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Water-Molecule-Driven Vapochromic Behavior of a Mononuclear Platinum(II) System with Mixed Bipyridine and Thioglucose

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Supporting Information

ABSTRACT: A mononuclear platinum(II) complex with mixed bpy and H_4tg^- ligands, $[Pt(H_4tg\text{-}S)_2(bpy)]\cdot 2H_2O$ (**1a**; bpy = 2,2′-bipyridine and H_5tg = 1-thio-*β*-D-glucose), is photoluminescent in the solid state and undergoes facile and reversible removal of solvated water molecules accompanied by changes in its absorption and emission wavelengths. The analogous dmbpy complex, $[Pt(H_4tg\text{-}S)_2(dmbpy)]\cdot H_2O$ (**2a**; dmbpy = 4,4′-dimethyl-2,2′-bipyridine), is also emissive in the solid state, but its absorption and emission spectra remain unchanged after dehydration. X-ray crystallographic analyses revealed that the difference in the chromism of **1a** and **2a** is due to the difference in their hydrogen-bonding networks, which involve solvated water molecules.

Platinum(II) complexes bearing chelating or bridging diimine ligands continue to attract attention because of their intriguing photochemical and photophysical properties, which make them potentially applicable as artificial photosynthetic chromophores, nonlinear-optical materials, chemosensors, light-emitting diodes, and low-power upconversion materials.[1,2] Of particular interest is the vapochromic behavior that is realized by the judicious choice of coligands that regulate intermolecular $\pi-\pi$ and Pt⋯Pt interactions.[2] For example, Kato and co-workers reported that the coordination polymer, $\{Zn[Pt(CN)_2(dcbpy)]\cdot 4H_2O\}_n$ (dcbpy = 5,5′-dicarboxy-2,2′-bipyridine), exhibits unique vapochromism triggered by the removal/incorporation of water (H_2O) molecules bound to the Zn^{II} centers, which results in a change in the intermolecular Pt⋯Pt interactions.[3] Nevertheless, vapochromic diimine platinum(II) species remain largely unexplored and to date have been limited to coordination systems that contain cyanides,[3,4] acetylide derivatives,[5] or aromatic thiolates as coligands.[6]

As part of our continuing efforts to create polynuclear and supramolecular architectures with aliphatic thiolate ligands,[7] we recently synthesized a 2,2′-bipyridine platinum(II) complex with 1-thio-*β*-D-glucose (H_5tg), $[Pt(H_4tg\text{-}S)_2(bpy)]\cdot 2H_2O$ (**1a**; bpy = 2,2′-bipyridine), which acts as a versatile multidentate metalloligand that binds via the thiolato and hydroxyl groups of H_4tg^-.[8] An important structural aspect of **1a** is the presence of both hydrophobic bpy and hydrophilic H_4tg^- groups in one molecule, leading to the formation of both $\pi-\pi$ and hydrogen-bonding interactions. While investigating the properties of **1a**, we noticed that this compound is photoluminescent in the solid state. Furthermore, the emission color was observed to change upon exposure to selected organic vapors with a concomitant change in the absorption color (Figure 1). Remarkably, such absorption and emission color changes were not observed for the corresponding newly synthesized 4,4′-dimethyl-2,2′-bipyridine (dmbpy) complex $[Pt(H_4tg\text{-}S)_2(dmbpy)]\cdot H_2O$ (**2a**). Herein, we report on the vapochromic behavior of this mononuclear platinum(II) system along with the structural characterization of **1a** and **2a**, which revealed the importance of solvated H_2O molecules involved in hydrogen-bonding interactions within the complex structures.

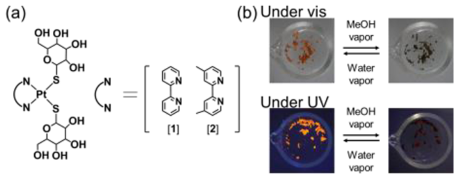

Figure 1. (a) Drawing of the complex molecules in **1a** and **2a**. (b) Photographs of **1a**: (upper) absorption and (lower) emission color changes upon exposure to vapors of MeOH and H_2O.

Complex **1a**, which is orange, was synthesized as described previously.[8] In the diffuse-reflection spectrum, a solid sample of **1a** exhibits a visible band at 430 nm (Figure S1a in the Supporting Information, SI).[9] While **1a** is nonemissive in water, it is emissive with an intense orange emission in the solid state when irradiated with UV light (365 nm) at room temperature (Figure 1b). The emission spectrum of solid **1a** exhibits a single band at 608 nm (Figure 2a) with an emission lifetime of 2.05 *μ*s,

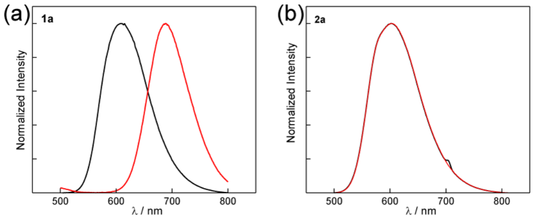

Figure 2. Emission spectra of (a) **1a** and (b) **2a** in the solid state. Black/red lines are before/after exposure to MeOH vapors. The excitation wavelength was 340 nm.

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indicative of phosphorescent character.[10] Density functional theory calculations revealed that the highest occupied molecular orbital (HOMO) and HOMO−1 are mainly composed of a mixture of p(S) and dπ(Pt) orbitals (Figure S2 in the SI),[9] while the lowest unoccupied molecular orbital is comprised of the π*(bpy) orbital, and thus the lowest excited state for **1a** can be assigned as p(S)/dπ(Pt)-to-π*(bpy) charge transfer (MLLCT).

When a solid sample of **1a** was exposed to a vapor of methanol (MeOH) or acetonitrile (MeCN) at room temperature, its orange color changed to brown within 10 min (Figure 1). In parallel with this absorption color change, its emission color also changed from orange to dark red. On the other hand, such absorption and emission color changes did not occur upon exposure of **1a** to a vapor of CH_2Cl_2 or *n*-hexane. In addition, a significant emission band shift from 608 to 687 nm was observed in the emission spectrum after exposure to a vapor of MeOH or MeCN (Figures 2a and S3 in the SI).[9] Furthermore, in the diffuse-reflection spectrum, the original visible band of **1a** at 430 nm shifted slightly to 438 nm and a new, broad, lower-energy band appeared at 544 nm (Figure S1a in the SI).[9] A similar low-energy band was observed for diimine-coordinated platinum complexes that possess intermolecular Pt···Pt interactions, and this band has been assigned to an MMLCT transition in which the HOMO is mainly composed of dσ*(Pt_2).[6b,11] Thus, the red shift of the emission band of **1a** is assumed to originate from generation of a triplet MMLCT state because of generation of intermolecular Pt···Pt interactions in the sample after exposure to a vapor of MeOH or MeCN. Notably, when the sample of **1a** after exposure to a vapor of MeOH or MeCN was exposed to a water vapor at room temperature, the original absorption and emission colors were recovered within 10 min, and its diffuse-reflection and emission spectra became identical with those of **1a**.

Contrary to our anticipation, the ^{1}H NMR spectrum (D_2O) of each sample after exposure to a vapor of MeOH or MeCN did not show any methyl proton signals for MeOH or MeCN, and the spectrum was identical with that of **1a** (Figure S4 in the SI) over the entire region.[9] Because the diffuse-reflection and emission spectra of the sample (**1b**) obtained by heating **1a** at 70 °C for 1 h were identical with those obtained following exposure to a vapor of MeOH or MeCN (Figure S3 in the SI),[12] it was concluded that this chromic behavior is due to the removal of solvated H_2O molecules by vapor diffusion of polar MeOH or MeCN and that these molecules are then recovered by vapor diffusion of water.[13] Consistent with this assumption, the elemental analytical data for **1b** are in good agreement with dehydrated [Pt(H_4tg-*S*)$_2$(bpy)].[9] In addition, thermogravimetric analysis indicated that the removal of solvated H_2O molecules from solid **1a** occurs over the low-temperature range 30−55 °C (Figure S7 in the SI),[9] which is compatible with facile removal of H_2O molecules via vapor diffusion of MeOH or MeCN.

Prompted by the intriguing chromic behavior of **1a**, an analogous platinum(II) complex bearing a dmbpy ligand, **2a**, was synthesized via the reaction of [$PtCl_2$(dmbpy)] with NaH_4tg in a 1:2 ratio in water.[9] Complex **2a**, which is also orange, was characterized by ^{1}H NMR and absorption spectra (Figures S4 and S8 in the SI) and elemental analysis.[9] The diffuse-reflection spectral features of a solid sample of **2a** are similar to those of **1a**, with a visible band at approximately 440 nm (Figure S1 in the SI).[9] In addition, **2a** is also photoluminescent at room temperature in the solid state and exhibits a single emission band centered at nearly the same wavelength (604 nm) as that for **1a** (Figure 2b). However, no changes in the absorption and emission spectra were observed for **2a** after the removal of solvated H_2O molecules. Indeed, the diffuse-reflection and emission spectra of its dehydrated form, [Pt(H_4tg-*S*)$_2$(dmbpy)], were the same as those of **2a** (Figures 2b and S1a in the SI).[9]

To elucidate the factors that govern the different chromic behaviors of **1a** and **2a**, single crystals of **1a** and **2a** were prepared, and their structures were determined via X-ray crystallography.[9] Compound **1a** crystallizes in the chiral monoclinic space group *P*2_1, which contains a complex molecule and two solvated H_2O molecules in the asymmetric unit. As shown in Figure 3a, the complex molecule has the expected mononuclear structure [Pt(H_4tg-*S*)$_2$(bpy)] in which the Pt^{II} center is coordinated by a bidentate N,N bpy and two monodentate *S* H_4tg$^-$ ligands in square-planar geometry. The two H_4tg$^-$ ligands are in an anticonfiguration, with one above and the other below the square plane. In the packing structure, the complex molecules in **1a** are arranged in a parallel, offset fashion to form a 1D chain structure with a linear array of Pt^{II} atoms (Figure 4a), such that the two pyridine rings in one complex molecule each stack with one pyridine ring from an adjacent molecule (av. C···C = 3.37 Å). A H_2O molecule exists between two of the H_4tg$^-$ ligands, forming intermolecular O−H···O hydrogen bonds (av. O_{tg}···O_{water} = 2.82 Å).[14] Thus, in addition to π−π interactions,[15] the 1D chain structure is sustained by hydrogen bonds mediated by solvated H_2O molecules, and no direct intermolecular hydrogen bonds are formed within each 1D chain between the H_4tg$^-$ ligands.[16] The Pt···Pt distance between two complex molecules in the 1D chain is 5.27 Å, indicating no metal−metal-bonding interactions.[17]

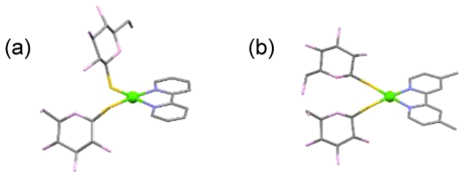

Figure 3. Perspective views of the molecular structures of (a) **1a** and (b) **2a**. H atoms are omitted for clarity. Color code: Pt, green; S, yellow; O, pink; N, blue; C, gray.

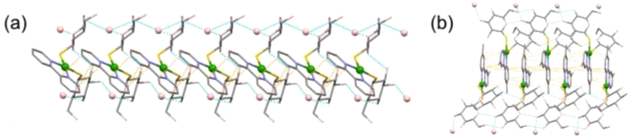

Figure 4. Perspective views of 1D chain structures of (a) **1a** and (b) **2a**. Blue and orange dashed lines represent O−H···O and π−π interactions, respectively.

Compound **2a** also crystallizes in a chiral monoclinic space group *P*2_1, containing a complex molecule and three solvated H_2O molecules in the asymmetric unit. The overall structure of the complex molecule in **2a**, [Pt(H_4tg-*S*)$_2$(dmbpy)], is very similar to that in **1a**, except for the presence of dmbpy in place of bpy (Figure 3b).

However, the packing structure for **2a** is quite different from that for **1a** (Figure 4b); i.e., the complex molecules in **2a** are arranged in an antiparallel fashion to give a zigzag array of Pt^{II} atoms, which appears to avoid steric crowding between the dmbpy ligands bearing methyl groups. As a result, each of the two pyridine rings in one complex molecule is stacked with two adjacent pyridine rings from neighboring molecules (av. C···C =

3.36 Å), forming a 1D chain structure supported by tight $\pi-\pi$ interactions between the dmbpy ligands. Moreover, this 1D chain is also supported by direct intermolecular $O-H\cdots O$ hydrogen bonds between the H_4tg^- ligands (av. $O_{tg}\cdots O_{tg} = 2.86$ Å), while the solvated H_2O molecules contribute little to the connectivity of the 1D chain.[16] Similar to **1a**, no significant Pt⋯Pt interactions exist in **2a**, as evidenced by the 6.69 Å distance between the Pt^{II} centers.

The most significant structural difference between **1a** and **2a** is the packing mode of the complex molecules. Although both form 1D chain structures, the 1D chain in **1a** is supported by $O-H\cdots O$ hydrogen bonds that involve solvated H_2O molecules in combination with single $\pi-\pi$ interactions between two complex molecules, whereas the 1D chain in **2a** is supported by direct $O-H\cdots O$ hydrogen bonds between H_4tg^- ligands and double $\pi-\pi$ interactions between two complex molecules. The removal of solvated H_2O molecules from **1a** is assumed to cause a slip of the complex molecules such that the bpy ligand in each complex molecule effectively overlaps with adjacent complex molecules in the 1D chain. This overlap leads to generation of appreciable intermolecular Pt⋯Pt interactions, resulting in the appearance of the low-energy band at 544 nm. Such a movement of the complex molecules in **2a** is not induced by the removal of solvated H_2O molecules because the H_2O molecules contribute little to stabilization of the 1D chain structure.

In summary, what appears to be the first instance, photoluminescence in mononuclear diimine platinum(II) complexes (**1a** and **2a**) that contain hydrophilic, aliphatic thiolate ligands was reported. Of note is the quite facile removal of solvated H_2O molecules upon exposure to a vapor of MeOH or MeCN or via moderate heating, which are reincorporated upon treatment with water vapor. Remarkably, this reversible removal/incorporation of H_2O molecules leads to significant changes in the absorption and emission colors of **1a**, whereas such chromic behavior was not recognized for **2a**.[18] The cause of this difference was elucidated via single-crystal X-ray analyses, which revealed different hydrogen-bonding behavior of the solvated H_2O molecules with H_4tg^- because of the different stacking modes of the bpy and dmbpy ligands. Thus, this study highlights the significance of the introduction of both hydrophilic and hydrophobic ligands in one complex molecule, as well as of the slight modification of ligands, for the creation of vapochromic coordination systems that are very sensitive toward water vapor under mild conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format and crystallographic, experimental, molecular orbital calculation, and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(12) The emission band for a sample obtained by heating **1a** at 40 °C for 30 min appeared at 645 nm, the wavelength of which is just between the bands for **1a** and **1b** (Figure S5 in the SI).

(13) This was also supported by the powder X-ray diffraction study (Figure S6 in the SI).

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