Organogel of an 8-quinolinol platinum(II) chelate derivative and its efficient phosphorescence emission effected by inhibition of dioxygen quenching†

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Received (in Cambridge, UK) 4th May 2005, Accepted 9th June 2005
First published as an Advance Article on the web 4th July 2005
DOI: 10.1039/b506148b

A newly synthesized 8-quinolinol platinum(II) chelate derivative gelates various organic solvents, and the gel formed shows unique thermo- and solvatochromism of visible and phosphorescent colour in response to a sol–gel phase transition and possesses an attractive ability to inhibit dioxygen quenching of excited triplet states.

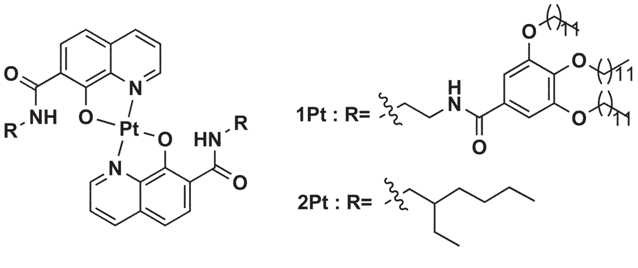
Phosphorescent materials composed of metal chelate derivatives have gained much interest due to their advantages of long-lived luminescence and high luminescence quantum yield for various applications such as EL displays,[1] sensors,[2] photovoltaic devices[3] and photocatalysts.[4] Considering the practical utilization of these materials, the most essential but difficult problem is how dioxygen quenching of their excited triplet states can be avoided. One of the successful examples in aqueous solution is to utilize micellar functions: therein, the collisional deactivation of excited triplet states can be minimized by solute-partitioning to the micellar phase.[5]

Recently, a low molecular-weight gel system has become a topic of growing interest because of novel supramolecular architectures created by gelator assemblies.[6] Low molecular-weight gel tissues are produced by micro (or nano) phase separation of gelator molecules and solvent molecules, where the gelator phase is well segregated from the solvent phase which contains dioxygen. In addition, the gelator assemblies have the crystal-like nature favourable to segregation, being different from the dynamic nature characteristic of micellar systems. It thus occurred to us that if the phosphorescent group is integrated in a gelator, deactivation of excited triplet states by collision with dioxygen molecules could be effectively inhibited. Here, we report on gel formation and phosphorescence properties of an 8-quinolinol platinum(II) chelate **1Pt** bearing 3,4,5-tris(*n*-dodecyloxy)benzoylamide substituents. 8-Quinolinol platinum(II) chelate derivatives are known to show red phosphorescence even at room temperature.[7] We expected that its square planar chelate structure would be of great advantage to gel formation because of their strong π–π interactions, which are one of the main driving forces for gelation.[6,8] In addition, it is well-known that introduction of 3,4,5-tris(alkoxy)phenyl substituents into a π-conjugated planar molecule is favourable to self-assembly into a columnar stacking structure to give highly ordered structures such as liquid crystals and gels.[9] The long alkyl chains of 3,4,5-tris(alkoxy)phenyl substituents, which usually occupy the outer layers of the columnar structure, are expected to insulate dioxygen in the solvent phase from the chelate moiety which occupies the inner core of the columnar structure. To clarify the gelation effect, we also designed a non-gelling reference compound **2Pt**, which has 2-ethylhexyl moieties as solubilizing substituents.

Firstly, we evaluated the gelation ability of compound **1Pt** in various organic solvents by the "stable-to-inversion of a test tube" method. As shown in Table S1,† **1Pt** gelates 18 organic solvents among 25 candidates, such as benzene, hexane, 1-butanol, 1,4-dioxane, *etc*. Additionally, **1Pt** shows the very low critical gelation concentration (c.g.c.), 0.10 mg ml^{-1} (0.050 mM) for cyclohexane, *p*-xylene, *etc*. From these results, one can conclude that **1Pt** is classified as a "good gelator".

The morphology of **1Pt** gel fibers was investigated by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). We could observe a network structure characteristic of the low molecular-weight organogels,[6,8,9] the approximate diameters and the length of the fibrous aggregate of the **1Pt** + 1-butanol gel being 50–200 nm and several μm, respectively (Fig. 1). We confirmed the creation of similar fibrous structures in gels prepared from other gelling solvents by SEM and TEM observations.

To obtain insights into the aggregation mode of chelate moieties in the gel tissue, we measured UV-Vis absorption spectra of the **1Pt** + *p*-xylene gel and the **1Pt** + 1,1,2,2-tetrachloroethane sol. As shown in Fig. 2, absorption bands for **1Pt** appearing at 353 nm and 459 nm in the sol phase, which are assigned to a ligand centered π–π transition and a singlet intraligand charge transfer (^{1}ILCT) transition, respectively, were shifted to longer wavelengths



Scheme 1 Structures of 3,4,5-tris(*n*-dodecyloxy)benzoylamide substituents-appended 8-quinolinol platinum(II) chelate gelator (**1Pt**) and its non-gelling reference compound (**2Pt**).

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† Electronic supplementary information (ESI) available: Experimental procedures for the preparation of **1Pt** and **2Pt**, their characterization data and gelation properties of **1Pt**. See http://dx.doi.org/10.1039/b506148b

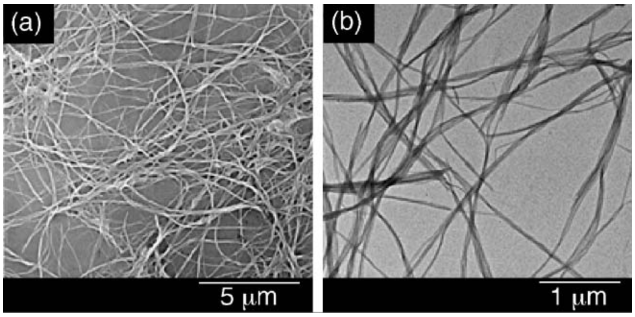

Fig. 1 (a) SEM and (b) TEM images of the **1Pt** + 1-butanol gel, [**1Pt**] = 2.0 mg ml^{-1}.

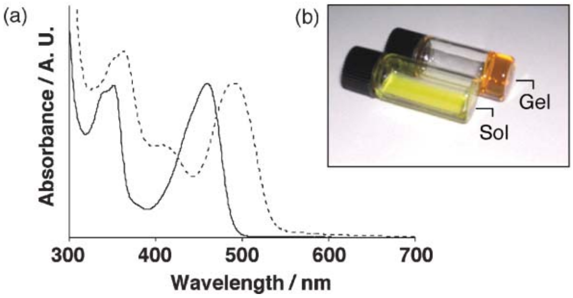

Fig. 2 (a) Absorption spectra of the **1Pt** + *p*-xylene gel (dashed) and the **1Pt** + 1,1,2,2-tetrachloroethane solution (solid), [**1Pt**] = 10 mg ml^{-1}, and (b) photograph of the **1Pt** + *p*-xylene gel and its heated solution (sol).

up to 364 nm and 492 nm, respectively, in the gel phase.[7] This result indicates that the 8-quinolinol platinum(II) chelate moieties in the **1Pt** + *p*-xylene gel tissues tend to adopt a *J*-aggregation mode, which causes unique thermochromism of **1Pt** in relation to a sol–gel transition phenomenon (Fig. 2b): the colour of a heated solution was yellow and that of a cooled gel was orange.[10] We also measured UV-Vis absorption spectra of the **1Pt** + decane, 1,4-dioxane and 1-butanol gels. The spectral patterns were almost the same with that of the *p*-xylene gel, indicating that the aggregation mode of **1Pt** in the gel phase is scarcely affected by solvents.

An XRD analysis of the xerogel prepared from the **1Pt** + benzene gel shows two strong peaks at $2\theta = 2.1^\circ$ (42 Å) and 3.4° (26 Å), which are assigned to the (100) diffraction and the (010) diffraction, respectively (Fig. 3). Taking a typical stacking distance (*ca.* 4.5 Å) between two closely packed 3,4,5-tris(alkoxy)phenyl substituents in the column and a density of $d = 1.3$ g cm^{-3} into consideration,[11] we can calculate $Z = 2$, that is, two molecules per unit cell. Therefore, a packing structure in Fig. 4b is proposed as the most likely aggregation model. The distance of the inter-columnar separation (42 Å) is shorter than the long axis of **1Pt** (*ca.* 52 Å). This result implies that the molecules in the gel tissue are stacked in a tilted fashion along the *c* axis (Fig. 4c). These π–π stacked structures were visually confirmed by high resolution TEM (HR-TEM) as strong stripe contrasts parallel to the fiber long axis (Fig. 4d).

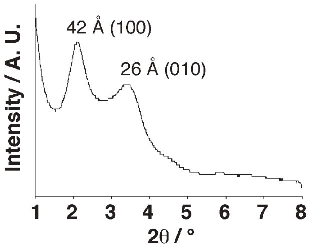

Fig. 3 Powder XRD diagram of the xerogel prepared from the **1Pt** + benzene gel, [**1Pt**] = 200 mg ml^{-1}.

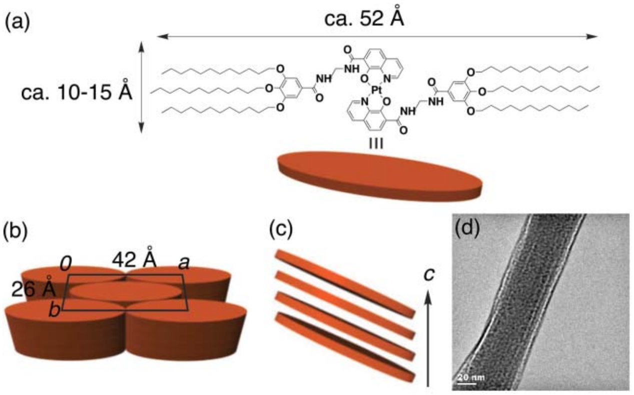

Fig. 4 (a) Molecular scales of **1Pt**, (b) proposed packing model of **1Pt** in the gel tissues, (c) tilted arrangement of **1Pt** along the *c* axis, (d) HR-TEM image of the **1Pt** + *p*-xylene gel, [**1Pt**] = 2.0 mg ml^{-1}.

Next, we discuss the influence of gel formation on phosphorescent properties of **1Pt**. It is well-known that 8-quinolinol platinum(II) chelates show red phosphorescence around 600–650 nm, which is emitted from the ligand-centred transitions ($^3\pi\pi$ or ^{3}ILCT).[7] We observed tangerine luminescence appearing at 610 nm from the **1Pt** + 1,1,2,2-tetrachloroethane solution, whereas red luminescence appearing at 640 nm from the **1Pt** + *p*-xylene gel (Fig. 5). These colours originated from *J*-aggregation of chelate moieties as confirmed by the UV-Vis absorption spectra and XRD analysis. Moreover, this red luminescence is emitted from a nano-scale fibrous structure, which is directly observable by a confocal laser scanning microscope (CLSM) (Fig. 5c).

To estimate the inhibition efficiency of dioxygen quenching ($E_{\text{v.s. O2}}$) we conducted the following experiment. Luminescence

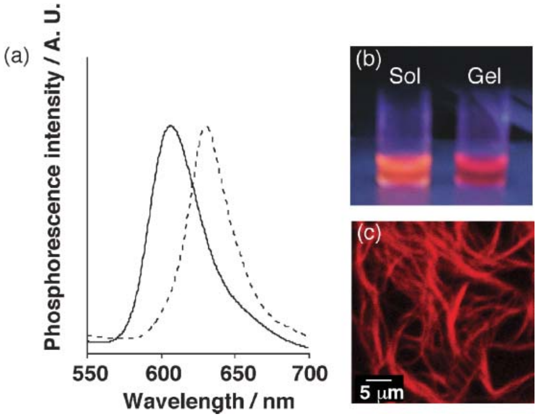

Fig. 5 Luminescence spectra of the **1Pt** + *p*-xylene gel (dashed) and **1Pt** + 1,1,2,2-tetrachloroethane solution (solid), [**1Pt**] = 2.0 mg ml^{-1}; excited at 490 nm for the gel and at 460 nm for the sol, (b) photograph of the **1Pt** gel and sol under UV light (365 nm), (c) CLSM image of the **1Pt** + *p*-xylene gel, [**1Pt**] = 2.0 mg ml^{-1}.

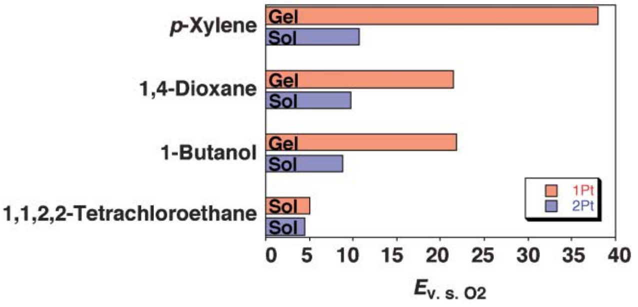

Fig. 6 $E_{\text{v.s. O2}}$ values of **1Pt** (red) and **2Pt** (blue) for four kinds of solvents, [**1Pt**] = [**2Pt**] = 1 mM.

spectra of **1Pt** and **2Pt** were measured under an argon atmosphere or a dioxygen-saturated atmosphere in the gel or sol phase,[12] where we defined $E_{\text{v.s. O2}}$ as $LI_{\text{dioxygen}}/LI_{\text{argon}}$ under each measurement condition. The experimental results are summarized in Fig. 6. We found that the $E_{\text{v.s. O2}}$ values of **1Pt** are larger than those of **2Pt** in all gelling solvents. On the other hand, the $E_{\text{v.s. O2}}$ values of **1Pt** and **2Pt** are almost the same in the non-gelling solvent, 1,1,2,2-tetrachloroethane. These results support the view that the enhancement of the $E_{\text{v.s. O2}}$ is not due to the difference in the peripheral substituent structure, but due to the molecular assembling effect in the gel.

In conclusion, we have demonstrated that 3,4,5-tris(*n*-dodecyloxy)benzoylamide substituents-appended 8-quinolinol platinum(II) chelate **1Pt** acts as a highly efficient gelator for various organic solvents. This gelation capability is attributed to the strong *J*-aggregated π–π interaction of chelate moieties, which results in thermo- and solvatochromism of visible colour and a colour change in the phosphorescence emission in response to a sol–gel phase transition. Furthermore, it was shown that dioxygen quenching of the excited triplet states is efficiently inhibited in the gel phase. Considering that the gel matrix, which occupies an intermediate state between a solid phase and a liquid phase and possesses a self-supported and transparent character, the phosphorescent organogel described here is believed to be a very attractive emitting material.[13]

This work was supported by the Grant-in-Aid for Young Scientists (B) (No. 16750122), Scientific Research on Priority Area (No. 17036051) and the 21st Century COE Program, "Functional Innovation of Molecular Informatics" from the MEXT of Japan and by JSPS fellows (M. S.).

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