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Luminescent Pincer-Type Cyclometalated Platinum(II) Complexes with Auxiliary Isocyanide Ligands: Phase-Transfer Preparation, Solvatomorphism, and Self-Aggregation

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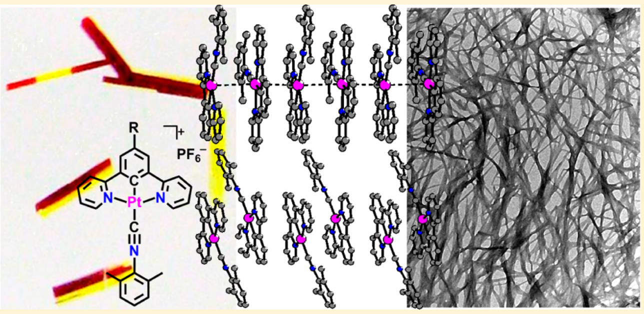
Supporting Information

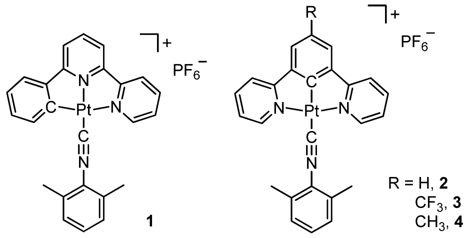
ABSTRACT: A series of luminescent pincer-type cyclometalated platinum(II) complexes, namely [4-R-(N^C^N)PtC≡N(C$_6$H$_3$-2,6-Me$_2$)]PF$_6$ (**2**–**4**; 4-R-(N^CH^N) represents substituted 1,3-bis(2′-pyridyl)benzene ligands), were prepared under phase-transfer conditions. Complex **2** shows two solvatomorphic crystal structures and exhibits vapoluminescent response toward acetonitrile vapor. The photophysical properties of and supramolecular nanowires formed from these complexes were also investigated.



There has been considerable interest in cyclometalated Pt(II) complexes supported by the pincer-type (N^C^N) ligands (N^CH^N = 1,3-bis(2′-pyridyl)benzene) and its analogues, since Williams and co-workers reported the intriguing intense $^3\pi\pi^*$ emission of this class of complexes in fluid solutions with emission quantum yields up to 0.68.[1] The dramatic increase in both emission quantum yield and lifetime, in comparison to their 6-phenyl-2,2′-bipyridine (CH^N^N) isoelectronic congeners,[2] have been ascribed to the shorter Pt–C bond distances of this class of Pt(II) complexes that raise the energy of the d–d state, thereby diminishing the nonradiative decay pathway(s).[3] The intense phosphorescence enables charge-neutral cyclometalated Pt(II) complexes of this type to be attractive candidates for applications in chemosensing and in optoelectronic devices.[4] Despite these advances, only limited examples of cationic pincer-type (N^C^N)Pt complexes have been reported in the literature. We report herein new members of cationic cyclometalated Pt(II) complexes of [4-R-(N^C^N)PtC≡N(C$_6$H$_3$-2,6-Me$_2$)]PF$_6$ type that display intriguing spectroscopic and self-assembling properties,

In previous works, we attempted to prepare [(N^C^N)PtC≡N(C$_6$H$_3$-2,6-Me$_2$)]Cl from a [(N^C^N)PtCl] precursor and 2,6-dimethylphenyl isocyanide by a simple ligand-substitution reaction in homogeneous solution,[5] as this method is useful for the synthesis of the C^N^N congeners, such as complex **1** in Chart 1. However, no pure product was obtained through this approach, even though a large excess of isocyanide ligand was used. Instead, two species, the starting material [(N^C^N)PtCl] and the desired product, were identified on the basis of ESI-MS and ^{1}H NMR data, most probably as a result of reversible ligand exchange reactions. To shift the reaction equilibrium to allow for the isolation of pure N^C^N-coordinated platinum(II) isocyanides **2**–**4** (Chart 1), we designed an aqueous/organic phase-transfer reaction to enrich the targeted cationic products in the aqueous solution phase.

Chart 1. Chemical Structures for Complexes 1 (Previous Work) and 2–4 (Present Work)



The two-phase reaction system for the synthesis of organoplatinum(II) salts in the present work, namely [4-R-(N^C^N)PtC≡N(C$_6$H$_3$-2,6-Me$_2$)]PF$_6$ (R = H for **2**, CF$_3$ for **3**, and Me for **4**), consisted of equivalent volumes of water and dichloromethane. When an excess amount of 2,6-dimethylphenyl isocyanide was added to the lower-layer dichloro-

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methane solution containing [4-R-(N^C^N)PtCl], the cationic [4-R-(N^C^N)PtC≡N(C_6H_3-2,6-Me_2)]Cl salt thus formed was quickly transferred to the aqueous phase. The luminescent color change in the course of the reaction could be monitored by human eyes under a 365 nm lamp (Figure 1). Generally, upon the addition of isocyanide ligand under vigorous stirring conditions, the pale yellow color of the organic layer faded, and this was accompanied by the disappearance of the green emission. Meanwhile, the aqueous phase changed from colorless to pink with a concomitant development of an intense red emission. The red emission from the aqueous solution is a signature of molecular aggregation of monomeric Pt(II) complexes through intermolecular Pt···Pt and/or ligand−ligand interactions.[5] When the pink aqueous phase containing cationic salts was separated and mixed with a saturated aqueous NH_4PF_6 solution, the corresponding salts **2**−**4** precipitated out and were isolated as red, yellow, and orange-red solids, respectively. Interestingly, the colors and luminescence of the organic phase could be restored by adding an excess of chloride ions into the aqueous layer. The charge-neutral precursor [(N^C^N)PtCl] was regenerated and was extracted back into the organic phase.

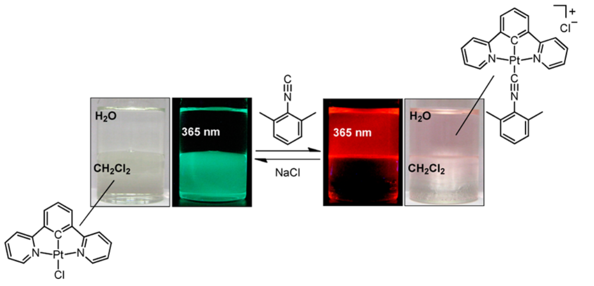

Figure 1. Changes in solution color and luminescence of the two-phase system upon the addition of isocyanide or chloride ions to induce the switching of the substitution reaction.

Two crystal forms of **2** were obtained, depending on the recrystallization conditions. Slow diffusion of diethyl ether vapor into a dichloromethane solution of **2** at ambient temperature afforded red needle-shaped crystals with an *Ima*2 space group, while yellow prism crystals with a $P\bar{1}$ space group were isolated from an acetonitrile solution. There have been many reports on the polymorphic behavior of square-planar Pt(II) complexes in the literature, all of which were found to be associated with the molecular arrangement and Pt···Pt distances in the crystal structures.[6] The crystal structure of the red form features infinite Pt···Pt chains along the *a* axis. Every two neighboring molecules are in a staggered arrangement with a torsion angle of 117° around the Pt−Pt axis. The uniform intermetal distance of 3.43 Å (slightly shorter than the sum of van der Waals radii of 3.44 Å) and Pt−Pt−Pt angle of 170° are indicative of extended $d^8\cdots d^8$ interactions along the near-linear Pt···Pt backbone (Figure 2a). The phenyl ring of the isocyanide ligand and the [(N^C^N)Pt] plane are coplanar, which is similar to the case for its C^N^N counterpart[7] but different from that for the [(N^C^N)PtC≡CPh] crystal,[8] where the acetylenic phenyl ring is perpendicular to the plane of the cyclometalated ligand. There is a solvated acetonitrile molecule in the unit cell of the yellow form of **2**. The cations in the yellow form are stacked into chains, with every two adjacent molecules in a head-to-tail fashion with an interplanar distance of ca. 3.5 Å. Close Pt···Pt interactions are excluded, as the alternating intermetal separations of 3.74 and 5.46 Å are much longer than the sum of van der Waals radii. Efforts to obtain crystals of **3** and **4** suitable for X-ray crystallographic studies were not successful. However, the yellow color of **3** and the orange-red color of **4** in the solid state are indicative that Pt···Pt interactions are absent in the former but could be present in the latter.

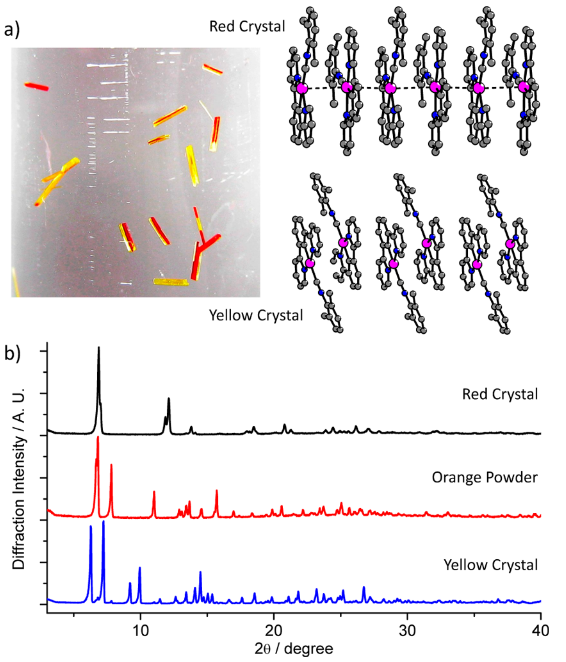

Figure 2. (a) Two solvatomorphic crystals grown for complex **2** and the crystal-packing diagrams of the red and yellow crystals with hydrogen atoms, counterions, and solvated molecules omitted for clarity. (b) Powder X-ray diffraction patterns of **2** in various forms.

The two solvatomorphs of crystal **2**, the red form and the yellow form (acetonitrile phase), can be converted into each other through sorption or desorption of the solvated acetonitrile molecules. When the needle-shaped crystal of **2** was immersed into a mixture of acetonitrile and diethyl ether, it changed from red to yellow within several minutes.[9] The powder X-ray diffraction (PXRD) pattern of the yellow solid thus obtained showed peaks at 2θ = 6.28, 7.24, 9.22, and 9.96°, which is identical with the pattern simulated from the crystal data of the yellow crystals obtained from the acetonitrile phase, indicative of a similar packing of molecules. The changes from the red form to the yellow form could be ascribed to structural reorganization induced by acetonitrile solvent molecules on the basis of X-ray crystallographic analysis. However, the red crystal form could not transform directly to the yellow form upon exposure to acetonitrile vapor. Instead, only an orange solid was obtained, and this solid was envisioned to be an intermediate state between the red and yellow forms. PXRD measurements on the resulting orange sample supported this assumption; the diffraction pattern of the orange powder was different from that of either the red or the yellow forms (Figure 2b). On the other hand, the yellow crystal was unstable and swiftly transformed to its red form upon aging in air (Figure 2a), leaving some colorful crystals with alternating red and yellow fragments. Several recent reports attributed the color and emission response of Pt(II) complexes toward volatile organic compounds (VOCs) to the vapochromic behavior arising from alterations in intermolecular packing.[10]

The absorption and emission spectra of complexes **2**−**4** were recorded under various conditions, with the results depicted in Figures 3 and Figures S2 and S3 (Supporting Information) and the photophysical data summarized in Table S1 (Supporting Information). All three complexes in CH_3CN exhibit similar absorption spectral profiles. The intense bands in the region 248−329 nm with large extinction coefficients (∼10^4 mol^{-1} dm^3 cm^{-1}) originate from intraligand $\pi-\pi^*$ transitions localized on the cyclometalated 1,3-bis(2′-pyridyl)benzene ligand. The low-energy absorptions at 350−450 nm are tentatively assigned to transitions having mixed charge-transfer/intraligand characters, with reference to previous works on the $[(N\text{^}C\text{^}N)PtC{\equiv}C(C_6H_4\text{-}4\text{-}R)]$ system.[8,11] As the 4-substituent on the phenyl ring of the cyclometalated ligand becomes more electron donating from **3** via **2** to **4**, the low-energy band red-shifts in energy.

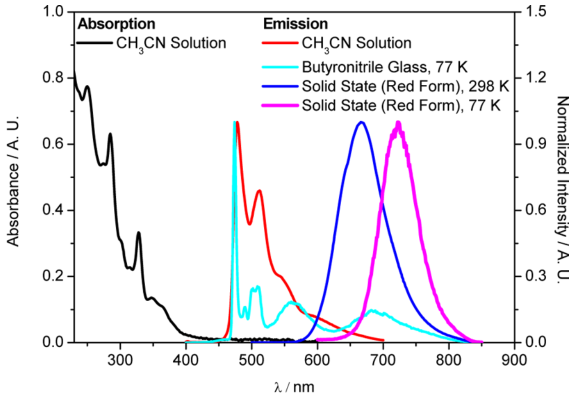

Figure 3. Absorption and emission spectra of complex **2**.

Complexes **2**−**4** emit brightly in the green spectral region in degassed CH_3CN at a concentration of 2.0×10^{-5} mol dm^{-3} at 298 K, with λ_{max} (lifetime, quantum yield) values of 478 nm (5.6 μs, 12%), 472 nm (3.5 μs, 8%), and 497 nm (4.60 μs, 14%), respectively. The emission maxima are red-shifted with the substituent attached to the phenyl unit of the cyclometalated ligand in the order $CF_3 < H < CH_3$, and the excitation spectra monitored at λ_{max} match well with the corresponding absorption spectra. The vibronically structured band reveals a spacing of about 1400 cm^{-1} in accordance with the C═C and C═N vibrational modes of the 1,3-bis(2′-pyridyl)benzene moiety, suggesting that the emission originates from a state of primarily ^{3}LC character. Lowering the temperature from 298 to 77 K resulted in a highly structured emission in the high-energy region, together with a lower energy broad band. For example, the emission spectrum of **2** in a glassy butyronitrile solution at 77 K is characterized by a vibronically resolved emission band with peak λ_{max} at 474 nm (τ = 25.4 μs) and two broad emission bands with peak λ_{max} at 560 nm (τ = 3.6 μs) and 683 nm (τ = 3.6 μs), respectively. The high-energy emissions are comparable in energy with those recorded in solution, whereas the low-energy bands with peaks λ_{max} 560 and 683 nm could be tentatively ascribed to be triplet $\pi\pi^*$ excimeric and triplet metal−metal-to-ligand charge-transfer (^{3}MMLCT) excited states, respectively.

Solid-state emission of oligopyridyl/cyclometated Pt(II) complexes could be significantly affected by the packing of molecules in their crystal structures.[12] The red form of **2** shows a broad and structureless emission at both room temperature and 77 K, with λ_{max} at 667 (τ = 0.2 μs) and 723 nm (τ = 1.0 μs), respectively. When a film of the red sample **2** drop-casted from a dichloromethane solution onto a quartz plate was exposed to acetonitrile vapor, a blue shift in emission energy and an enhancement of the emission intensity were observed (Figures 4), accompanied by a change in film color from red to orange. The emission of the yellow form of **2** with λ_{max} at 565 nm is further blue-shifted from that of the red and orange forms (Figure S1, Supporting Information). In contrast to **2**, both **3** and **4** show a broad structureless emission at room temperature and an intense vibronic structured band at 77 K (Figures S2 and S3, Supporting Information), suggesting that the emissive excited states are temperature dependent.

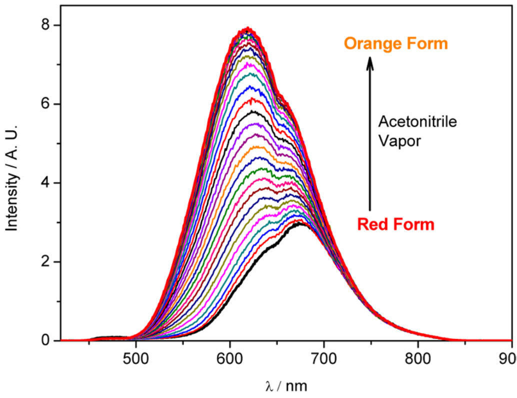

Figure 4. Emission spectral traces of the red form of **2** drop-casted on a quartz plate in response to acetonitrile vapors. The excitation wavelength was 365 nm. The emission spectra were recorded at intervals of approximately 1 min.

Recently, we and others have reported the usage of Pt(II) complexes to construct quasi-one-dimensional nanowires,[13] quasi-two-dimensional nanosheets,[8] and nanowheels.[14] We examined the self-assembly of complexes **2**−**4** and found that the molecular aggregates thus formed are affected by the extent of Pt···Pt interactions and/or $\pi-\pi$ stacking of cyclometalated ligands. Superstructures of all of the complexes in this work were obtained by a reprecipitation method without the aid of surfactants. As an example, a CH_3CN solution of **2** at a concentration of 1000 μM was prepared. The stock solution was diluted to 100 μM with water to give dispersions in CH_3CN/H_2O (1/9 v/v). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of a dispersion of **2** (Figure 5) in CH_3CN/H_2O revealed well-defined nanowires with width less than 50 nm and length up to 2 μm. Changing the solvent from water to diethyl ether in the course of reprecipitation could increase the lateral dimensions while keeping the morphology of nanowires unchanged. Under similar fabrication conditions, complexes **3** and **4** assembled into nanorods and nanowires, respectively, both with lower aspect ratios and ill-defined morphologies. We propose that the intermolecular Pt···Pt and/or $\pi-\pi$ interactions would contribute to directing the anisotropic growth and self-aggregation to one-dimensional nanostructures.

In conclusion, three new pincer-type cyclometalated Pt(II) isocyanides were prepared under phase-transfer conditions. These intensely phosphorescent complexes can be assembled into one-dimensional nanowires or nanorods driven by interamolecular Pt···Pt and/or $\pi-\pi$ stacking interactions. The solvatomorphism and vapoluminescent behaviors of **2** are rationalized by structural rearrangements induced by the

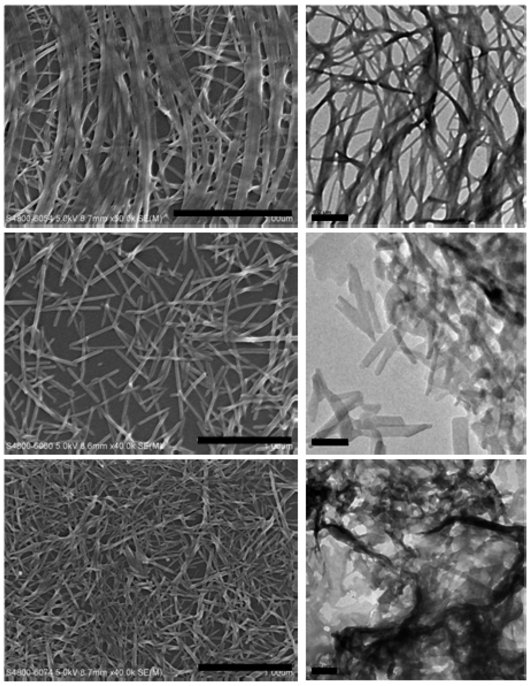

Figure 5. SEM (left) and TEM (right) images of nanostructures assembled from **2**–**4** (from top to bottom) in acetonitrile/water (1/10, v/v). The scale bars represent 1 μm in SEM and 200 nm in TEM micrographs.

sorption or desorption of solvated molecules, on the basis of X-ray crystallographic analysis. This work is supplementary to the surging study on the design and synthesis of cationic pincer-type cyclometalated Pt(II) complexes as supramolecular functional materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, text, tables, and figures giving crystallographic data for both the red and yellow forms of **2**, experimental details, structure characterization data, supplementary absorption and emission spectra, and spectroscopic and photophysical 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.

■ ACKNOWLEDGMENTS

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