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Solvent-Induced Aggregation through Metal···Metal/π···π Interactions: Large Solvatochromism of Luminescent Organoplatinum(II) Terpyridyl Complexes

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Square-planar complexes of platinum(II) have been shown to display intriguing spectroscopic and luminescence properties.[1−4] Examples include the rich polymorphism exhibited by a number of platinum(II) polypyridine complexes in the solid-state, with their solid-state colors dependent on the extent of metal−metal interactions and $\pi-\pi$ stacking of the polypyridyl ligands,[1,3,5,6] and recently, the interesting vapochromic and vapoluminescence properties displayed by a number of double salts of square-planar platinum(II)−palladium(II), platinum(II)−platinum(II) as well as $Pt(CNR)_2(CN)_2$ complexes.[7]

In this communication, we report the syntheses and crystal structures of two novel luminescent platinum(II) diynyl complexes of terpyridyl ligands, $[Pt(tpy)(C\equiv C-C\equiv CH)]OTf$ **1** and $[Pt(^tBu_3\text{-}tpy)(C\equiv C-C\equiv CH)]OTf$ **2** (tpy = 2,2′:6′,2″-terpyridine; $^tBu_3$-tpy = 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine). Complex **1** has been found to exist in two forms, a dark-green form and a red form; both of which have been structurally characterized and shown to exhibit different crystal-packing arrangements. Solutions of complex **1** were shown to display a dramatic color change and a tremendous emission enhancement upon varying the composition of the solvent mixtures. On the contrary, complex **2** with a bulky tri-*tert*-butyl-2,2′:6′,2″-terpyridine ligand crystallizes as discrete molecules and shows no observable color changes in various solvent mixtures.

Complexes **1** and **2** were prepared by the reaction of $TMS-C\equiv C-C\equiv C-TMS$ with the corresponding precursor complexes, $[Pt(tpy)(MeCN)](OTf)_2$[4d] and $[Pt(^tBu_3\text{-}tpy)(MeCN)](OTf)_2$, respectively, in the presence of an excess of KF in methanol. Their crystal structures have been revealed by X-ray crystallography.[8] The dark-green form and red form of **1** were obtained by recrystallization from the slow diffusion of diethyl ether vapor into acetonitrile and diluted acetone solution, respectively.

The crystal packing of the complex cation of **1** in dark-green form and red form are depicted in Figure 1. The molecular structures of them are very similar with the terpyridine and diynyl ligands coordinated to the platinum atom in a square-planar geometry. The dark-green form of **1** exists as a linear chain with the platinum atoms equally spaced, with short intermolecular Pt···Pt contacts of 3.388 Å. When viewed along the *b* axis, the platinum atoms are almost superimposable to give a nearly perfect linear $[Pt]_n$ chain with a Pt−Pt−Pt angle of 179.2°. The individual molecules are rotated with respect to their neighbors, with a C−Pt−Pt−C torsion angle of 134.4° and a partial stacking of the aromatic terpyridyl units. The red form, on the other hand, shows dimeric structure with alternating Pt···Pt distances of 3.394 and 3.648 Å. The "short" and "long" Pt···Pt bonds exhibit a zigzag arrangement with a Pt−Pt−Pt angle of 154.3°. Rotation of 49.7° of one square plane with respect to its adjacent molecules was observed. Other platinum(II) polypyridyl complexes have also shown similar extended linear-chain packing[1e,3a,5] and dimeric structure.[1d,3b,5b] Dimorphic forms of gold(I) dimer have also been reported as a result of different intermolecular interactions.[9] Unlike **1**, where the Pt metal center or the terpyridine ligand shows a strong propensity to aggregate to form chains with short intermolecular Pt···Pt contacts or $\pi-\pi$ stacking arrangements, **2** exists as discrete monomeric units with no evidence of short Pt···Pt contacts (>4.9 Å), as is required by the steric demand of the bulky 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine ligand. Such monomeric arrangement has also been demonstrated by the "yellow" form of $[Pt(bpy)Cl_2]$.[6]

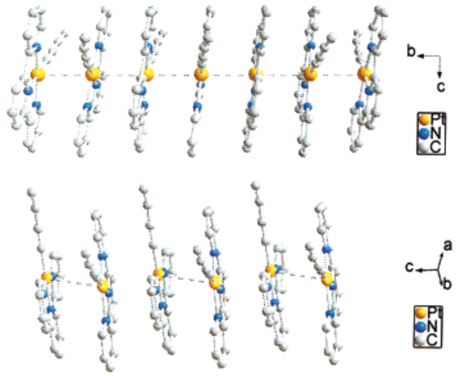

Figure 1. Perspective view of complex cation of **1** in dark-green form (top) exhibiting extended linear chain packing and in red form (bottom) showing zigzag arrangement. Hydrogen atoms are omitted for clarity.

Unlike the solid-state absorption spectra in which the dark-green and the red forms of **1** absorb at ca. 685 and 510 nm, respectively, dissolution of either of the two forms of **1** in acetonitrile or acetone gave a yellow solution with the same UV−vis absorption spectrum, which is dominated by high-energy intraligand absorptions at 313, 329, and 340 nm, and a low-energy metal-to-ligand charge-transfer (MLCT) absorption at 416 nm in the visible region, typical of monomeric platinum(II) terpyridyl complexes.[3,4] Ground-state aggregation or oligomerizaion of **1** by varying the concentration from 2×10^{-3} to 2×10^{-5} M in acetonitrile is unlikely to occur as indicated from the nice agreement with Beer's law. Upon increasing the diethyl ether content in solution, the color of the solution changes dramatically from yellow to green to blue (Figure 2). The solutions remain clear and macroscopically homogeneous and remain stable for more than 2 h with no precipitation. Similar changes were not observed in the corresponding solutions of **2**.

Figure 3a shows the UV−vis absorption changes with various solvent compositions. Upon increasing the diethyl ether content while maintaining the concentration constant, the absorption at 416 nm drops in intensity with a concomitant growth of a new band at 615 nm with well-defined isosbestic points, suggesting that a clean conversion of **1** in the monomeric form to another species has

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Figure 2. Solution of **1** (concentration = 1.47 × 10^{-4} M) in acetonitrile/diethyl ether mixture demonstrating the remarkable color changes. Diethyl ether composition (form left to right): 64, 68, 72, 74, 76, 78, 80%.

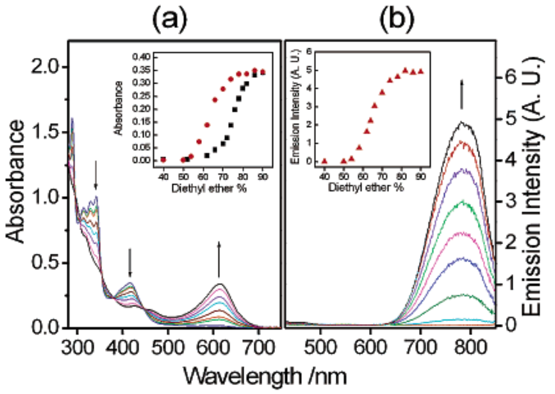

Figure 3. (a) UV−vis absorption changes of **1** (concentration = 1.47 × 10^{-4} M) in acetonitrile with increasing diethyl ether content. Inset: Plot of absorbance vs diethyl ether composition in acetonitrile at 615 nm (■) and in acetone at 610 nm (●, red). (b) Emission enhancement of **1** (concentration = 1.47 × 10^{-4} M) in acetone upon increasing diethyl ether content. Inset: Plot of corrected emission intensity as a function of diethyl ether composition (▲, red).

occurred. The inset shows the absorbance changes of the new band formed with increasing diethyl ether content in acetonitrile and acetone solutions. The drastic color changes displayed by solutions of **1** are believed to arise from the formation of aggregates in solution. In view of the fact that the dimeric red form of **1** shows an absorption at ca. 510 nm in the solid state as well as the fact that most other dimeric Pt(II)−terpyridine systems[3a,b] show absorption bands at 470−510 nm, the newly formed species that gives rise to the low-energy 615-nm absorption is likely to be either trimeric or oligomeric in nature. Since **1** is insoluble in diethyl ether, it is likely that molecules of **1** would tend to aggregate in acetonitrile/diethyl ether and acetone/diethyl ether mixtures as a result of the reduced solvation. The diethyl ether content required to induce aggregation in acetone (lower than that required in acetonitrile) is consistent with the lower solubility of **1** in acetone. Interestingly, excitation of solutions of **1** at 384 nm (one of the isosbestic points in the UV−vis spectroscopic studies) shows an intense emission at 785 nm that only becomes switched on and enhanced with increasing diethyl ether compositions (Figure 3b). The close resemblance of the emission intensity changes at 785 nm as a function of diethyl ether content (Figure 3b inset) to the absorbance changes at 615 nm with increasing diethyl ether content (Figure 3a inset) is indicative of their similar origin, that is, an origin that arises as a result of aggregate formation, probably facilitated by the propensity to form metal−metal interactions and $\pi-\pi$ stacking. This has been confirmed by the observation of an excitation band at ca. 605 nm in the excitation spectrum of **1** monitored at 785 nm. We tentatively assign the 615-nm band in the electronic absorption spectrum as a metal−metal-to-ligand charge-transfer (MMLCT) transition, and the 785-nm phosphorescence as derived from states of a ^{3}MMLCT character. Further support for the 785-nm emission to be derived from trimeric or oligomeric species is provided by the observation of the solid-state emission of the dimeric red form at ca. 680 nm. On the contrary, excitation of **2** shows an emission at 627 nm in acetonitrile, typical of ^{3}MLCT emission in related platinum(II) terpyridyl systems.[4c] No new emission band due to aggregate formation was observed.

The remarkable change of UV−vis absorption as well as emission characteristics induced by changes in the solvent composition may be regarded as a special type of solvatochromism. It is anticipated that such drastic solvent-induced sensitive changes in color and on−off switching of emission via aggregation of metal−metal-bonded and π-stacked species would serve as versatile reporters and probes of environmental changes and may find potential applications in materials science and sensor technology.

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Supporting Information Available: Characterization of **1** and **2**, crystallographic data of **1** (2 forms) and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Crystal data for **1** (dark-green form): orthorhombic, *Pbcn* (no.60), a = 22.543(5) Å, b = 6.776(1), Å, c = 28.608(6) Å, $\alpha = \beta = \gamma = 90$ °, V = 4369.9(15) Å^3, Z = 8, D_c = 1.904 g cm^{-3}, T = 301 K, no. of independent data [R(int) = 0.0820] = 3384, R1 = 0.0596 [$I > 2\sigma(I)$], GOF = 0.948. **1** (red form): monoclinic, *C2*, a = 19.847(4) Å, b = 14.801(3), Å, c = 6.867(1) Å, α = 90 °, β = 94.35(3) °, γ = 90 °, V = 2011.4(7) Å^3, Z = 4, D_c = 2.069 g cm^{-3}, T = 301 K, no. of independent data [R(int) = 0.0470] = 2849, R1 = 0.0896 [$I > 2\sigma(I)$], GOF = 1.070. **2**: triclinic, *P*-1, a = 10.040(2) Å, b = 14.759(3), Å, c = 15.488(3) Å, α = 72.86(3) °, β = 75.94(3) °, γ = 72.70(3) °, V = 2063.3(7) Å^3, Z = 2, D_c = 1.466 g cm^{-3}, T = 301 K, no. of independent data [R(int) = 0.414] = 6647, R1 = 0.0507 [$I > 2\sigma(I)$], GOF = 1.041.

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