

Three Redox States of a Diradical Acceptor-Donor-Acceptor Triad: Gating the Magnetic Coupling and the Electron Delocalization

Manuel Souto,[†] Vega Lloveras,[†] Sergi Vela,[‡] Maria Fumanal,[‡] Imma Ratera,^{†,} and Jaume Veciana^{†,*}*

[†] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC)/CIBER-BBN, Campus Universitari de la UAB, 08193 Cerdanyola del Vallès (Barcelona), Spain

[‡] Laboratoire de Chimie Quantique, Université de Strasbourg, 4 rue Blaise Pascal, F-67000 Strasbourg, France

AUTHOR INFORMATION

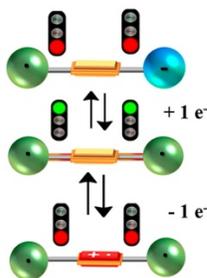
Corresponding Author

*E-mail: vecianaj@icmab.es, iratera@icmab.es

ABSTRACT: The diradical acceptor-donor-acceptor triad $\mathbf{1}^{\bullet\bullet}$, based on two polychlorotriphenylmethyl (PTM) radicals connected through a tetrathiafulvalene(TTF)-vinylene bridge, has been synthesized. The generation of the mixed-valence radical anion, $\mathbf{1}^{\bullet-}$, and triradical cation species, $\mathbf{1}^{\bullet\bullet+}$, obtained upon electrochemical reduction and oxidation, respectively, was monitored by optical and ESR spectroscopy. Interestingly, the modification of

electron delocalization and magnetic coupling was observed when the charged species were generated and the changes have been rationalized by theoretical calculations.

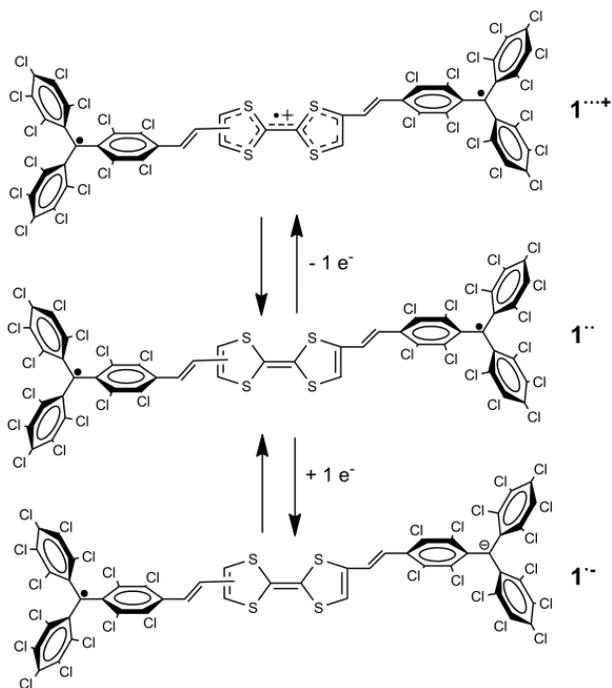
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In the last few years, there is an increasing interest in the design and synthesis of novel organic materials exhibiting intramolecular electron transfer (IET) phenomena. Challenging are dyadic systems formed by donor (D) and acceptor (A) units connected by conjugated bridges due to their potential applications as molecular wires or switches.¹⁻⁸ Organic mixed-valence (MV) compounds containing at least two redox sites with two different oxidation states connected through a conjugated bridge are good examples for this kind of compounds.⁹⁻¹⁴ On the other hand, research on organic molecules containing several stable radical centres linked through ferromagnetic coupling bridges have also received much attention during the past decades.¹⁵⁻²² In fact, there are recent examples of diradical compounds that can switch the magnetic interaction between the radical centres by changing the chemical nature of the bridge.^{19,20} Thus, switching the magnetic response of organic molecular materials through the application of an external stimulus is an interesting phenomenon since they mimic elemental electronic operations.

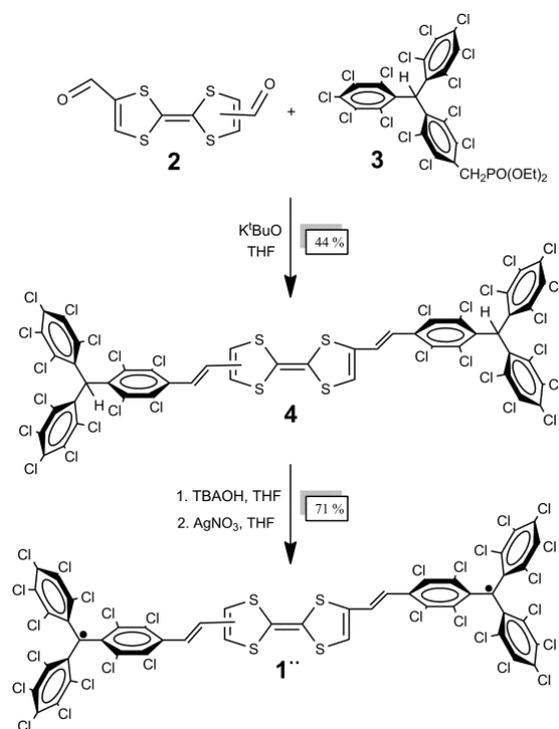
In our group, we have recently reported an organic radical D-A dyad, based on the electron π -donor tetrathiafulvalene (TTF) connected to the electron acceptor

polychlorotriphenylmethyl (PTM) radical, that exhibits bistability in solution through the application of external stimuli such as the polarity of the solvent or temperature.²³⁻²⁸ In order to study the effect of having two acceptor PTM units linked to the same TTF moiety, we have synthesized and characterized the quadrupolar species based on a diradical acceptor-donor-acceptor (A-D-A) triad **1**^{••} consisting on two PTM radical units connected by a bis-vinylene-TTF bridge. Moreover, we have studied the reversible formation of the mixed-valence **1**^{•+} and triradical cation **1**^{••+} species by one-electron reduction and oxidation respectively (Scheme 1). Both species exhibit different optical and magnetic properties as the electron delocalization was suppressed for the generated charged species. This molecular tristable redox system can gate their physical properties upon the application of an electrical input in a reversible way under ambient conditions.



Scheme 1. Molecular structures of diradical **1**^{••}, mixed-valence **1**^{•+} and triradical cation **1**^{••+}.

Diradical triad **1**^{••} was synthesized in three steps as shown in Scheme 2. First, the precursor diformyl TTF **2** was obtained as a mixture of (*E*) and (*Z*) isomers, as previously reported.²⁹ It is important to note that all the reported compounds derived from **2** were obtained as a mixture of isomers,³⁰⁻³⁴ which are difficult to isolate due to the easiness of a *E-Z* isomerisation during the chromatographic separation.³⁵ Crystallization also resulted fruitless for their purification. Compound **4** was obtained through a Horner-Wadsworth-Emmons reaction of diformyl TTF **2** and two equivalents of phosphonated PTM derivative **3**.⁹ The two vinylene units were obtained in *trans*-configuration according to the coupling constants in the ¹H-NMR spectra and to the nature of the base (*tert*-butoxide) that always favours the formation of *trans*-olefins³⁶ (see Figure S1). DFT calculations show that *E* and *Z* isomers of **4** lie extremely close in energy (*ca.* 0.1 kcal/mol). In addition the computational analysis suggests that the *cis* configuration of the vinylene units is *ca.* 2 kcal/mol disfavoured with respect to the *trans* one (see Table S4). Finally, subsequent deprotonation of **4** with two equivalents of TBAOH and oxidation of corresponding dicarbanions using silver nitrate yield diradical **1**^{••} (*E* + *Z*) in 71%, as a brownish powder.



Scheme 1. Three-step synthesis of **1''**. TBAOH = tetrabutylammonium hydroxide.

Cyclic voltammetry (CV) of diradical **1''** was recorded in CH_2Cl_2 at room temperature, with $[(n\text{-Bu})_4\text{N}] \text{PF}_6$ (0.1 M) as supporting electrolyte, a Pt wire as a working electrode, and Ag/Ag^+ as the reference electrode (Figure 1). The spectrum of **1''** shows two reversible oxidation processes (0.59 and 1.06 V vs Ag^+/Ag) assigned to the oxidation of the TTF bridge to $\text{TTF}^{+\cdot}$ and TTF^{2+} respectively, and one reversible reduction process (-0.21 V) that involves the simultaneous transfer of two electrons due to the reduction of the two PTM radical subunits. The CV suggests a negligible or very weak interaction between the two PTM radical subunits since we would expect to observe two electrochemical reduction waves in the case of a strong interaction between the two subunits.

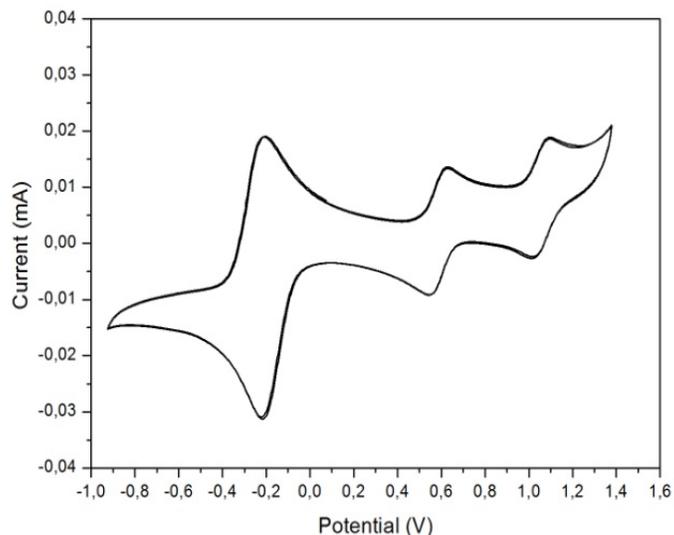


Figure 1. Cyclic voltammetry of solution of diradical $\mathbf{1}^{\bullet\bullet}$ in CH_2Cl_2 vs. Ag/AgCl using $n\text{-Bu}_4\text{PF}_6$ (0.1 M) as electrolyte at 300 K under argon at a scan rate of 0.1 V/s.

UV-Vis-NIR spectrum of diradical $\mathbf{1}^{\bullet\bullet}$ was obtained in CH_2Cl_2 at 300 K (Figure 2) showing an intense band at 385 nm, characteristic of PTM radical chromophores. The shoulders around 420 and 540 nm are attributed to the electronic conjugation of the unpaired electron into the π -framework. Regarding the low-energy region, the weak broad band that appears around 900 nm is assigned to the intramolecular charge transfer process from the electron-donor TTF bridge to the two electron-acceptor PTM radical subunits. TDDFT calculations confirmed such assignments enabling to ascribe each band to certain MO transitions (see Table S3).

Formation of radical anion mixed-valence species $\mathbf{1}^{\bullet\bullet}$ was carried out either by electrochemical or by chemical reduction using metallic Cu with $[(\text{Ph})_4\text{P}]\text{Br}$ (0.1 M) as supporting electrolyte in CH_2Cl_2 (see Figures 2 and S8). The reduction process was followed by UV-Vis-NIR spectroscopy until the mixed-valence species was completely generated. It was

observed two isosbestic points at 480 and 730 nm during the course of the reduction indicating that there are no byproducts due to decompositions or further reactions. During the reduction, the initial band at 385 nm, characteristic of PTM radical chromophore, gradually decreases and two new intense bands at 520 and 604 nm appear which are attributed to the PTM anion chromophore. Moreover, the lowest-energy band at 900 nm gradually decreases indicating the suppression of charge transfer from the TTF bridge to one of the PTM radical subunit as the later group is not electron-acceptor anymore. It is important to note that it was not observed any band in the NIR region that could be assigned to the intervalence transition (IVT) as observed for other mixed-valence compounds indicating a weak coupling of the two terminal PTM subunits.¹³ Finally, triradical cation $\mathbf{1}^{\bullet\bullet\bullet+}$ was generated either by electrochemical or by chemical oxidation of $\mathbf{1}^{\bullet}$ using FeCl_3 (see Figures 2 and S9). Absorption spectrum of the oxidized species shows a decreasing in intensity of the shoulders at 420 and 540 nm and the appearance of two new bands at 550 and 690 nm associated with the formation of $\text{TTF}^{\bullet+}$ species.³⁷⁻³⁹ Moreover, the band at 900 nm attributed to the IET gradually decreases in agreement with the lack of intramolecular charge transfer when the TTF bridge loses its electron-donor character.

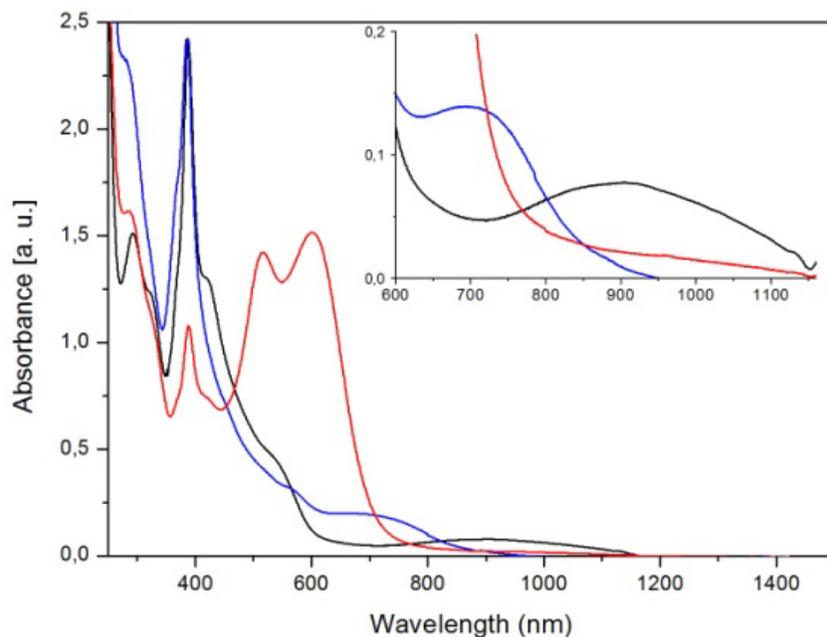


Figure 2. UV-Vis-NIR spectra of a solution 0.05 mM of diradical $\mathbf{1}^{\bullet\bullet}$ (black line), mixed-valence species $\mathbf{1}^{\bullet\bullet\bullet}$ (red line) and triradical cation $\mathbf{1}^{\bullet\bullet\bullet\bullet+}$ (blue line) in CH_2Cl_2 . Inset shows the low-energy range of the absorption spectra.

CW X-band ESR spectra of $\mathbf{1}^{\bullet}$ were recorded in CH_2Cl_2 in the temperature range of 300-200 K (Figure S10). The spectrum of $\mathbf{1}^{\bullet}$ at 240 K (Figure 3) shows at g_{iso} of 2.0027 three overlapped lines that are attributed to the coupling of the unpaired electron with two equivalent protons with a coupling constant $a_H = 0.9$ G ($\Delta H_{pp} = 0.9$ G) which is half of the value showed by a PTM monoradical with one vinylene bridge ($a_H = 2$ G). The appearance of three symmetrical lines indicate that the magnetic interaction of the two electrons of the PTM radicals have a magnetic exchange coupling constant, J , that fulfils the condition $|J| \gg |a_i|$, as it has been already observed for other PTM diradicals.⁹⁻¹³ The weak observed satellite lines are attributed to the hyperfine couplings with the naturally abundant ^{13}C nuclei of the PTM subunits with coupling constants of $a_{C,\alpha} = 14.9$ G and $a_{C,arom} = 6.9$ and 4.8 G that are also half the values for

typical PTM monoradicals. The spectrum of diradical $\mathbf{1}^{\bullet\bullet}$ was also recorded in frozen CH_2Cl_2 at 140 K and it was possible to observe the forbidden $\Delta m_s = 2$ transitions at half field in the ESR spectra suggesting the presence of the thermally-populated triplet state in the molecule (Figure S11). DFT calculations confirmed that the two unpaired electrons of $\mathbf{1}^{\bullet\bullet}$ are localized in each PTM unit (see Table S1 and Figure S15 in SI), and are coupled by an almost-negligible magnetic interaction (J_1 , see Table S2 and Figure S16 in SI). This is in agreement with the CV measurements discussed above. Even if the computed ground state is an open-shell singlet, the strength of the coupling suggests that the system effectively behaves as a paramagnet, with *ca.* 75% population of triplet states.

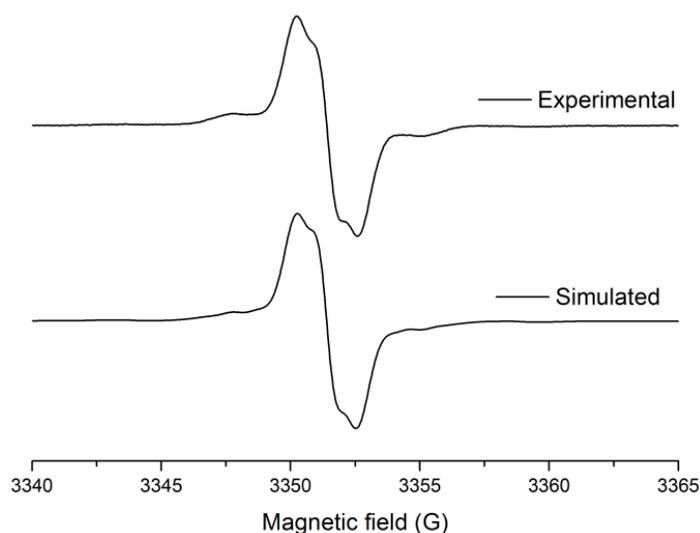


Figure 3. Experimental and simulated ESR spectra of 0.05 mM solution of diradical $\mathbf{1}^{\bullet\bullet}$ in CH_2Cl_2 at 240 K.

On the other hand, ESR spectra of the mixed-valence $\mathbf{1}^{\bullet\bullet}$ in CH_2Cl_2 species were recorded in the temperature range of 220-300 K (Figure S12). All the recorded spectra at different temperatures show two symmetrical lines at a *g* value of 2.0026 which indicates the coupling of the unpaired electron with only one hydrogen atom of the ethylene moiety directly linked to the

PTM radical with the isotropic hyperfine coupling constants typical for a PTM monoradical with a vinylene bridge ($a_H = 1.7$ G; $\Delta H_{pp} = 1.4$ G) (Figure 4).¹¹ This result, together with the lack of an intervalence (IVT) band transition in the absorption spectra, suggests that at these temperatures the unpaired electron of the radical anion $\mathbf{1}^{\cdot-}$ is always localized on only one half of the molecule, like in a monoradical (i.e. the intramolecular electron transfer rate is below the EPR time scale) showing that this MV compound belongs to Class I.

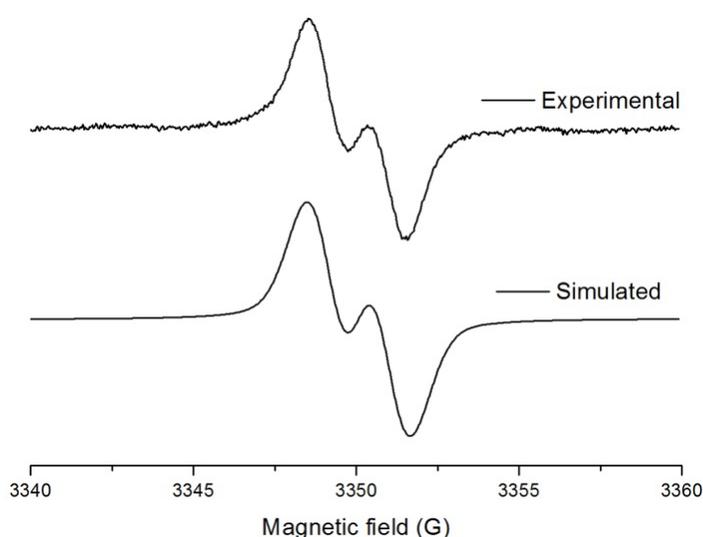


Figure 4. Experimental and simulated ESR spectra of 0.05 mM solution of mixed-valence $\mathbf{1}^{\cdot-}$ in CH_2Cl_2 at 240 K.

This localization effect observed for the radical anion $\mathbf{1}^{\cdot-}$ is in contrast to other fused A-D-A triads using a TTF as a bridge where the MV compounds have delocalized the unpaired electron at high temperatures.⁴⁰⁻⁴⁵ However, in all these examples the molecules are almost planar and in our case the molecule has several degrees of conformational freedom. Also it is important to mention the influence of the different topologies of the possible isomers on the ease of the electron transfer as it has been previously studied.⁹

Finally, ESR spectra of the oxidized $\mathbf{1}^{\cdot\cdot\cdot+}$ triradical cation species were recorded in CH_2Cl_2 in the temperature range of 240-300 K (Figure S13). The ESR spectrum of $\mathbf{1}^{\cdot\cdot\cdot+}$ consists of two

separated groups of lines centered at g -values of 2.0085 and 2.0034 that are attributed to the open-shell $\text{TTF}^{\cdot+}$ and PTM^{\cdot} radical subunits, respectively, that appear uncoupled (Figure 5). The ESR lines associated to the TTF bridge show a symmetric 5-lines signal indicating the coupling of the unpaired electron of the $\text{TTF}^{\cdot+}$ with two protons from the TTF subunit and two from the vinylene units ($a_{\text{H,TTF}} = 1.3$ and $a_{\text{H,vin}} = 0.8$ G). On the other hand, the group of lines corresponding to the PTM radical subunits shows only two overlapped symmetrical lines due to the coupling of the unpaired electron of the PTM subunits with only one proton of the bridge ($a_{\text{H,vin}} = 1.5$ G). The fact that the two group of lines related to the $\text{TTF}^{\cdot+}$ and PTM^{\cdot} radicals appear uncoupled and separated suggests that the electrons at the two terminal PTM radical subunits remain localized at the ESR time scale. A worth noticing point is the moderately-strong antiferromagnetic (AFM) interactions calculated for $\mathbf{1}^{\cdot\cdot+}$ between the oxidized TTF and each of the PTM moieties ($J_2 \approx J_3 \approx -60 \text{ cm}^{-1}$) (Table S2). Therefore, the resulting ground state is a doublet, with three unpaired electrons localized in the TTF and PTM (x2) units (see Figure S17). The quadruplet state lies higher in energy and, as a result, is poorly populated, which explains why the forbidden transition at half field in the ESR is not observed anymore. On the other hand, when temperature is lowered, the lines associated to the $\text{TTF}^{\cdot+}$ bridge do not disappear indicating the absence of dimerization process in contrast to the reported monoradical TTF-PTM dyad.²⁷ This is probably due to the steric hindrance of the two bulky PTM units that avoid the close interaction between the $\text{TTF}^{\cdot+}$ units.

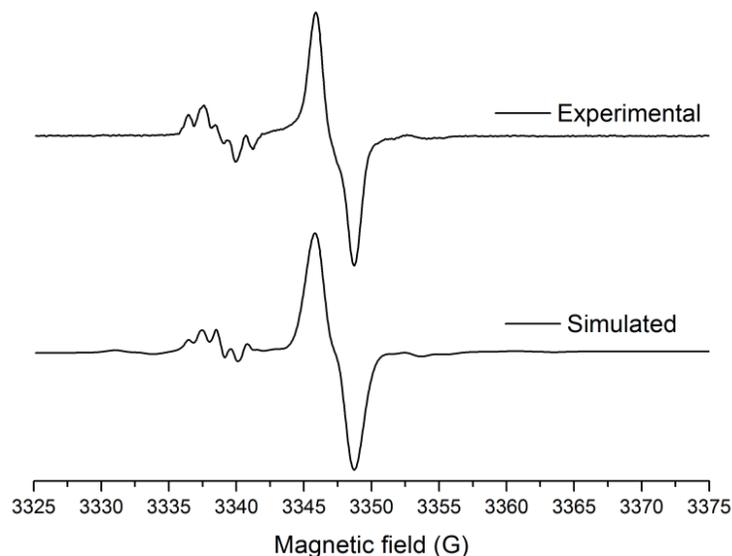


Figure 5. Experimental and simulated ESR spectra of 0.05 mM solution of radical cation $\mathbf{1}'''$ in CH_2Cl_2 at 240 K.

In order to demonstrate the reversibility of the system, we have carried out electrochemical redox reactions starting from $\mathbf{1}''$ that is oxidized to $\mathbf{1}'''$, then reduced to $\mathbf{1}'$ and oxidized back to the diradical species using CH_2Cl_2 with $[(n\text{-Bu})_4\text{N}] \text{PF}_6$ (0.1 M) as supporting electrolyte, Pt wire as a working electrode, and Ag/Ag^+ as the reference electrode (Figure 6). We performed several cycles and the electrochemical oxidation and reduction processes were monitored by UV-Vis spectroscopy at the wavelength of 650 nm showing that the absorbance intensity is completely recovered after each step demonstrating the high reversibility and stability of the resulted species.

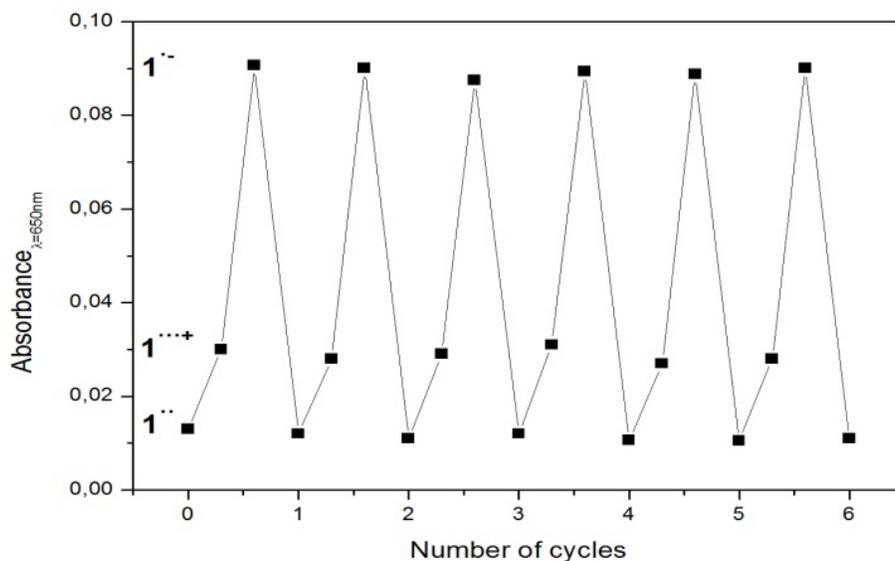


Figure 6. Evolution of the UV-Vis intensity at 650 nm recorded during the stepwise oxidation and reduction cycles of $1^{\bullet\bullet}$.

In conclusion, we have reported a diradical A-D-A triad composed by two PTM radical subunits connected through a TTF-vinylene bridge that can reversible modulate the optical, electronic and magnetic properties by one-electron reduction and oxidation in a reversible way. Interestingly, the suppression of the electron delocalization was observed when passing from the diradical to the anion radical mixed-valence species indicating the preferable localization of the unpaired electron on only one of the two PTM radical moieties. On the other hand, the switching from an almost negligible ferromagnetic (FM) magnetic interaction to a moderate-strong antiferromagnetic (AFM) interaction between TTF and PTM moieties was observed when the TTF bridge was oxidized. Finally, the system was found to be highly reversible and can be viewed as a promising building block for the development of molecular switches.

ASSOCIATED CONTENT

Supporting Information. General methods, synthesis and characterization, chemical reduction and oxidation of $\mathbf{1}^{\bullet}$, ESR spectra of $\mathbf{1}^{\bullet}$, $\mathbf{1}^{\bullet-}$ and $\mathbf{1}^{\bullet++}$ at different temperatures, and computational analysis are included.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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