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Synthesis and characterization of novel NLO-phores from π-extended tetrathiafulvalene (TTF) derivatives.

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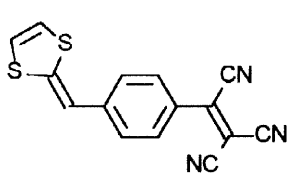
Abstract

Donor-π-Acceptor systems containing extended TTF derivatives with quinonoid structures have been synthesized and characterized. Their properties as second order NLO chromophores have been studied by experimental (EFISH) and theoretical methods.

Keywords: Electronic Spectra; Theoretical Studies; Thiafulvalenes.

Nonlinear optical chromophores (NLO-phores) are typically constituted by strong donor and acceptor units connected through a conjugated π-system [1]. Different classes of donor fragments have been used in the search of high first order hyperpolarizability (β) values, and, in this regard, the electron-donating dithiafulvenyl group has been successfully used in the preparation of highly efficient second-order nonlinear compounds such as **1** [2], **2a** [3] and **2b** [4]. In the search of novel chromophores, we have recently reported the first TTF-containing organic materials (**3**) exhibiting second-order optical nonlinearity [5,6].



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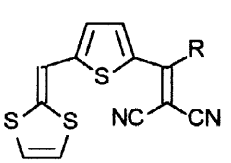
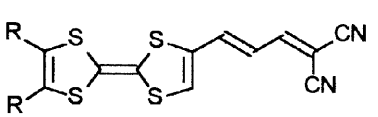


2a: R=CN
2b: R=H



3a: R=H
3b: R-R=$(SCH_2)_2$

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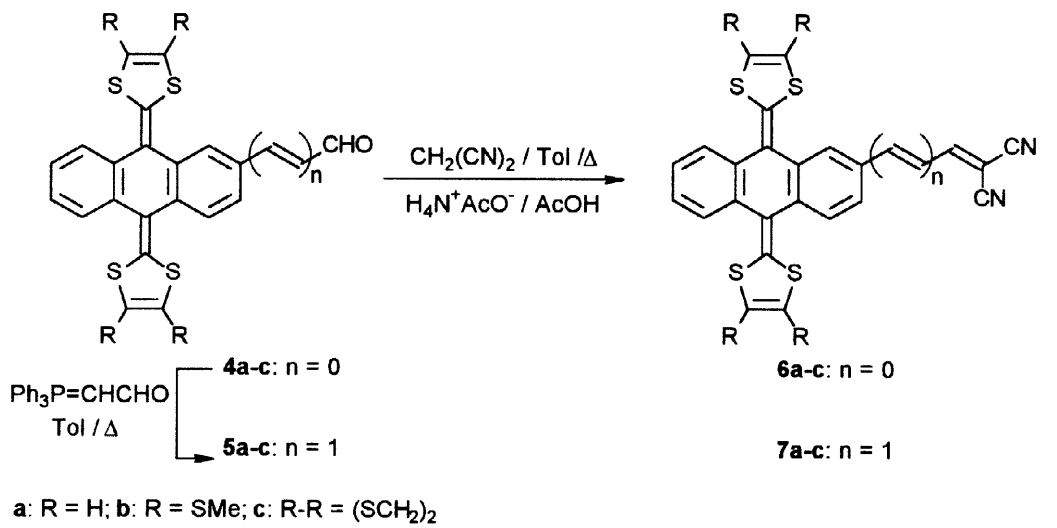
The presence of the ethylenedithio group as a substituent on the TTF framework (**3b**) resulted in an enhancement of the μβ values and an hypsochromic shift relative to **3a**, which is in contrast to the transparency-nonlinear efficiency trade-off.

In order to evaluate the effect that the separation of the two dithiafulvenyl groups of the TTF core has on the second harmonic generation, we have carried out the synthesis of the novel D-π-A systems (**6a-c** and **7a-c**) in which a π-extended TTF derivative is covalently attached to an acceptor dicyanovinyl group through ethylenic spacers. This donor fragment could be formally considered as the first example in which two dithiafulvenyl groups are linked to the acceptor unit through styrene or styrylvinylene spacers (**Scheme**).

The synthesis of the target molecules (**6a-c,7a-c**) was carried out from the respective aldehydes (**4a-c, 5a-c**) by Knoevenagel condensation of malononitrile in refluxing toluene, using ammonium acetate/acetic acid and azeotropic distillation of the water generated in the reaction medium. Compounds **6a-c** and **7a-c** were prepared as stable, high melting point solids in good yields (65-82%). The starting aldehydes **4a-c** [7] and **5a-c** [8] were previously prepared in our group in a multistep synthetic procedure from commercially available 2-hydroxymethylanthraquinone.



Scheme

Compounds **6a-c** and **7a-c** show the presence of a strong cyano stretching vibration at 2230 cm^{-1} in the FTIR spectrum. The vinyl proton appears as a singlet at δ ~ 7.7 in the ^{1}H-NMR spectra of compounds **6a-c**, meanwhile three sets of signals at δ=7.2-7.6 are clearly observed for the vinyl protons in compounds **7a-c** (see experimental).

The UV-Vis spectra of compounds **6a-c** and **7a-c** show a low energy charge-transfer band in the visible region which is bathochromically shifted (~100 nm) in comparison with the respective aldehydes (**4a-c** and **5a-c**) as a consequence of the stronger electron-acceptor character of the dicyanovinyl chromophore with regard to the carbonyl group. In agreement with the previously reported TTF derivatives (**3**) [5,6] and analogues thereof [9,10], a most

interesting observation is that compounds **7a-c** present a slight hypsochromic shift when compared to **6a-c**, in spite of their larger π-extension (**Table 1**).

Solvatochromic studies carried out on compounds **6b** and **7b** (R=SMe) in solvents of different polarity indicate a negative solvatochromic effect [**6b**: 560 nm (C_6H_{12}); 556 (CH_2Cl_2); 524 (EtOH); 522 (MeCN); **7b**: 566 nm (C_6H_{12}); 549 (CH_2Cl_2); 528 (EtOH); 508 (MeCN)]. This behaviour supports, in valence bond theory language, a major zwitterionic contribution to the ground state. This finding is also supported by the ^1H NMR spectra of compounds **7a** and **7c** which show a difference between CH=CH and CH-CH $^3J_{HH}$ coupling constants of only ΔJ=0.3-0.5 Hz. [11].

Table 1. UV-Vis, μβ values and redox potentials for compounds **6-7**.

Compound	λ_{max} (nm)[a]	μβ[a,b]	$\mu\beta_0$[b]	$\mu\beta_{0\ calc}$[b,c]	$E^{1,ox}_{a.p.}$[d]	$E^{1,red}_{c.p.}$[d]
6a	559	230	138	133	0.51	-1.10
6b	556	255	154	211	0.58	-0.97
6c	571	295	172	226	0.62	-1.04
7a	555	450	272	271	0.48	-0.99
7b	549	545	334	351	0.58	-0.97
7c	566	550	325	364	0.60	-0.95

[a] In CH_2Cl_2; [b] All μβ values in (10^{-48} esu) units. Measured at 1,907 nm by the EFISH technique, the estimated errors in μβ values are ± 10%; [c] FF PM3; [d] In Volts *vs* SCE; CH_2Cl_2 as solvent; $Bu_4N^+ClO_4^-$ 0,1 M; 200 mV/s.

Compounds **6a-c** and **7a-c** show a quasi reversible oxidation wave involving two electrons to form the respective dication, which is slightly influenced by the substituents on the 1,3-dithiole ring (**Table 1**). The electrochemical redox behaviour of these conjugated TTF analogues with a quinonoid structure is well established [12] and their structural and electronic properties have recently been characterized by both experimental and quantum-chemical calculations [13]. On the reduction side, a wave to form the radical-anion is observed which is anodically shifted in compounds **6a-c** and **7a-c,** in comparison with their carbonyl containing precursors **4a-c** and **5a-c,** due to the better acceptor ability of the dicyanovinyl chromophore [14].

μβ Values experience an important enhancement on going from compounds **6a-c** to **7a-c** due to the increase of conjugation length. The presence of the ethylenedithio or methylthio groups also results in an increase of μβ. These results are in agreement with those previously reported for TTF [6] and dithiafulvenyl [3] containing chromophores.

The geometry of compounds **6** and **7** has been optimized by theoretical calculations at both semiempirical (PM3) and *ab initio* (HF/3-21G*) levels. The proximity of sulfur atoms to the peri hydrogens of the anthracene ring causes the loss of planarity giving rise to a butterfly type geometry (see **Figure 1**) in agreement with theoretical calculations [13] and X-ray structures [12] of similar extended tetrathiafulvalenes. Thus, the S...H distance calculated to be 1.78 Å for a planar geometry [13] becomes 2.58-2.63 Å (PM3) or 2.82-2.83 Å (HF/3-21G*) in the optimized geometries.

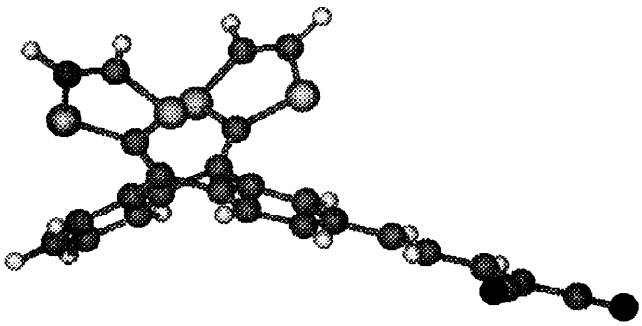
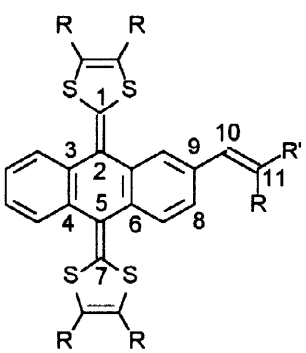


Figure 1. HF/3-21G* optimized geometry of **7a**.

Deviation from planarity is described in terms of the dihedral angles gathered in **Table 2**. Dihedral angle α corresponds to the angle formed by the two benzene rings while β and γ define the tilting of the two dithiole rings. While the geometry calculated at both levels of theory is quite similar, it can be seen that *ab initio* calculations give rise to a somewhat more folded geometry than PM3. A clear difference is however observed in the way used to avoid the sterical repulsion caused by the dicyanovinyl group and the hydrogen atom located at C8 on compound **6a**. Thus, while PM3 predicts a δ dihedral angle of 44.5°, in the HF/3-21G* optimized geometry the dicyanovinyl group is nearly coplanar (δ = -5.0°) with the benzene ring to which it is attached and the steric crowding is relieved by deformation of the C8-C9-C10, C9-C10-C11 and C10-C11-R angles from ideal 120° to 125.2°, 131.3° and 125.5° respectively.

Table 2. Selected dihedral angles[a] (degrees) in the optimized geometries of **6a** and **7a**.



6a: R = R' = CN
7a: R =H; R' = $CHC(CN)_2$

	PM3				HF/3-21G*			
Compound	α	β	γ	δ	α	β	γ	δ
6a	138.9	-138.7	138.9	44.5	135.9	-131.7	131.8	-5.0
7a	139.1	-138.7	138.7	0.1	135.9	-131.7	132.1	-5.4

[a]Dihedral angles have been defined as follows: α = C3-C2-C5-C6; β =C1-C2-C3-C4; γ = C7-C5-C4-C3; δ = C8-C9-C10-C11

The *ab initio* geometry is in better agreement with the X-ray structures of 2,2-dicyanovinylbenzene [15] and substituted derivatives [16,17]. For all these compounds the angle defined by the planes containing the benzene ring and the dicyanovinyl group ranges

from 3.8° to 14°. Furthermore, measured angles for 2,2-dicyanovinylbenzene (C8-C9-C10: 125.3°; C9-C10-C11: 130.4° and C10-C11-R: 126.7°) are very close to the above-mentioned calculated values.

Although PM3 has been reported to give a better description than *ab initio* HF calculations of the molecular structure of extended TTFs [13], the twisting of the dicyanovinyl side chain in **6a** is largely overestimated by this semiempirical method.

The PM3 calculated topologies of the HOMO and LUMO of **7a** are depicted in **Figure 2** and show that they are mainly located on the donor and acceptor moities respectively. This result supports the intramolecular charge-transfer character assigned to the first absortion band of compounds **7** and **6**. It is worth noting that the HOMO and the LUMO of 9,10-bis(1,3-dithiol-2-ylidene)dihydroanthracene are mostly located on the dithiafulvenyl moieties, so it displays its first absortion band, which has not charge-transfer character, at shorter wavelength (415 nm) [13].

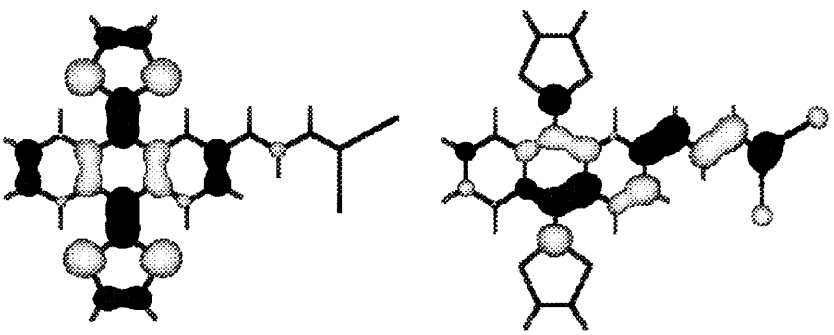


Figure 2. Calculated topologies of HOMO and LUMO of **7a**.

The second order NLO properties of these compounds have been evaluated using the semiempirical PM3 hamiltonian since it has already been succesfully applied to TTF-derived chromophores [6]. The calculated (FF-PM3) static $\mu\beta$ values gathered in **Table 1** are in good agreement with the experimental results, reproducing the trends observed on introduction of alkylthio groups on the dithiafulvenyl rings and on extension of the π-conjugated spacer. For the sake of comparison, *ab initio* (CPHF/6-31G*//HF/3-21G*) calculations were carried out on **6a** and **7a**, yielding somewhat overestimated $\mu\beta_0$ values: 168 and 322 (10^{-48}) esu, respectively. Theoretical calculations also show the partial overlap between the HOMO and LUMO (**Figure 2**) which is a requisite for obtaining good second-order responses in push-pull polyenes [18].

In conclusion, we have carried out the synthesis of novel D-π-A systems containing π-extended TTF derivatives with quinonoid structures which behave as efficient NLO chromophores. The presence of sulfur-containing substituents on the 1,3-dithiole ring and the length increase of the π-conjugated spacer are factors that significantly enhance the NLO response.

Experimental

General

Melting points were measured on a Thermolab apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a Varian Unity-300 and a Bruker AC-250. IR spectra were recorded using a Perkin-Elmer 781 spectrometer. Mass spectra (EI^{+}, 70 eV) were obtained on a VG Autospec EBE mass Spectometer. Cyclic voltammograms were measured using an EG&G PAR model 273 potentiostat. EFISH measurements were taken with a non-linear optics spectrometer from SOPRA S.A. The fundamental light source at 1.907 μm was the first Stokes peak of a hydrogen Raman cell pumped by the 1.064 μm light of a Q-switched Nd:YAG laser (Quantel YG 781, 10pps, 8 ns, pulse). That light was passed through a linear polarizer and focused on the EFISH cell. The polarizing dc electric field (paralell to the light polarization) used in this cell was 6 kV. The output light from the cell was passed thought an interference filter to select the second harmonic light (0.954 μm) which was finally detected with a R642 photomultiplier from Hamamatsu. Optical absortion spectra were measured with a Hitachi U-3400-UV-VIS-NIR spectrophotometer. Molecular orbital calculations were performed on Intel Pentium and Pentium Pro computers running under the Microsoft Windows NT 4.0 Workstation operating system. Geometry optimizations (PM3 and HF/3-21G*) were carried out using the Berny analytical gradient method implemented in Gaussian 94w [19]. Static (zero frequency) hyperpolarizabilities were obtained by single point calculations on the optimized geometries using the Finite Field approach implemented in MOPAC 6.0 [20] and the Coupled Perturbed Hartree-Fock (CPHF) algorithm included in Gaussian 94w. Definitions described in ref [18] have been used: $\mu\beta_{vec} = \beta_x\mu_x + \beta_y\mu_y + \beta_z\mu_z$ with $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$; $\beta_y = \beta_{yxx} + \beta_{yyy} + \beta_{yzz}$ and $\beta_z = \beta_{zxx} + \beta_{zyy} + \beta_{zzz}$

Synthesis of Substituted 2-(2,2-dicyanovinyl)-9,10-bis(1,3-dithiol-2-ylidene)dihydroanthracenes (6a-c). General Procedure. A solution of the corresponding substituted 2-formyl-9,10-bis(1,3-dithiol-2-ylidene)dihydroanthracenes (**4a-c**) [7] (0.5 mmol), malononitrile (1mmol), ammonium acetate (25 mg, 0.23 mmol) and acetic acid (1ml) in toluene (30 ml) was refluxed with azeotropic distillation using a Dean-Stark for 24h. The solvent was removed under reduced presure and the isolation of the final products was performed by careful flash chromatography, using silica-gel and methylene dichloride as eluent.

2-(2,2-dicyanovinyl)-9,10-bis(1,3-dithiol-2-ylidene)dihydroanthracene (6a). 82 % yield, mp 283-285 °C (dec.). IR (KBr disk) ν (cm^{-1}): 2230 (C≡N), 1580; 1550; 1500; 1460; 1420; 1290, 1230, 815, 765, 660, 640. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 8.14 (d, 1H, J=1.5 Hz), 7.87 (dd, 1H, J_1=6.5, J_2=1.5 Hz), 7.73 (s, 1H), 7.72 (d, 1H, J=6.3 Hz), 7.64-7.62 (m, 2H), 7.33 (m, 2H), 6.42 (s, 2H), 6.36 (s, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 158.7, 141.6, 141.4, 138.5, 136.4, 134.7, 134.4, 128.7, 127.9, 126.9, 126.4, 126.3, 125.7, 125.0, 124.7, 120.7, 119.8, 117.8, 117.5, 117.4, 116.8, 114.2, 112.9. UV-Vis (CH_2Cl_2) λ_{max} (log ε) nm: 229 (4.50), 324 (4.45), 415 (4.24), 559 (3.96), M.S. m/z: 456 (M^{+}). Anal. Calcd. for $C_{24}H_{12}N_2S_4$: %C: 63.13, %H: 2.65, %N: 6.14. Found: %C: 62.88, %H: 2.85, %N: 5.83.

2-(2,2-dicyanovinyl)-9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)dihydroanthracene (6b). 75 % yield, mp 282-284 °C (dec.). IR (KBr disk) ν (cm^{-1}): 2230 (C≡N), 1590, 1530, 1500, 1460, 1420, 1325, 1270, 1225, 1100, 1025, 810, 765. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.93 (d, 1H J=1.7 Hz), 7.80 (dd, 1H, J_1=8.1, J_2=1.7 Hz), 7.67 (s, 1H), 7.63 (d, 1H J=8.1 Hz), 7.52 (m, 2H), 7.29-7.19 (m, 2H), 2.24 (s, 12H). ^{13}C-NMR ($CDCl_3$, 62 MHz) δ: 158.9, 140.8, 135.9, 134.2, 133.9, 129.1, 128.5, 127.3, 127.0, 126.9, 126.3, 125.6, 125.4, 122.4, 121.4, 114.3, 113.1, 81.4, 29.8, 19.3, 19.2, 19.1. UV-Vis (CH_2Cl_2) λ_{max} (log ε) nm: 232 (4.51), 330 (4.43), 424 (4.24), 556 (3.98). M.S. m/z: 640 (M^+). Anal. Calcd. for $C_{28}H_{20}N_2S_8$: %C: 52.47, %H: 3.15, %N: 4.37. Found: %C: 51.94, %H: 3.44, %N: 3.93.

2-(2,2-dicyanovinyl)-9,10-bis(1,3-dithiol-4,5-ethylenedithio-2-ylidene)dihydroanthracene (6c). 71 % yield, mp 283-285 °C (dec.). IR (KBr disk) ν cm^{-1}: 2230 (C≡N), 1580, 1550, 1500, 1455, 1425, 1290, 1225, 1120, 765. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7,85 (d, 1H, J=1.6 Hz), 7.84 (dd, 1H, J_1=8.5, J_2=1.6 Hz), 7.67 (s, 1H), 7.59 (d, 1H, J=8.5 Hz), 7.46 (m, 2H), 7.28 (m, 2H), 3.24 (s, 8H). ^{13}C-NMR ($CDCl_3$, 62 MHz) δ: 158.8, 140.8, 135.9, 134.2, 134.0, 128.9, 128.5, 127.7, 127.0, 126.3, 125.8, 125.5, 122.4, 114.3, 113.1, 81.4, 29.5, 29,4. UV-Vis (CH_2Cl_2) λ_{max} (log ε) nm: 236 (4.93), 334 (4.79), 430 (4.55), 571 (4.36). Anal. Calcd. for $C_{28}H_{16}N_2S_8$: %C: 52.80, %H: 2.51, %N: 4.40. Found: %C: 53.28, %H: 2.89, %N: 4.10.

Synthesis of Substituted 2-(4,4-dicyanobutadienyl)-9,10-bis(1,3-dithiol-2-ylidene)dihydroanthracenes (7a-c). General Procedure. A solution of the corresponding substituted 2(E-2-formylvinyl-9,10-bis(1,3-dithiol-2-ylidene)dihydroanthracene (**5a-c**) [8] (0.2 mmol), malononitrile (0.4 mmol), ammonium acetate (11mg) and acetic acid (1ml) in toluene (20 ml) was refluxed with azeotropic elimination of the generated water in the reaction medium by using a Dean-Stark apparatus for 24h. The solvent was removed under reduced pressure and the isolation of the final products was performed by careful flash chromatography using silica-gel and methylene dichloride as eluent.

2-(4,4-dicyanobutadienyl)-9,10-bis(1,3-dithiol-2-ylidene)dihydroanthracene (7a). 80 % yield, mp 285-287 °C (dec.). IR (KBr disk) ν (cm^{-1}): 2230 (C≡N), 1600, 1565, 1550, 1500, 1455, 1420, 1380, 1320, 1270, 1180, 980, 850, 825, 805, 760, 650. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.86 (d, 1H, J=1.8 Hz), 7.75 (d, 1H, J=7.8 Hz), 7.69 (dd, 1H, J_1=9.3, J_2=9.0 Hz), 7.59-7.56 (m, 2H), 7.48 (dd, 1H, J_1=7.8, J_2=1.8 Hz), 7.31-7.28 (m, 2H), 7.3 (d, 1H, J=9.3 Hz), 7.25 (d, 1H, J=9.0 Hz), 6.31 (m, 4H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 160.3, 159.8, 149.7, 139.0, 137.3, 136.3, 134.8, 131.2, 126.0, 125.6, 125.4, 125.3, 124.9, 124.8, 121.6, 121.2, 120.7, 117.7, 117.3, 117.1, 117.0, 116.5, 113.7, 111.8. UV-Vis (CH_2Cl_2) λ_{max} (log ε) nm: 232 (4.40), 352 (4.50), 416 (4.37), 555 (4.02). M.S. m/z: 482 (M^+). Anal. Calcd. for $C_{26}H_{14}S_4N_2$: %C: 64.70, %H: 2.92, %N: 5.80. Found: %C: 64.22, %H: 3.15, %N: 5.74.

2-(4,4-dicyanobutadienyl)-9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)dihydroanthracene (7b). 65 % yield, mp 286-288 °C (dec.). IR (KBr disk) ν (cm^{-1}): 2230 (C≡N), 1600, 1555, 1495, 1420, 1315, 1260, 1180, 980, 895, 825, 760. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.68 (d, 1H, J=1.7 Hz), 7.59 (d, 1H, J=8.1 Hz), 7.60-7.52 (m, 4H), 7.31-7.23 (m, 4H), 2.40 (s,12H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 159.5, 149.4, 138.1, 135.5, 134.4, 134.0, 134.1, 132.8, 131.6, 126.5, 126.3, 125.1, 125.9, 125.8, 125.3, 125.2, 124.6, 122.2, 122.1, 113.5, 111.6, 19.1, 19.0, 18,9. UV-Vis (CH_2Cl_2) λ_{max} (log ε) nm: 238 (4.89), 354 (4.96), 424 (4.75), 549 (4.45). Anal. Calcd for

$C_{30}H_{22}S_8N_2$: %C: 54.02, %H: 3.32, %N: 4.20. Found: %C: 54.59, %H: 3.98, %N: 3.89.

2-(4,4-dicyanobutadienyl)-9,10-bis(1,3-dithiol-4,5-ethylenedithio-2-ylidene)dihydroanthracene (7c). 76 % yield, mp 288-290 °C (dec.). IR (KBr disk) ν (cm^{-1}): 2230 (C≡N), 1600, 1570, 1550, 1510, 1460, 1275, 1180, 985, 765. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.67 (d,1H, J=1.5 Hz), 7.63 (dd,1H, J_1=9.6, J_2=9.1 Hz), 7.60 (d,1H, J=7.8 Hz), 7.57 (dd,1H, J_1=7.8, J_2=1.5 Hz), 7.54-7.51 (m, 2H), 7.36-7.34 (m, 2H),7.32 (d,1H, J=9.6 Hz) 7.30 (d,1H, J=9.1 Hz), 3.32 (s, 8H). ^{13}C-NMR ($CDCl_3$, 62 MHz) δ: 159.9, 149.7, 138.3, 135.8, 134.3, 131.8, 126.8, 126.7, 126.4, 126.2, 125.7, 125.6, 123.1, 122.8, 122.4, 113.7, 111.8, 111.7, 29.7, 29.6. UV-Vis (CH_2Cl_2) λ_{max} (log ε) nm: 236 (4.68), 360 (4.67), 434 (4.41), 566 (4.16). Anal. Calcd for $C_{30}H_{18}S_8N_2$: %C: 54.35, %H: 2.74, %N: 4.23. Found: %C: 54.94, %H: 3.29, %N: 3.67.

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