

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

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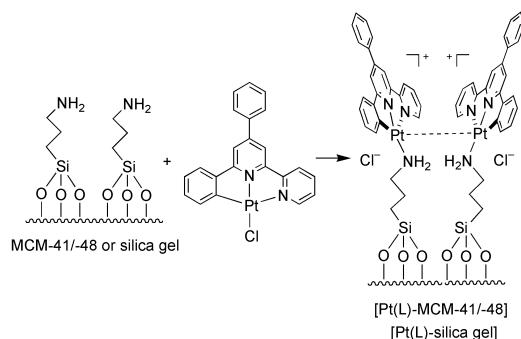
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Luminescent cyclometalated complex [Pt(L)py]⁺ (**1**) immobilised in Nafion film exhibits a solvatochromic shift in emission maximum from 530 to 650 nm upon immersion in ethanol but no effect is detected with aprotic organic solvents, whereas the emission of the [Pt(L)]⁺ luminophore anchored in silica materials shows a blue shift from ~665 to 550 nm upon exposure to pentane vapour but no shift is observed for ethanol vapour.

The susceptibility of metal–metal-to-ligand charge transfer (MMLCT) [$d\sigma^* \rightarrow p\sigma$] absorption and emission energies in weakly interacting platinum(II) diimine systems to be affected by subtle changes in the micro-environment has received tremendous attention over the past several years.¹ Perturbation of metal–metal and/or ligand–ligand interactions causes changes in photoluminescence excited states from triplet MMLCT (usually at $\lambda > 650$ nm) to MLCT (λ 500–550 nm) or *vice versa*, and this can be a useful operating principle for the design of luminescent sensory devices.² If the platinum(II) luminophore is embedded inside a host or supporting matrix,³ we envision that host–guest (analyte, such as volatile organic compounds (VOCs)) contacts could affect the metal–metal and/or ligand–ligand interactions and hence the interchange between ³MMLCT and ³MLCT states. Herein is described the employment of the cyclometalated [Pt(L)]⁺ (HL = 4,6-diphenyl-2,2'-bipyridine) moiety as a luminescent probe in Nafion 417 film and silica materials. Importantly, we demonstrate that the influence of guest molecules upon the nature of the emissive state and energy (³MLCT or/and ³MMLCT) can differ significantly depending on the supporting host material.

The complex [Pt(L)py]⁺ (**1**) was prepared according to the literature method.⁴ Incorporation of **1** into Nafion film was achieved by adopting the previously reported procedures.⁵ Immobilisation of [Pt(L)]⁺ moieties into MCM-41/-48 and silica gel were obtained by reacting [Pt(L)Cl] with the modified silica surfaces as depicted in Scheme 1.



Scheme 1

† Electronic supplementary information (ESI) available: characterisation data for **1** and [Pt(L)NH₂^tBu]ClO₄, and emission spectra for various loadings of [Pt(L)]⁺ on different supports and solvato-/vapochromic responses. See <http://www.rsc.org/suppdata/cc/b2/b210284f/>

A series of absorption spectra for the incorporation of **1** into a Nafion film (0.5×0.5 cm²) were obtained by the immersion of the Nafion film in an acetonitrile solution of **1** (3×10^{-5} mol dm⁻³) for extended periods (Fig. 1). The absorbance increases as the loading of **1** proceeds. The inset of Fig. 1 shows the absorbance at 350 nm as a function of loading time, which reaches a plateau after *ca.* 600 min of loading. The difference between the concentration of the solution before and after loading revealed that ~0.07 mg of **1** had been immobilised into the Nafion film.

The emission of the modified Nafion film depends on the loading time (see ESI[†]). After immersing a 0.5×0.5 cm² piece of Nafion film in an acetonitrile solution of **1** (5×10^{-5} mol dm⁻³) for up to 90 min, the film exhibits an intense emission at λ_{max} 530 nm, which is comparable to the ³MLCT emission of **1** in acetonitrile (λ_{max} 542 nm) at room temperature. As the loading time is increased (120–300 min), the intensity of the ³MMLCT emission at $\lambda > 600$ nm increases at the expense of the ³MLCT band at λ_{max} 530 nm. At loading times of more than 300 min, only the 665 nm emission is observed.

We investigated the solvatochromic response of the Nafion film that is not 'saturated' with **1** (loading time ~90 min), for which the intrinsic emission band appears at 530 nm. Upon immersing the film in solvents such as pentane, benzene, acetonitrile or dichloromethane, this emission showed no notable shift in energy (λ_{max} ~532 nm), whereas in ethanol, the emission maximum significantly red-shifted to 650 nm (Fig. 2). This shift in emission energy in ethanol was reversible and the yellow emission was restored after the film was dried in air for 24 h at room temperature. Such interchange between the ³MLCT (λ_{max} 530 nm) and ³MMLCT (λ_{max} 650 nm) emissions implies that intrusion of ethanol into the Nafion host can significantly alter the metal–metal and/or ligand–ligand interactions between [Pt(L)py]⁺ units when the Nafion film is partially loaded.‡

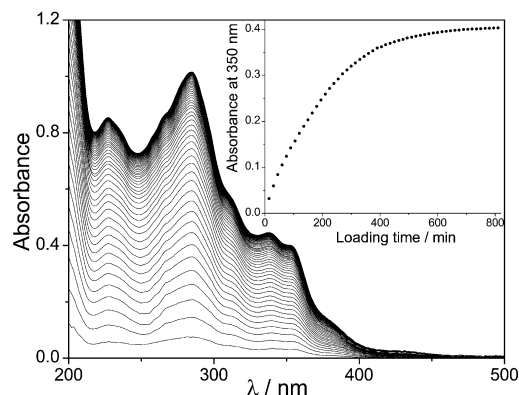


Fig. 1 UV-vis absorption spectra of **1** in Nafion at various times (15–810 min) after immersion into an acetonitrile solution of **1** (3×10^{-5} mol dm⁻³). The spectra represent the difference between the spectra recorded immediately after introducing the film into the solution and those recorded at later times. Inset: absorbance at 350 nm as a function of loading times.

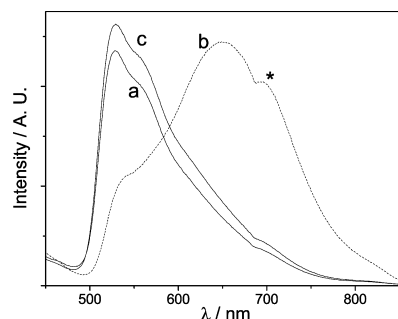


Fig. 2 Emission spectra (λ_{exc} 350 nm) of Nafion film incorporated with **1** (for 90 min) before (a), and after (b) immersion in ethanol for 20 min, and (c) after drying in air for 24 h; * denotes instrumental artifact.

The solvatochromic behaviour of **1** in Nafion film was compared with that of $[\text{Pt}(\text{L})]^+$ attached to silica materials. The FT Raman spectrum of $[\text{Pt}(\text{L})\text{Cl}]$ shows the $\nu(\text{Pt}-\text{Cl})$ stretching at 331 cm^{-1} , which disappears upon immobilisation into MCM-41 and -48. The X-ray powder diffraction patterns of MCM-41, APTES-modified MCM-41, and $[\text{Pt}(\text{L})\text{-MCM-41}]$ are almost identical, indicating that the structure of MCM-41 is retained.⁶ The platinum content ($[\text{Pt}]$) in $[\text{Pt}(\text{L})\text{-MCM-41}]$ determined by ICP atomic emission spectroscopy lies in the range 0.18–5.36 wt%, and increases with the concentration of $[\text{Pt}(\text{L})\text{Cl}]$ used in the incorporation procedure. When platinum loading is low ($[\text{Pt}] < 0.4\text{ wt}\%$), excitation at 380 nm results in an emission band at λ_{max} 550 nm ($\tau = 1.6\text{ }\mu\text{s}$) which is comparable to the $^3\text{MLCT}$ emission (λ_{max} 550 nm, $\tau = 1.0\text{ }\mu\text{s}$) of $[\text{Pt}(\text{L})\text{NH}_2\text{Bu}]\text{-ClO}_4$ in acetonitrile. As $[\text{Pt}]$ is increased, an emission band at $\lambda_{\text{max}} > 660\text{ nm}$ increases in intensity at the expense of the 550 nm emission. At $[\text{Pt}] > 2.8\text{ wt}\%$, only the emission at 670 nm ($\tau_1 = 0.24\text{ }\mu\text{s}$, $\tau_2 = 0.88\text{ }\mu\text{s}$) is observed and this is assigned to a $^3\text{MMLCT}$ excited state. Similar findings were noted using MCM-48 instead of MCM-41 (see ESI[†]).

Photoluminescence responses of $[\text{Pt}(\text{L})\text{-MCM-41}]$ and $[\text{Pt}(\text{L})\text{-MCM-48}]$ towards solvents were investigated using $[\text{Pt}]$ of 2.8 wt%, which displays a red emission at λ_{max} 662 nm at 298 K. The $[\text{Pt}(\text{L})\text{-MCM-41/-48}]$ materials were placed in an airtight tank saturated with vapours of a low-polarity solvent such as pentane, benzene, chloroform, or dichloromethane for 10 min, and a substantial blue-shift of the emission maximum to 548 nm was observed (Fig. 3). This process was reversible and the red emission was restored to its original intensity after the sample was removed from the tank and dried in air for 3 d. In contrast to the Nafion material, there was no noticeable shift in emission energy when $[\text{Pt}(\text{L})\text{-MCM-41/-48}]$ was similarly exposed to ethanol or methanol vapour. Similar vapochromic behaviour towards low-polarity solvents was observed for $[\text{Pt}(\text{L})\text{-silica gel}]$ with $[\text{Pt}]$ of 2.5 wt% (see ESI[†]), but in this case, incomplete conversion of the $^3\text{MMLCT}$ to $^3\text{MLCT}$ emission was observed. We expect that the high surface area and large pore volume of the MCM-41/-48 supports³ will facilitate rapid and reversible sorption/desorption of solvent molecules into the channels of the $[\text{Pt}(\text{L})\text{-MCM-41/-48}]$ materials, and we ascribe the lower optical response of $[\text{Pt}(\text{L})\text{-}$

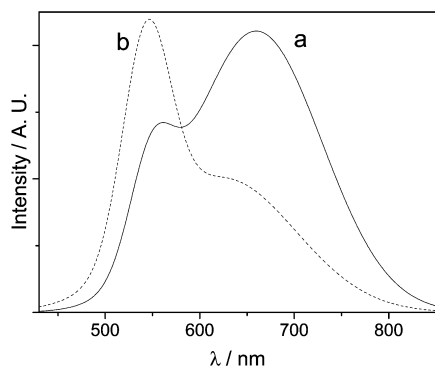


Fig. 3 Emission spectra (λ_{exc} 380 nm) of $[\text{Pt}(\text{L})\text{-MCM-41}]$ ($[\text{Pt}] = 2.8\text{ wt}\%$) before (a), and after (b) exposure to pentane vapour at 298 K.

silica gel] towards low-polarity solvents to the amorphous nature of the surface structure.

The dissimilar solvato-vapochromic behaviour of the $[\text{Pt}(\text{L})]^+$ sensory probe when incorporated into different supports deserves further discussion. The $[\text{Pt}(\text{L})]^+$ chromophore in Nafion film revealed a solvatochromic shift towards ethanol only, while embedding this luminescent probe into silica materials resulted in sensitivity towards low-polarity solvents but not alcohols. This demonstrates that the sensing mechanism of the emissive component $[\text{Pt}(\text{L})]^+$ is different when the supporting matrix is changed. Possible interaction of ethanol with the sulfonate ionic sites or fluorocarbon phase of the Nafion membrane⁷ may affect the remote phenyl rings attached to the cyclometalated $\text{C}^{\wedge}\text{N}^{\wedge}\text{N}$ ligands leading to aggregation of the luminophore **1**, and hence the low-energy $^3\text{MMLCT}$ emission. On the contrary, interaction between silica materials and alcohols could be less prevalent. Instead, the high sorption capacity of silica materials for low-polarity or nonpolar solvents such as benzene⁸ and pentane could lead to disruption and segregation of the metal–metal and/or ligand–ligand interactions among the incorporated $[\text{Pt}(\text{L})]^+$ moieties. It is apparent that the resulting matrix/solvent interaction consequently influences the micro-environment of the $\text{Pt}(\text{II})$ luminophore, and hence the metal–metal and/or ligand–ligand interactions, leading to a switching phenomenon. Thus, anchoring luminescent platinum(II) probes onto a variety of functionalised supporting frameworks could pave the way for new developments in luminescent sensory materials.

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Notes and references

† Photoluminescence response towards solvents was also examined using Nafion films with high loading of **1** (loading time > 400 min). The emission at 653 nm displayed no notable shift in energy upon immersing the film in ethanol. This suggests that when a Nafion film is fully loaded with **1**, the effect upon the intermolecular metal–metal and/or ligand–ligand interactions is less apparent.

§ MCM-41 and -48 were prepared by literature methods.⁹ The modified MCM-41/-48 with (3-aminopropyl)triethoxysilane (APTES)¹⁰ (100 mg) was stirred with $[\text{Pt}(\text{L})\text{Cl}]$ (0.7–25 mg) in CHCl_3 (10 mL) for 8 h at room temperature. The resultant $[\text{Pt}(\text{L})\text{-MCM-41/-48}]$ was washed with CHCl_3 and dried. Incorporation of $[\text{Pt}(\text{L})]^+$ moieties into APTES-modified silica gel¹¹ was similarly obtained.¹²

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