Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supporting Information

A Facile Strategy towards Highly Accessible and Hydrostable MOF-Phase within the Hybrid PolyHIPEs through *In-situ* Metal-Oxide Recrystallization

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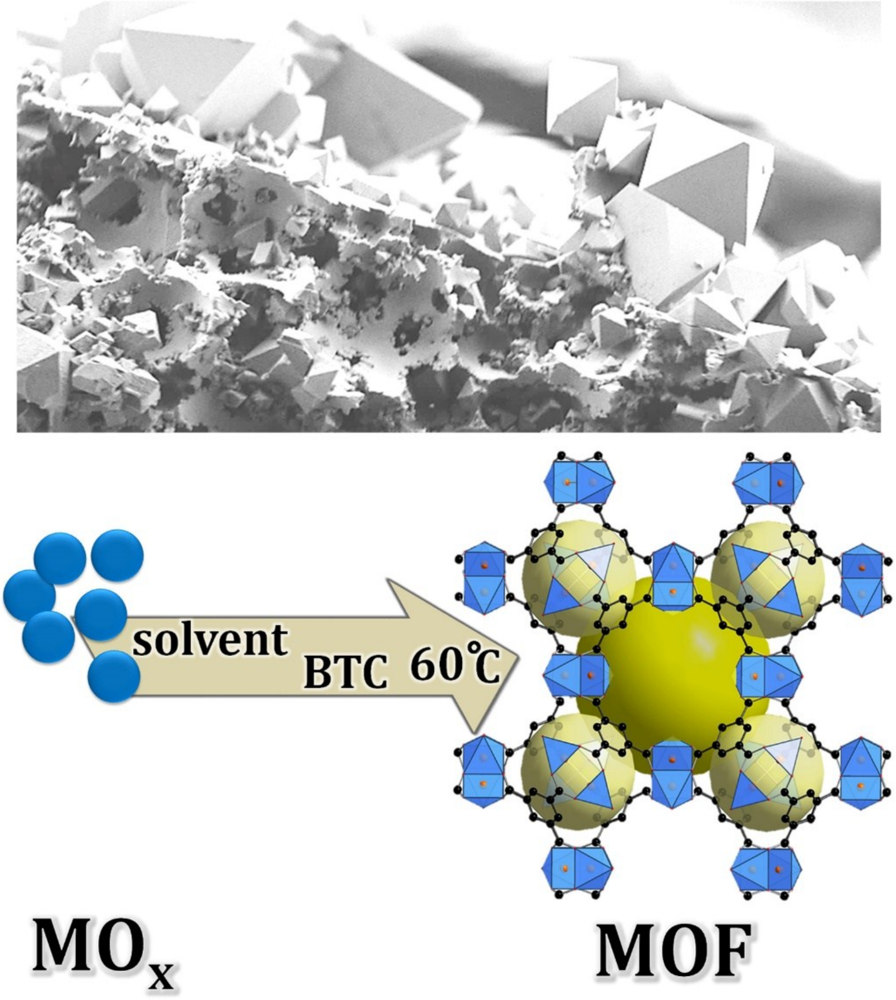

Experimental

Preparation of the oleic acid coated nanoparticles.

ZnO nanoparticles were first synthesized by the polyol method in ethylene glycol using zinc acetate dihydrate as a precursor and *p*-toluene sulphonic acid as an end capping agent. ZnO nanopowders were washed according to the previously described procedure[1] and finally dried on air. CuO nanoparticles were obtained by Sigma-Aldrich.

The surface of ZnO and CuO nanoparticles was further modified with oleic acid (OA). Both type of nanoparticles were suspended in the solution of OA and ethanol (the mass fractions of OA was 5 % to ZnO) by sonication using Hielscher sonicator for 10 min. Subsequently, the suspension was mixed with magnetic stirrer for 48 h at room temperature and dried in the oven at 50 °C overnight. The amount of OA attached onto the NPs' surface was determined by TGA.

Preparation of the microcellular nanocomposite foams (μCNF)

The DCPD monomer (9.8 mmol, 1.30 g), Pluronic® L121 (*cf.* Table S1), toluene (50µL) and NPs (*cf.* Table S1) were placed in a 3 neck round-bottomed flask equipped with a mechanical stirrer and a dropping funnel. The mixture was stirred at 400 rpm for 5 min and upon continuous stirring at 25°C deionized water (5.5 mL) was added drop-wise over about 1 h. Afterwards, the initiator **M2** (1.3 mg, 0.0007 mmol in respect to **DCPD)** dissolved in toluene (0.25 mL) was added and the emulsion was stirred for further 5 min. Subsequently, the emulsion was transferred to an appropriate mould (i.e. glass vials). The filled moulds were transferred into a preheated oven operating under air. Curing of the emulsions at 80 °C for 4 h resulted in the formation of white rigid monoliths in all cases. The specimens were purified by Soxhlet extraction with acetone for 24 h and subsequently dried in a desiccator under vacuum (10 mbar) until the weight was constant.

Table S1. Emulsions composition (80 vol. % aqueous phase)

sample	m(**DCPD**) [g]	Surfactant [g]	OA[a] [wt. %]	NPs [wt. %]	V(H_2O) [mL]
ZnO@pDCPD	2.27	0.126	3	30	10
CuO@pDCPD	2.27	0.126	2.5	30	10

[a] amount of OA attached to the nanoparticles's surface and determined by TGA

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[1] S. Kovačič, A. Anžlovar, B. Erjavec, G. Kapun, N. B. Matsko, M. Žigon, E. Žagar, A. Pintar and C. Slugovc, *ACS Appl. Mater. Interfaces*, 2014, **6**, 19075-19081.

Preparation of the MOF@polyHIPE hybrid materials

MOF@polyHIPE hybrid materials were solvothermally crystallized from metal oxide@pDCPD precursors. Crystallization procedure was based on optimized synthesis of the corresponding MOFs from the ZnO and CuO powders. In the case of MOF-5@polyHIPE, the ZnO@pDCPD monolith (0.25 g) cut with the razor was immersed in the solution containing 42 mg (0.25 mmol) of terephthalic acid in 10 ml of *N,N*-dimethylformamide and 0.01 ml of water. After the solvothermal treatment in the sealed vial at 60 °C for 2 days, the hybrid material was rinsed with acetone and dried at ambient conditions. Similar procedure was used for the synthesis of HKUST-1@polyHIPE: 0.25 g of CuO@pDCPD was placed in the solution containing 8 ml of ethanol and 2 ml of water. Recrystallization was taking place at 120 °C for 2 days. The product was recovered by rinsing with acetone and drying at room temperature.

For comparative studies, pure MOFs were prepared as well using modified procedures from the literature.[2] For the MOF-5(Zn) synthesis, the mixture of 0.450 g $Zn(NO_3)_2{\cdot}6H_2O$, 0.083 g of terephthalic acid, 49 ml of *N,N*-dimethylformamide and 1 ml of water was solvothermally treated at 100 °C for 7 hours. Cubic crystals were rinsed with chloroform and dried in vacuum. The HKUST-1(Cu) crystallized from the mixture of 0.15 g of $Cu(NO_3)_2{\cdot}3H_2O$ and 0.14 g of benzene-1,3,5-tricarboxylic acid in the 10 ml of ethanol/water mixture (4:1 volumetric ratio) after microwave heating at 130 °C for 20 minutes. The product was recovered by filtration and dried at ambient conditions.

Characterization methods

Electron microscopy investigations

The porous structures of the dry samples (gold-palladium sputter-coated cryogenic fracture surfaces) were described through scanning electron microscopy (SEM) (Ultra+ (Carl Zeiss). The average void size was determined by manually measuring 50 to 100 voids in SEM micrographs, calculating an average, and applying a correction (multiplying by $2/3^{1/2}$) to account for the random nature of the fracture plane through the void.[3] The average window size (d_{WN}) was determined by manually measuring 50 to 100 windows in SEM micrographs.

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[2] C. McKinstrya, R. J. Cathcarta, E. J. Cussenb, A. J. Fletchera, S. V. Patwardhana, J. Sefcika, Chem. Eng. J., 2016, **285**, 718-725.

[3] A. Barbetta, N. R. Cameron, *Macromolecules* 2004, **37**, 3188.

XRD analysis

X-ray diffraction (XRD) patterns of the hybrid materials were recorded by a PANalytical X'Pert PRO high-resolution diffractometer with a CuKα1 radiation (λ = 1.5406 Å). In order to focus only on indicative reflections assigned to the MOF-5 and HKUST-1 phase, a narrow 2θ region from 5 to 35° was selected with a step of 0.034° per 100 s using fully opened 100 channel X'Celerator detector.

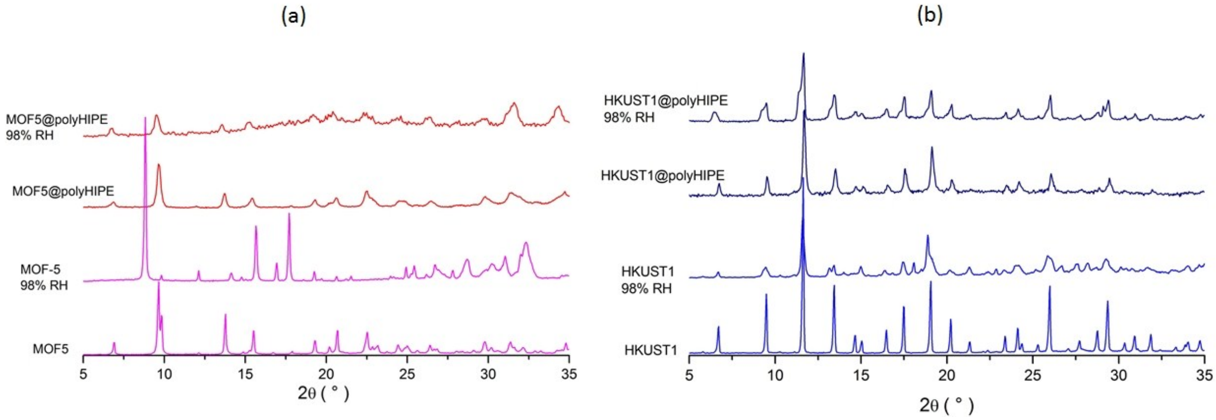

Figure S1. XRD patterns of as-pepared materials and after exposure at 98% RH for (a) MOF-5 pristine and corresponding composite and (b) HKUST-1 and corresponding composite.

Thermogravimetric analysis

Thermogravimetric analysis (TG/DTG) was carried out using a thermogravimeter Q5000IR (TA Instruments Inc.) in an air flow and a heating rate of 10 °C/min.

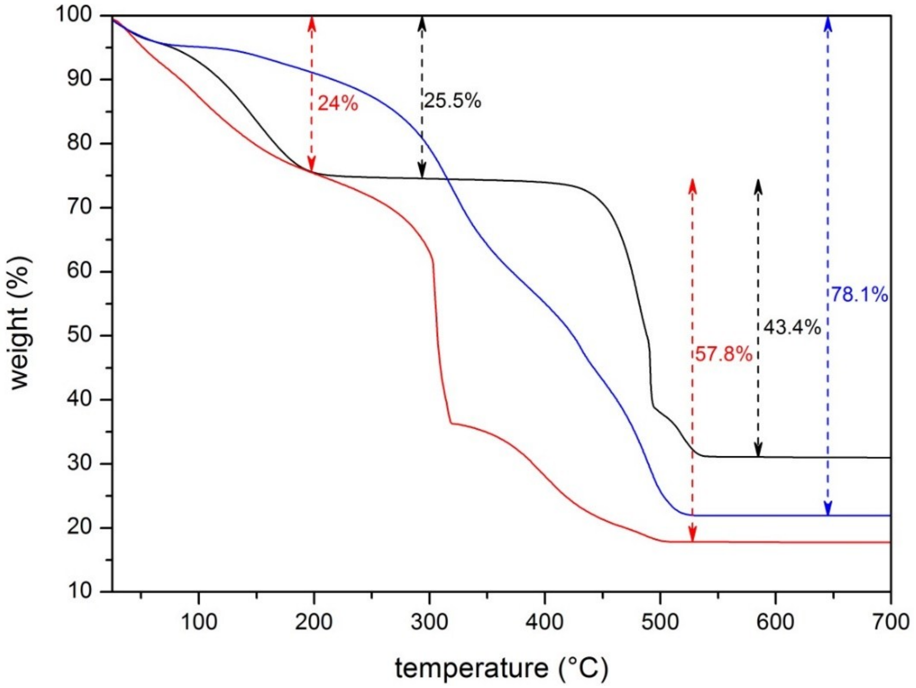

Figure S2. Thermogravimetric curves of pristine MOF-5 (black line), ZnO/polyHIPE (blue line) and MOF-5/polyhIPE (red line),and the corresponding weight losses.

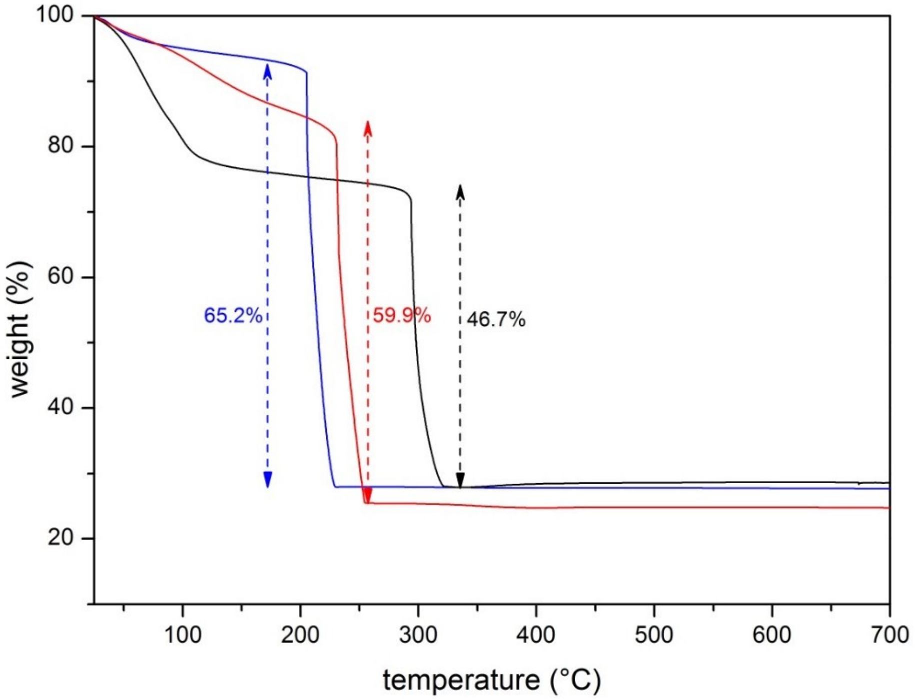

Figure S3. Thermogravimetric curves of pristine HKUST-1 (black line), CuO/polyHIPE (blue line) and HKUST-1/polyhIPE (red line), and the corresponding weight losses.

Nitrogen sorption measurements

Nitrogen sorption measurements were performed on an IMI-100 manometric gas sorption analyzer (Hiden Isochema, Inc.) at 77 K in the range of relative pressure values from 10^{-6} to 1. As-prepared samples were degassed at 150 °C for 16 h prior to the measurements. The specific surface areas were determined by BET method based on the obtained sorption isotherms.

Table S2. MOF loadings, surface area and accessible microporosity of synthesized hybrids compared with the published materials.

Material	**[1]wt.%**	**[2]MOF-S_{BET} (m^2/g)**	**[3]S_{BET}-m (m^2/g)**	**[4]S_{BET}-c (m^2/g)**	η	**ref**
MOF5/polyHIPE	55.1	2501	1298	1401	0.93	this work
HKUST1/polyHIPE	75.4	1211	794	921	0.86	this work
HKUST1/PAM	62.0	1075	654	667	0.98	4
MIL100(Fe)/polyHIPE	13.6	1136	130	154	0.84	5
HKUST1/polyHIPE	62.3	1340	570	846	0.67	6
MIL101(Cr)/polyHIPE	59	3060	990	1805	0.55	7
MIL101(Cr)/NIPAM	92	2860	980	2630	0.37	8
MIL100(Cr)/NIPAM	58	1370	150	800	0.19	7
MIL100(Fe)/NIPAM	78	2140	300	1650	0.18	7
HKUST1/polyHIPE	25.0	1100 - 1700 [5]	16	275 – 425	~0.05	9

[1]weight contribution of MOF within the polymer matrix, calculated from TG analysis; [2]measured S_{BET} of pure MOFs; [3]measured S_{BET} of the composites; [4]calculated S_{BET} of the composites (see ESI for details); [5]MOF microporosity accessibility within the polymers; [5]no data of S_{BET} of pristine MOF is available. Therefore, the range of expected S_{BET} values was taken into account.

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[4] L. D. O'Neill, H. Zhang and D. Bradshaw, *J. Mater. Chem.*, 2010, **20**, 5720.

[5] S. Kovačič, M. Mazaj, M. Ješelnik, D. Pahovnik, E. Žagar, C. Slugovc and N. Z. Logar, *Macromol. Rapid Commun.*, 2015, **36**, 1605–1611.

[6] M. G. Schwab, I. Senkovska, M. Rose, M. Koch, J. Pahnke, G. Jonschker and S. Kaskel, *Adv. Eng. Mater.*, 2008, **10**, 1151–1155.

[7] M. Wickenheisser and C. Janiak, *Microporous Mesoporous Mater.*, 2015, **204**, 242–250.

[8] M. Wickenheisser, T. Paul and C. Janiak, *Microporous Mesoporous Mater.*, 2016, **220**, 258–269.

[9] C. L. Calvez, M. Zouboulaki, C. Petit, L. Peeva and N. Shirshova, *RSC Adv*, 2016, **6**, 17314–17317

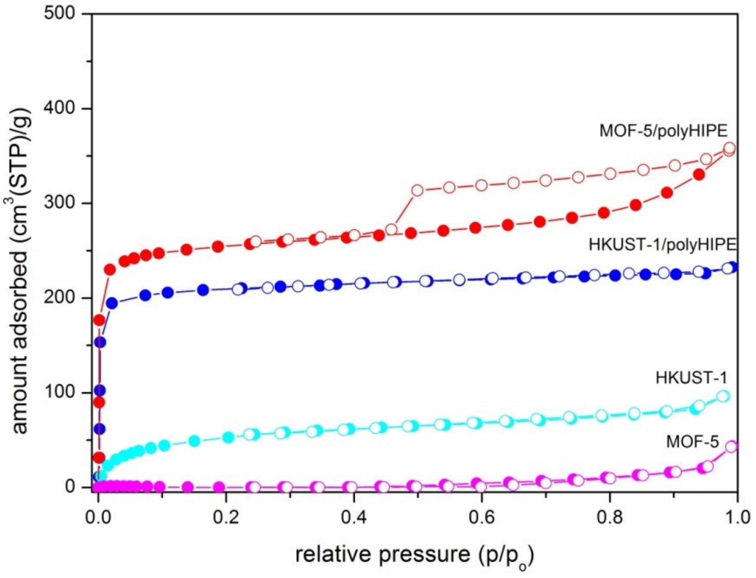

Figure S4. Samples' N_2 sorption isotherms measured at 77 K after exposure of the samples in controlled environment with 98 % RH for 3 days.

Calculations of MOF contribution within the composites based on the TG analysis

MOF-5/polyHIPE

Mass fraction of ZnO within MOF-5:

$$w(ZnO) = \frac{4.Mr(ZnO)}{Mr(Zn_4O(BDC)_3)} = 0.423$$

Theoretical weight contribution of MOF-5 within polyHIPE if all ZnO is recrystallized into MOF, based on ZnO/polyHIPE:

$$w_1(MOF5) = \frac{wt\,\%\,residue\,from\,ZnO/polyHIPE\;\;TG}{w(ZnO).(wt\%\;of\;solvent\,from\,ZnO/polyHIPE\;\;TG)} = 0.551$$

Calculated weight contribution of MOF-5 within polyHIPE if all ZnO is recrystallized into MOF, based on MOF-5/polyHIPE:

$$w_2(MOF5) = \frac{wt\,\%\,residue\,from\,MOF5/polyHIPE\;\;TG}{w(ZnO).(wt\%\;of\;solvent\,from\,MOF5/polyHIPE\;\;TG)} = 0.551$$

Recrystallization efficiency:

$$\frac{w_2(MOF5)}{w_1(MOF5)} = 1$$

HKUST-1/polyHIPE

Mass fraction of CuO within HKUST-1:

$$w(CuO) = \frac{3.Mr(ZnO)}{Mr(Cu_3(BTC)_2)} = 0.391$$

Theoretical weight contribution of HKUST-1within polyHIPE if all CuO is recrystallized into MOF, based on CuO/polyHIPE:

$$w_1(HKUST1) = \frac{wt\,\%\,residue\,from\,CuO/polyHIPE\;\;TG}{w(CuO).(wt\%\;of\;solvent\,from\,CuO/polyHIPE\;\;TG)} = 0.765$$

Calculated weight contribution of HKUST-1 within polyHIPE if all CuO is recrystallized into MOF, based on HKUST-1/polyHIPE:

$$w_2(HKUST1) = \frac{wt\,\%\,residue\;from\;HKUST1/polyHIPE\;\;TG}{w(CuO).(wt\%\;of\;solvent\;from\;HKUST1/polyHIPE\;\;TG)} = 0.754$$

Recrystallization efficiency:

$$\frac{w_2(HKUST1)}{w_1(HKUST1)} = 0.986$$

Calculations of MOF accessibility within the composites:

$$\eta = \frac{S_{BET} - measured}{S_{BET} - calculated}$$

S_{BET} –calculated = w(MOF).S_{BET} (MOF) + w(polymer).S_{BET}(polymer)

CO_2 adsorption cycling experiment

A CO_2 cycling was performed on an IMI-HTP manometric gas analyzer (Hiden Isochema Inc.). Prior the measurements, the samples were degassed overnight at 150 °C for the HKUST1 and polyHIPE-HKUST-1 and at 200 °C for the MOF-5 and polyHIPE-MOF5. Cycling tests were performed by a following sequence: degassing at 170 °C for 2 h, CO_2 dosing at 1 bar and 25 °C, desorption in vacuum, and pressurizing with air (relative humidity of 50 %) to 1 bar.