

Luminescent metallogels of platinum(II) terpyridyl complexes: interplay of metal···metal, π - π and hydrophobic-hydrophobic interactions on gel formation†

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A series of platinum(II) terpyridyl complexes has been demonstrated to show gelation properties driven by Pt···Pt and π - π interactions in addition to hydrophobic-hydrophobic interactions; counter-anions have been found to affect strongly the colour of the metallogel.

Luminescent square-planar d⁸ platinum(II) polypyridyl complexes have been extensively studied due to their intriguing spectroscopic and luminescence properties,¹⁻⁴ as well as their propensity to exhibit metal-metal and π - π interactions.^{1a-c,2a-c,g-h,3} A particular class of platinum(II) complexes that has attracted much attention is the platinum(II) terpyridyl complexes, in which the extents of the d⁸-d⁸ metal-metal interaction and the π - π interaction of the terpyridyl ligand have been shown to play a major role in governing the spectroscopic and luminescence properties.^{2a-c,g-h,3}

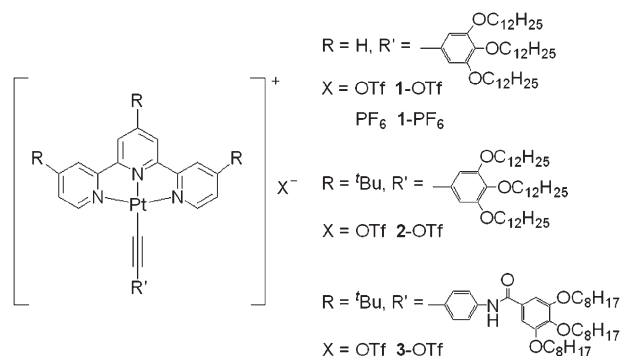
Recently, we reported that platinum(II) terpyridyl alkynyl complexes³ could show drastic colour changes and luminescence enhancement due to an intermolecular aggregation and oligomerisation process caused by polymer-induced^{3d} or solvent-induced^{3a,c} self-assembly as well as intramolecular self-association^{3e} of the metal complexes. The reason behind these remarkable spectroscopic changes upon the conformational and microenvironmental changes is suggested to be the formation of inter- or intramolecular Pt···Pt and π - π interactions in solution.

Despite recent growing interest in the development of low molecular-weight organogels, most of the work has been directed towards the utilisation of noncovalent van der Waals' forces, π - π stacking and hydrogen bonding interactions as the driving force for gelation.^{5,6} Recently, there has also been growing interest in the study of metallogels, owing to the rich spectroscopic and luminescence properties exhibited by a variety of transition metal complexes.⁶ Despite the recent interest in metallophilicity^{6b,f} and its utilisation in directing supramolecular assembly,^{6b,f} corresponding studies in the exploration of metal-metal interactions for metallogel formation are rare.^{6b,f} In view of the propensity of the platinum(II) terpyridyl system to form Pt···Pt and π - π interactions, it is anticipated that such interactions may provide an additional driving force for the gelation process. Moreover, the

interesting photophysical properties of the platinum(II) terpyridyl system may give rise to interesting changes in the spectroscopic and luminescence behaviour during the sol-gel transition and serve as a reporter for changes in the microenvironment. These, together with our previous work^{3c} on the effect of the counter anions in governing the extent of metal-metal and π - π interactions that impart the different colour changes,^{3c} have prompted us to explore the utilisation of the platinum(II) terpyridyl system in metallogel synthesis. Herein we describe the synthesis and characterisation of the platinum(II) terpyridyl alkynyl complexes, **1**-OTf and **1**-PF₆ (**1** in its trifluoromethanesulfonate and hexafluorophosphate salts), **2**-OTf and **3**-OTf (Scheme 1) as well as the study of their gelation properties.

Complex **1**-OTf was synthesized by the reaction of [Pt(tpy)Cl]OTf^{2b,d} and 3,4,5-tris(dodecyloxy)phenylacetylene⁷ in DMF in the presence of triethylamine and a catalytic amount of copper(I) iodide. **1**-PF₆ was prepared by a metathesis reaction of **1**-OTf with NH₄PF₆. Complexes **2**-OTf and **3**-OTf were similarly prepared by the Cu(I)-catalyzed reaction of [Pt(^tBu₃tpy)Cl]OTf^{2b,d} with 3,4,5-tris(dodecyloxy)phenylacetylene⁷ and *N*-(4-ethynylphenyl)-3,4,5-tris(octyloxy)benzamide respectively in CH₂Cl₂.

The electronic absorption spectra of **1**-OTf in DMSO, and **2**-OTf and **3**-OTf in MeCN were studied. Under dilute conditions (<10⁻⁴ M), **1**-OTf, **2**-OTf and **3**-OTf showed a similar absorption pattern. The photophysical data are summarised in Table S1.† With reference to previous related work,³ the high-energy absorption band at ca. 267–349 nm is assigned as intraligand (IL) [$\pi \rightarrow \pi^*$] transitions of the alkynyl and terpyridine ligands, while the low-energy absorption band at ca. 406 to 476 nm is assigned as a metal-to-ligand charge transfer (MLCT) [d π (Pt) \rightarrow π^* (tpy)] transition with mixing of an alkynyl-to-terpyridine ligand-to-ligand charge transfer (LLCT) character. Upon increasing the



Scheme 1

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† Electronic supplementary information (ESI) available: Experimental procedures, photophysical data of **1**-OTf, **1**-PF₆, **2**-OTf and **3**-OTf, concentration-dependent UV-vis spectrum of **1**-OTf and temperature-dependent UV-vis and emission spectra of **1**-PF₆ and **2**-OTf. See DOI: 10.1039/b705062c

concentration of **1**-OTf in DMSO, a new absorption shoulder at *ca.* 580 nm was formed and a plot of the absorbance at 580 nm *versus* concentration showed a nonlinear relationship that deviates from Beer's law (Fig. S1†) while no such phenomena were observed in **2**-OTf and **3**-OTf. This suggested the existence of ground-state complex aggregation of **1**-OTf in DMSO at concentrations higher than 10^{-4} M.^{3a-c} The electronic absorption at $\lambda > 560$ nm is attributed to metal-metal-to-ligand charge transfer (MMLCT) transition.

The study of the effect of concentration on the emission properties of **1**-OTf in DMSO was also performed. At concentrations $\geq 10^{-4}$ M, an emission band was observed at 780 nm while no emission band was observed in dilute solutions. Based on the UV-vis absorption studies, the emission band at concentrations $\geq 10^{-4}$ M was suggested to be derived from the ³MMLCT excited state as a result of the intermolecular Pt··Pt and π - π interactions in DMSO. The absence of ³MLCT emission in dilute solutions of **1**-OTf is ascribed to intramolecular reductive electron-transfer quenching of the ³MLCT state as well as energy transfer to the low-lying ³LLCT state arising from the presence of the three electron-rich alkoxy groups on the phenylethynyl ligand. A similar lack of emissive behaviour has also been observed in other related alkoxyphenylethynyl platinum(II) terpyridine complexes.⁴

1-OTf was tested for its gelation property in various organic solvents by the "stable-to-inversion of a test tube" method and **1**-OTf formed a stable and clear purple metallogel with a low critical gelation concentration (c.g.c.) (4.4 mg ml^{-1}) for DMSO, as shown in Fig. 1a and b. The corresponding free ligand alkyne was also tested for its gelation behaviour in DMSO, forming white opaque gel at 7.5 mg ml^{-1} . However, unlike the purple metallogel from **1**-OTf which was clear and stable for more than one week, the organogel formed out of the free ligand was opaque and collapsed after standing overnight. This indicates that the Pt··Pt and π - π interactions originating from the platinum(II) terpyridyl moieties serve to enhance the gelation ability and stability of 3,4,5-tris(dodecyloxy)phenylacetylene in DMSO upon coordination, and the incorporation of a platinum(II) terpyridyl chromophore into organogels may provide an effective colorimetric reporter for the sol-gel transition.

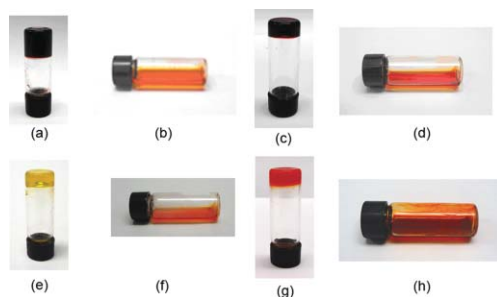


Fig. 1 Photographs of **1**-OTf in DMSO ($[\text{Pt}] = 4.4 \text{ mg ml}^{-1}$) in (a) the gel form at room temperature, (b) the sol form at elevated temperature. Photographs of **1**-PF₆ in DMSO ($[\text{Pt}] = 7.5 \text{ mg ml}^{-1}$) in (c) the gel form at room temperature, (d) the sol form at elevated temperature. Photographs of **2**-OTf in DMSO ($[\text{Pt}] = 7.8 \text{ mg ml}^{-1}$) in (e) the gel form at room temperature, (f) the sol form at elevated temperature. Photographs of **3**-OTf in benzene ($[\text{Pt}] = 80 \text{ mg ml}^{-1}$) in (g) the gel form at room temperature, (h) the sol form at elevated temperature.

To study the morphology of the DMSO xerogel formed by **1**-OTf (air-dried gel), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were recorded. As shown in Fig. 2, a network of fibrous structures, which is characteristic of low molecular-weight organogels,^{5a-d,6a-d} was observed. The approximate diameter and length of the fibres were 470 nm and 10 μm , respectively.

As the metallogel of **1**-OTf in DMSO was found to show drastic colour changes during the sol-gel transition, a temperature-dependent UV-vis absorption study was performed in the temperature range from 10 to 80 °C. Upon increasing the temperature from 10 to 41 °C, the MMLCT absorption shoulder at *ca.* 580 nm gradually dropped in absorbance, as a result of the decreasing extent of Pt··Pt and π - π interactions. At $T > 41$ °C, a new absorption band started to appear at 415 nm. Upon further increasing the temperature to $T_{\text{gel}} = 55$ °C, the MMLCT absorption shoulder disappeared completely, indicating that the Pt··Pt and π - π interactions are involved in the metallogel formation in addition to the hydrophobic interactions arising from the three long alkoxy chains, and no drastic changes were observed on further heating. The UV-vis absorption spectral traces at various temperatures are shown in Fig. 3a and b. In contrast, the DMSO gel of **2**-OTf (Fig. 1e and f) showed a slight blue shift in MLCT energy (Fig. S2a†) during gel-to-sol transition, confirming the lack of Pt··Pt and π - π interaction involvement in gel formation due to the steric bulk imparted by the ^tBu₃tpy ligand.

The DMSO gel of **1**-OTf was also subjected to variable-temperature emission studies. An emission band at 780 nm was observed at 20 °C upon excitation at 496 nm, which is assigned as ³MMLCT emission, similar to that observed at high concentrations in solution. Upon increasing the temperature from 20 to 45 °C, this ³MMLCT emission band gradually decreased in intensity. At $T = 50$ °C, the intensity of the ³MMLCT emission started to drop drastically and approached zero at the sol-gel transition temperature ($T_{\text{gel}} = 55$ °C). The emission spectral changes as a function of temperature are shown in Fig. 3c. Similar to the UV-vis absorption studies, the disappearance of the ³MMLCT emission was a result of the decrease in the Pt··Pt and π - π interactions, in addition to the increase in the rate of nonradiative decay upon an increase in temperature. Similar findings have been observed in a dinuclear platinum(II) terpyridine system.^{3e} The almost complete switching-off of the ³MMLCT emission at the sol-gel transition temperature is again indicative of the involvement of the Pt··Pt and π - π stacking interactions in the gelation process. On the other hand, a diminution of a slightly structured emission band was observed in DMSO gel of **2**-OTf upon gel-to-sol transition (Fig. S2b†) and this has been attributed

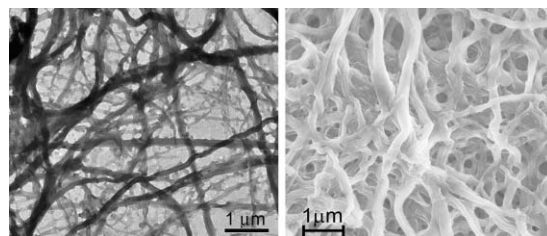


Fig. 2 TEM (left) and SEM (right) images of the DMSO gel of **1**-OTf.

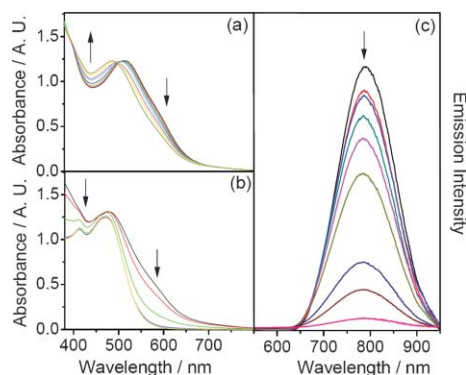


Fig. 3 UV-vis absorption spectra of **1-OTf** in the temperature range of (a) 10–41 °C and (b) 44–80 °C. (c) Corrected emission spectra of the DMSO gel of **1-OTf** at various temperatures in the range of 20–56 °C.

to the more effective nonradiative decay expected at higher temperatures and reduced rigidity.

Since the nature of the counter anions has previously been shown by us to influence the aggregation behaviour of the platinum(II) terpyridyl alkynyl systems,^{3c} the hexafluorophosphate salt of **1**, **1-PF₆**, was prepared (Scheme 1). **1-PF₆** was tested for its gelation behaviour. Interestingly, it formed a deep red gel in DMSO, with c.g.c. = 7.5 mg ml⁻¹ and $T_{\text{gel}} = 42$ °C, and also showed a remarkable colour change during the sol–gel transition (Fig. 1c and d). Its UV-vis absorption spectra at various temperatures were studied and are shown in Fig. S3a.† Similarly, a drop in the MMLCT absorption shoulder at 575 nm was observed upon an increase in temperature, approaching zero absorbance at 42 °C, which is close to the sol–gel transition temperature. In the corresponding emission studies at various temperatures, the emission band at 720 nm, typical of the ³MMLCT emission diminished in intensity upon elevated temperature and approached zero at $T_{\text{gel}} = 42$ °C (Fig. S3b†). Similar to **1-OTf**, the Pt··Pt and π - π interactions are involved in the gelation of **1-PF₆**. Interestingly, **1-OTf** which has a lower critical gelation concentration and higher T_{gel} than **1-PF₆**, shows lower-energy MMLCT absorption and ³MMLCT emission bands than the corresponding **1-PF₆**, providing a direct correlation of the extent of the Pt··Pt and π - π interactions (as revealed by the MMLCT energy) to the stability of the metallogels, and hence indicating the importance of the Pt··Pt and π - π interactions in enhancing the gel formation processes.

3-OTf was also studied for its gelation property and it was found that it only formed a stable orange gel in benzene at 80 mg ml⁻¹ (Fig. 1g and h). Together with the findings for **2-OTf**, it is likely that extra hydrophobic–hydrophobic interactions arising from the *tert*-butyl substituents also play a role in stabilising the gel formation although the role of interactions with the counter-anions and solvent in the gelation process cannot be completely excluded.

In conclusion, a platinum(II) terpyridyl alkynyl system is found to form metallogels which show drastic colour and emission changes during the sol–gel transition. This property can serve as a reporter for microenvironmental changes. Counter-anion-dependent colour changes and metallogel stability were observed

which is attributed to the different degrees of aggregation derived from the Pt··Pt and π - π interactions involved in the gelation process.

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