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## A self-assembled tetrathiafulvalene box

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### Introduction

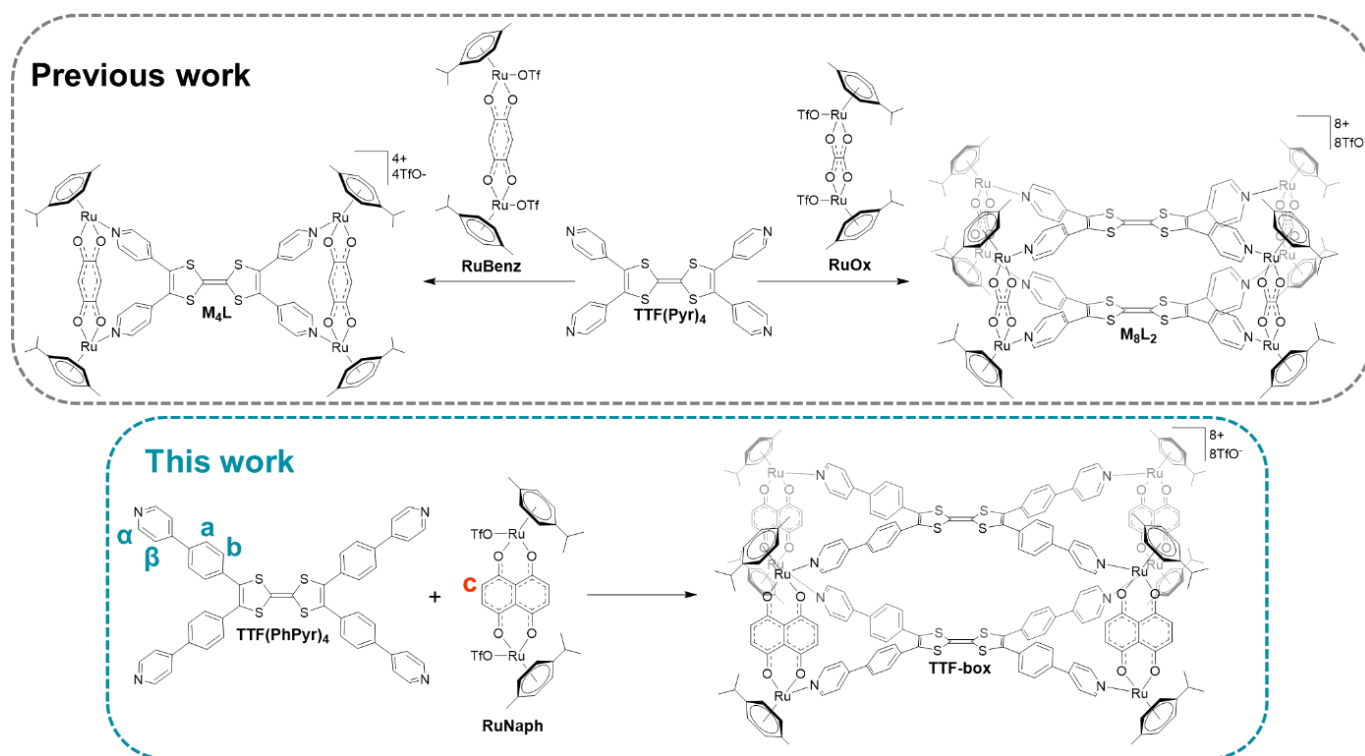
The dimerization of conjugated radical-cations constitutes an appealing interaction of the supramolecular tool-box, which has known a strong recent interest.<sup>1-4</sup> Interestingly, the latter can be controlled through a redox stimulation, as demonstrated with the prototypical electroactive cases of tetrathiafulvalene (TTF) or bipyridinium derivatives. Oxidation in solution of TTF derivatives<sup>5, 6</sup> into the corresponding  $\pi$ -dimer species (TTF<sup>•+</sup>)<sub>2</sub> has been characterized in very specific cases, *i.e.* highly concentrated solutions at low temperature,<sup>7, 8</sup> redox-active units confined in a molecular cavity,<sup>9-12</sup> covalently preorganized poly-TTF systems,<sup>13-22</sup> or stabilization of TTF units in interlocked structures.<sup>1, 23</sup>

To get a better control over the experimental parameters driving the radical-pairing interaction, there is a need to develop new molecular models. In this context, designing bis(TTF) architectures with two preorganized facing TTF units, prone to stack, is of interest notably if the intramolecular inter-TTF distance can be tuned. A similar approach was recently developed with success in the case of flexible viologen cyclophanes, through controlling the linker length between both redox units.<sup>24-26</sup>

To the best of our knowledge, only one organic macrocycle<sup>27</sup> featuring two facing TTF moieties has been described so far.<sup>28</sup> This electron-rich bis(TTF)derivative, prepared in several steps through covalent synthesis, was designed to afford a distance of *ca.* 7 Å between both TTF plans in order to bind planar electron-poor guests in a sandwich-like manner.

On the other hand, macrocyclic metalla-rings can be prepared in one step and in excellent yields through the coordination-driven self-assembly strategy between polytypic ligands and specific metal complexes.<sup>29-51</sup> For instance, this approach has allowed to target electro-active assemblies.<sup>52-58</sup> We have contributed to this field by synthesizing a large number of redox-active supramolecular cavities incorporating electron-rich dithiolyldiene units, such as with extended-TTF derivatives<sup>59-64</sup> or very recently, S-rich fluorene derivatives.<sup>65-67</sup> Despite well-defined redox properties, only two examples of discrete metalla-assemblies based on the parent TTF framework have been described so far.<sup>68, 69</sup> They were obtained upon self-assembling a tetratopic TTF-based ligand bearing four pyridyl units (**TTF(Pyr)**<sub>4</sub>), with either a *cis*-blocked M(II) complex (M = Pd or Pt),<sup>69</sup> or a bis-Ruthenium one **RuOx**<sup>68</sup> (Scheme 1). In the latter case, a M<sub>8</sub>L<sub>2</sub> assembly was obtained in good yields, for which two TTF units are facing each other. On the contrary, a M<sub>4</sub>L metalla-plate (*i.e.* one ligand associated to two bis-Ruthenium complexes) was obtained upon mixing **TTF(Pyr)**<sub>4</sub> with the longer bis-Ruthenium complex **RuBenz** (Scheme 1).<sup>68</sup> Such a difference is due to the respective Ru-Ru distance in both complexes (*i.e.* 5.5 Å in **RuOx** and 7.9 Å in **RuBenz**). The latter value well matches for the coordination of two adjacent pyridyl units in **TTF(Pyr)**<sub>4</sub> (Npyr...Npyr = 6.7 Å), favoring the M<sub>4</sub>L discrete structure (Scheme 1 and Figure 1). Driving the self-assembly to a new M<sub>8</sub>L<sub>2</sub> TTF-box for which two TTF units are forced to face each other, needs therefore a mismatch between both Npyr...Npyr and Ru...Ru distances. This can be achieved through changing the ligand size (*i.e.* the distance between two Npyr atoms) or the bis-Ruthenium complex (*i.e.* the distance between two Ru atoms).

We present hereafter the coordination-driven assembling of a new M<sub>8</sub>L<sub>2</sub> **TTF-box** using the new enlarged TTF-based ligand **TTF(PhPyr)**<sub>4</sub> and the bis-Ruthenium<sup>70</sup> complex **RuNaph** (Scheme 1). The interaction between both facing redox units in this system is investigated in solution. This study shows that both TTF units dimerize intramolecularly when oxidized to the radical-cation state, thanks to the rigidity of the assembly.

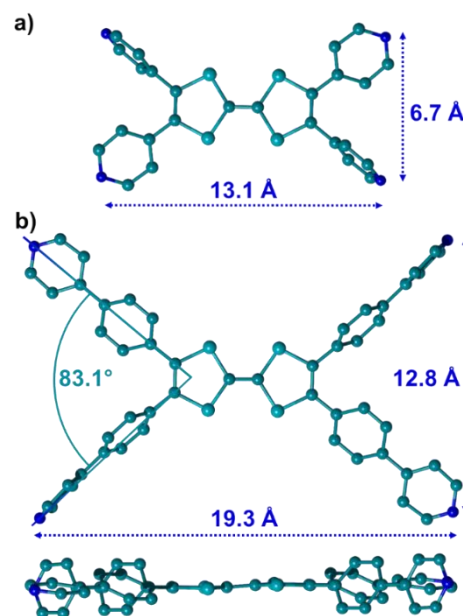


**Scheme 1.** Synthesis of the previously described complex  $M_8L_2$  and  $M_4L$  (top),<sup>68</sup> and of **TTF-box** from the current work.

## Results and discussion

We designed the tetratopic ligand **TTF(PhPyr)<sub>4</sub>** which differs from **TTF(Pyrr)<sub>4</sub>** by the presence of a paraphenylene spacer between the redox and coordinating units. Importantly, this design results in a much longer separation between adjacent Npyr atoms, prone to change drastically the reaction with a bis-Ruthenium complex of a given length ( $M_8L_2$  vs  $M_4L$  self-assemblies). The new ligand **TTF(PhPyr)<sub>4</sub>** was synthesized in 86% yield using a Palladium-catalyzed C-H activated tetraarylation,<sup>71</sup> starting from the commercially available TTF and (4-bromophenyl)pyridine.<sup>72</sup> This yield is remarkable given the formation of four new C-C bonds along this process. Single crystals of ligand **TTF(PhPyr)<sub>4</sub>**, suitable for a X-ray diffraction study, were obtained by slow evaporation of a dichloromethane/methanol mixture. X-ray data show a significant disorder of the phenyl units through rotation around the TTF-Pyr axis (Figure 1). The molecule is contained in a 12.8 x 19.3 Å rectangle, as defined by the four Npyr atoms. These values can be compared with those observed for **TTF(Pyrr)<sub>4</sub>** (6.7 x 13.1 Å).<sup>69</sup> In particular the distance between adjacent Npyr atoms in **TTF(PhPyr)<sub>4</sub>** appears significantly higher than in **TTF(Pyrr)<sub>4</sub>** (12.8 Å vs 6.7 Å) as well as when compared to the Ru-Ru distances for all the bis-Ruthenium complexes studied (Scheme 1). Such mismatching of the distances between the Npyr coordinating units on one hand, and both metals of the bis-Ruthenium complex on the other hand, is prone to favor the

formation of the desired  $M_8L_2$  self-assemblies. Reaction of **TTF(PhPyr)<sub>4</sub>** with the bis-Ruthenium complex **RuNaph** ( $d_{Ru-Ru} =$



**Fig. 1.** X-ray crystal structures of a) **TTF(Pyrr)<sub>4</sub>** and b) **TTF(PhPyr)<sub>4</sub>** ligands.

8.4 Å) in acetone was followed by <sup>1</sup>H NMR spectroscopy. After one night, the resulting spectrum shows well defined signals, suggesting the formation of a discrete self-assembled system (Figure 2). The  $\alpha$  pyridyl protons signals as well as those of the paraphenylene spacer are upfield shifted upon coordination to

the metal center. Occurrence of a single discrete structure is confirmed by a  $^1\text{H}$  DOSY NMR experiment, for which a single set of aligned signals is observed. The corresponding diffusion coefficient ( $D = 4.75 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ ) allows to estimate a hydrodynamic radius of  $r_H = 15 \text{ \AA}$  calculated from the Stokes-

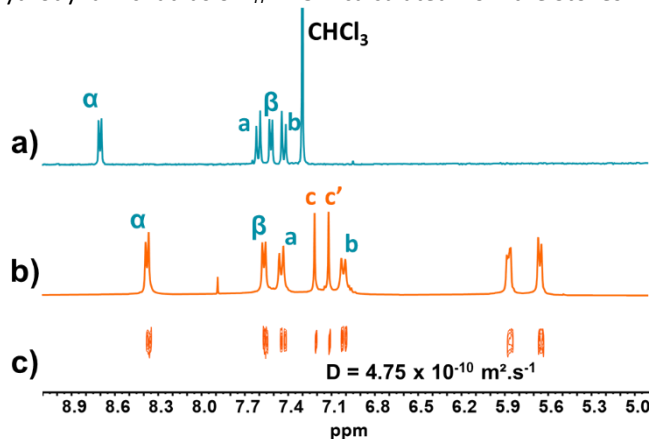


Fig. 2. (a)  $^1\text{H}$  NMR (aromatic region) of ligand **TTF(PhPyr)<sub>4</sub>** in  $\text{CDCl}_3$ , (b) **TTF-box** in  $\text{Acetone-d}_6$  and (c)  $^1\text{H}$  DOSY NMR corresponding to (b).

Einstein equation,<sup>73</sup> a value which is in agreement with the expected  $\text{M}_8\text{L}_2$  species.

An FTIR-MS analysis was carried out and confirms the formation of the  $\text{M}_8\text{L}_2$  **TTF-box**, as shown by the characteristic ions [**(TTF(PhPyr)<sub>4</sub>)<sub>2</sub>(RuNaph)<sub>4</sub>, 5TfO**] $^{3+}$  ( $m/z = 1671.4093$ ) and [**(TTF(PhPyr)<sub>4</sub>)<sub>2</sub>(RuNaph)<sub>4</sub>, 4TfO**] $^{4+}$  ( $m/z = 1216.3185$ ) (Figure S7).

Single-crystals were obtained by diffusion of methyl-*tert*-butyl ether into a solution of **TTF-box** in methanol (Figure 3) and the X-ray diffraction structure of the TTF dimeric structure could be solved. Two independent molecules are present in the crystal. From these data, a length of *ca.* 37  $\text{\AA}$

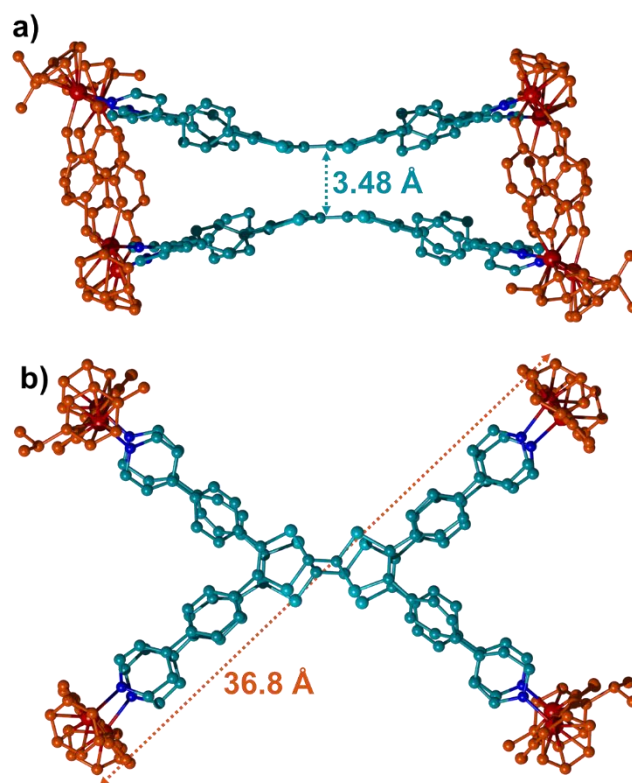


Fig. 3. X-ray structure of **TTF-box**, lateral view (a), top view (b). Hydrogens, anions and solvent molecules are omitted for clarity.

was found for the largest diagonal of **TTF-box**, a value which satisfactorily correlates with the calculation extracted from the DOSY  $^1\text{H}$  NMR study. The most striking feature of this structure relies on the close distance between both facing TTF units within the dimeric structure. A short distance of 3.48  $\text{\AA}$  is observed between both central C=C bonds of two opposite TTF units, and S $\cdots$ S distances as low as 3.83  $\text{\AA}$  for the smallest. These values are significantly smaller than the Ru-Ru distance in each of the four lateral pillars (8.38  $\text{\AA}$ ), meaning that the TTF dimeric structure is collapsed and fills the space between both TTF units. This observation means that a certain degree of conformational flexibility exists in the TTF framework, though there is no  $\text{sp}^3$  C atom in the entire system. In particular, one of the TTF units undergoes a bending of 20° around the S $\cdots$ S axis of one 1,3-dithiol ring. Though the design and size of this metallacage suggests the possibility to intercalate one planar electron-poor guest in a sandwich mode, all attempts failed, probably because of the close contacts occurring between both TTF panels. This observation is consistent with the study of J. Becher et al.<sup>28</sup> The electrochemical properties of **TTF(PhPyr)<sub>4</sub>** were studied (Figure 4a). and compared to those of **TTF(Pyr)<sub>4</sub>**<sup>69</sup> and the tetrakis(methylpyridinium) derivative of **TTF(PhPyr)<sub>4</sub>**, *i.e.* compound **TTF(PhPyrMe)<sub>4</sub>** (see SI). The latter can be considered as a model compound, reminiscent of ligand **TTF(PhPyr)<sub>4</sub>** when

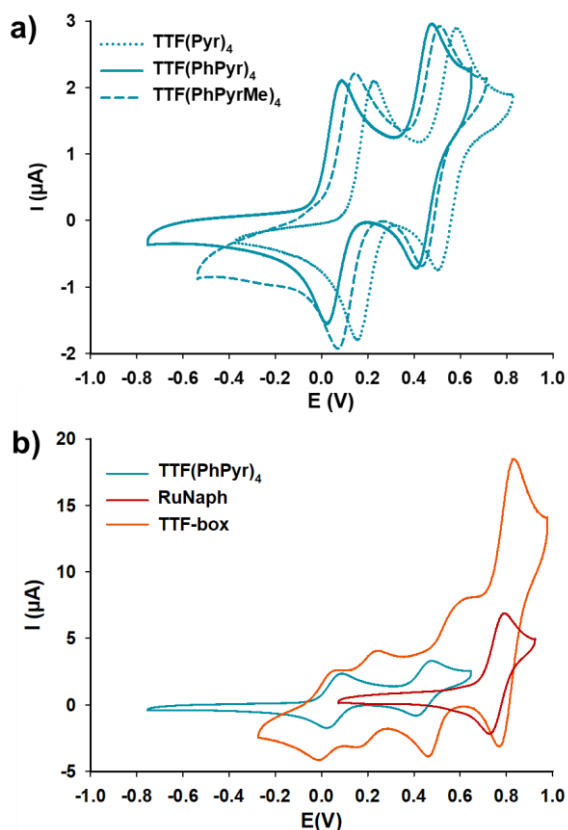


Fig. 4. Cyclic voltammetry in  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  1/1 ( $C = 1 \text{ mM}$ ,  $n\text{Bu}_4\text{NPF}_6$  (0,1 M)),  $100 \text{ mV}\cdot\text{s}^{-1}$ , glassy carbon, vs  $\text{Fc}/\text{Fc}^+$ ) of  $\text{TTF}(\text{PhPyr})_4$ ,  $\text{TTF}(\text{PhPyrMe})_4$ , and  $\text{TTF}(\text{Pyr})_4$  (a) and of  $\text{TTF-box}$ , compared to the starting ligand  $\text{TTF}(\text{PhPyr})_4$  and the bis-Ruthenium complex  $\text{RuNaph}$  (b). \* For solubility reasons  $\text{TTF}(\text{PhPyr})_4$  was recorded in  $\text{CH}_2\text{Cl}_2$ .

the latter is engaged in a coordination bond as it is the case in  $\text{TTF-box}$ . The pyridyl groups quaternization was carried out upon treating  $\text{TTF}(\text{PhPyr})_4$  with methyl iodide in DMF, followed by an anion exchange with  $\text{KPF}_6$ . The ligand  $\text{TTF}(\text{PhPyr})_4$  shows two reversible oxidation waves ( $E_{1^{\text{ox}}} = 0.08 \text{ V}$  and  $E_{2^{\text{ox}}} = 0.48 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$ ) corresponding to two successive one-electron oxidations to the radical-cation and dication states, as usually observed for TTF derivatives. It is worth noting that these oxidations occur at significantly lower potentials compared to  $\text{TTF}(\text{Pyr})_4$  ones ( $E_{1^{\text{ox}}} = 0.22 \text{ V}$  and  $E_{2^{\text{ox}}} = 0.58 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$ ). This difference can be explained by the presence of the phenyl spacer which isolates the pyridyl groups from the redox-active

TTF core, thereby attenuating the withdrawing inductive effect of Npyr atoms. On this basis, compound  $\text{TTF}(\text{PhPyr})_4$  exhibits a high  $\pi$ -donating ability and appears appropriate for generating electron-rich discrete assemblies. The corresponding tetrapyrindinium salt  $\text{TTF}(\text{PhPyrMe})_4$  shows redox waves ( $E_{1^{\text{ox}}} = 0.14 \text{ V}$  and  $E_{2^{\text{ox}}} = 0.51 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$ ) which are anodically shifted when compared to  $\text{TTF}(\text{PhPyr})_4$ , as expected from the positively charged nitrogen atoms.

Interestingly, under the same conditions,  $\text{TTF-box}$  exhibits a splitting of the first oxidation process into two reversible waves ( $E_{1^{\text{ox}}} = 0.04 \text{ V}$  and  $E_{2^{\text{ox}}} = 0.24 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$ , Figure 4b).<sup>74</sup> This observation is assigned to the successive formation of the mixed-valence dimer  $(\text{TTF})_2^{\bullet+}$  and of the corresponding  $\pi$ -dimer  $(\text{TTF}^{\bullet+})_2$ .<sup>14, 16, 18</sup> Such phenomenon is explained by the very close distance between both facing TTF subunits in  $\text{TTF-box}$ , prone to strongly interact upon oxidation. A third reversible oxidation process, located at  $E_{3^{\text{ox}}} = 0.60 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$  and anodically shifted compared to  $\text{TTF}(\text{PhPyrMe})_4$  because of coulombic repulsions, is assigned to the formation of the dication state for each TTF unit. The last reversible oxidation process is observed at  $E_{4^{\text{ox}}} = 0.83 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$  and is ascribed to one  $\text{Ru}(\text{II}) \rightarrow \text{Ru}(\text{III})$  oxidation per bimetallic pillar, as shown from comparison with  $\text{RuNaph}$  (Figure 4b). Finally, an additional irreversible process attributed to the oxidation of the second metal cation on each  $\text{RuNaph}$  pillar is located at  $E_{5^{\text{ox}}} = 1.21 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$  (Figure S8).<sup>75</sup> On this basis, it is important to highlight that: *i*) the charge on  $\text{TTF-box}$  can be monitored in a fully reversible manner from  $8+$  ( $E = -0.2 \text{ V}$ ) to  $16+$  ( $E = +1.0 \text{ V}$ ), *ii*) a remarkably high charge state of  $20+$  is reached at  $E = 1.2 \text{ V}$  and *iii*) the self-assembled  $\text{TTF-box}$  remains stable upon repeated cycles within this window of potentials. Intercalation of polyaromatic guests (*i.e.* pyrene or perylene) could not be detected along those electrochemical experiments (no variation of redox potentials). This may be explained by the presence of competitive counter anions that may obstruct the cavity when  $\text{TTF-box}$  is oxidized.<sup>60</sup>

Spectroelectrochemistry experiments were led to get a better insight on the electronic interactions occurring between both TTF moieties in the self-assembly. They were carried out on  $\text{TTF-box}$  as well as on  $\text{RuNaph}$  and the corresponding tetracationic salt  $\text{TTF}(\text{PhPyrMe})_4$ . The UV-vis spectra of the three compounds are shown in Figure 5a. The tetrakis(pyridinium) salt  $\text{TTF}(\text{PhPyrMe})_4$  exhibits two strong absorption bands at  $\lambda = 325 \text{ nm}$  ( $\epsilon = 41\,100 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) and  $\lambda = 460 \text{ nm}$  ( $\epsilon = 4\,200 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ), assigned to  $\pi$ - $\pi^*$

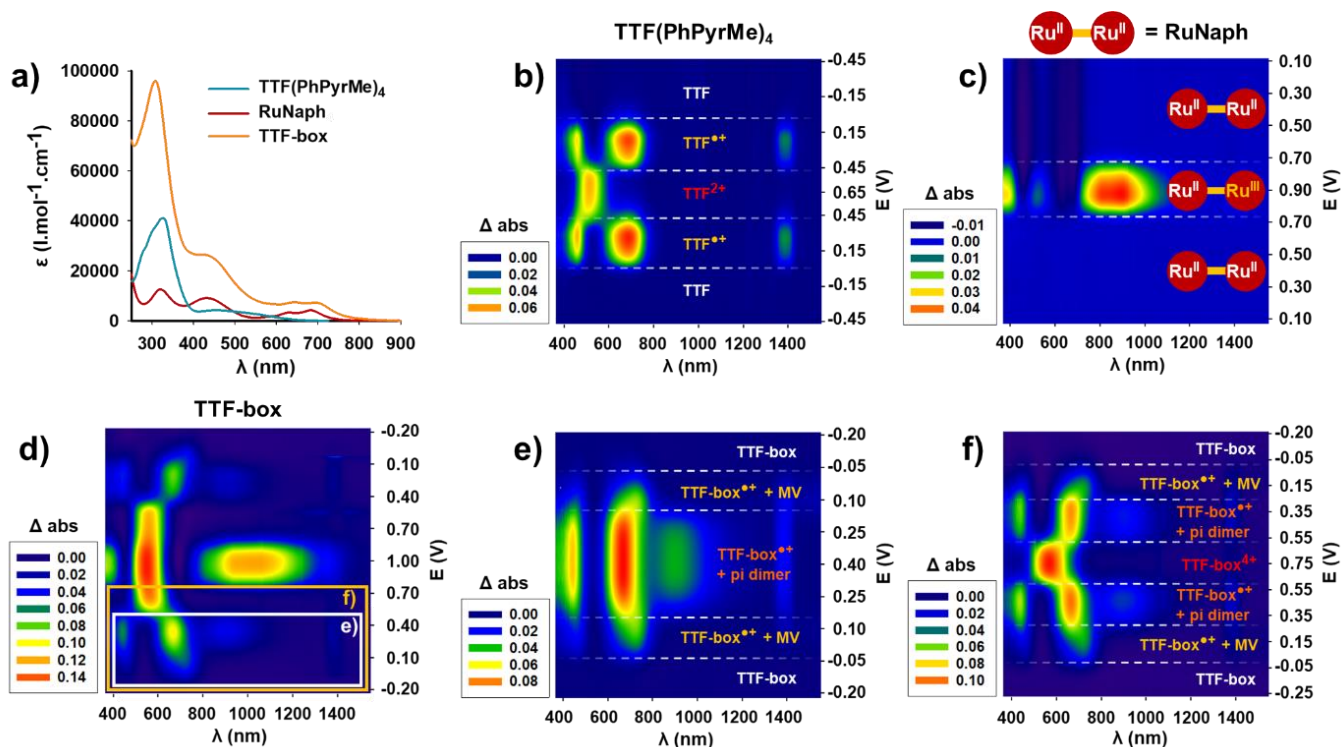


Fig. 5. UV-vis absorption spectra of **TTF(PhPyrMe)<sub>4</sub>**, **RuNaph** and **TTF-box** in CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> 1/1 (C = 5 × 10<sup>-5</sup> M) (a). Absorption spectroelectrochemistry experiment in thin layer conditions (~50 μm) during a cyclic voltammetry experiment in CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> 1/1 (C = 1 mM, n-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M)), 20 mV.s<sup>-1</sup>, 20°C) of **TTF(PhPyrMe)<sub>4</sub>** (b), **RuNaph** (c) and **TTF-box** in the -0.20 – 1.00 V range (d), oxidation and reduction scan limited to TTF radical cation, i.e. in the -0.20 – 0.40 V range (e) and finally oxidation and reduction scan limited to TTF dication, i.e. -0.25 – 0.75 V range (f); z axis = variation of absorbance Δ(Abs), MV = mixed valence.

transitions and intra-ligand charge transfer respectively. The **RuNaph** complex exhibits main absorptions at λ = 320 nm (ε = 12 600 l.mol<sup>-1</sup>.cm<sup>-1</sup>) and λ = 430 nm (ε = 9100 l.mol<sup>-1</sup>.cm<sup>-1</sup>), which correspond to the intra-ligand charge transfer in naphthalene and cymene, and minor absorptions at λ = 630 nm (ε = 3 300 l.mol<sup>-1</sup>.cm<sup>-1</sup>) and λ = 682 nm (ε = 4 200 l.mol<sup>-1</sup>.cm<sup>-1</sup>), that correspond to the metal-ligand charge transfer due to the coordination with naphthalene and cymene.<sup>76</sup> Finally, the spectrum of **TTF-box** essentially corresponds to the sum of the above respective contributions of **TTF(PhPyrMe)<sub>4</sub>** and **RuNaph** (λ = 305 nm (ε = 96 200 l.mol<sup>-1</sup>.cm<sup>-1</sup>), 435 nm (ε = 26 200 l.mol<sup>-1</sup>.cm<sup>-1</sup>), 645 nm (ε = 7 900 l.mol<sup>-1</sup>.cm<sup>-1</sup>) and 695 nm (ε = 7500 l.mol<sup>-1</sup>.cm<sup>-1</sup>)) which is typical for such systems.<sup>77</sup>

The spectroelectrochemistry experiments were carried out upon monitoring the variation in absorbance, Δ(Abs), recorded in the UV-VIS-NIR region, while performing a cyclic voltammetry of a millimolar solution of the compound under study (0.1 M nBu<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN-CH<sub>2</sub>Cl<sub>2</sub> 1/1) in thin layer conditions (TLCV experiment - thickness around 50 μm) (Figure 5b-f). The **TTF(PhPyrMe)<sub>4</sub>** pyridinium voltabsorptogram shows an increase of absorption upon formation of TTF<sup>•+</sup> (λ = 460 and 695 nm) and TTF<sup>2+</sup> (λ = 520 nm) at respectively E<sub>1</sub><sup>ox</sup> ≈ 0.20 V and E<sub>2</sub><sup>ox</sup> = 0.65 V vs Fc/Fc<sup>+</sup> (Figure 5b).<sup>78,79</sup> The oxidation of **NaphRu** (Ru<sup>II</sup> → Ru<sup>III</sup>) is characterized by the increase of distinctive bands around 375 nm, 525 nm (weak) and 900 nm (Figure 5c). The

spectroelectrochemical spectrum of **TTF-box** recorded from E = -0.20 to 1.00 V (Figure 5d), exhibits some differences compared to the superimposition of **TTF(PhPyrMe)<sub>4</sub>** and **RuNaph** contributions, as expected from the interaction occurring between both TTF units. A main difference concerns the region related to the first TTF oxidation step (-0.05 V < E < 0.40 V), for which additional absorption bands are detected (Figure 5e). At the very beginning of **TTF-box** first oxidation, spectral signatures are observed at λ = 465 and 725 nm, which are assigned to the radical-cation state (**TTF-box<sup>•+</sup>**) by analogy with above observations from **TTF(PhPyrMe)<sub>4</sub>**.<sup>80</sup> As in CV experiments (Figure 4b), a second close one-electron transfer occurs at E<sup>ox</sup> ≈ 0.30 V. The latter is assigned to the formation of the π-dimer state (**TTF-box<sup>(•+)<sup>2</sup></sup>**), with characteristic absorptions at λ = 440 and 665 nm and 920 nm.<sup>81</sup> On the other hand, a characteristic signature of TTF<sup>2+</sup>, without any confinement-dependent behavior, is observed at E<sup>ox</sup> ≈ 0.70 V (i.e. **TTF-box<sup>4+</sup>**) (Figure 5f). This observation suggests a strong repulsion between TTF<sup>2+</sup> moieties. Finally, at higher voltage, the spectral signature of the oxidized Ruthenium side panels is observed (Figure 5d) with a red shifting of about 100 nm compared to **RuNaph** precursor (Figure 5c). This set of spectroelectrochemical data demonstrates that **TTF-box** constitutes an original example of a bis-TTF derivative for which interactions occurring at oxidized states (mixed valence and π-

dimer) can be characterized at room temperature, a feature which is allowed by the spatial proximity of both TTF units in the coordination self-assembly.

## Conclusion

We have designed a tetratopic ligand **TTF(PhPyr)<sub>4</sub>** in order to favor the formation of a M<sub>8</sub>L<sub>2</sub> cage upon self-assembling with a bis-Ruthenium complex, providing a control over the inter-TTF distance. Whereas the Ru-Ru distance is 8.3 Å within the four pillars of the box, short interplanar C··C and S··S distances of respectively 3.48 Å and 3.83 Å are observed between both TTF units in **TTF-box**. This short distance results from a severe bending of the facing ligands, which collapse towards the center of the cavity. Electrochemical experiments including spectroelectrochemical measurements clearly show that the two facing TTF units interact upon oxidation, giving rise to an oxidized TTF dimer (**TTF-box**<sup>(•+)<sub>2</sub></sup>). This observation is imputable to the unique geometry of this M<sub>8</sub>L<sub>2</sub> assembly, for which the two TTF units are forced to stack together. **TTF-box** does not disassemble upon oxidation which attests to its robustness, and allows to reversibly generate up to eight positive charges upon oxidation. Given the strong interest in the recent literature for redox-controlled supramolecular interactions,<sup>2</sup> and considering the unique molecular design of **TTF-box** for which both redox units are forced to face, extension of this coordination-driven approach to the design of new related redox-active boxes is under study using alternative ligands and bis-metallic complexes.

## Author Contributions

SK, VCr and OA carried out experiments. EL supervised spectroelectrochemical measurements. MA carried out X-ray diffraction analysis. CM helped in growing crystals. VCa and FA performed HMRS FTIR measurements. ZV, SG and MS supervised and conceived the project. SG and MS wrote the manuscript. All authors discussed the results and contributed to the final manuscript.

## Conflicts of interest

There are no conflicts to declare

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