Supporting Information

Ultrafast Sonochemical Synthesis of Imine-linked Porous Organic Cages with High Surface Area for Gas Adsorption

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Table of contents

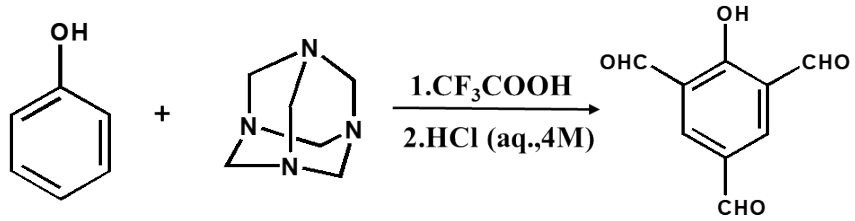
1. Instruments and materials

2-hydroxybenzene-1,3,5-tricarbaldehyde[1], and Bis(4-hydroxy-3,5-diformyl-phenyl)methane[2] was synthesized according to previously reported procedures. Other reagents and solvents were purchased from commercial sources and used without any further purification. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PA Nalytical diffractometer with Cu Ka radiation (λ = 1.5406 Å) using a scan speed of 1° min^{-1} and a step size of 0.02° in 2 Theta. The Fourier-transform infrared spectroscopy (FT-IR) was recorded on a Bruker TENSOR 37 FT-IR spectrometer using KBr pellets. Thermogravimetric analysis (TGA) analysis was performed on a TAQ500 under a nitrogen flow, heating from 25 °C to 800 °C at a rate of 10 °C min^{-1}. Scanning electron microscopy (SEM) images were obtained using a field emission SEM (JSM-7800F, imaged at 5 keV and 12 μA). The surface areas and N_2 adsorption isotherms of samples (at 77.3 K) were obtained using a Micromeritics ASAP 2020 plus HD88 volumetric adsorption analyzer. Before analysis, the samples were degassed at 100 °C for 12 h under vacuum (10^{-5} bar). All Sono-POCs were prepared using a Wenzhou Hongxiang Technology ultrasonic cleaner, operating at 100% power output.

2. Synthetic procedures

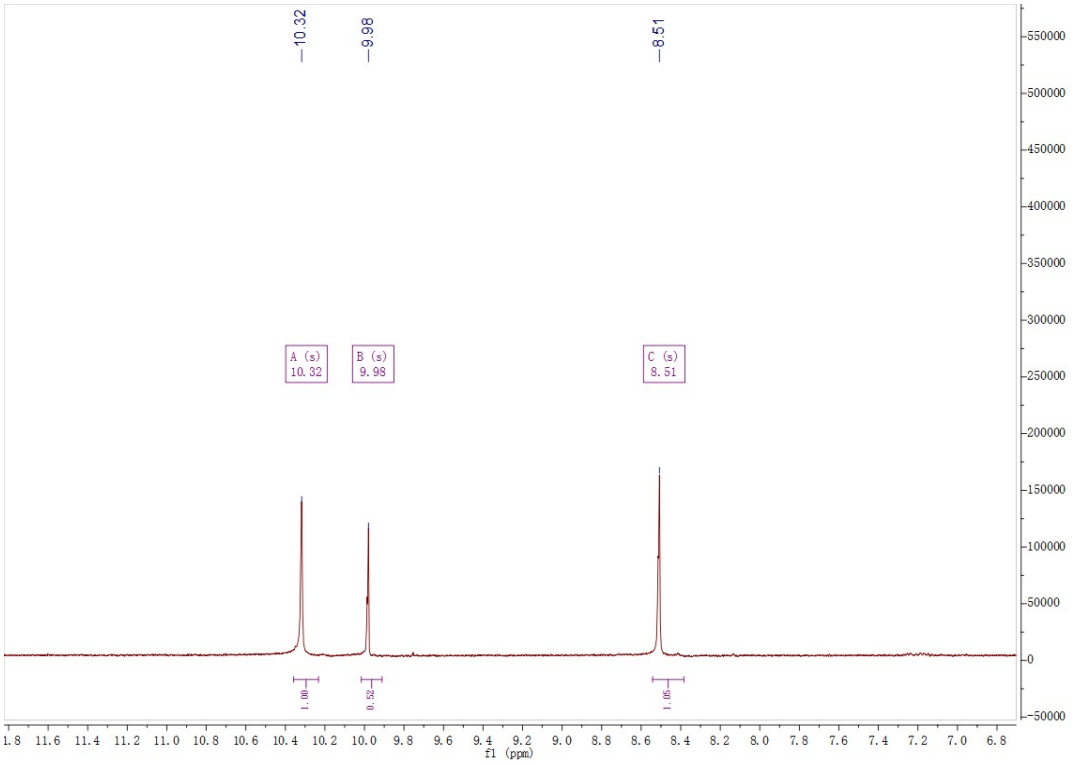
2.1 Monomer synthesis

Synthesis of 2-hydroxybenzene-1,3,5-tricarbaldehyde

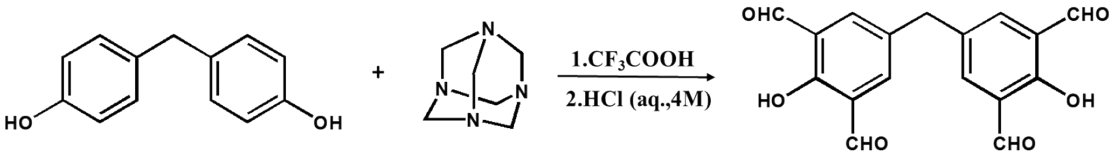


2-hydroxybenzene-1,3,5-tricarbaldehyde was synthesized following the reported procedure with minor modification[1]. Initially, phenol (5.93 g, 63 mmol) and hexamethylenetetramine (17.2 g, 123 mmol) were dissolved in trifluoroacetic acid (60 mL) under a nitrogen atmosphere. The mixture was stirred at 130 °C for 16 h, and

then heated to 150 °C for 3 h. After cooling to 120 °C, the mixture was treated with HCl (aq., 4 M, 100 mL) and then heated at 105 °C for another 30 min and cooled to room temperature. The crude products were filtered and washed with water, methanol, dichloromethane and dried in air. The crude product was recrystallized by DMF and the yield was 33%. ^{1}H NMR (400 MHz, DMSO-d_6, 298K, TMS): δ 10.32 (s, 1H), 9.98 (s, 1H), 8.51 (s, 1H) ppm.

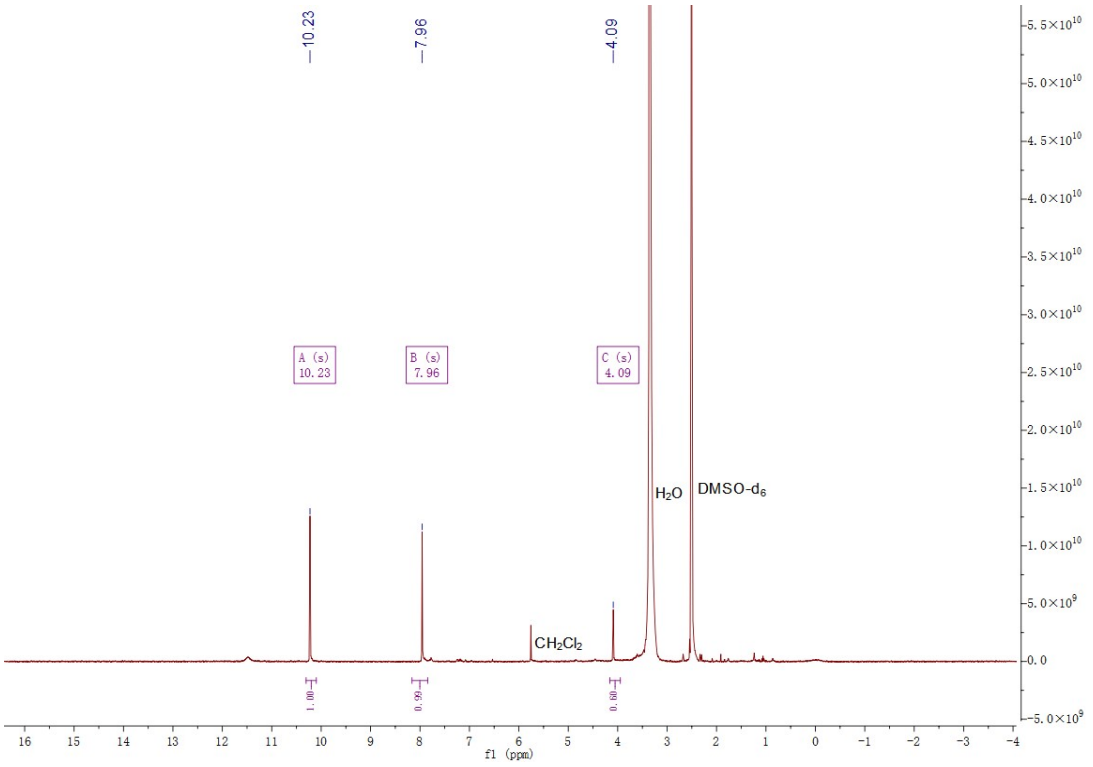


Synthesis of bis(4-hydroxy-3,5-diformylphenyl)methane

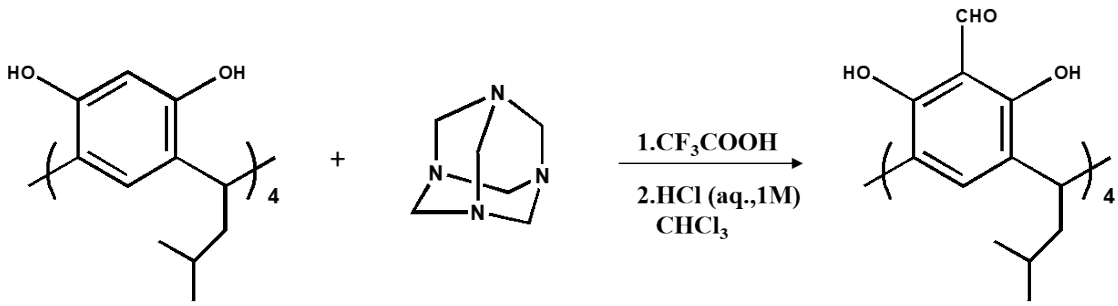


Bis(4-hydroxy-3,5-diformylphenyl)methane was synthesized according to the reported procedure[2]. 4,4'-Methylenediphenol (3 g, 14.98 mmol) and hexamethylenetetramine (20 g, 14.3 mmol) were mixed in a 250 mL round-bottom flask, then trifluoroacetic acid (70 mL) was added. The mixture was heated at 100 °C under nitrogen for 24 h via an oil bath. After cooling to room temperature, 4 M HCl (100 mL) was poured into the resultant red viscous solution and refluxed at 100 °C for 3 h. The mixture was then cooled to room temperature, and the precipitated yellow

product was filtered, dried under a vacuum and recrystallized from DMSO (< 20 mL), yielding 1.50 g (32%) of yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6, 298K, TMS) δ 10.23 (s, 1H), 7.96 (s, 1H), 4.09 (s, 1H) ppm.

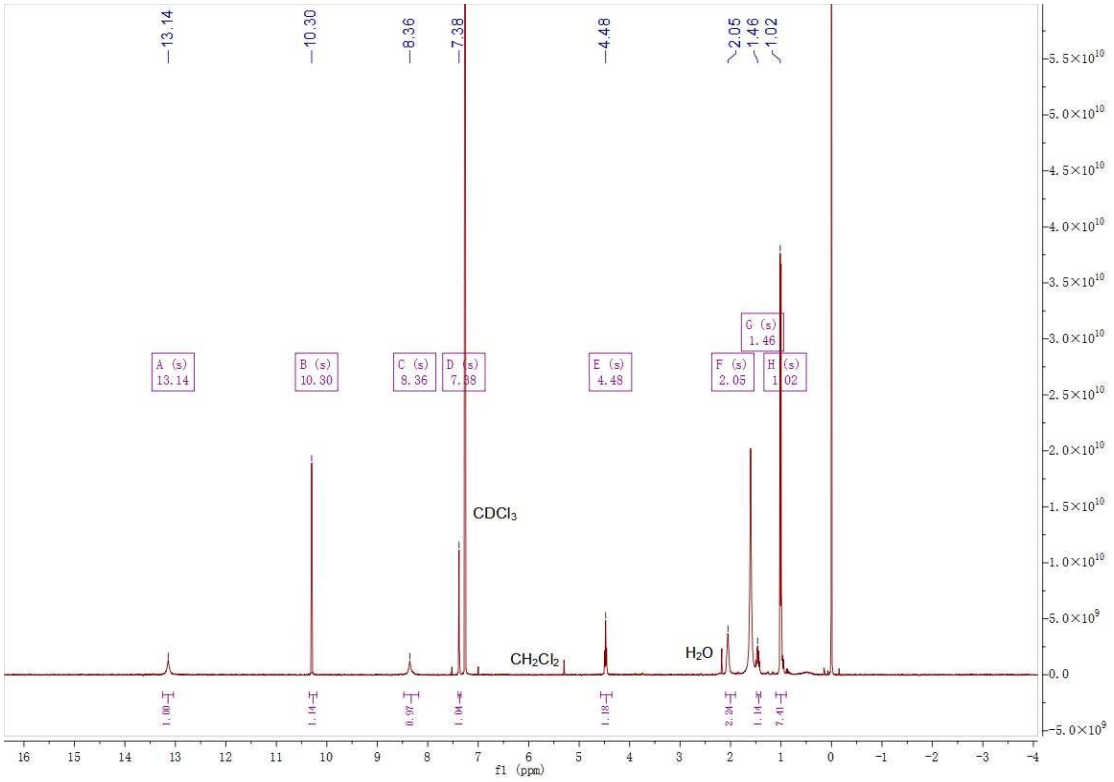


Synthesis of C4RACHO



C4RACHO was synthesized following established literature procedures with minor adjustments[3]. Resorcin[4]arene (98%, 7.2 g, 9.5 mmol) and hexamethylenetetramine (99.5%, 20 g, 143 mmol) were put in a 350 mL thick-walled pressure bottle. Trifluoroacetic acid (99.5%, 140 mL) was then added and vigorously stirred until the substrates were dispersed in the liquid. The suspension was heated to 120 °C with stirring for 1 h. The resulting dark solution was poured into a flask containing $CHCl_3$ (99.5%, 50 mL) and aqueous HCl (36~38%, 50 mL, 1 M). The mixture was stirred

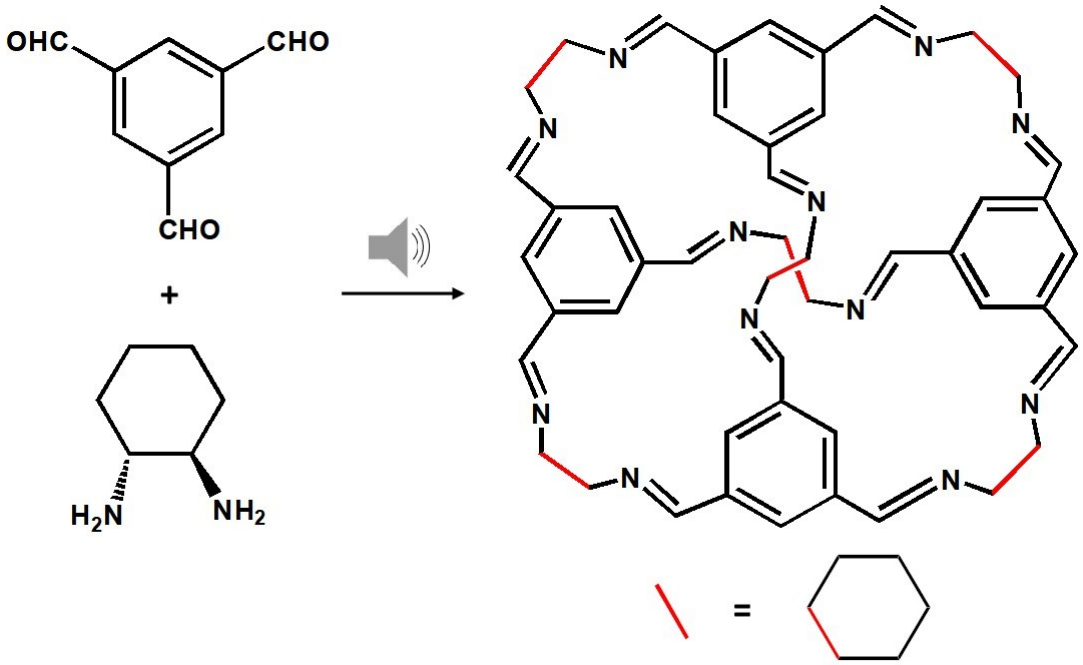
vigorously overnight. The organic phase was separated, and the aqueous phase was subsequently washed with $CHCl_3$ (99.5%, 500 mL) several times. The combined chloroform extracts were dried over anhydrous $MgSO_4$ (99.5%) and evaporated to dryness. The resulting crude precipitate was washed with acetone (99.5%, 50 mL), filtered off, and vacuum-dried to afford 4 g of the yellow product (56%). ^{1}H NMR (400 MHz, Chloroform-d, TMS, ppm) δ 13.14 (s, 1H), 10.30 (s, 1H), 8.36 (s, 1H), 7.38 (s, 1H), 4.48 (s, 1H), 2.05 (s, 2H), 1.46 (s, 1H), 1.02 (s, 7H).



2.2 Synthesis of POCs using ultrasonication

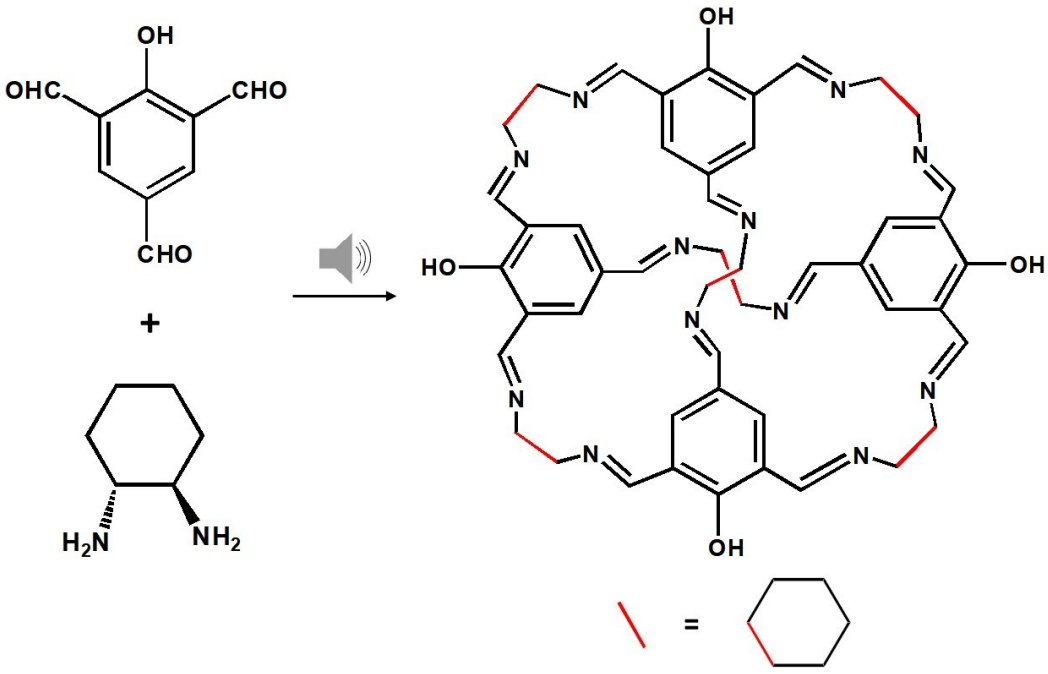
The amine and aldehyde monomers, along with the solvent were added into a 20 mL vial and sonicated in continuous mode and at 100% power for 1, 5, 10 ,30, 60, 90 min. The resulting solid was then washed by Soxhlet extraction with methanol for 24 h, followed by drying in an oven for 24 h.

Synthesis of Sono-CC3R



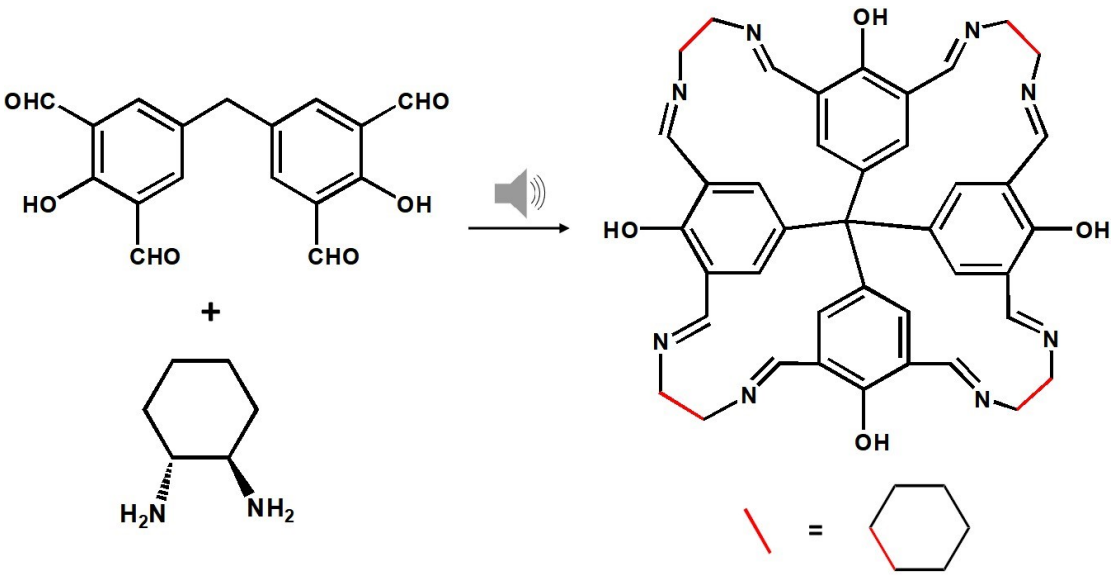
1,3,5-Benzenetricarboxaldehyde (145.93 mg, 0.9 mmol), (1R,2R)-(-)-1,2-diaminocy-clohexane (154.16 mg,1.35 mmol) and methanol solution in different volumes (5 mL, 10 mL, 15 mL) were sonicated for 5 min, respectively. Afterwards, the white powder was collected, filtered, and recovered, followed by Soxhlet extraction with methanol for 24 h, and finally dried in an oven.

Synthesis of Sono-CC3R-OH



2-Hydroxy-1,3,5-benzenetricarbaldehyde (160.33 mg, 0.9 mmol), (1R,2R)-(-)-1,2-diaminocyclohexane(154.16 mg, 1.35 mmol), and methanol solution in different volumes (5 mL, 10 mL, 15 mL) were sonicated for 5 min, respectively. Afterwards, the yellow powder was collected, filtered, and recovered, followed by Soxhlet extraction with methanol for 24 h, and finally dried in an oven.

Synthesis of Sono-NC2R



Bis(4-hydroxy-3,5-diformylphenyl)methane (210.79 mg, 0.675 mmol), (1R,2R)-(-)-1,2-diaminocyclohexane (154.16 mg,1.35 mmol) and methanol solution in different volumes (5 mL, 10 mL, 15 mL) were sonicated for 5 min, respectively. Afterwards, the yellow powder was collected, filtered, and recovered, followed by Soxhlet extraction with methanol for 24 h, and finally dried in an oven.

Synthesis of Sono-CPOC-201

C4RACHO (0.10 mmol, 82 mg) and m-phenylenediamine (0.2 mmol, 21.5 mg) were added into methanol (10 mL) and underwent ultrasonic treatment for 5 min. Afterwards, the red powder was collected, filtered, and recovered, followed by Soxhlet extraction with methanol for 24 h, and finally dried in an oven.

Synthesis of Sono-CPOC-301

C4RACHO (0.10 mmol, 82 mg) and p-phenylenediamine (0.2 mmol, 21.5 mg)

were added into methanol (10 mL) and underwent ultrasonic treatment for 5 minutes. Afterwards, the red powder was collected, filtered, and recovered, followed by Soxhlet extraction with methanol for 24 h, and finally dried in an oven.

2.3 Synthesis of POCs using solvothermal method

Synthesis of Solvo-CC3R and Solvo-CC3R-OH

Solvothermal CC3R was synthesized according to the reported procedure[4]. Typically, 1,3,5-triformylbenzene (145.8 mg, 0.9 mmol) and (1R,2R)1,2-diaminocyclohexane (154.2 mg, 1.35 mmol) were dispersed with 20 mL of ethanol in a single-necked flask under ultrasonication. The mixture was then heated to 90 °C under magnetic stirring and refluxed for 4 h. The white CC3R powder was collected, followed by Soxhlet extraction with ethanol for 24 h and then evacuated under vacuum at room temperature overnight. The CC3R-OH were synthesized under the same procedure by using 2-hydroxy-1,3,5-triformylbenzene and (1R,2R)-1,2-diaminocyclohexane as the reactants, and CC3R-OH was collected as yellow powder.

Synthesis of Solvo-NC2R

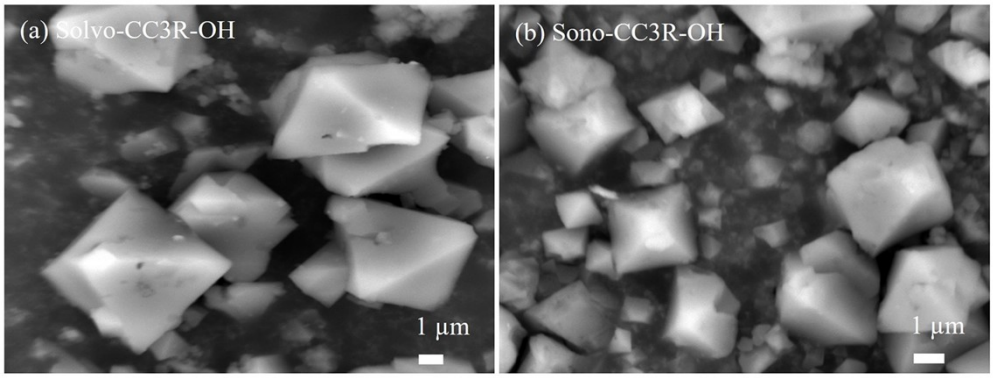
Solvothermal NC2R was synthesized based on reported literature[2]. Bis(4-hydroxy-3,5-diformylphenyl)methane (150 mg, 0.48 mmol) and NaOH(40 mg, 1 mmol) were dissolved in a mixture of water and ethanol (70/100 mL, v/v) and refluxed for 1 h. A 30 mL ethanol solution of (1R,2R)-cyclohexanediamine (137 mg, 2.5 equiv relative to tetraaldehyde) was added into the mixture, and refluxed for additional 24 h. The resulting clear solution was filtered and the filtrate was allowed to slow evaporation at higher ambient temperature (above approximate 30 °C) to afford cage crystals of NC2R (>80 mg, 35%). Afterwards, the yellow powder was collected, filtered, and recovered, followed by Soxhlet extraction with ethanol for 24 h, and finally dried in an oven.

2.4 Large-scale synthetic procedures for Sono-CC3R-OH

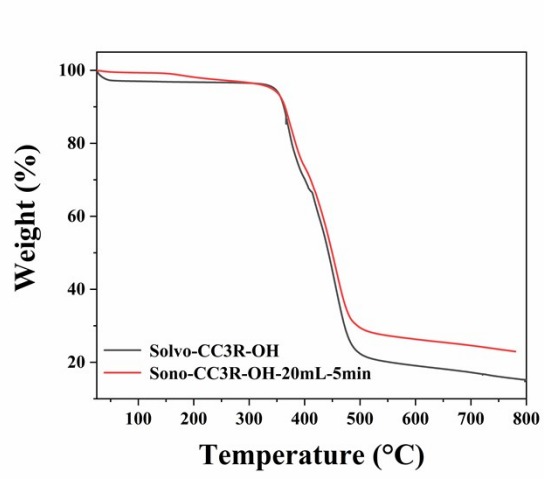
2-hydroxy-1,3,5-benzenetricarbaldehyde (32 g, 0.18 mol), (1R,2R)-(-)-1,2-Diam-

inocyclohexane (30.8 g, 0.27 mol), and methanol solution (1 L) were sonicated for 5 min. Afterwards, the yellow powder was collected, filtered, and recovered, followed by Soxhlet extraction with methanol for 24 h, and finally dried in an oven to achieve a yield of around 56%.

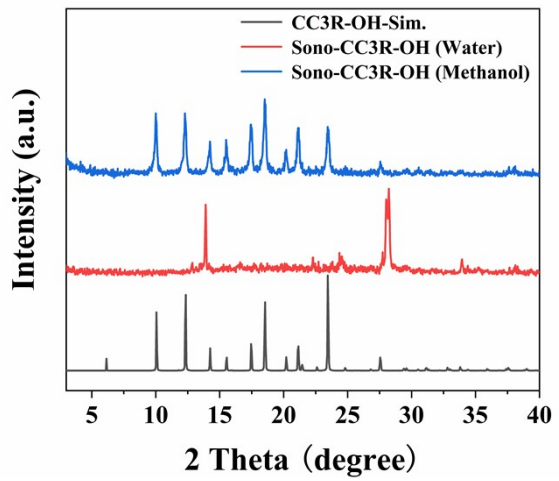
3. Characterization of Sono-POCs



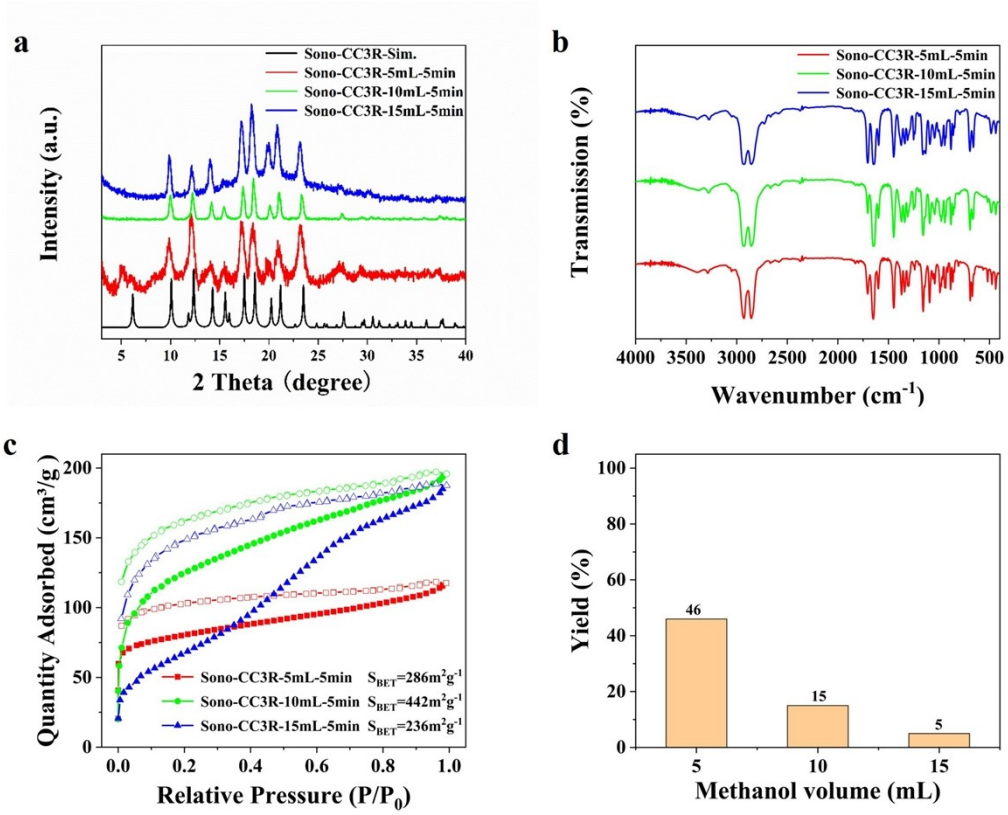
Supplementary Fig. 1. The SEM images of (a) Solvo-CC3R-OH, (b) Sono-CC3R-OH.



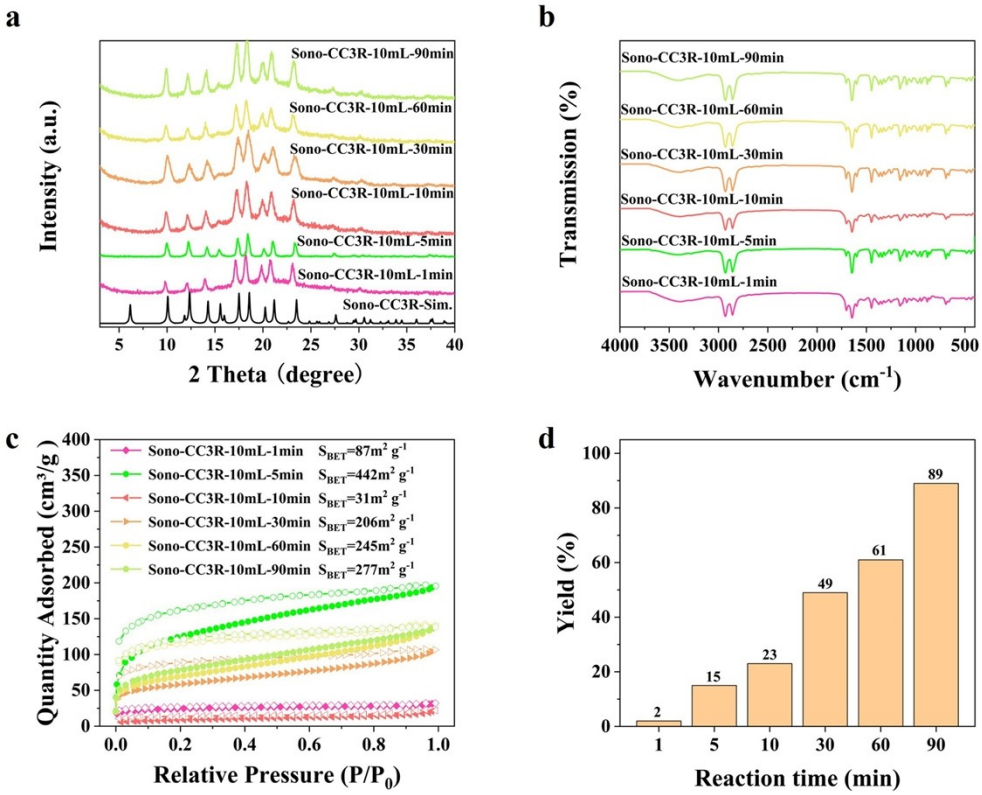
Supplementary Fig. 2. TGA diagram of Solvo-CC3R-OH and Sono-CC3R-OH-20mL-5min.



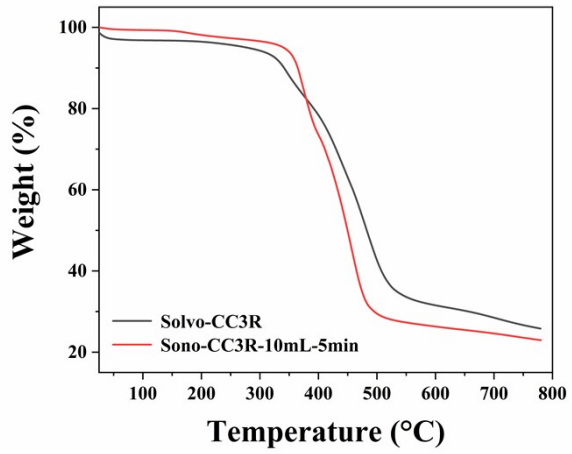
Supplementary Fig. 3. PXRD patterns of Sono-CC3R-OH (Water) and Sono-CC3R-OH (Methanol) obtained by ultrasound for 5 min.



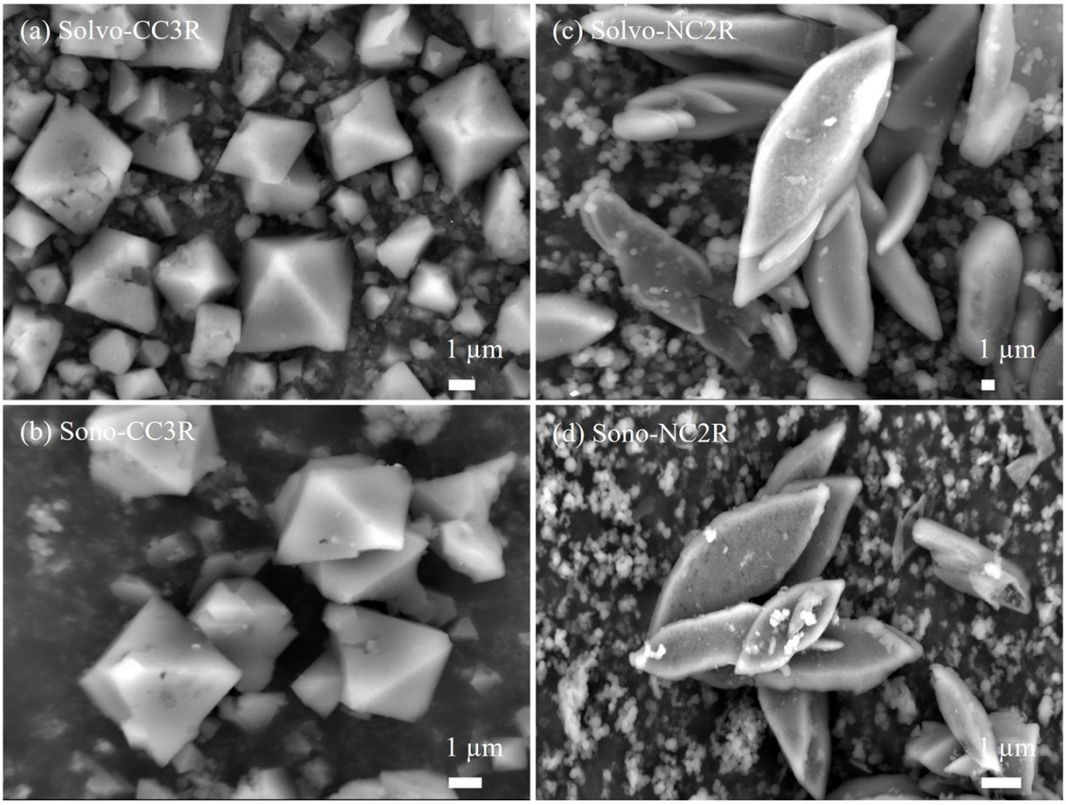
Supplementary Fig. 4. a. PXRD patterns, b. FTIR spectra, c. N_2 adsorption-desorption isotherms, and d. the yields of Sono-CC3R at different methanol volumes.



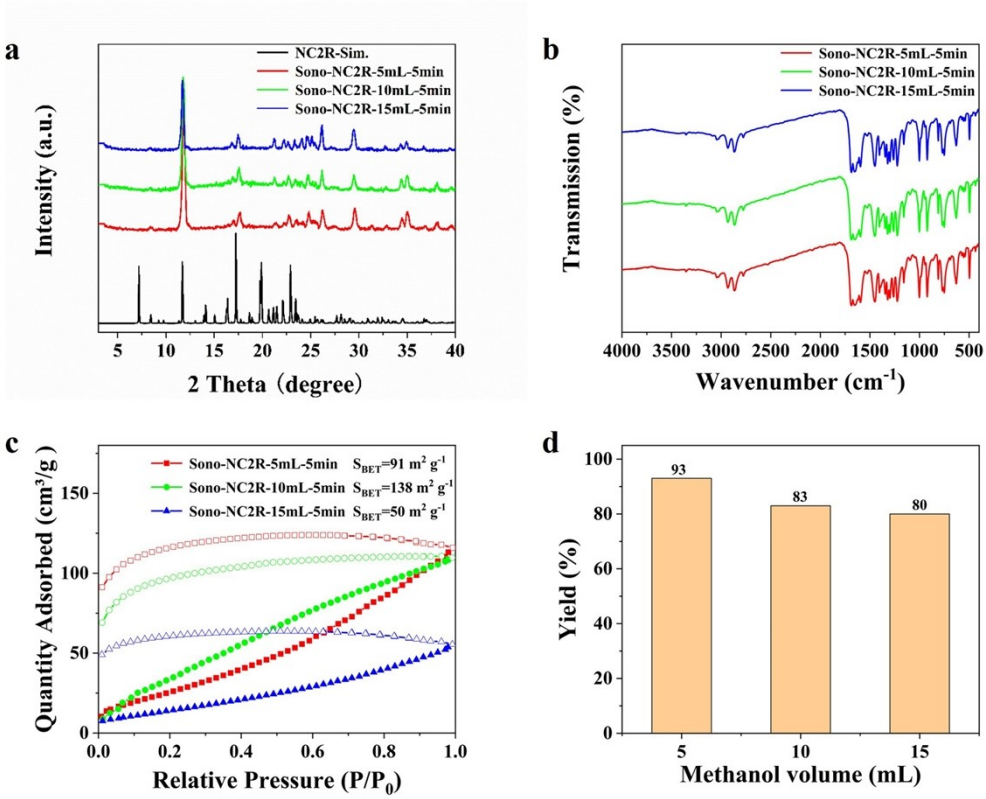
Supplementary Fig. 5. a. PXRD patterns, b. FTIR spectra, c. N_2 adsorption-desorption isotherms, and d. the yields of Sono-CC3R at different reaction times.



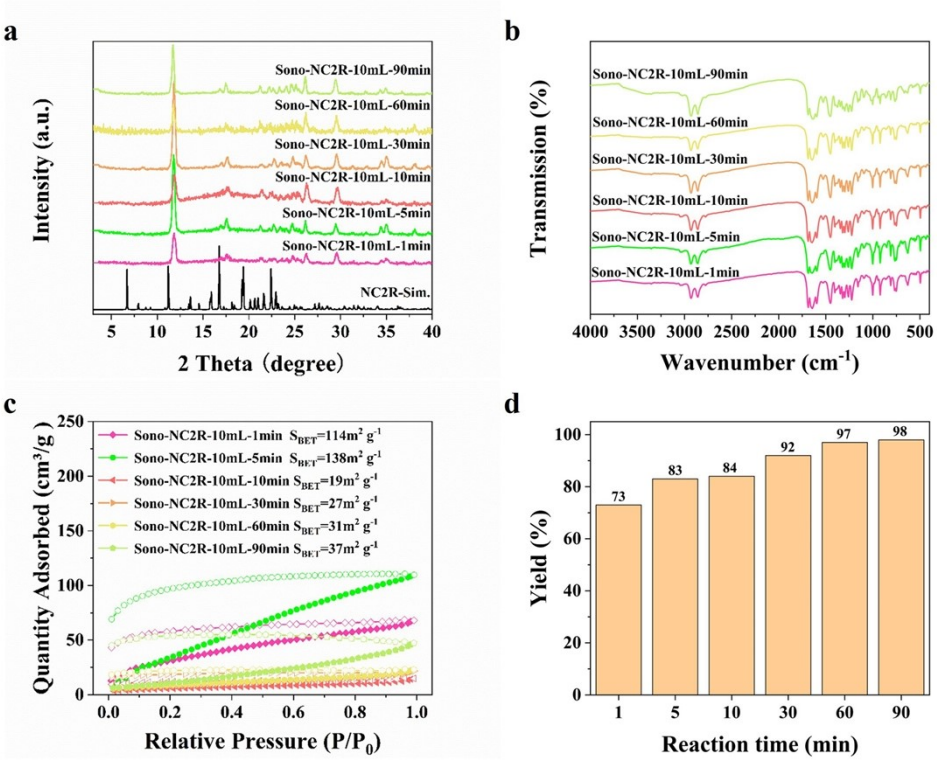
Supplementary Fig. 6. TGA diagram of Solvo-CC3R and Sono-CC3R-10mL-5min.



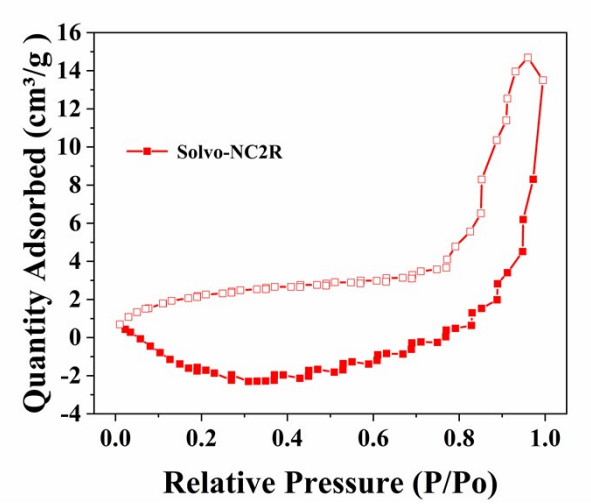
Supplementary Fig. 7. The SEM images of (a) Solvo-CC3R, (b) Sono-CC3R-10mL-5min, (c) Solvo-NC2R, and (d) Sono-NC2R-10mL-5min.



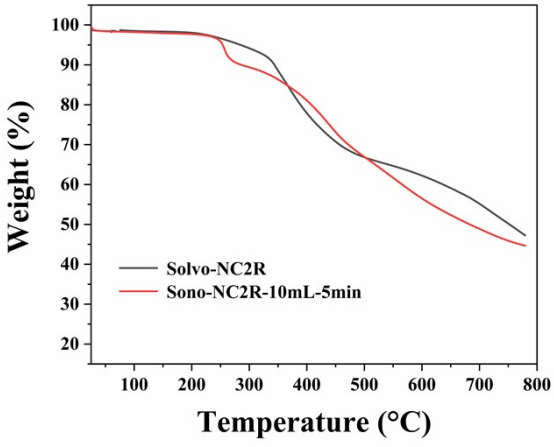
Supplementary Fig. 8. a. PXRD patterns, b. FTIR spectra, c. N_2 adsorption isotherms, and d. the yields of Sono-NC2R at different methanol volumes.



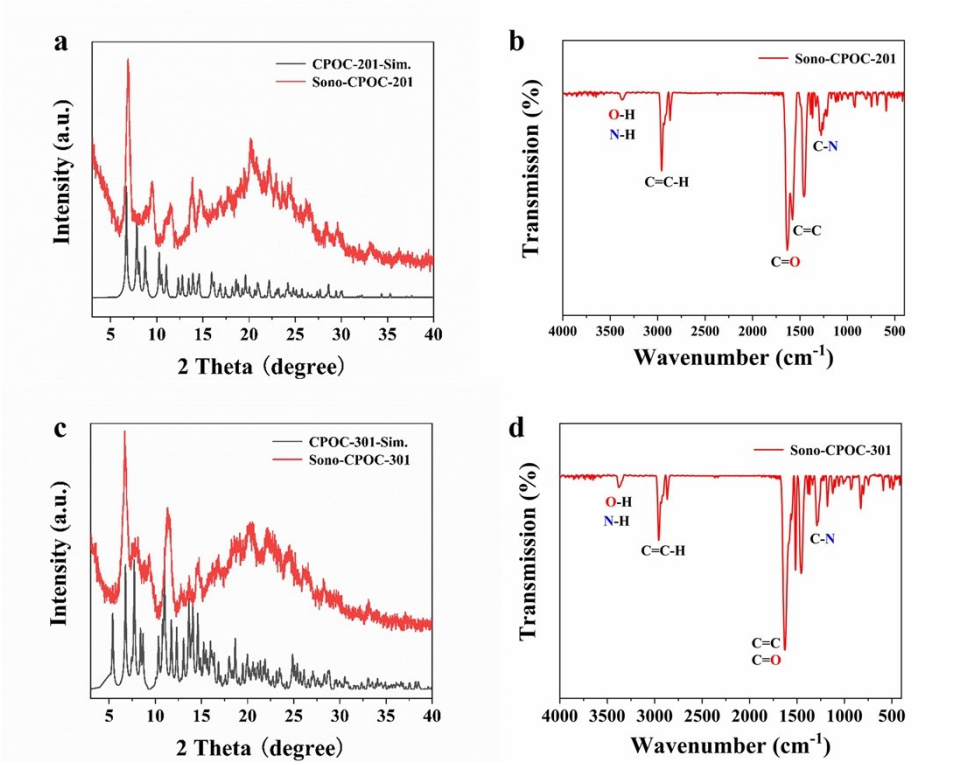
Supplementary Fig. 9. a. PXRD patterns, b. FTIR spectra, c. N_2 adsorption isotherms, and d. the yields of Sono-NC2R at different reaction times.



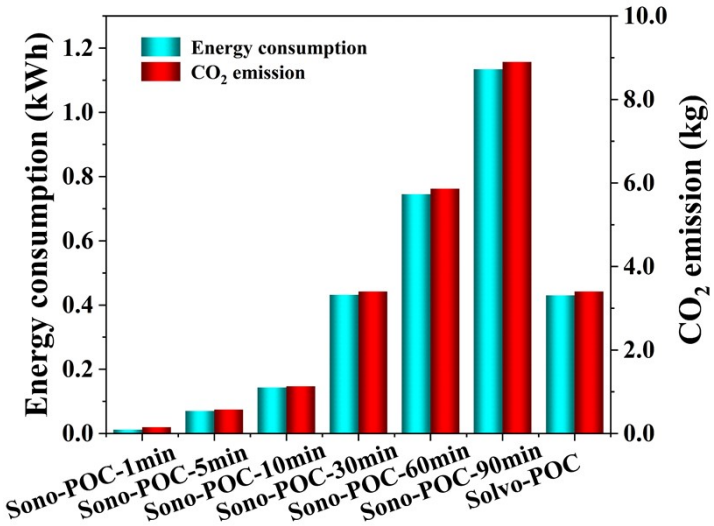
Supplementary Fig. 10. N_2 adsorption isotherms of NC2R synthesized by solvent thermal method as reported in the literature.



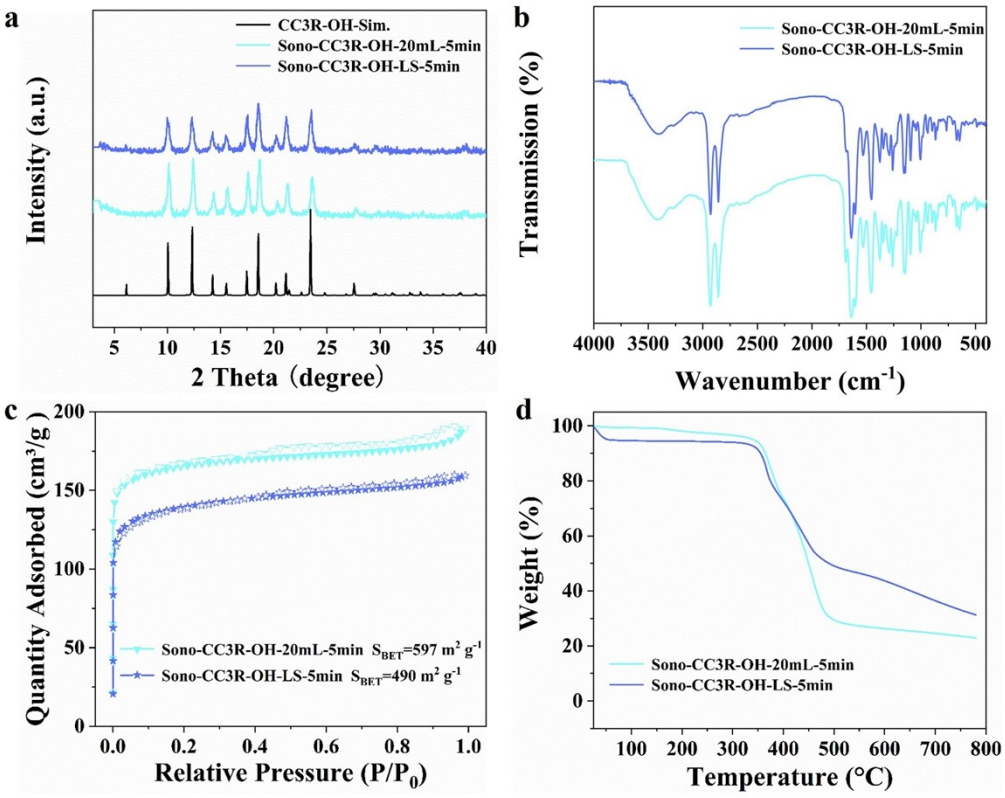
Supplementary Fig. 11. TGA diagram of Solvo-NC2R and Sono-NC2R-10mL-5min.



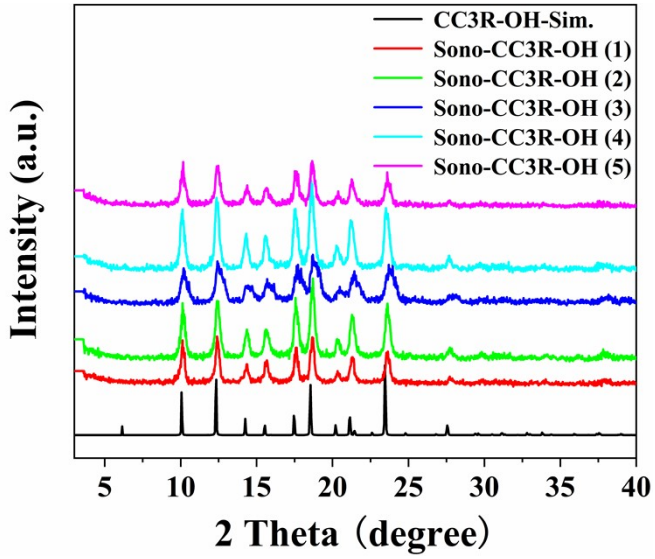
Supplementary Fig. 12. a. PXRD patterns, b. FTIR spectra, c. N_2 adsorption isotherms of Sono-CPOC-201 obtained by sonochemical approach using methanol as solvent. d. PXRD patterns, e. FTIR spectra, f. N_2 adsorption isotherms of Sono-CPOC-201 obtained by sonochemical approach using methanol as solvent.



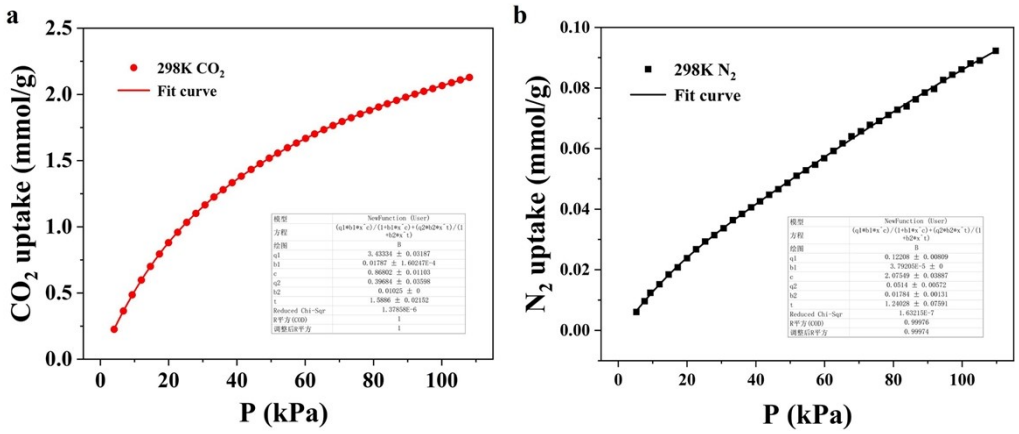
Supplementary Fig. 13. The comparison of power consumption for Sono-POCs.



Supplementary Fig. 14. a. PXRD patterns, b. FTIR spectra, c. N_2 adsorption isotherms, and d. the TGA diagram of the comparison of Sono-CC3R-OH-20mL-5min, Sono-CC3R-OH-LS (LS=Large-Scale) and Sono-CC3R-OH-simulated.



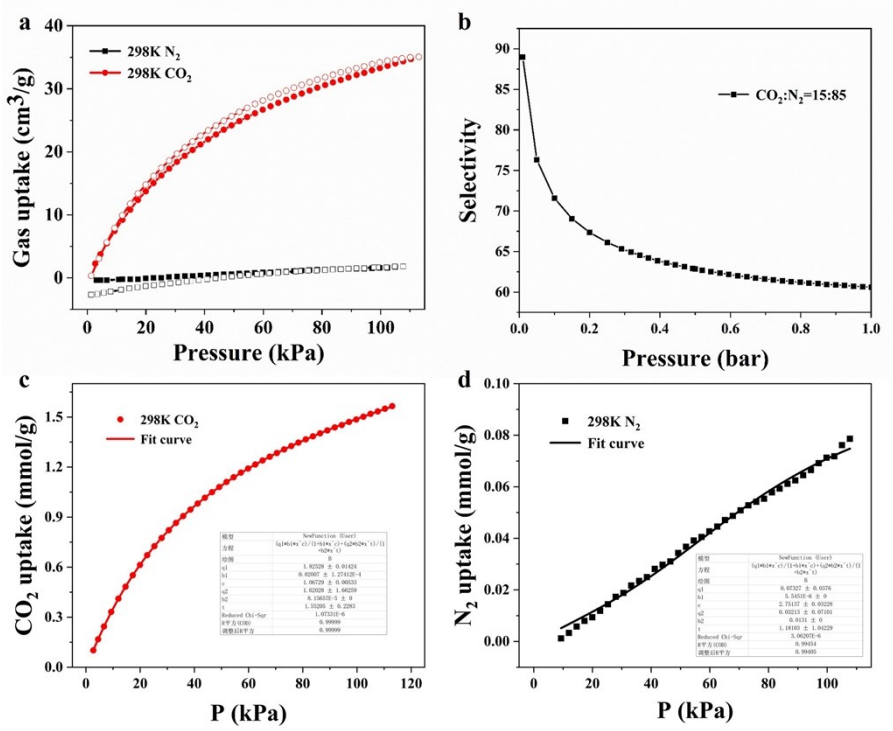
Supplementary Fig. 15. The PXRD patterns of Sono-CC3R-OH obtained by using the recycled solvent.



Supplementary Fig. 16. Virial fitting of a. CO_2 and b. N_2 adsorption data for Sono-CC3R-OH at 298 K.

Table S1. Summary of CO_2/N_2 selectivity in literature on Porous organic cages.

Compound	Condition	Selectivity	Reference
		CO_2/N_2 (15:85, v/v)	
Sono-CC3R-OH	298 K, 1 bar	77.5	This work
sp^2c-POC1	298 K, 1 bar	51.6	S[5]
CC6	300 K, 1 bar	11	S[6]
CC3	296 K, 1 atm	7.8	S[7]
CC2		8.7	
6	293 K, 1 bar	73	S[8]
1		100	S[9]
2		67	
3		36	
4		138	
cage 1	273 K, 1 bar	80	S[10]
5	273 K, 1 bar	32	S[11]
Tc-rp	273 K, 1 bar	4.8	S[12]



Supplementary Fig. 17. a. Comparison of experimental CO_2 and N_2 adsorption isotherms of Solvo-CC3R-OH at 298 K. b. IAST selectivity of CO_2/ N_2 mixtures for Solvo-CC3R-OH at 298 K. Virial fitting of c. CO_2 and d. N_2 adsorption data for Sono-CC3R-OH at 298 K.

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