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## Tuning the structure and the properties of dithiafulvene metalla-assembled tweezers

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Maksym Dekhtiarenko,<sup>a,b</sup> Serhii Krykun,<sup>a,b</sup> Vincent Carré,<sup>c</sup> Frédéric Aubriet,<sup>c</sup> David Canevet,<sup>a</sup> Magali Allain,<sup>a</sup> Zoia Voitenko,<sup>b</sup> Marc Sallé\*<sup>a</sup> and Sébastien Goeb\*<sup>a</sup>

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A  $M_2L_2$  metalla-macrocycles constructed through coordination driven self-assembly from the Pd(dppf)OTf<sub>2</sub> complex (dppf = 1,1'-Bis(diphenylphosphino)ferrocene) and an electron-rich 9-(1,3-dithiol-2-ylidene)fluorene bis-pyridyl ligand is depicted. This molecular tweezer exhibits a cavity able *i)* to promote dimerization upon oxidation and *ii)* to bind an electro-deficient substrate with a remarkable association constant. Those properties are compared with those of a previously described regioisomer.

### Introduction

The coordination-driven strategy has been successfully used to construct a considerable variety of discrete architectures with very high yields.<sup>1,2</sup> One reason for this success, lies on the high degree of predictability in the geometry of the resulting self-assembled structures.<sup>3</sup> On this basis, more and more complex systems have been produced, including chiral<sup>4-6</sup>, heteroleptic<sup>7-9</sup> and interlocked<sup>10-12</sup> ones. Those self-assembled discrete structures generally include a cavity,<sup>13</sup> and their host properties have been widely studied to target various applications (e.g. depollution,<sup>14</sup> drug delivery,<sup>15</sup> catalysis<sup>16-18</sup> and storage of reactive molecules<sup>19</sup>). Nevertheless, for most of these applications, there is an important need for controlling the intensity of the host-guest interaction,<sup>20</sup> which implies designing stimuli-responsive architectures.<sup>21-24</sup> On this basis, we described the preparation and properties of a series of redox-active rings<sup>25</sup> and cages<sup>26-31</sup> constructed from the tetrathiafulvalene (TTF) moieties and some of its derivatives. We also recently depicted the efficiency of the 9-(1,3-dithiol-2-ylidene)fluorene (DTF)-based ligands, in generating self-assembled discrete structures, be they rings<sup>32</sup>, tweezers<sup>33</sup> or cages.<sup>34</sup> The DTF moiety can be oxidized reversibly at low potential to the corresponding radical cation,<sup>35,36</sup> a species which is prone to form mixed valence or  $\pi$ -dimer species under specific conditions. This driving force can be exploited to control, reversibly, the release of a guest compound thanks to a redox driven dimerization process.<sup>33</sup>

We report herein that the shape, the redox and the binding properties of coordination-driven self-assembled metalla-cycles constructed from ditopic DTF based ligands and the *cis*-Pd(dppf)(OTf)<sub>2</sub> complex (dppf = 1,1'-bis(diphenylphosphino)ferrocene; OTf = trifluoromethanesulfonate), can be efficiently and readily tuned by a simple change from a 4-pyridyl coordinating unit to a 3-pyridyl one.

### Results and discussion

We already reported that the self-assembly of the **L4Pyr** ligand with *cis*-Pd(dppf)(OTf)<sub>2</sub> in dichloromethane at 40 °C converges to a single symmetrical  $M_2L_2$  discrete species (Scheme 1 left).<sup>32</sup> In the present study, we applied a similar synthetic protocol to **L3Pyr** (Scheme 1 right). The presence of the 3-pyridyl unit leads to a more complex <sup>1</sup>H NMR spectrum than the one obtained from **L4Pyr** (Figure 2). Nevertheless, all aromatic signals could be attributed using a COSY experiment (Figure S2). In particular, all signals of pyridyl proton in **Pd<sub>2</sub>L3Pyr<sub>2</sub>** are upfield shifted compared to the free **L3Pyr** ligand, except H<sub>6</sub> (Figure 1a). This global observation is assigned to the shielding effect promoted by the phenyl rings from the *dppf* coligand, which is compensated in the case of H<sub>6</sub> by coordination to the metal. The presence of only one discrete species is confirmed by <sup>1</sup>H DOSY NMR experiment (Figure 1c and S3). The latter shows a single set of signals with a diffusion coefficient of  $D = 4.96 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ , a value which is very similar to the one measured for the **Pd<sub>2</sub>L4Pyr<sub>2</sub>** metalla-cycle (Figure 1c'). This observation suggests that the self-assembled structure obtained from **L3Pyr** is similar in size to the one of **Pd<sub>2</sub>L4Pyr<sub>2</sub>**. The corresponding estimated hydrodynamic radius is of *ca* 10 Å, as extracted from the Stokes-Einstein equation ( $T = 298 \text{ K}$ ),<sup>37,38</sup> a value which is consistent with the formation of a  $M_2L_2$  architectures as in the case of **Pd<sub>2</sub>L4Pyr<sub>2</sub>**.<sup>32</sup>

<sup>a</sup> Laboratoire MOLTECH-Anjou, UMR CNRS 6200, UNIV Angers, SFR MATRIX, 2 Bd Lavoisier, 49045 Angers Cedex, France.

E-mails: marc.salle@univ-angers.fr; sebastien.goeb@univ-angers.fr

<sup>b</sup> Taras Shevchenko National University of Kyiv, 64/13 Volodymyrska st., Kyiv 01033, Ukraine

<sup>c</sup> LCP-A2MC, FR 3624, Université de Lorraine, ICPM, 1 Bd Arago, 57078 Metz Cedex 03, France

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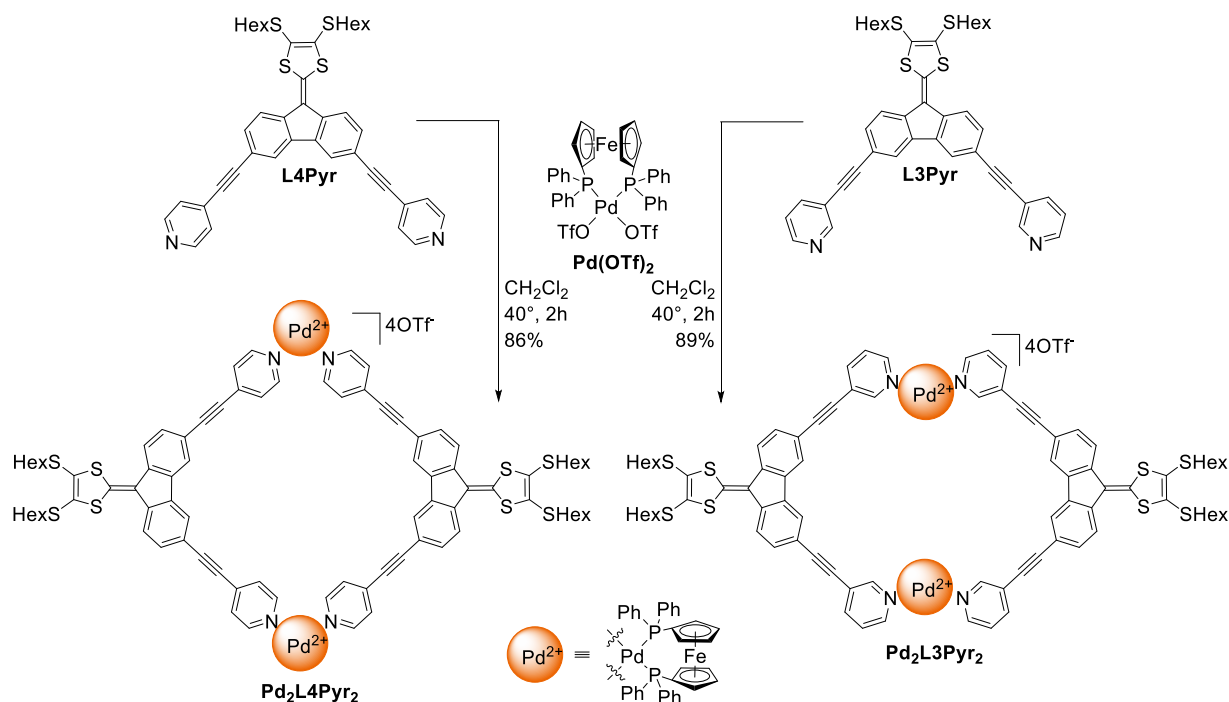
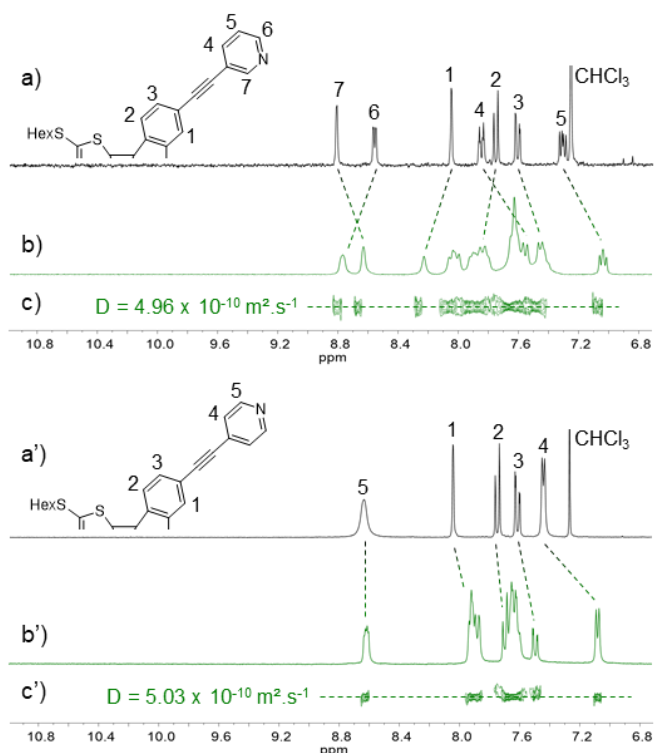
Scheme 1. Synthesis of metalla-macrocycles  $\text{Pd}_2\text{L4Pyr}_2$ <sup>32</sup> and  $\text{Pd}_2\text{L3Pyr}_2$ .

Fig. 1  $^1\text{H}$  NMR spectra (aromatic region) of ligands  $\text{L3Pyr}$  (a) and  $\text{L4Pyr}$  (a') in  $\text{CDCl}_3$ , metalla-macrocycles  $\text{Pd}_2\text{L3Pyr}_2$  (b) and  $\text{Pd}_2\text{L4Pyr}_2$  (b') in  $\text{CD}_2\text{Cl}_2$ , and corresponding  $^1\text{H}$  NMR DOSY spectra (c and c') related to (b) and (b').

The stoichiometry of the self-assembly  $\text{Pd}_2\text{L3Pyr}_2$  was confirmed by high-resolution ESI-FTICR-MS spectrometry (Figure S4). In addition to signals of the expected  $\text{M}_2\text{L}_2$  molecular clip [ $\text{Pd}_2\text{L3Pyr}_2 - 2\text{OTf}$ ]<sup>2+</sup>;  $m/z = 1510.667$ ), peaks corresponding to higher molecular masses were observed despite variations carried out on the instrumental conditions,

the concentration ( $10^{-5} \text{ M} < C < 10^{-3} \text{ M}$ ) and the solvent. Taken into account the above DOSY NMR data, these experiments suggest aggregation of the starting  $\text{M}_2\text{L}_2$  metalla-cycle upon ESI. Such behavior is known in the literature with soft ionization conditions<sup>39</sup> and was also observed in the case of the  $\text{Pd}_2\text{L4Pyr}_2$  analogue.<sup>32</sup>

Unfortunately, attempts to grow single crystals of  $\text{Pd}_2\text{L3Pyr}_2$  suitable for X-ray analysis were unsuccessful. Theoretical calculations using the MM+ model were undertaken and the results compared to similar experiments carried out for  $\text{Pd}_2\text{L4Pyr}_2$  (Figure 2). The calculated  $\text{Pd}_2\text{L4Pyr}_2$  structure (Figure 2a) is fully consistent with the one observed in the corresponding by X-ray crystallography (Figure S8c). In particular, a dihedral angle of ca.  $80^\circ$  between both fluorenyl mean planes, and an intramolecular S...S distance between facing dithiole rings of ca.  $15 \text{ \AA}$ , were found, and these values are very close to those observed in the crystal. Importantly, switching from a 4-pyridyl coordinating unit to a 3-pyridyl one, drastically modifies the shape of the metalla-clip. The metal coordination in the meta position of the pyridyl groups in  $\text{Pd}_2\text{L3Pyr}_2$ , results in a significant conformational change with much closer electroactive units. In particular,  $\text{Pd}_2\text{L3Pyr}_2$  shows a dihedral angle between both fluorenyl units of ca.  $27^\circ$  and a S...S distance of ca.  $8.5 \text{ \AA}$ .

The electrochemical properties of the metalla-clip  $\text{Pd}_2\text{L3Pyr}_2$  were studied by cyclic voltammetry (CV) in  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  and compared to the previously described  $\text{Pd}_2\text{L4Pyr}_2$  homolog<sup>32</sup>(Figure 3a). Both  $\text{L4Pyr}$  and  $\text{L3Pyr}$  ligands exhibit one reversible redox wave, centered on the DTF moiety at  $E^{\text{ox}} = 0.56$  and  $0.46 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$  respectively. One reversible oxidation is also observed for the DTF moieties in  $\text{Pd}_2\text{L4Pyr}_2$  ( $E_1^{\text{ox}} = 0.59 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$ ) which is followed by oxidation of the ferrocene moieties

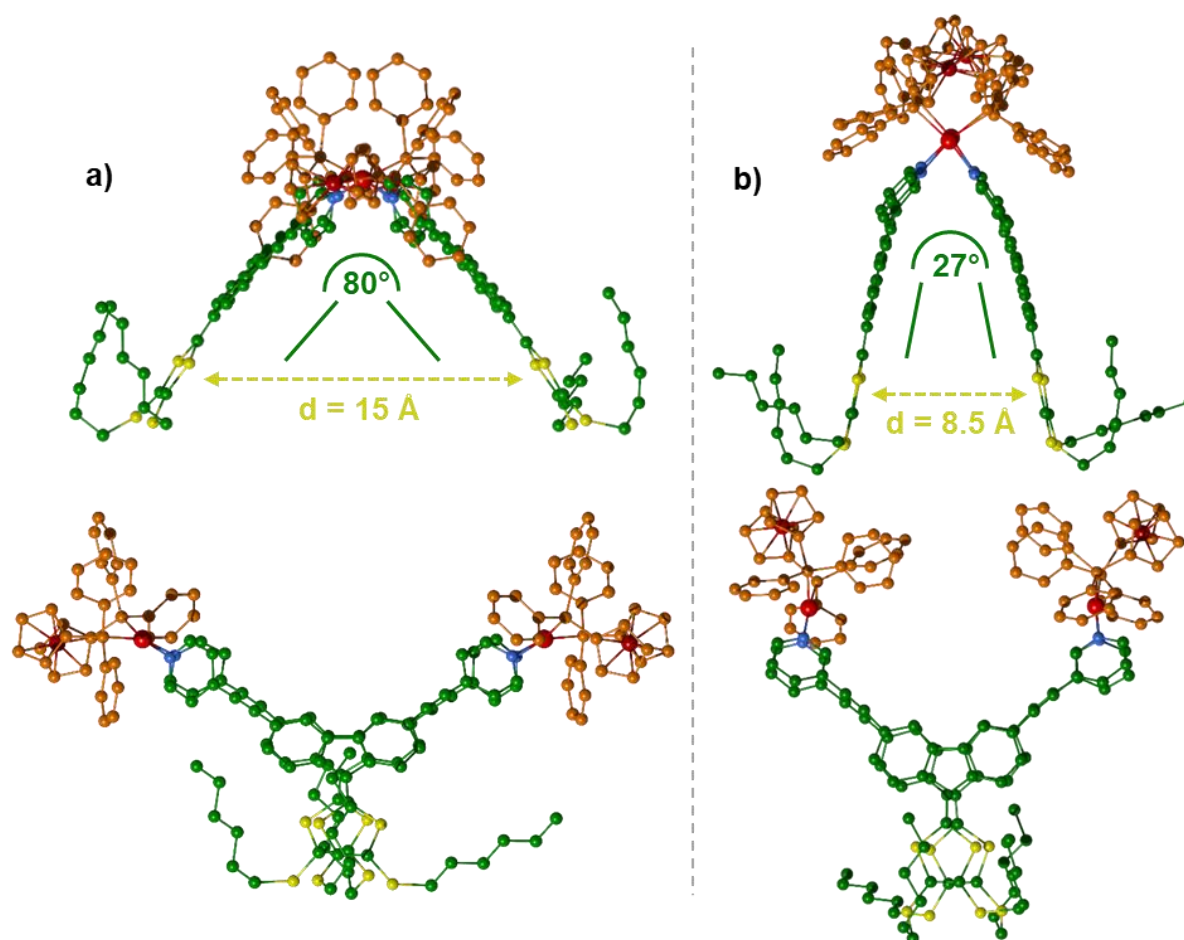
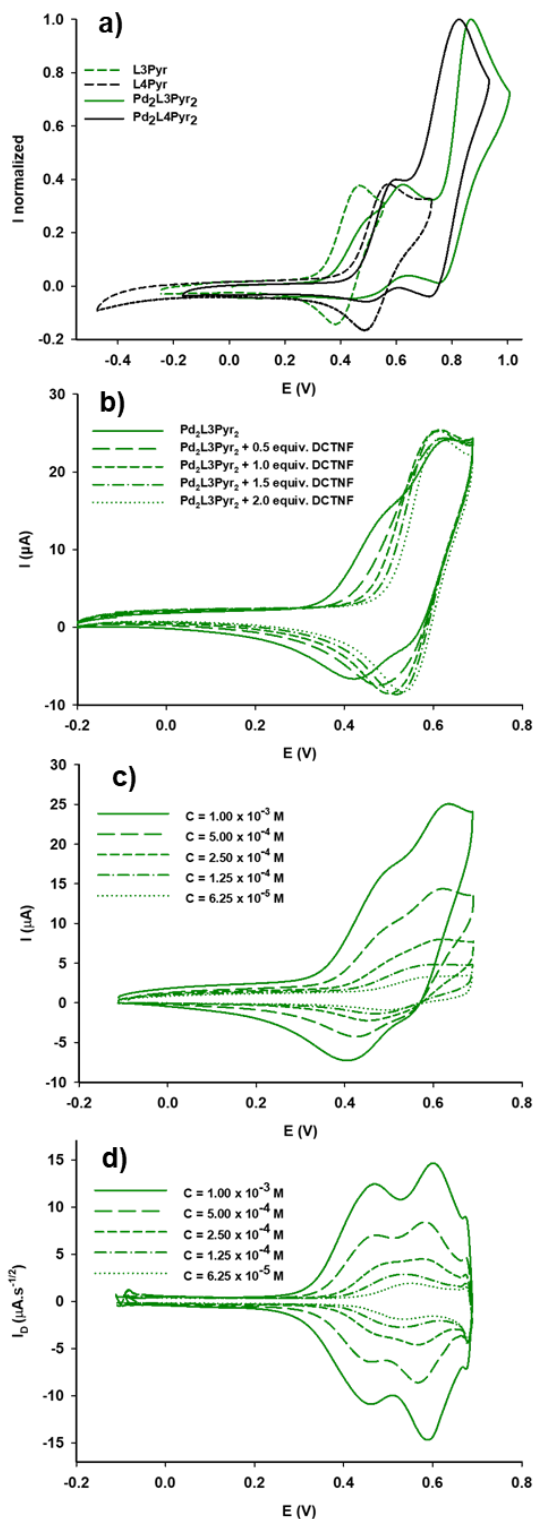


Fig. 2 Molecular force field (MM+) model of tweezers  $\text{Pd}_2\text{L}_4\text{Pyr}_2$  (a) and  $\text{Pd}_2\text{L}_3\text{Pyr}_2$  (b).

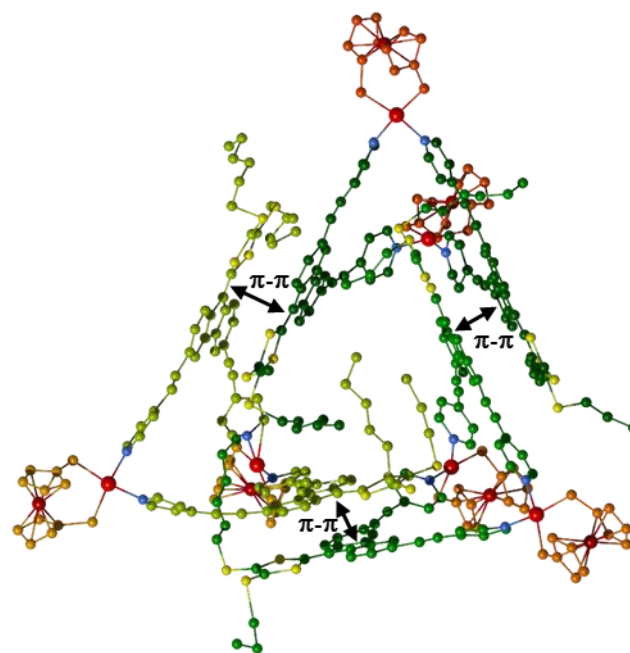
at  $E_2^{\text{ox}} = 0.82 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$ . This observation indicates that both DTF ligands are electronically equivalent and independent in  $\text{Pd}_2\text{L}_4\text{Pyr}_2$ . A striking different behavior is observed for tweezer  $\text{Pd}_2\text{L}_3\text{Pyr}_2$ . The CV of the latter exhibits a splitting of the redox wave corresponding to the DTF units, with 2 reversible oxidations occurring at  $E_1^{\text{ox}} = 0.49 \text{ V}$  and  $E_2^{\text{ox}} = 0.63 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$ , suggesting that both tips of the tweezer do not behave independently. Such splitting has already been reported in the case of molecular tweezers bearing TTF<sup>40</sup> and more recently with DTF tips,<sup>33</sup> and was ascribed to the formation of mixed-valence and  $\pi$ -dimer species upon oxidation. The above-mentioned estimated distance of  $8.5 \text{ \AA}$  between both panels in  $\text{Pd}_2\text{L}_3\text{Pyr}_2$  should in principle allow the sandwiching of a planar aromatic species between both tips,<sup>41, 42</sup> including a self-intercalation of two molecular tweezers if no other species is present in solution. This was confirmed by a concentration-dependent CV study of  $\text{Pd}_2\text{L}_3\text{Pyr}_2$ , which shows the disappearance of the splitting phenomenon upon diluting the solution from  $C = 10^{-3} \text{ M}$  to  $C = 6.25 \times 10^{-5} \text{ M}$  (Figures 3c,d). Such behavior is similar to the one reported by E. Levillain and P. Hudhomme for TTF-based molecular clips.<sup>40</sup> Thanks to the modelling of cyclic voltammetry experiments, these authors could demonstrate that the stepwise oxidation process follows a square scheme involving both neutral and radical cation

species, which interact either inside or outside the cavity (Figure S5a). This difference of the CV behavior between  $\text{Pd}_2\text{L}_3\text{Pyr}_2$  and  $\text{Pd}_2\text{L}_4\text{Pyr}_2$ , is therefore correlated to the distance separating both tips of the tweezer: whereas  $\text{Pd}_2\text{L}_3\text{Pyr}_2$  can bind a planar guest in the cavity through the simultaneous contribution of both tips ( $\text{S}\cdots\text{S}$  distance  $8.5 \text{ \AA}$ ) (Figure S5b),  $\text{Pd}_2\text{L}_4\text{Pyr}_2$  ( $\text{S}\cdots\text{S}$  distance  $15 \text{ \AA}$ ) cannot.

Based on those electrochemical experiments and geometrical optimizations, it appears that metalla-clip  $\text{Pd}_2\text{L}_3\text{Pyr}_2$  provides a cavity suitable for guest encapsulation. Additional cyclic voltammetry experiments were therefore carried out to monitor the host-guest interaction process, in presence of 9-dicyanomethylene-2,4,7-trinitrofluorene (DCTNF), an electro-deficient planar aromatic compound (Figure 3b). Interestingly, the addition of an increasing amount of DCTNF into a solution of  $\text{Pd}_2\text{L}_3\text{Pyr}_2$  shifts the first oxidation process to higher potential with the disappearance of the wave splitting. This suggests the intercalation of the DCTNF unit between both electron-rich DTF tips, which prevents therefore the above-mentioned self-intercalation process of two oxidized metalla-clips to occur. Moreover, the splitting observed during the reduction process of the oxidized molecular tweezer also disappears in the host-guest system (Figure 3b), ruling out a guest release phenomenon upon oxidation, a behavior that we recently



**Fig. 3** Cyclic voltammograms ( $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  (v/v 1/1), 0.1 M  $n\text{Bu}_4\text{NPF}_6$ , 100  $\text{mV}\cdot\text{s}^{-1}$ , CG, V vs.  $\text{Fc}/\text{Fc}^+$ ) of a) **L3Pyr**, **L4Pyr**, **Pd<sub>2</sub>L4Pyr<sub>2</sub>** and **Pd<sub>2</sub>L3Pyr<sub>2</sub>** at  $C = 10^{-3}$  M, b) **Pd<sub>2</sub>L3Pyr<sub>2</sub>** at  $C = 10^{-3}$  M in presence of DCTNF, c) **Pd<sub>2</sub>L3Pyr<sub>2</sub>** at different concentrations and d) the deconvoluted CV corresponding to (c).

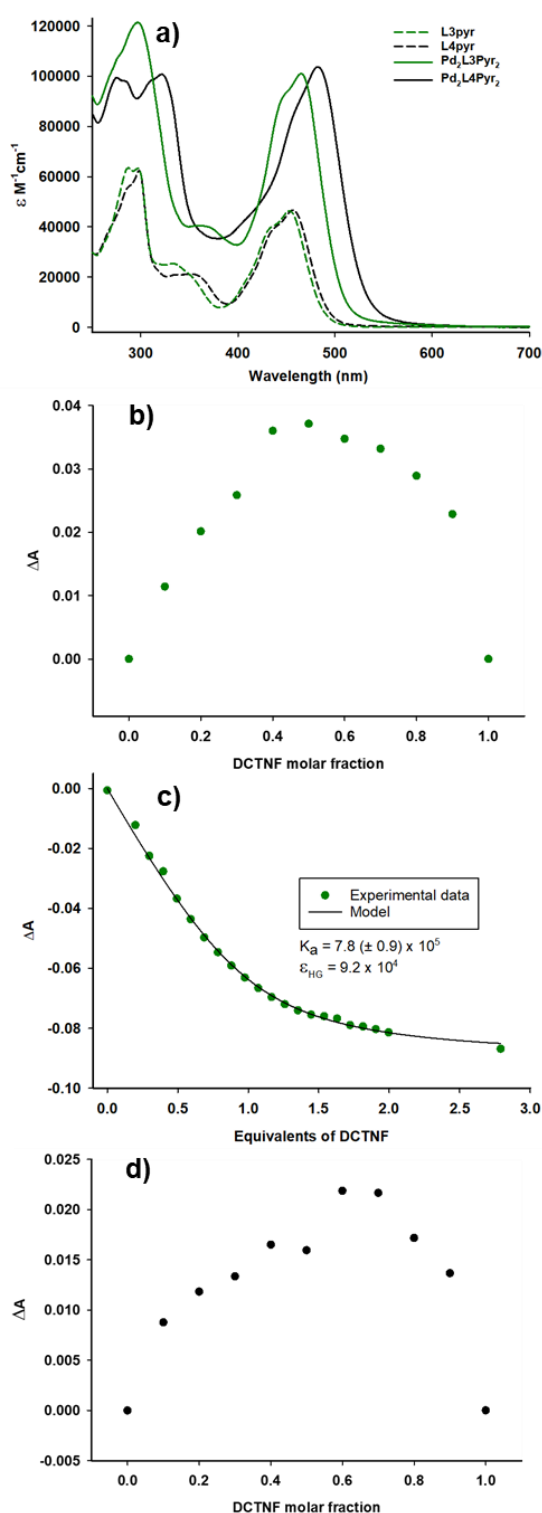


**Fig. 4** Crystal packing of **Pd<sub>2</sub>L4Pyr<sub>2</sub>** crystallized by slow diffusion of MeOtBu in a solution of  $\text{CH}_2\text{Cl}_2$  containing 2 equiv. of DCTNF (*dppf* phenyl rings omitted for clarity).

observed for a DTF-based Ruthenium tweezer.<sup>33</sup> As expected, similar studies carried out with **Pd<sub>2</sub>L4Pyr<sub>2</sub>** did not show any significant changes of the cyclic voltammogram, except a very weak anodic shift (Figure S6).

To get a better understanding of those interactions we tried to grow single crystals from solutions containing **Pd<sub>2</sub>L4Pyr<sub>2</sub>** or **Pd<sub>2</sub>L3Pyr<sub>2</sub>** and DCTNF (2 equiv.). Even though all attempts to get cocrystallized structures were unsuccessful, vapor diffusion of MeOtBu into a mixture of **Pd<sub>2</sub>L4Pyr<sub>2</sub>** and DCTNF lead to single crystals that does not show presence of DCTNF in the structure.<sup>43-45</sup> The latter exhibits a packing mode that differs from the one obtained in absence of DCTNF<sup>32</sup> (Figures S8c) and shows some specific features (Figure 4). It includes three independent  $\text{M}_2\text{L}_2$  metalla-clip units interacting through head-to-tail  $\pi$ - $\pi$  stacking between their respective DTF units, with interplanar distances of ca. 3.5 Å. As a result, they form an original discrete architecture constructed from two distinctive supramolecular interactions, *i.e.* coordination bonds and parallel displaced aromatic-aromatic interactions.

Deeper insights related to the interactions mode occurring between DCTNF and **Pd<sub>2</sub>L4Pyr<sub>2</sub>** or **Pd<sub>2</sub>L3Pyr<sub>2</sub>** were provided by UV-Vis experiments carried out in  $\text{CH}_2\text{Cl}_2$  (Figure 5). Both metalla-clips show absorption spectra close to those of their constitutive ligands (**L4Pyr** and **L3Pyr**) with, as expected, molar extinction coefficients which are twice higher. They are characterized by two absorption bands at high energy localized around 300 nm which are ascribed to  $\pi$ - $\pi^*$  transitions located on the pyridine and fluorene units as well as an intense ICT



**Fig. 5** UV-Vis spectra of ligands **L3Pyr**, **L4Pyr** and metalla-tweezers **Pd<sub>2</sub>L3Pyr<sub>2</sub>** and **Pd<sub>2</sub>L4Pyr<sub>2</sub>** recorded in  $\text{CH}_2\text{Cl}_2$  (a). Job plots for complexation of receptor **Pd<sub>2</sub>L3Pyr<sub>2</sub>** (b) and **Pd<sub>2</sub>L4Pyr<sub>2</sub>** (d) with DCTNF determined by UV-Vis spectroscopy at respectively 465 and 480 nm ( $\text{CH}_2\text{Cl}_2$ ,  $C = 10^{-5}$  M), and plots of absorbance of a UV-vis titration for complexation of receptor **Pd<sub>2</sub>L3Pyr<sub>2</sub>** ( $\text{CH}_2\text{Cl}_2$ ,  $C = 10^{-5}$  M) with DCTNF ( $\text{CH}_2\text{Cl}_2$ ,  $5 \times 10^{-4}$  M) at 465 nm (c).

band around 480 nm coming from the  $\text{HOMO}_{\text{DTF}} - \text{LUMO}_{\text{pyridine}}$  transition.<sup>46</sup> Job Plot experiments were carried out at  $\lambda_{\text{max}} = 465$  nm (**Pd<sub>2</sub>L3Pyr<sub>2</sub>**, Figure 5b) and 480 nm (**Pd<sub>2</sub>L4Pyr<sub>2</sub>**, Figure 5d), at  $C = 10^{-5}$  M in  $\text{CH}_2\text{Cl}_2$ , upon addition of aliquots of DCTNF ( $C = 5 \times 10^{-4}$  M in  $\text{CH}_2\text{Cl}_2$ ). As expected from CV experiments, both

metalla-tweezers exhibit highly distinctive behaviors. As clearly seen from Figure 5b, a maximum is observed for a molar fraction of 0.5 in the Job plot titration of **Pd<sub>2</sub>L3Pyr<sub>2</sub>** with DCTNF. This value is assigned to the formation of a 1:1 host-guest complex, for which both DTF unit cooperatively contribute to the guest binding, according to a sandwich-mode. A binding constant of  $K_a = 7.8 (\pm 0.9) \times 10^5$  was calculated<sup>47</sup>, a value which illustrates the remarkable ability of this tweezer to complex the electro-deficient DCTNF unit. On the other hand, the Job plot titration in the case of **Pd<sub>2</sub>L4Pyr<sub>2</sub>** (Figure 5d) exhibits a maximum for *ca.* 0.6-0.7. This value correlates with a 1:2 stoichiometry, meaning that even though the metalla-assembly **Pd<sub>2</sub>L4Pyr<sub>2</sub>** does not possess a cavity suitable for recognition of planar guests, it is able to interact with two DCTNF units. This is corroborated by a <sup>1</sup>H NMR experiment, which shows that signals of a mixture of a DTF ligand and DCTNF, are shifted related to the species recorded alone (Figure S7).

## Conclusions

In summary, the properties of two  $\text{M}_2\text{L}_2$  metalla-clips, **Pd<sub>2</sub>L4Pyr<sub>2</sub>** and **Pd<sub>2</sub>L3Pyr<sub>2</sub>**, constructed from the same *cis*-blocked  $\text{Pd}(\text{dppf})(\text{OTf})_2$  complex and two isomeric DTF-based ligands differing by the position of the nitrogen atom on the pyridyl coordinating units, are compared. While the molecular tweezer built from **L4Pyr** shows an intramolecular distance of *ca.* 15 Å between both redox-active tips, the one obtained from ligand **L3Pyr** features a cavity in which both DTF units are separated by 8.5 Å. The latter structural organization is favorable for promoting *i)* a tweezer dimerization upon oxidation, through formation of intercalated cationic dimeric species *ii)* formation of a host-guest complex with an electro-deficient DCTNF unit, with a remarkable association constant of  $7.8 \times 10^5$  in methylene chloride. These results illustrate at which extent minor structural changes led on the starting ligand, may drastically impact the geometry and host properties of the resulting metalla-species prepared through a coordination-driven self-assembled processes.

## Conflicts of interest

There are no conflicts to declare

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