Fused Porphyrin-Based Porous Crystals

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Porous crystals comprising extended π-conjugated systems have been actively studied in recent years.[1,2] We have developed "adaptive nanographene MOF" which exhibits unique structural phase transition by cooperatively rotating its large and planer π-system upon guest uptake.[1] Among extended π-conjugated systems, fused porphyrins are attractive candidates for further developing adaptive porous crystals taking advantage of their multiple coordination sites as well as absorption in the near infrared (NIR) region.[3] Herein, we will report the novel porous crystals composed of triply linked fused porphyrin and their NIR light responsive behavior.[4]

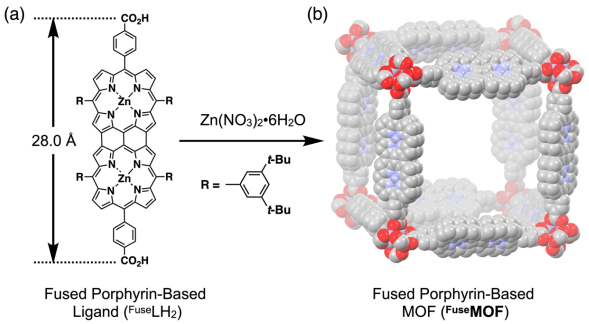

Fig. 1 (a) Structure of $^{Fuse}LH_2$. (b) Crystal structure of ^{Fuse}**MOF**.

We newly synthesized a fused porphyrin-based dicarboxylic acid ligand ($^{Fuse}LH_2$, Fig. 1a). Dark purple colored ^{Fuse}**MOF** crystals were obtained by the reaction of $^{Fuse}LH_2$ with $Zn(NO_3)_2$•$6H_2O$ in *N,N*-diethylformamide. The single crystal structure of ^{Fuse}**MOF** revealed that $^{Fuse}L^{2-}$ is mutually connected with hexatopic Zn_4O clusters to form its cubic lattice (Fig. 1b). Interestingly, despite the use of the extremely long ligand, interpenetration doesn't take place due to the bulky substituents, affording huge void spaces corresponding to 86% of the crystal volume.

We carried out *in situ* microscopic observation upon NIR laser irradiation (Fig. 2). Surprisingly, a single crystal of ^{Fuse}**MOF** dispersed in DMF immediately shrank by 18% in volume upon NIR irradiation, and then it recovered the original size and shape, reversibly. We will present in detail about this intriguing phenomenon.

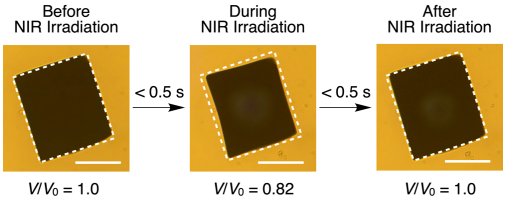

Fig. 2 Microscopic observation of ^{Fuse}**MOF** upon NIR laser irradiation (scale bar: 100 μm).

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