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ARTICLE

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

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Maksym Dekhtiarenko,^{a,b} Serhii Krykun,^{a,b} Vincent Carré,^c Frédéric Aubriet,^c David Canevet,^a Magali Allain,^a Zoia Voitenko,^b Marc Sallé*^a and Sébastien Goeb*^a

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A M_2L_2 metalla-macrocycles constructed through coordination driven self-assembly from the Pd(dppf)OTf₂ 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.^{1,2} One reason for this success, lies on the high degree of predictability in the geometry of the resulting self-assembled structures.³ On this basis, more and more complex systems have been produced, including chiral⁴⁻⁶, heteroleptic⁷⁻⁹ and interlocked¹⁰⁻¹² ones. Those self-assembled discrete structures generally include a cavity,¹³ and their host properties have been widely studied to target various applications (e.g. depollution,¹⁴ drug delivery,¹⁵ catalysis¹⁶⁻¹⁸ and storage of reactive molecules¹⁹). Nevertheless, for most of these applications, there is an important need for controlling the intensity of the host-guest interaction,²⁰ which implies designing stimuli-responsive architectures.²¹⁻²⁴ On this basis, we described the preparation and properties of a series of redox-active rings²⁵ and cages²⁶⁻³¹ 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 rings³², tweezers³³ or cages.³⁴ The DTF moiety can be oxidized reversibly at low potential to the corresponding radical cation,^{35,36} a species which is prone to form mixed valence or π -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.³³

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)₂ 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)₂ in dichloromethane at 40 °C converges to a single symmetrical M_2L_2 discrete species (Scheme 1 left).³² 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 ¹H 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 **Pd₂L3Pyr₂** are upfield shifted compared to the free **L3Pyr** ligand, except H₆ (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 H₆ by coordination to the metal. The presence of only one discrete species is confirmed by ¹H 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 **Pd₂L4Pyr₂** metalla-cycle (Figure 1c'). This observation suggests that the self-assembled structure obtained from **L3Pyr** is similar in size to the one of **Pd₂L4Pyr₂**. The corresponding estimated hydrodynamic radius is of *ca* 10 Å, as extracted from the Stokes-Einstein equation ($T = 298 \text{ K}$),^{37,38} a value which is consistent with the formation of a M_2L_2 architectures as in the case of **Pd₂L4Pyr₂**.³²

^a 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

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

^c LCP-A2MC, FR 3624, Université de Lorraine, ICPM, 1 Bd Arago, 57078 Metz Cedex 03, France

† Electronic Supplementary Information (ESI) available. See

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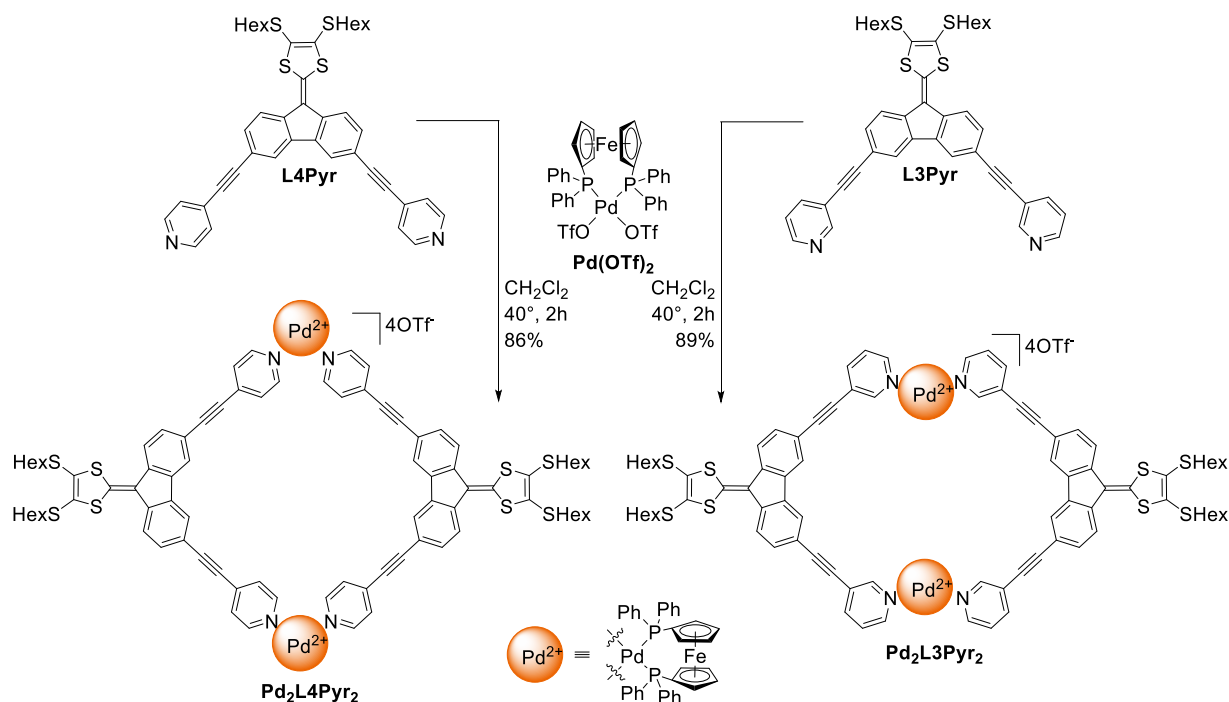
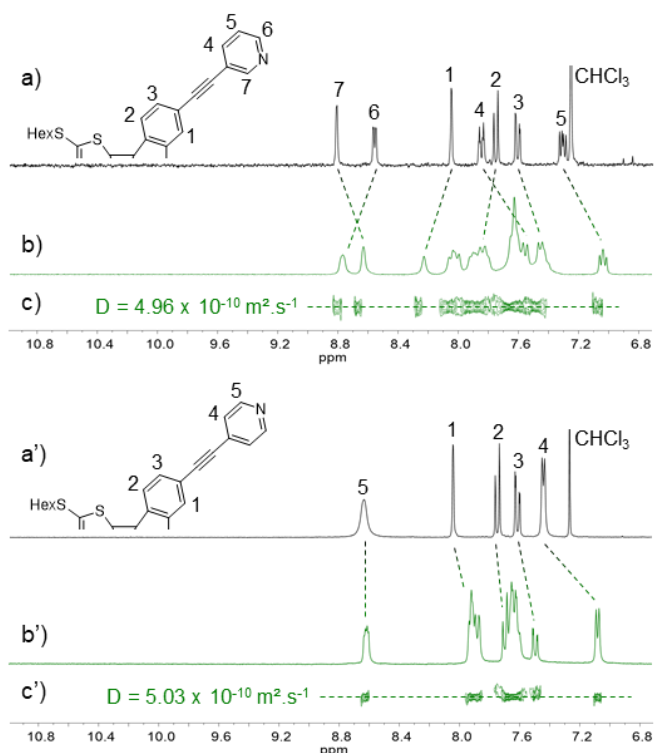
Scheme 1. Synthesis of metalla-macrocycles $\text{Pd}_2\text{L4Pyr}_2$ ³² and $\text{Pd}_2\text{L3Pyr}_2$.

Fig. 1 ^1H NMR spectra (aromatic region) of ligands L3Pyr (a) and L4Pyr (a') in CDCl_3 , metalla-macrocycles $\text{Pd}_2\text{L3Pyr}_2$ (b) and $\text{Pd}_2\text{L4Pyr}_2$ (b') in CD_2Cl_2 , and corresponding ^1H 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 M_2L_2 molecular clip [$\text{Pd}_2\text{L3Pyr}_2 - 2\text{OTf}$]²⁺; $m/z = 1510.667$), 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 M_2L_2 metalla-cycle upon ESI. Such behavior is known in the literature with soft ionization conditions³⁹ and was also observed in the case of the $\text{Pd}_2\text{L4Pyr}_2$ analogue.³²

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° between both fluorenyl mean planes, and an intramolecular S...S distance between facing dithiole rings of ca. 15 \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° and a S...S distance of ca. 8.5 \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 $\text{Pd}_2\text{L4Pyr}_2$ homolog³²(Figure 3a). Both L4Pyr and L3Pyr ligands exhibit one reversible redox wave, centered on the DTF moiety at $E^{\text{ox}} = 0.56$ and 0.46 V vs Fc/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 Fc/Fc^+) which is followed by oxidation of the ferrocene moieties

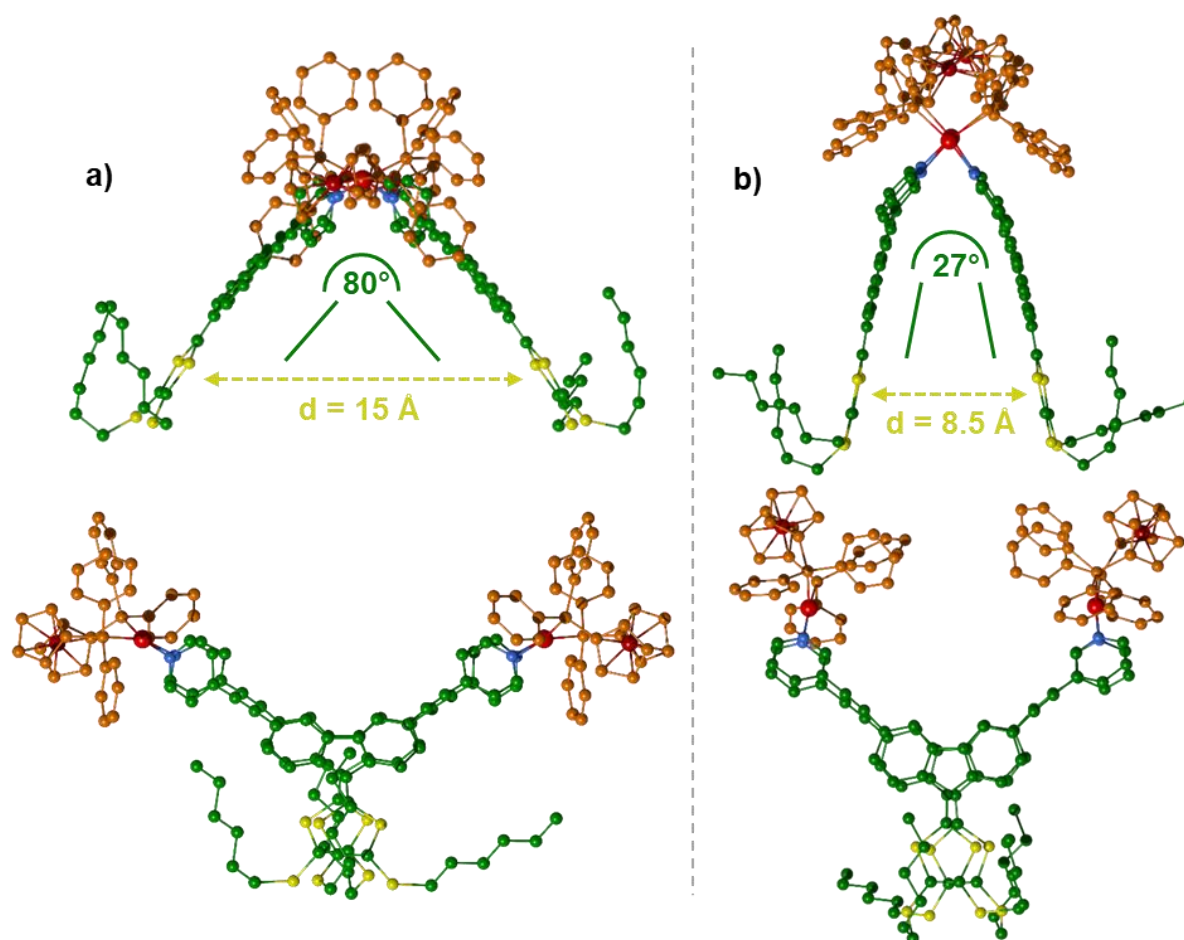


Fig. 2 Molecular force field (MM+) model of tweezers $\text{Pd}_2\text{L4Pyr}_2$ (a) and $\text{Pd}_2\text{L3Pyr}_2$ (b).

at $E_2^{\text{ox}} = 0.82\text{V}$ vs Fc/Fc^+ . This observation indicates that both DTF ligands are electronically equivalent and independent in $\text{Pd}_2\text{L4Pyr}_2$. A striking different behavior is observed for tweezer $\text{Pd}_2\text{L3Pyr}_2$. 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 Fc/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 TTF⁴⁰ and more recently with DTF tips,³³ and was ascribed to the formation of mixed-valence and π -dimer species upon oxidation. The above-mentioned estimated distance of 8.5Å between both panels in $\text{Pd}_2\text{L3Pyr}_2$ should in principle allow the sandwiching of a planar aromatic species between both tips,^{41, 42} 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 $\text{Pd}_2\text{L3Pyr}_2$, 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.⁴⁰ 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 $\text{Pd}_2\text{L3Pyr}_2$ and $\text{Pd}_2\text{L4Pyr}_2$, is therefore correlated to the distance separating both tips of the tweezer: whereas $\text{Pd}_2\text{L3Pyr}_2$ can bind a planar guest in the cavity through the simultaneous contribution of both tips ($\text{S}\cdots\text{S}$ distance 8.5Å) (Figure S5b), $\text{Pd}_2\text{L4Pyr}_2$ ($\text{S}\cdots\text{S}$ distance 15Å) cannot.

Based on those electrochemical experiments and geometrical optimizations, it appears that metalla-clip $\text{Pd}_2\text{L3Pyr}_2$ 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 $\text{Pd}_2\text{L3Pyr}_2$ 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

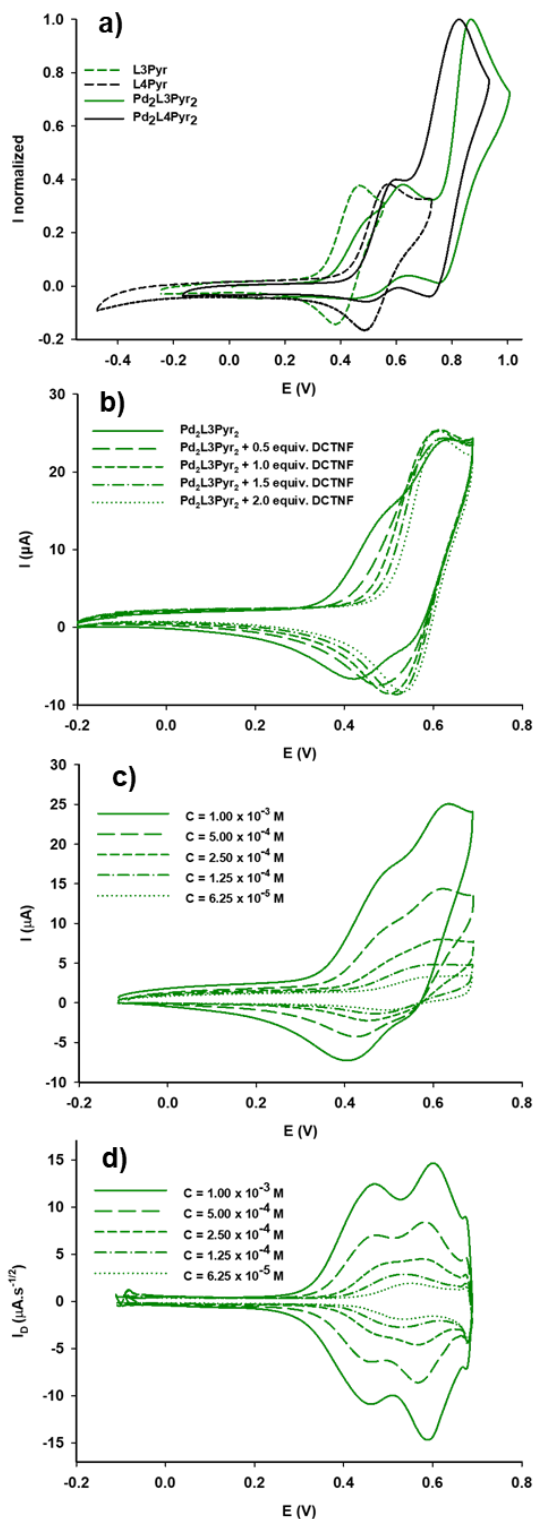


Fig. 3 Cyclic voltammograms ($\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (v/v 1/1), 0.1 M $n\text{Bu}_4\text{NPF}_6$, 100 $\text{mV}\cdot\text{s}^{-1}$, CG, V vs. Fc/Fc^+) of a) **L3Pyr**, **L4Pyr**, **Pd₂L4Pyr₂** and **Pd₂L3Pyr₂** at $C = 10^{-3}$ M, b) **Pd₂L3Pyr₂** at $C = 10^{-3}$ M in presence of DCTNF, c) **Pd₂L3Pyr₂** at different concentrations and d) the deconvoluted CV corresponding to (c).

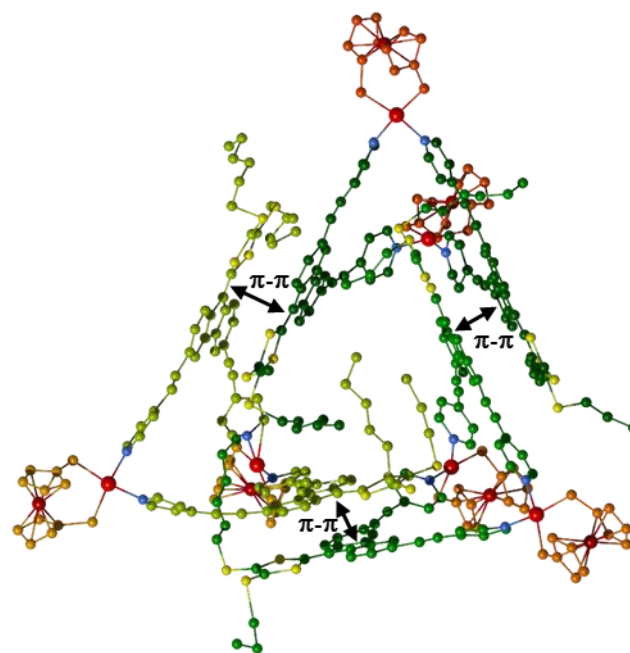


Fig. 4 Crystal packing of **Pd₂L4Pyr₂** crystallized by slow diffusion of MeOtBu in a solution of CH_2Cl_2 containing 2 equiv. of DCTNF (*dppf* phenyl rings omitted for clarity).

observed for a DTF-based Ruthenium tweezer.³³ As expected, similar studies carried out with **Pd₂L4Pyr₂** 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 **Pd₂L4Pyr₂** or **Pd₂L3Pyr₂** and DCTNF (2 equiv.). Even though all attempts to get cocrystallized structures were unsuccessful, vapor diffusion of MeOtBu into a mixture of **Pd₂L4Pyr₂** and DCTNF lead to single crystals that does not show presence of DCTNF in the structure.⁴³⁻⁴⁵ The latter exhibits a packing mode that differs from the one obtained in absence of DCTNF³² (Figures S8c) and shows some specific features (Figure 4). It includes three independent M_2L_2 metalla-clip units interacting through head-to-tail π - π 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 **Pd₂L4Pyr₂** or **Pd₂L3Pyr₂** were provided by UV-Vis experiments carried out in CH_2Cl_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 π - π^* transitions located on the pyridine and fluorene units as well as an intense ICT

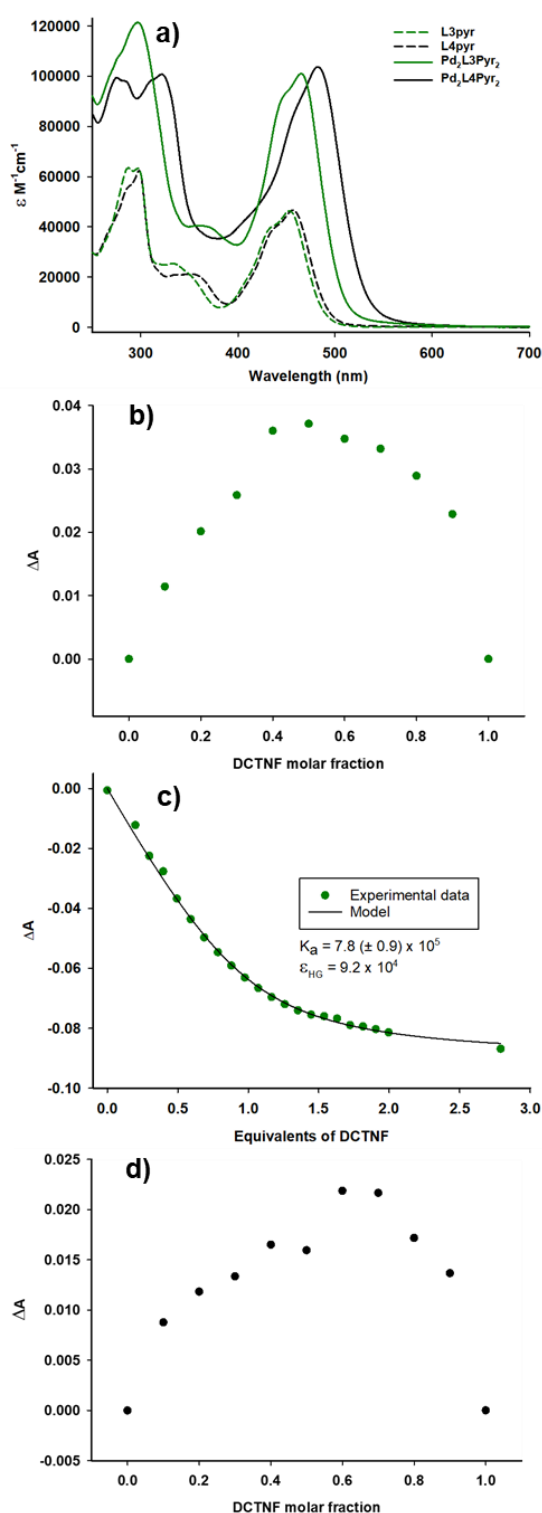


Fig. 5 UV-Vis spectra of ligands **L3Pyr**, **L4Pyr** and metalla-tweezers **Pd₂L3Pyr₂** and **Pd₂L4Pyr₂** recorded in CH_2Cl_2 (a). Job plots for complexation of receptor **Pd₂L3Pyr₂** (b) and **Pd₂L4Pyr₂** (d) with DCTNF determined by UV-Vis spectroscopy at respectively 465 and 480 nm (CH_2Cl_2 , $C = 10^{-5}$ M), and plots of absorbance of a UV-vis titration for complexation of receptor **Pd₂L3Pyr₂** (CH_2Cl_2 , $C = 10^{-5}$ M) with DCTNF (CH_2Cl_2 , 5×10^{-4} M) at 465 nm (c).

band around 480 nm coming from the $\text{HOMO}_{\text{DTF}} - \text{LUMO}_{\text{pyridine}}$ transition.⁴⁶ Job Plot experiments were carried out at $\lambda_{\text{max}} = 465$ nm (**Pd₂L3Pyr₂**, Figure 5b) and 480 nm (**Pd₂L4Pyr₂**, Figure 5d), at $C = 10^{-5}$ M in CH_2Cl_2 , upon addition of aliquots of DCTNF ($C = 5 \times 10^{-4}$ M in CH_2Cl_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 **Pd₂L3Pyr₂** 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 calculated⁴⁷, 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 **Pd₂L4Pyr₂** (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 **Pd₂L4Pyr₂** 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 ^1H 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 M_2L_2 metalla-clips, **Pd₂L4Pyr₂** and **Pd₂L3Pyr₂**, 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 7.8×10^5 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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