

Highly Conjugated π -Electron Donor and π -Electron Acceptor Dimers with p -Quinodimethane Structures

Nazario Martín,* Ignacio Pérez, Luis Sánchez, and Carlos Seoane*

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain

Received September 19, 1996[®]

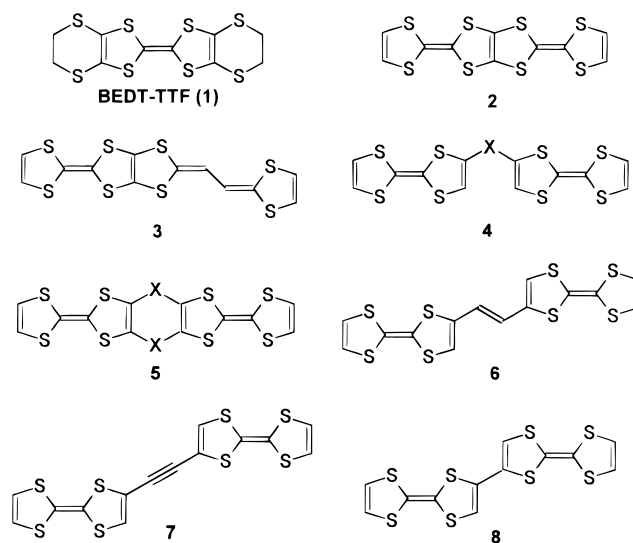
The syntheses of the first dimeric donors (**19a–c**) derived from TTF with p -quinodimethane structures as well as the analogues dimeric acceptors (**20**, **21**) derived from TCNQ and DCNQI have been carried out from the novel 2,2'-oxydianthraquinone (**18**). Depending upon the substitution pattern on the 1,3-dithiole ring of the donor molecules, eight (**19a**) or sixteen (**19b** and **19c**) sulfur atoms are contained in these dimers. The presence of the oxygen atom connecting both monomeric units has an influence on the redox properties of the novel dimers due to its electron-withdrawing effect. The CV data indicate that these dimers behave electrochemically as two independent monomers. This behavior defines rather unusual electrochemical properties in both donor (**19a–c**) and acceptor (**20**) molecules, which exhibit only one redox wave involving a four-electron overall process. In contrast, the dimeric DCNQI derivative (**21**) showed two-electron reduction waves to form, simultaneously in both monomeric units, the radical anions and dianions. The redox potential values show that although the dimeric acceptors **20** and **21** exhibit too negative potentials to form stable solid CT-complexes with donor molecules, the novel dimeric donors show a donating ability similar to that of BEDT-TTF. The dimeric donors (**19a–c**) did not form CT-complexes with TCNQ and DCNQI due to their distorted structures, but they form CT-complexes with stronger acceptor molecules such as TCNQF₄ and DDQ. These CT-complexes, which showed in all cases a 1:3 (donor: acceptor) stoichiometry, exhibit a paramagnetic and semiconducting electrical behavior.

Introduction

The search for new electron donor molecules for organic conductors and superconductors has recently been focused on the formation of two-dimensional electronic structures leading to the stabilization of the metallic state down to low temperatures.¹ In this regard, bis(ethylene-dithio)tetrathiafulvalene (BEDT-TTF) (**1**) has been widely used for the preparation of different organic superconductors² and, more recently, other molecular systems containing two or more fused (**2**, **3**)³ or covalently attached (**4–8**)⁴ tetrathiafulvalene (TTF) units (Chart 1) have attracted considerable interest as a consequence of their increasing dimensionality resulting in metallic cation radical salts or, in some cases, leading to the formation of superconducting salts.³

On the other hand, extended TTF derivatives bearing a p -quinodimethane structure (**9–12**) (Chart 2) have been

Chart 1. BEDT-TTF (**1**) Together with Some Representative Examples of Electron Donors Containing Two TTF Units (**2–8**)



used as strong electron donors due to the extended conjugation which results in a decrease of the intramolecular on-site Coulombic repulsion⁵ and the formation of nonstoichiometric complexes with acceptor molecules, on the basis of their different sizes.⁶ In contrast to TTF and its derivatives, the p -quinodimethane analogues of

[®] Abstract published in *Advance ACS Abstracts*, February 1, 1997.

(1) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Wangbo, M. H. *Organic Conductors (Including Fullerenes). Synthesis, Structure, Properties and Theory*; Pentrice Hall: New Jersey, 1992.

(2) For reviews see: (a) Yagubskii, E. B. *Mol. Cryst. Liq. Cryst.* **1993**, *230*, 139; Saito, G. *Phosphorus, Sulfur Silicon*. **1992**, *67*, 345. Williams, J. M.; Schulitz, A. J.; Geiser, U.; Carlson, K. D.; Kini, A. M.; Wang, H. H.; Kwo, W. K.; Whango, M. H.; Schirber, J. E. *Science* **1991**, *252*, 1501.

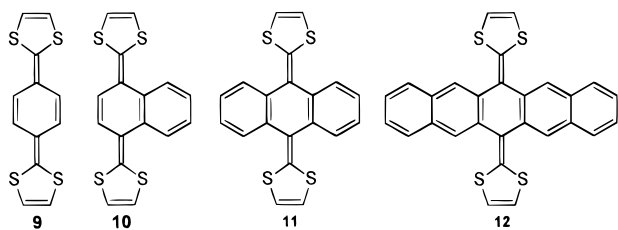
(3) (a) Misaki, Y.; Higuchi, N.; Fujiwara, H.; Yamabe, T.; Mori, T.; Mori, H.; Tanaka, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1222. (b) Misaki, Y.; Ohta, T.; Higuchi, N.; Fujiwara, H.; Yamabe, T.; Mori, T.; Mori, H.; Tanaka, S. *J. Mater. Chem.* **1995**, *5*, 570 and references cited therein.

(4) The synthesis of dimeric tetrathiafulvalenes as new electron donors has been recently reviewed: Otsubo, T.; Aso, Y.; Takimiya, K. *Adv. Mater. (Weinheim, Ger)* **1996**, *8*, 203. See also Adam, M.; Müllen, K. *Adv. Mater. (Weinheim, Ger)* **1993**, *6*, 439. Bryce, M. R. *J. Mater. Chem.* **1995**, *5*, 1481. For other more recent dimeric TTFs see: Leriche, P.; Giffard, M.; Riou, A.; Majani, J.-P.; Cousseau, J.; Jubault, M.; Gorgues, A.; Becher, J. *Tetrahedron Lett.* **1996**, *37*, 5115; Gerson, F.; Lamprecht, A.; Formigüé, M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1409.

(5) Yamashita, Y.; Kobayashi, Y.; Migashi, T. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1052. See also: Kitamura, Ch.; Tanaka, S.; Yamashita, Y. *Adv. Mater.* **1996**, *8*, 570 and references cited therein.

(6) Bryce, M. R.; Moore, A. J.; Hasan, M.; Ashwell, G. J.; Fraser, A. T.; Clegg, W.; Hursthouse, M. B.; Karaulov, A. I. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1450.

(7) (a) Bryce, M. R.; Moore, A. J. *Synth. Met.* **1988**, *25*, 203. (b) Bryce, M. R.; Coffin, M. A.; Hursthouse, M. B.; Karaulov, A. I.; Müllen, K.; Scheich, H. *Tetrahedron Lett.* **1991**, *32*, 6029. (c) Bryce, M. R.; Moore, A. J. *J. Chem. Soc., Perkin Trans 1* **1991**, 157.

Chart 2. Some π -Extended *p*-Quinodimethane Analogues of TTF

TTF form stable dication species which form CT-complexes with electrical and magnetic properties.^{6,7}

In spite of the interest of these π -extended *p*-quinodimethane analogues of TTF in the search for new optoelectronic properties, the synthesis of molecules containing two or more highly conjugated TTF units has not yet been carried out. We have recently reported the synthesis and redox properties of the highest known π -extended TTF analogues with only one quinoid structure (**12**) and the formation of CT-complexes with strong acceptor molecules.⁸ In this paper we describe the preparation of the first dimeric π -extended *p*-quinodimethane analogues of TTF (**19a–c**) in which both donor moieties are covalently attached by an oxygen atom. The presence of the oxygen as a spacer has an additional advantage in that it may participate in *inter*- and *intrastack* interactions, thus increasing the dimensionality in the donor system. The strong electron donor properties of these twin molecules (**19a–c**) have been measured by cyclic voltammetry in solution and can be accounted for by the aromatization that takes place upon oxidation of the quinoid structures.⁵

The synthetic approach followed for the preparation of the novel dimeric donors also allowed preparation of the first dimeric π -extended tetracyano-*p*-quinodimethane (TCNQ) and dicyano-*p*-quinondiimine (DCNQI) electron acceptors **20** and **21**. Although a wide variety of TCNQ and DCNQI derivatives have been reported in the last years, dimeric acceptors are almost unknown.⁹ Octacyanoanthradiquinotetramethane (**13**)¹⁰ and diquinotetraimide (**14**)¹¹ have been described as the only twin TCNQ-type and DCNQI-type known acceptors, respectively. In both compounds (**13**, **14**), the acceptor units are fused to a benzene ring in full conjugation. In this context, we have reported the synthesis of different electron acceptor molecules¹² and, more recently, the first sulfur-containing twin-DCNQI-type acceptor derived from thianthrene (**15**),¹³ which showed better acceptor ability than the parent DCNQI (Chart 3).

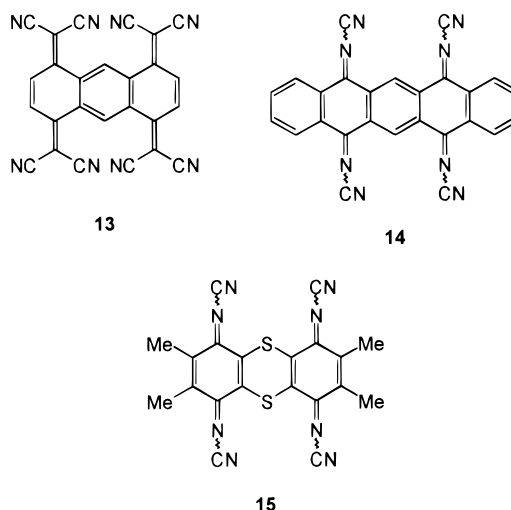
(8) Martín, N.; Sánchez, L.; Seoane, C.; Fernández, C. *Synth. Met.* **1996**, *78*, 137.

(9) Several twin type acceptors based on quinones are known, see: (a) Draber, W. *Chem. Ber.* **1967**, *100*, 1559. (b) Frank, W.; Gompfer, R. *Tetrahedron Lett.* **1987**, *28*, 3083. Watson, W. H.; Edouk, E. E.; Kashyap, R. P.; Krawieck, M. *Tetrahedron* **1993**, *49*, 3035. (c) Rak, S. F.; Jozefiak, T. H.; Miller, L. L. *J. Org. Chem.* **1990**, *55*, 4794.

(10) (a) Mitsuhashi, T.; Goto, M.; Honda, K.; Maruyama, Y.; Inabe, T.; Sugawara, T.; Watanabe, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 261. (b) Mitsuhashi, T.; Goto, M.; Honda, K.; Maruyama, Y.; Inabe, T.; Sugawara, T.; Watanabe, T. *J. Chem. Soc., Chem. Commun.* **1987**, 810.

(11) (a) Rak, S. F.; Liberko, C. A.; Miller, L. L. *Synth. Met.* **1991**, *42*, 2365. (b) Rak, S. F.; Liberko, C. A.; Miller, L. L. *J. Org. Chem.* **1992**, *57*, 1379.

(12) (a) De la Cruz, P.; Martín, N.; Miguel, F.; Seoane, C.; Albert, A.; Cano, F. H.; González, A.; Pingarrón, J. M. *J. Org. Chem.* **1992**, *57*, 6192. (b) Martín, N.; Segura, J. L.; Seoane, C.; De la Cruz, P.; Langa, F.; Ortí, E.; Viruela, P. M.; Viruela, R. *J. Org. Chem.* **1995**, *60*, 4077. (c) Martín, N.; Segura, J. L.; Seoane, C.; Ortí, E.; Viruela, P. M.; Viruela, R.; Albert, A.; Cano, F. H.; Vidal-Gancedo, J.; Rovira, C.; Veciana, J. *J. Org. Chem.* **1996**, *61*, 3041.

Chart 3. Twin TCNQ-Type (13**) and DCNQI-Type (**14**, **15**) Acceptors**

The presence of the oxygen bridge linking both acceptor moieties **20** and **21** should, in principle, lead to a different electrochemical behavior than that found for the twin-acceptors (**13–15**) previously reported. In this paper we describe the synthesis, spectroscopy, electrochemical characterization, and complexation studies of novel dimeric, highly conjugated, π -electron donors, and π -electron acceptors containing *p*-quinodimethane structures.

Results and Discussion

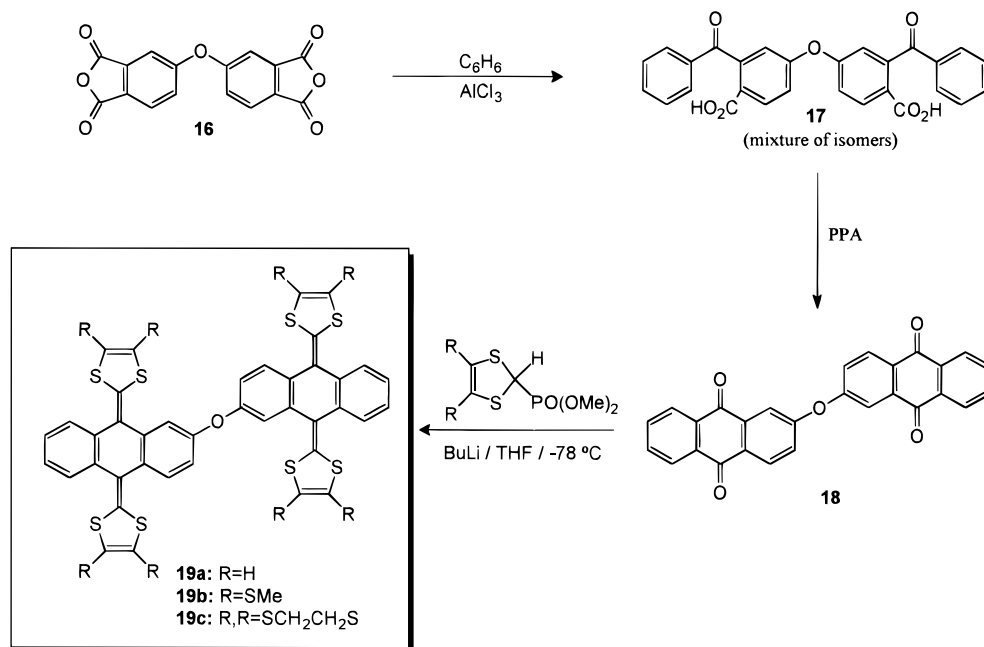
Synthesis. The preparation of the novel dimeric donors and acceptors was carried out from 2,2'-oxydianthraquinone (**18**) as shown the Scheme 1. Compound **18** could be easily obtained in a two-step procedure from the commercially available 4,4'-oxydiphthalic anhydride (**16**) by Friedel–Crafts reaction with benzene and aluminum trichloride as the catalyst. This reaction affords a mixture of three constitutional isomers of oxybis-(benzoylbenzoic acid)s (**17**) which were not separated, since all of them led, by subsequent cyclization with polyphosphoric acid as the dehydrating reagent, to the dianthraquinone (**18**) as the only product (Scheme 1). The structure of 2,2'-oxydianthraquinone (**18**) was supported on its analytical and spectroscopic data. Thus, the stretching vibration of the carbonyl group was observed as a strong band at 1680 cm^{-1} in the IR spectrum, and six signals were observed in the $^1\text{H-NMR}$ spectrum corresponding to the seven different protons of the monomer (see Experimental Section). The poor solubility of **18** in the most common organic solvents prevented us from recording the $^{13}\text{C-NMR}$ spectrum. However, the mass spectrum and the elemental analysis clearly confirm the proposed structure.

The synthesis of the dimeric donors (**19a–c**)¹⁴ was achieved from 2,2'-oxydianthraquinone (**18**) by Wittig–Horner reaction with the carbanion generated from the respective phosphonate ester in the presence of *n*-butyllithium. The different phosphonates used were in turn obtained in a multistep synthetic procedure by

(13) González, M.; De Miguel, P.; Martín, N.; Segura, J. L.; Seoane, C.; Ortí, E.; Viruela, P. M.; Viruela, R. *Adv. Mater. (Weinheim, Ger)* **1994**, *6*, 765.

(14) A part of the new dimeric donors was recently presented as a communication in the International Conference on Science and Technology of Synthetic Metals, ICSM'96, 28 July–2 August, 1996; Snowbird, Utah.

Scheme 1



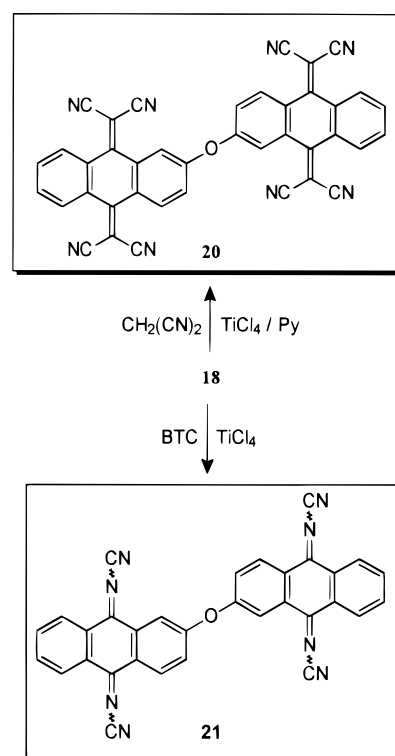
following the method previously reported in the literature.¹⁵ A 1:8 (oxydianthraquinone:phosphonate) stoichiometry was found to be the most appropriate for the preparation of compounds **19**, although a stoichiometric ratio of 1:10 was used for compound **19b**. In spite of the low solubility of compound **18**, this reaction proceeds gently to afford the *p*-quinodimethane analogues of TTF in moderate to good yields (45–56%). A further purification by careful flash chromatography is needed for the separation of byproducts containing one or more unreacted free carbonyl groups which were detected by TLC (Scheme 1).

The structure of the novel donors was established by their spectroscopic data. Particularly useful in these compounds was the absence of the carbonyl band in the IR spectrum to ascertain their analytical purity which was further confirmed by elemental analyses and positive FAB mass spectra.

Although attempts to obtain a single crystal for the X-ray analysis were unsuccessful, the structure of the monomeric units in compounds **19** is expected to be highly distorted out of the planarity as a consequence of the strong steric interaction of the *peri* hydrogens and the sulfur atoms of the 1,3-dithiolo subunits. These findings have been previously observed in the X-ray data of the monomer⁶ of compound **19a** and other related structures.¹⁶

The novel dimeric TCNQ acceptor derivatives were prepared in a one-step procedure from 2,2'-oxydianthraquinone (**18**) by following well-established procedures for simpler related molecules.¹⁷ Thus, the dimeric TCNQ derivative (**20**) was synthesized from **18** by reaction with

Scheme 2



Lehnert's reagent (malononitrile, titanium tetrachloride, and pyridine)¹⁸ in 45% yield (Scheme 2). From the different stoichiometric ratios tried, a 1:15 (compound **18**: malononitrile) ratio resulted to be the most appropriate leading to the reaction product in 24 h at room temperature. As observed in the preparation of the donor molecules (**19**), these multicondensation reactions take place with simultaneous formation of other byproducts containing unreacted carbonyl groups which can be easily detected by chromatography. The octacyano compound **20** is finally purified by rapid flash chromatography in

(15) (a) Bryce, M. R.; Moore, A. J. *Synthesis* **1991**, 26. (b) Parg, R. P.; Kilburn, J. D.; Ryan, T. G. *Synthesis* **1994**, 195 and references cited therein.

(16) Yamashita, Y.; Tanaka, S.; Imaeda, K.; Inokuchi, H.; Sano, M. *J. Org. Chem.* **1992**, 57, 5517.

(17) (a) Aümüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1984**, 618. (b) Martin, N.; Hanack, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1522. (c) Martin, N.; Behnisch, R.; Hanack, M. *J. Org. Chem.* **1989**, 54, 2563. (d) De la Cruz, P.; Martin, N.; Miguel, F.; Seoane, C.; Albert, A.; Cano, F. H.; Leverenz, A.; Hanack, M. *Synth. Met.* **1992**, 48, 59. See also reference 12.

(18) (a) Lehnert, W. *Tetrahedron Lett.* **1970**, 11, 4723. (b) Lehnert, W. *Synthesis* **1974**, 667.

silica gel and hexane:ethyl acetate as the eluent to avoid the hydrolysis to the starting quinone **18**.

Compound **20** showed the stretching cyano band at 2230 cm^{-1} in the IR spectrum. This high value found for a conjugated cyano group suggests that the molecule is highly distorted by the steric interaction between the *peri* hydrogens and the cyano groups. This fact has been previously observed in the X-ray analysis of the monomer tetracyano-9,10-anthraquinodimethane (TCAQ)¹⁹ and recently confirmed by quantum-chemical calculations.²⁰ The structure of compound **20** was supported on their spectroscopic data and ascertained by the negative FAB spectrum and elemental analysis.

On the other hand, the dimeric DCNQI derivative (**21**) was prepared from **18** by following Hünig's procedure.²¹ The reaction of **18** with a large excess of bis(trimethylsilyl)carbodiimide (BTC) (1:30 ratio) at room temperature in dichloromethane and in the presence of titanium tetrachloride for 24 h affords compound **21** in a moderate yield (28%), together with a mixture of compounds containing one or more unreacted carbonyl groups (Scheme 2). In contrast to the TCNQ derivative (**20**), attempts to separate them by using chromatographic procedures were unsuccessful due to their instability on silica gel, neutral silica gel, or florisil. Compound **21** could be finally isolated by precipitation using hexane and purified by washing with acetonitrile. The IR spectrum shows the cyano groups as a band at 2180 cm^{-1} . The spectroscopic assignment was confirmed by the negative FAB mass spectrum and elemental analysis (see Experimental Section).

The high resolution ¹H-NMR spectrum shows a wide signal at δ 9.0, thus indicating the existence of a syn \rightleftharpoons anti isomerization equilibrium in which the =N-CN groups adopt different orientations. This observation was first established by Hünig *et al.*^{21b} and, more recently, was thoroughly studied for a particular substitution pattern in our group.^{12c}

Electrochemistry. The redox properties of the novel π -extended donors (**19a–c**) and acceptors (**20, 21**) were measured in dichloromethane at room temperature by cyclic voltammetry (CV) and are collected in Table 1. The voltammograms of the donor molecules (**19a–c**) show the presence of only one oxidation wave involving four electrons to form the corresponding dication in both monomeric units of the dimer (Figure 1). In contrast to TTF derivatives which form stable radical cations and destabilized dications, donors **19a–c** form stable dication species in both monomers of the respective dimers.

As shown in Table 1, these compounds (**19a–c**) show slightly higher oxidation potentials than that measured for the monomer under the same experimental condi-

tions. This fact could be accounted for by the presence of the electron-withdrawing oxygen atom linking both donor units. The comparison with the parent TTF confirms that these molecules are slightly poorer donors. However, these compounds donate the second electron from the donor moieties better than TTF as a consequence of the decrease of the on-site Coulomb repulsion with increasing the conjugation length.

Donors **19a** and **19c** show the same first oxidation potential value which is cathodically shifted 50 mV in comparison to the ethylenedithio derivative **19b**. This result indicates that the donating ability of these π -extended donors (**19a–c**) is very similar to that found to the well-known donor BEDT-TTF (**1**) ($E_1 = +0.51\text{ V}$) and other bis-TTF derivatives previously reported.^{4,22} Interestingly, and to the best of our knowledge, this is the first example in which a TTF derivative shows only one oxidation wave corresponding to a four-electron transfer to form the tetracation. Resolution of the oxidation peaks could not be reached by reducing the scan rate, and the two two-electron redox processes of these donors (**19a–c**) are observed as a single wave. The coalescence of these two two-electron processes of each donor unit of the dimer into a single-wave is a clear indication that both donor fragments, connected by the oxygen atom as spacer, behave independently. This finding is in contrast to that observed for the dimeric TTFs bearing heteroatoms as spacers (**4**) which show three oxidation waves, thus indicating an interaction between both donor moieties.⁴ The larger distance between the active donor centers in compounds **19a–c** could account for this different result. These observed redox trends for the dimeric TTFs could not be explained by extended Hückel calculations for compounds of type **4** which showed a negligible through-space and through-bond orbital interaction between the two TTF units.²³ The geometric distortion found in the monomer of **19** is responsible for the coalescence of the first and second oxidation potentials into a single oxidation wave involving two electrons to form a planar and aromatic hydrocarbon skeleton.^{7,8} The high stability of the dication species has been used to explain the reduction wave to the neutral molecule, which appears at negative values in the voltammograms of largely π -extended *p*-quinodimethane analogues of TTF.^{7,8} Although in compounds **19a** and **19c** the same trend was observed, this is not the case for **19b** which showed a reversible oxidation wave as is shown in Figure 1. This behavior is not totally understood, and deep theoretical calculations on π -extended TTF analogues are currently under investigation.

Regarding the dimeric electron acceptors (**20, 21**), they showed a totally different electrochemical behavior. Thus, the dimeric TCNQ-type derivative (**20**) shows only a quasireversible reduction wave in the CV. This finding indicates that both tetracyano-9,10-anthraquinodimethane (TCAQ) moieties in **20** behave independently and, consequently, the voltammogram of **20** is similar to that of the monomeric TCAQ as it is shown in Figure 2.

The number of electrons involved in the reduction process of TCAQ has been previously confirmed by controlled potential coulometric analysis to be $2e^-$.^{17,24}

(19) Schubert, U.; Hünig, S.; Aümüller, A. *Liebigs Ann. Chem.* **1985**, 1216.

(20) (a) Ortí, E.; Viruela, P. M.; Viruela, R.; Martín, N. *Synth. Met.* **1995**, 70, 1031. (b) Ortí, E.; Viruela, P. M.; Viruela, R. *J. Phys. Chem.* **1996**, 100, 6138.

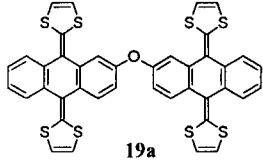
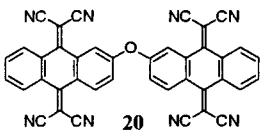
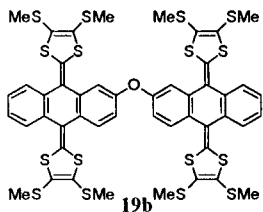
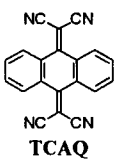
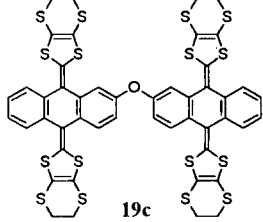
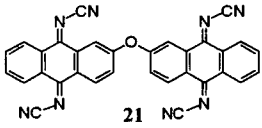
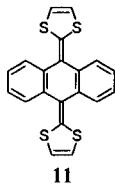
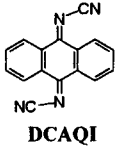
(21) (a) Aümüller, A.; Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1984**, 96, 437. (b) Aümüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1986**, 142. (c) Hünig, S. *Pure Appl. Chem.* **186**, 62, 385. (d) Hünig, S.; Erk, P. *Adv. Mater. (Weinheim, Ger)* **1991**, 5, 225. (e) Martín, N.; Navarro, J. A.; Seoane, C.; Albert, A.; Cano, F. H.; Becker, J. Y.; Khodorkovsky, V.; Harlev, E.; Hanack, M. *J. Org. Chem.* **1992**, 57, 5726. (f) Hünig, S.; Sinzger, K.; Jopp, M.; Baner, D.; Bietsch, W.; Ulrich, J.; Wolf, H. C. *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 859. (g) Martín, N.; Segura, J. L.; Seoane, C.; De la Cruz, P.; Langa, F.; González, A.; Pingarrón, J. M. *Tetrahedron* **1993**, 49, 4881. (h) Martín, N.; Seoane, C.; Garin, J.; Orduna, J. *Rapid Commun. Mass Spectrom.* **1995**, 9, 71. See also reference 13.

(22) Lahlil, K.; Moradpour, A.; Bowlas, C.; Menou, F.; Cassoux, P.; Bonvoisin, J.; Launay, J. P.; Dive, G.; Dehareg, D. *J. Am. Chem. Soc.* **1995**, 117, 995.

(23) Formigué, M.; Huang, Y. S. *Organometallics* **1993**, 12, 797.

(24) Kini, A. M.; Cowan, D. O.; Gerson, F.; Möckel, R. *J. Am. Chem. Soc.* **1985**, 107, 556.

Table 1. Redox Potentials of Novel Dimeric Donors (19a–c) and Acceptors (20 and 21) (in volts)

Compound	$E_{a.p.}^a$	$E_{c.p.}^a$	Compound	$E^{1, red. \frac{1}{2} a}$	$E^{2, red. \frac{1}{2} a}$
	0.50 (4 e ⁻)	-0.17		-0.34 (4 e ⁻)	
	0.50 (4 e ⁻)	0.35		-0.36 (4 e ⁻)	
	0.55 (4 e ⁻)	0.10		-0.23 (2 e ⁻)	-0.54 (2 e ⁻)
	0.45	-0.02		-0.29	-0.62
TTF	0.37 ^b	0.67 ^b	TCNQ	0.21	-0.35
			DCNQI	0.20	-0.43

^a In CH₂Cl₂; SCE vs Pt; Bu₄N⁺ClO₄⁻ as supporting electrolyte; scan rate 200 mV/s; ^b Half-wave oxidation potentials

Table 2. Spectroscopic, Stoichiometric, and Conductivity Measurements of the Prepared CT-Complexes

complex	ν (cm ⁻¹) ^a	λ (nm) ^b	D:A stoichiometry ^c	σ_{RT} (S cm ⁻¹)
19a-TCNQF ₄	2190, 2170	857, 754, 688	1:3	—
19b-TCNQF ₄	2190, 2170	857, 754, 688	1:3	—
19c-TCNQF ₄	2190, 2170	856, 753, 688	1:3	1.81 × 10 ⁻⁶ ^d
19a-DDQ	2210	588, 547, 430	1:3	<10 ⁻⁷
19b-DDQ	2210	580, 546, 433	1:3	<10 ⁻⁷
19c-DDQ	2210	583, 548, 447	1:3	<10 ⁻⁷

^a KBr pellets. ^b In CH₂Cl₂. ^c Determined by elemental analysis. ^d Measured at 370 K.

Thus, the redox wave in the CV of dimer **20** is indicative of a rather unusual overall process leading to the tetra-anion ($A-A + 4e^- \rightleftharpoons A^{2-}-A^{2-}$). However, it has been previously suggested from ESR studies carried out on TCAQ²⁴ that a coproportionation reaction ($A + A^{2-} \rightleftharpoons 2A^-$) could also be operative to some extent and, consequently, it may also occur in the dimeric system **20**.

The half-wave reduction potential value of **20** together with those of the monomer TCAQ and the parent TCNQ are summarized in Table 1. The reduction potential of **20** is slightly shifted to more positive values than TCAQ. This fact could be accounted for by the spacer oxygen atom and its electron-withdrawing effect. Nevertheless, the acceptor strength of **20** is far away from that of the parent TCNQ as a consequence of benzannulation which significantly deviates the TCAQ units in **20** from planarity due to the well-known steric interaction between the

peri hydrogen atoms and the dicyanomethylene groups.^{19,20,24}

On the other hand, the dimeric DCNQI derivative (**21**) shows, in contrast to the dimeric TCNQ analogue (**20**), two quasireversible reduction waves in the CV. Thus, compound **21** presents the same electrochemical behavior than the previously reported monomer (DCAQI),²⁵ which exhibits two single-wave reductions to the corresponding radical anion and dianion. However, the redox behavior of dimer **21** involves two two-electron reduction processes to form the radical anion ($A-A + 2e^- \rightleftharpoons A^{\cdot-}-A^{\cdot-}$) in both monomers and the dianions ($A^{\cdot-}-A^{\cdot-} + 2e^- \rightleftharpoons A^{2-}-A^{2-}$). Dimer **21** shows a better acceptor ability than its monomer (Table 1) measured under the same experimental conditions due to the electron-withdrawing effect

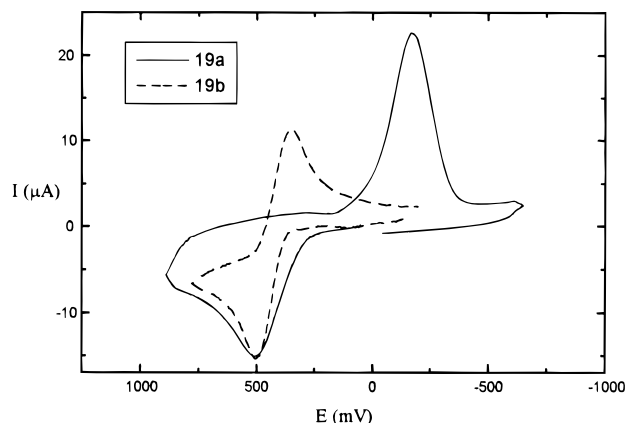


Figure 1. Cyclic voltammogram of compounds **19a** and **19b** (200 mV/s).

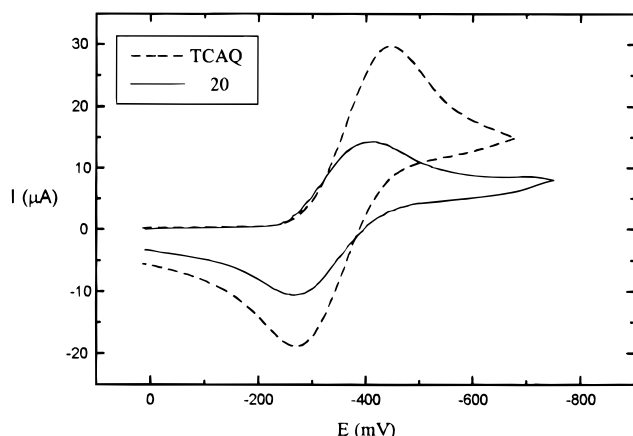


Figure 2. Cyclic voltammogram of TCAQ and acceptor **20** (200 mV/s).

of the oxygen atom connecting both acceptor units. However, dimer **21** is a weaker acceptor than the parent DCNQI which shows a positive first reduction potential value. Although it has been previously shown that DCNQI systems are substantially more planar than the TCNQ analogues,¹⁹ the lateral extension of the π -system reduces the bonding interactions in the DCNQI ring and introduces new antibonding interactions, resulting in a destabilization of the LUMO, thus justifying the lower reduction potential of **21** and its monomer compared to the parent DCNQI.^{12c}

DCNQI derivative **21** shows a better acceptor ability than its TCNQ analogue (**20**) due to its more planar geometry.¹⁹ This trend is also observed for the respective monomers as it is shown in Table 1.

The starting 2,2'-oxydianthraquinone (**18**) shows a similar electrochemical behavior than that found for its monomer 9,10-anthraquinone, exhibiting two quasi-reversible reduction waves ($E^{1,\text{red}}_{1/2} = -0.87$ V and $E^{2,\text{red}}_{1/2} = -1.40$ V) involving an overall process leading to the acceptance of two and four electrons, respectively. Now the first reduction potential is strongly shifted to more negative values as a consequence of the poorer acceptor ability of the carbonyl groups compared to the =N-CN and C(CN)₂ groups.

Charge Transfer Complexes. In agreement with the negative reduction potential values showed by the dimeric acceptors **20** and **21**, attempts to form CT-complexes with TTF were unsuccessful. However, evidence of complexation in solution was observed in the

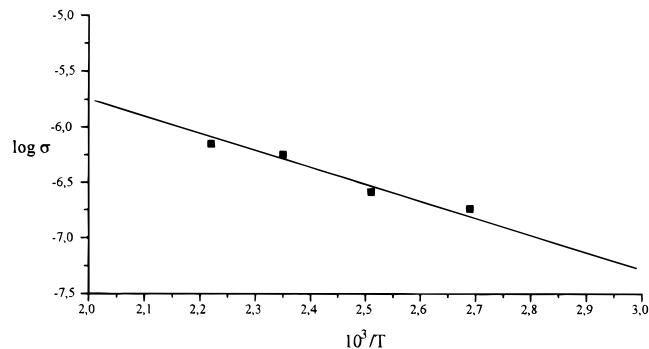


Figure 3. Temperature dependence of the conductivity for **19c**-TCNQF₄.

UV-vis spectrum in the reaction of **21** with *N,N,N,N*-tetramethyl-*p*-phenylenediamine ($\lambda_{\text{max}} = 580, 622, 640$ nm). This complexation reaction could not be, however, observed for the TCNQ analogue (**20**) due to its lower acceptor ability and also higher distorted structure.

Dimeric donors (**19a-c**), although exhibiting a strong donor ability, did not form complexes with acceptors such as TCNQ and DCNQI. The lack of complexation is explained by their weaker electron-donating ability than that of TTF and also than that of their respective monomers which formed electrically conducting CT-complexes with TCNQ.⁶ The small difference observed between the oxidation potentials of the monomer (**11**) and dimeric donors (**19a-c**) suggests that geometrical factors are also diffculting the complexation reaction. However, dimers **19a-c** form stable CT-complexes with stronger acceptors such as tetrafluorotetracyano-*p*-quinodimethane (TCNQF₄) and dichlorodicyano-*p*-benzoquinone (DDQ). Thus, when donors **19a-c** were mixed in hot acetonitrile with TCNQF₄ or DDQ a rapid reaction occurred, and the black microcrystalline solid formed was collected by filtration. The novel complexes showed the presence of characteristic charge-transfer bands in the visible region of the electronic spectra as well as the stretching cyano band shifted to lower values in the IR spectra than the neutral molecules, thus confirming the charge transfer interaction (Table 2).

As summarized in Table 2, all complexes showed 1:3 (D:A) stoichiometry according to the elemental analyses. This result, as well as the vibrational frequency values found for the cyano groups in the IR spectra, should rule out the presence of the TCNQF₄ or DDQ molecules as the dianion in the complexes (TCNQF₄²⁻: 2167, 2133; DDQ²⁻: 2192, 2169 cm⁻¹).²⁶ Although according to the IR spectra of the TCNQF₄ complexes, a complete charge transfer does not occur ($\nu_{\text{CN}} = 2201$ cm⁻¹ for the sodium salt of TCNQF₄ radical anion),²⁷ the room-temperature conductivities of the complexes, measured on compressed pellets by a standard two-probe technique, were very low ($\sigma_{\text{RT}} < 10^{-6}$ S cm⁻¹). The temperature dependence of the conductivity carried out for the **19c**-TCNQF₄ complex ($\sigma_{370} = 1.8 \times 10^{-6}$ S cm⁻¹) showed a semiconducting behavior with an activation energy of 0.33 eV (Figure 3).

Additionally, we measured the magnetic susceptibility for the **19c**-TCNQF₄ complex, finding values of 1.33×10^{-3} and 2.77×10^{-3} emu mol⁻¹ at 286.34 and 74.92 K, respectively, thus confirming the paramagnetic behavior

(26) Miller, J. S.; Dixon, D. A. *Science* **1987**, *235*, 871.

(27) Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Pöhler, P. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442.

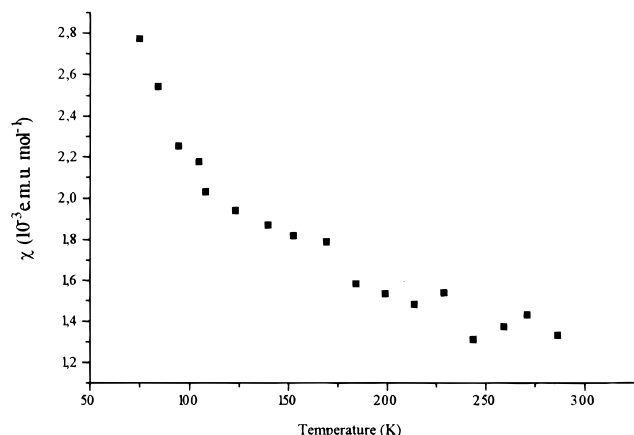


Figure 4. Temperature dependence of the magnetic susceptibility for **19c**-TCNQF₄.

of this complex, which follows the Curie-Weiss law in the measured range of temperatures as it is shown in Figure 4.

Summary and Conclusions

We have synthesized the first dimeric highly conjugated π -electron donors derived from TTF with a *p*-quinodimethane structure and π -electron acceptors derived from TCNQ and DCNQI in which both monomeric units are connected through an oxygen atom as spacer. The CV data indicate, in contrast to the dimeric TTF analogues, that both donor and also acceptor dimers behave electrochemically as molecules formed by two independent monomeric units. To the best of our knowledge, these dimeric donors (**19a**-**c**) are the first example in which an oxidation wave involving four electrons is observed for a TTF derivative. The dimeric acceptors also showed the same trend and, consequently, only one reduction wave involving an overall reduction process of four electrons was observed in the CV of the TCNQ derivative **20**. The dimeric DCNQI derivative **21** exhibited two two-electron reduction waves as it was observed for its monomer. Although the nonplanar geometry and the poor reduction potential values exhibited by the novel dimeric acceptors did not allow the preparation of stable CT-complexes, this was not the case for the dimeric donors (**19a**-**c**) which showed oxidation potentials similar to that of BEDT-TTF. Thus, stable CT-complexes were obtained by mixing donors **19a**-**c** with strong acceptor molecules such as TCNQF₄ and DDQ. In contrast to the monomer of **19a**, which formed an electrically conducting CT-complex with TCNQ, no CT-complexes were obtained with its dimer (**19a**). Considering the close oxidation potential values for the donor **19a** and its monomer, steric factors could also have a significant influence in the complexation process due to the higher distorted geometry of the dimeric molecules (**19a**-**c**) in comparison to their respective monomer.

In agreement with the above considerations, low electrical conductivities were observed for these CT-complexes which showed a semiconducting and paramagnetic behavior.

We believe that particularly the dimeric donor molecules bearing eight (**19a**) and sixteen (**19b** and **19c**) sulfur atoms per molecule are promising candidates for the preparation of interesting salts and CT-complexes with increasing of dimensionality. Work is in progress

directed to the preparation of novel π -extended dimeric donors in which both monomeric units are covalently attached by a conjugated ethylenic spacer or by two bridges which will lead to more planar dimers. The different connectivity between both monomeric units may modify this interesting and rather unusual electrochemical behavior resulting in multistage redox systems, thus satisfying the essential molecular design strategy for the preparation of new molecular conductors.²⁸

Experimental Section

4,4'-Oxybis(2-benzoylbenzoic acid)s (17). To a solution of 4,4'-oxydiphthalic anhydride (**16**) (3.1 mmol) in dry benzene (8 mL) was added AlCl₃ (12.5 mmol) in several portions during 1 h. After stirring the reaction mixture for 5 h, water (15 mL) and concd HCl (5 mL) were added, and a solid precipitated. The unreacted benzene was removed by steam distillation. The solid was filtered off, and a second crop was obtained by concentrating the mother liquors. This solid was a mixture of three constitutional isomers: 58% yield; IR (KBr) 3100, 1720, 1680, 1605, 1580, 1500, 1430, 1280, 1230, 1150, 1080 cm⁻¹; ¹H NMR (CDCl₃; 300 MHz) δ 7.00 (m), 7.15 (m), 7.33 (m), 7.41 (m), 7.54 (m), 7.71 (m), 8.09 (m). Anal. Calcd for C₂₈H₁₆O₅: C, 77.77, H, 3.73. Found: C, 77.53, H, 4.00.

2,2'-Oxydianthraquinone (18). A mixture of benzoylbenzoic acids (**17**) (12.8 mmol) and polyphosphoric acid (PPA) (9.18 mL) was heated at 120 °C for 24 h. The mixture was hydrolyzed with water (30 mL), and the resulting solid was filtered off and washed with hot ammonium hydroxide. The solid was purified by silica gel chromatography (CH₂Cl₂): 66% yield; ¹H NMR (CDCl₃; 300 MHz) δ 7.51 (2H, dd, *J* = 8.7 Hz, *J* = 2.4 Hz), 7.83 (4H, m), 7.92 (2H, d, *J* = 2.4 Hz), 8.31 (2H, m), 8.36 (2H, m), 8.42 (2H, d, *J* = 8.7 Hz); IR (KBr) 1680, 1595, 1490, 1390, 1340, 1300, 1235, 1160, 1140, 1100, 900, 720 cm⁻¹; MS *m/z*: 431 (M⁺ + 1), 370, 297, 254, 241, 167, 140, 111, 59; UV-vis (CH₂Cl₂) λ_{\max} (nm) (log ϵ): 258 (4.68), 330 (4.00). Anal. Calcd for: C₂₈H₁₄O₅: C, 78.14; H, 3.28. Found: C, 77.86; H, 3.38.

Synthesis of Donors (19). General Procedure. To a solution of the corresponding 1,3-dithiolyolphosphonate in dry THF was added BuLi (1.6 M in hexane) dropwise under argon atmosphere. The resulting solution was stirred at -78 °C for 30 min. A suspension of 2,2'-oxydianthraquinone (**18**) in dry THF was then added and kept under these conditions for an additional 1 h and then at room temperature overnight. The solvent was removed under reduced pressure and the residue washed with water (75 mL) and extracted with CH₂Cl₂ (3 × 75 mL). The organic layer was dried, and the solvent was removed under reduced pressure. The resulting solid was purified by silica gel chromatography using hexane:methylene dichloride as eluent.

2,2'-Oxybis[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene] (19a). The reaction was carried out using a stoichiometric ratio of 1:8 (oxadanthraquinone:phosphonate): 45% yield; ¹H NMR (CDCl₃; 300 MHz) δ 6.14 (2H, m), 6.27 (6H, m), 7.04 (3H, m), 7.28 (4H, m), 7.36 (2H, m), 7.68 (5H, m); ¹³C NMR (CDCl₃; 75 MHz) δ 91.8, 116.9, 117.1, 117.2, 121.4, 121.8, 124.9, 125.8, 126.2, 135.1, 148.2, 157.7; IR (KBr) 1550, 1520, 1460, 1420, 1280, 1225, 805, 760, 650 cm⁻¹; MS *m/z* (FAB⁺) 774 (M⁺), 573, 516, 485, 429, 401, 364; UV-vis (CH₂Cl₂) λ_{\max} (nm) (log ϵ) 240 (4.71), 366 (4.40), 430 (4.56). Anal. Calcd for C₄₀H₂₂OS₈: C, 61.98; H, 2.86. Found: C, 61.76; H, 2.73.

2,2'-Oxybis[9,10-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene] (19b). A stoichiometric ratio of 1:10 (oxadanthraquinone:phosphonate) was used: 49% yield; ¹H NMR (CDCl₃; 300 MHz) δ 2.29 (3H, s), 2.35 (6H, s), 2.37 (3H, s), 2.39 (6H, s), 2.40 (6H, s), 7.06 (2H, m), 7.19 (1H, m), 7.31 (4H, m), 7.54 (7H, m); ¹³C NMR (CDCl₃; 75 MHz) δ 18.7, 18.9, 22.5, 26.7, 31.4, 115.4, 116.31, 122.6, 123.0, 125.0, 125.2, 125.6, 125.8, 126.0, 126.2, 126.6, 126.7, 130.1, 130.1,

131.9, 134.2, 134.5, 136.2, 154.7, 155.3; IR (KBr) 2920, 1550, 1500, 1460, 1430, 1320, 1280, 1230, 960, 900, 760 cm^{-1} ; MS m/z (FAB⁺) 1142, 1096, 992, 949, 735, 574, 486, 391, 364; UV-vis (CH_2Cl_2) λ_{max} (nm) (log ϵ) 244 (4.54), 372 (4.15), 438 (4.34). Anal. Calcd for $\text{C}_{48}\text{H}_{38}\text{OS}_{16}$: C, 50.41; H, 3.35. Found: C, 50.26 H, 3.22.

2,2'-Oxybis[9,10-bis[4,5-(ethylenedithio)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene] (19c). A stoichiometric ratio of 1:8 (oxadanthraquinone:phosphonate) was used: 56% yield; ^1H NMR (CDCl_3 ; 300 MHz) δ 3.28 (16H, m), 7.06 (2H, m), 7.19 (1H, m), 7.32 (4H, m), 7.5 (7H, m); ^{13}C NMR (CDCl_3 ; 75 MHz) δ 29.4, 31.4, 110.7, 111.1, 115.8, 116.1, 116.3, 123.2, 123.6, 124.5, 125.4, 126.1, 126.9, 127.2, 128.7, 129.9, 130.8, 133.3, 133.9, 134.3, 134.5, 135.8, 136.4; IR (KBr) 2920, 1590, 1550, 1510, 1450, 1410, 1280, 1220, 1160, 1100, 930, 870, 810, 750 cm^{-1} ; MS m/z (FAB⁺) 1134 (M^+), 988, 960, 879, 798, 766, 735, 623, 573, 515, 486, 391, 364; UV-vis (CH_2Cl_2) λ_{max} (nm) (log ϵ) 244 (4.79), 388 (4.29), 448 (4.53). Anal. Calcd for $\text{C}_{48}\text{H}_{30}\text{OS}_{16}$: C, 50.76 H, 2.66. Found: C, 50.33 H, 2.45.

2,2'-Oxybis(11,11,12,12-tetracyano-9,10-anthraquinodimethane) (20). To a refluxing solution of quinone **18** (0.25 mmol) in dry methylene dichloride (50 mL) were added malononitrile (3.75 mmol), titanium tetrachloride (3.75 mmol), and dry pyridine (7.50 mmol) dropwise under argon atmosphere. After stirring for 24 h, the solvent was removed under vacuum. The solid obtained was washed with water (50 mL) and methylene dichloride (3 \times 50 mL). The organic extracts were dried with MgSO_4 . Further purification was accomplished by silica gel chromatography using hexane:ethyl acetate (4:1) as eluent: 56% yield; ^1H NMR (CDCl_3 , 300 MHz) δ 7.52 (2H, dd, $J_1 = 8.7$, $J_2 = 2.5$), 7.76 (4H, m), 7.92 (2H, d, $J = 2.5$), 8.16 (2H, m), 8.27 (2H, m), 8.35 (2H, d, $J = 8.7$); ^{13}C NMR (CDCl_3 , 75 MHz) δ 112.4, 112.7, 112.8, 112.9, 117.1, 122.9, 126.1, 127.5, 127.6, 129.7, 130.3, 132.4, 132.5, 132.6, 156.0, 157.6, 157.6, 157.6, 157.7, 159.4; IR (KBr) 2230 ($\text{C}\equiv\text{N}$), 1590, 1560, 1535, 1430, 1340, 1325, 1280, 1250, 770, 700 cm^{-1} ; MS m/z (FAB⁻/NPOE) 872 ($[\text{M} + \text{NPOE}]^-$), 761, 622 (M^-), 590, 574, 502, 486, 451, 388, 372, 319; UV-vis (CH_2Cl_2) λ_{max} (nm) (log ϵ) 230 (4.36), 296 (4.58), 348 (4.52). Anal. Calcd for $\text{C}_{40}\text{H}_{14}\text{N}_8\text{O}$: C, 77.17; H, 2.27; N, 18.00. Found: C, 76.47; H, 2.32, N, 17.89.

2,2'-Oxybis(*N,N'*-dicyano-9,10-anthraquinonediimine) (21). To a refluxing solution of quinone **18** (0.5 mmol) in dry methylene dichloride were added titanium tetrachloride (15 mmol) and then bis(trimethylsilyl)carbodiimide (BTC) (15 mmol) dropwise under argon atmosphere. After stirring for 24 h, ice-water (100 mL) and methylene dichloride were added, and the mixture was shaken vigorously. The organic layer was separated and dried over MgSO_4 . Half of the solvent was removed under vacuum, and then hexane was added. The solid obtained was collected by filtration and purified by washing with acetonitrile: 28% yield; ^1H NMR (CDCl_3 , 300 MHz) δ 7.54 (4H, m), 7.85 (2H, m), 9.00 (8H, m, br); ^{13}C NMR (CDCl_3 , 75 MHz) δ 86.9, 103.9, 110.0, 117.2, 120.9, 125.0, 127.8, 130.8, 134.7, 135.0, 147.3, 160.1, 169.9, 170.7; IR (KBr) 2180 ($\text{C}\equiv\text{N}$), 1560, 1490, 1330, 1280, 1250, 930, 880, 840, 780, 695 cm^{-1} ; MS m/z (FAB⁻/NPOE) 526 (M^-), 502, 429, 389, 363,

319. Anal. Calcd for $\text{C}_{32}\text{H}_{14}\text{N}_8\text{O}$: C, 73.00; H, 2.68; N, 21.28. Found: C, 72.91; H, 2.57; N, 21.19.

Preparation of Charge Transfer Complexes. General Procedure. To a boiling solution of the corresponding donor (**19a–c**) (0.010 mmol) in dry acetonitrile (10 mL), a solution of the corresponding acceptors (TCNQF₄ or DDQ) (0.040 mmol) in dry acetonitrile (5 mL) was added under argon atmosphere. The resultant dark green solution was slowly cooled to 0 °C. The solid precipitated was collected by filtration, washed with cold acetonitrile (3 \times 10 mL), and dried in vacuo to afford the corresponding CT-complex.

Complex 2,2'-Oxybis[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene] (19a)–TCNQF₄: 26% yield; IR (KBr) 2190 ($\text{C}\equiv\text{N}$), 2170 ($\text{C}\equiv\text{N}$), 1640, 1610, 1530, 1490, 1450, 1390, 1340, 1200, 1140, 970, 725 cm^{-1} ; UV-vis (CH_2Cl_2) λ_{max} (nm) 688, 754, 857. Anal. Calcd for $\text{C}_{76}\text{H}_{22}\text{F}_{12}\text{N}_{12}\text{OS}_8$: C, 56.93; H, 1.38, N, 10.48. Found: C, 57.69; H, 1.63; N, 10.60.

Complex 2,2'-Oxybis[9,10-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene] (19b)–TCNQF₄: 31% yield; IR (KBr) 2190 ($\text{C}\equiv\text{N}$), 2170 ($\text{C}\equiv\text{N}$), 1670, 1530, 1500, 1450, 1390, 1340, 1200, 1140, 970, 750 cm^{-1} ; UV-vis (CH_2Cl_2) λ_{max} (nm) 688, 754, 857. Anal. Calcd for $\text{C}_{84}\text{H}_{38}\text{F}_{12}\text{N}_{12}\text{OS}_{16}$: C, 51.16, H, 1.94, N, 8.52. Found: C, 50.32, H, 2.08, N, 9.37.

Complex 2,2'-Oxybis[9,10-bis[4,5-(ethylenedithio)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene] (19c)–TCNQF₄: 25% yield; IR (KBr) 2190 ($\text{C}\equiv\text{N}$), 2170 ($\text{C}\equiv\text{N}$), 1630, 1530, 1500, 1450, 1390, 1340, 1200, 1140, 970, 750 cm^{-1} ; UV-vis (CH_2Cl_2) λ_{max} (nm) 688, 753, 856. Anal. Calcd for $\text{C}_{84}\text{H}_{30}\text{F}_{12}\text{N}_{12}\text{O}$ S₁₆: C, 51.37, H, 1.54, N, 8.56. Found: C, 51.54, H, 1.85, N, 8.66.

Complex 2,2'-Oxybis[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene] (19a)–DDQ: 35% yield; IR (KBr) 2210 ($\text{C}\equiv\text{N}$), 1550, 1490, 1450, 1190, 1040, 880, 790. cm^{-1} ; UV-vis (CH_2Cl_2) λ_{max} (nm) 430, 547, 588. Anal. Calcd for $\text{C}_{64}\text{H}_{22}\text{Cl}_6\text{N}_6\text{O}_7\text{S}_8$: C, 52.79, H: 1.52, N: 5.77. Found: C, 52.38, H, 1.98, N, 5.60.

Complex 2,2'-Oxybis[9,10-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracene] (19b)–DDQ: 29% yield; IR (KBr) 2210 ($\text{C}\equiv\text{N}$), 1550, 1490, 1450, 1370, 1320, 1190, 1040, 880, 790, 750 cm^{-1} ; UV-vis (CH_2Cl_2) λ_{max} (nm) 433, 546, 589. Anal. Calcd for $\text{C}_{72}\text{H}_{38}\text{Cl}_6\text{N}_6\text{O}_7\text{S}_{16}$: C, 47.39, H, 2.10, N: 4.61. Found: C, 46.97, H, 2.39, N, 4.36.

Complex 2,2'-Oxybis[9,10-bis(4,5-(ethylenedithio)-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene] (19c)–DDQ: 23% yield; IR (KBr) 2210 ($\text{C}\equiv\text{N}$), 1560, 1450, 1380, 1290, 1210, 880 cm^{-1} ; UV-vis (CH_2Cl_2) λ_{max} (nm) 447, 548, 583. Anal. Calcd for $\text{C}_{72}\text{H}_{30}\text{Cl}_6\text{N}_6\text{O}_7\text{S}_{16}$: C, 48.35, H: 1.66, N, 4.63. Found: C, 47.91, H: 2.03, N, 4.44.

Acknowledgment. This work has been financially supported by the DGICYT of Spain (Project PB95-0428-CO2). One of the authors (L.S.) is indebted to the M.E.C.

JO9617950