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Synthesis and Properties of the First Highly Conjugated Tetrathiafulvalene Analogues Covalently Attached to [60]Fullerene

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The synthesis of the first C_{60}-based donor−acceptor (D−A) systems (**12a**−**c**) in which the C_{60} core is covalently linked to strong, highly conjugated π-electron donors derived of tetrathiafulvalene (TTF) with *p*-quinodimethane structure has been carried out by cyclization with azomethine ylides following Prato's procedure. The synthetic strategy requires the preparation of the novel formyl-substituted π-extended donors which, in turn, are prepared in a multistep synthetic procedure by reaction of 2-formyl-9,10-anthraquinone (**6**) with the appropriately substituted phosphonate esters (**8**). Semiempirical PM3 calculations predict a geometry highly distorted from planarity for the donor fragment and a most stable conformation in which both 1,3-dithiole rings are far away from the [60]fullerene surface. The redox properties were determined by cyclic voltammetry in solution and reveal the presence of four cathodically shifted reduction waves, relative to C_{60} and corresponding to the C_{60} core, and a two-electron single oxidation wave to form stable dication species of the π-extended donor units. Magnetic susceptibility measurements clearly indicate a paramagnetic behavior in the solid state, and a remarkable conductivity is observed for these single component organic compounds.

Introduction

An area of increasing interest in fullerene chemistry is the preparation of [60]fullerene-based donor−acceptor (D−A) systems due to the interesting optoelectronic properties they could exhibit. Electron transfer processes play an important role in chemical and biological reactions and, consequently, a wide variety of bridge donor−acceptor molecules have been synthesized in order to study the intramolecular electron-transfer mechanisms.[1] Donor−spacer−acceptor (D−s−A) structures are the basis of the development of molecular electronic devices,[2] the design of artificial photosynthetic systems,[3] or for the obtention of molecular chromophores exhibiting nonlinear optical response.[4] Moreover, organic compounds exhibiting semiconducting properties based on a single component have only recently been described.[5]

Much less is known, however, about covalently attached [60]fullerene−electron-donor systems. A variety of donor moieties such as porphyrin,[6] phthalocyanine,[7] ferrocene,[8] ruthenium complexes,[9] carotenoid polyenes,[10] and aniline derivatives[11] have been bound to the C_{60} cage and very weak or negligible charge-transfer (CT) interactions were observed. A direct observation of an *intra*molecular CT interaction from an *N*-phenyl group to the C_{60} core has been recently reported.[12] Photoinduced *intra*molecular electron-transfer processes, generating a charge-separated state, have been studied in some of the prepared donor−bridge−[60]fullerene dyads using time-resolved spectroscopic methods.[6,8−11] In fact, porphyrin−

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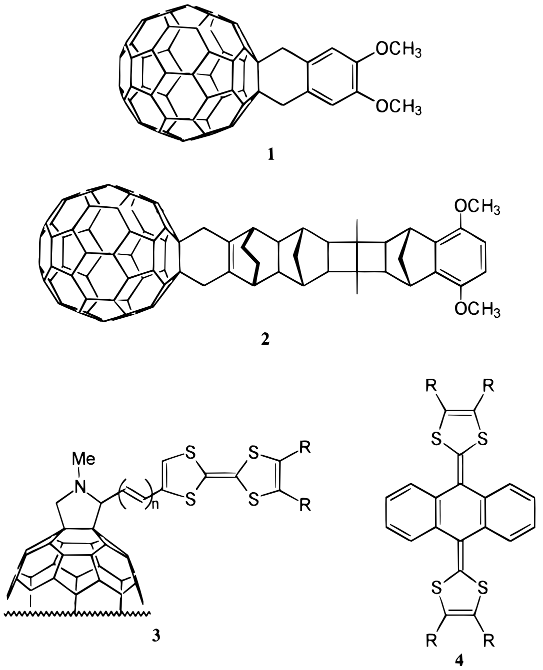
Chart 1. Some Representative Examples of [60]Fullerene-Based Donor−σ−Acceptor (1−3) and the π-extended *p*-Quinodimethane Analogue of TTF (4)



C_{60} bichromophoric compounds have been proposed as models to study artificial photosynthetic systems.[6]

Donor−acceptor interactions between methoxybenzene donor fragments and [60]fullerene in compounds **1** and **2** were observed in the solid state by X-ray analysis as a specific solid state effect with a significant influence on their electronic properties.[13,14]

The attachment of the well-known donor tetrathiafulvalene (TTF) to the C_{60} core (**3**) has been recently reported by Prato[15] and us[16] and, apparently, no CT interaction was observed in solution.[17] Considering the interest of C_{60}-based D−A dyads for the preparation of self-doping bichromophoric materials, we have carried out the synthesis of the first highly conjugated TTF derivatives with *p*-quinodimethane structure (**4**) linked to the C_{60} framework. In contrast to TTF and its derivatives, which are known to form stable radical-cations, π-extended TTF analogues (**4**) form stable dication species which form CT complexes with electrical and magnetic properties[18] (Chart 1).

TTF analogues with π-extended conjugation (**4**) represent an interesting class of electron-donors because of their strong donor character, similar to the parent TTF, and to the decreasing of the on-site Coulombic repulsions in the charged species. This electrochemical behavior has been accounted for by the fact that the quinoid structures form a new aromatic ring upon oxidation.[18,19]

In this paper we describe a new type of single-component donor−acceptor organic compounds (**12a**−**c**) in which the π-extended TTF donors **4** are covalently linked to the C_{60} cage, acting as an electron-accepting moiety, through a pyrrolidine ring. The presence of eight sulfur atoms as substituents on the donor fragment in some of the prepared molecules (**12b** and **12c**) may reinforce the *inter*molecular interactions in the solid state.[20] The synthesis, spectroscopy, electrochemistry, semiempirical theoretical calculations and magnetic and electrical conductivity measurements have been performed for the understanding of these donor−C_{60} dyads.

Results and Discussion

The target molecules **12a**−**c** were prepared by 1,3-dipolar cycloadditions of the appropriate azomethine ylides to [60]fullerene by following the previously well-established procedure first reported by Prato.[21] The synthetic procedure followed for the preparation of the C_{60}−donor systems is shown in Scheme 1. The starting 2-formyl-9,10-anthraquinone (**6**) was obtained by oxidation with PCC of the commercially available 2-(hydroxymethyl)-9,10-anthraquinone (**5**) in high yield. The shorter route to prepare compounds **12a**−**c** involved, in principle, the attachment of the quinone moiety to C_{60} by following the azomethine ylide cycloaddition from **6** to form the interesting fulleropyrrolidine **7**. A further Wittig−Horner reaction of **7** with the corresponding 1,3-dithiole phosphonate ester (**8**)[22] should afford **12a**−**c**. However, the reaction did not take place and no condensation products were obtained, in spite of this being the general procedure followed for the preparation of extended TTF analogues with *p*-quinodimethane structure.[18,19] This result could be accounted for by the presence of the C_{60} cage either by reacting with the carbanion generated from phosphonate ester **8** in the presence of *n*-butyllithium, giving rise to noncharacterizable polyaddition compounds, or by deactivation of the carbonyl groups as a consequence of their close proximity to the surface of the ball. This fact has been previously observed in other unreactive ester groups in methanofullerenes.[23]

An alternative route for the preparation of **12a**−**c** is also shown in Scheme 1. It involves firstly the formation of the formyl-substituted donor molecules **11a**−**c** and subsequent 1,3-dipolar cycloaddition reaction with C_{60}. Thus, the preparation of **11a**−**c** requires the previous protection of the formyl group in the 2-formyl-9,10-anthraquinone (**6**) by formation of the cyclic ketal, followed by Wittig−Horner reaction with the carbanion generated from the respective phosphonate esters (**8**). Treatment of compounds **10a**−**c** under acid conditions

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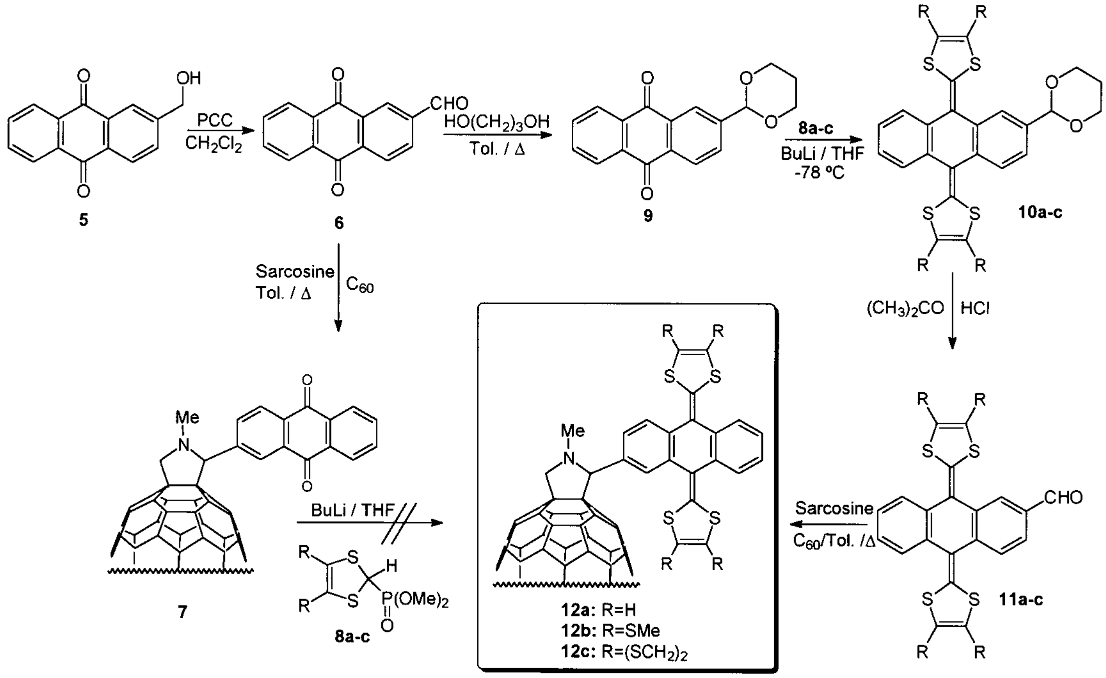
Scheme 1



led to the formyl-free donors **11a**−**c**, which react with [60]fullerene and sarcosine (*N*-methylglycine) in refluxing toluene to afford the π-extended donor containing fulleropyrrolidines (**12a**−**c**) in moderate yields (27−31%) (78−87% based on recovered C_{60}).

The structure of the novel compounds was supported by their analytical and spectroscopic data. The low solubility exhibited by these compounds (**12a**−**c**) in common organic solvents made it difficult to record the ^{1}H-NMR and prevented the collection of the ^{13}C-NMR spectra for compounds **12a** and **12c**. In fact, the ^{1}H-NMR spectra of compounds **12a**−**c** in chloroform at room temperature show wide and weak signals due, probably, to the presence of a conformational equilibrium between conformations A and B (see Figure 1). A good resolution was achieved for **12b** and **12c** by recording the ^{1}H-NMR spectra at higher temperature (50 °C), thus accelerating the isomers interconversion. Under these conditions, the signals of the pyrrolidine protons appear at δ 4.9 and 4.2 as doublets ($J \approx 9.3$ Hz; geminal hydrogens) and δ 4.9−5.0 (CH), in agreement with other related derivatives. The ^{13}C-NMR spectrum of compound **12b** shows, in addition to the N−Me group at δ 39.8, the signals at δ 68.8, 69.8, 77.1, and 83.4 for the sp^3 carbons of the pyrrolidine ring and those at the 6,6-junction of the C_{60} cage, in accordance with that previously observed for other related fulleropyrrolidine derivatives.[21] The UV−vis spectra of the novel fulleropyrrolidines (**12a**−**c**) show an absorption band at 438−452 nm which is assigned to the π-extended donor moiety,[18,19] thus hiding the typical weak absorption band at around 430 nm of dihydrofullerenes. The mass spectral molecular ions were observed using FAB technique in positive or negative ion modes for **12a**−**c** at *m/z* 1156, 1340, and 1337 ($M + H^+$) respectively (**12b**: accurate mass 1338.9710, calculated for $C_{87}H_{25}NS_8$ 1338.9752).

Although X-ray diffraction of compounds **12a**−**c** has not yet been accomplished because of difficulty in growing single crystals, we have obtained the structure of the adduct **12a** by molecular geometry optimization at the semiempirical PM3 level (Hyperchem 3.0), and the results are shown in Figure 1. Theoretical data clearly indicate that the geometry of the donor fragment is severely distorted from planarity due to the strong steric interactions between the sulfur atoms of the 1,3-dithiole rings and the CH units in adjacent *peri* positions. To avoid these interactions, the donor moiety adopts a butterfly-type structure, similar to that observed for the donor molecule (**4**, R = H) from X-ray data,[24] in which the lateral benzene rings preserve their planarity, with the central quinonoid ring adopting a boat conformation. The distortion from planarity of this structure (**12a**) can be described in terms of the angles α and γ. Angle α corresponds to the angle formed by the "wings of the butterfly" (dihedral angle C2−C1−C4−C5), and angle γ defines the tilting of the 1,3-dithiole rings with respect to the C2−C3−C5−C6 plane (dihedral angle C6−C1−C2−C3). α and γ have values of 139.6° and 38.4°, respectively.

These values are in good agreement with those from X-ray data[24] ($\gamma = 34.9°$) since the packing forces tend to planarize the molecules in the crystal to achieve the most compact packing along the molecular stacks.

The presence of the fulleropyrrolidine fragment covalently linked to the donor moiety gives rise to two possible isomers depending upon the orientation of the two dithiole rings (up and down). Theoretical calculations predict that conformation A with the dithiole rings pointing upward, is 1.45 kcal/mol more stable than B (Figure 1).

The distance predicted between the closest sulfur atom to the surface of the ball in conformation B (3.80 Å) is too long to consider the existence of an *intra*molecular CT interaction in the ground state. This prediction is in full agreement with the UV−vis observations, which did not show the presence of a low-energy charge-transfer band from the HOMO (−8.09 eV), which is localized on the π-extended donor moiety, to the LUMO (−2.74 eV), which spreads on the C_{60} acceptor unit. These findings

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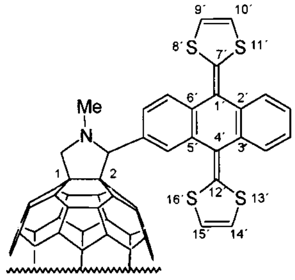
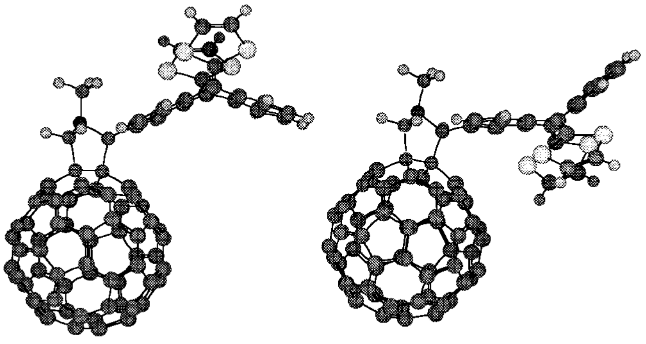


12a



A B

Figure 1. Minimum energy conformations (A and B) calculated for the donor−σ−acceptor **12a**. The aleatory atom numbering used in the text for **12a** is represented in the top figure.

were confirmed by EPR measurements in solution, which showed the absence of radical species. On the other hand, the geometry of the donor fragment produces a cavity with a distance between the outer carbons (C9−C15) of the 1,3-dithiole rings larger (8.8 Å) than the diameter (7.1 Å) of C_{60}.[25] These geometrical features could lead to an arrangement in the solid state in which a part of the fullerene surface is recognized by a neighboring π-extended donor moiety of a different molecule, thus giving rise to charge transfer and/or van der Waals interactions in the solid state. Similar findings have been recently observed by X-ray analysis by Kräutler *et al.* for anthracene 6,6-monoadducts[26] and previously for *inter*molecular CT complexes with TTF dimers.[27]

The bond length predicted between C1 and C2 (1.583 Å) is quite similar to that found by X-ray analysis for the recently reported triazolinyl-1,2-dihydro[60]fullerene[28] (1.574 Å) and [60]fullereno[1,2]isoxazole[29] (1.576 Å) in which a pentagonal ring is fused to the C_{60} core, being slightly shorter than that reported for some methanofullerenes,[30] benzocyclobutene structures[31] (1.645 Å), or Diels−Alder adducts (1.62 Å).[14]

The electrochemical properties of compounds **12a**−**c** have been studied by cyclic voltammetry in toluene: acetonitrile (4:1) as solvent at room temperature and the data are collected in the Table along with those of

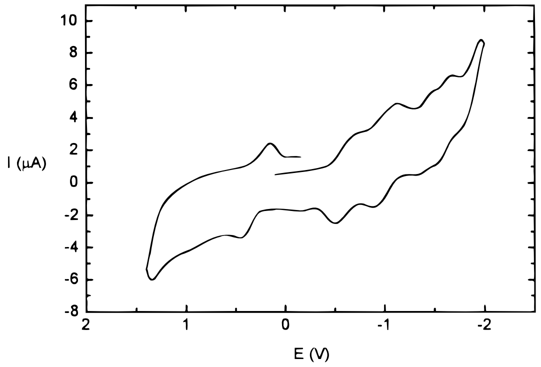


Figure 2. Cyclic voltammogram of compound **12a** at 200 mV/s.

[60]fullerene and the parent π-extended donor (**4**) for comparison purposes.

The cyclic voltammogram of these compounds (**12a**−**c**) show the presence of four quasi-reversible reduction waves, similar to those found for the parent [60]fullerene, corresponding to the first four reduction steps of the fullerene moiety. These reduction potentials appear at slightly more negative potentials than those of C_{60}, as it corresponds to 1,2-dihydrofullerenes.[32] This fact has been accounted for by the saturation of a double bond in the C_{60} framework, which raises the LUMO energy of the resulting organofullerene. In addition, another quasi-reversible reduction was observed in compound **12a** (R = H) between the second and the third reduction waves of the [60]fullerene moiety which could be reasonably assigned to the reduction of the organic addend (Figure 2). In compounds **12b** and **12c** this wave is apparently buried under the second reduction wave of the C_{60} core, which appears more intense that the remaining waves.

On the oxidation side, all these compounds undergo a two-electron redox behavior which is observed in the voltammogram as a single wave to form the dication. These findings are in full agreement with that observed for the electron donor **4**[18c] and other largely π-extended analogues[19] which present a single oxidation wave involving two electrons. This fact had been previously confirmed by Coulometric analysis.[18c] The coalescence of the two one-electron processes characteristic of TTF and its derivatives into a single oxidation wave reveals that the presence of the quinonoid structure between the two 1,3-dithiole rings leads to unstable, highly distorted from planarity, radical-cations, which upon oxidation form stable dication species in which the Coulombic repulsion is remarkably decreased.

Despite the absence of an intramolecular CT band in the UV−vis spectrum in solution for these D−A compounds (**12a**−**c**), the electroactive character of both π-extended donor and C_{60} acceptor partners are clearly observed in the CV measurements (Table 1). Consequently, we carried out the room temperature conductivity of compound **12a** measured on a compressed pellet by a standard two-probe technique, and a value of $\sigma_{rt} = 10^{-6}$ S cm^{-1} was obtained which still represents a high value for an undoped single component organic compound.

In order to confirm the possible electronic interactions in the solid state, we have measured the molar magnetic susceptibility (χ_m) of the novel D−A compounds (**12a**−**c**)

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Table 1. Redox Properties of the New Organofullerenes 12a−c (V *vs* SCE)

compound	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}	E^1_{ox}
12a (R = H)[a]	−0.66	−1.01	−1.67 (−1.48)[b]	−1.96	0.46
12b (R = SMe)[a]	−0.67	−1.10	−1.67	−2.20	0.60
12c (R = $(SCH_2)_2$)[a]	−0.64	−0.99	−1.67	−1.95	0.50
C_{60}[a]	−0.60	−1.00	−1.52	−2.04	
4[c]					0.45

[a] In toluene:MeCN (4:1); SCE *vs* Pt; $Bu_4N^+ClO_4^-$ as supporting electrolite; scan rate 200 mV/s. [b] Reduction of the organic addend. [c] In CH_2Cl_2; SCE *vs* Pt; $Bu_4N^+ClO_4^-$ as supporting electrolite; scan rate 200 mV/s.

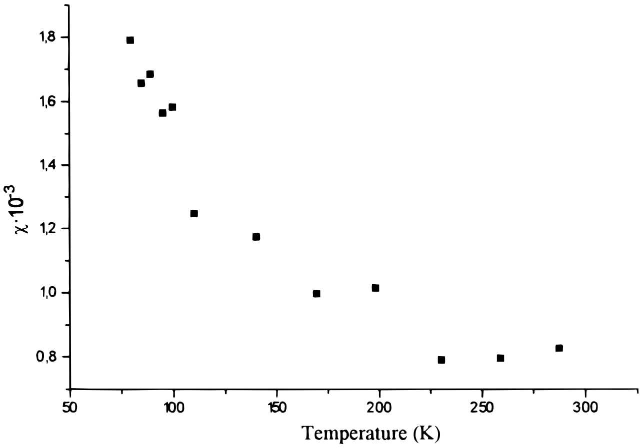

Figure 3. Temperature dependence of the magnetic susceptibility for compound **12a**.

with a Faraday balance. The values found (**12a**, 8.24 × 10^{-4}, 1.78 × 10^{-3} emu mol^{-1}; **12b**, 2.07 × 10^{-3}, 5.39 × 10^{-3} emu mol^{-1}; **12c**, 2.25 × 10^{-3}, 4.83 × 10^{-3} emu mol^{-1}) measured at 290 and 75 K, respectively, clearly confirm the paramagnetic behavior of these D−A systems in the solid state, showing magnetic moments of $\mu = 1.38$ (**12a**), $\mu = 2.22$ (**12b**), and $\mu = 2.28$ (**12c**) μ_B at 290 K. These compounds obey the Curie−Weiss law in the range of temperatures measured, and the variation of the magnetic susceptibility with temperature for compound **12a** is shown in Figure 3.

Summary and Conclusions

We have described the synthesis of novel covalently linked D−A systems (**12a**−**c**) formed by the moderate acceptor [60]fullerene and highly conjugated TTF derivatives with the *p*-quinodimethane structure. The synthesis has been carried out by formation of the respective formyl-substituted electron donors (**11a**−**c**) and subsequent 1,3-dipolar cycloaddition by reaction with [60]-fullerene and sarcosine.

The molecular geometry of compound **12a** was calculated from semiempirical PM-3 calculations and reveals a highly distorted electron-donor moiety with a butterfly-type structure, in full agreement with that previously observed for the parent donor molecule (**4**, R = H) by X-ray diffraction. The presence of the C_{60} core gives rise to two different conformations, depending upon the orientation of the two dithiole rings (up and down). Theoretical calculations predict a minimum energy geometry in which both 1,3-dithiole rings are pointing away from the ball surface. Although no CT interactions were observed in solution, the particular geometry of the donor fragment produces a cavity in which a C_{60} cage of a neighboring molecule could be allocated, thus giving rise to a specific solid state interaction. In agreement with this prediction, the magnetic susceptibility clearly confirms the paramagnetic behavior in the solid state.

The electrochemical properties of the donor−acceptor systems **12a**−**c** were measured by cyclic voltammetry showing the electroactive character of both donor and acceptor moieties. Thus, the π-extended donor fragment shows a two-electron single wave to form the dication, in contrast to the behavior of TTF itself and its derivatives, which form stable radical-cations, and in good agreement with the redox properties of the parent unsubstituted π-extended donors **4**. In accordance with the presence of donor−acceptor units, the electrical conductivity measurements carried out on compound **12a** show a remarkable value for a single-component C_{60}-based organic compound.

Work is in progress directed to the preparation of novel D_2−A systems bearing two donor units covalently attached to the C_{60} cage and to the synthesis of stronger π-extended donors which could increase the *intra*- and/or *inter*molecular CT interactions. In addition, these novel C_{60}-based donor compounds could be considered as precursors of a particular type of C_{60}-based CT complexes by reaction with strong acceptors, including C_{60}-based electron-acceptor molecules.[33]

Experimental Procedures

2-Formyl-9,10-anthraquinone (6). To a suspension of 2-(hydroxymethyl)anthraquinone (**5**) (2.0 g, 8 mmol) in CH_2Cl_2 (100 mL) was added pyridinium chlorochromate (PCC) (2.6 g, 12 mmol). The mixture was stirred at room temperature for 12 h. Then, the excess of PCC was removed by filtration. The solvent was evaporated under reduced pressure and the residue was washed with water (75 mL) and extracted with CH_2Cl_2 (3 × 75 mL). The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The resulting solid was purified by silica gel chromatography using hexane:methylene dichloride (1:5) as eluent: 98% yield; mp 181−183 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 10.25 (1H, s), 8.81 (1H, d, $J = 1.5$), 8.49 (1H, d, $J = 7.8$), 8.38−8.33 (2H, m), 8.31 (1H, dd, $J_1 = 7.8$, $J_2 = 1.5$), 7.87 (2H, m); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 190.7, 171.7, 169.9, 139.7, 134.5, 134.4, 132.9, 129.4, 128.0, 127.3; IR (KBr) 1700 (CHO), 1675 (CO), 1660 (CO), 1585, 1330, 1300, 1260, 1200, 975, 930, 855, 710 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (nm) (log ϵ) 250 (4.40), 390 (4.10), 460 (4.07); MS (*m*/*z*) 236 (M^+). Anal. Calcd for $C_{15}O_3H_8$: C, 76.27; H, 3.39. Found: C, 75.80; H, 3.89.

9,10-Dihydro-9,10-dioxoanthracene-2-carbaldehyde Trimethylene Acetal (9). A solution of 2-formylanthraquinone (**6**) (1.8 g, 7.5 mmol), propylene glycol (0.85 g, 11.25 mmol), and *p*-toluenesulfonic acid (traces) in toluene (100 mL) was refluxed with azeotropic destillation using a Dean−Stark for 48 h. The solvent was removed under reduced pressure and the residue washed with water (100 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The organic layer was dried and the solvent was removed under reduced pressure. The resulting solid was purified by recrystallization from ethyl acetate: 87% yield; mp 230−231 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 8.43 (1H, s), 8.32 (3H, m), 7.95 (1H, d, $J = 7.8$), 7.86 (2H, m), 5.65 (1H, s), 4.33 (2H, t, $J = 10.5$), 4.06 (2H, t, $J = 12.3$), 2.27 (2H, m); ^{13}C-NMR ($CDCl_3$, 62 MHz) δ 183.0, 182.9, 144.8, 134.2, 133.7, 133.6, 133.5, 131.8, 127.5, 127.4, 127.3, 125.9, 100.3, 67.6, 25.7; IR (KBr) 1675, 1660, 1600, 1385, 1290, 1160, 975, 850, 720 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 254 (4.50), 280 (4.47), 326 (4.48); MS (*m*/*z*) 299 (M^+). Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.17; H, 4.89.

Synthesis of Protected π-Extended Donors (10a−c). General Procedure. To a solution of the corresponding 1,3-

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[33] Martín, N.; Illescas, B. M.; Seoane, C. *Tetrahedron Lett.* **1997**, *38*, 2015.

dithiolephosphonate **8** in dry THF was added dropwise BuLi (1.6 M in hexane) under argon atmosphere. The resulting solution was stirred at −78 °C for 30 min. A suspension of the acetal **9** in dry THF was then added and kept under these conditions for an additional hour and then at room temperature overnight. The solvent was removed under reduced pressure and the residue washed with water (75 mL) and extracted with CH_2Cl_2 (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 (1:1) as eluent.

9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene-2-carbaldehyde Trimethylene Acetal (10a). 90% yield; mp 273−275 °C (dec); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.85 (1H, s), 7.67 (3H, m), 7.39 (1H, d, $J = 8.1$), 7.26 (2H, m), 6.28 (4H, s), 5.54 (1H, s), 4.29 (2H, t, $J = 10.5$), 4.00 (2H, t, $J = 12.3$), 2.24 (2H, m); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 136.2, 135.2, 125.7, 124.8, 123.5, 122.6, 122.0, 117.3, 117.1, 116.9, 101.3, 67.3, 25.7; IR (KBr) 1600, 1520, 1390, 1150, 770, 650 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 238 (4.44), 366 (3.94), 430 (4.17); MS (m/z) 466 (M^+). Anal. Calcd for $C_{24}H_{18}O_2S_4$: C, 61.77; H, 3.89. Found: C, 61.42; H, 4.09.

9,10-Bis(4,5-(methylthio)-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene-2-carbaldehyde trimethylene acetal (10b): 92% yield; mp 278−280 °C (dec); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.67 (1H, s), 7.55 (1H, d, $J = 7.8$), 7.51 (2H, m), 7.45 (1H, d, $J = 7.8$), 7.30 (2H, m), 5.54 (1H, s), 4.27 (2H, t, $J = 10.7$), 4.02 (2H, t, $J = 12.4$), 2.39 (12H, s), 2.21 (2H, m); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 125.7, 124.7, 123.5, 122.6, 117.2, 117.1, 116.9, 116.8, 101.2, 67.2, 29.6, 25,7; IR (KBr) 1545, 1450, 1380, 1100, 890, 760 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 242 (4.86), 368 (4.33), 438 (4.57); MS (m/z) 650 (M^+). Anal. Calcd for $C_{28}H_{26}O_2S_8$: C, 51.66; H, 4.03. Found: C, 51.46; H, 4.00.

9,10-Bis(4,5-(ethylenedithio)-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene-2-carbaldehyde trimethylene acetal (10c): 89% yield; mp 278−280 °C (dec); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.61 (1H, s), 7.50 (1H, m), 7.49−7.42 (2H, m), 7.39 (1H, m), 7.38−7.27 (2H, m), 5.57 (1H, s), 4.15 (2H, m), 3.80 (2H, m), 3.29 (8H, s), 2.18 (2H, m); IR (KBr) 1545, 1460, 1375, 1290, 1235, 1200, 1155, 1065, 1050, 955, 905, 840, 770, 705, 650 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 242 (3.75), 388 (3.15), 446 (3.44). Anal. Calcd for $C_{28}H_{22}O_2S_8$: C, 51.98; H, 3.40. Found: C, 51.82; H, 2.98.

Synthesis of Substituted 2-Formyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracenes (11a−c). General Procedure. To a suspension of the corresponding protected donor (**10a**−**c**) (2.5 mmol) in acetone (75 mL) was slowly added hydrochloric acid (35%) (6 mL). The reaction was monitorized by TLC. After addition of HCl, the reaction mixture was neutralized by addition of sodium bicarbonate (5%). The solvent was evaporated and the crude mixture was washed with water (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was dried and the solvent was removed under vacuum. The compound obtained was purified by silica gel chromatography [hexane:CH_2Cl_2 (1:2)].

2-Formyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (11a): 98% yield; mp 264−266 °C (dec); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 10.01 (1H, s), 8.21 (1H, s), 7.85 (1H, d, $J = 8.0$ Hz), 7.79 (1H, d, $J = 8.0$ Hz), 7.71 (2H, m), 7.30 (2H, m), 6.35 (4H, d, $J = 7.8$ Hz); ^{13}C-NMR ($CDCl_3$, 62 MHz) δ 191.4, 127.5, 126.3, 126.1, 126.0, 125.3, 124.9, 124.8, 117.3, 117.1, 116.9; IR (KBr,) 1695 (CHO), 1600, 1550, 1430, 1210, 805, 650 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 250 (4.40), 390 (4.09), 460 (4.06), MS (m/z) 408 (M^+). Anal. Calcd for $C_{21}H_{12}OS_4$: C, 61.74; H, 2.96. Found: C, 61.32; H, 3.47.

2-Formyl-9,10-bis(4,5-(methylthio)-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (11b): 98% yield; mp 262−264 °C (dec); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.96 (1H, s), 7.98 (1H, d, $J = 1.5$ Hz), 7.75 (1H, dd, $J_1 = 8.0$ Hz, $J_2 = 1.8$ Hz), 7.64 (1H, d, $J = 8.0$ Hz), 7.52 (2H, m), 7.28 (2H, m), 2.32 (12H, s); ^{13}C-NMR ($CDCl_3$, 62 MHz) δ 191.4, 140.3, 135.4, 134.9, 134.4, 134.2, 134.0, 133.2, 127.9, 126.8, 126.7, 126.6, 126.4, 125.9, 125.6, 125.5, 122.9, 122.4, 19.3, 19.2; IR (KBr) 1695 (CHO), 1600, 1530, 1420, 1210, 810, 760 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 250 (4.72), 400 (4.32), 466 (4.35); MS (m/z) 592 (M^+). Anal. Calcd for $C_{25}H_{20}OS_8$: C, 50.64; H, 3.40. Found: C, 50.94; H, 3.75.

2-Formyl-9,10-bis(4,5-(ethylenedithio)-1,3-dithiol-2-ylidene)dihydroanthracene (11c): 97% yield; mp 263−265 °C (dec); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 10.04 (1H, s), 8.00 (1H, d, $J = 1.5$ Hz), 7.81 (1H, dd, $J_1 = 7.7$ Hz, $J_2 = 1.5$ Hz), 7.67 (1H, d, $J = 7.7$ Hz), 7.54 (2H, m), 7.35 (2H, m), 3.31 (8H, s); ^{13}C-NMR ($CDCl_3$, 62 MHz) δ: 191.1, 140.1, 135.3, 134.2, 134.1, 133.8, 133.4, 131.6, 127.8, 126.6, 125.8, 125.5, 125.4, 122.8, 122.6, 111.3, 111.1, 110.9, 110.7, 24.50; IR (KBr) 1695 (CHO), 1600, 1505, 1280, 1180, 810, 760 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 248 (4.48); 418 (4.00); 478 (4.10). Anal. Calcd for $C_{25}H_{16}OS_8$: C, 51.03; H, 2.74. Found: C, 51.41; H, 2.72.

Synthesis of Fulleropyrrolidines 7 and 12a−c. General Procedure. A toluene solution containing C_{60} (0.14 mmol), *N*-methylglycine (0.70 mmol), and the appropriate aldehyde (0.14 mmol) was heated to reflux for 24−48 h. The solvent was then evaporated and the crude material was carefully chromatographed on a neutral silica gel column (cyclohexane and cyclohexane−toluene mixtures). Further purification was accomplished by repetitive precipitation and centrifugation.

***N*-Methyl-2-(9,10-dioxo-9,10-dihydroanthracenyl)-3,4-fulleropyrrolidine (7):** 40% yield (57%); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 8.69 (1H, s), 8.38 (2H, m), 8.31 (2H, m); 7.79 (2H, m), 5.14 (1H, s), 5.03 (1H, d, $J = 9.3$), 4.33 (1H, d, $J = 9.3$), 2.83 (3H, s); FTIR (KBr) 1674, 1593, 1322, 1288, 707, 668, 526 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 254 (4.10), 280 (4.37), 326 (4.28); MS (FAB^+) (m/z) 983 (M^+).

***N*-Methyl-2-[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracenyl]-3,4-fulleropyrrolidine (12a):** 32% yield (78%); ^{1}H-NMR (300 MHz, 50 °C, $CDCl_3$:CS_2, 2:1) δ 8.10 (1H, s), 7.59 (3H, m), 7.33 (3H, m), 4.98 (2H, m), 4.27 (2H, m), 2.74 (3H, m); FTIR (KBr) 1451, 1422, 1179, 1084, 798, 639, 625 cm^{-1}; UV−vis (CH_2Cl_2), λ_{max} (log ϵ) 438 (4.32), 326 (4.61), 256 (5.12); MS (FAB^+) (m/z) 1156 (M^+).

***N*-Methyl-2-[9,10-bis(4,5-(methylthio)-1,3-dithiol-2-ylidene)-9,10-dihydroanthracenyl]-3,4-fulleropyrrolidine (12b):** 27% yield (87%); ^{1}H-NMR (300 MHz, 50 °C, $CDCl_3$:CS_2, 2:1) δ 8.07 (1H, s), 7.87 (1H, m), 7.49 (3H, m), 7.24 (2H, m), 4.95 (1H, d, $J = 9.5$), 4.91 (1H, s), 4.21 (1H, d, $J = 9.5$), 2.67 (3H, s), 2.27 (12H, s); ^{13}C-NMR (75 MHz, $CDCl_3$:CS_2, 2:1) δ 155.9, 153.6, 153.1, 152.6, 147.0, 145.9, 145.8, 145.6, 145.2, 144.9, 144.4, 144.1, 142.6, 142.3, 142.2, 142.0, 141.8, 141.7, 141.3, 139.8, 139.5, 139.2, 136.4, 135.5, 134.9, 134.2, 131.6, 130.4, 129.3, 128.7, 128.5, 127.9, 126.1, 125.2, 125.1, 124.5, 123.5, 123.3, 118.4, 83.3, 77.1, 69.7, 68.8, 39.8, 31.9, 29.7; FTIR (KBr) 1491, 1451, 1424, 1174, 1107, 752, 625 cm^{-1}; UV−vis (CH_2Cl_2), λ_{max} (log ϵ) 438 (4.25), 326 (4.49), 256 (5.00); MS (FAB^+) (m/z) 1338.9752 (M^+) (calcd 1338.9710).

***N*-Methyl-2-[9,10-bis(4,5-(ethylenedithio)-1,3-dithiol-2-ylidene)-9,10-dihydroanthracenyl]-3,4-fulleropyrrolidine (12c):** 37% yield (83%); ^{1}H-NMR (300 MHz, 50 °C, $CDCl_3$:CS_2, 2:1) δ 8.13 (1H, s), 7.91 (1H, m), 7.76 (3H, m), 7.51 (2H, m), 5.06 (1H, s), 4.90 (1H, m, $J = 9.7$), 4.33 (1H, m, $J = 9.7$), 3.41 (8H, s), 2.83 (3H, s); FTIR (KBr) 1500, 1304, 1211, 798, 754, 651, 625 cm^{-1}; UV−vis (CH_2Cl_2), λ_{max} (log ϵ) 452 (4.12), 328 (4.36), 256 (5.08); MS (FAB^+) (m/z) 1337 ($M + H^+$).

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