

# Highly Phosphorescent Crystals of Vaulted *trans*-Bis(salicylaldiminato)platinum(II) Complexes

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Supporting Information

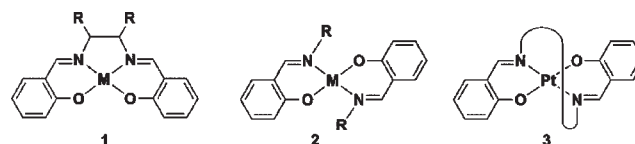
**ABSTRACT:** Unprecedented strong phosphorescent emission in the crystalline state is observed for a variety of vaulted *trans*-bis(salicylaldiminato)platinum(II) complexes which are newly synthesized as a third coordination mode of well-studied bis(salicylaldiminato) complexes. This Communication describes the dynamic photophysical properties of these complexes in the liquid and crystalline states and a mechanistic rationale for the strong emission in the crystalline state.

Solid-state emission is important not only for the development of future light-emitting devices with high luminance<sup>1</sup> but also in regard to fundamental research for new functions of molecular aggregations.<sup>2,3</sup> High-density integration is a straightforward concept to increase the brightness of light-emitting materials; however, most materials that exhibit intense emission under low-density environments cannot maintain their emission efficiencies in the crystalline state due to inevitable energy loss by non-radiative pathways through intermolecular connection.<sup>2a,b</sup> It is this dilemma that long prevented the systematic and continuous research on solid-state emission, especially on emissive crystals. The major strategy to overcome this difficulty is to design the molecular array in order to decrease the negative intermolecular contact between packed molecular units. Highly emissive fluorescent solids and crystals have been recently formed by the introduction of sterically bulky units<sup>1f–h,2b</sup> and ionic spacers.<sup>2d</sup> An alternative topic in this field is the aggregation-induced enhancement of fluorescent emission (AIEE) in solid<sup>3</sup> and gel<sup>4</sup> states, which is attributable to overcoming the positive effect on fixation of conformationally flexible  $\pi$ -conjugate systems by suitable molecular aggregations.

Phosphorescent emission in crystals remains unascertained<sup>5,6</sup> despite its potential importance in material science.<sup>7</sup> This is probably due to the significant negative effect of bimolecular triplet–triplet annihilations between transition metal complexes.<sup>8</sup> It is entirely fair to state that related information on phosphorescent solids is limited to that of the emissive tris(phenylpyridine)iridium [Ir(ppy)<sub>3</sub>] complex, whose extremely high emission properties in solution [photoluminescence (PL) quantum yield:  $\Phi = 0.97$ ]<sup>9</sup> decrease in condensed solid systems such as a neat film (0.03)<sup>10</sup> due to self-quenching through intermolecular  $\pi$ -stacking interactions.<sup>11,12</sup> To the best of our knowledge, the highest PL quantum yield of crystals is that of Pt(*t*-BuCN)<sub>2</sub>(CN)<sub>2</sub> ( $\Phi = 0.33$ ),<sup>13</sup> where infinite Pt–Pt interactions and the staggered coordination of linear cyano and

isonitrile ligands minimize the deactivation for metal-to-ligand charge transfer (MLCT) emission.

As part of our program, which is aimed at the development of transition metal-based functional materials, we have investigated new properties of *trans*-bis(salicylaldiminato) d<sup>8</sup> transition metal complexes **2**,<sup>14</sup> almost untouched analogues of the well-studied *cis*-fused complexes **1**.<sup>15,16</sup> Consequently, we have synthesized a bridged *trans*-form of divalent platinum complex **3**, a novel third mode of bis(salicylaldiminato) transition metal complexes, and found that complex **3** exhibits extraordinarily high phosphorescent properties in the crystalline state due to its characteristic molecular array of vaulted units, which leads to minimization of the energy loss. Complex **3** is nonemissive in the solution state, which therefore provides remarkable switching of emission properties between solution (OFF) and solid (ON), in contrast to typical solution (strong)–solid (weak) properties.

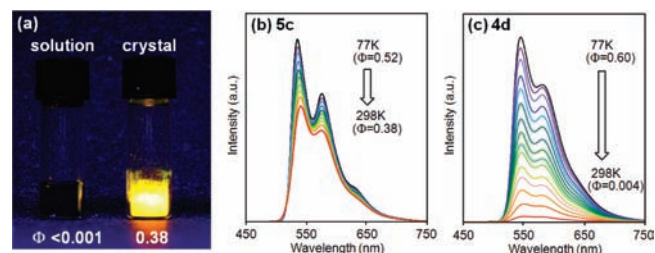


Yellow plates of polyethylene glycol (PEG)-bridged *trans*-bis(salicylaldiminato)platinum complex **5c**, derived by recrystallization from ethyl acetate, exhibit an intense yellow phosphorescent emission ( $\lambda_{\text{max}} = 546, 578 \text{ nm}$ ;  $\lambda_{\text{ex}} = 420 \text{ nm}$ ;  $\tau = 3.4 \mu\text{s}$ ) at 298 K (Figure 1a,b). The quantum yield of the crystals<sup>17</sup> at 298 K has been determined to be  $\Phi = 0.38 \pm 0.01$ , which is the highest yield for phosphorescent crystal emission at ambient temperature. An amorphous solid of **5c** exhibits a lower quantum yield ( $\Phi = 0.14 \pm 0.01$ ), which implies that the crystal packing minimizes the energy loss for phosphorescence. It is noteworthy that a solution of **5c** in any solvent is almost nonemissive at 298 K (cyclohexane,  $\Phi < 0.001$ ; 2-methyltetrahydrofuran,  $\Phi < 0.001$ ). The present switching of emission properties between solution and solid states is very rare and in contrast to the typical steep decay of emission of solids as observed for highly emissive Ir(ppy)<sub>3</sub> [ $\Phi = 0.34 \pm 0.01$  (crystal),<sup>17</sup>  $0.004 \pm 0.001$  (amorphous solid),<sup>17</sup>  $0.97 \pm 0.05$  (2-methyltetrahydrofuran solution)<sup>9,17</sup>].

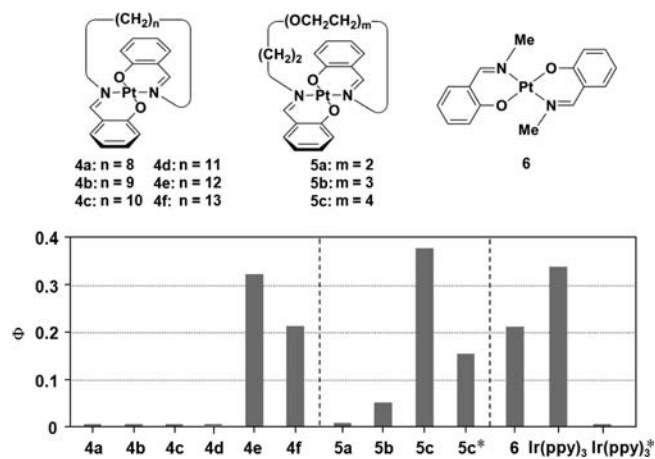
Such strong emission properties in the crystalline state appear specifically in vaulted complexes with an appropriate linker length. Figure 2 summarizes the PL quantum yields of a series of *trans*-bis(salicylaldiminato)platinum(II) crystals at 298 K ( $\lambda_{\text{ex}} = 420 \text{ nm}$ ). The crystalline emission of these complexes can be controlled by

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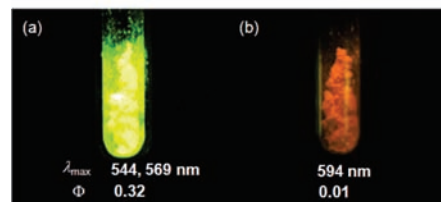
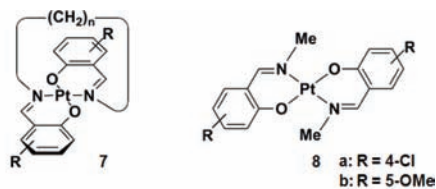
**Figure 1.** (a) Contrasting emission properties of **5c** in solution ( $2 \times 10^{-4}$  M, 2-methyltetrahydrofuran) and crystalline states at 298 K under UV illumination ( $\lambda_{\text{ex}} = 365$  nm). (b,c) Temperature dependence in emission intensity of **5c** and **4d** crystals between 77 K (black line) and 298 K (red line) ( $\lambda_{\text{ex}} = 420$  nm).



**Figure 2.** Absolute quantum yield for crystalline-state emission of complexes **4–6** ( $\lambda_{\text{ex}} = 420$  nm) and Ir(ppy)<sub>3</sub> (380 nm) at 298 K. \*Amorphous solid.

selection of the type and length of the linkers. Crystals of vaulted complexes **4e,f** bearing dodeca- and tridecamethylene linkers exhibit higher quantum yields of  $0.32 \pm 0.01$  and  $0.21 \pm 0.01$ , respectively, while related analogues **4a–d** with shorter linkers ( $n = 8–11$ ) are nonemissive in the crystalline state. A PEG-bridged crystal **5c** ( $m = 4$ ) exhibits the highest quantum yield at 298 K, although crystals **5a** and **5b** with shorter PEG linkers ( $m = 2$  and  $3$ ) are nonemissive or less emissive ( $\Phi = 0.002 \pm 0.001$  and  $0.051 \pm 0.001$ ). A bridged structure has proven to be indispensable for strong emission, and the nonvaulted crystal **6** exhibits a much smaller quantum yield ( $\Phi = 0.21 \pm 0.01$ ). Despite the high emission properties of some crystals, all complexes **4–6** do not exhibit any significant luminescence properties in 2-methyltetrahydrofuran solution at 298 K (Figure 1a, see Supporting Information).

Quantum yields of crystals of **4** at 77 K are as follows: **4a**, 0.09  $\pm$  0.03; **4b**, <0.001; **4c**, 0.18  $\pm$  0.02; **4d**, 0.60  $\pm$  0.02; **4e**, 0.51  $\pm$  0.01; and **4f**, 0.53  $\pm$  0.03. It is noteworthy that crystal **4d** exhibits the highest quantum yield at 77 K among all the complexes examined, although it is nonemissive at 298 K. In contrast, the PEG-bridged crystals have increased quantum yields at 77 K without significant changes in their relative intensity (**5a**, 0.12  $\pm$  0.01; **5b**, 0.43  $\pm$  0.01; **5c**, 0.52  $\pm$  0.01). It can be mentioned that emissive crystals **4e**, **4f**, and **5c** have higher heat resistance in emission intensity. Contrasting temperature dependence in emission intensity of **5c** and **4d** crystals at 77–298 K is shown in Figure 1b,c.

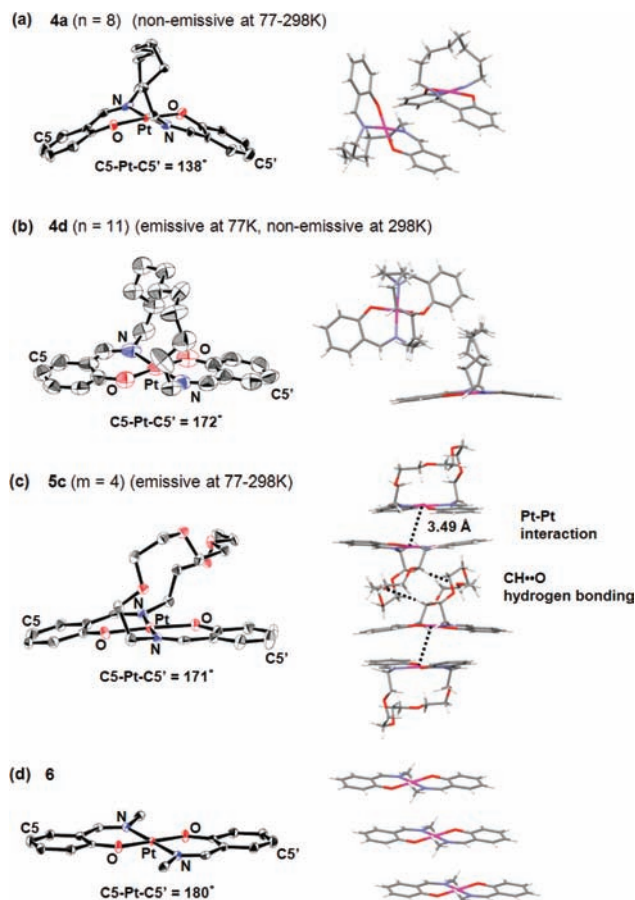


**Figure 3.** Effect of dodecamethylene bridge on emission of (a) **7a** and (b) **8a** under UV irradiation at 365 (photo) and 420 nm (quantum yield) at 298 K.

Note that the *trans*-complexes are better motifs for easy color change. Brilliant green-yellow [**7a**:  $\lambda_{\text{max}} = 544, 569$  nm;  $\Phi = 0.32 \pm 0.01$  (298 K)] and red [**7b**: 599, 630 nm;  $\Phi = 0.06 \pm 0.01$  (298 K)] crystal emission can be generated by introduction of 4-chloro and 5-methoxy substituents on the aromatic rings. It should also be emphasized that the emission colors are different in many cases from those of nonvaulted crystals. Typical examples are brilliant green-yellow in vaulted **7a** and dull orange in nonvaulted **8a** (Figure 3).

TD-DFT (B3LYP/6-31G\*, LanL2DZ) calculation of excited states ordering of **4a–e** showed that both  $T_1$  and  $T_2$  states lie below  $S_1$ , which indicates that phosphorescent emission principally occurs via  $S_1–T_2$  intersystem crossing. The calculation also indicates that major electronic configurations of  $S_1$  ( $T_1$ ) and  $S_2$  ( $T_2$ ) are HOMO-to-LUMO and HOMO-to-LUMO+1, respectively. Complexes bearing shorter methylene linkers tend to have larger  $S_1–T_2$  and smaller  $S_2–S_1$  gaps (see Supporting Information), as typically shown on comparison of nonemissive **4a** [ $\Delta E(S_1–T_2) = 0.28$  eV,  $\Delta E(S_2–S_1) = 0.25$  eV] and **4b** (0.27 eV, 0.27 eV) with emissive **4e** (0.23 eV, 0.34 eV) and **4f** (0.23 eV, 0.35 eV). Given the DFT calculation indicating that HOMO, LUMO, and LUMO+1 are principally Pt(5d)–O(2p), C=N( $\pi^*$ ), and Pt(5d)–C=N( $\pi^*$ ), respectively, these results strongly suggest that nonemissive **4a,b** crystals have slower intersystem crossing process and faster d–d transition process for nonradiative decay compared to those with emissive **4e,f**.<sup>19</sup> Contributions of a metal–metal-to-ligand charge transfer (MMLCT) and ligand–ligand  $\pi$  excimeric states seem to be less significant, since diluted solutions and crystals of these complexes show very similar emission spectrum patterns at 77 K (Supporting Information).

Molecular structure and packing of crystals **4–6** are shown in Figure 4.<sup>18</sup> Short-linked complexes **4a–c**, nonemissive at 77–298 K, have strongly bent coordination sites, which would explain the foregoing energy loss (Figure 4a). Medium-linked complex **4d**, emissive only at low temperature, has a planar coordination site without any significant intermolecular interactions (Figure 4b). The absence of intermolecular interactions would lead to a remarkable decay in emission at higher temperature (Figure 1c) by increasing the mobility of the packing units. In contrast, long-linked, planar complexes **4e**, **4f**, and **5c**, highly emissive at 77–298 K, form dimeric arrays which are firmly supported by the vaulted structure, a planar coordination plane, and Pt–Pt interactions. Cofacial coordination planes are located on



**Figure 4.** Molecular structure and packing of (a) **4a**, (b) **4d**, (c) **5c**, and (d) **6**.

pseudo-staggered positions to minimize the steric and electric repulsion between the aromatic rings (Supporting Information). Crystal **5c**, which exhibits the highest quantum yield at ambient temperature, stabilizes its beneficial molecular array by an intermolecular H-bonding network<sup>20</sup> through neighboring PEG units (Figure 4c). These intermolecular factors would suppress a steep increase in the molecular mobility, leading to minimization of energy loss for their original strong phosphorescent emission at higher temperature. The less emissive, nonvaulted crystals **6** form highly regulated aggregates of very flat coordination planes (Figure 4d), which would lead to significant energy loss from excited states. The unprecedented, drastic quenching of **4e**, **4f**, and **5c** in the solution state would be due to planarity and flexibility of the *trans*-bis(salicylaldiminato)metal coordination sites.<sup>14</sup> Research is currently underway to elucidate the mechanism and to apply these materials to the development of new light-emitting devices.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental details and characterization data for **4a–f**, **5a–c**, **6**, **7a,b**, and **8a**; X-ray crystallographic files, in CIF format, for **4a–f**, **5b,c**, and **6**; and a short movie, in MPEG video format, of the phosphorescent emission of crystals **5c**, **7a**, and **7b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

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