Supporting Information

Solvatochromic response imposed by environmental changes in matrix/chromophore entities: luminescent cyclometalated platinum(II) complex in Nafion and silica materials

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Experimental procedures and characterisation data for $[Pt(L)py]^+$ (**1**) and $[Pt(L)NH_2{}^tBu]ClO_4$. Emission spectra for various loadings of $[Pt(L)]^+$ on different supports and solvato-/vapochromic responses.

Experimental Section

Materials. Nafion film 417 with thickness of 0.017 inch was purchased from Aldrich. Acetonitrile for photophysical measurements was distilled over potassium permanganate and calcium hydride. All other solvents were of analytical grade and purified according to conventional methods.[1]

Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan Mat 95 mass spectrometer. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra were recorded on DPX 500 Bruker FT-NMR spectrometers respectively with chemical shift (in ppm) relative to tetramethylsilane. Elemental analysis was performed by the Institute of Chemistry at the Chinese Academy of Sciences, Beijing. UV-vis spectra were recorded on a Perkin Elmer Lambda 19 UV/vis spectrophotometer.

Emission and Lifetime Measurements. Steady-state emission spectra were recorded on a SPEX 1681 Fluorolog-2 series F111AI spectrophotometer. The emission spectra were corrected for monochromator and photomultiplier efficiency and for xenon lamp stability.

Emission lifetime measurements were performed with a Quanta Ray DCR-3 pulsed Nd:YAG laser system (pulse output 355 nm, 8 ns). The emission signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix model 2430 digital oscilloscope. Errors for λ values (± 1 nm), τ (± 10 %), ϕ (± 10 %) are estimated.

General Procedures. $[Pt(L)py]ClO_4$ (**1**) (HL = 4,6-diphenyl-2,2'-bipyridine) was prepared similarly by procedure for $[Pt(C^\wedge N^\wedge N)py]ClO_4$ ($HC^\wedge N^\wedge N$ = 6-phenyl-2,2'-bipyridine).[2] A mixture of [Pt(L)Cl] (0.30 g, 0.56 mmol) and excess pyridine (0.20 g, 2.53 mmol) in CH_3CN/CH_3OH (20/20 mL) was stirred for 3 hours at room temperature. Excess

$LiClO_4$ (0.2 g) was added to the resultant mixture, which was stirred for five hours, then filtered and evaporated to ~5 mL. Addition of diethyl ether yielded a yellow solid, which was filtered and washed with diethyl ether. Recrystallisation by vapour diffusion of diethyl ether into an acetonitrile solution yielded 0.32 g (84 %) of yellow crystals. ^{1}H NMR (DMSO-d_6): δ 7.09 (t, 1H, *J* = 7.3 Hz), 7.15 (t, 1H, *J* = 7.2 Hz), 7.35–7.39 (m, 2H, py), 7.50 (d, 1H, *J* = 7.3 Hz), 7.58–7.63 (m, 3H), 7.77 (t, 1H, *J* = 7.6 Hz, py), 7.82 (d, 1H, *J* = 7.4 Hz), 7.92 (t, 1H, *J* = 6.4 Hz), 8.11 (d, 2H, *J* = 6.9 Hz), 8.27 (s, 1H), 8.37 (t, 1H, *J* = 7.8 Hz), 8.52 (s, 1H), 8.56 (d, 2H, *J* = 4.1 Hz, py), 8.75 (d, 1H, *J* = 8.0 Hz), 8.92 (d, 1H, *J* = 5.1 Hz). MS (FAB, +ve NBA matrix): *m/z* 581 (M^+).

$[Pt(L)NH_2{}^tBu]ClO_4$ was prepared by stirring an equimolar amount of *tert*-butylamine and [Pt(L)Cl] in acetonitrile for 3 h. Excess $LiClO_4$ was added to yield an orange precipitate, which was collected and washed with diethyl ether. The product was purified by vapour diffusion of diethyl ether into an acetonitrile solution. Anal. Found: C, 46.02; H, 3.78; N, 6.45. $C_{26}H_{26}N_3ClO_4Pt$ requires: C, 46.26; H, 3.88; N, 6.22%. ^{1}H NMR (DMSO-d_6): δ 1.41 (s, 9H, ^{t}Bu), 5.76 (broad s, 2H, NH_2), 7.17 (t, 1H, *J* = 7.3 Hz), 7.25 (t, 1H, *J* = 7.2 Hz), 7.52 (d, 1H, *J* = 7.3 Hz), 7.58–7.65 (m, 3H), 7.92 (d, 1H, *J* = 7.9 Hz), 7.97 (t, 1H, *J* = 6.2 Hz), 8.13 (d, 2H, *J* = 7.8 Hz), 8.36 (s, 1H), 8.43 (t, 1H, *J* = 7.8 Hz), 8.59 (s, 1H), 8.83 (d, 1H, *J* = 8.0 Hz), 9.19 (d, 1H, *J* = 4.9 Hz). MS (FAB, +ve NBA matrix): *m/z* 575 (M^+).

Figure 1. Emission spectra (λ_{ex} 350 nm) of **1** in Nafion film at 298 K after immersion in an acetonitrile solution of **1** (5×10^{-5} M) for various times; * denotes instrumental artifact.

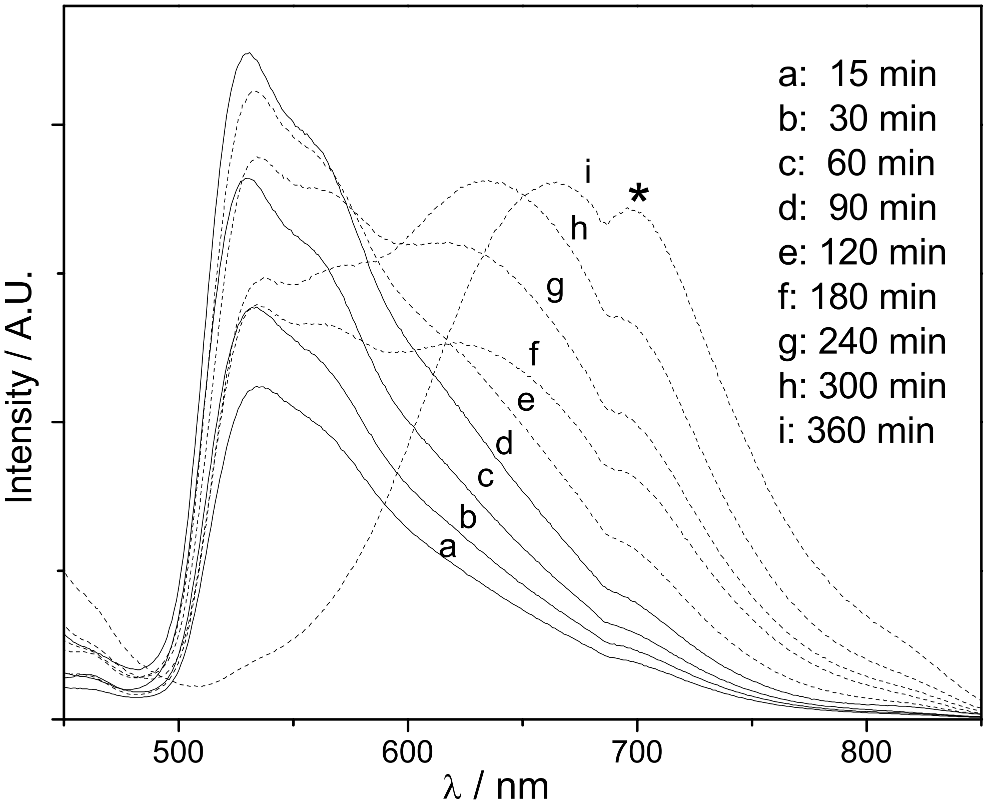


Figure 2. Emission spectra (λ_{ex} 380 nm) of [Pt(L)-MCM-41] afforded using different concentrations of [Pt(L)Cl] in the incorporation procedure: (a) 3.72×10^{-4}, (b) 9.30×10^{-4}, (c) 1.86×10^{-3}, (d) 2.79×10^{-3}, (e) 3.72×10^{-3} mol dm^{-3}; * denotes instrumental artifact.

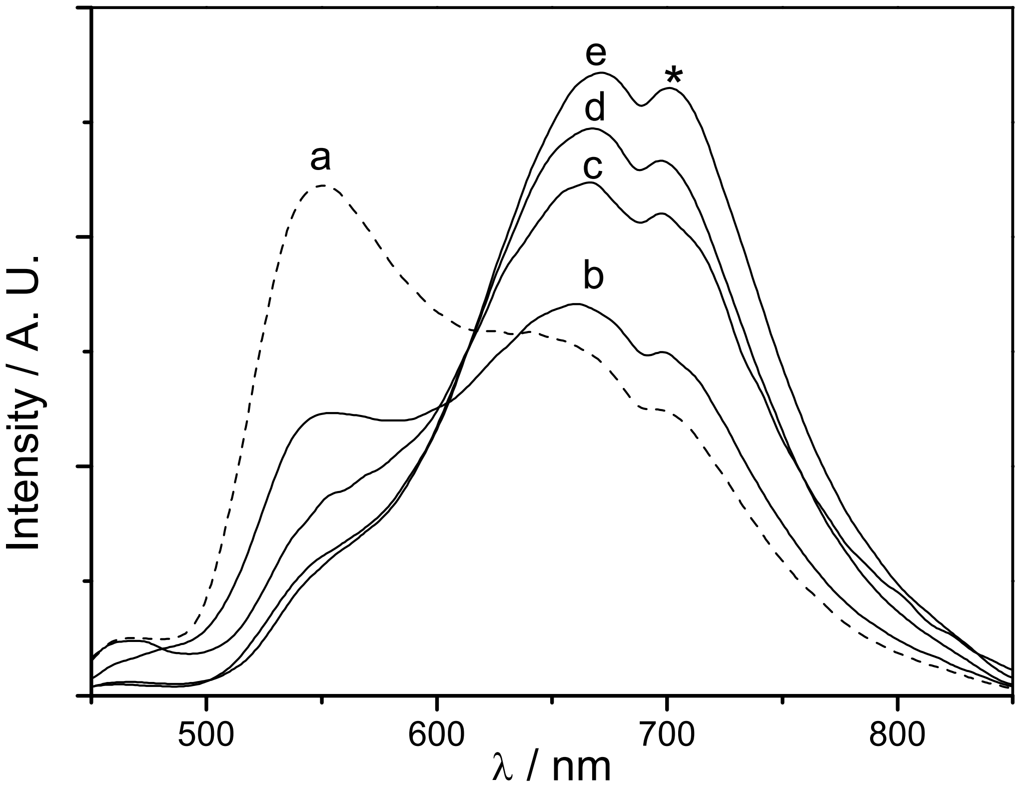


Figure 3. Emission spectra (λ_{ex} 380 nm) of [Pt(L)-MCM-48] afforded using different concentrations of [Pt(L)Cl] in the incorporation procedure: (a) 1.86 × 10^{-4}, (b) 3.72 × 10^{-4}, (c) 9.30 × 10^{-4}, (d) 1.86 × 10^{-3}, (e) 2.79 × 10^{-3}, (f) 3.72 × 10^{-3} mol dm^{-3}; * denotes instrumental artifact.

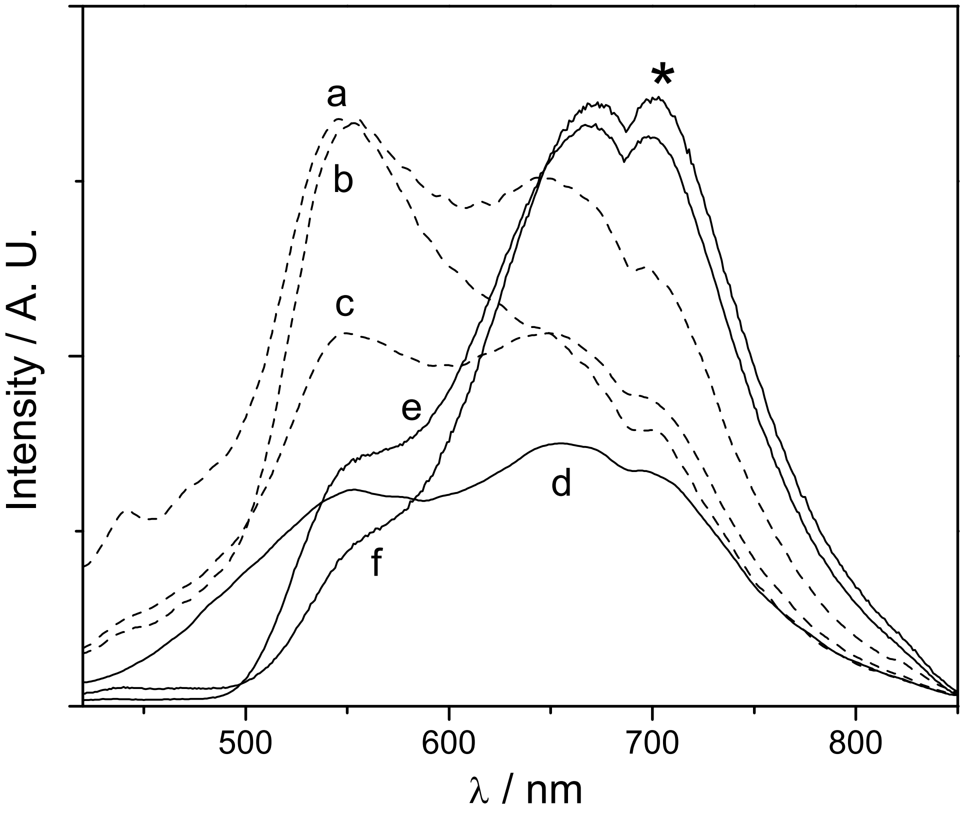


Figure 4. Emission spectra (λ_{ex} 380 nm) of [Pt(L)-MCM-48] with high platinum content before (a), and after (b) exposure to benzene vapour for 10 minutes at 298 K; * denotes instrumental artifact.

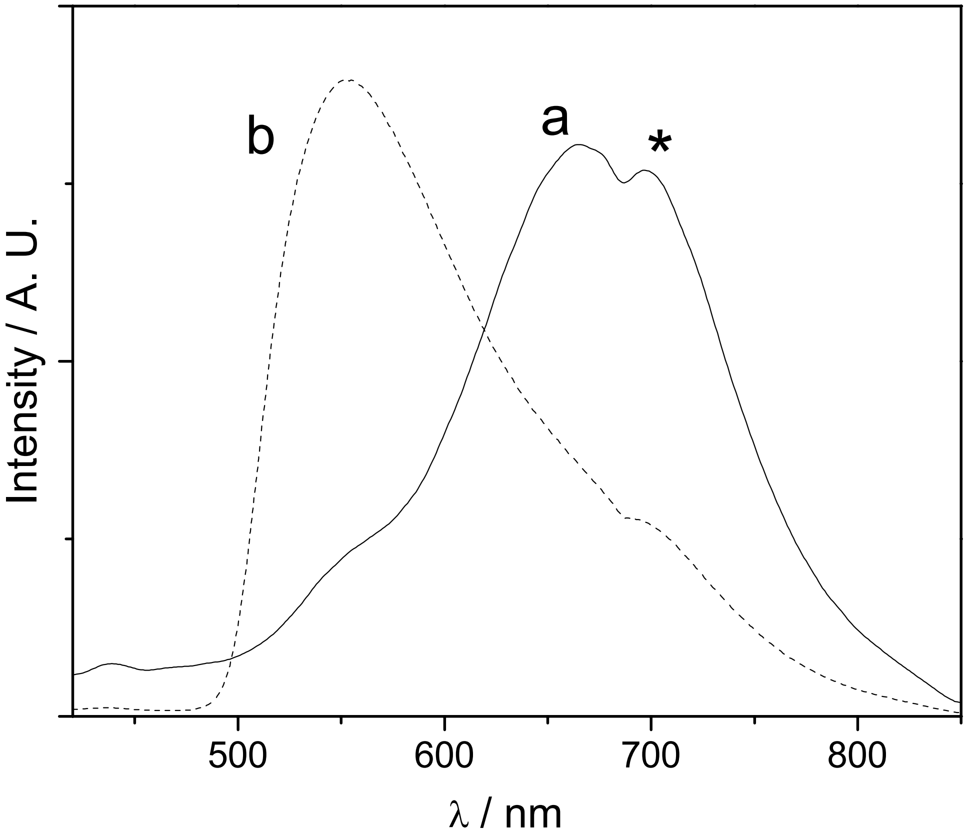
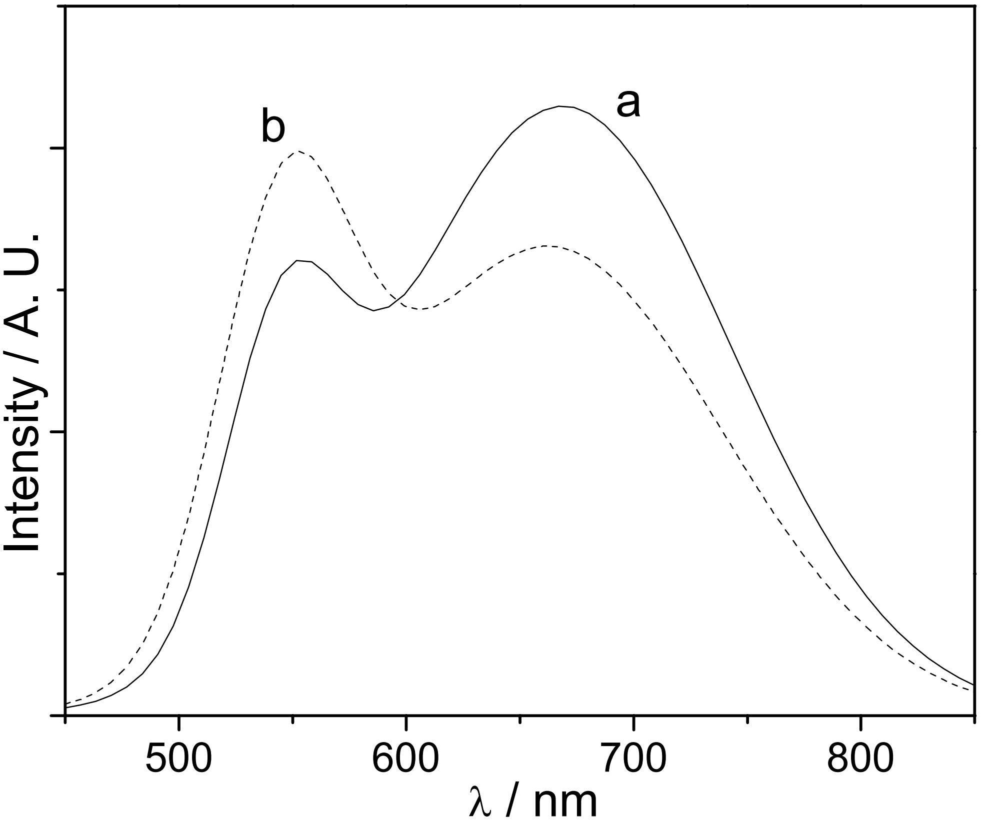


Figure 5. Emission spectra (λ_{ex} 380 nm) of [Pt(L)-silica gel] ([Pt] = 2.5 wt %) before (a), and after (b) exposure to pentane vapour at 298 K.



References

1 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*; 2nd ed., Pergamon: Oxford, 1980.

2 S. W. Lai, M. C. W. Chan, T. C. Cheung, S. M. Peng and C. M. Che, *Inorg. Chem.*, 1999, **38**, 4046.