

Electronic Supplementary Information for:

Ionic Liquid-in-Ionic Liquid Nanoemulsions

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1. Experimental Section

Materials The surfactant AOT (>95%) was purchased from Guangzhou Leelchem Corporation. The ionic liquid (IL) PAF was purchased from Centre of Green Chemistry and Catalysis, LICP, CAS (purity >99%). [Omim]PF₆ was synthesized following the method reported^{S1} and its purity was determined by ¹H NMR. La(NO₃)₃·6H₂O (A. R. grade) was purchased from Sinopharm Chemical Reagent Co., Ltd. H₃BTC (purity 95%) was purchased from Aldrich.

Emulsion formation The appropriate amount of PAF and AOT were first loaded into a capped glass vessel with a magnetic bar inside, and the mixture was vigorously stirred (1800 rpm) until a mono-phase solution was generated. The desired amount of [omim]PF₆ was added into the solution, and the mixture was stirred for 1 hour for the formation of emulsions. The concentration of AOT was fixed at 0.5 mol/dm³.

Electrical conductivities The electrical conductivities of PAF/[omim]PF₆/AOT systems were detected by a Model DDS-307 conductivity meter produced by Shanghai Precision Scientific Instrument Co., Ltd. The KCl solutions at different concentrations (1.0×10⁻¹ mol/dm³, 1.0×10⁻² mol/dm³ and 1.0×10⁻³ mol/dm³) were used to calibrate the cell constant. Data were collected while the emulsions were kept stirring.

SAXS experiment on nanoemulsions The SAXS experiments were carried out on Beamline 4B9A at Beijing Synchrotron Radiation Facility (BSRF). The data were collected using a CCD detector (MAR) with a maximum resolution of 2048×2048 pixels. The wavelength used was 1.53 Å, and the distance from the sample to the detector was 1.64 m. In a typical experiment, the freshly prepared nanoemulsion was added into the sample cell, and the X-ray scattering data were recorded.

Confocal laser scanning microscopy on macroemulsion The image of the macroemulsion was measured on an OLYMPUS FV1000-IX81 confocal laser scanning microscopy with the magnification of

1000 times. A 5.0 μL newly formed macroemulsion was trickled through microsyringe on a 0.7 mm thick coverslip and covered with another, and was monitored and captured by a digital CCD.

MOF synthesis and characterization $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol) and H_3BTC (0.2 mmol) were added into a sealed vessel containing 10 mL newly prepared emulsion ($[\text{AOT}] = 0.5 \text{ mol/dm}^3$). After the mixture was stirred at 30 $^\circ\text{C}$ for 24 hours, the precipitate was collected by centrifugation, washed by acetone for 5 times, and dried under vacuum at 75 $^\circ\text{C}$ for 12 hours. The morphology of the obtained products was characterized by SEM HITACHI S-4800 and TEM JeoL-1011 operated at 100 kV. The nitrogen adsorption–desorption isotherms were determined by using a Micromeritics ASAP 2020M system with the desorbing temperature at 200 $^\circ\text{C}$. The mesopore size of the MOF was calculated from the adsorption branch by using the BJH model while the micropore size by HK model. Powder XRD analysis of the sample was performed on the X-ray diffractometer (Model D/MAX2500, Rigaka) with Cu-K_α radiation. Thermogravimetric analysis was carried out on a PerkinElmer TGA instrument. The temperature range was from 50 to 800 $^\circ\text{C}$ with a heating rate of 10 $^\circ\text{C}/\text{min}$, and the experiment was carried out in nitrogen atmosphere. FT-IR spectra were obtained using a Bruker Tensor 27 spectrometer, and the samples were prepared by the KBr pellets method.

2. Results

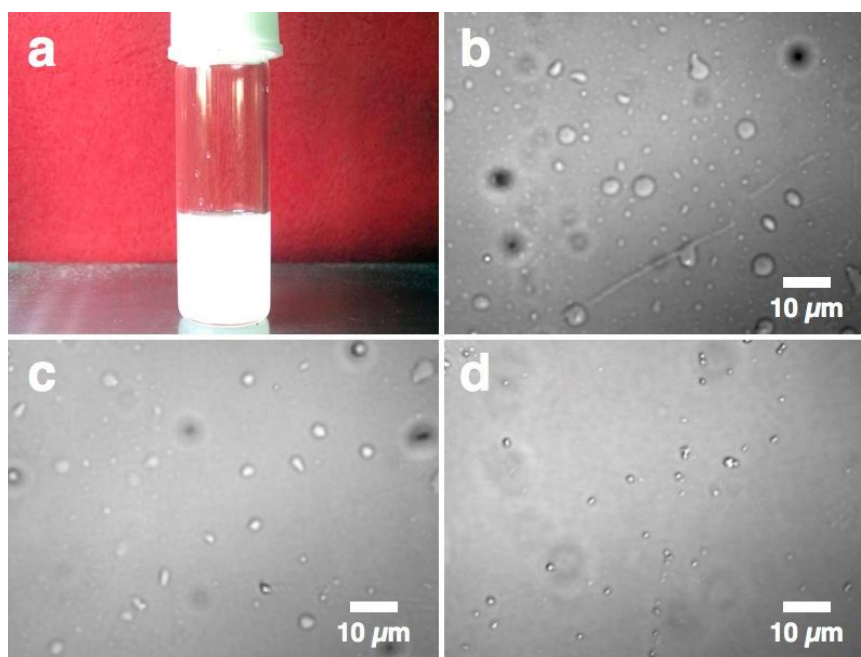


Fig. S1 A photograph of PAF-in-[omim]PF₆ macroemulsion (a) and confocal laser scanning microscopy images of macroemulsions with [omim]PF₆ volume fraction of 0.40 (b), 0.50 (c) and 0.70 (d).

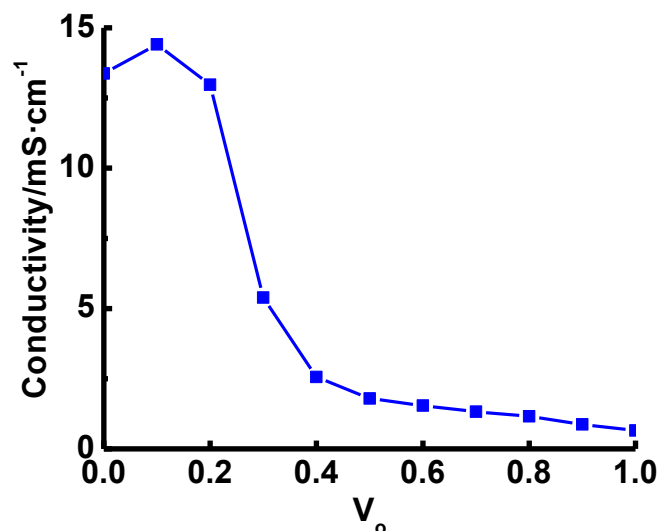


Fig. S2 Conductivities of PAF/[omim]PF₆ emulsions with different [omim]PF₆ volume fraction (V₀).

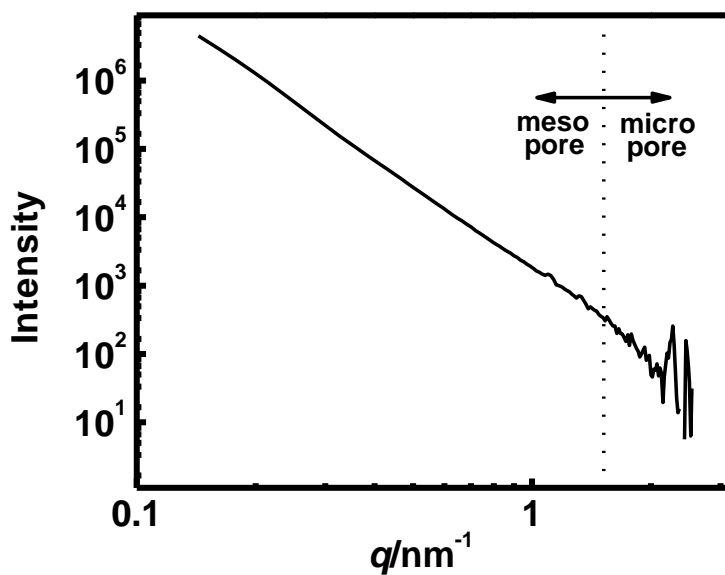


Fig. S3 Small-angle X-ray scattering pattern of the MOF synthesized in the nanoemulsion with [omim]PF₆ volume fraction of 0.30. There are some arrows in the low q region ($<1.5 \text{ nm}^{-1}$) and the medium q region ($1.5\text{-}3.0 \text{ nm}^{-1}$), indicative of the existence of both mesopores and micropores in the MOF.

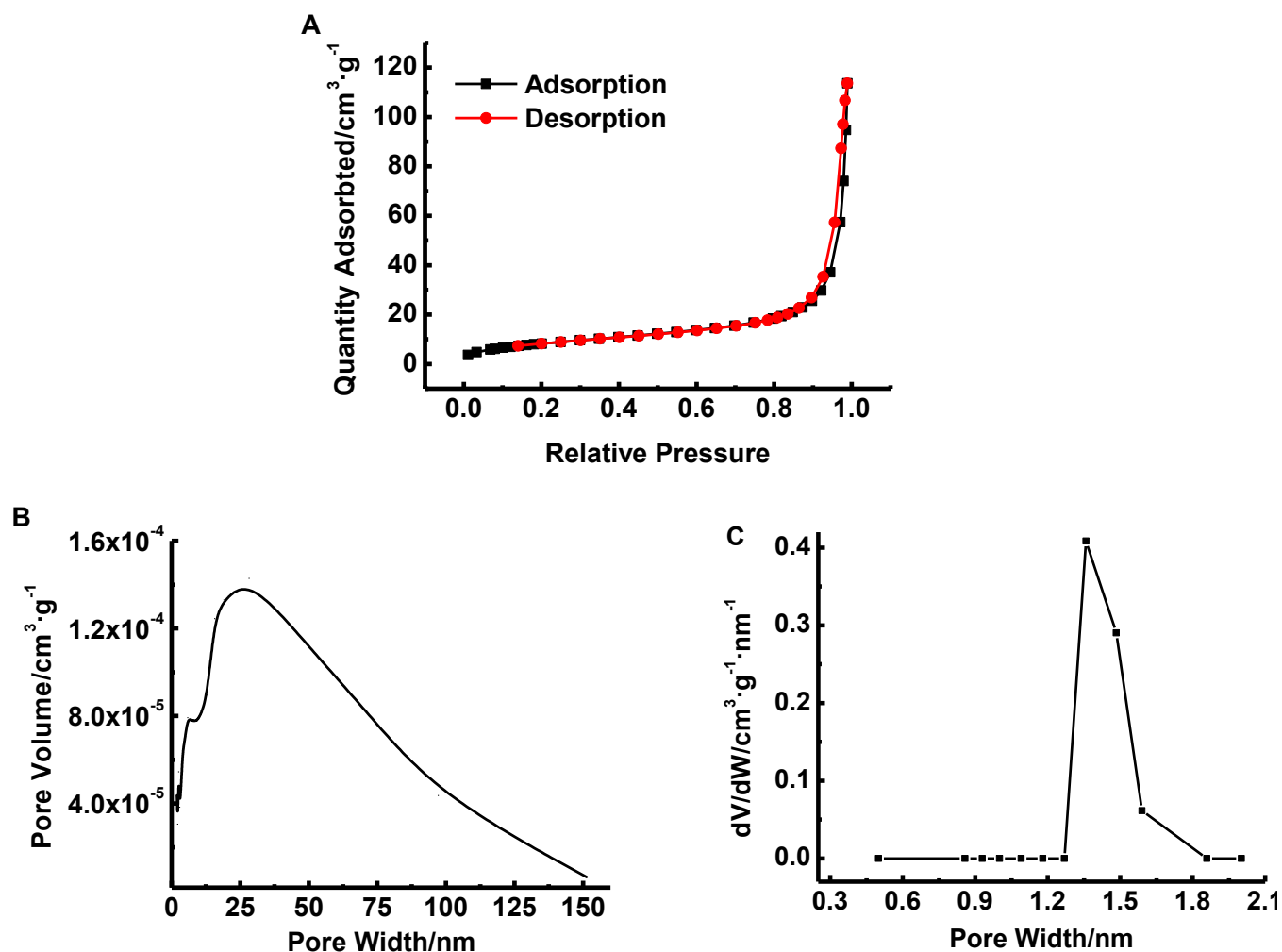


Fig. S4 A: N₂ adsorption-desorption isotherm of the MOF synthesized in the nanoemulsion with [omim]PF₆ volume fraction of 0.30. It exhibits an intermediate mode between type I and type IV, which is related to mesoporous materials and microporous materials, respectively.^{S2} B and C show the mesopore size distribution curve and micropore size distribution, respectively. The BET surface area and total specific pore volume of the as-synthesized MOF are 32.72 m²/g and 0.1279 cm³/g, respectively. Such low surface area and pore volume can be attributed to the closed porosity,^{S3} given the volume fraction of [omim]PF₆ (0.30) and the schematic formation of MOF (show in Scheme 1). The micropore surface area was determined to be 7.71 m²/g, indicating the low microporosity.

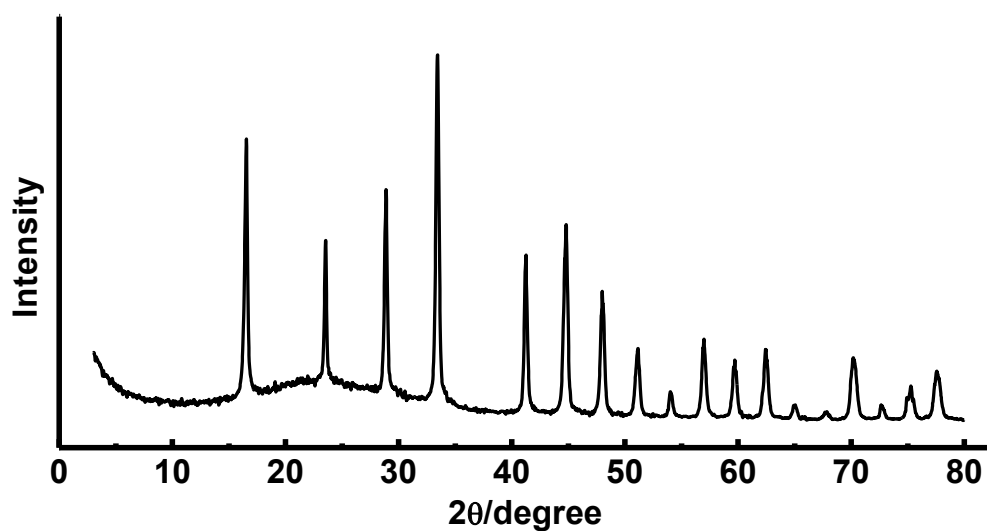


Fig. S5 Powder X-ray diffraction pattern of the MOF synthesized in nanoemulsion with [omim]PF₆ volume fraction of 0.30.

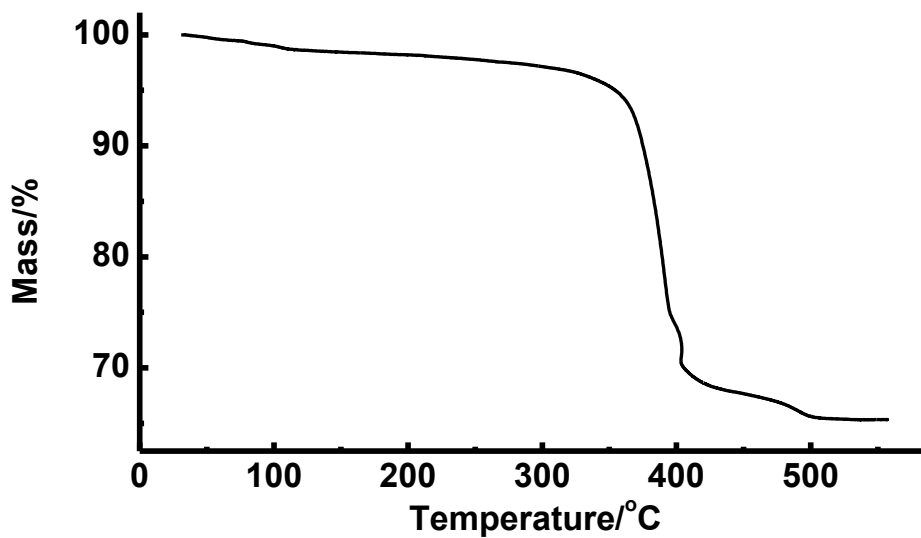


Fig. S6 Thermogravimetric analysis curve of the MOF synthesized in nanoemulsion with [omim]PF₆ volume fraction of 0.30. The MOF is stable up to 360 °C.

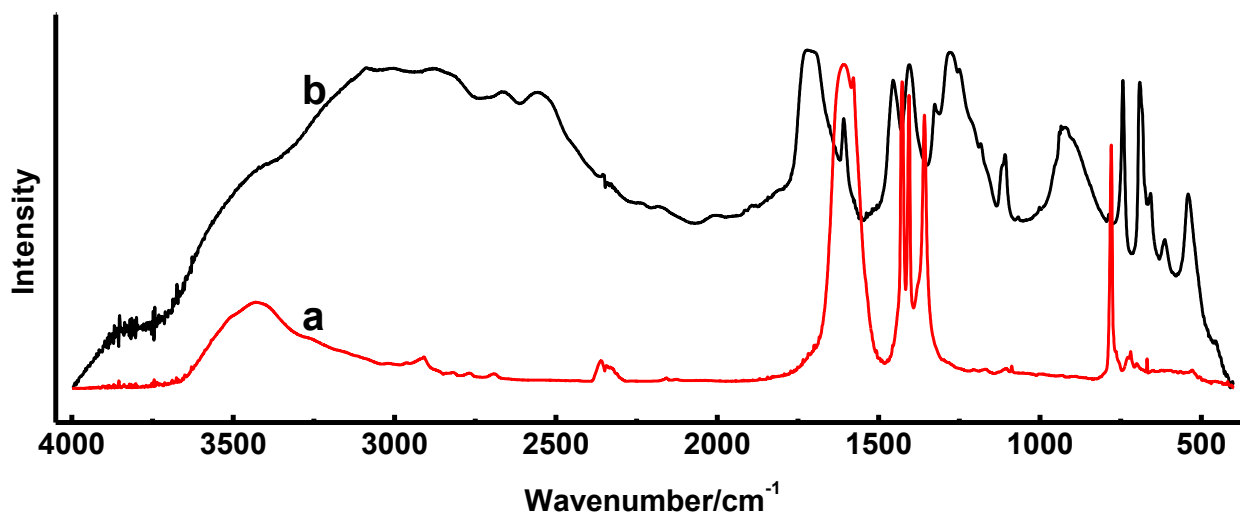


Fig. S7 FT-IR spectra of the MOF synthesized in nanoemulsion with [omim]PF₆ of 0.30 (a) and 1, 3, 5-benzenetricarboxylic acid (b). The H₃BTC shows two absorption bands at about 1680 cm⁻¹ and 1380 cm⁻¹. In sharp contrast, the MOF shows the strong characteristic absorption for the symmetric and asymmetric vibration of BTC groups at about 1620 cm⁻¹ and 1375 cm⁻¹. The wavenumber difference of the two bands for the MOF narrows, indicating that the carboxylate groups of BTC are coordinated to La (III) ions.^{S4}

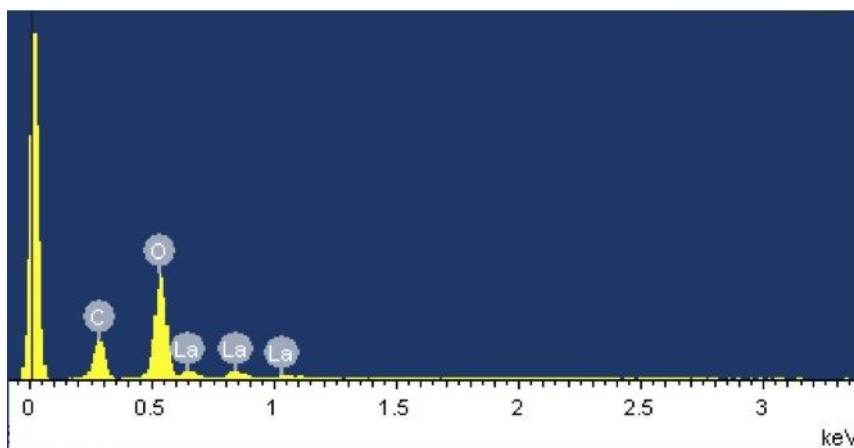


Fig. S8 Energy dispersive spectrum of the MOF synthesized in nanoemulsion with [omim]PF₆ volume fraction of 0.30. It shows the presence of lanthanum, oxygen, and carbon in the MOF.

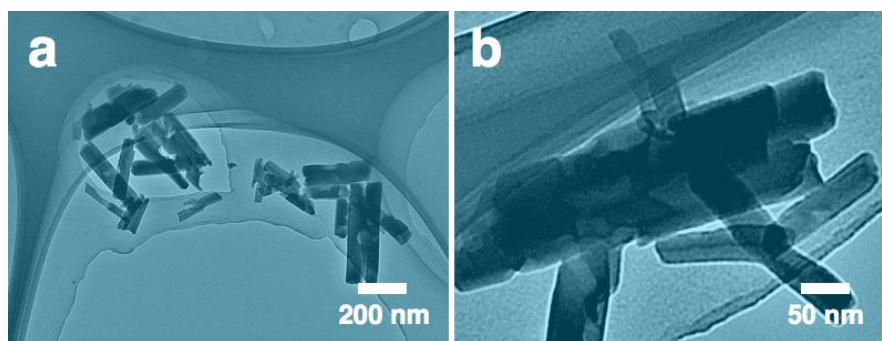


Fig. S9 TEM images of the MOF synthesized in pure PAF with different magnification.

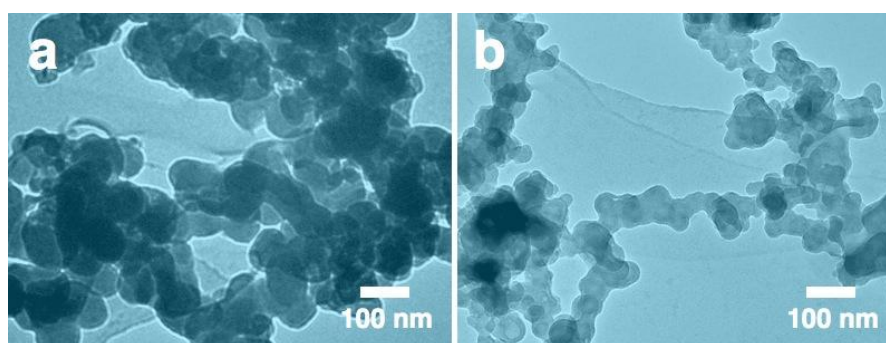


Fig. S10 TEM images of the MOFs synthesized in PAF-in-[omim]PF₆ emulsion with [omim]PF₆ volume fraction of 0.50 (a) and 0.70 (b).

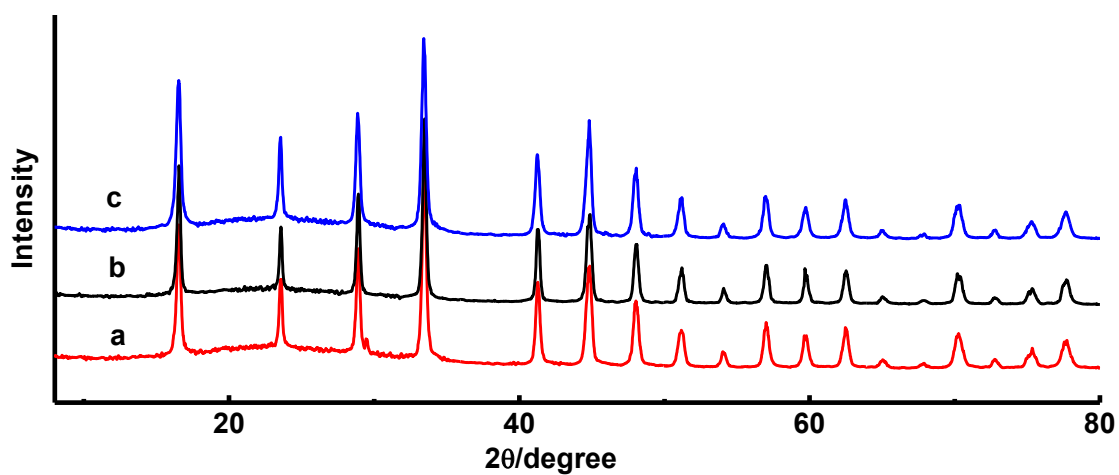


Fig. S11 The powder X-ray diffraction patterns of MOFs synthesized in pure PAF (a) and PAF-in-[omim]PF₆ emulsions with [omim]PF₆ volume fraction of 0.50 (b) and 0.70 (c).

References

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