

Inverse Guest Adsorption and Luminescent Response in an Au(I)-based Metal–Organic Framework

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Stimuli-responsive luminescent coordination polymers (CPs) and metal-organic frameworks (MOFs) composed of metal ions and organic ligands have attracted considerable attention for the development of novel photofunctional materials such as chemical sensors owing to their highly regular, flexible, and designable frameworks.

Here, we prepared a novel CP $\{\text{Zn}^{\text{II}}(\text{pz})[\text{Au}^{\text{I}}(\text{CN})_2]_2\}$ (pz = pyrazine; **1**) with an interpenetrated 3-D structure based on cyanide-bridged Au–Zn–Au linkages and bidentate pz ligands (**Fig. (a)**). **1** showed a light-blue phosphorescence ($\lambda_{\text{em}} = 462 \text{ nm}$, $\lambda_{\text{ex}} = 365 \text{ nm}$) originating from aurophilic interactions in the framework. In addition, Guest adsorption properties were investigated to explore the guest-sensing ability of **1**. Despite no adsorption for nitrogen (N_2), carbon dioxide (CO_2), methane (CH_4), oxygen (O_2), and carbon monoxide (CO) and solvent guests, **1** displayed size-inverse and selective adsorption behavior for carbon disulfide (CS_2) at the room temperature with efficient host-guest interactions, in which the emission intensity of the framework drastically and reversibly changed along with CS_2 ads/desorption process (**Fig. (b), (c)**). Therefore, we focus on the details of the CS_2 -responsivity of **1** because this harmful guest is one of the important chemicals in the field of industrial society; however, it is also known the detrimental effects on human health and the environment.

The correlation between the luminescent property and the structural change was investigated by *ex situ* single-crystal X-ray diffraction and photoluminescent measurements under CS_2 vapor. The CS_2 -adsorbed state of **1** possessed an interpenetrated 3-D structure with two types of Au–Au distances induced by CS_2 adsorption. The resultant size-inverse and guest-selective luminescent change of **1** might be due to the CS_2 -driven changes in structure and emission decay process.

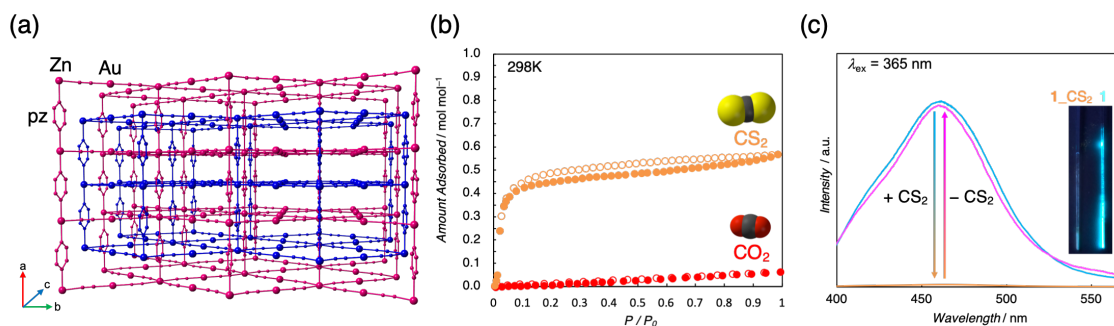


Fig.(a) Crystal structure of **1**, **(b)** size-inverse guest adsorption at 298 K, **(c)** CS_2 -induced luminescent variations at room temperature.