Stability Control and Luminescence of Porous Crystals of Self-assembled Platinum(II) Complexes Based on the Electronic Tuning of Ligands

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Porous molecular crystals (PMCs) have been actively studied as next-generation sensing and adsorption materials because of their structural/electronic flexibility and porosity. On the other hand, it is sometimes difficult to selectively obtain the desired porous structure due to the competition of weak intermolecular interactions during the crystallization. Previously, we developed a PMC built from a luminescent Pt(II) complex **1** (Fig. 1), which exhibited the assembly-induced emission owing to the Pt···Pt interactions.[1)] However, this porous structure was a kinetically trapped phase, and a thermodynamically more stable non-porous structure was favorably formed.

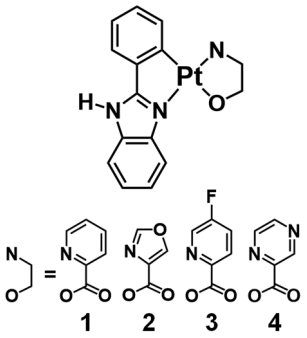

Fig. 1 Structures of **1**-**4**.

In this study, we have investigated to obtain the desired porous structure as the thermodynamically most stable phase by controlling the intermolecular interactions through ligand modification (**2**-**4** in Fig. 1). Although the complex **2** never formed the porous structure, the desired porous crystals were preferentially obtained for complexes **3** and **4** (Fig. 2) bearing the electron-deficient ligands. In contrast to the negligible Pt···Pt interactions in the non-porous crystal of **2**, the Pt···Pt interactions were enhanced by the electron-deficient ligands (d(Pt···Pt) = 3.4994(4) Å for **1**, 3.4503(4) Å for **3**, and 3.3390(3) Å for **4**). Importantly, depending on the strength of Pt···Pt interactions, these crystals exhibited distinctly different UV-vis absorption (Fig. 3) and luminescence behavior. The photophysical properties as well as the guest adsorption behavior of these crystals will be discussed.

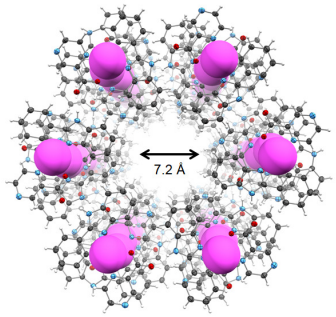

Fig. 2 Porous structure of **4**.

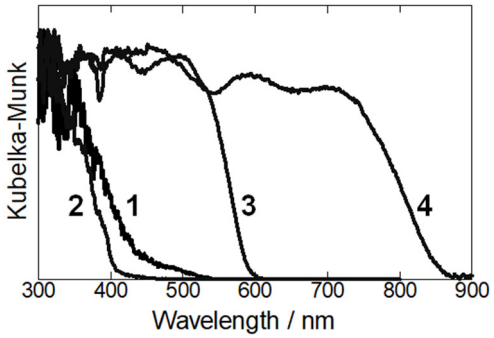

Fig. 3 UV-vis spectra of crystals **1**-**4**.

1) M. Yoshida, M. Kato, *et al.*, *Chem. Commun.* **2020**, *56*, 12989.