

Synthesis, X-ray Structure, and Electrochemical Oxidative Coupling Reactions of 1,5- and 2,6-Bis(1,4-dithiafulven-6-yl)naphthalenes

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Novel π -extended tetrathiafulvalene (TTF) derivatives (**12a–c**, **13a–c**, **15a–c**) in which the two 1,3-dithiole units are connected through a naphthalene spacer have been prepared in high yields by Wittig–Horner olefination reaction from dialkoxy-substituted diformyl naphthalenes (**11a,b**, **14**) and differently substituted phosphonate esters (**10a–c**). The electrochemical study revealed a similar behavior for the novel electron donor molecules (**12a–c**, **13a–c**, **15a–c**) regardless of the position of the 1,3-dithiole rings on the naphthalene core. The extended donors undergo an efficient electrooxidation process affording new oligomeric extended TTF species which exhibit lower oxidation potential values than their precursor donors. EPR experiments confirm the presence of the cation radical derived from the oligomeric TTF vinylogues and support an ECE process. The structural study has been carried out by X-ray analysis of **12a** and semiempirical PM3 calculations and reveals a distorted geometry from the planarity with the naphthalene moiety forming an angle of $\sim 35^\circ$ with the thiafulvalene rings. A good agreement was found between the experimental and calculated values, thus validating the PM3 method. The chemical oxidation of the synthesized donors (**12a–c**, **13a–c**, **15a–c**) with strong electron acceptors give rise to charge transfer complexes (CTC) which were characterized by UV–vis, FTIR, and EPR spectroscopy.

Introduction

Tetrathiafulvalene (TTF)¹ (**1**) is the best known π -electron donor molecule which has been successfully used in the preparation of electrically conducting and superconducting salts and charge transfer (CT) complexes.² Since the discovery of TTF, a wide variety of modifications have been performed on its skeleton in the search of new molecular-based organic metals.^{3,4} Among the modifica-

tions known to date, the extension of conjugation between the two 1,3-dithiole units of TTF has recently received particular attention due to the expected increased dimensionality,⁵ nonlinear optical properties,⁶ or the interest in the preparation of small-gap semiconductors.⁷

Representative examples of extended TTFs are shown in Chart 1. Yoshida et al.⁸ reported the first vinylogue of TTF (**2**) which exhibits a lower oxidation potential than the parent TTF as a consequence of the decreasing of the intramolecular Coulombic repulsion in the dication species. Substituted analogues (**3**) have been recently and efficiently prepared by Lorcy et al.⁹ by electrochemical synthesis from 1,4-dithiafulvenes (**4**).

Elongated π -donors bearing a heterocyclic spacer (**5**) have also been prepared and behave as strong donors, forming highly conducting CT complexes.¹⁰

π -Extended TTFs in which both 1,3-dithiole units are connected through a *p*-quinodimethane moiety (**6**) were first reported by Yamashita¹¹ and Bryce.¹² These com-

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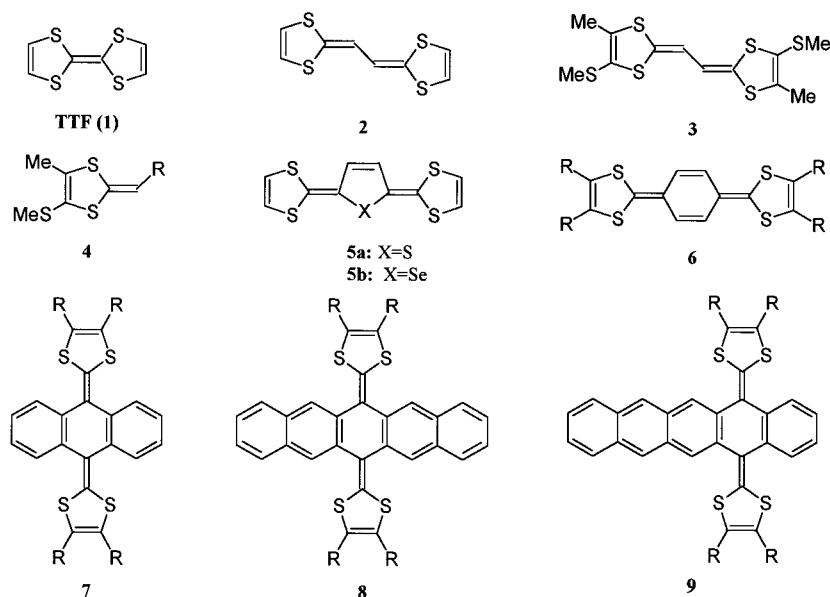
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Chart 1



pounds present strong electron donor properties [**6**: (R=H) $E^{1/2} = -0.11$; $E^{2/2} = -0.04$ V]¹¹ due to the formation of a new aromatic sextet upon oxidation, forming easily the dication species as a result of the decreased Coulombic repulsion. In contrast to **6**, compounds bearing fused benzene rings (**7**) show a highly distorted structure out of the planarity and only one oxidation wave to form the dication. The instability of the radical cation in **7** is determined by the reduced gain of aromaticity due to its still folded structure. Compound **7** (R = Me), however, readily form electrically conducting CT complexes by mixing with tetracyano-*p*-quinodimethane (TCNQ) in a donor:acceptor stoichiometry of 1:4.^{12,13}

We have synthesized very recently a series of highly conjugated TTF analogues (**8**, **9**) and their structural and electronic properties characterized by both experimental techniques and quantum-chemical calculations.¹⁴ These compounds form CT complexes with strong electron acceptors showing a semiconducting behavior. Interestingly, the benzannulation gives rise to new unoccupied low-energy orbitals localized on the polyacenic units. A HOMO \rightarrow LUMO transition is observed in the UV-vis spectra corresponding to an electron transfer from the 1,3-dithiole moieties to the fused acene units acting as the acceptor.¹⁴

Taking into account the effect that the π -extension between the two 1,3-dithiole rings plays on the electron donor properties of the analogous TTF derivatives, in this paper we report a detailed study of the synthesis, electrochemistry, X-ray structure determination, quantum-chemical calculations, and EPR measurements of the novel π -extended donors **12a-c**, **13a-c**, and **15a-c**. In

addition, from these donor systems, charge transfer complexes were prepared by mixing with different electron acceptor molecules.

Results and Discussion

Synthesis. The target molecules (**12a-c**, **13a-c**, and **15a-c**) were prepared by a Wittig-Horner olefination reaction from phosphonate ester **10a-c**. In the presence of *n*-butyllithium at -78 °C, esters **10a-c** generate the respective intermediate carbanions which react with dialkoxy-substituted diformylnaphthalenes **11a,b** and **14** leading to the respective π -extended TTF derivatives **12a-c**, **13a-c**, and **15a-c** bearing a naphthalene unit connecting both 1,3-dithiole rings¹⁵ (Scheme 1).

Phosphonate esters (**10a-c**)¹⁶ were prepared in several steps from substituted 1,3-dithiole-2-thiones by following the well-established method previously reported in the literature.¹⁷ Dialkoxy-substituted diformylnaphthalenes **11a,b** and **14** were in turn prepared in a multistep synthetic procedure by using literature procedures.¹⁸ Compounds **12a-c** and **13a-c** were obtained by using different stoichiometries of the starting dicarbonyl compounds (**11a,b**) and phosphonate esters **10a-c**. The yield is optimized with a ratio of 4:1 (**10:11**) since an excess of phosphonate ester avoids extensive formation of the monocondensated compound. Thus, compounds **12a-c** and **13a-c** are obtained in high yields (85–95%). In a similar way, compounds **15a-c** are prepared in good yields (70–95%) by using a larger excess of phosphonate **10** (ratio 6:1) (see Experimental Section).

During the preparation of this manuscript, the paper by Christensen reporting the synthesis and electrochemistry of related structures using naphthalene spacers connecting two 4,5-dimethyl-1,5-dithiole units was brought

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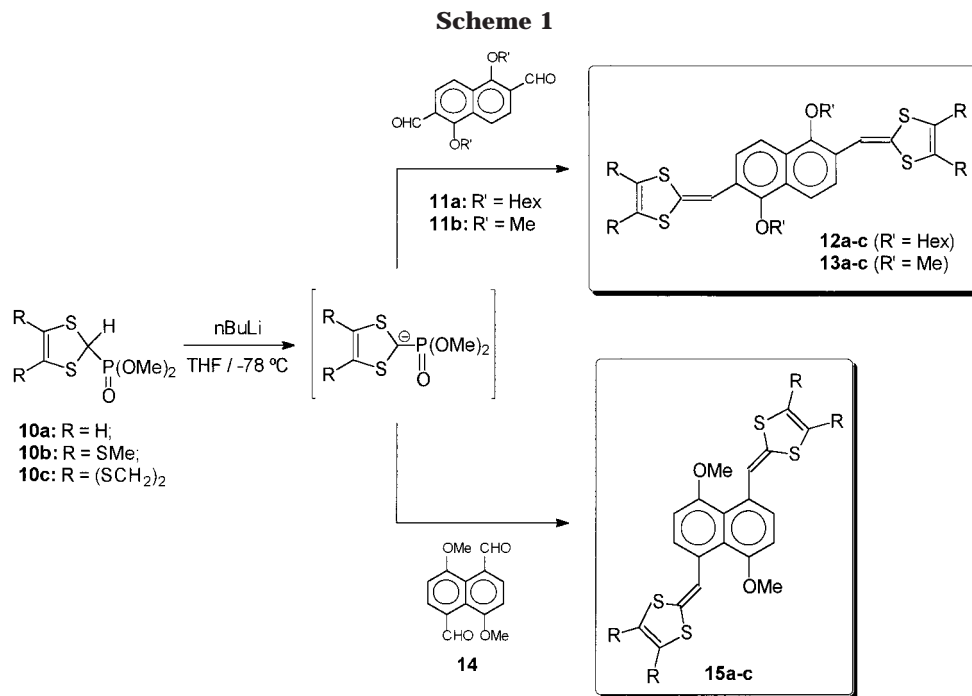
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to our attention.¹⁹ The analogous compounds were prepared using potassium *tert*-butoxide in considerably lower yields (36–62%).

The analytical and spectroscopic data (UV–vis, IR, ¹H NMR, ¹³C NMR, MS) of the compounds prepared clearly support the proposed structures. The novel π -extended donors (**13a–c** and **15a–c**) show low solubility in common organic solvents and especially those compounds bearing the ethylenedithio groups on the 1,3-dithiole rings (**13c** and **15c**) for which the ¹³C NMR spectra could not be recorded. In contrast, compounds **12a–c** endowed with long alkyl chains on the naphthalene unit present a remarkable solubility in most organic solvents.

Electrochemistry. The redox properties of the novel π -extended donors were determined by cyclic voltammetry (CV) measurements carried out in CH₂Cl₂ at room temperature using a glassy carbon as working electrode, Bu₄N⁺ClO₄[−] as supporting electrolyte, and SCE as reference electrode.

It is important to note that the observed electrochemical behavior is quite similar for these compounds, independent of the position of the substituents on the

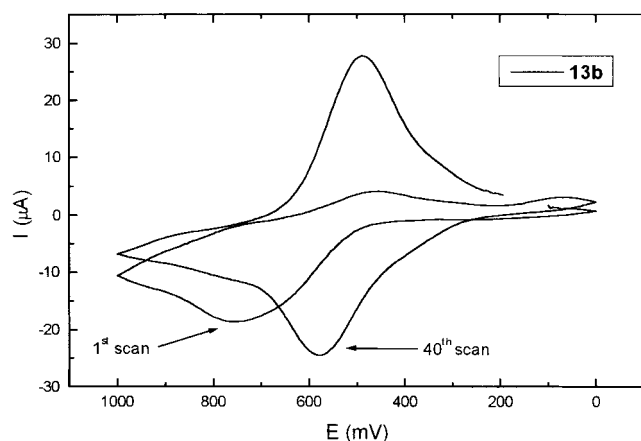


Figure 1. Cyclic voltammogram of compound **13b** at different scan numbers (scan rate 200mV/s).

naphthalene framework. Thus, on the first scan, compounds **12**, **13**, and **15** show an irreversible oxidation peak. Upon successive scans the intensity of this anodic peak decreases and a new reversible redox system appears at remarkably lower oxidation potential values (Figure 1).

Compounds **15a–c** with a different substitution pattern on the naphthalene moiety than in **12** and **13** also exhibit a first irreversible oxidation peak on the first scan. However, a larger number of scans are needed (~30–40 scans) for the observation of the reversible peak which also appears at lower oxidation potential values.

The above electrochemical behavior indicates an ECE process as it has been previously reported for other related dithiafulvene derivatives (Scheme 2).⁹ Thus, formation of a radical cation in the first electrochemical oxidation process (E) is followed by a further homolytic coupling chemical reaction (C) to form the neutral dimeric or oligomeric species derived from TTF which undergoes a subsequent reversible electrochemical process (E) at lower oxidation potential values. The mechanism of dimerization of 1,4-dithiafulvenes into TTF vinylogues has been recently well-established by Hapiot et al.²⁰ and skilfully used by Lorcy²¹ for the preparation of interesting π -redox cyclophanes endowed with TTF derivatives and also by Roncali for the electrogeneration of TTF-derivatized polymers.²² A first observation of formation by electrooxidation of dimeric species from furan-containing dithiafulvene derivatives, which were characterized by UV–vis/NIR spectrochemistry as well as by an alternative synthesis of the dimer, was previously reported by Daub.²³

Interestingly, compounds **12a–c** show, on the first scans, the presence of a broad irreversible oxidation wave which, after 100 scans still persists, with the reversible

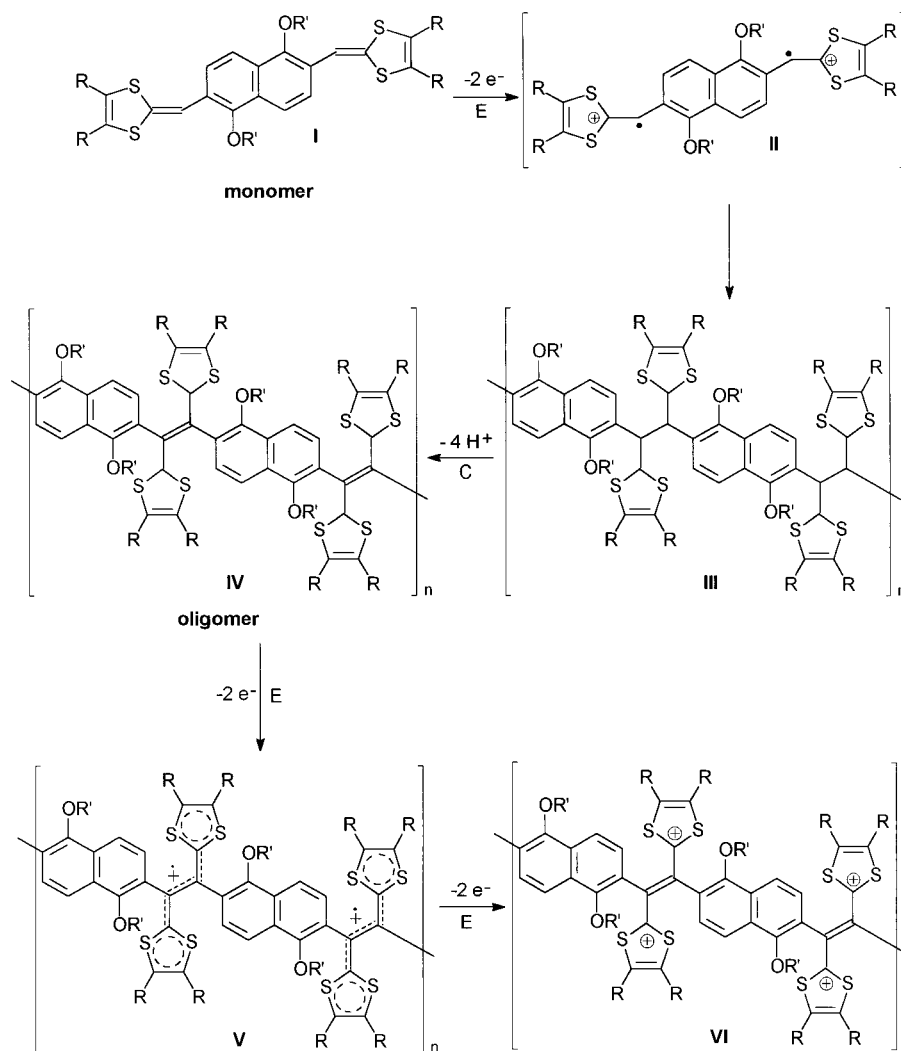
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Scheme 2



oxidation wave appearing at lower values, corresponding to the formation of the oligomer. The presence in the voltammogram of the first oxidation wave to form the radical cation after a high number of scans could be explained by the higher solubility of compounds **12a–c** due to the presence of the two hexyloxy groups, thus preventing the deposition of the dimeric or oligomeric species on the electrode surface.²⁴

The above electrochemical coupling processes are related, according to theoretical calculations carried out on π -donor molecules bearing the 1,3,5-substituted benzene moiety, to a high electronic density at the linking site.²⁵ Consequently, molecules exhibiting a *meta* linkage connecting both 1,4-dithiafulvenyl groups are good candidates to present a high density of unpaired electrons at the vinyl carbon in the cation radical.²² In this regard, the molecules presented in this work bearing a naphthalene unit as a spacer connecting the two dithiafulvenyl moieties are very attractive due to the possibilities for different substitution patterns on the naphthalene skeleton (**12**, **13**, and **15**) and to the presence of solubilizing chains which allow for improved solubility. In addition,

the distortion of the planarity (see below) favors a high electron density at the vinyl linkage. Distorted π -donors derived from dithiafulvene derivatives have previously been reported by Yamashita as useful compounds for the electrogeneration of polymers.²⁶

In an attempt to characterize the intermediate radical-cation species involved in the electrochemical dimerization of dithiafulvene derivatives **12**, **13**, and **15** into the corresponding TTF vinylogues, we have monitored the electrochemical oxidation of compounds **13a**, **13b**, and **15a** by EPR spectroscopy. From the beginning of the spectroelectrochemical experiment a signal, which increases with the electrolysis time, appears in all cases. Nevertheless, these signals cannot be attributed in any case to the intermediate radical-cation species formed by the first oxidation process. This result indicates that the further homolytic coupling of the radical-cation species II (Scheme 2) is too fast to be detected by EPR in the experimental conditions used. Figure 2 shows the spectrum obtained from oxidation of compound **13a**. From the *g* values and the proton and ³³S coupling constants (Table 1), the signals can be ascribed to the radical-cation V (Scheme 2), derived from the condensed species IV. Indeed, all *g* values and H and ³³S coupling constants are very similar to those found for other vinylogous

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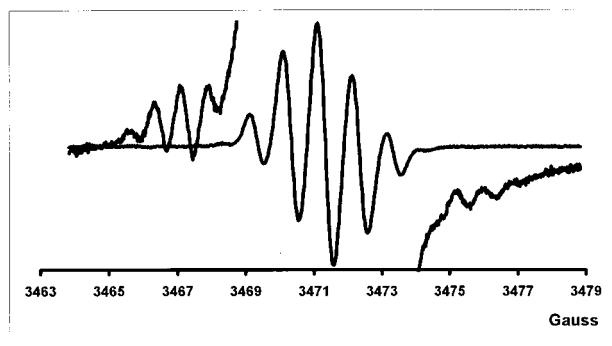


Figure 2. EPR spectrum of the cation-radical derived from electrochemical products following the oxidation of **13a** in dichloromethane with tetrabutylammonium hexafluorophosphate as electrolyte. The ^{33}S satellite lines are observed in the amplified spectrum.

Table 1. Proton and ^{33}S Coupling Constants, a_{H} and a_{S} (mT), and g Factors for the Radical-Cations Derived from Electrogenerated Products from **13** and **15**

compd	a_{H}	a_{S}	g
13a	0.101 (4H)	0.362	2.0079
13b	<i>a</i>	0.236	2.0074
15a	0.096 (4H)	<i>a</i>	2.0074

^a Not observed.

tetratiafulvalene derivatives.²⁷ Oxidation products derived from **12a** and **15a** show five lines due to the coupling of the unpaired electron with four equivalent protons of the TTF core²⁸ whereas coupling with the naphthyl protons, if it exists, is too small to be observed. This fact can be explained by the expected high deviation from coplanarity of the naphthyl rings with respect to the TTF core due to steric hindrance.

The above spectroelectrochemical experiments are a direct evidence of the formation of dimeric species from the dithiafulvene derivatives **12**, **13**, and **15**, supporting therefore the ECE process previously reported for other dithiafulvene derivatives.⁹

Structural Study. The structural properties of the novel π -extended TTF derivatives (**12**, **13**, and **15**) play a very active role in the electrochemical behavior of these compounds since a high electronic density at the ethylene linkage could be closely related with a highly distorted molecule out of the planarity.²⁶ We have determined the structure of compound **12a** by X-ray crystallographic analysis (Figure 3). Theoretical calculations at the semiempirical PM3 method of compounds **13a** and **15a** have also been carried out and the data compared with those obtained experimentally in order to have a reliable computational method.

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(28) In the previously studied unsubstituted vinylogous TTF's, two different sets of two equivalent protons of the TTF core were found in EPR and the same trend was observed for more extended TTF vinylogues.²⁷ The bulkiness of the naphthyl substituents in **12a** and **15a** seems to promote a coplanarity of the two 1,4-dithiafulvenyl groups in the vinylogous TTF core of compound **V** responsible for the equivalence of the four protons found in EPR. The same behavior was previously found when two bulky substituents were introduced in the central bonds of extended vinylogous TTF's, since the four protons of the two dithiafulvenyl moieties became equivalent in the EPR spectrum. The same happens for a similar derivative in which the planarity of both dithiafulvenyl moieties have been forced by covalent bonds.^{27a}

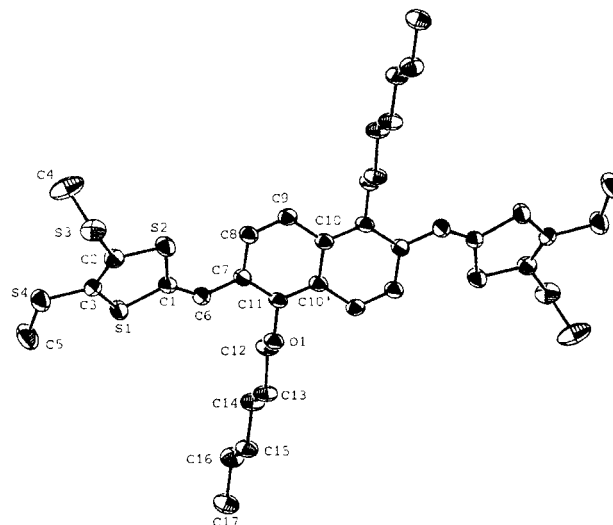


Figure 3. ORTEP³¹ X-ray structure of compound **12a** showing the numbering scheme.

The X-ray structure of compound **12a** shows that the molecule has a center of symmetry which coincides with a crystallographic center. All bond distances and angles are in the range of values found for other related TTF derivatives. Thus, the bond distances C1–C6 [1.345(5) Å] and C6–C7 [1.458(3) Å] are typical for double and single bond values, respectively. The naphthalene moiety forms an angle of 35.33(6)° with the thiafulvene, and therefore, this compound is clearly distorted from planarity. The torsion angles around C6 are 177.5(2)° (S1–C1–C6–C7) and 28.9(5)° (C1–C6–C7–C8), and the hexyl chain is located perpendicular to the naphthalene plane [torsion angle: 91.5(3)°]. The bond distances and angles of the sulfur atoms attached to the methyl groups are larger than those of the sulfurs of the ring. The remaining bond distances and angles are, as expected, within the experimental error for this type of compounds (see Supporting Information).

In the crystal packing the relatively short distance [3.453(4) Å] between the centroid of one of the phenyl rings of the naphthalene moiety and the methyl group (C4) linked to the 1,3-dithiole unit is remarkable, through the symmetry operation $-x, 1 - y, 1 - z$. Considering this interaction, it gives rise to a zigzag packing along the *cb* plane (see Figure 4).

Predicted values compare, in general, quite well with the experimental data for both bond distances and valence angles. The optimized geometry of **13a** bearing methoxy groups on the naphthalene unit is shown in Figure 5. The good agreement between the torsion angles around C6 predicted by theory and found by X-ray analysis is remarkable. Thus, S1–C1–C6–C7 presents a value of 178.6° which is quite similar to that found experimentally [177.5(5)°], and the torsion angle calculated for C8–C7–C1–S2 was found to be 48.8° which shows the angle formed between the naphthalene and thiafulvalene moieties. This value (48.8°) is larger than that found experimentally [35.33(6)°] and can be accounted for by the packing forces which tend to planarize the molecules in order to achieve the most compact crystal packing along the molecular stacks. These findings validate the utility of the PM3 methods for predicting geometrical features on this type of compound.

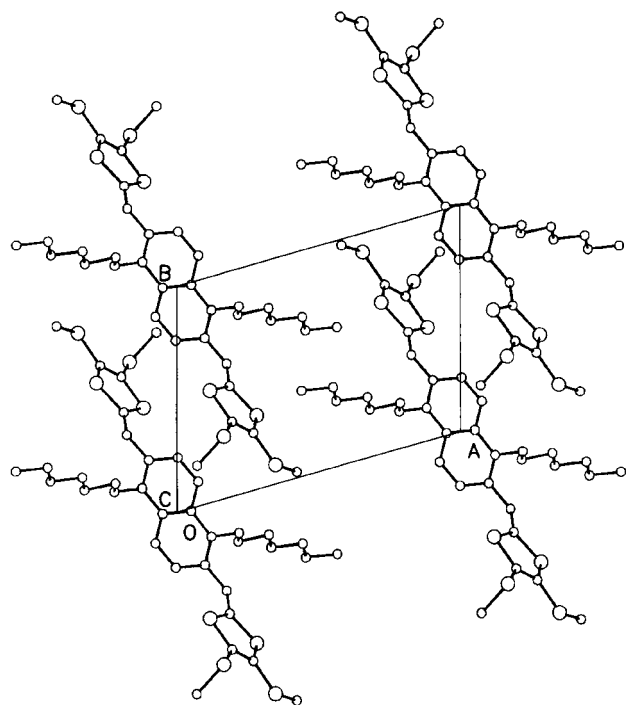


Figure 4. Crystal packing of compound **12a** viewed down the *c* axis.

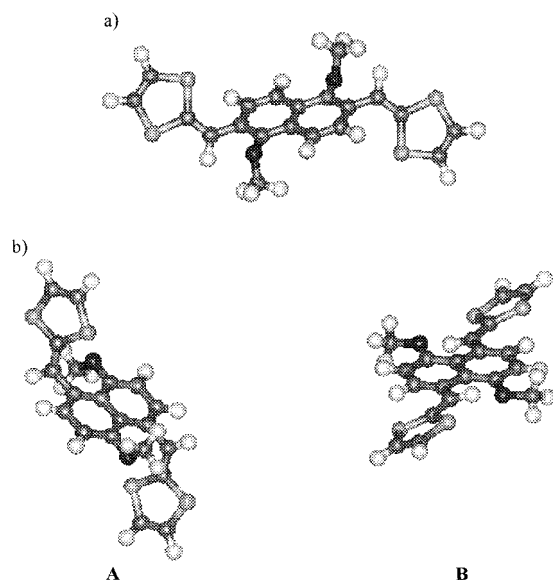


Figure 5. (a) PM3-optimized geometry of compound **13a**. (b) PM3-optimized geometries of compound **15a**.

Attempts to obtain a single crystal for the X-ray analysis of compounds **15a–c** were unsuccessful. Therefore, we have carried out theoretical calculations (PM3) on compound **15a** in order to obtain information about its geometrical features. It is important to note that two different geometries (A and B) (Figure 5) were found for **15a**. Conformer A was found to be 5.6 kcal/mol more stable than B despite the more planar geometry of conformation B. This fact could be explained by the releasing of steric hindrance in A due to the almost orthogonal position of the thiafulvalene units related to the naphthalene framework, thus avoiding the strong steric interaction between the vinylic hydrogen and the *peri* methoxy groups on the naphthalene unit.

Chart 2

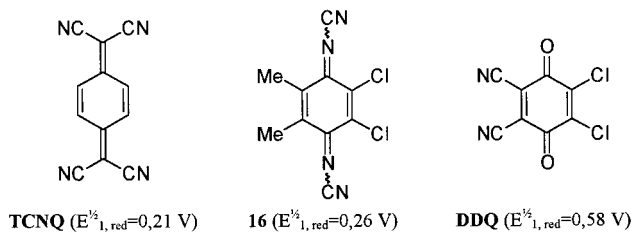


Table 2. Spectroscopic Data of CT Complexes Prepared by Chemical Oxidation of Donors **13a,b and **15a,b** with Different Acceptors**

donor	acceptor	ν_{CN}^a (cm^{-1})	λ_{max}^b (nm)
13b	TCNQ	2226, 2218	748, 560, 478
15a	TCNQ	2220, 2195	750, 560, 476
13a	DDQ	2231	642, 604, 486
13b	DDQ	2232	646, 584
15a	DDQ	2231, 2222	680, 598, 540
15b	DDQ	2231	718, 564, 458
13a	16	2145	702, 610, 512
13b	16	2145	714, 586, 500
15a	16	2145	696, 598, 520
15b	16	2149	686, 608, 550

^aDetermined by FTIR in KBr pellets. ^bIn CH_2Cl_2 .

Compound **15a** presents bond distances and angles very similar to those found by X-ray analysis for **12a**. Interestingly, the dihedral angle C11–C7–C1–S2 is 116.1° , that is, the 1,3-dithiole units are scarcely conjugated with the naphthalene unit. These findings clearly support the CV data since the geometrical features favor a high electronic density at the vinyl linkage of the radical cation, thus favoring a further polymerization process.

Charge Transfer Complexes. The novel π -extended donors (**12**, **13**, and **15**) were found to form CT complexes with different electron acceptor molecules such as tetracyano-*p*-quinodimethane (TCNQ) (0.21 V), the acceptor prepared in our laboratory, 2,3-dichloro-5,6-dimethyldicyano-*p*-quinonediimine (**16**)²⁹ (0.26 V), and the stronger acceptor 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (0.58 V) (Chart 2).

The chemical oxidation of donors (**12**, **13**, and **15**) should lead to the formation of the respective transient radical cation species which, subsequently, give rise to the formation of the oligomer by a chemical coupling reaction. The stronger donor molecules formed in situ readily form CT complexes in the presence of the strong electron acceptors. Although complexes thus formed were spectroscopically characterized by IR and UV–vis techniques (Table 2), their stoichiometries could not be accurately established from the elemental analysis determinations, probably due to the formation of oligomeric species. The room-temperature conductivities of the formed complexes were measured on compressed pellets by a standard two-probe technique. All CT complexes showed electrical conductivity values lower than $\sigma_{rt} < 10^{-6} \text{ S cm}^{-1}$.

In fact, the EPR spectra of CT complexes obtained from **13a** and **13b** with DDQ and TCNQ in anhydrous dichloromethane with exclusion of oxygen clearly showed that the complexes contain the vinylogous TTF species as a cation-radical. In all cases two signals with different *g*

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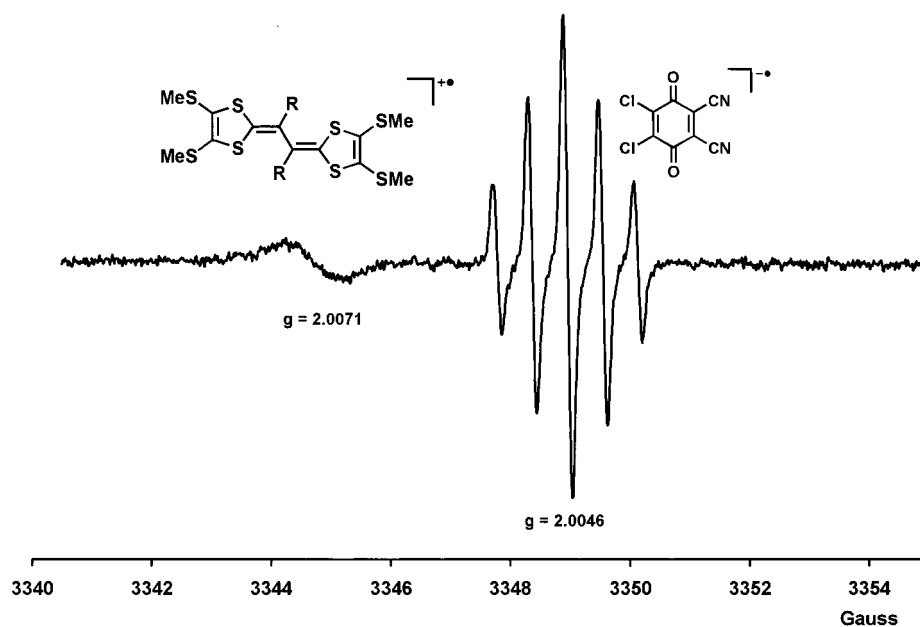


Figure 6. EPR spectrum of the complex formed upon reaction of compound **13b** with DDQ in dichloromethane solution as described in the caption for Figure 2.

values are observed in the EPR spectra. The signals with the highest g values are, in the four complexes studied, identical to those obtained by electrochemical oxidation of compounds **13a** and **13b** that have been assigned to the TTF derived species V (Scheme 2). At lower g values the characteristic structured signals of the radical anions derived from the acceptor (DDQ or TCNQ) appear.³⁰ In Figure 6 the EPR spectrum of the CT complex formed by reaction of **13b** with DDQ is shown.

Summary and Conclusions

The synthesis of novel π -extended donors derived from TTF in which the 1,3-dithiole rings are separated by a naphthalene spacer has been carried out by Wittig–Horner reaction of dialkoxy-substituted diformylnaphthalenes (**11a,b**, **14**) and substituted phosphonate esters (**10a–c**). The naphthalene core has allowed the preparation of several new donors with the same substitution pattern on different positions and the determination of the effect that the different connectivity of the two 1,3-dithiole rings plays on the electron donor properties. The cyclic voltammetry studies reveal that donors **15a–c** undergo a slower electrooxidation process than compounds **12** and **13** which have the same substitution

scheme. All new donors show an irreversible oxidation peak on the first scan which decreases upon successive scans, with formation of a new reversible wave at lower oxidation potential values, which is attributed to the generation of dimeric or oligomeric TTF vinylogues. This electrochemical behavior suggests an ECE mechanism which is in agreement with the experiments performed within the EPR cavity. Attempts to characterize the intermediate radical-cation species involved in the electrochemical dimerization of donors **12**, **13**, and **15** by EPR spectroscopy were unsuccessful due to their fast dimerization process. Nevertheless, the obtained EPR data clearly confirm the presence of the radical-cation derived from the condensed species.

The structural properties of these new donors were determined by X-ray diffraction of compound **12a** as well as theoretical calculations at the semiempirical (PM3) level. The predicted values compare quite well with those determined experimentally and reveal a distorted geometry with the naphthalene core and the thiafulvalene ring forming an angle of 35.33(6)°. This finding supports the dimerization process since a distorted structure favors a high electronic density at the ethylene linkage.

Reactions of donors **13a,b**, and **15a–c** with strong electron acceptor molecules such as **16**, DDQ, or TCNQ resulted in the chemical oxidation of the donors and a subsequent oligomerization process to afford solid CT complexes containing the vinylogue TTF species as the cation radical.

Experimental Section

Cyclic voltammograms were recorded on a potentiostat/galvanostat Versastat EG & G PAR, equipped with a software of electrochemical analysis model 250, by using a GCE (glassy carbon) as working electrode, SCE as reference electrode, $\text{Bu}_4\text{N}^+\text{ClO}_4^-$ (0.1 M), CH_2Cl_2 as solvent, and at scan rate of 200 mV/s.

EPR spectra were recorded on a Bruker ESP 300E X-band spectrophotometer, equipped with temperature controller ER 412HT and a field frequency (F/F) lock accessory and a built-in NMR gaussmeter. The spectroelectrochemical experiments

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were performed by in situ electrochemical oxidation, monitored by an EG & G PAR 263A potentiostat/galvanostat, on an EPR cell equipped with Pt wires as working and counter electrodes and using the Ag/AgCl system as a reference electrode. Experimental conditions were +0.8 V, CH₂Cl₂ 0.2 M in Bu₄-NPF₆.

X-ray data were recorded on a Philips PW 1100 diffractometer and averaged to give 2916 unique observed reflections [$I > 2\sigma(I)$] which were used to solve the structure by direct methods and to refine it to $R = 0.055$ ($wR = 0.070$) by full-matrix least-squares analysis (all non-hydrogen atoms anisotropic). Hydrogen atoms were located in a difference Fourier map and refined isotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Wittig–Horner Reactions. General Procedure. To a solution of phosphonate esters (**10b,c**) (2 mmol) in dry THF (20 mL) at -78°C and under an argon atmosphere was added *n*-BuLi (1.6 M) (2.2 mmol) with a syringe. After 30 min at -78°C , a solution of the corresponding aldehyde (0.5 mmol) in dry THF (20 mL) was added with a syringe into the solution of the phosphonate carbanion. The mixture was stirred for 1 h at -78°C and then allowed to warm to 20°C and stand overnight. The THF was evaporated under reduced pressure, water (75 mL) was added, and the residue was extracted with CH₂Cl₂ (3 × 75 mL). The combined extracts were dried (MgSO₄) and filtered out, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane:dichloromethane mixtures as eluent.

1,5-Dihexyloxy-2,6-bis(1,3-dithiol-2-ylidenemethyl)naphthalene (12a) (Table 3): 90% yield; mp $103\text{--}105^\circ\text{C}$ (dec); ¹H NMR (CDCl₃, 300 MHz) δ 7.87 (2H, d, $J = 8.55$ Hz), 7.65 (2H, d, $J = 8.79$ Hz), 6.91 (2H, d, $J = 1.47$ Hz), 6.36 (2H, d, $J = 6.83$ Hz), 6.27 (2H, dd, $J_1 = 6.83$, $J_2 = 1.47$ Hz), 3.90 (4H, t, $J = 6.25$ Hz), 2.2–0.7 (22H, m); ¹³C NMR (CDCl₃, 62 MHz) δ 151.2, 137.2, 128.1, 125.8, 123.9, 118.1, 117.6, 108.1, 77.6, 31.8, 30.5, 29.8, 26.0, 22.8, 14.2; IR (KBr) 1590, 1560, 1530, 1245, 1235 cm⁻¹; UV–vis (CH₂Cl₂) λ_{max} (log ϵ) 424 (7.46), 406 (7.45), 316 (7.34), 246 (7.23) nm; MS m/z , 556 (M⁺). Anal. Calcd for C₃₀H₃₆O₂S₄: C, 64.73; H, 6.52. Found: C, 64.45; H, 6.52. CV: $E_{\text{a.p.}}^1$ 0.59 V.

1,5-Dihexyloxy-2,6-bis(4,5-dimethylthio-1,3-dithiol-2-ylidenemethyl)naphthalene (12b): 91% yield; mp $105\text{--}107^\circ\text{C}$ (dec); ¹H NMR (CDCl₃, 300 MHz) δ 7.86 (2H, d, $J = 8.7$ Hz), 7.53 (2H, d, $J = 8.7$ Hz), 6.83 (2H, s), 3.91 (4H, t, $J = 6.90$ Hz), 2.47 (6H, s), 2.43 (6H, s), 2.0–0.8 (22H, m); ¹³C NMR (CDCl₃, 62 MHz) δ 151.6, 132.9, 128.4, 125.4, 124.6, 124.4, 118.3, 110.3, 75.3, 31.8, 30.4, 29.8, 26.0, 22.8, 19.1, 18.9, 14.2; IR (KBr) 1590, 1555, 1245, 1235 cm⁻¹; UV–vis (CH₂Cl₂) λ_{max} (log ϵ) 430 (7.60), 414 (7.58), 318 (7.47), 260 (7.38), 232 (7.33) nm; MS m/z , 740 (M⁺). Anal. Calcd for C₃₄H₄₄O₂S₈: C, 55.13; H, 5.94. Found: C, 55.26; H, 6.02. CV: $E_{\text{a.p.}}^1$ 0.74 V.

1,5-Dihexyloxy-2,6-bis(1,3-dithiol-4,5-ethylenedithio-2-ylidenemethyl)naphthalene (12c): 65% yield; mp $143\text{--}145^\circ\text{C}$ (dec); ¹H NMR (CDCl₃, 300 MHz) δ 7.84 (2H, d, $J = 8.7$ Hz), 7.50 (2H, d, $J = 8.7$ Hz), 6.87 (2H, s), 3.90 (4H, t, $J = 6.6$ Hz), 3.34 (8H, s), 2.0–0.5 (22H, m); ¹³C NMR (CDCl₃, 62 MHz) δ 151.8, 131.2, 128.4, 125.4, 124.6, 118.3, 110.7, 75.4, 31.8, 30.4, 29.9, 29.8, 26.0, 22.8, 14.2; IR (KBr) 1590, 1560, 1235 cm⁻¹; UV–vis (CH₂Cl₂) λ_{max} (log ϵ) 438 (7.60), 424 (7.59), 324 (7.47), 266 (7.39), 238 (7.34) nm; MS m/z , 736 (M⁺) Anal. Calcd for C₃₄H₄₀O₂S₈: C, 55.43; H, 5.43. Found: C, 55.70; H, 5.50. CV: $E_{\text{a.p.}}^1$ 0.76 V.

1,5-Dimethoxy-2,6-bis(1,3-dithiol-2-ylidenemethyl)naphthalene (13a): 91% yield; mp $221\text{--}223^\circ\text{C}$ (dec); ¹H NMR (CDCl₃, 300 MHz) δ 7.88 (2H, d, $J = 8.7$ Hz), 7.69 (2H, d, $J = 8.7$ Hz), 6.92 (2H, d, $J = 1.5$ Hz), 6.37 (2H, d, $J = 6.6$ Hz), 6.29 (2H, dd, $J_1 = 6.6$ Hz, $J_2 = 1.5$ Hz), 3.89 (6H, s); ¹³C NMR (CDCl₃, 62 MHz) δ 151.7, 137.6, 127.6, 125.5, 123.9, 118.0, 117.4, 107.5, 62.0; IR (KBr) 1590, 1560, 1530, 1245, 1230 cm⁻¹; UV–vis (CH₂Cl₂) λ_{max} (log ϵ) 424 (4.87), 406 (4.90), 316 (4.51), 244 (4.84) nm; MS m/z , 416 (M⁺). Anal. Calcd for C₂₀H₁₆O₂S₄: C, 57.69; H, 3.88. Found: C, 57.69; H, 3.99. CV: $E_{\text{a.p.}}^1$ 0.59 V.

Table 3. Crystal Data, Data Collection, and Structure Refinement of 12a

Crystal Data	
formula	C ₃₄ S ₈ O ₂ H ₄₄
M_r	741.200
crystal size (mm)	0.33 × 0.24 × 0.21
symmetry	triclinic, $P-1$
unit cell determ	least-squares fit from 73 reflcns ($7 < \theta < 85^\circ$)
unit cell dimns	13.472 (2), 9.903 (1), 7.386 (1) Å
$\alpha = 99.12(1)$, $\beta = 104.34(1)$, $\gamma = 72.56(1)^\circ$	
packing: V (Å ³), Z	907.0 (2), 2
D_c (g cm ⁻³), $F(000)$	1.3570, 392.0
μ (cm ⁻¹)	47.908
T	294 K
Experimental Data	
technique	four-circle diffractometer:
Philips PW1100 bisecting geometry graphite oriented monochromator:	
Cu K α 1.5418 Å $\omega/2\theta$ scan	
scanning range for θ	$2 < \theta < 65^\circ$
no. of reflcns:	
measd	3085
obsd	2916 ($I > 2\sigma(I)$ criterion)
range of hkl	$-15/15\text{--}12/12\ 0/9$
absortion correction	none
two standard reflcns frequency: 90 min	
Solution and Refinement	
solution	direct methods
refinement	L.s. on F_{obs}
parameters	419
weighting scheme ($w\Delta^2 F$) vs ($ F_o $) and ($\sin \theta/\lambda$)	empirical as to give no trends in
final R and R_w	0.055, 0.070
S	0.9733
$(\Delta/\sigma)_{\text{max}}$	0.026
ρ_{max}	0.58 e Å ³
computer and programs	Vax 6410, SIR92, ³² XRAY80, ³³ PESOS, ³⁴ PARST ³⁵
scattering factors	<i>Intl Tables for X-ray Crystallog.</i> ³⁶
anomalous dispersion	<i>Intl Tables for X-ray Crystallog.</i> ³⁶

1,5-Dimethoxy-2,6-bis(4,5-dimethylthio-1,3-dithiol-2-ylidenemethyl)naphthalene (13b): 94% yield; mp $210\text{--}212^\circ\text{C}$ (dec); ¹H NMR (CDCl₃, 300 MHz) δ 7.89 (2H, d, $J = 9$ Hz), 7.55 (2H, d, $J = 9$ Hz), 6.84 (2H, s), 3.88 (6H, s), 2.47 (6H, s), 2.43 (6H, s); ¹³C NMR (CDCl₃, 75 MHz) δ 152.1, 133.4, 127.9, 125.1, 124.7, 124.6, 118.2, 109.7, 62.1, 18.9, 18.8; IR (KBr) 1590, 1555, 1250, 1230 cm⁻¹; UV–vis (CH₂Cl₂) λ_{max} (log ϵ) 430 (5.11), 262 (5.13), 234 (5.03) nm; MS m/z , 600 (30%). Anal. Calcd for C₂₄H₂₄O₂S₈: C, 48.00; H, 4.03. Found: C, 48.23; H, 4.07. CV: $E_{\text{a.p.}}^1$ 0.76 V.

1,5-Dimethoxy-2,6-bis(4,5-ethylenedithio-1,3-dithiol-2-ylidenemethyl)naphthalene (13c): 65% yield; mp 370°C (dec); ¹H NMR (CDCl₃, 300 MHz) δ 7.87 (2H, d, $J = 9$ Hz), 7.53 (2H, d, $J = 9$ Hz), 6.88 (2H, s), 3.87 (6H, s), 3.34 (8H, s); IR (KBr) 1595, 1560, 1530, 1245, 1235 cm⁻¹; UV–vis (CH₂Cl₂) λ_{max} (log ϵ) 438 (3.05), 266 (3.10), 236 (3.04) nm; MS m/z , 596 (25%). Anal. Calcd for C₂₄H₂₀O₂S₈: C, 48.33; H, 3.38. Found: C, 48.42; H, 3.69. CV: $E_{\text{a.p.}}^1$ 0.74 V.

4,8-Dimethoxy-1,5-bis(1,3-dithiol-2-ylidenemethyl)naphthalene (15a): 71% yield; mp $249\text{--}251^\circ\text{C}$ (dec); ¹H NMR (CDCl₃, 300 MHz) δ 7.43 (2H, d, $J = 8.2$ Hz), 7.25 (2H, d, $J = 1.5$ Hz), 6.83 (2H, d, $J = 8.2$ Hz), 6.22 (2H, d, $J = 6.6$ Hz), 6.05 (2H, dd, $J_1 = 6.6$ Hz, $J_2 = 1.5$ Hz), 3.91 (6H, s); ¹³C NMR (CDCl₃, 75 MHz) δ 139.1, 137.2, 131.0, 128.6, 126.0, 125.0, 124.6, 118.9, 116.8, 116.1, 113.9, 106.5, 53.3; IR (KBr) 1595, 1580, 1520, 1270, 1220 cm⁻¹; UV–vis (CH₂Cl₂) λ_{max} (log ϵ) 388 (2.92), 272 (2.87), 240 (3.25) nm; MS m/z , 416 (M⁺). Anal. Calcd

for $C_{20}H_{16}O_2S_4$: C, 57.69; H, 3.88. Found: C, 57.73; H, 3.95. CV: $E_{a.p.}^1$ 0.53 V.

4,8-Dimethoxy-1,5-bis(4,5-dimethylthio-1,3-dithiol-2-ylidenemethyl)naphthalene (15b): 91% yield; mp 202–203 °C (dec); 1H NMR ($CDCl_3$, 300 MHz) δ 7.32 (2H, d, $J = 8.1$ Hz), 7.26 (2H, s), 6.83 (2H, d, $J = 8.1$ Hz), 3.93 (6H, s), 2.44 (6H, s), 2.32 (6H, s); ^{13}C NMR ($CDCl_3$, 62 MHz) δ 156.7, 137.2, 126.9, 126.7, 126.5, 125.3, 125.1, 123.7, 121.0, 106.4, 56.0, 18.7, 18.6, 18.4; IR (KBr) 1590, 1570, 1515, 1265, 1220 cm^{-1} ; UV-vis (CH_2Cl_2) λ_{max} (log ϵ) 390 (3.12), 240 (3.45) nm; MS m/z , 600 (M^+). Anal. Calcd for $C_{24}H_{24}O_2S_8$: C, 48.00; H, 4.03. Found: C, 47.63; H, 4.49. CV: $E_{a.p.}^1$ 0.65 V.

4,8-Dimethoxy-1,5-bis(1,3-dithiol-4,5-ethylenedithio-2-ylidenemethyl)naphthalene (15c): 78% yield; mp >400 °C; 1H NMR ($CDCl_3$, 300 MHz) δ 7.31 (2H, d, $J = 8.0$), 7.27 (2H, s), 6.90 (2H, d, $J = 8.0$), 3.91 (6H, s), 3.29 (8H, s); IR (KBr) 1595, 1570, 1520, 1280, 1230 cm^{-1} ; UV-vis (CH_2Cl_2) λ_{max} (log ϵ) 398 (3.21), 352 (3.08), 240 (3.45) nm; MS m/z , 596 (32%). Anal. Calcd for $C_{34}H_{40}O_2S_8$: C, 48.33; H, 3.38. Found: C, 47.74; H, 3.70. CV: $E_{a.p.}^1$ 0.66 V.

Synthesis of Charge Transfer Complexes. General Procedure. To a boiling solution of the corresponding donor (0.1 mmol) in dry CH_2Cl_2 (10 mL) under an argon atmosphere was added a solution of the corresponding acceptor [TCNQ, DDQ or 2,3-dichloro-5,6-dimethyl-*N,N*-dicyano-*p*-quinonediimine (**16**)] (0.4 mmol). The resultant dark-blue solution was refluxed for 30 min, and the mixture was slowly cooled to 0 °C. The solid precipitated was collected by filtration, washed with cold CH_2Cl_2 (3×5 mL), and dried in vacuo to give the corresponding complex.

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