

Electronic supplementary information

Heterogeneous nucleation and growth of highly crystalline imine-linked covalent organic frameworks

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Chemicals

All reagents were purchased from commercial sources and used without further purification. Solvents were used without prior drying procedures.

Characterizations

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/max 2500 Diffractometer operated at 40 kV and 20 mA with Cu K α radiation ($\lambda = 1.5416 \text{ \AA}$) ranging from 2° to 30° with a speed of $2^\circ/\text{min}$ at ambient temperature.

FT-IR spectra were recorded with a Bruker RFS100/S instrument in the range of 400 to 4000 cm^{-1} with an interval of 4 cm^{-1} .

Scanning electron microscope (SEM) images were collected using HITACHI SU8020 scanning electron microscopy at an accelerating voltage of 5 kV and accelerating current of $10 \mu\text{A}$.

Transmission Electron Microscope (TEM) images were collected using JEM-2100F transmission electron microscopy at an accelerating voltage of 200 kV. The TEM samples were prepared by dropping the sample from anhydrous ethanol on copper grids.

Nitrogen adsorption and desorption isotherms were measured using Micromeritics ASAP-2460 Surface Area and Porosity Analyzer. The samples loaded in sample tubes were heated to $100 \text{ }^\circ\text{C}$ under a vacuum of 0.5 mtorr for 24 h, and the measurements

were conducted at liquid nitrogen temperature (77 K) using ultrahigh-purity grade nitrogen (99.999%).

Solid state ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 M NMR spectrometer.

Experimental details

Synthesis of SiO_2 nanospheres: SiO_2 nanospheres were synthesized based on modification of protocols reported by Mondal et al.¹ and Song et al.² Uniform SiO_2 nanospheres with an average particle size of ~ 200 nm were synthesized according to the modification of the StÖber method. Briefly, 3.40 mL of aqueous ammonia (32 wt.%) was added to the mixture solution of 20 mL of deionized and 120 mL of ethanol after stirring for 30 min at 25 °C. 12 mL of tetraethoxysilane (TEOS) was added to the above solution quickly and was kept stirring for another 1 h to yield monodisperse SiO_2 spheres. After washing three times with ethanol by centrifugation and redispersion and dried under vacuum for 24 hours.

Amino-functionalization of SiO_2 nanospheres: 1g SiO_2 nanospheres were dispersed in 180 mL ethanol by sonication. A mixture of 300 μL APTES and 20 mL ethanol was slowly added to the previous solution under vigorous stirring at 25 °C, stirring for another 6 h to functionalize the silica surface with $-\text{NH}_2$ groups. The surface modified particles were washed with ethanol and dried under vacuum for 24 hours for further use.

Synthesis of heterogeneous nuclei: 1,3,5-triformylbenzene (TFB, 6.46 mg, 0.04 mmol) was dissolved in 1 mL of NH_2 -f- SiO_2 suspension (100 mg mL^{-1} in dioxane). The mixture was stirred for 1 h before 1,4-phenylenediamine (PDA, 6.46 mg, 0.06 mmol) and 18 μL of acetic acid were added. The final concentration of NH_2 -f- SiO_2 suspension is 50 mg/mL. After reaction, the solution was used right away in the following procedures.

Synthesis of highly crystalline NH_2 -f- SiO_2 @LZU1: TFB (32.4 mg, 0.2 mmol) and PDA (32.4 mg, 0.3 mmol) was dissolved in 1 mL of seed solution (50 mg/mL), respectively. These two solutions were mixed and 90 μL of acetic acid was added. The reaction mixture (2 mL in total) was transferred into a 5-mL two-neck round-bottle flask and heated for 3 h at 120 °C. One neck of the flask was equipped with a rubber stopper and the other neck was connected with a condenser. After reaction, the precipitates were collected by centrifugation and washed with THF for several times. Finally, the precipitates were dried at 70 °C for 12 h in vacuum.

Synthesis of highly crystalline NH_2 -f- SiO_2 @LZU1 with different thickness of LZU1: all procedures were the same as above expect that the seed solution was diluted with 1,4-dioxane before use.

Synthesis of SiO₂@LZU1: All procedures were the same as before except that the NH₂-f-SiO₂ was replaced by SiO₂.

Preparation of hollow LZU1: 5 mg of highly crystalline NH₂-f-SiO₂@LZU1 was dispersed in 5 mL of 1% HF aqueous solution. The mixture was stirred at room temperature for 12 h. The remaining solids were collected by centrifugation, rinsed with ethanol and finally dried under vacuum.

Synthesis of imine-linked polymer particles without NH₂-f-SiO₂: TFB (32.4 mg, 0.2 mmol) and PDA (32.4 mg, 0.3 mmol) was dissolved in 0.5 mL of Dioxane, respectively. The mixture was sonicated at room temperature until the monomers were fully dissolved. The two solution were combined and 18 μL of acetic acid were added. The reaction mixture (1 mL in total) was transferred into a 5-mL two-neck round-bottle flask and heated for 5 min at 120 °C. One neck of the flask was equipped with a rubber stopper and the other neck was connected with a condenser. After reaction, the precipitates were collected by centrifugation and washed with THF for several times. Finally, the precipitates were dried at 70 °C for 12 h in vacuum.

Synthesis of highly crystalline COF-LZU1 without NH₂-f-SiO₂: TFB (32.4 mg, 0.2 mmol) and PDA (32.4 mg, 0.3 mmol) was dissolved in 0.5 mL of Dioxane, respectively and sonicated at room temperature until the monomers were fully dissolved. The two solutions were added into 1 mL of Schiff-base polymer solution (50 mg/mL in dioxane). 90 μL of acetic acid were added to the mixture. The final concentration of the imine-linked polymer was 25 mg/mL. The reaction mixture (2 mL in total) was transferred into a 5-mL two-neck round-bottle flask and heated for 3 h at 120 °C. One neck of the flask was equipped with a rubber stopper and the other neck was connected with a condenser. After reaction, the precipitates were collected by centrifugation and washed with THF for several times. Finally, the precipitates were dried at 70 °C for 12 h in vacuum.

Synthesis of COF-LZU1 through homogeneous nucleation method: TFB (32.4 mg, 0.2 mmol) and PDA (32.4 mg, 0.3 mmol) was dissolved in 1 mL of Dioxane, respectively and sonicated at room temperature until the monomers were fully dissolved. 90 μL of acetic acid were added to the mixture. The reaction mixture (2 mL in total) was transferred into a 5-mL two-neck round-bottle flask and heated for 3 h at 120 °C. One neck of the flask was equipped with a rubber stopper and the other neck was connected with a condenser. After reaction, the precipitates were collected by centrifugation and washed with THF for several times. Finally, the precipitates were dried at 70 °C for 12 h in vacuum.

Synthesis of heterogeneous nuclei for TpPa-1: 1,3,5-triformylphloroglucinol (TFP, 8.40 mg, 0.04 mmol) was dissolved in 1 mL of NH₂-f-SiO₂ suspension (100 mg mL⁻¹ in dioxane). The mixture was stirred for 1 h before PDA (6.46 mg, 0.06 mmol) and 18

μL of acetic acid were added. The reaction mixture was further stirred for 3 h at room temperature. After reaction, the solution was used right away in the following procedures.

Synthesis of highly crystalline $\text{NH}_2\text{-f-SiO}_2\text{@TpPa-1}$: TFP (43.0 mg, 0.2 mmol) and PDA (32.4 mg, 0.3 mmol) was dissolved in 1 mL of heterogeneous nuclei solution (50 mg/mL), respectively. These two solutions were mixed and 90 μL of acetic acid was added. The reaction mixture (2 mL in total) was transferred into a 5-mL two-neck round-bottle flask and heated for 3 h at 120 °C. One neck of the flask was equipped with a rubber stopper and the other neck was connected with a condenser. After reaction, the precipitates were collected by centrifugation and washed with THF for several times. Finally, the precipitates were dried at 70 °C for 12 h in vacuum.

Synthesis of TpPa-1 through homogeneous nucleation method: TFP (43.0 mg, 0.2 mmol) and PDA (32.4 mg, 0.3 mmol) was dissolved in 1 mL Dioxane, respectively. These two solutions were mixed and 90 μL of acetic acid was added. The reaction mixture (2 mL in total) was transferred into a 5-mL two-neck round-bottle flask and heated for 3 h at 120 °C. One neck of the flask was equipped with a rubber stopper and the other neck was connected with a condenser. After reaction, the precipitates were collected by centrifugation and washed with THF for several times. Finally, the precipitates were dried at 70 °C for 12 h in vacuum.

Calculation of the number of seeds in a given volume

The average diameter of SiO_2 nanospheres = 200 nm

The volume of a single SiO_2 nanospheres = 4188790.20 nm^3

The mass density of SiO_2 = 2.2 g/cm^3 = 2.2 * 10⁻²¹ g/nm^3

Then, the mass of a single SiO_2 = 9.22 * 10⁻¹⁵ g

The average thickness of amorphous polymer shell in seeds = 23 nm

The volume of the amorphous polymer shell in a single seed = 3605991.257 nm^3

The molecular weight of a two-dimensional single cell in COF-LZU1 = 540.576 g/mol

The lattice parameters of COF-LZU1: a = b = 2.181 nm, c = 0.346 nm

The volume of a three-dimensional single cell = 6.583 nm^3

The area of a two-dimensional single cell in COF-LZU1 = 19.027 nm^2

The number of cells in a single seeds =
$$\frac{3605991.257}{6.583} = 547744.7863$$

The mass of amorphous polymer shell in a single seed = 4.92 * 10⁻¹⁶ g

From above calculation, the mass of a single seed is 9.22 * 10⁻¹⁵ g + 4.92 * 10⁻¹⁶ g = 9.71 * 10⁻¹⁶ g = 9.71 * 10⁻¹³ mg.

When the concentration of seeds is 1 mg/mL, the number density of seeds in solution

is $1.03 \times 10^{12}/\text{mL}$.

Additional figures

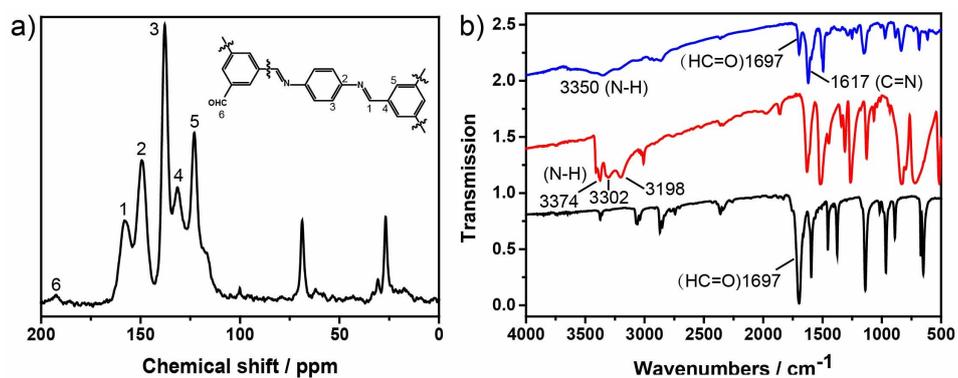


Figure S1. (a) solid-state ^{13}C NMR and (b) FT-IR spectra of amorphous seeds (blue), PDA (red) and TPB (black). The number 1, 2, 3, 4, 5, and 6 in (a) represent the characteristic peaks in 157, 148, 137, 130, 122, and 191 ppm, respectively.

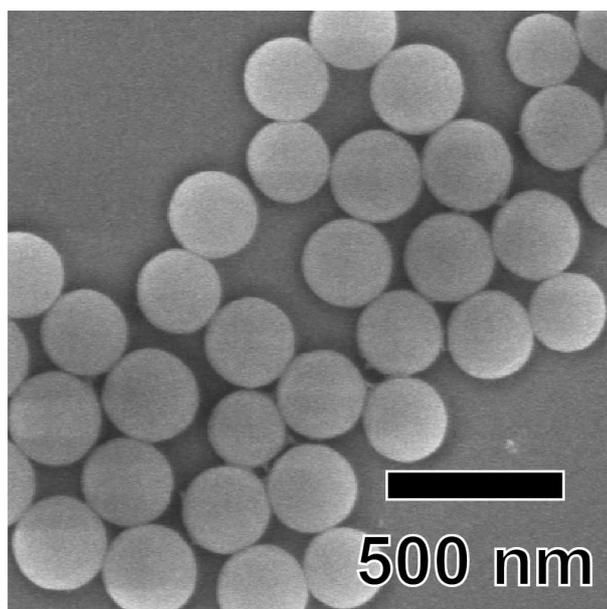


Figure S2. SEM image of SiO_2

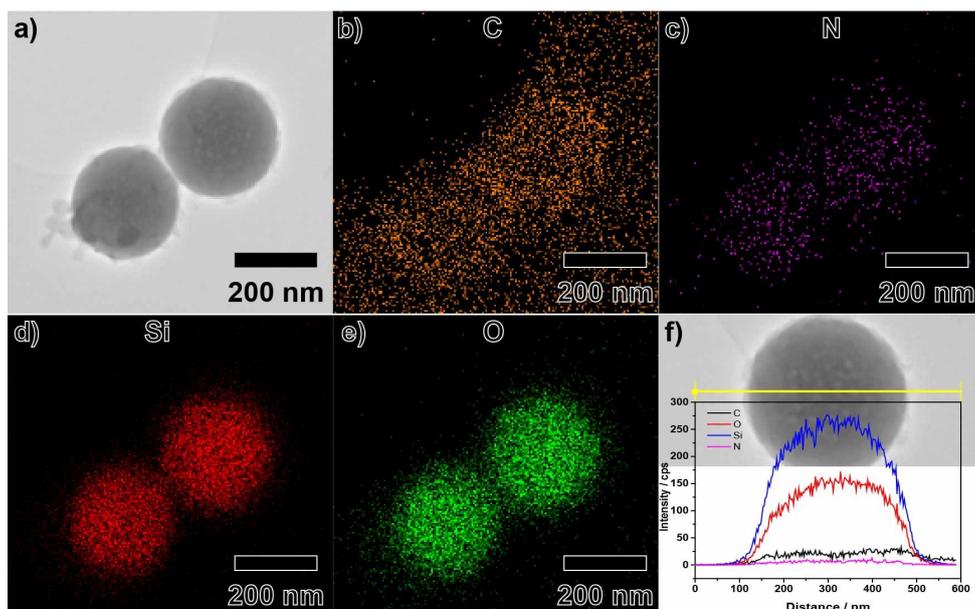


Figure S3. TEM EDS mapping and linear analysis. (a) TEM image for EDS mapping, (b)-(e) element mapping distributions and (f) Linear analysis of elements across the sphere.

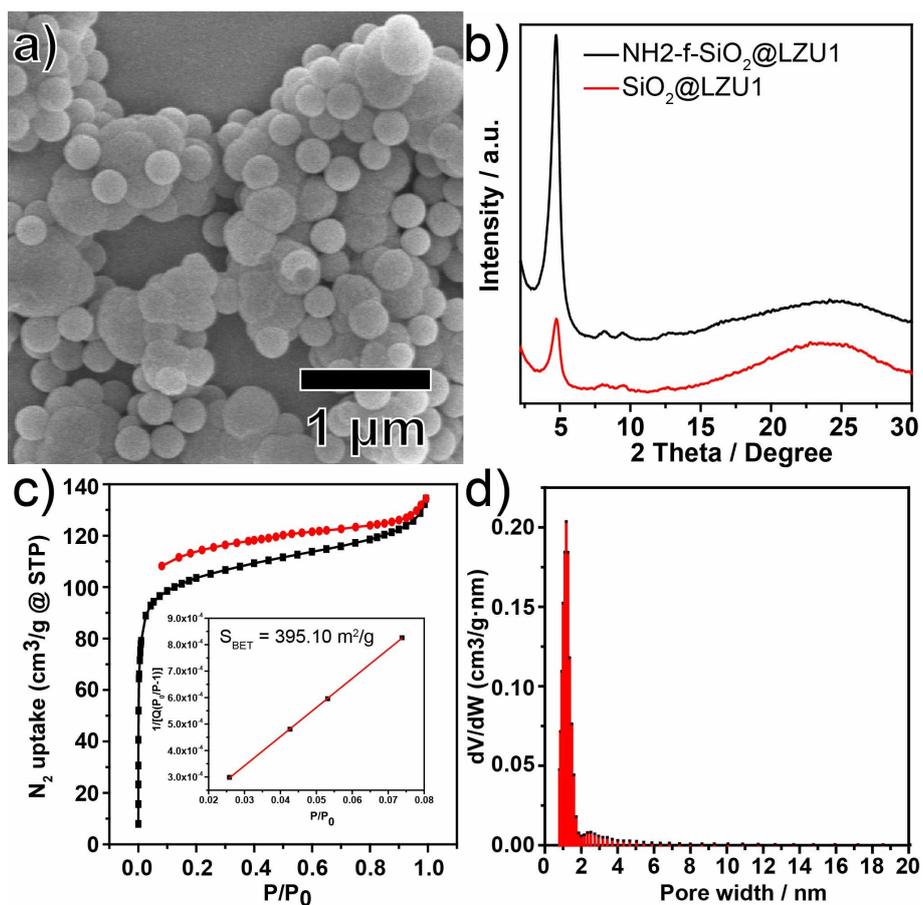


Figure S4. (a) SEM images, (b) PXRD pattern (red) and (c) N_2 sorption isotherm of LZU1 growth on SiO_2 without amino functionalization ($SiO_2@LZU1$)

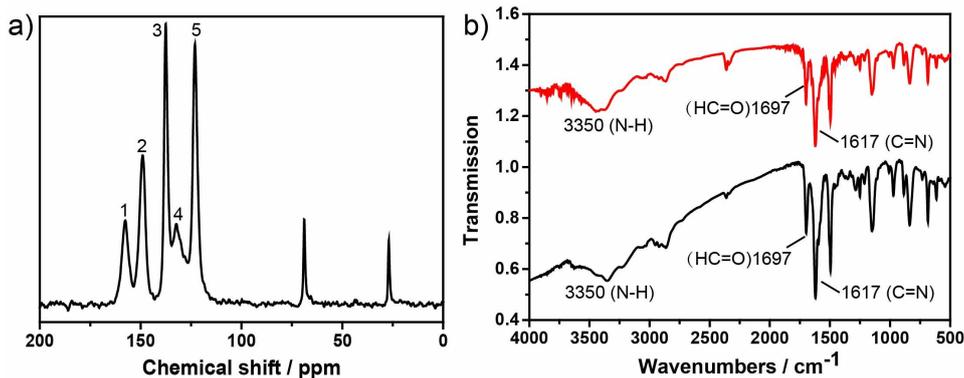


Figure S5. (a) solid-state ^{13}C NMR of COF hollow spheres, (b) FT-IR spectra of $\text{NH}_2\text{-f-SiO}_2\text{@LZU1}$ (red) and COF hollow spheres (black).

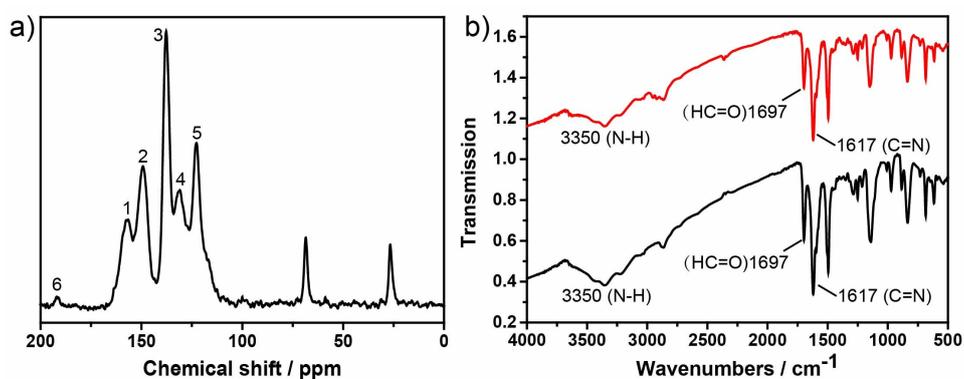


Figure S6. (a) solid-state ^{13}C NMR of highly crystalline COF-LZU1 microspheres synthesized without the help of $\text{NH}_2\text{-f-SiO}_2$, (b) FT-IR spectra of amorphous imine-linked polymer microspheres synthesized without the help of $\text{NH}_2\text{-f-SiO}_2$ (red) and highly crystalline COF-LZU1 microspheres (black).

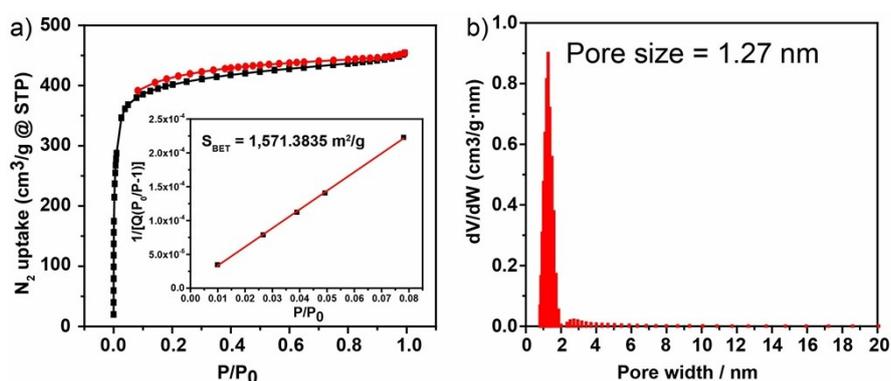


Figure S7. (a) The N_2 sorption isotherm (inset shows the BET surface area) and (b) pore size distribution of COF-LZU1 hollow spheres. Concentration of seeds: 25 mg/mL.

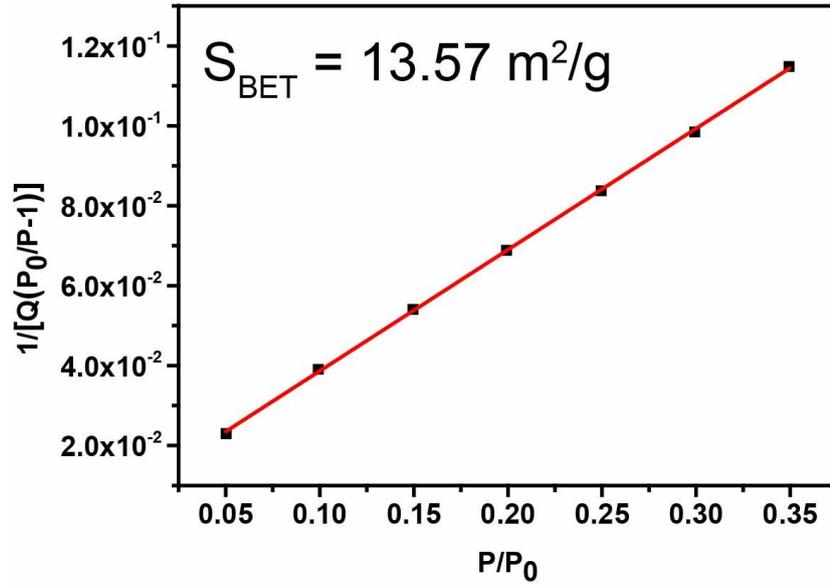


Figure S8. The BET specific area of amorphous seeds

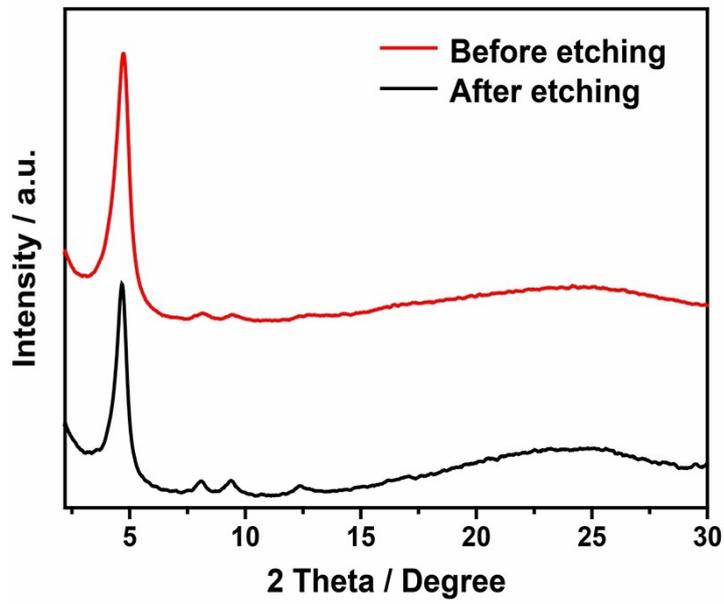


Figure S9. Comparison of crystallinity between before and after etching.

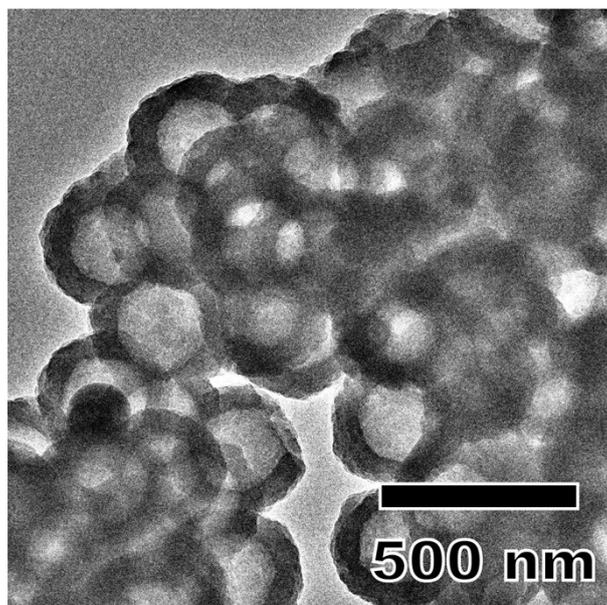


Figure S10. The TEM image of hollow COFs. The concentration of seeds is 12.5 mg/mL.

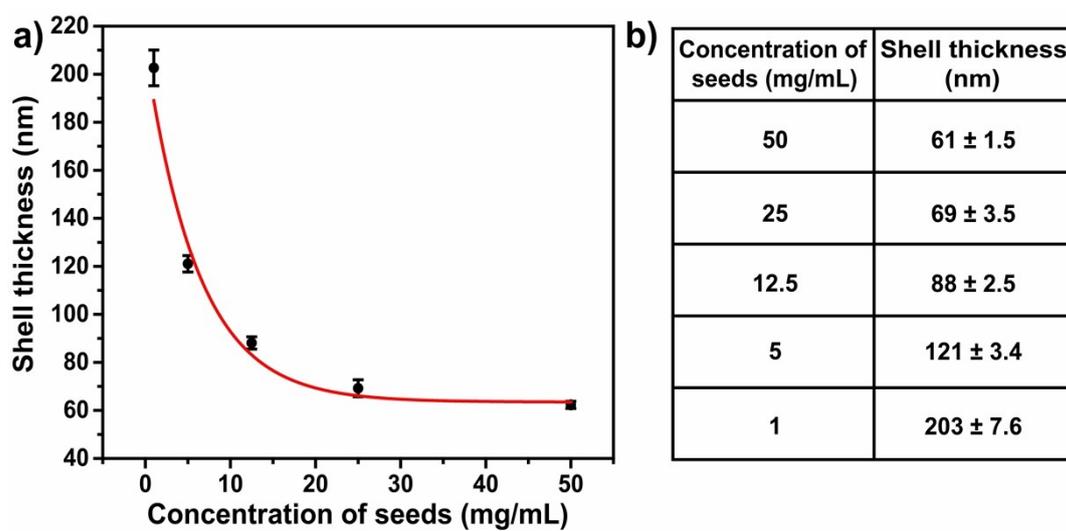


Figure S11. (a) The scatter plot of the concentration of seeds and the shell thickness, (b) The table of the concentration of seeds and the shell thickness.

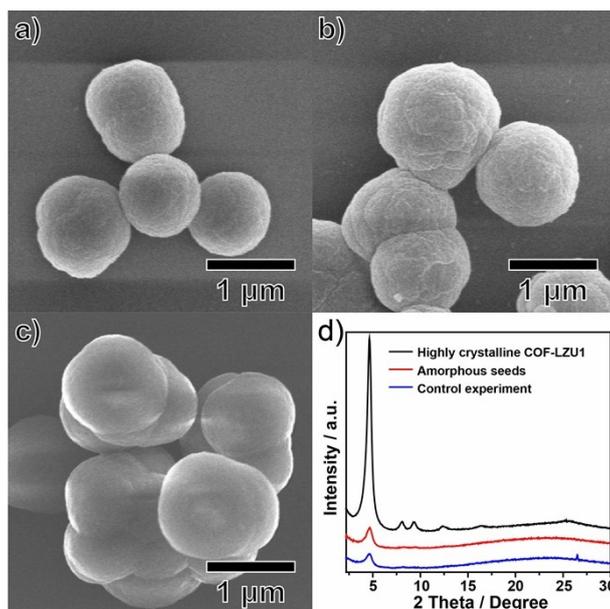


Figure S12. The SEM images of (a) amorphous imine-linked polymer microspheres, (b) highly crystalline COF-LZU1 microspheres and (c) particles obtained through one-step homogeneous method; (d) The corresponding PXRD patterns.

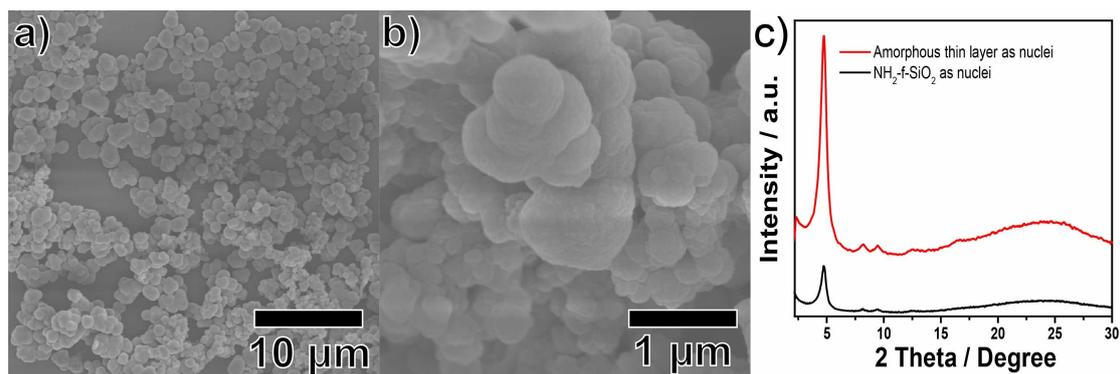


Figure S13. We directly used NH₂-f-SiO₂ as seeds to synthesize COFs. (a) and (b) SEM images of as-synthesized materials, (c) PXRD patterns of as-synthesized materials using amorphous thin layer as seeds (red) and using NH₂-f-SiO₂ as seeds.

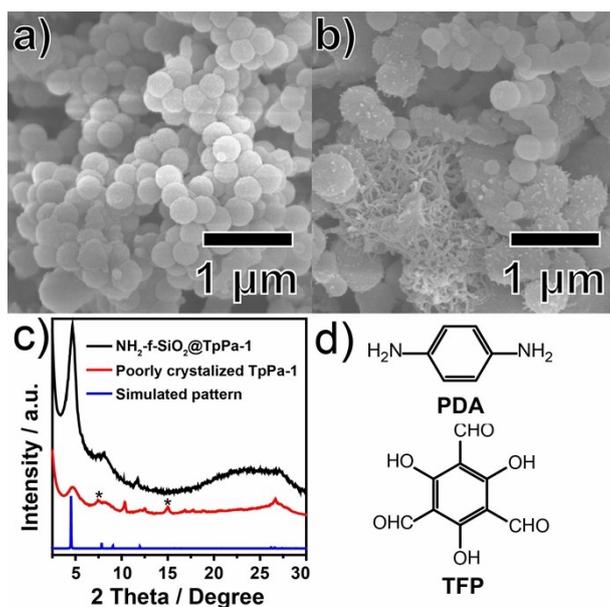


Figure S14. SEM images of (a) highly crystalline $\text{NH}_2\text{-f-SiO}_2\text{@TpPa-1}$ and (b) TpPa-1 obtained through homogeneous nucleation method; (c) The corresponding XRD patterns and (d) Molecular structure of PDA and TFP.

In the pattern of poorly crystallized TpPa-1 (Fig. S13c), the identity of peaks marked with asterisk may arise from the residual intensity of monomers. In the fig. S8 of ref. 3, the blue pattern shows the XRD peaks of PDA which is matched with marked peaks in fig. S13c.

Notes and references

1. B. Banerjee, R. Singuru, S. K. Kundu, K. Dhanalaxmi, L. Bai, Y. Zhao, B. M. Reddy, A. Bhaumik and J. Mondal, *Catal. Sci. Technol.*, 2016, **6**, 5102.
2. P. Li, C-Y. Cao, Z. Chen, H. Liu, Y. Yu and W-G. Song, *Chem. Commun.*, 2012, **48**, 10541.
3. S.-Y. Ding, J. Gao, Q. Wang, Y. Zhang, W.-G. Song, C.Y. Su and W. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 19816.