Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information for

Growth of large single MOF crystals and effective separation of organic dyes

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EXPERIMENT

All the reagents were purchased from Aldrich without any purication.

Powder X-ray diffractions (XRD) were carried out on Scintag X1 diffractometer with Cu-K α (λ = 1.5418 Å) at 40 kV, 35 mA. The FCFM photographs were from Laser Confocal Scanning Fluorescence Microscopy FV1000. All digital photographs were taken by Sony w630 and Canon D500, while the magnified photographs were taken by operating camera LED 1000 from Leica Microsywtems.

THE AVERAGE SIZE OF CRYSTALS AND THE CHANGE OF PH

the composition ratio (DMF : nitric acid)	pH before reaction	The concentration of hydroin before reaction (mol/ L)	The largest crystal size (mm)	pH after reaction
1:4	Below 0	1.6	4.0	6.5
1:2	Below 0	1.33	2.4	6.3
1:1	Below 0	1	0.9	6.5
2:1	Below 1	0.67	0.4	6.4

Table s1 the demonstration of pH change before and after the reaction.

THE EFFECTS OF DIFFERENT ACIDS ON $CU_2(BTC)_3$ CRYSTALS

	A	B	C	D	E
Nitric acid	Y	4.0	Y	1.636	7.77E-8
Hydrochloric acid	Y	0.5	Y	1.556	8.17E-8
Sulfuric acid	Y	1.3	Y	1.600	7.95E-8
Phosphoric acid	N	-	Y	-	-
Perchloric acid	Y	1.7	Y	1.000	1.272E-7
Citric acid	N	-	N	-	-
Acetic acid	Y	Powder	N	-	-
Formic acid	Y	Powder	N	-	-
Benzenesulfonic acid	N	N	N	-	-

Table s2 the demonstration of acid selection and relevant results. A: whether HKUST-1 materials can be obtained (according to XRD pattern) B:the max diameter (unit millimeter) C: whether the crystals obtained in the mixed system of the specific acid and nitric acid can reach 2mm D: the molar concentration of hydrion in the optimum system (mol/L) E: the molar concentration of [BTC^{3-}] in the initial system. F: the (according to Ka3=K1K2K3=7.6×10-3×7.9×10-5×6.6× 10-6=3.963×10-12 K=1.582×10-4)

Considering the effects from the hydions, several experiments using different acids were conducted. Just as shown in the table 2, the reaction system was constituted by DMF and specific dilute acid, e.g. Hydrochloric acid, sulfuric acid, phosphoric, perchloric acid, citric acid, acetic acid, formic acid, benzenesulfonic acid etc.. According to the experiment results, most of the inorganic acids would lead to large single crystals in millimeter level. On the contrary, the results of organic acids varied greatly, which was even hard to obtain macroscopic crystals. This might be illustrated with the self coordination of the acids with the metal ions themselves. Indeed only sulfuric acid, hydrochloric acid and perchloric acid seemed to be effective when it comes to the growth of large MOF crystals. And if these three acids could be mixed with nitric acid at the rate of 1:1, the diameter of crystals obtained could reach nearly 2 mm. Even different sizes from different acids, it was general that with the increase of acid, the crystal size was enlarged. The acids without coordination effects, such as nitric acid and perchloric, were especially effective when it came to large single crystal growth. And the types of acid seemed all stimulated effects as long as it would not take part in the coordination part.

THE PHOTOGRAPHS OF $CU_3(BTC)_2$ SYNTHESIZE WITH DIFFERENT ACIDS

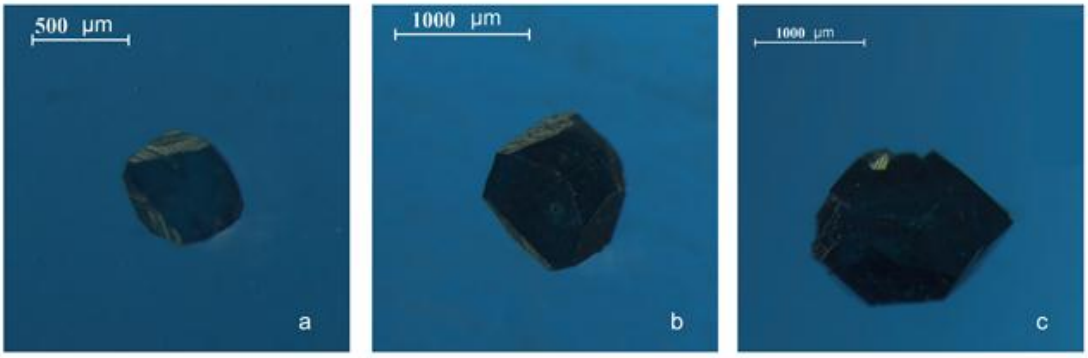

Figure S1 The photographs of $Cu_3(BTC)_2$ synthesize with different acids: a. hydrochloric acid; b sulfuric acid; c. perchloric acid.

THE INFLUENCE OF ACIDS ON MOF CRYSTALS

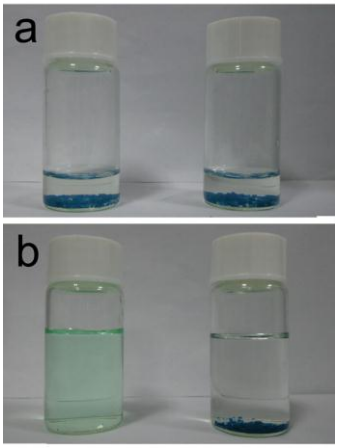

Figure s2 the photograghs of (a) two bottles of $Cu_3(BTC)_2$ crystals with 3 ml ethanol; (b) the same two bottles of $Cu_3(BTC)_2$ after adding 5 ml hydrocloric acid and 5 ml ethanol respectively.