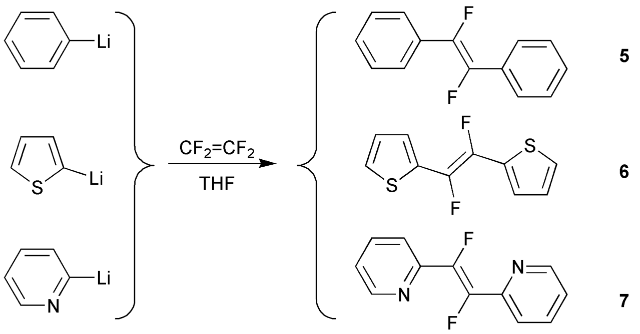


Compound	5	6	7
Yield (%)	50	30	10
Mp/°C	74	98	91

Scheme 2 Synthesis of three 1,2-difluoro-1,2-diarylethenes as reported by Dixon.[6]

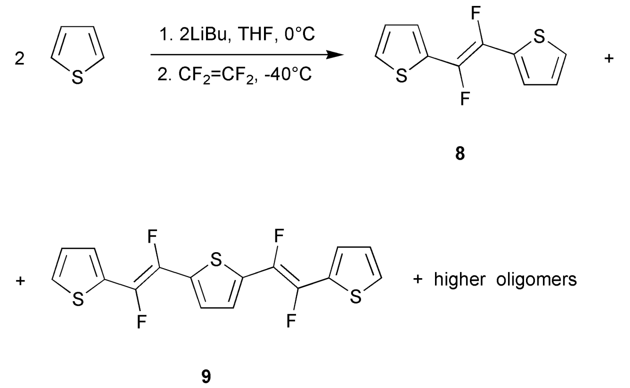
In the present work we provide a detailed description of the synthesis and the characterisation of a series of (*E*)-1,2-difluoro-1,2-bis(2-thienyl)ethenes (DFDTEs) by low temperature reactions of 2-lithiothiophenes with tetrafluoroethene (TFE). We also report the low temperature crystal structure and discuss the solid state organisation of a representative system. Spectroscopic and structural data pertaining to these molecules provide a unique insight into the effect of fluorination of the ethene double bond on the chemical, optical and electronic properties of 1,2-bis(2-aryl)ethenes such as PDTEs. The interest of these systems is heightened by their potential as monomers for oxidative polymerisation to give poly[(*E*)-1,2-difluoro-1,2-bis(2-thienyl)ethenes]. The synthetic method outlined can also be extended, by changing the stoichiometry, to the one pot synthesis of 1,2-difluoro-2-thienylethene oligomers or polymers.

Results and discussion

A first attempt was made to prepare alkoxy-substitued DFDTEs by reacting 2 equivalents of the lithium derivatives of the alkoxythiophenes with TFE according to the procedure described in the literature.[6] We used two alkoxy derivatives namely a methoxy and an octyloxythiophene; the lithium derivatives were prepared using LDA at −78 °C and butyllithium at 0 °C to room temperature in THF, in order to obtain the desired regiochemistry: 2-lithium-4-alkoxy and 2-lithium-3-alkoxythiophene respectively. In all cases, the gross product was a red pitch from which we were unable to isolate the expected compounds even after repeated flash chromatographic purification. TLC analysis showed that we had indeed obtained a complicated mixture of compounds, suggested by UV-vis absorption spectra to be higher oligomers (λ_{max}($CHCl_3$)/nm 430–450). Faced with these problems, we decided to repeat the synthesis starting from thiophene itself, attempting to reproduce Dixon's work with respect to this etherocycle (Scheme 3). The result was similar to our previous results, but in this case we were able to isolate both the expected product **8** and one of its higher analogues **9** as yellow solids. Yields of pure compounds were quite low (9% and 4% respectively). Under these conditions the reaction clearly does not stop at the stoichiometric product. On the other hand, the same experiment carried out at lower temperatures did not proceed at all, in agreement with observations reported by Starostina *et al.*[7,8]

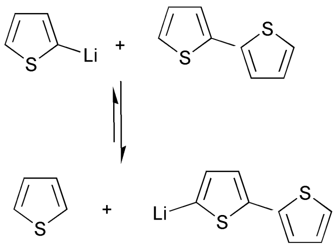
A thorough analysis of all available information lead us to formulate the following hypothesis on the reaction mechanism:

I. In a broad perspective, the lithiation process can be considered an acid-base reaction in which the strongest acid (*i.e.* the substrate) displaces the weakest acid from its salt (*i.e.* the lithiating agent).



Scheme 3 Synthesis of 1,2-difluoro-1,2-dithienylethenes following the experimental conditions reported by Dixon.[6]

II. It is known from the literature that α-protons of oligothiophenes are more acidic than the α-protons of the corresponding monomers. For instance, in the synthesis of 2,2′-bithiophene by oxidative coupling of 2-lithiothiophene the equilibrium in Scheme 4 takes place and the formation of higher oligomers is observed.[9]



Scheme 4 Equilibrium reactions during the oxidative coupling of 2-lithiothiophene.

III. In the reaction of 2-lithiothiophene derivatives with TFE, the resulting product bears a fluoroethene group in the 2-position with respect to the 5-α-proton of the thiophene ring. Under our working hypothesis (*i.e.* exploiting the electronegativity of fluorine atoms), this group should withdraw electrons from thiophene thus increasing the acidity of its α-proton. This hypothesis is also confirmed by the low field 0.2 ppm shift of the 5-proton of 2-thienyltrifluoroethene (isolated as an intermediate of the reaction) with respect to the starting thiophene unit. As a result, the unreacted 2-lithiothiophene derivatives present in the reaction mixture could favourably exchange lithium with the formed compounds, leading to a chain lengthening irrespective of the starting stoichiometric ratios (Scheme 5).

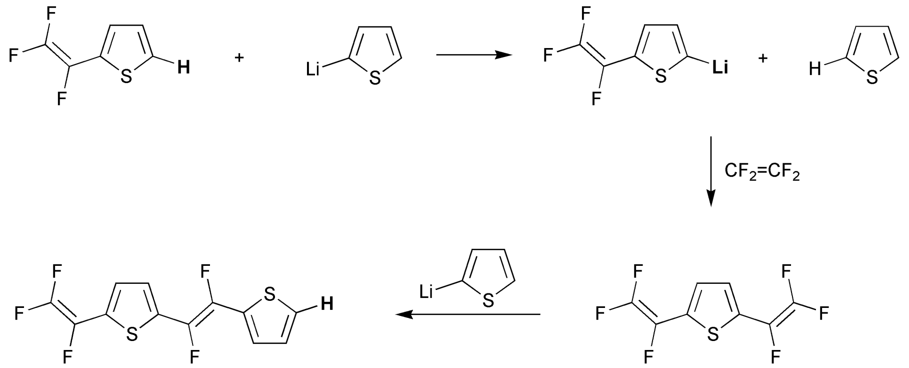
If this explanation is correct, the same experiment carried out on an α-capped thiophene compound would afford a higher yield of the (*E*)-1,2-difluoro-1,2-bis(2-thienyl)ethene derivative and no higher oligomers, since the product would be unable to exchange lithium with the unreacted lithiothiophene molecules at any stage of the reaction. We thus performed a synthesis analogous to those in Scheme 3 but starting from 2-methylthiophene (Scheme 6): after flash-chromatographic purification and recrystallisation from petroleum ether pure compound **11** was obtained in a 43% yield. Furthermore, parallel TLC analysis of **11** and of the gross product showed the former as being the main product of only two products, the other one most probably being the *cis*-isomer.

In accordance with the results reported above, we addressed the possibility of using a protective group for one of the two α positions of the thiophene ring in order to prepare alkyl and alkoxy substituted (*E*)-1,2-difluoro-1,2-bis(2-thienyl)ethene in higher yields. The trimethylsilyl (TMS) group was chosen since it can be easily and selectively introduced and removed from the thiophene ring and is claimed to favour the oxidative

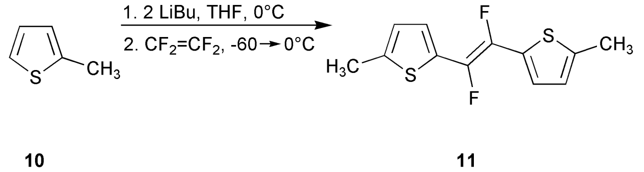
Table 1 Yields, melting points and UV-vis absorption spectra data of compounds **8**, **9**, **11** and **14(a–c)** in $CHCl_3$ solution. Commercial (Aldrich) 1,2-bis(2-thienyl)ethene (DTE) reported for comparison. Notation (sh) means shoulder

			UV-vis	
Compound	Yield (%)	Mp/°C[a]	λ	$\varepsilon(\lambda_{max})$
DTE	—	132	338	25000
8	9	90	318, 332, 352	36000 (332)
9	4	160	374, 396, 420	62000 (396)
11	43	79	328, 344, 362	39000 (344)
14a	31	105	332, 348, 368	49500 (348)
14b	8	120	353 (sh), 370, 388	31600 (370)
14c	20	72	327, 352 (sh), 372 (sh)	20000 (327)

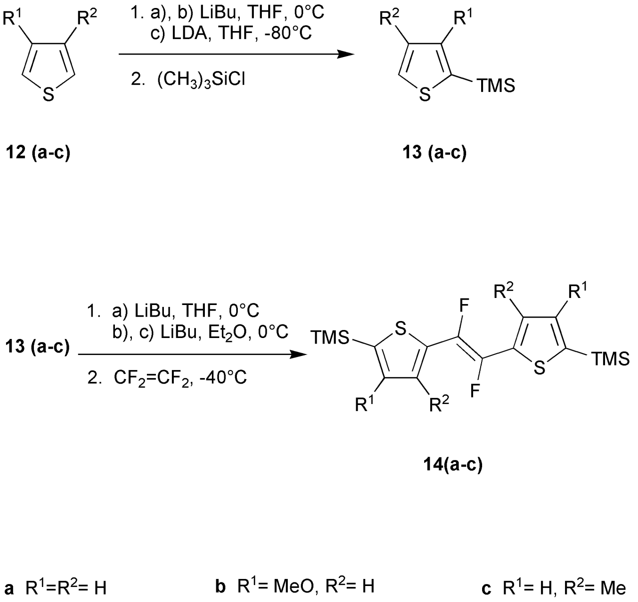
[a] Determined as onset by differential scanning calorimetry (DSC).



Scheme 5 Proposed mechanism for the formation of higher oligomers in the reaction between 2-lithiothiophene derivatives and TFE.



Scheme 6 Synthesis of (*E*)-1,2-difluoro-1,2-bis(5-methyl-2-thienyl)-ethene.



Scheme 7 Trimethylsilyl protection in the synthesis of (*E*)-1,2-difluoro-1,2-dithienylethenes.

polymerisation of the final compounds.[10-19] TMS protected thiophene derivatives **13(a–c)** were thus prepared by the lithiation of thiophene compounds **12(a–c)** followed by quenching with trimethylsilyl chloride (Scheme 7). After distillation under reduced pressure, all the products were isolated in high yields. Further reaction with butyllithium (BuLi) followed by addition of TFE in a 2 : 1 ratio, purification by flash chromatography and recrystallisation from petroleum ether afforded pure **14** as a yellow solid. In the case of unsubstituted thiophene **13a**, protection of one of the α positions with TMS resulted in a three-fold increase (from 9% to 31%) of the reaction yield. The same protective group allowed us to isolate a β-methoxy (**14b**) and a β-methyl (**14c**) substituted DFDTE though with lower yields and in the presence of some by-products, as shown by the TLC analysis of the gross products. Two of the by-products of **14b** and **14c**, even if present in small amounts were isolated and characterised as the *cis* isomer and the monosubstituted trifluoroethene. Even taking into consideration the difficulty in measuring accurately the volume of TFE actually introduced into the reaction mixture, these data suggest that the presence of other substituents at the β position of the thiophene ring decreases the effectiveness of TMS as a protecting group. Since it is known that trimethylsilyl bonds are easily cleaved by a fluorine ion because of the high affinity that fluorine has for silicon and the strength of the Si–F bond, we performed the reactions in diethyl ether instead of THF in order to reduce the concentration of fluorine ions in solution derived from the presence of the by-product LiF.

Table 1 summarises the yields, melting points, and UV-vis absorption data of compounds **8**, **9**, **11** and **14**. For the sake of comparison, the same data for (*E*)-1,2-bis(2-thienyl)ethene (DTE), *i.e.* the non-fluorinated analogues of **8**, are also reported. ^1H, ^{13}C and ^{19}F NMR, IR and Raman characterisation are reported in the Experimental section.

All spectroscopic data are consistent with the expected structures and vibrational spectra clearly indicate that the configuration of all the compounds is *trans*. In fact, in all cases the C=C stretching of the ethene double bond is Raman active but not IR active, as is the case for symmetrically substituted bonds. The most intense band in the Raman spectra pertain to the double bonds collective skeletal motion frequently called Я mode[20] between 1400 and 1450 cm^{-1}. Furthermore all fluorinated products have C=C stretching frequencies of the ethene double bond 13–48 cm^{-1} higher than for DTE. In the IR spectra, the C–F symmetric stretching band can be seen around 1100–1130 cm^{-1}.

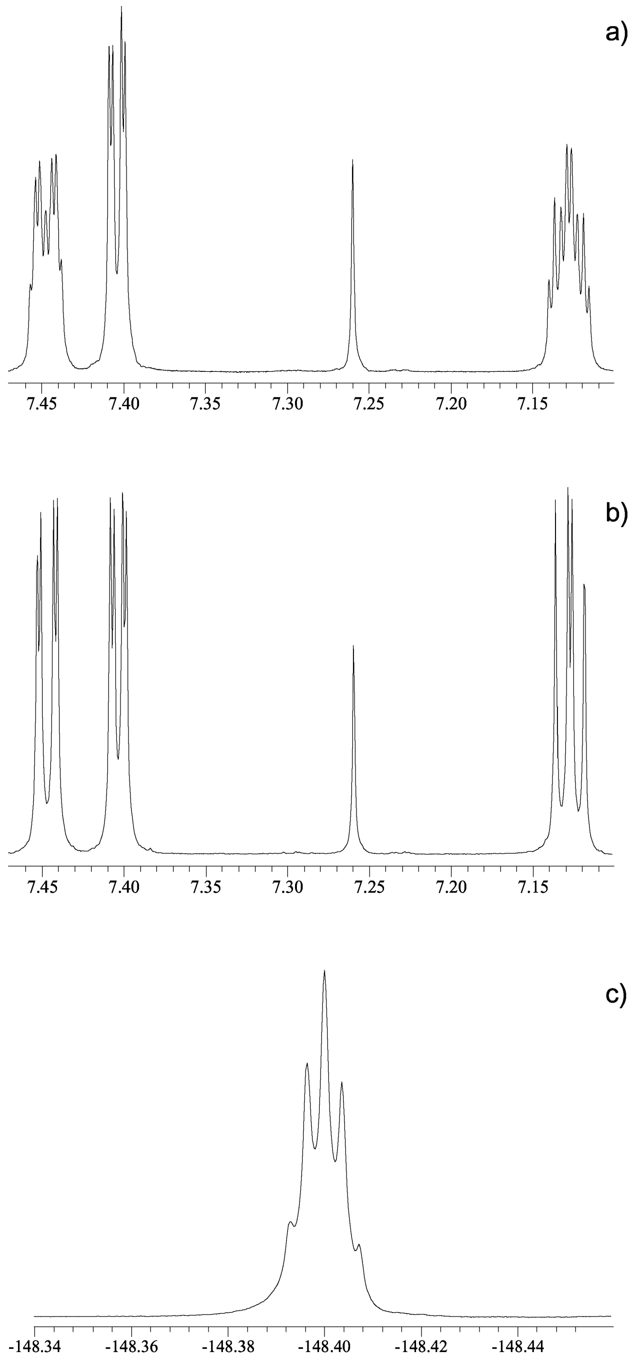


Fig. 1 NMR spectra ($CDCl_3$) of **8**: ^1H-NMR (a), ^1H-NMR, ^{19}F broad decoupling (b), ^{19}F-NMR, ^1H coupled (c).

For the correct interpretation of the ^1H-NMR spectra, decoupling from ^{19}F nuclei was necessary, the later causing a splitting of the signals with a $J_{H,F}$ of about 1.7 Hz.

As a representative example of the NMR characterisation, the spectra of compound **8** are reported in Fig. 1. The comparison of ^1H spectra (Fig. 1a and 1b) shows that proton 3 does not couple with fluorine while protons 4 and 5 are coupled with both fluorine atoms with the same coupling constant (J = 1.7 Hz). The quintet in the ^{19}F spectrum can be explained considering the coupling of fluorine with protons 4, 5, 4′ and 5′ with the same coupling constant. A comparison of the chemical shifts of the aromatic protons of DTE and of **8** show the latter as being shifted towards lower magnetic fields of 0.12–0.34 ppm, depending on the position. This effect is distinctive of an electron-withdrawing group and can also be observed for **9** and **14a** while in **14b** and **14c** it is partially counterbalanced by the presence of the electron-donating β-methoxy and -methyl substituents. The aromatic protons of compound **11**, instead, are shielded by 0.25–0.35 ppm with respect to **8** and a coupling constant of 1.1 Hz can be observed between the methyl protons and C(4)H. A strong hyperconjugation between the α-methyl substituents and the π electrons can thus be inferred. Comparison of the UV-vis spectra of (*E*)-1,2-bis(2-thienyl)ethene and **8** shows the latter as having an absorption band much better resolved in its vibrational components. A similar vibronic structure is also observed in compounds **9**, **11**, **14a** and, to a lesser degree, in **14b**. On the contrary, **14c** presents a quite different spectrum with a single broad absorption with a maximum at 327 nm and two shoulders at 352 and 372 nm. UV-vis spectra of **8**, **14a** and **14b** are reported in Fig. 2.

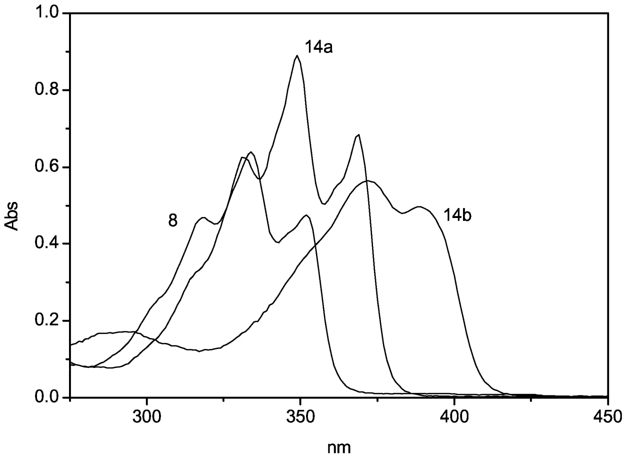


Fig. 2 UV-vis spectra in $CHCl_3$ of **8**, **14a** and **14b**.

To improve our understanding of the effect of 1,2 fluorine substitution on conjugated double bonds in (*E*)-1,2-bis(2-thienyl)ethenes a single crystal X-ray diffraction study of **14b** was carried out. Because crystals were very small and highly unstable in the beam, data had to be acquired at low temperature (120 K) using synchrotron radiation at ESRF. A view of the molecular structure of **14b** is shown in Fig. 3 and selected molecular dimensions are reported in Table 2. The *trans*-ethene system is very close to planarity, as apparent from the torsion angles in Table 2, and has a crystallographic inversion centre at its midpoint. The atomic displacement parameters of C(1) and F(1) are small and closely comparable to those of the thiophene ring atoms. This fact implies the absence of significant torsional disorder along the C(2)–C(1) bond, of the kind found, especially at room temperature, in some molecules of the (*E*)-

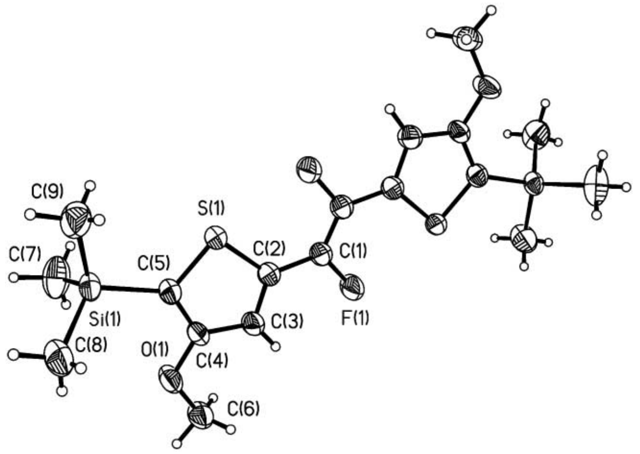


Fig. 3 A view of molecule **19b** at 120 K, with atomic displacement parameters drawn at 90% probability level with the labelling used in the text. The molecule has a crystallographic inversion centre at the midpoint of the ethene double bond while symmetry related atoms are primed in the text and in Table 2.

Table 2 Selected molecular dimensions of **14b**

Bond lengths (Å)	
S(1)–C(5)	1.7189(15)
S(1)–C(2)	1.7253(15)
F(1)–C(1)	1.3492(17)
O(1)–C(4)	1.3614(17)
C(2)–C(3)	1.378(2)
C(2)–C(1)	1.4402(19)
C(1)–C(1)′	1.341(3)
C(5)–C(4)	1.379(2)
C(3)–C(4)	1.4208(19)
Bond angles (°)	
C(5)–S(1)–C(2)	93.36(7)
C(4)–O(1)–C(6)	116.23(12)
C(3)–C(2)–C(1)	124.84(13)
C(3)–C(2)–S(1)	111.08(11)
C(1)–C(2)–S(1)	124.05(11)
C(1)′–C(1)–F(1)	115.91(16)
C(1)′–C(1)–C(2)	129.68(17)
F(1)–C(1)–C(2)	114.41(12)
C(4)–C(5)–S(1)	109.20(11)
C(2)–C(3)–C(4)	111.37(13)
C(5)–C(4)–C(3)	114.99(13)
O(1)–C(4)–C(5)	119.22(13)
O(1)–C(4)–C(3)	125.78(13)
C(4)–C(5)–Si(1)	128.80(11)
S(1)–C(5)–Si(1)	122.00(8)
Torsion angles (°)	
C(5)–S(1)–C(2)–C(1)	−177.49(13)
C(3)–C(2)–C(1)–C(1)′	−177.4(2)
S(1)–C(2)–C(1)–C(1)′	0.5(3)
C(3)–C(2)–C(1)–F(1)	1.4(2)
C(6)–O(1)–C(4)–C(3)	−3.6(2)

stilbene family.[21,22] Accordingly the bond lengths in the crystal structure of **14b** are expected to be accurate. The C(1)–C(1)′ bond measures 1.341(3) Å and is at the upper end of values found in (*E*) and (*Z*)-difluoro substituted, alternated double bonds: for tetrafluoro-*p*-benzoquinone (at 113 K) a value of 1.339(2) Å was reported,[23] 1.333(2) and 1.307(9) for potassium hydrogen difluorofumarate (at 123 K) and maleate (at rt) respectively,[24] while values between 1.329(5) and 1.315(3) Å, depending essentially on the degree of conjugation and the deviations from planarity, have been reported at rt for two α,ω-diarylperfluoropolyenes.[25,26] Electron diffraction studies[27] of (*E*)- and (*Z*)-difluoroethenes give C=C double bond values of 1.331(4) and 1.329(4) Å, to be compared with 1.331(1) and 1.311(3) Å for monofluoroethene and tetrafluoroethene. In **14b** the length of the C(1)–C(2) bond, adjacent to the double bond is 1.440(2) Å: it is at the lower end of values of corresponding bond lengths in conjugated 1,2 difluorinated systems. In the case of tetrafluoro-*p*-benzoquinone we have 1.475 (2) Å,[23] 1.499(1) Å for the planar potassium hydrogen difluoromaleate and 1.502(6) Å for the corresponding non-planar fumarate.[24] Values between 1.455(3) and 1.431(5) Å, depending upon the degree of conjugation and the deviations from planarity are found in the two cited α,ω-diarylperfluoropolyenes.[25,26] Note that in low temperature crystal structures of non-fluorinated stilbenes, bonds adjacent to the central double bond measure typically between 1.479(1) and 1.472(1) Å[21,22] while the only crystal structure of a vinylene thiophene has a value of 1.445(5) Å.[28] Inter-ring C–C bond lengths of 1.454(4) and 1.467(5) Å, respectively, have been reported[28] for coplanar 3,3′- and 4,4′-dipentoxy-2,2′-bithiophenes. All these data give a subtle but consistent picture confirming that in **14b** the difluorovinylene system is significantly conjugated. Consistent with gas-phase electron diffraction data on fluorinated ethenes, the tendency of fluorine substitution to shorten double bonds[27,30] is hardly relevant in the present case: note that the average length of alternated double and single bonds in hydrocarbon multiply conjugated systems are 1.345 and 1.443 Å respectively.[31]

Irrespective of the dissymmetric substitution pattern, endocyclic thiophene bond lengths are quite symmetric and closely correspond with the expected values. The bond angle at the oxygen substituted C(4) atom is nearly 4 degrees larger than all the other intraannular bond angles, consistent with the expected substituent effects.[29,32] A similar but much larger widening occurs at the fluorine substituted C(1) atom, the C(2)–C(1)–C(1)′ bond angle measuring 129.7(2)° as compared to angles C(2)–C(1)–F(1) and F(1)–C(1)–C(1)′ which are 114.4(1)° and 115.9(2)° respectively. Comparable values of 127.7(7)° and 129.2(9)° respectively of the H–C–C bond angles at fluorine substituted carbons have been reported in gas-phase electron diffraction studies of mono and *trans*-difluoroethene.[27] At fluorine substituted C–C–C bond angles, values ranging from 127.2(3) to 132.6(2)° result also in α,ω-diarylperfluoropolyenes[25,26] while 131.4(1) and 127.7(4)° were found in potassium hydrogen difluoromaleate and fumarate.[24] The widening of this angle in fluorinated conjugated systems needs further investigation; we suggest that steric factors are likely to play some role, especially determining the larger values, while electronic effects may well be dominant in most other cases.

The torsion angles in Table 2 show that, with the obvious exception of the trimethylsilyl groups, the molecule is closely planar and even the methoxy group, which shows the largest deviation, is only 4° away from coplanarity with the conjugated system [C(6)–O(1)–C(4)–C(5) = 176.1(2)°]. The angle between the central ethene and the thiophene planes is roughly 2° as compared to *ca.* 18° found at 118 K in (*E*)-stilbene.[21,22]

The planar conformation of **14b** appears to be favoured by weak interactions[33] involving the fluorine atoms. The distances from F(1) to H(3), the hydrogen atom on C(3), and to S(1)′ are 2.547 and 2.831(2) Å respectively, amounting to about 0.1 and 0.5 Å less than the sum of Van der Waals radii (1.20, 1.47 and 1.80 Å for H, F and S). The F ··· S distance is identical to the shorter O ··· S interactions (2.835(2) Å) found in planar 3,3′-dialkoxy-2,2′-bithiophene.[29] The angles C(1)–C(2)–C(3) and C(1)–C(2)–S(1) are 124.8(1)° and 124.1(1)°, suggesting the more favourable nature of the F ··· S interaction as compared to the H ··· F interaction. An additional short intermolecular contact involving F(1) and one of the trimethylsilyl group hydrogens [H(9A)″ ··· F(1) = 2.477 Å] is likely to play a stabilising role in the packing.

Conclusions

In this paper we present effective synthetic routes to 1,2-difluoro-1,2-bis(2-thienyl)ethenes along with their spectroscopic and structural characterisation. It was demonstrated that protection of the α position of the thiophene units greatly enhanced the reaction yield, suppressing H–Li exchange in the intermediate products. If unprotected thiophene units were used with a 1 : 1 stoicheometry between the Li derivative and TFE, longer oligomers or polymers could be obtained. One short oligomer **9** was isolated and characterised. Fluorine substitution appears to be compatible with significant π-delocalisation and favours the planarity of the systems. The crystal structure of derivative **14b** shows intramolecular interactions which may play a role stabilising planar arrangements: they involve the fluorine atoms and both the hydrogen and the sulfur atoms on adjacent thiophenes. Dynamic torsional disordering of the kind observed in (*E*)-stilbenes is virtually absent in our systems at 120 K. Comparative bond length examination suggests that effective conjugation occurs: the C–C bonds adjacent to the difluorinated double bond are in fact quite short, while the ethene bond in the fluorinated system seems marginally shorter than in non-fluorinated conjugated systems, consistent with the higher C=C stretching frequency determined in fluorinated systems. In **14b** it is on the other hand significantly longer than in most 1,2-difluorinated ethene moieties. The observed features relate the modest steric requirements of the fluorine substituent to the fact that its strong σ-acceptor properties are complemented by significant π-donor abilities. Rather small effects on bond lengths result while large effects can be expected on charge mobility. Synthesis, characterisation and potential applications of polymers based on the building blocks described herein, have been discussed elsewhere.[34]

Experimental

General methods

All reactions were carried out under an inert atmosphere of argon and in anhydrous conditions. Reaction solvents were dried by distillation over a K–Na alloy while reagents were dried overnight on 4 Å molecular sieves. Trimethylsilyl chloride and TFE were used as received and the required amount of gas calculated according to the equation of state for a perfect gas. TFE solutions were prepared by dissolving the gas in the reaction solvent at −80 °C (bp of TFE −75.6 °C). Melting points were determined as onset by Differential Scanning Calorimetry using a Mettler DSC 30 with Mettler TA3000 processor (heating rate 10 °C min^{-1}). UV-vis absorption spectra in $CHCl_3$ solution were recorded by a Jasco V-570 spectrometer. Vibrational spectroscopy was performed using a Nicolet FT-IR Magna 560 (solid in KBr), a Nicolet FT-Raman 910 (solid). NMR spectra in $CDCl_3$ were collected using Bruker Instruments as specified for single spectra data.

X-Ray analysis†

Preliminary data collections of **14b** with a laboratory X-ray source yielded very poor quality data because of small crystal size and very rapid crystal decay. Intensity data were therefore collected at the Swiss–Norwegian Beamlines at ESRF, at T = 120(2) K on a minute crystal of **14b** (size 0.10 × 0.02 × 0.02 mm) with a MAR345 image plate using synchrotron radiation (λ = 0.7000(2) Å). The 345 mm diameter of the image plate has been used with a pixel resolution of 0.15 μm. A full rotation around the spindle axis of the MAR345 has been performed, with a rotation width of 2°; the sample to detector distance was set to 120 mm for a resolution at the edge of the image plate of 0.70 Å ($2\theta_{\max}$ = 59.82°). 178 images were processed and scaled with the program CrysAlisRED.[35] Cell dimensions and space group were determined from 2894 very intense reflections selected throughout the data collection. A total of 22604 reflections have been integrated, 3262 of which are unique (R_{int} = 0.0364), for a final completeness of the data set of 98%. The structure was solved by direct methods using the program SIR92[36] and was refined by full matrix least-squares on F^2 using SHELX97.[37] All non-hydrogen atoms have been refined anisotropically. Clear difference Fourier maps enabled the location and free refinement of all the hydrogen atoms in the structure.

Crystal data for **14b**: $C_{18}H_{26}F_2O_2S_2Si_2$, FW 432.69, Monoclinic, space group $C2/c$, T = 120(2) K, a = 15.537(3) Å, b = 16.739(2) Å, c = 10.481(2) Å, β = 126.46(2)°, V = 2192.3(14) Å^3, Z = 4, D_C = 1.311 mg m^{-3}, μ = 0.379 mm^{-1}, $F(000)$ = 912, 3262 unique reflections, 162 parameters, final agreement factors (all data): $R1$ = 0.0389, $wR2$ = 0.0975, Goof = 1.136.

Materials

Butyllithium (hexane solution), diisopropylamine, 2-methylthiophene, 3-methylthiophene, thiophene and trimethylsilyl choride were purchased from Aldrich. Sodium sulfate, ammonium chloride and the molecular sieves were purchased from Fluka. All solvents were Riedel-de Haën. Petroleum ether refers to bp 40–60 °C. Tetrafluoroethene was a kind gift of Ausimont SpA., 3-methoxythiophene was prepared according to the literature.[38]

(*E*)-1,2-Difluoro-1,2-bis(2-thienyl)ethene (8) and 2,5-bis{(*E*)-[1,2-difluoro-2-(2-thienyl)]ethenyl}thiophene (9)

Butyllithium (1.6 M, 27.5 ml, 44 mmol) was cautiously added dropwise over 10 min to a stirred solution of thiophene (3.7 g, 44 mmol) in THF (100 ml) at 0 °C. The resulting mixture was allowed to warm up to room temperature over a period of 1 h before being cooled down to −40 °C and a solution of TFE (20.3 mmol) in THF (200 ml) at −70 °C being added. After 15 min at −40 °C the reaction was quenched with saturated aqueous NH_4Cl and the solvent evaporated under reduced pressure. The gross product was then extracted with diethyl ether (2 × 100 ml) and the combined extracts washed with water to neutrality, dried over sodium sulfate, filtered and evaporated under reduced pressure to leave a red–orange oil. Purification by flash chromatography using petroleum ether as eluent and recrystallisation from the same solvent afforded **8** (0.46 g, 9%) and **9** (0.20 g, 4%) as yellow solids.

(*E*)-1,2-Difluoro-1,2-bis(2-thienyl)ethene (8). δ_H (500 MHz; $CDCl_3$; ^{19}F decoupling) 7.13 (2H, dd, $J_{4,3}$ 3.8, $J_{4,5}$ 5.0, Th(4)-H), 7.40 (2H, dd, $J_{3,4}$ 3.8, $J_{3,5}$ 1.2, Th(3)-H), 7.45 (2H, dd, $J_{5,3}$ 1.2, $J_{5,4}$ 5.0, Th(5)-H); δ_H (500 MHz; $CDCl_3$) 7.13 (2H, m, $J_{4,3}$ 3.8, $J_{4,5}$ 5.0, $J_{4,F}$ 1.7, Th(4)-H), 7.40 (2H, dd, $J_{3,4}$ 3.8, $J_{3,5}$ 1.2, Th(3)-H), 7.45 (2H, m, $J_{5,3}$ 1.2, $J_{5,4}$ 5.0, $J_{5,F}$ 1.7, Th(5)-H); δ_F (500 MHz; $CDCl_3$; ^1H broad decoupling) −148.4 (2F, s); δ_C (250 MHz; $CDCl_3$; ^1H broad decoupling) 125.8 (2C, t, J_{CF1} 3.7, J_{CF2} 3.7), 127.8 (2C, t, J_{CF1} 3.7, J_{CF2} 3.7), 128.0 (2C, s), 131.7 (2C, t, J_{CF1} 9.25, J_{CF2} 9.25), 144.7 (2C, dd, J_{CF1} 275.5, J_{CF2} 92.6, = CF); $\nu_{\max}$/cm^{-1} (FTIR) 3112s (ring CH), 1439s (ring C=C), 1356s (ring C=C), 1256s, 1228s, 1121s (CF), 1046s (ring CH), 853s (ring CH), 828s (ring CH), 714vs (ring CH), 698vs (ring CH); $\nu_{\max}$/cm^{-1} (FT-Raman) 3112w (ring CH), 1665vs (vinyl C=C), 1649vs (vinyl C=C), 1420vs (Я mode), 1080w, 853w, 635w.

2,5-Bis[(*E*)-1,2-difluoro-2-(2-thienyl)ethenyl]thiophene (9). δ_H (500 MHz; $CDCl_3$; ^{19}F decoupling) 7.14 (2H, dd, $J_{4,3}$ 3.8, $J_{4,5}$ 5.1, Th(4)-H), 7.38 (2H, s, Th(3′)-H and Th(4′)-H), 7.43 (2H, dd, $J_{3,4}$ 3.7, $J_{3,5}$ 1.2, Th(3)-H), 7.48 (2H, dd, $J_{5,3}$ 1.2, $J_{5,4}$ 5.1, Th(5)-H); δ_H (500 MHz; $CDCl_3$) 7.14 (2H, m, $J_{4,3}$ 3.7, $J_{4,5}$ 5.1, $J_{4,F}$ 1.5, Th(4)-H), 7.38 (2H, br s, Th(3′)-H), 7.43 (2H, dd, $J_{3,4}$ 3.7, $J_{3,5}$ 1.2, Th(3)-H), 7.48 (2H, m, $J_{5,3}$ 1.2, $J_{5,4}$ 5.1, $J_{5,F}$ 3.2, Th(5)-H); δ_F (500 MHz; $CDCl_3$; ^1H broad decoupling) −144.4 (2F, d, $J_{F1,F2}$ 114.9), −147.6 (2F, d, $J_{F2,F1}$ 114.9); $\nu_{\max}$/cm^{-1} (FTIR) 3103br (ring CH), 1428s (ring C=C), 1240s, 1133vs (CF), 1052s (ring CH), 851s (ring CH), 804vs (ring CH), 712 (ring CH), 696vs (ring CH), 525s; $\nu_{\max}$/cm^{-1} (FT-Raman) 1646s (vinyl C=C), 1630vs (vinyl C=C), 1449s, 1418vs (Я mode).

(*E*)-1,2-Difluoro-1,2-bis[5-methyl-(2-thienyl)]ethene (11)

Butyllithium (1.6 M, 20 ml, 32 mmol) was cautiously added dropwise over 10 min to a stirred solution of 2-methylthiophene (3.1 ml, 32 mmol) in THF (50 ml) at 0 °C. The resulting mixture was allowed to warm up to room temperature over a period of 1 h before being cooled down to −40 °C and a solution of TFE (16 mmol) in THF (200 ml) at −70 °C being added. The reaction mixture was then allowed to warm up to room temperature overnight and was quenched with saturated aqueous NH_4Cl. Work-up and purification as for **8** afforded **11** (1.75 g, 43%) as a yellow solid; δ_H (500 MHz; $CDCl_3$; ^{19}F decoupling)

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† CCDC reference number 185122. See http://www.rsc.org/suppdata/p2/b2/b203589h/ for crystallographic files in .cif or other electronic format.

2.52 (6H, d, $J_{Me,4}$ 1.2, Th(5)Me), 6.76 (2H, dd, $J_{4,3}$ 3.7, $J_{4,Me}$ 1.1, Th(4)-H), 7.15 (2H, d, $J_{3,4}$ 3.7, Th(3)-H); δ_H (500 MHz; $CDCl_3$) 2.52 (6H, dd, $J_{Me,4}$ 1.2, $J_{Me,F}$ 0.5, Th(5)Me), 6.76 (2H, m, $J_{4,3}$ 3.7, $J_{4,Me}$ 1.1, $J_{4,F}$ 1.7, Th(4)-H), 7.15 (2H, d, $J_{3,4}$ 3.7, Th(3)-H); δ_F (500 MHz; $CDCl_3$; ^1H broad decoupling) −148.7 (2F, s); δ_C (300 MHz; $CDCl_3$; ^1H decoupling) 15.6 (2C, s, Th(5)Me), 125.4 (2C, t, $J_{C,F1}$ 5.0, $J_{C,F2}$ 5.0), 126.1 (2C, s), 129.3 (2C, t, $J_{C,F1}$ 9.9, $J_{C,F2}$ 9.9), 142.4 (2C, t, $J_{C,F1}$ 4.1, $J_{C,F2}$ 4.1), 144.0 (2C, dd, $J_{C,F1}$ 273.5, $J_{C,F2}$ 92.6, = CF); ν_{max}/cm^{-1} (FTIR) 1472s (ring C=C), 1378s (ring C=C), 1225s, 1118vs (CF), 1039s (ring CH), 797vs (ring CH), 788vs (ring CH), 524s; ν_{max}/cm^{-1} (FT-Raman) 1662vs (vinyl C=C), 1651vs (vinyl C=C), 1447vs (Я mode).

2-Trimethylsilylthiophene (13a)

Butyllithium (2.5 M, 54 ml, 134 mmol) was cautiously added dropwise over 10 min to a stirred solution of thiophene (10.7 ml, 128 mmol) in THF (80 ml) at 0 °C. The resulting mixture was allowed to warm up to room temperature over a period of 1 h before being cooled down again to 0 °C and trimethylsilyl chloride (17.9 ml, 141 mmol) was cautiously added dropwise over a period of 20 min. The reaction mixture was then allowed to warm up to room temperature and was quenched with 3 ml of water. The solvent was evaporated under reduced pressure and the gross product extracted with diethyl ether (2 × 100 ml). The combined extracts were washed with water to neutrality, dried over sodium sulfate, filtered and evaporated under reduced pressure to leave a pale yellow liquid. Distillation under reduced pressure (60 °C, 15 mmHg) afforded **13a** (18.3 g, 91%) as a colourless liquid (99% GC pure).

δ_H (300 MHz; $CDCl_3$) 0.35 (9H, s, -$SiMe_3$), 7.21 (1H, dd, $J_{4,3}$ 3.3, $J_{4,5}$ 4.6, 4-H), 7.29 (1H, dd, $J_{3,4}$ 3.3, $J_{3,5}$ 0.8, 3-H), 7.62 (1H, dd, $J_{5,3}$ 0.8, $J_{5,4}$ 4.6, 5-H).

3-Methoxy-2-trimethylsilylthiophene (13b)

Butyllithium (1.6 M, 52.5 ml, 84 mmol) was cautiously added dropwise over 10 min to a stirred solution of 3-methoxythiophene (9.13 g, 80 mmol) in THF (50 ml) at 0 °C. The resulting mixture was allowed to warm up to room temperature over a period of 1 h before being cooled down again to 0 °C and trimethylsilyl chloride (11.2 ml, 88 mmol) cautiously added dropwise over a period of 20 min. The reaction mixture was then allowed to warm up to room temperature and was quenched with 3 ml of water. The solvent was evaporated under reduced pressure and the gross product extracted with diethyl ether (2 × 100 ml). The combined extracts were washed with water to neutrality, dried over sodium sulfate, filtered and evaporated under reduced pressure to leave a pale yellow liquid which was mainly the 2-trimethylsilyl derivative, with a minor content of the 5-trimethylsilyl isomer. Distillation under reduced pressure (40 °C, 2 × 10^{-1} mbar) afforded **13b** (11.2 g, 75%) as a colourless liquid (98% pure).

δ_H (300 MHz; $CDCl_3$) 0.37 (9H, s, -$SiMe_3$), 3.87 (3H, s, -OMe_3), 6.99 (1H, d, $J_{4,5}$ 5.0, 4-H), 7.47 (1H, d, $J_{5,4}$ 4.9, 5-H).

3-Methyl-5-trimethylsilylthiophene (13c)

Butyllithium (1.6 M, 17 ml, 27.2 mmol) was cautiously added dropwise over 10 min to a stirred solution of diisopropylamine (3.4 ml, 25 mmol) in THF (180 ml) at 0 °C. The resulting mixture was cooled to −80 °C over a period of 1 h after which time 3-methylthiophene (2.4 ml, 25 mmol) was added. After 1 h at −80 °C, trimethylsilyl chloride (3.5 ml, 37.5 mmol) was cautiously added dropwise over a period of 20 min and the reaction maintained at the same temperature for 30 min before being quenched with 3 ml of water. The solvent was then evaporated under reduced pressure and the gross product extracted with diethyl ether (2 × 100 ml). The combined extracts were washed with water to neutrality, dried over sodium sulfate, filtered and evaporated under reduced pressure to leave a pale yellow liquid which was mainly the 5-trimethylsilyl derivative, with a minor content of the 2-trimethylsilyl isomer. Distillation under reduced pressure (70 °C, 15 mmHg) afforded **13c** (2.6 g, 61%) as a colourless liquid (98% GC pure).

δ_H (300 MHz; $CDCl_3$) 0.32 (9H, s, 5-$SiMe_3$), 2.32 (3H, s, 3-Me_3), 7.06 (1H, d, $J_{4,2}$ 0.9, 4-H), 7.17 (1H, d, $J_{2,4}$ 1.0, 2-H).

(*E*)-1,2-Difluoro-1,2-bis(5-trimethylsilyl-2-thienyl)ethene (14a)

Butyllithium (2.5 M, 10.8 ml, 27 mmol) was cautiously added dropwise over 10 min to a stirred solution of 2-trimethylsilylthiophene (4.5 ml, 27 mmol) in diethyl ether (100 ml) at 0 °C. The resulting mixture was then allowed to warm up to room temperature over a period of 1 h before being cooled down to −30 °C and a solution of TFE (13.5 mmol) in diethyl ether (200 ml) added at −70 °C. The reaction mixture was kept at −40 °C overnight and was finally quenched with saturated aqueous NH_4Cl. Work-up and purification as for **8** afforded **14a** (1.57 g, 31%) as a white–pale yellow solid; δ_H (500 MHz; $CDCl_3$; ^{19}F decoupling) 0.36 (18H, s, -$SiMe_3$), 7.23 (2H, d, $J_{4,3}$ 3.7, Th(4)-H), 7.44 (2H, d, $J_{3,4}$ 3.7, Th(3)-H); δ_H (500 MHz; $CDCl_3$) 0.36 (18H, s, -$SiMe_3$), 7.23 (2H, m, $J_{4,3}$ 3.7, $J_{4,F}$ 1.8, Th(4)-H), 7.44 (2H, d, $J_{3,4}$ 3.7, Th(3)-H); δ_F (500 MHz; $CDCl_3$; ^1H broad decoupling) −145.1 (2F, s); δ_C (250 MHz; $CDCl_3$) 0.46 (6C, s, Th(5)$SiMe_3$), 127.0 (2C, t, $J_{C,F1}$ 3.7, $J_{C,F2}$ 3.7), 134.8 (2C, s), 136.6 (2C, t, $J_{C,F1}$ 9.2, $J_{C,F2}$ 9.2), 143.4 (2C, t, $J_{C,F1}$ 3.7, $J_{C,F2}$ 3.7), 144.7 (2C, dd, $J_{C,F1}$ 275.5, $J_{C,F2}$ 92.5, = CF); ν_{max}/cm^{-1} (FTIR) 2953 (CH_3), 1515s, 1252vs, 1029s, 1118s (CF), 1061s (ring CH), 988vs, 839vs (ring CH), 811vs (ring CH), 758s, 538s; ν_{max}/cm^{-1} (FT-Raman) 1653vs (vinyl C=C), 1422vs Я mode).

(*E*)-1,2-Difluoro-1,2-bis(4-methoxy-5-trimethylsilyl-2-thienyl)-ethene (14b)

Butyllithium (1.6 M, 12.1 ml, 19.4 mmol) was cautiously added dropwise over 10 min to a stirred solution of 3-methoxy-2-trimethylsilylthiophene (3.61 g, 19.4 mmol) in diethyl ether (100 ml) at 0 °C. The resulting mixture was then allowed to warm up to room temperature over a period of 1 h before being cooled down to −30 °C and a solution of TFE (9.7 mmol) in diethyl ether (250 ml) added at −70 °C. The reaction mixture was kept at −40 °C overnight and was finally quenched with saturated aqueous NH_4Cl. Work-up and purification as for **8** afforded **14b** (0.33 g, 8%) as a pale yellow solid; δ_H (500 MHz; $CDCl_3$; ^{19}F decoupling) 0.32 (18H, s, -$SiMe_3$), 3.85 (6H, s, -OMe), 7.16 (2H, s, Th(3)-H); δ_H (500 MHz; $CDCl_3$) 0.32 (18H, s, -$SiMe_3$), 3.85 (6H, s, -OMe), 7.16 (2H, s, Th(3)-H); δ_F (500 MHz; $CDCl_3$; ^1H broad decoupling) −147.6 (2F, s); δ_C (400 MHz; $CDCl_3$; ^1H broad decoupling) 0.57 (6C, s, Th(5)$SiMe_3$), 71.8 (2C, s, OMe), 115.0 (2C, t, $J_{C,F1}$ 4.8, $J_{C,F2}$ 4.8), 117.8 (2C, s), 134.6 (2C, t, $J_{C,F1}$ 9.6, $J_{C,F2}$ 9.6), 144.8 (2C, dd, $J_{C,F1}$ 274.6, $J_{C,F2}$ 91.4, = CF), 163.9 (2C, s); ν_{max}/cm^{-1} (FTIR) 2957s (CH_3), 1352s (ring C=C), 1460s (ring C=C), 1374vs, 1249s, 1214s, 1172s, 1092s (CF), 1026vs (ring CH), 842 (ring CH), 823s (ring CH); ν_{max}/cm^{-1} (FT-Raman) 1651vs (vinyl C=C), 1409vs Я mode).

(*E*)-1,2-Difluoro-1,2-bis(3-methyl-5-trimethylsilyl-2-thienyl)-ethene (14c)

Butyllithium (1.6 M, 9.6 ml, 15.3 mmol) was cautiously added dropwise over 10 min to a stirred solution of 3-methyl-5-trimethylsilylthiophene (2.61 g, 15.3 mmol) in diethyl ether (100 ml) at 0 °C. The resulting mixture was then allowed to warm up to room temperature over a period of 1 h being cooled down to −30 °C and a solution of TFE (7.7 mmol) in diethyl ether (250 ml) added at −70 °C. The reaction mixture was kept at −40 °C overnight and finally quenched with saturated aqueous NH_4Cl. Work-up and purification as for **8** afforded **14c** (0.60 g, 20%) as a pale-yellow solid; δ_H (500 MHz; $CDCl_3$; ^{19}F

decoupling) 0.35 (18H, s, -SiMe$_3$), 2.39 (6H, s, Th(3)-Me), 7.02 (2H, s, Th(4)-H); δ_H (500 MHz; CDCl$_3$) 0.35 (18H, s, -SiMe$_3$), 2.39 (6H, t, $J_{Me,F}$ 2, Th(3)-Me), 7.02 (2H, s, Th(4)-H); δ_F (500 MHz; CDCl$_3$; ^{1}H broad decoupling) −137.0 (2F, s); δ_C (250 MHz; CDCl$_3$; ^{1}H broad decoupling) 0.60 (6C, s, Th(5)SiMe$_3$), 15.9 (2C, t, $J_{C,F1}$ 3.7, $J_{C,F2}$ 3.7, Th(3)Me), 129.9 (2C), 138.2 (2C, br s), 140.3 (2C, s), 141.7 (2C, dd, $J_{C,F1}$ 353.4, $J_{C,F2}$ 183.1, = CF), 143.0 (2C, s); ν_{max}/cm^{-1} (FTIR) 1526s, 1122s (CF), 1021 (ring CH), 1000s (ring CH), 831s (ring CH), 702s (ring CH); ν_{max}/cm^{-1} (FT-Raman) 2896w (CH$_3$), 1656s (vinyl C=C), 1406s (Я mode), 626s, 459vs.

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