Supramolecular Chemistry

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Induced Self-Assembly of a Tetrathiafulvalene-Based Open-Shell Dyad through Intramolecular Electron Transfer**

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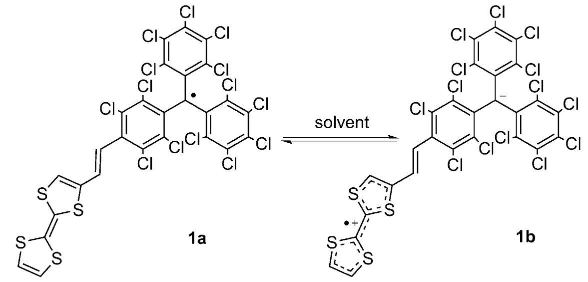
Substituted tetrathiafulvalene (TTF) compounds and their cation radical (TTF$^{+\bullet}$) derivatives have received a great deal of attention in recent years on account of their fascinating electrical[1] and electrochemical properties.[2] The self-assembling of TTF derivatives plays a key role in both types of properties since it controls the molecular structures in solid state and in solution. While a great deal of knowledge exists in the self-assembling of TTF molecules in solid state, little is known in solution because of the weakness of noncovalent interactions involved in this media. Therefore, the observation and study of TTF aggregates in solution remains a challenging task unless suitable hosts, cages, or special conditions are employed.[3,4] Rosokha and Kochi were able to observe the self-assembling of the TTF$^{+\bullet}$ cation radical in solution at room temperature using high concentrations of its salt with a large and non-coordinating carboranate anion. Specifically, they studied the diamagnetic [TTF$^{+\bullet}$-TTF$^{+\bullet}$] dimer as well as the association of the TTF$^{+\bullet}$ cation radical with its parent neutral TTF donor forming the mixed valence [TTF$^{+\bullet}$-TTF] species.[4] Nevertheless, in this case and others the generation of the dimerized species is always driven by the presence of the cation radical which is generated ex situ by an (electro)chemical oxidation stimulus. Remarkably no examples of such dimerizations induced by an intramolecular activation with neutral TTF derivatives have been reported up to date. One possible way to achieve this goal is to use a donor–acceptor dyad, based on a TTF electron π-donor connected to an electron acceptor, which exhibits a reversible switching between two states through an intramolecular electron transfer (IET) process in response to an external stimulus like temperature, pressure, light, solvent, or electrical field. One of the two resulting states of such dyad will have a neutral structure while the other will exhibit a zwitterionic structure with a charged TTF subunit which should induce the desired dimerization. Among the existing TTF-based dyads, few have open-shell acceptor units. There are examples of TTFs connected to stable neutral radicals to develop "spin-polarized donors" since they are excellent candidates for developing responsive solid-state materials with coexisting magnetic and conducting properties.[5] There is only one example of a TTF-based dyad where the IET process and the reversible switching between the two involved states have been studied in solution but without paying attention to the self-assembling phenomena.[6] Hence, it is highly desirable to design new open-shell dyads formed by building blocks that exhibit IET and, as a consequence, assemble in a functional way such as the TTF$^{+\bullet}$ derivatives. With this goal in mind, the neutral organic open-shell dyad **1** (Scheme 1), consisting of the electron acceptor perchlorotriphenylmethyl (PTM) radical subunit linked to the electron π-donor TTF subunit through a vinylene π-bridge, was synthesized. Along the same research line we previously reported IET studies based on PTM dyads using ferrocenes as electron donor subunits in solution.[7] Moreover, the bistability phenomenon of one of these dyads in solid state was properly rationalized.[8] Here we focus on the study of the self-assembly of dyad **1** in solution induced by the associated IET process. The understanding of such a phenomenon will



Scheme 1. Dyad **1** in the neutral **1a** and zwitterionic **1b** electronic states obtained through an IET process.

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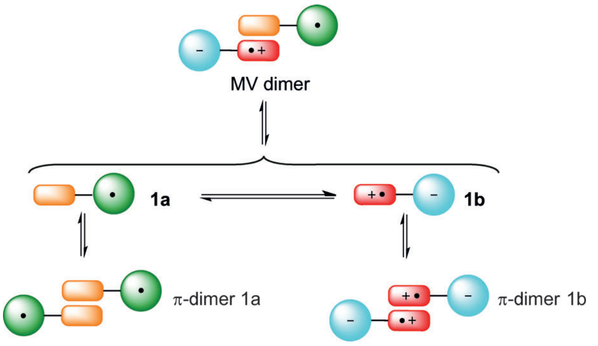
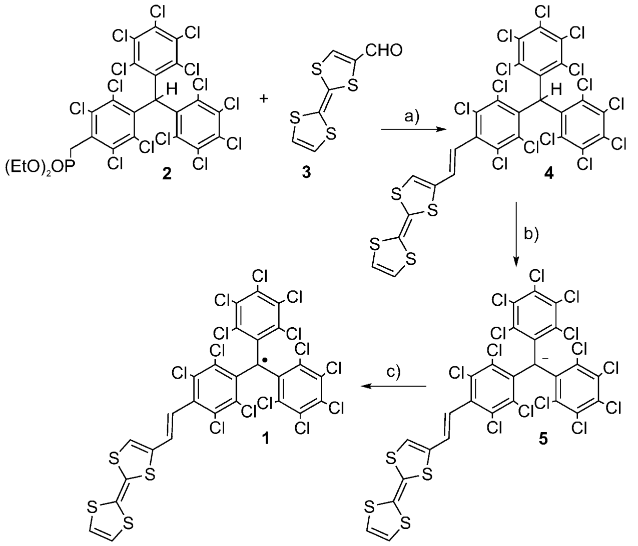
be of fundamental interest for the achievement of new supramolecular switches and logic gates with **1** as well as for the comprehension of its solid-state physical properties.

Remarkably, moderate changes of solvent properties induce an IET with the consequent reversible switching between the neutral **1a** and the zwitterionic **1b** states. Moreover, the dipolar nature of the molecule and more specifically the cation radical character introduced on the TTF subunit by the IET process induces the TTF-based self-assembly of dyad **1**. To the best of our knowledge, this is the first time that an IET process induces the self-assembly of a neutral TTF-based dyad (Scheme 2).



Scheme 2. Supramolecular structures of dyad **1** induced by the IET process and associated equilibria occurring in solution (MV = mixed valence).

Dyad **1** was synthesized in three steps with a good yield (Scheme 3). Compound **4** was first obtained through a Horner–Wadsworth–Emmons reaction[9] of the protonated PTM derivative **2**[10] functionalized with a phosphonate group and the 2-formyltetrathiafulvalene **3**[11] using potassium *tert*-butoxide as a base. Subsequent deprotonation of **4** with



Scheme 3. Synthesis of dyad **1**: a) Potassium *tert*-butoxide (1.1 equiv), THF, −78 °C, 70%; b) KOH (10 equiv), [18]crown-6 (1 equiv), CH_2Cl_2, RT, 90%; c) $AgNO_3$, CH_2Cl_2/CH_3CN (4:1), RT, 95%.

potassium hydroxide in the presence of [18]-crown-6 yielded **5**. Finally, the oxidation of **5** with silver nitrate afforded dyad **1**, which is stable under ambient conditions and shows a remarkable solvatochromism (Figure 1).

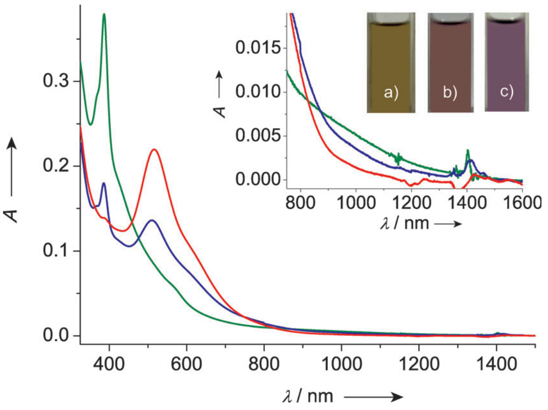


Figure 1. UV/Vis/NIR spectra of dyad **1** in CH_2Cl_2 (green line), acetone (blue line), and DMF (red line). Inset: Low-energy range of the absorption spectra and colors of **1** exhibited in a) CH_2Cl_2, b) acetone, and c) DMF solutions.

UV/Vis/NIR spectra of dyad **1** at 300 K in different aprotic solvents were measured (Figure 1). Dichloromethane (CH_2Cl_2), acetone, acetonitrile, and *N*,*N*-dimethylformamide (DMF) were chosen because of their different polarity. The absorption spectrum of **1** in CH_2Cl_2 (0.05 mM) at 300 K shows an intense absorption band at 387 nm which is characteristic of the radical chromophore of the PTM subunit.[12] Moreover, a weak broad band is observed in the region of 900–1100 nm which is ascribed to the photoinduced IET process between the TTF donor and the PTM acceptor subunits.[7,13] These two bands unequivocally prove the presence of **1** in CH_2Cl_2 in the neutral state **1a**. In contrast, a solution of **1** in DMF (0.05 mM) presents an intense band at 512 nm and a shoulder at 605 nm which clearly correspond to the anionic form of the PTM moiety.[7,13–14] Moreover, both the sharp band at 387 nm and the low-energy IET band observed in the neutral state **1a** disappear confirming the presence of the zwitterionic state **1b** in DMF.

Interestingly, the spectra of **1** (0.05 mM) in acetone and acetonitrile (see Figure S1 in the Supporting Information), simultaneously exhibit the bands located at 387 nm and around 900–1100 nm attributed to **1a** as well as a band at 505 nm and the shoulder related to **1b**. Thus, these spectra prove the coexistence of both species **1a** and **1b** in equilibrium in both solvents. These results indicate that polar solvents favor the zwitterionic state **1b** whereas less polar ones stabilize the neutral state **1a**.[15] Therefore, it is possible to tune the equilibrium between **1a** and **1b** simply by the modification of the molecular environment.

To confirm such a tuning of the equilibrium, solutions of **1** with a nominal concentration of 0.05 mM were prepared in mixtures of CH_2Cl_2/acetone and CH_2Cl_2/DMF with increasing proportions of acetone and DMF, respectively. UV/Vis/NIR spectra of these solutions were performed at 300 K and the absorbance of the sharp radical band at 387 nm and the anionic band around 500 nm were plotted versus the acetone or DMF proportions (Figure S2). The increment of the polarity of the solvent, achieved by increasing the relative amount of acetone or DMF, enhances the intensity of the broad band located around 500 nm related to the zwitterionic state **1b** at expenses of the sharp band centered at 387 nm attributed to the neutral state **1a**. The equilibrium is more shifted towards the zwiterionic state **1b** in mixtures of CH_2Cl_2/DMF than in CH_2Cl_2/acetone in accordance with the higher polarity of DMF.

To corroborate the electronic structure of the **1a** and **1b** states, the ESR spectra of dyad **1** in CH_2Cl_2, acetone, acetonitrile, and DMF at 300 K were measured (Figure 2 and Figure S8). The neutral form **1a** is expected to present an ESR signal produced by the PTM radical subunit with a g value close to 2.0026,[13–14] whereas the zwitterionic state **1b** is supposed to show under isotropic conditions a signal associated to the $TTF^{+\bullet}$ cation radical subunit with a g value around 2.0084.[16]

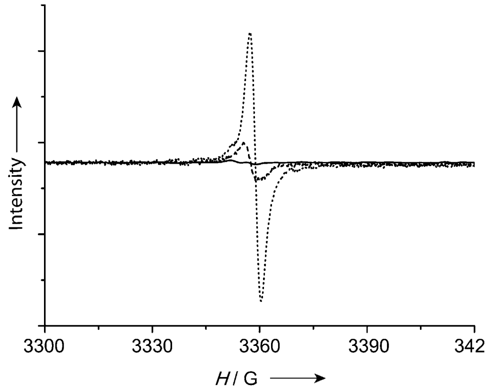


Figure 2. ESR spectra of 0.05 mM solutions of dyad **1** at 300 K in CH_2Cl_2 (dotted line), acetone (dashed line), and DMF (solid line).

Indeed, the ESR spectrum at 300 K of dyad **1** in CH_2Cl_2 shows one broad line located at a g value of 2.0025 confirming the presence of the neutral **1a** state. Similarly, a solution of **1** in acetone exhibits a broad line centered at a g value of 2.0027, the intensity of which is considerably lower than that observed in CH_2Cl_2 at the same concentration. This result is in agreement with the UV/Vis/NIR spectra confirming the coexistence of **1a** and **1b** species in acetone. Similar agreement is obtained in DMF since no signal related to the PTM radical subunit was observed proving that all molecules exist in the zwitterionic state **1b**. Surprisingly, no signals related to the presence of the $TTF^{+\bullet}$ cation radical subunit were detected in the ESR spectra of solutions of **1** in acetone, acetonitrile, or DMF. Considering that the existence of the zwitterionic species **1b** is directly proved by the UV/Vis/NIR spectra and indirectly demonstrated by the relative intensities of the ESR signal related to the PTM subunit, the lack of the ESR signal of the $TTF^{+\bullet}$ subunit indicates the existence of an additional phenomenon. We suggest that under such conditions the species **1b** evolves towards supramolecular diamagnetic structures that are ESR silent, like the π-dimer **1b** (Scheme 2). The weak absorption band associated to the **1b** dimer expected at around 750 nm cannot be detected in optical spectra (Figure S3) because of the overlap with the tail of the much more intense band of the PTM anion. To shed some light on this complex dynamic behavior, temperature-dependent ESR spectra of dyad **1** in CH_2Cl_2, acetone, acetonitrile, and DMF were also measured.[17] The ESR signal of dyad **1** in CH_2Cl_2 at 300 K consists of an unstructured line at a g value of 2.0025 which becomes partially resolved into three lines when the temperature is decreased (see Figure S5 for ESR experimental and simulated spectra of dyad **1** at two extreme temperatures and Figure S6 for spectra at other temperatures). The three lines observed at low temperatures are assigned to the coupling of the unpaired electrons of the resulting species with two equivalent protons with a coupling constant of $a_H = 1.1$ G. This hyperfine coupling together with the temperature behavior resemble those exhibited by some PTM diradical derivatives incorporating a p-phenylenevinylene or a 1,1′-ferrocenylendivinylene bridges between the two PTM subunits which are magnetically coupled through the bridges.[10,13b,18] Therefore, the observation of the three-lines signal at low temperatures suggests the presence of a fast equilibrium between the neutral molecule **1a** and the homodimer π-dimer **1a** (Scheme 2), which is driven by the known tendency of neutral TTFs to dimerize at low temperature in solution, that here may be enhanced by the dipolar character of **1**.[4]

Variable temperature ESR spectra of dyad **1** in DMF (0.05 mM) do not give any signal in the whole temperature range of 260–350 K indicating that the zwitterionic **1b** species are completely dimerized producing the stable and ESR-silent π-dimer **1b**,[4] in accordance with the well-known tendency of the $TTF^{+\bullet}$ cation radicals to aggregate in solution forming diamagnetic supramolecular structures.

Temperature-dependent ESR spectra of **1** in acetone and acetonitrile (0.05 mM) were also performed to study the dynamic equilibrium between the coexisting neutral **1a** and the zwitterionic **1b** species (Figures S7 and S8). At 300 K a broad unstructured signal centered at a g value of 2.0027 is observed which is progressively shifted towards higher g values when the temperature is lowered reaching a g value of 2.0032 at 190 K (Figure 3). In this temperature range, no changes on the shape of the signal neither the appearance of further signals related to the $TTF^{+\bullet}$ cation radical subunit were detected. These results can be interpreted by the existence of a fast equilibrium between the coexisting species **1a** and **1b** and a supramolecular mixed valence species, the MV dimer, that takes place at faster rates than the ESR time scale (Scheme 2). Therefore, the ESR spectra obtained at low temperatures should be the averaged ESR signals of the different species present in solution. In line with this interpretation, the ESR signals of **1** in acetone and acetonitrile move towards the g value of the $TTF^{+\bullet}$ subunit (Figure 3) when the temperature is decreased. Thus, the signal appears at a position given by the weighted mean of the g values of the three species in equilibrium; given by $g = g_{1a} \cdot p_{1a} + g_{1b} \cdot p_{1b} + g_{MVdimer}(1 - p_{1a} - p_{1b})$, where p_{1a} and p_{1b} are the probabilities of the molecules to be in the **1a** or the **1b** states, respectively, at

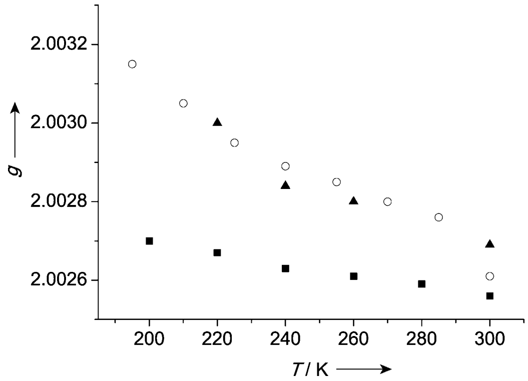


Figure 3. Temperature dependence of the g values of **1** in solutions of acetone (empty circles), CH_2Cl_2 (full squares), and acetonitrile (full triangles).

the observed temperature.[19] The direct confirmation of the formation of MV dimer species was obtained by nanoelectrospray ionization ion-mobility mass spectrometry (Nano-ESI-IM-MS) using acetonitrile as solvent since this technique allows to discriminate between species with the same m/z ratios but with different charge, size, and shape.[20] Therefore, it enables the separation in the gas phase of a species with a $2m/2z$ ratio from another with a m/z ratio. After background removal by ion mobility separation we could resolve a clear peak at a mobility drift time of 5.51 ms that corresponds to the double-charged dimeric species of **1** appearing at m/z 954 amu. The observed isotope mass distribution agrees well with the theoretical expectation; a notable result in view of the specific distribution of the chlorine isotopic mass (Figure S9). Low proportions of other less stable dimeric species like the π-dimers **1a** or **1b** are discarded because of their known lower stability in solution compared with the MV dimer.

More information is obtained from the ESR spectrum of the frozen solution (140 K) of dyad **1** in acetone since the fast dynamic equilibrium between the species is quenched under such conditions. The resulting spectrum can be nicely simulated as the sum of two main contributions, one associated with species having a $TTF^{+\bullet}$ cation radical and another with species containing a PTM radical with a ratio of 2/3 (Figure S10). Indeed, this spectrum corresponds to that of a sample containing a randomly oriented rigid collection of molecules of **1a** and MV dimer. The TTF signal related to the dimeric species exhibits the magnetic anisotropy of a $TTF^{+\bullet}$ cation radical with the typical turning points associated with the principal components of the g tensor of $g_x = 2.0239$, $g_y = 2.0040$, and $g_z = 1.9812$,[21] whereas the signal related to the **1a** species exhibits the typical low magnetic anisotropy of PTM radicals with g-tensor components of $g_x \approx g_y \approx g_z \approx 2.0025$. The latter signal has also the contribution of the PTM subunit of the MV dimer. Cyclic voltammograms of dyad **1** in different solvents (Figures S11 and 12) show a solvent dependence of the potentials exhibited by the two first redox waves [$\Delta E_{\mathrm{red}}(CH_2Cl_2) > \Delta E_{\mathrm{red}}(\mathrm{acetone}) > \Delta E_{\mathrm{red}}(\mathrm{DMF})$] in agreement with the easiness of IET and thus, corroborating the solvent effect on such a phenomenon. Therefore, these results support again the presence of **1a** in CH_2Cl_2 and the absence in DMF, as well as the mixture **1a**/**1b** in acetone. Finally, quantum chemical calculations confirmed the possibility to tune dyad **1** from a neutral to a zwitterionic state by application of a uniform electric field. Spin distributions calculated for the two forms are in line with a switching of the spin density from the PTM to the TTF unit when going from the neutral to the zwitterionic structures (Figures S14 and S15). The molecular orbitals show that in the neutral state the highest occupied molecular orbital (HOMO) energy is higher than for the singly occupied molecular orbital (SOMO; Figures S16 and S17), as required to construct solid-state conductive organic radical crystals.

In summary, we have described a neutral organic open-shell TTF-based dyad **1** which exhibits an intramolecular electron transfer phenomenon that enables the reversible switching from its neutral state **1a** to its zwitterionic state **1b** simply by modification of the solvent polarity being possible to attain the coexistence of both states **1a** and **1b** under certain conditions. Moreover, it has been demonstrated for the first time that the TTF-based self-assembly of this dyad is induced by the IET process between the donor and acceptor groups. In conclusion, we obtained a complex responsive molecular system that can be switched applying an external stimulus between different supramolecular architectures. This type of system can be viewed as a promising building block for "smart" functional supramolecular materials which can modify their electronic structure in response to external stimuli and are interesting because of their conductive and magnetic properties in solid state.

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[15] It is worth mentioning that the equilibrium between **1a** and **1b** may not only be controled by the polarity of the solvent but also by other specific solute–solvent interactions.

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