Guest-dependent thermochromic feature in metal-organic framework and its thin film on different supports fabricated by seeded growth approach

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Experimental section

Materials

1, 1′-ethynebenzene-3, 3′, 5, 5′-tetracarboxylate (H_4EBTC) was prepared according the literatures [1]. Copper (II) dinitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, Fluka, 98%) and copper (II) acetate monohydrate ($Cu(CH_3COO)_2 \cdot H_2O$, Shanghai Sinpeuo Fine Chemical Co., Ltd., 99%) were used without further purification. DMF and DMSO were employed as solvents.

Synthesis of MOF crystal

$[Cu_2(EBTC)(H_2O)_2 \cdot G]$ (**1**) was prepared following the published procedure [2]. $[Cu_2(EBTC)(H_2O)_2][(H_2O)_x(CH_3OH)_y]$ (**2**) was obtained by soaking **1** in methanol for 24 h at ambient temperature and then refreshing for three times.

Seed deposition

The substrate is porous alumina disk with an average pore size of ca. 110 nm and about 35% porosity. One side of the substrate was polished using 1200-mesh SiC sandpaper, washed using abundant deionized water and dried before seeding. The polished side of the substrate was sequentially processed (1) dipping in DMF/DMSO solution with 1 mM H_4EBTC in a volume ratio of 1:1 for 30 min (2) washing with the DMF/DMSO solvents (3) dipping in DMF/DMSO solution with 1 mM $Cu(CH_3COO)_2 \cdot H_2O$ for 20 min and (4) washing with the DMF/DMSO solvents. The procedures from (1) to (4) were repeated for a substrate several times, and the substrate with seed layer was dried at 50 ^oC in vacuum for 30min for the fabrication of the film.

Film fabrication

H_4EBTC (17.7mg) and $Cu(NO_3)_2 \cdot 3H_2O$ (53.3mg) were dissolved in DMF (2.5ml) and DMSO (2.5ml), and a drop of 1M HNO_3 in DMF was added to the nixed solution. The solution was directly transferred into a 25 ml Teflon-lined autoclave in which the seeded substrate was horizontally stood in the bottom of autoclave for growth of **F-1**. The autoclave was cooled to ambient temperature with a cooling rate of 20 $^oC \cdot h^{-1}$ after crystallization at 65 ^oC for 24 h. The as-prepared films were cleaned with DMF/DMSO and cleanly stored after drying at 25 ^oC under vacuum for 12 h. The

$[Cu_2(EBTC)(H_2O)_2][(H_2O)_x(CH_3OH)_y]$ film (**F-2**) was obtained by soaking **F-1** in CH_3OH solvent for 24 h and drying at ambient temperature.

Characterization

The UV-visible spectra were carried using an UV-vis spectrophotometer (Shimadzu UV-2401TC). The crystalline phases of the Cu-EBTC film was determined using Powder X-ray diffractometry (PXRD, D8-advance, Bruker, Germany) with Cu Kα radiation (λ = 1.5418 Å) in the range of $5^o \leq 2\theta \leq 50^o$ at room temperature. The film morphologies were observed via scanning electron microscopy (SEM) (FEI, model Quanta-200, Holland) using gold-coated specimens to increase conductivity. TGA experiments were performed with STA449 F3 thermogravimetric analyzer in the 30-700 °C range at a warming rate of 10 °C/min under a nitrogen atmosphere and the polycrystalline samples were placed in an Al_2O_3 crucible.

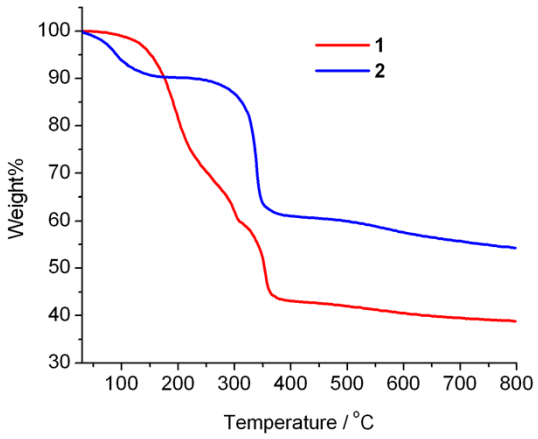


Figure S1 TGA plots of **1** and **2**

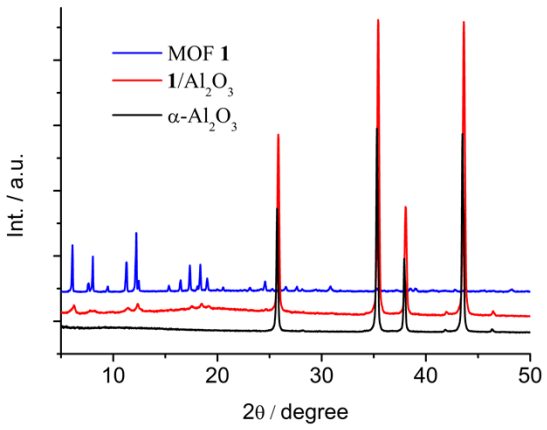


Figure S2 PXRD patterns of Al_2O_3support, **1** and the **1**/Al_2O_3 film

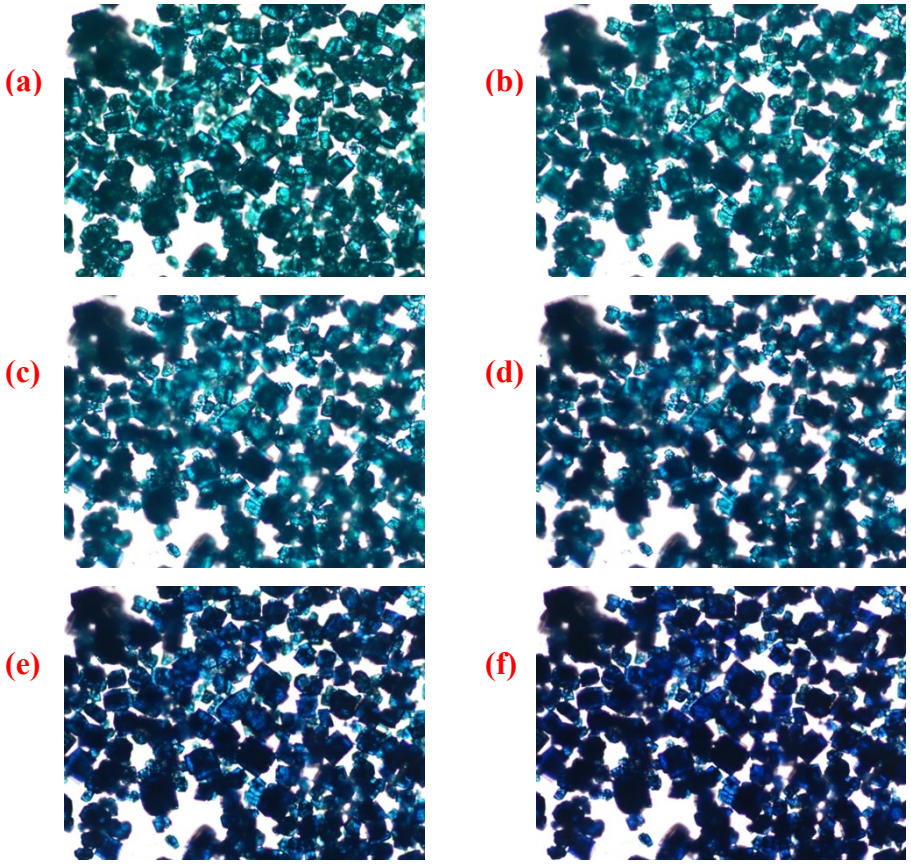
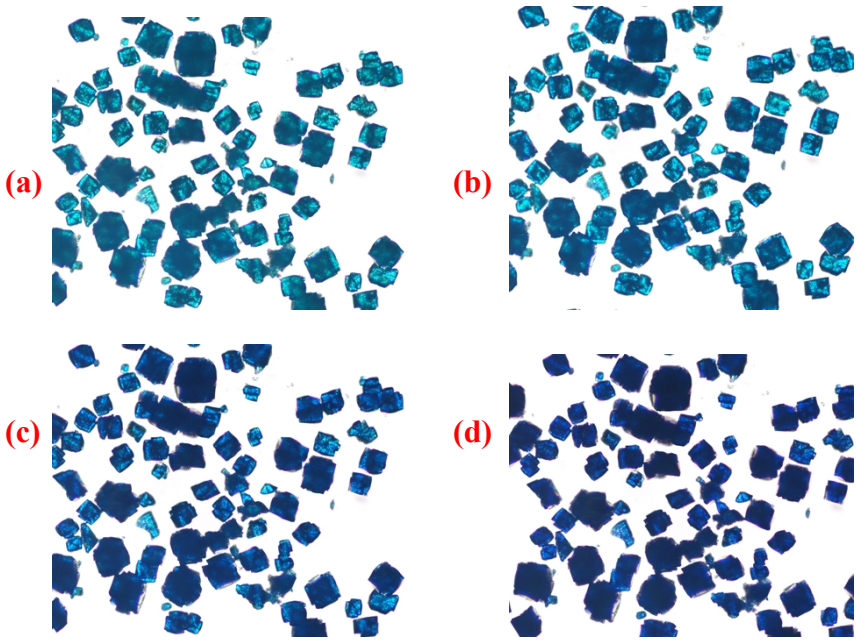


Figure S3 Photographs of the **1** at (a) 25 °C (b) 120 °C (c) 140 °C (d) 160 °C (e) 180 °C and (f) 200 °C.



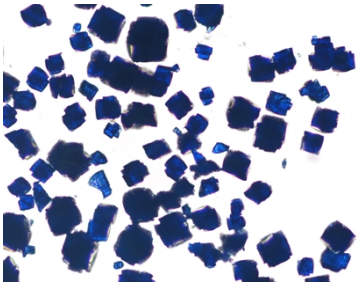
(e) 

Figure S4 Photographs of the **2** at (a) 25 °C (b) 30 °C (c) 40 °C (d) 50 °C and (e) 60 °C.

References

1. H. Zhou, H. Dang, J. H. Yi, A. Nanci, A. Rochefort and J. D. Wuest, *J. Am. Chem. Soc.*, 2007, **129**, 13774.
2. Y. X. Hu, S. C. Xiang, W. W. Zhang, Z. X. Zhang, L. Wang, J. F. Bai and B. L. Chen, *Chem. Commun.*, 2009, 7551.