

A Self-assembled M_2L_2 Truncated Square and its Application as a Container for Fullerenes

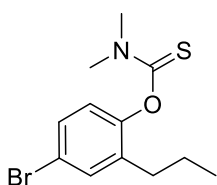
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Section A. Materials and General Methods

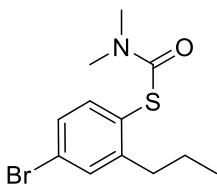
4-bromo-2-propylphenol^[S1], 1,4-dibromo-2,5-bis(methylsulfinyl)benzene^[S2], and [Pt(**dppp**)(OTf)₂]^[S3] were synthesized according to literatures. All other reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. Tetrahydrofuran (THF), dichloromethane (DCM) and dimethylformamide (DMF) were degassed and dried under nitrogen by passing them through a Vigor VSGS-5 Solvent Purification System. Reaction progress was monitored by thin layer chromatography (TLC) or on an Advion Plate Express[®] Automated TLC plate reader (TLC/CMS). Flash column chromatography was performed over silica gel (200-300 mesh). NMR spectra were recorded on the JEOL 400YH instrument. NMR spectra were internally referenced to tetramethylsilane (¹H) or alternatively to the residual proton solvent signal. All ¹³C NMR spectra were recorded with complete proton decoupling. Fluorescence measurements were conducted on a Perkin-Elmer LS-55 spectrofluorophotometer using a xenon lamp as the light source, an excitation wavelength of 370 nm was used. High resolution mass spectra of new compounds were recorded on LTQ Orbitrap Elite LC/MS (ESI or APCI) or MAT 95XP (Thermo, EI). Cyclic voltammetry (CV) experiments were carried out on a Chenhua CHI600E electrochemical workstation.

Section B. Synthesis and Characterization of compounds



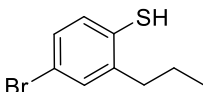
O-(4-bromo-2-propylphenyl) dimethylcarbamothioate: A 250 mL dry Schlenk flask was charged with 4-bromo-2-propylphenol (3.0 g, 14.0 mmol, 1.0 equiv.), dimethylthiocarbamoyl chloride (2.3 g, 18.2 mmol, 1.3 equiv.), DABCO (2.1 g, 18.2 mmol, 1.3 equiv.) and anhydrous acetonitrile (60 mL). Then the reaction mixture was stirred at 90 °C for 16 h under N₂ atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure. HCl (1 M, 100 mL) was then added, and the mixture was extracted with CH₂Cl₂ (50 mL × 3). The organic layers were combined and dried over Na₂SO₄, then the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (petroleum ether/dichloromethane = 2:1) to give desired compound as a white oil (3.26 g, 77% yield). ¹H NMR (400 MHz, Chloroform-d, room temperature) δ 7.40 – 7.30 (m, 2H), 6.88 (d, J = 8.5 Hz, 1H), 3.41 (dt, J = 44.6, 0.6 Hz, 6H), 2.53 – 2.39 (m, 2H), 1.68 – 1.58 (m, 2H),

0.94 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 187.20, 151.32, 137.38, 132.99, 129.76, 125.29, 119.27, 43.49, 38.70, 32.18, 23.00, 14.08. HRMS (APCI) (m/z): calcd. for C₁₂H₁₇BrNOS⁺ [M+H]⁺ 302.0209, found: 302.0202.



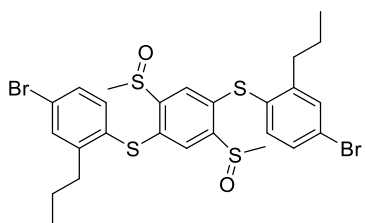
S-(4-bromo-2-propylphenyl) dimethylcarbamothioate: Under an N₂ atmosphere, a 100 mL dry round-bottom flask was charged with O-(4-bromo-2-propylphenyl) dimethylcarbamothioate (3.8 g, 12.62 mmol) and anhydrous tetraethylene glycol dimethyl ether (38 mL). The reaction mixture was reflux for

1.5 h at 275 °C. The reaction mixture was subsequently cooled to room temperature, poured into 150 mL ethyl acetate, and then washed with saturated sodium chloride (50 mL × 3). The organic layers were combined and dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel with DCM/PE (v/v = 1/2) as eluent to give the titled product (3.10 g, 81% yield) as a yellow oil. ¹H NMR (400 MHz, Chloroform-d) δ 7.43 (d, J = 1.5 Hz, 1H), 7.34 – 7.32 (m, 2H), 3.07 (d, J = 36.4 Hz, 6H), 2.75 – 2.66 (m, 2H), 1.65 – 1.56 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 166.31, 149.08, 139.09, 132.68, 129.66, 127.07, 124.38, 37.10, 36.45, 24.05, 14.06. HRMS (APCI) (m/z): calcd. for C₁₂H₁₇BrNOS⁺ [M+H]⁺ 302.0209, found: 302.0204.



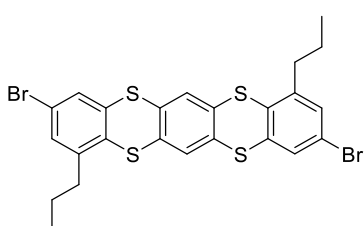
4-bromo-2-propylbenzenethiol: Under an N₂ atmosphere, a dry 100 mL round-bottom flask was charged with compound S-(4-bromo-2-propylphenyl) dimethylcarbamothioate (2.51 g, 8.3 mmol, 1.0 equiv.), KOH (3.27 g, 58.2 mmol,

7 equiv.) and 12 mL of CH₃OH. The reaction mixture was reflux for 1 h. After cooling to room temperature, poured into 100 mL ice water. Then a solution of 37% aq. HCl was added to reach pH < 3, and the mixture was extracted with CH₂Cl₂ (50 mL × 3). The organic layers were combined and dried over Na₂SO₄, filtered, and concentrated in vacuum to give the product as a yellow oil (1.9 g, 99% yield). ¹H NMR (400 MHz, Chloroform-d) δ 7.28 (d, J = 2.2 Hz, 1H), 7.20 – 7.11 (m, 2H), 3.28 (s, 1H), 2.64 – 2.56 (m, 2H), 1.69 – 1.56 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H). ¹³C NMR (400 MHz, Chloroform-d) δ 142.76, 132.38, 132.03, 129.62, 129.51, 119.61, 36.59, 22.66, 13.98. HRMS (EI) (m/z): calcd. for C₉H₁₁BrS⁺ [M]⁺ 229.97594, found: 229.97625.



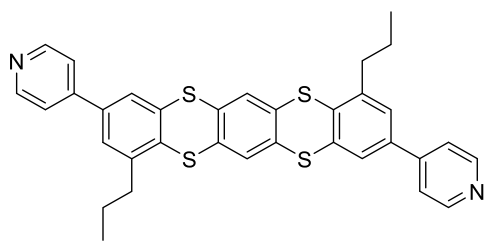
(2): A 250 mL dry Schlenk flask was charged with 1,4-dibromo-2,5-bis(methylsulfinyl)benzene (1.19 g, 3.3 mmol, 1.0 equiv.), 4-bromo-2-propylbenzenethiol (1.83 g, 8.0 mmol, 2.4 equiv.), K_2CO_3 (1.38 g, 10.0 mmol, 3.0 equiv.) and anhydrous DMAc (45 mL). Then the reaction

mixture was stirred at 120 °C for 24 h under N_2 atmosphere. After cooling to room temperature, the mixture was filtered and concentrated in vacuum. The residue was dissolved in DCM (150 mL) and washed several times with saturated solution of NaCl. The organic layers were combined and dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel with CH_2Cl_2 as eluent to give **2** (1.72 g, 79% yield) as a white solid. 1H NMR (400 MHz, Chloroform- d) δ 7.71 (d, J = 4.6 Hz, 2H), 7.44 (dd, J = 3.9, 2.2 Hz, 2H), 7.30 (dt, J = 8.3, 2.4 Hz, 2H), 7.03 (dd, J = 8.3, 5.0 Hz, 2H), 2.81 (s, 3H), 2.75 (s, 3H), 2.73 – 2.61 (m, 3H), 1.69 – 1.57 (m, 2H), 0.95 (dd, J = 7.7, 7.0 Hz, 7H). ^{13}C NMR (100 MHz, Chloroform- d) δ 150.09, 146.29, 134.28, 133.68, 133.48, 130.67, 129.95, 127.24, 123.60, 77.41, 77.30, 77.10, 76.78, 42.48, 36.17, 23.84, 14.01. HRMS (ESI) (m/z): calcd. for $C_{26}H_{29}Br_2O_2S_4^+$ [$M+H$] $^+$ 660.9391, found: 660.9388.

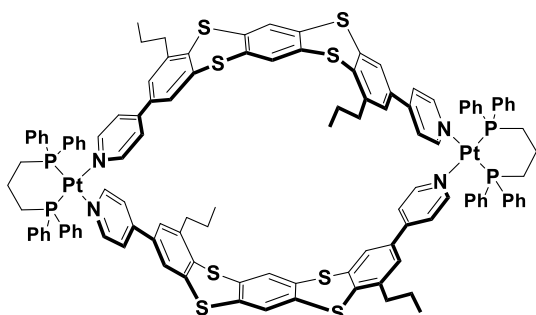


(3): Under an N_2 atmosphere, a dry 100 mL round-bottom flask was charged with **2** (1.6 g, 2.42 mmol, 1.0 equiv.), P_2O_5 (3.44 g, 24.2 mmol, 10 equiv.) and 30 mL of trifluoromethanesulfonic acid. The reaction mixture was stirred for 12 h at room temperature and then cooled to

0 °C in an ice bath. 100 mL of ice water and 25 mL of pyridine added dropwise with stirring. The reaction mixture was subsequently heated to 110 °C and stirred for another 6 h. After cooling to room temperature, the mixture was filtered and filter cake was washed with H_2O (100 mL) to give **3** (1.30 g, 90% yield) as an earthy yellow solid, and **3** can be used directly for the next reaction without further purification. 1H NMR (400 MHz, Chloroform- d) δ 7.62 (d, J = 0.7 Hz, 2H), 7.49 (d, J = 2.1 Hz, 2H), 7.27 (d, J = 2.1 Hz, 2H), 2.82 – 2.68 (m, 5H), 1.70 – 1.57 (m, 4H), 0.99 (t, J = 7.3 Hz, 7H). ^{13}C NMR (100 MHz, Chloroform- d) δ 143.94, 137.15, 136.04, 135.73, 134.03, 131.56, 129.43, 128.29, 121.23, 36.71, 23.82, 13.97. HRMS (ESI) (m/z): calcd. for $C_{24}H_{20}Br_2S_4^+$ [M] $^+$ 595.8788, found: 595.8793.



(1): A 50 mL dry Schlenk flask was charged with **3** (596 mg, 1.0 mmol, 1 equiv.), 4-Pyridylboronic acid (351 mg, 2.85 mmol, 2.85 equiv.), K_2CO_3 (1.38 g, 10 mmol, 10 equiv.), $Pd(PPh_3)_4$ (118 mg, 0.1 mmol, 0.1 equiv.), H_2O (7 mL) and DMF (52 mL). Then the reaction mixture was stirred at 100 °C for 16 h under N_2 atmosphere. After cooling to room temperature, the mixture was filtered and concentrated in vacuum. The residue was dissolved in DCM (150 mL) and washed several times with saturated solution of NaCl. The organic layers were combined and dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel with DCM/MeOH (v/v = 30/1) as eluent to give **1** (442 mg, 74% yield) as a white solid. 1H NMR (400 MHz, Chloroform-d) δ 8.67 (s, 5H), 7.69 (s, 2H), 7.63 (d, $J = 1.9$ Hz, 2H), 7.54 (s, 4H), 7.41 (d, $J = 2.0$ Hz, 2H), 2.96 – 2.83 (m, 5H), 1.71 (h, $J = 7.4$ Hz, 5H), 1.04 (t, $J = 7.3$ Hz, 7H). ^{13}C NMR (100 MHz, Chloroform-d) δ 150.26, 147.14, 143.18, 137.56, 136.35, 136.18, 136.09, 135.71, 128.35, 127.39, 125.33, 121.63, 37.02, 24.01, 14.06. HRMS (APCI) (m/z): calcd. for $C_{34}H_{29}N_2S_4^+$ $[M+H]^+$ 593.1208, found: 593.1199.



[Pt₂(dppp)₂(1)₂(OTf)₄]: **1** (0.30 mg, 0.51 μ mol, 1 equiv.) and $[Pt(dppp)(OTf)_2]$ (0.459 mg, 0.51 μ mol, 1 equiv.) were dissolved in 0.6 mL of CH_2Cl_2 in a 2 mL vial. The reaction mixture was allowed to stir for 2 h at room temperature to give the $[Pt_2(dppp)_2(1)_2(OTf)_4]$. Further purification of the product was carried out by slow evaporation of a similar sample in $CH_2Cl_2/1,4$ -dioxane. 1H NMR (CD_2Cl_2 , 298K, 400 MHz) δ (ppm): δ 8.91 (s, 4H), 7.78 – 7.52 (m, 12H), 7.30 (d, $J = 26.1$ Hz, 18H), 7.22 – 7.09 (m, 6H), 3.26 (s, 4H), 2.82 – 2.65 (m, 4H), 2.43 – 2.04 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 10H). The $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 298K, 162MHz) δ (ppm): -14.39 ppm. ESI-TOF-MS: m/z 600.1146 $[M-4OTf]^{4+}$, 849.8026 $[M-3OTf]^{3+}$, 1349.1776 $[M-2OTf]^{2+}$.

Section C. Self-assembly of **1** with [Pt(dppp)(OTf)₂]

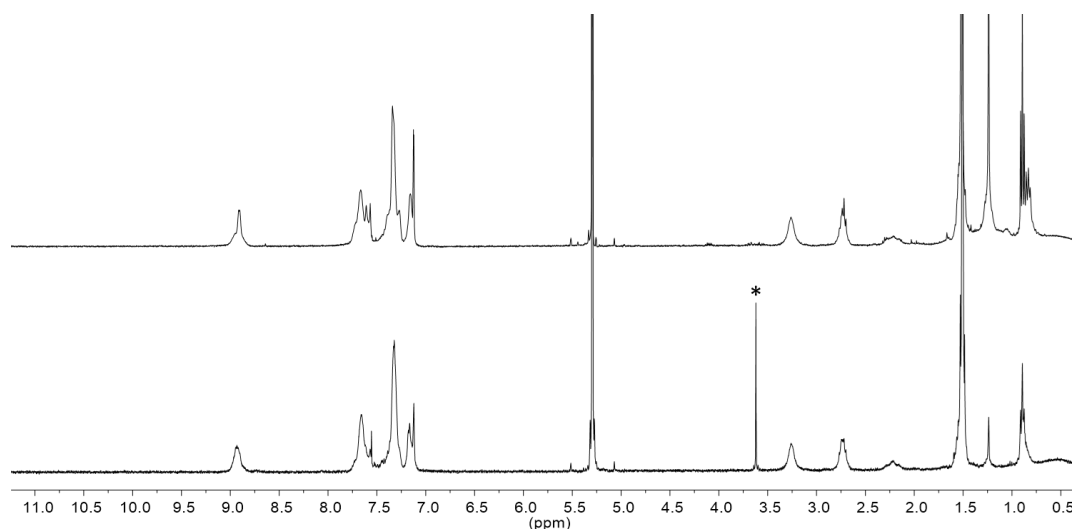


Figure S1. ¹H NMR (400 MHz, 298K, CD₂Cl₂) spectra of (top) purified [Pt₂(dppp)₂(**1**)₂(OTf)₄] and (bottom) an equimolar (1.70 mM) mixture of [Pt(dppp)(OTf)₂] and **1**. (* 1,4-dioxane).

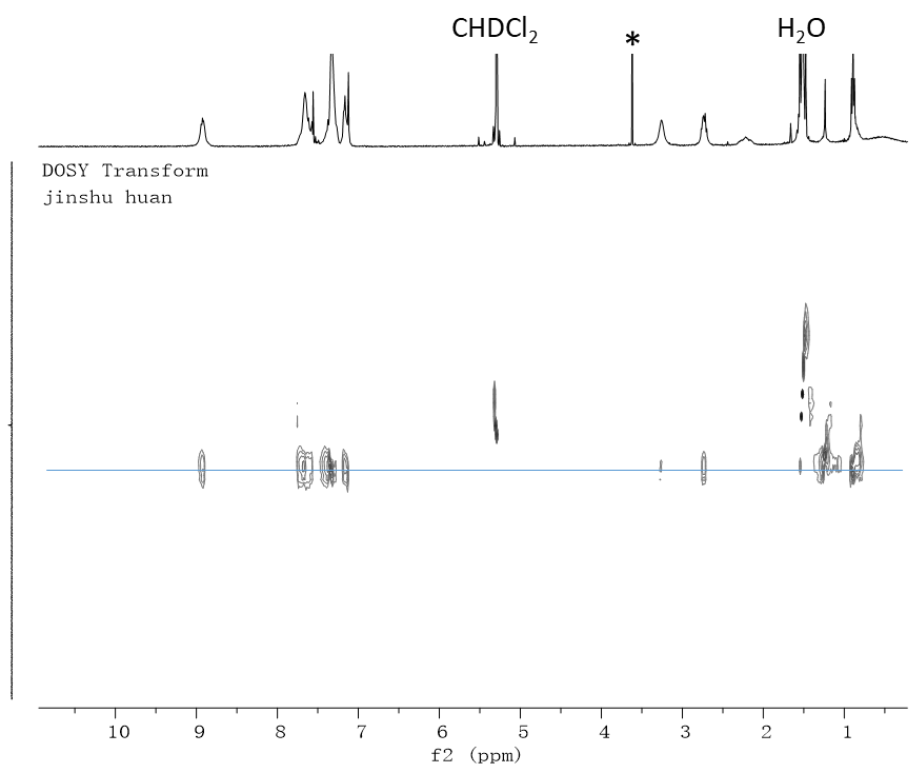


Figure S2. DOSY spectrum of an equimolar mixture of [Pt(dppp)(OTf)₂] and **1** in CD₂Cl₂ (1.70 mM, 400 MHz, 298K). Diffusion time = 100 ms, Grad 1 = 1 ms, Grad 1 amp = 100 mT/m ~ 0.297 T/m. Relaxation delay = 10 s.

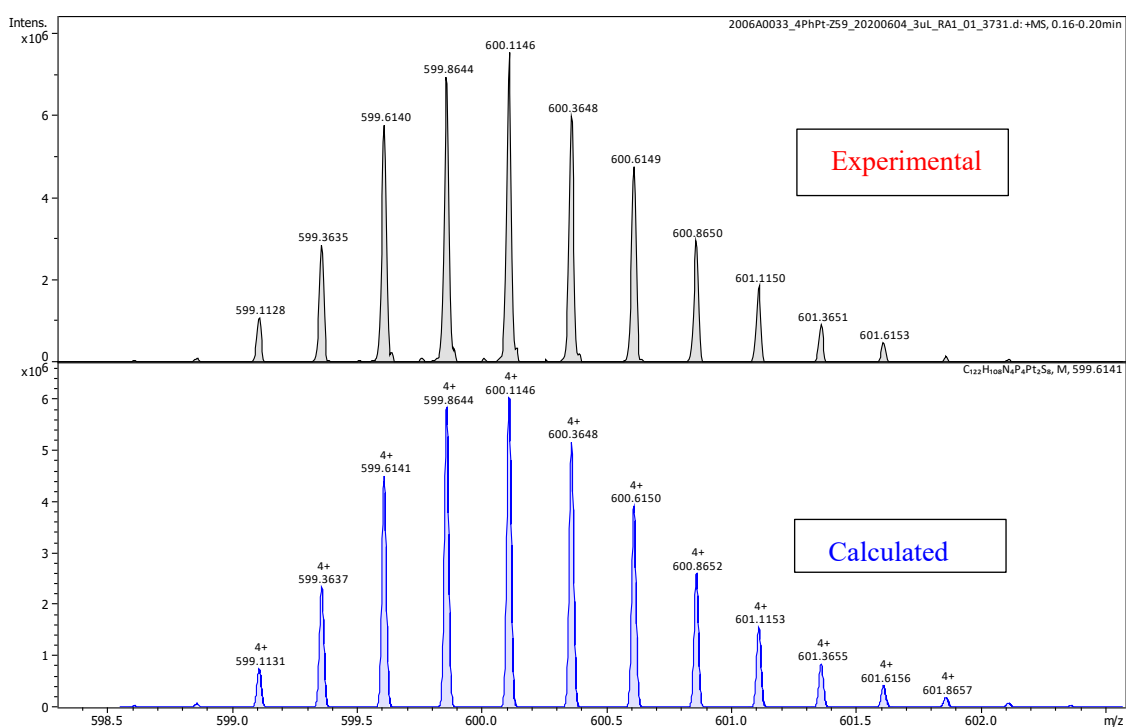
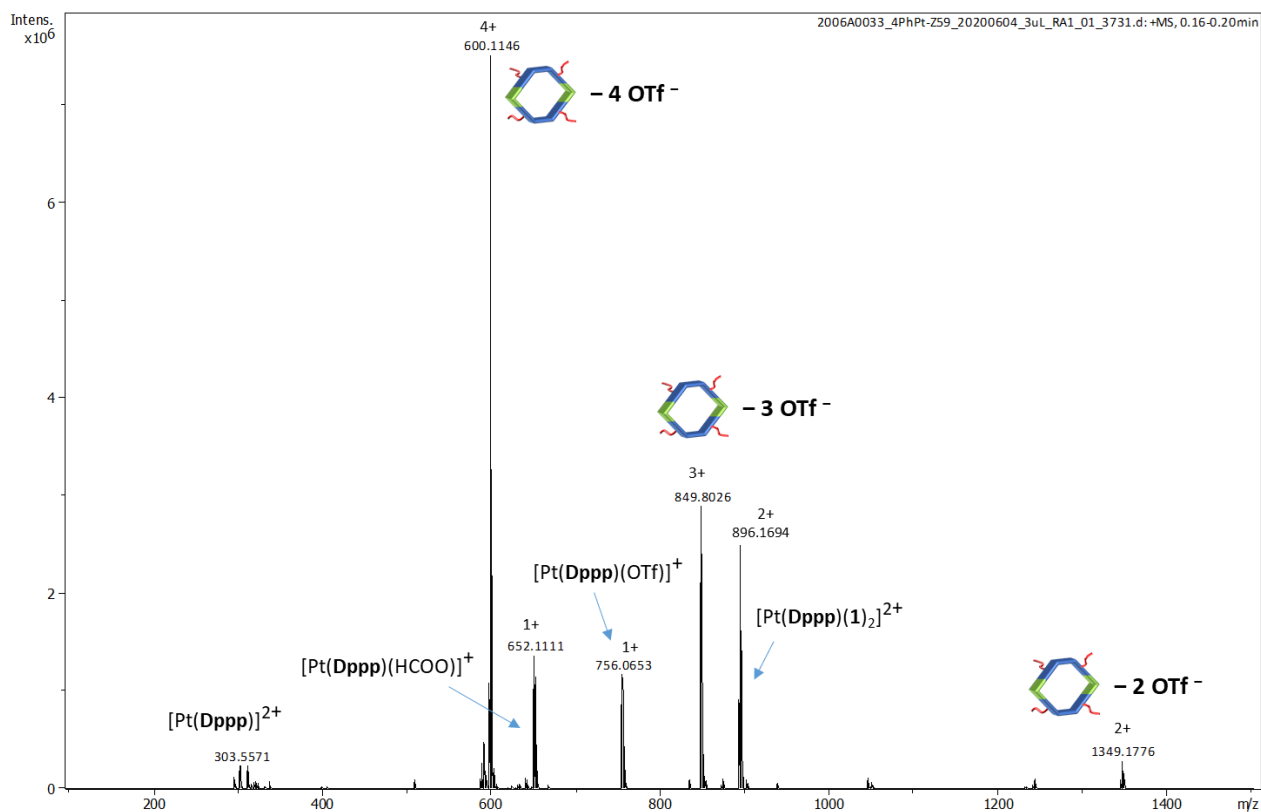


Figure S3. ESI-TOF-MS spectra of an equimolar mixture of $[Pt(\mathbf{dppp})(OTf)_2]$ and **1** in CD_2Cl_2 . Full spectrum (top), and experimental and simulated isotopic pattern for $[Pt_2(\mathbf{dppp})_2(\mathbf{1})_2]^{4+}$ (bottom).

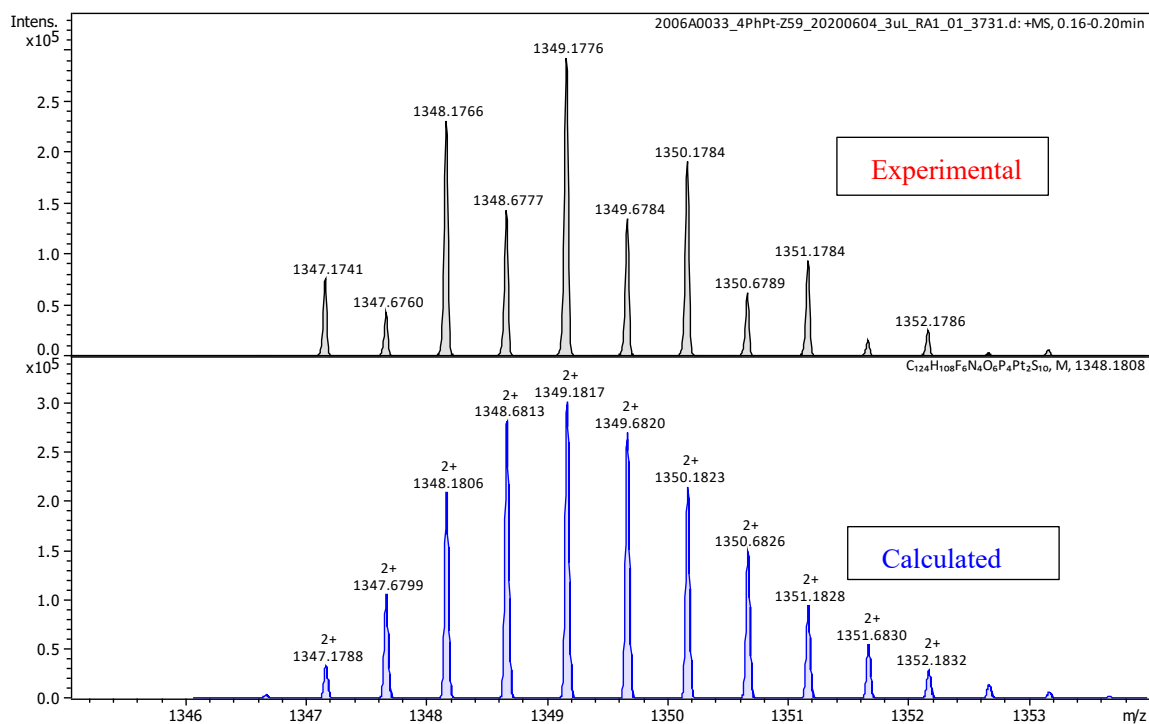
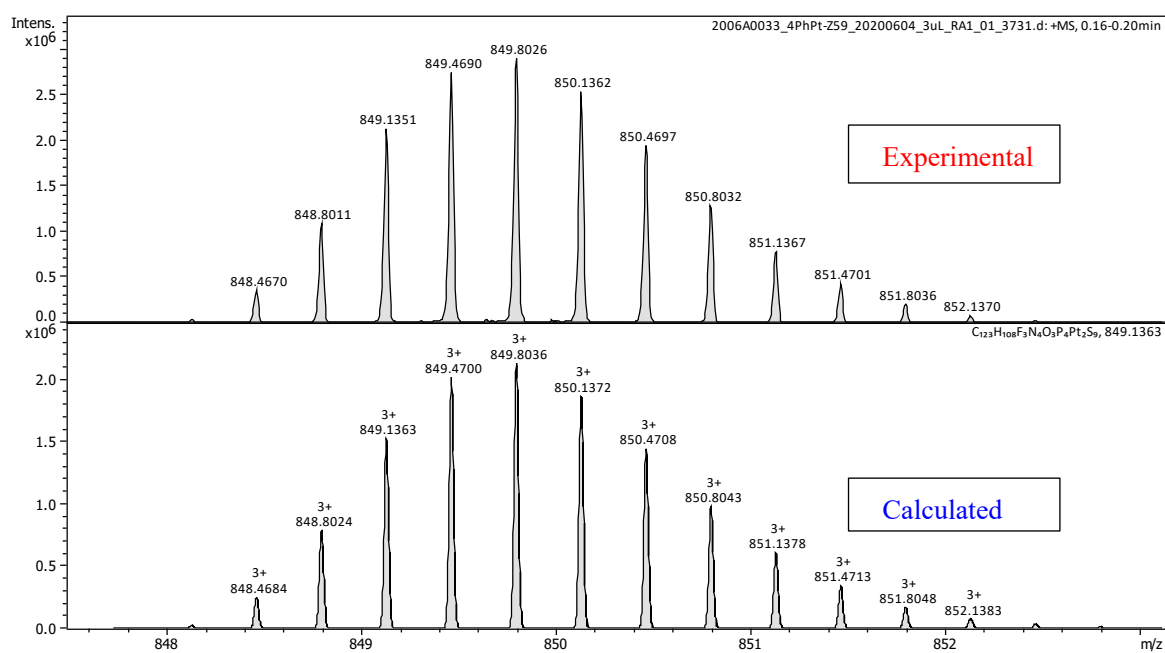


Figure S4. Experimental and simulated isotopic pattern for $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})]^{3+}$ (top) and $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_2]^{2+}$ (bottom) on ESI-TOF-MS spectra of an equimolar mixture of $[\text{Pt}(\text{dppp})(\text{OTf})_2]$ and $\mathbf{1}$ in CD_2Cl_2 .

Section D. Host-guest chemistry of $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ towards C_{60} and C_{70} .

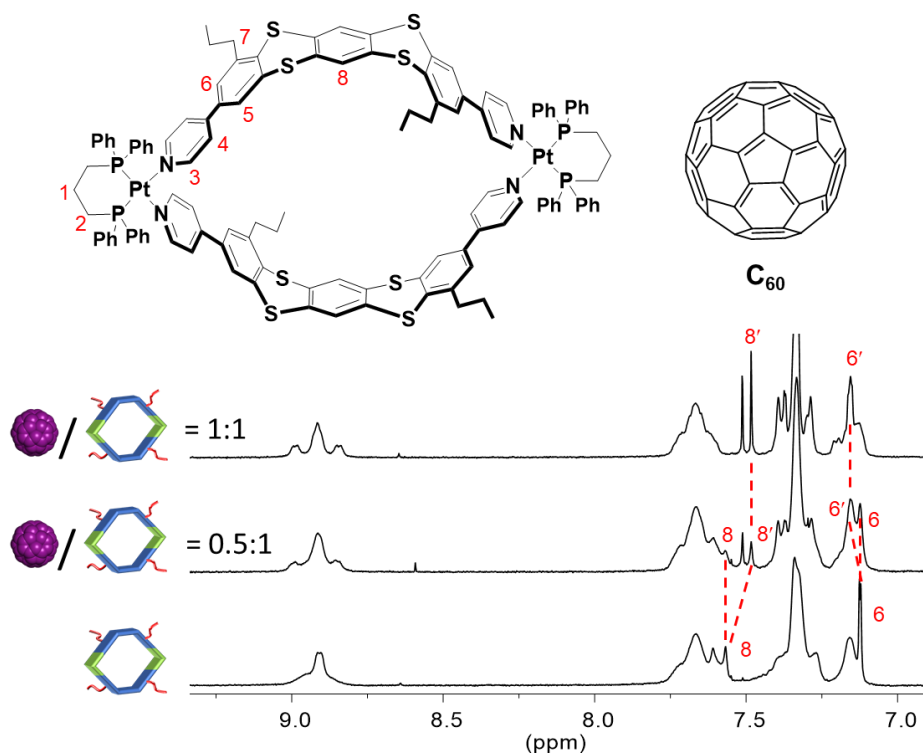


Figure S5. ^1H NMR spectra (400 MHz, 298K, CD_2Cl_2) comparison of $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ (1.0 mM) added with various equivalents of C_{60} . From bottom to top: 0.0, 0.5, and 1.0 equiv. of C_{60} .

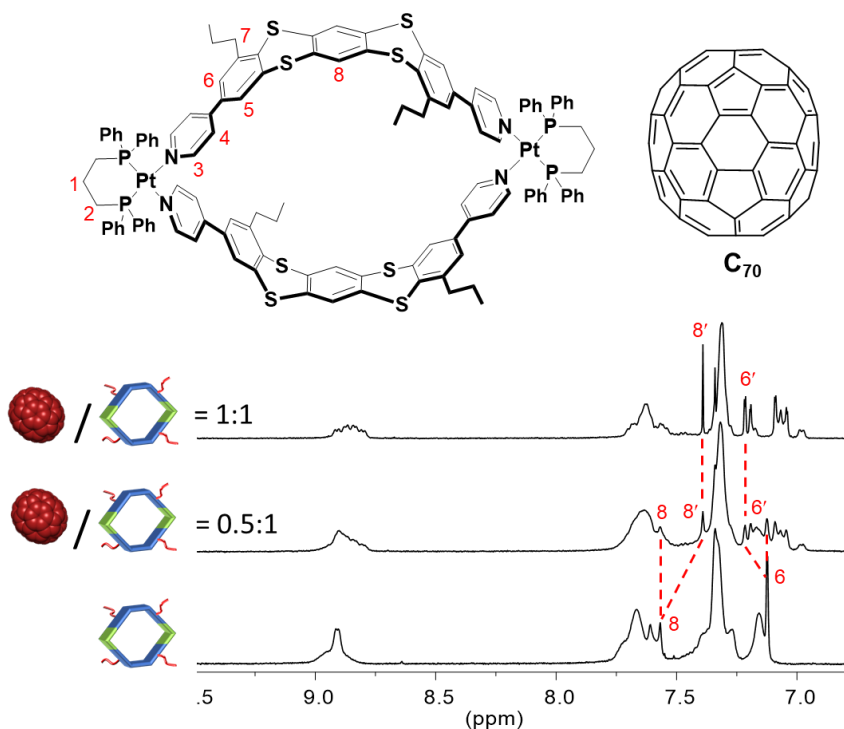


Figure S6. ^1H NMR spectra (400 MHz, 298K, CD_2Cl_2) comparison of $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ (1.0 mM) added with various equivalents of C_{70} . From bottom to top: 0.0, 0.5, and 1.0 equiv. of C_{70} .

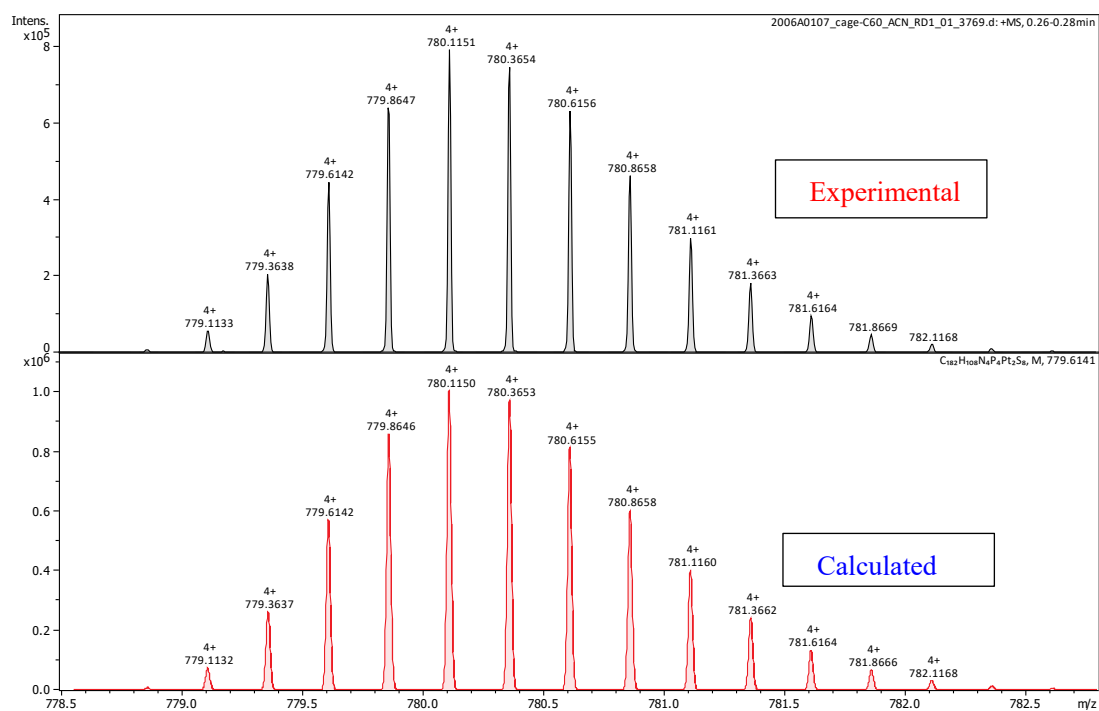
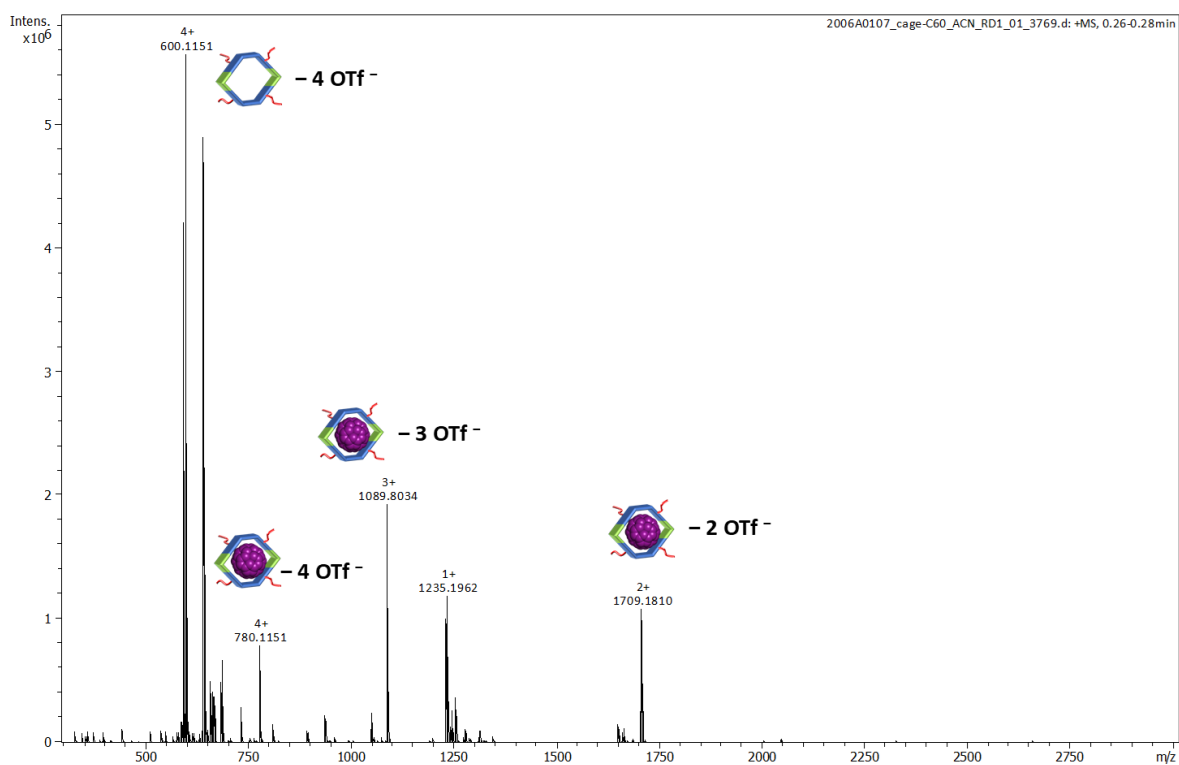


Figure S7. ESI-TOF-MS spectra of an equimolar mixture of $[Pt_2(\mathbf{dppp})_2(\mathbf{1})_2(OTf)_4]$ and C_{60} in CD_2Cl_2 . Full spectrum (top), and experimental and simulated isotopic pattern for $\{C_{60}C[Pt_2(\mathbf{dppp})_2(\mathbf{1})_2]\}^{4+}$ (bottom).

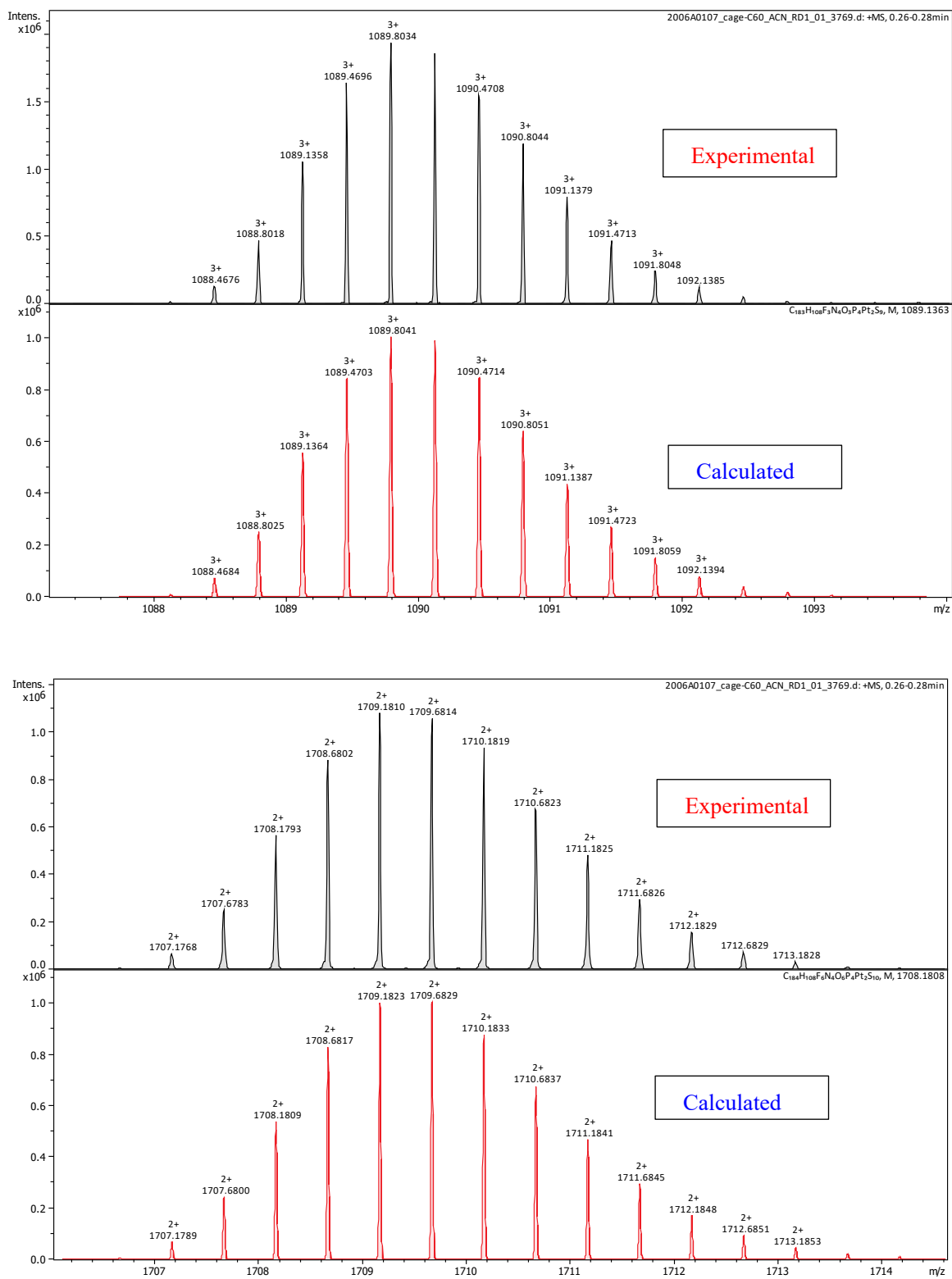


Figure S8. Experimental and simulated isotopic pattern for $\{C_{60}[Pt_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})]\}^{3+}$ (top) and $\{C_{60}[Pt_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_2]\}^{2+}$ (bottom) on ESI-TOF-MS spectra of an equimolar mixture of $[Pt_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ and C_{60} in CD_2Cl_2 .

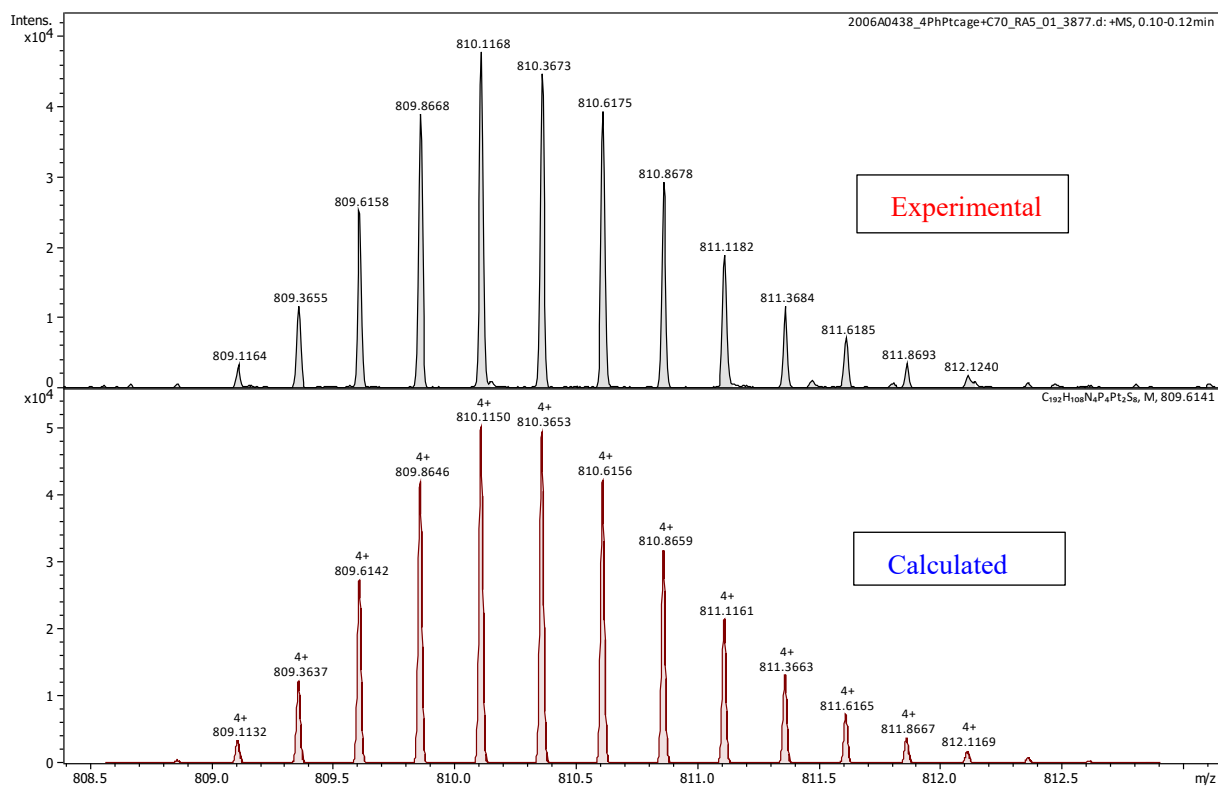
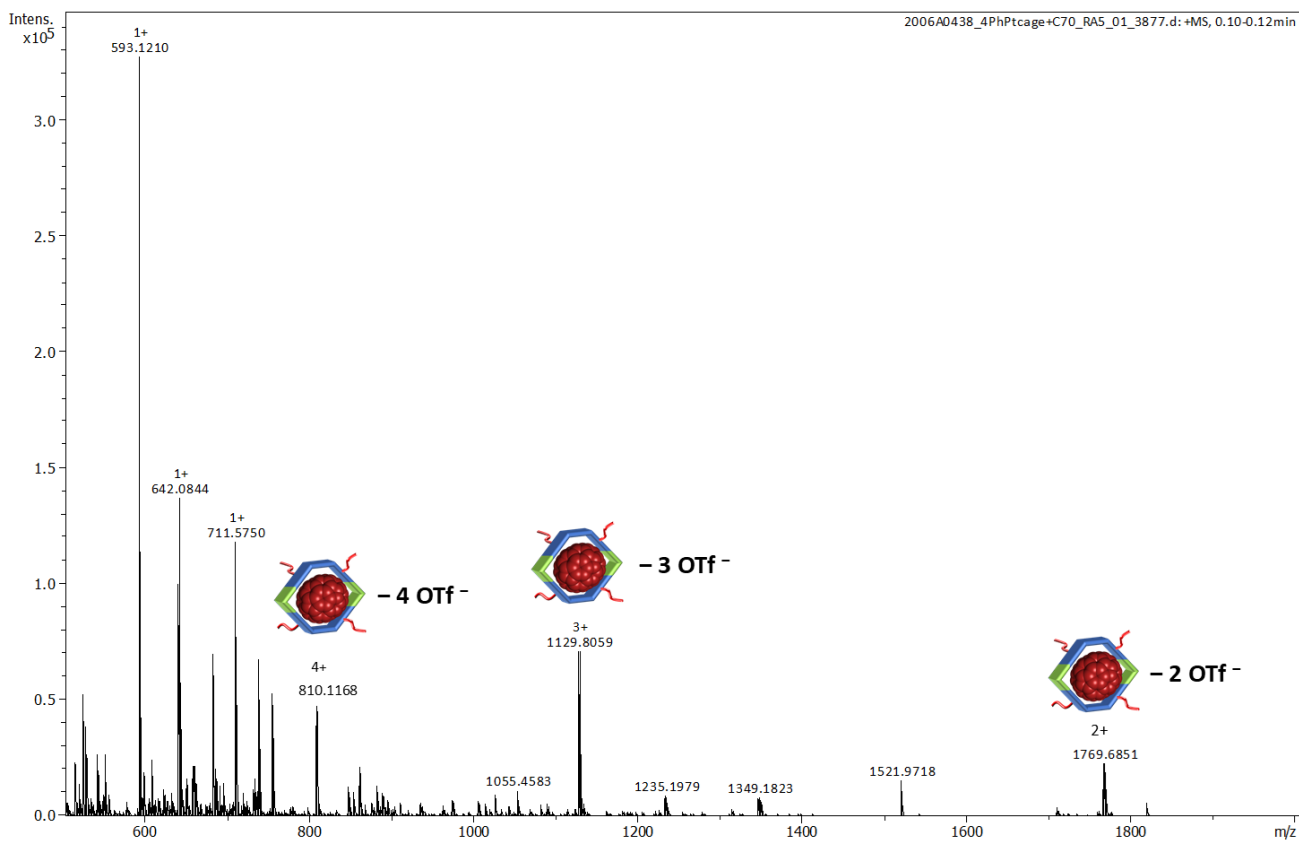


Figure S9. ESI-TOF-MS spectra of an equimolar mixture of $[Pt_2(\mathbf{dppp})_2(\mathbf{1})_2(OTf)_4]$ and C_{70} in CD_2Cl_2 . Full spectrum (top), and experimental and simulated isotopic pattern for $\{C_{70} \subset [Pt_2(\mathbf{dppp})_2(\mathbf{1})_2]\}^{4+}$ (bottom).

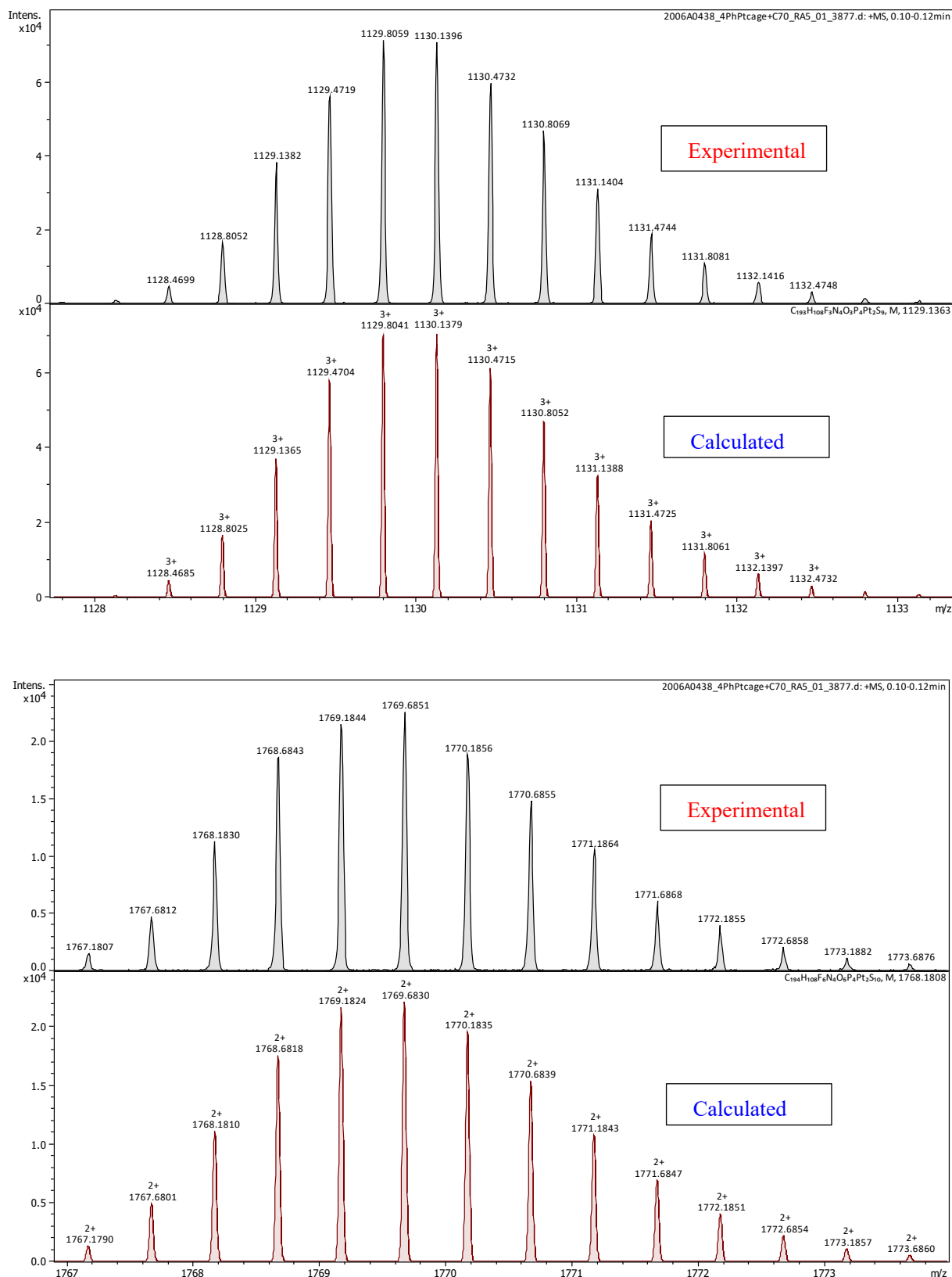


Figure S10. Experimental and simulated isotopic pattern for $\{C_{70}[Pt_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})]\}^{3+}$ (top) and $\{C_{70}[Pt_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_2]\}^{2+}$ (bottom) on ESI-TOF-MS spectra of an equimolar mixture of $[Pt_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ and C_{70} in CD_2Cl_2 .

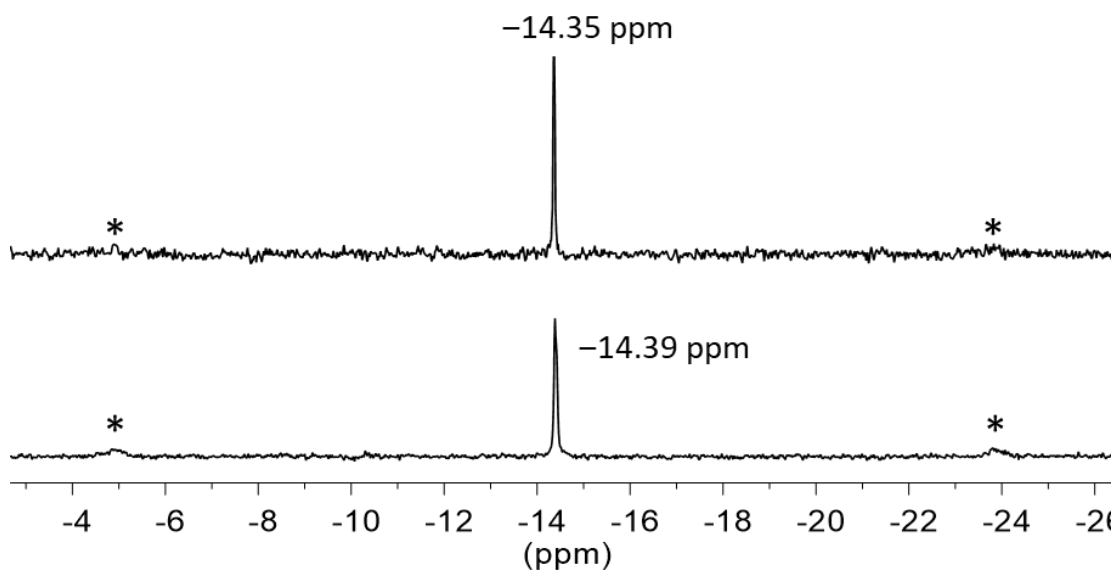


Figure S11. ^{31}P NMR spectra (162 MHz, 298K, CD_2Cl_2) comparison of $\text{C}_{60}\text{C}[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ (top) and $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ (bottom). *satellite peak arise from coupling with ^{195}Pt .

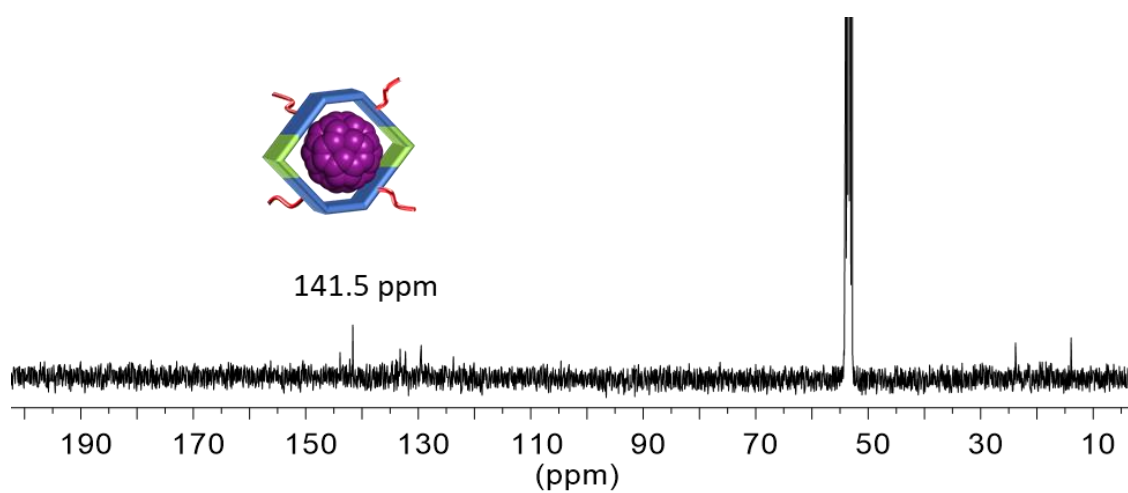


Figure S12. ^{13}C NMR spectrum (100 MHz, 298K, CD_2Cl_2) of $\text{C}_{60}\text{C}[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$.

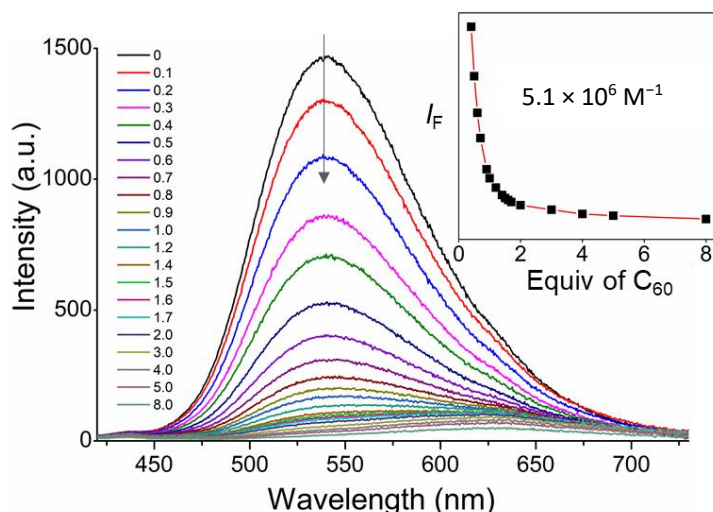


Figure S13. Fluorescence titration of $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ ($9.9 \mu\text{M}$) in dichloromethane upon addition of fullerene C_{60} (1.5 mM in toluene) from 0 to 8 equiv. in a 1.0 cm path cuvette while the concentration of $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ was maintained constant. Association constants were obtained by a global fitting analysis to a 1:1 binding model using Bindfit^[S4,S5] (<http://supramolecular.org/>).

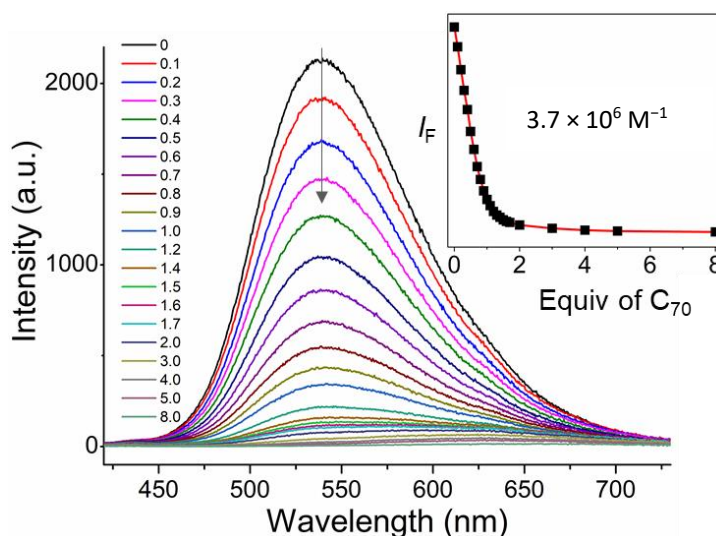


Figure S14. Fluorescence titration of $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ ($10 \mu\text{M}$) in dichloromethane upon addition of fullerene C_{70} (1.5 mM in toluene) from 0 to 8 equiv. in a 1.0 cm path cuvette while the concentration of $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ was maintained constant. Association constants were obtained by a global fitting analysis to a 1:1 binding model using Bindfit^[S3,S4] (<http://supramolecular.org/>).

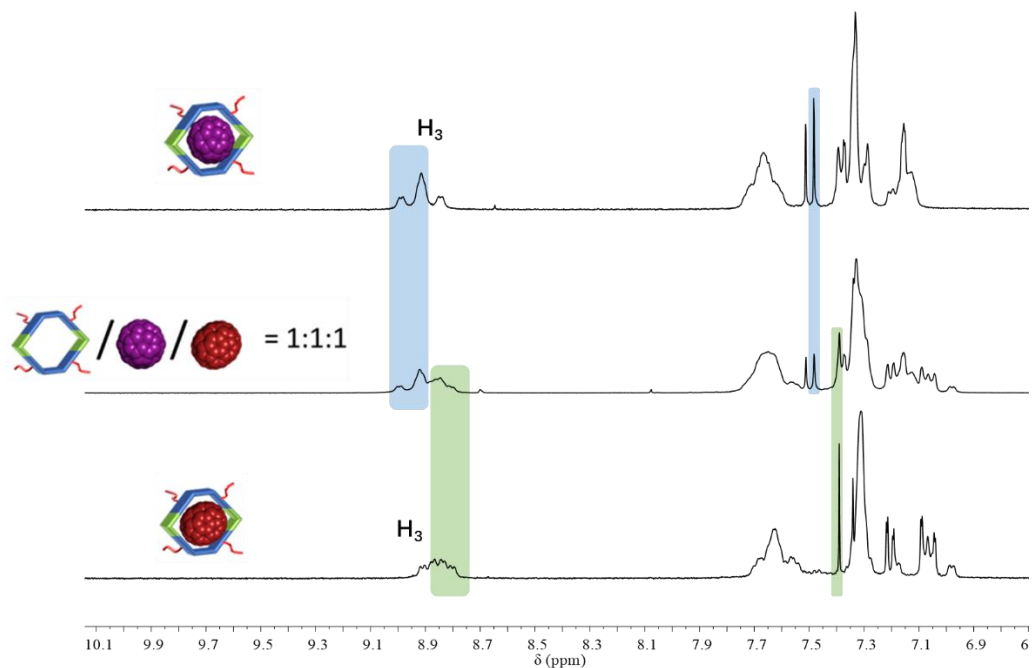


Figure S15. ^1H NMR spectra (400 MHz, 298K, CD_2Cl_2) of a 1:1:1 mixture of $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$, C_{60} , and C_{70} . The signals arise from complex $\text{C}_{60}\text{C}[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_2]$ are highlighted in blue; signals for complex $\text{C}_{70}\text{C}[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_2]$ are highlighted in green. The ratio of the complexed C_{60} to C_{70} is estimated to be 1/0.9 based on the resonance of pyridyl proton H_3 .

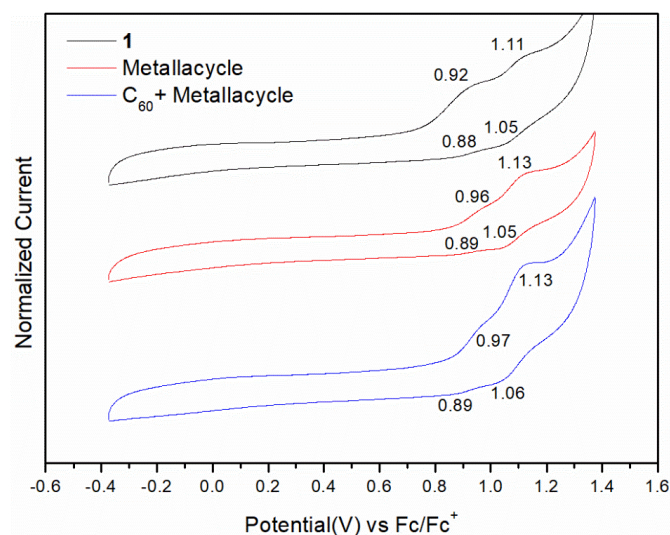


Figure S16. Cyclic voltammograms of $\mathbf{1}$, $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$, and an equimolar mixture of C_{60} and $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ (0.2 mM) in 1,1,2,2-tetrachloroethane/ acetonitrile (1:1) containing 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ as a supporting electrolyte. Scan rate: $100 \text{ mV}\cdot\text{s}^{-1}$. A three-electrode cell configuration consisting of a saturated calomel reference electrode, a glassy carbon electrode (1.6 mm in diameter) working electrode, and a Pt coil counter electrode was used. All potentials were referenced to the Fc/Fc^+ redox couple.

Section F. Details of X-ray Crystallography

Single crystals of **1** were obtained from vapor diffusion of hexanes into a tetrahydrofuran solution. Single crystals of $[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ were obtained via slow evaporation of a $\text{CH}_2\text{Cl}_2/1,4\text{-dioxane}$ mixture at room temperature for 2 days. Single crystals of $\text{C}_{60}\text{C}[\text{Pt}_2(\text{dppp})_2(\mathbf{1})_2(\text{OTf})_4]$ were obtained from vapor diffusion of hexanes into a tetrachloroethane solution at RT for a week.

Crystals were frozen in paratone oil inside a cryoloop under a cold stream of N_2 . Reflection data were collected either on a Rigaku SuperNova, Dual, AtlasS2 diffractometer using monochromatized $\text{Cu K}\alpha$ radiation or on a BRUKER D8 VENTURE PHOTON II diffractometer using $\text{MoK}\alpha$ radiation. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved using OLEX² crystallography software.^[S6,S7] When practical, non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in idealized positions and refined using a riding model. Figures were drawn with Pymol. Details can be obtained from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk for CCDC accession numbers 2113304, 2113305 and 2113306.

Table S1. Crystal Data, Solution and Refinement Parameters.

	1	[Pt ₂ (dppp) ₂ (1) ₂ (OTf) ₄](C ₄ H ₈ O ₂) ₆	C ₆₀ C-[Pt ₂ (dppp) ₂ (1) ₂ (OTf) ₄]
CCDC number	2113304	2113305	2113306
formula	C ₃₄ H ₂₈ N ₂ S ₄	C ₁₅₀ H ₁₅₆ F ₁₂ N ₄ O ₂₄ P ₄ Pt ₂ S ₁₂	C ₁₈₆ H ₁₀₈ F ₁₂ N ₄ O ₁₂ P ₄ Pt ₂ S ₁₂
formula weight	592.82	3525.56	3717.54
crystal system	Monoclinic	Triclinic	C2/c
space group	<i>P</i> 21/n	<i>P</i> -1	<i>P</i> 21/n
T (K)	223(2)	173(2)	173(2)
a (Å)	8.0280(1)	11.9342(2)	38.3955(6)
b (Å)	10.8723(2)	17.2712(2)	17.1804(3)
c (Å)	37.5335(5)	25.9639(3)	35.9313(7)
α (°)	90	103.668(1)	90
β (°)	94.368(1)	98.429(1)	103.070(2)
γ (°)	90	104.350(1)	90
V (Å³)	3266.52(9)	4916.75(12)	23088.1(7)
Z	4	1	4
ρ, g cm⁻³	1.205	1.191	1.069
μ, mm⁻¹	2.853	4.668	3.969
reflections used	6639	20261	20276
variables	363	991	1365
restraints	0	1356	14006
R₁ [<i>I</i> > 2σ(<i>I</i>)]^[a]	0.0526	0.0736	0.1267
R₁ (all data)	0.0580	0.0789	0.1627
R_{2w}[<i>I</i> > 2σ(<i>I</i>)]^[b]	0.1681	0.1898	0.3068
R_{2w} (all data)	0.1738	0.1952	0.3249
GoF on <i>F</i>²	0.967	1.087	1.125

^[a] R₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$; ^[b] R_{2w} = $[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, where $w = q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$

Section H. NMR spectra of compounds.

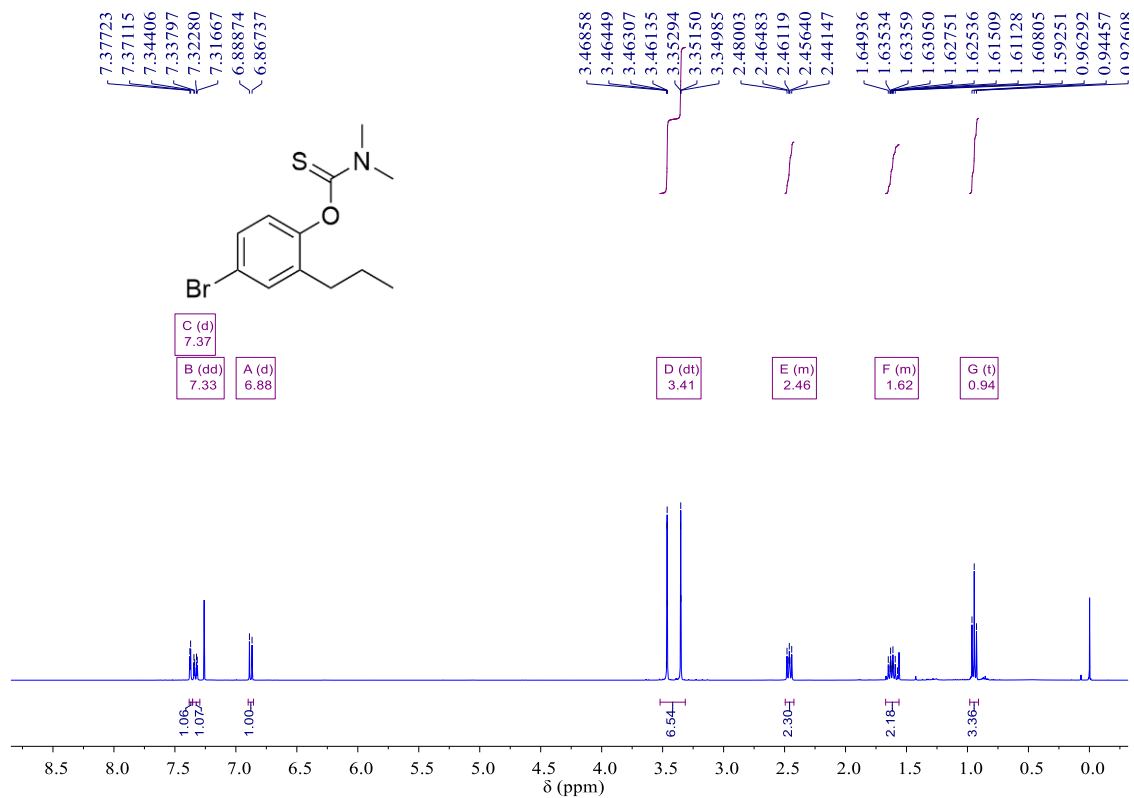


Figure S17. ¹H NMR (400 MHz, CDCl₃, 298 K) spectrum of O-(4-bromo-2-propylphenyl) dimethylcarbamothioate.

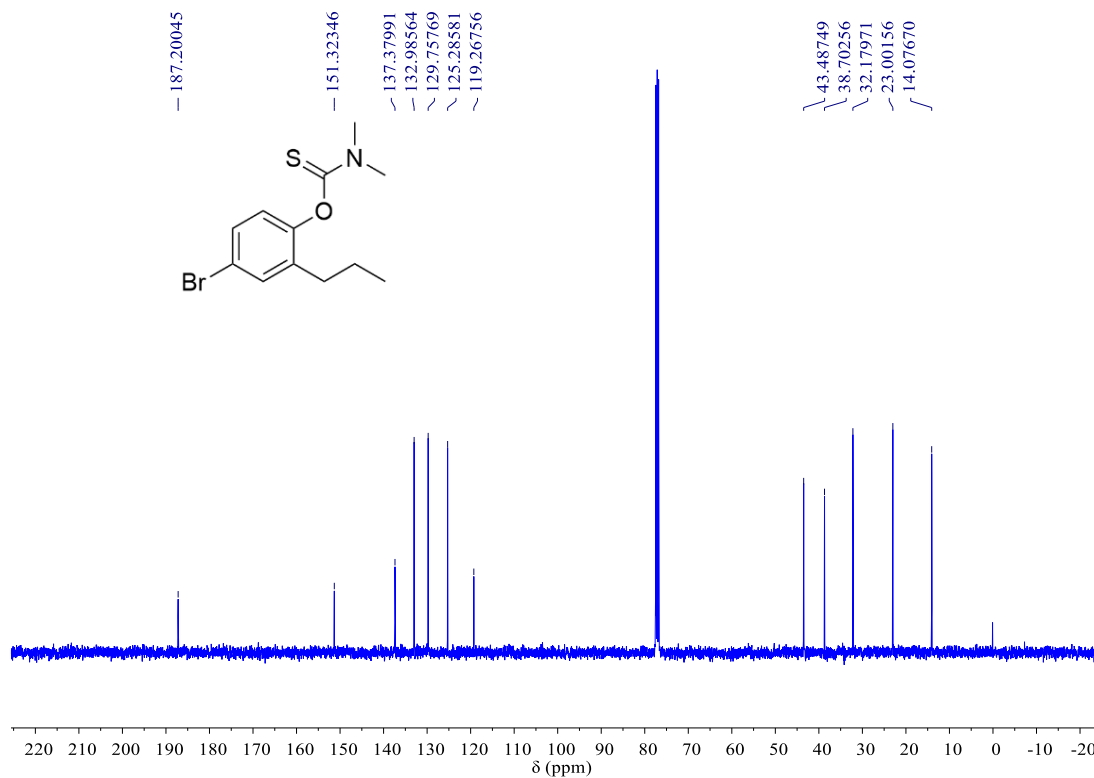


Figure S18. ¹³C NMR (100 MHz, CDCl₃, 298 K) spectrum of O-(4-bromo-2-propylphenyl) dimethylcarbamothioate.

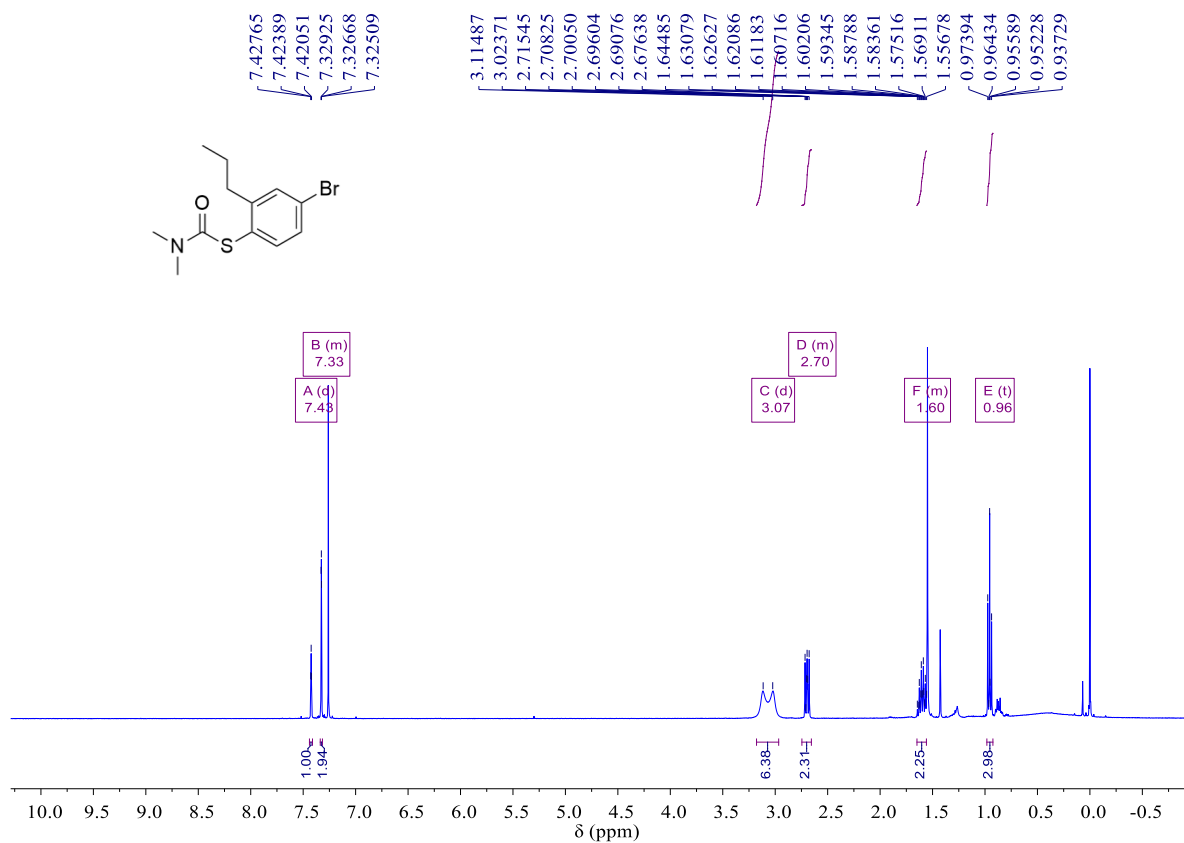


Figure S19. ¹H NMR (400 MHz, CDCl₃, 298 K) spectrum of S-(4-bromo-2-propylphenyl) dimethylcarbamothioate.

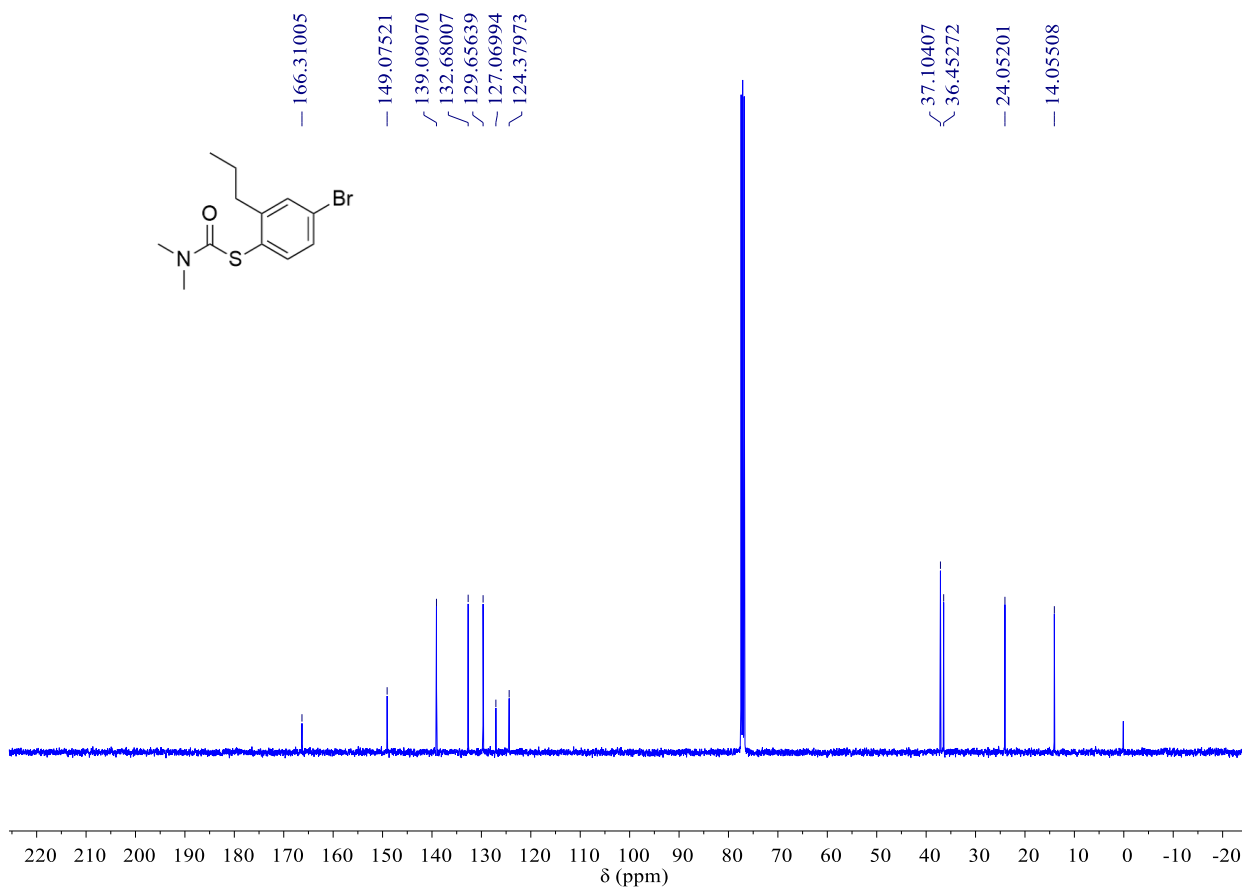


Figure S20. ¹³C NMR (100 MHz, CDCl₃, 298 K) spectrum of S-(4-bromo-2-propylphenyl)

dimethylcarbamothioate.

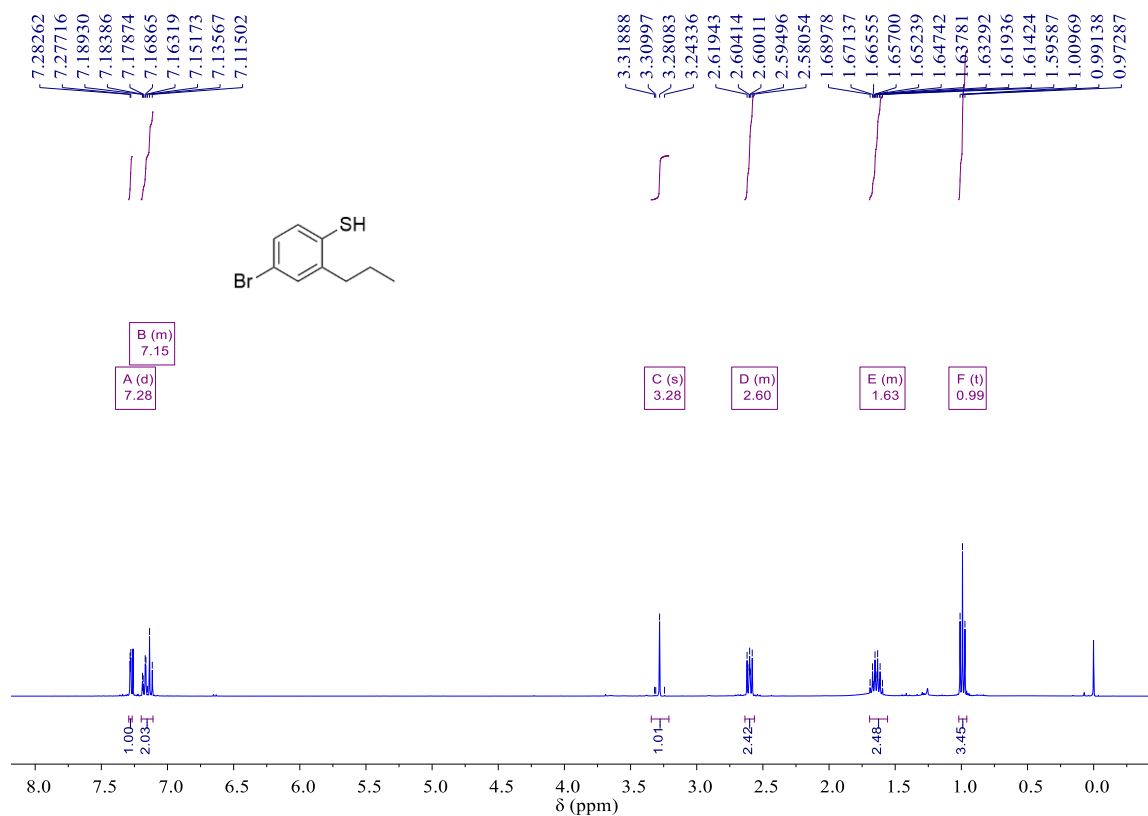


Figure S21. ¹H NMR (400 MHz, CDCl₃, 298 K) spectrum of 4-bromo-2-propylbenzenethiol.

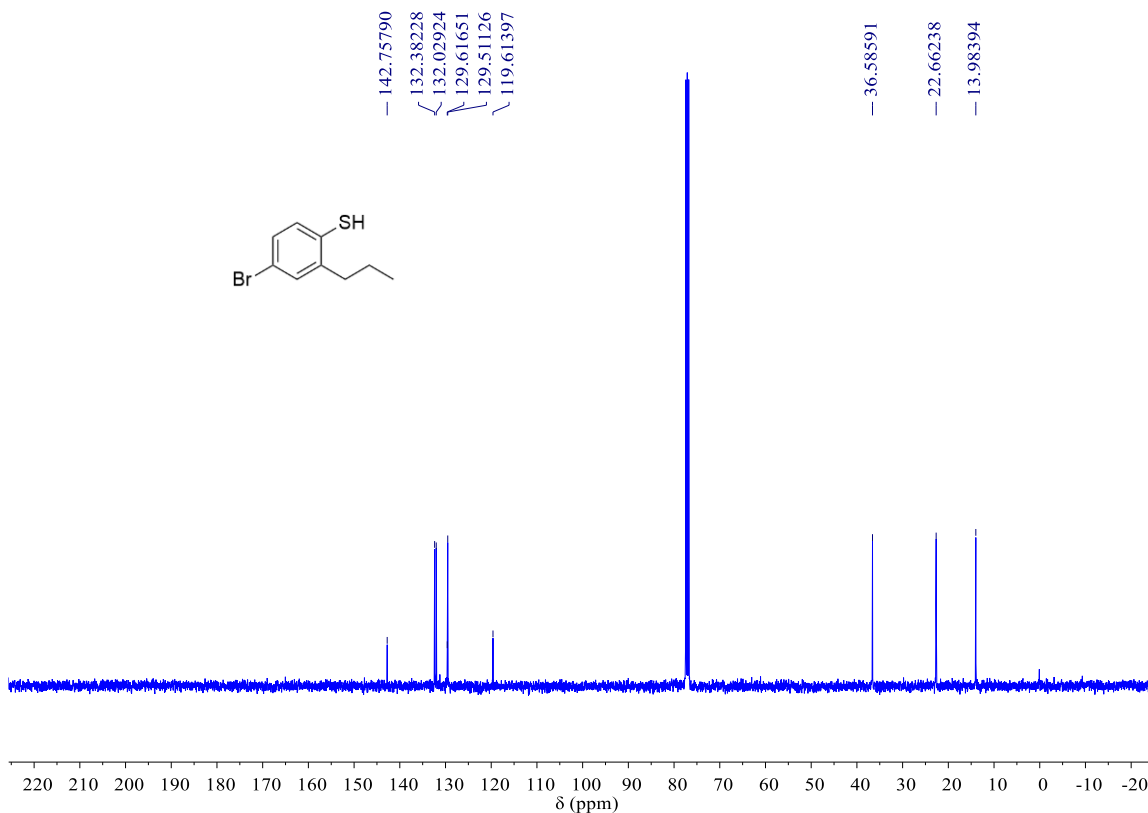


Figure S22. ^{13}C NMR (100 MHz, CDCl_3 , 298 K) spectrum of 4-bromo-2-propylbenzenethiol.

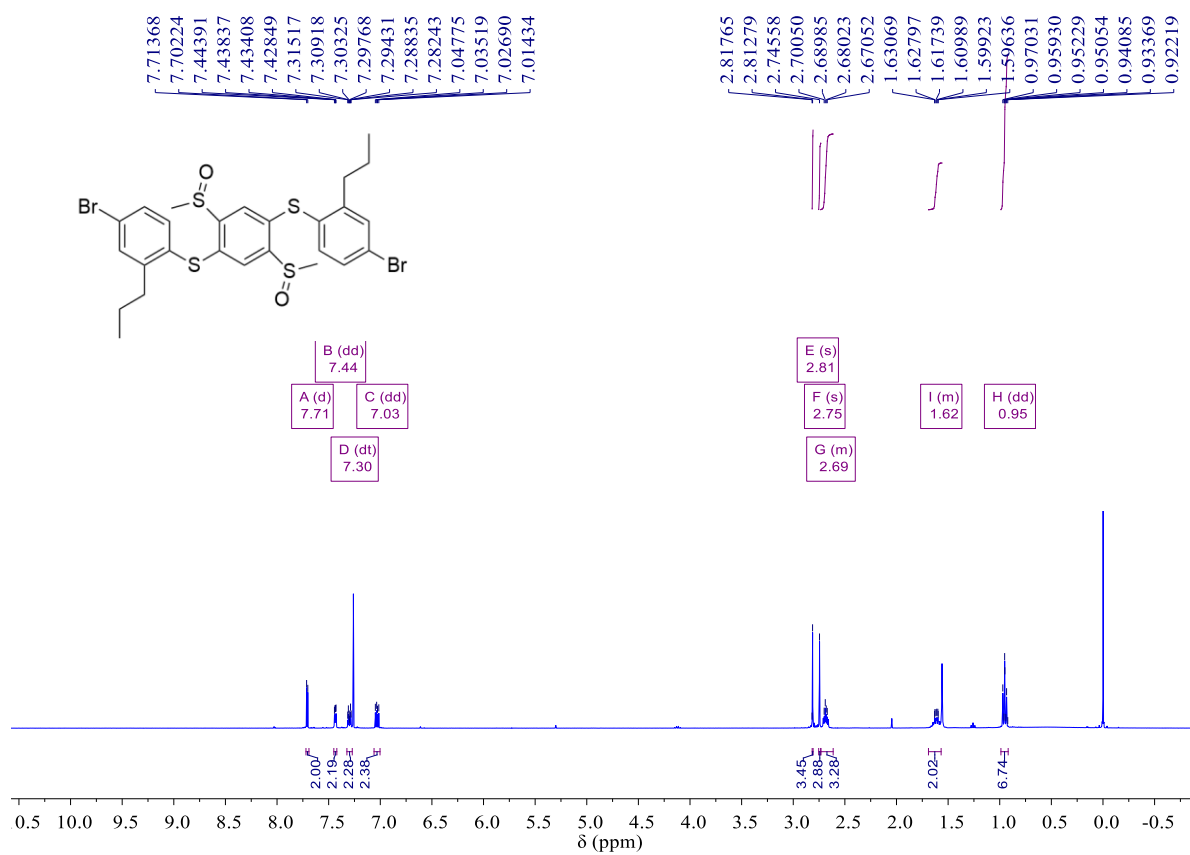


Figure S23. ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of **2**.

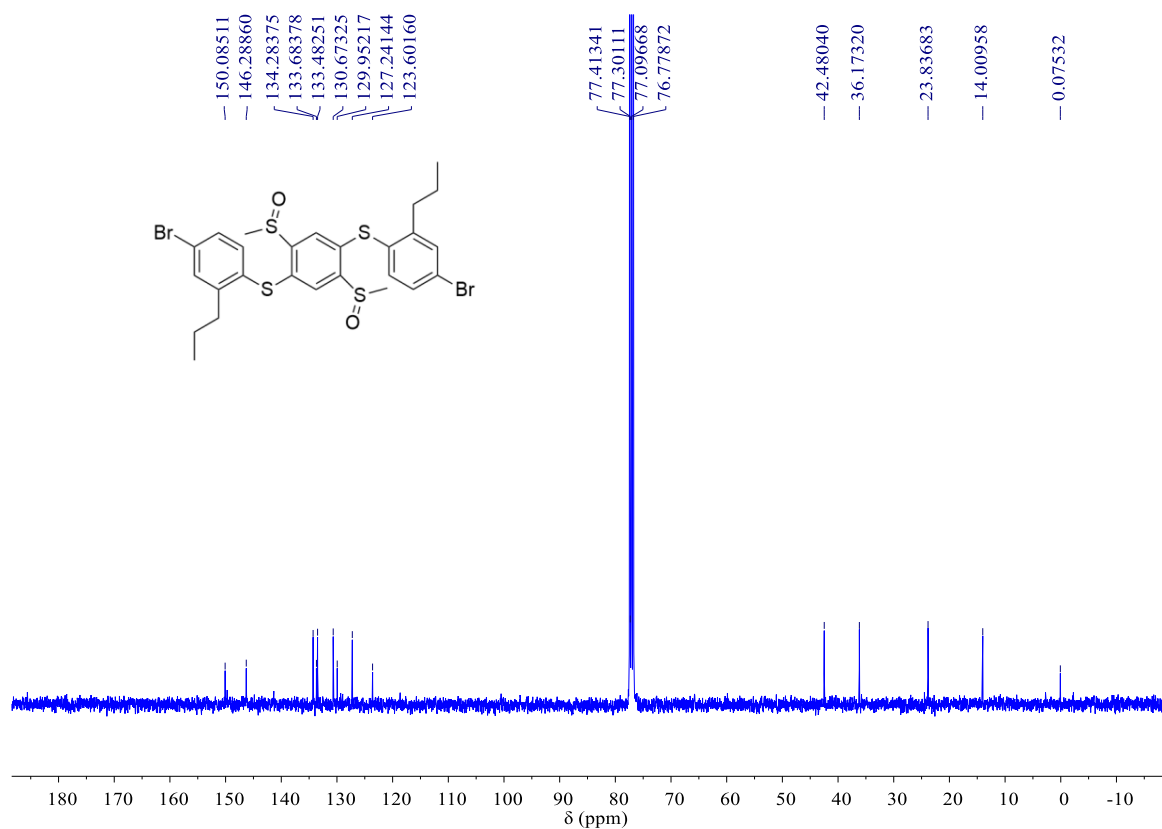


Figure S24. ^{13}C NMR (100 MHz, CDCl_3 , 298 K) spectrum of **2**.

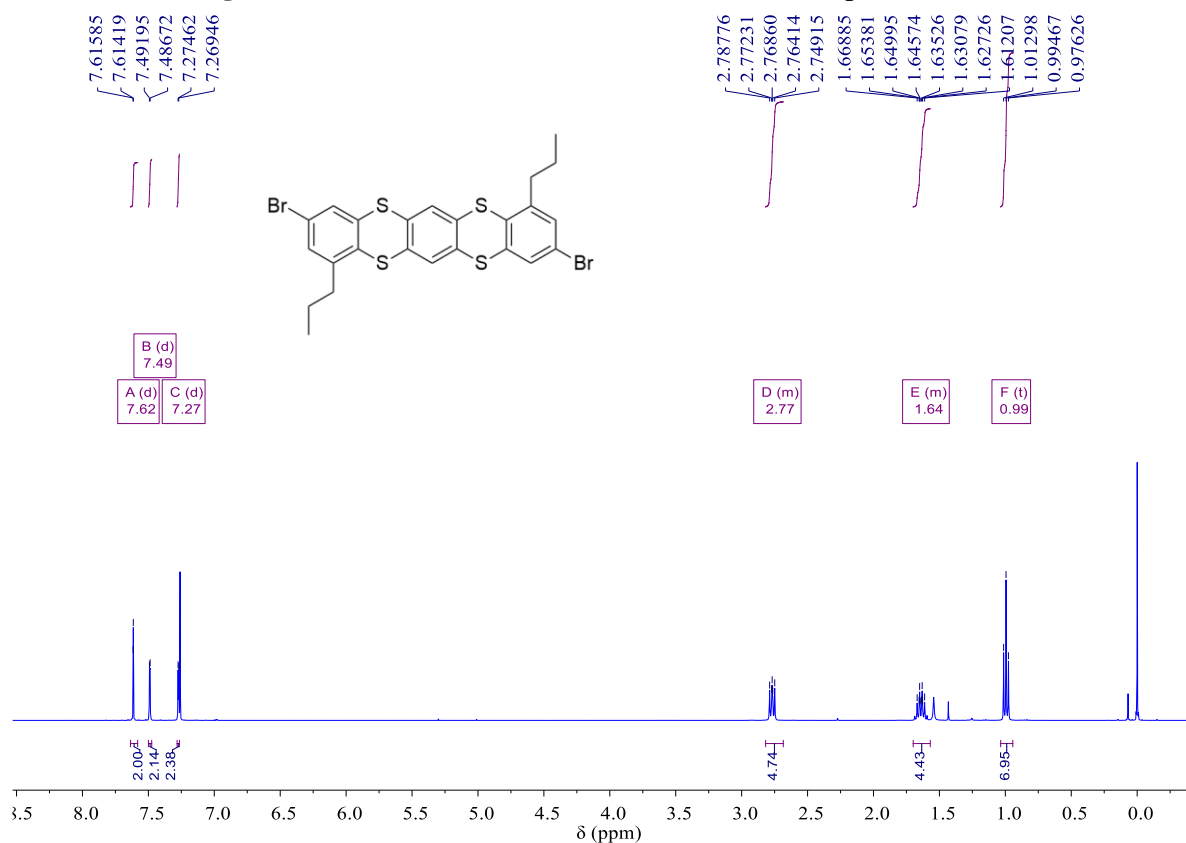


Figure S25. ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of **3**.

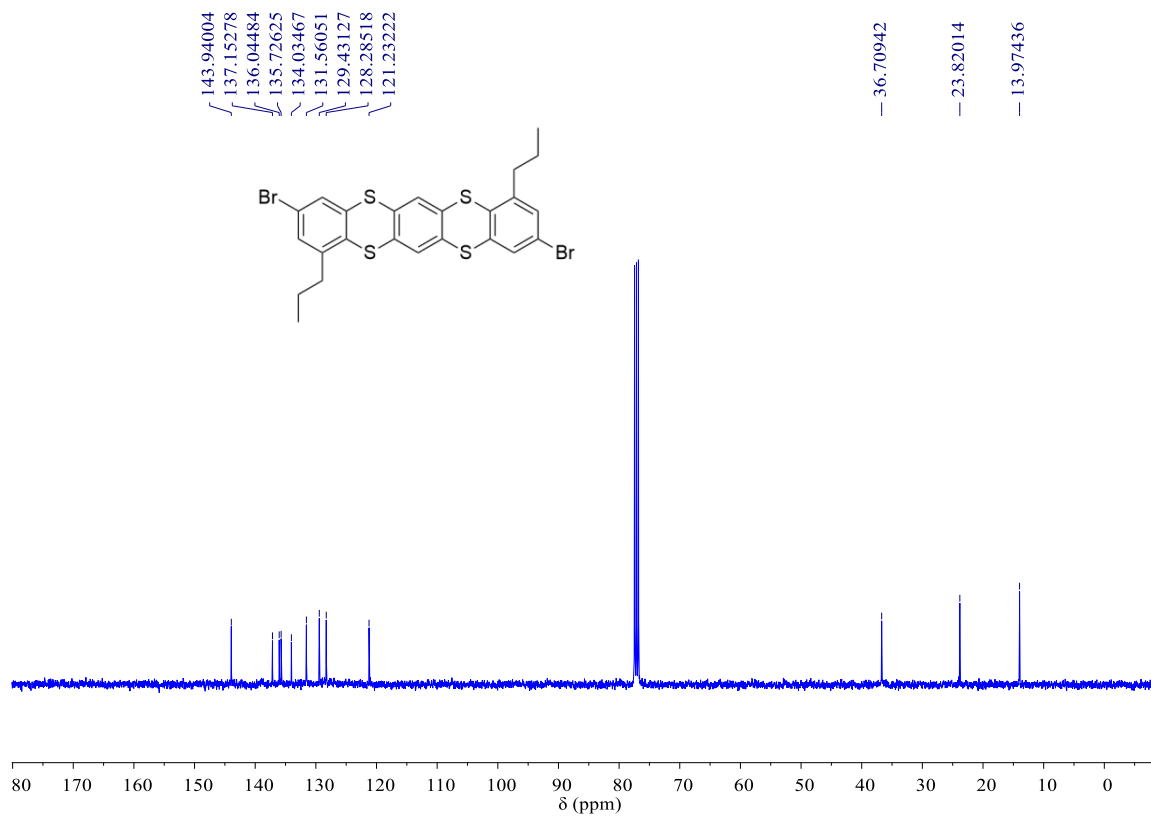


Figure S26. ^{13}C NMR (100 MHz, CDCl_3 , 298 K) spectrum of **3**.

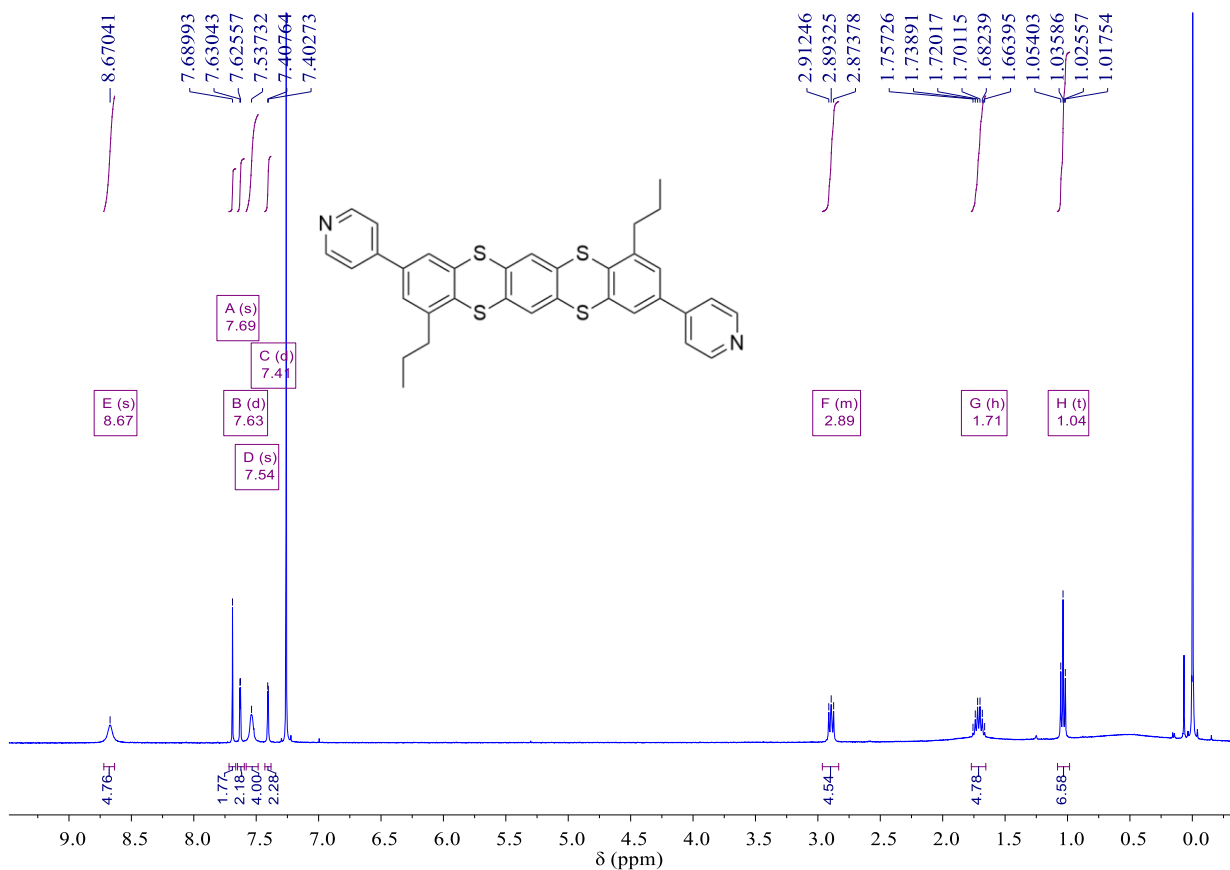


Figure S27. ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of **1**.

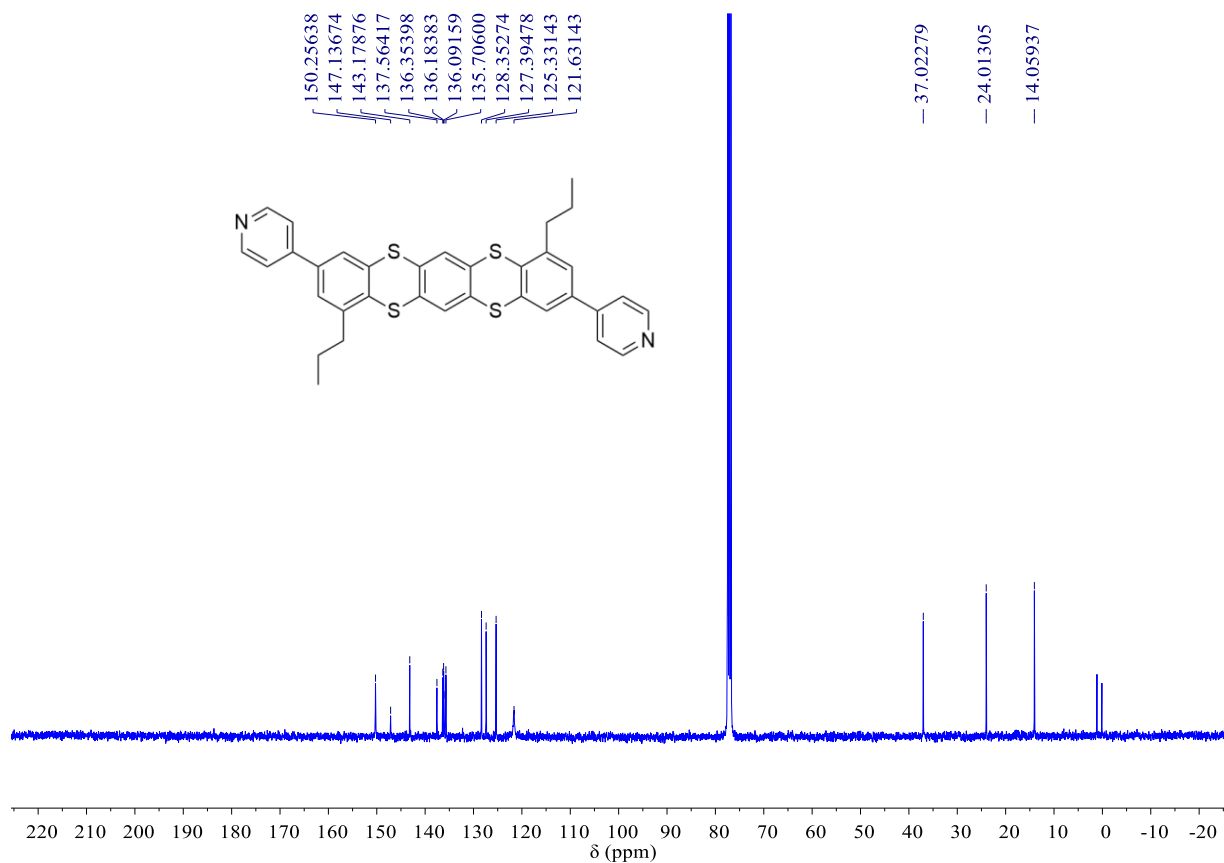


Figure S28. ^{13}C NMR (100 MHz, CDCl_3 , 298 K) spectrum of **1**.

jinshu huan DCM -2
single_pulse

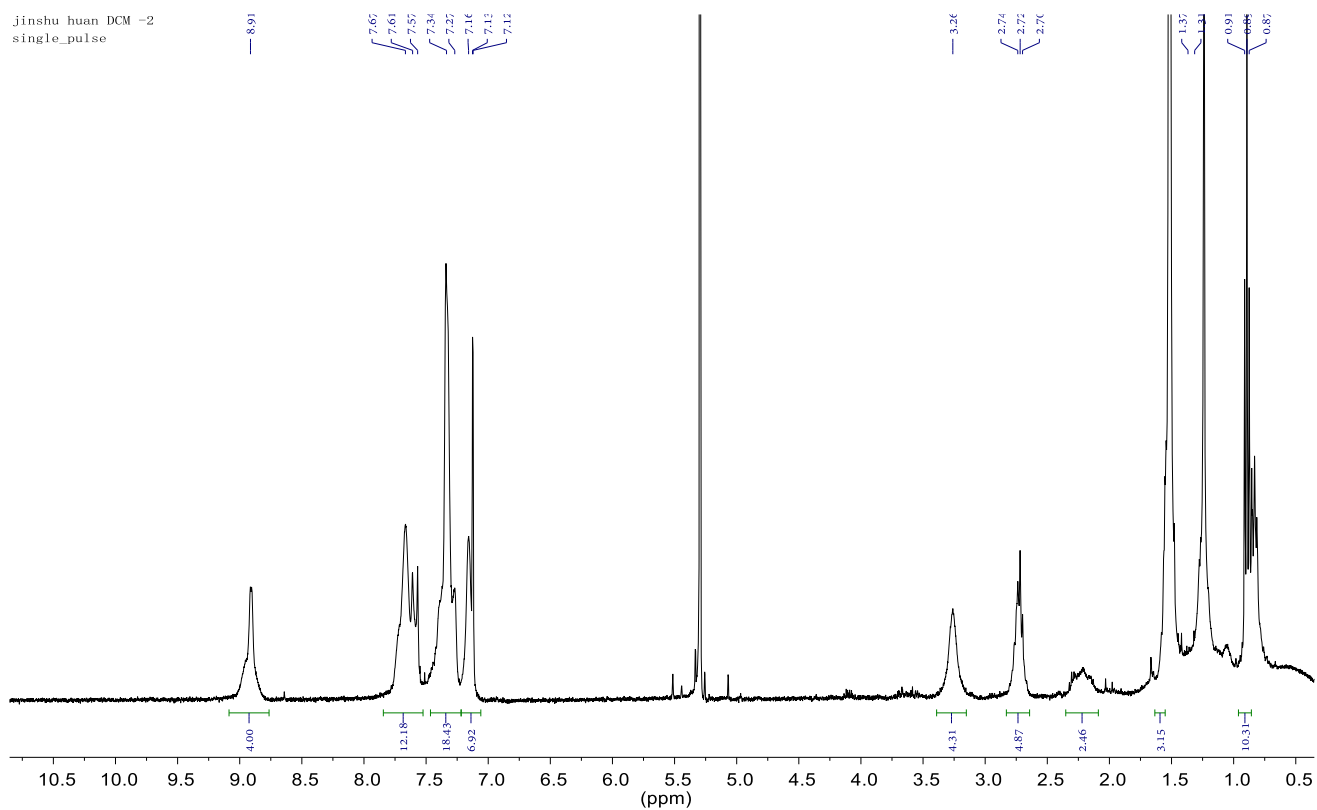


Figure S29. ¹H NMR (400 MHz, CD₂Cl₂, 298 K) spectrum of [Pt₂(dppp)₂(**1**)₂(OTf)₄].

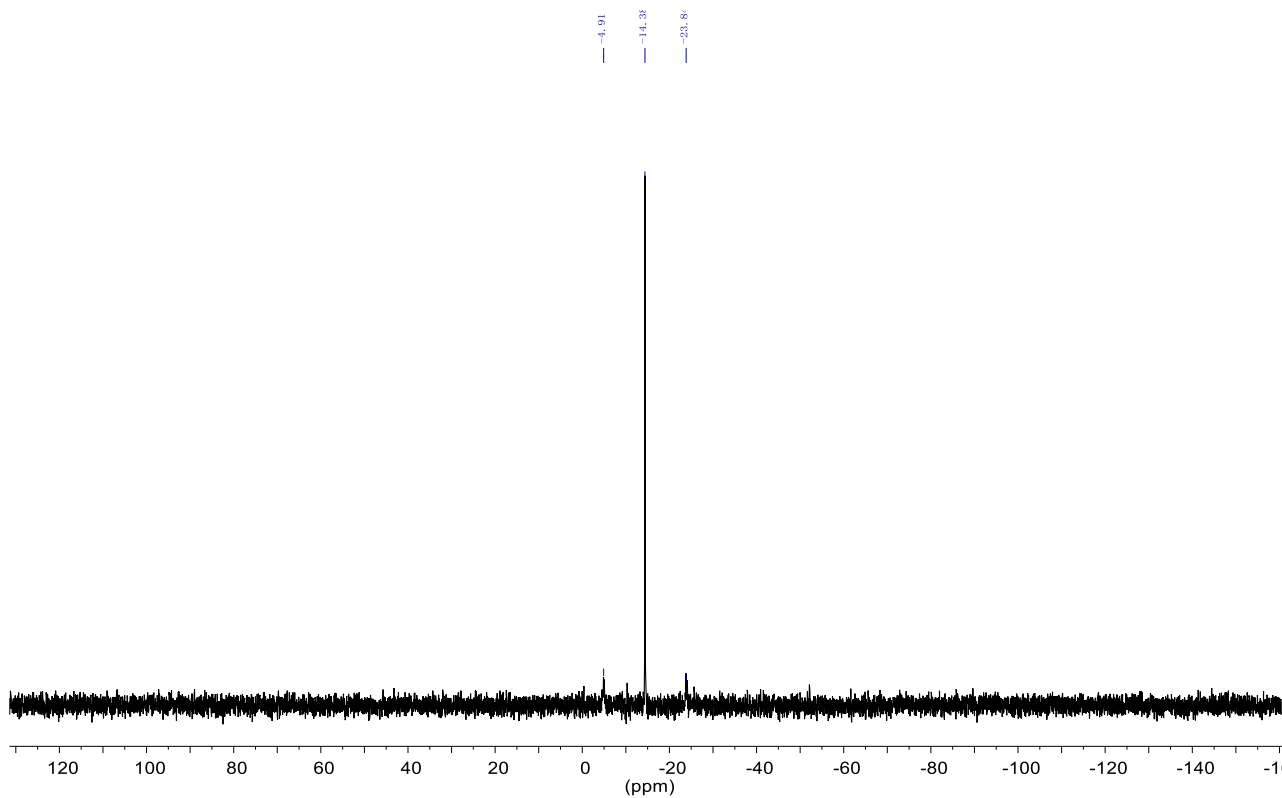


Figure S30. ³¹P NMR (192 MHz, CD₂Cl₂, 298 K) spectrum of [Pt₂(dppp)₂(**1**)₂(OTf)₄].

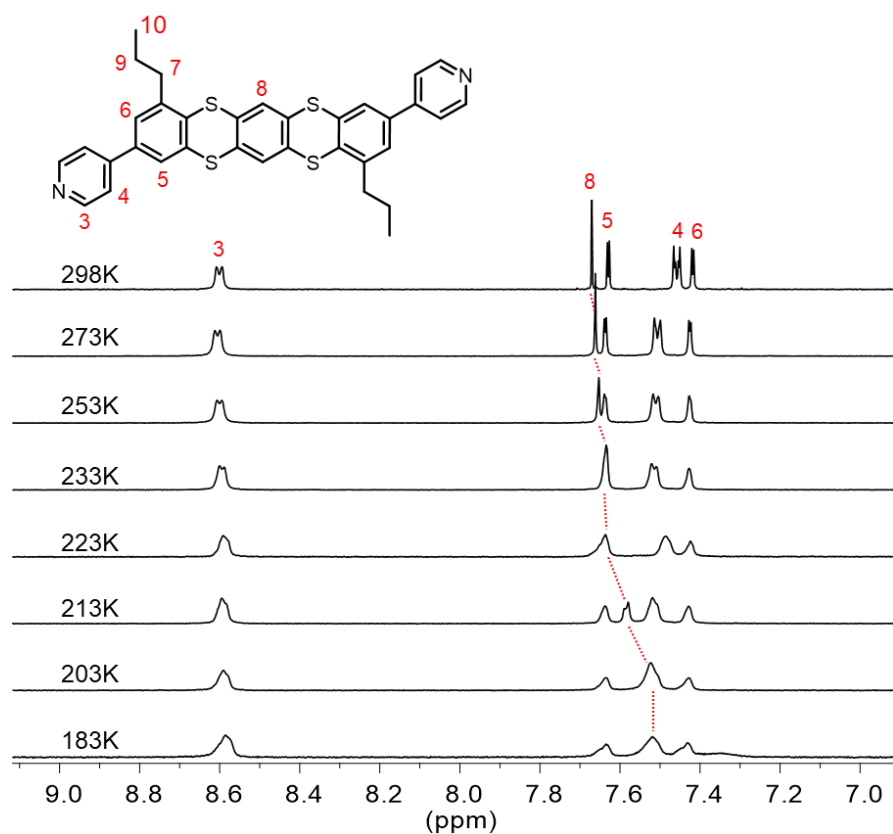


Figure S31. Variable temperature ^1H NMR (CD_2Cl_2 , 400 MHz) spectra for aromatic region of **1**.

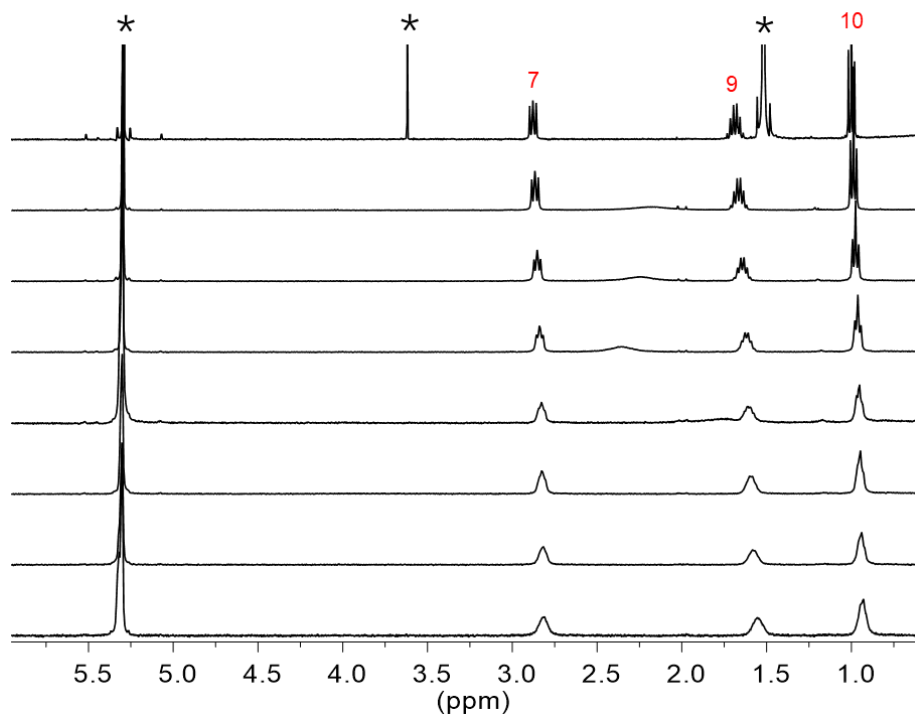


Figure S32. Partial variable temperature ^1H NMR (CD_2Cl_2 , 400 MHz) spectra of **1**. (*solvents)

Section G. UV-vis Absorption Spectra

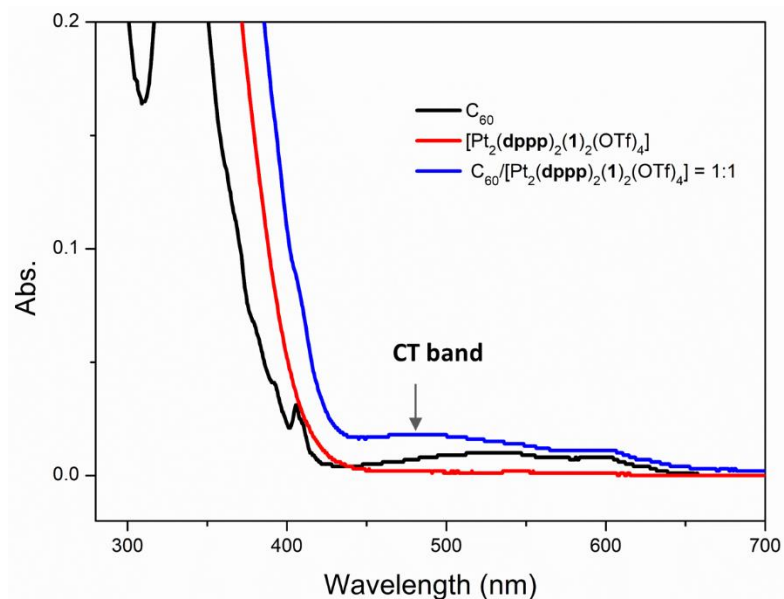


Figure S33. UV-vis spectra of **C₆₀**, **[Pt₂(dppp)₂(1)₂(OTf)₄]**, and a 1:1 mixture (10 μ M in dichloromethane at 298K). A charge transfer (CT) band centred at 486 nm was observed for the complex $\{C_{60}\llbracket Pt_2(dppp)_2(1)_2(OTf)_4 \rrbracket\}$.

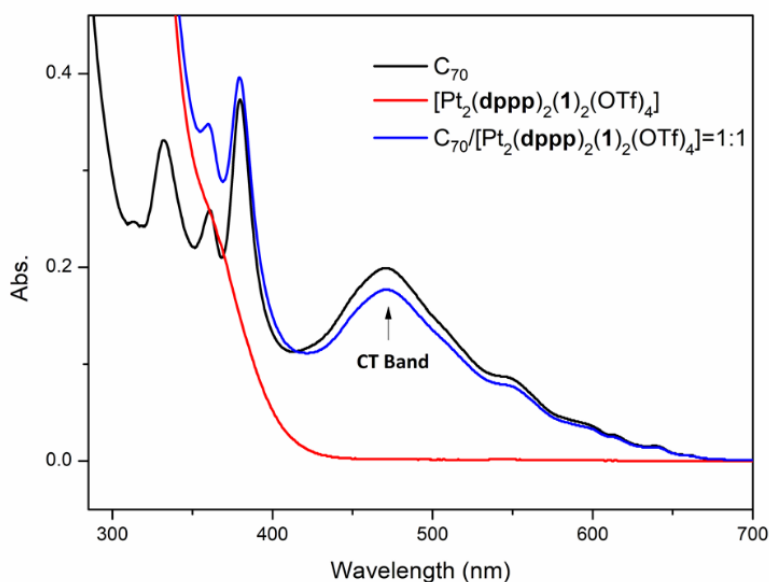


Figure S34. UV-vis spectra of **C₇₀**, **[Pt₂(dppp)₂(1)₂(OTf)₄]**, and a 1:1 mixture (10 μ M in dichloromethane at 298K). A charge transfer (CT) band centred at 471 nm was observed for the complex $\{C_{70}\llbracket Pt_2(dppp)_2(1)_2(OTf)_4 \rrbracket\}$.

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