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

Ping-Chun Guo,a, b Tian-Ru Chen,a, b Xiao-Ming Ren,*a, b Zhenyu Chu,a Wanqin Jin* a

a State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, P.R. China

b College of Science, Nanjing University of Technology, Nanjing 210009, P.R. China

Tel.: +86 25 58139476
Fax: +86 25 58139481

E-mail: xmren@njut.edu.cn (X.M.R.) and wqjin@njut.edu.cn (W.Q.J.)
Experimental section

Materials

1, 1’-ethynebenzene-3, 3’, 5, 5’-tetracarboxylate (H$_4$EBTC) was prepared according the literatures [1]. Copper (II) dinitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O, Fluka, 98%) and copper (II) acetate monohydrate (Cu(CH$_3$COO)$_2$·H$_2$O, 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$_2$O)$_2$·G] (1) was prepared following the published procedure [2]. [Cu$_2$(EBTC)(H$_2$O)$_2$][(H$_2$O)$_x$(CH$_3$OH)$_y$] (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$_4$EBTC 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$_3$COO)$_2$·H$_2$O 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 °C in vacuum for 30 min for the fabrication of the film.

Film fabrication

H$_4$EBTC (17.7 mg) and Cu(NO$_3$)$_2$·3H$_2$O (53.3 mg) were dissolved in DMF (2.5 ml) and DMSO (2.5 ml), and a drop of 1 M HNO$_3$ in DMF was added to the mixed 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 °C·h$^{-1}$ after crystallization at 65 °C for 24 h. The as-prepared films were cleaned with DMF/DMSO and cleanly stored after drying at 25 °C under vacuum for 12 h. The
[Cu₂(EBTC)(H₂O)₂][(H₂O)₆(CH₃OH)₃] film (F-2) was obtained by soaking F-1 in CH₃OH 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° ≤ 2θ ≤ 50° 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 Al₂O₃ crucible.

![Figure S1](image1.png) **Figure S1** TGA plots of 1 and 2

![Figure S2](image2.png) **Figure S2** PXRD patterns of Al₂O₃ support, 1 and the 1/Al₂O₃ 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.
Figure S4 Photographs of the 2 at (a) 25 °C (b) 30 °C (c) 40 °C (d) 50 °C and (e) 60 °C.

References
