# Neutral versus Polycationic Coordination-Cages: Experimental Evidence of the Charge Effect onto Neutral Guest Inclusion

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# Supporting Information

## Chemicals and instrumentation

### Chemicals

Complex $Pd(dctbf)_2(cod)$[1] (dctfb = 3,5-dichloro-2,4,6-trifluorobenzene) and ligand **L**[2] were synthetized as described in the literature. All reagents were commercial reagent grade and were used without further purification. For synthesis and crystallizations analytical grade non dry solvents were used. 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 ($^1$H), 75.5 ($^{13}$C) and 282.6 MHz ($^{19}$F) NMR spectra were recorded at room temperature using perdeuterated solvents as internal standards ($^1$H), external $CFCl_3$ ($^{19}$F), on a NMR Bruker Avance III 300 spectrometer. DOSY NMR spectra were analyzed with MESTRENOVA software. ESI-FTICR spectra were performed on a IonSpec (Agilent), 9,4 T hybride ESI q-Q-q in $CH_2Cl_2/CH_3NO_2$ (5 x $10^{-4}$ M). Cyclic voltammetry experiments were carried out on a BioLogic SP-150 potentiostat and the conditions were the following: 0.1 M $n$$Bu_4NPF_6$ in acetonitrile or methylene chloride, GC working electrode, Ag wire reference electrode and Pt counter electrode, calibrated using internal ferrocene. Elemental analyses were achieved on a Thermo Electron analyzer.

## Experimental procedures and characterizations

Synthesis of self-assembly $\mathbf{M_4L_2}$

The ligand **L** (90 mg, 0.07 mmol) and $Pd(dctbf)_2(cod)$ (83 mg, 0.14 mmol, 2 equiv.) were dissolved in acetone (8.0 mL) and stirred for 48h at RT. The precipitate was filtered, washed with cold acetone and dried under vacuum to give compound $\mathbf{M_4L_2}$ (138 mg, 0.03 mmol, 87%) as red needles. m.p.>250 °C; IR $\bar{\upsilon}$ = 2867, 1606, 1400 cm$^{-1}$; $^1$H NMR (ppm, $CDCl_3$): 8.12 (8H, d, $J$ = 6.5, $CH_{pyr.}$), 7.03 (8H, d, $J$ = 6.5, $CH_{pyr.}$), 6.96 (4H, s, $CH_{anthr.}$), 4.25-4.07 (8H, m, $CH_2$), 3.85 (8H, t, $J$ = 5.2, $CH_2$), 3.73-3.67 (8H, m, $CH_2$), 3.66-3.58 (16H, m, $CH_2$), 3.55-3.50 (8H, m, $CH_2$), 3.36 (12H, s, $CH_3$); $^{19}$F NMR (ppm, $CDCl_3$): -90.4 ($F^o$), -118.0 ($F^p$); ESI-FTICR ($CH_2Cl_2/CH_3NO_2$) *m/z* calculated: $[\mathbf{M_4L_2}.(KOTf)_4\text{-}4TfO^-]^{4+}$ 1213.95434, $[\mathbf{M_4L_2}.(KOTf)_4\text{-}3TfO^-]^{3+}$ 1668.58965; found: $[\mathbf{M_4L_2}.(KOTf)_4\text{-}4TfO^-]^{4+}$ 1213.94871, $[\mathbf{M_4L_2}.(KOTf)_4\text{-}3TfO^-]^{3+}$ 1668.58600; Anal. Calcd for $C_{184}H_{160}Cl_{16}F_{24}N_8O_{32}Pd_4S_8$: C, 47.02; H, 3.43; N, 2.38; S, 5.46. Found: C, 46.40; H, 3.34; N, 2.35; S, 5.32 %.

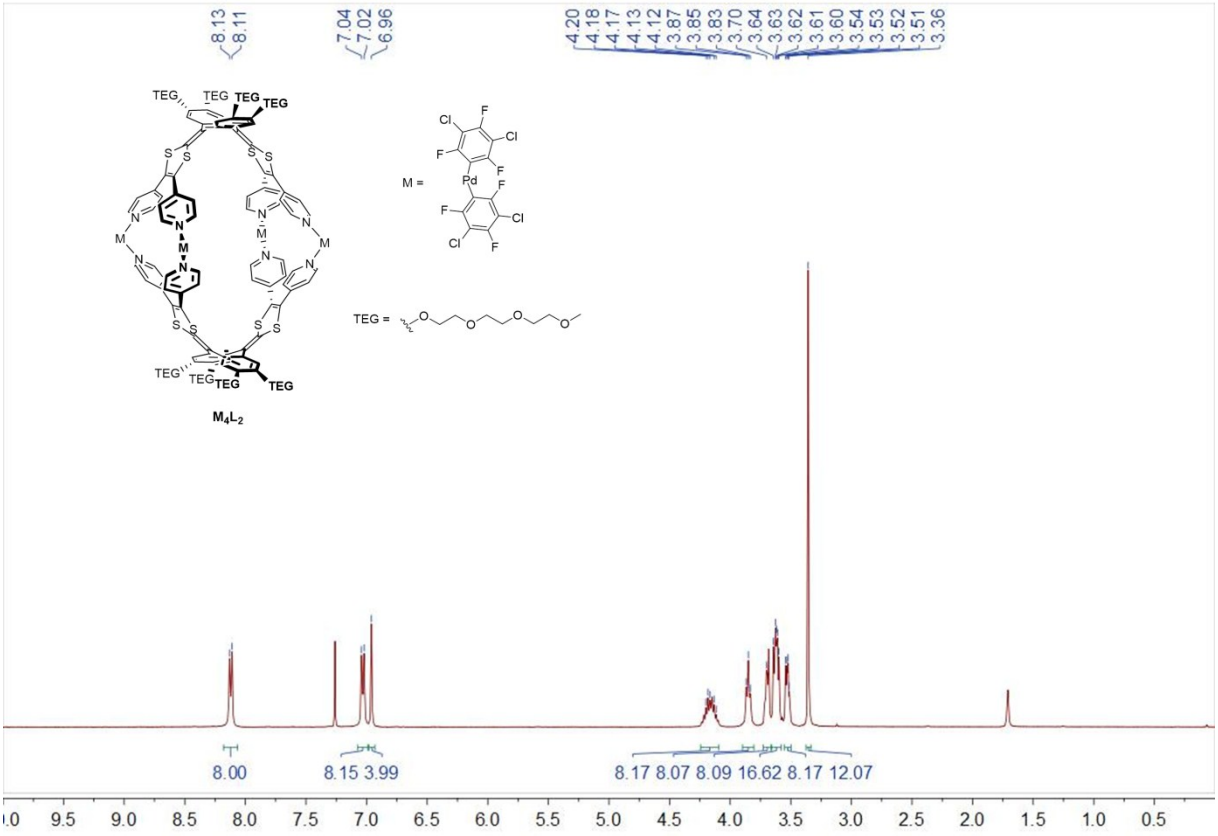


**Figure S1. $^{1}$H-NMR spectrum of $M_4L_2$ in $CDCl_3$.**

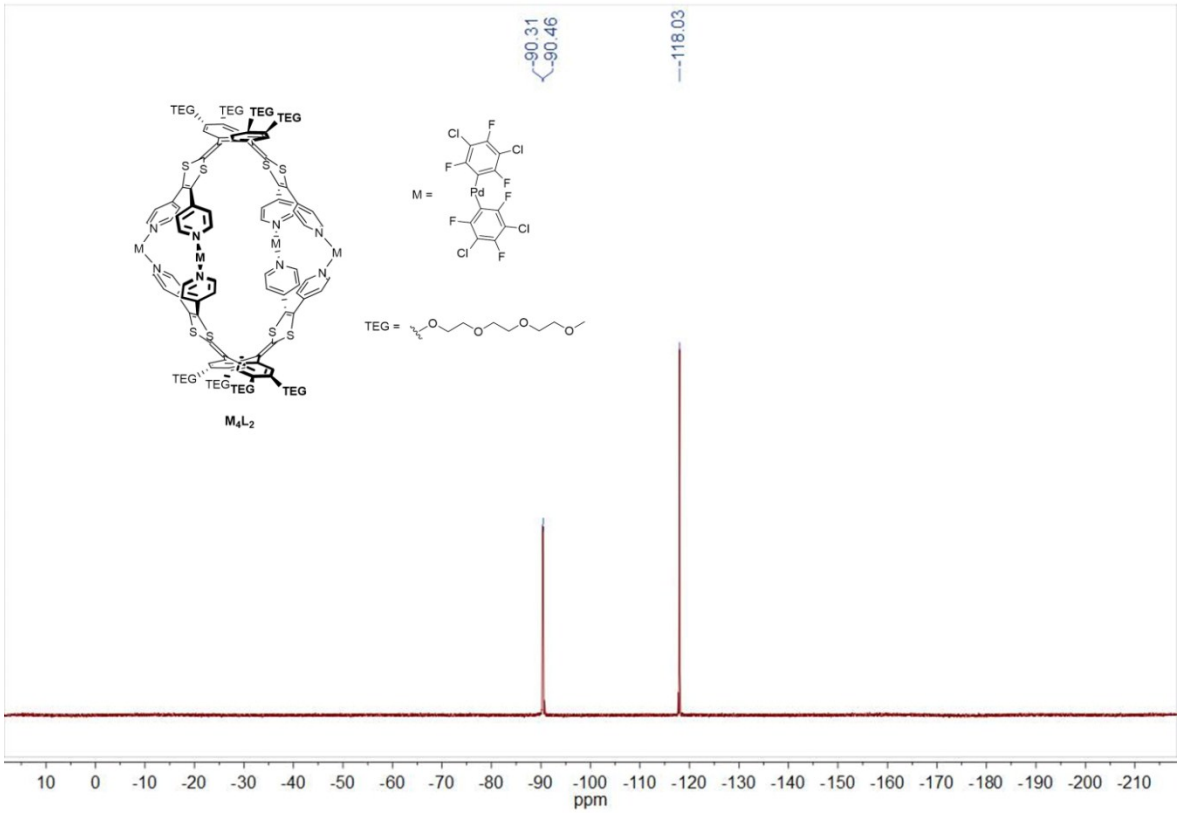


**Figure S2. $^{19}$F-NMR spectrum of $M_4L_2$ in $CDCl_3$.**

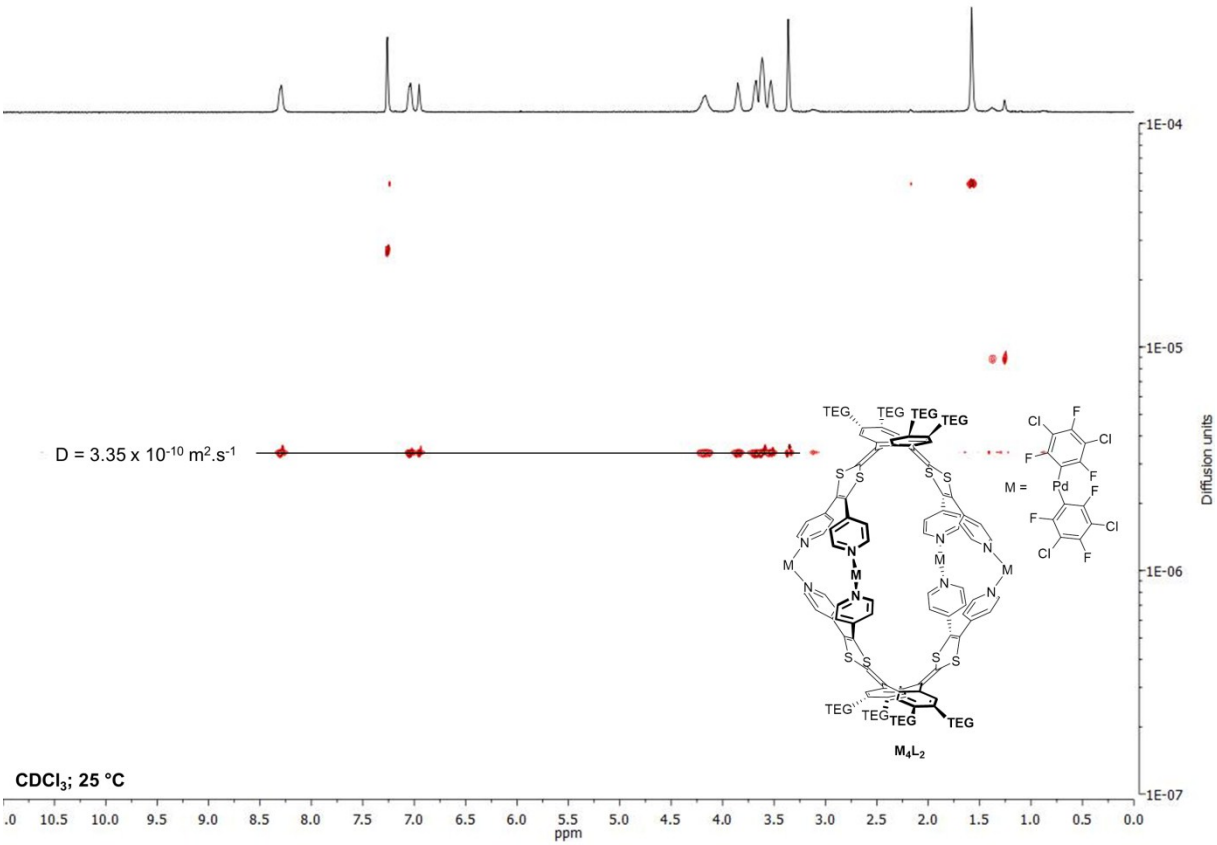


**Figure S3. $^1$H DOSY NMR of $M_4L_2$ in $CDCl_3$ ($10^{-3}$ M).**

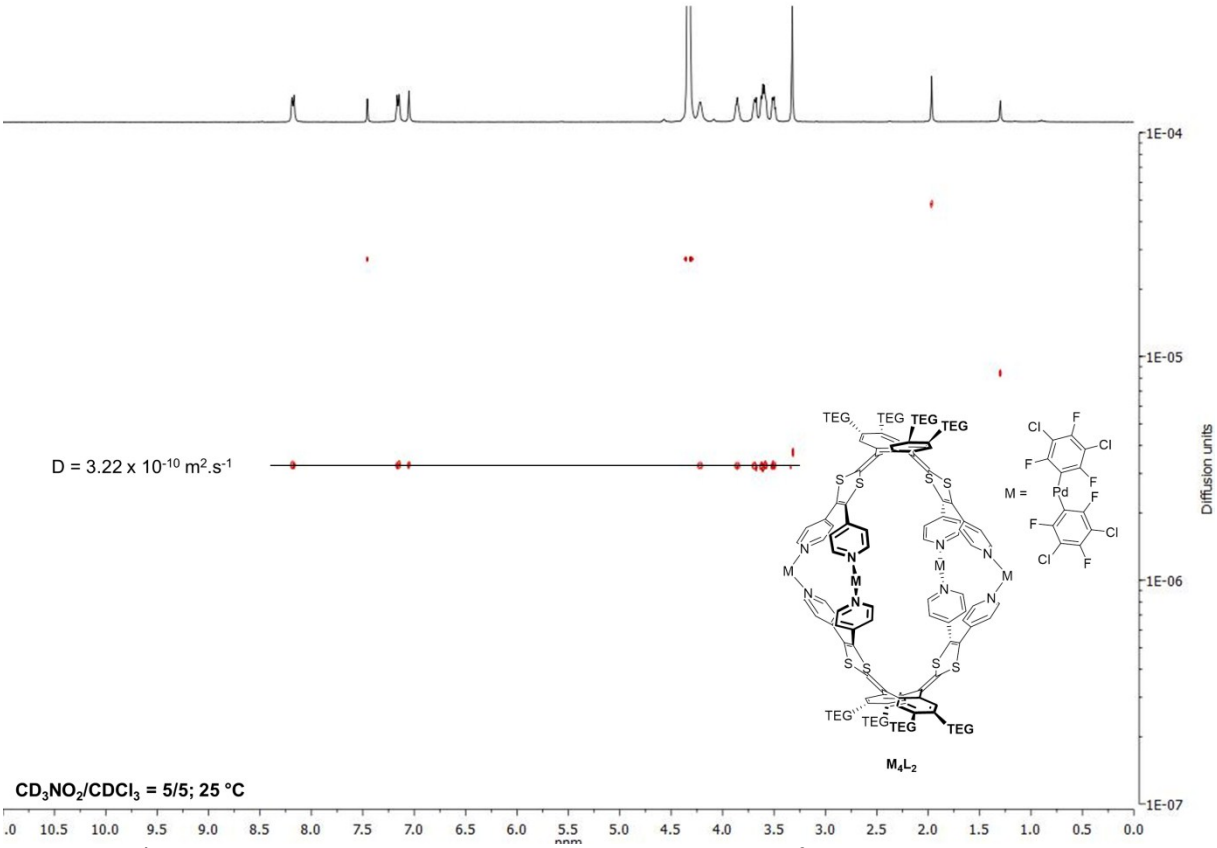


**Figure S4. $^1$H DOSY NMR of $M_4L_2$ in $CDCl_3/CD_3NO_2$ = 5/5 (2 x $10^{-3}$ M).**

## ESI-FTICR experiment

For ESI-FTICR experiment, 8 equivalents of KOTf in $CH_3NO_2$ (C = 1.6 x $10^{-2}$ M) was added to a solution of $\mathbf{M_4L_2}$ in $CH_2Cl_2$ (C = 2 x $10^{-3}$ M).

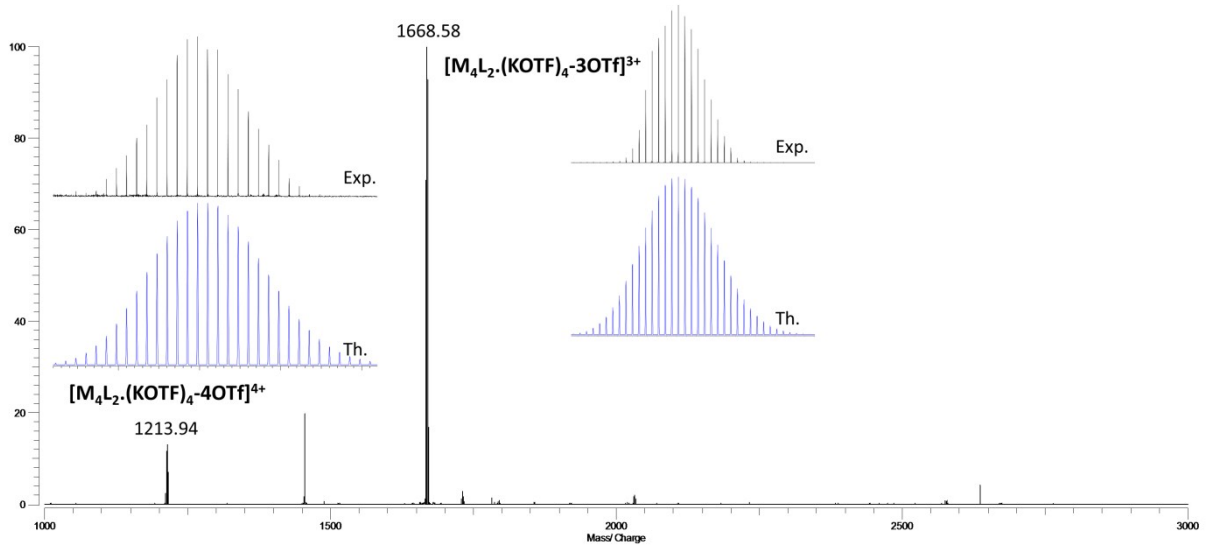


**Figure S5. ESI-FTICR spectrum of $M_4L_2.(KOTf)_4$ recorded in $CH_2Cl_2/CH_3NO_2$ = 5/5.**

## $K_a$ determination method

A DOSY experiment was run with a solution (0.5 mL) of cage $\mathbf{M_4L_2}$ or $\mathbf{M_4L_2^{8+}}$ (C = 2.0 x $10^{-3}$M) in $CDCl_3/CD_3NO_2$ (1/1) containing 1 equiv. of planar polyaromatic guest at 298K. $K_a$ was calculated from diffusion coefficients $D_{free}$ (free guest in $CDCl_3/CD_3NO_2$ (5/5)), $D_{comp}$ (cages $\mathbf{M_4L_2}$ or $\mathbf{M_4L_2^{8+}}$ in $CDCl_3/CD_3NO_2$ (1/1)), and $D_{obs}$ (guest in presence of cages $\mathbf{M_4L_2}$ or $\mathbf{M_4L_2^{8+}}$). The bounded fraction X was calculated using equation: $D_{obs} = X\ D_{comp} + (1 - X)D_{free}$ and $K_a$ using equation $K_a = (1 - X) / (C \times X^2)$.

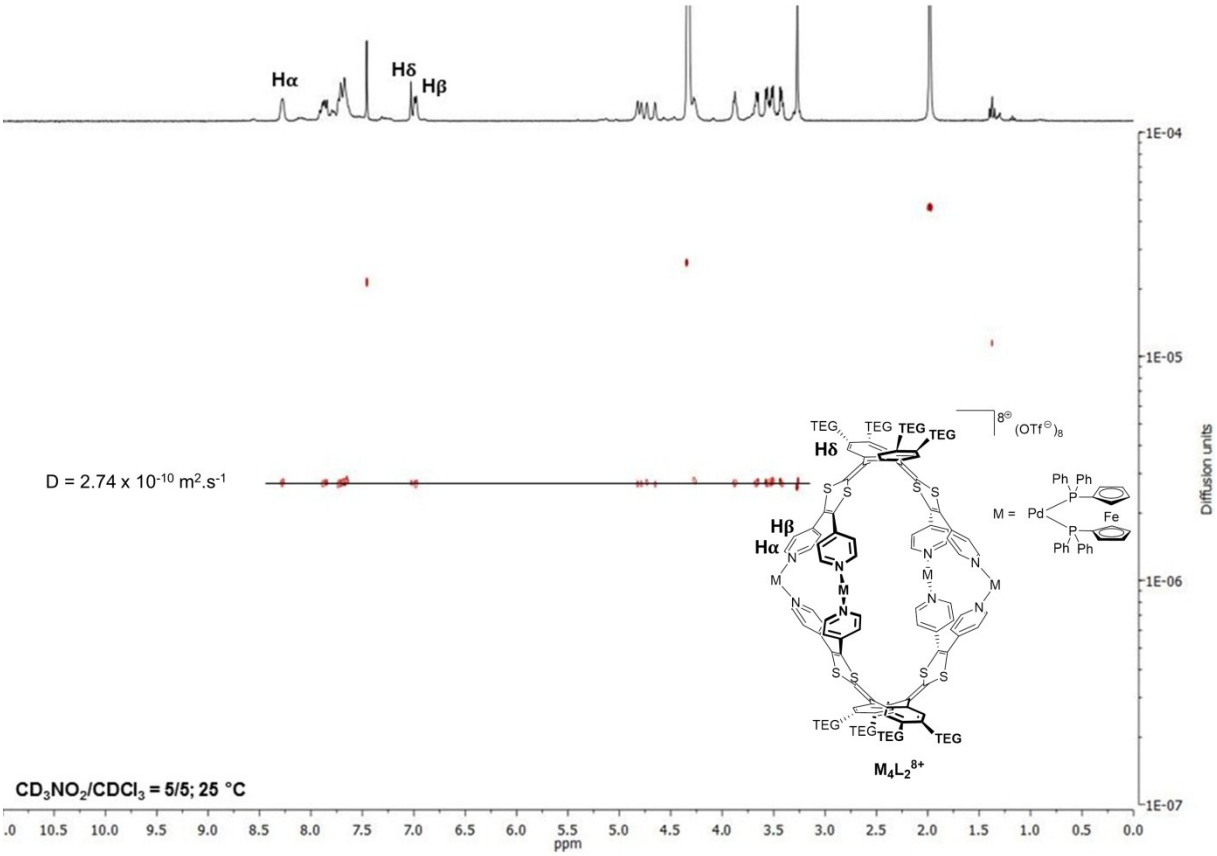


**Figure S6. $^{1}$H DOSY NMR of $M_4L_2^{8+}$ in $CDCl_3/CD_3NO_2$ = 5/5 (2 x $10^{-3}$ M).**

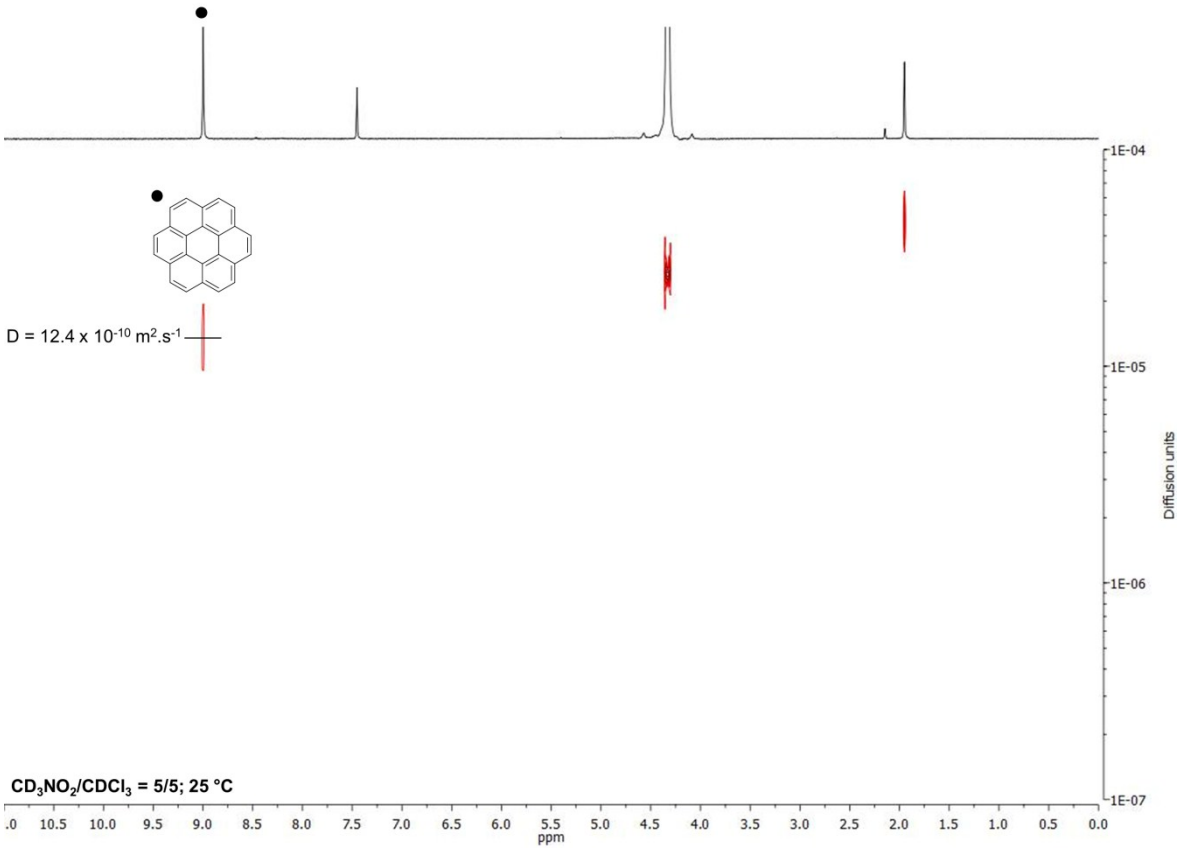


**Figure S7. $^{1}$H DOSY NMR spectrum of coronene in $CD_3NO_2/CDCl_3$ = 5/5 (2 x $10^{-3}$ M).**

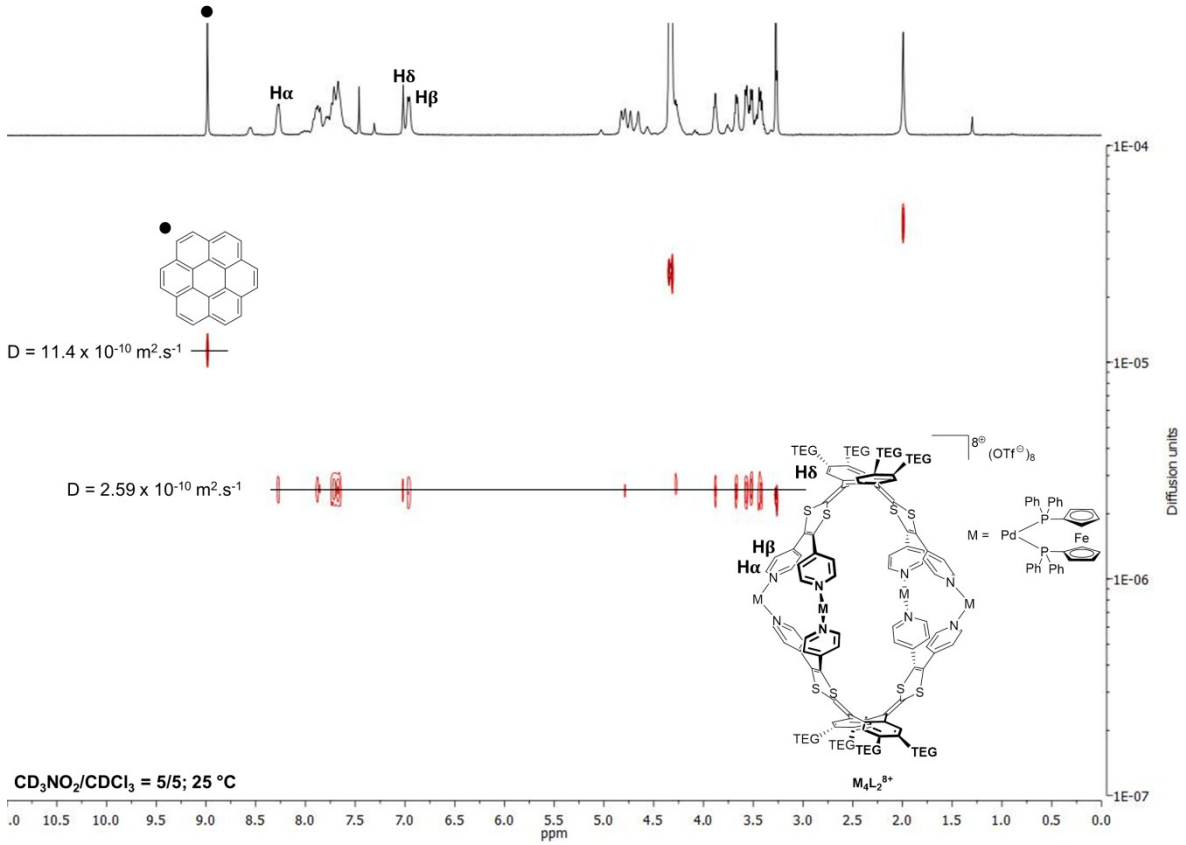


**Figure S8. $^1$H DOSY NMR spectrum of a stoichiometric mixture of coronene and $M_4L_2^{8+}$ in $CD_3NO_2/CDCl_3$ = 5/5 (2 x $10^{-3}$ M).**

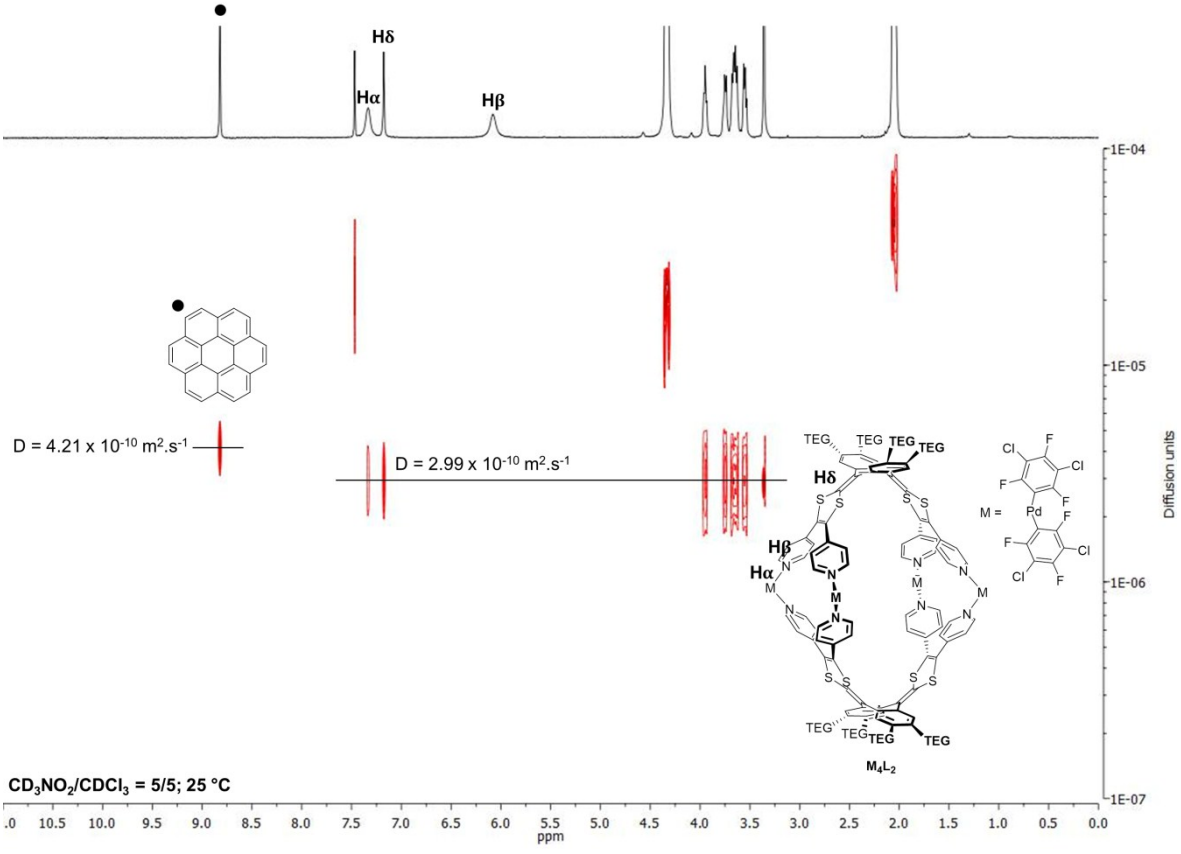


**Figure S9. $^1$H DOSY NMR spectrum of a stoichiometric mixture of coronene and $M_4L_2$ in $CD_3NO_2/CDCl_3$ = 5/5 (2 x $10^{-3}$ M).**

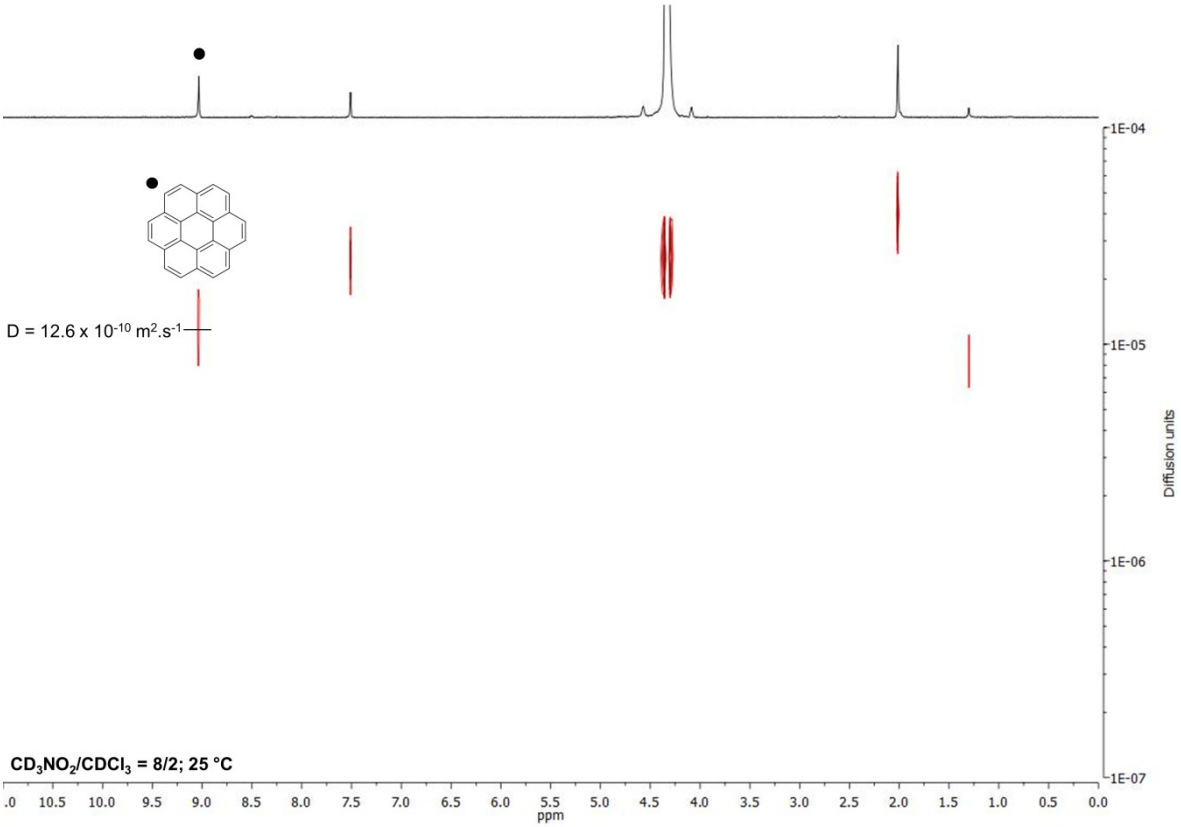


**Figure S10. $^{1}$H DOSY NMR spectrum of coronene in $CD_3NO_2/CDCl_3$ = 8/2 (2 x $10^{-3}$ M).**

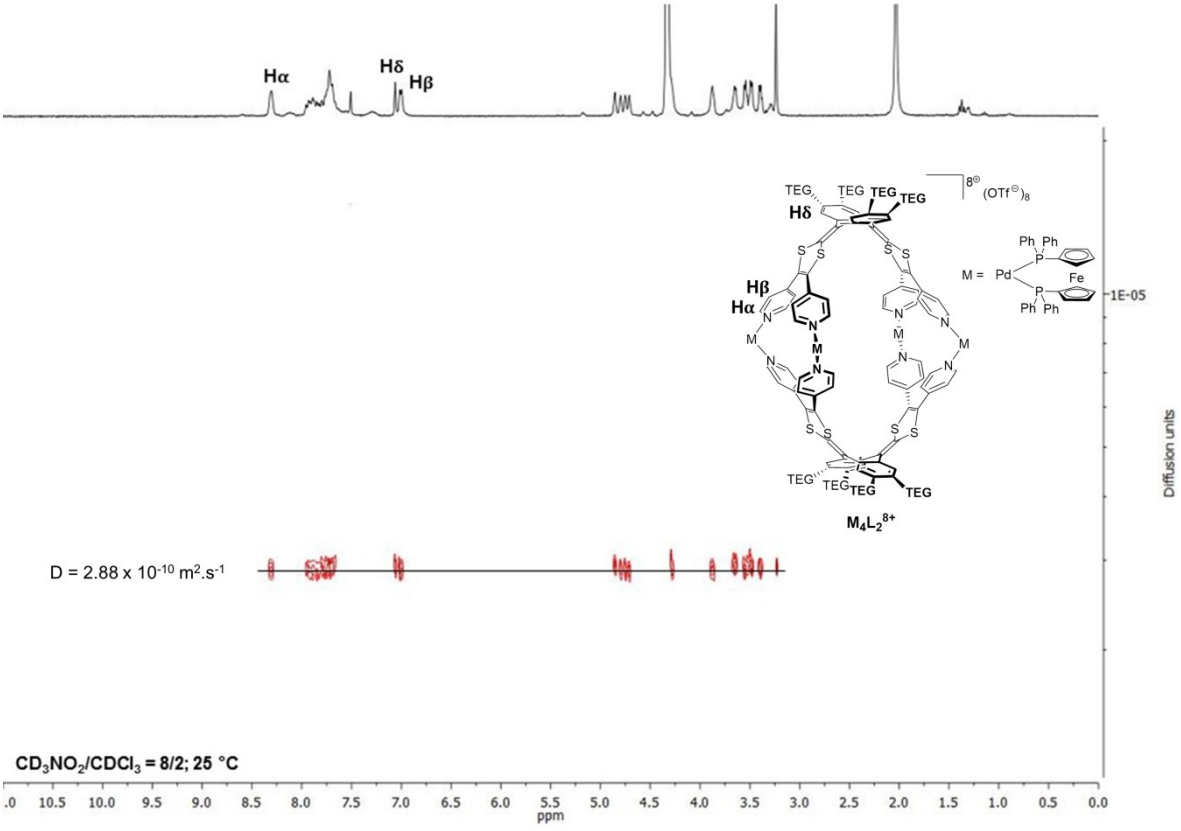


**Figure S11. 1H DOSY NMR spectrum of $M_4L_2^{8+}$ in $CD_3NO_2/CDCl_3$ = 8/2 (2 x $10^{-3}$ M).**

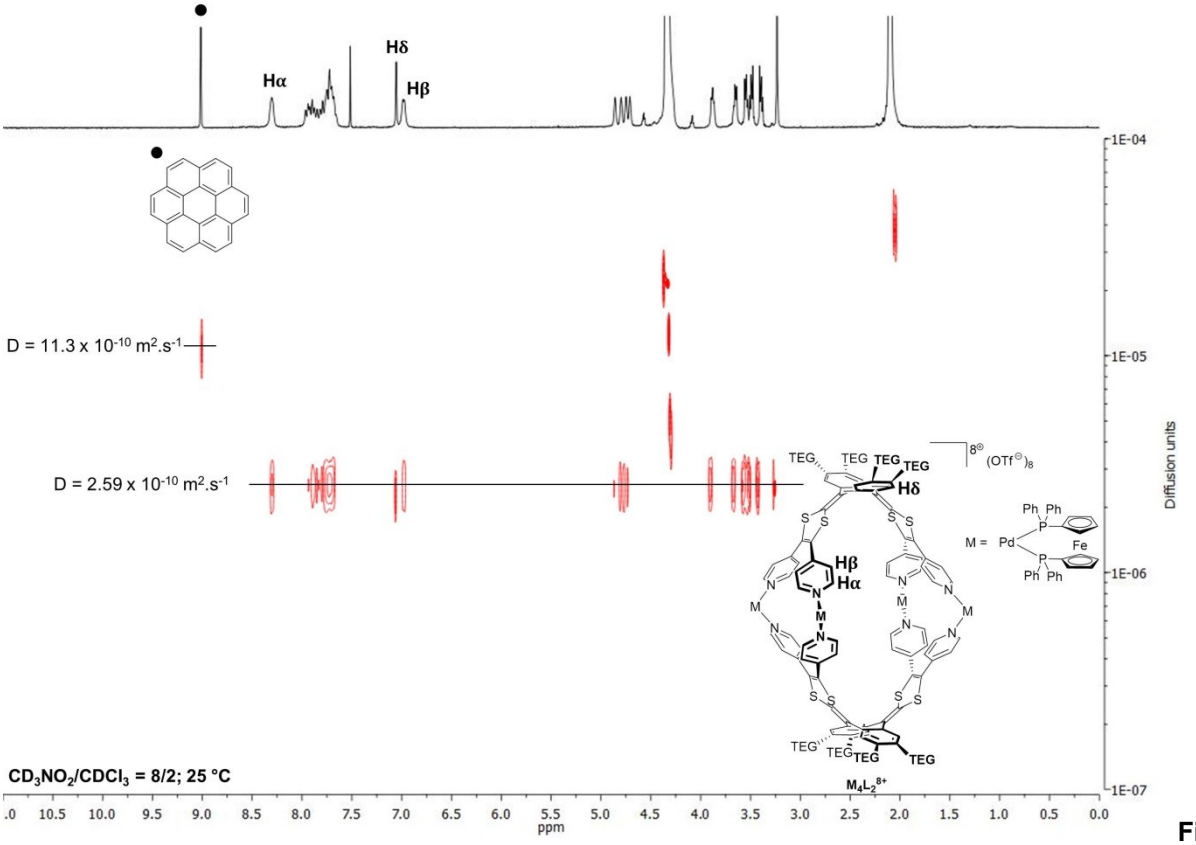


**Figure S12. $^1$H DOSY NMR spectrum of a stoichiometric mixture of coronene and $M_4L_2^{8+}$ in $CD_3NO_2/CDCl_3$ = 8/2 (1 x $10^{-3}$ M).**

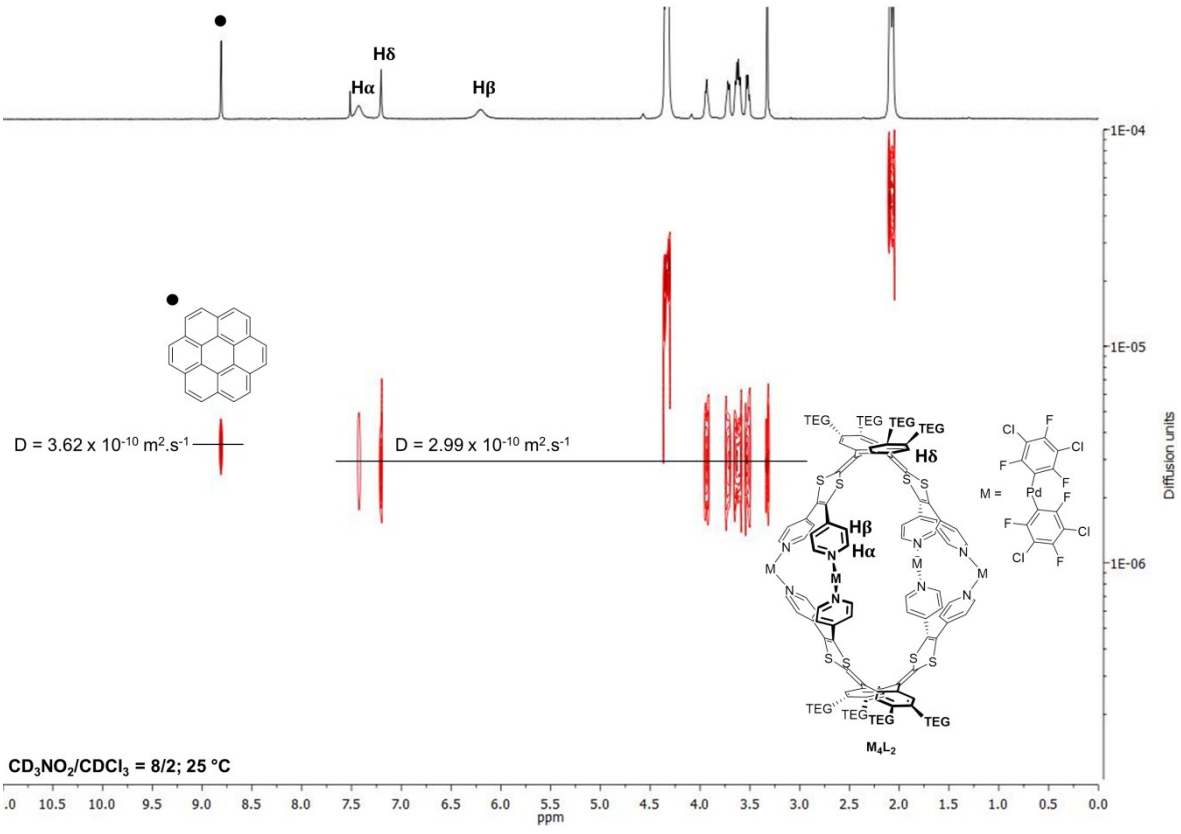

**Figure S13. $^1$H DOSY NMR spectrum of a stoichiometric mixture of coronene and $M_4L_2$ in $CD_3NO_2/CDCl_3$ = 8/2 (2 x $10^{-3}$ M).**

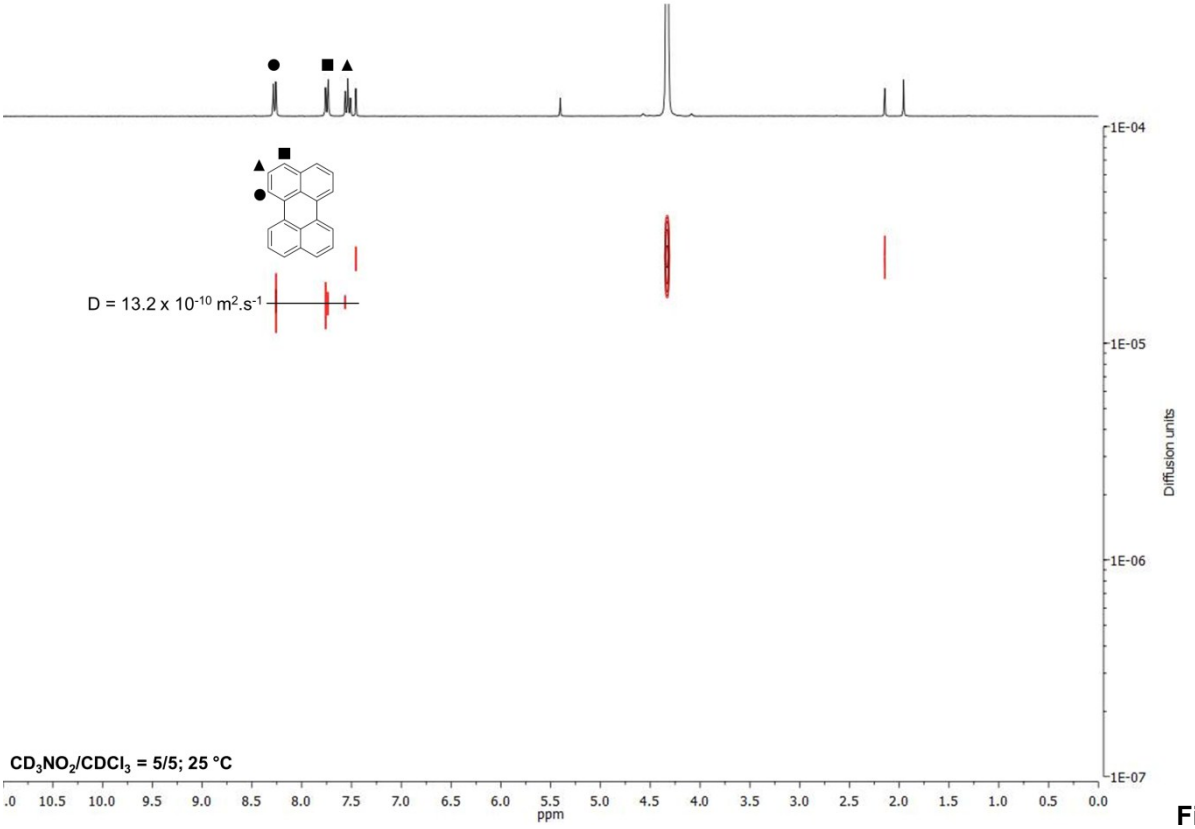


**Figure S14. $^1$H DOSY NMR spectrum of perylene in $CD_3NO_2/CDCl_3$ = 5/5 (2 x $10^{-3}$ M).**

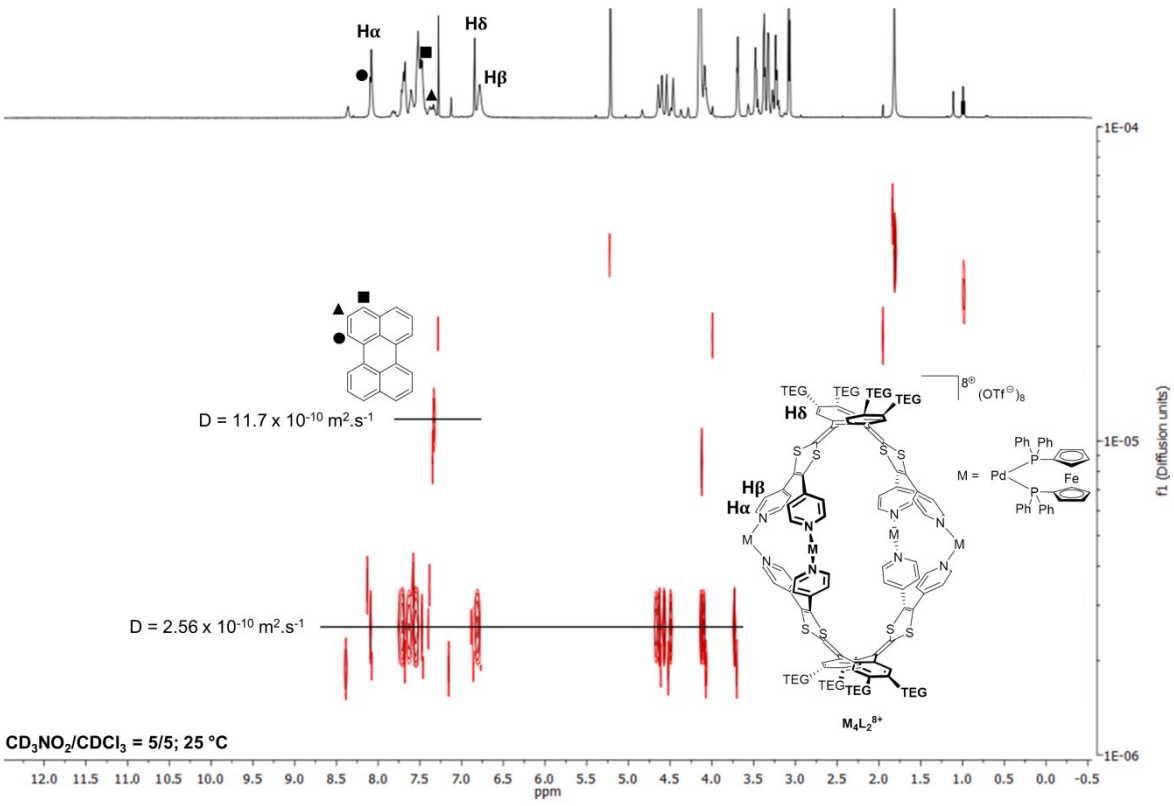

**Figure S15. $^1$H DOSY NMR spectrum of a stoichiometric mixture of perylene and $M_4L_2^{8+}$ in $CD_3NO_2/CDCl_3$ = 5/5 (2 x $10^{-3}$ M).**

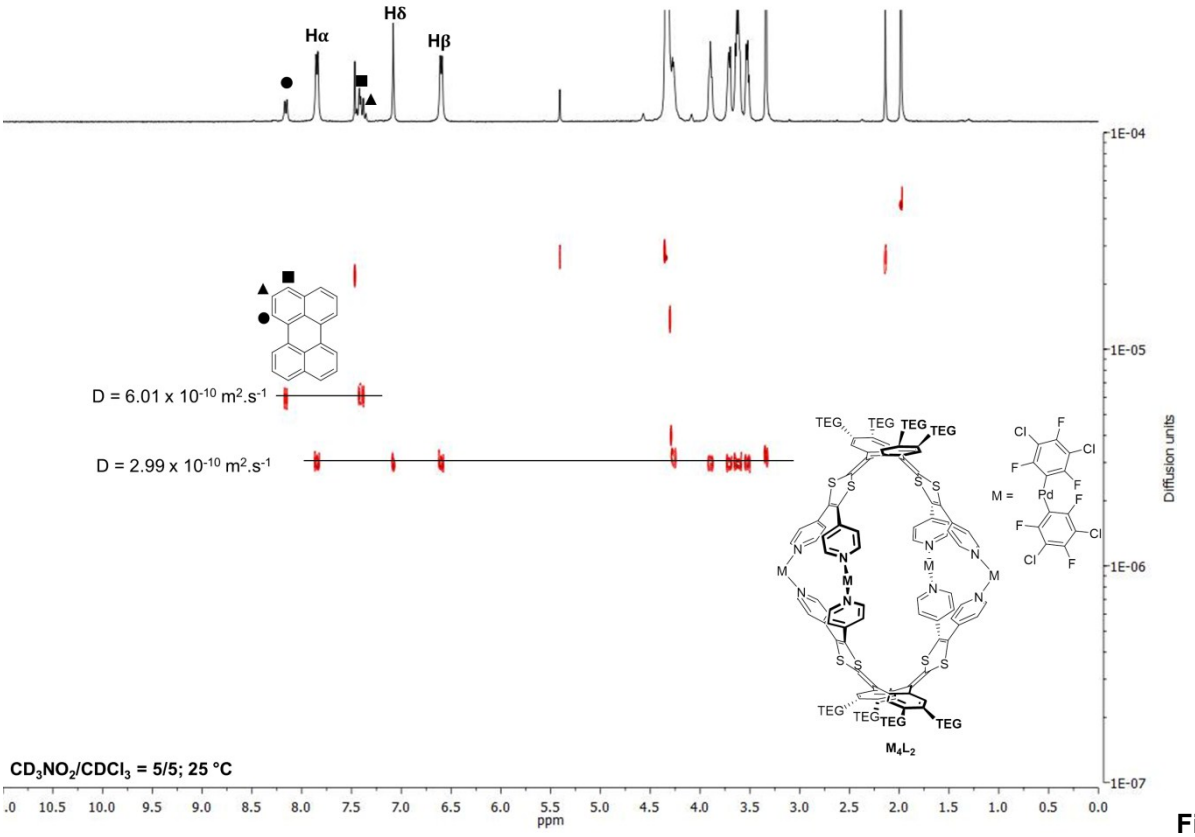


**Figure S16. $^1$H DOSY NMR spectrum of a stoichiometric mixture of perylene and $M_4L_2$ in $CD_3NO_2/CDCl_3$ = 5/5 (2 x $10^{-3}$ M).**

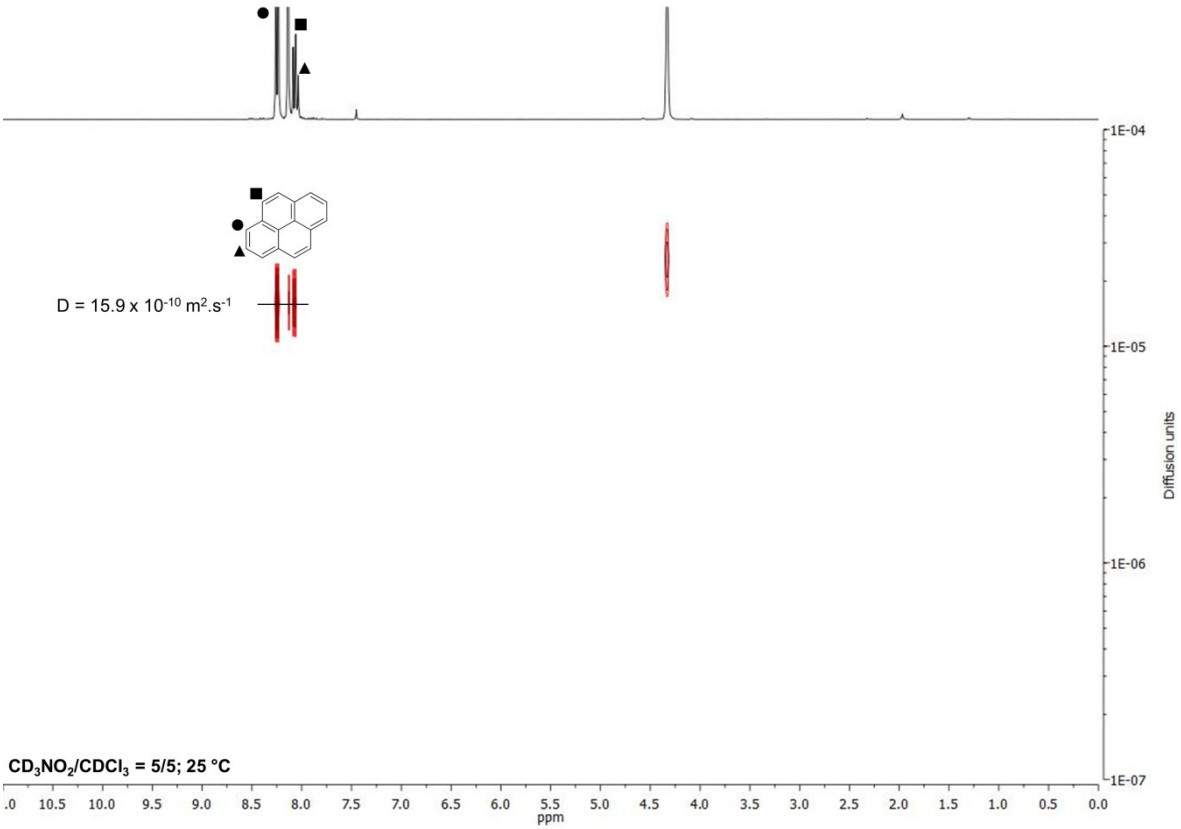


**Figure S17. $^1$H DOSY NMR spectrum of pyrene in $CD_3NO_2/CDCl_3$ = 5/5 (2 x $10^{-3}$ M).**

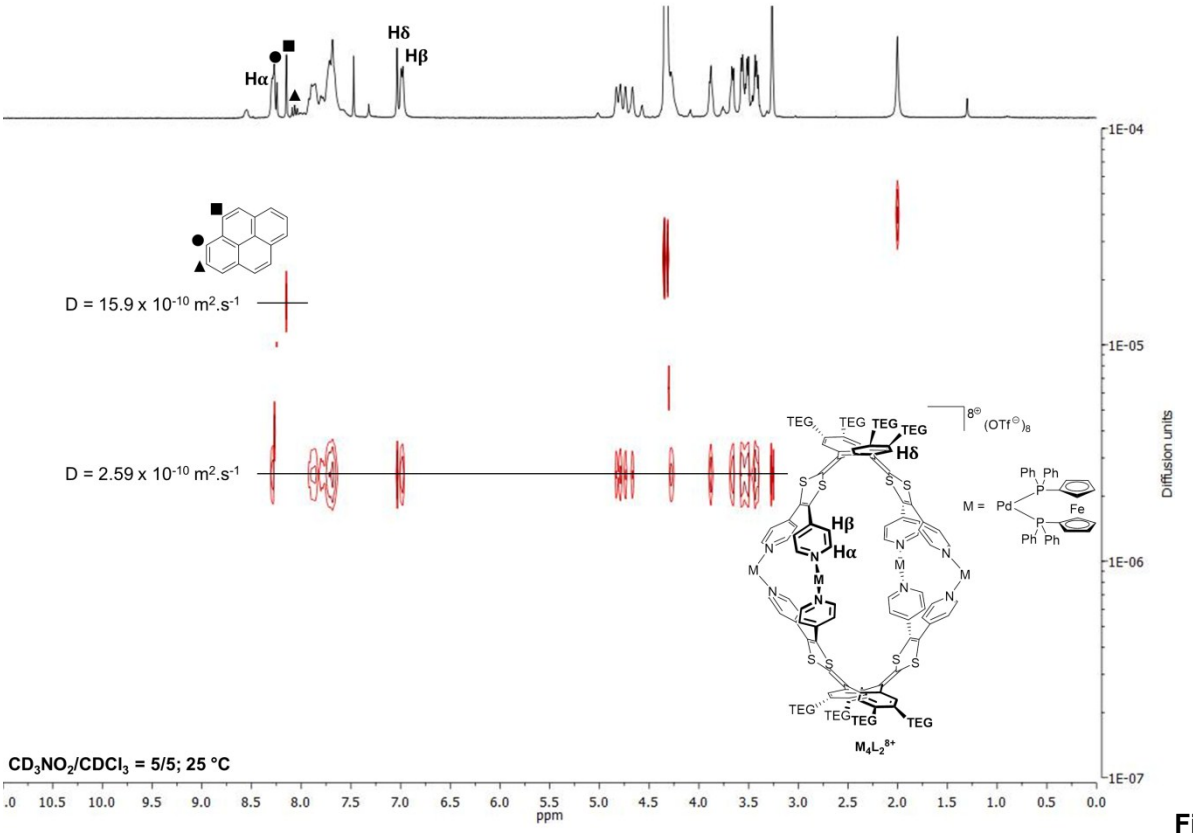


**Figure S18. $^1$H DOSY NMR spectrum of a stoichiometric mixture of pyrene and $M_4L_2^{8+}$ in $CD_3NO_2/CDCl_3$ = 5/5 (2 x $10^{-3}$ M).**

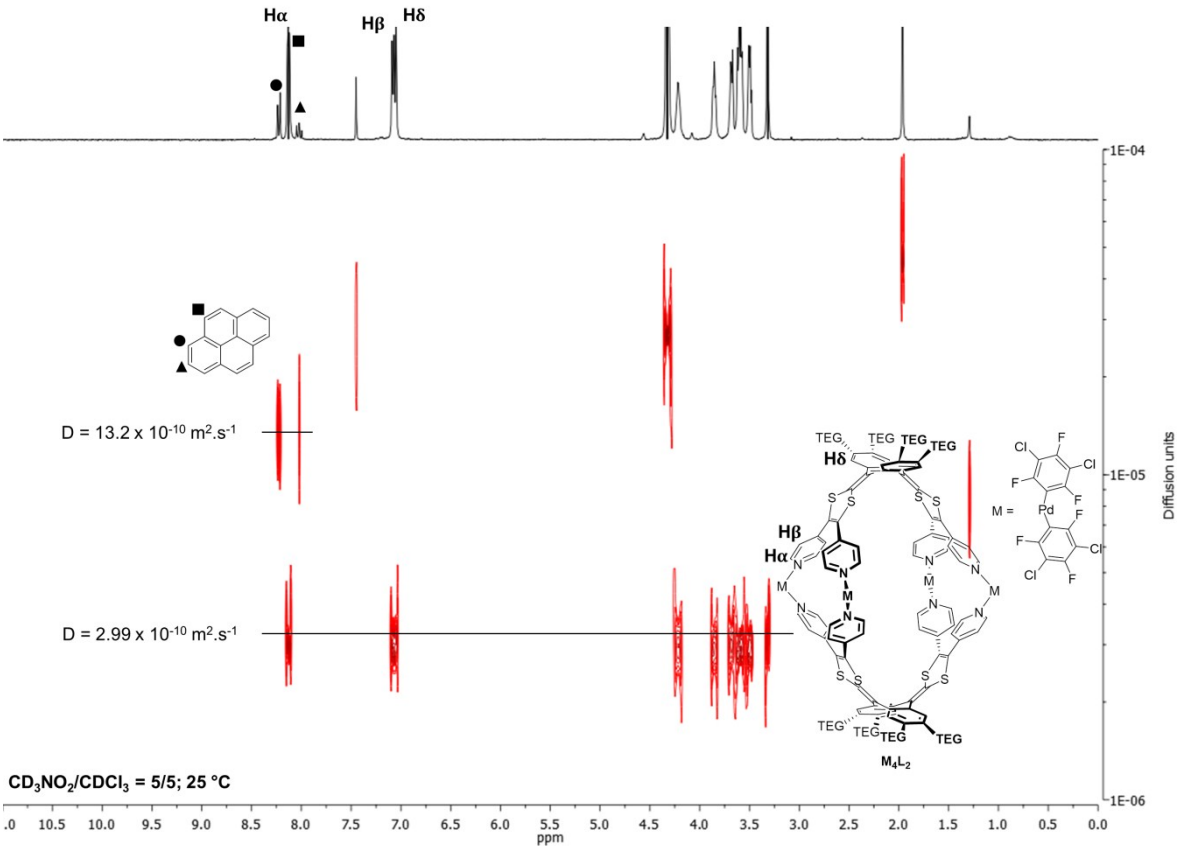


**Figure S19. $^1$H DOSY NMR spectrum of a stoichiometric mixture of pyrene and $M_4L_2$ in $CD_3NO_2/CDCl_3$ = 5/5 (2 x $10^{-3}$ M).**

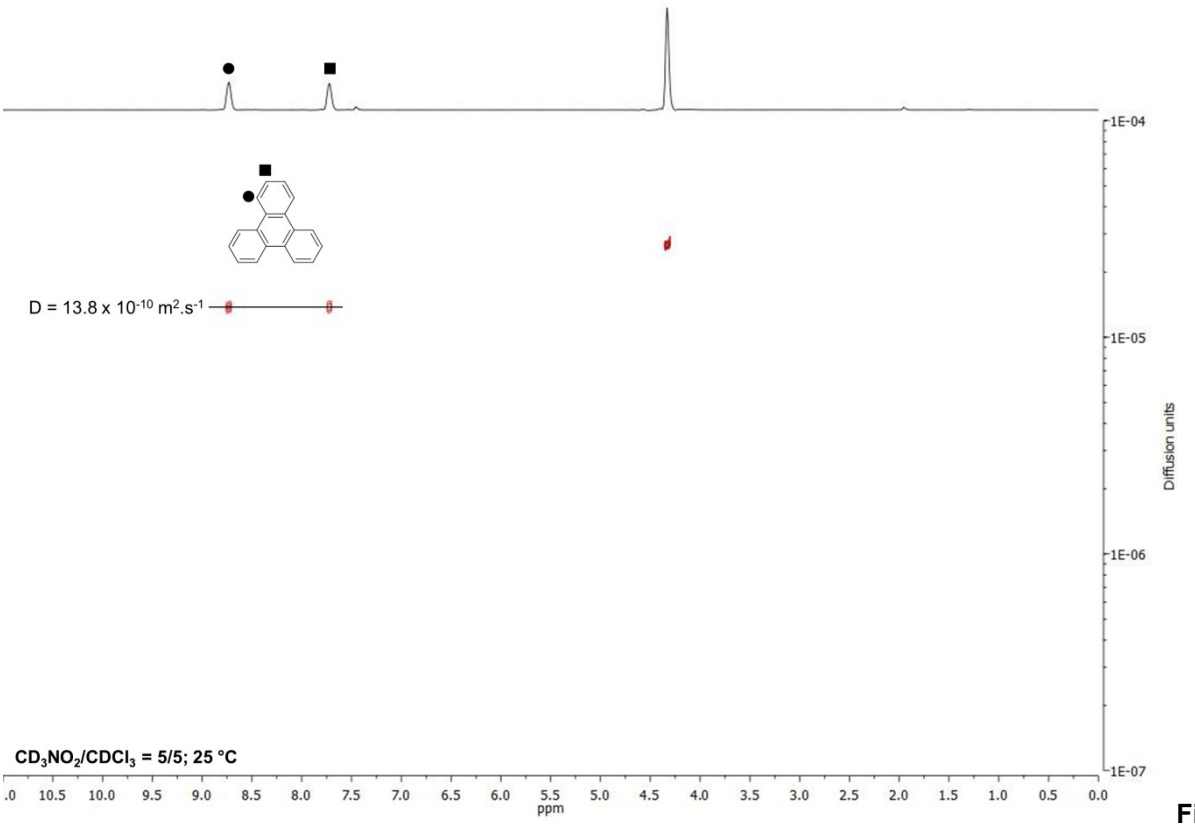


**Figure S20. $^1$H DOSY NMR spectrum of triphenylene in $CD_3NO_2/CDCl_3$ = 5/5 (2 x $10^{-3}$ M).**

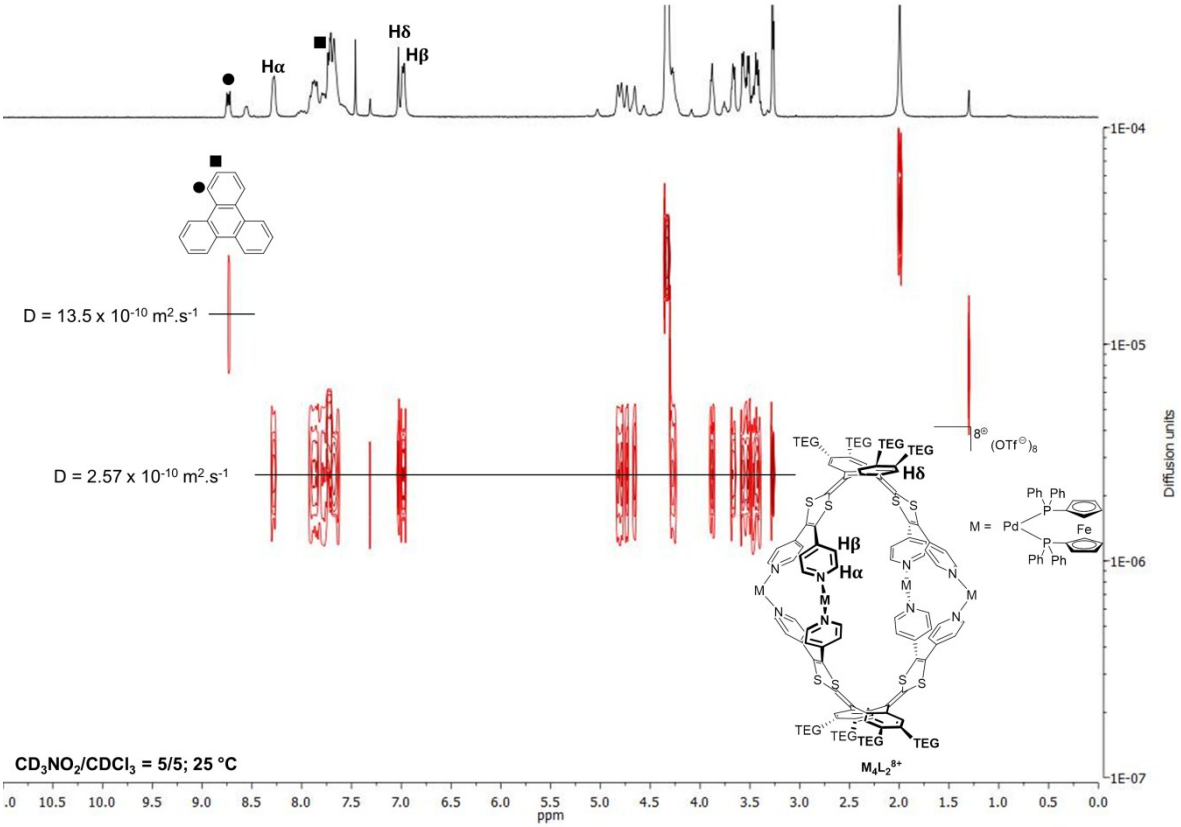


**Figure S21. $^1$H DOSY NMR spectrum of a stoichiometric mixture of triphenylene and $M_4L_2^{8+}$ in $CD_3NO_2/CDCl_3$ = 5/5 (2 x $10^{-3}$ M).**

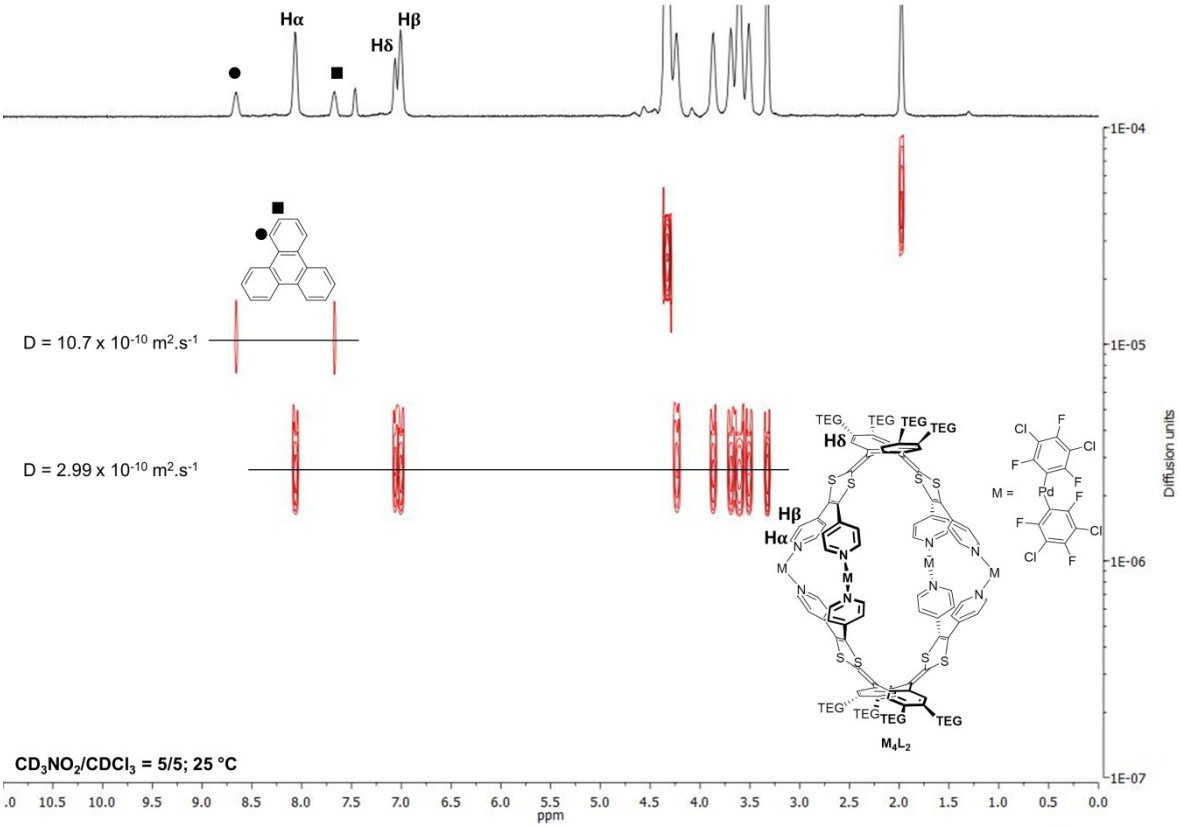


**Figure S22. $^1$H DOSY NMR spectrum of a stoichiometric mixture of triphenylene and $M_4L_2$ in $CD_3NO_2/CDCl_3$ = 5/5 (2 x $10^{-3}$ M).**

## Procedure for triflate anion exchange

For $B_{12}F_{12}^{2-}$:
Cage $\mathbf{M_4L_2^{8+}}$ (30 mg, 0.005 mmol) and $(TBA)_2B_{12}F_{12}$ (30 mg, 0.037 mmol, 8 equiv.) were dissolved in acetonitrile (2.0 mL) and stirred at 40°C for 10 minutes. Then, diethyl ether (10.0 mL) was added and the resulting precipitate was isolated by centrifugation, washed with diethyl ether (3 x 3.0 mL) and dried under vacuum. This procedure was repeated 2 times to give the product $\mathbf{M_4L_2^{8+}(B_{12}F_{12}^{2-})_4}$ (24 mg, 75%) as an orange solid. $^1$H NMR (ppm, $CD_3NO_2$): 8.36 (8H, bs, $CH_{pyr.}$), 8.16-7.41 (40H, m, Ph), 7.11 (4H, s, $CH_{anthr.}$), 7.02 (8H, d, *J* = 5.6, $CH_{pyr.}$), 5.26 (4H, s, $H_{Fc}$), 4.98 (4H, s, $H_{Fc}$), 4.83 (4H, s, $H_{Fc}$), 4.75 (4H, s, $H_{Fc}$), 3.87 (8H, m, $CH_2$), 3.67-3.34 (40H, m, $CH_2$), 3.21 (12H, s, $CH_3$); $^{19}$F NMR (ppm, $CD_3NO_2$): -267.1.

For $BF_4^-$:
Cage $\mathbf{M_4L_2^{8+}}$ (30 mg, 0.005 mmol) and $TBABF_4$ (25 mg, 0.073 mmol, 16 equiv.) were dissolved in acetonitrile (2.0 mL) and stirred at 40°C for 10 minutes. Then, diethyl ether (10.0 mL) was added and the resulting precipitate was isolated by centrifugation, washed with diethyl ether (3 x 3.0 mL) and dried under vacuum. This procedure was repeated 2 times to give the product $\mathbf{M_4L_2^{8+}(BF_4^-)_8}$ (27 mg, 97%) as an orange solid. $^1$H NMR (ppm, $CD_3NO_2$): 8.28 (8H, d, *J* = 4.6, $CH_{pyr.}$), 8.05-7.62 (40H, m, Ph), 7.08 (4H, s, $CH_{anthr.}$), 6.97 (8H, d, *J* = 4.6, $CH_{pyr.}$), 4.90 (4H, s, $H_{Fc}$), 4.80 (4H, s, $H_{Fc}$), 4.75 (8H, s, $H_{Fc}$), 3.89 (8H, m, $CH_2$), 3.67-3.34 (40H, m, $CH_2$), 3.20 (12H, s, $CH_3$); $^{19}$F NMR (ppm, $CD_3NO_2$): -151.9 ($^{11}BF_4$), -152.0 ($^{10}BF_4$).

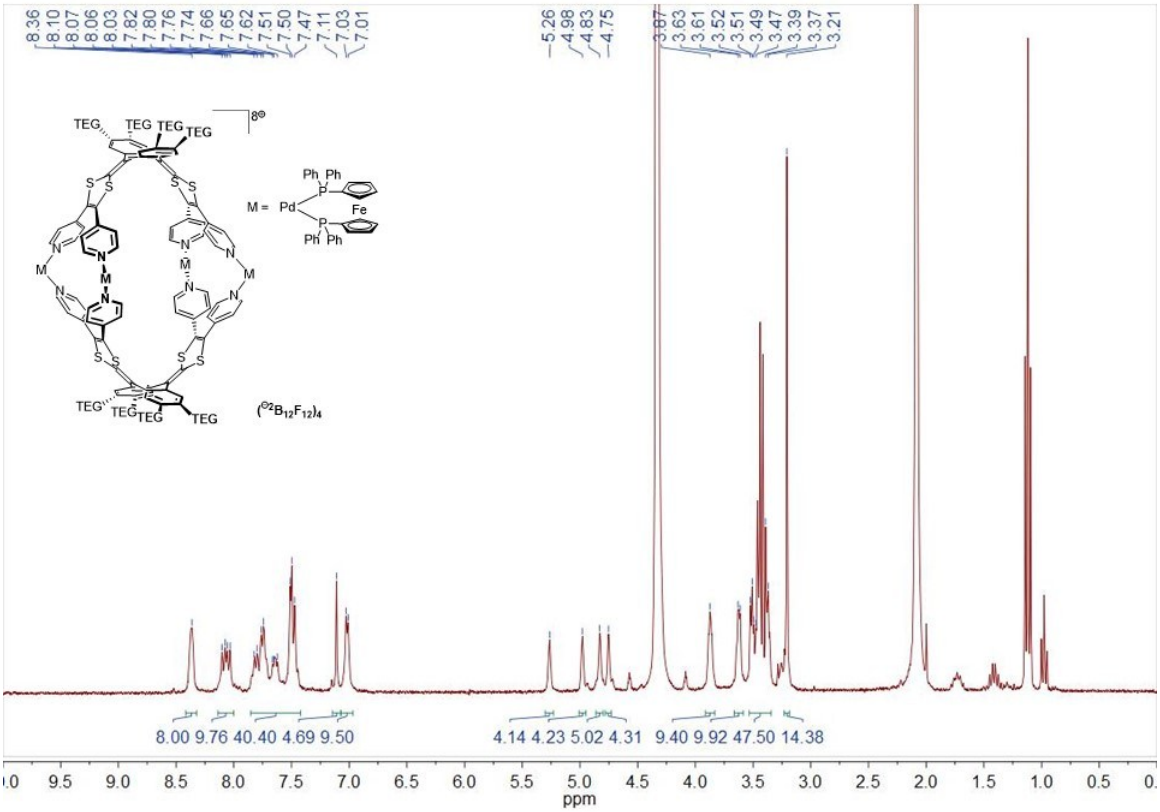


**Figure S23. $^1$H-NMR spectrum of $\mathbf{M_4L_2^{8+}(B_{12}F_{12}^{2-})_4}$ in $CD_3NO_2$.**

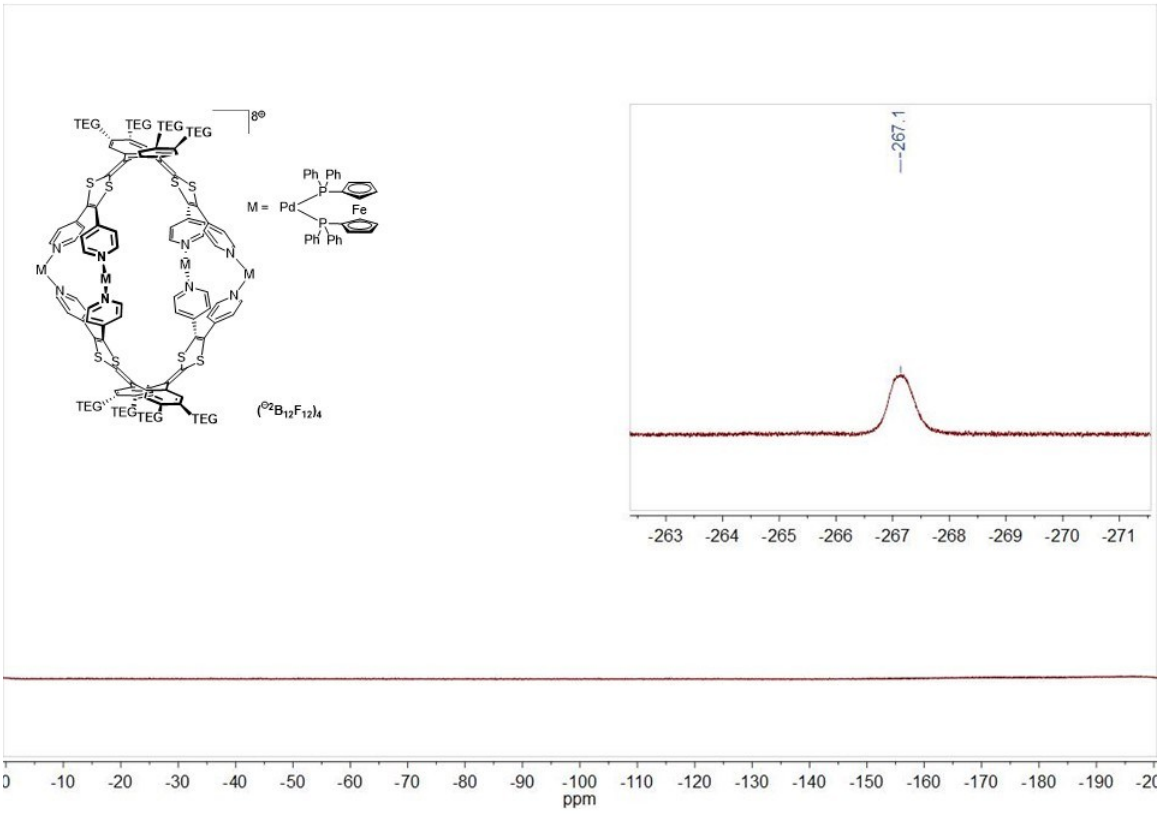


**Figure S24. $^{19}$F-NMR spectrum of $M_4L_2^{8+}(B_{12}F_{12}^{2-})_4$ in $CD_3NO_2$.**

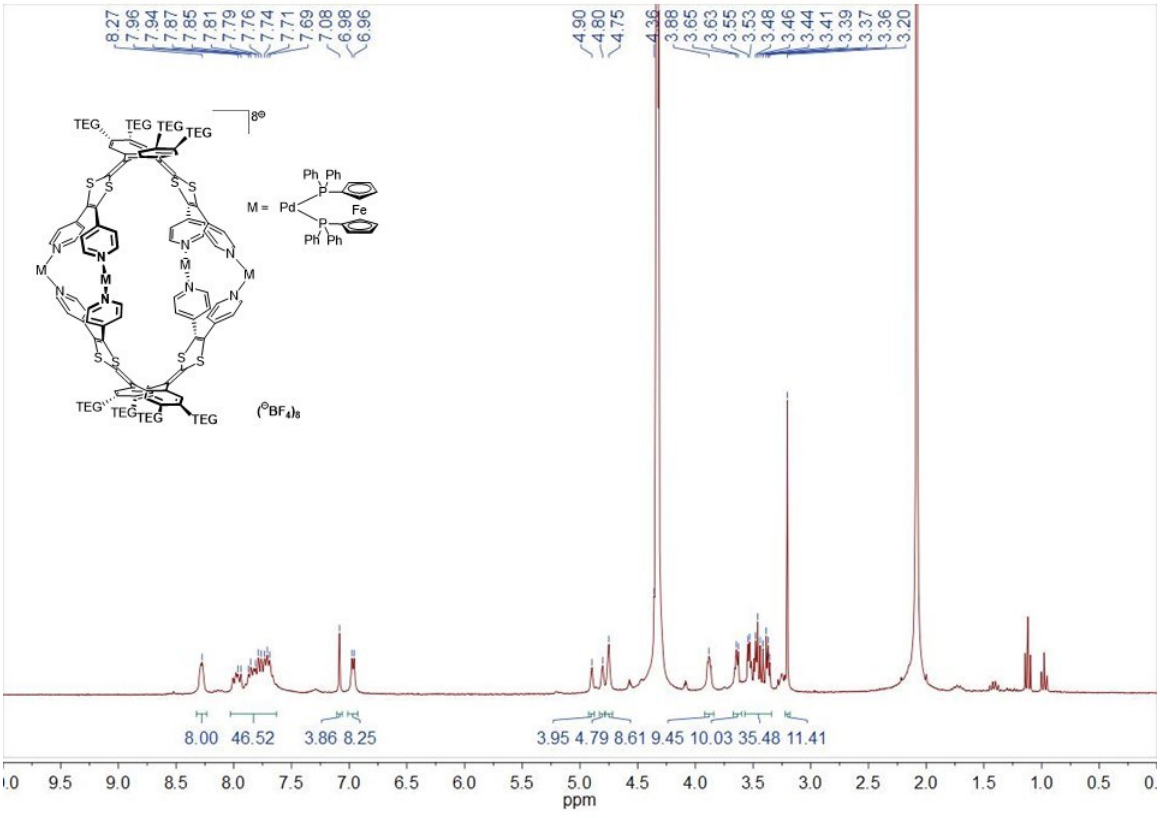


**Figure S25. $^{1}$H-NMR spectrum of $M_4L_2^{8+}(BF_4^-)_8$ in $CD_3NO_2$.**

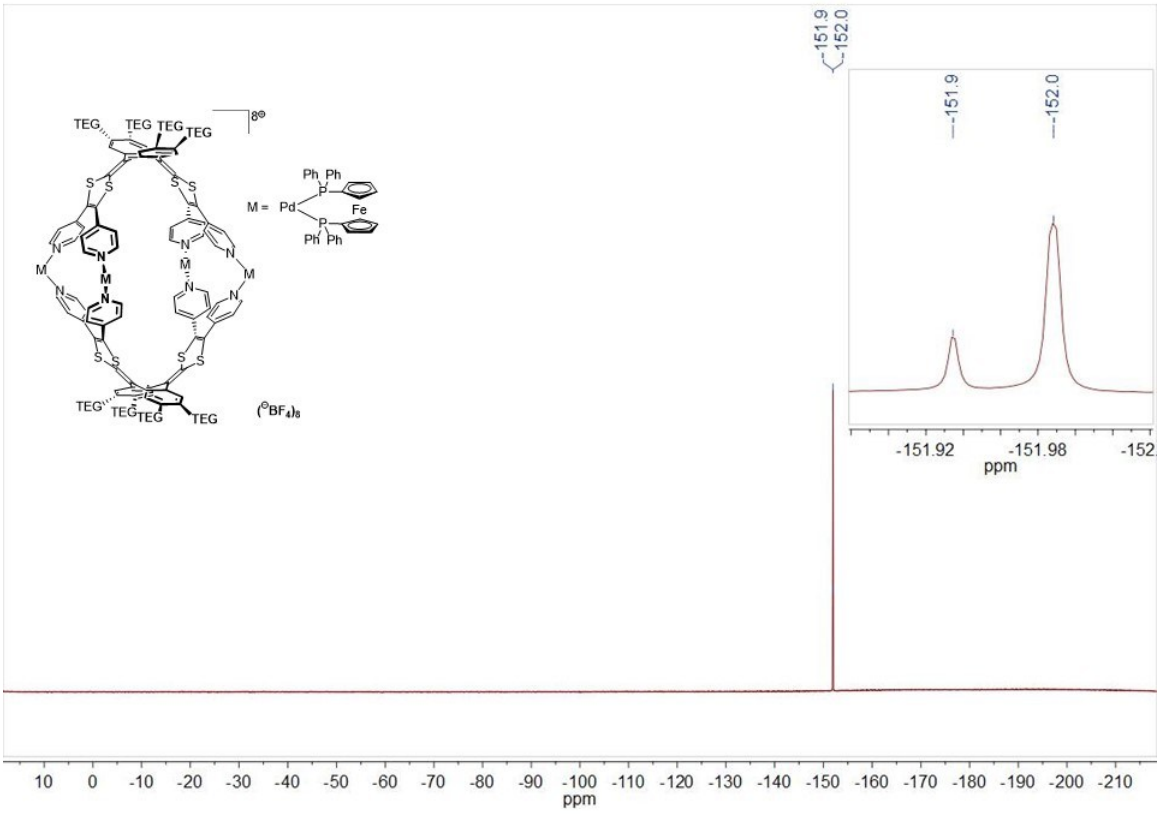


**Figure S26. $^{19}$F-NMR spectrum of $M_4L_2^{8+}(BF_4^-)_8$ in $CD_3NO_2$.**

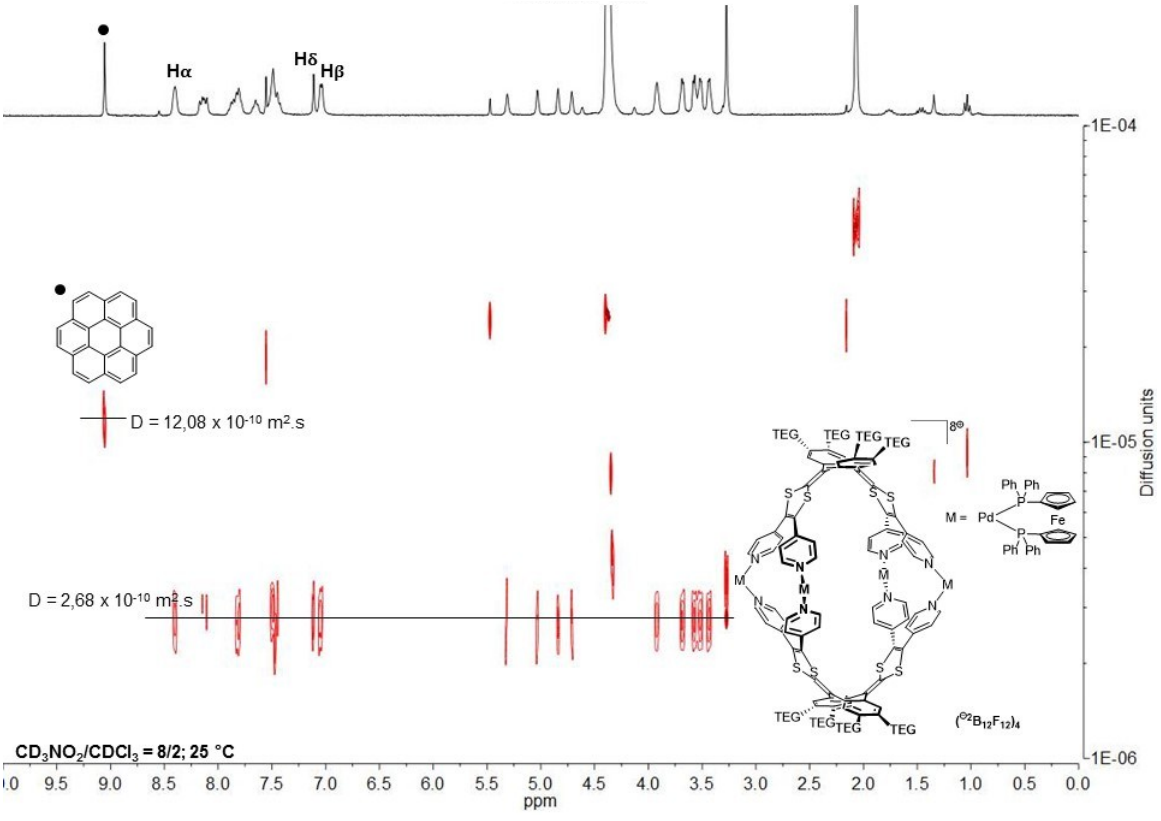

**Figure S27. $^1$H DOSY NMR spectrum of a stoichiometric mixture of coronene and $M_4L_2^{8+}(B_{12}F_{12}^{2-})_4$ in $CD_3NO_2/CDCl_3$ = 8/2 (1 x $10^{-3}$ M).**

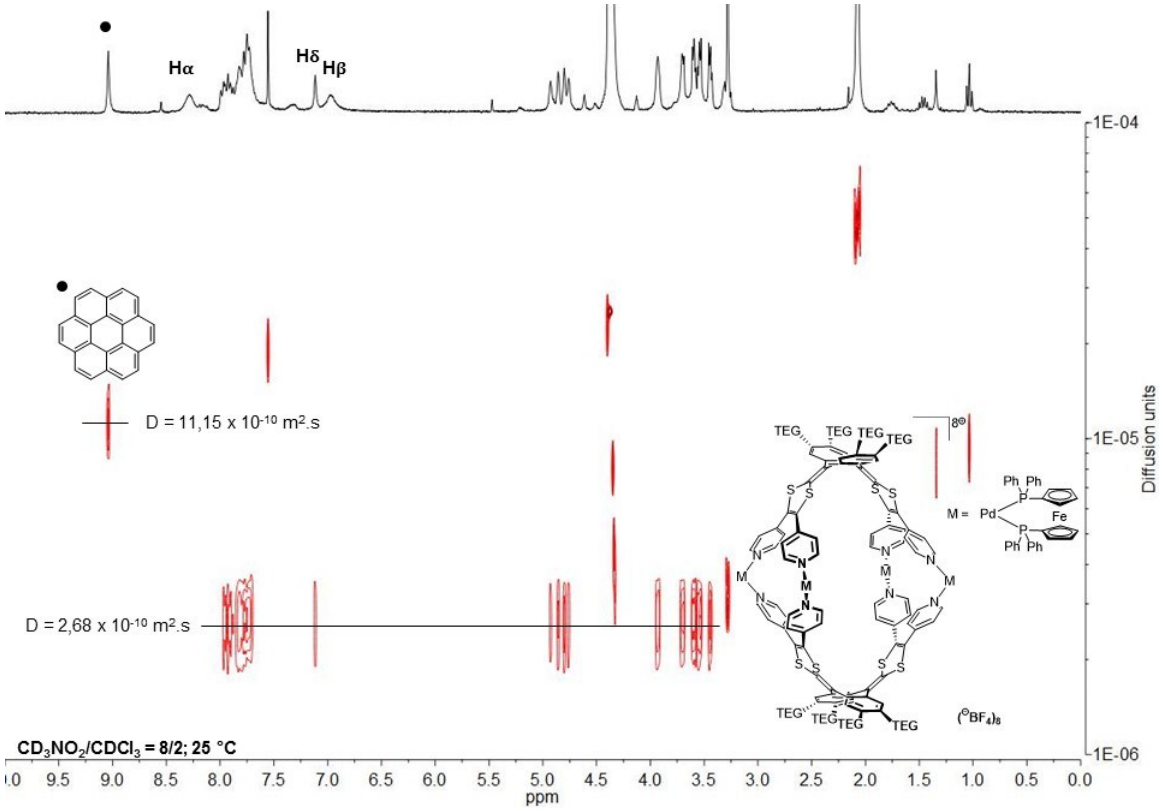


**Figure S28. $^1$H DOSY NMR spectrum of a stoichiometric mixture of coronene and $M_4L_2^{8+}(BF_4^-)_8$ in $CD_3NO_2/CDCl_3$ = 8/2 (1 x $10^{-3}$ M).**

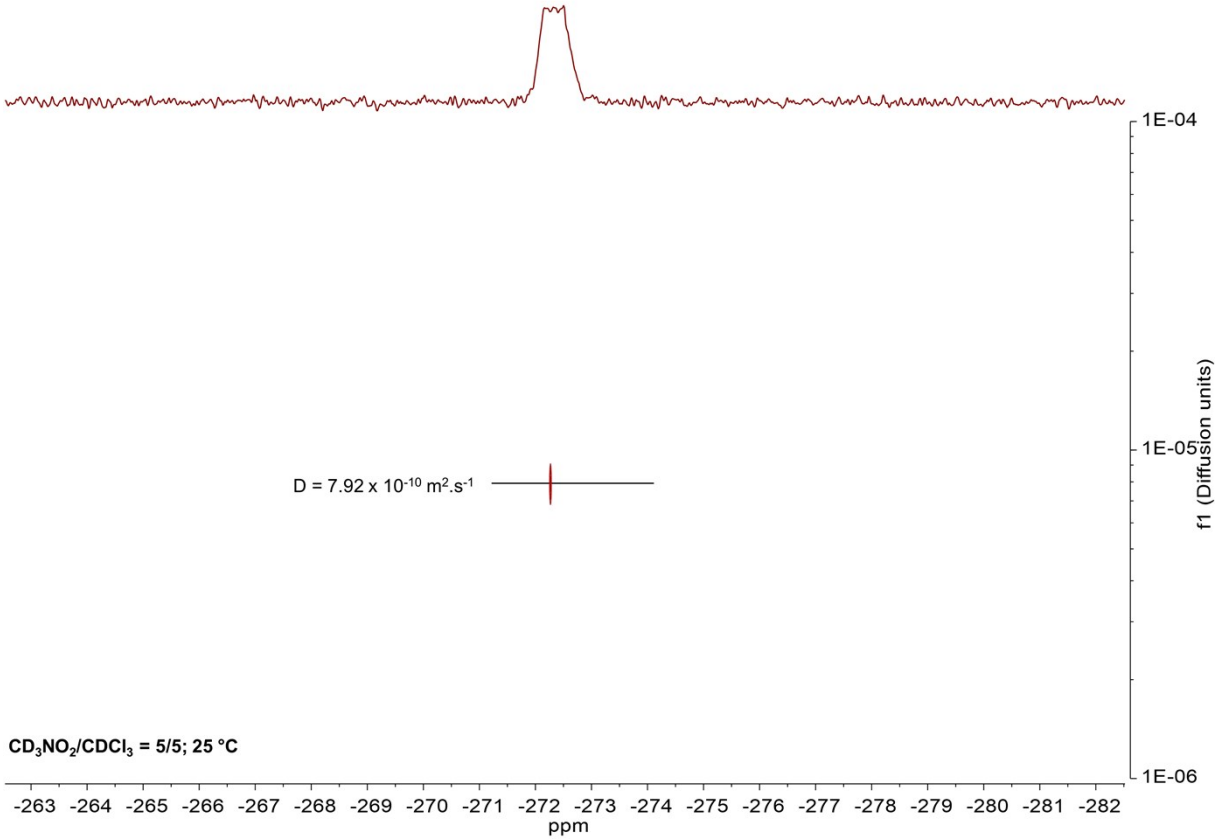


**Figure S29. $^{19}F$ DOSY NMR spectrum of $TBA_2\ B_{12}F_{12}$ in $CD_3NO_2/CDCl_3$ = 1/1 (2 x $10^{-3}$ M).**

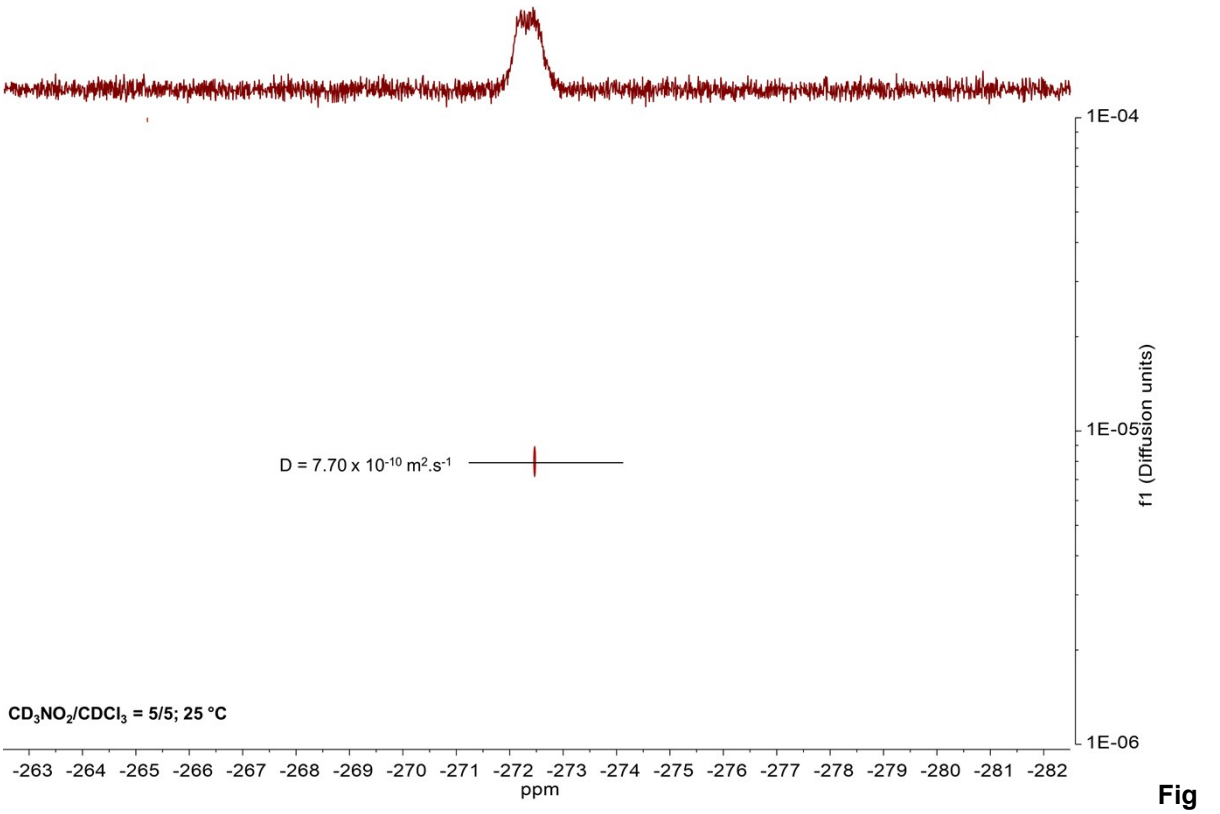


**Figure S30. $^{19}F$ DOSY NMR spectrum of a stoichiometric mixture of $TBA_2\ B_{12}F_{12}$ and $M_4L_2$ in $CD_3NO_2/CDCl_3$ = 1/1 (2 x $10^{-3}$ M).**

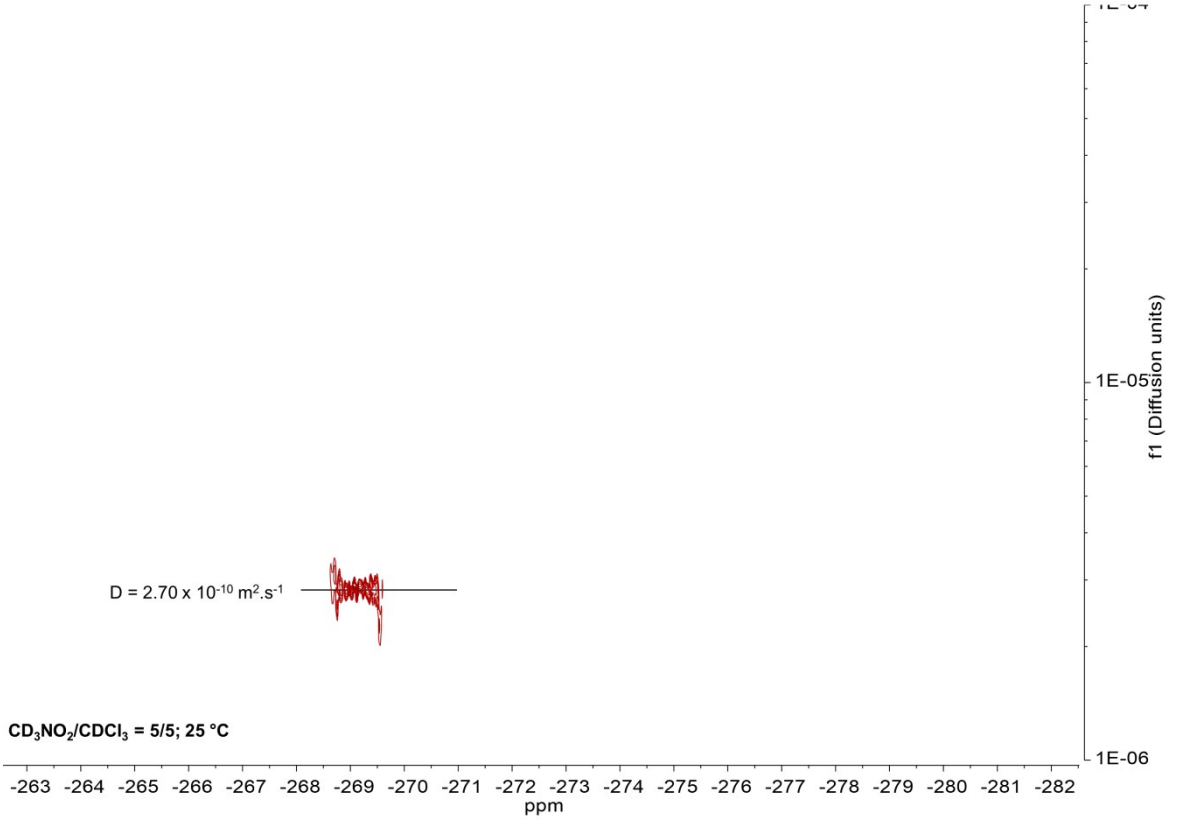


**Figure S31. $^{19}F$ DOSY NMR spectrum of a stoichiometric mixture of $TBA_2B_{12}F_{12}$ and $M_4L_2^{8+}(BF_4^-)_8$ in $CD_3NO_2/CDCl_3$ = 1/1 (2 x $10^{-3}$ M).**

# Job Plot

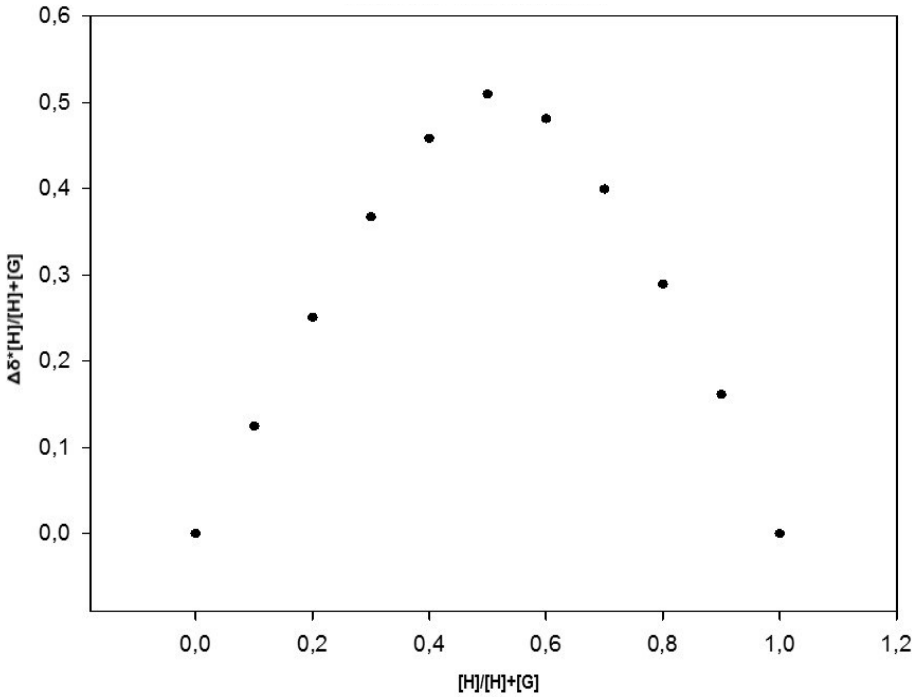


**Figure S32. Job plots for complexation of receptor $M_4L_2$ (H) with Coronene (G) determined by $^1H$ NMR ($M_4L_2$ $H_\beta$) in $CDCl_3/CD_3NO_2$ 1/1 at 298K, [H] + [G] = $10^{-3}$ mol.$L^{-1}$.**

# X-Ray

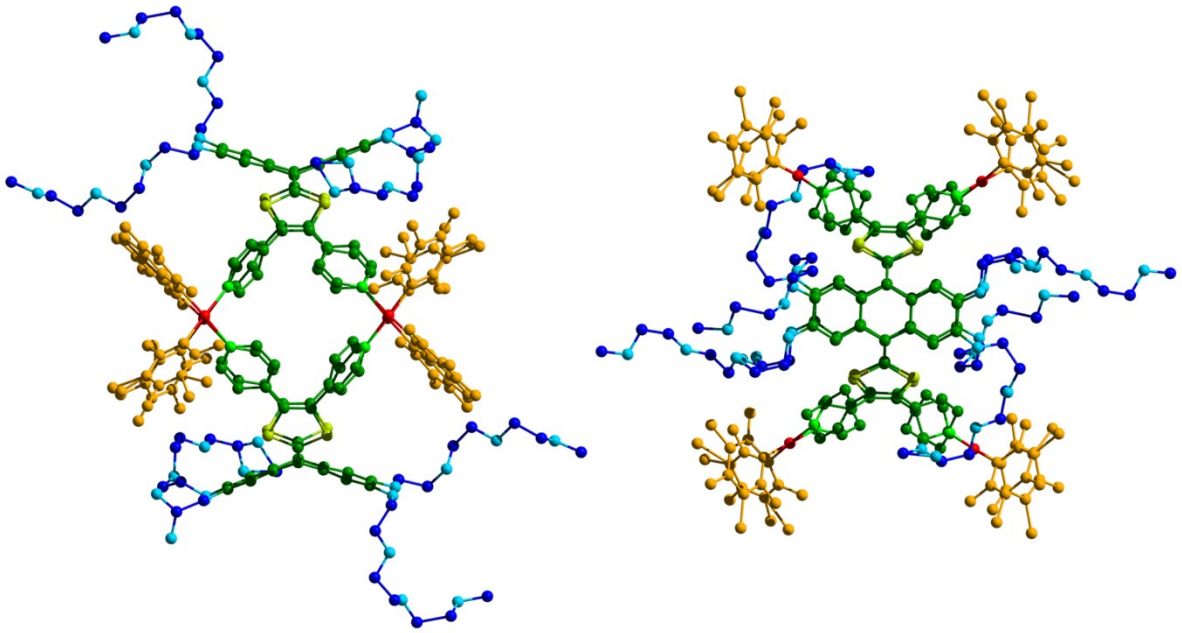

**Figure S30. X-Ray crystal structure of host structure $M_4L_2$**

For **$M_4L_2$:** 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 0.67 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, 2012). The crystal was very sensitive to decomposition and only poor diffraction data with low intensity was observed, involving low completeness. Nevertheless, main structure was solved (minus 10 C and 4 O on terminal PEG chains). The H atoms were not placed at their calculated positons since the main molecule was incomplete. The structure refinement showed disordered electron density which could not be reliably modeled and the program PLATON/SQUEEZE was used to remove the scattering contribution corresponding to acetonitrile solvent and missing atoms in the main structure from intensity data. The assumed solvent composition (26 $CH_3CN$ 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 **$M_4L_2$**: $C_{210}H_{199}Cl_{16}F_{24}N_{21}O_{32}P_8Pd_4S_8$, M = 5234.18, red prism, 0.28 x 0.17 x 0.08 $mm^3$, monoclinic, space group *P* $2_1/c$, a = 16.3201(3) Å, b = 29.0112(3) Å, c = 27.2545(3) Å, β = 105.883(1)°, V = 12411.4(3) $Å^3$, Z = 2, ρcalc = 1.401 $g/cm^3$, μ = 0.609$mm^{-1}$, F(000) = 5324, θmin = 1.60°, θmax = 32.60°, 271014 reflections collected, 38045 unique ($R_{int}$ = 0.115), parameters / restraints = 1202 / 0, R1 = 0.0794 and wR2 = 0.2232 using 26089 reflections with I>2σ(I), R1 = 0.1039 and wR2 = 0.2423 using all data, GOF = 1.065, -0.854 < Δρ < 2.675.$Å^{-3}$. CCDC 1441971.

For coronene⊂**$M_4L_2$**: X-ray single-crystal diffraction data were collected at 180K on an Agilent Technologies SuperNova diffractometer equipped with Atlas CCD detector and mirror

monochromated micro-focus Cu-$K_\alpha$ radiation (λ = 1.54184 Å). The structure was solved by direct methods, expanded 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, V1.171.37.35g, 2014). The H atoms were included in the calculation without refinement. The structure refinement showed disordered electron density which could not be reliably modeled and the program PLATON/SQUEEZE was used to remove the scattering contribution corresponding to nitromethane solvent from the intensity data. The assumed solvent composition (18 $CH_3NO_2$ 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 coronene⊂**$M_4L_2$**: $C_{226}H_{226}Cl_{16}F_{24}N_{26}O_{68}Pd_4S_8$, M = 6099.61, red prism, 0.21 x 0.11 x 0.06 $mm^3$, triclinic, space group *P*-1, a = 17.8945(6) Å, b = 19.5103(6) Å, c = 20.5070(7) Å, $\alpha$ = 90.134(2)°, $\beta$ = 99.808(3)°, $\gamma$ = 110.635(3)°, V = 6587.2(4) $Å^3$, Z = 1, ρcalc = 1.538 $g/cm^3$, μ = 5.131 $mm^{-1}$, F(000) = 3108, θmin = 2.43°, θmax = 76.49°, 54466 reflections collected, 26411 unique ($R_{int}$ = 0.072), parameters / restraints = 1427 / 51, R1 = 0.0866 and wR2 = 0.2317 using 16298 reflections with I>2σ(I), R1 = 0.1165 and wR2 = 0.2625 using all data, GOF = 0.969, -1.703 < Δρ < 2.396.$Å^{-3}$. CCDC 1441826.


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[2] V. Croué, S. Goeb, G. Szalóki, M. Allain and M. Sallé, *Angew. Chem. Int. Ed.*, **2016**, *55*, 1746.