Supporting Information

Tuning the structure and the properties of dithiafulvene metallaassembled tweezers

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Chemicals and instrumentation

Chemicals

Complex *cis*-Pd(*dppf*)(OTf)₂ (*dppf* = 1,1'-bis(diphenylphosphino)ferrocene; OTf = trifluoromethane-sulfonate),¹ 9dicyanomethylene-2,4,7-trinitrofluorene (**DCNTF**),² ligands **L3Pyr**,³ **L4Pyr**⁴ and self-assembly **Pd**₂**L4Pyr**₂⁴ were synthesized using procedures described in the literature. All reagents were commercial reagent grade and were used without further purification. For synthesis and crystallization, analytical grade solvents were used.

Instrumentation

Characterizations and NMR experiments were carried out on an NMR Bruker Avance III 300 spectrometer at room temperature or 298 K (¹H NMR DOSY), using perdeuterated solvents. Chemical shifts are reported in ppm relative to the solvent residual value. ¹H DOSY NMR spectra were analyzed with MestReNova software. ESI-FTICR spectra were performed on an IonSpec (Agilent), 9.4 T hybride ESI q-Q-q in CH₃CN (C = 10^{-3} M). Cyclic voltammetry experiments were carried out on a BioLogic SP-150 potentiostat, Pt counter electrode and Ag/AgNO₃ (0.1 M *n*Bu₄NPF₆ in CH₃CN) reference electrode.



Experimental procedures and characterizations

Synthesis of metalla-twezzer Pd₂L3Pyr₂

A stoichiometric mixture of ligand L3Pyr (7.01 mg, 0.01 mol) and *cis*-Pd(*dppf*)(OTf)₂ (9.57 mg, 0.01 mol) in CH₂Cl₂ (1 mL) was stirred for 2 h at room temperature. Then, Et₂O was added and the resulting suspension was centrifuged. The solid was rinsed 3 times with Et₂O and dried under vacuum to give Pd₂L3Pyr₂ as a red powder (15.10 mg, 89%).

¹H NMR (300 MHz, CD_2Cl_2) δ 8.85 (s, 4H), 8.72 (s, 4H), 8.31 (s, 4H), 8.11 – 8.08 (m, 8H), 7.98 – 7.91 (m, 12H), 7.71 – 7.62 (m, 24H), 7.54 (d, *J* = 7.7 Hz, 8H), 7.12 (t, *J* = 7.5 Hz, 4H), 4.93 (s, 4H), 4.78 (s, 4H), 4.57 (s, 4H), 4.33 (s, 4H), 2.97 (t, *J* = 7.3 Hz, 8H), 1.73 – 1.69 (m, 16H), 1.48 – 1.39 (m, 8H), 1.31 – 1.29 (m, 8H), 0.86 (t, *J* = 7.8, 7.0 Hz, 12H). ¹H DOSY NMR (300 MHz, CD_2Cl_2 , $C = 10^{-3}$ M) $D = 4.96 \times 10^{-10}$ m².s⁻¹.

FTICR-HRMS (m/z), [[Pd₂L3Pyr₂]⁴⁺ - 2TfO⁻]²⁺: found: 1510.667, calculated 1510.667.



Figure S1. ¹H NMR spectrum of Pd₂L3Pyr₂ in CD₂Cl₂.



Figure S2. COSY NMR spectrum of Pd₂L3Pyr₂ in CD₂Cl₂.



Figure S3. ¹H DOSY NMR spectrum of Pd₂L3Pyr₂ in CD₂Cl₂.



Figure S4. ESI-FTICR spectrum of Pd_2L3Pyr_2 recorded in CH_2Cl_2/CH_3NO_2 (v/v 1/1) (C = 10⁻³ M).



Figure S5. Schematic representation of the stepwise oxidations mechanism proposed by P. Hudhomme and E. Levillain in case of TTF based molecular clips (a),⁵ and square scheme involved in the oxidation of Pd₂L3Pyr₂ (b).



Figure S6. Cyclic voltammograms (CH₃CN/CH₂Cl₂ (v/v 1/1), 0.1 M nBu₄NPF₆, 100 mV·s⁻¹, CG, V vs. Fc/Fc⁺) of Pd₂L4Pyr₂ at C = 10⁻³ M in presence of DCTNF.



Figure S7. ¹H NMR of ligand L3Pyr (a), DCTNF (b) and their 1/1 mixture (b) in CDCl₃ at C = 10^{-3} M.

Molecular Modeling

Molecular modeling was performed by using the molecular mechanics force field MM+ method from the HyperChem Professional 8.0.3 program (Hypercube, Inc., Waterloo, ON, Canada,) configured *in vacuo*, with an RMS of 10⁻⁵ kcal/mole, a number of maximum cycles of 32500, and a Polak-Ribiere algorithm. Counter anions were omitted to simplify the calculation.

Determination method of the Ka constant (Pd2L3Pyr2 and DCTNF)⁶

In order to determine the binding constant, UV-Vis titration experiment was led in DCM by adding a solution of **DCTNF** ($C = 5 \times 10^{-4} \text{ M}$) and **Pd₂L3Pyr₂** ($C = 10^{-5} \text{ M}$) onto a solution of pure **Pd₂L3Pyr₂** ($C = 10^{-5} \text{ M}$). In this way, the host concentration was maintained constant during the titration.⁷ In the case of a 1:1 complex, the equilibrium under consideration can be described by equation 1:

H + G \longleftarrow HG : K_a

The evolution of the absorbance A at a given wavelength can be expressed according to equation 2:

 $\Delta A = (\epsilon HG - \epsilon H - \epsilon G) \frac{[H]0 + [G]0 + 1/Ka \pm \sqrt{([H]0 + [G]0 + 1/Ka)^2 - 4[H]0[G]0}}{2}$

Where ε_{H} , ε_{G} and ε_{HG} are the molar extinction coefficients of the host, the guest and the host-guest association respectively, I is the optical path of the quartz cell and K_a the binding constant. Concentrations [H]₀ and [G]₀ correspond to the introduced concentrations of host and guest within the quartz cell.

This theoretical equation was fitted to the corresponding experimental data with the least-squares method, affording an evaluation of the desired binding constant.

X-ray diffraction





X-ray single-crystal diffraction data for Pd_2L4Pyr_2 (from single crystals obtained in presence of DCTNF) were collected at 150K on a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Atlas CCD detector and micro-focus Cu-K_a radiation (λ = 1.54184 Å). The structure was solved by dual space algorithm, expanded and refined on F² by full-matrix least-squares techniques using SHELX programs (G. M. Sheldrick, SHELXT 2018/2 and SHELXL 2018/3). All non-hydrogen atoms were refined anisotropically and the H atoms were included in the calculation without refinement. Multiscan empirical absorption was corrected using CrysAlisPro program (CrysAlisPro, Agilent Technologies, V1.171.38.46, 2015).

The structure refinement showed disordered electron density which could not be reliably modeled and the program PLATON/SQUEEZE (A.L. Spek V290617 (1980-2019)) was used to remove the corresponding scattering contribution from the intensity data. Because of incomplete data collection and too low resolution, we only

calculate void space (16286 A3) in the structure even if the program limits have been exceeded. In the same way, only the known composition (without solvent) was included in the calculation of the empirical formula, formula weight, density, linear absorption coefficient and F(000).

Crystallographic data for Pd₂L4Pyr₂.

 $C_{468}H_{408}F_{36}Fe_6N_{12}O_{36}P_{12}Pd_6S_{36}$, solvent / [6($C_{42}H_{40}N_2S_4$), 6($C_{34}H_{28}Fe_1P_2Pd$), 12(CF_3SO_3), solvent], M = 9959.34, orange prism, 0.251 x 0.184 x 0.082 mm³, triclinic, *P*-1 space group, a = 26.626(1) Å, b = 34.233(2) Å, c = 37.535(2) Å, $\alpha = 69.996(5)^{\circ}$, $\beta = 87.800(5)^{\circ}$, $\gamma = 73.300(5)^{\circ}$, V = 30724(3) Å³, Z = 2, pcalc = 1.077 g/cm³, $\mu = 4.413$ mm⁻¹, F(000) = 10200, θ min = 2.779°, θ max = 62.024°, 110690 reflections collected, 78748 unique (R_{int} = 0.0987), parameters / restraints = 3871 / 713, R1 = 0.1374 and wR2 = 0.3594 using 18381 reflections with I>2 σ (I), R1 = 0.2744 and wR2 = 0.4660 using all data, GOF = 0.924, -0.859 < $\Delta\rho$ < 0.697 e.Å⁻³. CCDC 1996862.

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