Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of well dispersed polymer grafted metal-organic framework nanoparticles

Ke Xie, Qiang Fu, Yingdian He, Jinguk Kim, Sook Jin Goh, Eunhyung Nam, Greg Qiao and Paul Webley**

Experimental section

Chemicals. Zirconium(IV) chloride ($ZrCl_4$, >99.5%), 2-aminoterephthalic acid (99%), α-bromoisobutyryl bromide (BiBB, 98%), poly(ethylene glycol) methyl ether methacrylate (PEGMA, Avg. MW 475), copper(II) bromide ($CuBr_2$, 99%), sodium ascorbate (>98%), palladium(II) chloride ($PdCl_2$, >99.9%), 4-nitrophenol (NP, >99%) and sodium borohydride ($NaBH_4$, >99%) were purchased from Sigma-Aldrich and used as received. Triethylamine (TEA) was distilled from calcium hydride under argon. Tetrahydrofuran (THF) was distilled from benzophenone and sodium metal under argon. Tris [2-(dimethylamino) ethyl] amine (Me_6Tren) was prepared according to a reference.[1] H_2PdCl_4 solution was prepared by dropwise adding 1 mol L^{-1} HCl solution onto a certain amount of $PdCl_2$ powder under stirring until an orange solution was formed, and then diluted to a desired volume.

Preparation of nano-sized NH_2-UiO-66. The nano-sized NH_2-UiO-66 was prepared *via* an up-scaled preparation process using water to tune the particle size.[2] Briefly, $ZrCl_4$ (0.320 g, 1.372 mmol) was dissolved by 80 mL DMF in a 120 mL Teflon-lined, stainless steel autoclave. Into the solution 2-aminoterephthalic acid (0.248 g, 1.372 mmol) was added and dissolved by sonification. 1.236 mL water (68.7 mmol, 50 equiv to $ZrCl_4$) was added into the solution under stirring. Then the autoclave was sealed and kept in an oven at 120 ^oC for 24 hours. The precipitate was isolated by centrifuge and washed with DMF and methanol for 3 times respectively. The obtained solid was immersed in methanol for 24 hours, washed again with methanol and dried under reduced pressure for 24 hours at 80 ^oC.

Preparation of Br-functionalized NH_2-UiO-66 (Br@MOF). The Br@MOF was obtained by functionalizing NH_2-UiO-66 with BiBB under nitrogen atmosphere in a 100 mL flask. In a typical procedure, 0.60 g (containing 2 mmol $–NH_2$) of NH_2-UiO-66 was dispersed in 40 mL anhydrous THF by sonification. TEA (418 μL, 0.303g, 3 mmol for 0.5Br) and BiBB (124 μL, 0.23g, 1 mmol for 0.5Br) were dissolved in 10 mL THF respectively. The TEA solution was injected into the NH_2-UiO-66 suspension under stirring. Then the BiBB solution was dropwise added into the mixture (in *ca.* 30 min) at room temperature under stirring. The reactant was then stirred at 50 ^oC for 24 hours. The product was washed with THF and methanol to remove the unreacted precursors and TEA•HBr salt by-product. The resulted Br@MOF was immersed in methanol for 24 hours, washed with methanol and dried under reduced pressure at 40 ^oC. The obtained products are named xBr where x denotes to the mole feeding ratio of the BiBB *vs.* amino group.

Preparation of P@MOFs. The P@MOF samples were synthesized *via* an atom-transfer radical-polymerization (ATRP) procedure using xBr as the initiator. Typically, 0.3 g of xBr and the desired amount of PEGMA was sonicated with 100 mL deionized water in a 150 mL glass bottle (solution A). $CuBr_2$ (43.4 mg, 0.19 mmol), Me_6Tren (260 μL, 224 mg, 0.97 mmol) and sodium ascorbate (114 mg, 0.57 mmol) were dissolved in 20 mL deionized water (solution B). Then solution B was added into the solution A which was kept at 30 ^oC for 15 min. The reactant was stirred at 30 ^oC for 24 hours, resulting in a light green suspension. The obtained suspension was centrifuged at RCF=0.4g for 60s to obtain a green, transparent solution. This solution was purified by dialysis (cut-off MW=3500) and a light yellow solution was obtained. The resulted P@MOFs are named xBr-yP where y denotes to the weight feeding ratio of the PEGMA *vs.* the xBr. The light yellow solution was concentrated to *ca.* 40 mL and dried by lyophilisation to obtain the product. 0.5Br-1P, 0.5Br-2P are yellow powder, 0.5Br-4P is (a little) sticky yellow powder and 0.5Br-12P is yellow, amorphous, sticky solid.

Preparation of Pd(0) catalysts. The Pd(0) catalysts were prepared via a widely reported ethylene glycol reduction method. [3,4] 50 mg of P@MOF or NH_2-UiO-66 was dispersed in 10 mL of water by sonication. The pH of the dispersion was adjusted to 3 by HCl solution. Then a solution of H_2PdCl_4 (Pd concentration 0.6 mg mL^{-1}) was added into the dispersion followed by 4 hours of stirring at 25 °C. The $PdCl_4^{2-}$ ions were trapped by protonated amino groups in the NH_2-UiO-66 core. After washed with pH=3 HCl solution, the $PdCl_4^{2-}$ trapped particles was dispersed in 1 mL of ethylene glycol and sonicated for 3 hours. The ethylene glycol dispersion was diluted with 2 mL of pH=3 HCl solution and the Pd(0) loaded particles were isolated and washed to neutral by deionized water. The products were dried by lyophilisation.

Measurement on catalytic performance of Pd(0) loaded particles. For the 1st cycle,15 mg of Pd(0) loaded particles was dispersed in 10 mL of deionized water. 2.4 mL of $NaBH_4$ solution (0.2 mol L^{-1}) was introduced into this dispersion to obtain a pH=9, homogeneous colloid solution. The volume of this solution was adjusted by water to 15 mL.0.6 mL of 4-nitrophenol (5 mmol L^{-1}) was then added to this solution. Immediately 3 mL of the mixture solution was put into a quartz cuvette and measured the UV-vis absorption on a Shimadzu UV-1800 Spectrophotometer every 10 minutes. After 2 hours, the pH of the solution was adjusted to 4 (except Pd-NH_2-UiO-66) and centrifuged to obtain the precipitate. The precipitate was thoroughly washed with HCl solution (pH=3, twice) and deionized water. The precipitate was then dried by lyophilisation to measure the weight. The recycled catalyst was used in the same condition (except catalyst weight) as the 1st cycle for the rest of the cycles. Turnover number (TON) and turnover frequency (TOF) are calculated based on their definitions in reference.[5,6]

Characterizations. Scanning electron microscope (SEM) images were acquired using a FEI Quanta 200 ESEM FEG. Samples were pre-coated with gold using a Dynavac Mini Sputter Coater prior to imaging. X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance instrument with Cu Kα radiation (40 kV, 40 mA) and a nickel filter, and the samples were exposed at a scanning rate of $2\theta = 0.020$ $°\cdot s^{-1}$ in the range of 3-70°. X-ray photoelectron spectroscopy (XPS) analysis was performed on a VG ESCALAB 220i-XL spectrometer under ultra-high vacuum (6×10^{-9} mbar). Thermogravimetric analysis (TGA) was performed on a Diamond TG/DTA, PerkinElmer in air with heating rate of 10 °C min^{-1}. Dynamic light scattering (DLS) was measured on Zetasizer, Malvern. The inductively coupled plasma optical emission spectrometry (ICP-OES) was performed on a Varian 720-ES spectrometer using calibration curves generated from standard solutions. To investigate the contact angle, 10 mg of sample powder was sonicately dispersed in 2 mL THF, then the dispersion was casted on an aluminum foil to form an even sample film. Contact angle measurements were conducted with a Data Physics OCA 20 Tensiometer. Measurements were recorded with OCA software, using sessile drop profile.

SI1 Investigation on dispersity.

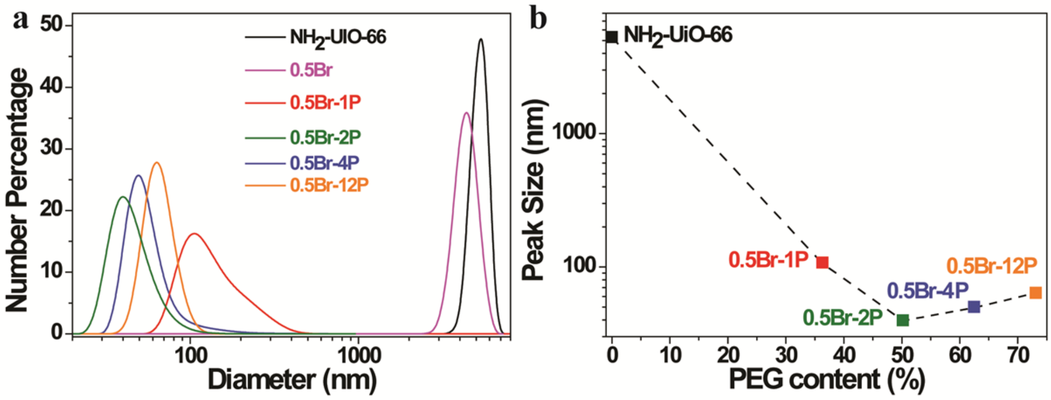

Figure S1 (a) DLS curves for NH_2-UiO-66 (black), 0.5Br (magenta), 0.5Br-1P (red), 0.5Br-2P (green), 0.5Br-4P (blue) and 0.5Br-12P (orange) aqueous dispersion at pH=7. All the P@MOF samples were filtered through a 450 nm filter before measurement. (b) The peak of size distribution (from (a)) *vs.* PEG content (from Table S1). The size distribution of NH_2-UiO-66 is 3~7 µm, and 2.5~6 µm for 0.5Br, much larger than the sizes observed in SEM (Figure 1a, 1b in main text) due to the aggregation. The 0.5Br-1P is less aggregated than 0.5Br but still exhibit some aggregation because the PEG brush is too short to make it 100% dispersed. 0.5Br-2P particle size is in good agreement to the raw MOF size acquired in SEM (Figure 1a in main text). 0.5Br-4P particle size is in consistent to the SEM image (Figure 1c in main text). For the well-dispersed samples, the size distribution peak shift from 30 to 70 nm as the PEG feeding ratio increases, reflecting the increasing shell thickness of P@MOF. This result suggests the improved dispersity of the P@MOF comparing with the raw MOF.

SI2 Contact angles for NH_2-UiO-66 and 0.5Br-2P films.

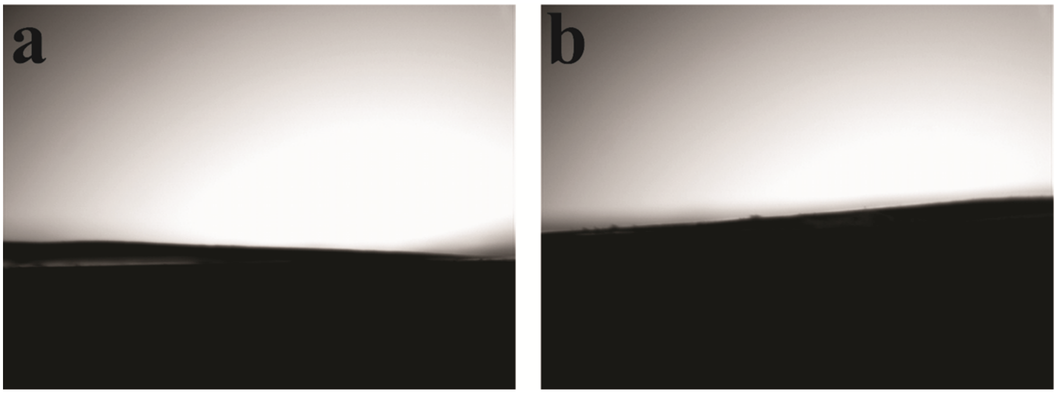

Figure S2 Typical images reflecting water contact angles for NH_2-UiO-66 (a) and 0.5Br-2P (b) films. The water droplets were adsorbed within 1 second after dropped on the films in both cases, suggesting the super hydrophilicity of both samples.

SI3 Retention of MOF porosity.

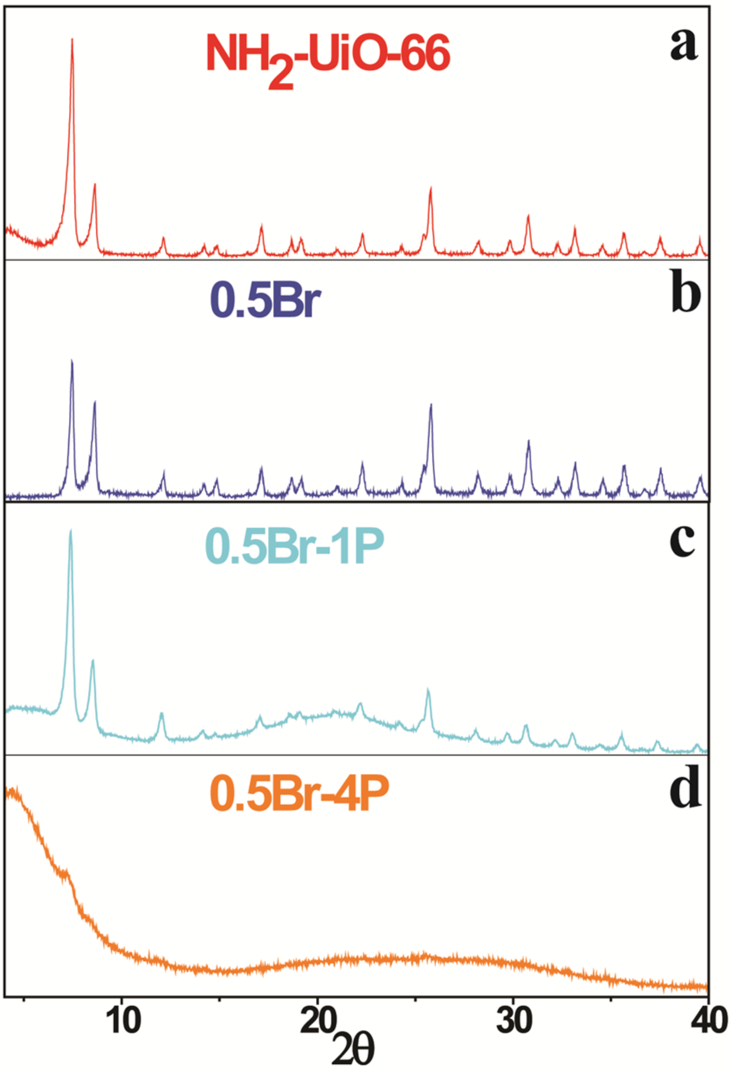

Figure S3 XRD spectra for NH_2-UiO-66 (a), 0.5Br (b), 0.5Br-1P (c) and 0.5Br-4P (d).

SI4 Measurement on degree of polymerization

The typical weight loss curves are displayed in Figure S5, and the corresponding calculated results are summarized in Table S1. The NH_2-UiO-66 started to lose weight at *ca.* 380 ^{o}C and the weight residual (Wr) at 550 ^{o}C is 40.0% (ZrO_2), agreeing with the previous reports.[2,7] Moreover, the weight loss curves of the xBr indicate that 16.1% of the amino groups were functionalized with bromide for 0.5Br. The degree of polymerization (DP) of PEGMA initiated by Br@MOF can be tuned by changing the feeding ratio of PEGMA to Br@MOF, as advised by the TGA curves of the P@MOFs in Figure S5b. It is observed that the weight losing onset temperature for the P@MOFs are in the range of 150-300 ^{o}C, close to that of pure PEG [8] but much lower than that of *ca.* 380 ^{o}C for NH_2-UiO-66. This is ascribed to the lower decomposition temperature of PEG. Moreover, dramatic slope changes on the weight loss curves can be observed for the P@MOF samples, implying the binary phase feature of the P@MOF. That is, the polymer shell was firstly burnt at high weight losing rate. After the oxidation of polymer shell was nearly finished, the MOF core started to decompose at relatively lower rate. The polymer content in the P@MOF can be calculated from the Wr of the samples and summarized in Table S1.

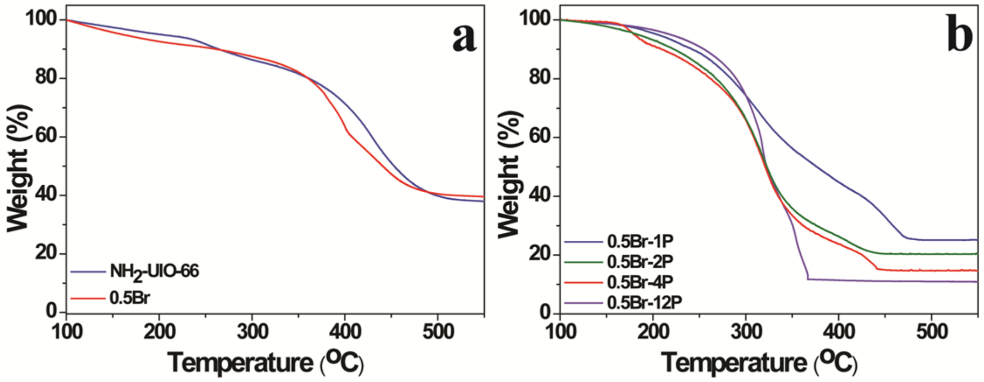

Figure S4 The TGA measurements for the samples as indicated. All the tests were performed in air with the heating rate of 10 ^{o}C min^{-1}.

Table S1 The calculated results from TGA curves.

Sample	**Weight Residual (Wr, %)**	**Content Beyond NH_2-UiO-66 (%)**	**Simulated Particle Image**[a)]
PEG	0.04	0	-
NH_2-UiO-66	40.0	0	
0.5Br	37.1	7.25 (16.1% NH-Br) [b)]	-
0.5Br-1P	25.5	36.2	
0.5Br-2P	20.5	50.2	
0.5Br-4P	15.0	62.5	
0.5Br-12P	10.8	73.0	

a) Orange circle refers to the NH_2-UiO-66 core and grey loop refers to the PEG based shell. The ratio between radius of core and thickness of thickness are calculated from PEG content, density of NH_2-UiO-66[9] and PEG[10], assuming the PEG chains are densely packed on the core surface.

b) The percentage of bromide-functionalization is calculated by finding the *r* value in the following equation:

$$\frac{123.2}{308+149r} = Wr .$$

Where 123.2, 308 and 149 are the mole weight of ZrO_2, NH_2-UiO-66 in our study and the α-bromoisobutyryl group, respectively, and *Wr* is the weight residual.

SI5 pH sensitive property of P@MOF.

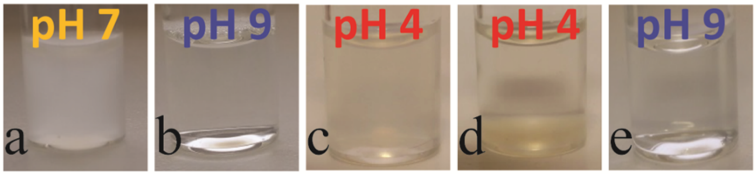

Figure S5 pH responsive property of 0.5Br-1P solution (0.5 mg normalized MOF per mL). The 0.5Br-1P water suspension transformed from the emulsion looking to a clear, transparent liquid as the pH value was adjusted to 9 (a to b). Then the pH was adjusted to 4, the transparent dispersion quickly turned to cloudy (c) and then the particles precipitated to the bottom within 3 minutes (d), and transformed to clear dispersion again if the pH returned to 9 (e). pH does not affect the dispersity of raw MOF.

Reference

1 E. H. H. Wong, M. P. van Koeverden, E. Nam, S. N. Guntari, S. H. Wibowo, A. Blencowe, F. Caruso and G. G. Qiao, *Macromolecules*, 2013, **46**, 7789–7796.

2 A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem. - A Eur. J.*, 2011, **17**, 6643–6651.

3 S. Jiang, Y. Ma, G. Jian, H. Tao, X. Wang, Y. Fan, Y. Lu, Z. Hu and Y. Chen, *Adv. Mater.*, 2009, **21**, 4953–4956.

4 Y. Xiong, J. M. Mclellan, J. Chen, Y. Yin, Z. Li and Y. Xia, *J. Am. Chem. Soc.*, 2005, **127**, 17118–17127.

5 M. Boudart, *Chem. Rev.*, 1995, **95**, 661–666.

6 H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A. F. England, T. Ikariya and R. Noyori, *Angew. Chemie Int. Ed.*, 1998, **37**, 1703–1707.

7 S. J. Garibay and S. M. Cohen, *Chem. Commun.*, 2010, **46**, 7700–7702.

8 L. Wang, J. Wang, X. Gao, Z. Liang, B.-K. B. Zhu, L. L. Zhu and Y. Y.-Y. Xu, *Polym. Chem.*, 2014, **5**, 2836.

9 Q. Yang, A. D. Wiersum, P. L. Llewellyn, V. Guillerm, C. Serre and G. Maurin, *Chem. Commun.*, 2011, **47**, 9603–9605.

10 H. Lin and B. D. Freeman, *J. Memb. Sci.*, 2004, **239**, 105–117.