

Complexation of Pyrene in Aqueous Solution with a Self-assembled Palladium Metallocycle

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Supporting Information

Table of Contents

General Methods.....	2
Crystal Structure Analysis.....	2
Ligand 1·NO ₃	2
Ligand 1·PF ₆	2
Metallocycle 3a·6NO ₃	2
Metallocycle 3a·4OTf·2PF ₆	3
Inclusion Complex PYR⊂3a·6NO ₃	3
Figure S1 ¹ H NMR (500 MHz, D ₂ O) (top) and ¹³ C NMR and DEPT (125 MHz, D ₂ O) (bottom) spectra of 3a·6NO ₃	4
Figure S2 COSY (500 MHz, D ₂ O) spectrum of 3a·6NO ₃	5
Figure S3 HSQC (top) and HMBC (500 MHz, D ₂ O) (bottom) spectra of 3a·6NO ₃	6
Figure S4 ¹ H NMR (500 MHz, CD ₃ CN) spectrum of 3a·4OTf·2PF ₆	7
Figure S5 ¹³ C NMR (500 MHz, CD ₃ CN) spectrum of 3a·4OTf·2PF ₆	7
Figure S6 ¹ H NMR (500 MHz, CD ₃ CN) spectrum of 3b·6PF ₆	8
Figure S7 ¹³ C NMR (500 MHz, CD ₃ CN) spectrum of 3b·6PF ₆	8
Figure S8 ¹ H NMR (500 MHz, D ₂ O) spectrum of PYR⊂3a·6NO ₃	9
Figure S9 COSY (500 MHz, D ₂ O) spectrum of PYR⊂3a·6NO ₃	10
Figure S10 HSQC (500 MHz, D ₂ O) spectrum of PYR⊂3a·6NO ₃	10
Figure S11 HMBC (500 MHz, D ₂ O) spectrum of PYR⊂3a·6NO ₃	11
Table S1. Crystal data and structure refinement for PYR⊂3a·6NO ₃	12
Figure S12. Job plot showing the 1:1 (H:G) stoichiometry of a complex formed between pyrene and 3a·6NO ₃ (total concentration 1 mM) in MeOH (384 nm).....	13
Titration data for pyrene with metallocycle 3a·6NO ₃ in MeOH:.....	14
Titration data for pyrene with metallocycle 3a·4OTf·2PF ₆ in CH ₃ CN:.....	15
Determination of the association constant (K _a) by liquid-liquid extraction.....	16
Computational Methods.....	17

General Methods

Compound **1**·Cl was prepared according to literature procedures.¹ All other reagents used were commercial grade chemicals from freshly opened containers. Milli-Q water was purified with a Millipore Gradient A10 apparatus. Merck 60 F₂₅₄ foils were used for thin layer chromatography, and Merck 60 (230-400 mesh) silica gel was used for flash chromatography. Proton and carbon nuclear magnetic resonance spectra were recorded on Bruker Avance 300 or Bruker Avance 500 spectrometers equipped with a dual cryoprobe for ¹H and ¹³C, using the deuterated solvent as lock and the residual protiated solvent as internal standard. Mass spectrometry experiments were carried out in a LC-Q-q-TOF Applied Biosystems QSTAR Elite spectrometer for low- and high-resolution ESI. UV-vis spectra were obtained using a Perkin-Elmer Lambda 900 spectrometer. Melting points were measured using Stuart Scientific SMP3 apparatus. Microanalyses for C, H and N were performed by the elemental analyses general service of the University of A Coruña.

Crystal Structure Analysis

The structures were solved by direct methods and refined with the full-matrix least-squares procedure (SHELX-97)² against F^2 . The X-ray diffraction data were collected on a Bruker X8 APEXII or a Bruker SMART 1k diffractometer. Hydrogen atoms were placed in idealized positions with $U_{\text{eg}}(\text{H})$ 1.2 $U_{\text{eg}}(\text{C})$ and were allowed to ride on their parent atoms.

Ligand **1**·NO₃

A solution of **1**·Cl (0.050 g, 0.139 mmol) and AgNO₃ (0.024 g, 0.139 mmol) in water (3 mL) was stirred at room temperature for 3h with the exclusion of light. The suspension was then filtered, and the filtrate concentrated in vacuo to give **1**·NO₃ (0.053 g, 99%). ¹H NMR (300 MHz, D₂O) δ : 4.24 (s, 2H); 7.41 (d, J = 6.1 Hz, 2H); 7.65 (d, J = 8.6 Hz, 2H); 7.75 (d, J = 8.6 Hz, 2H); 8.00 (d, J = 4.7, 2H); 8.47 (d, J = 6.1 Hz, 2H); 8.58 (d, J = 6.9 Hz, 2H); 8.83 (d, J = 4.7, 2H); 9.20 (d, J = 6.9 Hz, 2H). ¹³C NMR (75 MHz, D₂O) δ : 39.9 (CH₂); 122.5 (CH); 124.3 (CH); 124.9 (CH); 126.0 (CH); 131.1 (CH); 140.9 (C); 142.4 (C); 143.4 (C); 144.6 (CH); 148.3 (CH); 150.1 (CH); 151.7 (C); 154.6 (C). Anal. Calc. C₂₂H₁₈N₄O₃: C, 68.38; H, 4.70; N, 14.50. Found C, 68.07; H, 4.62; N, 14.81.

Ligand **1**·PF₆

An excess of KPF₆ was added to a solution of **1**·Cl (0.050 g, 0.139 mmol) and AgNO₃ (0.024 g, 0.139 mmol) in water (3 mL). The solid formed was filtered to give **1**·PF₆ (0.061 g, 94%). ¹H NMR (300 MHz, CD₃CN) δ : 4.20 (s, 2H); 7.33 (d, J = 6.0 Hz, 2H); 7.67 (d, 8.7 Hz, 4H); 7.89 (d, J = 4.5, Hz, 2H); 8.49 (d, J = 7.0 Hz, 2H); 8.54 (d, J = 4.6, 2H); 8.90 (d, J = 4.5, 2H); 8.97 (d, J = 5.3, Hz, 2H). ¹³C NMR (75 MHz, CD₃CN) δ : 39.9 (CH₂); 121.9 (CH); 124.4 (CH); 124.7 (CH); 126.0 (CH); 131.0 (CH); 140.9 (C); 143.9 (C); 144.9 (CH); 149.4 (CH); 150.1 (C); 151.3 (CH); 154.9 (C). Anal. Calc. C₂₂H₁₈F₆N₃P: C, 56.30; H, 3.87; N, 8.95. Found C, 56.53; H, 3.62; N, 9.23.

Metallocycle **3a**·6NO₃

The addition of (en)Pd(NO₃)₂ (1.5 mg, 5.2·10⁻³ mmol) to a solution of **1**·NO₃ (2.0 mg, 5.2·10⁻³ mmol) in D₂O (0.6 mL) gave **3a**·6NO₃. ¹H NMR (500 MHz, D₂O) δ : 2.95 (s, 8H); 4.19 (s, 4H); 7.54 (s, 8H); 7.56 (d, J = 6.6 Hz, 4H); 7.96 (d, J = 5.4, 4H); 8.34 (d, J = 7.0 Hz, 4H); 8.65 (d, J = 6.6 Hz, 4H); 8.69 (d, J = 5.4, 4H); 9.01 (d, J = 7.0 Hz, 4H). ¹³C NMR (125 MHz, D₂O) δ : 40.1 (CH₂); 46.8 (CH₂); 124.2 (CH); 125.0 (CH); 126.0 (CH); 127.2 (CH); 130.6 (CH); 140.8 (C); 143.1 (C); 144.4 (CH); 145.0 (C); 150.9 (CH); 151.9 (C); 152.0 (CH); 155.2 (C).

¹ Bongard, D.; Möller, M.; Nagaraja Rao, S.; Corr, D.; Walder, L. *Helv. Chim. Acta* **2005**, 88, 3200.

² G. M Sheldrick, SHELX-97, *An Integrated System for Solving and Refining Crystal Structures from Diffraction Data*, University of Göttingen, Germany, 1997.

Metallocycle **3a**·4OTf·2PF₆.

The addition of (en)Pd(OTf)₂ (2.1 mg, 4.5·10⁻³ mmol) to a solution of **1**·PF₆ (2.1 mg, 4.5·10⁻³ mmol) in CD₃CN (0.6 mL) gave **3a**·4OTf·2PF₆. ¹H NMR (300 MHz, CD₃CN) δ: 2.90 (s, 8H); 4.19 (s, 4H); 4.50 (br s, 8H); 7.54 (m, 12H); 7.95 (d, *J* = 6.8 Hz, 4H); 8.32 (d, *J* = 7.0 Hz, 4H); 8.71 (d, *J* = 6.6 Hz, 4H); 8.90 (d, *J* = 7.1 Hz, 4H); 8.98 (d, *J* = 6.8 Hz, 4H). ¹³C NMR (125 MHz, CD₃CN) δ: 154.9 (C); 152.7 (CH); 152.1 (C); 151.6 (CH); 145.1 (C); 144.9 (CH); 143.4 (C); 140.9 (C); 130.6 (CH); 127.3 (CH); 126.6 (CH); 125.1 (CH); 124.7 (CH); 46.8 (CH₂); 46.7 (CH₂); 39.7 (CH₂).

Metallocycle **3b**·6PF₆

A solution of (en)Pt(OTf)₂ (2.1 mg, 4.5·10⁻³ mmol) and **1**·PF₆ (2.1 mg, 4.5·10⁻³ mmol) in H₂O (25 mL) was heated at 100 °C for 4 d. After cooling to room temperature, an excess of KPF₆ was added and a white solid precipitated. The precipitate was filtered and washed with H₂O. The solid was purified by recrystallization in CH₃CN to afford **3b**·6PF₆ (0.0113 mmol, 50 %). Mp = 172 (decomp). ¹H RMN (CD₃CN, 500 MHz) δ: 2.77 (s, 8H); 4.18 (s, 4H); 4.84 (br s, 8H); 7.45-7.53 (m, 12H); 7.87 (d, *J* = 6.8 Hz, 4H); 8.29 (s, 4H); 8.62 (d, *J* = 6.6 Hz, 4H); 8.90 (d, *J* = 7.0 Hz, 4H). ¹³C NMR (125 MHz, CD₃CN) δ: 155.0 (C); 153.5 (CH); 152.3 (CH); 152.2 (C); 145.0 (C); 144.9 (CH); 143.3 (CH); 141.0 (CH); 130.7 (C); 127.4 (C); 126.5 (CH); 124.8 (CH); 124.7 (CH); 47.7 (CH₂); 39.7 (CH₂). HRMS-ESI (*m/z*): calcd for [M-4PF₆]⁴⁺ 362.0733, found 362.0740; calcd for [M-5PF₆]⁵⁺ 260.6657, found 260.6664.

Inclusion Complex PYR⊂**3a**·6NO₃.

Pyrene (0.5 mg, 2.4·10⁻³ mmol) was added to a solution of **3a**·6NO₃ in D₂O (4 mM, 0.6 mL). The mixture was sonicated for 1 h at 50 °C to give a red solution of PYR⊂**3a**·6NO₃. ¹H NMR (500 MHz, D₂O) δ: 2.78 (s, 8H); 4.05 (s, 4H); 5.85 (t, *J* = 7.6 Hz, 2H); 6.50 (d, *J* = 7.6 Hz, 4H); 6.82 (br s, 8H); 7.31 (s, 8H); 7.36 – 7.46 (m, 8H); 7.70 – 7.73 (m, 4H); 8.82 – 8.92 (m, 8H).

Single crystals of PYR⊂**3a**·6NO₃ suitable for X-ray crystallography were grown from 30 mM NaNO₃ solution of **1**·NO₃, **2a**, and PYR (in a 2:2:1 mol ratio).

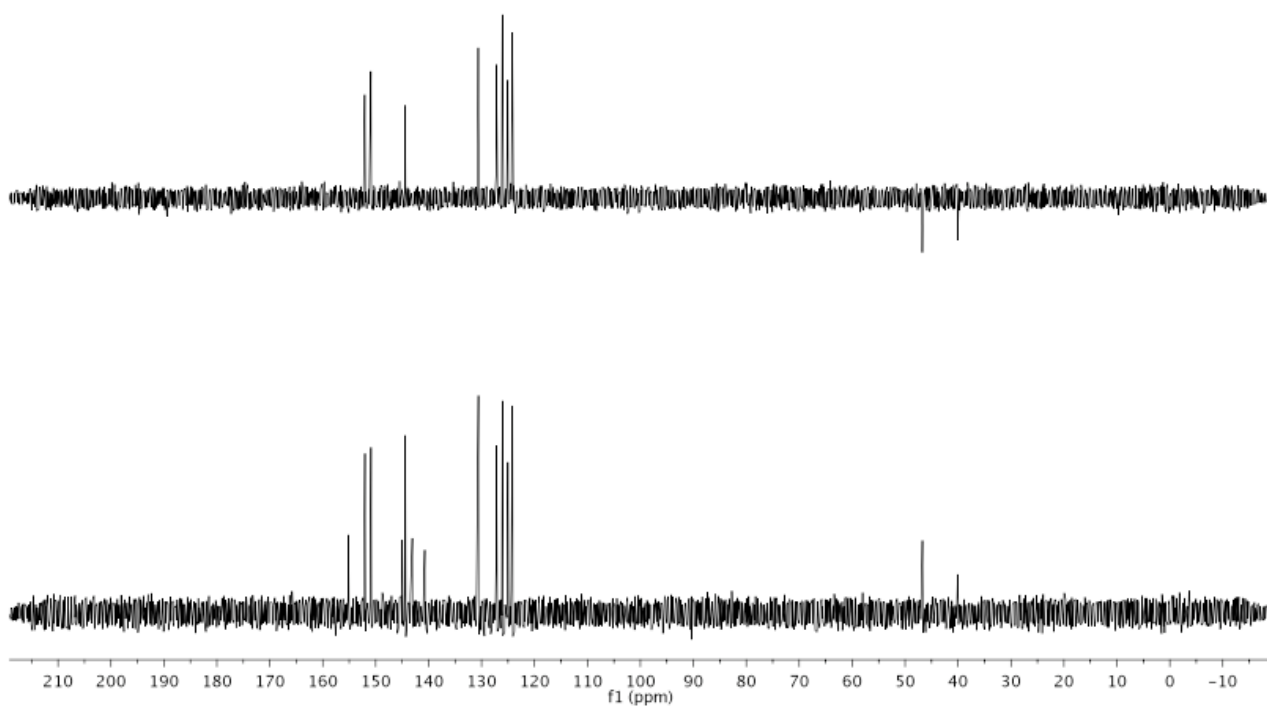
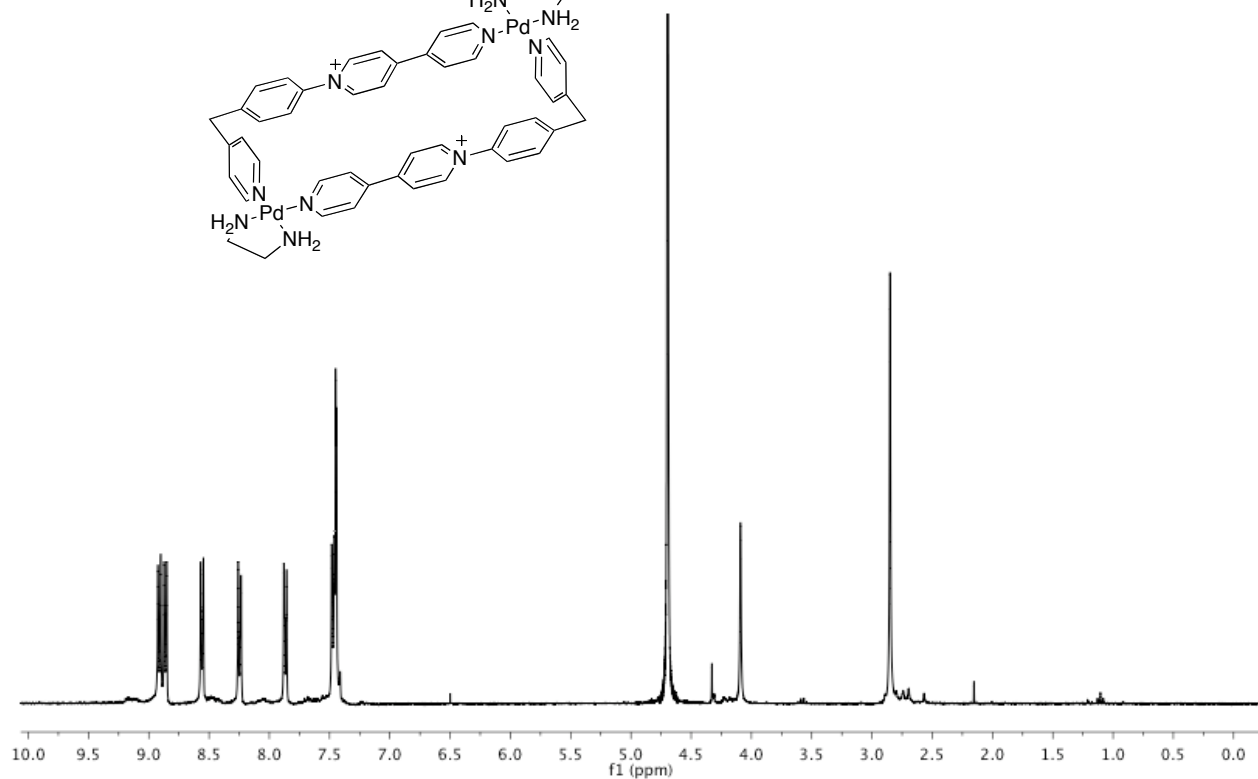


Figure S1 ^1H NMR (500 MHz, D_2O) (top) and ^{13}C NMR and DEPT (125 MHz, D_2O) (bottom) spectra of $3\text{a}\cdot 6\text{NO}_3$

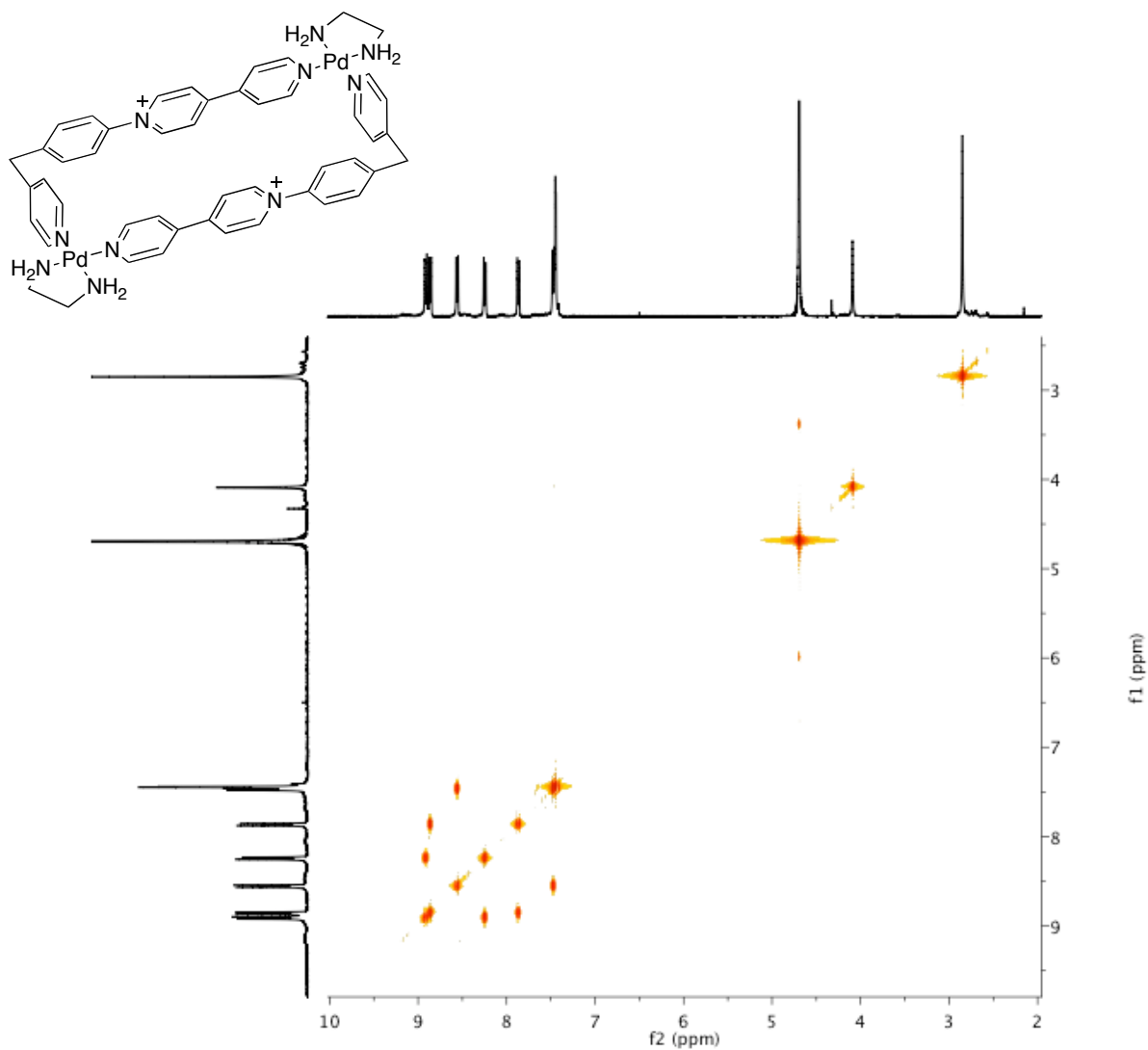


Figure S2 COSY (500 MHz, D₂O) spectrum of 3a·6NO₃

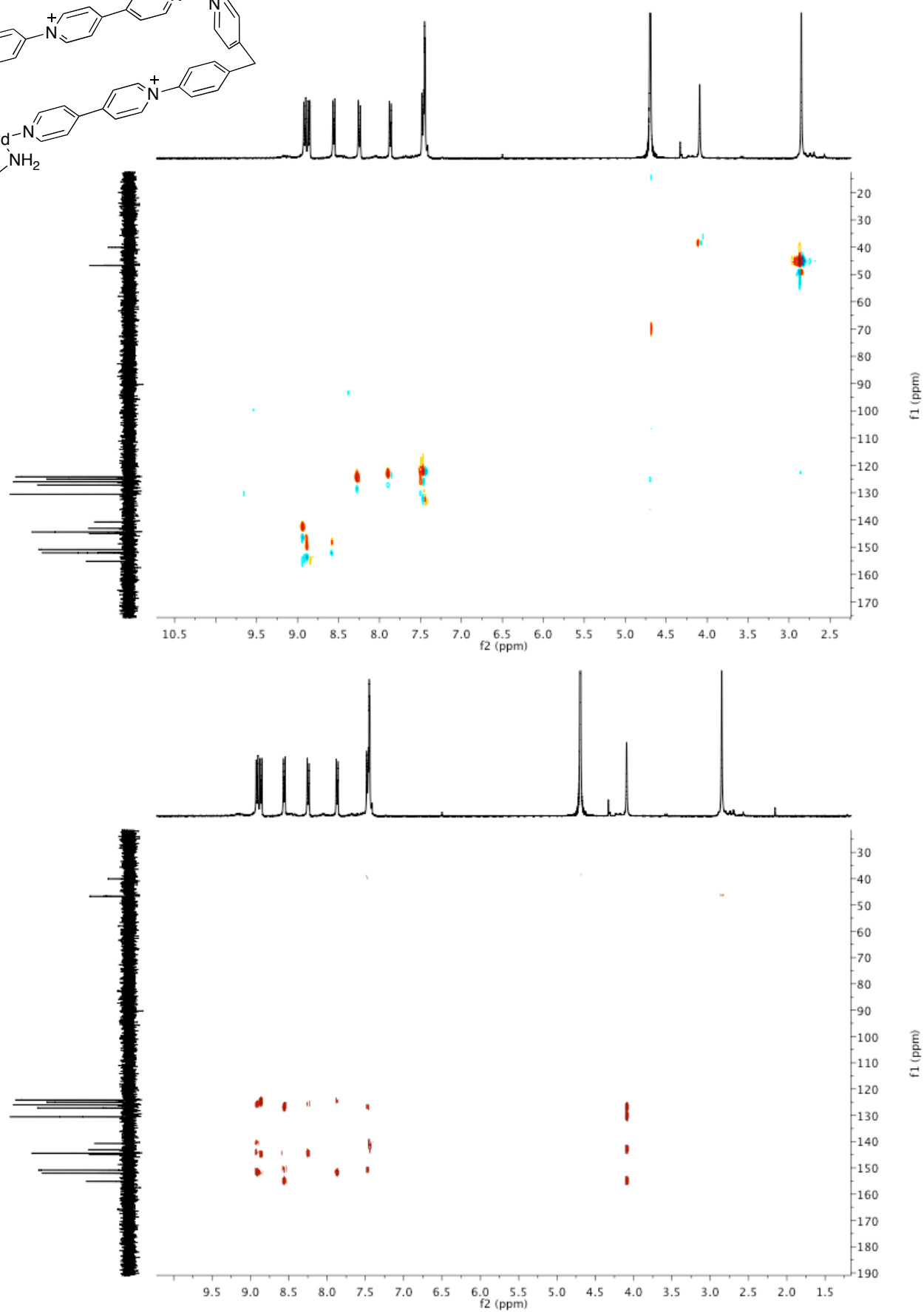


Figure S3 HSQC (top) and HMBC (500 MHz, D₂O) (bottom) spectra of 3a·6NO₃.

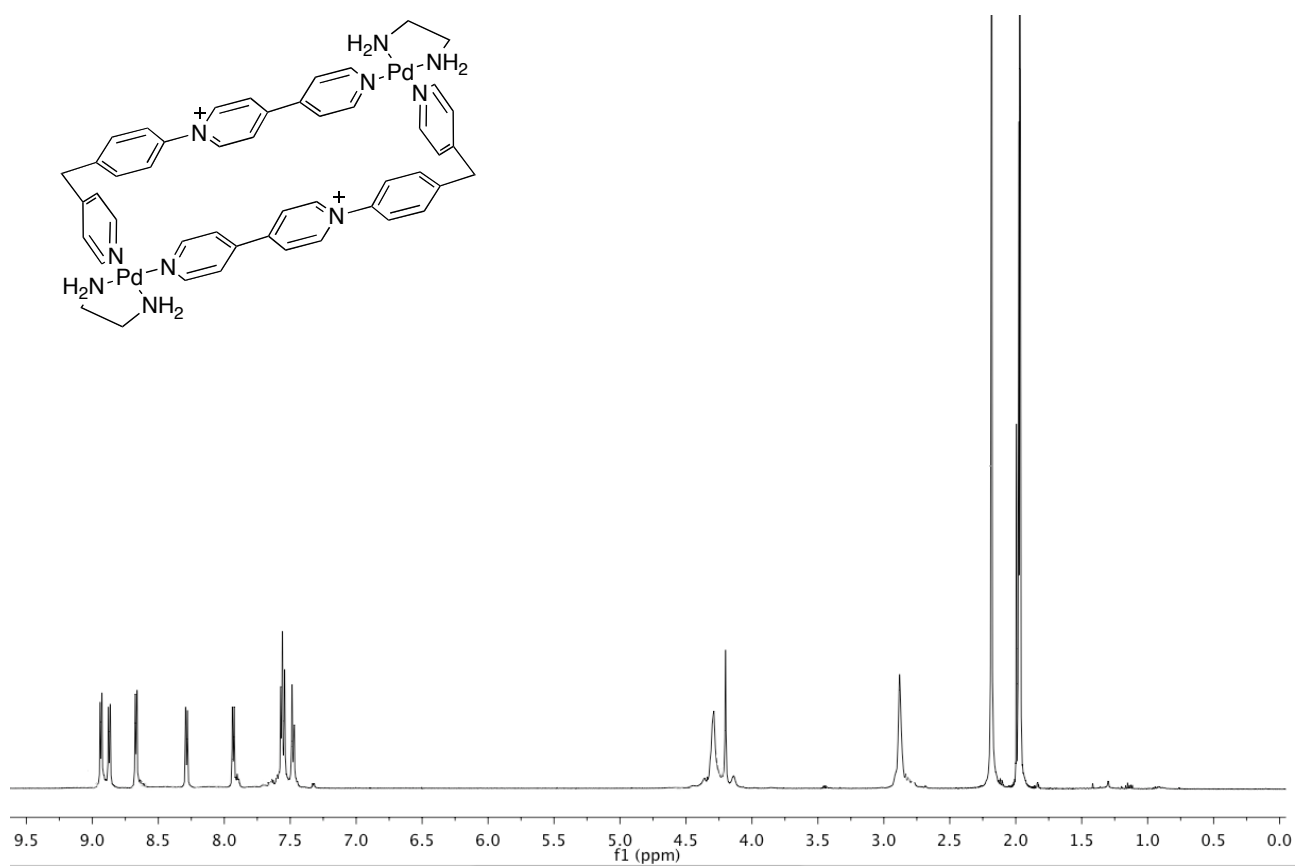


Figure S4 ^1H NMR (500 MHz, CD_3CN) spectrum of $3\text{a}\cdot 4\text{OTf}\cdot 2\text{PF}_6$.

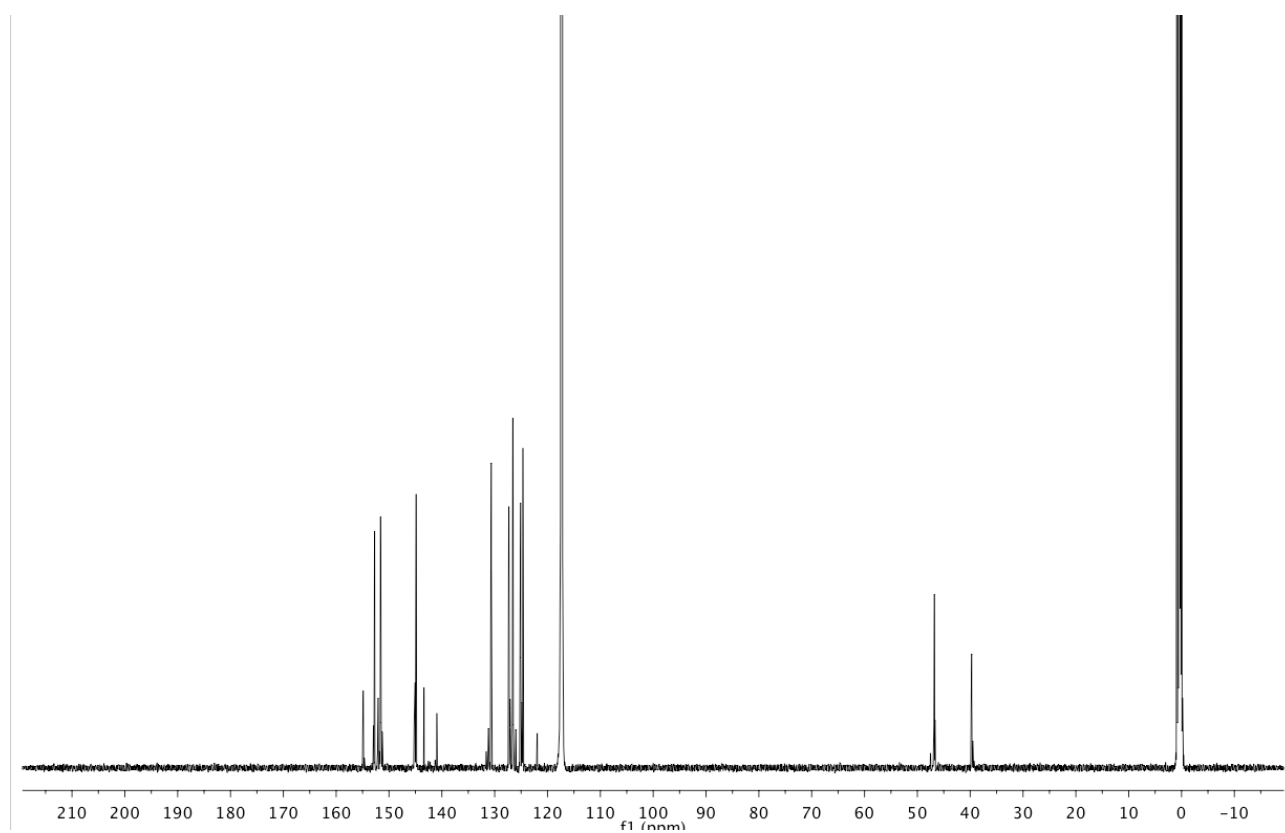


Figure S5 ^{13}C NMR (500 MHz, CD_3CN) spectrum of $3\text{a}\cdot 4\text{OTf}\cdot 2\text{PF}_6$.

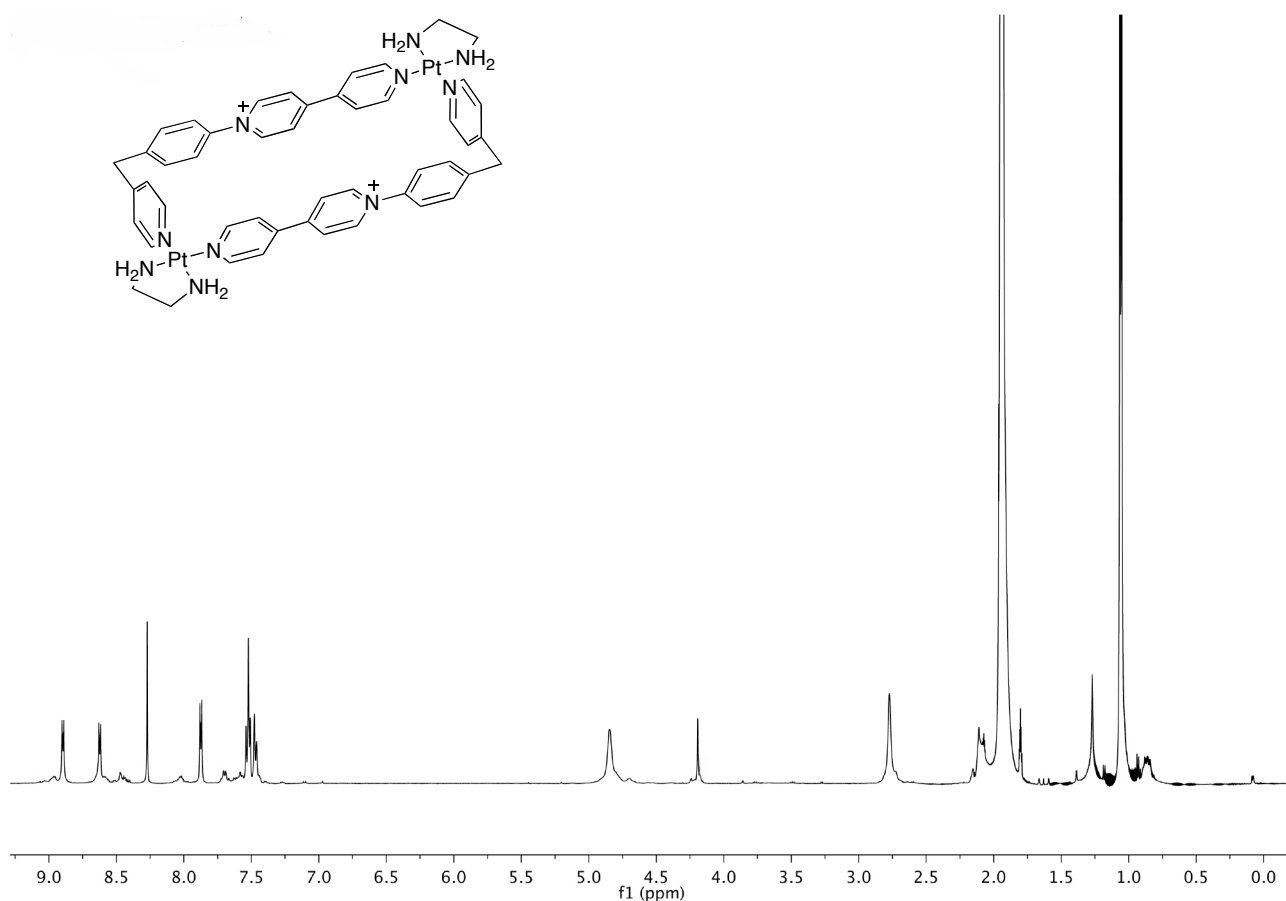


Figure S6 ¹H NMR (500 MHz, CD₃CN) spectrum of 3b·6PF₆.

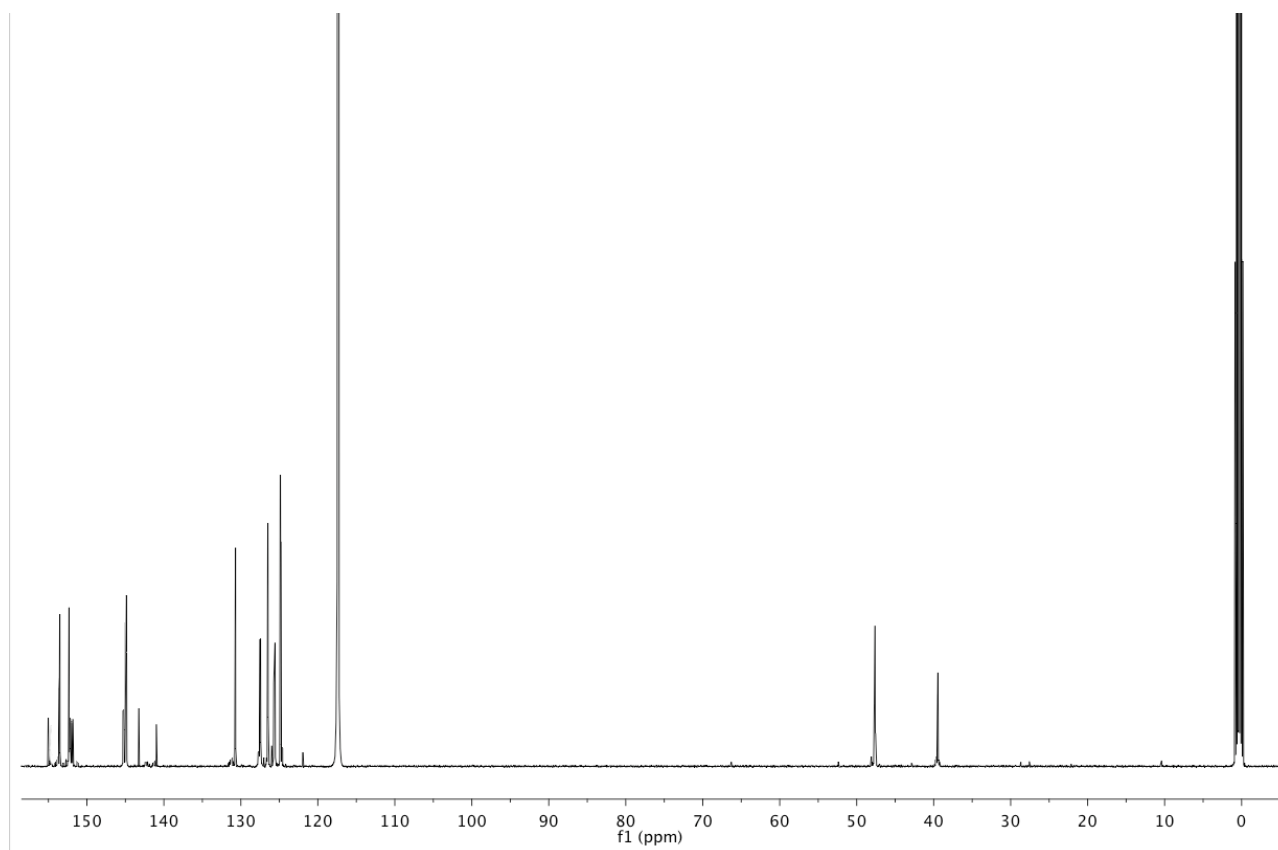


Figure S7 ¹³C NMR (500 MHz, CD₃CN) spectrum of 3b·6PF₆.

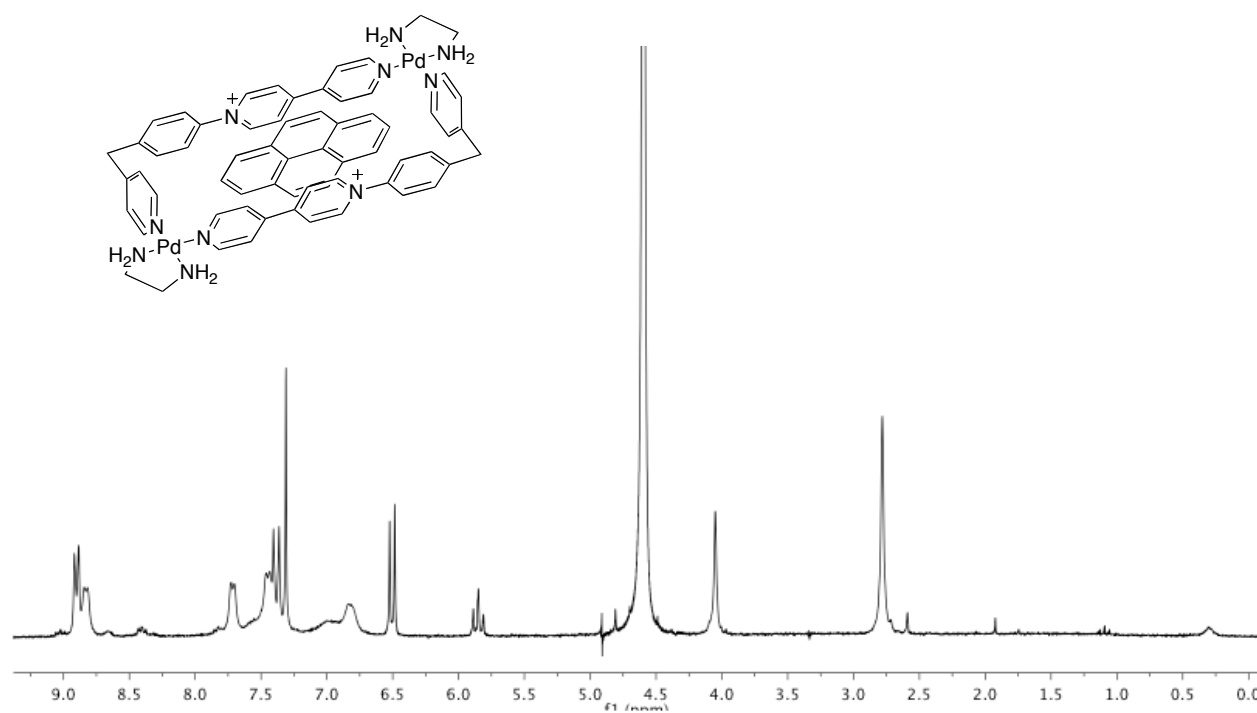


Figure S8 ^1H NMR (500 MHz, D_2O) spectrum of $\text{PYRC3a} \cdot 6\text{NO}_3$.

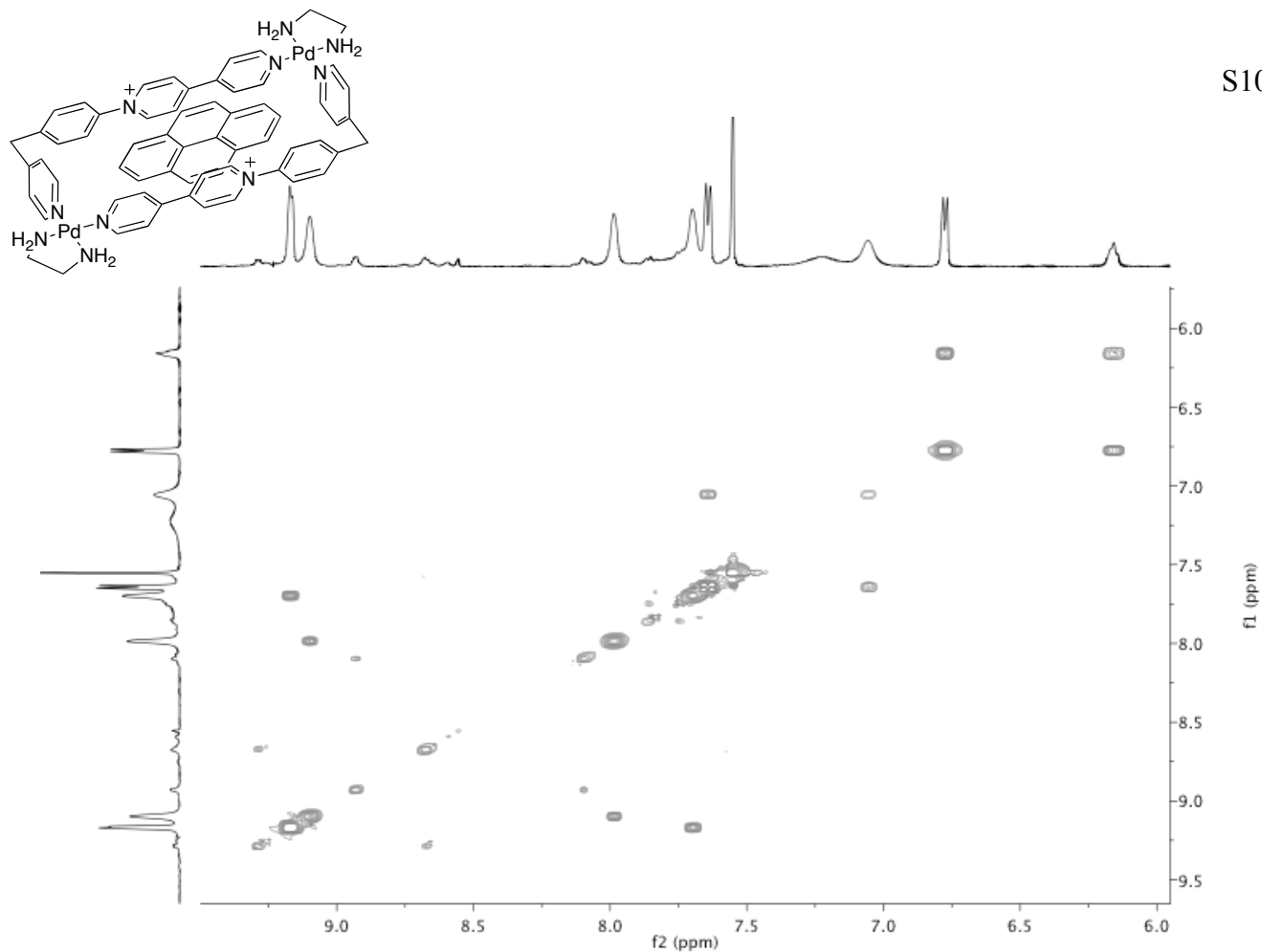


Figure S9 COSY (500 MHz, D₂O) spectrum of PYRC3a·6NO₃.

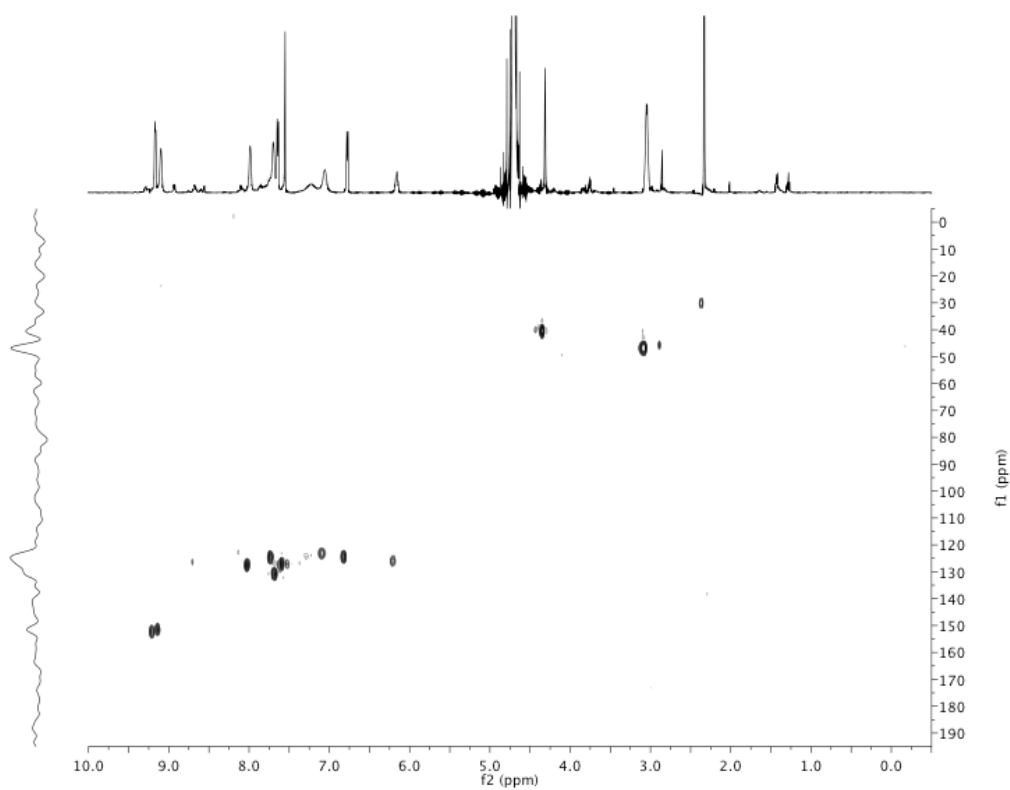


Figure S10 HSQC (500 MHz, D₂O) spectrum of PYRC3a·6NO₃.

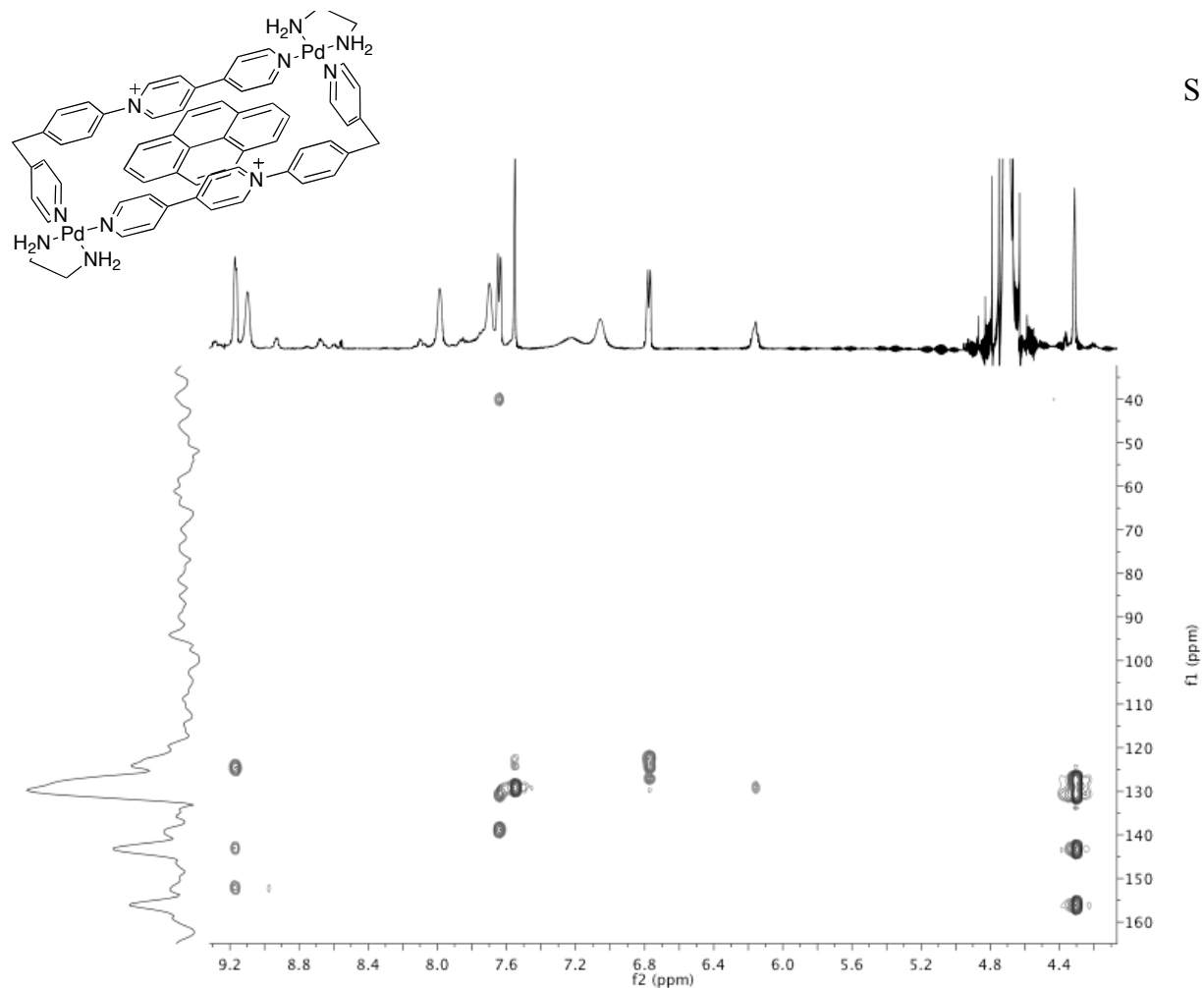
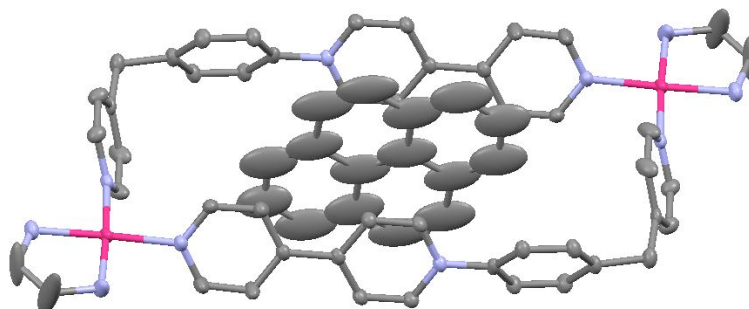


Figure S11 HMBC (500 MHz, D₂O) spectrum of PYRC3a·6NO₃.

Table S1. Crystal data and structure refinement for PYRC3a·6NO₃

Empirical formula	$C_{64}H_{62}N_{16}O_{33}Pd_2$	
Formula weight	1796.10	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 14.326(5)$ Å	$\alpha = 89.769(5)^\circ$
	$b = 17.092(5)$ Å	$\beta = 70.447(5)^\circ$
	$c = 17.164(5)$ Å	$\gamma = 84.337(5)^\circ$
Volume	$3939(2)$ Å ³	
<i>Z</i>	2	
D_{calc}	1.514 Mg/m ³	
μ	0.552 mm ⁻¹	
$F(000)$	1828	
Crystal size	$0.48 \times 0.30 \times 0.13$ mm ³	
θ range for data collection	1.20 to 26.44°	
Index ranges	$-16 \leq h \leq 17$, $-21 \leq k \leq 21$, $0 \leq l \leq 21$	
Reflections collected	16203	
Independent reflections	16203 [$R_{\text{int}} = 0.0000$]	
Completeness to $\theta = 28.28^\circ$	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9316 and 0.7774	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16203 / 126 / 1064	
Goodness-of-fit on F^2	0.916	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0680$, $wR_2 = 0.1678$	
R indices (all data)	$R_1 = 0.0818$, $wR_2 = 0.1807$	

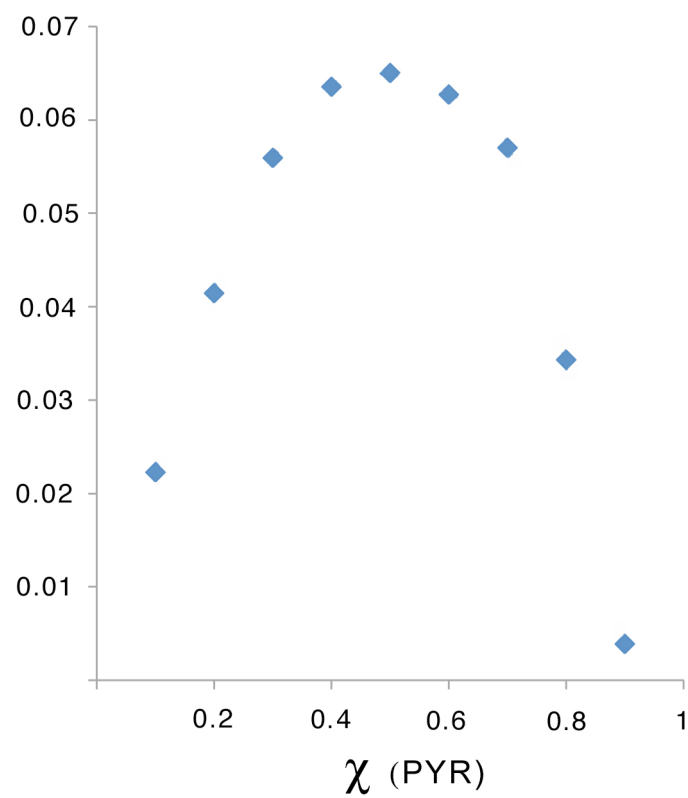


Figure S12. Job plot showing the 1:1 (H:G) stoichiometry of a complex formed between pyrene and 3a·6NO₃(total concentration 1 mM) in MeOH (384 nm).

Determination of binding constant (K_a) using the UV/Vis dilution method.

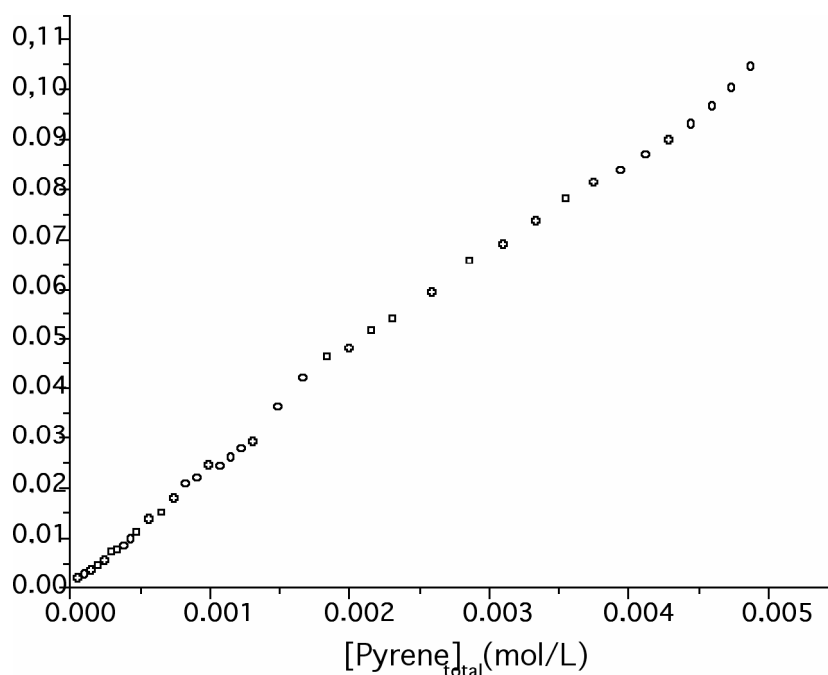
Titration data for pyrene with metallocycle **3a**·6NO₃ in MeOH:

A 1 mM solution of host (**3a**·6NO₃) in MeOH and a solution of host (1 mM) and guest (pyrene, 10 mM) in MeOH were separately prepared. Aliquots of the guest/host solution (10 μ L initially, then 20 μ L, then 50 μ L, and finally 100 μ L) were added to the host solution (2 mL). The spectrum was recorded after each addition and overall 39 data points were obtained.

The association constants were determined by using the nonlinear least squares fitting of the titration curves plotting A of the host-guest complex charge-transfer band against the molar equivalent of the guest. All of the titration curves were well fitted to the expression of a 1:1 binding isotherm.

Temperature: 300 K. $\lambda_{\text{max}} = 460$ nm. $K_a = 49 \pm 5 \text{ M}^{-1}$ (adj. $R^2 = 0.99847$).

Total volume added (μ L)	A	[pyrene] _{total} (mol/L)	Total volume added (μ L)	A	[pyrene] _{total} (mol/L)
10	0.001981	4.97512E-05	350	0.036262	0.001489362
20	0.002747	9.90099E-05	400	0.042143	0.001666667
30	0.003689	0.000147783	450	0.046411	0.001836735
40	0.004554	0.000196078	500	0.048247	0.002
50	0.005515	0.000243902	550	0.051921	0.002156863
60	0.007234	0.000291262	600	0.054103	0.002307692
70	0.007663	0.000338164	700	0.059498	0.002592593
80	0.008449	0.000384615	800	0.06582	0.002857143
90	0.009799	0.000430622	900	0.069067	0.003103448
100	0.011255	0.00047619	1000	0.073657	0.003333333
120	0.013759	0.000566038	1100	0.078253	0.003548387
140	0.015077	0.000654206	1200	0.081479	0.00375
160	0.017911	0.000740741	1300	0.084087	0.003939394
180	0.020814	0.000825688	1400	0.087165	0.004117647
200	0.021956	0.000909091	1500	0.09005	0.004285714
220	0.024567	0.000990991	1600	0.09319	0.004444444
240	0.024319	0.001071429	1700	0.096616	0.004594595
260	0.026146	0.001150442	1800	0.100556	0.004736842
280	0.027891	0.00122807	1900	0.104701	0.004871795
300	0.029228	0.001304348			



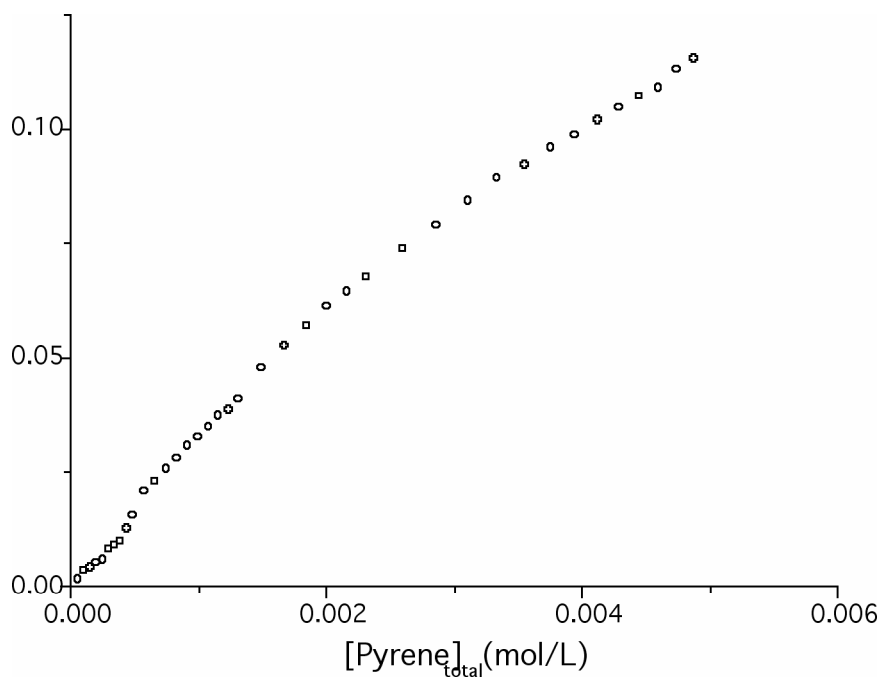
Titration data for pyrene with metallocycle **3a**·4OTf·2PF₆ in CH₃CN:

A 1 mM solution of host (**3a**·4OTf·2PF₆) in CH₃CN and a solution host (1 mM) and guest (pyrene, 10 mM) in CH₃CN were separately prepared. Aliquots of the guest/host solution (10 μ L initially, then 20 μ L, then 50 μ L, and finally 100 μ L) were added to the host solution (2 mL). The spectrum was recorded after each addition and overall 39 data points were obtained. The association constants were determined by using the nonlinear least squares fitting of the titration curves plotting A of the host-guest complex charge-transfer band against the molar equivalent of the guest. All of the titration curves were well fitted to the expression of a 1:1 binding isotherm.

Temperature: 300 K. $\lambda_{\text{max}} = 452$ nm. $K_a = 145 \pm 7$ M⁻¹ (adj. R² = 0.99887).

Total volume added (μ L)	A	[Pyrene] _{total} (mol/L)	Total volume added (μ L)	A	[Pyrene] _{total} (mol/L)
10	0.001754	4.97512E-05	350	0.048022	0.001489362
20	0.001982	9.90099E-05	400	0.052782	0.001666667
30	0.003699	0.000147783	450	0.0571	0.001836735
40	0.005462	0.000196078	500	0.061409	0.002
50	0.006118	0.000243902	550	0.064521	0.002156863
60	0.008311	0.000291262	600	0.067749	0.002307692
70	0.008008	0.000338164	700	0.074008	0.002592593
80	0.009966	0.000384615	800	0.079089	0.002857143
90	0.012795	0.000430622	900	0.084436	0.003103448
100	0.01556	0.00047619	1000	0.089472	0.003333333
120	0.021043	0.000566038	1100	0.092324	0.003548387
140	0.023101	0.000654206	1200	0.096177	0.00375
160	0.025808	0.000740741	1300	0.098983	0.003939394
180	0.028067	0.000825688	1400	0.10213	0.004117647
200	0.030938	0.000909091	1500	0.10474	0.004285714
220	0.032818	0.000990991	1600	0.107243	0.004444444
240	0.035053	0.001071429	1700	0.109135	0.004594595

260	0.037603	0.001150442	1800	0.113285	0.004736842
280	0.038885	0.00122807	1900	0.115629	0.004871795
300	0.041304	0.001304348			



Determination of the association constant (K_a) by liquid-liquid extraction.

Freshly prepared solutions of host (**3a**·4OTf·2PF₆, 5 mL 1mM in H₂O saturated with heptane) and guest (pyrene, 5 mL 10mM in heptane saturated with H₂O) were mixed and the mixture sonicated at room temperature for 2 hours. An aliquot of the resulting organic phase was diluted and analyzed.

Computational Methods

All calculations were performed using the Gaussian 03 (Revision C.01)¹ program package with the B3LYP^{2, 3} three parameter hybrid density functional. In vacuo geometry optimization of **3a** was carried out without constraints. Initial geometries were constructed using the GaussView program⁴ and standard bond distances and angles. In these calculations we used the standard 6-31G(d) basis set for C, H and N atoms, while for Pd the LanL2DZ valence and effective core potential functions were used.⁵ The stationary points found on the potential energy surfaces as a result of the geometry optimizations have been tested to represent energy minima rather than saddle points via frequency analysis.

	Coordinates (Angstroms)		
	X	Y	Z
C1	11.586	-1.419	0.365
H2	12.369	-2.124	0.067
H3	11.616	-1.318	1.454
C4	2.734	-4.328	-1.021
H5	3.305	-4.557	-1.914
C6	-2.734	4.327	-1.021
H7	-3.305	4.556	-1.915
C8	-1.396	4.691	-0.997
H9	-0.911	5.183	-1.832
C10	1.397	-4.691	-0.997
H11	0.911	-5.184	-1.831
C12	-6.399	1.851	-1.134
H13	-6.785	1.406	-2.044
C14	7.386	1.997	-1.203
H15	7.894	1.628	-2.088
C16	6.600	3.144	-1.262
H17	6.524	3.671	-2.209
C18	6.955	1.755	1.066
H19	7.134	1.198	1.979
C20	6.152	2.889	1.069
H21	5.710	3.209	2.008
C22	5.956	3.625	-0.112
C23	5.149	4.919	-0.127
H24	5.486	5.539	0.711
H25	5.399	5.477	-1.037
C26	3.629	4.771	-0.052
C27	2.915	4.134	-1.079
H28	3.443	3.704	-1.926
C29	2.904	5.342	1.006
H30	3.423	5.883	1.793
C31	1.509	5.268	1.058
H32	0.972	5.753	1.868
C33	1.525	4.046	-1.047
H34	0.996	3.528	-1.841

C35	0.831	4.610	0.030
C36	-3.323	3.696	0.091
C37	-4.690	3.099	0.045
C38	-5.487	2.965	1.195
H39	-5.205	3.410	2.143
C40	-5.196	2.551	-1.145
H41	-4.652	2.619	-2.081
C42	-6.681	2.251	1.131
H43	-7.294	2.127	2.018
C44	6.399	-1.852	-1.134
H45	6.786	-1.406	-2.044
C46	6.681	-2.251	1.131
H47	7.294	-2.126	2.018
C48	5.487	-2.964	1.195
H49	5.205	-3.410	2.143
C50	5.196	-2.551	-1.145
H51	4.652	-2.620	-2.081
C52	4.690	-3.099	0.045
C53	-0.831	-4.610	0.030
C54	3.323	-3.696	0.091
C55	-1.525	-4.047	-1.047
H56	-0.996	-3.529	-1.842
C57	-2.914	-4.134	-1.080
H58	-3.442	-3.706	-1.927
C59	-3.629	-4.771	-0.052
C60	-2.904	-5.342	1.006
H61	-3.423	-5.881	1.793
C62	-1.509	-5.267	1.058
H63	-0.973	-5.752	1.869
C64	-5.149	-4.919	-0.127
H65	-5.399	-5.477	-1.037
H66	-5.486	-5.540	0.711
C67	-5.955	-3.625	-0.112
C68	-6.152	-2.889	1.069
H69	-5.710	-3.209	2.008
C70	-6.599	-3.144	-1.262
H71	-6.524	-3.671	-2.209
C72	-6.955	-1.755	1.066
H73	-7.135	-1.198	1.980
C74	-7.386	-1.997	-1.202
H75	-7.894	-1.628	-2.087
C76	2.521	-3.560	1.240
H77	2.903	-3.109	2.149
C78	1.186	-3.920	1.213
H79	0.523	-3.759	2.054
C80	-1.187	3.921	1.213
H81	-0.524	3.760	2.054
C82	11.755	-0.078	-0.322
H83	12.680	0.419	-0.011
H84	11.774	-0.184	-1.410
C85	-2.521	3.560	1.240
H86	-2.903	3.110	2.149
C87	-11.586	1.419	0.365
H88	-11.617	1.318	1.454
H89	-12.369	2.124	0.067
C90	-11.755	0.078	-0.322

H91	-11.774	0.184	-1.410
H92	-12.680	-0.419	-0.011
N93	-7.567	-1.305	-0.055
N94	-7.122	1.674	-0.008
N95	-0.619	4.435	0.090
N96	7.567	1.305	-0.055
N97	7.122	-1.674	-0.008
N98	0.619	-4.435	0.090
N99	-10.225	1.959	-0.004
H100	-9.978	2.735	0.617
H101	-10.258	2.360	-0.947
N102	-10.561	-0.774	0.032
H103	-10.513	-1.590	-0.584
H104	-10.670	-1.149	0.980
N105	10.561	0.774	0.032
H106	10.513	1.590	-0.584
H107	10.670	1.149	0.980
N108	10.225	-1.959	-0.004
H109	9.978	-2.735	0.617
H110	10.258	-2.360	-0.947
Pd111	8.818	-0.390	-0.008
Pd112	-8.818	0.390	-0.008

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