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Impact of a Carboxyl Group on a Cyclometalated Ligand: Hydrogen-Bond- and Coordination-Driven Self-Assembly of a Luminescent Platinum(II) Complex

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Supporting Information

ABSTRACT: A new luminescent cyclometalated platinum(II) complex containing a carboxyl group, *trans*-[Pt(*p*cppy)(pic)][**1-COOH**; H*p*cppy = 2-(*p*-carboxyphenyl)pyridine and Hpic = picolinic acid] has been synthesized and characterized. The luminescence behavior of **1-COOH** in the solid and solution states is completely different despite the similarity of the luminescence in both states for the nonsubstituted complex, [Pt(ppy)(pic)] (**1-H**; Hppy = 2-phenylpyridine). Interestingly, **1-COOH** exhibits concentration-dependent absorption and emission behavior based on its aggregation in a basic aqueous solution despite the absence of amphiphilic character.

Square-planar platinum(II) complexes have been extensively studied for several decades because of their unique color and photophysical properties attributed to the various stacking interactions (e.g., Pt–Pt- and/or $\pi-\pi$-stacking interactions).[1] Taking advantage of these unique stacking interactions, several platinum(II) complexes have been reported to exhibit drastic and reversible color changes.[2] In addition, notably, such chromic behavior is observed not only in the solid state but also in the solution state. For instance, amphiphilic platinum(II) complexes, such as [Pt(tpy)($C\equiv CC\equiv CH$)]OTf (tpy = 2,2′:6′,2″-terpyridine and OTf = triflate) and K[Pt(bzimpy)($C\equiv CC_6H_4OR$)] [bzimpy = 2,6-bis(benzimidazol-2′-yl)pyridine], have been reported to exhibit interesting solvatochromism based on aggregation of the square-planar molecules, which involves the change of Pt–Pt- and/or $\pi-\pi$-stacking interactions.[3] This type of interesting behavior in the solution state is believed to be necessary for exhibiting amphiphilicity in the platinum(II) complex molecule (e.g., a hydrophobic long alkyl chain group with a hydrophilic platinum(II) cationic or anionic molecule). Thus, marginal attention has been focused on the formation of molecular aggregation based on other mechanisms.[4]

We have reported several luminescent platinum(II) complexes exhibiting interesting vapochromic behavior, attributed to the change of the Pt–Pt interactions in the solid state.[5,6] From the viewpoint of crystal engineering, hydrogen-bonding interaction is useful for regulating the molecular arrangement in the solid state; for example, a platinum(II) complex bearing both proton-accepting and proton-donating groups, [Pt(H_2dcbpy)$(CN)_2$] (H_2dcbpy = 4,4′-dicarboxy-2,2′-bipyridine), forms an interesting porous structure constructed by a two-dimensional hydrogen-bonding sheet network and effective Pt–Pt interactions between the sheets.[6] In contrast to their unique behavior in the solid state, in the dilute solution state, several platinum(II) diimine complexes are well-known to exhibit marginal emission, with the exception of a system exhibiting effective intermolecular Pt–Pt- and/or $\pi-\pi$-stacking interactions.[7]

In this study, we focused on cyclometalated ligands, which have afforded several strongly luminescent platinum(II) complexes not only in the solid state but also in the solution state.[8] We envisioned that the combination of a cyclometalated ligand and a hydrogen-bonding functional group can lead to the construction of a novel, strong luminescent system, which exhibits chromic behavior in both the solid and solution states. Herein, we report the syntheses, crystal structures, and photoluminescence properties of two cyclometalated platinum(II) complexes, [Pt(ppy) (pic)] (**1-H**; Hppy = 2-phenylpyridine and Hpic = picolinic acid) and [Pt(*p*cppy)(pic)] [**1-COOH**; H*p*cppy = 2-(*p*-carboxyphenyl)pyridine] (Scheme 1) in which the carboxyl groups of *p*cppy and pic ligands are expected to act as proton-donating and proton-accepting hydrogen-bonding sites, respectively. In addition, **1-COOH** exhibits strong concentration-dependent absorption and emission behavior in basic aqueous solutions despite the absence of amphiphilicity in the molecule.

Scheme 1. Schematic Structures of 1-H and 1-COOH

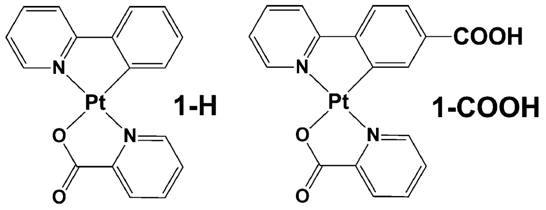

Figure 1 shows the crystal structures of **1-H** and **1-COOH**. Both **1-H** and **1-COOH** were obtained as trans isomers, in which the N atom of the pic ligand was coordinated in a position trans to the N atom of the ppy or *p*cppy ligand. The Pt–C and Pt–N

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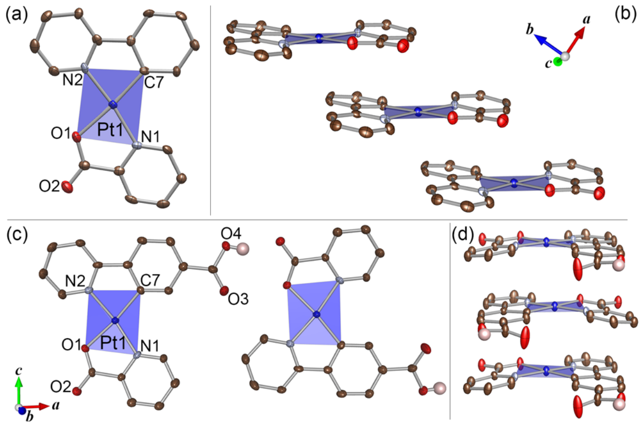

Figure 1. Molecular and stacking structures of (a and b) **1-H** and (c and d) **1-COOH** with thermal vibrational ellipsoids at the 50% probability level. Coordination spheres of Pt^{II} are shown as blue planes. Brown, light-blue, and red ellipsoids and pink balls represent the C, N, O, and H atoms, respectively. C-bound H atoms are omitted for clarity.

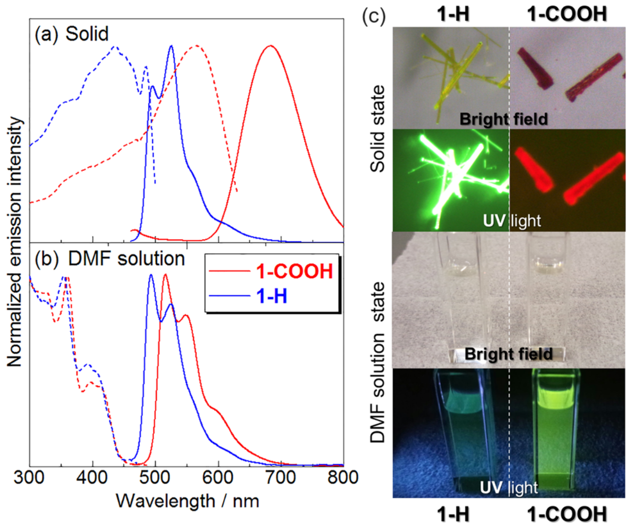

Figure 2. Normalized excitation (dotted lines)[9] and emission spectra (solid lines; λ_{ex} = 400 nm) of **1-H** (blue) and **1-COOH** (red) in the solid state (a) and in DMF solution (b): **1-H**, 0.06 mM; **1-COOH**, 0.04 mM. (c) Bright-field and luminescence images of **1-H** and **1-COOH** in the solid and DMF solution states.

bond distances in **1-COOH** [1.990(7)−2.054(7) Å] were comparable to those in **1-H**, indicating that the carboxyl group of the *p*cppy ligand barely affects the coordination environment of Pt^{II}. The almost planar molecules of **1-H** were stacked along the *c* axis; however, the intermolecular Pt−Pt interaction was negligibly weak because of the stairlike stacking structure [the nearest Pt−Pt distance was 5.572(2) Å; Figure 1b]. On the other hand, the crystal structure of **1-COOH** was significantly different from that of **1-H**. As expected from the hydrogen-bonding ability, a one-dimensional (1D) ribbonlike structure was formed by the hydrogen bonds between the carboxylic acid group of the *p*cppy ligand and the carboxylate of the pic ligand of the adjacent molecule (Figure 1c). In addition, a 1D *π*−*π*-stacking columnar structure was also formed along the *c* axis, which is almost perpendicular to the direction of the 1D hydrogen-bonded ribbon (Figure 1d). Although the distance between adjacent molecular planes [3.386(2) Å] in **1-COOH** was longer than that of **1-H** [3.291(2) Å], infinite stacking with the alternate arrangement of the *p*cppy and pic ligands may enhance the *π*−*π*-stacking interaction. As a result, the intermolecular Pt−Pt distance [3.595(2) Å] in **1-COOH** is shorter than that in **1-H**.

1-H exhibited vibronic-structured green emission at approximately 495 nm in both the solid and *N*,*N*-dimethylformamide (DMF) solution states (Figure 2), suggesting that the emission possibly originates from the intramolecular excited state. In contrast, a significantly different luminescent behavior was observed for **1-COOH**. A broad red emission without any vibronic structure was observed at 683 nm in the solid state, which is a remarkably lower energy by approximately 158 nm compared to that of **1-H**, whereas the emission spectrum in the DMF solution was very similar to that of **1-H** with a small red shift (ca. 23 nm). This small shift is due to the more stable *π** orbital of the *p*cppy ligand compared with that of the ppy ligand, owing to the electron-withdrawing carboxyl group. In fact, time-dependent density functional theory (TD-DFT) calculations for **1-H** and **1-COOH** suggest that the lowest unoccupied molecular orbital of **1-COOH** is delocalized on the carboxyl group, and the estimated absorption energy of **1-COOH** is marginally smaller than that of **1-H** (Figure S1 and Tables S3−S5). In addition, our preliminary DFT calculations of the dimerized **1-COOH** suggest that the highest occupied molecular orbital mainly comprises two d_{z^2} orbitals of Pt ions having antibonding character. Thus, the red emission observed for **1-COOH** in the solid state could be attributed to the metal−metal-to-ligand charge-transfer transition. Although the emission quantum yield of **1-COOH** (Φ_{em} = 0.15) was smaller than that of **1-H** (Φ_{em} = 0.67) in the solid state, the value in the DMF solution (Φ_{em} = 0.03) was comparable to that of **1-H** (Φ_{em} = 0.01). Thus, the lower emission quantum yield of **1-COOH** in the solid state is possibly attributed to the smaller energy gap between the emissive and ground states in **1-COOH** compared to that in **1-H**.

Interestingly, the emission and absorption properties of **1-COOH** were found to depend on its concentration in a 4% NaOH aqueous solution (Figures 3 and S2). A new absorption band was clearly observed around 520 nm at a higher concentration region (>0.1 mM; Figure S3). Furthermore, a new emission band was also observed at longer wavelength in the same concentration region (Figure 3b), and a red emission similar to that in the solid state was observed in the 1 mM solution by excitation at 550 nm (see Figure S4). Notably, one isosbestic point was observed at 418 nm in the concentration-dependent absorption spectrum of **1-COOH**, suggesting that only one new species, probably the dimerized one, is generated at a higher concentration region. Considering the fact that the ^1H NMR spectrum of **1-COOH** was also shifted to upfield by

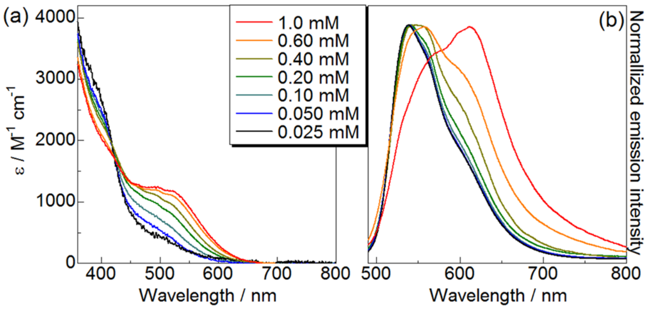

Figure 3. Concentration dependences of (a) UV−vis absorption and (b) emission spectra (λ_{ex} = 400 nm) of **1-COOH** in a 4% NaOH aqueous solution.

approximately 0.1 ppm at higher concentration (Figure S5), dimerization possibly occurs owing to effective intermolecular Pt−Pt/π−π interactions. The particle-size distributions estimated by a dynamic light scattering method revealed that the size in the 1 mM solution was 2 times larger than that in the 0.1 mM solution (Figure S6). In contrast, such concentration-dependent behavior was barely observed in the DMF solutions of **1-COOH** or **1-H** (Figures S7−S9). In addition, the solubility of **1-COOH** was poor in the acidic aqueous solution, implying that the deprotonated **1-COO$^-$** plays an important role on this concentration-dependent behavior.

As mentioned above, amphiphilic cationic and/or anionic platinum(II) complexes with hydrophobic long alkyl chains are well-known to form various self-assembled structures.[3] However, no hydrophobic functional group was present in **1-COOH**, indicating the lack of amphiphilicity. The other possibility for dimerization is that **1-COOH** can coordinate to a metal cation (in this case, Na^+) via the deprotonated carboxylate group of the *p*cppy ligand (**1-COO$^-$**). In fact, drastic changes were observed in the UV−vis absorption and emission spectra by the addition of 15-crown-5, a crown ether well-known for trapping Na^+ by forming a complex with it (Figure 4). As shown in Figure 4, characteristic bands for the dimerized species completely disappeared. In addition, in the presence of 15-crown-5 (1 equiv to Na^+), all signals in the ^{1}H NMR spectrum of **1-COOH** were observed to be shifted to lower field by approximately 0.7 ppm compared to those in the absence of 15-crown-5 (Figure S5), suggesting that 15-crown-5 effectively binds Na^+, which leads to the suppression of aggregation in **1-COO$^-$**. These results clearly indicate that Na^+ in a basic aqueous solution plays an important role in forming the dimerized structure of **1-COO$^-$** via coordination of the carboxylate group of the *p*cppy ligand.

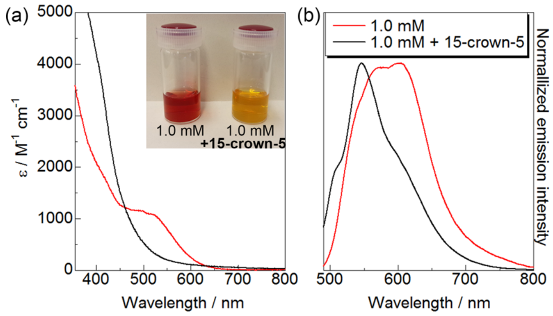

Figure 4. Changes of (a) UV−vis absorption and (b) emission spectra (λ_{ex} = 400 nm) of **1-COOH** in a 4% NaOH aqueous solution by the addition of 800 μL of 15-crown-5 (1 equiv to Na^+). The inset in panel (a) shows the bright-field images of the solutions.

In summary, we synthesized a new cyclometalated platinum(II) complex, **1-COOH**, containing a hydrogen-bonding carboxylic acid group. **1-COOH** and **1-H**, which does not contain a carboxyl group, exhibited vibronic-structured green emission in a DMF solution. In contrast, **1-COOH** exhibited red emission without any vibronic structure in the solid state, attributed to intermolecular Pt−Pt/π−π-stacking interactions. Moreover, **1-COOH** exhibited strongly concentration-dependent absorption and emission behavior in a NaOH aqueous solution despite the absence of amphiphilicity, probably attributed to the dimerization induced by coordination of the carboxylate of a deprotonated **1-COO$^-$** species to Na^+. Currently, the metal-ion dependence of **1-COOH** is underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01343.

Experimental details, TD-DFT calculations and MO diagrams and concentration dependence of the UV−vis and ^{1}H NMR spectra (PDF)

X-ray crystallographic data in CIF format of **1-H** and **1-COOH** (CIF)

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Author Contributions

The manuscript was written with the contributions of all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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(9) Emission wavelengths for excitation spectra in the solid and DMF solution states are 525 and 494 nm for **1-H** and 683 and 516 nm for **1-COOH**, respectively.