

Supplementary Information for *Chem. Commun.*

Self-aggregated phosphorescent platinum(II) polymeric materials from modified poly(4-vinylpyridine)

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General experimental procedure, syntheses, photophysical properties and morphology of the reported PVP-Pt(C^NN) are described.

General Experimental Procedure

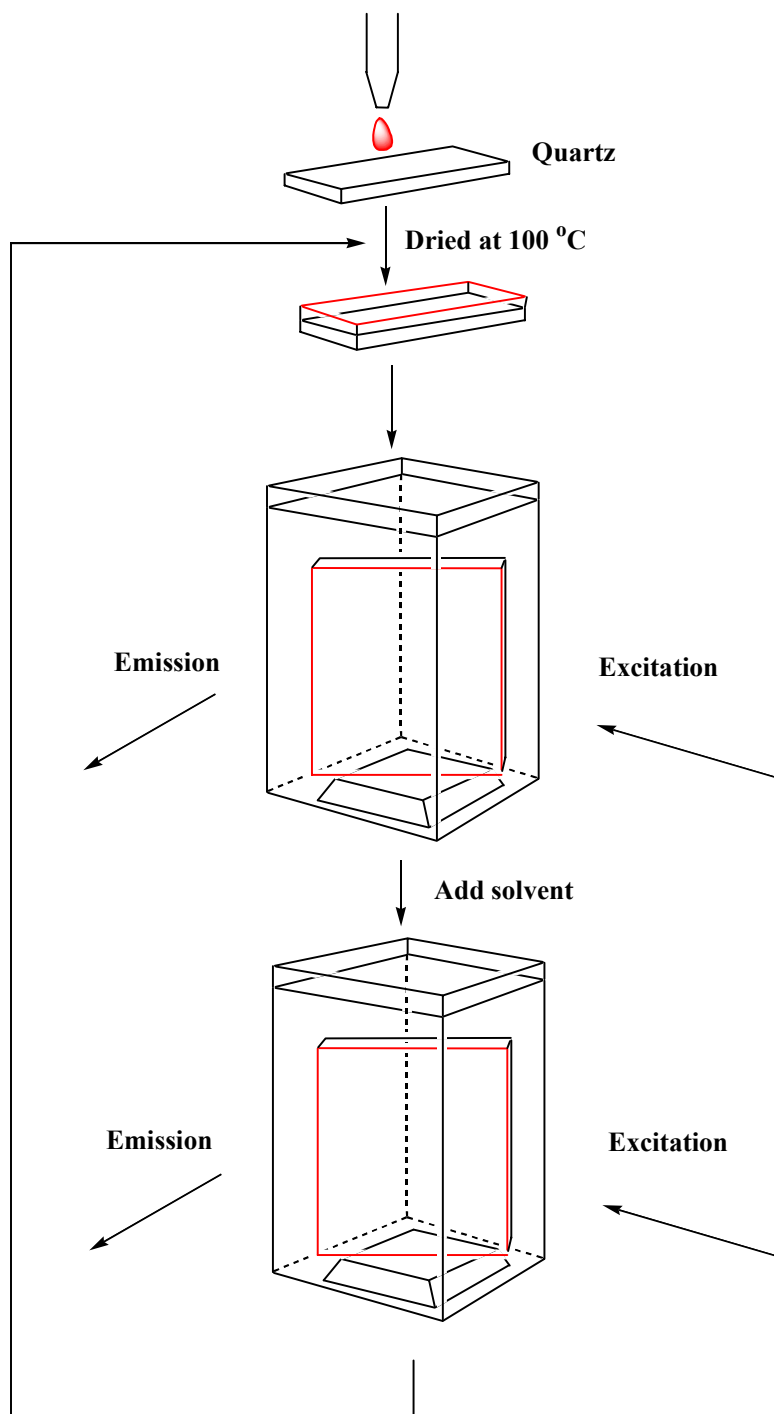
Synthesis of PVP-Pt(C[^]N[^]N)

The (C[^]N[^]N) ligand and [Pt(C[^]N[^]N)Cl] complex were prepared according to method published previously.^{1, 2} PVP (0.2 g) was dissolved in methanol (100 mL). [Pt(C[^]N[^]N)Cl] (0.23 g) was suspended in a further solution of methanol (100 mL) and added to the methanolic solution of PVP. The reaction mixture was warmed to 60 °C under argon for 12 hours, until all the solids had dissolved. The reaction mixture was filtered and concentrated. The polymer product was precipitated using diethyl ether, collected and washed with cold methanol. Yield: 0.41 g (95.4 %). ¹H NMR (270 MHz, CDCl₃) 8.21 (bs, 18H), 6.63 (bs, 20H), 3.87 (bs, 3H), 2.40 (bs, 1H), 1.63 (bs, 12H). Anal. Found: C, 64.69; H, 5.46; N, 9.61; ICP-MS: Pt content = 14.5 % by weight. Both the results from elemental analysis and ICP-MS are consistent with n – m : m = 6 : 1.

Preparation of Polymer Micelles for TEM Measurement

A solution of PVP-Pt(C[^]N[^]N) dissolved in CH₂Cl₂ (0.5 mg / mL) was filtered through a 0.2 μm PTFE member filter. Filtered toluene was added slowly and continuously to the CH₂Cl₂ solution of PVP-Pt(C[^]N[^]N) using a syringe pump at a constant rate of 1.7 mL / hour, until turbidity in the solution was observed. To prepare a polymer film for TEM measurement, the PVP-Pt(C[^]N[^]N) micelle solution was dropped into water for precipitation.

Procedure of studying the solvochromic behaviour of PVP-Pt(C^NN) film in saturated solvent vapour



Scheme S1. Study of the solvochromic behaviour of PVP-Pt(C^NN) film in saturated solvent vapour

Physical characterization of PVP-Pt(C[^]N[^]N[^])

¹H and ¹³C NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR system, with chemical shifts (in ppm) determined relative to tetramethylsilane. UV/vis spectra were recorded on a PerkinElmer Lambda 900 UV/vis spectrophotometer. Emission spectra were obtained on a SPEX Fluorolog-3 fluorescence spectrophotometer. The decomposition temperature was determined using a PerkinElmer TGA 7 in N₂ atmosphere with heating rate of 15 °C / min. Particle diameters in various solvents were measured using a Malvern Zetasizer 3. Transmission electron micrographs were recorded on a JEOL-100 electron microscope operated at 80 kV.

Table S1. Data illustrating the change in physical and photoluminescent behaviour of PVP-Pt(C[^]N[^]N[^]) (n – m : m = 6 : 1) with various solvents

	CH ₂ Cl ₂	CHCl ₃	CH ₃ OH	DMF	Hexane	Benzene
PL solution emission λ _{max} of PVP-Pt(C [^] N [^] N [^]) (nm)	558	637	645	550	N / A ^a	N / A ^a
PL film emission ^b λ _{max} of PVP-Pt(C [^] N [^] N [^]) (nm)	623	598	633	N / A ^c	583	572
PL solution emission λ _{max} of [Pt(C [^] N [^] N [^])py]Cl ^d (nm)	558	560	547	551	N / A ^a	571
Particle diameter of PVP (nm)	19	17	19	15	N / A ^a	N / A ^a
Particle diameter of PVP-Pt(C [^] N [^] N [^]) (nm)	27	92	49	24	N / A ^a	N / A ^a

^a N / A = not applicable. No measurement was made since PVP-Pt(C[^]N[^]N[^]) is insoluble in these solvents.

^b PL emission λ_{max} of PVP-Pt(C[^]N[^]N[^]) film in air is 573 nm.

^c N / A = not applicable. No measurement was made since an atmosphere of saturated DMF vapour cannot be achieved at room temperature.

^d $[\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{py}]\text{Cl}$ (py = pyridine) is the model compound for PVP- $\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})$.

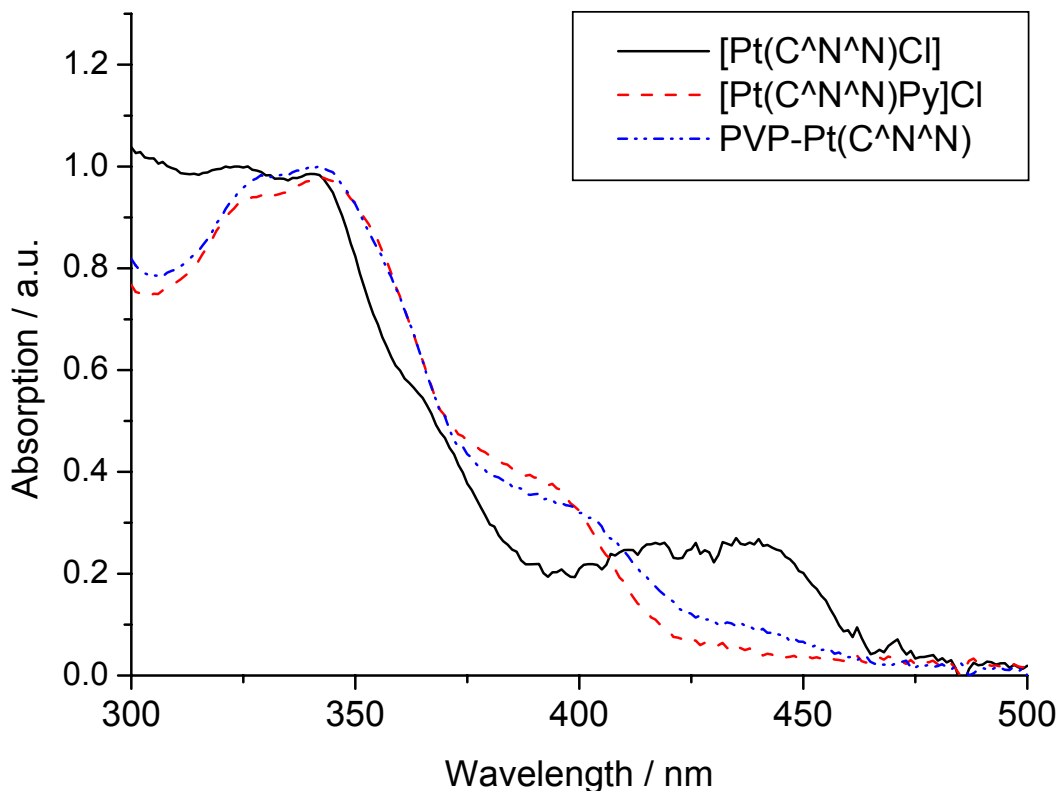


Figure S1. Absorption spectra of $[\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{Cl}]$, $[\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{py}]\text{Cl}$ (py = pyridine) and PVP- $\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})$ in DMF solutions. The blue-shifting of the $^3\text{MLCT}$ absorption λ_{max} of $[\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{Cl}]$ at 437 nm to 394 and 401 nm for $[\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{py}]\text{Cl}$ (py = pyridine) and PVP- $\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})$ respectively is expected upon coordination of a pyridine moiety to a platinum complex.³

References:

- 1 E. C. Constable, R. P. G. Henney, T. A. Leese, and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1990, 513.
- 2 F. Kröhnke, *Synthesis*, 1976, 1.
- 3 S.-W. Lai, M. C.-W. Chan, T.-C. Cheung, S.-M. Peng, and C.-M. Che, *Inorg. Chem.*, 1999, **38**, 4046.