

[Supporting Information]

[COF-300]-[UiO-66] Composite Membrane with
Remarkably High Permeability and H₂/CO₂
Separation Selectivity

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Table of Contents

Sections	Topics	Pages
1	Materials	S3
2	Defect-included UiO-66 structure in the UiO-66 membrane	S4
3	Variable temperature X-ray diffraction (XRD) study	S5
4	Variable temperature Fourier transform infrared (FT-IR) spectroscopic analysis	S7
5	Thermogravimetric analysis (TGA)	S9
6	Low pressure gas sorption measurements 6.1. Low pressure N ₂ sorption measurements 6.2. Low pressure H ₂ and CO ₂ sorption measurements	S11
7	References	S14

Section 1. Materials

Polyaniline emeraldine base, terephthalic acid and acetic anhydride (99.5%) were purchased from Sigma-Aldrich, Inc. Raney-nickel was purchased from Aladdin. Unless otherwise stated, all other starting materials and solvents were supplied by J&K Scientific Ltd. and used as received without further purification.

Tetrakis(4-aminophenyl)methane was synthesized as per previous reports^[1] with some alterations, as follows:

Synthesis of tetrakis(4-nitrophenyl)methane: Briefly, 30.0 mL of fuming nitric acid was poured into a 500 mL flask and cooled to -10 °C. Tetraphenylmethane (5.0 g, 15.6 mmol) was slowly added to the flask under vigorous stirring. After this, 16.7 mL of acetic anhydride and 33.3 mL of acetic acid were added dropwise to the mixture. The mixture was stirred at -10 °C for 1 h, following which 160.0 mL of acetic acid was added to it and stirred for another 2 h. It was filtered, washed subsequently with acetic acid (100 mL × 2), methanol (100 mL × 2), cold THF (50 mL × 2) and degassed at 60 °C for 8 h affording a yellow powder (3.0 g, yield: 38.4%).

Synthesis of tetrakis(4-aminophenyl)methane: Tetrakis(4-nitrophenyl)methane (1.8 g, 3.6 mmol) was dissolved in 120.0 mL THF. After this, ca. 12.0 g of Raney-nickel was carefully added to it. The solution thereby obtained was refluxed at 70 °C with dropwise addition of N₂H₄·H₂O (8.0 mL, 164.6 mmol). After a reflux time of 4 h, the precipitate was later isolated by filtration, washed with ethanol, and rotary evaporated under reduced pressure to obtain a white solid. The white solid was washed with ethanol (50 mL × 2), and finally degassed at 80 °C for 8 h to give tetrakis(4-aminophenyl)methane as white powder (1.0 g, yield: 73.2%).

Section 2. Defect-included UiO-66 structure in the UiO-66 membrane

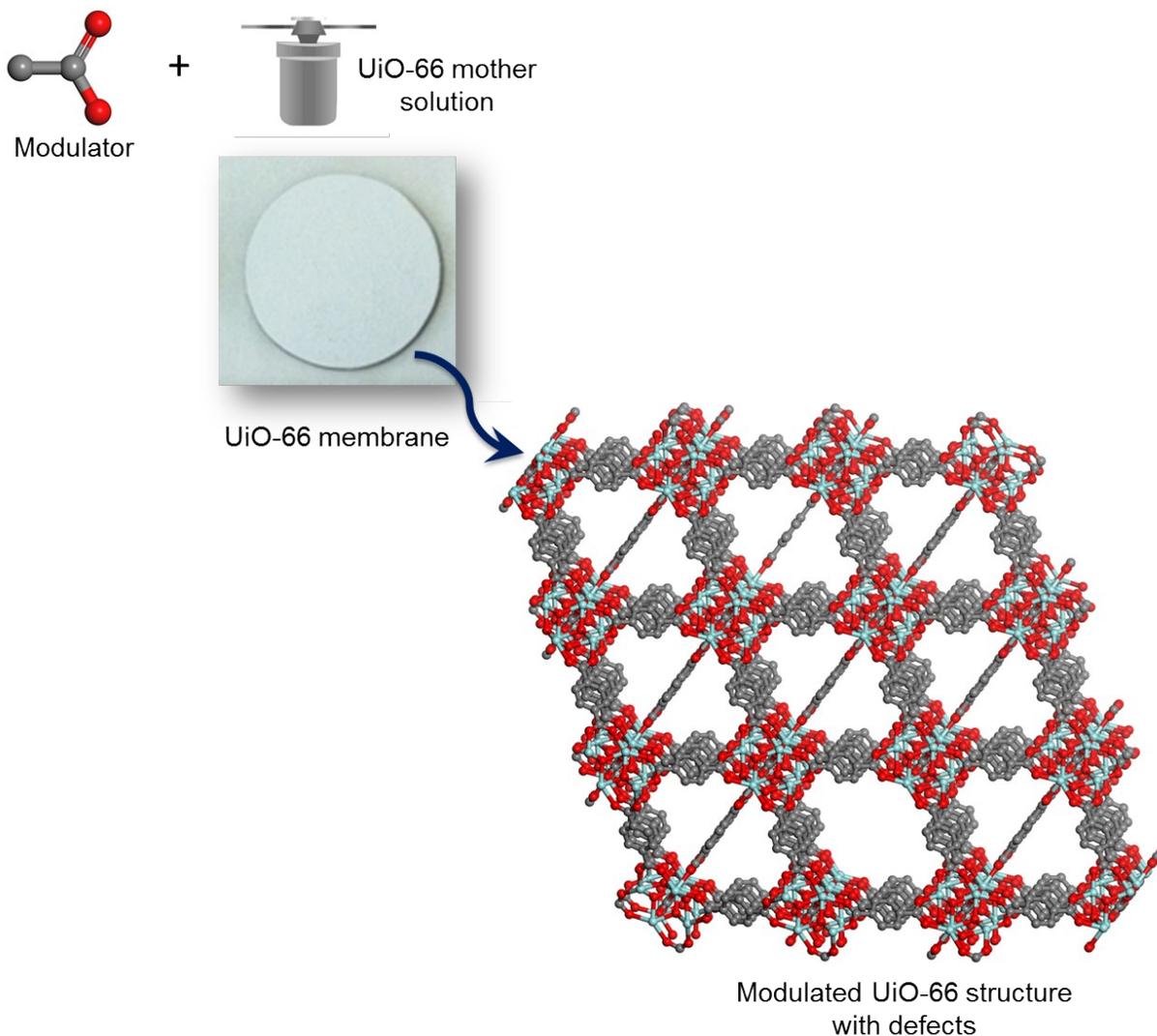


Figure S1. Modulated UiO-66 structure with defects where the missing ligands impart the MOF with unsaturated metal sites. Zr, C and O atoms are shown as cyan, gray and red, respectively. H atoms are excluded for clarity.

Section 3. Variable temperature X-ray diffraction (XRD) study

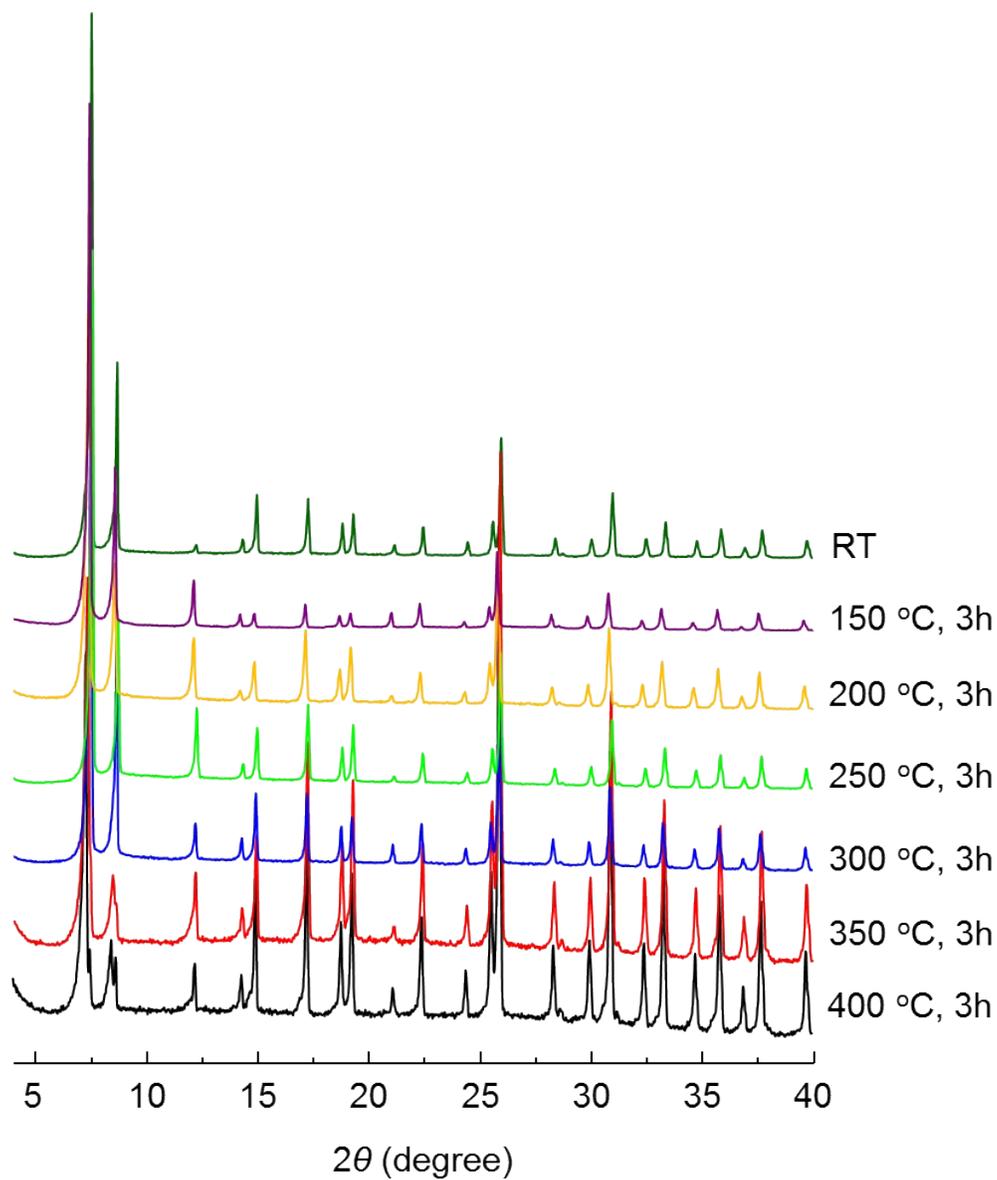


Figure S2. PXRD patterns of degassed UiO-66 after heating for 3 h at high temperatures from 150 °C to 400 °C.

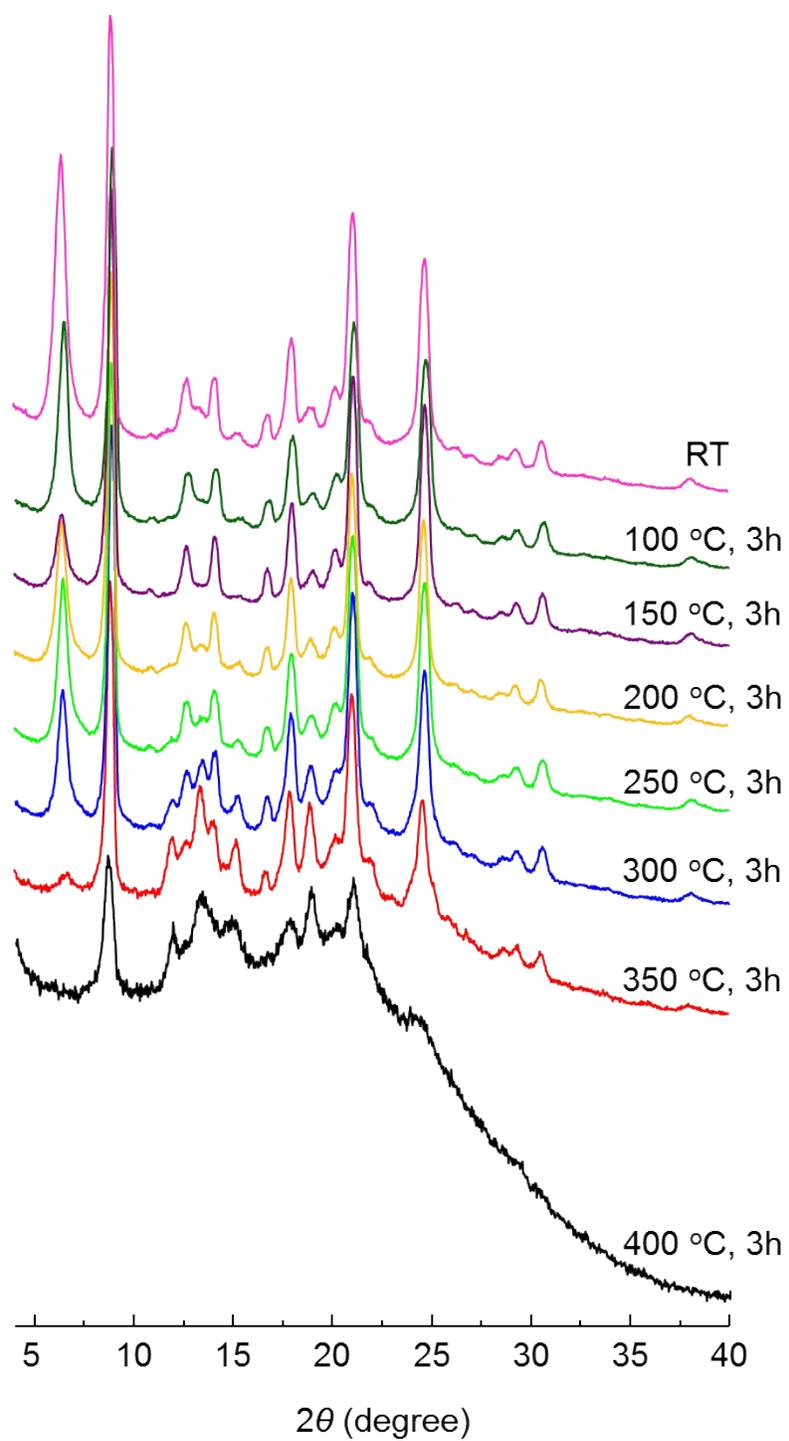


Figure S3. PXRD patterns of degassed COF-300 after heating for 3 h at high temperatures from 100 °C to 400 °C.

Section 4. Variable temperature Fourier transform infrared (FT-IR) spectroscopic analysis

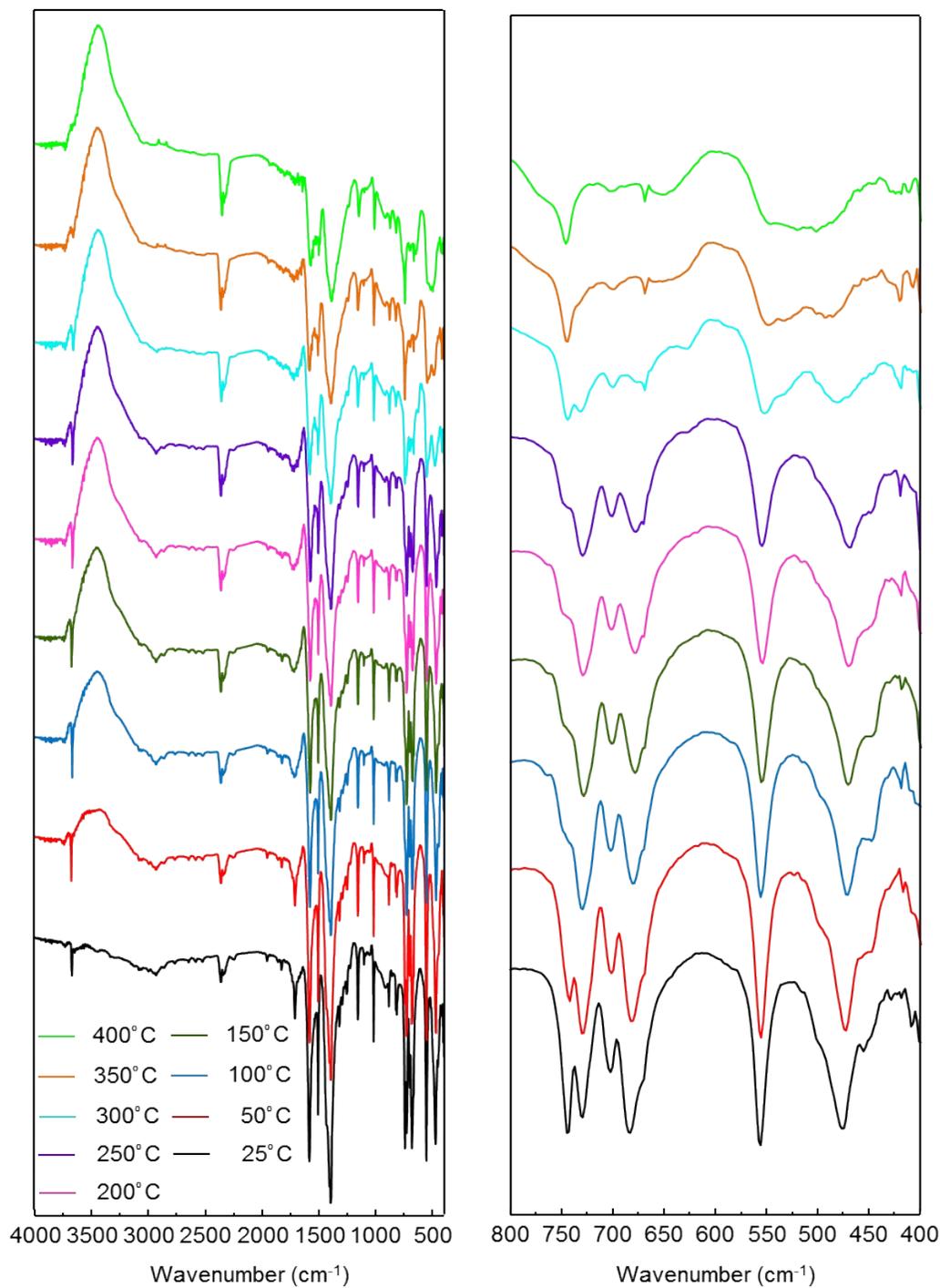


Figure S4. FT-IR spectra of UiO-66 from 25 °C to 400 °C in the spectral range of 4000 cm⁻¹-400 cm⁻¹ (left) and 800 cm⁻¹-400 cm⁻¹(right).

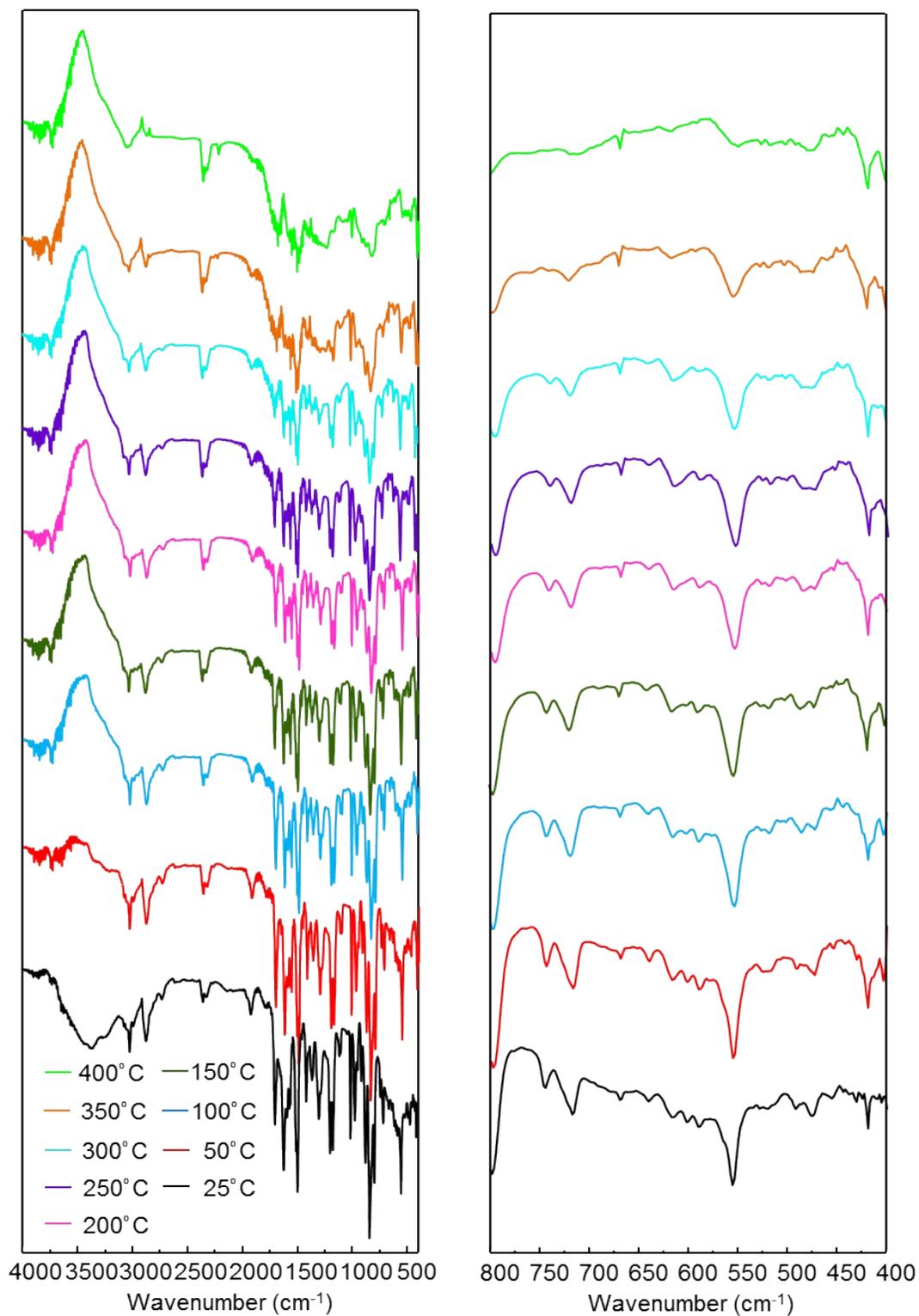


Figure S5. FT-IR spectra of COF-300 from 25 °C to 400 °C in the spectral range of 4000 cm^{-1} -400 cm^{-1} (left) and 800 cm^{-1} -400 cm^{-1} (right).

Section 5. Thermogravimetric analysis (TGA)

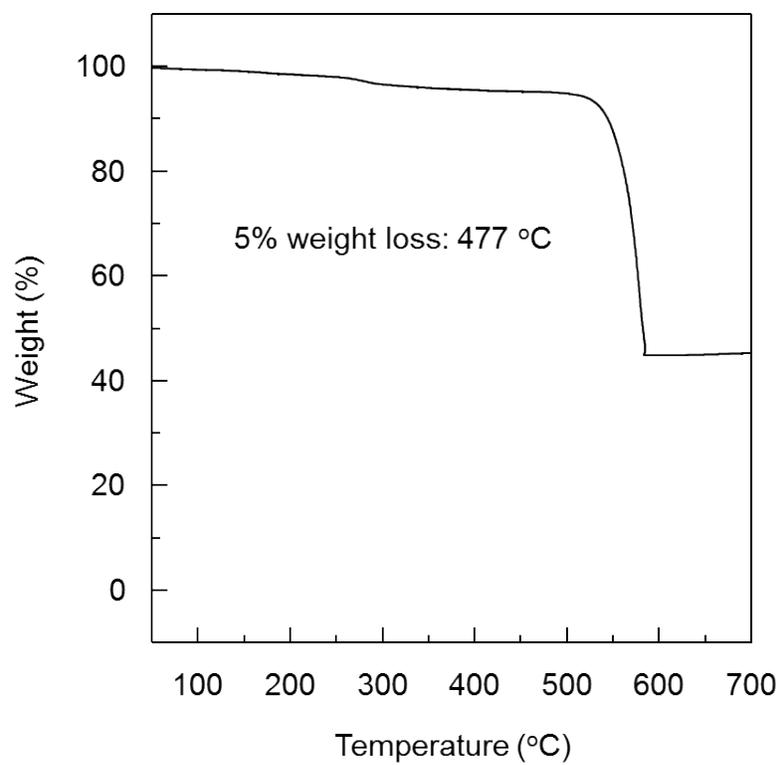


Figure S6. TGA curve of UiO-66 under dry air at a heating rate of 10 °C min^{-1} .

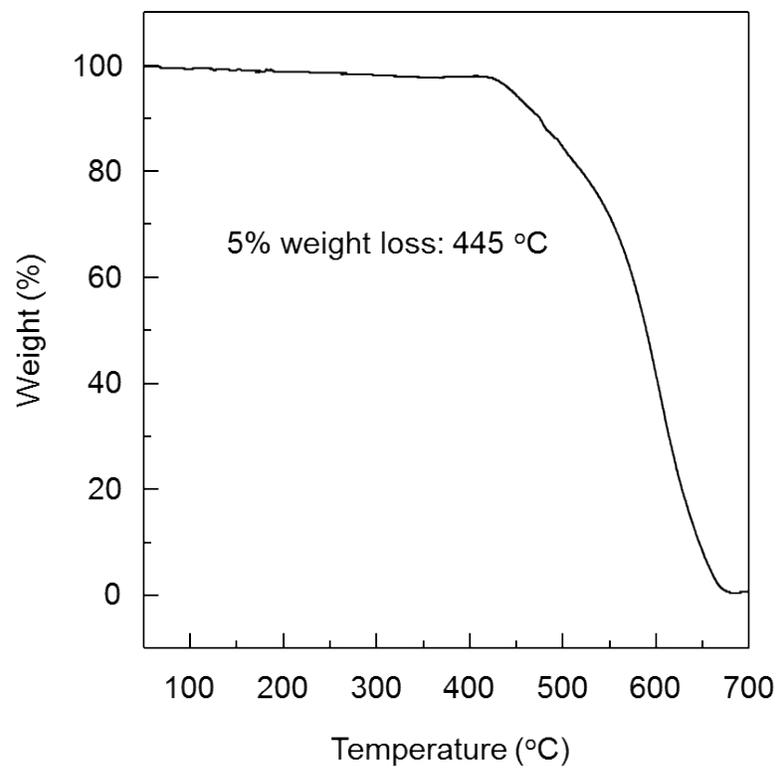


Figure S7. TGA curve of COF-300 under dry air at a heating rate of 10 °C min⁻¹.

Section 6. Low pressure gas sorption measurements

6.1. Low pressure N₂ sorption measurements

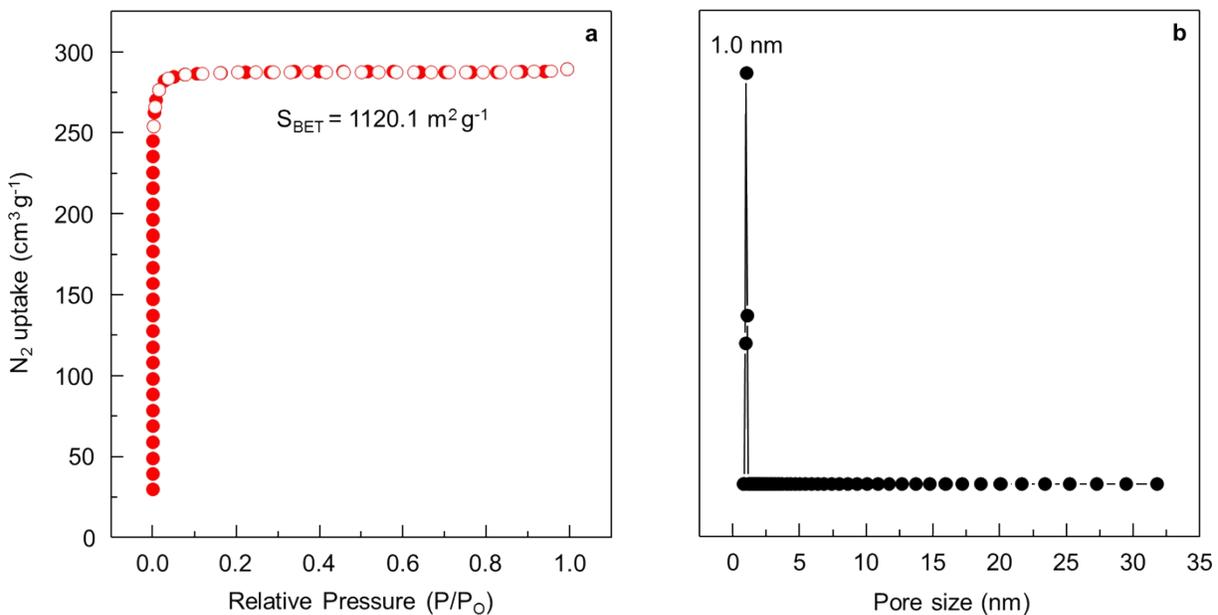


Figure S8. (a) N₂ sorption isotherms of degassed UiO-66 measured at 77 K. The solid symbols denote adsorption and the open symbols denote desorption. (b) Pore size distribution of UiO-66 determined from the N₂ adsorption isotherms using the Density Functional Theory (DFT) method.

6.2. Low pressure H₂ and CO₂ sorption measurements

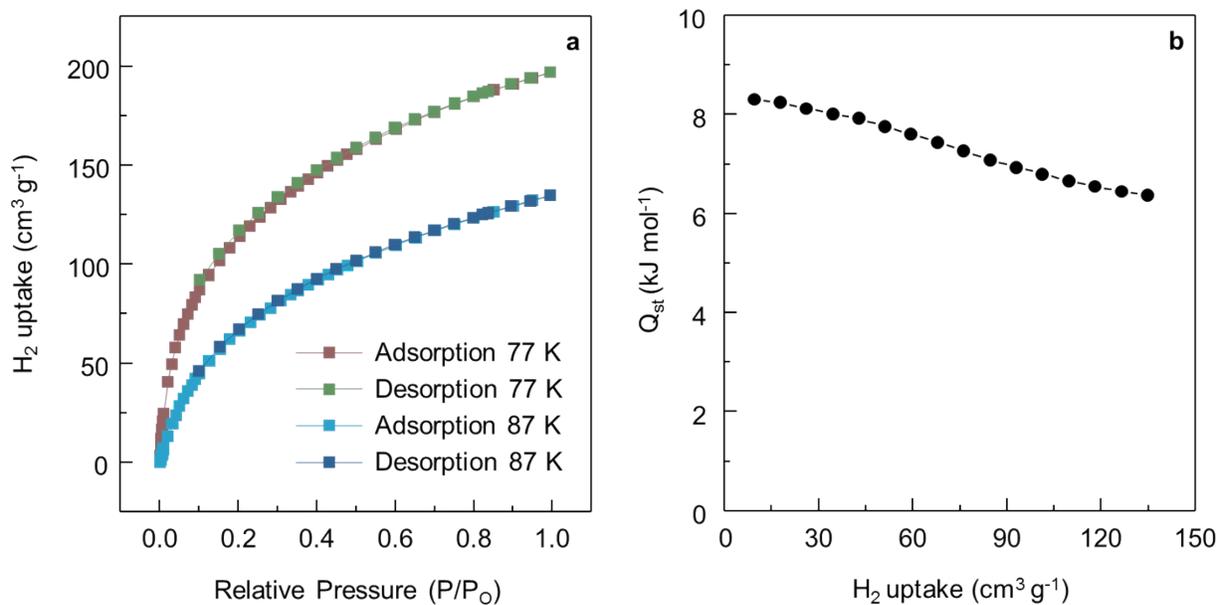


Figure S9. (a) H₂ sorption isotherms of degassed UiO-66 measured at 77 K and 87 K. (b) Isothermic enthalpy (Q_{st}) of H₂ adsorption for degassed UiO-66 powder.

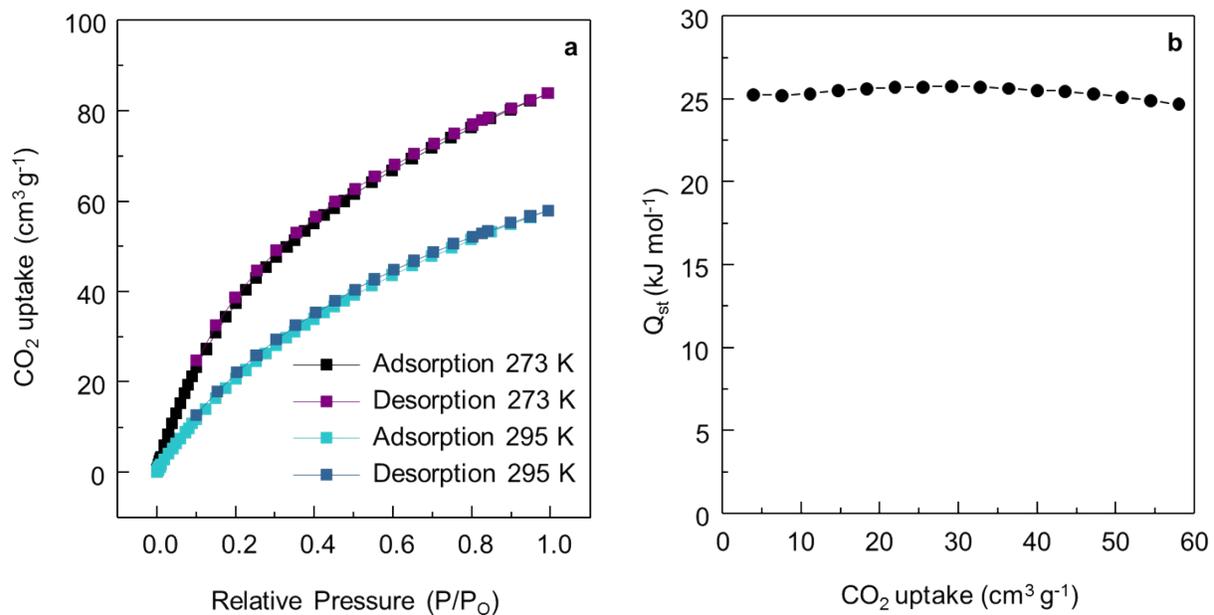


Figure S10. (a) CO₂ sorption isotherms of degassed UiO-66 measured at 273 K and 295 K. (b) Isothermic enthalpy (Q_{st}) of CO₂ adsorption for degassed UiO-66 powder.

Section 7. References

1. P. Ganesan, X. Yang, J. Loos, T. J. Savenije, R. D. Abellon, H. Zuilhof, E. J. R. Sudhölter, *J. Am. Chem. Soc.*, 2005, 127, 14530-14531.