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Synthesis and Electron-Donor Ability of the First Conjugated π-Extended Tetrathiafulvalene Dimers[†]

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A series of novel conjugated homo (**16a**,**b**) and heterodimers (**20**) of π-extended tetrathiafulvalenes with *p*-quinodimethane structures (exTTFs) linked by a conjugative vinyl spacer have been prepared by olefination Wittig−Horner reaction from the corresponding quinones (**14**, **19**) and phosphonates (**15a**,**b**). The redox properties, determined by cyclic voltammetry, reveal a strong donor character and the presence of only one four-electron oxidation wave to form the tetracation species at oxidation potential values quite similar to those found for the related monomers. Theoretical calculations (PM3) show a planar central stilbene moiety and highly distorted exTTF units. The electronic spectra support as well as the electrochemical data and theoretical calculation the lack of significant communication between the exTTF units.

Introduction

Tetrathiafulvalene (TTF, **1**) is a well-known electron-donor molecule that is currently receiving renewed interest due to its application in fields other than electrical conductivity.[1] In particular, π-extended TTFs with *p*-quinodimethane structure (exTTF, **2**) incorporating an anthracene spacer between the dithiole rings[2] have been successfully used as electron-donating building blocks in the preparation of photosynthetic models (**3**)[3] or as materials with marked nonlinear optical properties (**4**).[4] Another remarkable applications involve crown-annelated exTTFs (**5**), in which the crown ether moiety is fused to the dithiole rings, as complexing agents for metal ions recognition,[5] as well as for the synthesis of electroactive donor−acceptor dyads (**6**).[6] Recently, a molecular wire-like behavior has been found in a series of C_{60}-wire-exTTF systems (**7**) over distances of 40 Å and beyond, in which a strong paraconjugation takes place between the π-conjugated oligomer and the exTTF electron donor, resulting in high coupling constant values ($V \sim 5.5$ cm^{-1})[7] (Chart 1).

In contrast to the parent TTF, π-extended TTFs exhibit only a single, quasireversible oxidation wave involving two electrons to form stable dicationic species. In fact, the oxidation potential for exTTF (**2**: R = H, $E^1_{\mathrm{ox}} = 0.44$ V vs SCE) is slightly higher than that reported for the parent TTF (**1**: $E^1_{\mathrm{ox}} = 0.34$ V vs SCE). Formation of the oxidized state in exTTFs (**2**) occurs with a strong structural change from the highly distorted and non aromatic neutral butterfly shape molecule to the planar and fully aromatic dication state in which the 1,3-dithiolium cations are in an almost orthogonal geometry to the planar anthracene unit.[8] This feature has been exploited in our group to improve the lifetime of the charge-separated state due to the gain of aromacity and planarity associated with the oxidation process in the photolytically generated radical pair in C_{60}-exTTF dyads.[9]

One of the strategies followed to prepare novel TTF-based donors with increased dimensionality as well as to obtain multistep redox systems has been the synthesis of molecular species bearing two or more TTF units, and

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[†] This work is dedicated to Professor José L. Soto on the occasion of this retirement.

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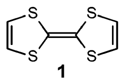
CHART 1. Some Representative Examples of Functional Molecules Containing the ExTTF Moiety



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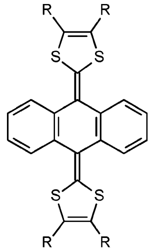
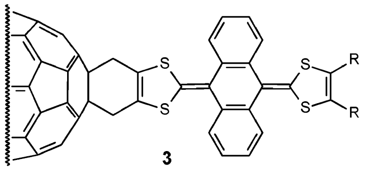


exTTF, **2**

R = H, CH_3, SCH_3, $(\text{-}SCH_2\text{-})_2$



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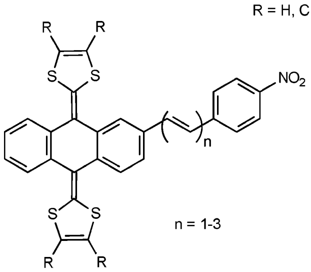

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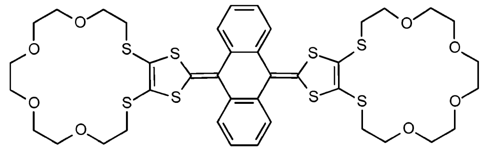

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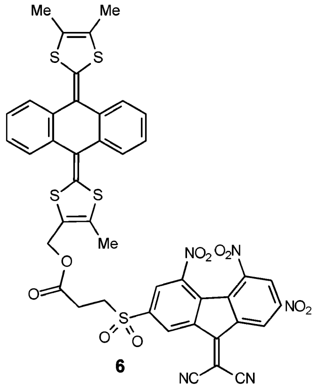

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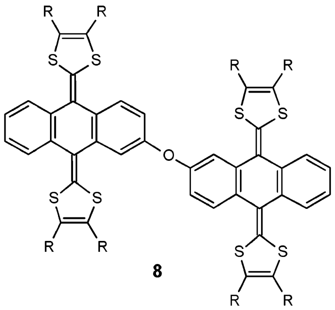

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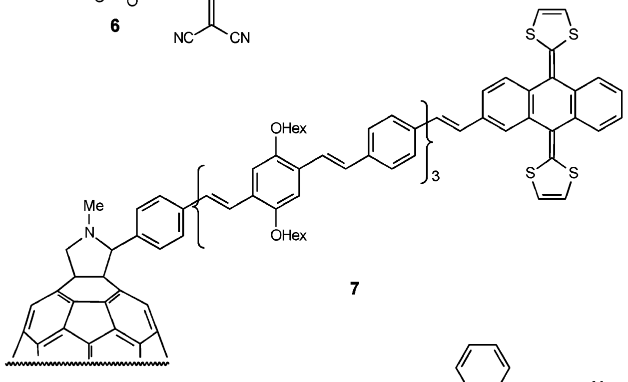

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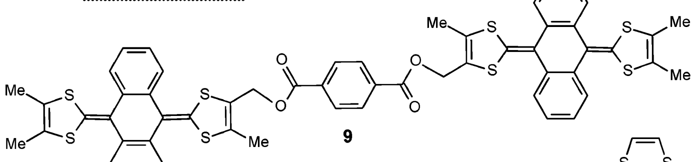

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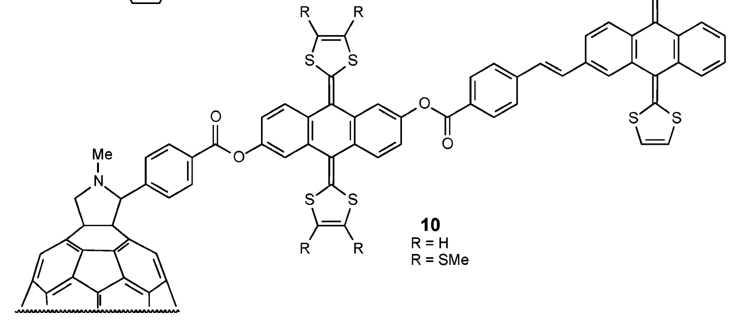

10

R = H

R = SMe

a wide variety of molecular, macromolecular and supramolecular systems have been reported.[1,10] In contrast, only a very few examples of double donors involving one exTTF unit are known,[11] and only two dimeric systems (**8**, **9**) formed with exTTF have been reported so far. The electrochemical study of compounds **8**[12] and **9**[13] reveals the presence of only one oxidation wave, thus confirming that both exTTF moieties, connected either by an oxygen atom in **8** or by means of a more complex spacer involving multiple single and double bonds in **9**, behave independently.

We have recently reported a suitably functionalyzed exTTF dimer which has been covalently connected to the C_{60} molecule affording a new electroactive triad (C_{60}-exTTF$_1$-exTTF$_2$, **10**) in which the photoinduced electron transfer gives rise to the radical pair $C_{60}^{\bullet -}$−exTTF$_1$−exTTF$_2^{\bullet +}$ showing the highest lifetime reported so far for a C_{60}-based triad (~100 μs).[14] This remarkable finding has been accounted for by the low reorganization energy of the C_{60} molecule[15] and the gain of aromaticity and planarity undergone by the exTTF units upon oxidation.

To have a better understanding of unprecedented exTTF dimers in which both exTTF units are covalently connected through a conjugated bridge, in this paper we report on the synthesis of a series of novel exTTF dimers bound by a vinyl spacer. The presence of a conjugated bridge linking both donor units could, in principle, lead to a different electrochemical behavior than that found for the twin-donors (**8**, **9**) previously reported. The geometry of the novel compounds has been determined by semiempirical PM3 theoretical calculations in order to determine the planarity of the novel donor molecules and, hence, the degree of electronic communication between the two exTTF units.

Results and Discussion

Synthesis. The preparation of the novel exTTF dimers was carried out in a multistep synthetic procedure from commercially available 2-amino-9,10-anthraquinone (**11**) as shown in Scheme 1. It is worth mentioning that suitably functionalized *p*-quinodimethane analogues of TTF (exTTFs) have been less studied, and only recently, the chemical functionalization of exTTFs has been undertaken by different groups.[16] Therefore, we decided to carry out the synthesis of exTTFs **17** and **18** endowed with iodine and vinyl groups, respectively. Compound **18** was synthesized in three steps from 2-amino-9,10-anthraquinone (**11**) by functional group transformation to 2-iodo-9,10-anthraquinone (**12**)[17] and further Stille coupling reaction with tritertbutylvinyltin in the presence of $Pd(PPh_3)_4$[18] to afford 2-vinyl-9,10-anthraquinone **13**. Transformation of **13** into the exTTF **18** was carried out by Wittig−Horner olefination reaction with phosphonate **15a**. Phosphonates **15a,b** were in turn obtained in a multistep synthetic procedure by following the procedure reported in the literature.[19]

Compounds **17** and **18** are appealing building blocks for the construction of conjugated exTTF dimers by Heck coupling reaction. However, all attempts to obtain compound **16a** from its precursors (**17** and **18**) were unsuccessful and formation of dimer **16a** was only detected by TLC and mass spectroscopy.

Compound **16** could be, however, prepared from bis-anthraquinone **14** which was in turn obtained by reacting quinones **12** and **13** by Heck coupling,[20] using $(CH_3CN)_2PdCl_2$ as the catalyst in refluxing toluene.[21] Compound **14** was thus obtained in 24% yield using triethylamine as base and tetrabutylammonium bromide as phase-transfer agent. Other conditions used such as $Pd(OAc)_2$ as a catalyst or adding LiCl led to **14** in lower yields. Compound **14** was also prepared by an alternative olefin metathesis reaction from 2-vinyl-9,10-anthraquinone **13** using the Grubbs ruthenium catalyst $[Cl_2Ru(Pcy_3)_2]$ in refluxing dichloromethane. However, this cycloaddition/cycloreversion process led to bis-anthraquinone **14** in 18% yield.

Olefination Wittig−Horner reaction of bis-anthraquinone **14** with the carbanion generated from the respective phosphonate ester (**15a**,**b**) in the presence of *n*-butyllithium afforded exTTF dimers **16a**,**b** as orange stable solids in reasonably good yields (54%−62%) (see the Experimental Section). It is important to note that a stoichiometric ratio of 1:10 (bis-anthraquinone/phosphonate) was found to be the most appropriate to complete the reaction and to avoid major compounds containing one or more unreacted free carbonyl groups. Anyway, a further purification by careful flash cromatography is needed for the separation of these byproducts which were detected by TLC (Scheme 1).

The structure of exTTF dimers **16a**,**b** was established by their analytical and spectroscopic data. The FTIR spectrum showed the absence of carbonyl band, thus

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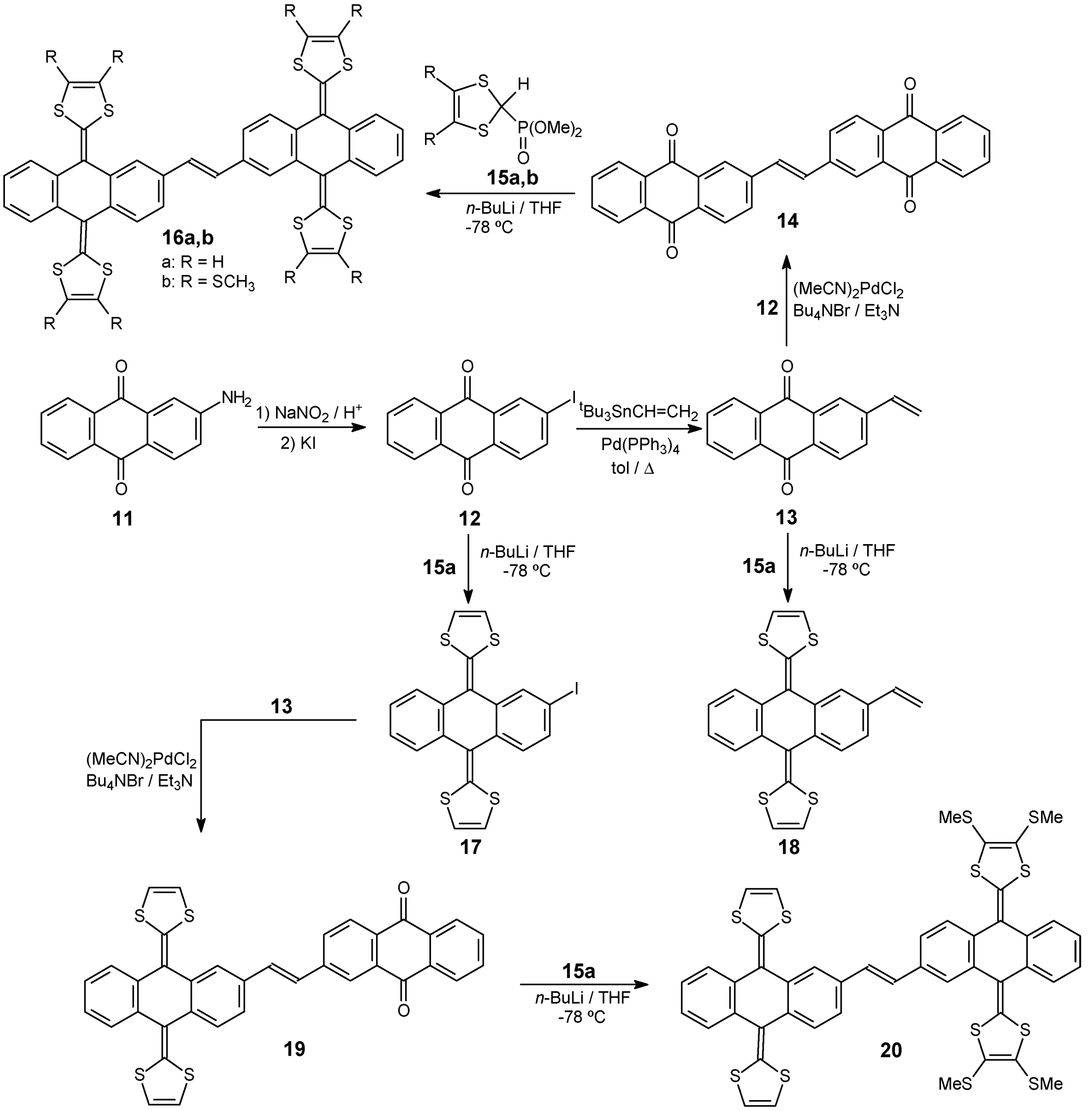
SCHEME 1



showing the purity of the final compounds which was confirmed by elemental analysis and electrospray mass spectrometry.

The ^{1}H NMR and ^{13}C NMR spectra of **16a**,**b** showed only the half of the expected signals due to the existence of a C_2 rotational axis. Therefore, the ^{1}H NMR spectra of **16a**,**b** showed, in addition to the expected aromatic and dithiole ring signals, the vinyl protons as a singlet at δ ~7.2. The *E* configuration of the vinyl moiety was confirmed by the IR band appearing at 968 cm^{-1}.

As shown in Scheme 1, the synthetic procedure followed for obtaining exTTF dimers (**16a**,**b**) is limited to the preparation of symmetric systems bearing the same substituents on the 1,3-dithiole ring. Therefore, we have carried out a different synthetic strategy to obtain asymmetric dimers which is based in the preparation of the valuable intermediate **19** constituted by one exTTF unit and one anthraquinone moiety able to undergo further chemical transformations.

Intermediate **19** was synthesized by Heck coupling reaction between iodine-containing exTTF (**17**) and vinylanthraquinone (**13**) using $(CH_3CN)_2PdCl_2$ as catalyst in refluxing toluene. Compound **19** contains the strong electron donor exTTF conjugated with the electron acceptor 9,10-anthraquinone, and consequently, its electronic spectrum shows the presence of an intense intramolecular charge-transfer band centered at $\lambda_{max} \approx 520$ nm (Figure 1). This absorption band is responsible for the violet color of this compound and suggests the interest of this compound, as well as other further D−π−*A* derivatives prepared by transformation of the quinone moiety into other acceptors, in the field of nonlinear optics.

Conjugated hetero exTTF dimer **20** was finally prepared from **19** by following the standard above procedure for the introduction of the 1,3-dithiole rings by Wittig−Horner olefination reaction using a stoichiometry **19**/phosphonate of 1:6 (Scheme 1).

Thus, compound **20** was obtained as a stable orange solid in 58% yield. The structure of **20** was confirmed by analytical and spectroscopic data and the ^{1}H and ^{13}C NMR spectra revealed the lack of symmetry. The UV−vis spectrum of **20** is similar to that of **16a**,**b** and shows a significant hypsochromic shift in comparison with its

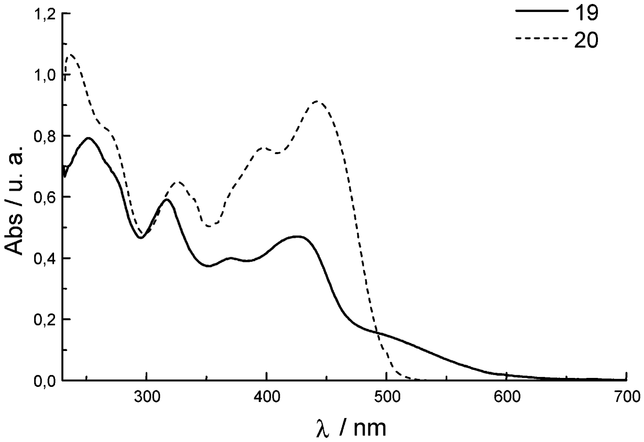


FIGURE 1. UV−vis absorption spectra of compounds **19** and **20** in dichloromethane.

TABLE 1. Redox Potentials (V vs Ag/AgCl) of Novel Donors Synthesized[a]

compd	$E^{1,\mathrm{ox}}{}_{\mathrm{pa}}$	$E_{\mathrm{pc}}{}^{b}$	$E^{1,\mathrm{red}}{}_{\mathrm{pc}}$	$\lambda_{\max}{}^{c}$ (nm)
2a (R = H)	0.33 (2e$^-$)			415
2b (R = SCH_3)	0.47 (2e$^-$)			435
17	0.38 (2e$^-$)	0.19		430
18	0.36 (2e$^-$)	0.11		434
16a	0.36 (4e$^-$)	0.17		428
16b	0.46 (4e$^-$)	0.25		434
19	0.37 (2e$^-$)		−0.86 −1.19	523
20	0.32 (2e$^-$) 0.44 (2e$^-$)	0.25 0.34		443

[a] In MeCN/CH_2Cl_2 (1/1), Ag/AgCl vs Pt, scan rate 100 mVs^{-1}. [b] Reduction process from the dication to the neutral molecules. [c] In CH_2Cl_2.

precursor **19** as a consequence of the lack of the donor−acceptor character in **20** (Figure 1).

Electrochemistry. The redox properties of the novel π-extended dimers (exTTF) were measured by cyclic voltammetry (CV) in CH_3CN/CH_2Cl_2 (1/1) as solvent at room temperature using a glassy carbon (GC) as working electrode, the standard Ag/AgCl as reference electrode, and using tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte. The data are collected in Table 1 together with the parent exTTF (**2**: R = H; R = SCH_3) as references.

Unlike the parent TTF, exTTFs **2a**,**b** exhibit only one, two-electron, quasireversible oxidation wave to form a dication, which has been confirmed by Coulombimetric analysis.[22] The coalescence of the two one-electron processes into one two-electron process reveals that the presence of the quinonoid structure between the two 1,3-dithiole rings leads to unstable, highly distorted, nonplanar, radical cations.[8] Only recently, the first experimental evidence for the formation of the π-radical cation and dication species of a series of exTTFs by using time-resolved and steady-state radiolytic techniques, has been reported.[23]

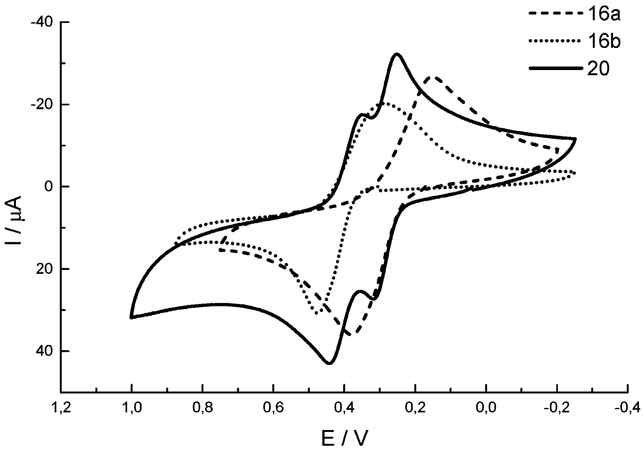


FIGURE 2. Room-temperature cyclic voltammograms of **16a**, **16b**, and **20** in MeCN/CH_2Cl_2 (1/1).

In agreement with the above data, functionalized exTTFs **17** and **18** show only one oxidation wave to form the dication species at the same value as reported for the parent unsubstituted **2a** under the same experimental conditions. Iodine substituted compound **17** showed, however, a sligthly poorer oxidation potential than **2a** (see Table 1), due to the presence of the iodine atom and its electronegative character.

The CV of all three new dimers **16a**,**b** and **20** show several common features. All of the compounds essentially retain the electronic porperties of both exTTF moieties. Thus, compounds **16a**,**b** showed only one oxidation wave involving 4e$^-$ at values quite similar to those found for the respective monomer components (**2a** and **2b**, respectively). In contrast, heterodimer **20** showed two oxidation waves corresponding to the formation of the dication and tetracation species of the two constituent exTTF units of the dimer. The first anodic peak corresponding to the oxidation of the exTTF unit with the unsubtituted 1,3-dithiole rings and the second one corresponding to the exTTF unit bearing the SCH_3 groups. Interestingly, these values are sligthly shifted to lower oxidation potentials compared to the respective dimers **16a**,**b** (Figure 2).

The reduction wave at positive values is associated to the process of formation of the neutral molecule from the tetracation state. As shown in Figure 2, the cyclic voltammograms of the novel dimeric donors exhibit a chemically reversible behavior which is in contrast to other irreversible behaviors observed for exTTFs under different experimental conditions.[24]

Interestingly and most importantly, when comparing the CVs of the dimeric exTTF donors **16a**,**b** and **20** with those of the model compounds **2a**,**b** and **18**, it is obvious that the CV of the dimers is not exactly the sum of the CVs of the respective monomers. This could suggest the presence of weak electronic interactions between the two donor moieties (Table 1). This small electronic interaction in the ground state is in agreement with the recorded electronic spectra. The UV−vis spectra of the dimers is dominated by the absorption of the exTTF moiety in the

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visible region (~430 nm), and the found values for the λ_{max} of the dimers are slightly shifted in comparison with the respective monomers (see Table 1).

These electrochemical findings are in agreement with those found for other related doubly donor molecules such as the TTF−CH═CH−exTTF heterodimer, for which a weak electronic interaction between the two donor (TTF and exTTF) moieties was observed by CV.[24a] In contrast, this weak interactions were not reported for the related TTF dimer (TTF−CH═CH−TTF) which showed only two redox couples, implying that there is no Coulombic effect between the two TTF units.[24b]

Finally, D−π−A compound **19** showed, in addition to the oxidation wave of the exTTF unit (0.34 V), the two single-electron reduction waves to form the radical anion and dianion species of the anthraquinone moiety, thus confirming its amphoteric redox behavior.

Molecular Structure. The molecular structure of the parent exTTF dimer **16a** has been optimized by using semiempirical calculations at the PM3 level. Previous theoretical calculations carried out on exTTFs (**2**) have shown a good agreement with experimental data and demonstrated that the PM3 method provides a good description, even better than ab initio HF/6-31G* calculations, for the molecular structure of this type of compounds.[8]

The minimum energy conformations (A and B) found for **16a** reveal an energy difference of only 0.272 kcal/mol. As expected, the exTTF units show a butterfly-shaped nonplanar geometry due to the strong steric hindrance between the peri hydrogens and the sulfur atoms (1.78 Å). To avoid these interactions, the molecule is distorted out of the planarity with the central ring in a boat conformation (distance S···H, 2.53 Å).

Distortions from planarity in the exTTF units can be described in terms of the angles α and γ. Angle α corresponding to the angle formed by the outer benzene rings (the wings of the butterfly), and γ defines the tilting of the dithiole units and is obtained as the supplement of the C7−C2−C6−C5 dihedral angle.[8] The calculated angles are basically the same for both exTTF units, being α = 140.0° and γ = 33.2° for the more stable conformation (B). Theses values are in good agreement with those determined experimentally in the crystal for compound **2** (R = SCH_3)[22] (α = 143.8° and γ = 33.3°) (Figure 3).

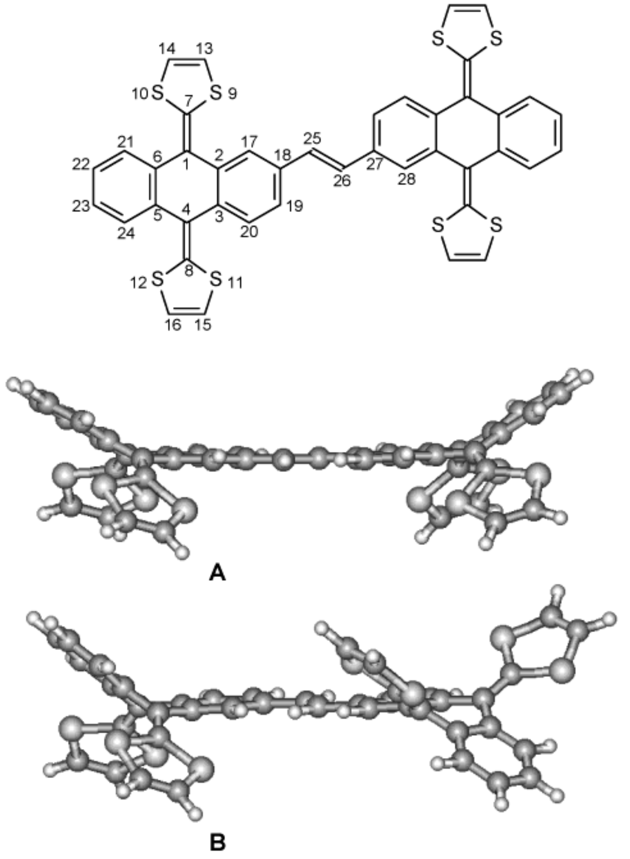

FIGURE 3. Syn (A) and anti (B) minimum energy PM3-optimized conformations for compound **16a**.

Although two different geometries [syn (A) and anti (B)] are possible for **16a** depending upon the orientation of the two dithiole rings in each exTTF moiety (up and down), no significant energy differences were found between them. Finally, the planarity of the vinyl group connecting the two benzene rings has been determined by the dihedral angle C18−C25−C26−C27. The calculated value of 179.3° as well as the dihedral angles C17−C18−C25−C26 = 178.0° and C25−C26−C27−C28 = 175.4° confirm that both π-extended TTF units are in conjugation through the vinyl spacer, thus supporting the electronic communication between both benzene rings of the exTTF units.

Conclusions

In summary, we have synthesized a series of novel exTTF dimers covalently connected through a vinyl spacer from the corresponding bis-anthraquinone by Wittig−Horner olefination reaction with the respective phosphonates of 1,3-dithiole rings. The starting bis-anthraquinone was prepared either by Heck coupling reaction or by olefination metathesis. A new donor heterodimer involving two different exTTF units with different substitution pattern on the 1,3-dithiole rings was prepared from D−π−A molecule **19** constituted by one exTTF unit connected by a vinyl spacer to the anthraquinone moiety.

The electrochemical data reveal a similar redox behavior in the exTTF dimers showing only one quasireversible oxidation wave to form the corresponding tetracation species. This finding suggest that although a certain degree of electronic interaction takes place between the exTTF units, both electroactive units behave independently and, therefore, no significant electronic communication occurs between the 1,3-dithiole rings in the ground state. This electrochemical behavior is in agreement with that previously reported for the analogue system constituted by two TTF units connected by a vinyl spacer which showed only two oxidation waves corresponding to the radical cation and dication species of each TTF moiety.[25]

Theoretical calculations (PM3) carried out on compound **16a** reveal two highly distorted exTTF units and a planar moiety involving the vinyl group and the two adjacent benzene rings. This geometry favors the electronic communication between the adjacent benzene

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(25) Green, D. C.; Allen, R. W. *J. Chem. Soc., Chem. Commun.* **1978**, 832.

units and, at the same time, shows the lack of planarity between the 1,3-dithiole rings in the ground state, thus underpinning the lack of a strong electronic interaction between the donor 1,3-dithiole rings as is also suggested by the electrochemical results.

Experimental Section

2-Amino-9,10-anthraquinone (**11**) and *n*-butyllithium (1.6 M) were commercially available. 2-Iodo-9,10-anthraquinone (**12**)[17] and phosphonate esters (**15a,b**)[19] were obtained by previously reported procedures.

2-Vinyl-9,10-anthraquinone (13). To a stirred solution of 2-iodo-9,10-anthraquinone (**12**) (334 mg, 1 mmol) in dry toluene (20 mL) was added $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) under argon atmosphere. While stirring, tributyl(vinyl)tin (634 mg, 2 mmol) was added. The resulting reaction mixture was refluxed for 20 h. The solvent was then removed under vacuum and the residue extracted with ethyl acetate (2 × 100 mL). The combined organic extracts were washed with brine (3 × 75 mL). After drying over $MgSO_4$, the solvent was removed under reduced pressure to afford a solid, which was further purified by column chromatography on silica gel using hexane/dichloromethane (1:1): 71% yield; mp 175−177 °C (lit.[26] mp 175−176 °C dec); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.35−8.26 (m, 4H, ArH), 7.83−7.78 (m, 3H, ArH), 6.87 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.7 Hz), 6.05 (d, 1H, J_1 = 17.4 Hz), 5.54 (d, 1H, J_2 = 10.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 183.2, 179.9, 143.3, 135.4, 134.1, 134.0, 133.6, 132.6, 131.4, 127.8, 127.3, 127.2, 124.8, 118.3; FTIR (KBr) 1678, 1626, 1589, 1325, 1290, 995, 933, 920, 899, 740, 710 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 334, 267 nm; MS (EI) *m*/*z* 234 (M^+). Anal. Calcd for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 82.23; H, 4.36.

1,2-Di(anthraquinon-2-yl)ethylene (14). To a solution of 2-iodo-9,10-anthraquinone (**12**) (428 mg, 1.3 mmol) and 2-vinyl-9,10-anthraquinone (**13**) (300 mg, 1.3 mmol), in dry toluene (250 mL) and under argon atmosphere, were added $(MeCN)_2PdCl_2$ (111 mg, 427 μmol), NBu_4Br (413 mg, 1.3 mmol) and triethylamine (4.3 mL). The resulting reaction mixture was refluxed for 48 h. The solvent was removed under vacuo, and the residue was chromatographed on silica gel using hexane/dichloromethane (3:7) as eluent: 24% yield; mp > 250 °C (lit.[21] mp 434 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.33−8.26 (m, 4H, ArH), 8.21 (d, 2H, J_2 = 1.7 Hz, ArH), 8.17 (d, 2H, J_1 = 8.1 Hz, ArH), 7.82−7.79 (m, 4H, ArH), 7.62 (dd, 2H, J_1 = 8.1 Hz, J_2 = 1.7 Hz, ArH), 6.95 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 183.3, 180.1, 154.7, 134.9, 134.3, 133.7, 133.3, 132.9, 129.6, 126.4, 126.3, 121.1, 118.1; FTIR (KBr) 2924, 1672, 1626, 1587, 1572, 1344, 1305, 1282, 986, 932, 847, 712, 663 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 570, 428, 330, 255 nm; MS (EI) *m*/*z* 440 (M^+). Anal. Calcd for $C_{30}H_{16}O_4$: C, 81.81; H, 3.66. Found: C, 82.03; H, 3.84.

ExTTF Dimers 16a,b. General Procedure. To a solution of the corresponding phosphonate ester (**15a**,**b**) (10 mmol) in dry THF (200 mL) at −78 °C and under argon atmosphere was added *n*-BuLi (1.6 M) (11 mmol) with a syringe. After 30 min at −78 °C, the quinone **14** (1 mmol) in dry THF (50 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 kept at this temperature overnight. The THF was evaporated under reduced pressure, water (100 mL) was added, and the residue was extracted with CH_2Cl_2 (3 × 75 mL). The combined extracts were dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane/dichloromethane as eluent.

1,2-Di[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl]ethylene (16a): 54% yield; mp 225−227 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69−7.64 (m, 4H, ArH), 7.49 (d, 2H, J_1 = 8.2 Hz, ArH), 7.30−7.25 (m, 4H, ArH), 7.23 (s, 2H), 7.01 (d, 2H, J_2 = 2.4 Hz, ArH), 6.61 (dd, 2H, J_1 = 8.2 Hz, J_2 = 2.4 Hz, ArH), 6.29 (s, 4H), 6.27 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.4, 134.1, 132.2, 131.7, 130.8, 130.3, 128.8, 128.0, 127.2, 125.9, 124.9, 117.3, 117.2, 117.1; FTIR (KBr) 2922, 2850, 1545, 1514, 1454, 1444, 1259, 1091, 1020, 800, 754, 654 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 428, 363, 279, 239 nm; MS (EI) *m*/*z* 784 (M^+). Anal. Calcd for $C_{42}H_{24}S_8$: C, 64.25; H, 3.08. Found: C, 64.42; H, 3.25.

1,2-Di{9,10-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracen-2-yl}ethylene (16b): 62% yield; mp 194−195 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55−7.51 (m, 4H, ArH), 7.36 (d, 2H, J_1 = 8.2 Hz, ArH), 7.32−7.28 (m, 4H, ArH), 7.20 (s, 2H), 6.86 (d, 2H, J_2 = 2.3 Hz, ArH), 6.63 (dd, 2H, J_1 = 8.2 Hz, J_2 = 2.3 Hz, ArH), 2.39 (s, 24H, SCH_3); ^{13}C NMR (CD_3COCD_3, 75 MHz) δ 147.8, 134.7, 134.1, 133.7, 129.3, 126.6, 126.5, 126.3, 125.2, 125.1, 125.0, 124.8, 124.6, 124.3, 124.2, 124.0, 121.8, 111.6, 110.2, 18.6 (SCH_3), 18.4 (SCH_3); FTIR (KBr) 2918, 1618, 1560, 1533, 1499, 1471, 1417, 1292, 1252, 968, 879, 758, 675 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 434, 368, 276, 242 nm; MS (ES), *m*/*z* 1154 (M^+). Anal. Calcd for $C_{50}H_{40}S_{16}$: C, 52.04; H, 3.49. Found: C, 52.26; H, 3.55.

Preparation of Donors 17 and 18. General Procedure. To a solution of the phosphonate ester (**15a**) (1 mmol) in dry THF (20 mL) at −78 °C and under argon atmosphere was added *n*-butyllithium (1.6 M) (1.1 mmol). After 1 h at −78 °C, a solution of the corresponding quinone (**12** or **13**) (0.25 mmol) in dry THF (15 mL) was added with a syringe. The mixture was stirred for 1 h at −78 °C and then allowed to warm to 20 °C and kept at this temperature overnight. The THF was evaporated under reduced pressure, water (75 mL) was added, and the residue was extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane/dichloromethane (9:1) as eluent.

2-Iodo-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (17): 62% yield; mp 259−260 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.01 (d, 1H, J_2 = 1.8 Hz, ArH), 7.71−7.66 (m, 2H, ArH), 7.60 (dd, 1H, J_1 = 8.2 Hz, J_2 = 1.8 Hz, ArH), 7.43 (d, 1H, J_1 = 8.2 Hz, ArH), 7.32−7.28 (m, 2H, ArH), 6.33 (s, 2H), 6.31 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.2, 142.3, 139.8, 139.3, 134.0, 132.0, 128.8, 127.9, 127.1, 119.6, 117.2, 114.3; FTIR (KBr) 2924, 2852, 2183, 1545, 1516, 1452, 1394, 756, 646, 623, 501 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 430, 366, 238 nm; MS (EI) *m*/*z* 506 (M^+, 68), 380 (M^+ − I, 36). Anal. Calcd for $C_{20}H_{11}IS_4$: C, 47.43; H, 2.19. Found: C, 47.23; H, 2.09.

2-Vinyl-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (18): 65% yield; mp 186−187 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.77 (d, 1H, J_2 = 1.7 Hz, ArH), 7.71−7.68 (m, 2H, ArH), 7.66 (d, 1H, J_1 = 8.2 Hz, ArH), 7.34−7.28 (m, 3H, ArH), 6.77 (dd, 1H, J_1 = 17.4 Hz, J_2 = 11.0 Hz), 6.32 (s, 2H), 6.31 (s, 2H), 5.80 (d, 1H, J_1 = 17.4 Hz), 5.28 (d, 1H, J_2 = 11.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 136.6, 135.7, 135.3, 125.9, 125.1, 124.9, 123.9, 122.6, 117.2, 113.8; FTIR (KBr) 2924, 2852, 2362, 2345, 1630, 1545, 1508, 995, 800, 752, 648 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 434, 370, 287 (sh), 250 nm; MS (EI), *m*/*z* 406 (M^+). Anal. Calcd for $C_{22}H_{14}S_4$: C, 64.98; H, 3.47. Found: C, 64.75; H, 3.18.

1-(Anthraquinon-2-yl)-2-[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl]ethylene (19). To a solution of the exTTF iodo derivative (**17**) (230 mg, 0.45 mmol) and 2-vinyl-9,10-anthraquinone (**13**) (106 mg, 0.45 mmol), in dry toluene (100 mL) and under argon atmosphere, were added $(MeCN)_2PdCl_2$ (39 mg, 150 μmol), NBu_4Br (145 mg, 0.45 mmol) and triethylamine (1.5 mL). The resulting reaction mixture was refluxed for 22 h. The solvent was removed under vacuo, and the residue was chromatographed on silica gel using hexane/dichloromethane (1:1) as eluent. The isolated product was obtained as a deep red solid: 31% yield; mp 204−205 °C;

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[26] Fernández-Refojo, M.; Pan, Y.-L.; Kun, K. A.; Cassidy, H. G. *J. Org. Chem.* **1960**, *25*, 416.

^{1}H NMR (DMSO-d_6, 300 MHz) δ 8.41 (s, 1H, ArH), 8.26−8.21 (m, 4H, ArH), 8.00 (s, 1H, ArH), 7.96−7.93 (m, 2H, ArH), 7.73−7.66 (m, 5H), 7.58 (d, 1H, $J = 16.3$ Hz), 7.39−7.36 (m, 2H, ArH), 6.79 (m, 4H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 182.5 (CO), 181.9 (CO), 143.0, 137.2, 137.1, 135.2, 134.8, 134.5, 134.4, 134.2, 133.5, 133.1, 133.0, 132.2, 131.6, 131.5, 127.5, 127.0, 126.6, 126.2, 125.0, 124.9, 124.6, 123.3, 120.4, 120.3, 118.3, 118.2, 118.0; FTIR (KBr) 2924, 2363, 2343, 1672, 1591, 1545, 1508, 1327, 1298, 957, 933, 750, 708, 658 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} 523, 428, 371, 317, 252 nm; MS (ES) m/z 612 (M$^+$). Anal. Calcd for $C_{36}H_{20}O_2S_4$: C, 70.56; H, 3.29. Found: C, 70.28; H, 3.36.

1-[9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl]-2-{9,10-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-9,10-dihydroanthracen-2-yl}ethylene (20). To a solution of the phosphonate ester (**15b**) (1.8 g, 6 mmol) in dry THF (120 mL) at −78 °C and under argon atmosphere was added *n*-butyllithium (1.6 M) (4.1 mL, 6.6 mmol). After 1 h at −78 °C, a solution of the quinone **19** in dry THF (612 mg, 1 mmol) was added with a syringe. The mixture was stirred for 1 h at −78 °C and then allowed to warm to 20 °C and kept at this temperature overnight. The THF was evaporated under reduced pressure, water (100 mL) was added, and the residue was extracted with CH$_2$Cl$_2$ (3 × 50 mL). The combined extracts were dried (MgSO$_4$) and filtered, and the solvent was removed under reduced pressure. Purification of the product was achieved by column chromatography on silica gel using hexane/dichloromethane (2:1) as eluent. The purified product was isolated as a yellow solid: 58% yield; mp 232−233 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.89−7.85 (m, 1H, ArH), 7.72−7.68 (m, 4H, ArH), 7.59−7.53 (m, 3H), 7.48−7.41 (m, 2H, ArH), 7.36−7.28 (m, 4H, ArH), 7.19−7.17 (m, 2H, ArH), 6.30 (d, 4H, $J = 1.5$ Hz), 2.39 (s, 12H, 4SMe), ^{13}C NMR (CDCl$_3$, 75 MHz) δ 135.9, 135.8, 135.7, 135.6, 135.5, 135.3, 135.2, 135.0, 134.8, 134.5, 133.8, 131.2, 131.0, 129.0, 128.9, 128.2, 126.4, 126.3, 125.9, 125.7, 125.6, 125.4, 125.3 (2C), 124.9, 124.4, 124.3, 123.6, 123.5, 123.4, 123.1, 123.0, 122.9, 122.8, 117.3, 117.2 (2C), 117.1, 19.2 (SCH$_3$), 19.1 (SCH$_3$); FTIR (KBr) 2920, 2852, 2281, 1701, 1545, 1508, 1498, 1452, 1420, 1257, 959, 800, 754, 638 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} 443, 396, 327, 273, 236 nm; MS (ES), m/z 968 (M$^+$). Anal. Calcd for $C_{46}H_{32}S_{12}$: C, 56.99; H, 3.33. Found: C, 57.25; H, 3.48.

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