TTF-Based Mixed-Valence Acceptor-Donor-Acceptor Triads: A Joint Theoretical and Experimental Approach

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Abstract

This work presents a joint theoretical and experimental characterization of the structural and electronic properties of two tetrathiafulvalene (TTF)-based acceptor-donor-acceptor triads (BQ-TTF-BQ and BTCNQ-TTF-BTCNQ, where BQ is naphthoquinone and BTCNQ is benztetracyano-*p*-quinodimethane) in their neutral and reduced states. The study is performed making use of electrochemical, electron paramagnetic resonance (EPR), and UV-Vis-NIR spectroelectrochemical techniques guided by quantum-chemical calculations. Emphasis is especially made on the mixed-valence properties of both triads in their radical anion states. The electrochemical and EPR results reveal that both BQ-TTF-BQ and BTCNQ-TTF-BTCNQ triads in their radical anion states behave as class II mixed-valence compounds with significant electronic communication between the acceptor moieties. Density functional theory calculations (BLYP35/cc-pVTZ) taking into account the solvent effects predict charge-localized species ($\text{BQ}^{\cdot-}$ -TTF-BQ and $\text{BTCNQ}^{\cdot-}$ -TTF-BTCNQ) as the most stable structures for the radical anion states of both triads. A stronger localization is found both experimentally and theoretically for the BTCNQ-TTF-BTCNQ anion in accordance with the more electron-withdrawing character of the BTCNQ acceptor. CASSCF/CASPT2 calculations suggest that the low-energy, broad absorption bands experimentally observed for BQ-TTF-BQ and BTCNQ-TTF-BTCNQ radical anions are associated with the intervalence charge transfer (IV-CT) electronic transition and two nearby donor-to-acceptor CT excitations. The study highlights the molecular efficiency of the electron-donor TTF unit as a molecular wire connecting two acceptor redox centres.

1. Introduction

Mixed-valence (MV) compounds are excellent models to get insight into the understanding of the fundamental intramolecular electron-transfer (IET) phenomena.^[1-4] MV systems usually consist of two or more redox centres with different oxidation states that are connected by conjugated or non-conjugated bridges. Three main types of MV systems exist according to the Robin-Day classification,^[5] which is based on the balance between the strength of the electronic coupling between the redox sites (V_e) and the reorganization energy (λ_{reorg}). Class I MV compounds ($2V_e \ll \lambda_{\text{reorg}}$) are localized MV systems with the charge excess placed in one redox centre and no electronic interaction between the redox sites. In class II systems, the charge excess is also localized in one redox centre ($2V_e < \lambda_{\text{reorg}}$) but a low activation energy for IET from one redox centre to the other is commonly found and the process can be thermally induced. Class III or delocalized MV systems ($2V_e > \lambda_{\text{reorg}}$) display the charge excess equally distributed between the two redox centres. The ground-state potential energy surface (PES) of the two last classes of MV systems is distinguished by (see Figure 1): i) two minima separated by an energy barrier related to the λ_{reorg} and V_e values for localized class II systems, and ii) a single minimum for delocalized class III systems. Although mixed valency is typically associated with polynuclear transition metal complexes, there is an increasing number of organic systems that can be conceived as MV systems.^[3-4]

Figure 1. Scheme of potential energy surfaces for class II and class III mixed-valence systems. The drawing above the energy diagrams represents the charge distribution in mixed-valence anions.

From the experimental perspective, the study of organic MV systems is not an easy task. In many cases, MV compounds are difficult to handle due to their instabilities, especially when the mixed-valence systems are radical species. In addition, the solubility of the MV ionized species can be very small preventing the study of the kinetics of the electron transfer process in a broad range of temperatures since the compounds precipitate on lowering the temperature. It is also found that similar compounds cannot be solubilised in the same solvents making difficult the comparison between them. In this sense, quantum-chemical calculations can play a key role to characterize MV compounds, to analyze the IET phenomenon, and to establish trends in a family of compounds in the same conditions. In the last years, new computational strategies based on the density functional theory (DFT) have been successfully employed to study organic MV compounds. Among them, the constrained DFT approach developed by Van Voorhis and co-workers^[6-7] and the computational DFT protocol proposed by Kaupp and co-workers^[8-11] should be pointed out. The former approach allows to constrain the charge excess to one redox centre in the MV system and provides a reliable description of class II MV systems, which are difficult to be dealt with common standard functionals due to the self-interaction error.^[12-13] However, this approach lacks of predictive character because it requires a prior knowledge about the localized/delocalized nature of the MV system under study. The protocol developed by Kaupp and co-workers is based on using a nonstandard density functional together with an appropriate continuum model to take into account the solvent effects, and has been widely used for class II and class III MV compounds as well as for the challenging class II/III borderline systems.^[8-10] The protocol has provided accurate estimates of the IET barriers and intervalence charge transfer (IV-CT) excitations in different organic MV systems.^[10]

Since the discovery of the first organic metal,^[14] the charge-transfer complex formed by the electron donor tetrathiafulvalene (TTF) and the electron acceptor tetracyano-*p*-quinodimethane (TCNQ), TTF and its derivatives have aroused a great interest as building blocks for low-dimensional organic conductors and superconductors.^[15-16] TTF derivatives have been also used as donor units covalently linked to acceptor compounds through molecular bridges to promote efficient photoinduced intramolecular electron transfer.^[17] However, the behaviour of the TTF conjugated unit as a molecular wire between redox centres has been scarcely explored. Over the last years, there has been an effort to synthesize acceptor-donor-acceptor (A-D-A) triads, which behave as MV compounds in their radical anion states and where the donor linker is the TTF conjugated backbone.^[18-21] In particular, acceptor fragments such as naphthoquinone (BQ) and benztetracyano-*p*-quinodimethane (BTCNQ) have been coupled to the TTF moiety and triads such as BQ-TTF-BQ and BTCNQ-TTF-BTCNQ (Figure 2) have been recently synthesized and characterized.^[20-21] The MV properties of the BTCNQ-TTF-BTCNQ triad have been

investigated using variable-temperature electron paramagnetic resonance (EPR) measurements.^[20] In contrast, although BQ-TTF-BQ has received great interest as a promising ambipolar semiconductor to fabricate organic field-effect transistors (OFETs),^[21] its MV behaviour has not been unraveled up to date.

Herein, a joint theoretical and experimental characterization of the structural and electronic properties of the BQ-TTF-BQ and BTCNQ-TTF-BTCNQ triads is performed by using quantum-chemical calculations and electrochemical, electron paramagnetic resonance (EPR), and UV-Vis-NIR spectroelectrochemical techniques. The main goal is to shed light onto the mixed-valence properties of the BQ-TTF-BQ triad, which has not been investigated in this context. The quantum-chemical and spectroscopic characterization of the BTCNQ-TTF-BTCNQ compound will also be helpful to compare with BQ-TTF-BQ and to establish valuable structure-property relationships in these TTF-based acceptor-donor-acceptor triads.

Figure 2. Chemical structures of the BQ-TTF-BQ and BTCNQ-TTF-BTCNQ triads.

2. Experimental and Computational Details

UV-Vis-NIR spectra were recorded in a VARIAN CARY 5000 spectrophotometer. Cyclic voltammograms (CV) were registered with a conventional three-electrode configuration consisting of platinum wires as working and auxiliary electrodes and a saturated Ag/AgCl reference electrode and containing 0.1 M of $N(n\text{-C}_4\text{H}_9)_4\text{PF}_6$ (TBAHP) as supporting electrolyte. Deoxygenation of the solutions was performed previously to the experiments by bubbling nitrogen for at least 10 min, and the working electrode was cleaned after each run. Ferrocene was used as an internal reference both for potential calibration and for reversibility criteria. All the potential values reported are relative to the Fc^+/Fc couple. Reduction of compounds ($c = 5 \times 10^{-4}$ M) was performed with Cu metal in *o*-DCB:BZN 7:1 (BQ-TTF-BQ and BQ-thione) and DMSO:BZN 45:55 (BTCNQ-TTF-BTCNQ) containing tetraphenylphosphonium bromide (0.015 M). EPR spectra were recorded on a Bruker ELEXYS E500 X-band spectrometer equipped with a field-frequency (F/F) lock accessory and built in NMR Gaussmeter. A

rectangular TE102 cavity was used for the measurements. The signal-to-noise ratio of the spectra was increased by accumulation of scans using the F/F lock accessory to guarantee large field reproducibility. Precautions to avoid undesirable spectral distortions and line broadenings, such as those arising from microwave power saturation and magnetic field over modulation, were also taken into account. To avoid dipolar line broadening from dissolved oxygen, solutions were always carefully degassed with pure Argon.

DFT calculations were carried out using the Gaussian 09 program package (revision B.01).^[22] According to the quantum-chemical protocol suggested by Kaupp *et al.*, the nonstandard global hybrid functional BLYP35, which uses the Becke's exchange (B88)^[23] and the LYP correlation^[24] functionals with an exact-exchange portion of 35%, was chosen. The extended cc-pVTZ basis set^[25] was used in all calculations. Geometry optimizations were done under C_{2v} symmetry constraints for the neutral species and the delocalized anions, and using C_s symmetry restrictions for the localized anions. The radical anion species were calculated as open-shell doublet systems using the spin-unrestricted UBLYP35 approach. To take into account the interaction with the solvent, both neutral and charged species were also optimized in the presence of the solvent, *o*-DCB. Solvent effects, which are crucial to provide a reliable description concerning the localized/delocalized nature of organic MV systems, were taken into account within the self-consistent reaction field (SCRF) theory using the conductor-like polarizable continuum model (CPCM) approach.^[26-27] Vertical electronic excitation energies for the localized anion species were first computed at the BLYP35/cc-pVTZ level using the time-dependent DFT (TDDFT) approach^[28-30] and the optimized ground-state molecular geometries. TDDFT calculations of the lowest-lying doublet states were carried out in the presence of the solvent. The complete active space self-consistent field (CASSCF) method combined with a second-order perturbation approach (CASSCF/CASPT2) was employed to calibrate the accuracy of the TDDFT results using the MOLCAS 7.6 program package.^[31] CASSCF calculations were done making use of the cc-pVDZ basis set and an active space of 3 electrons within 3 orbitals (one located on the TTF fragment and the other two on each acceptor moiety). The CASPT2 technique was applied to correct the CASSCF energies of the five lowest-lying electronic states of the two anionic triads. Molecular orbitals were plotted using Chemcraft 1.6.^[32]

3. Results and Discussion

3.1. Structural and Electronic Properties of BQ-TTF-BQ and BTCNQ-TTF-BTCNQ

To investigate the effect of fusing the acceptor units (BQ and BTCNQ) on the molecular and electronic structure of the TTF backbone, geometry optimizations of the BQ-TTF-BQ and BTCNQ-TTF-BTCNQ triads and the constituting molecules (BQ, BTCNQ, and TTF) were performed at the BLYP35/cc-pVTZ level in the presence of the solvent (*o*-DCB). Figure 3 displays the minimum-energy structures computed for the BQ-TTF-BQ and BTCNQ-TTF-BTCNQ triads. Calculations predict a minimum-energy C_{2v} -boat conformation with a folding angle θ along the S $\cdots$ S axes of 11.9° and 17.8° for BQ-TTF-BQ and BTCNQ-TTF-BTCNQ, respectively. This folding angle θ is similar to that previously reported both experimentally^[33] and theoretically^[34] for isolated TTF. In the case of the BQ-TTF-BQ triad, the fully-planar D_{2h} conformation turns out to be also a minimum in the potential energy surface and is found to be mostly degenerate in energy with the boat conformation (0.06 kcal mol⁻¹). The small energy difference between the C_{2v} -boat and D_{2h} -planar conformation is in accord with the X-ray diffraction data reported for BQ-TTF-BQ where the fully D_{2h} -planar structure is observed.^[21] In contrast to BQ-TTF-BQ, only the C_{2v} -boat conformation is computed as a minimum-energy structure for the BTCNQ-TTF-BTCNQ triad and, accordingly, is the one found in the X-ray diffraction analysis.^[20] The steric hindrance between the C $\equiv$ N groups and the vicinal sulfur and hydrogen atoms determines that the BTCNQ moieties fold along the C $\cdots$ C axes (angle ϕ) and adopt a butterfly-like structure (Figure 3). The folding angle is more accentuated in the triad ($\phi = 146^\circ$) than in the isolated BTCNQ molecule ($\phi = 160^\circ$) due to the additional interaction with the sulphur atoms.

Figure 3. Minimum-energy conformations obtained for the two neutral triads at the BLYP35/cc-pVTZ level in the presence of *o*-DCB. Left, BQ-TTF-BQ, right BTCNQ-TTF-BTCNQ.

Table 1 compares the optimized values calculated for selected bond lengths of BQ-TTF-BQ and BTCNQ-TTF-BTCNQ with those obtained for the isolated TTF, BQ, and BTCNQ molecules. The main differences are found for the bonds connecting the donor and acceptor

moieties. For BQ-TTF-BQ, the carbon-carbon (CC) double bond shared by the TTF and BQ units (bond 4) elongates from 1.324 and 1.300 Å in TTF and BQ, respectively, to 1.341 Å in the triad. In addition, the carbon-sulphur (CS) bonds 3 of the TTF fragment undergo a notably shortening (from 1.753 to 1.743 Å) compared with isolated TTF, and the CC single bonds 5 of the BQ moieties shrink from 1.477 in BQ to 1.472 Å in the triad. These structural changes are mainly ascribed to the electron density transfer that takes place in the BQ-TTF-BQ triad from the central TTF moiety, which accumulates a positive charge of +0.40e, to the BQ centres, which bear a negative charge of −0.20e each. For the BTCNQ-TTF-BTCNQ triad, despite the fact that a greater charge transfer from central TTF (+0.60e) to the BTCNQ acceptor units (−0.30e) occurs since BTCNQ is better acceptor than BQ, the BTCNQ moieties are slightly more quinoid than isolated BTCNQ. For example, the single and double CC bonds 5 and 6 slightly lengthen and shorten, respectively, compared to BTCNQ (Table 1). This may stem from the larger geometrical distortion induced by the dicyanovinylene groups in the BTCNQ-TTF-BTCNQ triad, which leads to a less effective conjugation path.

Table 1. Selected BLYP35/cc-pVTZ-optimized bond lengths (Å) calculated in *o*-DCB for BQ-TTF-BQ, BTCNQ-TTF-BTCNQ, and their constituting molecular fragments (TTF, BQ, and BTCNQ).

Bond	BQ-TTF-BQ	BTCNQ-TTF-BTCNQ	TTF	BQ	BTCNQ
1	1.336	1.338	1.338	-	-
2	1.774	1.761	1.773	-	-
3	1.743	1.753	1.753	-	-
4	1.341	1.352	1.324	1.300	1.336
5	1.472	1.458	-	1.477	1.447
6	1.212	1.363	-	1.214	1.370
7	1.484	1.472	-	1.484	1.464
8	1.400	1.407	-	1.398	1.416
9	1.387	1.389	-	1.388	1.393
10	1.386	1.385	-	1.384	1.382
11	1.387	1.382	-	1.389	1.383
12	-	1.427	-	-	1.423
13	-	1.146	-	-	1.146
14	-	1.427	-	-	1.427
15	-	1.146	-	-	1.146

Figure 4. Electron density contours (0.03 e bohr⁻³) calculated for the HOMO/HOMO-1 and LUMO/LUMO+1 of BQ-TTF-BQ and BTCNQ-TTF-BTCNQ at the BLYP35/cc-pVTZ level. The HOMO/HOMO-1 of TTF and the LUMO of BQ are shown on the left for comparison purposes.

Figure 4 displays the atomic orbital composition computed for the frontier molecular orbitals of the BQ-TTF-BQ and BTCNQ-TTF-BTCNQ triads and the TTF and BQ fragments. In the BQ-TTF-BQ triad, the highest occupied molecular orbital (HOMO) and the HOMO-1 spread over the electron-donor TTF unit and match exactly the HOMO and HOMO-1 of the TTF molecule. The lowest unoccupied molecular orbital (LUMO) and the LUMO+1 are completely localized on the electron-acceptor BQ unit and clearly resemble the LUMO of the naphthoquinone molecule. They correspond to the in-phase and out-of-phase combination of the LUMO of the BQ units, respectively. An equivalent description is obtained for the BTCNQ-TTF-BTCNQ triad (Figure 4). An aspect to be kept in mind is that the delocalized description of the LUMO and LUMO+1 over the two identical BQ or BTCNQ moieties is perfectly compatible with a localized description where the LUMO and LUMO+1 would be degenerate and localized over different acceptor moieties. Although the localized/delocalized notation is

not relevant for neutral A-D-A triads, it will be used below for the electronic description of the anions since they give rise to MV species. In oxidation/reduction terms, the topology of the MOs clearly suggests that first oxidations will occur on the TTF unit, whereas first reductions will take place on the acceptor moieties.

3.2. Mixed-Valence Species

To reveal if there exists any electronic coupling between the acceptor units assisted by the TTF bridge in the BQ-TTF-BQ and BTCNQ-TTF-BTCNQ triads, their electrochemical properties were studied by cyclic voltammetry. The cyclic voltammetry of BTCNQ-TTF-BTCNQ shows two very close reduction processes at $E_{1/2}(1) = -0.20$ V and $E_{1/2}(2) = -0.31$ V (vs Fc^+/Fc) (Figure 5b) that correspond to the consecutive two-electron reduction of each of the two BTCNQ moieties. Two-electron reduction processes to the dianion are usually found for benzoannulated TCNQs,^[35-38] and the detection of a double two-electron reduction process in BTCNQ-TTF-BTCNQ can be an indication that there exists an electronic interaction between the two BTCNQ moieties through the TTF bridge.^[20] The cyclic voltammetry of BQ-TTF-BQ was only possible to be recorded in *o*-DCB at 120 °C due to the very low solubility of the triad. As in the previous case, although less well defined, two single-electron reduction processes can be envisaged in the broad wave centred at $E_{1/2} = -1.23$ V (vs Fc^+/Fc) (Figure 5a), also indicating the existence of an electronic communication between both BQ moieties.

Figure 5. Cyclic voltammetry of a) BQ-TTF-BQ in *o*-dichlorobenzene at 120 °C and b) BTCNQ-TTF-BTCNQ in DMSO/benzonitrile (45:55) at room temperature.

The IET process for the BQ-TTF-BQ triad in its radical anion state was studied by variable-temperature EPR spectroscopy (VT-EPR). Previously, we performed the study of the radical

anion derived from the model compound BQ-thione, a precursor in the synthesis of the triad,^[19] that has only one naphthoquinone moiety (Figure 6). Chemical reduction of BQ-thione with copper metal in a tetraphenylphosphonium bromide solution (BrPPh₄) leads to the radical anion species BQ-thione^{•-}. This species shows the EPR spectrum displayed in Figure 6, which is characterized by seven lines resulting from the coupling of the unpaired electron with two sets of equivalent aromatic protons ($a_H(2H) = 0.626$ G and $a_H(2H) = 0.355$ G). The EPR spectrum of BQ-thione^{•-} remains invariant with temperature. In contrast, the EPR spectrum recorded at the first reduction stage of BQ-TTF-BQ, which corresponds to the radical anion species (BQ-TTF-BQ)^{•-}, exhibits a significant change upon heating from 240 K to 340 K (Figure 7). The spectrum at 240 K is essentially identical to that of the BQ-thione model compound (7 lines with $a_H(2H) = 0.657$ G and $a_H(2H) = 0.322$ G). As the temperature is gradually increased from 240 to 340 K, the lines split and the new lines start to increase in intensity due to extensive dynamic electron exchange between both BQ moieties through the TTF bridge. The final spectrum is characterized by 13 lines, which result from the coupling of the unpaired electron with two sets of four equivalent aromatic protons of both BQ moieties with half the value of the coupling constants ($a_H(4H) = 0.329$ G and $a_H(4H) = 0.161$ G). The lowest temperature spectrum unequivocally demonstrate that, on the EPR time scale, the odd electron of the BQ-TTF-BQ anion is localized on one BQ unit and, as the temperature is raised, the activation energy barrier is overcome promoting a faster IET process between the two BQ moieties.

Figure 6. EPR spectrum of model compound BQ-thione^{•-} P(C₆H₅)₄⁺ at 320 K in *o*-DCB:BZN 7:1 with PPh₄Br.

Figure 7. Experimental and simulated EPR spectra of BQ-TTF-BQ^{•-} P(C₆H₅)₄⁺ at different temperatures in *o*-DCB:BZN 7:1 with PPh₄Br.

The dynamics of the intramolecular exchange process was theoretically simulated and first-order rate constants were extracted by fitting the experimental EPR spectra (Figure 7). Kinetic data leads to a linear Arrhenius plot over the 340–240 K temperature range, which gives the activation parameters $E_{\text{act}} = 3.4 \text{ kcal mol}^{-1}$, $\log A = 9.5$ ($\Delta G^{\ddagger}_{300 \text{ K}} = 7.9 \text{ kcal mol}^{-1}$, $\Delta H^{\ddagger} = 2.8 \text{ kcal mol}^{-1}$, and $\Delta S^{\ddagger} = -16.9 \text{ e.u.}$). The IET rate constants for the BQ-TTF-BQ anion are computed in the range of $2.2 \times 10^6 - 1.8 \times 10^7 \text{ s}^{-1}$.

The IET process for the BTCNQ-TTF-BTCNQ radical anion was previously studied.^[20] Spectroelectrochemistry and EPR spectroscopy measurements unambiguously revealed that the BTCNQ-TTF-BTCNQ anion behaves as a class II MV compound, where the extra electron is localized in one of the BTCNQ units. The kinetic and thermodynamic parameters obtained by fitting the experimental temperature-dependent EPR spectra to the Arrhenius equation were: $E_{\text{act}} = 1.13 \text{ kcal mol}^{-1}$, $\log A = 7.53$ ($\Delta G^{\ddagger}_{300 \text{ K}} = 8.3 \text{ kcal mol}^{-1}$, $\Delta H^{\ddagger} = 0.52 \text{ kcal mol}^{-1}$, and $\Delta S^{\ddagger} = -25.8 \text{ e.u.}$). The estimated rate constants ($4.3 \times 10^6 - 6.2 \times 10^6 \text{ s}^{-1}$) for the IET process in the BTCNQ-TTF-BTCNQ anion are smaller than those found in the BQ-TTF-BQ anion, which is in

concordance with the obtained thermodynamic data since the $\Delta G^\ddagger$ value for the IET process in the BTCNQ-TTF-BTCNQ anion is larger than that for the BQ-TTF-BQ anion.

The theoretical characterization of the BQ-TTF-BQ and BTCNQ-TTF-BTCNQ triads in their radical anion states is much more complex due to the possibility to form localized ($\text{BQ}^{\bullet-}$ -TTF-BQ and $\text{BTCNQ}^{\bullet-}$ -TTF-BTCNQ) or delocalized ($(\text{BQ-TTF-BQ})^{\bullet-}$ and $(\text{BTCNQ-TTF-BTCNQ})^{\bullet-}$) radical anions (class II or class III MV systems, respectively). To explore the electronic and structural properties of the reduced species, geometry optimizations of the radical anions were performed at the BLYP35/cc-pVTZ level in *o*-DCB. The localized C_s -symmetry anions (class II MV systems) are found to be minimum-energy structures more stable than the delocalized C_{2v} -symmetry anions by 4.94 and 7.02 kcal mol⁻¹ for BQ-TTF-BQ and BTCNQ-TTF-BTCNQ, respectively. The localized/delocalized nature of the radical anion species is illustrated in Figure 8 by the unpaired-electron spin density and NPA charge distributions calculated for the respective anions. Whereas localized $\text{BQ}^{\bullet-}$ -TTF-BQ and $\text{BTCNQ}^{\bullet-}$ -TTF-BTCNQ structures (C_s -symmetry) are characterized by concentrating the extra electron in one of the acceptor moieties, the charge in the delocalized $(\text{BQ-TTF-BQ})^{\bullet-}$ and $(\text{BTCNQ-TTF-BTCNQ})^{\bullet-}$ structures (C_{2v} -symmetry) is equally distributed among the acceptor units. The free energy ($\Delta G^\ddagger$) computed from frequency calculations at the BLYP35/cc-pVTZ level for the IET process is 6.58 and 8.31 kcal mol⁻¹ for the $\text{BQ}^{\bullet-}$ -TTF-BQ and $\text{BTCNQ}^{\bullet-}$ -TTF-BTCNQ anions, respectively. These theoretical values are in notable agreement with those experimentally estimated by EPR (*vide supra*).

Figure 8. a) Unpaired-electron spin density distribution and b) NPA charge distribution computed for the localized/delocalized radical anions at the UBLYP35/cc-pVTZ level. A and D denote acceptor and donor, respectively.

Table 2. Selected BLYP35/cc-pVTZ-optimized bond distances (Å) computed in *o*-DCB for the BQ-TTF-BQ and BTCNQ-TTF-BTCNQ triads in their radical anion states.

Bond	BQ-TTF-BQ		BTCNQ-TTF-BTCNQ	
	Localized (C_s)	Delocalized (C_{2v})	Localized (C_s)	Delocalized (C_{2v})
1	1.338	1.336	1.338	1.337
2	1.768	1.772	1.752	1.756

2'	1.778	1.772	1.765	1.756
3	1.760	1.749	1.770	1.758
3'	1.742	1.749	1.751	1.758
4	1.372	1.359	1.393	1.372
4'	1.343	1.359	1.354	1.372
5	1.424	1.446	1.408	1.435
5'	1.471	1.446	1.456	1.435
6	1.252	1.231	1.428	1.389
6'	1.213	1.231	1.364	1.389
7	1.467	1.467	1.451	1.465
7'	1.485	1.467	1.472	1.465
8	1.412	1.406	1.417	1.412
8'	1.399	1.406	1.406	1.412
9	1.400	1.393	1.406	1.396
9'	1.387	1.393	1.389	1.396
10	1.376	1.381	1.372	1.380
10'	1.386	1.381	1.385	1.380
11	1.398	1.392	1.393	1.386
11'	1.387	1.392	1.382	1.386
12	-	-	1.411	1.421
12'	-	-	1.427	1.421
13	-	-	1.152	1.149
13'	-	-	1.146	1.149
14	-	-	1.408	1.420
14'	-	-	1.427	1.420
15	-	-	1.153	1.149
15'	-	-	1.146	1.149

Table 2 gathers the BLYP35/cc-pVTZ-optimized bond distances computed for the localized and delocalized radical anions of the BQ-TTF-BQ and BTCNQ-TTF-BTCNQ triads in the presence of *o*-DCB. The most important structural changes affect the acceptor units because, as mentioned above, the extra electrons are mainly injected in the BQ and BTCNQ moieties. The single and double CC bonds of the quinone-type benzene rings shrink and lengthen, respectively, and these benzene rings become more aromatic upon reduction. This aromatization is accompanied by a remarkable lengthening of the exocyclic double bonds 6 and 6'. Table 2 clearly illustrates that the structural changes in the localized anions of the triads are concentrated on one of the acceptor BQ and BTCNQ moieties in good agreement with the unpaired-electron spin densities and charge distributions shown in Figure 8.

The localized BQ⁻-TTF-BQ radical anion exhibits boat-like and fully-planar minimum-energy conformations as it was found for the neutral BQ-TTF-BQ triad. At the BLYP35/cc-pVTZ level, the energy difference between both conformations is also negligible (0.06 kcal mol⁻¹), the planar conformation being slightly favoured. For the BTCNQ⁻-TTF-BTCNQ anion, only the boat-like conformation is theoretically predicted as a minimum-energy structure. In the boat-like conformations, the bending angle θ defining the folding of the TTF unit changes from 168.1° (162.2°) in the BQ (BTCNQ) units of the neutral triads to 170.7° (162.4°) and 167.8° (161.4°) in the BQ⁻¹ (BTCNQ⁻¹) and BQ⁰ (BTCNQ⁰) units, respectively, of the radical anion

triads. The difference between the values of the folding angle is an additional structural signature which corroborates that the extra electron enters only one acceptor moiety.

To analyze the evolution of the optical properties with the reduction state, *in situ* UV-Vis-NIR spectroelectrochemistry experiments were performed. The UV-Vis-NIR absorption spectra of compounds BQ-TTF-BQ and BTCNQ-TTF-BTCNQ show the expected bands of the BQ/BTCNQ and TTF subunits, along with a broad absorption in the limit of the infrared region (Figure 9). This band peaks around $\lambda = 730$ nm ($\epsilon = 310$ M⁻¹ cm⁻¹) for BQ-TTF-BQ and shifts to the red at $\lambda = 800$ nm ($\epsilon = 890$ M⁻¹ cm⁻¹) for BTCNQ-TTF-BTCNQ. The band is assigned to an optically induced charge-transfer (CT) process between the donor TTF core and the acceptor BQ or BTCNQ moieties, respectively. Its intramolecular nature was confirmed by dilution experiments (from $5 \cdot 10^{-4}$ to $2.5 \cdot 10^{-4}$ and $1.25 \cdot 10^{-4}$ M), which showed that the intensity of the corresponding absorption follows the Beer–Lambert law. The broad absorption bands decrease in intensity as the acceptor moieties of the triads are reduced, thus confirming their donor-acceptor CT nature.

At the first stages of the reduction of BTCNQ-TTF-BTCNQ, its electronic spectrum shows a decreased intensity of the absorption band at 389 nm and the appearance of a new narrow and weak band at 592 nm, which is ascribed to the formation of BTCNQ radical anions. Along with these changes, a new band appears at lower energies as a broad shoulder of the CT band (green spectrum in Figure 9b). The deconvolution of the spectrum shows that this new band appears at 9246 cm⁻¹ (1080 nm) with a full width at half maximum of 3193 cm⁻¹. When the reduction process continues further, both the new band and the initial CT band tend to disappear (red spectrum in Figure 9b). Therefore, the band at 1080 nm is assigned to an intervalence charge-transfer (IV-CT) band of the class II mixed-valence BTCNQ⁻-TTF-BTCNQ anion, in which an IET from the reduced BTCNQ⁻ moiety to the nonreduced BTCNQ unit occurs as previously observed in the closely-related, one-electron-reduced Q-TTF-Q triad.^[18] Due to the insolubility of compound BQ-TTF-BQ in all common solvents, the reduction was carried out at high temperature (80 °C) using a mixture of *o*-dichlorobenzene and benzonitrile as solvent. In the UV-Vis-NIR spectra acquired during the reduction process, the CT band observed for the neutral compound at $\lambda = 730$ nm is slightly blue shifted ($\lambda = 665$ nm) and a shoulder grows in the region around $\lambda = 450$ nm (Figure 9a and Figure S1 in the Supporting Information). When the reduction process goes further, the band at $\lambda = 665$ nm tends to vanish while the shoulder at $\lambda = 450$ nm is defined as a new band at $\lambda = 405$ nm accompanied by a shoulder around $\lambda = 500$ nm. Simultaneously, a very wide and weak band centered around $\lambda = 1400$ nm appears at the beginning of the reduction (inset of Figure 9a, green line) and vanishes when the reduction of the molecule goes on. This small band, due to its width, position, and behavior during the reduction has been assigned to the intervalence charge-transfer band of the BQ⁻-TTF-BQ anion.

Figure 9. UV-Vis-NIR spectra of a) BQ-TTF-BQ in *o*-DCB:BZN 7:1 at 80 °C and b) BTCNQ-TTF-BTCNQ in DMSO:BZN 45:55 in their neutral state (blue) and at increasing reduction stages (green and red).

Table 3. Vertical excitation energies (ΔE) and oscillator strengths (f) computed for the localized $\text{BQ}^{\cdot-}$ -TTF-BQ and $\text{BTCNQ}^{\cdot-}$ -TTF-BTCNQ anions at the CASSCF/CASPT2 and TDDFT levels.

Method	$\text{BQ}^{\cdot-}$ -TTF-BQ			$\text{BTCNQ}^{\cdot-}$ -TTF-BTCNQ		
	ΔE (eV)	f	Description	ΔE (eV)	f	Description
CASSCF/CASPT2 (3,3) ^[a]	0.43	0.006	$D_1 (\text{BQ}^{\cdot-} \rightarrow \text{BQ}^0)$	0.84	0.007	$D_1 (\text{TTF} \rightarrow \text{BTCNQ}^0)$
	0.90	0.006	$D_2 (\text{TTF} \rightarrow \text{BQ}^0)$	0.86	0.002	$D_2 (\text{BTCNQ}^{\cdot-} \rightarrow \text{BTCNQ}^0)$
	0.91	0.002	$D_3 (\text{TTF} \rightarrow \text{BQ}^0)$	0.88	0.013	$D_3 (\text{TTF} \rightarrow \text{BTCNQ}^0)$
	2.76	0.059	$D_4 (\text{TTF} \rightarrow \text{BQ}^{\cdot-})$	1.92	0.075	$D_4 (\text{TTF} \rightarrow \text{BTCNQ}^{\cdot-})$
TDDFT ^[b]	0.98	0.000	$D_1 (\text{TTF} \rightarrow \text{BQ}^0)$	0.85	0.001	$D_1 (\text{TTF} \rightarrow \text{BTCNQ}^0)$
	1.05	0.012	$D_2 (\text{BQ}^{\cdot-} \rightarrow \text{BQ}^0)$	1.14	0.183	$D_2 (\text{TTF} \rightarrow \text{BTCNQ}^{\cdot-})$
	1.39	0.011	$D_3 (\text{TTF} \rightarrow \text{BQ}^0)$	1.30	0.010	$D_3 (\text{TTF} \rightarrow \text{BTCNQ}^0)$
	2.15	0.017	$D_4 (\text{TTF} \rightarrow \text{BQ}^{\cdot-})$	1.46	0.005	$D_4 (\text{BTCNQ}^{\cdot-} \rightarrow \text{BTCNQ}^0)$

[a] CASSCF/CASPT2 calculations have been performed using the cc-pVDZ basis set and without taking into account solvent effects. [b] Time-dependent DFT calculations have been carried out with the cc-pVTZ basis set considering solvent effects using the CPCM model and *o*-DCB as solvent.

To gain more insight into the nature of the absorption bands experimentally observed, the lowest-energy doublet excited states of $\text{BQ}^{\cdot-}$ -TTF-BQ and $\text{BTCNQ}^{\cdot-}$ -TTF-BTCNQ were first calculated at the CASSCF/CASPT2 level using an active space of 3 electrons within 3 orbitals (one located on the TTF fragment and the other two located on each acceptor moiety), the cc-pVDZ basis set, and the BLYP35-optimized geometries. For $\text{BQ}^{\cdot-}$ -TTF-BQ, three doublet excited states (D_n) are calculated below 1.0 eV with small oscillator strengths ($f < 0.01$) for the respective $D_0 \rightarrow D_n$ electronic transitions (Table 3). The first $D_0 \rightarrow D_1$ transition is described by a

one-electron promotion from the single-occupied molecular orbital (SOMO) to the LUMO, which are located on different BQ moieties. It therefore corresponds to the $\text{BQ}^{\cdot-} \rightarrow \text{BQ}^0$ electron transfer (IV-CT excitation) and is computed at 0.43 eV with a weak oscillator strength of 0.006. At slightly higher energies, the $\text{D}_0 \rightarrow \text{D}_2$ and $\text{D}_0 \rightarrow \text{D}_3$ transitions are calculated at 0.90 ($f = 0.006$) and 0.91 eV ($f = 0.002$), respectively, and involve an electron transfer from the TTF moiety to the neutral BQ^0 fragment. The CASSCF/CASPT2 results therefore suggest that the first three electronic transitions (the $\text{BQ}^{\cdot-} \rightarrow \text{BQ}^0$ IV-CT transition and the two $\text{TTF} \rightarrow \text{BQ}^0$ CT transitions) contribute to the very low-intense and broad absorption band experimentally observed around 0.89 eV (1400 nm). These theoretical results for the localized $\text{BQ}^{\cdot-}$ -TTF-BQ radical anion are in good agreement with those previously reported for the closely related Q-TTF-Q triad.^[39]

For $\text{BTCNQ}^{\cdot-}$ -TTF-BTCNQ, the $\text{D}_0 \rightarrow \text{D}_1$ and $\text{D}_0 \rightarrow \text{D}_3$ transitions associated with the CT excitations from TTF to the BTCNQ^0 unit are computed at 0.84 ($f = 0.007$) and 0.88 eV ($f = 0.013$), and the IV-CT transition ($\text{D}_0 \rightarrow \text{D}_2$) is now predicted at 0.86 eV with an oscillator strength of 0.002. Hence, the broad band experimentally observed at around 1.15 eV (1080 nm) is associated to both the $\text{BTCNQ}^{\cdot-} \rightarrow \text{BTCNQ}^0$ IV-CT excitation and the two $\text{TTF} \rightarrow \text{BTCNQ}^0$ CT excitations. CASSCF/CASPT2 calculations predict a blue shift of the IV-CT transition in going from $\text{BQ}^{\cdot-}$ -TTF-BQ (0.43 eV) to $\text{BTCNQ}^{\cdot-}$ -TTF-BTCNQ (0.86 eV) in agreement with the lower IET barrier experimentally inferred and theoretically computed for the BQ-TTF-BQ triad (*vide supra*). The IV-CT excitation predicted at lower energies for $\text{BQ}^{\cdot-}$ -TTF-BQ also implies a larger broadening of the corresponding band in the UV-Vis-NIR spectrum. This feature contributes to the difficulties experimentally found to clearly determine the IV-CT transition for the $\text{BQ}^{\cdot-}$ -TTF-BQ MV system.

TDDFT calculations at the BLYP35/cc-pVTZ level in *o*-DCB were also performed to estimate the energy and nature of the lowest-energy excited states of the MV triads (Table 3). For $\text{BQ}^{\cdot-}$ -TTF-BQ, the description of the first three electronic states is similar to that obtained by CASSCF/CASPT2 although the electronic transitions are computed at higher energies. For $\text{BTCNQ}^{\cdot-}$ -TTF-BTCNQ, BLYP35 predicts an unexpected intense $\text{TTF} \rightarrow \text{BTCNQ}^{\cdot-}$ transition ($f = 0.183$) at low energies (1.14 eV), which correlates with that computed at 1.92 eV by CASSCF/CASPT2, whereas the IV-CT electronic transition is calculated higher in energy at 1.46 eV ($f = 0.005$). These results indicate that although the protocol based on the nonstandard BLYP35 functional in combination with an appropriate continuum model has provided good estimates of the IV-CT transitions for different organic mixed-valence compounds,^[8-10] it seems not to offer a reliable description neither for the relative energies nor for the intensity of the lowest-lying excitations for the MV compounds investigated in this study, specially for the $\text{BTCNQ}^{\cdot-}$ -TTF-BTCNQ radical anion.

4. Conclusions

A joint theoretical and experimental characterization of the structural and electronic properties of the two TTF-based acceptor-donor-acceptor triads BQ-TTF-BQ and BTCNQ-TTF-BTCNQ has been performed by quantum-chemical calculations, and electrochemical, electron paramagnetic resonance, and spectroelectrochemical UV-Vis-NIR techniques. Emphasis has been made on the mixed-valence properties of both triads in their radical anion states. The donor TTF core and the acceptor BQ and BTCNQ units preserve their electronic structure in the neutral system, for which a charge transfer takes place from the central TTF fragment to the peripheral BQ/BTCNQ moieties. The electrochemical and EPR measurements revealed that both BQ-TTF-BQ and BTCNQ-TTF-BTCNQ behave as class II mixed-valence compounds in their radical anion state and exhibit a significant electronic communication between the acceptor moieties. DFT calculations (BLYP35/cc-pVTZ) performed in the presence of the solvent predict localized $\text{BQ}^{\cdot-}$ -TTF-BQ and $\text{BTCNQ}^{\cdot-}$ -TTF-BTCNQ structures as the most stable ones for both radical anions, which fully supports the experimental evidences. Compared to $\text{BQ}^{\cdot-}$ -TTF-BQ, the $\text{BTCNQ}^{\cdot-}$ -TTF-BTCNQ radical anion has been shown to have a stronger class II character (higher localization) both experimentally and theoretically. The latter exhibits a larger $\Delta G^\ddagger$ value for the intramolecular electron transfer process between the acceptor units, which is in agreement with the higher electron-withdrawing character of BTCNQ compared to BQ. CASSCF(3,3)/CASPT2 calculations suggest that the broad low-energy absorption bands experimentally observed for the $\text{BQ}^{\cdot-}$ -TTF-BQ and $\text{BTCNQ}^{\cdot-}$ -TTF-BTCNQ radical anions are associated with both the IV-CT electronic transition ($\text{BQ}^{\cdot-}/\text{BTCNQ}^{\cdot-} \rightarrow \text{BQ}^0/\text{BTCNQ}^0$) and two $\text{TTF} \rightarrow \text{BQ}^0/\text{BTCNQ}^0$ CT excitations. This study therefore highlights that the electron-donor TTF molecule can be viewed as an efficient molecular wire when coupled to two acceptor redox centres. It is also important to mention that the studied A-D-A triads belong to the family of so-called quadrupolar molecules, for which interesting studies as quadrupolar chromophores in both neutral and charged states are being developed.^[40]

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TTF-Based Mixed-Valence Acceptor-Donor-Acceptor Triads: A Joint Theoretical and Experimental Approach

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Jumping electrons! The BQ-TTF-BQ and BTCNQ-TTF-BTCNQ acceptor-donor-acceptor triads in their radical anion states are shown to behave as class II mixed-valence compounds with significant electronic communication between the acceptor moieties assisted by the TTF bridge.

Supporting Information

TTF-Based Mixed-Valence Acceptor-Donor-Acceptor Triads: A Joint Theoretical and Experimental Approach

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Figure S1. Evolution of the UV-Vis-NIR spectra upon reduction of BQ-TTF-BQ.