Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Additive-mediated size control of MOF nanoparticles

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Materials and methods

Chemicals

Benzene-1,3,5-tricarboxylic acid (H_3BTC, 98%), *N*,*N*-dimethylformamide (DMF, p.a.) and copper acetate monohydrate ($Cu(OAc)_2 \cdot H_2O$, 98+%) were purchased from Acros. Poly(acrylic acid) (PAA, MW = 1,800), 2-aminoterephthalic acid ($H_2BDC\text{-}NH_2$, 99+%) and polyvinylpyrrolidone (PVP, MW = 40,000) were purchased from Sigma-Aldrich. Zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$, p. a.) was purchased from ACS. Hexadecyltrimethylammonium bromide (CTAB, 98%) was purchased from Alfa Aesar. Ethanol (99%) was purchased from BfB. All chemicals were used as received without further purification.

Synthesis of HKUST-1

In a typical synthesis, H_3BTC (73.8 mg, 0.344 mmol) was dissolved in ethanol (1.4 mL) and DMF (4.2 mL) under stirring and combined with PAA (221 mg, 0.123 mmol). To this mixture, a solution of $Cu(OAc)_2 \cdot H_2O$ (70 mg, 0.344 mmol) in 2.8 mL deionized water was added under vigorous stirring, which rapidly induced the formation of a blue precipitate. The product was separated from the reaction mixture by centrifugation and washed in DMF, ethanol and water for at least 3 times. Stable colloidal suspensions were obtained by redispersing the washed product in DMF using ultrasound (Elmasonic S100H ultrasonic bath, 550 W).

For further experiments, the reaction conditions were varied, including reaction time (5 min, 30 min), reaction temperature (0 °C, room temperature (RT), 55 °C) and amount of PAA (depending on the weight ratio of H_3BTC:PAA = 1:2, 1:3, 1:4, 1:5, 1:6, 1:15, corresponding to 0.082 mmol, 0.123 mmol, 0.164 mmol, 0.205 mmol, 0.246 mmol, 0.615 mmol of PAA).

Synthesis of IRMOF-3

In a typical synthesis, $Zn(OAc)_2 \cdot 2H_2O$ (35.12 mg, 0.160 mmol) was dissolved in DMF (2 mL) and rapidly added to a solution of $H_2BDC\text{-}NH_2$ (10.86 mg, 0.059 mmol), CTAB (10 mg, 0.027 mmol) and PVP (10 mg, 0.00025 mmol) in 3 mL DMF under stirring. The reaction mixture turned turbid within the first minute and was stirred additionally for at least 5 min. The product was separated by centrifugation and washed in DMF and ethanol for at least 3 times. Stable colloidal suspensions were obtained by redispersing the washed product in DMF using ultrasound (Elmasonic S100H ultrasonic bath, 550 W).

For further experiments, the reaction conditions were varied, including reaction time (5 min, 30 min, 60 min, 3 d, 11 d) and amount of additive (0.0135 mmol/0.00013 mmol, 0.027 mmol/0.00025 mmol, 0.054 mmol/0.0005 mmol of CTAB/PVP; 0.00013 mmol, 0.00025 mmol, 0.0005 mmol, 0.00125 mmol of PVP).

Thin film deposition

Thin films consisting of HKUST-1 and IRMOF-3 nanoparticles, respectively, were obtained by spin-coating the respective colloidal suspensions on pre-cleaned silicon substrates. Prior to film deposition, silicon substrates (1x1 cm^2) were treated with piranha acid (96% H_2SO_4/30% H_2O_2, 2:1) for 1 h, rinsed intensively with water, dried under nitrogen stream and plasma-cleaned (Femto plasma cleaner, Diener Electronic GmbH, air, 100 W) for 5 min. A rotational speed of 4000 rpm for 1 min was used for the deposition of the layers, while the acceleration speed was fixed to 1500 $rpms^{-1}$. Thicker films were obtained by multiple coating steps.

Characterization

Powder X-ray diffraction (XRD) measurements were carried out on a Huber G670 diffractometer in Guinier geometry or on a Stadi P type diffractometer (Stoe & Cie) in transmission using Ge(111)-monochromated Cu-Kα_1 radiation (λ = 1.54051 Å). Data were collected between 5° and 50°.

Dynamic light scattering (DLS) measurements were carried out with a Nano ZS Zetasizer with a 4 mW HeNe laser (λ = 633 nm). The scattered light was detected in back-scattering geometry at an angle of 173°.

Infrared (IR) spectroscopy was carried out with the help of a Perkin Elmer Spektrum BX II spectrometer with an attenuated total reflectance unit.

Scanning electron (SE) micrographs were recorded either with a JEOL JSM-6500F SEM equipped with an Oxford EDX analysis system or with a Merlin (Zeiss) FE-SEM.

AFM measurements were performed on a MFP-3D Stand alone AFM (Asylum Research, Santa Barbara). Tapping-mode was applied using OMCL-AC160TS-R3 (Olympus, Tokio) cantilevers with a resonant frequency of 300 kHz.

Ellipsometric measurements were carried out using a Woollam M2000D at angles of 65°, 70° and 75° in the spectral range of 190-1000 nm. The data were fitted between 300 and 1000 nm using a Cauchy-type material as the model layer to determine the effective refractive index (RI) and the thickness of the investigated layers (using average values deduced by SEM images as starting values). The effective RI of the MOF layer is made up of RI contributions from textural porosity (RI_{por} = 1), the MOF itself, and possible residues of the additives ($RI_{res} > 1$).

Additional analytical data

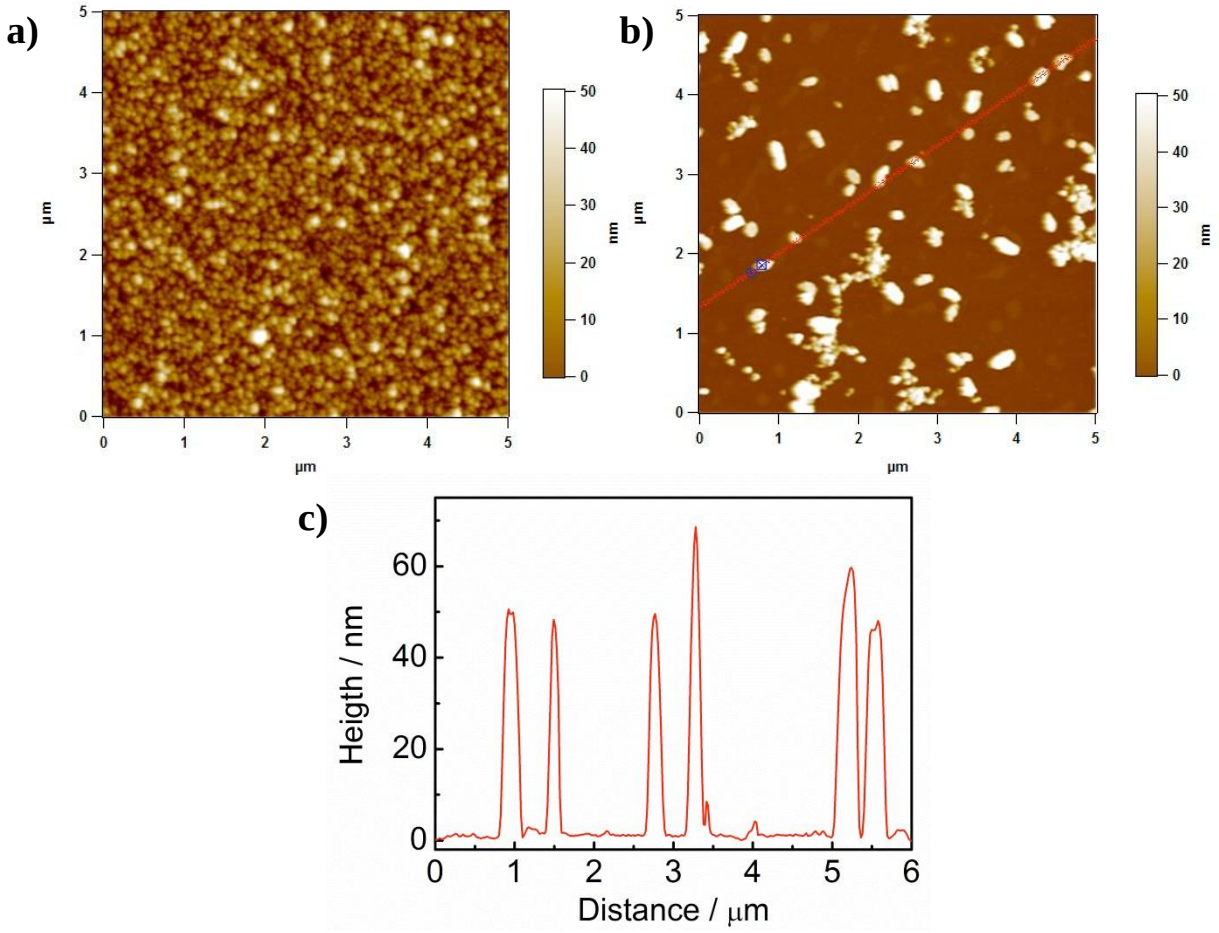

Figure S1 AFM measurements (a, b) and height profile (c) of HKUST-1 particles synthesized at 0 °C.

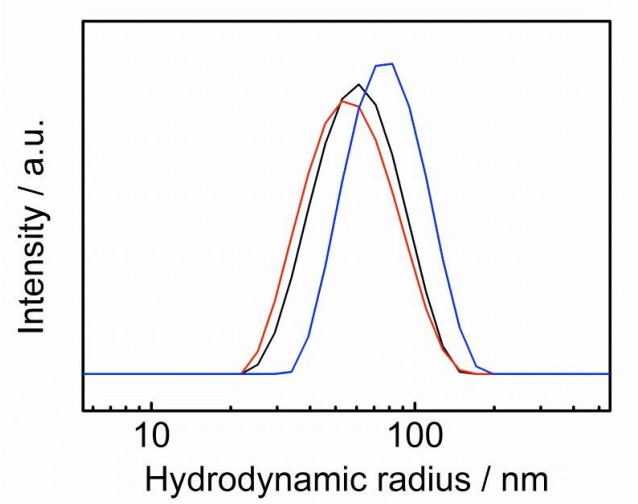

Figure S2 DLS measurements of HKUST-1 particles synthesized at different temperatures (black: 0 °C, red: RT, blue: 55 °C) after centrifugation and redispersion in DMF.

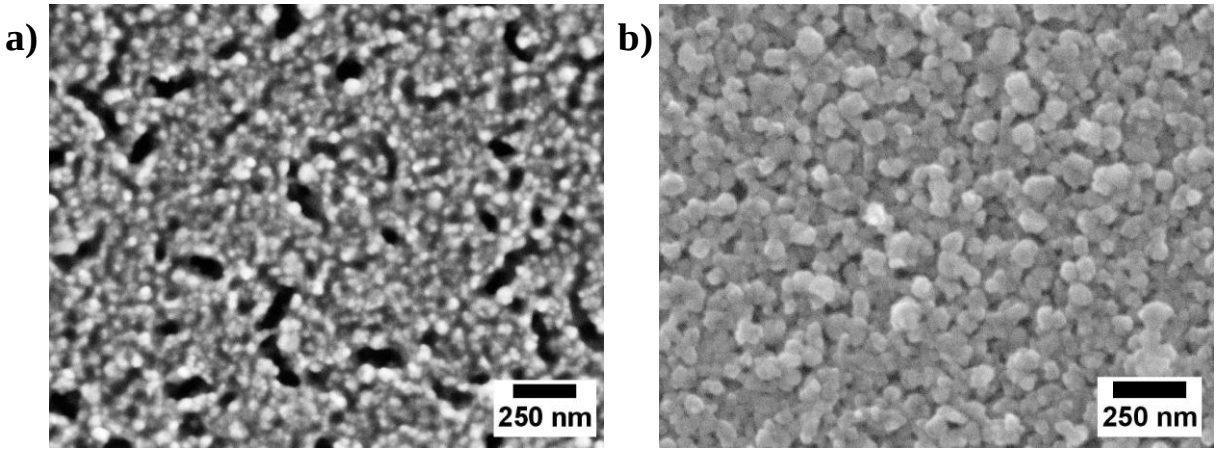

Figure S3 SEM images of HKUST-1 particles synthesized at different temperatures: a) 0 °C, b) RT.

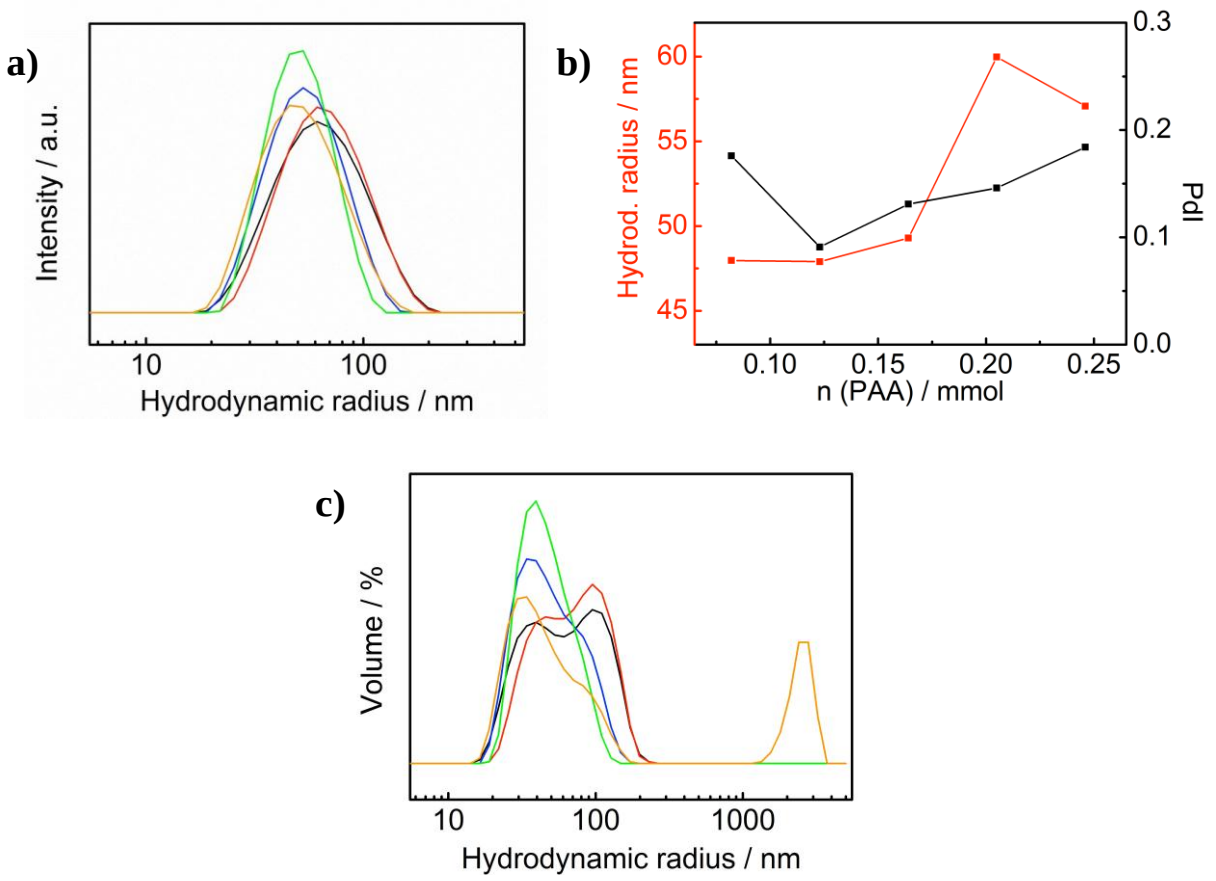

Figure S4 DLS measurements (shown as a) intensity distribution and c) volume distribution) of HKUST-1 particles synthesized at 0 °C with different ratios of H_3BTC:PAA (black: 1:6 / 0.246 mmol PAA, red: 1:5 / 0.205 mmol PAA, blue: 1:4 / 0.164 mmol PAA, green: 1:3 / 0.123 mmol PAA, orange: 1:2 / 0.082 mmol PAA) after centrifugation and redispersion in DMF; b) evolution of the size (red) and the polydispersity index (PDI) (black), with the PAA concentration.

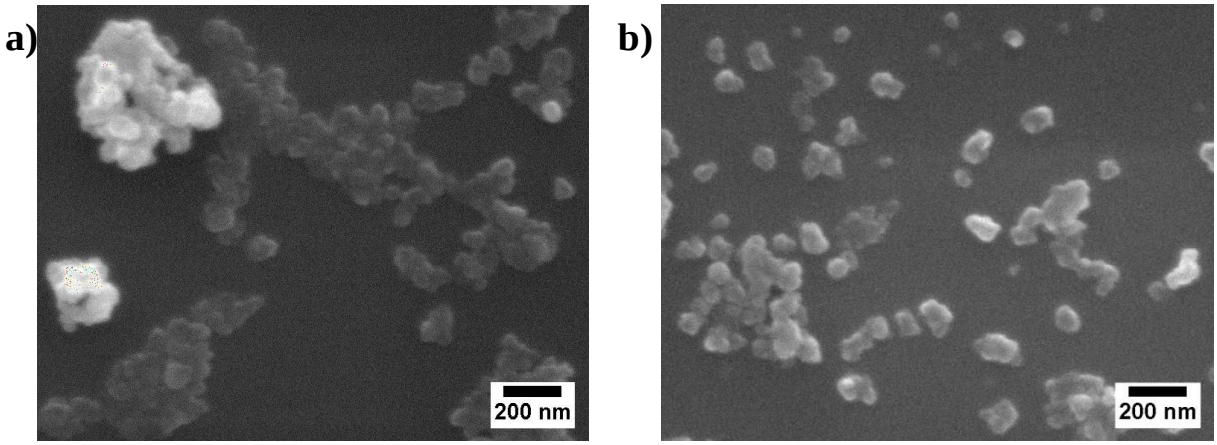

Figure S5 SEM images of HKUST-1 particles synthesized at RT after different reaction times: a) 5 min, b) 30 min.

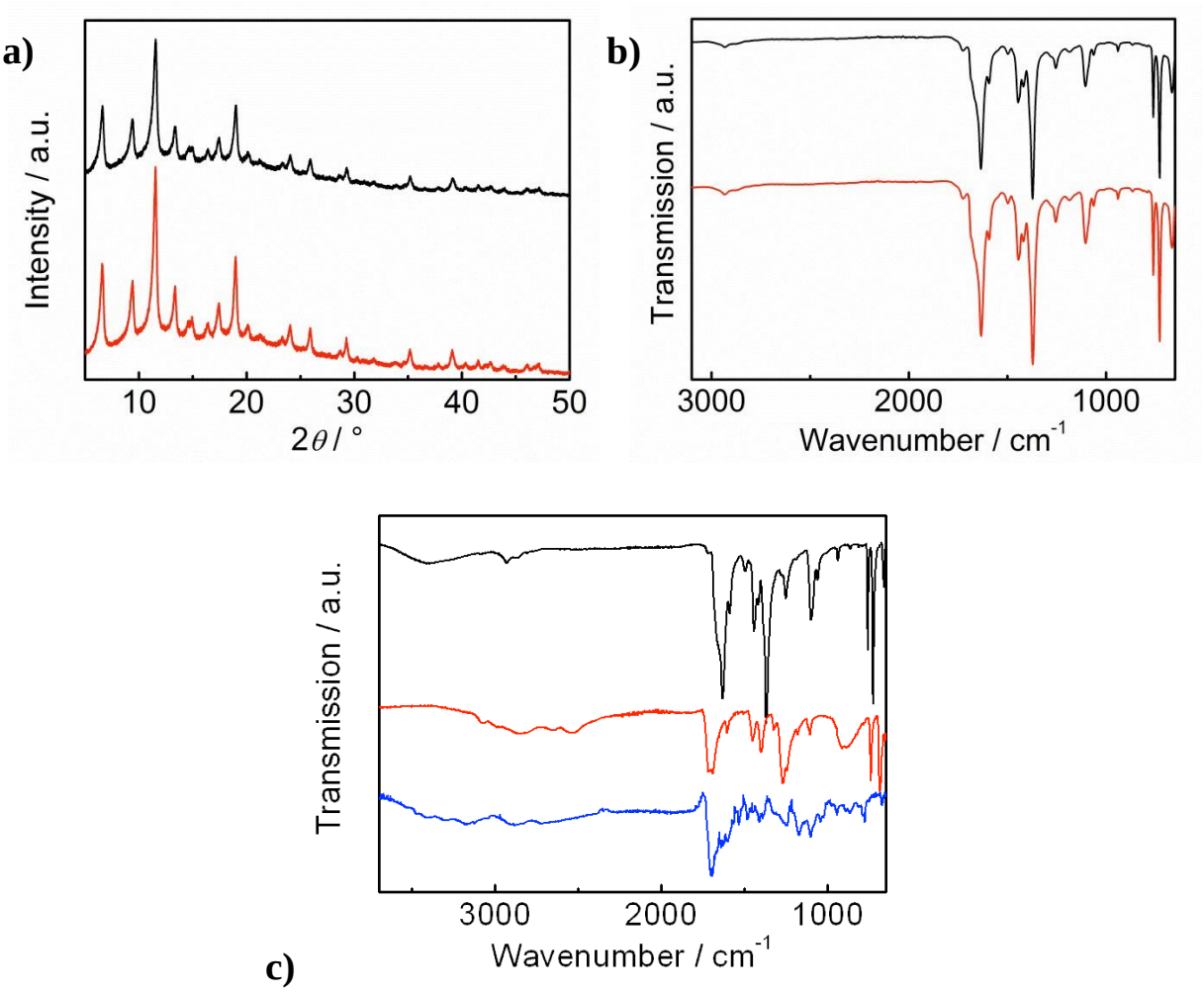

Figure S6 PXRD patterns (a) and IR spectra (b) of HKUST-1 particles synthesized at RT after different reaction times (black: 5 min, red: 30 min). c) IR spectra of HKUST-1 (black, synthesized without additives), H_3BTC (red) and PAA (blue), showing good agreement between the products synthesized with and without PAA (note that PAA and H_3BTC have similar IR bands, in particular around 1700 cm^{-1} corresponding to C=O vibrations of carboxylic acid groups).

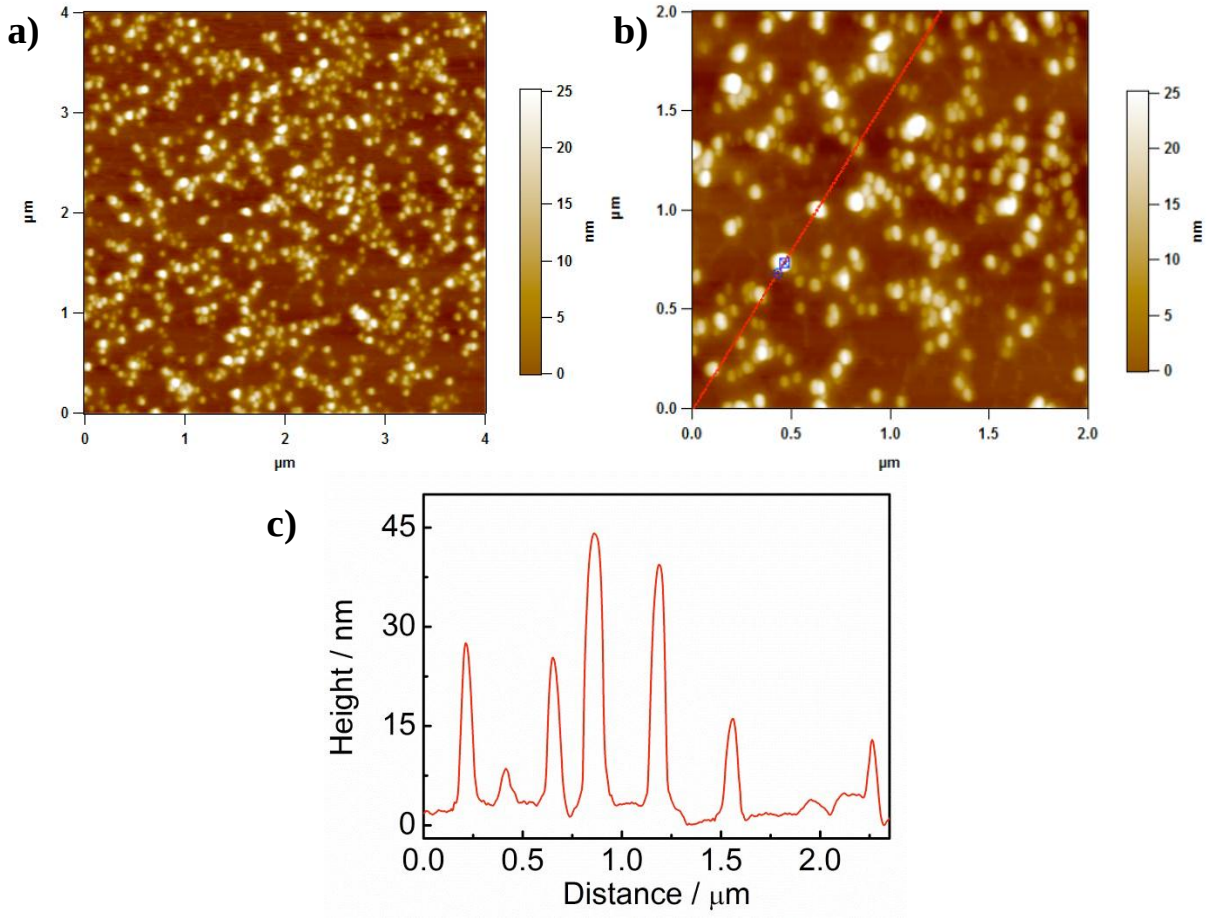

Figure S7 AFM measurements (a, b) and height profile (c) of IRMOF-3 particles.

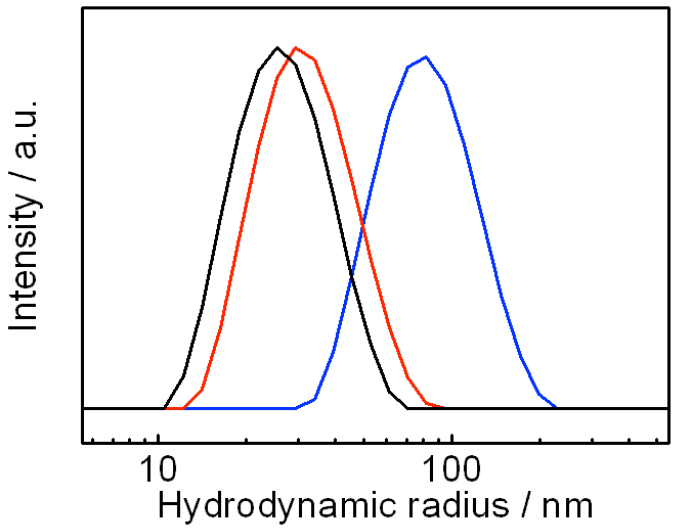

Figure S8 DLS measurements of IRMOF-3 particles synthesized with different total amounts of CTAB/PVP at weight ratios of 1:1 (black: 0.054 mmol/0.0005 mmol, red: 0.027 mmol/0.00025 mmol, blue: 0.0135 mmol/0.00013 mmol) after centrifugation and redispersion in DMF.

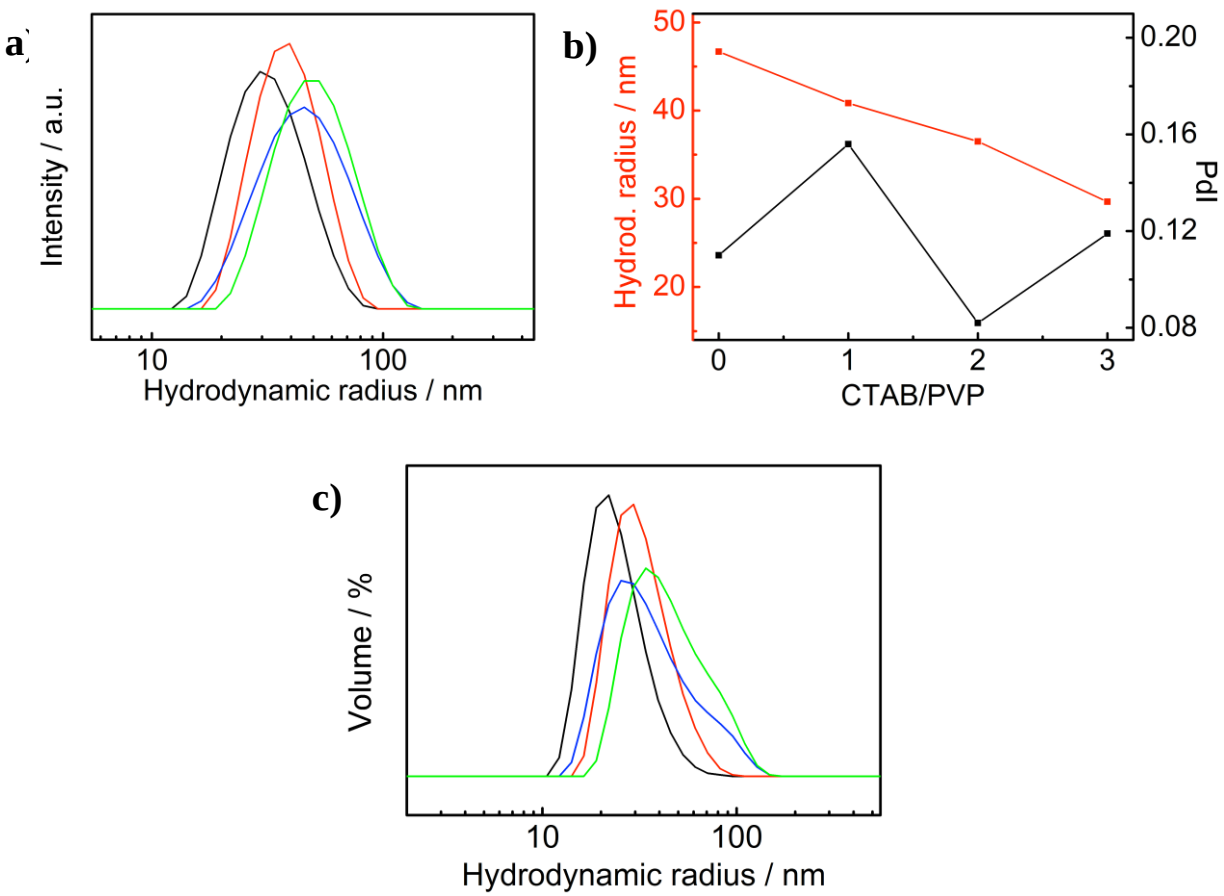

Figure S9 DLS measurements (shown as a) intensity distribution and c) volume distribution) of IRMOF-3 particles synthesized with different amounts of CTAB and/or PVP (black: weight ratio 1:1 of CTAB/PVP (0.027 mmol/0.00025 mmol), red: 0.027 mmol of CTAB, blue: 0.00025 mmol of PVP, green: no additives) after 5 min reaction time; b) evolution of the mean radius and the PdI with the amount of additives (0: no additives, 1: 0.027 mmol of CTAB, 2: 0.00025 mmol of PVP, 3: 0.027 mmol/0.00025 mmol of CTAB/PVP).

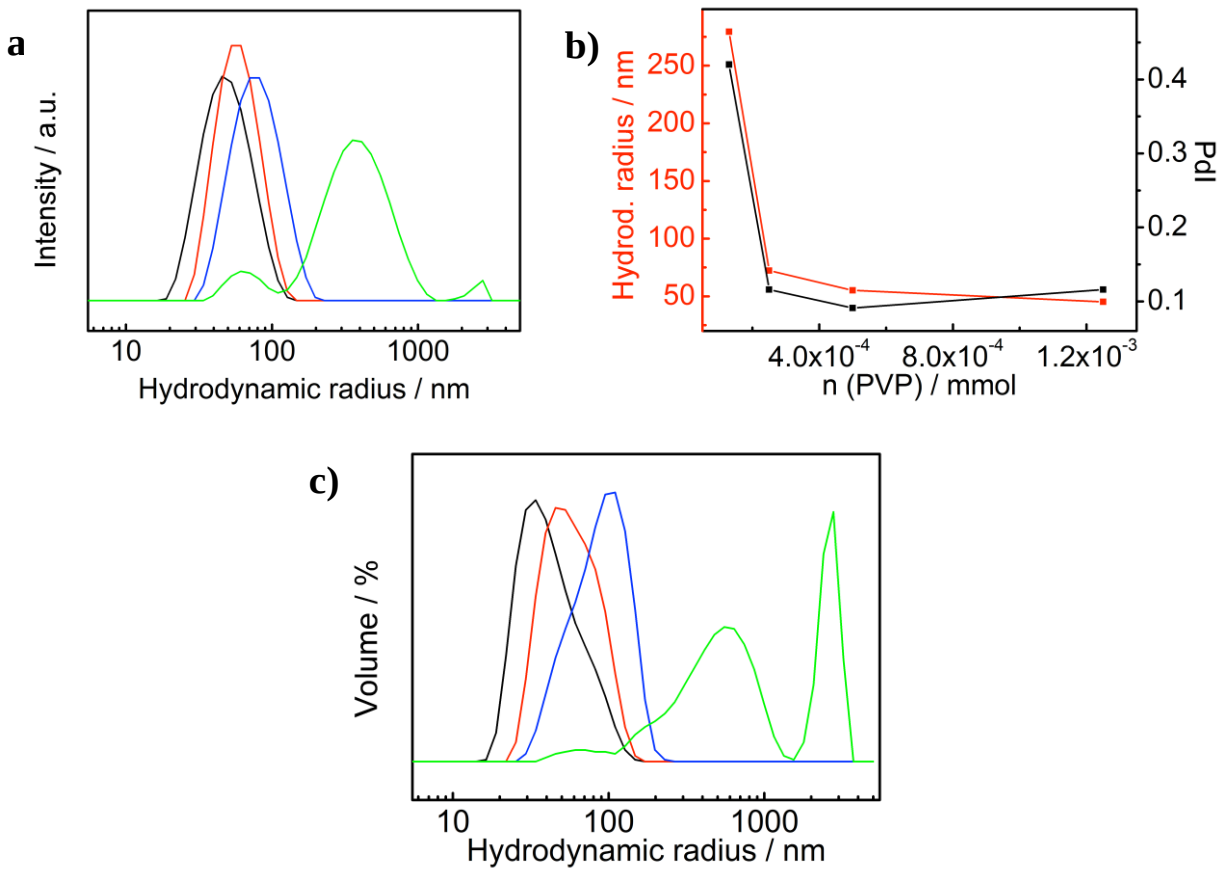

Figure S10 DLS measurements (shown as a) intensity distribution and c) volume distribution) of IRMOF-3 particles synthesized with different amounts of PVP (black: 0.00125 mmol, red: 0.0005 mmol, blue: 0.00025 mmol, green: 0.00013 mmol) after centrifugation and redispersion in DMF; b) evolution of the size (red) and the PdI (black) with the amount of PVP.

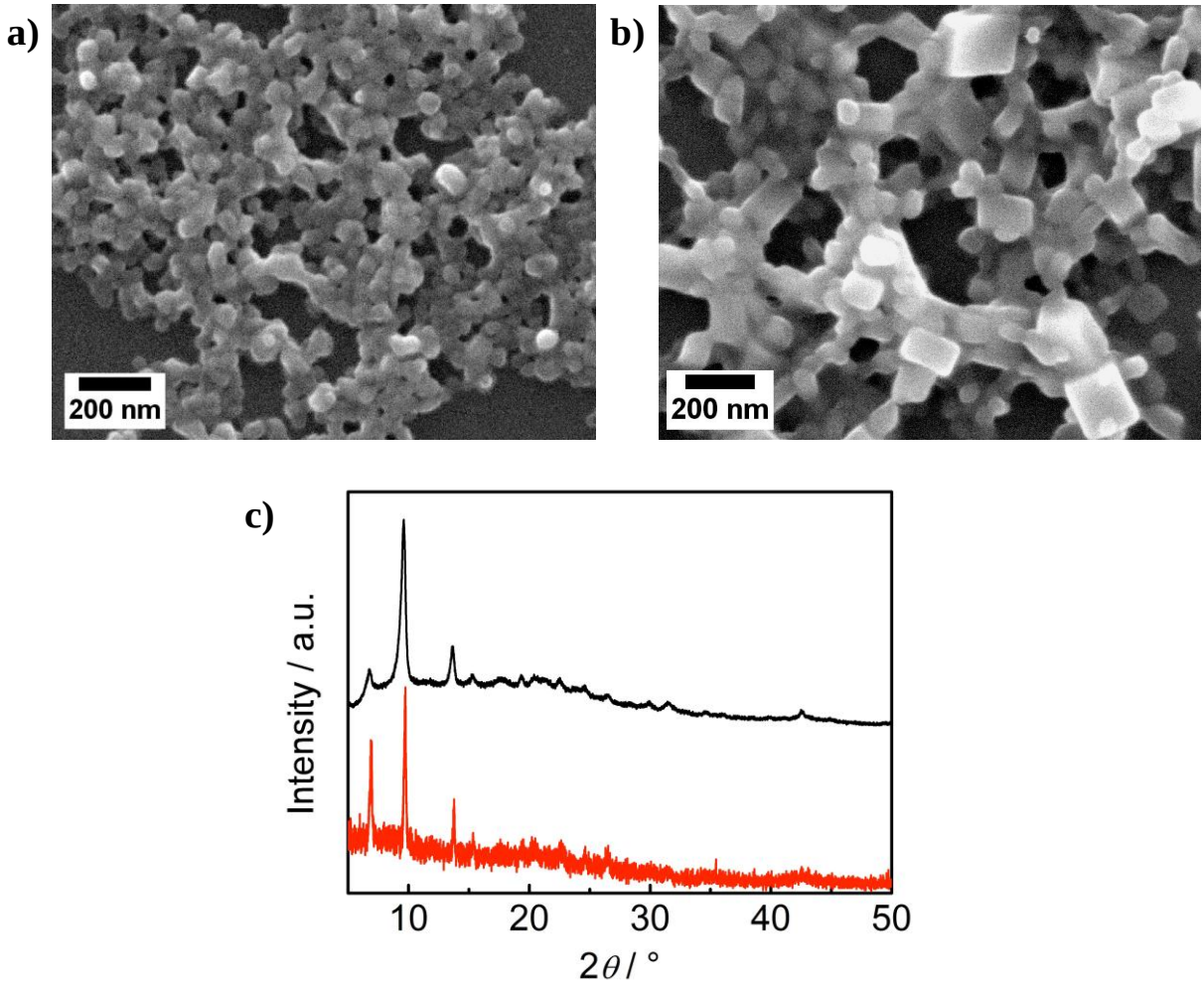

Figure S11 SEM images of IRMOF-3 particles synthesized a) with CTAB/PVP (0.027 mmol/0.00025 mmol) and b) without additives; c) corresponding PXRD patterns of IRMOF-3 particles synthesized with additives (black) and without additives (red).

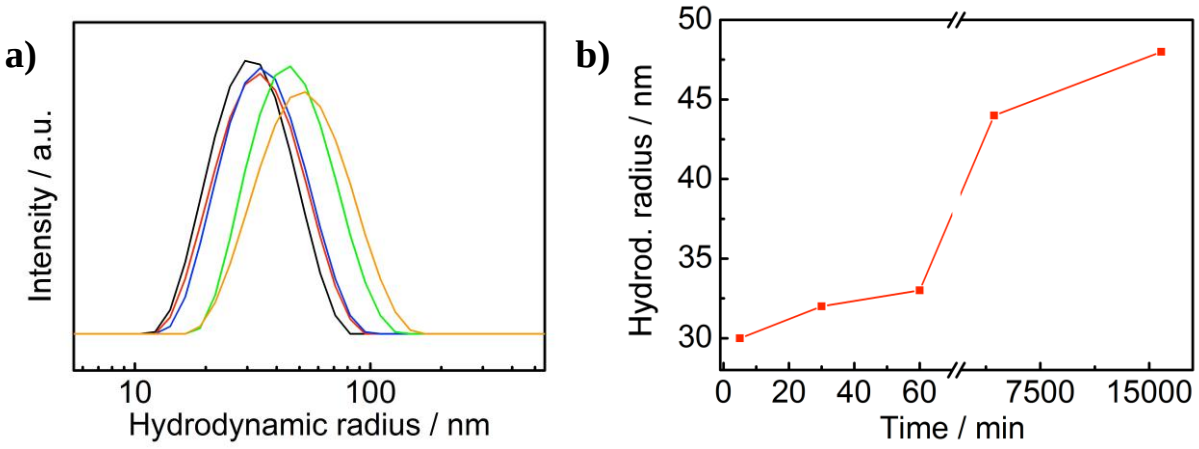

Figure S12 DLS measurements of IRMOF-3 particles as a function of time: a) evolution of the size distribution of the reaction mixture (black: 5 min, red: 30 min, blue: 60 min, green: 3 d, orange: 11 d); b) evolution of the mean radius.

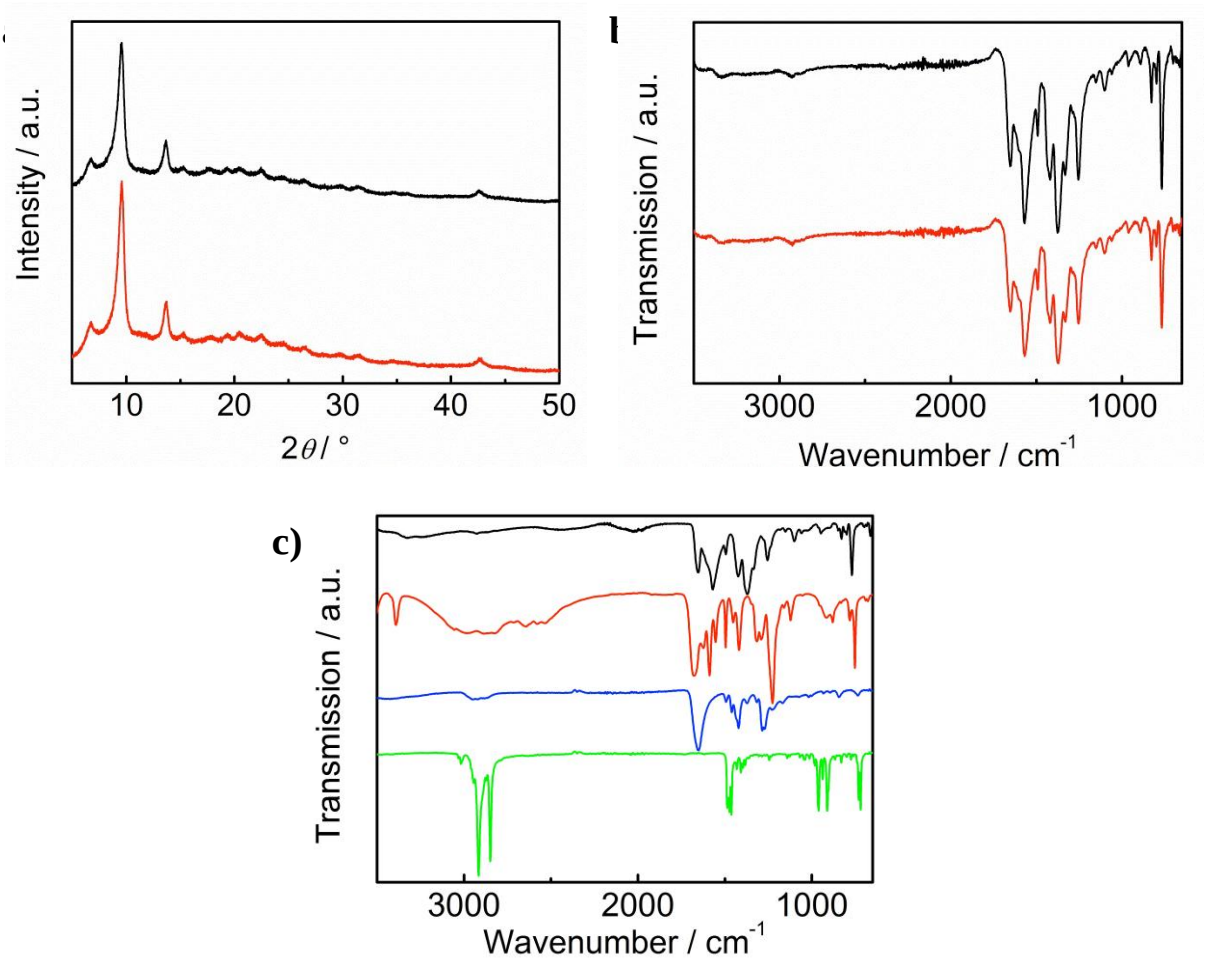

Figure S13 PXRD patterns (a) and IR spectra (b) of IRMOF-3 particles synthesized at different reaction times (black: 5 min, red: 30 min). c) IR spectra of IRMOF-3 (black, synthesized without additives), $H_2BDC\text{-}NH_2$ (red), PVP (blue) and CTAB (green), demonstrating the good agreement of the IR spectra of the products synthesized with and without CTAB/PVP as well as the absence of major residues from the additive mixture.

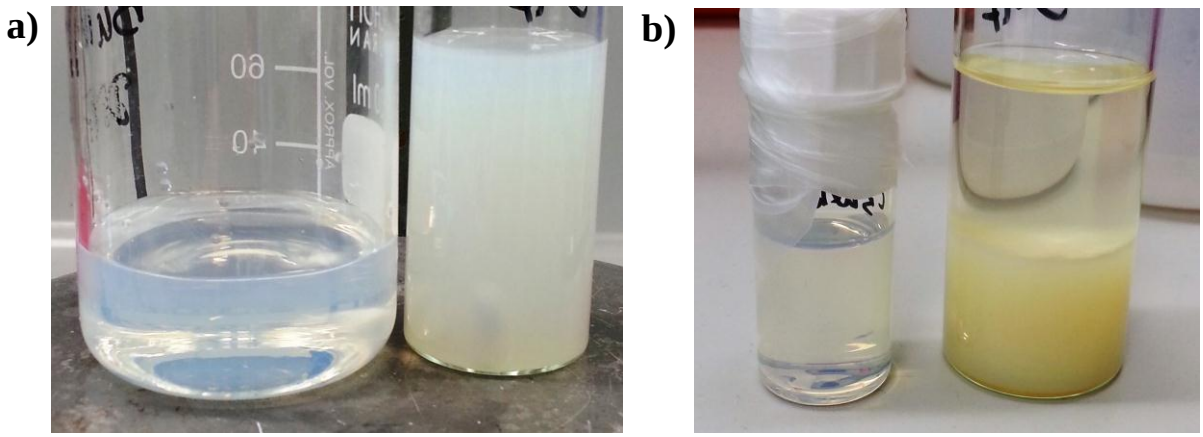

Figure S14 Photographs of suspensions of IRMOF-3 particles synthesized with additives (vessel on the left) and without additives (vessel on the right) after a) 30 min and b) 1 day.