

Gate-Open-Close Vapochromism of Rhenium(I) Molecular Crystals Supported by Non-Covalent Interactions: In-Situ Observation of the Guest-Induced Structural Transformation Dynamics

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Recently, vapochromic materials, which adsorb guest molecules to exhibit reversible changes of the photoluminescence property, have been the subject of intense research. It is essential for this property to design and control the molecular arrangement in the crystalline state. In this work, a novel luminescent molecular rhenium(I) complex *fac*-ReBr(CO)₃(ppt) (**1**), where ppt = 2-pyridyl-4-phenylthiazole, has been synthesized and characterized. Complex **1** has a non-porous guest-free crystal (**1**) (Type O) and several solvated crystals, and they are molecular crystals supported by multiple non-covalent interactions. The solvated crystals have been formulated **1**·*n*Sol, where *n* = 0.5 (Type A) or 1 (Type B). We have also investigated the vapochromic behavior of guest-free **1**. The crystal has given an emission peak at 574 nm upon irradiation at 365 nm. The emission wavelength has displayed a blue shift by ca. 20 nm under volatile organic compound (VOC) vapors. We have also observed vapor-induced emission enhancement (VIEE). Interestingly, in spite of the non-porous structure, guest-free crystal **1** has showed gate-open-close behavior, and this result has been suggested by adsorption isotherm measurement. The guest-adsorption process has been monitored by synchrotron *in-situ* powder X-ray diffraction (*in-situ* PXRD) analysis (SPRING-8, BL02B2). During the structural transformation from Type O to Type A or B, no intermediates have been observed, indicating crystal-to-crystal transformation. In addition, guest-substitution process has also occurred between several solvated crystals (Type A and Type B). However, this process was irreversible, suggesting that the strength of the host-guest interactions varied depending on the kinds of solvents. The guest-induced and guest-exchange structural transformation dynamics is shown in Fig. 1.

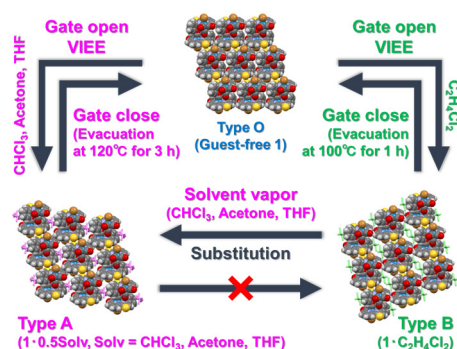


Fig. 1. Crystal-to-crystal transformation dynamics