

# Redox-Active 17- and 19-Membered Metallamacrocycles Incorporating Tetrathiafulvalene

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Redox-active 17- and 19-membered metallamacrocycles were prepared thanks to the chelating ability of bis[(diphenylphosphane)alkylthio]TTF towards the  $M(CO)_4$  fragment ( $M = Mo, W$ ). The TTF unit can adopt either a *cis* or a *trans* configuration as can the phosphorus atoms coordinated to the metal center. Moreover, an element of planar chirality is generated by the *trans* isomer of the TTF. Thus, the reaction affords six stereoisomers as evidenced by  $^{31}P$  NMR and X-ray crystallographic analyses. The electrochemical properties of the title compounds have been investigated by cyclic voltammetry. Within the 19-membered metallamacrocycles, no

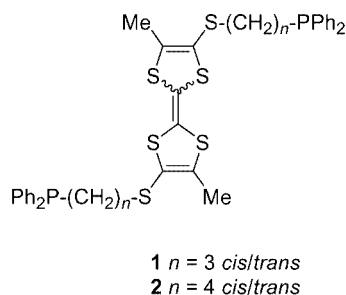
significant influence of the two redox moieties was detected, whereas in the 17-membered metallamacrocycles, the oxidized TTF modifies the redox behavior of the metal center. Two crystalline complexes obtained with tetracyanoquinodimethane (TCNQ) and the tungsten 17- and 19-membered metallamacrocycles are reported. Comparison of the crystal structures shows that these metallamacrocycles appear to be rather flexible even with strained structures.

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## Introduction

Various cyclophanes or cage molecules incorporating one or more electroactive units such as a tetrathiafulvalene core (TTF) have been studied with the aim of creating, through intramolecular or intermolecular interactions, nanoelectronic devices.<sup>[1]</sup> Among the electroactive macrocycles described so far, none of them contain a metallic fragment. Association of the TTFs with one appropriate metal will lead to a macrocycle with multiple redox sites and the possibility of interaction between the inorganic and organic moieties.<sup>[2]</sup> Various potential applications can be envisioned for these hybrid molecules, as molecular materials or in catalytic systems as it is well known that the steric and electronic properties of the ligand have an enormous effect on the reactivity of metal complexes.<sup>[3]</sup> A simple route toward the formation of large metallamacrocycles involves the coordination of a bidentate  $\alpha,\omega$ -diphosphane ligand to the transition metal center.<sup>[4]</sup> Therefore, we have studied the ability of bis-substituted [(diphenylphosphanyl)propylthio]-TTF **1**<sup>[5]</sup> to form metal carbonyl complexes upon chelation of the  $Mo(CO)_4$  and  $W(CO)_4$  fragments. Moreover, we also present the synthesis of the diphosphanyl ligand **2** where the phosphane moieties are linked to the donor core through a longer spacer group such as a thiobutyl one and the influence of this longer chain on the structural and electrochemi-

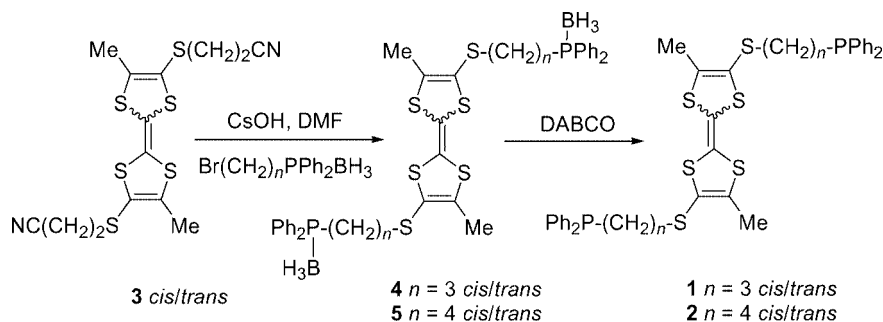
cal properties of the metallamacrocycles. Comparison of the effect of the length of the spacer group on the molecular structure and the redox behavior will then be discussed. Another interesting feature that will be presented is the influence of the complexation with TCNQ on the conformation of these metallamacrocycles.



## Results and Discussion

The synthesis of the ligand **2** was accomplished as depicted in Scheme 1 according to the chemical pathway used for the synthesis of bis[(diphenylphosphanyl)propylthio]-TTF **1** using the preformed TTF derivative **3** as the starting material.<sup>[5]</sup> The methodology consists first of the synthesis of the bis[(boronatodiphenylphosphanyl)butylthio]TTF **5**. The use of phosphane–borane substituents in the synthesis of the target TTFs presents several advantages as they are very stable compared to phosphane derivatives towards the

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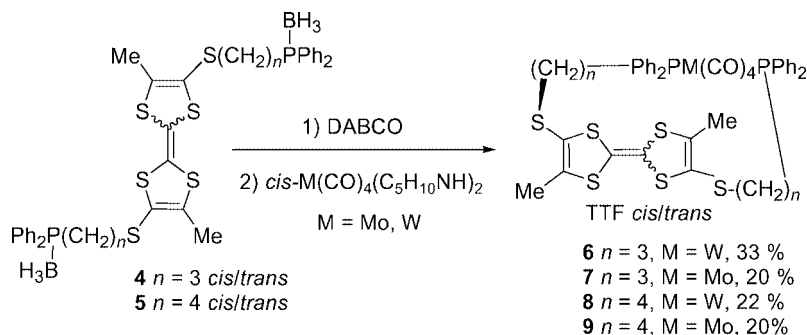
Scheme 1.

usual oxidizing or electrophilic reagents, and very easy to handle and to purify.<sup>[6,7]</sup> The bis(cyanoethylthio)TTF **3** was treated with cesium hydroxide and reacted with the bromobutylidiphenylphosphane–borane leading to TTF **5**. Decomplexation of the phosphane–borane complex was performed in the presence of DABCO under an inert atmosphere to give the bis[(diphenylphosphanyl)butylthio]TTF **2**.<sup>[8]</sup> These TTFs **1–2** should be kept under an inert atmosphere to avoid the formation of the corresponding phosphane oxides. Note that all these TTFs **1–5** are obtained as a mixture of the *cis* and *trans* isomers and attempts to separate these isomers are worthless as TTFs are prone to isomerization in solution upon light exposure or in the presence of traces of acid.<sup>[9,10]</sup>

In order to form metal carbonyl complexes with these TTF ligands, we used *cis*-M(CO)<sub>4</sub>(C<sub>5</sub>H<sub>10</sub>NH)<sub>2</sub> derivatives (M = Mo, W) where the two labile piperidine ligands can be easily replaced by other ligands such as two phosphanes.<sup>[11]</sup> As mentioned earlier for monosubstituted phosphanylTTF derivatives, the metal carbonyl complexation can be realized directly from the phosphane–borane TTF complexes,<sup>[12]</sup> in a one-pot procedure by a two-step chemical synthesis: firstly decomplexation of the phosphane–borane complex in the presence of DABCO and then addition of one equivalent of *cis*-M(CO)<sub>4</sub>(C<sub>5</sub>H<sub>10</sub>NH)<sub>2</sub> in the medium where the bis[(diphenylphosphanyl)alkylthio]TTFs were formed. The solution was warmed at 80 °C for 2 h. Actually, because of the flexibility of the alkylthio spacer groups, two types of metal carbonyl complexes were obtained, the

expected metallamacrocycles **6–9** (Scheme 2) but also polymeric derivatives resulting respectively from an intramolecular and an intermolecular complexation. The mononuclear metallamacrocycles formed can be easily isolated after column chromatography upon silica gel in an overall yield of 20–33%.

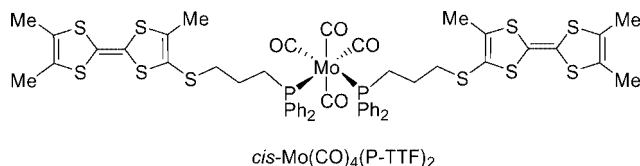
Analysis of the fraction containing the mononuclear complexes by <sup>31</sup>P NMR, after the chromatographic separation, reveals the presence of four signals for each of the four investigated derivatives **6–9** (Table 1). Indeed, besides the *cis/trans* isomerism of the TTF core, the phosphorus atoms can also be either *cis* or *trans* coordinated to the metal center. For the tungsten metallamacrocycles **6** and **8**, a small doublet due to the coupling of the phosphorus atom with the <sup>183</sup>W isotope is associated with the four singlets. Thanks to the coupling constant, it is possible to distinguish the *cis*-P–W–P isomers from the *trans*-P–W–P ones.<sup>[13]</sup> Indeed, the phosphorus atoms resonate at high field for **6** and **8** with <sup>1</sup>J<sub>PW</sub> = 230 Hz characteristic for the *cis*-P–W–P isomers while the two signals observed at low field for **6** and **8** exhibit a <sup>1</sup>J<sub>PW</sub> = 279 Hz characteristic for the *trans*-P–W–P one. For the molybdenum metallamacrocycles, by analogy with previous results on monodiphenylphosphanylpropylthio-TTF (P–TTF) *cis* coordinated to the Mo(CO)<sub>4</sub>, *cis*-Mo(CO)<sub>4</sub>(P–TTF)<sub>2</sub>,<sup>[12]</sup> where the phosphorus atoms resonated at δ = 26.6 ppm, the singlets observed at high field for **7** and **9** can be attributed to *cis*-P–Mo–P isomers while the signals observed at low field for **7** and **9** are assigned to the *trans* isomers.



Scheme 2.

Table 1.  $^{31}\text{P}$  chemical shifts for compounds **6–9** in  $\text{CDCl}_3$  solution.

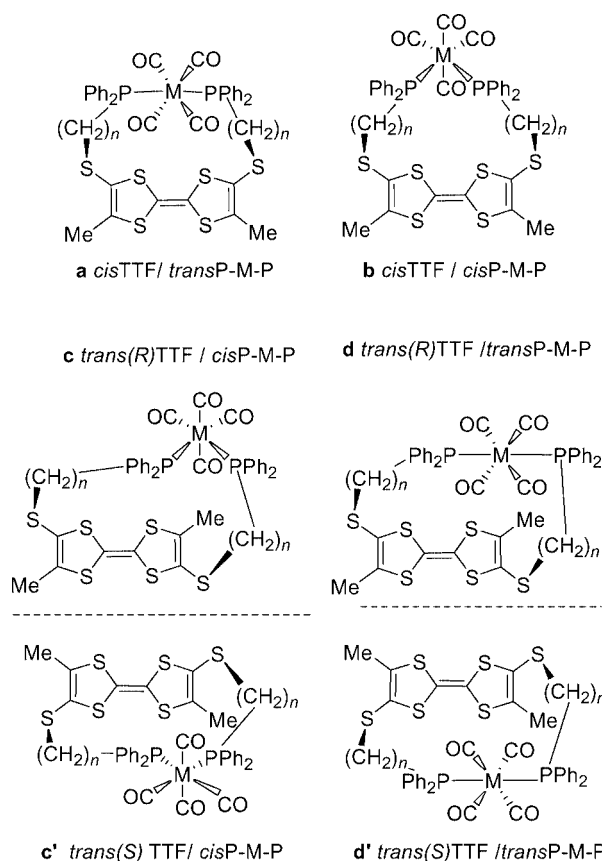
| Compound (metal, $n$ ) | $\delta = ^{31}\text{P}$ ppm ( $^1J_{\text{PW}}$ [Hz]) |
|------------------------|--------------------------------------------------------|
| <b>6</b> (W, 3)        | 5.9 (230), 6.9 (230), 13.5 (279), 14.6 (279)           |
| <b>7</b> (Mo, 3)       | 24.2, 24.7, 38.4, 39.3                                 |
| <b>8</b> (W, 4)        | 8.0 (230), 8.6 (230), 14.8 (279), 14.9 (279)           |
| <b>9</b> (Mo, 4)       | 25.5, 25.7, 39.0, 39.1                                 |



Interestingly, the intensity of the various signals observed indicates that a majority of the *trans* isomers on the metal center are formed in all the cases with an estimated *trans* P–M–P/*cis* P–M–P ratio of 5:2. The obtention of *cis/trans* isomers on the metal center, starting from the *cis*-M(CO)<sub>4</sub>(piperidine)<sub>2</sub> derivatives (M = Mo, W), finds its origin in the temperature used to form these metallamacrocycles.<sup>[11]</sup> Indeed, when the reaction was performed at 50 °C, no isomerization occurs as previously observed for monosubstituted TTF but the reaction rate is very low, while at 80 °C substitution of the two piperidine ligands occurs, especially for the *cis*-W(CO)<sub>4</sub>(piperidine)<sub>2</sub> derivative, but also isomerization on the metallic center. The TTF core can also adopt either a *cis* or *trans* configuration. The presence of isomers on the TTF moiety is not surprising as we started from a mixture of *cis* and *trans* isomers for both TTFs **4** and **5**. Moreover, the *trans* form of the TTF introduces an element of planar chirality. Therefore, as depicted in Scheme 3, six stereoisomers can be envisioned for each metallamacrocycle, **6–9**, corresponding to the following isomers: (i) **a** *cis* TTF/*trans* P–M–P, (ii) **b** *cis* TTF/*cis* P–M–P, (iii) **c** *trans* (R)TTF/*cis* P–M–P and **c'** *trans* (S)TTF/*cis* P–M–P and (iv) **d** *trans* (R)TTF/*trans* P–M–P, and **d'** *trans* (S)TTF/*trans* P–M–P, hence the four  $^{31}\text{P}$  NMR signals since the enantiomers **clc'** and **ddl'** can not be distinguished in this way.

Crystals of the metallamacrocycles **6**, **7**, and **8** were isolated from a mixture of dichloromethane and methanol. The crystal structure determinations reveal that in the case of the macrocycles **6** ( $n = 3$ , M = W) and **8** ( $n = 4$ , M = W), the isomers **a** (*cis* TTF/*trans* P–W–P), were isolated (Figure 1), while for **7** ( $n = 3$ , M = Mo) the two enantiomeric forms **7 clc'** [*trans* (R/S) TTF/*cis* P–Mo–P] (Figure 2) were crystallized in the racemic mixture.

All the TTF moieties adopt a boat conformation within these metallacyclophanes where both dithiole rings are folded along the S...S vector with asymmetric folding angles, which are more pronounced for the most strained 17-membered metallamacrocycles **6a** (17 and 28°) and **7 clc'** (19 and 36°) than for the 19-membered metallamacrocycle **8a** (9 and 11°). Comparison of the crystal structure of **6a** ( $n = 3$ ) with **8a** ( $n = 4$ ), where the difference is only due to the length of the spacer group between the TTF and the phosphorus atoms, shows that in both cases, the W–P distances and P–W–P interligand angles are similar and in the



Scheme 3.

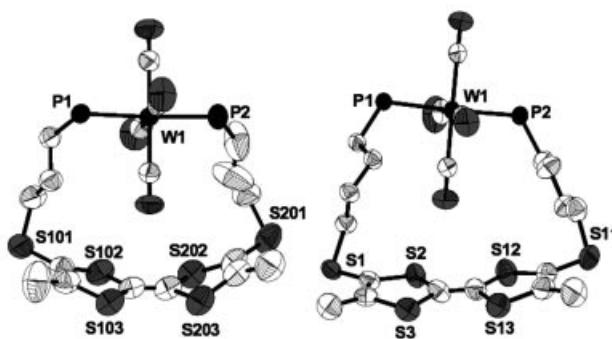


Figure 1. Molecular structure of (left) **6a** and (right) **8a**. The hydrogen atoms and the phenyl rings are not shown for clarity (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: W(1)–P(1) 2.4636(12), W(1)–P(2) 2.4644(14), P(1)–W(1)–P(2) 177.36(5) for **6a** and: W(1)–P(1) 2.4717(8), W(1)–P(2) 2.4652(8), P(1)–W(1)–P(2) 176.20(2) for **8a**.

usual range. Therefore, constraints brought by the formation of the metallamacrocycle are more effective on the fulvalene skeleton than on the inorganic part. Analysis of the crystals **6a** and **8a**, dissolved in  $\text{CDCl}_3$ , by  $^{31}\text{P}$  NMR reveals that the isomers **a** (*cis* TTF/*trans* P–W–P) exhibit only one set of signals at  $\delta = 13.5$  ppm for **6a** and at  $\delta = 14.8$  ppm for **8a**. The same  $\text{CDCl}_3$  solution left under ambient light exposure and analyzed again one day later exhibits this time two sets of signals caused by the presence of the *cis* and *trans* TTF isomers.<sup>[9]</sup>

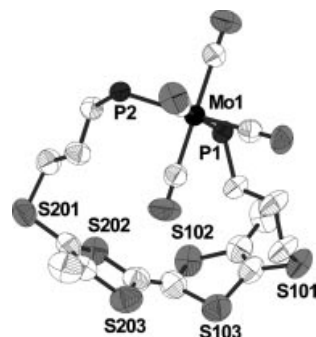
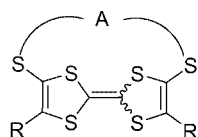


Figure 2. Molecular structure of **7c**. The hydrogen atoms and the phenyl rings are not shown for clarity (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Mo(1)–P(1) 2.5386(13), Mo(1)–P(2) 2.5666(12), P(1)–Mo(1)–P(2) 99.85(4).



TTF *cis/trans*

- 14-membered ring : R = Ar, A = (CH<sub>2</sub>)<sub>6</sub>  
                               R = Ar, A = CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>  
                               R = H, A = CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>  
                               R = CO<sub>2</sub>Me, A = CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>  
 18-membered ring : R = Me, A = (CH<sub>2</sub>)<sub>10</sub>  
 20-membered ring : R = Me, A = (CH<sub>2</sub>)<sub>12</sub>

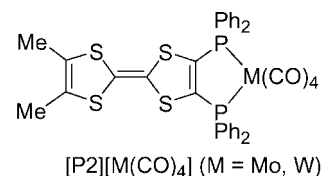
The redox properties of the metallacyclopheanes **6–9** were studied by cyclic voltammetry and peak potentials of the various complexes are collected in Table 2 together with the data for the starting ligands TTF **1** and **2**. In order to obtain an insight into the effect of the ligand environment on the redox potentials of the metal center, we also added to Table 2 the data for complexes Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> and W(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>. It is worth noting that *cis*-M(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> and *trans*-M(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> (M = Mo, W) present almost identical *E*<sup>o</sup> values [15] and exhibit cyclic voltammograms which are partially reversible for the molybdenum complex and irreversible for the tungsten one because of the loss of carbon monoxide on the metallic center upon oxidation.[15] Concerning the various metallamacrocycles, two oxidation waves are observed. The first reversible oxidation step corresponds to the oxidation of the TTF in its radical cation while the second oxidation process is due to the concomitant oxidation of the TTF radical cation into the dication and the oxidation of the metallic center. However, this process is not fully reversible due to the loss of the carbonyl ligand upon oxidation (Figure 3). This concomitant oxidation of the organic and inorganic moieties was also observed on phosphane TTF linked to a metal via a nonconjugated spacer group, such as *cis*-Mo(CO)<sub>4</sub>-(P–TTF)<sub>2</sub>. [12] Within the metallamacrocycles of the same size, the nature of the metal center, Mo or W, does not modify the redox potentials. Moreover, comparison of the first redox potentials of the complexes with those of the starting ligands (**1** and **2**) shows that there is no significant influence of the cyclization despite the strained structures

described above. Interestingly, comparison can also be made with TTF cyclophanes where fully covalent bridges of various lengths link the two dithiole moieties leading to 14-, 18-, and 20-membered rings.[16–18] Indeed, among those cyclophanes, the most constrained one with the shortest bishthioalkyl link (–S(CH<sub>2</sub>)<sub>6</sub>S–[16] and –SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>–CH<sub>2</sub>S–[16,17]) were found to exhibit a single irreversible oxidation wave, while by contrast, longer links [–S(CH<sub>2</sub>)<sub>10–12</sub>S][18] or the redox active metallamacrocycles described here display a first fully reversible oxidation wave. The lack of reversibility of the redox system on the 14-membered TTF cyclophanes was attributed to the severe bending of the TTF core as for instance the *cis*-substituted TTF with a bishthiohexyl bridge, [–S(CH<sub>2</sub>)<sub>6</sub>S], is folded by 47 and 34° along the S...S vector.[16b] Although, in **6–9**, the metallic fragment with the CO ligands brings a novel inner constraint to the TTF unit, the bridge is long enough to enable the two typical redox waves of a TTF core.

Table 2. Oxidation potentials V vs. SCE, Pt-working electrode with *n*Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) in CH<sub>2</sub>Cl<sub>2</sub>, scanning rate 0.1 V/s.

| Compound (metal, <i>n</i> )                          | <i>E</i> <sup>1</sup> | <i>E</i> <sub>pa</sub> <sup>2</sup> / <i>E</i> <sub>pc</sub> <sup>2</sup> |
|------------------------------------------------------|-----------------------|---------------------------------------------------------------------------|
| W(CO) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub>  | 0.87[a]               |                                                                           |
| Mo(CO) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub> | 0.85/0.76             |                                                                           |
| <b>6</b> (W, 3)                                      | 0.45                  | 0.93/0.82                                                                 |
| <b>7</b> (Mo, 3)                                     | 0.47                  | 0.91/0.82                                                                 |
| <b>8</b> (W, 4)                                      | 0.41                  | 0.88/0.77                                                                 |
| <b>9</b> (Mo, 4)                                     | 0.41                  | 0.85/0.76                                                                 |
| <b>1</b> ( <i>n</i> = 3)                             | 0.46                  | 0.86/0.80                                                                 |
| <b>2</b> ( <i>n</i> = 4)[14]                         | 0.39                  | 0.82[a]                                                                   |

[a] Irreversible process.



Considering the second redox process, the comparison of the anodic peak potential *E*<sub>pa</sub><sup>2</sup> in the complexes **6–9** with the value of the noncyclic Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> and W(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> shows a significant positive shift of *E*<sub>pa</sub><sup>2</sup> in the 17-membered cyclic compounds **6** and **7** (+60 mV for Mo, W) while the *E*<sub>pa</sub><sup>2</sup> potentials are almost identical in the less-constrained **8** and **9** molecules. This indicates that through-space interactions occur between the two-organic and organometallic-redox moieties in the smallest metallamacrocycles. This effect on *E*<sub>pa</sub><sup>2</sup> is most probably due to electrostatic repulsion and the close proximity of the TTF dication to the bound metal. Note that by contrast, when the phosphane is directly linked to the TTF core, as in [P2][M(CO)<sub>4</sub>] (M = Mo, W), oxidation of the coordinated metallic center occurs at a more positive potential than the TTF<sup>+</sup>/TTF<sup>2+</sup> redox system because of even stronger electrostatic interactions.[19] In this case the donating ability of the TTF core within the complexes was also significantly decreased as a positive shift of about 200 mV was observed, while in our metallamacrocycle **6–9** the redox properties of the donor are conserved.

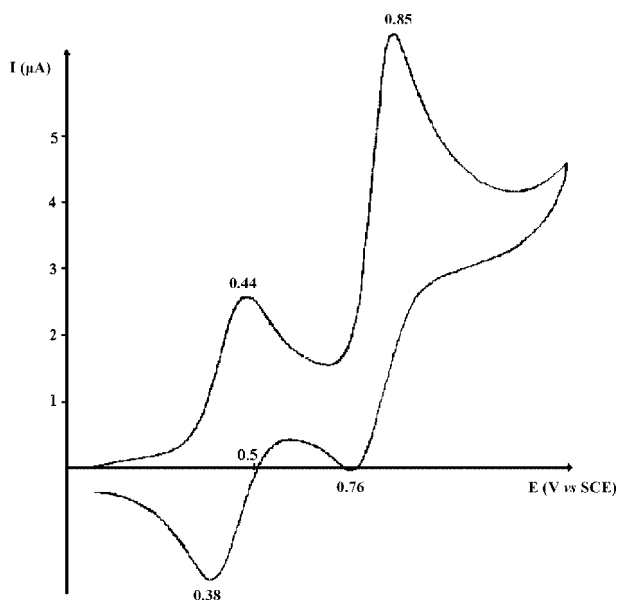


Figure 3. Cyclic voltammogram of **9**,  $n\text{Bu}_4\text{NPF}_6$  (0.1 M) in  $\text{CH}_2\text{Cl}_2$ , scanning rate 0.1 V/s.

Formation of charge transfer salts with TCNQ depends on the relative redox potentials of the donor ( $E_D^1$ ) and TCNQ ( $E_A^1 = 0.18$  V vs. SCE). These metallamacrocycles with their first redox potentials above 0.40 V are a rather borderline case as precursors of such charge transfer salts since  $E_D^1 - E_A^1 > 0.22$  V. Indeed, it is known that a partial or full charge transfer is only possible when  $E_D^1 - E_A^1 < 0.25$  V.<sup>[20–21]</sup> Mixing a dichloromethane solution of the metallamacrocycles **6** or **8** with an acetonitrile solution of TCNQ afforded deep purple shiny single crystals after slow evaporation. X-ray crystal structure determinations reveal a stoichiometry of two metallamacrocycles for one TCNQ in each case with inclusion of acetonitrile, that is  $(\mathbf{6})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_3$  and  $(\mathbf{8})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_2$ . The former complex with **6** ( $n = 3$ ) crystallizes in the triclinic system, space group  $P\bar{1}$ , with molecule **6** in a general position

in the unit cell, one TCNQ located on an inversion center, one acetonitrile disordered on an inversion center, and one acetonitrile in a general position. Complex  $(\mathbf{8})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_2$  crystallizes in a triclinic system, space group  $P\bar{1}$ , with molecule **8** in a general position in the unit cell, TCNQ located on an inversion center with only one acetonitrile in a general position. In the solid state, the TCNQ molecule is, in each case, sandwiched by two TTF cores of the metallamacrocycles in a  $\cdots\text{DAD}\cdots$  (D = **6** or **8** and A = TCNQ) motif. The TCNQ ring overlaps the central C=C bond of the TTF core and the interplanar separations between the donor and the acceptor are 3.48 and 3.53 Å for  $(\mathbf{6})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_3$  and  $(\mathbf{8})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_2$ , respectively (Figure 4). Using the empirical formula of Kistenmacher, which correlates the bond lengths to the formal charge of the TCNQ in various charge transfer salts,<sup>[22]</sup> we found that in both complexes the TCNQ is neutral. This is supported by the EPR analyses carried out on the crystals and no EPR signal was observed from room to liquid helium temperature. This is also confirmed by the diamagnetic behavior found in the whole temperature range by SQUID susceptibility measurements. Therefore, both complexes,  $(\mathbf{6})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_3$  and  $(\mathbf{8})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_2$ , are neutral donor/acceptor complexes. Concerning  $(\mathbf{8})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_2$ , the DAD motifs form stacks with a lateral slip between two neighboring TTF cores with S $\cdots$ S distances at 4.499(9) Å, while for  $(\mathbf{6})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_3$  the DAD motifs are isolated from each other by the inorganic moieties of the macrocycles (Figure 5).



Figure 4. TTF/TCNQ overlap in  $(\mathbf{6a})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_3$  (left) and  $(\mathbf{8a})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_2$  (right).

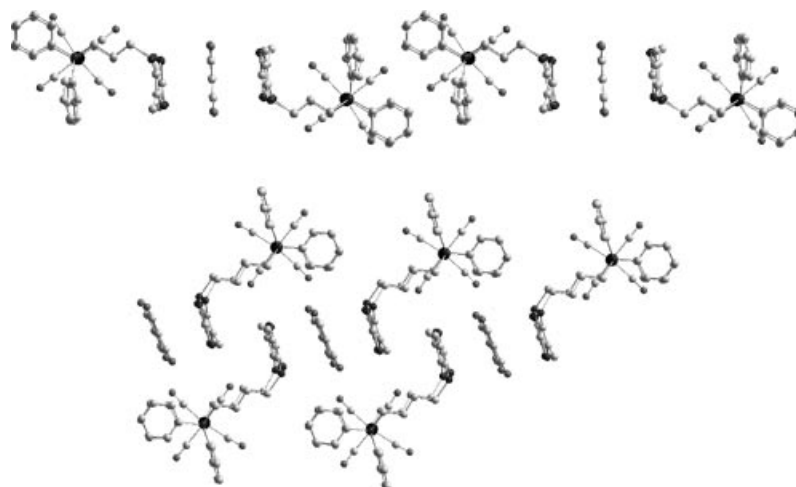


Figure 5. Stacking arrangement of  $(\mathbf{6a})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_3$  (top) and  $(\mathbf{8a})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_2$  (bottom).

Also noticeable, among the six possible stereoisomers for each metallamacrocycle **6** and **8** present in the starting solution for the elaboration of the TCNQ complexes, the isomers that crystallized within these complexes are the isomers **a** (*cis* TTF/*trans* P–W–P), which were independently crystallographically characterized and described above. The complexation with TCNQ has a significant influence on the conformation of the metallamacrocycles **6a** and **8a** as depicted in Figure 6. Comparison of the molecular structures shows that the TTF core for the 17-membered metallamacrocycle **6a** is more planar within the complex as the folding angles along the S...S vector for the dithiole rings are smaller (11 and 15° instead of 17 and 28°). The planarization of the TTF core in  $(\mathbf{6a})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_3$  brings the metal closer to the TTF core with a distance of about 5.85 vs. 6.25 Å in the starting complex. Contrariwise, for the 19-membered metallamacrocycle **8a**, the folding angles are in the same range (10 and 10° instead of 11 and 9°). Actually, the difference brought by the complexation on **8a** lies in the location of the metal in relation to the TTF core. Indeed, within the complex  $(\mathbf{8a})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_2$  the side chain with the metallic moiety is located in a plane perpendicular to the plane of the TTF core, while before complexation the chain with the metallic fragment was located more on the side of the TTF (Figure 6).

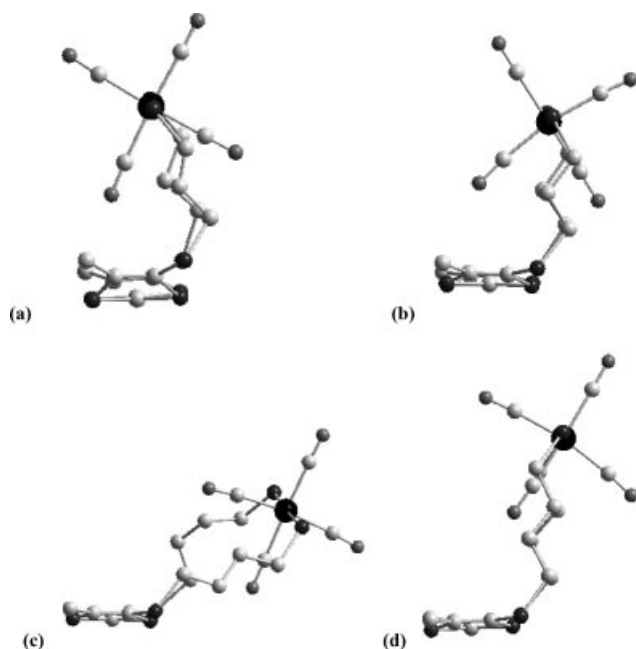


Figure 6. Side view of the metallamacrocycles, (a) **6a**, (b)  $(\mathbf{6a})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_3$ , (c) **8a**, (d)  $(\mathbf{8a})_2(\text{TCNQ}) \cdot (\text{CH}_3\text{CN})_2$ .

Analysis of the bond lengths of the metallamacrocycles within the TCNQ complexes shows that in both cases the bond lengths of the TTF core are in the usual range for neutral TTF moieties with the central C=C bond lengthened by 1.340 Å, but still within the range for the neutral TTF core. Similarly, the W–P distances are not significantly modified (Table 3). On the contrary, the P–W–P angles are

altered and for **6a** it amounts to 169.16(3)° instead of 177.36(5)° and for **8a** 176.20(2)° instead of 172.58(4)°, accounting for the consequences of the complexation with TCNQ (Table 3). Therefore, even with a constrained structure such as **6a** these metallamacrocycles remain flexible and the planarization of the TTF core, within the TCNQ complexes, induces a transfer of the constraints onto the metallic fragment.

Table 3. Significant bond lengths [Å] and angles [°].

| Compound                       | <i>d</i> W–P | <i>d</i> C=C | Angle P–W–P | Folding angles along S...S vector |
|--------------------------------|--------------|--------------|-------------|-----------------------------------|
| <b>6a</b>                      | 2.4636(12)   | 1.310(9)     | 177.36(5)   | 17                                |
|                                | 2.4644(14)   |              |             | 28                                |
| $(\mathbf{6a})_2(\text{TCNQ})$ | 2.4655(10)   | 1.340(6)     | 169.16(3)   | 11                                |
|                                | 2.4697(9)    |              |             | 15                                |
| <b>8a</b>                      | 2.4652(8)    | 1.312(6)     | 176.20(2)   | 9                                 |
|                                | 2.4717(8)    |              |             | 11                                |
| $(\mathbf{8a})_2(\text{TCNQ})$ | 2.4550(12)   | 1.340(9)     | 172.58(4)   | 10                                |
|                                | 2.4606(12)   |              |             | 10                                |

## Conclusions

In this study, redox active 17- and 19-membered metallamacrocycles incorporating one TTF unit have been synthesized through the coordination of the bidentate [(diphenylphosphanyl)alkylthio]TTFs to the  $\text{Mo}(\text{CO})_4$  and  $\text{W}(\text{CO})_4$  fragments. As a consequence of the possible *cis/trans* isomerization of the TTF core and the metallic fragment six stereoisomers were formed. As evidenced by the X-ray diffraction studies, the central TTF unit in these metallamacrocycles is not planar, however it is significantly less folded in the 19-membered ring than in the 17-membered ring. Nevertheless, the bending of the TTF is not sufficient to negate the electron-donating ability of this redox unit. Furthermore, in the 17-membered metallamacrocycles, the close proximity of the metallic fragment to the TTF produces electrostatic interactions as evidenced by the shift of the oxidation peak potentials of the metallic fragment to more positive potentials. Two TCNQ complexes with the 17- and 19-membered metallamacrocycles ( $\text{M} = \text{W}$ ) have been obtained and crystallographically analyzed. Although no charge transfer was observed, comparison of the crystal structures provide valuable information on the relative flexibility of these strained structures. An attractive feature of these metallamacrocycles lies in the modification of the TTF core upon oxidation which should modify the molecular organization in the neighborhood of the metal fragment and attempts at isolating cation radical salts are currently under way.

## Experimental Section

$^1\text{H}$  NMR and  $^{31}\text{P}$  NMR spectra were recorded with a Bruker AC 300P spectrometer. Chemical shifts are reported in ppm referenced to TMS for  $^1\text{H}$  NMR and to  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  NMR spectroscopy. Elemental analyses were obtained from the Laboratoire Central de Microanalyse du CNRS, Lyon. Mass spectra were recorded with

a ZABSpec TOF instrument by the Centre Régional de Mesures Physiques de l'Ouest, Rennes.  $\text{CH}_2\text{Cl}_2$  was distilled from  $\text{P}_2\text{O}_5$ . Toluene was dried with sodium wire. Chromatography was performed using silica gel Merck 60 (70–260 mesh).  $\text{Mo}(\text{CO})_6$  and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased from ACROS Organics,  $\text{W}(\text{CO})_6$  was purchased from Aldrich.  $\text{M}(\text{CO})_4(\text{NHC}_5\text{H}_{10})_2$  was prepared from  $\text{M}(\text{CO})_6$  according to published procedures.<sup>[11]</sup> Cyclic voltammetry was carried out in dichloromethane, containing 0.1 M  $n\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte. Voltammograms were recorded at 0.1  $\text{Vs}^{-1}$  on a platinum disk electrode ( $A = 1 \text{ mm}^2$ ). The potentials were measured vs. a saturated calomel electrode. TTF **2** was prepared following known procedures.<sup>[5]</sup>

**General Procedure for the Synthesis of Complexes 6–9:** To a solution of the TTF **4** or **5** (0.5 mmol) in dried, degassed toluene (30 mL) DABCO (112 mg, 1 mmol) was added under argon. The mixture was stirred for 4 h at 50 °C after which  $\text{M}(\text{CO})_4(\text{NHC}_5\text{H}_{10})_2$  (0.5 mmol) in degassed  $\text{CHCl}_3$  (10 mL) was added. The resulting solution was stirred at 80 °C for 2 h and then the solvent was removed under reduced pressure. The solid residue was dissolved in  $\text{CH}_2\text{Cl}_2$ , washed with water, and dried with  $\text{Na}_2\text{SO}_4$ . The solvent was removed and chromatography of the residue over silica gel (3:1  $\text{CH}_2\text{Cl}_2/\text{PE}$ ) afforded the complexes **6–9** as a mixture of isomers.

**Complex 6:** Yield 170 mg (33%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.20$ – $1.40$  (4 m, 4 H), 1.99, 2.01, 2.09, 2.14 (4 s, 6 H), 2.25–2.64 (4 m, 4 H), 2.70–3.0 (4 m, 4 H), 7.19–7.70 (m, 20 H) ppm.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 5.9$  ( $^1J_{\text{PW}} = 230 \text{ Hz}$ ), 6.9 ( $^1J_{\text{PW}} = 230 \text{ Hz}$ ), 13.5 ( $^1J_{\text{PW}} = 279 \text{ Hz}$ ), 14.6 ( $^1J_{\text{PW}} = 279 \text{ Hz}$ ) ppm.  $\text{C}_{42}\text{H}_{38}\text{O}_4\text{P}_2\text{S}_6\text{W}$ : HRMS calcd. 1044.0075; found 1044.0075.  $\text{C}_{42}\text{H}_{38}\text{O}_4\text{P}_2\text{S}_6\text{W} \cdot \text{CH}_3\text{OH}$ : calcd. C 47.95, H 3.90, S 17.84; found C 47.58, H 3.80, S 17.53.

**Complex 7:** Yield 100 mg (20%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.20$ – $1.40$  (4 m, 4 H), 1.98, 2.02, 2.14, 2.16 (4 s, 6 H), 2.25–2.64 (4 m, 4 H), 2.70–3.0 (4 m, 4 H), 7.19–7.70 (m, 20 H) ppm.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 24.2$ , 24.7, 38.4, 39.3 ppm.  $\text{C}_{42}\text{H}_{38}\text{MoO}_4\text{P}_2\text{S}_6$ : HRMS calcd. 957.9626; found 957.9626.

**Complex 8:** Yield 120 mg (22%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.18$ – $1.80$  (4 m, 8 H), 2.00, 2.02, 2.10, 2.12 (4 s, 6 H), 2.41–2.62 (4 m, 8 H), 7.15–7.50 (m, 20 H) ppm.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 8.0$  ( $^1J_{\text{WP}} = 230 \text{ Hz}$ ), 8.6 ( $^1J_{\text{WP}} = 230 \text{ Hz}$ ), 14.8 ( $^1J_{\text{WP}} = 279 \text{ Hz}$ ), 14.9 ( $^1J_{\text{WP}} = 279 \text{ Hz}$ ) ppm.  $\text{C}_{44}\text{H}_{42}\text{O}_4\text{P}_2\text{S}_6\text{W}$ : HRMS calcd. 1072.0392; found 1072.0395.

**Complex 9:** Yield 100 mg (20%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.18$ – $1.40$  (4 m, 4 H), 1.40–1.55 (4 m, 4 H), 1.92–2.09 (4 s, 6 H), 2.38–2.62 (4 m, 8 H), 7.12–7.49 (m, 20 H) ppm.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 25.5$ , 25.7, 39.0, 39.1 ppm.  $\text{C}_{44}\text{H}_{42}\text{MoO}_4\text{P}_2\text{S}_6$ : HRMS calcd. 985.9940; found 985.9946.

Crystallization of the derivatives **6**, **7**, and **8** from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  afforded prisms of complexes **6a**, **7c'**, and **8a** that were suitable for X-ray crystal structure analyses.

**Single-Crystal Structure Determination:** A single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin fiber glass. Single crystal data collection was performed at room temperature with a Nonius KappaCCD diffractometer (Centre de Diffractométrie, Université de Rennes, France), with  $\text{Mo-K}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). A crystal-to-detector distance of 25.0 mm was used for all the crystals and the data collection strategy (determination and optimization of the goniometer positions) was performed with the help of the COLLECT program.<sup>[23]</sup> Experimental details of the data collection are summarized in Table 4.

The integration process and data reduction was carried out using the DENZO-SCALEPACK<sup>[24]</sup> program. Numerical absorption corrections were performed using the multiscan procedure<sup>[25a]</sup> implemented in the WinGX program suite.<sup>[25b]</sup> Structure determination was performed with the direct methods solving program SIR97,<sup>[26]</sup> which revealed all the non-hydrogen atoms. SHELXL 97<sup>[27]</sup> was used to refine the structure. Finally, hydrogen atoms were placed geometrically and held in the riding mode in the least-square

Table 4. Crystallographic data.

| Structure parameter                      | <b>6a</b>                                                            | <b>7c'</b>                                                   | <b>8a</b>                                                            | <b>(6a)<sub>2</sub>(TCNQ)·(CH<sub>3</sub>CN)<sub>3</sub></b>                       | <b>(8a)<sub>2</sub>(TCNQ)·(CH<sub>3</sub>CN)<sub>2</sub></b>                 |
|------------------------------------------|----------------------------------------------------------------------|--------------------------------------------------------------|----------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------|
| Empirical formula                        | $\text{C}_{42}\text{H}_{38}\text{O}_4\text{P}_2\text{S}_6\text{W}_1$ | $\text{C}_{42}\text{H}_{38}\text{MoO}_4\text{P}_2\text{S}_6$ | $\text{C}_{44}\text{H}_{42}\text{O}_4\text{P}_2\text{S}_6\text{W}_1$ | $\text{C}_{51}\text{H}_{44.5}\text{N}_{3.5}\text{O}_4\text{P}_2\text{S}_6\text{W}$ | $\text{C}_{52}\text{H}_{47}\text{N}_3\text{O}_4\text{P}_2\text{S}_6\text{W}$ |
| Molecular weight                         | 1044.87                                                              | 956.96                                                       | 1072.93                                                              | 1208.55                                                                            | 1216.05                                                                      |
| Color                                    | orange                                                               | yellow                                                       | orange                                                               | purple                                                                             | purple                                                                       |
| Cryst. system                            | triclinic                                                            | monoclinic                                                   | triclinic                                                            | triclinic                                                                          | triclinic                                                                    |
| Space group                              | $P\bar{1}$                                                           | $P2_1/c$                                                     | $P\bar{1}$                                                           | $P\bar{1}$                                                                         | $P\bar{1}$                                                                   |
| $a$ [Å]                                  | 10.4523(2)                                                           | 13.0628(2)                                                   | 10.4360(1)                                                           | 12.31580(10)                                                                       | 12.1689(3)                                                                   |
| $b$ [Å]                                  | 12.1755(2)                                                           | 17.6849(4)                                                   | 12.5218(1)                                                           | 15.0526(2)                                                                         | 12.9499(4)                                                                   |
| $c$ [Å]                                  | 18.1465(4)                                                           | 19.7180(4)                                                   | 18.1813(3)                                                           | 16.5610(3)                                                                         | 18.5932(5)                                                                   |
| $\alpha$ [°]                             | 79.438(1)                                                            | 90                                                           | 79.8321(5)                                                           | 68.7400(10)                                                                        | 101.823(2)                                                                   |
| $\beta$ [°]                              | 78.558(1)                                                            | 105.2488(10)                                                 | 84.1490(5)                                                           | 69.4250(10)                                                                        | 92.619(2)                                                                    |
| $\gamma$ [°]                             | 80.787(1)                                                            | 90                                                           | 85.6027(5)                                                           | 85.3210(10)                                                                        | 109.5750(10)                                                                 |
| $V$ [Å <sup>3</sup> ]                    | 2206.69(7)                                                           | 4394.77(15)                                                  | 2322.21(5)                                                           | 2675.01(6)                                                                         | 2681.27(13)                                                                  |
| $Z$                                      | 2                                                                    | 4                                                            | 2                                                                    | 2                                                                                  | 2                                                                            |
| $F(000)$                                 | 1044                                                                 | 1960                                                         | 1076                                                                 | 1214                                                                               | 1224                                                                         |
| $D_{\text{calcd.}}$ [g/cm <sup>3</sup> ] | 1.573                                                                | 1.446                                                        | 1.535                                                                | 1.501                                                                              | 1.506                                                                        |
| $M$ [mm <sup>−1</sup> ]                  | 3.014                                                                | 0.696                                                        | 2.867                                                                | 2.499                                                                              | 2.493                                                                        |
| Data collected                           | 42143                                                                | 44160                                                        | 46842                                                                | 52690                                                                              | 41261                                                                        |
| Independent data                         | 10104                                                                | 9658                                                         | 13458                                                                | 11779                                                                              | 11380                                                                        |
| $R_{\text{int}}$                         | 0.0611                                                               | 0.0985                                                       | 0.0829                                                               | 0.082                                                                              | 0.0836                                                                       |
| Observed data                            |                                                                      |                                                              |                                                                      |                                                                                    |                                                                              |
| $[I > 2\sigma(I)]$                       | 8380                                                                 | 5587                                                         | 11327                                                                | 9492                                                                               | 9154                                                                         |
| Parameters refined                       | 497                                                                  | 497                                                          | 515                                                                  | 625                                                                                | 615                                                                          |
| $R(F)$                                   | 0.0426                                                               | 0.0532                                                       | 0.0386                                                               | 0.0383                                                                             | 0.0459                                                                       |
| $wR(F^2)$                                | 0.1137                                                               | 0.1578                                                       | 0.1005                                                               | 0.0799                                                                             | 0.1058                                                                       |
| GoF                                      | 1.044                                                                | 1.02                                                         | 1.052                                                                | 1.05                                                                               | 1.085                                                                        |
| Residual $d$ [e·Å <sup>−3</sup> ]        | 1.305/−1.198                                                         | 0.676/−0.589                                                 | 1.408/−1.501                                                         | 0.921/−0.882                                                                       | 1.717/−1.46                                                                  |

refinement procedure. The last cycles of the refinement included atomic positions for all the atoms, anisotropic displacement parameters for all the non-hydrogen atoms, and isotropic displacement parameters for all the hydrogen atoms.

CCDC-297239 to -297243 [for **6a**, (**6a**)<sub>2</sub>(TCNQ)·(CH<sub>3</sub>CN)<sub>3</sub>, **7c/c'**, **8a**, and (**8a**)<sub>2</sub>(TCNQ)·(CH<sub>3</sub>CN)<sub>2</sub>, respectively] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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