Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Unbalanced MOF-on-MOF growth for the production of lopsided core-shell of MIL-88B@MIL-88A with mismatched cell parameters

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General Methods

Solvents and all other chemicals were obtained from commercial sources and used as-received unless otherwise stated. All scanning electron microscopy (SEM) images were acquired using a JEOL JSM-7001F field-emission SEM. All scanning transmission electron microscopy (STEM) images were acquired on a FEI Tecnai G2 F30 ST using dark-field imaging in the STEM mode at 300 kV (Korea Basic Science Institute, Seoul, Korea). All transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were acquired using a JEOL JEM-2100F at 200 kV (Center for Microcrystal Assembly, Sogang University). X-ray diffraction patterns were obtained using a Rigaku Ultima IV equipped with a graphite-monochromated Cu Kα radiation source (40 kV, 40 mA). Thermogravimetric analysis (TGA) measurements were conducted using a Shimadzu TGA-50 under a nitrogen atmosphere at a heating rate of 10 ℃ min^{-1}. To ensure similar experimental conditions, all PXRD and TGA data for the samples were measured after the same pre-treatment (under dynamic vacuum at room temperature for 30 min). MDI Jade 9.0 software was used to calculate the cell parameters of the samples.

Preparation of MIL-88B

A precursor solution was prepared by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ (64.0 mg, 0.16 mmol) and 1,4-benzenedicarboxylic acid (30.0 mg, 0.18 mmol) in 4 mL of *N*,*N*-dimethylformamide (DMF). Next, 4 mL of CH_3CN was added to the precursor solution.[1] The resulting mixture was placed in an oil bath (110 ℃) for 40 min. The resulting MIL-88B particles after the reaction were isolated by cooling to room temperature, and subsequently washed with fresh DMF and methanol via several centrifugation-redispersion cycles.

Preparation of MIL-88A

A precursor solution was prepared by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ (64.0 mg, 0.16 mmol) and fumaric acid (21.0 mg, 0.18 mmol) in 8 mL of DMF. After sonication for 30 min, the resulting mixture was placed in an oil bath (110 ℃) for 10 min. The resulting MIL-88A particles after the reaction were isolated by cooling to room temperature, and subsequently washed with fresh DMF and methanol via several centrifugation-redispersion cycles.

Preparation of MIL-88B@MIL-88A

A precursor solution was prepared by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ (64.0 mg, 0.16 mmol) and fumaric acid (21.0 mg, 0.18 mmol) in 8 mL of DMF in the presence of MIL-88B template (2.5 mg). After sonication for 30 min, the resulting mixture was placed in an oil bath (110 ℃) for 10 min. The resulting MIL-88B@MIL-88A particles were isolated by cooling to room temperature, and subsequently washed with fresh DMF and methanol via several centrifugation-redispersion cycles.

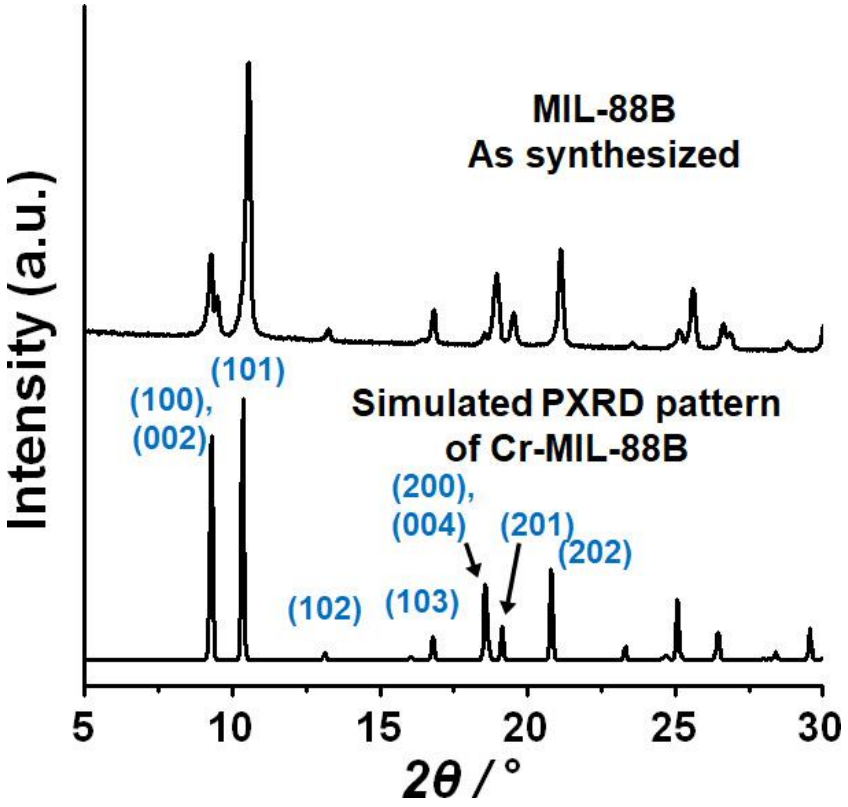

Fig. S1 PXRD pattern of MIL-88B (top) and simulated PXRD pattern[2] of Cr-MIL-88B (bottom).

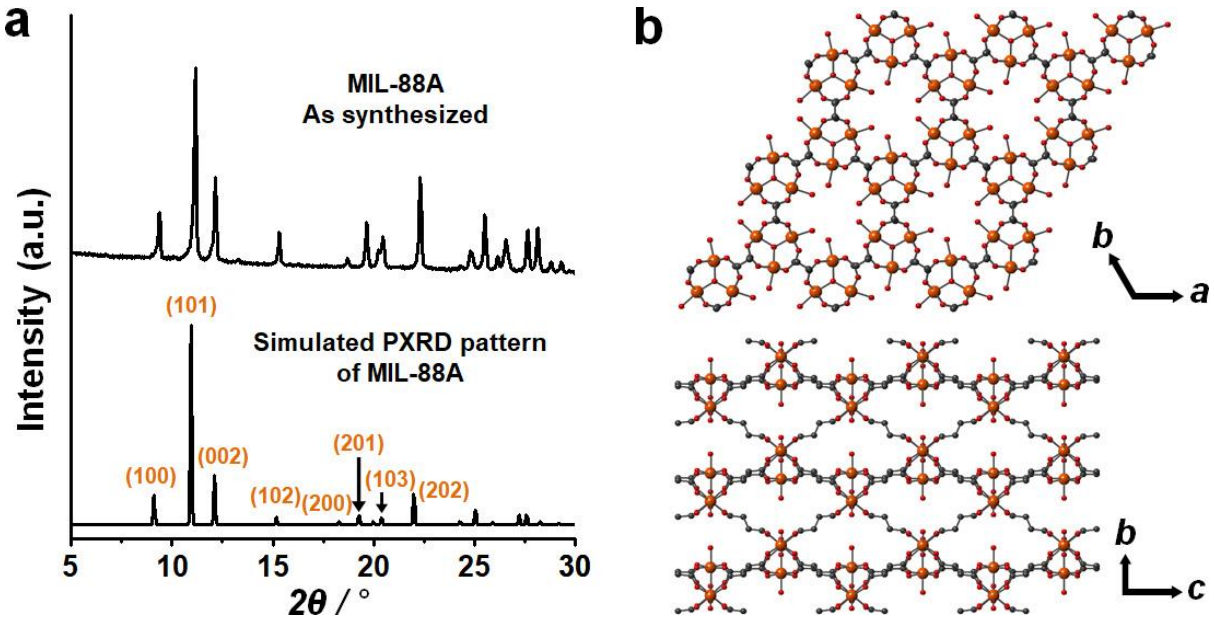

Fig. S2 (a) PXRD pattern of MIL-88A (top) and simulated PXRD pattern[3] of MIL-88A (bottom). (b) Ball-and-stick representation for MIL-88A.

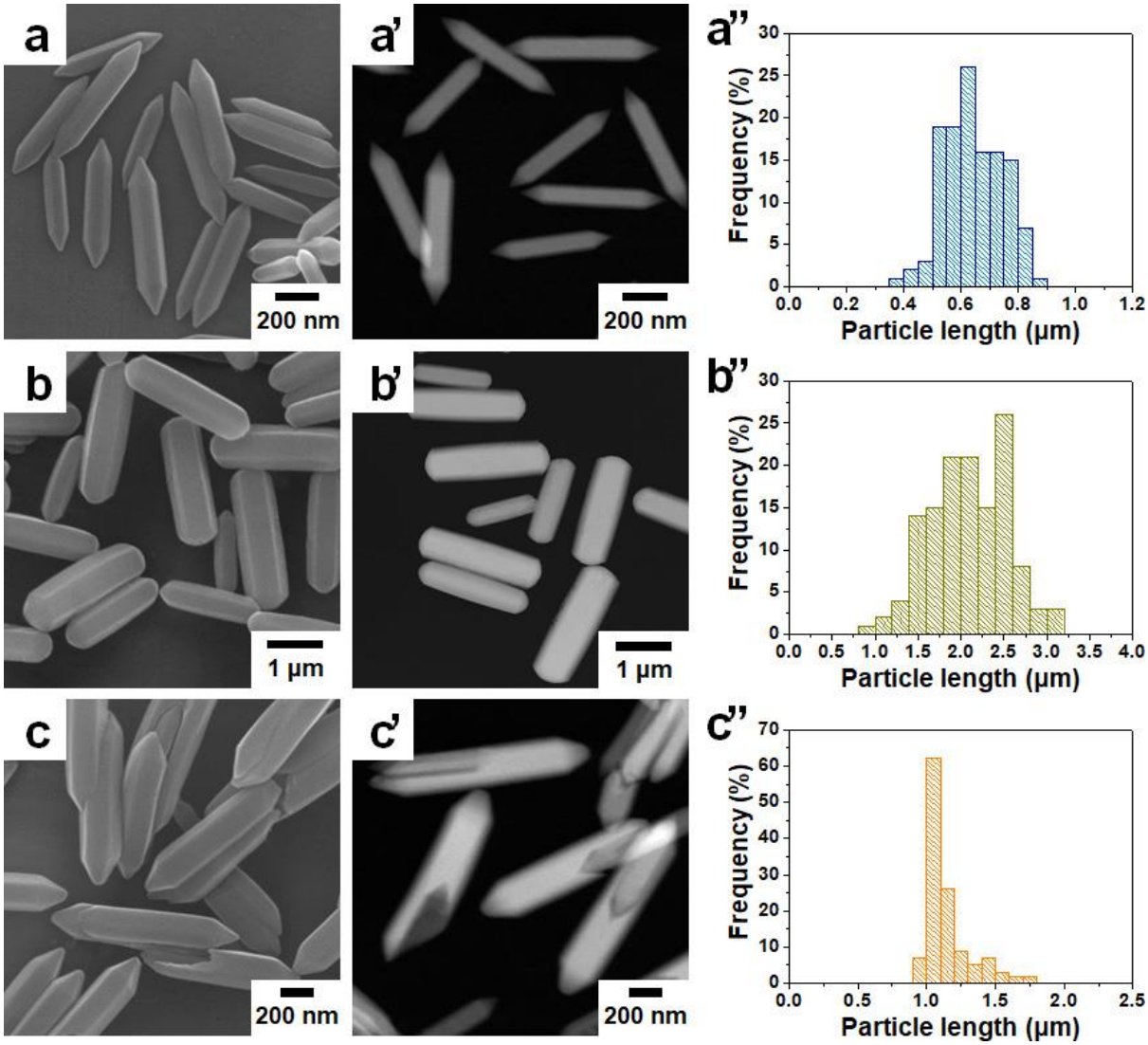

Fig. S3 SEM images, STEM images, and size distributions of (a) MIL-88B template, (b) pure MIL-88A obtained in the absence of MIL-88B template, and (c) lopsided core-shell of MIL-88B@MIL-88A obtained in the presence of MIL-88B template. The size distributions of MIL-88B, MIL-88A, and MIL-88B@MIL-88A were measured from SEM images and the average sizes (length) of MIL-88B, MIL-88A, and MIL-88B@MIL-88A were 0.65 ± 0.10, 2.09 ± 0.45, and 1.15 ± 0.17 μm, respectively.

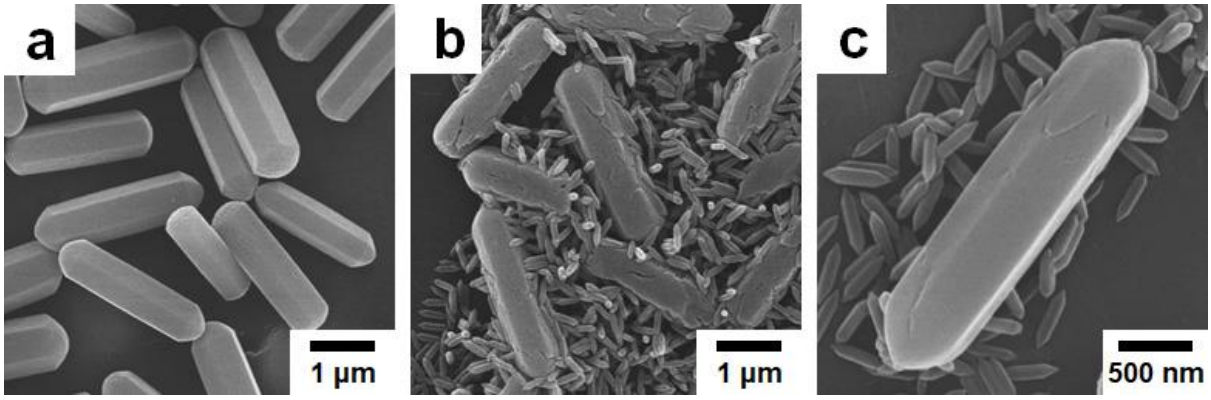

Fig. S4 (a) SEM image of pure MIL-88A template. (b,c) SEM images of product obtained from the reaction of $Fe(NO_3)_3 \cdot 9H_2O$ (64.0 mg) and H_2BDC (30.0 mg) in the presence of MIL-88A template (2.5 mg) during 40 min.

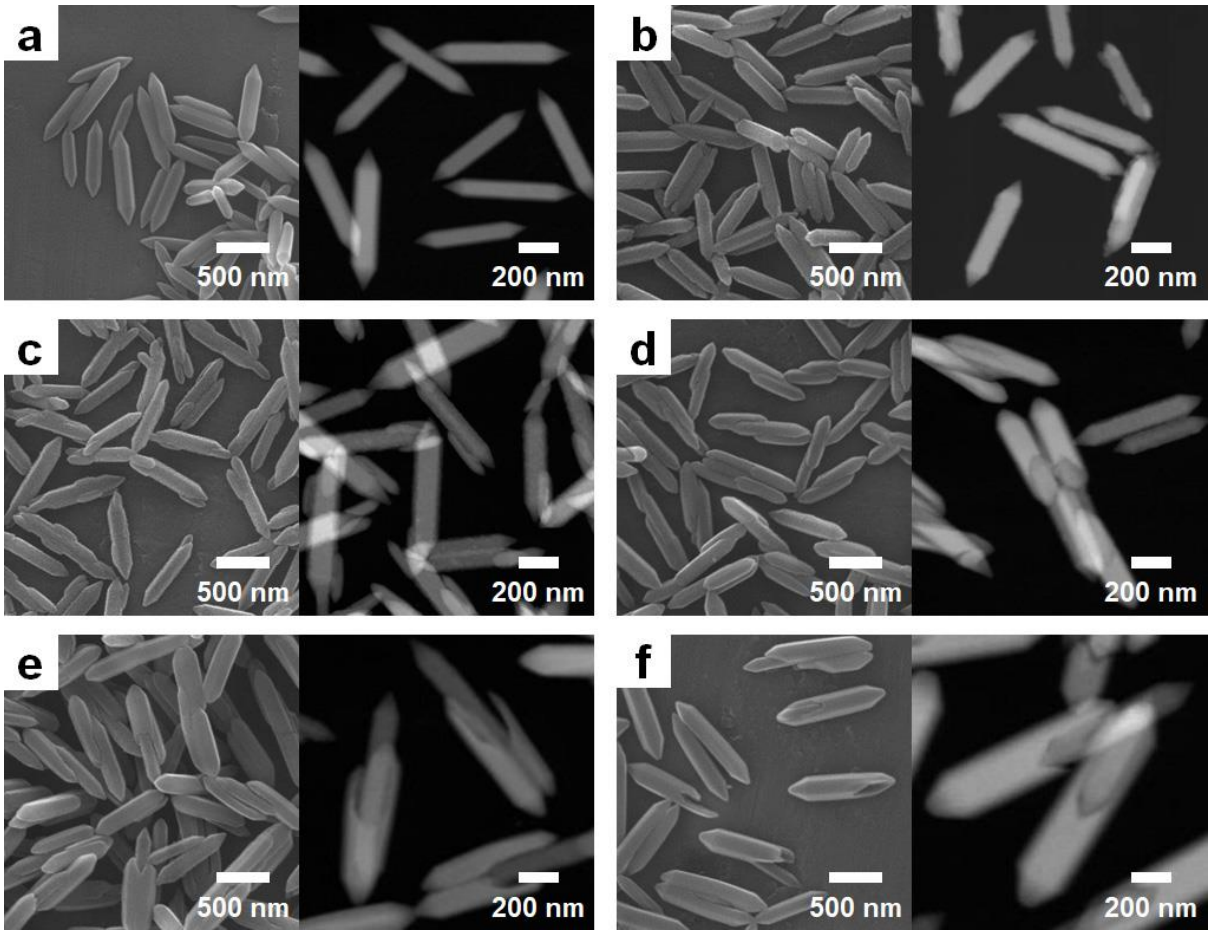

Fig. S5 SEM and STEM images monitoring the formation of the lopsided core-shell of MIL-88B@MIL-88A. SEM and STEM images acquired from the samples collected from the reaction solution at different times (a) 0 min (initial template), (b) 2 min, (c) 4 min, (d) 6 min, (e) 8 min, and (f) 10 min.

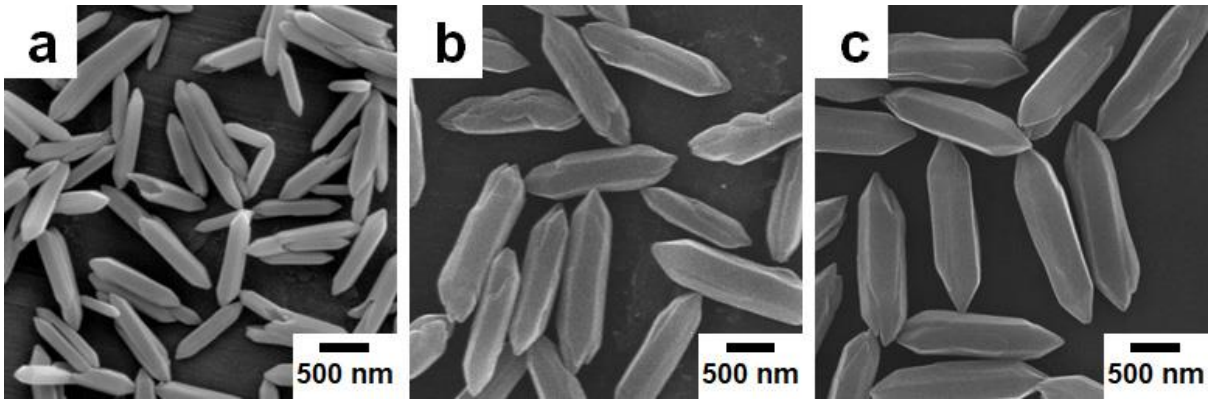

Fig. S6 (a) SEM image of core-shell of MIL-88B@MIL-88A obtained from the reaction of $Fe(NO_3)_3 \cdot 9H_2O$ (64.0 mg) and fumaric acid (21.0 mg) in the presence of MIL-88B template (2.5 mg) during 10 min. (b) SEM image of core-shell of MIL-88B@MIL-88A obtained from the reaction of $Fe(NO_3)_3 \cdot 9H_2O$ (128.0 mg) and fumaric acid (42.0 mg) in the presence of MIL-88B template (2.5 mg) during 10 min. (c) SEM image of core-shell of MIL-88B@MIL-88A obtained from the reaction of $Fe(NO_3)_3 \cdot 9H_2O$ (128.0 mg) and fumaric acid (42.0 mg) in the presence of MIL-88B template (2.5 mg) during 30 min.

Table S1. The numbers of core-shell MIL-88B@MIL-88A, empty MIL-88A shell, naked MIL-88B core, and pure MIL-88A counted from several SEM images.

	MIL-88B@ MIL-88A	Empty MIL-88A shell	Naked MIL-88B core	Pure MIL-88A	Total
Number of particles counted	154	123	106	0	383
Percent (%)	40.2	32.1	27.7	0	100

Table S2. The relative ratios between MIL-88B and MIL-88A within samples obtained at different time points.

Reaction Time	Ratio[a] (MIL-88B : MIL-88A)
4 min	0.70 : 0.30
6 min	0.39 : 0.61
8 min	0.28 : 0.72
10 min	0.26 : 0.74

[a]The relative ratios between MIL-88B and MIL-88A within samples were determined from the TGA curves. The weight loss percentages related to the decomposition of MIL-88B to metal oxide and MIL-88A to metal oxide in the TGA curves of MIL-88B and MIL-88A are different and characteristic. And so the approximation on the relative ratios between MIL-88B and MIL-88A within samples can be calculated from the weight loss percentages in the TGA curves of the samples obtained at different time points.

References

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2 S. Surblé, C. Serre, C. Mellot-Draznieks, F. Millange and G. Férey, *Chem. Commun.*, 2006, 284-286.

3 C. Serre, F. Millange, S. Surblé and G. Férey, *Angew. Chem., Int. Ed.*, 2004, **43**, 6286-6289.