Vapor-controlled Assembly/Disassembly of an Anionic Pt(II) Complex Loaded on a Cationic Nanosheet

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Layered double hydroxides (LDHs; Fig. 1(a)), which consist of positively charged nanosheet-like structures and interlayer anions, are well-known to electrostatically load anionic molecules. In this work, we have focused on the controlled assembly of electrostatically loaded anionic molecules on the LDH by external stimuli. Here we report a stimuli-responsive nanohybrid material based on an anionic Pt(II) complex $[Pt(CN)_2(ppy)]^-$ (Fig. 1(b); Hppy = 2-phenylpyridine) and the LDH consisting of Mg^{2+} and Al^{3+} ions (Mg-Al LDH), in which the Pt(II) complex was found to assemble on the LDH under water vapor, causing vapochromic luminescence.

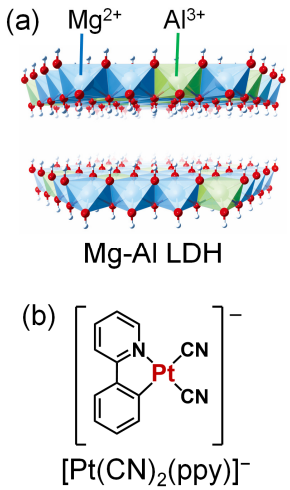

Fig. 1 (a) Mg-Al LDH and (b) $[Pt(CN)_2(ppy)]^-$.

The Pt(II)-loaded Mg-Al LDH nanoparticles (hereafter termed as **Pt-LDH**) have been synthesized by heating $K[Pt(CN)_2(ppy)]$ together with $MgCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, and tris(hydroxymethyl)aminomethane. Importantly, the obtained **Pt-LDH** exhibited obvious vapochromism. As shown in Fig. 2, dry **Pt-LDH** displayed green emission consisting of several vibronic satellite bands (λ_{em}^{max} = 480 and 520 nm; RH 0% in Fig. 2), while the emission color changed to orange under water vapor (λ_{em}^{max} = 604 nm; RH 97% in Fig. 2). The variable-temperature emission lifetime measurements revealed that the luminescence of the dry **Pt-LDH** originated from the ligand-centered $^3\pi\pi^*$ luminescence of discrete $[Pt(CN)_2(ppy)]^-$, whereas the luminescence of **Pt-LDH** under water vapor originated from the assembled state. Thus, these results indicate that the assembly of Pt(II) complex molecules was controlled on the LDH nanosheets by water vapor absorption. The detailed vapochromic mechanism will be discussed in detail based on differential scanning calorimetry (DSC) and water vapor adsorption measurements.

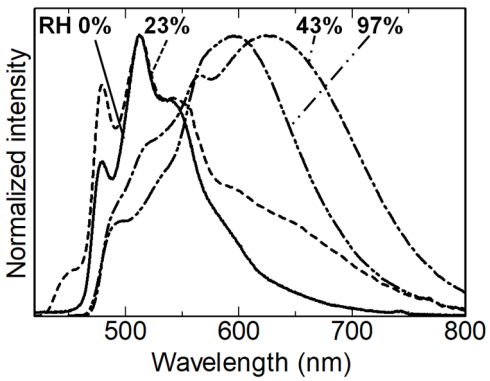

Fig. 2 Emission spectra of **Pt-LDH** under various relative humidity (RH).