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Synthesis and properties of π-extended triads (A_2D) derived from tetrathiafulvalene (TTF) and tetracyano-*p*-quinodimethane (TCNQ)

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Abstract—A new series of electroactive triads (**10a–c**) has been prepared by Knoevenagel condensation of formyl-containing π-extended TTFs (**9a–c**) to a suitably functionalized dimer (**8**) derived from the electron acceptor TCAQ. The electronic spectra of the triads (**10a–c**) show the presence of an intramolecular charge transfer (ICT) band from the donor π-extended TTF unit to the conjugated carbonyl groups. Theoretical calculations at the semiempirical PM3 level predict different geometrical structures for the triads which rule out a through space electronic interaction between the donor (π-extended TTF) and acceptor (TCAQs) moieties. Cyclic voltammetric measurements reveal the amphoteric behaviour of triads **10a–c** and a negligible electronic interaction between the redox chromophores. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Electroactive molecules bearing both electron-donor and electron-acceptor moieties covalently connected through a chemical spacer have received a great deal of attention as they are of interest in fields such as molecular electronics,[1] artificial photosynthetic models,[2] non-linear optics[3] and solvatochromic effects.[4] Among the wide variety of electron donor and acceptor molecules used in the preparation of donor-acceptor (D–A) systems, tetrathiafulvalene (TTF)[5] and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ)[6] have been successfully modified in the search of unconventional optoelectronic properties.

Extended π-donor analogues (**1**) in which both dithiole rings are separated by a *p*-quinodimethane moiety are of particular interest since they oxidize at lower potential values[7] and form highly stable dicationic species.[8]

We have recently reported that π-extended TTF derivatives linked to the electron-acceptor C_{60} (**2**) result in long lifetime charge-separated states which is a basic requirement for their application in photovoltaic devices.[9] In addition, π-extended TTF derivatives of type D-π-A (**3**) behave as efficient NLO chromophores.[10]

On the other hand, extended π-acceptors (such as **4**) derived from TCNQ present unique geometrical and electrochemical properties which have been used for the preparation of systems exhibiting intra- and intermolecular photoinduced electron-transfer properties.[11,12] It is interesting to note that, despite the interest of the TCNQ molecule for many applications which has allowed the synthesis of a wide variety of TCNQ derivatives,[6] dimeric acceptors are almost unknown.[13] The first example of dimeric highly conjugated π-electron acceptors derived from TCNQ in which both monomeric units are connected through an oxygen atom as spacer (**5**) has been only recently reported.[14] Cyclic voltammetric studies carried out on compound **5** indicate that this dimer behaves electrochemically as two independent units, showing only one, four-electron, chemically reversible reduction wave at -0.340 ($4e^-$) V vs. SCE in CH_2Cl_2. This behaviour has been accounted for by the oxygen bridge which prevents conjugation between the two electron-acceptor units (Chart 1).

In this paper we describe the synthesis and electrochemistry of a novel TCNQ dimer (**8**) which is suitably functionalized with an active methylene unit for further chemical transformations. From dimer **8** a series of novel electroactive triads (**10a–c**) has been prepared by linking a π-extended donor derived from TTF with a *p*-quinodimethane moiety. The electronic spectra of the novel triads **10a–c** reveal the presence of an intramolecular charge-transfer (CT) band and the cyclic voltammetry (CV) measurements carried out in solution at different temperatures show that these compounds exhibit an amphoteric redox behavior.

Keywords: tetrathiafulvalene; synthesis; donor–acceptor systems; tetracyano-*p*-quinodimethane.

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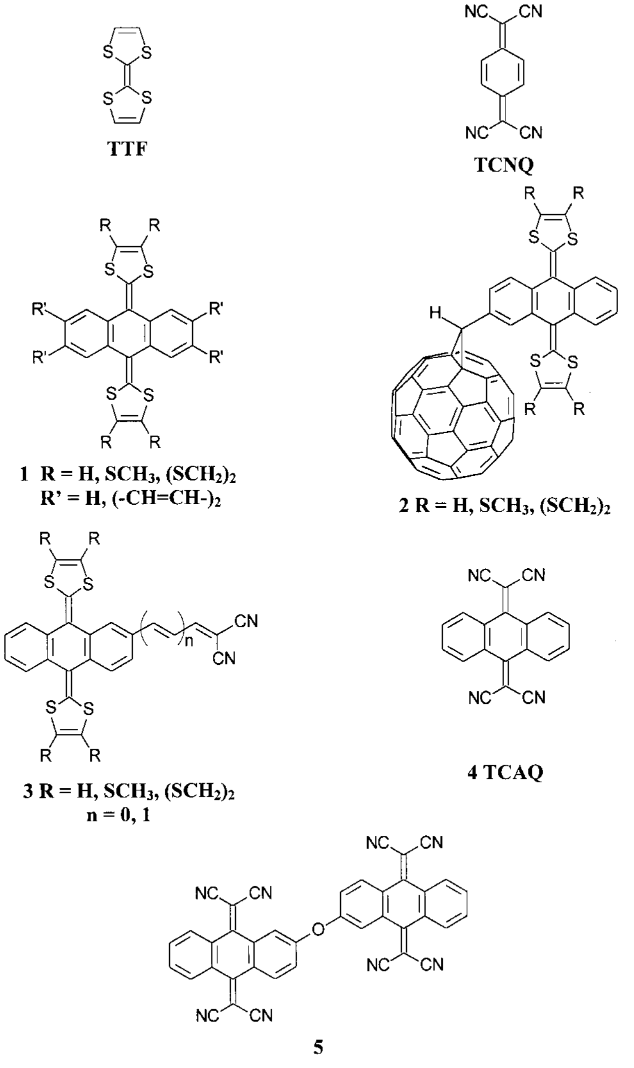
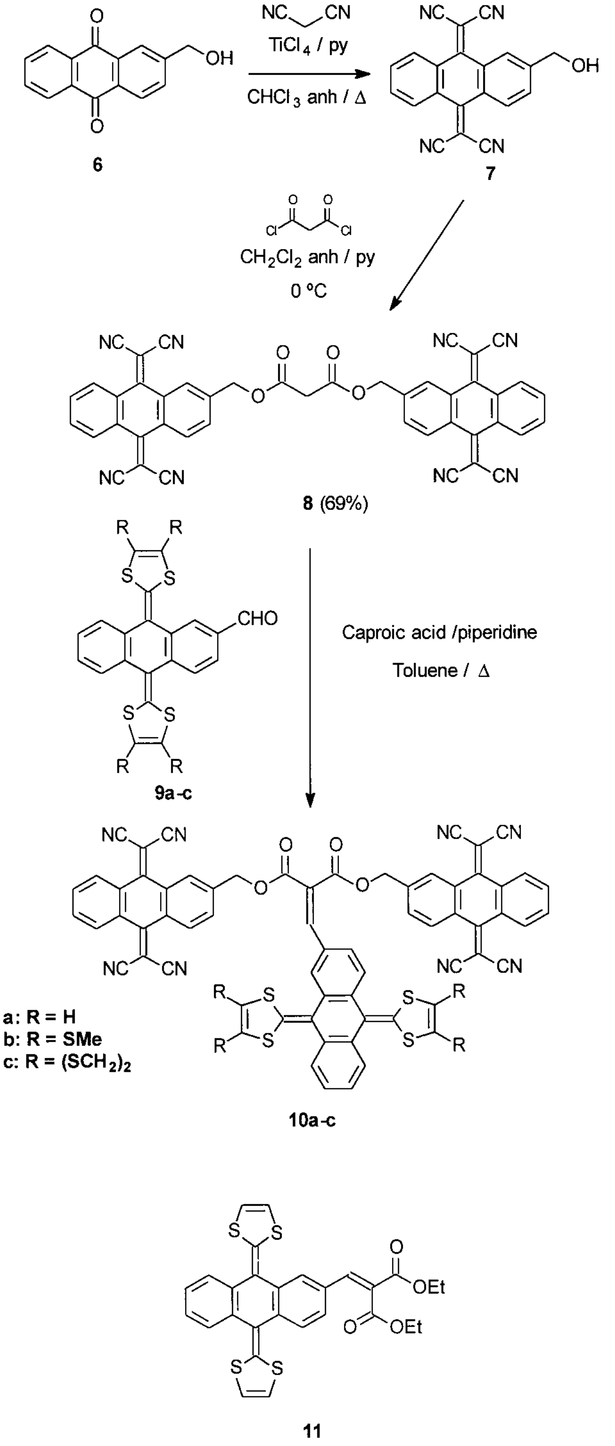


Chart 1.



Scheme 1.

2. Results and discussion

2.1. Synthesis

The preparation of the new TCAQ dimer **8** as well as the further formation of triads **10a–c** are depicted in Scheme 1. The synthesis of dimer **8** was carried out in two steps from commercially available 2-hydroxymethyl-9,10-anthraquinone (**6**) by reaction with Lehnert reagent[15] ($TiCl_4$, malononitrile, pyridine) by following Hünig's procedure.[16] Thus, 2-hydroxymethyl substituted TCAQ (**7**)[17] was obtained as a stable yellow solid in 64% yield. Dimer **8** was obtained from **7** by reaction with malonyl dichloride at 0°C in the presence of pyridine in 69% yield. Dimer **8** shows in the FTIR spectrum the presence of the conjugated cyano groups at 2227 cm^{-1}. This relatively high value for the stretching vibration of the cyano group clearly indicates the lack of planarity of the TCAQ units, which is in agreement with the data found for the parent TCAQ (2212 cm^{-1}) and other related structures.[18] In addition, the carbonyl groups in **8** appear as a band at 1739 cm^{-1}.

Triads **10a–c** were prepared from **8** by Knoevenagel condensation with the formyl containing donors **9a–c**[19] using caproic acid/piperidine as the catalyst in refluxing toluene with azeotropic distillation (Dean–Stark) of the water generated in the reaction medium. Compounds **10a–c** were obtained as stable red solids in moderate yields (23–30%).

The FTIR spectra of triads **10a–c** show the cyano groups at 2226 cm^{-1} and the carbonyl groups at 1732 cm^{-1} which suggests a strong influence of the donor moiety on the carbonyl groups. The presence of the TTF derivative in **10a–c** breaks the symmetry showed by dimer **8** and, therefore, two carbonyl groups are observed in the ^{13}C NMR spectra (see Experimental).

Interestingly, triads **10a–c** show in the UV–V is spectra the presence of a weak and broad band centered at around 500 nm which is not present neither dimer **8** nor donor **9a–c**. This band clearly indicates the presence of a charge-transfer from the electron-donor unit to an acceptor moiety. Since both π-extended TTF donor and the TCAQ acceptors are not in conjugation through the chemical spacer, two plausible explanations could account for the experimental UV–Vis findings: (i) a through space intramolecular donor-acceptor electronic interaction or (ii) a through π-bond charge-transfer process from the π-extended TTF donor to the conjugated carbonyl groups acting as acceptors. (Fig. 1).

Theoretical calculations carried out at the semiempirical PM3 level clearly indicate that triads **10a–c** do not present a suitable geometry for the through space intramolecular electronic interaction (see below), thus ruling out this possibility. This finding is also supported by the stretching vibration of the cyano groups of **10a–c** (2226–2227 cm^{-1}) and their precursor **8** (2227 cm^{-1}) which suggest no significant ICT process onto the TCAQ units.

Fig. 1 shows the UV–Vis spectra of triads **10a–c** as well as that of dimer **8** and donor **1** (R=R′=H) for comparison purposes. From the observation of Fig. 1 it is clear that the CT band stems from the interaction of donor unit with the dicarbonyl moiety. Fig. 2 displays the electronic spectra of **10a** in solvents of different polarity, namely CH_2Cl_2 (ϵ=8.93), toluene (ϵ=2.38) and CH_3CN (ϵ=35.94). From this Fig. 2, no significant solvatochromic effect is observed on the position of the 500 nm band.

In order to prove the intramolecular CT character of these bands, we carried out the synthesis of compound **11** in which the donor unit is covalently connected to the malonic ester through a vinyl spacer. A similar CT-band was observed at 470 nm which is in agreement with some related structures exhibiting NLO behavior (Fig. 1).[10]

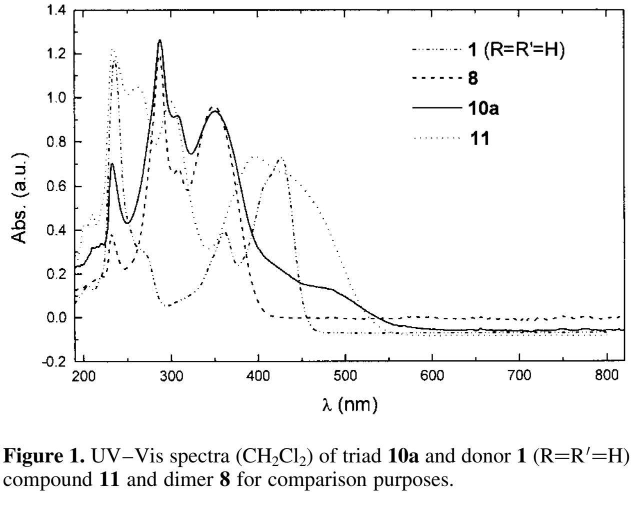


Figure 1. UV–Vis spectra (CH_2Cl_2) of triad **10a** and donor **1** (R=R′=H), compound **11** and dimer **8** for comparison purposes.

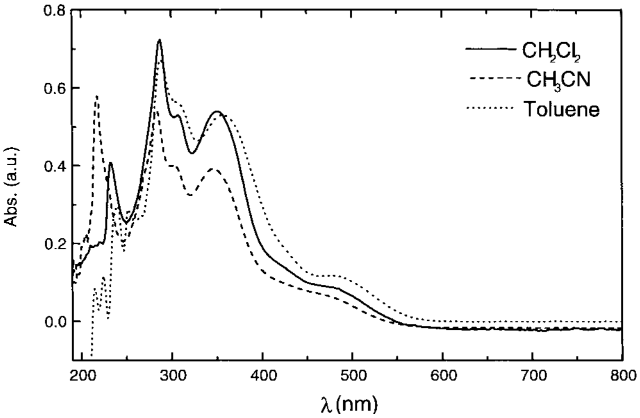


Figure 2. Electronic spectra of **10a** in solvents of different polarity, namely CH_2Cl_2, toluene, CH_3CN.

2.2. Electrochemistry

The redox properties of dimer **8** and triads **10a–c** were studied by cyclic voltammetry (CV) in methylene dichloride solution at different temperatures. Table 1 shows the redox potential values of the novel compounds along with that of TCAQ (**4**) and donor **1** (R=R′=H) for comparison purposes.

As expected, dimer **8** shows the presence of only one quasireversible reduction wave at −0.371 V which indicates that both tetracyano-9-10-anthraquinodimethane (TCAQ) moieties behave independently and, therefore, is quite similar to that found for the monomeric TCAQ (see Table 1).

It has been previously reported that the number of electrons involved in the reduction process of TCAQ is of 2e$^-$ according to the controlled potential coulometric analysis.[20] Therefore, the redox wave in the CV of **8** corresponds to an overall process leading to the tetraanion ($A–A+4e^- \rightleftharpoons A^{2-}–A^{2-}$). ESR studies carried out on the parent TCAQ suggest that a coproportionation reaction ($A+A^{2-} \rightleftharpoons 2A^{\cdot -}$) could also take place is some extent[21] and, consequently, this process can not be ruled out in the dimeric compound **8**.

Triads **10a–c** also show the quasireversible reduction wave of the two TCAQ moieties which appear at reduction potential values which are slightly cathodically shifted related to the parent TCAQ than dimer **8**. On the oxidation side, triads

Table 1. Redox potentials of the structures **8**, **10a–c**, and TCAQ as reference compounds at room temperature

Compounds	E^a_{Red}	E^a_{ox}
1 (R=R′=H)	–	0.44
8	−0.371 (−0.299)[b]	–
10a	−0.389 (−0.249)	0.496 (0.201)
10b	−0.370 (−0.255)	0.585 (0.270)
10c	−0.423 (−0.238)	0.627 (0.252)
TCAQ (**4**)	−0.375 (−0.191)	–

[a] All potentials in V vs. SCE; CH_2Cl_2 as solvent; scan rate 200 mV/s; 0.1 mol dm^{-3} $Bu_4N^+ClO_4^-$ as supporting electrolyte; GCE as working electrode.

[b] Re-oxidation potential values.

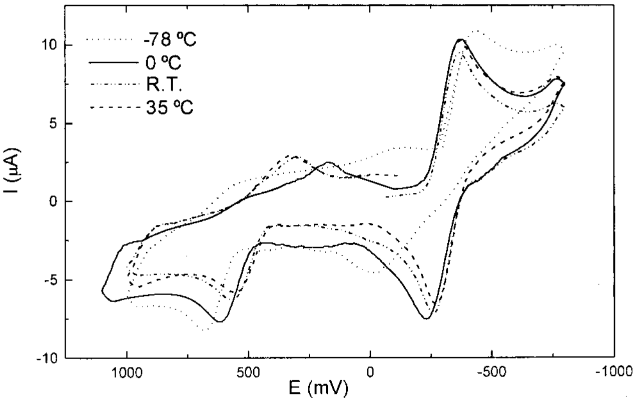


Figure 3. Cyclic voltammetry of triad **10b** at different temperatures in CH_2Cl_2 at 200 mV s^{-1}.

10a–c exhibit the presence of only one oxidation wave involving two electrons to form the dication, in a similar way to that found for the parent compound **1** (R=R′=H).

As it is shown in Table 1, substitution on the 1,3-dithiole ring has a profound impact on the oxidation potential values. Thus, **10a** is slightly easier to oxidize than **10b** and **10c**.

Fig. 3 displays the electrochemical redox behavior of compound **10b** at different temperatures. The voltammograms were recorded at 35°C, RT, 0°C and −78°C. The oxidation potential values are anodically shifted with decreasing the temperature [E_{ox} (35°C)=0.560 V; E_{ox} (RT)= 0.585 V; E_{ox} (0°C)=0.620 V; E_{ox} (−78°C)= 0.690 V]; which indicates a higher difficulty for the formation of the dication species. The reduction wave associated to the reduction of the dication to the neutral molecule also undergoes a remarkable cathodic shift to lower potentials when lowering the temperature [E_{red} (35°C)=0.315 V; E_{red} (RT)= 0.270 V; E_{red} (0°C)=0.170 V; E_{red} (−78°C)=−0.130 V]. This loss of electrochemical reversibility of these systems with decreasing the temperature is in agreement with that previously observed for compounds of type **1**[7,8] which has been accounted for by the high stability of the dication species.[8]

Fig. 3 also shows the reduction wave involving four electrons of the two TCAQ units. In this case, the reduction potentials are much less affected by the decreasing of the temperature. Thus, the reduction potential values are almost the same from 35°C to 0°C and only at lower temperatures deviate significantly [E_{red} (35°C)=−0.375 V; E_{red} (RT)= −0.370 V; E_{red} (0°C)=−0.380 V; E_{red} (−78°C)= −0.450 V]. The oxidation wave associated to the process 2(acceptor^{2-}→acceptor°) is more influenced by the temperature [E_{ox} (35°C)=−0.270 V; E_{ox} (RT)=−0.255 V; E_{ox} (0°C)=−0.230 V; E_{ox} (−78°C)=−0.004 V] which results in a much more irreversible system at −78°C.

The cyclic voltammetry reveals the high stability of the formed dication species upon oxidation on the donor fragment, as well as the stability of the dianion species formed upon reduction on both TCAQ moieties. This remarkable stability of the different ionic species formed upon oxidation as well as reduction processes has been accounted for by gain of aromaticity and planarity.

Therefore, these largely π-extended acceptor-donor-acceptor triads are appealing systems for further photophysical studies in the search of systems exhibiting long live charge separated states.

2.3. Molecular structure

The molecular geometry of compound **10a** has been optimized by using semiempirical calculations at the PM3 level.[22] This method provides a good description of the interactions taking place between nonbonded atoms such as hydrogen bonding or steric interactions. The latter are especially important for the molecules studied in this work since they determine the planarity of the system.

It has been previously reported that theoretical calculations carried out for π-extended TTFs[8] as well as TCAQ derivatives[23] show a good agreement between theory and experiment and demonstrate that the PM3 method provides a good description, even better than ab initio HF/6-31G* calculations, of the molecular structure of π-extended TTFs.[8]

Fig. 4 displays the minimum-energy conformation of **10a**.

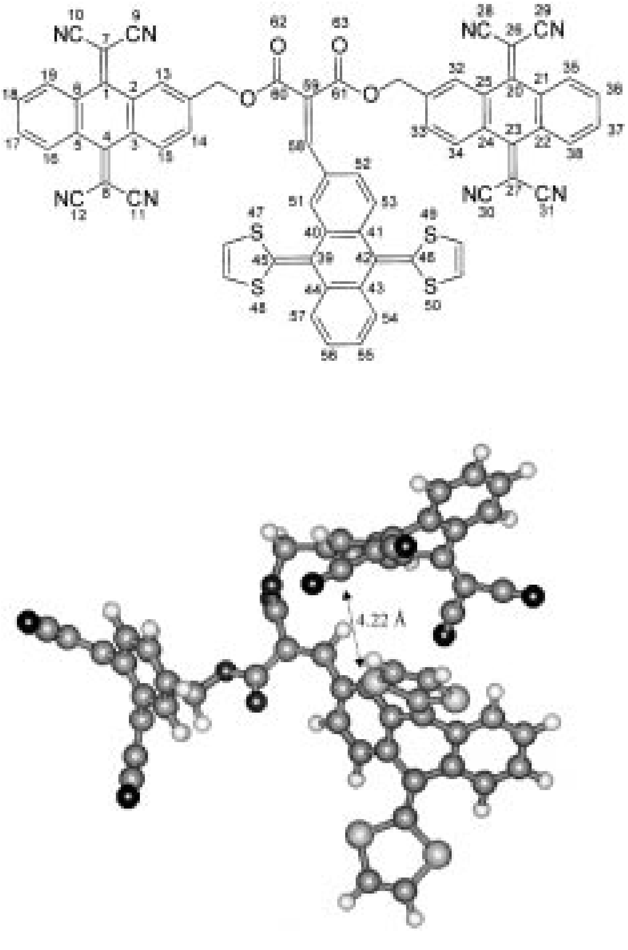


Figure 4. Optimized molecular geometry of **10a** at the semiempirical PM3 level, showing the closest distance between the donor and acceptor moieties.

In addition to this molecular structure, some other different conformations were found depending upon the orientation of the fused benzene rings on the TTF and TCNQ moieties. These conformations exhibited heats of formation with energy differences lower than 1 kcal/mol in comparison with that depicted in Fig. 4.

Both π-extended TTF moiety and the two TCAQ units showed, as expected, a highly distorted geometry out of the planarity. The planar conformation of the π-extended TTF moiety is strongly hindered by the sort distance between the *peri* hydrogens and the sulfur atoms (1.78 Å). To avoid these interactions the molecule adopts a butterfly-shaped non-planar geometry with the central ring in a boat conformation. (distance S···H. 2.62 Å).

The same behavior is observed for both TCAQ systems which also show a butterfly-shaped geometry. The calculated distance C···H and N···H between the CN groups and the hydrogens in *peri* positions are 1.898 and 2.256 Å, respectively.[23] These distances are remarkably shorter than the sum of the van der Waals radii (2.90 and 2.75 Å, respectively).[24] To alleviate the steric hindrance, the molecule adopts a nonplanar structure.

Distortions from the planarity can be described in terms of the angles α and γ. Angle α corresponds to the angle formed by the outer benzene rings (the wings of the butterfly), and γ defines the tilting of the dithiole units in the donor moiety and the $C(CN)_2$ groups in the TCAQs, with respect to the C2–C3–C5–C6 and C40–C41–C43–C44, respectively. These calculated angles (α=139.7° and γ=36.1° for the π-extended TTF unit; α=140.1° and γ=36.5° for the TCAQ units) are in good accord with those from X-ray data for the parent TCAQ (**4**) (146.1° and 30.4°, respectively)[25] as well as the parent donor **1** (R=R′=SMe) (143.8 and 33.3°, respectively).[7b] These small differences can be accounted for since theoretical calculations are performed on isolated molecules and packing forces tend to planarize the molecules in the crystal to achieve the most compact packing along the molecular stacks.

Fig. 4 shows that both carbonyl groups of compound **10a** are not coplanar, showing angles of C58–C59–C60–C62=94.3° and C58–C59–C61–C63=29.4°. The calculated energy for the molecule with both coplanar carbonyl groups resulted to be 11.6 kcal/mol higher in energy, thus supporting the loss of planarity for the most favorable conformation.

Fig. 4 also presents the closest distance between the π-extended TTF donor and the acceptor TCAQ which is of 4.2 Å (distance S(dithiole)···C(C≡N)). This finding rules out a possible through space electronic interaction between both donor and acceptor redox chromophores, thus confirming the through bond charge-transfer between the donor unit and the conjugated carbonyl groups.

In summary, we report a new type of triads (**10a–c**) constituted by two π-extended acceptors (TCAQ) and one π-extended TTF unit, obtained by Knoevenagel condensation from a suitably functionalized TCAQ dimer (**8**) and the formyl-containing TTF derivatives (**9a–c**). Although the cyclic voltammetric measurements reveal no significant electronic interactions between the redox active units, the electronic spectra of triads **10a–c** present an intramolecular charge transfer band (ICT) from the TTF derivative donor unit to the conjugated carbonyl groups. Theoretical calculations present a highly distorted molecule out of the planarity and confirm the lack of through space electronic interaction between both donor and acceptors moieties.

The molecules now reported are appealing systems for further photophysical studies due to the high stability of the dication and dianion species formed upon oxidation and reduction, respectively. This study is currently under investigation.

4. Experimental

4.1. General

Melting points were measured on a Thermolab apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were measured with a Varian Unity XL-300 and a Bruker AC-200. Mass spectra (EI^+, 70 eV) were obtained on a VG Autospec EBE mass spectrometer. The FTIR spectra were recorded with a Nicolet Magna-IR spectrometer 5550 or with an FTIR-8300. Optical absorption spectra were measured with a Hewlett–Packard-8452 A Spectrophotometer. Cyclic voltammetry measurements were performed on an EG & G PAR Versastat potentiostat using 250 Electrochemical Analysis Software. A Metrohm 6.0804.C10 glassy carbon electrode was used as indicator electrode in voltammetric studies, 1×10^{-5} M solutions of the compound in methylene dichloride, 0.1 M Bu_4NClO_4 as the supporting electrolyte, platinum working as counter electrode, saturated calomels electrode (SCE) as reference electrode at 20°C.

All reagents were used as purchased unless otherwise stated. All solvents were dried according to standard procedures.

Semiempirical calculations were carried out at the PM3/RHF level with the Hyperchem 5.1 program package.

4.1.1. Di-[9,10-bis(dicyanomethylen)-2-anthraquinonyl-methyl]malonate (8). To a solution of 2-hidroxymethyl-9,10-bis(dicyanomethylen)anthraquinone **7**[17] (167 mg, 0.5 mmol) in 30 mL of dry methylene dichloride, dry pyridine (0.03 mL, 0.495 mmol) was added under argon atmosphere. The resulting solution was cooled on an ice bath to 0°C, and then, malonate dichloride (0.02 mL, 0.245 mmol) in a methylene dichloride solution (1 mL) was added slowly. After the mixture was stirred for 2 h at 0°C, stirring continued at rt overnight. Water was added (75 mL), and the solution was washed three times with methylene dichloride (3×75 mL). The organic phase was dried over sodium sulfate. After solvent evaporation, the crude material was purified by column chromatography (silica gel) using a mixture hexane/ethyl acetate (1:1) as eluent. 69% yield, mp 170–172°C (dec.). FTIR (KBr disk) ν (cm^{-1}): 2227 (C≡N), 1739 (C=O); 1538; 1562, 1465, 1375, 1335, 1280, 1261, 1136, 1017, 831, 815 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ: 8.28–8.23 (m, 8H, ArH), 7.80–7.67 (m, 6H, ArH), 5.35 (s, 4H, CH_2O–), 3.63 (s, 2H, $COCH_2CO$). ^{13}C NMR ($CDCl_3$, 62 MHz) δ: 165.7 (C=O), 159.6, 159.5, 140.6, 132.6, 131.1, 130.6, 130.1, 130.0, 129.8, 127.8, 127.6, 126.4, 113.0 (CN), 112.9 (CN), 83.49, 65.4 (CH_2O–); 40.9 ($COCH_2CO$). UV–Vis (CH_2Cl_2) λ_{max} (log ϵ) nm: 350 (453), 308 (438), 288 (462), 232 (413). MS m/z: 759 (M^++Na, 56). $C_{45}H_{20}O_4N_8$: calcd C 73.35; H 2.74; N 15.22; found C 73.56; H 2.78; N 14.91.

4.2. Synthesis of triads 10a–c

General Procedure. A solution of the di-[9,10-bis(dicyanomethylen)-2-anthraquinonylmethyl] malonate (**8**) (50 mg, 0.068 mmol) or diethyl malonate (**11**) (25 mg, 0.156 mmol), the corresponding substituted 2-formyl-9,10-bis-(1,3-dithiol-2-ylidine)dihydroanthracene (**9a–c**) (0.068 or 0.156 mmol, respectively), and drops of caproic acid and piperidine in toluene (50 mL), was refluxed with azeotropic distillation using a Dean–Stark for 5 h. The solvent was removed under reduced pressure and the isolation of the final products was performed by careful flash chromatography, using silica gel and hexane/ethyl acetate (1:1) as eluent.

4.2.1. 2-{2′,2′-Di[9,10-bis(dicyanomethylen)-2-anthraquinonylmethyloxycarbonyl]}vinyl-9,10-bis (1,3-dithiol-2-ylidene)dihydroanthracene (10a). 23 mg (30% yield), mp 241–243°C. FTIR (KBr disk) ν (cm^{-1}): 3071, 2954, 2226 ($C{\equiv}N$), 1732 (C=O), 1621, 1549, 1507, 1453, 1419, 1385, 1329, 1283, 1250, 1190, 1114, 1066, 1012, 899, 833, 802, 764, 693, 656, 584, 502. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 8.27–8.22 (m, 12H, ArH), 7.80–7.69 (m, 10H, ArH), 6.36–6.29 (m, 4H), 5.46 (m, 4H, CH_2O–). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 165.7 (C=O), 163.4 (C=O), 159.9, 159.7, 159.6 (3C), 140.9, 140.1, 138.5, 137.3, 136.0, 135.0, 134.7, 132.5, 132.4, 130.9, 130.7, 130.1, 130.0, 129.9, 129.8, 129.7, 127.9, 127.7, 127.6, (2C), 127.5 (2C), 127.4, 127.1, 126.3, 126.2, 126.1, 125.0, 124.9, 124.8, 124.6, 117.7, 117.5, 117.4, 117.3, 117.1, 113.0, 112.9 (4C, $C{\equiv}N$), 83.6, 83.4, 83.2, 83.1, 77.2, 65.4 (CH_2O–). UV–Vis (CH_2Cl_2) λ_{max} (log ϵ) nm: 486 (4.02), 352 (4.76), 308 (4.75), 288 (4.89), 232 (4.64). M.S. m/z: 1026 (M^+). $C_{66}H_{30}O_4N_8s_4$·1 AcOEt: calcd C 71.05; H 3.24; N 9.48; S 10.82; found C 70.42; H 3.66; N 9.20; S 9.71.

4.2.2. 2-{2′,2′-Di[9,10-bis(dicyanomethylen)-2-anthraquinonylmethyloxycarbonyl]}vinyl-9,10-bis (1,3-dithiol-4,5-dimethylthio-2-ylidene)dihydroanthracene. (10b). 20 mg (23% yield), mp 220–222°C. FTIR (KBr disk) ν (cm^{-1}): 2924, 2227 ($C{\equiv}N$), 1735 (C=O), 1632, 1554, 1494, 1454, 1426, 1341, 1284, 1251, 1194, 1066, 834, 766, 694, 640. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 8.27–8.23 (m, 10H, ArH), 7.77–7.32 (m, 12H, ArH), 5.46 (m, 4H, CH_2O–), 2.41 (m, 3H), 2.40 (m, 3H), 2.39 (m, 3H), 2.38 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 165.6 (C=O), 163.5 (C=O), 159.9, 159.7, 159.6, 156.0, 155.9, 140.8, 140.3, 135.3, 134.3, 134.0, 133.9, 132.6, 131.0, 130.7, 130.5, 130.0, 129.9, 129.8, 127.9 (2C), 127.8, 127.7, 127.6, 127.5, 126.6, 126.5, 126.3, 126.2, 125.6, 125.4, 125.3, 125.2, 113.0 ($C{\equiv}N$), 112.9 (3C, $C{\equiv}N$), 83.6, 83.6 (4C), 77.2, 65.8 (CH_2O–), 65.5 (CH_2O–), 19.2, (SCH_3), 19.1 (SCH_3). UV–Vis (CH_2Cl_2) λ_{max} (log ϵ) nm: 450 (4.20), 348 (4.74), 308 (4.75), 286 (4.89), 234 (4.73). M.S. m/z: 1310 (M^+). $C_{70}H_{38}O_4N_8S_8$·1 AcOEt: calcd C 64.12; H 2.92; N 8.55; S 19.52; found C 63.50; H 3.31; N 8.01; S 19.32.

4.2.3. 2-{2′,2′-Di[9,10-bis(dicyanomethylen)-2-anthraquinonylmethyloxycarbonyl]}vinyl-9,10-bis (1,3-dithiol-4,5-ethylenedithio-2-ylidene)dihydroanthracene. (10c). 22 mg (25% yield), mp 249–252°C. FTIR (KBr disk) ν (cm^{-1}): 2924, 2227 ($C{\equiv}N$), 1735 (C=O), 1623, 1555, 1509, 1454, 1416, 1385, 1341, 1285, 1251, 1194, 1114, 1066, 1012, 923, 835, 765, 693, 639, 506. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 8.32–7.11 (m, 22H, ArH), 5.47 (m, 4H, CH_2O–), 3.42–3.27 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 163.3 (2C, C=O), 159.7, 159.6, 140.9, 140.1, 134.1, 133.9, 132.5, 132.3, 131.1, 130.8, 130.7, 130.1, 139.8, 127.9, 127.7, 127.6, 126.7, 126.6, 126.3, 125.3, 125.1, 113.2 ($C{\equiv}N$), 113.0 (3C, $C{\equiv}N$), 112.8, 111.1, 110.42, 83.7, 83.6, 83.2, 77.2, 65.5 (CH_2O–), 29.5 (SCH_2), 29.4 (SCH_2). UV–Vis (CH_2Cl_2) λ_{max} (log ϵ) nm: 434 (4.20), 346 (4.73), 310 (4.75), 288 (4.89), 234 (4.76). MS m/z: 1306 (M^+). $C_{70}H_{34}O_4N_8S_8$·1 AcOEt: calcd C 63.68; H 3.03; N 8.03; S 18.38; found C 61.98; H 3.36; N 7.68; S 18.33.

4.2.4. 2(2′,2′-Diethoxycarbonyl)vinyl-9,10-bis(1,3-dithiol-2-ylidene)dihydroanthracene. (11). 39 mg (46% yield), mp 194–197°C. FTIR (KBr disk) ν (cm^{-1}): 2922, 2851, 1718 (C=O), 1707, 1624, 1599, 1543, 1508, 1500, 1448, 1252, 1207, 1059, 796, 754, 741, 685, 644, 631, 617. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.78 (d, 1H, J=1.70 Hz), 7.75–7.66 (m, 3H), 7.40 (dd, 1H, J_1=8.06 Hz, J_2=1.70 Hz), 7.35–7.28 (m, 2H), 6,33 (m, 4H), 4.38 (m, 4H, CH_2O–), 1.33 (m, 6H, CH_3CH_2O–). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 166.8 (C=O), 164.4 (C=O), 141.7, 137.8, 137.6, 136.8, 135.9, 135.2, 135.0, 130.1, 127.2, 126.4, 126.1 (2C), 125.3, 125.2, 125.0, 124.8, 121.4, 121.1, 117.4, 117.3, 117.2, 117.1. UV–Vis (CH_2Cl_2) λ_{max} (log ϵ) nm: 470 (4.12), 396 (4.18), 299 (4.29), 261 (4.32), 234 (4.38). M.S. m/z: 550 (M^+).

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