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Functionalized polyolefinic nonlinear optic chromophores incorporating the 1,3-dithiol-2-ylidene moiety as the electron-donating part

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The synthesis of a series of push-pull systems [donor (D)–acceptor (A)], associating the 1,3-dithiol-2-ylidene moiety (D) to various (A) fragments through polyolefinic linkages of various lengths, is described. Design optimization of these NLO phores is *via* systematic determination of the molecular first hyperpolarizabilities β by the EFISH method. Selected compounds of this series, displaying the highest β values, are then chemically functionalized in order to promote their covalent grafting to polymeric backbones.

The quest for new chromophores possessing large molecular second-order nonlinearity is of current interest because of their potential applications in electro-optic devices. In this context, the design and synthesis of new D–π–A systems, where the electron-donor (D) and electron-acceptor (A) groups are separated by a π-conjugated linker, are presently a major focus. Moreover, a growing effort is devoted to the preparation of polymers covalently functionalized with such chromophores, in order to produce long-term stable nonlinear optical (NLO) systems.[1]

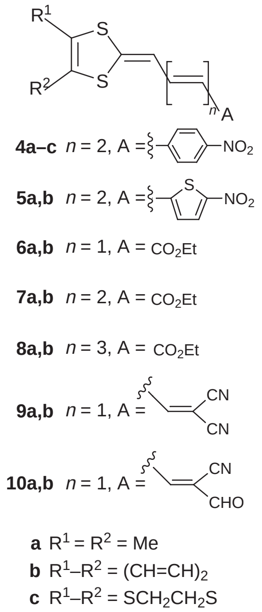
The 1,3-dithiol-2-ylidene moiety is well known for its electron-donating properties, and has been extensively used as such, notably in the synthesis of π-donating molecules of the tetrathiafulvalene family.[2] This donating ability has also been explored in the design of NLO chromophores.[3] Nevertheless, very few examples of push-pull chromophores possessing the 1,3-dithiol-2-ylidene moiety have been designed to further incorporate main-chain or side-chain polymers.

In this paper, we report on the synthesis of new push-pull conjugated polyenic systems incorporating the 1,3-dithiol-2-ylidene fragment as the donor part and various acceptor moities. A careful structural optimization of this class of chromophores has been carried out in order to reach high second-order hyperpolarizabilities as well as to introduce functionalities which could favour their subsequent incorporation into polymeric backbones.

Synthesis

The access to chromophores **4–10** involves key precursors **2** and **3**, whose syntheses were performed *via* adaptation of the previously described procedures.[4] Taking advantage of the great synthetic potential of the aldehyde functionality in **2** and **3**, we prepared target compounds **4–10** either through Wittig (–Horner) type olefinations or Knoevenagel condensations (Scheme 1).

Treatment of aldehydes **2** with the commercially available 4-nitrobenzyl(triphenyl)phosphonium bromide in presence of BuLi furnished chromophores **4** bearing the 4-nitrophenyl substituent as the acceptor part (only the *E*-configuration is observed for the double-bond formed during the olefination step). On the other hand, compounds **5–8** were obtained *via* Wittig–Horner olefinations of **1** and **2** with a phosphonate anion generated under basic conditions from the corresponding phosphonate esters.



All of these compounds were fully characterized using different spectroscopic methods, a careful NMR study (^{1}H NMR, ^{13}C NMR, COSY, HMQC, HMBC) being often needed to fully assign the molecular structures of compounds **4–8**. Whereas **4** and **5** were obtained as mixtures of *Z* and *E* isomers, the *trans* configuration of the double bond formed in the synthesis of compounds **6–8** was fully ascertained by NMR studies, as well as the *s-trans* conformation adopted by **8a** in [$^{2}H_{6}$]DMSO, assigned *via* an NOE experiment.

Furthermore, methanol recrystallization of **8a** produced

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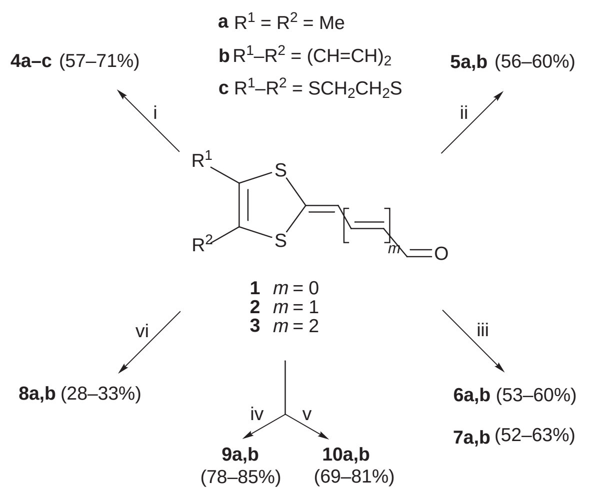


Scheme 1 *Reagents and conditions*: i, 4-nitrobenzyl(triphenyl)phosphonium bromide, BuLi, THF, reflux; ii, dimethyl (5-nitro-2-thienyl)methylphosphonate, BuLi, THF, reflux; iii, triethyl phosphonoacetate, BuLi, THF, 0 °C; iv, $CH_2(CN)_2$, Et_3N, dioxane, 0 °C; v, $NCCH_2CHO$, MeONa, THF, room temp.; vi, triethyl 4-phosphonocrotonate, BuLi, THF, 0 °C

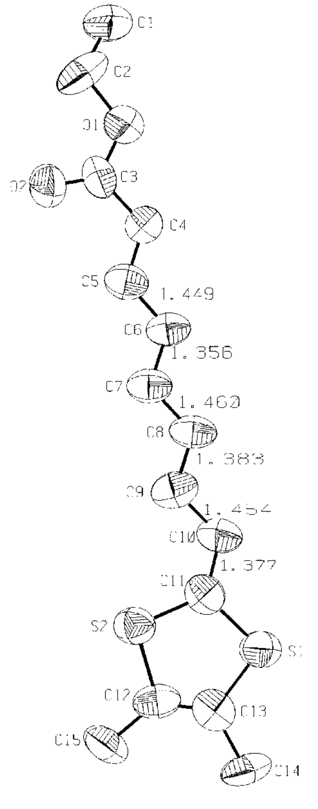
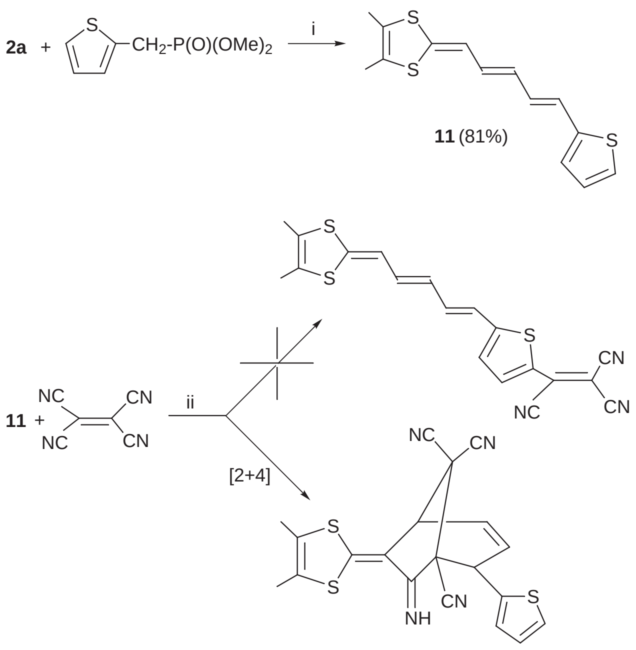


Fig. 1 ORTEP view of compound **8a**

crystals suitable for a X-ray structural determination[5] (Fig. 1). The most noticeable features of this structure lie in the occurrence of a perfectly planar *s-trans* structure, with relatively low Δr values between single and double bond lengths (average $r_{C=C}=1.372$ Å; average $r_{C-C}=1.454$; $\Delta r=0.08$ Å), corresponding to an optimized bond alternation for enhancement of quadratic and cubic NLO properties.[6] This Δr value has to be compared with the one encountered in the case of an unsubstituted polyene such as octa-1,3,5,7-tetraene, which displays a Δr value of 0.11 Å (average $r_{C=C}=1.340$ Å; average $r_{C-C}=1.445$ Å).[7] This comparison provides direct evidence for a low bond-length alternation in **8a**, associated to an important contribution from the charge-separated resonance form to the ground-state structure.



Scheme 2 *Reagents and conditions*: i, Bu^tOK, THF, room temp.; ii, DMF, room temp.

In our quest to synthesize new push-pull systems, we also attempted to graft the 2-(tricyanovinyl)thiophene fragment as the acceptor (A) group. For this purpose, we first synthesized the unsubstituted 2-thienyl derivative **11** through a Wittig–Horner olefination of **2a** with diethyl (2-thienyl)methylphosphonate (Scheme 2). Unfortunately this compound, when treated with tetracyanoethylene in DMF, did not give the required addition of the tricyanovinyl group to the terminal position of **2a**, but to compound **12** thanks to a [4+2] cycloaddition of tetracyanoethylene to the central polyolefinic linkage, followed either by a [2+2] process or an intramolecular nucleophilic addition, with prototropy. This unexpected structure was confirmed *via* an X-ray structural determination using a single crystal of **12** (Fig. 2).[8]

Alternatively, new push-pull systems **9** and **10** were prepared using Knoevenagel type condensations between aldehydes **2** and either malononitrile or cyanoacetaldehyde.

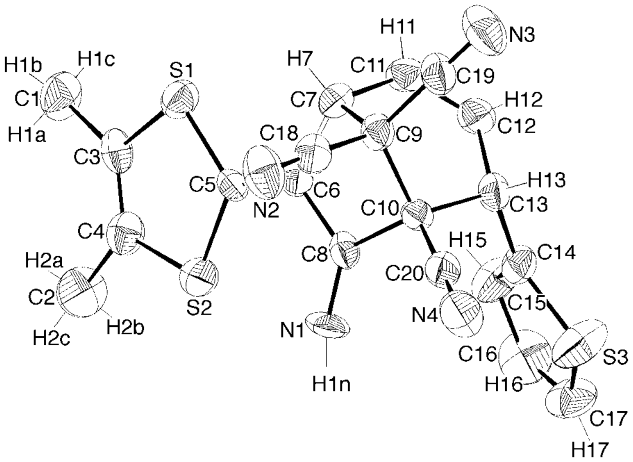


Fig. 2 ORTEP view of compound **12**

NLO properties

The second-order hyperpolarizabilities β of chromophores **1–5**, **9** and **10** were determined using an the electric field induced second harmonic (EFISH) generation experiment[9] using a laser source operating at 1.34 μm, the compounds being dissolved in chloroform (Table 1). The relevant parameter for electro-optic applications is $\mu\beta$, where μ is the ground state dipole moment. Static $\mu\beta(0)$ values are calculated from experimental $\mu\beta$ (1.34 μm) ones using a two-level dispersion model for β.[9]

All of the NLO-phores studied present large $\mu\beta$ and $\mu\beta(0)$ values. As expected for donor–acceptor substituted polyenes, extension of the conjugation length from **1a** to **3a** results in a significant enhancement of the second-order nonlinearity [$\mu\beta(0)$ values: **2a**/**1a** = 9.0, **3a**/**2a** = 1.3].

Compounds **3a**, **4a**, **10a** and **9a** on the one hand, and **3b**, **4b**, **10b** and **9b** on the other hand essentially display the same qualitative increase of $\mu\beta(0)$ values when increasing the acceptor character of the end group for both series, with confirmation of the superiority of the dicyanovinyl moiety over the aldehyde group, the $\mu\beta(0)$ values being increased by a factor of 2.6 and 2.3 for the **a** and **b** series, respectively. Additionally, the introduction of the nitrothienyl substituent in compound **5b** results in a strong increase of the nonlinearity when compared to **4b**, which confirms the utility of this electron-attracting substituent in the designing of new D–π–A NLO-phores.

Investigation of the donor part was limited to the study of the influence of the R groups at the 4,5-positions of the 1,3-dithiol-2-ylidene electron donating moiety. Of course, varying the R groups leads to smaller differences in $\mu\beta(0)$ than in the preceding study on the acceptor part, where the whole A fragment was changed. The superiority of the methyl group as a donating substituent (**3a**, **4a**, **9a**, **10a**) over the benzo-fused fragment (**3b**, **4b**, **9b**, **10b**) was established in all cases, with as expected a very small increase in $\mu\beta(0)$ [$\mu\beta(0)$ values: **3a**/**3b** = 1.02, **4a**/**4b** = 1.18, **9a**/**9b** = 1.18, **10a**/**10b** = 1.01]. Moreover, the 4,5-(ethane-1,2-diyldisulfanyl) substituted derivative **4c** displays a $\mu\beta(0)$ value between those of **4a** and **4b**, as expected from previous studies of its electron-donating behavior.[3b]

Synthesis of polymer precursors

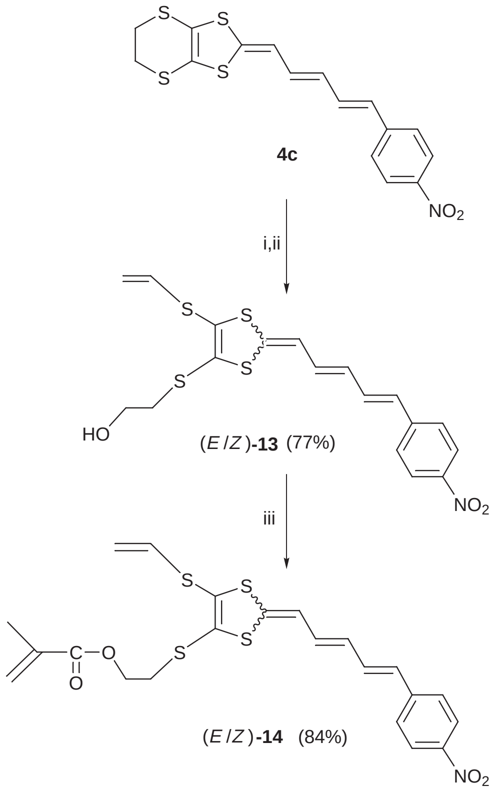
In order to obtain long-term stable nonlinear systems, these chromophores have been functionalized to allow further polymerization and to reach side-chain polymers bearing pendant active NLO moieties. This was achieved by introducing methyl methacrylate fragments[10] on the donor extremity of the push-pull system.

Addition of the methyl methacrylate fragment was carried out at the periphery of chromophores of type **4**, which were selected among structures **4–10** as the best candidates to be structurally modified due to easy chemical accessibility and good hyperpolarizability values.

Prior to the target NLO active monomers **14** and **23**, we needed to synthesize mono- and bis-(2-hydroxyethylsulfanyl) derivatives **13** and **22**.

In the case of **13**, we took advantage of the specific ability of the ethane-1,2-diyldisulfanyl group to undergo a ring opening under basic conditions[11] (Scheme 3). Thus, the successive treatment of compound **4c** with an excess of Bu_4NF and bromoethanol allowed the formation of the hydroxy intermediate **13** as a mixture of *Z* and *E* isomers, the hydroxyethyl and vinyl groups being disposed in a random fashion with respect to the polyene part. Subsequent esterification of **13** with methacryloyl chloride finally afforded the required **14**.

On the other hand, the two-fold introduction of the methacrylate moiety first involved the preparation of the 1,3-dithiolium salt **19a** (scheme 4). This synthesis was achieved in



Scheme 3 *Reagents and conditions*: i, Bu_4NF, THF, room temp.; ii, $BrCH_2CH_2OH$ (1.1 equiv.), THF, room temp.; iii, methacryloyl chloride, pyridine, THF, reflux

Table 1 Experimental data: λ_{max}, ground state dipole moment μ, $\mu\beta$ measured at 1.34 μm and static $\mu\beta(0)$ values deduced from experimental $\mu\beta$ ones using a two-level dispersion model for β

compound	$\lambda_{max}(CH_2Cl_2)$/nm[a]	μ/D	$\mu\beta/10^{-48}$ esu	$\mu\beta(0)/10^{-48}$ esu
1a	397 (4.26)	6.9	25	16
2a	432 (4.43)	8.2	273	144
3a	463 (4.24)	8.4	436	193
3b	431 (4.36)	6.1	369	189
4a	499 (4.50)	8.1	1130	464
4b	465 (4.40)	8.0	860	392
4c	479 (4.05)	8.6	981	403
5b	521 (4.27)	8.1	2540	850
9a	541 (4.37)	9.4	1870	508
9b	502 (4.81)	7.9	1200	431
10a	550 (4.56)	9.2	1590	401
10b	507 (4.44)	8.2	1147	397

[a] Values in parentheses are log ε.

several steps from thioxo derivative **15**,[12] whose hydroxy functionalities are first reacted with benzoyl chloride to produce **16a**. This compound could be further *S*-methylated with methyl trifluoromethanesulfonate to afford **17a**; no reaction was observed when using methyl iodide or dimethyl sulfate as alkylating agents. Reduction of the latter with sodium borohydride and subsequent treatment with hexafluorophosphoric acid furnished the required dithiolium intermediate **19a**. Formation of the corresponding phosphonate ester by addition of trimethyl phosphite was followed by Wittig–Horner olefination with fumaraldehyde mono(diethyl acetal). Further hydrolysis led to aldehyde **20a**, which was converted to the push-pull system **21** thanks to a Wittig olefination with 4-nitrobenzyl(triphenyl)phosphonium bromide. Deprotection of the alcohol functionalities and two-fold esterification of **22** with methacryloyl chloride afforded the expected polymer precursor **23**.

Attempts to copolymerise monomers **14** or **23** with methyl methacrylate in the presence of AIBN all resulted in chemical evolution of the NLO active part, as evidenced by extinction of the absorption bands related to the individual chromophores in the electronic spectra. This observation strongly suggests a lack of stability of the conjugated backbone under these polymerisation conditions.

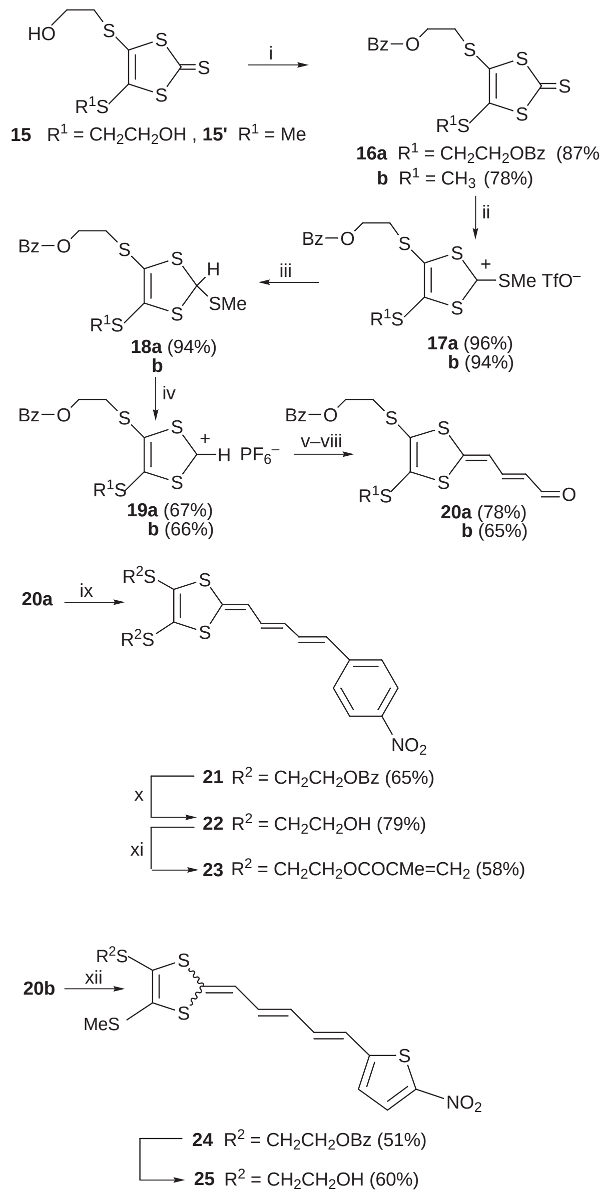
Alternatively, we attempted to prepare polyesters, containing the same optimized optically active group, by polycondensation between diol **22** and terephthaloyl chloride. Using various experimental conditions, we have been unable to isolate the target polymer, finding only short oligomers beside the [2+2] cyclocondensation product (*m*/*z* 1142). The introduction of these chromophores into other classes of polymers, notably polyimides, is underway.

Conclusion

We have synthesized a wide range of D–π–A systems incorporating 4,5-disubstituted 1,3-dithiol-2-ylidene moieties as the D part. EFISH measurements have shown these NLO phores to possess high second order nonlinearities, and have allowed us to evaluate the effect of (i) the length of the π-conjugating spacer and (ii) the nature of the electron-withdrawing and electron-releasing substituents on the $\mu\beta(0)$ values. Chemical modifications on one model chromophore allowed us to introduce polymerizable fragment(s) at the periphery of the D–π–A system. Considering the very attractive $\mu\beta(0)$ value obtained with compound **5b** possessing a nitrothienyl group as the acceptor part, chemical modification of this chromophore to hydroxy derivative **25** has been performed according to a similar synthetic strategy as for compound **22** (Scheme 4). Attempts to covalently graft this chromophore onto poly(imide-co-siloxanes) are in progress.

Experimental

Melting points were obtained using a Rechert-Jung hot-stage microscope apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer model 841 spectrophotometer, samples being embedded in KBr discs or Fluorolube mulls. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX270WB spectrometer operating respectively at 270 and 67.5 MHz or on a Bruker Avance DRX500 operating at 500 and 125.7 MHz, respectively; δ values are given in ppm (relative to TMS) and coupling constants (*J*) in Hz. Mass spectra were recorded in EI or FAB mode on a VG Autospec. UV–VIS spectra were recorded on a Perkin-Elmer Lambda 2 spectrometer. Elemental analyses were performed by the Service central d'analyses du CNRS (Vernaison, France). Column chromatography separations and purifications were carried out on Merck silica gel 60 (0.040–0.0063 nm).



Scheme 4 *Reagents and conditions*: i, BzCl, pyridine, THF, room temp.; ii, TfOMe, CH$_2$Cl$_2$, room temp.; iii, NaBH$_4$, Pr^{i}OH, MeCN, 0 °C; iv, HPF$_6$, Ac$_2$O, 0 °C; v, NaI, P(OMe)$_3$, MeCN, room temp.; vi, BuLi, −80 °C; vii, fumaraldehyde mono(dimethyl acetal), THF, −80 °C→room temp.; viii, Amberlyst-15, H$_2$O–acetone; ix, 4-nitrobenzyl(triphenyl)phosphonium bromide, BuLi, THF, reflux; x, KOH, THF–MeOH–H$_2$O (10:5:1), reflux; xi, methacryloyl chloride, pyridine, THF, reflux; xii, dimethyl (5-nitro-2-thienyl)methylphosphonate, BuLi, THF, reflux; xiii, KOH, THF–MeOH–H$_2$O (10:5:1), reflux

Syntheses of 4a–c

4-Nitrobenzyl(triphenyl)phosphonium bromide (2.2 mmol) was dissolved in dried THF (10 ml), and Bu^{n}Li (1.6 M in hexane; 2.2 mmol) was added at room temperature. The mixture was stirred for 15 min and aldehyde **2** (2 mmol) was added dropwise. The reaction mixture was refluxed for 2 h. After cooling, the solvents were removed under reduced pressure and the residue was dissolved in CH$_2$Cl$_2$, washed with water and dried (MgSO$_4$). The crude material obtained after evaporation of CH$_2$Cl$_2$ was chromatographed over silica gel (CH$_2$Cl$_2$ as eluent) to produce **4a–c** as brown powders.

5-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-1-(4-nitrophenyl)penta-1,3-diene 4a. Yield 71%, mp 173–174 °C; ^{1}H NMR (CDCl$_3$) 8.14 (d, 2H, $^3J=8.5$ Hz), 7.66 (d, 2H, $^3J=8.7$ Hz), 7.29 (dd, 1H, $^3J=10.5$, 15.5 Hz), 6.63 (d, 1H, $^3J=15.5$ Hz), 6.38–6.20 (m, 3H), 1.94 (s, 6H); ^{13}C NMR (CDCl$_3$)

145.4, 144.1, 139.5, 133.9, 132.7, 126.8, 125.9, 125.6, 123.7, 121.6, 110.9, 13.1, 12.8 (Calc. for $C_{16}H_{15}NO_2S_2$: C, 58.53; H, 4.06. Found: C, 58.10; H, 4.17%); *m/z* (EI) (%) 317 (M^+, 100), 195 (18), 131 (22), 59 (18); ν_{max}(KBr)/cm^{-1} 1504, 1336 (NO_2).

5-(1,3-Benzodithiol-2-ylidene)-1-(4-nitrophenyl)penta-1,3-diene 4b. Yield 57%, mp 246–248 °C; ^{1}H NMR ($CDCl_3$) 8.16 (d, 2H, $^3J=8.7$ Hz), 7.49 (d, 2H, $^3J=8.7$ Hz), 7.20 (m, 4H), 7.03 (dd, 1H, $^3J=11.0$, 15.5 Hz), 6.54 (d, 1H, $^3J=15.5$ Hz), 6.42 (dd, 1H, $^3J=11.3$, 13.8 Hz), 6.26 (dd, 1H, $^3J=11.0$, 13.8 Hz), 6.22 (d, 1H, $^3J=11.3$ Hz); ^{13}C NMR ($CDCl_3$) 151.5, 135.7, 133.9, 132.5, 128.2, 126.2, 126.0, 125.8, 125.5, 124.2, 121.7, 121.5, 114.1 (Calc. for $C_{18}H_{13}NO_2S_2$: C, 63.71; H, 3.83; N, 4.13; O, 9.44; S, 18.88. Found: C, 63.83; H, 4.03; N, 4.23; O, 9.91; S, 18.58%); *m/z* (EI) (%) 339 (M^+, 100), 292 (29), 153 (26), 140 (30), 77 (7); ν_{max}(KBr)/cm^{-1} 1565, 1335 (NO_2).

5-[4,5-(Ethane-1,2-diyldisulfanyl)-1,3-dithiol-2-ylidene]-1-(4-nitrophenyl)penta-1,3-diene 4c. Yield 60%, mp 220–221 °C; ^{1}H NMR ($CDCl_3$) 8.17 (d, 2H, $^3J=8.9$ Hz), 7.47 (d, 2H, $^3J=8.9$ Hz), 6.98 (dd, 1H, $^3J=10.1$, 15.5 Hz), 6.53 (d, 1H, $^3J=15.5$ Hz), 6.41 (dd, 1H, $^3J=10.3$, 13.8 Hz), 6.23 (dd, 1H, $^3J=10.1$, 13.8 Hz), 6.22 (d, 1H, $^3J=10.3$Hz), 3.33 (s, 4H); ^{13}C NMR ($CDCl_3$) 146.2, 144.2, 135.1, 133.8, 132.2, 128.7, 128.4, 127.5, 126.3, 124.2, 114.3, 29.7, 29.6 (Calc. for $C_{16}H_{13}NO_2S_4$: C, 50.66; H, 3.43; N, 3.69. Found: C, 50.46; H, 3.53; N, 3.49%); *m/z* (EI) (%) 379 (M^+, 100), 184 (92), 152 (34), 88 (35); ν_{max}(KBr)/cm^{-1} 1526, 1332 (NO_2).

Syntheses of 5a,b

Using a similar procedure as for **4a–c**, aldehyde **2** was reacted with dimethyl (5-nitro-2-thienyl)methylphosphonate as Wittig–Horner reagent.

5-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-1-(5-nitro-2-thienyl)penta-1,3-diene 5a. Yield 56%, black powder, mp 179–180 °C; ^{1}H NMR ($CDCl_3$) 7.78 (d, 1H, $^3J=4.2$ Hz), 6.85 (dd, 1H, $^3J=10.8$, 15.3 Hz), 6.81 (d, 1H, $^3J=4.0$ Hz), 6.47 (d, 1H, $^3J=15.0$ Hz), 6.35 (dd, 1H, $^3J=11.3$, 14.6 Hz), 6.09 (d, 1H, $^3J=11.5$ Hz), 6.05 (dd, 1H, $^3J=11.0$, 14.6 Hz), 1.98 (s, 3H), 1.95 (s, 3H); ^{13}C NMR ($CDCl_3$) 151.9, 143.0, 141.8, 135.2, 134.2, 130.0, 125.3, 123.5, 122.5, 120.7, 111.3, 13.6, 13.2; *m/z* (EI) (%) 323 (M^+, 100), 147 (67), 131 (26), 59 (24); ν_{max}(KBr)/cm^{-1} 1520, 1317 (NO_2).

5-(1,3-Benzodithiol-2-ylidene)-1-(5-nitro-2-thienyl)penta-1,3-diene 5b. Yield 60%, violet powder, mp 203–205 °C; ^{1}H NMR ($CDCl_3$) 7.8 (d, 1H, $^3J=4.2$ Hz), 7.21 (m, 4H), 6.88 (dd, 1H, $^3J=10.6$, 15.5 Hz), 6.85 (d, 1H, $^3J=4.5$ Hz), 6.54(d, 1H, $^3J=15.5$ Hz), 6.44 (dd, 1H, $^3J=11.3$, 14.3 Hz), 6.23 (d, 1H, $^3J=11.3$ Hz), 6.14 (dd, 1H, $^3J=14.3$ Hz); ^{13}C NMR ($CDCl_3$) 151.9, 138.4, 135.3, 135.1, 134.1, 133, 129.5, 126.7, 125.7, 125.5, 121.5, 121.4, 123.5, 113.5 (Calc. for $C_{16}H_{11}NO_2S_3$: C, 55.63; H, 3.21; N, 4.05; O, 9.26; S, 27.84. Found: C, 55.49; H, 3.13; N, 4.05; O, 9.57; S, 27.52%); *m/z* (EI) (%) 345 (M^+, 100), 147 (77), 69 (60); ν_{max}(KBr)/cm^{-1} 1526, 1324 (NO_2).

Syntheses of 6a,b, 7a,b and 8a,b

A solution of aldehyde **1** (1 mmol) and triethyl phosphonoacetate (1 mmol) (for **6a,b**), aldehyde **2** (1 mmol) and triethyl phosphonoacetate (1 mmol) (for **7a,b**) or aldehyde **2** (1 mmol) with triethyl 4-phosphonocrotonate (1 mmol) (for **8a,b**) in dried THF (10 ml) was treated with Bu^{n}Li (1.6 M in hexane, 1.1 equiv.) at 0 °C. The reaction mixture was stirred for 2 h, the solvents were removed under reduced pressure and the residue was dissolved in CH_2Cl_2, washed with water and dried ($MgSO_{4)}$. Evaporation of the solvent and silica gel chromatography (CH_2Cl_2 as eluent) produced **6a,b**, **7a,b** and **8a,b** as yellow powders.

Ethyl 4-(4,5-dimethyl-1,3-dithiol-2-ylidene)but-2-enoate 6a. Yield 60%; ^{1}H NMR ($CDCl_3$) 7.37 (dd, 1H, $^3J=11.8$, 14.8 Hz), 6,10 (d, 1H, $^3J=11.75$ Hz), 5.54 (d, 1H, $^3J=14.8$ Hz), 4.22 (q, 2H), 1.96 (s, 3H), 1.93 (s, 3H), 1.30 (t, 3H); *m/z* (EI) (%) 242 (M^+, 87), 197 (100), 170 (74), 116 (53), 71 (48), 59 (20).

Ethyl 4-(1,3-Benzodithiol-2-ylidene)but-2-enoate 6b. Yield 53%, mp 80–82 °C; ^{1}H NMR ($CDCl_3$) 7.34 (dd, 1H, $^3J=11.5$, 14.8 Hz,), 7.22 (m, 4 H), 6.24 (d, 1H, $^3J=11.5$ Hz), 5.65 (d, 1H, $^3J=14.8$Hz), 4.22 (q, 2H), 1.30 (t, 3H); ^{13}C NMR ($CDCl_3$) 167.0, 145.6, 139.3, 135.2, 134.7, 125.7, 125.6, 121.4, 121.2, 115.4, 110.9, 59.7, 13.9; *m/z* (EI) (%) 264 (M^+, 98), 236 (8), 219 (70), 192 (100), 147 (28), 69 (12); ν_{max}(KBr)/cm^{-1} 1696 (CO).

Ethyl 6-(4,5-Dimethyl-1,3-dithiol-2-ylidene)hexa-2,4-dienoate 7a. Yield 52%, mp 120–123 °C; ^{1}H NMR ($CDCl_3$) 7.31 (dd, 1H, $^3J=11.5$, 15.0 Hz), 6.43 (dd, 1H, $^3J=11.5$, 14.6 Hz), 6,06 (d, 1H, $^3J=11.5$ Hz), 6.03 (dd, 1H, $^3J=11.5$, 14.6 Hz), 5.76(d, 1H, $^3J=15.0$ Hz), 4.17 (q, 2H), 1.96, (s, 3H), 1.93 (s, 3H), 1.28 (t, 3H); ^{13}C NMR ($CDCl_3$) 168.0, 145.6, 143.7, 137.5, 124.3, 122.7, 122.9, 118.2, 111.1, 60.5, 14.8, 14.0, 13.7; *m/z* (EI) (%) 268 (M^+, 41), 223 (8), 195 (100), 59 (8); ν_{max}(KBr)/cm^{-1} 1697 (CO).

Ethyl 6-(1,3-Benzodithiol-2-ylidene)hexa-2,4-dienoate 7b. Yield 63%, mp 103 °C; ^{1}H NMR ($CDCl_3$) 7.34 (dd, 1H, $^3J=11.5$, 15 Hz), 7.19 (m, 4 H), 6.53 (dd, 1H, $^3J=11.3$, 14.3 Hz), 6.21 (d, 1H, $^3J=11.3$ Hz), 6.13 (dd, 1H, $^3J=11.5$, 14.3 Hz), 5.83 (d, 1H, $^3J=15$ Hz), 4.20 (q, 2H), 1.29 (t, 3H); ^{13}C NMR ($CDCl_3$) 167.3, 144.6, 140.4, 136.3, 135.7, 135.5, 126.1, 125.9, 121.8, 121.6, 125.8, 119.2, 113.4, 60.2, 14.3 (Calc. for $C_{15}H_{14}O_2S_2$: C, 62.02; H, 4.82; O, 11.03; S, 22.06. Found: C, 61.70; H, 4.90; O, 10.88; S, 21.63%); *m/z* (EI) (%) 290 (M^+, 36), 245 (9), 217 (100), 184 (23), 69 (8); ν_{max}(KBr)/cm^{-1} 1711 (CO).

Ethyl 8-(4,5-Dimethyl-1,3-dithiol-2-ylidene)octa-2,4-dienoate 8a. Yield 33%, mp 135 °C; Chemical shifts of different ^{1}H and ^{13}C nuclei were assigned from COSY [^{1}H,^{1}H] and HMQC spectra. The all-*trans* configuration of the conjugated spacer was confirmed from NOE measurements and X-ray diffraction: ^{1}H NMR ($CDCl_3$) 7.18 (dd, 1H, $^3J=11.5$, 15.2 Hz), 6.47 (dd, 1H, $^3J=10.9$, 14.7 Hz), 6.13 (m, 2H), 5.93 (d, 1H, $^3J=11.9$Hz), 5.91 (dd, 1H, $^3J=11.0$, 16.2 Hz), 5.18 (d, 1H, $^3J=15.2$ Hz), 4.10 (q, 2H), 1.96 (s, 3H), 1.93 (s, 3H), 1.20 (t, 3H); ^{13}C NMR ($CDCl_3$) 166.4, 144.9, 141.9, 139.3, 133.6, 127.9, 126.7, 122.3, 122.1, 118.6, 111.7, 59.6, 14.2, 13.3, 12.9 (Calc. for $C_{15}H_{18}O_2S_2$: C, 61.22; H, 6.12; O, 10.88; S, 21.76. Found: C, 61.29; H, 6.12; O, 10.89; S, 21.57%); *m/z* (EI) (%) 294 (M^+, 35), 265 (10), 221 (100), 157 (15), 91 (19); ν_{max}(KBr)/cm^{-1} 1702 (CO).

Ethyl 8-(1,3-Benzodithiol-2-ylidene)octa-2,4-dienoate 8b. Yield 28%, mp 135 °C; ^{1}H NMR ($CDCl_3$) 7.35 (m, 4H), 7.28 (dd, 1H, $^3J=11.5$, 15.0 Hz), 6.85 (dd, 1H, $^3J=10.8$, 14.6 Hz), 6.50–6.21 (m, 4H), 5.93 (d, 1H, $^3J=15.0$ Hz), 4.11 (q, 2H), 1.21 (t, 3H); ^{13}C NMR ($CDCl_3$) 166.3, 144.7, 141.5, 136.6, 134.8, 133, 129, 128.6, 126.6, 126.4, 122.3, 122.2, 119.4, 114.6, 59.7, 14.3 (Calc. for $C_{17}H_{16}O_2S_2$: C, 64.55; H, 5.06; O, 10.12. Found: C, 64.39; H, 5.03; O, 10.21%); *m/z* (EI) (%) 316 (M^+, 35), 287 (11), 243 (100); ν_{max}(KBr)/cm^{-1} 1698 (CO).

Syntheses of 9a,b

A mixture of aldehyde **2** (1 mmol), malononitrile (1.1 mmol) and triethylamine (1 ml) in dioxane (20 ml) was stirred for 10 min at 0 °C. The reaction mixture was then diluted with CH_2Cl_2 (100 ml), washed with water and dried ($MgSO_4$). The solvent was removed and the reaction product was purified by silica gel chromatography (CH_2Cl_2 as eluent) to produce **9a,b** as blue powders.

6-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-2-cyanohexa-2,4-dienenitrile 9a. Yield 78%, mp 227–232 °C; ^{1}H NMR ($CDCl_3$) 7.33 (d, 1H, $^3J = 12.2$ Hz), 6.88 (dd, 1H, $^3J = 12.0, 13.4$ Hz), 6.46 (dd, 1H, $^3J = 11.8, 13.4$ Hz), 6.28 (d, 1H, $^3J = 11.8$ Hz), 2.09 (s, 6H); ^{13}C NMR ($CDCl_3$) 160.3, 159.1, 146.5, 126.3, 126.2, 118.9, 116.0, 114.0, 111.0, 74.4, 14.1, 13.7; *m/z* (EI) (%) 246 (M^+, 100), 249 (12), 71 (22), 59 (22), 54 (35); ν_{max}(KBr)/cm^{-1} 2211 (CN).

6-(1,3-Benzodithiol-2-ylidene)-2-cyanohexa-2,4-dienenitrile 9b. Yield 85%, mp 242 °C; ^{1}H NMR ($CDCl_3$) 7.42 (d, 1H, $^3J =$ 12.7 Hz), 7.31 (m, 4H), 6.97 (dd, 1H, $^3J = 12.0, 13.9$ Hz), 6.49 (dd, 1H, $^3J = 12.0, 13.9$ Hz), 6.42 (d, 1H, $^3J_{ab} = 12.0$ Hz); ^{13}C NMR ($CDCl_3$) 159.4, 155.1, 144.9, 140.8, 135.8, 127.4, 122.7, 121.4, 114.8, 112.8 (Calc. for $C_{14}H_8N_2S_2$: C, 62.68; H, 2.98; N, 10.44; S, 23.88. Found: C, 62.33; H, 3.00; N, 10.33; S, 23.97%); *m/z* (EI) (%) 268 (M^+, 100), 242 (8), 152 (25), 108 (14), 69 (11); ν_{max}(KBr)/cm^{-1} 2220, 2204 (CN).

Syntheses of 10a,b

A solution of aldehyde **2** (1 mmol), cyanoacetaldehyde diethyl acetal (1 mmol) and sodium methoxide (2 mmol) in dried THF (10 ml) was stirred at room temperature for three days (in the case of **10a**) or one day (in the case of **10b**). Instantaneous hydrolysis was carried out by adding 50 ml of THF and 50 ml of HCl (2 M). The solution was diluted with CH_2Cl_2 and successively washed with water, saturated $NaHCO_3$ and brine. The organic phase was dried, evaporated and the residue was chromatographed on silica gel (CH_2Cl_2 as eluent) to give **10a,b** as violet powders.

6-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-2-cyanohexa-2,4-dienal 10a. Yield 69%, mp 231 °C; ^{1}H NMR ($CDCl_3$) 9.39 (s, 1H), 7.57 (d, 1H), 7.02 (dd, 1H), 6.48 (dd, 1H), 6.36 (d, 1H), 2.11 (s, 3H), 2.09 (s, 3H); *m/z* (EI) (%) 249 (M^+, 70), 220 (100), 170 (12), 144 (12), 116 (21), 71 (24), 59 (28); ν_{max}(KBr)/cm^{-1} 2211 (CN), 1659 (CO).

6-(1,3-Benzodithiol-2-ylidene)-2-cyanohexa-2,4-dienal 10b. Yield 81%, mp 218 °C; ^{1}H NMR ($CDCl_3$) 9.44 (s, 1H), 7.63 (d, 1H, $^3J = 12$ Hz), 7.52 (m, 4 H), 7.09 (dd, 1H, $^3J = 12.0$, 13.6 Hz), 6.63 (dd, 1H, $^3J = 12.0, 13.6$ Hz), 6.49 (d, 1H, $^3J =$ 12Hz); ^{13}C NMR ($CDCl_3$) 185.7, 157.1, 153.6, 144.8, 134.9, 126.4, 126.3, 121.8, 121.4, 114.0, 112.5, 109.1, 76.1 (Calc. for $C_{14}H_9NOS_2$: C, 61.97; H, 3.34; O, 5.89. Found: C, 61.92; H, 3.25; O, 5.22%); *m/z* (EI) (%) 271 (M^+, 85), 242 (100), 108 (34), 69 (30); ν_{max}(KBr)/cm^{-1} 2216 (CN), 1681 (CO).

Synthesis of 11

Potassium *tert*-butoxide (1.5 mmol) was slowly added at room temperature to a solution of aldehyde **2a** (1 mmol) and diethyl (2-thienyl)methylphosphonate (1.5 mmol) in THF (10 ml). The mixture was stirred for 30 min and diluted with CH_2Cl_2 (50 ml), washed with water and dried ($MgSO_4$). The solvent was evaporated and the solid product was recrystallized from methanol.

5-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-1-(2-thienyl)penta-1,3-diene 11. Yield 81%, yellow powder; ^{1}H NMR ($CDCl_3$) (chemical shifts of different protons were assigned *via* a COSY 45 ^{1}H,^{1}H experiment) 7.12 (d, 1H, $^3J = 4.9$ Hz), 6.94 (d, 1H, $^3J = 3.7$ Hz), 6.91 (dd, 1H), 6.62 (m, 2H), 6.10 (m, 3H), 1.94 (s, 3H), 1.91 (s, 3H); ^{13}C NMR ($CDCl_3$) 143.5, 136.2, 130.0, 129.5, 127.6, 127.0, 125.0, 123.7, 123.1, 121.7, 121.6, 111.9, 13.6, 13.25; *m/z* (EI) (%) 278 (M^+, 100), 191 (20), 160 (26), 147 (48), 131 (42), 115 (33).

Synthesis of 12

Tetracyanoethylene (1.5 mmol) was added portionwise to a solution of compound **11** (1 mmol) in DMF (10 ml). The homogeneous mixture was stirred for one day at room temperature, and then diluted with CH_2Cl_2 (100 ml), washed with water and dried ($MgSO_4$). Solvent was removed under reduced pressure and the yellow solid residue was chromatographed over silica gel (CH_2Cl_2 as eluent). Crystals suitable for X-ray analysis were obtained from chloroform.

1,8,8-Tricyano-2-(2-thienyl)-6-(4,5-dimethyl-1,3-dithiol-2-ylidene)-7-iminobicyclo[3.2.1]oct-3-ene 12. Yield 84%, yellow powder, mp 245 °C; ^{1}H NMR ($CDCl_3$) 9.08 (s, 1H), 7.31 (d, 1H, $^3J = 4.9$ Hz), 7.03 (d, 1H, $^3J = 3.7$ Hz), 6.99 (m, 1H), 6.47 (dd, 1H, $^3J = 6.5, 9.6$ Hz), 5.90 (dd, 1H, $^3J = 2.8, 9.6$ Hz), 4.61 (t, 1H), 3.92 (d, 1H, $^3J = 6.5$ Hz), 2.14 (s, 3H), 2.11 (s, 3H); *m/z* (EI) (%) 406 (M^+, 100), 297 (23), 160 (26), 233 (85), 208 (40), 131 (47); ν_{max}(KBr)/cm^{-1} 3267 (NH), 2247 (CN).

Synthesis of 13

To a solution of **4c** (0.5 mmol) in THF (10 ml) was added in one portion an excess (5 mmol) of Bu_4NF (1 M solution in THF) at room temperature. The red solution was stirred for 15 min, the colour turning to violet, and 2-bromoethanol (0.55 mmol) was added. The reaction mixture was stirred for 6 h. The THF was then evaporated and the residue was dissolved in CH_2Cl_2, washed with water and dried ($MgSO_4$). The CH_2Cl_2 was evaporated and the residue was chromatographed over silica gel (CH_2Cl_2 as eluent) to give **13** as a brown powder (probably as a mixture of *Z* and *E* isomers which are spectroscopically indistinguishable).

5-[4-Ethenylsulfanyl-5-(2-hydroxyethylsulfanyl)-1,3-dithiol-2-ylidene]-1-(4-nitrophenyl)penta-1,3-diene 13. Yield 77%; ^{1}H NMR ($CDCl_3$) 8.17 (d, 2H), 7.48 (d, 2H), 6.98 (dd, 1H, $^3J =$ 9.8, 15.4 Hz), 6.55 (d, 1H, $^3J = 15.4$ Hz), 6.40 (dd, 1H, $^3J = 9.4$, 15.6 Hz), 6.25 (m, 3H), 5.48 (m, 2H), 3.79 (m, 2H), 3.00, (t, 2H), 2.17 (t, 1H); ^{13}C NMR ($CDCl_3$) 146.3, 144, 135.6, 133.6, 131.5, 128.9, 128.8, 128.7, 126.3, 126.1, 117.7, 117.6, 114.9, 60.2, 39.0 (Calc for $C_{18}H_{17}NO_3S_4$: C, 51.04; H, 4.04; N, 3.30; O, 11.33; S, 30.27. Found: C, 50.91; H, 4.02; N, 3.32; O, 11.04; S, 30.32%); *m/z* (EI) (%) 423 (M^+, 100), 184 (84), 152 (43), 103 (43), 71 (44), 59 (12); ν_{max}(KBr)/cm^{-1} 3337 (OH), 1524, 1334 (NO_2).

Synthesis of 14

To a solution of **13** (0.5 mmol) and pyridine (0.1 ml) in dried THF (10 ml) was added dropwise a solution of freshly distillated methacryloyl chloride (1 mmol) in dried THF (5 ml). The reaction mixture was refluxed for 3 h, THF was removed under reduced pressure and the residue was dissolved in CH_2Cl_2, washed with water and dried ($MgSO_4$). After removing the solvent, the residue was chromatographed over silica gel (CH_2Cl_2 as eluent) to give **14** as a brown powder.

5-[4-Ethenylsulfanyl-5-(2-methacryloyloxyethylsulfanyl)-1,3-dithiol-2-ylidene]-1-(4-nitrophenyl)penta-1,3-diene 14. Yield 84%; ^{1}H NMR ($CDCl_3$) 8.17 (d, 2H), 7.49 (d, 2H), 6.99 (dd, 1H, $^3J = 9.9, 15.5$ Hz), 6.54 (d, 1H, $^3J = 15.5$ Hz), 6.36 (dd, 1H, $^3J = 9.4, 16.4$ Hz), 6.20 (m, 4H), 5.62 (1H), 5.45 (2H), 4.37 (t, 2H), 3.09 (m, 2H), 1.96 (s, 3H); *m/z* (EI) (%) 491 (M^+, 14), 184 (19), 113 (100), 69 (67); ν_{max}(KBr)/cm^{-1} 1720 (CO), 1530, 1335 (NO_2).

Synthesis of 16a

To a solution of **15**[11] (10 mmol) and pyridine (3.2 ml, 40 mmol) in THF (20 ml) was added dropwise benzoyl chloride (40 mmol) in dry THF (10 mL) at room temperature. After stirring for 3 h, the THF was evaporated. The residue was dissolved in CH_2Cl_2, washed with water and dried over $MgSO_4$. After removing the solvent, **16** was purified by chromatography over silica gel (light petroleum–CH_2Cl_2 1:2 as eluent) and obtained as a yellow powder.

4,5-Bis(2-benzoyloxyethylsulfanyl)-2-thioxo-1,3-dithiole 16a. Yield 87%, mp 82–85 °C; ^{1}H NMR ($CDCl_3$) 8.10 (dd, 4H), 7.52 (m, 6H), 4.50 (t, 4H), 3.20 (t, 4H); *m*/*z* (EI) (%) 494 (M^+, 25), 149 (100), 105 (61), 77 (33).

Synthesis of 16b

Using a similar procedure as for **16a**, a solution of thione **15′** (10 mmol) and pyridine (20 mmol) was reacted with benzoyl chloride (20 mmol) in dry THF.

4-(2-Benzoyloxyethylsulfanyl)-5-methylsulfanyl-2-thioxo-1,3-dithiole 16b. Yield 78%, mp <50 °C; ^{1}H NMR ($CDCl_3$) 8.10 (dd, 2H), 7.50 (m, 3H), 4.57 (t, 2H), 3.23 (t, 2H), 2.43 (s, 3H); *m*/*z* (EI) (%) 360 (M^+, 40), 149 (100), 105 (65), 77 (35).

Synthesis of 17a,b

Methyl trifluoromethanesulfonate (15.3 mmol) was added dropwise to a solution of **16a,b** (8.5 mmol) in dry CH_2Cl_2 (30 ml). The solution was stirred at room temperature for 4 h. After addition of diethyl ether (200 ml), a yellow precipitate was formed, filtered and rinsed with diethyl ether.

2-Methylsulfanyl-4,5-bis(2-benzoyloxyethylsulfanyl)-1,3-dithiolium trifluoromethanesulfonate 17a. Yield 96%, mp 102–103 °C; ^{1}H NMR ($CDCl_3$) 8.06 (dd, 4H), 7.46 (m, 6H), 4.63 (t, 4H), 3.53 (t, 4H), 3.10 (s, 3H).

2,5-Dimethylsulfanyl-4-(2-benzoyloxyethylsulfanyl)-1,3-dithiolium trifluoromethanesulfonate 17b. Yield 94%, mp 92–93 °C; ^{1}H NMR ($CDCl_3$) 8.10 (dd, 2H), 7.50 (m, 3H), 4.60 (t, 2H), 3.50 (t, 2H), 3.16 (s, 3H), 2.76 (s, 3H).

Synthesis of 18a,b

Compound **17a** or **17b** (8 mmol), dissolved in a minimal amount of acetonitrile, was added dropwise to a suspension of sodium borohydride (8.8 mmol) in isopropyl alcohol (4 ml) cooled at 0 °C, the temperature of the reaction mixture being maintained below 5 °C. The mixture was then stirred at room temperature for h, extracted with diethyl ether, washed with water and dried ($MgSO_4$). The solvents were evaporated and the resulting pinkish oil was used without further purification for the next step.

2-Methylsulfanyl-4,5-bis(2-benzoyloxyethylsulfanyl)-1,3-dithiole 18a. Yield 94%; ^{1}H NMR ($CDCl_3$) 8.10 (dd, 4H) 7.55 (m, 6H), 5.83 (s, 1H), 4.53 (t, 4H), 3.20 (t, 4H), 2.30 (s, 3H).

2,5-Dimethylsulfanyl-4-(2-benzoyloxyethylsulfanyl)-1,3-dithiole 18b. Quantitative yield; the crude product was immediately used in the subsequent step (synthesis of **19b**) without further characterization.

Synthesis of 19a,b

Hexafluorophosphoric acid solution (1.97 g, 8 mmol, 60%) was added dropwise at 0 °C to a solution of **18a** or **18b** in acetic anhydride (10 ml). The mixture was stirred for 10 min and ethyl acetate (20 ml) was added. Stirring was maintained for 15 min before adding diethyl ether (100 ml). The resulting precipitate was filtered and washed twice with anhydrous diethyl ether .

4,5-Bis(2-benzoyloxyethylsulfanyl)-1,3-dithiolium hexafluorophosphate 19a. Yield 67%, pinkish powder, mp 148 °C; ^{1}H NMR ($CDCl_3$) 8.20 (dd, 4H), 7.43 (m, 6H), 6.38 (s, 1H), 4.49 (t, 4H), 3.16 (t, 4H).

4-(2-Benzoyloxyethylsulfanyl)-5-methylsulfanyl-1,3-dithiolium hexafluorophosphate 19b. Yield 66%, violet powder, mp 110 °C; *m*/*z* (DAB) (%) 329 (100, $M-PF_6$).

Synthesis of 20a,b

To a solution of **19a** or **19b** (1 mmol) in dry acetonitrile (10 mL) were added successively potassium iodide (1 mmol) and trimethyl phosphite (1 mmol) at room temperature. The mixture was stirred for 15 min, the solvent was evaporated and the residue was immediately dissolved in dry THF (10 ml). The phosphonate anion was generated from Bu^{n}Li (=1.1 equiv., 1.6 M in hexane) at -80 °C. A stoichiometric amount of fumaraldehyde mono(dimethyl acetal) in dry THF was then added dropwise and the reaction was allowed to warm to room temperature. THF was removed *in vacuo*, the residue was dissolved in CH_2Cl_2 and washed with water. The obtained acetal was hydrolyzed with Amberlyst-15 (0.4 g) in wet acetone. The course of the reaction was monitored by TLC. After removing the solvent, the residue was purified by chromatography over silica gel (CH_2Cl_2 as eluent) and **20a** or **20b** was obtained as a yellow oil.

4-[4,5-Bis(2-benzoyloxyethylsulfanyl)-1,3-dithiol-2-ylidene]but-2-enal 20a. Yield 78%; ^{1}H NMR ($CDCl_3$) 9.49 (d, 1H, $^3J=8$ Hz), 8.02 (dd, 4H), 7.54, 7.41 (m, 6H), 6.87 (dd, 1H, $^3J=11.5$, 14.5 Hz), 6.21 (d, 1H, $^3J=11.5$ Hz), 5.91 (dd, 1H, $^3J=8.0$, 14.5 Hz), 4.52 (t, 2H), 4.51 (t, 2H), 3.19 (t, 4H); ^{13}C NMR ($CDCl_3$) 192.9, 161.1, 148.6, 145.7, 133.3, 129.7, 128.4, 128.2, 126.6, 111.7, 63.4, 34.7; *m*/*z* (EI) (%) 530 (M^+, 11), 149 (100), 105 (66), 77 (33); ν_{max}(KBr)/cm^{-1} 1718 (CO), 1667 (CO).

4-[4-(2-Benzoyloxyethylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]but-2-enal 20b. Yield 65%; ^{1}H NMR ($CDCl_3$) 9.50, 9.47 (2d, 1H, $Z+E$ isomers), 8.02 (dd, 2H), 7.45 (m, 3H), 6.95 (m, 1H, $^3J=11.5$, 14.5 Hz), 6.25 (m, 1H, $^3J=11.5$ Hz), 5.93 (m, 1H, $^3J=8.0$, 14.5 Hz), 4.55 (t, 2H), 3.20 (t, 2H), 2.42, 2.40 (2s, 3H); *m*/*z* (EI) (%) 396 (M^+, 25), 149 (100), 105 (54), 77 (30).

Synthesis of 21

Using a similar procedure as for **4a–c**, aldehyde **20a** was reacted with 4-nitrobenzyl(triphenyl)phosphonium bromide as the Wittig reagent.

5-[4,5-Bis(2-benzoyloxyethylsulfanyl)-1,3-dithiol-2-ylidene]-1-(4-nitrophenyl)penta-1,3-diene 21. Yield 65%, brown powder, mp 95–99 °C; ^{1}H NMR ($CDCl_3$) 8.16 (d, 2H, $^3J=8.9$ Hz), 8.05 (m, 4H), 7.49 (m, 8H), 6.98 (dd, 1H, $^3J=10.1$, 15.5 Hz), 6.54 (d, 1H, $^3J=15.5$ Hz), 6.17 (m, 3H), 4.51 (t, 4H), 3.18 (t, 4H); ^{13}C NMR ($CDCl_3$) 166.2, 146.2, 144.1, 135.6, 133.7, 133.2, 131.7, 129.6, 128.8, 128.6, 128.4, 126.4, 124.2, 114.8, 63.5, 34.4 (Calc. for $C_{32}H_{27}NO_6S_4$: C, 59.15; H, 4.19; N, 2.15; O, 14.77; S, 19.73. Found: C, 59.02; H, 4.39; N, 2.26; O, 15.20; S, 19.87%); *m*/*z* (EI) (%) 649 (M^+, 11), 149 (100), 105 (93), 77 (47); ν_{max}(KBr)/cm^{-1} 1731, 1719 (CO), 1537, 1333 (NO_2).

Synthesis of 22

A solution of **21** (1.2 mmol) and KOH (12 mmol) in a mixture of THF (10 ml), MeOH (5 ml) and H_2O (1 ml) was refluxed for 1 h. The solution was diluted in CH_2Cl_2, washed with water and dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed over silica gel (ethyl acetate–CH_2Cl_2 1:1 as eluent). Compound **22** was obtained as a black powder.

5-[4,5-Bis(2-hydroxyethylsulfanyl)-1,3-dithiol-2-ylidene]-1-(4-nitrophenyl)penta-1,3-diene 22. Yield 79%, mp 137–141 °C; ^{1}H NMR ($CDCl_3$) 8.17 (d, 2H), 7.49 (d, 2H) 6.98 (d, 1H, $^3J=8.0, 15.5$ Hz), 6.55 (d, 1H, $^3J=15.5$ Hz), 6.25 (m, 3H), 3.78 (t, 4H), 3.00 (t, 4H), 2.81 (s, 2H); ^{13}C NMR ($CDCl_3$) 146.3, 144.0, 135.2, 133.6, 131.5, 129.1, 128.9, 127.7, 126.4, 124.2 115.2, 59.9, 39.2 (Calc. for $C_{18}H_{19}NO_4S_4$: C, 48.96; H, 4.33; N, 3.17; O, 14.49; S, 29.04. Found: C, 48.44; H, 4.22; N, 3.29; O, 14.95; S, 29.36%); *m*/*z* (EI) (%) 441 (M^+, 100), 184 (75), 121 (35); ν_{max}(Fluorolube)/cm^{-1} 3319 (OH), 1566, 1333 (NO_2).

Synthesis of 23

Using a similar procedure as for **14**, diol **22** was reacted with methacryloyl chloride. Diester **23** was obtained as black crystals.

5-[4,5-Bis(2-methacryloyloxyethylsulfanyl)-1,3-dithiol-2-ylidene]-1-(4-nitrophenyl)penta-1,3-diene 23. Yield 58%, mp 76–79 °C; ^{1}H NMR ($CDCl_3$) 8.17 (d, 2H), 7.48 (d, 2H), 6.98 (dd, 1H, $^3J=9.9$ Hz), 5.48 (m, 2H), 5.61 (s, 1H), 4.35 (q, 4H), 3.10 (q, 4H), 1.96 (s, 6H); ^{13}C NMR ($CDCl_3$) 170, 146.2, 144.1, 135.8, 135.6, 133.7, 131.7, 128.8, 128.6, 127.6, 126.6, 126.2, 124.2, 114.8, 63.2, 34.3, 18.3; *m*/*z* (EI) (%) 577 (M^+, 7), 184 (8), 113 (100), 69 (29); ν_{max}(KBr)/cm^{-1} 1711 (CO), 1528, 1330 (NO_2).

Synthesis of 24

Using a similar procedure as for **5a,b**, aldehyde **20b** (1 mmol) was reacted with dimethyl (5-nitro-2-thienyl)methylphosphonate (1.1 mmol) as the Wittig–Horner reagent in the presence of Bu^{n}Li (=1.1 equiv., 1.6 M in hexane).

5-[4-(2-Benzoyloxyethylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]-1-(5-nitro-2-thienyl)penta-1,3-diene 24. Yield 51%, black powder; *m*/*z* (EI) (%) 521 (M^+, 20), 489 (10), 149 (100), 105 (76), 77 (47).

Synthesis of 25

Using a similar procedure as for **22**, ester **24** (1.2 mmol) was hydrolyzed to alcohol **25**.

5-[4-(2-Hydroxyethylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]-1-(5-nitro-2-thienyl)penta-1,3-diene 25. Yield 60%, dark violet powder; ^{1}H NMR ($CDCl_3$) 7.79 (d, 1H, $^3J=4.2$ Hz), 6.85 (d, 1H, $^3J=4.2$ Hz), 6.83 (dd, 1H, $^3J=10.6, 15.1$ Hz), 6.53 (d 1H, $^3J=15.1$ Hz), 6.28 (m, 1H), 6.15 (m, 2H), 3.74 (m, 2H), 2.96, 2.94 (2t, 2H), 2.48, 2.45 (2s, 3H), 2.37 (t, 1H); ^{13}C NMR ($CDCl_3$) 151.1, 137.5, 134.4, 132.6, 129.9, 127.4, 124.1, 122.2, 114.5, 59.9, 39.0, 19.0, 18.9; *m*/*z* (EI) (%) 417 (M^+, 100), 385 (38), 249 (40), 204 (45), 190 (60), 147 (67), 135 (62), 103 (68); ν_{max}(KBr)/cm^{-1} 3419 (OH), 1525, 1320 (NO_2).

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5 *Crystal data* for compound **8a**: $C_{15}H_{18}O_2S_2$, $M=294.43$, triclinic, $P\bar{1}$, $Z=2$, $a=8.395(3)$, $b=9.830(4)$, $c=10.909(4)$ Å, $\alpha=114.09(2)$, $\beta=99.99(3)$, $\gamma=96.42(3)$, $V=792.5(6)$ Å^3, $\lambda=0.71073$ Å. Data collection was carried out by the zig-zag $\omega/2\theta$ scan technique ($2<\theta<25°$) on an Enraf–Nonius CAD4 diffractometer. Conditions of measurements were $t_{max}=40$ s, range *h*, *k*, *l* [*h* (0, 10); *k* (−12, 12); *l* (−13, 13)]. Intensity control reflections were measured every 2 h without appreciable decay (0.15%). A total of 3098 independent reflections were collected from which 1153 corresponded to $I>3\sigma(I)$. Structure refinement: after Lorentz polarisation corrections, the structure was solved by direct methods using the general tangent phasing procedure (GENTAN), which revealed all the non-hydrogen atoms. After anisotropic refinement of S, O and C atoms, the coordinates of the H atoms were generated from the molecular geometry. The whole structure was refined by full-matrix least-squares techniques (refinement on F, x, y, z, U_{ij} for S, O and C atoms, x, y, z, and U fixed for H atoms). 172 variables for 1153 observations, with the resulting $R=0.073$, $Rw=0.078$. All the calculations were performed using the XTAL 3.2 package.

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