Electronic Supplementary Material (ESI) for New Journal of Chemistry.

A Self-Assembled M_2L_4 Cage incorporating Electron-rich 9-(1,3-dithiol-2-ylidene)Fluorene Units

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Supporting Information

Chemicals, instrumentation and titration

Chemicals

All reagents were of commercial reagent grade and were used without further purification. Compound **1** was synthetized as described in the literature.[1] Silica gel chromatography was performed with a SIGMA Aldrich Chemistry SiO_2 (pore size 60 Å, 40-63 µm technical grades).

Instrumentation

The 300.3 MHz (^{1}H) and 75.5 MHz (^{13}C) NMR spectra were recorded at room temperature using perdeuterated solvents as internal standards (^{1}H), on a NMR Bruker Avance III 300 spectrometer. DOSY NMR spectra were analysed with MESTRENOVA software. MALDI-TOF-MS spectra were recorded on a MALDI-TOF Bruker Biflex III instrument using a positive-ion mode. ESI-FTICR spectra were achieved on a IonSpec (Agilent), 9,4 T hybride ESI q-Q-q. Cyclic voltammetry experiments were carried out on a BioLogic SP-150 potentiostat, calibrated using internal ferrocen.

Experimental procedure and Characterization data

3,6-bis(pyridin-3-ylethynyl)-9H-fluoren-9-one (**2**)

Reaction was carried in the MW tube. To an argon degassed solution of 3,6-dibromo-9H-fluoren-9-one (100 mg, 0.295 mmol) and 3-ethynylpyridine (122 mg, 1.18 mmol, 4 equiv.) in triethylamine/toluene 1/1 (2 ml) were added $Pd(PPh_3)_4$ (68.3 mg, 0.059 mmol, 0.2 equiv.) and CuI (11.3 mg, 0.059 mmol, 0.2 equiv.). The solution was irradiated for 30 min at constant 250 W. The solvent was evaporated under vacuum. The residue was treated with water and extracted with dichloromethane (50 mL). The organic extracts were washed with water (3 x 50 mL) and dried over magnesium sulfate. The solvent was evaporated under vacuum. A chromatography column on silica gel was performed using dichloromethane/petroleum ether (1/1) as eluent. Compound was further purified by recrystallization from a mixture of dichloromethane/pentane. Compound **2** (85 mg) was obtained as a yellow powder, 75 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (s, 2H), 8.59 (s, 2H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.74 – 7.64 (m, 4H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.37 – 7.29 (m, 2H); ^{13}C NMR (76 MHz, $CDCl_3$) δ 191.77, 152.08, 148.88, 143.71, 138.97, 134.09, 133.00, 128.99, 124.54, 123.56, 123.35, 119.95, 92.21, 89.45; FAB-HRMS: found: 382.1104, calculated: 382.1106

3,3'-((9-(4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)-9H-fluorene-3,6-diyl)bis(ethyne-2,1-diyl))dipyridine (**L**)

To a solution of bisthiohexyl phosphonate (165 mg, 0.37 mmol, 1.5 equiv.) in anhydrous tetrahydrofuran (10 mL) at -78°C, was slowly added *n*-butyl lithium (0.149 mL, 0.37 mmol, 1.6 M, 1.5 equiv.). The mixture was stirred for one hour at -78°C and a suspension of 3,6-bis(pyridin-3-ylethynyl)-9H-fluoren-9-one (95 mg, 0.25 mmol, 1 equiv.) in anhydrous tetrahydrofuran (10 mL) at -78°C was added *via* cannula. The mixture was stirred 1 h at -78°C and overnight at room temperature. The solvent was removed under vacuum. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water, and dried over magnesium sulfate. The solvent was removed under vacuum. A chromatography column on silica gel was performed using a gradient of eluent: petroleum ether/dichloromethane (1/1) to dichloromethane/methanol (98/2). Compound was further purified by recrystallization in a mixture of dichloromethane/methanol. Ligand **L** (94 mg) was obtained as an orange solid, 54 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (d, *J* = 1.8 Hz, 2H), 8.57 (dd, *J* = 4.9, *J* = 1.8 Hz, 2H), 8.06 (d, *J* = 1.6 Hz, 2H), 7.86 (ddd, *J* = 7.9, *J* = 1.8, *J* = 1.8 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.62 (dd, *J* = 8.2, *J*= 1.6 Hz, 2H), 7.31 (dd, *J* = 7.9, 4.9 Hz, 2H), 2.99 (m, 4H), 1.71 (m, 2H), 1.48 (m, 4H), 1.33 (m, 8H), 0.90 (*J* = 6.8 Hz, 6H); ^{1}H NMR (300 MHz, DMSO) δ 8.792 (d, *J* = 1.7 Hz, 2H), 8.60 (dd, *J* = 4.8, *J* = 1.7 Hz, 2H), 8.33 (s, 2H), 8.00 (ddd, *J* = 7.8, *J* = 1.7, *J* = 1.7 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.67 (dd, *J* = 8.2, *J*= 1.7 Hz, 2H), 7.48 (dd, *J* = 7.8, 4.8 Hz, 2H), 3.07 (t, *J* = 7.1 Hz, 4H), 1.65 (m, 2H), 1.42 (m, 4H), 1.27 (m, 8H), 0.85 (*J* = 6.8 Hz, 6H); ^{1}H DOSY NMR (300 MHz, DMSO) *D* = 1.86 x 10^{-10} m^2s^{-1}; ^{13}C NMR (76 MHz,$CDCl_3$) δ 152.27, 148.43, 141.61, 138.38, 137.04,

136.80, 130.49, 129.22, 123.08, 123.04, 122.57,120.70, 119.55, 119.04, 93.64, 86.37, 36.67, 31.37, 29.74, 28.29, 22.57, 14.08; FAB-HRMS: found: 700.2067, calculated: 700.2074.

Cage $[Pd_2L_4]^{4+},4BF_4^-$

A mixture of ligand **L** (10.00 mg, 14.2 µmol) and $Pd(BF_4)_2(CH_3CN)_4$ (3.16 mg, 7.10 µmol) in DMSO (1.0 mL) were heated at 50°C for 5 min until complete dissolution. Then, ethyl acetate was added and mixture was centrifuged. The residue was washed with diethyl ether and dried under vacuum to give complex **1** (10.5 mg) as a dark red solid, yield 80%. Monocristals were obtained by slow diffusion of ethyl acetate in DMSO (gaz-liquid). ^{1}H NMR (300 MHz, DMSO) δ 9.17 (m, 4H), 8.43 (d, *J* = 8.1 Hz, 2H), 8.23 (s, 2H), 7.98 – 7.70 (m, 6H), 3.06 (t, *J* = 7.0 Hz, 4H), 1.69 – 1.52 (m, 4H), 1.40 (s, 4H), 1.32 – 1.16 (m, 8H), 0.83 (t, *J* = 6.7 Hz, 6H); ^{1}H DOSY NMR (300 MHz, DMSO) *D* = 7.90 x 10^{-11} m^2s^{-1}; FTICR-HRMS: found for $[[\mathbf{Pd_2L_4}]^{4+},4BArF^- - 3BArF^-]^{3+}$: 1293.2362, calculated: 1293.2350.

NMR spectra

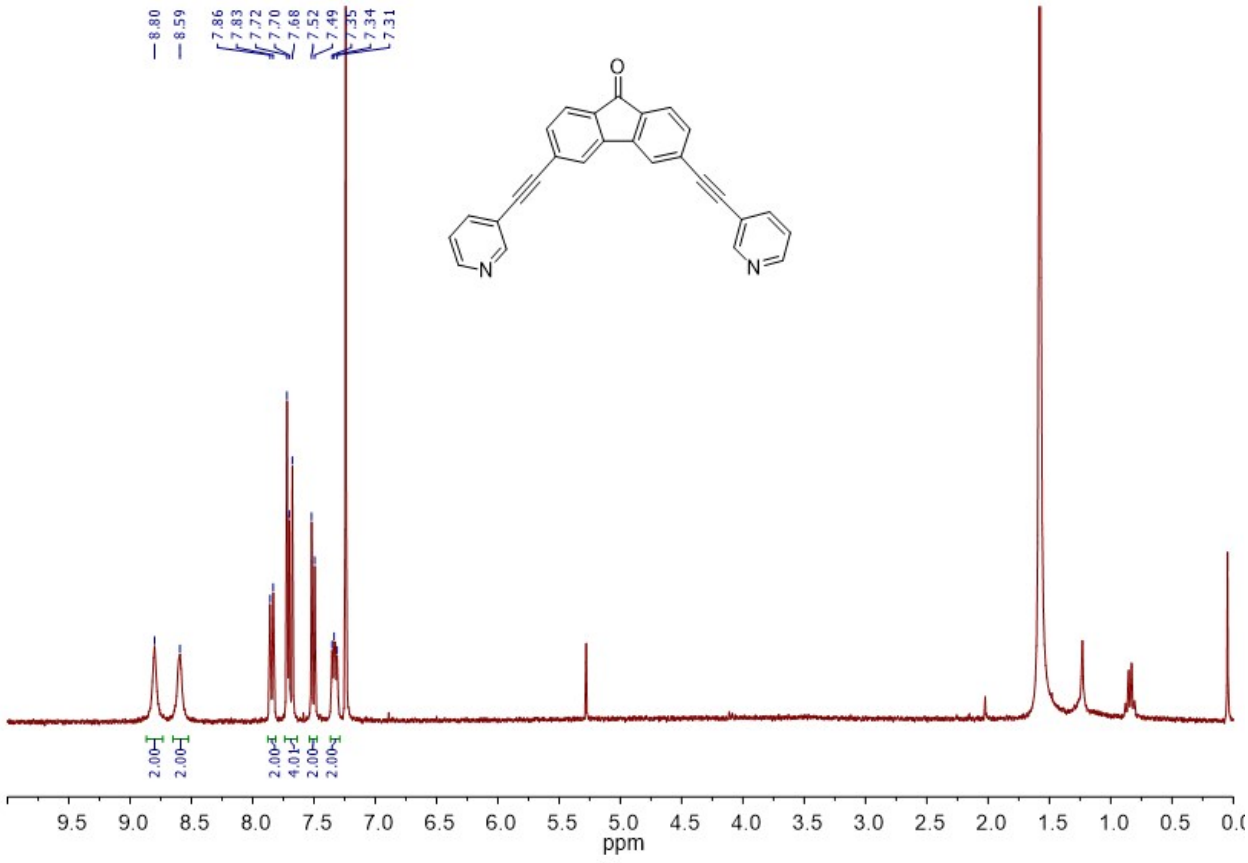

Figure S1. ^{1}H NMR spectra of **2** in $CDCl_3$

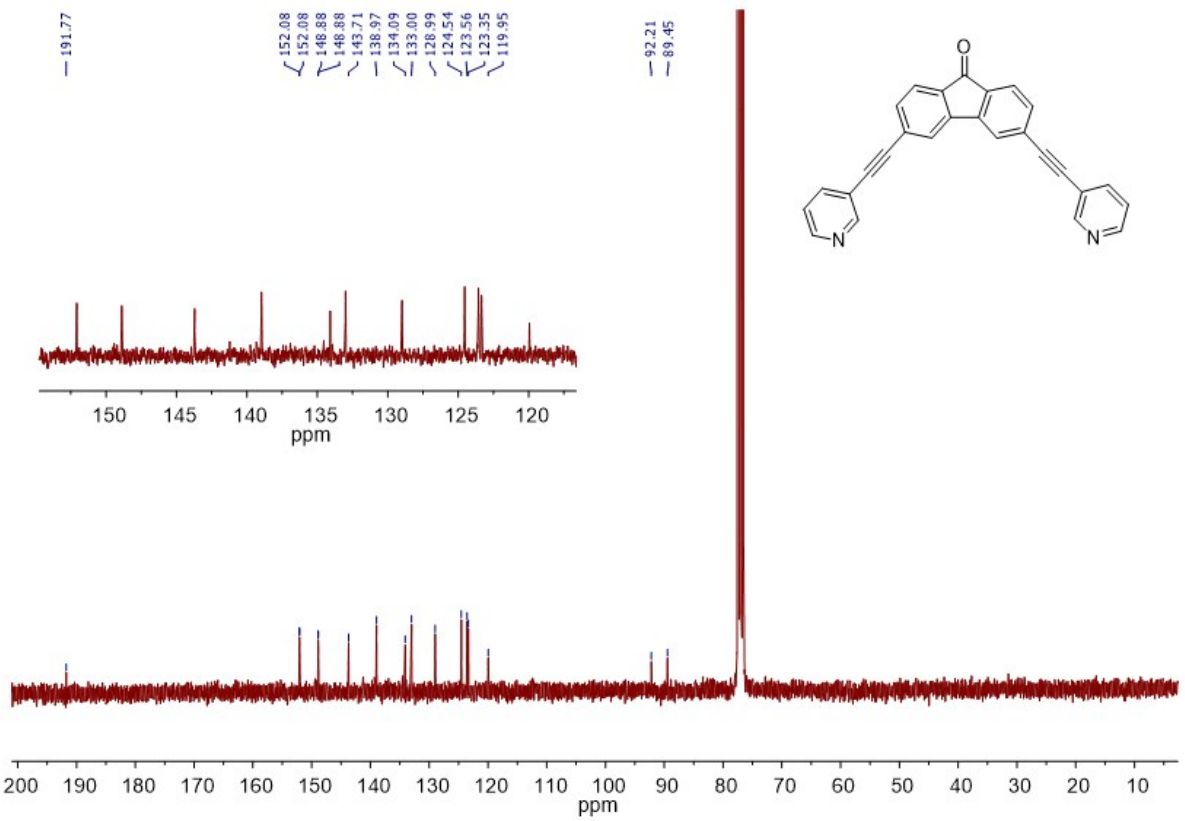

Figure S2. ^{13}C NRM spectrum of **2** in $CDCl_3$

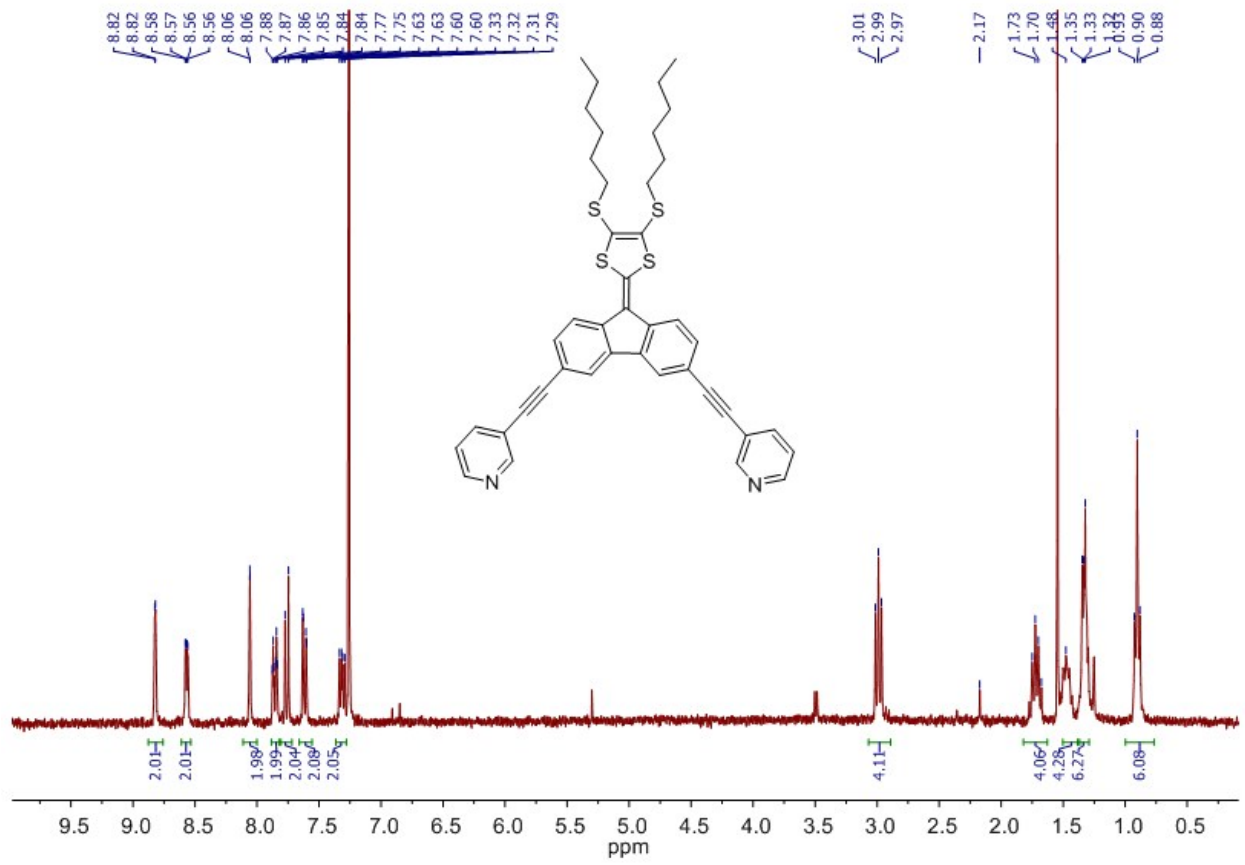

Figure S3. ^{1}H NMR spectra of **L** in $CDCl_3$

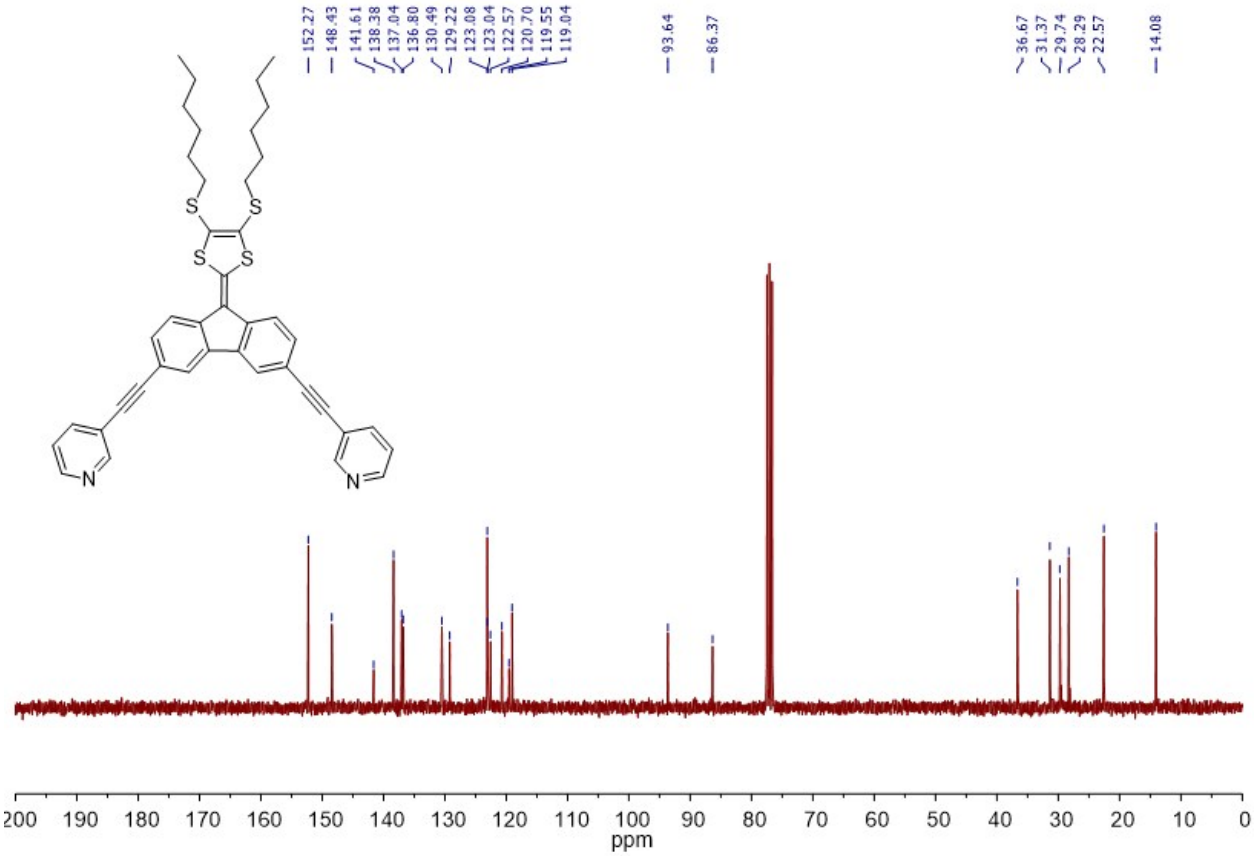

Figure S4. ^{13}C NMR spectra of **L** in $CDCl_3$

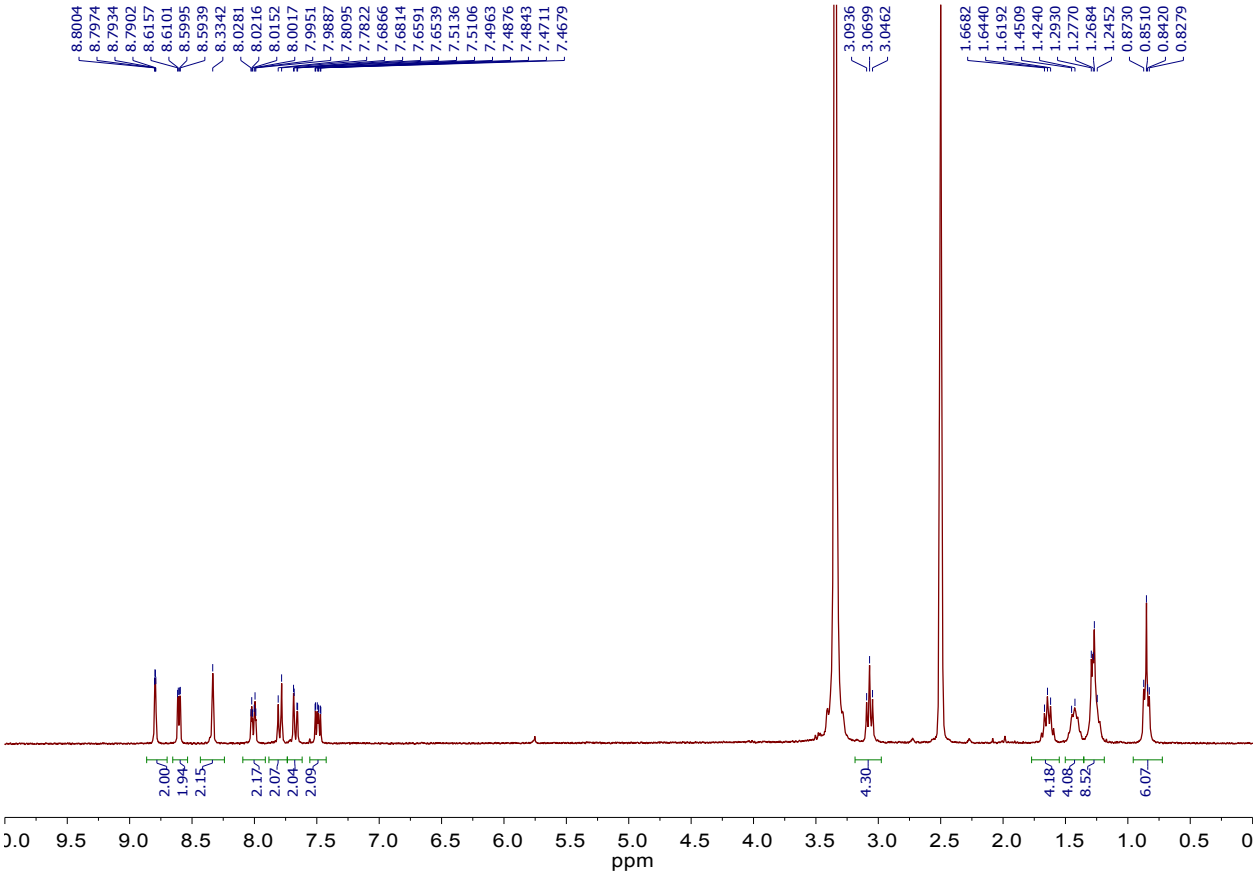

Figure S5. ^{1}H NMR spectra of **L** in DMSO-d6

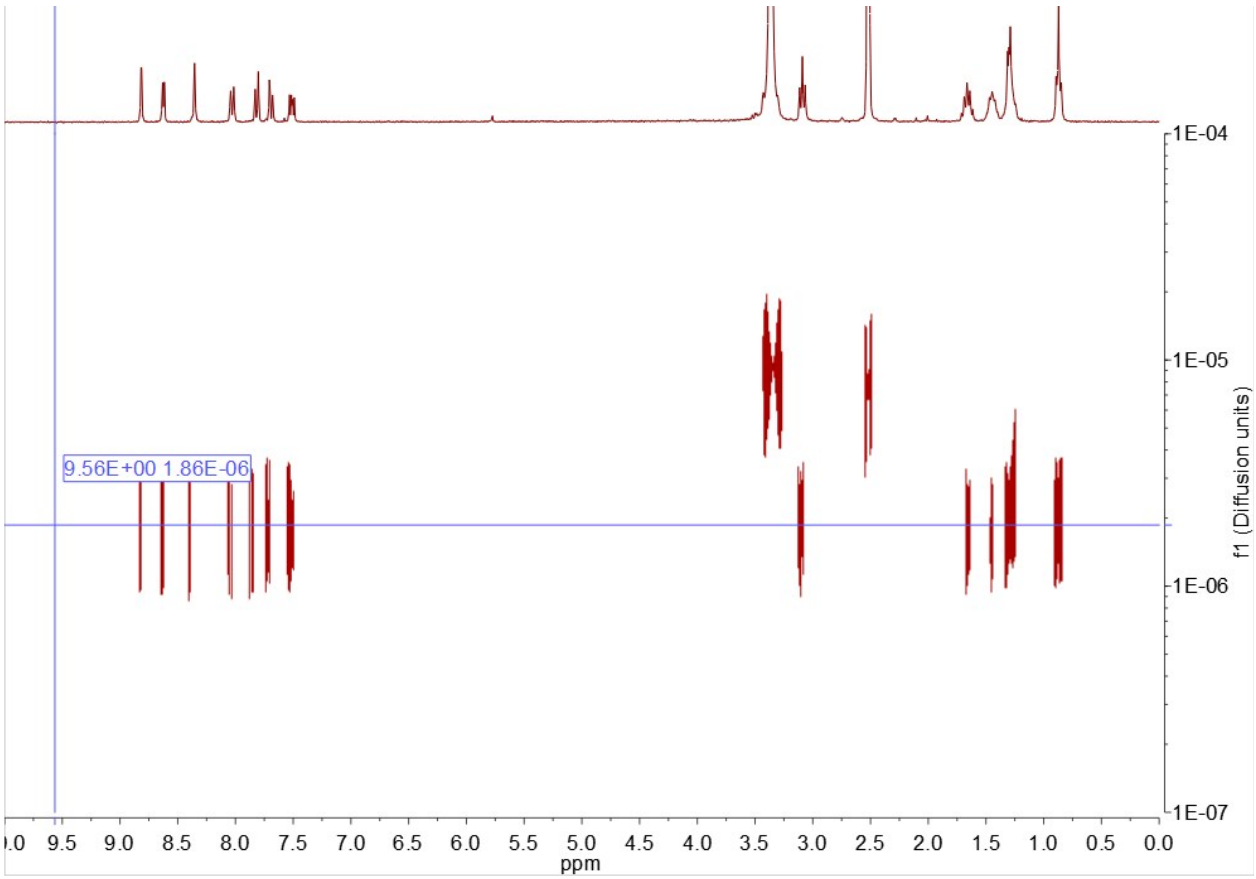

Figure S6. ^{1}H DOSY NMR spectra of **L** in DMSO-d6

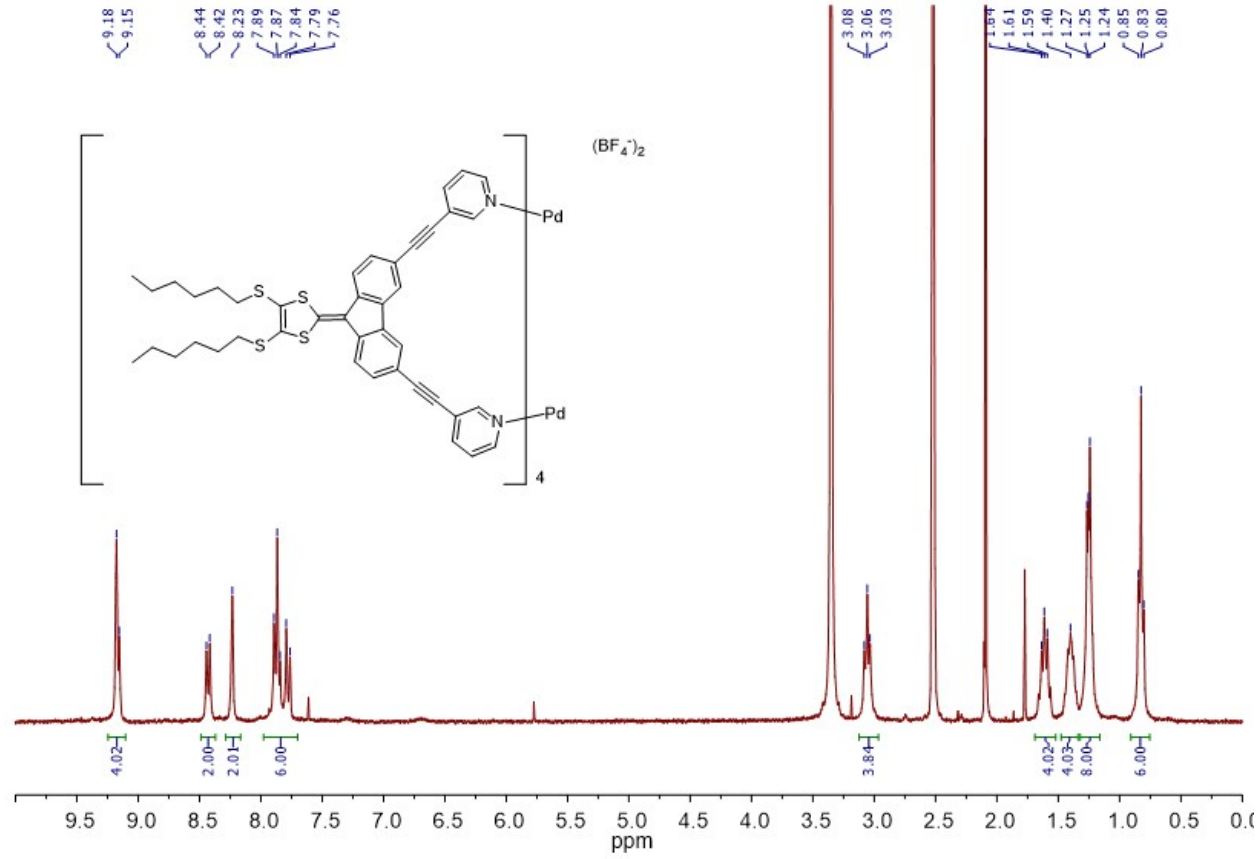

Figure S7. ^{1}H NMR spectra of **$[Pd_2L_4]^{4+}$,$4BF_4^-$** in DMSO-d6

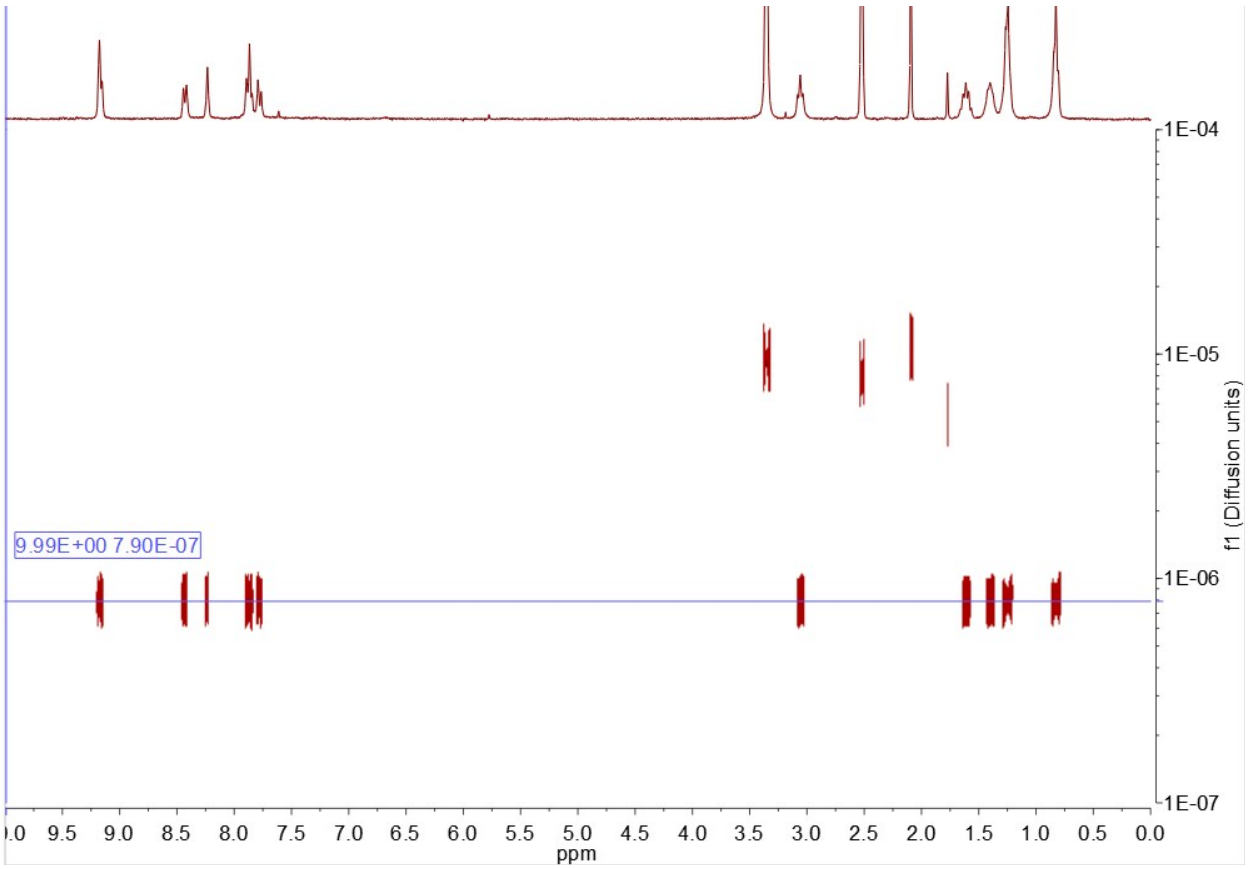

Figure S8. ^{1}H DOSY NMR spectra of **$[Pd_2L_4]^{4+}$,$4BF_4^-$** in DMSO-d6

Cyclic voltammetry

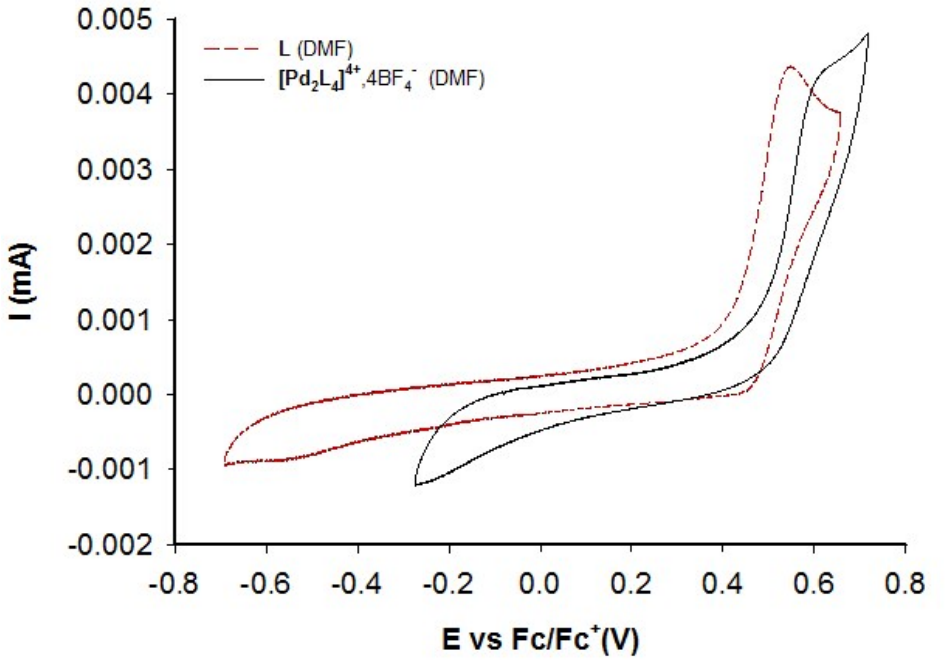

Figure S9. Cyclic voltammogram of ligand **L** and cage **$[Pd_2L_4]^{4+}$,$4BF_4^-$**
For **L**, (C = 10^{-3} M, DMF, 0.1 M nBu_4NPF_6, 100 mV·s^{-1}, glassy C) and for cage **$[Pd_2L_4]^{4+}$,$4BF_4^-$**, (C = 5×10^{-4} M, DMF, 0.1 M nBu_4PF_6, 20 mV·s^{-1}, glassy C), V vs Fc/Fc+.

X-Ray structures

For **$[Pd_2L_4]^{4+}$**,$4BF_4^-$: X-ray single-crystal diffraction data were collected at 120K on the Cristal beamline at SOLEIL Synchrotron (Saint-Aubin-France) on an Agilent 4-circles diffractometer equipped with an Atlas CCD detector. The radiation wavelength was 0.67221 Å.

The structure was solved by direct methods, expanded and refined on F^2 by full matrix least-squares techniques using SHELX97 package. All non-H atoms were anisotropically refined and multiscan empirical absorption was applied with CrysAlisPro program (CrysAlisPro, Agilent Technologies, V1.171.37.35, 2014). The crystal was twinned and very sensitive to decomposition and only poor diffraction data with low intensity was observed. Nevertheless, main structure was solved (minus 2 C and 7 H on one terminal hexyl chain). The H atoms were included in the calculation without refinement, except on the missing hexyl carbon atoms. The structure refinement showed disordered electron density which could not be reliably modeled and the program PLATON/SQUEEZE were used to remove the scattering contribution corresponding to dimethylsulfoxide solvent and missing atoms in the main structure, from the intensity data. The assumed solvent composition (16 DMSO in the unit cell) was used in the calculation of the empirical formula, formula weight, density, linear absorption coefficient and F(000).

Crystallographic data for **$[Pd_2L_4]^{4+}$,$4BF_4^-$** + 16 DMSO: $C_{200}H_{256}B_4F_{16}N_8O_{16}Pd_2S_{32}$, M = 4614.08, yellow prism, 0.12 x 0.10 x 0.06 mm^3, triclinic, space group *P* -1, a = 17.4676(7) Å, b = 17.8158(6) Å, c = 20.064(1) Å, α = 74.016(4)°, β = 67.644(4)°, γ = 89.049(3)°, V = 5524.0(4) $Å^3$, Z = 1, ρcalc = 1.387 g/cm^3, μ = 0.412mm^{-1}, F(000) = 2408, θmin = 1.558°, θmax = 32.304°, 68110 reflections collected, 68110 unique, parameters / restraints = 969 / 25, R1 = 0.0908 and wR2 = 0.2262 using 12796 reflections with I>2σ(I), R1 = 0.2912 and wR2 = 0.2725 using all data, GOF = 0.708, -1.052 < Δρ < 1.100.$Å^{-3}$. CCDC 1515148.

For ligand **L**: X-ray single-crystal diffraction data were collected at 293K on an Agilent Technologies SuperNova diffractometer equipped with Atlas CCD detector and micro-focus Cu-K_α radiation (λ = 1.54184 Å). The structure was solved by direct methods and refined on F^2 by full matrix least-squares techniques using SHELX97 (G.M. Sheldrick, 1998) package. All non-H atoms were refined anisotropically and multiscan empirical absorption was applied using CrysAlisPro program (CrysAlisPro, Agilent Technologies, V1.171.38.41r, 2015). The H atoms were included in the calculation without refinement.

Crystallographic data for ligand **L**: $C_{42}H_{40}N_2S_4$, M = 701.00, orange needle, 0.304 x 0.073 x 0.056 mm^3, tetragonal, space group *P* 4/n, a = 37.5699(7) Å, b = 37.5699(7)) Å, c = 5.3064(1) Å, V = 7490.0(2) $Å^3$, Z = 8, ρcalc = 1.243 g/cm^3, μ = 2.566 mm^{-1}, F(000) = 2960, θmin = 3.33°, θmax = 75.35°, 15624 reflections collected, 7536 unique (R_{int} = 0.0293), parameters / restraints = 435 / 13, R1 = 0.0727 and wR2 = 0.205 using 5562 reflections with I>2σ(I), R1 = 0.0944 and wR2 = 0.2286 using all data, GOF = 1.057, -0.471 < Δρ < 0.517.$Å^{-3}$. CCDC 1515147.

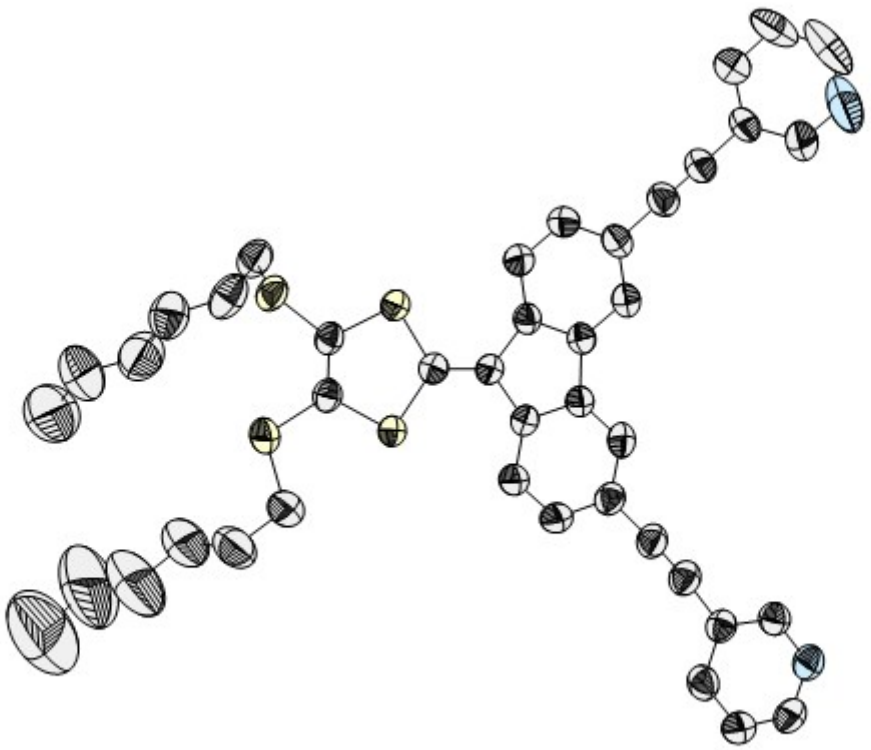

Figure S10. ORTEP view of ligand **L**
The dispalcement ellipsoids are drawn at 50% probability level. H atoms omitted for clarity.

(1) Estrada, L. A.; Neckers, D. C., *J. Org. Chem.* **2009,** *74*, 8484-8487.