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Multichromic behavior of a bimetallic Pt-Zn coordination polymer

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Porous Coordination Polymers (PCPs) have attracted increasing attention because of their interesting gas adsorption property, controllable framework, and so on.[1] However, gas adsorption properties of PCPs have been studied thoroughly for past dozen years, to introduce other functions to PCPs is an important subject. Utilization of functional metal complexes as bridging ligands is one of the most useful method to build a new functional PCPs. It is well known that a series of Pt(II)-diimine complexes show colorful vapochromism derived from the change of the MMLCT (metal-metal-to-ligand charge transfer) transition state whose energy strongly depends on the Pt···Pt contact distance.[2] In this work, taking advantage of the sensitive luminescence to the Pt-Pt interaction, we have designed and synthesized new luminescent Pt/Zn-based PCP, Zn[Pt(CN)$_2$(dcbpy)]·nH$_2$O (**1**; dcbpy = 5,5'-dicarboxy-2,2'-bipyridine, n = 0-4) which exhibits multichromic behavior coupled with the adsorption of the water vapor.

The PCP **1** was synthesized by a cation exchange reaction of K$_2$[Pt(CN)$_2$(dcbpy)]·2H$_2$O with Zn metal source, Zn(NO$_3$)$_2$·6H$_2$O in aqueous solution. The [Pt(CN)$_2$(dcbpy)]$^{2-}$ complex anion acts as a bridging ligand to produce an infinite one-dimensional polymeric chain along *a*+*c* direction (Figure 1). The Zn^{2+} ion had six-coordinated octahedral geometry with four coordinated water molecules and two O atoms of carboxyl groups of [Pt(CN)$_2$(dcbpy)]$^{2-}$. The [Pt(CN)$_2$(dcbpy)]$^{2-}$ units were stacked and formed 1-D columns along *b* axis. In the 1-D column, the shortest and longest adjacent Pt-Pt distances were 3.25 and 3.48 Å, respectively, suggesting moderate Pt-Pt interactions within the column.

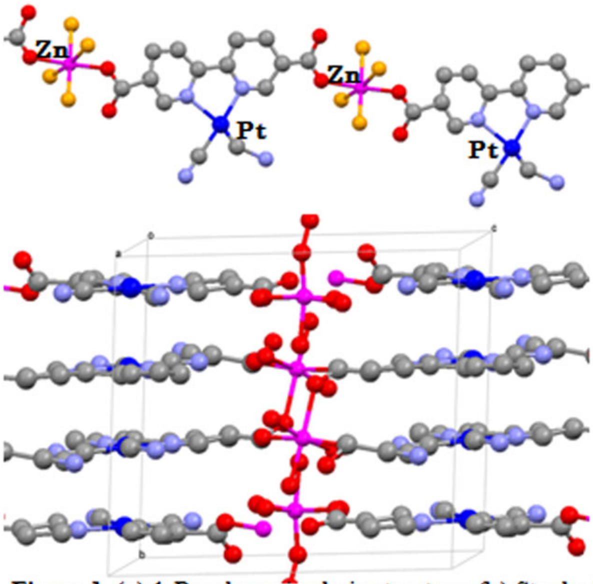

Figure 1. (a) 1-D polymeric chain structure. (b) Stacked structure along b axis.

Interestingly, the color and luminescence of **1** strongly depend on temperature, relative humidity and the surrounding vapor. The orange powder of **1** gradually changed to red and finally to dark purple with increasing temperature up to 373 K (Figure 2). Simultaneously, the emission spectrum of **1** also changed with increasing temperature, that is, emission band attributed to ^{3}MMLCT state was observed around 616 nm at 303 K and shifted to longer wavelength to 660 nm with increasing temperature up to 373 K. These changes were observed reversibly in humid air. And the similar color change was observed when **1** was exposed to hydrophilic organic vapors, such as MeOH, DMF and so on. At higher temperature region above 373 K, 040 reflection shifted to higher angle in powder X-ray diffraction pattern, and the stretching mode of OH bond disappeared. These results suggest that the release of water molecules above 373 K induces the shortening of the Pt-Pt distance.

In summary, we have synthesized a new Pt/Zn-based coordination polymer Zn[Pt(CN)$_2$(dcbpy)]·nH$_2$O (n = 0-4), which exhibits thermo- and vapor-controlled multichromic behavior. It is noteworthy that the Zn^{2+} ion can be substituted to the other divalent metal ions such as Ca^{2+}, Ni^{2+}. Further works to develop a series of multichromic coordination polymers M[Pt(CN)$_2$(dcbpy)] are now in progress.

[1] S. Kitagawa et al., Angew. Chem. Int Ed. 43, 2334 (2004).
[2] M.Kato., Bull. Chem. Soc. Jpn. 80, 287 (2007).

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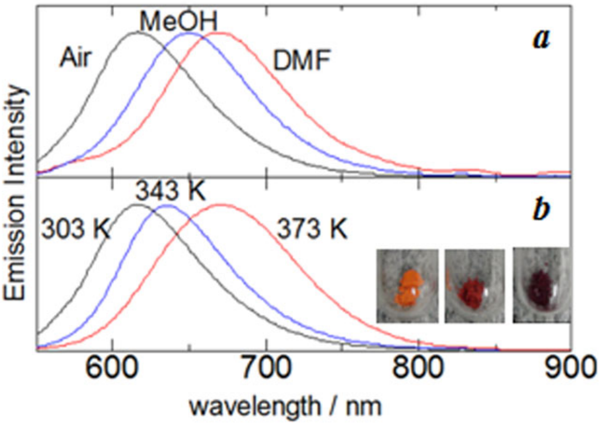

Figure 2. Luminescence spectra of **1** (*a*) under organic vapors and at various temperatures (*b*) Inset pictures show the color of **1** at 303, 343 and 373 K from the left.