

Supporting Information

Towards a Self-Assembled Honeycomb Structure via Diaminotriptycene Metal Complexes

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Experimental Details

Triptycenediamine **4** and hexanitrotriptycene were synthesized by previously published procedures.¹ ¹H and ¹³C NMR spectra were recorded on a Bruker AV-300 spectrometer. ¹³C NMR spectra were recorded using a proton decoupled pulse sequence. ¹H and ¹³C NMR spectra were calibrated to the residual protonated solvent at δ 7.26 and δ 77.00, respectively, in CDCl₃, or at δ 2.49 and δ 39.52, respectively, in DMSO-*d*₆. Electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker Esquire LC instrument. Matrix assisted laser desorption/ionization (MALDI) mass spectra were obtained on a Bruker Biflex IV time-of-flight (TOF) mass spectrometer equipped with a MALDI ion source. Elemental analyses (C,H,N) were performed at the UBC Microanalytical Services Laboratory. UV-vis spectra were obtained in DMSO (ca. 5×10^{-5} M) on a Varian Cary 5000 UV-vis-near-IR spectrophotometer using a 1 cm quartz cuvette. SEM images were collected on a Hitachi S4700 scanning electron microscope. TEM micrographs were obtained with a FEI Technai at an acceleration voltage of 200 kV. Gas adsorption data were obtained using a Micromeritics ASAP 2010 analyzer and analyses were carried out at 77K. XPS data were recorded with Leybold MAX200 analyzer at a vacuum in the range 10⁻⁹ torr, using achromatic Al K-alpha X-ray. For survey scans, the pass energy used is 192 eV, and for narrow scans, the pass energy used is 48 eV. A Bruker D8 Advance with Cu radiation and a NaI scintillation detector was used for powder X-ray diffraction analysis.

Synthesis of Hexaaminotriptycene **5**.

Compound **5** has been made previously,¹ but we used a modified procedure: To a solution of compound of hexanitrotriptycene (0.128 g, 0.244 mmol) in THF (50 mL) was added hydrazine monohydrate (1 mL) and a scoopula tip (~50 mg) of Raney Ni. After heating the mixture to 50 °C under N₂ for 1 h until all of the hydrazine was

reacted, the mixture was cooled to room temperature. The solution was filtered through a small pad of Celite under N₂, and then the solvent was removed by rotary evaporation to give the product as an off-white solid (0.06 g, 70% yield). ¹H NMR spectroscopy indicated that the desired product was obtained and the purity was typically >95% by ¹H NMR. The product was used directly for the synthesis of **7** and **8** without further purification.

Synthesis of Pt(*o*-triptycenesemiquinonediiimine)₂ **6.** A mixture of triptycenediamine **4** (0.068 g, 0.24 mmol) and potassium tetrachloroplatinate (0.047 g, 0.11 mmol) in methanol (10 mL) was heated at reflux for 15 h under nitrogen. After cooling the reaction mixture to room temperature, the precipitated solid was collected by suction filtration and washed with methanol and ethanol, yielding **6** as a dark blue powder (0.031 g, 36% yield). ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.81 (br s, 4H, NH), 7.45-7.40 (m, 12H, Ar), 7.01-6.99 (m 8H, Ar), 5.76 (s, 4H, bridgehead). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 145.1, 137.3, 136.7, 125.8, 124.3, 123.9, 52.1. ESI-MS (MeOH) *m/z* = 759.4 [(M+H)⁺]. IR ν = 3170, 2948, 1548, 1462, 1336, 1210, 1136, 902, 750, 694, 644 cm⁻¹. Mp > 300 °C. HR-MS (ESI) calcd for C₄₀H₂₈N₄¹⁹⁴Pt: 758.1941 [(M + H)⁺]. Found: 758.1956. UV-vis (DMSO): λ_{max} = 753 nm (ε = 8.2 x 10³ L mol⁻¹ cm⁻¹).

Product 7. A mixture of hexaminotriptycene **5** (0.033 g, 0.096 mmol) and potassium tetrachloroplatinate (0.079 g, 0.192 mmol) in methanol (10 mL) was heated to reflux under nitrogen. When the temperature reached 70 °C, a black solid was noticed depositing on the bottom of the flask. After 15 h, the reaction mixture was cooled to room temperature, the precipitate was collected by suction filtration, and the black powder was washed with methanol and ethanol (0.031 g, 84% yield). PXRD and TEM showed that the sample contains Pt-nanoparticles.

Disordered Pt honeycomb 8. A mixture of hexaaminotriptycene **5** (0.046 g, 0.134 mmol) and potassium tetrachloroplatinate (0.089 g, 0.214 mmol) were dissolved in 10 mL methanol, and a solution of potassium carbonate (0.055 g, 0.402 mmol) in 10 mL

of water was added at room temperature. After 2 h, a precipitate began to form. The reaction mixture was stirred for a further 12 h at room temperature, and then the precipitate was collected by centrifugation and washed with water (3 x 20 mL) and dichloromethane (2 x 20 mL) to yield **8** as a dark purple powder (0.043 g, 51% yield).

IR (*inter alia*): 3200–3400 (v. broad), 1623, 1539, 1441, 1338, 1213, 734, 596, 476.

XPS (Figure S10) showed the presence of Pt, C, N and O.

It is notoriously difficult to obtain satisfactory elemental analyses of disordered polymeric framework materials, due to both the propensity of these compounds to retain solvents and absorb atmospheric moisture, and the presence of unknown end-groups at the edge of the polymer. Despite this, we were able to obtain reasonable elemental analyses for the material as synthesized (which appears to retain methanol from the reaction mixture) and the solvent-exchanged material (which appears to retain some alkane, and absorb some atmospheric moisture). Table S1 shows the elemental analyses before and after solvent exchange for two different replicates; these analyses could be matched to theoretical values by incorporating different amounts of methanol or hexane/water. A representative “fitted” analysis is given for both the pre- and post-solvent exchanged material in the Table.

The inclusion of methanol (in the pre-solvent exchanged material) and hexane/water (in the post-solvent exchanged material) seems sensible, based on the sample preparation. Samples were initially prepared in MeOH/H₂O mixtures, and the resulting solids washed sequentially with H₂O, MeOH, EtOH and CH₂Cl₂ (see previous). The solvent exchange procedure involved stirring the complexes overnight in EtOH and then hexanes (Replicate 1). Elemental analysis of this complex suggested residual hexane in the pores, even after thorough drying *in vacuo*, and so for Replicate 2 more volatile pentane was used in place of hexane; however some amount of the alkane still appears to remain in the pores of the complex.

Table S1 Elemental analyses obtained for compound **8** before and after solvent exchange procedures.

Complex	%C	%H	%N
Replicate 1 (prior to solvent exchange)	38.91	4.47	11.32
Replicate 2 (prior to solvent exchange)	38.49	3.57	11.35
$[C_{20}H_{14}N_6Pt_{1.5}]_n \cdot 3CH_3OH$ (= $C_{23}H_{26}N_6O_3Pt_{1.5}$)	37.99	3.60	11.56
Replicate 1 (after solvent exchange)	40.54	3.80	12.10
Replicate 2 (after solvent exchange)	41.40	3.40	11.86
$[C_{20}H_{14}N_6Pt_{1.5}]_n \cdot 0.6(\text{hexane}) \cdot H_2O$ (= $C_{23.6}H_{24.4}N_6OPt_{1.5}$)	40.45	3.51	11.99
Theoretical value of solventless complex $[C_{20}H_{14}N_6Pt_{1.5}]_n$	38.07	2.24	13.32

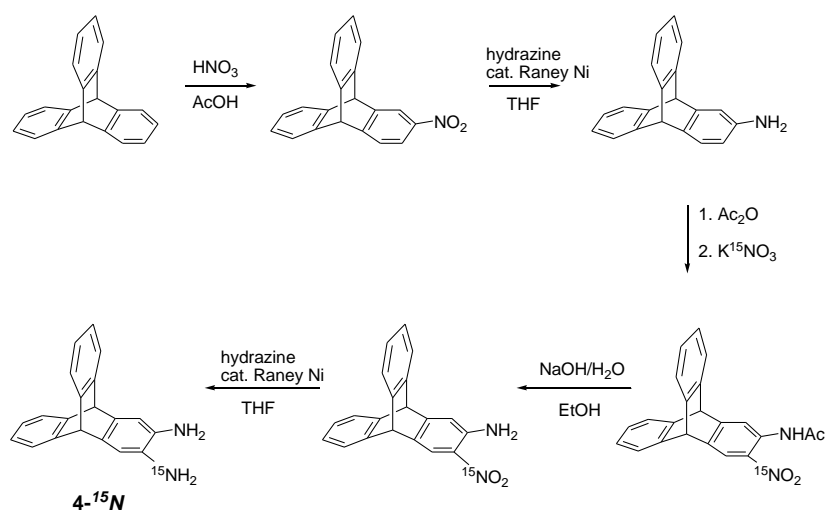
TGA showed the loss of approximately 7.5% mass by 120 °C and 10% mass by 200 °C. While this analysis is complicated by the tendency of the complex to decompose at elevated temperatures, this is roughly in accord with the proposed formulation (where solvent accounts for 10% of the mass of the complex).

X-ray Crystallography. Crystals of **6** suitable for X-ray diffraction were grown by slow cooling of a solution of **6** in hot DMSO. All measurements were made on a Bruker X8 diffractometer at 173 ± 1 K using graphite monochromated Mo- K_α radiation ($\lambda = 0.71069$ Å). Data was collected to a maximum 2θ value of 52.96° in a series of φ and ω scans in 0.50° oscillations with 20 s exposures. Of the 41855 reflections that were collected, 4676 were unique ($R_{\text{int}} = 0.0316$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.² Data were corrected for absorption effects using a multi-scan technique (SADABS)³, with max and min transmission coefficients of 0.725 and 0.464, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.⁴ The material crystallizes with two molecules of DMSO in the asymmetric

unit. One of these DMSO molecules could be adequately modeled and refined with little difficulty, but the other DMSO molecule appears to be disordered in multiple orientations. As it was impossible to model this molecule adequately, the SQUEEZE⁵ function in PLATON⁶ was used to adjust the data to account for residual electron density found within lattice void spaces. The SQUEEZE output suggests a total of 181 electrons per unit cell were eliminated from the structure, which is equivalent to approximately 2 DMSO molecules (@ 42 electrons per molecule) per asymmetric unit. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to the nitrogen atoms were located by difference mapping and refined isotropically; all other hydrogen atoms were included in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement on F^2 was based on 4676 reflections and 256 variable parameters and converged (largest parameter shift was 0.001 times its esd).⁷

Isotopic Labeling Experiment

In order to prove that the ligand in complex **6** was in the o-semibenzoquinonediimine form with 2 NH groups, we prepared complex **4-¹⁵N** with one ¹⁵NH₂ and one ¹⁴NH₂ group. This was done exactly in the same way that compound **4** was prepared, but using K¹⁵NO₃ for the second nitration step. The sequence is shown below:



Scheme S1. Synthesis of ¹⁵N-labelled compound **4**.

The ^1H NMR spectrum appears exactly as for **4**, but with one significant difference – the singlet at 4.22 ppm observed in **4** (corresponding to the NH_2 resonance) is split into a singlet (for $^{14}\text{NH}_2$) and a doublet (for $^{15}\text{NH}_2$). ESI-MS: $m/z = 286.1$ (100, $[\text{M}+\text{H}]^+$). The ^1H NMR spectrum of **4- ^{15}N** is shown in Figure S2.

Compound **6- $^{15}\text{N}_2$** was synthesized by the same procedure used to make **6**, but with **4- ^{15}N** used in the place of **4**. The ^1H NMR spectrum appears exactly as for **6**, but with the NH resonances split as described in the text. ESI-MS: $m/z = 764.2$ ((100, $[\text{M}+\text{H}]^+$). The ^1H NMR spectrum is shown in Figure S5.

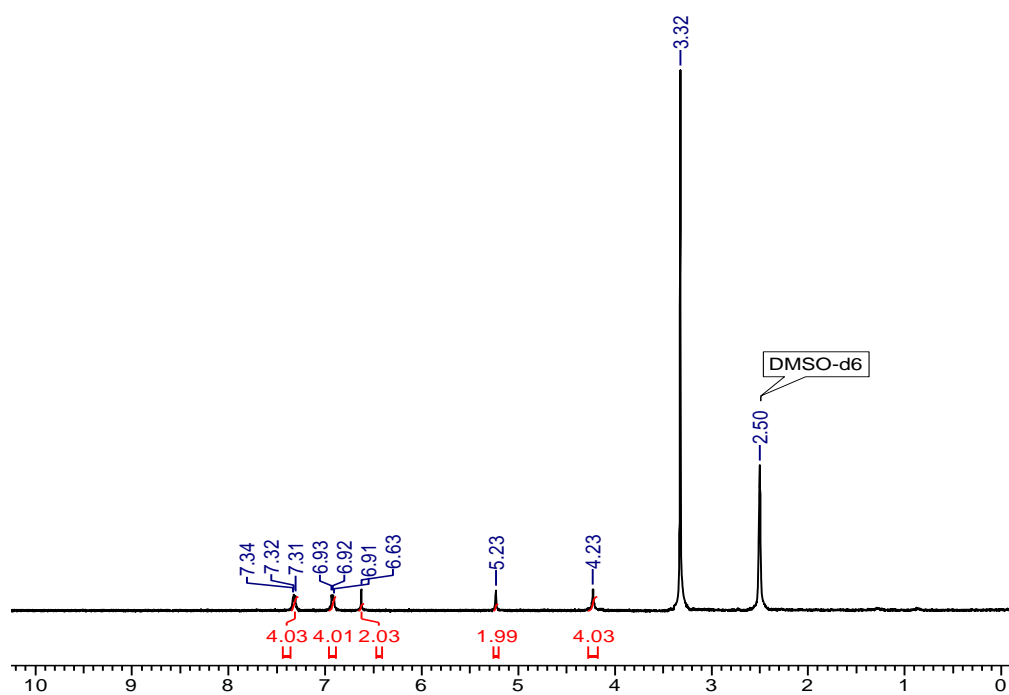


Figure S1. ^1H NMR spectrum (300 MHz, DMSO- d_6) of **4**

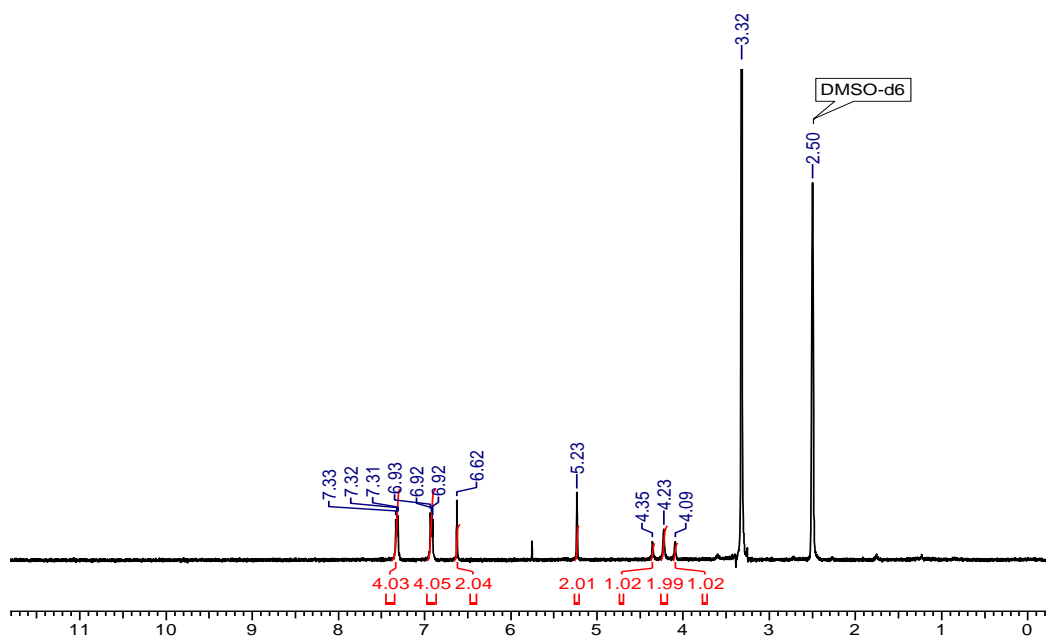


Figure S2. ^1H NMR spectrum (300 MHz, $\text{DMSO-}d_6$) of $4\text{-}^{15}\text{N}$

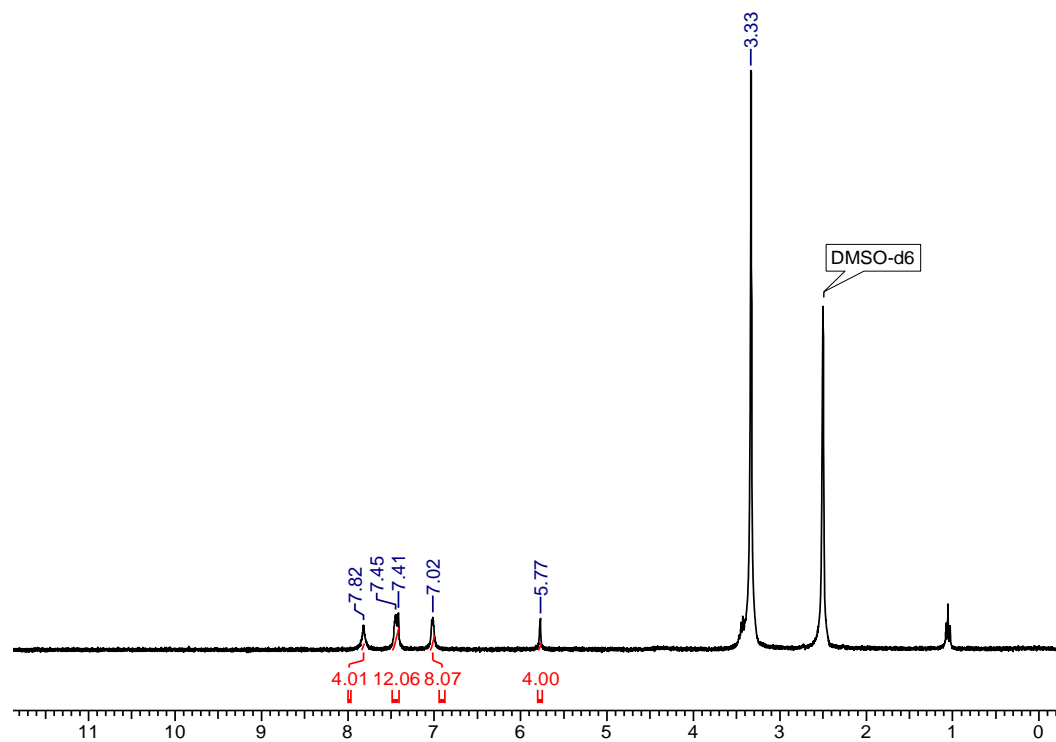


Figure S3. ^1H NMR spectrum (300 MHz, $\text{DMSO-}d_6$) of **6** (the resonance at 3.33 ppm is H_2O , 2.54 ppm is residual DMSO, and 1.09 ppm is residual Et_2O in the NMR solvent)

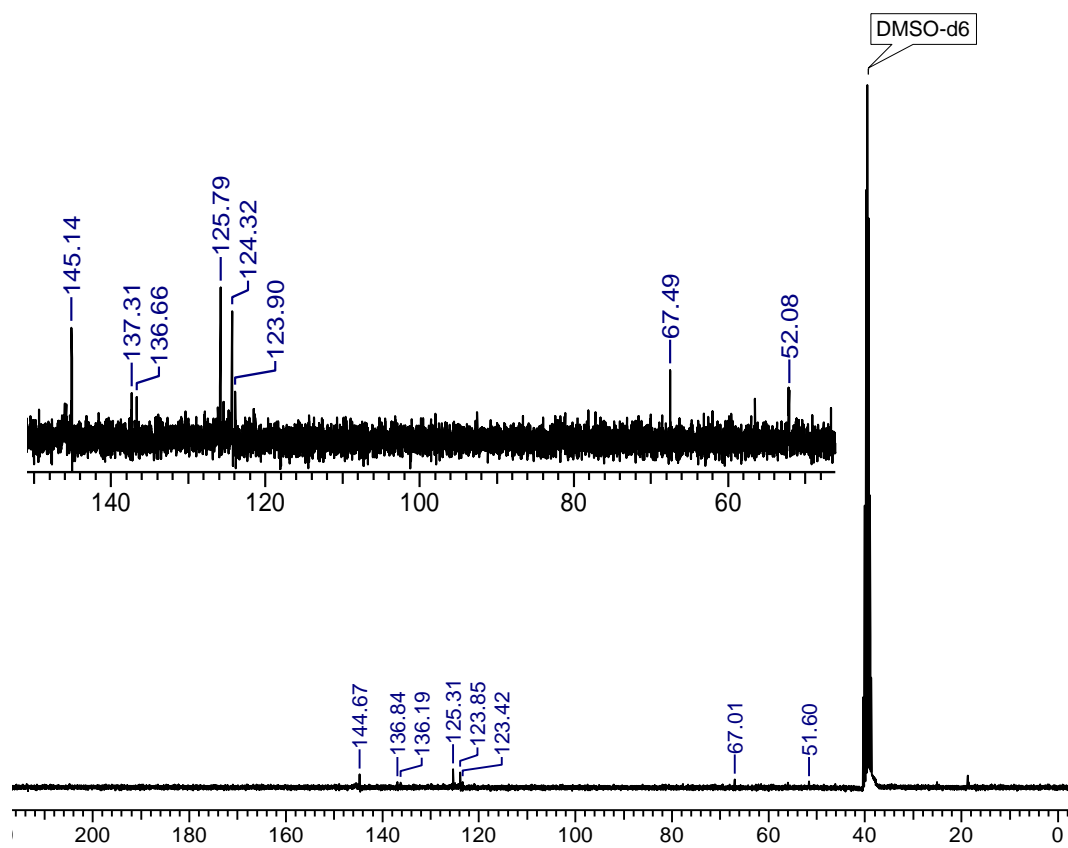


Figure S4. ^{13}C NMR spectrum (75 MHz, $\text{DMSO-}d_6$) of **6** (the resonance at 67 ppm is residual THF in the NMR solvent)

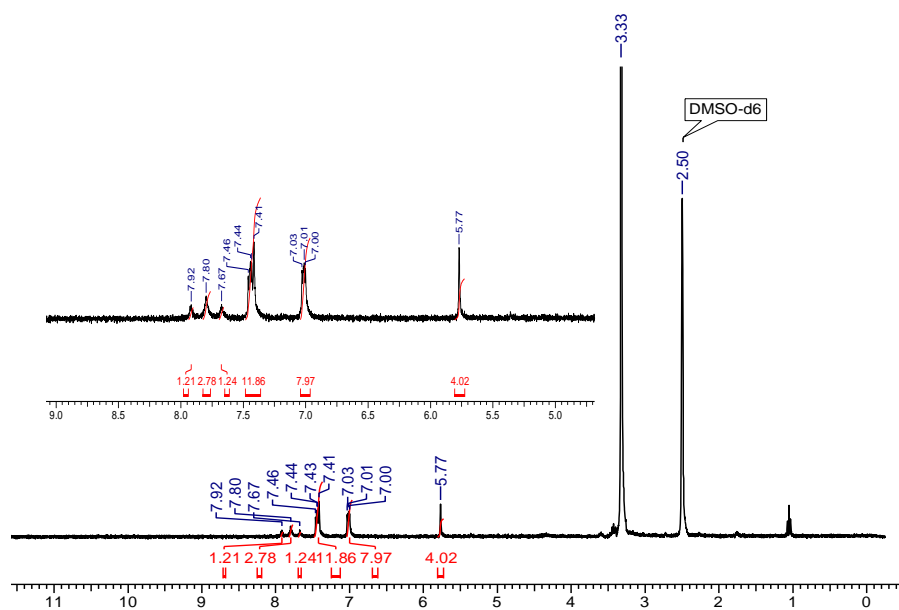


Figure S5. ^1H NMR spectrum (300 MHz, $\text{DMSO-}d_6$) of $6\text{-}^{15}\text{N}_2$

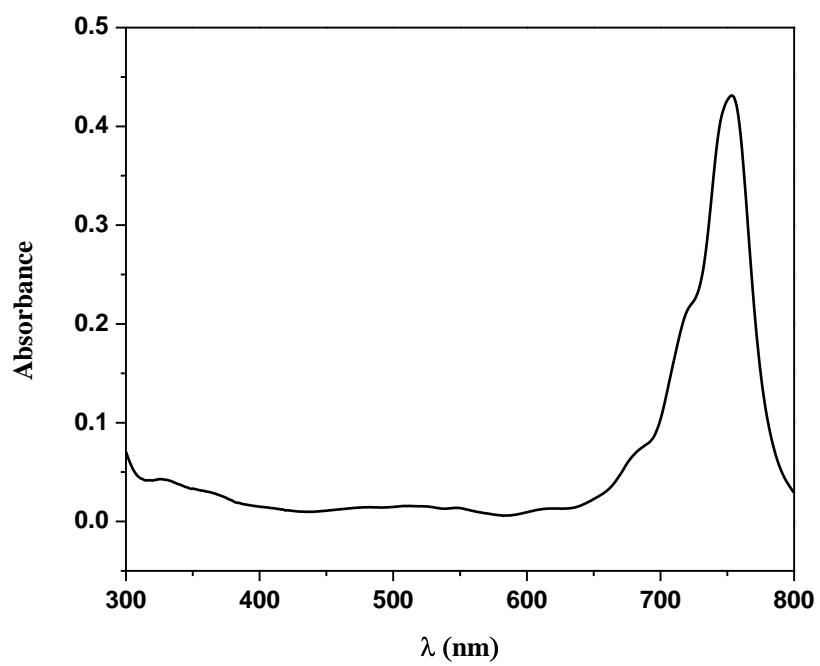


Figure S6. UV-Vis spectrum of Pt complex **6** (5.26×10^{-5} mol/L in DMSO)

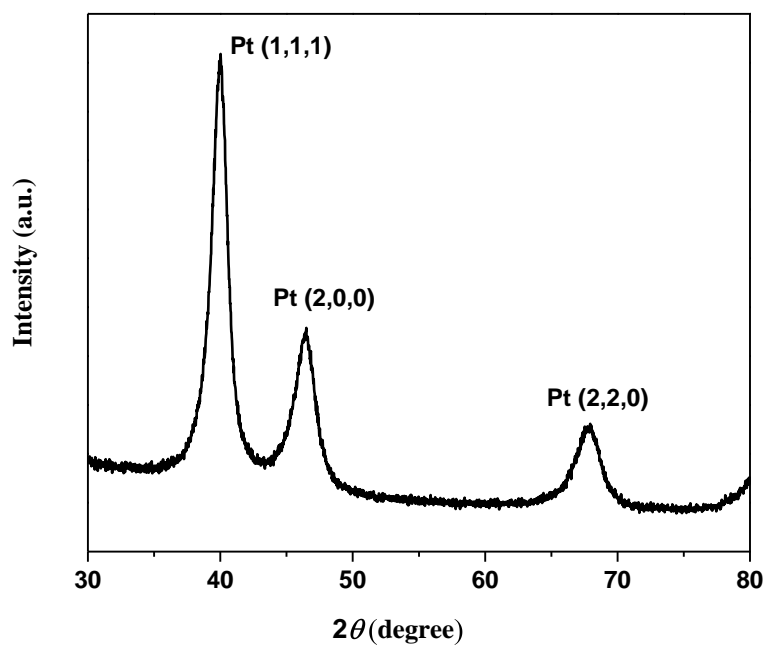


Figure S7. Powder X-ray diffraction (PXRD) pattern of product **7** shows Pt nanoparticles.

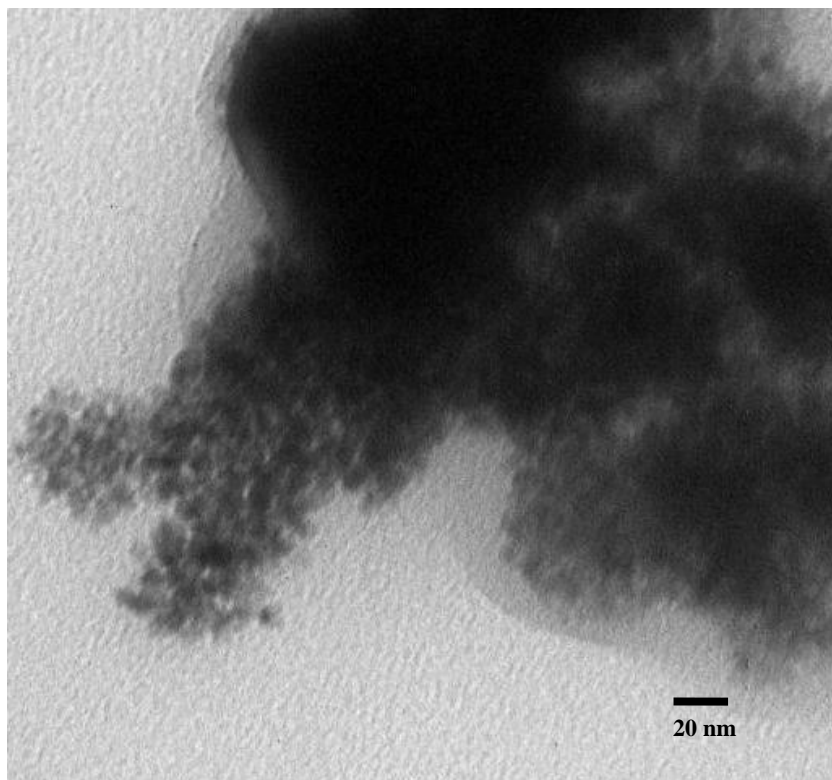


Figure S8. TEM micrograph of Pt nanoparticle-containing product **7**

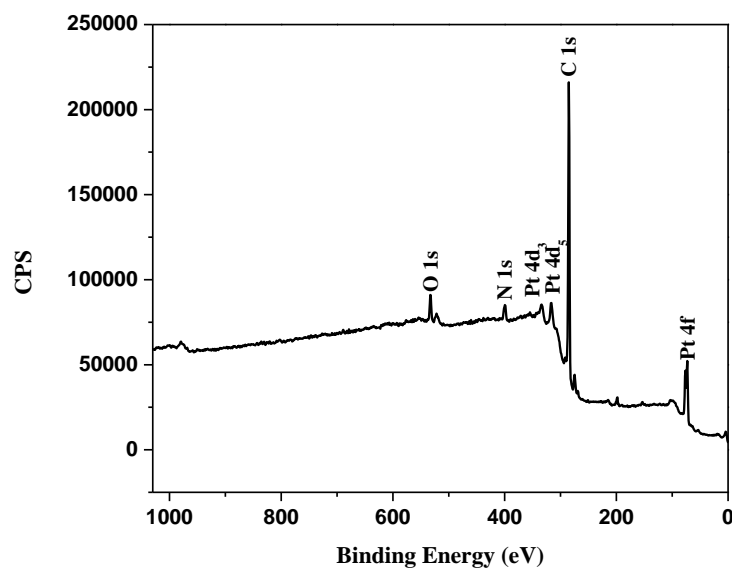


Figure S9. XPS wide scan spectrum of compound **6**

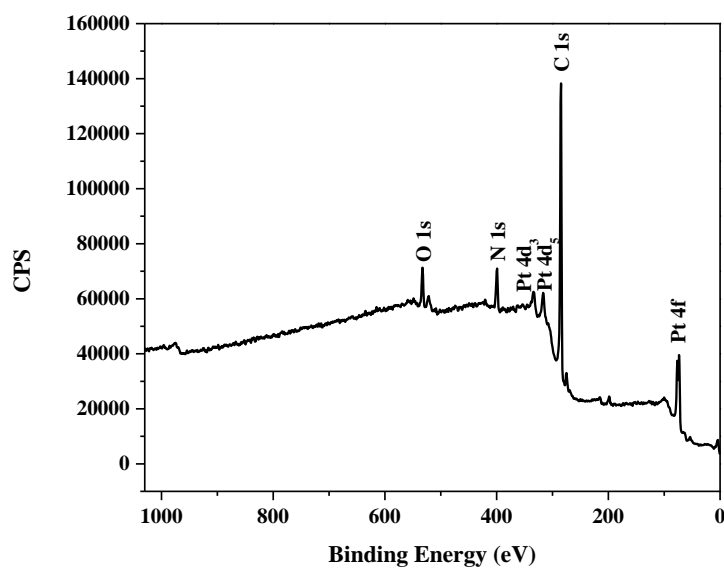


Figure S10. XPS wide scan spectrum of **8**

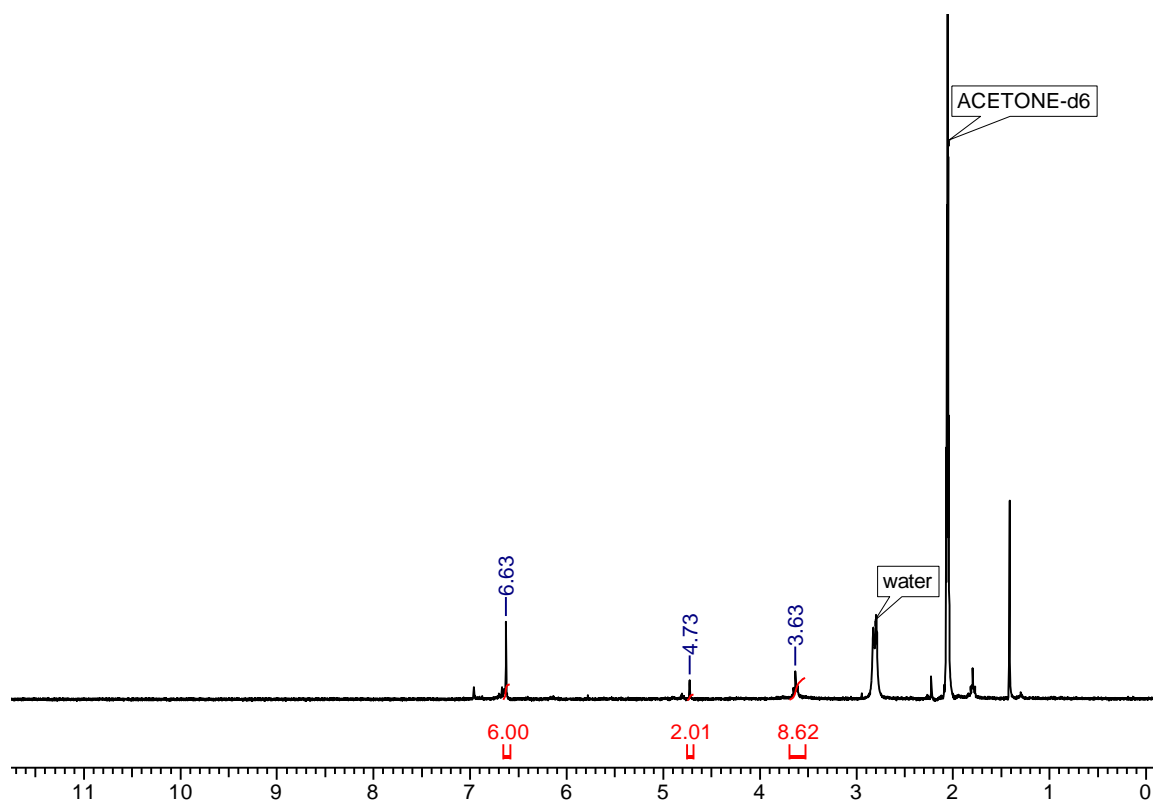


Figure S11. ¹H NMR spectrum (300 MHz, acetone-d₆) of **5**

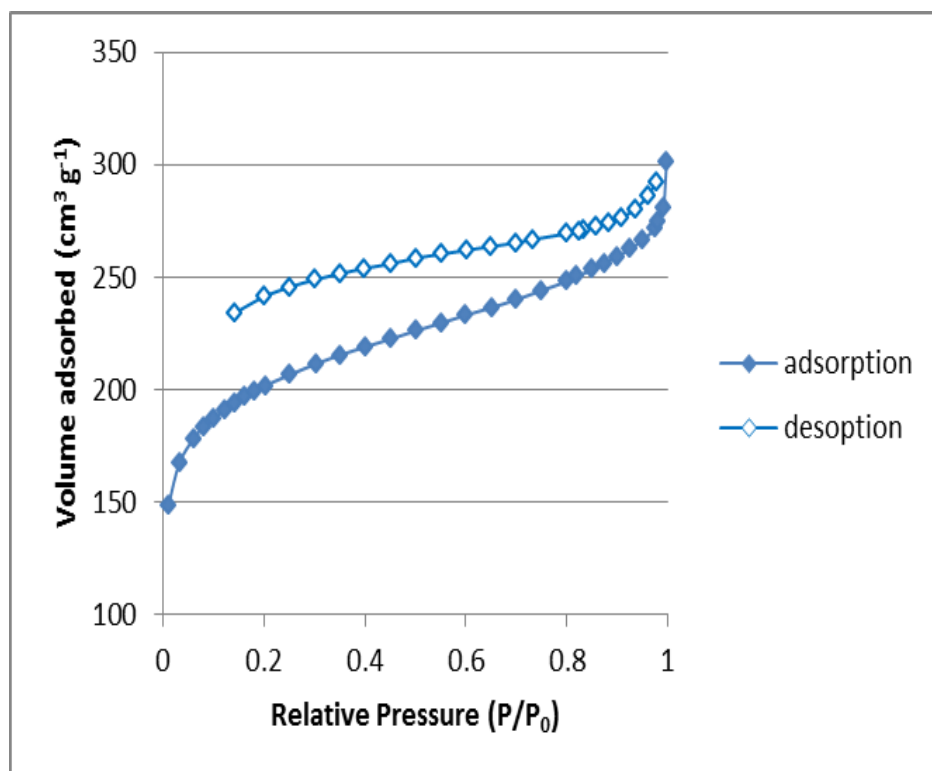


Figure S12. N₂ adsorption / desorption isotherm for **8**

References

- ¹ J. H. Chong and M. J. MacLachlan, *Inorg. Chem.* 2006, **45**, 1442; V. K. Shalaev and V. R. Skvarchenko, *Vestnik Moskovskogo Universiteta, Seriya 2: Khimiya* 1974, **15**, 726; V. K. Shalaev, E. V. Getmanova and V. R. Skvarchenko, *Zh. Org. Khim.* 1976, **12**, 191; M. Mastalerz, S. Sieste, M. Cenić and I. M. Oppel, *J. Org. Chem.* 2011, **76**, 6389.
- ² SAINT. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA. 1999.
- ³ SADABS. Bruker Nonius area detector scaling and absorption correction - V2.05, Bruker AXS Inc., Madison, Wisconsin, USA.
- ⁴ SIR92. Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Cryst.* **1994**, *26*, 343.
- ⁵ SQUEEZE – P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect A*, 1990, **46**, 194.
- ⁶ PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, Spek, A. L. (1998).
- ⁷ Least Squares function minimized:

$$\sum w(F_o^2 - F_c^2)^2$$