Synthesis, Structures and Nonlinear Optical Properties of Novel D−π−A Chromophores: Intramolecular Charge Transfer from 1,3-Dithiole or Ferrocene Moieties to Polynitrofluorene or Dicyanomethylene Moieties through Conjugated Linkers[‡]

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Keywords: Ab initio calculations / Charge transfer / Donor-linker-acceptor systems / Nonlinear optics / Ferrocene / Fluorene

Electron donor–π–acceptor chromophores **5**, **9**, **11**, **18**–**20**, **21**, **22**, **27**, **28a**, **28c**, **31**, **32**, **34**–**36**, **38a**–**c**, **41a**, **41c**, and **42** have been synthesised. The donor units are 1,3-dithiole and ferrocene; conjugated ethylenic, phenyl, phenylenevinylene, thienyl, bithienyl, terthienyl, or thienylenevinylene linkers act as a central π-electron relay unit, and dicyanomethylene and polynitrofluorene groups as the acceptor unit. The electronic absorption spectra display a broad low-energy intramolecular charge transfer band in the visible region (500–700 nm) the energy ($h\nu_{ICT} \approx 1.7$–2.5 eV) and intensity ($\varepsilon \approx 5000$–50000 $m^{-1}cm^{-1}$) of which depend substantially on the nature of both D and A moieties and on the structure of the linker unit. Nonlinear optical properties have been evaluated using the EFISH technique: the highest μβ(0) values are observed for **38b** [(900±300)×10^{-48} esu] and **42** [(1800±300)×10^{-48} esu] establishing that polynitrofluorene is a promising acceptor terminal moiety in this context. The molecular and electronic structures of **49** and **50** have been calculated by the RHF/6-31G(d)//RHF/6-31G(d) ab initio method. The HOMO is located mostly in the 1,3-dithiolium ring, and the LUMO mostly at the dicyanomethylene fragment (and the phenyl ring of **50**) although the electronic population at C2 of the 1,3-dithiolium rings is also considerable. The X-ray crystal structures of **9**, **18** and **27** are reported. In all three structures the conjugated π-systems are effectively planar with extensive π-electron delocalisation between the donor and acceptor moieties. The planar conformation of **18** gives rise to a close intramolecular S···S contact of 3.095(3) Å between the dithiole and thiophene units.

Introduction

The design of second-order nonlinear optical (NLO) materials is now well advanced and the basic tenets for large hyperpolarisabilities are universally accepted.[2] The molecules must be polarisable with asymmetric charge distribution and possess a pathway of π-conjugated electrons. Many of these donor−π−acceptor (D−π−A) systems are substituted benzenes, biphenyls, stilbenes, azostilbenes and tolanes, e.g. *p*-nitroaniline and 4-(dimethylamino)-4′-nitrostilbene (DANS). Bond length alternation (BLA), i.e. the difference in length between single and double bonds in the molecule, is a relevant parameter in the optimisation of the hyperpolarisability.[3−6] Molecules with aromatic ground states tend to posses a greater BLA (less polarised) for a given combination of donor and acceptor moieties than a simple polyene of comparable length. A high degree of BLA is indicative of an insufficient contribution of the charge-separated resonance form to the ground state and is a direct consequence of the loss of aromatic stabilisation in the charge-separated form. Therefore, molecules have been designed with less aromatic character in the ground state, or alternatively, where loss of aromaticity in the ground state is compensated for by a gain in aromaticity in the charge-separated form. Replacement of benzene by thiophene decreases the aromatic character of the ground state and leads to enhanced hyperpolarisabilities.[7,8] Consequently, novel thiophene-containing D−π−A systems are of current interest,[9,10] and theoretical work demonstrates a dramatic increase in NLO efficiency when a thiazole unit is a π-linker due to its inherent dipolar nature.[11]

1,3-Dithiole moieties provide a terminal electron-donating group in second-order NLO chromophores,[12−15] al-

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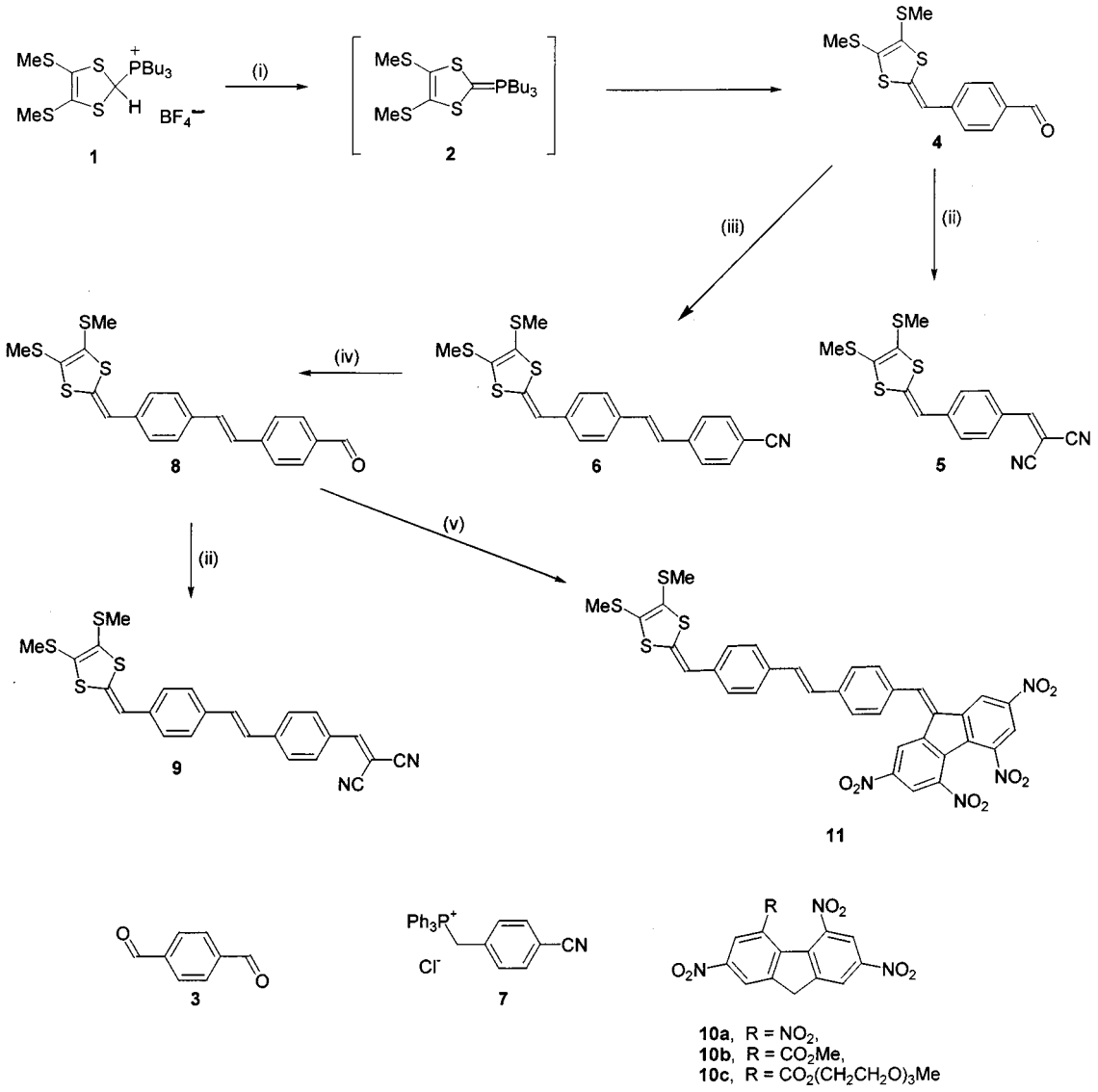
though generally only low to moderate second-harmonic generation (SHG) efficiencies have been achieved. Recently, third-order NLO properties of bis(1,3-dithiole) polymethine dyes were also reported.[16] Green et al.[17] demonstrated the great potential of ferrocene as an electron-donating group for second-order NLO materials,[18,19] which has also been used in third-order NLO materials.[19] While many electron-withdrawing groups have been exploited in NLO materials[20], polynitrofluorenes have not been used in this context, although fluorene acceptors are promising materials for optoelectronic applications.[21] Fluorene acceptors incorporating electron donor substituents[1,22–27] resulting in *intra*molecular charge transfer can keep sufficiently high electron affinity to be involved in *inter*molecular single-electron transfer processes. Therefore, the use of polynitrofluorene moieties in D–π–A systems is attractive in the design of molecules combining both electronic and NLO properties.

In this paper we describe the synthesis, linear and nonlinear optical properties of D–π–A systems comprising 1,3-dithiole and ferrocene as electron-donating groups, dicyanomethylene and polynitrofluorene as electron-accepting groups, with a wide variation in the structure of the π-linker. Compounds **9**, **18**, and **27** were characterised by single-crystal X-ray diffraction, and theoretical ab initio calculations for **49** and **50** were performed.

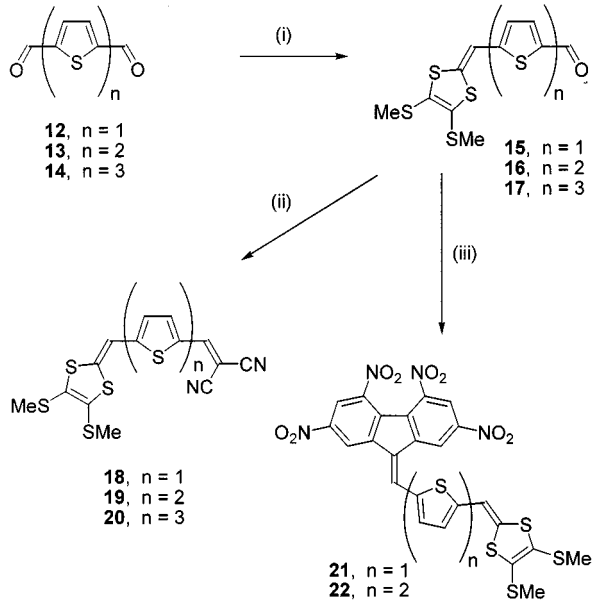
Results and Discussion

Synthesis of 1,3-Dithiole–π–A Systems 5, 9, 11, 18–20, 21, and 22

Terephthalaldehyde **3** reacted with ylide **2**[14] to afford aldehyde **4**, which was refluxed with Lehnert's reagent (malononitrile, titanium tetrachloride, and pyridine)[28] in



Scheme 1. Synthesis of dithiole–phenylene–acceptor compounds; reagents and conditions: (i) compound **3**, Et_3N, THF, 20 °C, 16 h; (ii) $CH_2(CN)_2$, $TiCl_4$, pyridine, CH_2Cl_2, reflux, 16 h; (iii) compound **7**, Et_3N, toluene, reflux, 16 h; (iv) Dibal-H, chlorobenzene, 0 °C, 2 h, then 20 °C, 2 h; (v) compound **10a**, DMF, 20 °C, 3.5 h

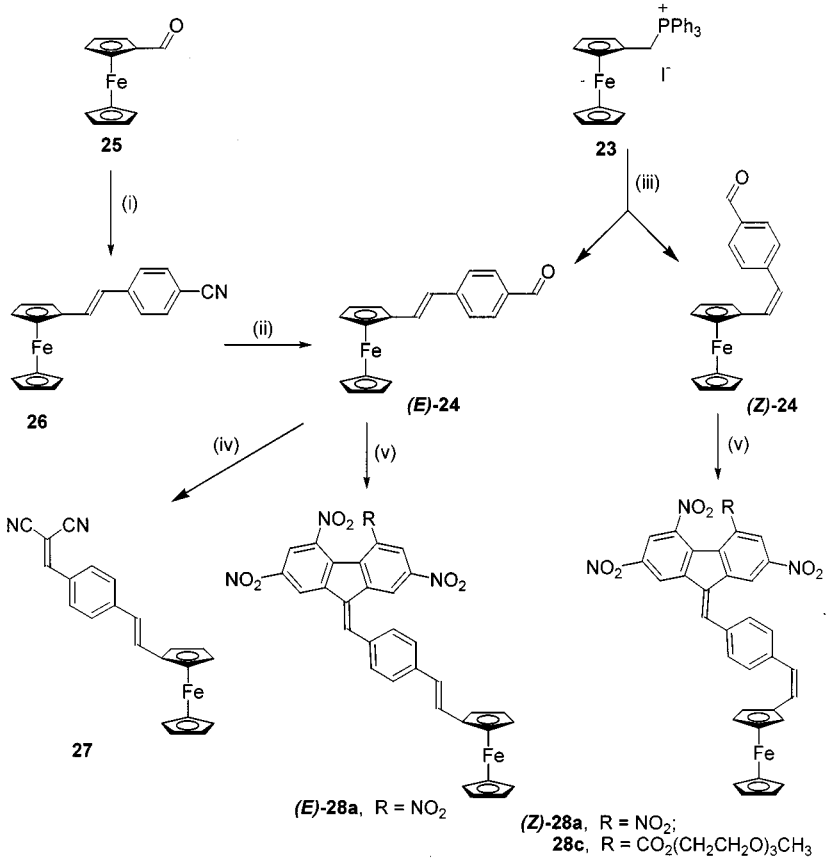


Scheme 2. Synthesis of dithiole−thienylene−acceptor compounds; reagents and conditions: (i) compound **1**, Et_3N, THF, 20 °C, 16 h; (ii) $CH_2(CN)_2$, $TiCl_4$, pyridine, CH_2Cl_2, reflux, 16 h; (iii) compound **10a**, DMF, 20 °C, 0.5−1.5 h

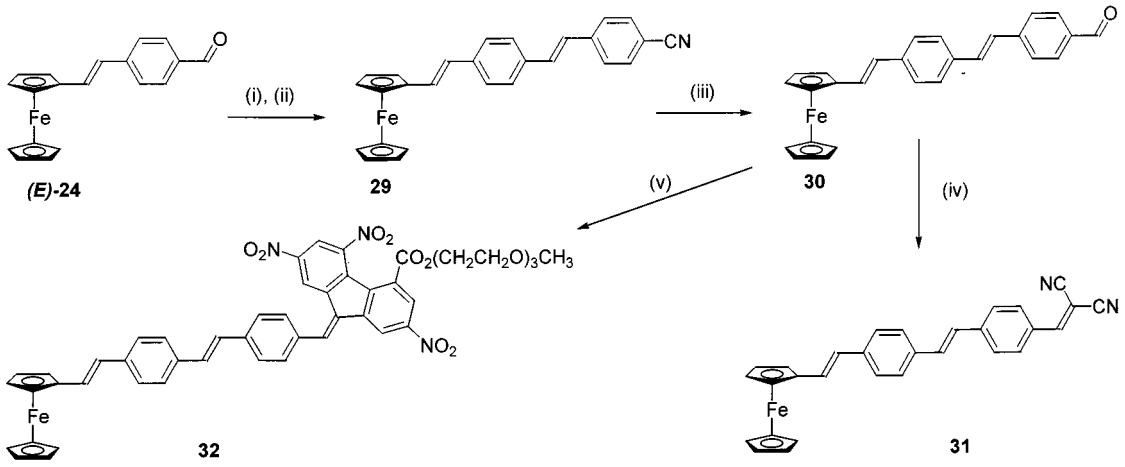
dichloromethane (DCM) yielding compound **5** (Scheme 1). Reaction of aldehyde **4** with phosphonium salt **7** gave nitrile **6** which was reduced to aldehyde **8** by diisobutylaluminium hydride (Dibal-H). Condensation of aldehyde **8** with Lehnert's reagent afforded compound **9**, whereas condensation with 2,4,5,7-tetranitrofluorene (**10a**)[29] in *N*,*N*-dimethylformamide (DMF) yielded system **11**. Polynitrofluorenes are quite strong C−H acids[30] and they react readily with aldehydes,[31] ketones,[32] amides,[30] and dithiolium salts.[23−25,33,34] In a similar manner, dialdehydes **12**−**14** were converted into aldehydes **15**−**17**, respectively, and hence compounds **18**−**20**, **21**, and **22**, respectively (Scheme 2).

Synthesis of Ferrocene−π−A Systems 27, 28a, 28c, 31, 32

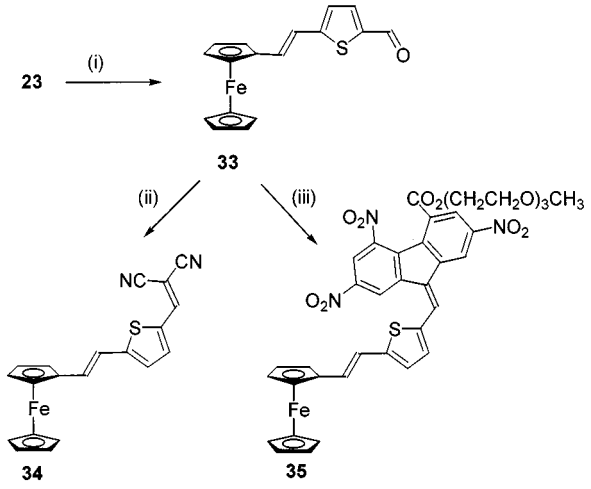
Terephthalaldehyde **3** reacted with the ylide, generated in situ from phosphonium salt **23** (by addition of potassium *tert*-butoxide in THF), affording aldehyde **24** as a mixture of (*E*)/(*Z*) isomers [(*E*)/(*Z*) ≈ 10:1, as judged by ^{1}H NMR] which were separated by column chromatography (Scheme 3). Alternatively, aldehyde ***(E)*-24** was prepared from ferrocenecarboxaldehyde (**25**) via the nitrile **26**. The overall yield via **26** (**25** → **26** → **24**) is 67% which is higher than from **23** [**23** → ***(E)*-24**; ca. 40%]. Reaction of aldehyde ***(E)*-24** with Lehnert's reagent or the tetranitrofluorene **10a**



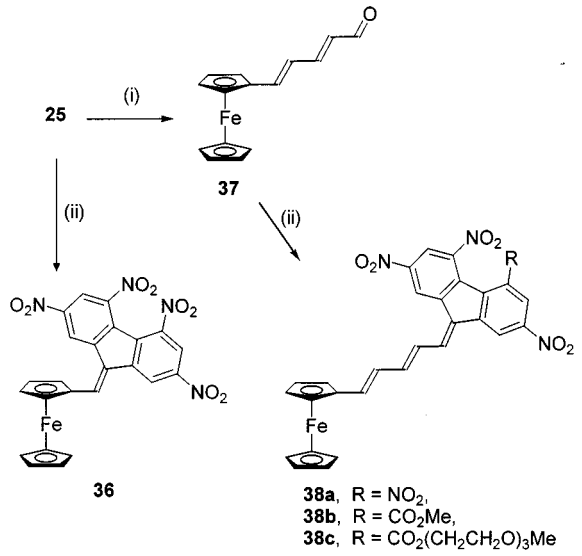
Scheme 3. Synthesis of ferrocene−phenylene−acceptor compounds; reagents and conditions: (i) compound **7**, Et_3N, toluene, reflux, 16 h; (ii) Dibal-H, chlorobenzene, 0 °C, 2 h, then 20 °C, 2 h; (iii) KO*t*Bu, THF, 0 °C, 0.5 h, followed by compound **3**, THF, 20 °C, 2 h; (iv) $CH_2(CN)_2$, $TiCl_4$, pyridine, CH_2Cl_2, reflux, 16 h; (v) compound **10a**,**c**, DMF, 20 °C, 1−6 h (**10a**) or 30−35 °C, 6 h (**10c**)



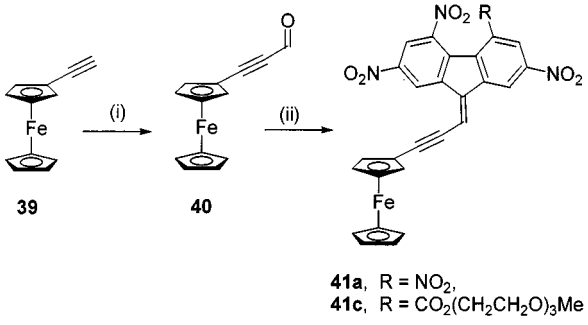
Scheme 4. Synthesis of extended ferrocene−phenylene−acceptor compounds; reagents and conditions: (i) compound **7**, KO*t*Bu, THF, 20 °C, 15 min; (ii) compound **24**, THF, reflux, 4 h; (iii) Dibal-H, chlorobenzene, 0 °C, 2 h, then 20 °C, 2 h; (iv) $CH_2(CN)_2$, $TiCl_4$, pyridine, CH_2Cl_2, reflux, 16 h; (v) compound **10c**, DMF, 20 °C, 24 h



Scheme 5. Synthesis of ferrocene−thienylene−acceptor compounds; reagents and conditions: (i) KO*t*Bu, THF, 0 °C, 0.5 h, followed by compound **12**, THF, 20 °C, 2 h; (ii) $CH_2(CN)_2$, $TiCl_4$, pyridine, CH_2Cl_2, reflux, 16 h; (iii) compound **10c**, DMF, 30−35 °C, 6 h



Scheme 6. Synthesis of ferrocene−vinylene−acceptor compounds; reagents and conditions: (i) *N*-*tert*-butyl-γ-trimethylsilylcrotonaldimine, CsF, DMSO, 20 °C, 0.5 h, then 100 °C, 0.5 h, then $ZnCl_2$/H_2O, 20 °C; (ii) compound **10a−c**, DMF, 20 °C, 0.5−20 h

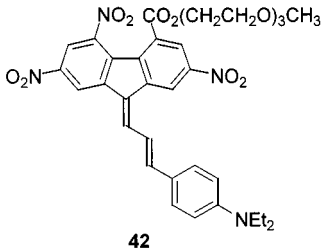


Scheme 7. Synthesis of ferrocene−ethynylene−fluorene compounds **41a**,**c**; reagents and conditions: (i) BuLi; then DMF, (ii) compound **10a**,**c**, DMF, 20 °C, 40 min to 20 h

afforded compounds **27** or ***(E)*-28a,** respectively. Similar reactions of *cis*-aldehyde ***(Z)*-24** gave *cis* isomers ***(Z)*-28a**,**c**. By analogy with the transformation **4** → **6** → **8**, aldehyde ***(E)*-24** was converted into **30**, and then into **31** or **32** by reaction with either Lehnert's reagent or with fluorene **10c** (Scheme 4). Reaction of salt **23** with dialdehyde **12** gave aldehyde **33**, and subsequently compounds **34** and **35** (Scheme 5).

Reaction of ferrocenecarboxaldehyde (**25**) with 2,4,5,7-tetranitrofluorene (**10a**) in DMF afforded derivative **36** in which the D and A moieties are connected via a short π-bridge.[35] We converted aldehyde **25** into its vinylogue **37** by reaction with *N*-*tert*-butyl-γ-trimethylsilylcrotonaldimine[36] and subsequent hydrolysis of the intermediate imine. Reaction of aldehyde **37** with fluorenes **10a−c** afforded compounds **38a−c** with the longer π-linker (Scheme 6). To access fluorene derivatives with a C≡C bond in the π-linker we formylated ferrocenylacetylene **39** as reported,[37] and

the resulting aldehyde gave compounds **41a**,**c** (Scheme 7). To compare the effects of ferrocene and 1,3-dithiole with the *p*-(dialkylamino)phenyl donor moiety, which is a known donor functionality for NLO chromophores,[38] we synthesised fluorene derivative **42** by reaction of fluorene **10c** with *p*-(diethylamino)cinnamaldehyde in acetic anhydride.



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X-ray Molecular Structures of Compounds 9, 18, and 27

The asymmetric unit of **9** comprises two molecules, A (Figure 1) and B (with one MeS group disordered) of similar geometry. The conjugated π-systems of the dicyanomethylene group, benzene rings, C=C double bonds and the heterocycle, are coplanar except for folding along the S(3)···S(4) vector by 7.3° (A) and 8.0° (B) and a twist around the C(18)−C(21) bond by 14.0° (A) and 4.8° (B). Molecule **27** (Figure 2), also exhibits a near-coplanarity of the dicyanomethylene group, the benzene ring, the C(11)=C(12) bond and the substituted cyclopentadiene ring, with twists around the C(1)−C(11), C(12)−C(13), and C(16)−C(19) bonds of 5.8, 10.2, and 12.0°, respectively. In both **9** and **27**, the C−C single bonds are shortened in comparison with the standard "non-conjugated" C(sp^2)−C(sp^2) bond (1.478 Å) although not the "conjugated" one (1.455 Å).[39] π-Conjugation along the chain is also manifested in partially quinoid geometry of the benzene rings, wherein the quinoid C−C bonds are 0.02−0.03 Å shorter than the others.

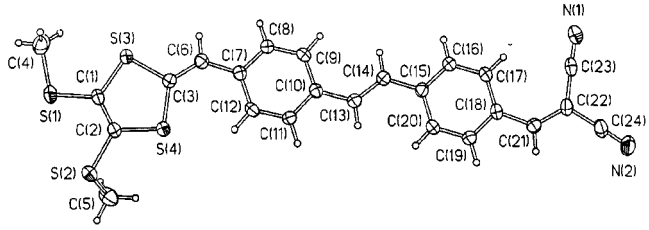


Figure 1. Molecule A of **9**, showing 50% probability displacement ellipsoids; bond lengths (mean of two molecules) [Å]: S(1)−C(1) 1.758(3), S(2)−C(2) 1.762(3), C(1)−C(2) 1.346(5), S(3)−C(1) 1.753(3), S(4)−C(2) 1.764(4), S(3)−C(3) 1.774(3), S(4)−C(3) 1.761(3), C(3)−C(6) 1.348(5), C(6)−C(7) 1.454(4), C(10)−C(13) 1.465(4), C(13)−C(14) 1.341(5), C(14)−C(15) 1.463(4), C(18)−C(21) 1.455(4), C(21)−C(22) 1.356(4), C(22)−CN 1.448(5)

The structure of **9** contains four-molecule stacks BAA′B′ in which molecules are parallel within 2°, with the interplanar separations *d* of 3.4−3.5 Å (Figure 3), but no *infinite* stacks. The crystal of **27** contains pairs of molecules contacting face-to-face (*d* = 3.44 Å). The long axes of all pairs in the structure are parallel to the crystallographic [1 0 1] direction. Viewed along the latter, the packing motif is a checker-board order with the planes of adjacent molecules approximately perpendicular and contacting edge-to-face, i.e. a distorted κ-mode.

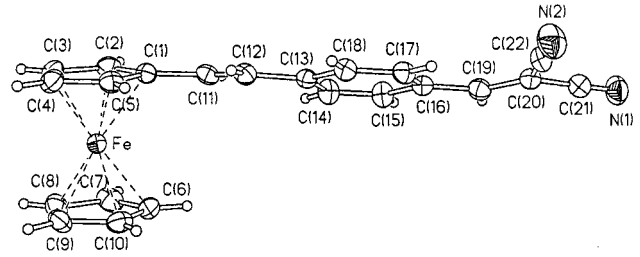


Figure 2. Molecular structure of **27**, showing 30% probability displacement ellipsoids; bond lengths [Å]: C(1)−C(11) 1.463(5), C(11)−C(12) 1.334(5), C(12)−C(13) 1.465(5), C(16)−C(19) 1.452(5), C(19)−C(20) 1.352(5), C(14)−C(15) 1.369(5), C(17)−C(18) 1.373(5), other benzene ring bonds average 1.400(5) Å

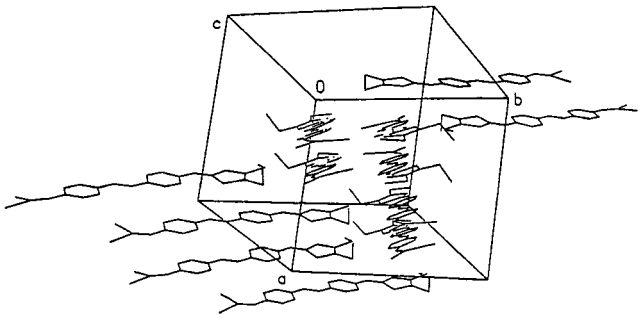


Figure 3. Crystal packing of **9**, showing tetramers

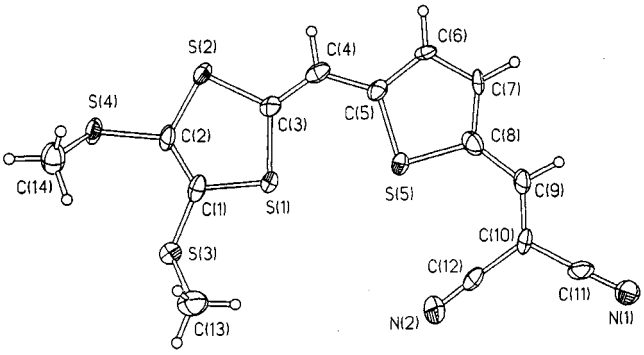
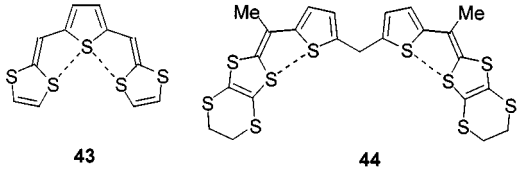


Figure 4. Molecular structure of **18**, showing 50% probability displacement ellipsoids; bond lengths [Å]: C(1)−S(1) 1.755(9), C(1)−C(2) 1.366(12), C(2)−S(2) 1.722(9), S(1)−C(3) 1.742(9), S(2)−C(3) 1.757(10), C(3)−C(4) 1.355(12), C(9)−C(10) 1.353(12)

The molecule of **18** (Figure 4) is planar, but for twists of 4.1(5) and 6.5(4)° around the (formally single) C(8)−C(9) and C(4)−C(5) bonds. These bonds, 1.428(12) and 1.432(13) Å respectively, are 0.03 Å shorter than the bonds between π-conjugated moieties in **9** or **27**. In the thiophene ring, the formally double bonds C(5)−C(6) 1.393(12) and C(7)−C(8) 1.383(12) Å are essentially equal with the "single" bond C(6)−C(7) 1.385(12) Å, cf. the standard[39] C=C and C−C bonds of 1.362 and 1.424 Å in thiophenes. Thus, **18** has a push-pull π-electron delocalisation (absent

in **9** or **27**) along the chain and by the C(5)C(6)C(7)C(8) path through the thiophene ring. The lone pairs of S(5) are effectively excluded from this conjugation: compare C(5)−S(5) and S(5)−C(8) distances of 1.745(9) and 1.747(9) Å with the standard C−S 1.712 Å in thiophene. The planar conformation of **18** gives rise to the intramolecular S(1)···S(5) contact of 3.095(3) Å (cf. the van der Waals radius of sulfur, 1.81 Å[40]). Molecular packing is characterised by step-like stacks (d = 3.41 Å), in which the donor (dithiole) part of each molecule overlaps with the acceptor (dicyanomethylene) part of the next.

The *syn-syn* configuration of both the C(3)=C(4) and C(9)=C(10) bonds with respect to the thiophene sulfur atom in **18** has been predicted correctly by MO ab initio calculations at the HF/3-21G* level,[41,42] while the PM3 method gave the *anti* configuration, demonstrating its poor ability to allow for intramolecular S···S interactions.[43] A similar planar s*yn-syn* configuration is observed in crystal structures of **43**,[44] its radical cation perchlorate salt[45] and **44**[46] with the intramolecular S···S distances of 3.12, 3.06−3.11, and 3.01 Å, respectively.



43 **44**

Electronic Absorption Spectra

The push-pull nature of the D−π−A compounds listed in Table 1 is manifested in their electronic absorption spectra: low-energy bands arising from intramolecular charge transfer (ICT) are seen in the visible region (500−700 nm). Their energies ($h\nu_{ICT} \approx 1.7-2.5$ eV) and intensities ($\varepsilon \approx 5000-50000$ м$^{-1}$ cm^{-1}) depend substantially on the nature of both D and A moieties as well as on the linker between them. Pure ICT character of these bands had been proven by concentration experiments (e.g., for compound **42** from $2\cdot10^{-6}$ to 10^{-3} м) indicating no observable intermolecular interactions between D and A moieties. Nevertheless, we cannot completely exclude some extent of such an interaction for all the compounds, especially at high concentrations. Thus, as was mentioned above, compound **27** forms dimers in the solid state and the lower than expected NLO response in SHG experiments for some compounds (see next section) can be attributed to such an aggregation.

Compounds with the *p*-phenylenevinylene linkers are characterized by short-wavelength ICT bands at ca. 500−550 nm (see, e.g. **11**, Figure 5, and **5**, **9**, **11**, **27**, **28**, **31**,

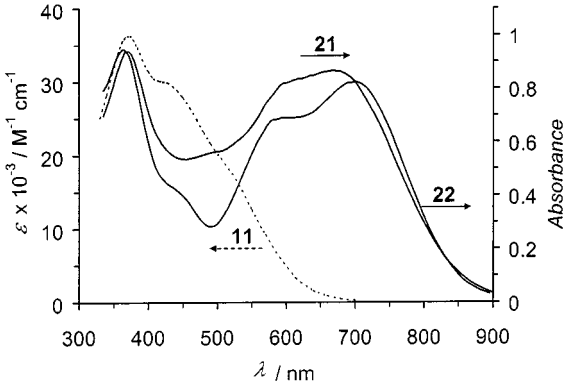


Figure 5. Electronic absorption spectra of 1,3-dithiole−π−fluorene push-pull compounds **11** (in acetone), **21** and **22** (in 1,2-dichloroethane), 25 °C

Table 1. Electronic absorption spectroscopic data and ICT energies ($h\nu_{ICT}$) derived from the longest wavelength absorbances

Compound	Solvent: λ_{max} [nm] (ε [м$^{-1}$ cm^{-1}])	$h\nu_{ICT}$ [eV]
5	DCM: 500 (31600), 324 (17800)	2.48
9	DCM: 474 (38000), 356 (32400)	2.67
11	acetone: 510sh (19000), 430sh (29500)	ca. 2.4
18	DCM: 547 (46500), 339 (10500), 293 (14500)	2.27
19	DCM: 564 (28000), 380 (16000), 275 (12900)	2.21
20	DCM: 550 (23800), 415 (23200), 272 (14200)	2.29
21	$C_2H_4Cl_2$: 700, 600sh	1.77
22	$C_2H_4Cl_2$: 670, 590sh	1.85
27	DCM: 543 (10000), 395 (17400)	2.28
(*E*)-**28a**	DCM: 625sh, 465, 367	ca. 2.0
(*Z*)-**28a**	$C_2H_4Cl_2$: 600sh, 430sh, 369	ca. 2.1
28c	$C_2H_4Cl_2$: 570sh, 430sh, 365	ca. 2.2
31	DCM: 500sh (12000), 420 (30500), 340 (13500), 327 (13500), 255 (12500)	2.50
32	$C_2H_4Cl_2$: 570sh (4470), 450sh (22900), 358 (39800)	ca. 2.2
34	DCM: 577 (10500), 344 (7400)	2.15
35	$C_2H_4Cl_2$: 640sh (11000), 502 (20900), 360 (21400)	ca. 1.9
36	$C_2H_4Cl_2$: 623 (4800), 430 (12000)	1.99
38a	$C_2H_4Cl_2$: 706, 514, 464; acetone: 690 (17000), 505 (28200), 461 (28200), 371 (24000)	1.76; 1.80
38b	$C_2H_4Cl_2$: 663, 485sh, 450sh	1.87
38c	$C_2H_4Cl_2$: 660 (15100), 490sh (25000), 455sh (25000), 371 (19500)	1.88
41a	$C_2H_4Cl_2$: 658, 451, 372	1.88
41c	$C_2H_4Cl_2$: 616 (4570), 431 (13500), 367 (20000)	2.01
42	DCM: 624 (46000), 536 (46000), 366 (25000), 294 (30000), 254 (35000)	1.99

and **32**, Table 1). These bands undergo a hypsochromic shift by lengthening the linker by adding an additional *p*-phenylenevinylene bridge [cf. **5** and **9**, **27** and **31**, **(*E*)-28a** and **32**, Figure 6, a, and Table 1]. Substitution of a phenyl ring in the linker by a more electron-rich thiophene ring resulted in a bathochromic shift of the ICT band and an increase in its intensity [**11** → **22**, Figure 5; **(*E*)-28a** → **35**, Figure 6, a; Table 1]. Such behaviour is well documented in the literature.[8] The number of thiophene rings in the bridge in 1,3-dithiole−π−A compounds **18**−**22** has little effect on the energies of ICT (Table 1), with even a hypsochromic shift of λ_{ICT} for **22** of ca. 30 nm as compared to **21** (Figure 5, Table 1), in contrast to polyene π-linker in D−π−A systems where lengthening the linker results in a substantial bathochromic shift of λ_{ICT}[23,47,48] (cf. **36** and **38a**, Table 1) and an increase in the ground state dipole moments.[49]

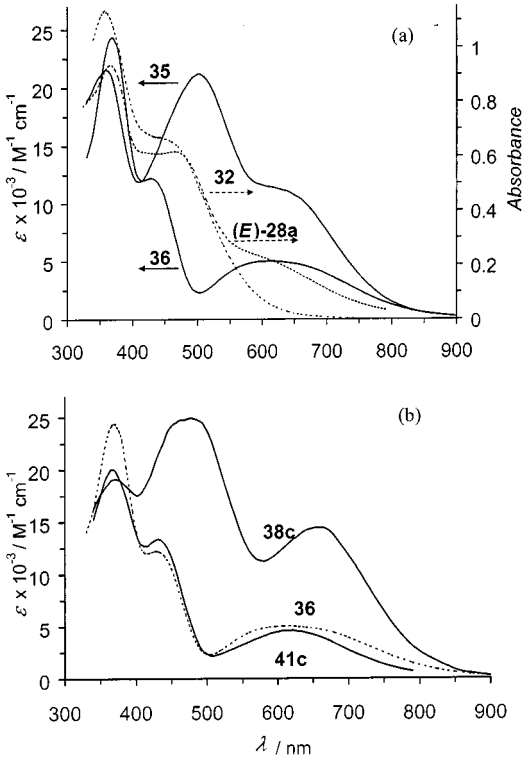


Figure 6. Electronic absorption spectra of ferrocene−π−fluorene push-pull compounds in 1,2-dichloroethane, 25 °C: (a) **28c**, **32**, **35**, and **36**; (b) **36**, **38c**, and **41c**

Usually, the long-wavelength absorption bands in conjugated oligomers undergo a bathochromic shift with an exponential saturation[50−53] with lengthening of the number of repeated units, although hypsochromic effects via the extention of conjugation in donor−acceptor systems have precedent in the literature, e.g. for stilbenoid squaraines and a series of 4′-(dimethylamino)-4-nitrostilbene homologues.[54]

Linkage of fluorene and ferrocene moieties via a short =C− linker (compound **36**) results in a broad ICT band at ca. 550−700 nm with a maximum at 623 nm. The additional incorporation of the 2,5-thienylenevinylene bridge (compound **35**) results in an increase in the intensity of the ICT band, whereas a *p*-phenylenevinylene bridge decreases the intensity due to the aromatic character of the phenyl ring making the quinoid zwitterionic structures for compounds **28** and **32** unfavourable. Surprisingly, the acetylene bridge (**36** → **41c**) has almost no effect on the electronic absorption spectra (Figure 6, b). As expected from the high polarisability of the polyene chain, incorporating additional −CH=CH−CH=CH− units into the π-linker of **36** results in a substantial bathochromic shift and an increase in the intensity of the ICT band (compound **38c**, Figure 6, b) and, as we show below, compound **38c** displays considerable first-order hyperpolarisability μβ(0) according to electric field induced second harmonic (EFISH) generation experiments.

Comparing dicyanomethylene and polynitrofluorene acceptor moieties one can conclude that ICTs in fluorene-based compounds are of lower energies (cf. **9**/**11**, **18**/**21**, **19**/**22**, **31**/**32**, **34**/**35**, Table 1); nevertheless, fluorene compounds with ICT usually keep their electron acceptor properties to some extent[22−26,35] due to larger π-extension than the dicyanomethylene fragment.

Nonlinear Optical Properties

The nonlinear optical properties were determined using the EFISH technique at λ = 1.54 μm. As seen from Table 2,

Table 2. λ_{max}, μβ values measured at λ = 1.54 μm (DCM), and static μβ(0) values deduced from the experimental μβ values using a two-level dispersion model for β

Compound	λ_{max} [nm]	μβ [10^{-48} esu]	μβ(0) [10^{-48} esu][a]
5	500	400±150	200±100[b]
9	474	850±50	470±30
18	547	650±50	280±30
27	543	450±50	200±20
***(Z)*-28c**	570sh, 430sh	1300±130	830±80[c]
31	500sh	570±30	370±20
32	570sh, 460sh	410±35	240±20[c]
38b	663	5000±1500	900±300[b]
38c	660	2700±200	470±50
41c	616	700±100	170±30
42	624	7200±700	1800±300
45a[d] [14]	556	4554	1170
45b[e] [15]	541	1870	508
45c[e] [15]	502	1200	431
46a[f][g] [47]	443	460	340
46b[f] [g] [47]	507	1410	940
47a[g][h] [48]	640	3470	1700
47b[g] [h] [48]	661	5490	2500
47c[g] [h] [48]	601	1820	990
47d[g] [h] [48]	611	2040	1080
47e[g] [h] [48]	662	5490	2500
47f[g] [h] [48]	655	7410	3450

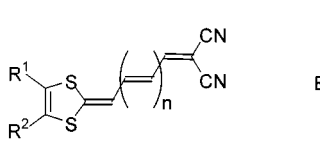
[a] μβ(0) = 300±20 was determined for DANS under the same conditions. − [b] The uncertainty in μβ and μβ(0) for this molecule is relatively large due to its low solubility. − [c] μβ(0) calculated using the energy of the main peaks (430 and 460 nm for **28c** and **32**, respectively) and not low-intensity, low-energy shoulders. − [d] Measured in chloroform at λ = 1.34 μm. − [e] Measured in dichloromethane at λ = 1.34 μm. − [f] Measured in chloroform at λ = 1.907 μm. − [g] Data for μβ and μβ(0) recalculated by dividing by a factor of 1.93 (see Exp. Sect.). − [h] Measured in dioxane λ = 1.907 μm.

compounds **5**, **9**, **18**, **27**, **31**, **32**, and **41c** show moderate second-order nonlinear properties [static first-order hyperpolarisability $\mu\beta(0) \approx 100-470 \times 10^{-48}$ esu], whereas compounds **28c**, **38b**, and **42** show quite high $\mu\beta(0)$ values.

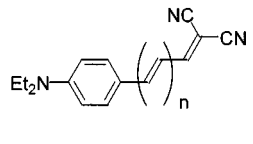
In spite of the hypsochromic shift in λ_{ICT} with an additional *p*-phenylenevinylene bridge (**5** → **9**, **27** → **31**, Table 1) such a lengthening of the linker results in ca. 2 times increase in their $\mu\beta(0)$ values (Table 2). Comparison of $\mu\beta(0)$ values for compounds with dithiole and ferrocene donor moieties (**5** vs. **27** and **9** vs. **31**, Table 2) shows that both these groups are comparable in their effects on SHG efficiencies. On the other hand, a comparison of compounds **27** and **28c** indicates that the polynitrofluorene moiety is much more favourable as an acceptor terminal group in NLO chromophores than the dicyanomethylene moiety.

Unexpectedly low $\mu\beta(0) = 240 \cdot 10^{-48}$ esu was obtained for compound **32**, that is 3.5 times lower than for its homologue predecessor **28c**, although as mentioned above, the *p*-phenylenevinylene linker increased $\mu\beta(0)$ values for other systems. Based on the complicated ^{1}H NMR spectrum of this compound, such a behaviour can be due to isomerism in **32** which is not the pure (*E*,*E*,*E*) isomer, but a mixture of geometrical isomers, or due to an aggregation of **32** (see below).

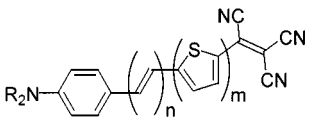
The incorporation of the acetylenic −C≡C− linker into the bridge (compound **41c**, Table 2) did not give rise to high non-linear efficiency of the compound. A much more pronounced effect on $\mu\beta(0)$ occurs with the polyene =CH−CH=CH−CH=CH− linker: Compound **38b** showed a $\mu\beta(0)$ value as high as $900 \cdot 10^{-48}$ esu. A similar $\mu\beta(0)$ value ($1800 \cdot 10^{-48}$ esu) was obtained for compound **42** with a shorter polyene linker =CH−CH=CH− and with the *p*-$Bu_2NC_6H_4$− moiety as the terminal donor group. A somewhat unexpected lowering of the $\mu\beta(0)$ value was observed for compound **38c** having a long-chain solubilising substituent $CO_2(CH_2CH_2O)_3CH_3$ as compared with its analogue **38b** having a CO_2CH_3 substituent (Table 2). This is probably due to an aggregation resulting from intramolecular D−A interaction that leads to formation of the dimers or oligomeric aggregates (especially at high concentrations). Such aggregates, having low or zero dipole moments, will drastically diminish the observed SHG signal. Comparison of our results on fluorene-based NLO chromophores with literature data (compounds **45**,[14,15] **46**,[47] and **47**[48]) confirms our conclusion that polynitrofluorenes are promising acceptors as terminal moieties for second-order NLO chromophores.



45a, n = 2, $R^1 = R^2$ = MeS
45b, n = 1, $R^1 = R^2$ = Me
45c, n = 1, $(R^1 + R^2)$ = $(CH{=}CH)_2$



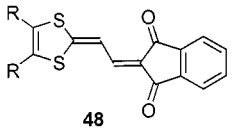
46a, n = 1
46b, n = 2



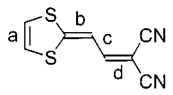
47a: R = Et, n = 1, m = 1
47b: R = Bu, n = 1, m = 2
47c: R = Ph, n = 1, m = 1
47d: R = Ph, n = 1, m = 2
47e: R = Et, n = 2, m = 1
47f: R = Et, n = 2, m = 2

Theoretical Calculations

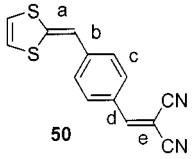
Low $\mu\beta(0)$ values for D−π−A compounds with a 1,3-dithiole donor moiety seem to be related to the fact that this moiety can exhibit electron-accepting properties. We obtained, for instance, very low $\mu\beta(0)$ values (50−100) for model compounds **48**.[55] This phenomenon can be illustrated by quantum mechanical calculations on compound **49**. Calculations were made using the Hartree−Fock (HF) level of theory with Pople's 6-31G split valence basis set and d-polarisation functions on heavy atoms [RHF/6-31G(d)//RHF/6-31G(d)].



48



49



50

Thus, although the first excitation for derivative **49** involves mostly HOMO−LUMO transition, the dithiole moiety contributes to both HOMO and LUMO (Figure 7). The calculated ground-state dipole moment is 9.4 D and the excited-state dipole moment is 14.2 D, i.e. the change in dipole moments upon excitation is not very large. According to the two-level model, the value of β is proportional to the difference in excited- and ground-state dipole moments, and, therefore, large hyperpolarisability cannot be expected for **49**. Indeed, the direct hyperpolarisability calculation using the same level of theory gave $\beta_z = 0.3 \cdot 10^{-30}$ esu and $\mu_g\beta_z = 3 \cdot 10^{-48}$ esu (cf. $\beta_z = 10.3 \cdot 10^{-30}$ esu and $\mu_g\beta_z = 81.5 \cdot 10^{-48}$ esu for *N*,*N*-dimethyl-*p*-nitroaniline at the same level of theory). The same trend was found for this molecule and its vinylogues using a PM3 semiempirical approach.

The molecular and electronic structure of compound **49** has recently been studied within a higher level of theory, i.e. by density functional theory (DFT) approach [B3P86/6-31G(d)] which includes electron correlation effects.[14] The results generally agree with those reported here, although the HF approach predicts a higher contribution to the LUMO from the 1,3-dithiole moiety (Figure 7). Comparison of calculated geometries of **49** by HF (Figure 8, a) and DFT methods,[14] and X-ray data for 1-[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-3,3-dicyanoprop-2-ene,[14] in-

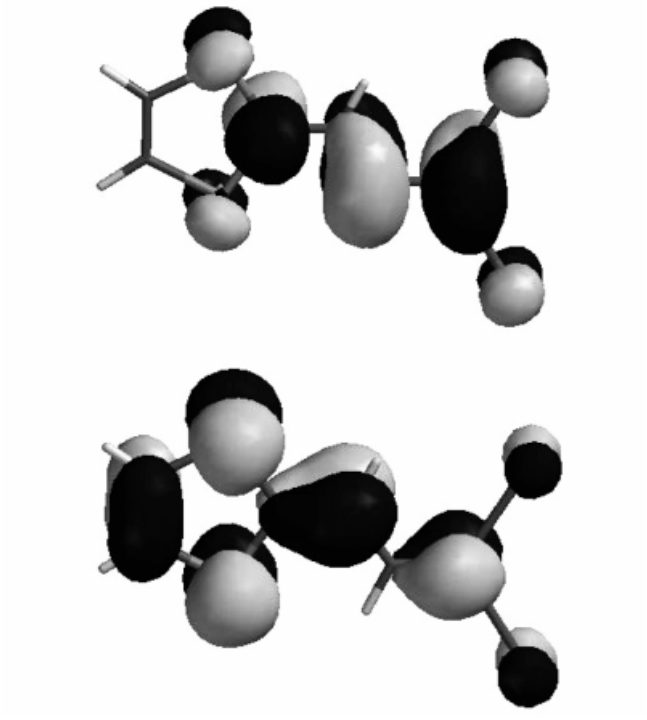


Figure 7. Frontier orbitals of **49** calculated by RHF/6-31G(d)// RHF/6-31G(d) ab initio method (top: LUMO, buttom: HOMO)

dicates good agreement between DFT and X-ray data, whereas the HF method predicts slightly higher bond alternation. Thus, the HF method predicts (Figure 8, a) shorter bond lengths a, c, and d, and longer bond length c (see enumeration on structure **49**) than DFT or X-ray: a = 1.338 and 1.343 Å, b = 1.370 and 1.387 Å, d = 1.376 and 1.384 Å, c = 1.412 and 1.402 Å, respectively.

The molecular structure of **50** optimised at the RHF/6-31G(d) level of theory, revealed a bent structure (Figure 8, b). Bond a (1.330 Å) (see enumeration on formula **50**) is shorter than bond e (1.340 Å) and bond b (1.471 Å) is longer than bond d (1.460 Å). Bond c (1.376 Å) is somewhat shorter than the other aromatic C−C bonds (1.381−1.395 Å). The HOMO is located mostly on the 1,3-dithiole ring, with the LUMO mostly on the dicyanovinyl and the phenyl fragments, although the electron population on C2 of the 1,3-dithiole ring is also considerable (Figure 9).

CIS calculations using 20×20 orbitals [RHF/6-31G(d)] predict the first excitation to be essentially charge transfer, involving mostly an HOMO−LUMO transition (almost no quantitative changes compared to results using 15×15 orbitals). Analysis of atomic charges (by Mulliken, with hydrogen atoms summed into heavy atoms) showed that the charge on the 1,3-dithiol-2-ylidene moiety is +0.04 e and on the dicyanovinyl moiety is −0.15 e in the ground state and +0.25 e and −0.31 e, correspondingly, in the first excited state. The calculated dipole moments of 9.14 D in the ground state and 16.53 D in the excited state are close to those calculated for *N*,*N*-dimethyl-*p*-nitroaniline. The hyperpolarisability tensor was calculated and the value of β

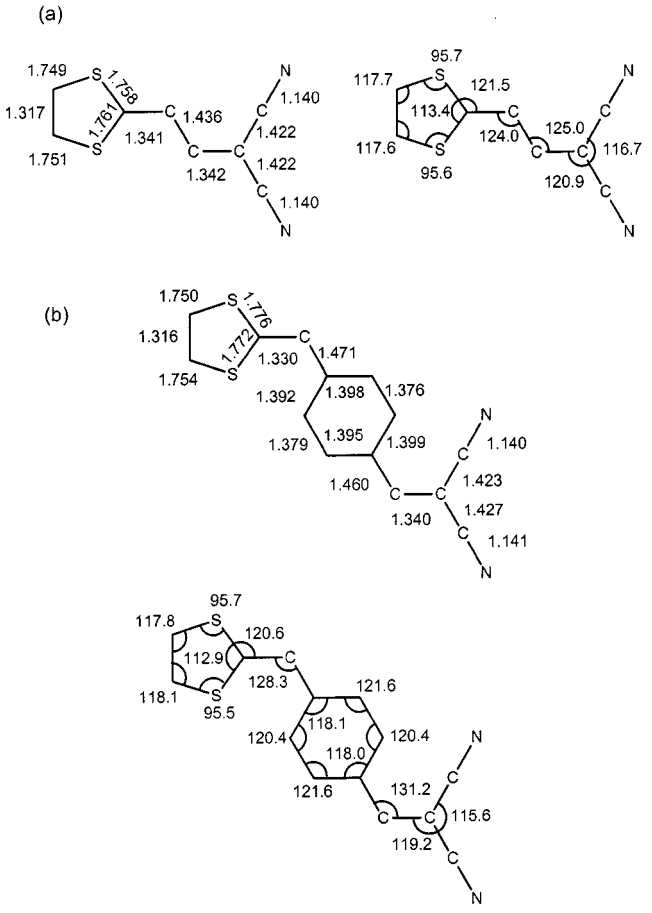


Figure 8. RHF/6-31G(d)-optimised minimum energy structures of (a) **49** and (b) **50**; bond lengths are in Å and bond angles are in °; dihedral angles in **50**: ω(dithiol-2-ylidene/phenylene) = 147.3°, ω(dicyanovinylene/phenylene) = 0.5°

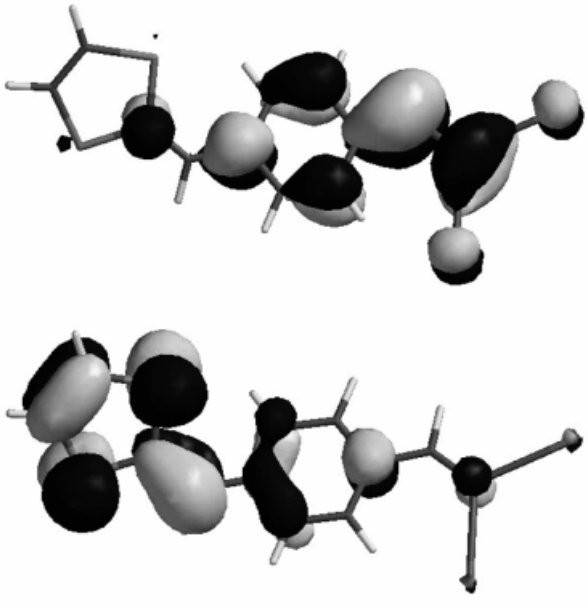


Figure 9. Frontier orbitals of **50** calculated by RHF/6-31G(d)// RHF/6-31G(d) ab initio method (top: LUMO, buttom: HOMO)

along the dipole moment was derived: $\beta_\mu = 31.3 \cdot 10^{-30}$ esu, $\mu_g\beta_\mu = 286 \cdot 10^{-48}$ esu. These values are higher than that calculated at the same level of theory for *N*,*N*-dimethyl-*p*-nitroaniline ($8.5 \cdot 10^{-30}$ and $67.5 \cdot 10^{-48}$, correspondingly).

Conclusions

A series of donor−π−acceptor chromophores **5**, **9**, **11**, **18**−**22**, **31**, **32**, **34**, **35**, **36**, **38**, **41**, and **42** have been synthesized. Broad low-energy bands (1.76−2.67 eV) are observed in the electron absorption spectra due to intramolecular charge transfer from the donor onto the acceptor moiety. Moderate second-order NLO properties are observed for compounds **5**, **9**, **18**, **27**, **31**, **32**, **36**, and **41c** [$\mu\beta(0) \approx 100-470 \times 10^{-48}$ esu], whereas compound **28c**, **38b**, and **42** show quite high $\mu\beta(0)$ values ($800-1800 \times 10^{-48}$ esu). We have demonstrated, therefore, that polynitrofluorenes are promising acceptor moieties for NLO chromophores: (a) they show quite high SHG, (b) the properties of the chromophore can be easily tuned by variation of substituents in the fluorene moiety and synthetic procedures for fluorene intermediates are well elaborated,[24,25,29−31,56] (c) at a certain balance of D/A moieties the molecule can posses both high electron-acceptor ability and NLO properties bringing new possibilities for optoelectronic applications.[21b]

Experimental Section

General Remarks: ^{1}H NMR spectra were obtained with a Bruker AC 250 spectrometer operating at 250.134 MHz, a Varian Unity 300 operating at 299.909 MHz or a Varian VXR 400S spectrometer operating at 399.958 MHz. ^{13}C NMR spectra were obtained with a Varian Unity 300 operating at 75.420 MHz and a Varian VXR 400S spectrometer operating at 100.581 MHz. − Mass spectra were recorded with a VG7070E spectrometer operating at 70 eV. − IR spectra were recorded with a Perkin−Elmer 1615 FTIR spectrometer operated from a Grams Analyst 1600. − UV/Vis spectra were obtained with Kontron Uvicon 930 and Specord M-40 spectrophotometers using quartz cells; extinction coefficients (ε) are quoted in M^{-1} cm^{-1}. − Melting points were obtained with a Kofler hot-stage microscope apparatus and are uncorrected. − Column chromatography was performed on Merck silica gel (70−230 mesh). − All reagents were of commercial quality and used as supplied unless otherwise stated; solvents were dried where necessary using standard procedures and distilled for chromatographic use. − Compounds **10a**,[29] **10b**,[25] and **10c**[25] were prepared as described previously.

General Procedure for the Preparation of Compounds 4 and 15−17: To a solution of phosphonium salt **1**[14] and a dialdehyde (either **3**, **12**, **13**, or **14**) (excess) in dry THF (ca. 75 mL) at 20 °C under argon was added dry triethylamine (excess) and the reaction mixture stirred at 20 °C for 16 h. After evaporation of the solvent, the residue was extracted into DCM. The organic phase was washed with water, dried ($MgSO_4$), and the solvent evaporated. Silica column chromatography of the residue as indicated afforded the products.

Benzaldehyde 4: Prepared from salt **1** (4.50 g, 9.3 mmol) and terephthaldehyde (**3**) (2.18 g, 16.3 mmol); elution with DCM/hexane (1:1, v/v) afforded compound **4** (2.50 g, 86%) as a yellow solid, m.p. 112 °C. − $C_{13}H_{12}OS_4$ (312.48): calcd. C 49.97, H 3.87; found C 49.68, H 3.71. − MS (CI); *m*/*z* (%): 313 (100) [MH^+]. − ^{1}H NMR ($CDCl_3$): δ = 9.94 (s, 1 H, C*H*O), 7.85 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.32 (d, 2 H, *J* = 8 Hz, *p*-Ph), 6.53 (s, 1 H, dithiole=C*H*), 2.46 (s, 3 H, Me), 2.45 (s, 3 H, Me). − ^{13}C NMR ($CDCl_3$): δ = 191.4 (*C*HO), 141.9, 138.2, 132.8, 130.1, 128.3, 126.7, 124.2, 112.8, 19.1 (Me), 18.9 (Me). − IR (KBr): 1669 (C=O), 1596, 1554, 1415, 1159, 836 cm^{-1}. − UV (DCM): λ_{max} (log ε) = 410 (4.71), 264 (4.50) nm.

Carbaldehyde 15: Prepared from salt **1** (11.6 g, 21.3 mmol) and thiophene-2,5-dialdehyde (**12**) (0.60 g, 4.3 mmol); elution with DCM/hexane (2:1, v/v) afforded compound **15** (0.93 g, 80%) as an orange solid, m.p. 96−97 °C. − $C_{11}H_{10}OS_5$ (318.50): calcd. C 41.48, H 3.16; found C 41.26, H 3.02. − MS (CI); *m*/*z* (%) = 319 (100) [MH^+]. − ^{1}H NMR ($CDCl_3$): δ = 9.84 (s, 1 H, C*H*O), 7.67 (d, 1 H, *J* = 4 Hz, thiophene), 6.90 (d, 1 H, *J* = 4 Hz, thiophene), 6.78 (s, 1 H, dithiole=C*H*), 2.49 (s, 3 H, Me), 2.46 (s, 3 H, Me). − ^{13}C NMR ($CDCl_3$): δ = 182.1 (*C*HO), 149.9, 140.6, 139.3, 137.0, 128.4, 126.9, 124.4, 107.1, 19.1 (Me), 19.0 (Me). − IR (KBr): 1638 (C=O), 1548, 1429, 1275 cm^{-1}. − UV (DCM): λ_{max} (log ε) = 440 (4.02), 269 (3.87) nm.

Carbaldehyde 16: Prepared from salt **1** (3.68 g, 6.75 mmol) and 2,2′-bithiophene-5,5′-dialdehyde (**13**) (300 mg, 1.35 mmol) and triethylamine (2 mL, excess). Initial elution with dichloromethane/hexane (2:1, v/v) gave tetrakis(methylsulfanyl)tetrathiafulvalene; the next fraction was the desired product which was eluted with dichloromethane and rechromatographed with DCM/hexane (3:1, v/v) to afford compound **16** (355 mg, 66%) as an orange solid, m.p. 104−105 °C. − $C_{15}H_{12}OS_6$ (400.63): calcd. C 45.0, H 3.0; found C 44.8, H 3.1. − MS (DCI); *m*/*z* (%) = 401 (100) [MH^+]. − ^{1}H NMR ($CDCl_3$): δ = 9.79 (s, 1 H, C*H*O), 7.60 (d, 1 H, *J* = 4 Hz, thiophene), 7.23 (d, 1 H, *J* = 4 Hz, thiophene), 7.16 (s, 1 H, *J* = 4 Hz, thiophene), 6.73 (d, 1 H, *J* = 4 Hz, thiophene), 6.59 (s, 1 H, dithiole=C*H*), 2.44 (s, 3 H, Me), 2.42 (s, 3 H, Me). − ^{13}C NMR ($CDCl_3$): δ = 182.1 (*C*HO), 147.2, 142.2, 140.9, 137.5, 133.8, 133.4, 128.7, 126.5, 125.1, 124.8, 123.3, 107.4, 19.0 (Me), 18.8 (Me). − IR (KBr): $\tilde{\nu}$ = 1646 (C=O) cm^{-1}. − UV (DCM): λ_{max} = 468, 344 nm.

Carbaldehyde 17: Prepared from salt **1** (1.43 g, 2.63 mmol), 2,2′′-terthiophene-5,5′′-dialdehyde (**14**) (200 mg, 0.66 mmol); elution initially with DCM/hexane (1:1, v/v) removed tetrakis(methylsulfanyl)tetrathiafulvalene; subsequent use of DCM/hexane (3:1, v/v) afforded compound **17** (210 mg, 66%) as a red solid, m.p. 157−158 °C. − $C_{19}H_{14}OS_7$ (482.74): calcd. C 47.3, H 2.9; found C 47.0, H 3.1. − MS (DCI); *m*/*z* (%) = 483 (100) [MH^+]. − ^{1}H NMR ($CDCl_3$): δ = 9.94 (s, 1 H, C*H*O), 7.76 (d, 1 H, *J* = 4 Hz, thiophene), 7.35 (d, 1 H, *J* = 4 Hz, thiophene), 7.31 (d, 1 H, *J* = 4 Hz, thiophene), 7.24 (d, 1 H, *J* = 4 Hz, thiophene), 7.20 (d, 1 H, *J* = 4 Hz, thiophene), 6.86 (d, 1 H, *J* = 4 Hz, thiophene), 6.74 (s, 1 H, dithiole=C*H*), 2.57 (s, 3 H, Me), 2.54 (s, 3 H, Me). − ^{13}C NMR ($CDCl_3$): δ = 182.4 (*C*HO), 146.9, 141.4, 140.5, 139.3, 137.4, 137.2, 134.7, 134.1, 131.9, 127.1, 124.8, 124.0, 123.9, 107.9, 19.2 (Me), 19.0 (Me). − IR (KBr): $\tilde{\nu}$ = 1651 (C=O) cm^{-1}. − UV (DCM): λ_{max} = 400, 264 nm.

General Procedure for the Preparation of Compounds 6 and 26: To a solution of an aldehyde (either **4** or **25**) and (4-cyanobenzyl)triphenylphosphonium chloride (**7**) in dry toluene (75 mL) under argon was added dry triethylamine (excess) and the mixture stirred at reflux for 16 h. After cooling, water (150 mL) was added. The organic phase was separated and the aqueous phase extracted with DCM (3×75 mL). The combined organic extracts were washed with water (2×100 mL), brine (50 mL), dried ($MgSO_4$), and the

solvent was evaporated. Silica column chromatography of the residue as indicated afforded the products.

Nitrile 6: Prepared from compounds **4** (1.00 g, 3.20 mmol) and **7** (5.29 g, 12.8 mmol); elution with DCM/hexane (1:1, v/v) afforded the product as a mixture of (*Z*)/(*E*) isomers (ca. 1:3 ratio as judged by ^{1}H NMR; this mixture may be utilised in the next reaction step as the separation of isomers of **8** is significantly easier). The (*Z*) isomer of **6** elutes first from the column and may be removed completely from the mixture by repeated chromatography (typically two further separations were required) to afford the product ***(E)*-6** as an orange solid, (0.54 g, 41%), m.p. 160 °C. − $C_{21}H_{17}NS_4$ (411.61): calcd. C 61.3, H 4.2, N 3.4; found C 61.2, H 4.2, N 3.5. − MS (CI); *m*/*z* (%) = 412 (100) [MH$^+$]. − ^{1}H NMR [(CDCl$_2$)$_2$]: δ = 7.64 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.58 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.53 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.23 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.16 (d, 1 H, *J* = 16 Hz, C*H*=CH), 7.04 (d, 1 H, *J* = 16 Hz, CH=C*H*), 6.50 (s, 1 H, dithiole=C*H*), 2.45 (s, 3 H, Me), 2.44 (s, 3 H, Me). − ^{13}C NMR [(CDCl$_2$)$_2$]: δ = 142.2, 136.7, 133.8, 133.6, 132.8, 132.1, 128.1, 127.5, 127.4, 127.1, 126.6, 124.3, 119.8, 114.4 (*C*N), 110.4, 19.5 (Me), 19.3 (Me).

Nitrile 26: Prepared from ferrocenecarboxaldehyde (**25**) (0.34 g, 1.60 mmol) and **7** (1.0 g, 2.4 mmol); elution with DCM afforded the product as a mixture of (*Z*)/(*E*) isomers (ca. 1:20 ratio as judged by ^{1}H NMR; this mixture may be utilised in the next reaction step as the separation of isomers of **24** is significantly easier). The (*Z*) isomer elutes first from the column and may be removed completely from the mixture by repeated chromatography to afford compound ***(E)*-26** (0.40 g, 80%) as an orange solid, m.p. 155−156 °C (from hexane/DCM, 1:1, v/v). − $C_{19}H_{15}FeN$ (313.18): calcd. C 72.87, H 4.83, N 4.47; found C 72.56, H 4.79, N 4.55. − MS (CI); *m*/*z* (%) = 331 (30) [MNH$_4^+$], 314 (100) [MH$^+$]. − ^{1}H NMR (CDCl$_3$): δ = 7.58 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.40 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.05 (d, 1 H, *J* = 16 Hz, C*H*=CH), 6.67 (d, 1 H, *J* = 16 Hz, CH=C*H*), 4.49 (t, 2 H, *J* = 2 Hz, cp), 4.36 (t, 2 H, *J* = 2 Hz, cp), 4.15 (s, 5 H, cp). − IR (KBr): ν̃ = 2219 (CN), 1632, 1596, 1171, 968, 817 cm^{-1}.

Benzaldehydes *(E)*-24 and *(Z)*-24: To a solution of (ferrocenylmethyl)triphenylphosphonium iodide (**23**) (1.16 g, 1.97 mmol) in dry THF (50 mL) at 0 °C under argon, was added potassium *tert*-butoxide (0.24 g, 2.2 mmol). The solution was stirred for 30 min, whereupon it turned rapidly from yellow to red, at which point, terephthaldehyde (**3**) (1.00 g, 7.9 mmol) was added as a solution in anhydrous THF (20 mL). The resultant mixture was stirred at 20 °C for 2 h, whereupon, the solvent was removed in vacuo and the residue purified by column chromatography on silica gel with DCM/hexane (1:1, v/v) as the eluent, followed by recrystallisation from the same solvent mixture to give **24** (0.28 g, 45%) as a red crystalline solid, m.p. 150−151 °C. The reaction affords a mixture of (*E*)/(*Z*) isomers (ca. 10:1 ratio as judged by ^{1}H NMR); the (*Z*) isomer elutes first from the column and the isomers can thereby be separated. − $C_{19}H_{16}FeO$ (316.18): calcd. C 72.18, H 5.10; found C 72.30, H 5.05. − MS (CI); *m*/*z* (%) = 317 (100) [MH$^+$].

***(E)*-24:** ^{1}H NMR (CDCl$_3$): δ = 9.97 (s, 1 H), 7.83 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.56 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.08 (d, 1 H, *J* = 16 Hz, C*H*=CH), 6.73 (d, 1 H, *J* = 16 Hz, C*H*=CH), 4.51 (t, 2 H, *J* = 2 Hz, cp), 4.36 (t, 2 H, *J* = 2 Hz, cp), 4.16 (s, 5 H, cp). − ^{13}C NMR (CDCl$_3$): δ = 191.6 (*C*HO), 151.0, 144.0, 131.5, 130.3, 126.0, 124.5, 82.2 (cp), 69.7 (cp), 69.4 (cp), 67.3 (cp). − IR (KBr): ν̃ = 1685 (C=O), 1591, 1561, 1215, 1163, 969, 815 cm^{-1}.

***(Z)*-24:** ^{1}H NMR (CDCl$_3$): δ = 9.99 (s, 1 H, C*H*O), 7.80 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.52 (d, 2 H, *J* = 8 Hz, *p*-Ph), [6.46, 6.45 (2 H, C*H*=C*H*)], 4.22 (s br., 2 H, cp), 4.18 (s br., 2 H, cp), 4.13 (s, 5 H, cp).

Carbaldehyde 33: Prepared analogously to the above compound from **23** (800 mg, 1.43 mmol), potassium *tert*-butoxide (180 mg, 1.56 mmol), and thiophene-2,5-dicarboxaldehyde (**12**) (420 mg, 3.00 mmol). Column chromatography on silica gel with DCM/hexane (1:4, v/v) as the eluent, followed by recrystallisation from the same solvent afforded compound **33** (216 mg, 47%) as a red solid, m.p. 136−138 °C. − $C_{17}H_{14}FeOS$ (322.20): calcd. C 63.37, H 4.38; found C 63.49, H 4.22. − MS (CI); *m*/*z* (%) = 323 (100) [MH$^+$]. − ^{1}H NMR (CDCl$_3$): δ = 9.84 (s, 1 H, C*H*O), 7.63 (d, 1 H, *J* = 4 Hz, thiophene), 7.03 (d, 1 H, *J* = 4 Hz, thiophene), 6.92 (d, 1 H, *J* = 15 Hz, C*H*=CH), 6.82 (d, 1 H, *J* = 15 Hz, C*H*=CH), 4.49 (s, 2 H, *J* = 2 Hz, cp), 4.38 (t, 2 H, *J* = 2 Hz, cp), 4.37 (s, 5 H, cp). − ^{13}C NMR (CDCl$_3$): δ = 182.3 (*C*HO), 153.3, 140.3, 137.5, 132.7, 124.7, 117.9, 81.2 (cp), 70.0 (cp), 69.3 (cp), 67.3 (cp). − IR (KBr): ν̃ = 1665 (C=O), 1618, 1437, 1231, 1102, 801 cm^{-1}.

Nitrile *(E,E)*-29: To a solution of **7** (0.62 g, 1.5 mmol) in dry THF (100 mL) at 20 °C under argon, was added potassium *tert*-butoxide (0.17 g, 1.5 mmol). The resultant mixture was stirred at 20 °C for 15 min, whereupon aldehyde ***(E)*-24** (0.32 g, 0.98 mmol) in anhydrous THF (10 mL) was added. The mixture was stirred at reflux for 4 h, cooled and the solvent removed in vacuo. The resultant residue was dissolved in DCM (150 mL) and washed successively with water (2 × 50 mL) and brine (50 mL), dried (MgSO$_4$), and the solvent removed. The brown solid obtained was purified by column chromatography on silica gel using DCM/hexane (1:1, v/v) as the eluent to afford a mixture of ***(E,E)*-29**/***(E,Z)*-29** (ca. 3:1 ratio, 0.31 g, 75%) as an orange solid. − $C_{27}H_{21}FeN$ (415.32): calcd. C 78.08, H 5.10, N 3.37; found C 78.03, H 5.25, N 3.52. − ***(E,E)*-29** and ***(E,Z)*-29** isomers are difficult to separate, therefore, we used a mixture of isomers in the synthesis of aldehyde **30**. Pure isomers can be isolated by repeated chromatography followed by recrystallisation from DCM/hexane.

***(E,E)*-29:** M.p. > 250 °C. − MS (CI); *m*/*z* (%) = 416 (100) [MH$^+$]. − ^{1}H NMR [(CDCl$_2$)$_2$]: δ = 7.63 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.60 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.49 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.45 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.19 (d, 1 H, *J* = 16 Hz, C*H*=CH), 7.05 (d, 1 H, *J* = 16 Hz, C*H*=CH), 6.92 (d, 1 H, *J* = 16 Hz, C*H*=CH), 6.66 (d, 1 H, *J* = 16 Hz, C*H*=CH), 4.50 (s, 2 H, cp), 4.33 (s, 2 H, cp), 4.16 (s, 5 H, cp). − ^{13}C NMR [(CDCl$_2$)$_2$]: δ = 141.9, 138.1, 134.6, 132.4, 132.0, 127.9, 127.3, 126.7, 126.3, 126.0, 125.2, 119.3, 109.9 (*C*N), 81.6 (cp), 69.4 (cp), 67.0 (cp). − IR (KBr): ν̃ = 2219 (CN), 1627, 1590, 1511, 1171, 1105, 968, 832 cm^{-1}.

***(E,Z)*-29:** M.p. 126−128 °C. − MS (CI); *m*/*z* (%) = 416 (100) [MH$^+$]. − ^{1}H NMR (CDCl$_3$): δ = 7.54 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.39 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.31 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.16 (d, 2 H, *J* = 8 Hz, *p*-Ph), 6.89 (d, 1 H, *J* = 16 Hz, C*H*=CH), 6.72 (d, 1 H, *J* = 12 Hz, C*H*=CH), 6.66 (d, 1 H, *J* = 16 Hz, C*H*=CH), 6.56 (d, 1 H, *J* = 12 Hz, C*H*=CH), 4.47 (t, 2 H, *J* = 1 Hz, cp), 4.30 (t, 2 H, *J* = 1 Hz, cp), 4.15 (s, 5 H, cp). − ^{13}C NMR (CDCl$_3$): δ = 142.3, 137.5, 134.4, 133.0, 132.0, 129.5, 129.2, 127.8, 127.7, 125.7, 125.2, 119.4, 110.3 (*C*N), 83.0 (cp), 69.2 (cp), 66.9 (cp). − IR (KBr): ν̃ = 2222 (CN), 1624, 1599, 1509, 1176, 1103, 959, 817 cm^{-1}.

General Procedure for the Preparation of Compounds 8, 24, and 30 by Dibal-H Reduction: To a solution of a nitrile (either **6**, **26** or **29**) (1.0 equiv.) in anhydrous chlorobenzene (ca. 30 mL) at 0 °C was added diisobutylaluminium hydride (Dibal-H, 1.3 equiv., 1 M solution in hexane) over a period of 10 min. After stirring for a further 2 h, the reaction mixture was allowed to warm to 20 °C and main-

tained at this temperature until the starting material was consumed (TLC evidence, typically 2 h). Chloroform (100 mL) and concentrated hydrochloric acid (5 mL) were added and the solution stirred vigorously at 20 °C for 20 min. Water (ca. 50 mL) was added, the organic phase separated, washed with water (2 × 50 mL) and brine (50 mL), dried ($MgSO_4$), and the solvent evaporated. The residue was purified by column chromatography on silica gel as indicated to afford the products.

Benzaldehyde 8: Prepared from **6** (500 mg, 1.22 mmol, mixture of *cis*/*trans* isomers) and Dibal-H; elution with toluene afforded first the (*Z*) isomer and subsequently the desired (*E*) isomer (226 mg, 45%) as an orange solid, m.p. 157−159 °C. − $C_{21}H_{18}OS_4$ (414.61): calcd. C 60.84, H 4.38; found C 60.83, H 4.27. − MS (EI); *m*/*z* (%) = 414 (100) [M^+]. − ^{1}H NMR [$(CDCl_2)_2$]: δ = 9.96 (s, 1 H, C*H*O), 7.87 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.66 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.56 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.23 (d, 2 H, *J* = 8 Hz), 7.25 (d, 1 H, *J* = 16 Hz, C*H*=CH), 7.13 (d, 1 H, *J* = 16 Hz), 6.51 (s, 1 H, dithiole=C*H*), 2.46 (s, 3 H), 2.45 (s, 3 H) − ^{13}C NMR [$(CDCl_2)_2$]: δ = 191.7 (*C*HO), 143.4, 136.2, 134.9, 133.7, 133.0, 131.6, 130.2, 127.6, 127.1, 127.0, 126.8, 123.9, 114.0, 19.1 (Me), 18.9 (Me). − IR (KBr): $\tilde{\nu}$ = 1693 (C=O), 1591, 1564, 1537, 1483, 1415, 1161, 972, 827 cm^{-1}. − UV (MeCN): λ_{max} (log ε) = 422 (4.35), 328 (4.16) nm.

Alternative Preparation of Benzaldehyde (*E*)-24: Prepared from nitrile **26** (0.33 g, 1.00 mmol) and Dibal-H; elution with DCM/hexane (1:1, v/v) afforded compound **24** (0.27 g, 84%) which was spectroscopically identical to that obtained above.

Benzaldehyde 30: Prepared from nitrile **29** (100 mg, 0.25 mmol) and Dibal-H; elution with DCM/hexane (1:2, v/v) afforded compound **30** (62 mg, 62%), m.p. > 250 °C (from DCM/hexane, 1:1, v/v). − $C_{27}H_{22}FeO$ (418.32): calcd. C 77.52, H 5.30; found C 77.31, H 5.02. − MS (CI); *m*/*z* (%) = 419 [MH^+] (50%). − ^{1}H NMR [$(CDCl_2)_2$]: δ = 9.99 (C*H*O) 7.87 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.65 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.51 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.44 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.25 (d, 1 H, *J* = 16 Hz, C*H*=CH), 7.19 (d, 1 H, *J* = 16 Hz, C*H*=CH), 6.93 (d, 1 H, *J* = 16 Hz, C*H*=CH), 6.69 (d, 1 H, *J* = 16 Hz, C*H*=CH), 4.47 (t, 2 H, *J* = 2 Hz, cp) 4.3 (t, 2 H, *J* = 2 Hz, cp), 4.14 (s, 5 H, cp). − IR(KBr): $\tilde{\nu}$ = 1697 (C=O), 1601, 1513, 1211, 1167, 1105, 819 cm^{-1}.

General Procedure for Preparation of Compounds 5, 9, 18−20, 27, 31, and 34: To a stirred solution of an aldehyde [either **4**, **8**, **15−17**, ***(E)*-24**, **30**, or **33**] (1.0 equiv.) in dry DCM (ca. 75 mL) at 20 °C under argon was added sequentially (i) malononitrile (1.1 equiv.), (ii) titanium tetrachloride (1 M in DCM, 1.1 equiv.) and (iii) dry pyridine (excess). The resultant mixture was stirred at reflux for 16 h. After cooling, water (ca. 100 mL) was added and the mixture extracted with DCM (3× 100 mL). The combined extracts were washed with water (2×75 mL), dried ($MgSO_4$), and the solvent was evaporated. Silica column chromatography of the residue as indicated afforded the products. UV/Vis spectra of the obtained compounds are collected in Table 1.

Dicyanomethylene Compound 5: Prepared from compound **4** (750 mg, 2.40 mmol); elution with DCM/hexane (1:1, v/v) afforded compound **5** (640 mg, 74%) as a purple solid, m.p. 134 °C. − $C_{16}H_{12}N_2S_4$ (360.52): calcd. C 53.30, H 3.36, N 7.77; found C 52.74, H 3.54, N 7.60. − ^{1}H NMR ($CDCl_3$): δ = 7.89 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.64 [1 H, s, C*H*=C(CN)$_2$], 7.27 (d, 2 H, *J* = 8 Hz, *p*-Ph), 6.53 (s, 1 H, dithiole=C*H*), 2.47 (s, 3 H, Me), 2.46 (s, 3 H, Me). − ^{13}C NMR ($CDCl_3$): δ = 158.3, 142.3, 141.0, 131.5, 128.7, 127.5, 127.0, 125.3, 114.4 (*C*N), 113.3 (*C*N), 112.3, 79.6 [*C*(CN)$_2$], 19.1 (Me), 18.9 (Me). − IR (KBr): $\tilde{\nu}$ = 2217 (CN), 1574, 1552, 1513, 1475, 1418, 1183, 835 cm^{-1}.

Dicyanomethylene Compound 9: Prepared from compound **8** (200 mg, 0.48 mmol); elution with toluene afforded compound **9** (138 mg, 62%) as a purple solid, m.p. 163 °C. − $C_{24}H_{18}N_2S_4$ (462.66): calcd. C 62.31, H 3.92, N 6.05; found C 61.86, H 3.83, N 5.88. − MS (CI); *m*/*z* (%) = 463 (100) [MH^+]. − ^{1}H NMR (CD_2Cl_2): δ = 7.90 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.74 [1 H, s, C*H*=(CN)$_2$], 7.64 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.55 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.29 (d, 1 H, *J* = 16 Hz, C*H*=CH), 7.23 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.13 (d, 1 H, *J* = 16 Hz, C*H*=CH), 6.50 (s, 1 H, dithiole=C*H*), 2.44 (s, 3 H, Me), 2.43 (s, 3 H, Me). − ^{13}C NMR (CD_2Cl_2): δ = 159.2, 144.2, 137.1, 134.0, 133.9, 132.9, 131.9, 130.3, 127.7, 127.5, 127.4, 126.6, 124.6, 114.6, 114.2 (*C*N), 113.5 (*C*N), 81.2 [*C*(CN)$_2$], 19.2 (Me), 19.1 (Me). − IR (KBr): $\tilde{\nu}$ = 2216 (CN), 1598, 1575, 1553, 1513, 1475, 1416, 1184, 1159, 836 cm^{-1}.

Dicyanomethylene Compound 18: Prepared from compound **15** (250 mg, 0.78 mmol); elution with DCM afforded compound **18** (188 mg, 65%) as a purple solid, m.p. 166−167 °C. − $C_{14}H_{10}N_2S_5$ (366.55): calcd. C 45.88, H 2.75, N 7.64; found C 45.65, H 2.66, N 7.46. − MS (CI); *m*/*z* (%) = 367 (100) [MH^+]. − ^{1}H NMR ($CDCl_3$): δ = 7.68 [1 H, s, C*H*=C(CN)$_2$], 7.66 (d, 1 H, *J* = 4 Hz, thiophene), 6.92 (d, 1 H, *J* 4 Hz, thiophene), 6.83 (s, 1 H, dithiole=C*H*), 2.50 (s, 3 H, Me), 2.48 (s, 3 H, Me). − ^{13}C NMR ($CDCl_3$): δ = 152.3, 149.1, 143.3, 139.3, 132.9, 130.0, 127.5, 125.0, 115.1 (*C*N), 114.2 (*C*N), 106.6, 72.7 [*C*(CN)$_2$], 19.3 (Me), 19.0 (Me). − IR (KBr): $\tilde{\nu}$ = 2207 (CN), 1567, 1524, 1402, 1346, 1276, 1225, 1141, 1057, 846 cm^{-1}.

Dicyanomethylene Compound 19: Prepared from aldehyde **16** (150 mg, 0.375 mol); elution with DCM afforded compound **19** as a purple solid (75 mg, 45%); two separations were required to obtain a sample of analytical purity, m.p. 184−185 °C. − $C_{18}H_{12}N_2S_6$ (448.67): calcd. C 48.19, H. 2.70, N. 6.24; found C 48.3, H 2.7, N 6.3. − MS (CI); *m*/*z* (%) = 449 (100) [MH^+]. − ^{1}H NMR ($CDCl_3$): δ = 7.72 [1 H, s, C*H*=C(CN)$_2$], 7.60 (d, 1 H, *J* = 4 Hz, thiophene), 7.38 (d, 1 H, *J* = 4 Hz, thiophene), 7.26 (d, 1 H, *J* = 4, thiophene), 6.83 (d, 1 H, *J* = 4, thiophene), 6.71 (s, 1 H, dithiole=C*H*), 2.50 (s, 3 H, Me), 2.48 (s, 3 H, Me). − ^{13}C NMR ($CDCl_3$): δ = 149.8, 149.7, 143.9, 140.5, 135.3, 133.0, 132.9, 128.0, 125.3, 123.7, 114.6 (*C*N), 113.7 (*C*N), 107.3, 74.8 [*C*(CN)$_2$], 19.3 (Me), 19.0 (Me). − IR (KBr): $\tilde{\nu}$ = 2214 (CN) cm^{-1}.

Alternative Synthesis of Dicyanomethylene Compound 19: A solution of aldehyde **16** (20 mg, 0.050 mol), malononitrile (6 mg, 0.09 mmol), and piperidine acetate (1 drop of 10% solution in 2-propanol) in 2-propanol was refluxed for 40 min, then cooled and the black-purple precipitate was filtered off, washed with 2-propanol, giving compound **19** (15.5 mg, 69%), m.p. 184−185 °C.

Dicyanomethylene Compound 20: Prepared from aldehyde **17** (150 mg, 0.31 mol); elution with DCM afforded compound **20** as a purple solid (70 mg, 42%); two separations were required to obtain a sample of analytical purity, m.p. 175 °C. − $C_{22}H_{14}N_2S_7$ (530.79): calcd. C 49.78, H. 2.66, N. 5.28; found C 49.7, H 2.8, N 5.3. − MS (CI); *m*/*z* (%) = 531 (100) [MH^+]. − ^{1}H NMR ($CDCl_3$): δ = 7.73 [1 H, s, C*H*=C(CN)$_2$], 7.61 (d, 1 H, *J* = 4 Hz, thiophene), 7.35 (d, 1 H, *J* = 4 Hz, thiophene), 7.24 (d, 1 H, *J* = 4, thiophene), 7.18 (d, 1 H, *J* = 4 Hz, thiophene), 7.15 (d, 1 H, *J* = 4, thiophene), 6.79 (d, 1 H, *J* = 4, thiophene), 6.66 (s, 1 H, dithiole=C*H*), 2.48 (s, 3 H, Me), 2.45 (s, 3 H, Me). − IR (KBr): $\tilde{\nu}$ = 2211 (CN) cm^{-1}.

Dicyanomethylene Compound 27: Prepared from aldehyde **24** (*E*) (280 mg, 0.88 mmol); elution with DCM followed by recrystallis-

ation from DCM/hexane (1:1, v/v), afforded compound **27** (154 mg, 51%) as a black solid; m.p. 197−199 °C. − $C_{22}H_{16}FeN_2$ (364.23): calcd. C 72.55, H 4.43, N 7.69; found C 72.69, H 4.80, N 7.37. − MS (CI); *m/z* (%) = 365 (100) [MH^+]. − ^{1}H NMR ($CDCl_3$): δ = 7.80 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.69 [1 H, s, C*H*=C(CN)$_2$], 7.53 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.15 (d, 1 H, *J* = 16 Hz, C*H*=CH), 6.69 (d, 1 H, *J* = 16 Hz, CH=C*H*), 4.54 (s br., 2 H, cp), 4.41 (s br., 2 H, cp), 4.18 (s, 5 H, cp). − ^{13}C NMR ($CDCl_3$): δ = 158.8, 144.5, 133.3, 131.6, 129.0, 126.4, 123.9, 114.4 (*C*N), 113.2 (*C*N), 81.8 [*C*(CN)$_2$], 80.1 (cp), 70.2 (cp), 69.5 (cp), 67.6 (cp). − IR (KBr): $\tilde{\nu}$ = 2225 (CN), 1627, 1599, 1572, 1542, 1181, 815 cm^{-1}.

Dicyanomethylene Compound 31: Prepared from aldehyde **30** (40 mg, 0.095 mmol); elution with DCM, followed by recrystallisation from DCM/hexane (1:1, v/v), afforded compound **31** (38 mg, 87%) as a black solid; m.p. > 250 °C. − $C_{30}H_{22}FeN_2$ (466.37): calcd. C 77.26, H 4.75, N 6.01; found C 77.09, H 4.52, N 5.78. − MS (CI); *m/z* (%) = 467 (20) [MH^+]. − ^{1}H NMR (CD_2Cl_2): δ = 7.94 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.76 [1 H, s, C*H*=C(CN)$_2$], 7.68 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.54 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.46 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.33 (d, 1 H, *J* = 16 Hz, C*H*=CH), 7.17 (d, 1 H, *J* = 16 Hz, CH=C*H*), 6.96 (d, 1 H, *J* = 16 Hz, C*H*=CH), 6.69 (d, 1 H, *J* = 16 Hz, CH=C*H*), 4.53 (s br., 2 H, cp), 4.35 (s br., 2 H, cp), 4.17 (s, 5 H, cp). − IR (KBr): $\tilde{\nu}$ = 2221 (CN), 1627, 1575, 1544, 1174, 962, 819 cm^{-1}.

Dicyanomethylene Compound 34: Prepared from aldehyde **33** (67 mg, 0.21 mmol); elution with DCM followed by recrystallisation from DCM/hexane (1:1, v/v), afforded compound **34** (47 mg, 61%) as a black solid; m.p. 160−162 °C. − $C_{20}H_{14}FeN_2S$ (370.25): calcd. C 64.88, H 3.81, N 7.57; found C 64.95, H 3.77, N 7.47. − MS (EI); *m/z* (%) = 370 (100) [M^+]. − ^{1}H NMR ($CDCl_3$): δ = 7.73 [1 H, s, C*H*=C(CN)$_2$], 7.55 (d, 1 H, *J* = 4 Hz, thiophene), 7.09 (d, 1 H, *J* = 16 Hz, C*H*=CH), 7.03 (d, 1 H, *J* = 4 Hz, thiophene), 6.81 (d, 1 H, *J* = 16 Hz, CH=C*H*), 4.52 (s, 2 H, *J* = 2 Hz, cp), 4.45 (t, 2 H, *J* = 2 Hz, cp), 4.19 (s, 5 H, cp). − ^{13}C NMR ($CDCl_3$): δ = 156.1, 150.1, 140.7, 135.9, 132.5, 125.4, 117.3, 114.7 (*C*N), 113.9 (*C*N), 80.8, 70.8 (cp), 69.7 (cp), 67.8 (cp). − IR (KBr): $\tilde{\nu}$ = 2221 (CN), 1609, 1571, 1427, 1260, 1103, 805 cm^{-1}.

Fluorene 11: Aldehyde **8** (44.6 mg, 0.127 mmol) was added to a solution of fluorene **10a** (45.3 mg, 0.131 mmol) in DMF (0.5 mL) and stirred at 20 °C for 3.5 h. After removing the solvent in vacuo at 20 °C, the residue was recrystallised from chlorobenzene (2 mL) yielding compound **11** (74.5 mg, 79%) as a black powder, m.p. 260 °C (dec). − $C_{34}H_{22}N_4O_8S_4$ (742.81): calcd. C 54.98, H 2.99, N 7.54; found C 54.91, H 3.10, N 7.00. − MS (EI); *m/z* (%) = 742 (100) [M^+]. − ^{1}H NMR ([D$_6$]DMSO): δ = 9.58 (d, 1 H, *J* = 2 Hz, fluorene), 9.10 (s, 1 H, fluorene=C*H*), 9.06 (d, 1 H, *J* = 2 Hz, fluorene), 8.82 (d, 1 H, *J* = 2 Hz, fluorene), 8.80 (d, 1 H, *J* = 2 Hz, fluorene), 7.90 (s, 4 H; *p*-Ph), 7.70 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.39−7.55 (m, 2 H, CH=CH), 7.26 (d, 2 H, *J* = 8 Hz, *p*-Ph), 6.76 (s, 1 H, dithiole=C*H*), 2.48 (s, 3 H, Me), 2.46 (s, 3 H, Me). − IR (KBr): $\tilde{\nu}$ = 1584, 1561, 1541 (s), 1527 (s), 1411, 1340, 1299, 1167, 968, 842 cm^{-1}.

Fluorene 21: Aldehyde **15** (96 mg, 0.30 mmol) was added to a solution of fluorene **10a** (136 mg, 0.39 mmol) in DMF (1.5 mL) and stirred at 20 °C for 1.5 h resulting in precipitation of a dark solid. The reaction mixture was diluted with methanol (6 mL), the solid was filtered off and washed with methanol yielding compound **21** (190 mg, 98%) which was then purified by column chromatography on silica gel (DCM), m.p. 320 °C (dec). − $C_{24}H_{14}N_4O_8S_5$ (646.70): calcd. C 44.57, H 2.18, N 8.66, S 24.8; found C 44.7, H 2.2, N 8.5, S 24.9. − MS (EI); *m/z* (%) = 646 (17) [M^+]. − ^{1}H NMR ([D$_6$]DMSO; 90 °C): δ = 9.90 (1 H, br), 9.50 (1 H, br), 9.06 (1 H, br), 8.76 (2 H, br), 8.10 (1 H, br), 7.35 (s br., 1 H), 7.28 (s br., 1 H), 2.56 (s, 3 H, Me), 2.55 (s, 3 H, Me). − IR (KBr): $\tilde{\nu}$ = 1585, 1527, 1434, 1405, 1387, 1356, 1341, 1313, 1290, 1243, 1208, 1155, 1068, 831, 801 cm^{-1}.

Fluorene 22: Aldehyde **16** (15.5 mg, 0.039 mmol) was added to a solution of fluorene **10a** (17.0 mg, 0.049 mmol) in DMF (0.5 mL), stirred at 20 °C for 0.5 h and then left standing overnight at 0−5 °C. The black precipitate was filtered off, washed with DMF (1 mL), acetone (5 mL) and 2-propanol (excess) yielding crude **22** (23.5 mg, 83%). Recrystallisation from chlorobenzene (15 mL) afforded compound **22** (16.5 mg, 58%) as a black powder, m.p. > 300 °C (dec.). − $C_{28}H_{16}N_4O_8S_6$ (728.82): calcd. C 46.14, H 2.21, N 7.69; found C 46.11, H 2.20, N 7.42. − HRMS (EI): *m/z* = 727.92831 [M^+] (calcd. 727.92925).

Fluorene (*E*)-28a: To a solution of fluorene **10a** (34 mg, 0.10 mmol) in DMF (1 mL) aldehyde ***(E)*-24** (35 mg, 0.11 mmol) was added and the mixture was stirred for 2 h at 20 °C resulting in precipitation of the product. After diluting with acetone (2 mL), the precipitate was filtered off and thoroughly washed with acetone yielding ***(E)*-28a** (55 mg, 87%). Recrystallisation from chlorobenzene (15 mL) afforded pure ***(E)*-28a** (35 mg, 56%) as a dark-brown solid, m.p. > 320 °C. − $C_{32}H_{20}FeN_4O_8$ (646.38): calcd. C 59.65, H 3.13, N 8.69; found C 58.82, H 3.03, N 8.52. − MS (EI); *m/z* (%) = 644 (63) [M^+]. − ^{1}H NMR ([D$_6$]DMSO): δ = 9.59 (s br., 1 H, fluorene), 9.10 (s br., 1 H, fluorene), 9.08 (s, 1 H., fluorene=C*H*), 8.82 (s br., 1 H., fluorene), 8.80 (s br., 1 H, fluorene), 7.87 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.77 (d, 2 H, *J* = 8 Hz, *p*-Ph), 7.29 (d, 1 H, *J* = 16 Hz, C*H*=CH), 6.95 (d, 1 H, *J* = 16 Hz, C*H*=CH), 4.67 (s, 2 H, cp), 4.54 (s, 2 H, cp), 4.32 (s, 5 H, cp).

Fluorene *(Z)*-28a: To a solution of fluorene **10a** (46.6 mg, 0.136 mmol) in DMF (0.5 mL) aldehyde ***(Z)*-24** (33.0 mg, 0.104 mmol) was added and the mixture was stirred for 1 h at 20 °C. After diluting with methanol (5 mL), the resulting precipitate was filtered off yielding crude ***(Z)*-28a** (54.0 mg, 80%). Column chromatography on silica gel (DCM) afforded pure ***(Z)*-28a** (46.0 mg, 68%) as a dark-brown solid, m.p. 265 °C (dec). − $C_{32}H_{20}FeN_4O_8$ (644.38): calcd. C 59.65, H 3.13, N 8.69; found C 59.4, H 3.1, N 8.6. − MS (EI); *m/z* (%) = 644 (2) [M^+]. − ^{1}H NMR ($CDCl_3$): δ = 9.18 (d, 1 H, *J* = 2 Hz, fluorene), 9.06 (d, 1 H, *J* = 2 Hz, fluorene), 8.91 (d, 1 H, *J* = 2 Hz, fluorene), 8.86 (d, 1 H, *J* = 2 Hz, fluorene), 8.39 (s, 1 H, fluorene=C*H*), 7.63 (s, 4 H, *p*-Ph), 6.55 (d, 1 H, *J* = 12 Hz, C*H*=CH), 6.46 (d, 1 H, *J* = 12 Hz, CH=C*H*), 4.38 (s, 2 H, cp), 4.32 (s, 2 H, cp), 4.19 (s, 5 H, cp). − ^{13}C NMR ([D$_6$]DMSO): δ = 147.8, 147.1, 145.4, 145.3, 145.1, 142.1, 140.8, 140.7, 132.2, 130.9, 130.6, 130.4, 129.6, 129.1, 128.3, 125.7, 122.5, 121.1. 119.9, 119.6, 80.6 (cp), 69.3 (cp), 69.2 (cp), 69.0 (cp).

Fluorene 28c: To a solution of fluorene **10c** (66 mg, 0.13 mmol) in DMF (1 mL) aldehyde ***(Z)*-24** (43 mg, 0.14 mmol) was added and the mixture was stirred for 6 h at 30−35°C. After removing the solvent in vacuo, the residue was chromatographed on silica gel (eluent: chloroform/ethanol, 99:1). The dark-red fraction was collected, concentrated in vacuo to a volume of ca. 0.5 mL, and diluted with petroleum ether (3−4 mL). The resulting brown solid was filtered off and washed with petroleum ether yielding **28c** (69 mg, 67%) as a black powder, m.p. 95−100 °C. − $C_{40}H_{35}FeN_3O_{11}$ (789.58): calcd. C 60.85, H 4.47, N 5.32; found C 59.73, H 4.48, N 5.39. − HRMS (EI): *m/z* = 789.16094 [M^+] (calcd. 789.16210). − ^{1}H NMR ($CDCl_3$): δ = [9.07 (s br.), 9.03 (s br.), 8.98 (s br.), 8.92 (s br.), 8.84 (s br.), 8.78 (s br.), 8.77 (s br.), 8.72 (s br.) (Σ = 4 H, *E*,*Z*: fluorene)], [8.26 (s), 8.23 (s) (Σ = 1 H,

E,*Z*: fluorene=C*H*)], 7.60 (s, 4 H, *p*-Ph), 6.51 (d, 1 H, J = 12 Hz, C*H*=CH), 6.47 (d, 1 H, J = 12 Hz, CH=C*H*), 4.54 (s br., 2 H, COOCH_2), 4.35 (s br., 2 H., cp), 4.31 (s br., 2 H, cp), 4.18 (s br., 5 H, cp), 3.89 (2 H, t, J = 4 Hz, CH_2), 3.62−3.80 (m, 6 H, CH_2), 3.51−3.60 (m, 2 H, CH_2), 3.37 (s, 3 H, Me). − ^{13}C NMR ($CDCl_3$): δ = [165.7, 165.6 (*E*,*Z*: *C*HO)], 147.8, 147.5, 147.0, 146.8, 146.6, 146.4, 145.1, 143.9 141.7, 141.4, 140.6, 138.5, 137.70, 137.66, 136.3, 134.8, 132.6, 131.6, 131.0, 130.8, 129.85, 129.81, 129.77, 125.7, 124.8, 124.5, 122.3, 121.3, 119.4, 119.0, 118.7, 117.8, [81.5, 71.9, 70.63, 70.58, 68.7−70.1 (br), 68.8 (*E*,*Z*: *C*H_2 and cp)], 65.7 (*C*H_2), 59.0 (*C*H_3).

Fluorene 32: To a solution of fluorene **10c** (49 mg, 0.10 mmol) in DMF (1 mL) aldehyde **30** (34 mg, 0.081 mmol) was added and the reaction mixture was stirred at 20 °C for 24 h. The solvent was distilled off in vacuo, and the residue was chromatographed on silica gel, eluting with chloroform/ethanol (500:1, v/v). The brown-violet fraction of the target product was concentrated in vacuo, the residue was dissolved in hot CCl_4 and stored for 2−3 h at 0−5° C. The precipitate was filtered off and washed with CCl_4/petroleum ether (1:1, v/v), yielding fluorene **32** (28 mg, 39%), m.p. ca. 110 °C. − HRMS (EI): m/z = 891.20738 [M$^+$] (calcd. for $C_{48}H_{41}FeN_3O_{11}$ 891.20905). − ^{1}H NMR ($CDCl_3$): δ = 8.5−9.1 (m br., 4 H, fluorene), 8.24 (s br., 1 H, fluorene=C*H*), 6.2−7.8 (m br., 12 H, 2 *p*-Ph + 2 C*H*=C*H*), 4.1−4.6 (m br., 11 H, CH_2 and cp), 3.89 (s br., 2 H, CH_2), 3.58−3.82 (m br., 6 H, CH_2), 3.55 (s br., 2 H, CH_2), 3.37 (s, 3 H, Me).

Fluorene 35: Prepared similarly to **28c** from fluorene **10c** (127 mg, 0.26 mmol) and aldehyde **33** (86 mg, 0.27 mmol), obtaining **35** (144 mg, 70%); m.p. 164−170 °C. − $C_{38}H_{33}FeN_3O_{11}S$ (795.60): calcd. C 57.37, H 4.18, N 5.28; found C 57.11, H 4.16, N 5.29. − MS (EI); m/z (%) = 795 (6) [M$^+$]. − ^{1}H NMR ($CDCl_3$): δ = [9.82 (s br.), 9.75 (s br.) (Σ = 1 H, *E*,*Z*: 1 H, fluorene)], [8.86 (s br.), 8.76 (s br.), 8.73 (s br.), 8.69(br.), 8.62(s br.) (Σ = 3 H, *E*,*Z*: fluorene)], 8.06 (s br., 1 H, fluorene=C*H*), 7.59 (br., 1 H, thiophene), 7.11 (br., 1 H, thiophene), 7.00 (d, 1 H, J = 16 Hz, C*H*=CH), 6.83 (d, 1 H, J = 16 Hz, CH=C*H*), 4.53 (br., 4 H, cp + COOCH_2), 4.43 (s br., 2 H, cp), 4.23 (s, 5 H, cp), 3.60−3.85 (m br., 6 H, CH_2), 3.53 (s br., 2 H, CH_2), 3.35 (s, 3 H, Me). − ^{13}C NMR ($CDCl_3$): δ = [165.85, 165.78 (*E*,*Z*: C=O)], 152.8, 147.3, 146.51, 146.44, 146.38, 146.25, 145.7, 144.6, 140.5, 139.5, 139.2, 139.1, 137.0, 134.4, 133.8, 133.7, 133.3, 130.73, 130.67, 130.60, 128.98, 128.89, 125.74, 125.66, 123.8, 123.2, 122.1, 121.1, 118.4, 118.2, 117.8, 117.5, 117.3, [81.5, 70.61, 70.56, 69.7, 68.8, 67.7 (*E*,*Z*: *C*H_2 and cp)], 65.64 (*C*H_2), 65.61 (*C*H_2), 59.0 (Me). − IR (KBr): $\tilde{\nu}$ = 1719 (C=O), 1585, 1541, 1526, 1432, 1398, 1342, 1293, 1238, 1158, 1105, 1058, 932, 833 cm^{-1}.

Fluorene 36: Ferrocenecarboxaldehyde (**25**) (93 mg, 0.44 mmol) was added to a solution of fluorene **10a** (137 mg, 0.40 mmol) in DMF (1 mL) and stirred at 20 °C until complete conversion of the fluorene (ca. 0.5 h; TLC monitoring). The mixture was diluted with 2-propanol (5 mL), left for 2−3 h at 0−5 °C and the resulting precipitate was filtered off and washed with 2-propanol. After drying, the resulting black powder was chromatographed on silica gel (eluent: chloroform). A dark-green fraction was collected, the solvent was removed under reduced pressure and the residue was washed with hexane and dried, yielding **36** (184 mg, 85%), m.p. 320 °C. − $C_{24}H_{14}FeN_4O_8$ (542.24): calcd. C 53.16, H 2.60, Fe 10.30; found C 53.21, H 2.69, Fe 10.50. − MS (EI); m/z (%) = 542 (100) [M$^+$]. − ^{1}H NMR ([D$_6$]acetone): δ = 9.71 (d, 1 H, J = 2 Hz, fluorene), 9.47 (d, 1 H, J = 2 Hz, fluorene), 8.96 (s, 1 H, fluorene=CH), 8.83 (d, 2 H, J = 2 Hz, fluorene), 5.20 (m, 2 H, cp), 5.09 (m, 2 H, cp), 4.46 (s, 5 H, cp).

Carbaldehyde 37: Ferrocenecarboxaldehyde (**25**) (0.50 g, 2.3 mmol) and dry CsF (0.26 g, 1.7 mmol) were dissolved in DMSO (0.25 mL) and *N*-*tert*-butyl-γ-trimethylsilylcrotonaldimine[36] (now available commercially from Acros) (0.60 g, 3.1 mmol) was added at 20 °C. The mixture was stirred for 0.5 h at 20 °C and then for 0.5 h at 100 °C. After cooling to room temperature, a degassed solution of $ZnCl_2$ in water (10 mL; 10%) and ether (10 mL) were added. ***Caution! A strong exothermic reaction took place during this operation; external cooling is necessary.*** The mixture was stirred for 2 h, the organic layer was separated and the water layer was extracted with ether (2×10 mL). The combined ether solutions were washed with brine, dried with $CaCl_2$ and the solvent was removed in vacuo. The residue was chromatographed on silica gel using chloroform as the eluent. The first orange fraction of unconverted **25** was immediately followed by a violet fraction of impure product which was reduced in vacuo to 1−2 mL, diluted with hot hexane (6 mL), filtered while hot, and left to crystallise affording violet needles of aldehyde **37** (92 mg, 15%), m.p. 129−131 °C. [The residue after concentration of the mother liquor contained an additional portion of desired product **37** (ca. 20 mg, 3%) together with some amount of unconverted ferrocenecarboxaldehyde (**25**).] − MS (EI); m/z (%) = 266 (100) [M$^+$]. − ^{1}H NMR ($CDCl_3$): δ = 9.57 (d, 1 H, J = 8 Hz, C*H*O), 7.16 (1 H, ddd, J = 15, 11 and 0.6 Hz, −CH=CH−C*H*=CH−CHO), 6.89 (d, 1 H, J = 15 Hz, −C*H*=CH−CH=CH−CHO), 6.60 (1 H, ddd, J = 15, 11 and 1 Hz, −CH=C*H*−CH=CH−CHO), 6.15 (1 H, ddt, J = 15, 8 and 1 Hz, −CH=CH−CH=C*H*−CHO), 4.50 (t, 2 H, J = 2 Hz, cp), 4.43 (t, 2 H, J = 2 Hz, cp), 4.16 (s, 1 H, cp). − ^{13}C NMR ($CDCl_3$): δ = 193.80 (*C*=O), 152.89, 143.65, 128.88, 123.77, 80.41 (cp), 70.83 (cp), 69.70 (cp), 68.15 (cp).

Fluorene 38a: Aldehyde **37** (3.0 mg, 0.011 mmol) was added to the solution of fluorene **10a** (6.7 mg, 0.019 mmol) in DMF (0.3 mL) and the mixture was stirred at 20 °C for 2 h. The resulting precipitate was filtered off, washed with DMF, then with acetone and dried in vacuo, yielding pure **38a** (6.5 mg, 97%) as a black powder, m.p. > 300 °C. − HRMS (EI): m/z = 594.04761 [M$^+$] (calcd. for $C_{28}H_{18}FeN_4O_8$ 594.04740). − ^{1}H NMR ([D$_6$]DMSO): δ = 9.46 (s, 1 H, fluorene), 9.28 (s, 1 H, fluorene), 8.77 (s, 1 H, fluorene), 8.63 (d, 1 H, J = 12 Hz, fluorene=C*H*), 7.68 (t, 1 H, J = 12 Hz, C*H*=CH), 7.39−7.53 (m, 1 H, C*H*=CH), 7.13 (br, 2 H, C*H*=CH), 4.78 (s, 2 H, cp), 4.63 (s, 2 H, cp), 4.24 (s, 5 H, cp).

Fluorene 38b: Aldehyde **37** (50 mg, 0.19 mmol) was added to the solution of fluorene **10b** (79 mg, 0.22 mmol) in DMF (1 mL) and the mixture was stirred at 20 °C for 12 h. The resulting precipitate was filtered off, washed with acetone (3 mL), then with acetone/ethanol mixture (3:1, v/v; 5 mL) and dried in vacuo, yielding pure **38b** (76 mg, 67%) as a black powder, m.p. > 300 °C. − $C_{30}H_{21}FeN_3O_8$ (607.36): calcd. C 59.33, H 3.49, N 6.92; found C 59.11, H 3.50, N 6.92. − MS (EI); m/z (%) = 607 (6) [M$^+$]. − ^{1}H NMR ($CDCl_3$): δ = [9.20 (d, J = 2 Hz), 8.92 (d, J = 2 Hz) (Σ = 1 H, *E*,*Z*: fluorene)], [8.85 (d, J = 2 Hz), 9.13 (d, J = 2 Hz) (Σ = 1 H, *E*,*Z*: fluorene)], [8.83 (d, J = 2 Hz), 8.77 (d, J = 2 Hz) (Σ = 1 H, *E*,*Z*: fluorene)], [8.73 (d, J = 2 Hz), 8.67 (d, J = 2 Hz) (Σ = 1 H, *E*,*Z*: fluorene)], [7.78 (d, J = 13 Hz), 7.76 (d, J = 13 Hz) (Σ = 1 H, *E*,*Z*: fluorene=C*H*)], 7.36−7.52 (m, 1 H, C*H*=CH), 7.10−7.20 (m, 1 H, C*H*=CH), 7.00−6.83 (m, 2 H, C*H*=CH), 4.62 (t, 2 H, J = 2 Hz, cp), 4.55 (t, 2 H, J = 2 Hz, cp), 4.21 (s, 5 H, cp), [3.884 (s), 3.877 (s) (Σ = 3 H, *E*,*Z*: Me)].

Fluorene 38c: Aldehyde **37** (45 mg, 0.17 mmol) was added to the solution of fluorene **10c** (82 mg, 0.17 mmol) in DMF (1 mL), stirred for 20 h at 20 °C. The solvent was distilled off in vacuo and the residue was chromatographed on silica gel (eluent chloroform/

ethanol, 99:1, v/v). A dark-coloured fraction containing compound **38c** was concentrated to a volume of 0.5−1 mL and diluted with petroleum ether (2 mL). The solid was filtered off, washed with petroleum ether and dried in vacuo yielding pure fluorene **38c** (93 mg, 75%). − HRMS (EI): *m/z* = 739.14318 [M^+] (calcd. for $C_{36}H_{33}FeN_3O_{11}$: 739.14645). − ^{1}H NMR ($CDCl_3$): δ = [9.19 (d, *J* = 2 Hz), 8.92 (d, *J* = 2 Hz) (Σ = 1 H, *E*,*Z*: fluorene)], [8.85 (d, *J* = 2 Hz), 9.13 (d, *J* = 2 Hz) (Σ = 1 H, *E*,*Z*: fluorene)], [8.82 (d, *J* = 2 Hz), 8.76 (d, *J* = 2 Hz) (Σ = 1 H, *E*,*Z*: fluorene)], [8.75 (d, *J* = 2 Hz), 8.69 (d, *J* = 2 Hz) (Σ = 1 H, *E*,*Z*: fluorene)], [7.78 (d, *J* = 12 Hz), 7.76 (d, *J* = 12 Hz) (Σ = 1 H, *E*,*Z*: fluorene=C*H*)], 7.36−7.52 (m, 1 H, C*H*=CH), 7.11−7.21 (m, 1 H, C*H*=CH), 6.82−7.00 (m, 2 H, C*H*=CH), 4.63 (s br., 2 H, cp), 4.57 (s br., 2 H, cp), 4.23 (s, 5 H, cp), 3.90 (m br., 2 H, COOCH_2), 3.73−3.78 (m, 2 H, CH_2), 3.63−3.72 (m, 6 H, CH_2), 3.51−3.58 (m, 2 H, CH_2), 3.37 (s, 3 H, Me).

Carbaldehyde 40: Obtained by lithiation of ferrocenylacetylene (**39**) with *n*BuLi in THF and subsequent reaction with DMF similarly to the procedure described earlier.[37] After column chromatography on silica gel with DCM/hexane (1:1, v/v), aldehyde **40** was isolated in 72% yield.

Fluorene 41a: Aldehyde **40** (24 mg, 0.10 mmol) was added to a solution of fluorene **10a** (35 mg, 0.10 mmol) in DMF (0.3 mL) and the mixture was stirred for 40 min (full conversion of the starting fluorene occurs in this period; TLC monitoring). An additional portion of fluorene **10a** (5 mg, 0.015 mmol) was added and the mixture was stirred for further 40 min. TLC (silica gel; DCM) showed the appearance of some by-product (R_f = 0.4) along with the desired green product (R_f = 0.85). The solvent was removed in vacuo and the residue was chromatographed on silica gel (eluent DCM) yielding ferrocene **41a** (20 mg, 35%), m.p. 300 °C. − $C_{26}H_{14}FeN_4O_8$ (566.27): calcd. C 55.15, H 2.49, N 9.89; found C 55.30, H 2.59, N 9.85. − MS (EI); *m/z* (%) = 566 (100) [M^+]. − ^{1}H NMR ($CDCl_3$): δ = 10.05 (d, 1 H, *J* = 2 Hz, fluorene), 8.96 (d, 1 H, *J* = 2 Hz, fluorene), 8.94 (d, 1 H, *J* = 2 Hz, fluorene), 8.88 (d, 1 H, *J* = 2 Hz, fluorene), 7.44 (s, 1 H, fluorene=C*H*), 4.93 (t, 2 H, *J* = 2 Hz, cp), 4.67 (t, 2 H, *J* = 2 Hz, cp), 4.35 (s, 5 H, cp). − From the fraction of the second product (R_f = 0.4) a green-grey powder (9.3 mg) was isolated which was not characterised.

Fluorene 41c: Aldehyde **40** (55.5 mg, 0.233 mmol) was added to a solution of fluorene **10c** (106 mg, 0.216 mmol) in DMF (1 mL) and the mixture was stirred for 20 h (full conversation of the starting fluorene, monitored by TLC). The solvent was removed in vacuo and the residue was chromatographed on silica gel (eluent chloroform/ethanol, 99:1 v/v). The main green-grey fraction was concentrated to a volume of 0.5 mL and diluted with petroleum ether (2 mL). The solid was filtered off and washed with petroleum ether affording pure fluorene **41c** (68 mg, 44%), m.p. 110 °C. − HRMS (EI): *m/z* = 711.11725 [M^+] (calcd. for $C_{34}H_{29}N_3O_{11}Fe$: 711.11515). − ^{1}H NMR ([D_6]acetone): δ = [9.95 (d, *J* = 2 Hz), 9.86 (d, *J* = 2 Hz), 9.19 (d, *J* = 2 Hz), 9.07 (d, *J* = 2 Hz), 8.85 (d, *J* = 2 Hz), 8.76 (d, *J* = 2 Hz), 8.72 (d, *J* = 2 Hz), 8.61 (d, *J* = 2 Hz) (Σ = 4 H, *E*,*Z*: fluorene)], [7.85 (s), 7.84 (s) (Σ = 1 H, *E*,*Z*: fluorene=C*H*)], 4.93 (t, 2 H, *J* = 2 Hz, cp), 4.67 (t, 2 H, *J* = 2 Hz, cp), 4.52 (m, 2 H, COOCH_2), [4.367 (s), 4.365 (s) (Σ = 5 H, *E*,*Z*: cp)], 3.90 (m, 2 H, CH_2), 3.52−3.72 (m, 6 H, CH_2), 3.40−3.49 (m, 2 H, CH_2), [3.25 (s), 3.23 (s) (Σ = 3 H, *E*,*Z*: Me)]. − ^{13}C NMR ($CDCl_3$): δ = [165.7, 165.6 (*E*,*Z*: *C*HO)], 148.0, 147.9, 147.3, 147.1, 146.7, 146.4, 143.8, 142.6, 141.9, 140.9, 137.1, 135.5, 134.8, 133.4, 131.8, 131.2, 130.9, 124.7, 124.4, 121.8, 120.9, 119.3, 118.9, 118.2, 117.3, 115.5, 115.4, 114.9, 86.85, 86.81, 72.82, 72.79, 71.9, 71.80, 70.89, 70.88, 70.63, 70.59, 68.8, 65.7, 61.98, 61.95, 59.0.

Fluorene 42: A mixture of ester **10c** (213 mg, 0.52 mmol) and 4-(diethylamino)cinnamaldehyde (90 mg, 0.44 mmol) in acetic anhydride (3 mL) was stirred for 2 h at 100 °C. Methanol (4 mL) was added to the reaction mixture and the solid was collected. Upon recrystallisation from a minimal amount of acetonitrile, compound **42** (200 mg, 67%) was obtained as a black powder, m.p. 182−183 °C. − HRMS (EI): *m/z* = 676.23511 [M^+] (calcd. for $C_{34}H_{36}N_4O_{11}$: 676.23806). − ^{1}H NMR ($CDCl_3$): δ = [9.16 (d, *J* = 2 Hz), 9.08 (d, *J* = 2 Hz), 8.84 (d, *J* = 2 Hz), 8.75 (d, *J* = 2 Hz), 8.68 (d, *J* = 2 Hz), 8.64 (d, *J* = 2 Hz), 8.63 (d, *J* = 2 Hz), 8.58 (d, *J* = 2 Hz) (Σ = 4 H, *E*,*Z*: fluorene)], 7.78 (d, 1 H, *J* = 12 Hz, fluorene=C*H*), 7.65 (dd, 1 H, *J* = 12 Hz, *J* = 14 Hz, CH−C*H*=CH), 7.54 (d, 2 H, *J* = 9 Hz, *p*-Ph), 7.28 (d, 1 H, *J* = 14 Hz, C*H*−Ph), 6.73 (d, 2 H, *J* = 9 Hz, *p*-Ph), 4.54 (m, 2 H, CO_2CH_2), 3.89 (m, 2 H, CH_2), 3.76 (m, 2 H, CH_2), 3.69 (m, 2 H, CH_2), 3.66 (m, 2 H, CH_2), 3.54 (m, 2 H, CH_2), 3.49 (q, 4 H, *J* = 7 Hz, CH_2Me), 3.35 (s, 3 H, OMe), 1.26 (t, 6 H, *J* = 7 Hz, Me).

X-ray Crystallography: Single-crystal X-ray diffraction experiments were carried out with a SMART 3-circle diffractometer with a 1 K CCD area detector, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[57] Crystal data and experimental details are summarised in Table 3; full structural data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-140255 (**9**), -140256 (**18**), and -140257 (**27**).

Table 3. Crystal data for compounds **9**, **18**, and **27**

Compound	**9**	**18**	**27**
Formula	$C_{24}H_{18}N_2S_4$	$C_{14}H_{10}N_2S_5$	$C_{22}H_{16}FeN_2$
M	462.64	366.54	364.22
T [K]	150	150	295
Crystal system	monoclinic	monoclinic	monoclinic
a [Å]	15.317(3)	16.359(4)	10.982(1)
b [Å]	18.565(4)	7.765(1)	7.482(1)
c [Å]	15.626(3)	13.016(5)	21.053(2)
β [°]	98.30(1)	101.43(4)	96.23(1)
V [Å^3]	4397(2)	1620.6(8)	1719.7(3)
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
Z	8	4	4
μ [cm^{-1}]	4.5	7.1	8.8
$2\theta_{max}$ [°]	56	50	52
Data total	50623	9279	9935
Data unique	10298	2853	3256
Data obsvd., $I > 2\sigma(I)$	6157	1325	2314
$wR(F^2)$, all data	0.137	0.229	0.117
$R(F)$, obs. data	0.058	0.085	0.055

EFISH Experiments: EFISH generation measurements have been performed in order to measure μβ values of the chromophores. Samples were prepared at three different concentrations generally in the range $(1-10)\times10^{-4}$ mol·L^{-1} in dichloromethane and tested using the EFISH setup. Our experimental setup, which is described elsewhere,[58] consists of a commercial (Surelite-II, "Continuum") Q-switched Nd:YAG laser (λ = 1.064 μm, 10 Hz) Raman-shifted to λ = 1.54 μm (CH_4 at 30 atm). The EFISH cell is wedge-shaped (3°) according to the conventional design.[59] Experimental data is acquired using a boxcar integrator (PCI-200, "Becker & Huckl") and normalised for each laser pulse relative to a quartz reference. The molecular μβ value is calculated from the EFISH signal,[60]

which for chromophores with tail absorption at the SH wavelength (770 nm) is corrected according to published procedures.[60][61] The zero frequency hyperpolarisability values μβ(0) were then deduced using the two-level model approximation, taking into account (where necessary) the spectral width of the absorption to the lowest excited state.[61] Note that our μβ and μβ(0) values are defined according to the "traditional" EFISH definition, so we have converted literature data (refs.[47,48]) based on the revised definition by the suggested factor of 1.93.[62]

Computational Procedure: The computations were carried out using ab initio methods with the Gaussian98[42] program. The geometries of compounds **49** and **50** were fully optimised at the Hartree−Fock level of theory using a 6-31 basis set supplemented by d-polarisation functions on heavy atoms. Restricted HF formalism was applied. Visualisation of HOMO−LUMO orbitals was performed by Gopenmol software (Leif Laaksonen, Centre for Scientific Computing, Espoo, Finland). The hyperpolarisability (β_μ) is defined as $\beta_\mu = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$ where $\beta_i = 1/3\Sigma_{k=x,y,z}(\beta_{ikk} + \beta_{kik} + \beta_{kki})$; $i = x, y, z$.

Acknowledgments

We thank EPSRC for funding (A. C., A. J. M., A. S. B., D. F. P.) the Royal Society for a Leverhulme Senior Research Fellowship (J. A. K. H.) and for funding visits to Durham (I. F. P.).

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Received February 1, 2001
[O01048]