Electronic Supplementary Information

Probing Excited State Electronic Communications Across Bisethynyl-[2.2]Paracyclophane-Containing Conjugated Organometallic Polymers

Sébastien Clément, Thomas Goudreault, Diana Bellows, Daniel Fortin, Laurent Guyard, Michael Knorr and Pierre D. Harvey

Contents Page

Experimental section.

Materials. The starting materials 4,16-diethynyl[2.2]paracyclophane (**6**),[1] 1-ethynyl-2,4,5-trimethylbenzene,[2] *trans*-Pt(PBu_3)$_2$$Cl_2$,[3] and Pt_2(dppm)$_2$$Cl_2$[4] were prepared according the literature. Mercury(II) chloride was purchased from Aldrich and was used as received. All reactions were performed in Schlenk-tube flasks under purified argon. All flasks were dried under a flame to eliminate moisture. All solvents were distilled from appropriate drying agents.

Bis(1-ethynyl-2,4,5-trimethylbenzene)bis(bis(diphenylphosphino)methane)diplatinum(I). $Pt_2dppm_2Cl_2$ (0.153 g, 0.124 mmol) was placed in a 100 mL round bottomed flask, followed by the addition of 40 mL of distilled methanol. To the above mixture, an excess of NaOMe (0.074 g, 1.363 mmol) was added and the reaction vessel was capped and flushed with argon. The ethynyl-2,4,5,-trimethylbenzene (0.036 g, 0.248 mmol) was then dissolved in a minimal amount of methanol and added via a syringe. The reaction was left to stir at room temperature overnight. A yellow precipitate was formed and collected by filtration and washed twice with cold methanol. The product, [Pt_2(μ-dppm)$_2$(CC-C_6H_2(2,4,5-Me_3))$_2$] (0.113 g, 63 %) was then dried on the vacuum pump overnight. Found: C, 59.54; H, 4.80 $C_{72}H_{68}P_4Pt_2$ requires C, 59.75; H, 4.74, IR (KBr) ν: 2088 (C≡C) cm^{-1}. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 2.85 ppm ($^1J_{Pt–P}$ = 2920 Hz). ^1H NMR (C_6D_6): δ 7.66 – 6.28 (m, 44 H, CH_{ar}), 4.66 (m, br., 4 H, PCH_2P, $^3J_{P\text{-}H}$ = 69 Hz), 1.94 (s, 3 H, CH_3), 1.91 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3). λ_{max}(2-MeTHF)/nm 298 nm (ε/$dm^3.mol^{-1}.cm^{-1}$ 42300), 336 (58800), 502 (23400).

Poly(4,16-diethynyl[2.2]paracyclophane)mercury(II) (**1**). A solution of $HgCl_2$ (135 mg, 0.5 mmol) in MeOH was mixed with **6** (128 mg, 0.5 mmol) in THF (5 mL). To this mixture, 12.5 mL of 0.4 M basic MeOH (prepared by dissolving 0.8 g of NaOH in 50 mL of MeOH) was added. Within several minutes, an off-white solid precipitated from the homogeneous solution. The reaction was complete after stirring for 12 h, and the solid was collected by filtration, washed with MeOH (2 x 20 mL), THF (10 mL), and air-dried to furnish the polymer in 80 % yield. Found : C, 52.64, H, 2.87 $C_{20}H_{14}Hg$ requires: C, 52.80, H, 3.10. IR (KBr): ν(C≡C): 2135 (m) cm^{-1}. ^1H MAS NMR: δ 6.87 (m, 6 H, CH aro.), 3.48 (m, 8 H, CH_2) ppm. ^{13}C MAS NMR: δ 143.4, 139.9, 133.8, 131.5, 125.8 (Ph), 34.8 (*C*H_2).

Poly(trans-4,16-diethynyl[2.2]paracyclophane)bis(tributylphosphine)platinum(II)) **(2)**. 0.031 g (0.12 mmol) of **6**, 0.081 g (0.12 mmol) of *trans*-$Pt(PBu_3)_2Cl_2$ and 0.002 g of CuI were dissolved in 10 mL of $CHCl_3$. 5 mL of Et_2NH were added and the reaction was stirred at 50°C for 2 d. The solvent was evaporated. The residue was dissolved in CH_2Cl_2 and washed 3 times with water. The solution was dried with $MgSO_4$ and filtered. The solvent was then evaporated. The polymer was reprecipitated in dichloromethane and Et_2O. (0.085 g, 83 %). IR (KBr)/cm^{-1} ν: 2088 (C≡C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 5.7 (2 P, s, $^1J_{Pt\text{-}P}$ = 2400) ppm. ^1H NMR ($CDCl_3$): δ 6.89 (d, 2 H, CH aro., $^3J_{H\text{-}H}$ = 7.5), 6.38 (m, 4 H, CH aro.), 3.28 (8 H, m, CH_2); 2.27 (m, br., 12 H, C*H_2*); 1.68 (m, br., 12 H, C*H_2*), 1.49 (m, 12 H, C*H_2*) 0.95 (t, 18 H, CH_3, $^3J_{H\text{-}H}$ = 6.8) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.9, 138.9, 136.7, 132.7, 130.2, 126.9 (Ph), 110.9 (C≡C), 42.2, 34.2 (*C*H_2); 26.5, 24.5, 23.7 (P(*C*H_2)$_3$); 14.0 (*C*H_3); λ_{max}(2-MeTHF)/nm 292 nm (ε/$dm^3.mol^{-1}.cm^{-1}$ 12700), 328 (13600), 354 (20200).

Poly(4,16-diethynyl[2.2]paracyclophane)bis(bis(diphenylphosphino)methane)platinum(I) **(3)**. To a THF solution (5 mL) of 0.021 g (0.08 mmol) of **6** was added a sodium methoxide solution (0.043 g (0.80 mmol) of sodium methoxide in MeOH (10 mL)). The solution was stirred at room temperature for 0.5 h. Then, 0.100 g (0.080 mmol) of $ClPt(\mu\text{-dppm})_2PtCl$ were added. Within a few minutes, an orange solid began to precipitate The reaction was stirred for 12 h. The solid was isolated by filtration, washed with MeOH (5 mL), THF (2 mL) and dried under vacuum (0.080 g, 70 %). Found: C, 59.29; H, 4.36. $C_{70}H_{58}P_4Pt_2$ requires C, 59.49; H, 4.11, IR (KBr)/cm^{-1} ν: 2085 (C≡C). ^{31}P MAS NMR: 6.0 (2 P, s) ppm. ^1H MAS NMR: δ 6.99 (m, 46 H, CH aro.), 3.53 (m, 12 H, CH_2) ppm. ^{13}C MAS NMR: δ 138.1, 132.1, 129.0 (Ph), 34.4 (*C*H_2).

Intruments. The NMR spectra for **2** were acquired on a Bruker AC-300 spectrometer (^1H 300.15 MHz, ^{13}C 75.48 MHz, ^{31}P 121.50 MHz) using the solvent as chemical shift standard, except in ^{31}P NMR, where the chemical shifts are relative to D_3PO_4 85% in

D_2O. All chemical shifts (δ) and coupling constants (J) are given in ppm and Hertz, respectively. All solid-state NMR experiments were performed at the National Ultrahigh-field NMR Facility for Solids (Ottawa, Canada) on a Bruker Avance II NMR spectrometer operating at 21.1 T. A double-resonance 3.2 mm Bruker probe with magic angle spinning, MAS, was used to acquire ^1H and ^{13}C MAS NMR spectra. ^1H and ^{13}C NMR chemical shifts were referenced to neat TMS using adamantane as a secondary chemical shift reference. 1H MAS NMR spectra were recorded at a resonance frequency of 900.2 MHz. Samples were spun at a spinning speed of 20 kHz in 3.2 mm o.d. ZrO_2 rotors. A single pulse sequence with background suppression was used in ^1H NMR experiments with the r.f. pulse length of 2.5 mks (pi/2 pulse) and a 10 s relaxation delay between pulses, which was found sufficient for a complete relaxation. Total 64 scans were accumulated in each ^1H NMR experiment. ^{13}C CP/MAS NMR spectra were recorded at a resonance frequency of 226.4 MHz under 15 kHz MAS. The CP contact time in all experiments was 1 ms, and a 5 s relaxation delay between pulses. From 2k to 10k scans were accumulated in ^{13}C CP/MAS NMR experiments, depending on the amount of sample available. SPINAL-64 proton decoupling was employed during spectra acquisition. ^{31}P CP/MAS NMR spectra were acquired using a double-resonance 2.5 mm MAS Bruker probe at a resonance frequency of 364.4 MHz under 20 kHz MAS. The CP contact time in all experiments was 3 ms with a delay between acquisitions of 20 seconds. SPINAL-64 proton decoupling was used during spectra acquisition. From 256 to 2048 scans were collected depending on the amount of sample available. ^{31}P NMR chemical shifts were referenced to 85% H_3PO_4 using solid $(NH_4)H_2PO_4$ (ADP) as a secondary chemical shift reference. The same ADP sample was used to setup ^{31}P CP/MAS conditions. The spectra were measured from freshly prepared samples. The IR spectra were acquired on a Bomem FT-IR MB series spectrometer equipped with a baseline-diffused reflectance. Molecular weights and molecular weight distributions of all polymers were determined by using gel permeation chromatography (GPC). The GPC set-up consisted of a Waters 515 HPLC pump, a Waters 996 Photodiode Array Detector and a Waters 410 Differential Refractometer, with a Styragel HR4E column (7.8*300 mm). The GPC eluent was HPLC grade THF, at a flow rate of $0.5 mL.min^{-1}$. Calibration curve was obtained using seven PS standards (Aldrich), with M_n ranging from 3400 to

382 000 g.mol^{-1}. TGA were acquired on a Perkin-Elmer TGA 7 between 50 and 950 °C at 3°C/ min under a nitrogen atmosphere.–Emission and excitation spectra were first obtained using a double monochromator Fluorolog 2 instrument from Spex. Fluorescence lifetimes were measured on a Timemaster Model TM-3/2003 apparatus from PTI using a N_2 laser excited at 330 nm (for **6**). Some phosphorescence lifetime measurements and time-resolved spectra were also performed on a PTI LS-100 using a 1μs tungsten-flash lamp. Second, steady-state and lifetime measurements were also performed on a double grafting FLS920 spectrometer from Edinburgh Instruments. The standard Xe900 continuous xenon lamp (450W), was used for excitation in the steady-state measurements. The standard microsecond flash lamp μF900H (60W, 1μs), was used for excitation in lifetime measurements of the powder samples. The standard red cooled PMT (Hamamatsu R928P) was used for photon detection in steady state and microseconds lifetime measurements. The PMT detector was set on the second monochromator of the emission arm. In all cases, the samples were measured in capillary tubes placed into EPR Dewar mounted on the sample holder of the FLS920. Measurements were carried out at r.t. and for samples cooled down to 77K by N_2(l). Cut-off filters were used to remove higher order effects.

DFT computations. Calculations were performed with Gaussian 09[5] at the Université de Sherbrooke with Mammouth super computer supported by le Réseau Québécois de Calculs de Haute Performances. The DFT[6-9] and TDDFT[10-12] were calculated with the B3LYP[13-15] method. 3-21G*[16-21] basis sets were used for all atoms but VDZ (valence double ζ) with SBKJC effective core potentials[22-24] were used for platinum and mercury. A THF quantum mechanical continuum solvation model was employed .[25]

References

1. S. Clément, L. Guyard, M. Knorr, S. Dilsky, C. Strohmann, and M. Arroyo, *J. Organomet. Chem.,* 2007, **692**, 839.
2. K. Gagnon, S. M. Aly, A. Brisach-Wittmeyer, D. Bellows, J.-F. Bérubé, L. Caron, A. S. Abd-El-Aziz, D. Fortin, and P. D. Harvey *Organometallics* 2008, **27***,* 2201.
3. G. B. Kauffmann and L. A. Teterm, *Inorg. Synth.* 1963, **7,** 245.

4. M. C. Grossel, J. R. Batson, R. P. Moulding, and K. R. Seddon, *J. Organomet. Chem.* 1986, **304,** 391.
5. M. J. Frisch, *et al. Gaussian, Inc.* Pittsburgh P.A., 1998.
6. P. Hohenberg, W. Kohn, *Phys. Rev.* 1964, **136**, B864.
7. W. Kohn and L. J. Sham, *Phys. Rev.* 1965, **140**, A1133.
8. D. R. Salahub and M. C. Zerner (The Challenge of d and f Electrons), *ACS, Washington, D.C.,* 1989.
9. R. G. Parr and W. Yang, (Density-functional theory of atoms and molecules) *Oxford Univ. Press, Oxford,* 1989.
10. R. E. Stratmann, G. E. Scuseria, and M. J. Frisch, *J. Chem. Phys.* 1998, **109**, 8218.
11. R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.* 1996, **256**, 454.
12. M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, *J. Chem. Phys.* 1998, **108***,* 4439.
13. A.D. Becke, *J. Chem. Phys.* 1993, **98**, 5648.
14. L. W. Yang, and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.* 1988, 785.
15. A. Miehlich, H. Savin, and H. Stoll, *Preuss, Chem. Phys. Lett.* 1989, **157**, 200.
16. Binkley, Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* 1980, **102**, 939.
17. M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, *J. Am. Chem. Soc.* 1982, **104**, 2797.
18. W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. Defrees, J. A. Pople, and J. S. Binkley, *J. Am. Chem. Soc.* 1982, **104**, 5039.
19. K. D. Dobbs and W. J. Hehre, *J. Comp. Chem.* 1986, *7,* 359.
20. K. D. Dobbs and W. J. Hehre, *J. Comp. Chem.* 1987, **8***,* 861.
21. K. D. Dobbs and W. J. Hehre, *J. Comp. Chem.* 1987**, 8***,* 880.
22. N. Godbout, D. R. Salahub, J. Andzelm, and E. Wimmer, *Can. J. Chem.* 1992**, 70***,* 560.
23. SBKJC ECP *EMSL Basis Set Exchange Library*.
24. W.J. Stevens, M. Krauss, H. Basch, and P. G. Jasien, *Can. J. Chem.* 1992, **70***,* 612.
25. J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.* 2005, **105***,* 2999.

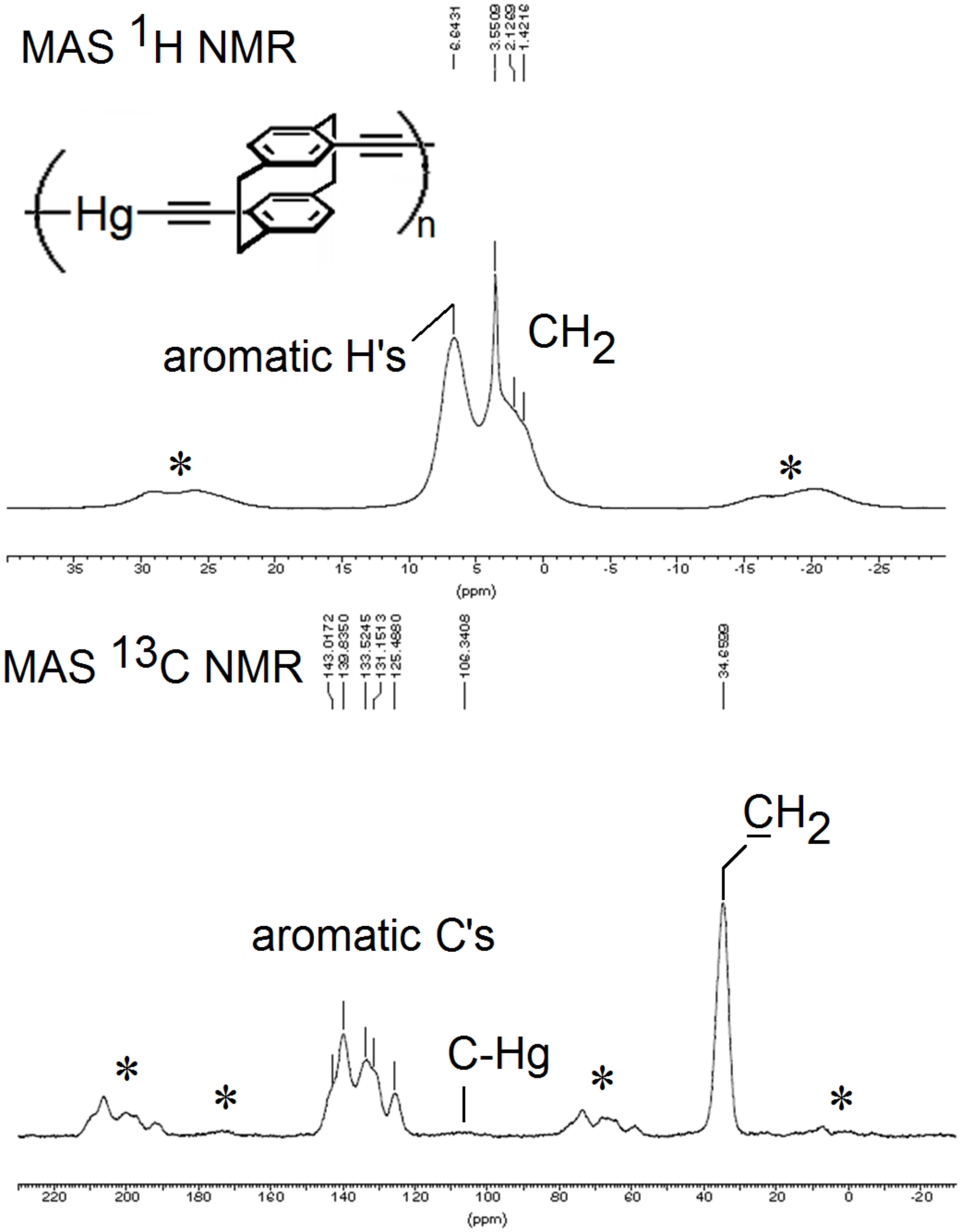


Figure S1. MAS ^{1}H and ^{13}C NMR spectra of polymer **1** at 298 K. The signals marked with stars correspond to spinning side bands.

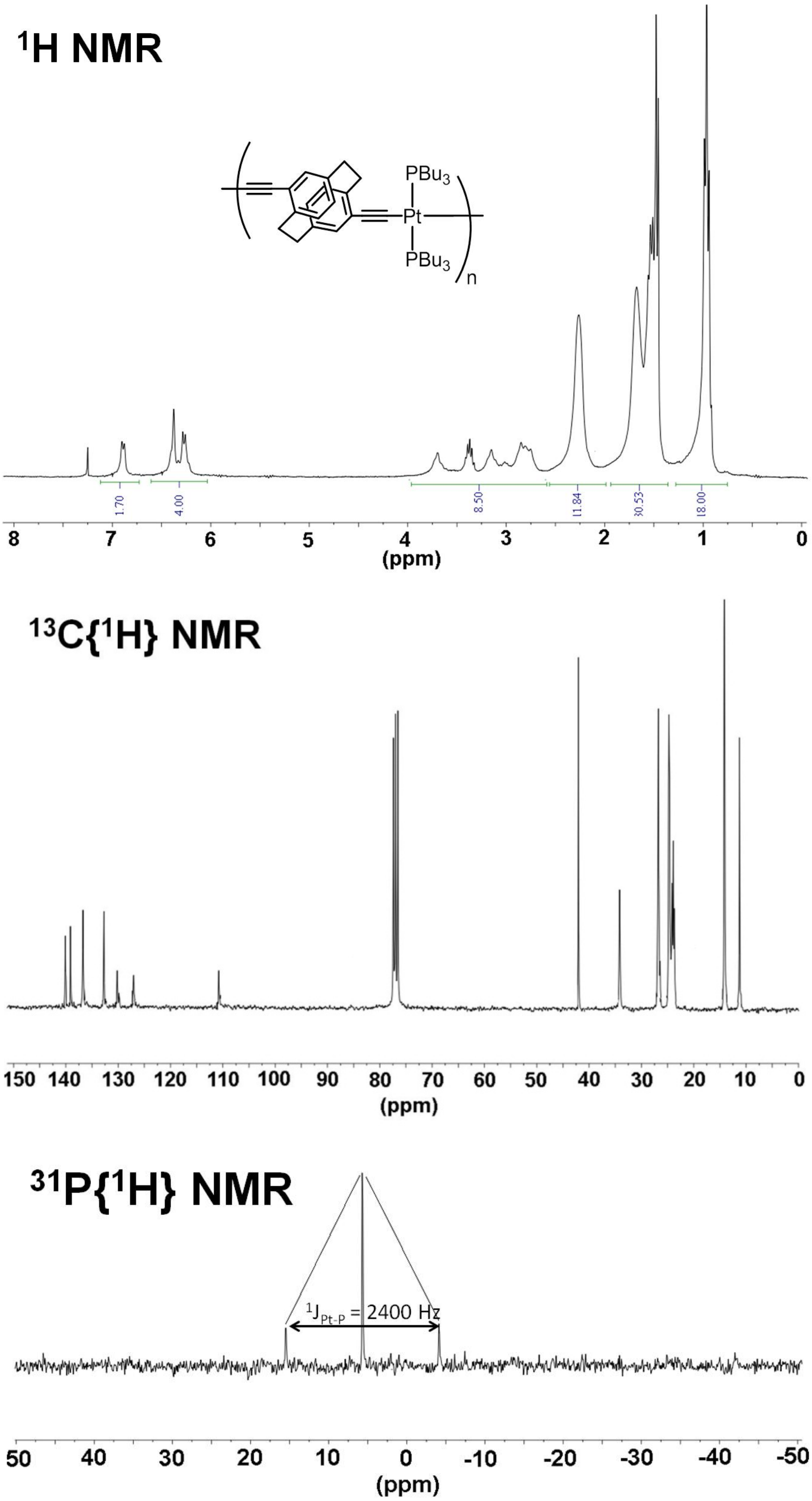


Figure S2. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of polymer **2** in $CDCl_3$ at 298 K.

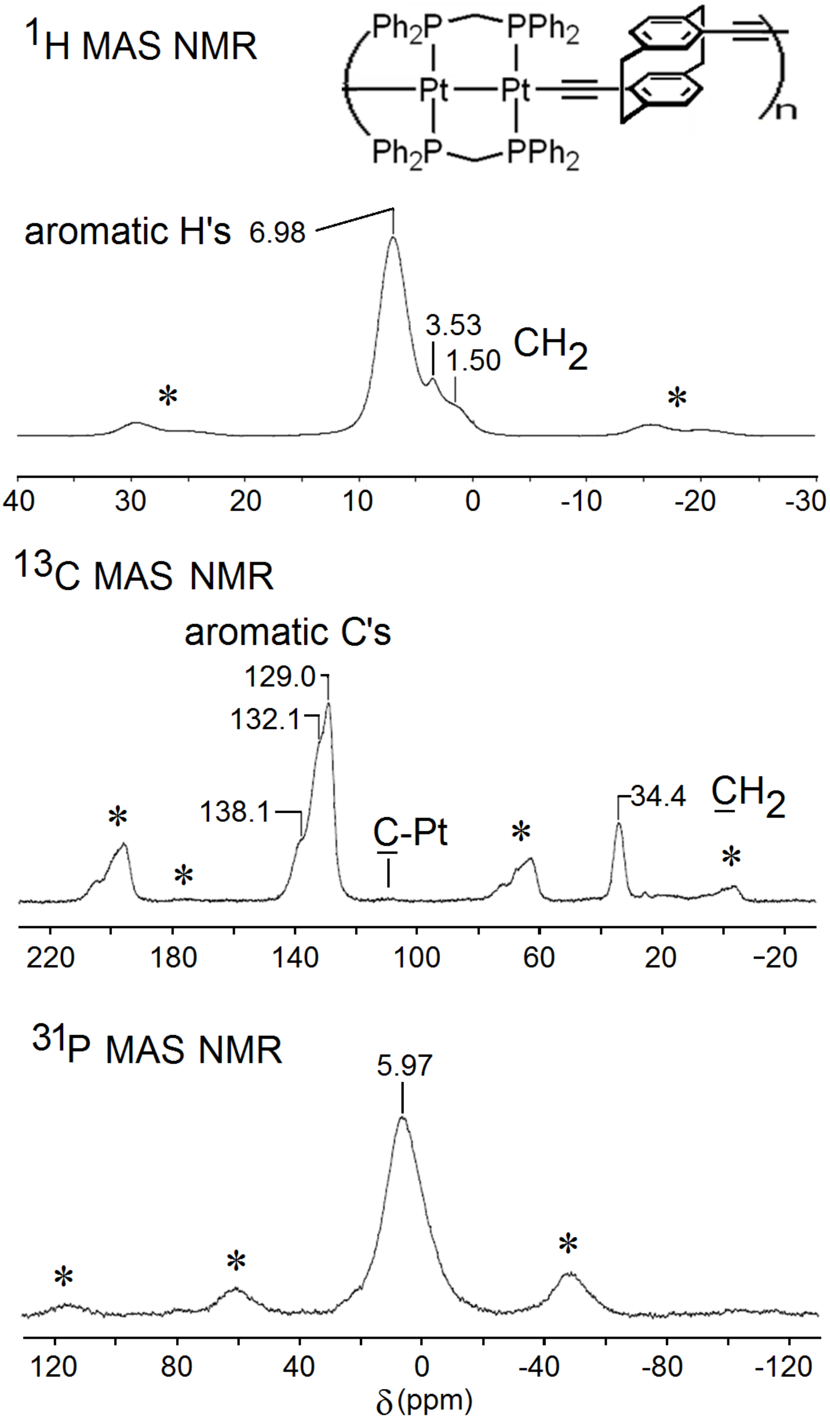


Figure S3. ${}^{1}H$, ${}^{13}C$ and ${}^{31}P$ MAS NMR spectra of polymer **3**. The signals marked with stars correspond to spinning side bands.

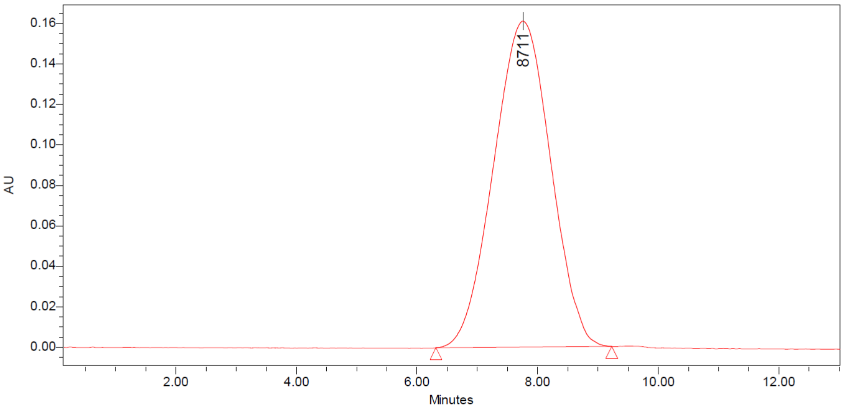


Figure S4. GPC trace for polymer **2** in THF.

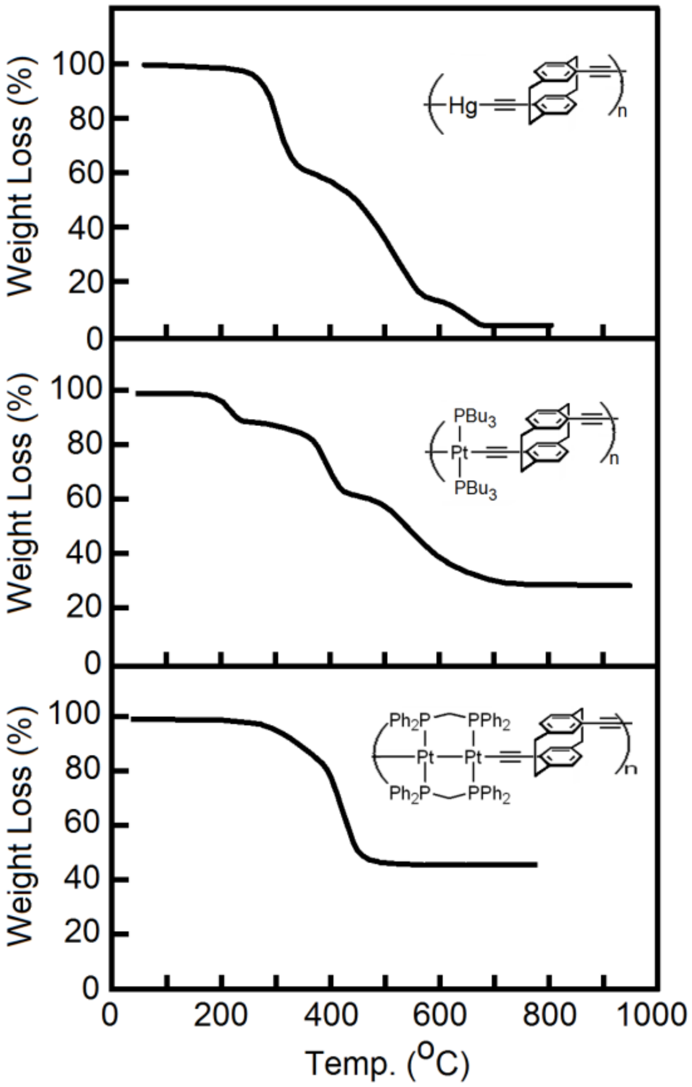


Figure S5. TGA traces for polymers **1**, **2** and **3**. Scan rate = 2°C/min.

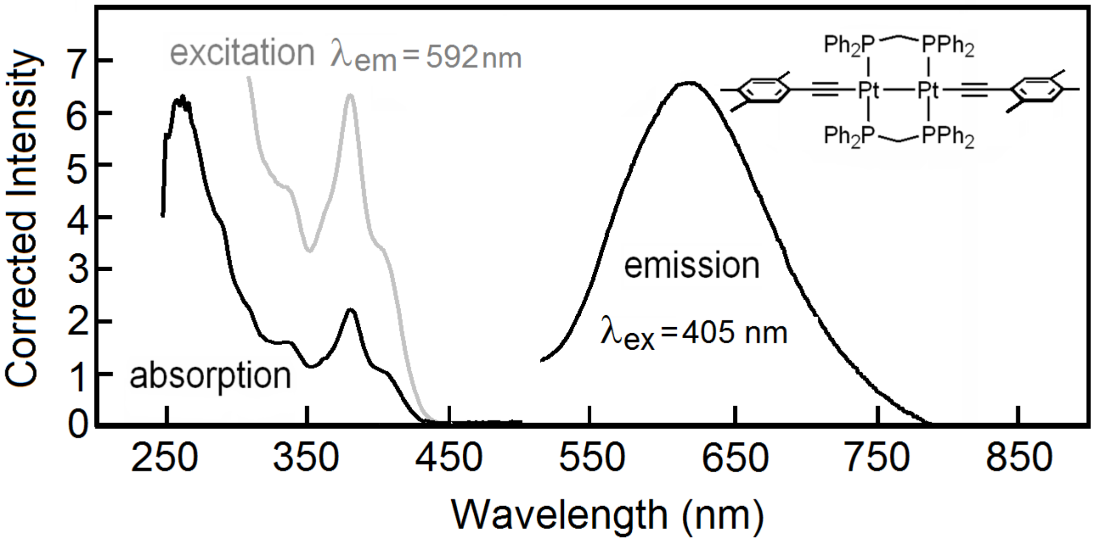
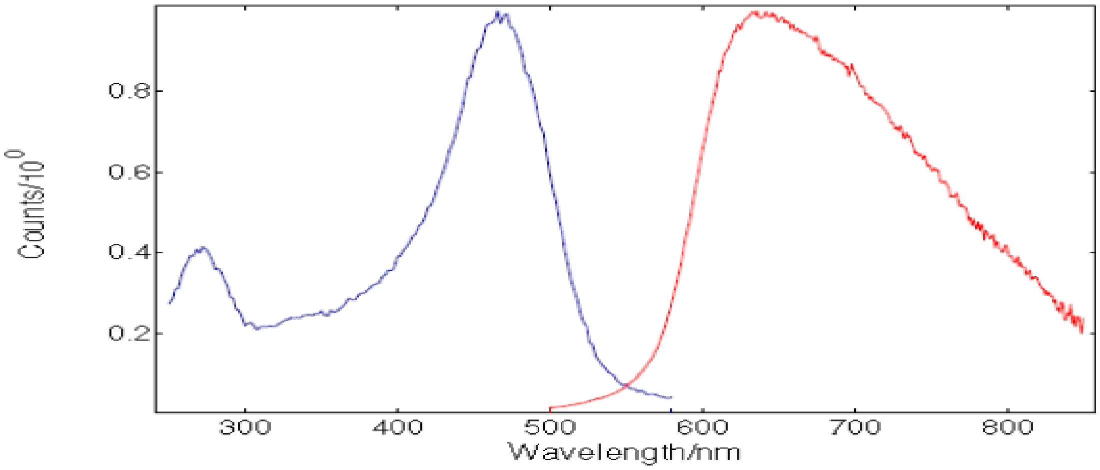


Figure S6. Absorption, excitation and emission spectra of $Pt_2(dppm)_2(C\equiv C(2,4,5\text{-}Me_3C_6H_2))_2$ in 2-MeTHF at 77K.



Normalized excitation and emission spectra of **Pt2PCP** sample at r.t.
Blue – excitation spectrum, λ_{em} = 640nm;
Red – emission spectrum, λ_{exc} = 450nm.

Figure S7. Excitation and emission spectra of polymer **3** in the solid state at 298 K.