# Electronic Supplementary Information (ESI)

# Enhanced carbon dioxide uptake by metalloporphyrin-based

# microporous covalent triazine framework

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### Section A. Methods

<sup>1</sup>H spectra were recorded on a Varian Mercury-300 NMR spectrometer, where chemical shifts ( $\delta$  in ppm) were determined with a residual proton of the solvent as Matrix-assisted laser desorption ionization time-of-flight standard. mass (MALDI-TOF MS) spectra were performed on an Applied Biosystems BioSpectrometry model Voyager-DE-STR spectrometer in reflector or linear mode using 9-nitroanthracene or dithranol as a matrix. The diffuse reflectance spectra (Kubleka-Munk spectrum) were recorded on a JASCO model V-670 spectrometer equipped with integration sphere model IJN-727. Infrared spectra were recorded on a JASCO model FT IR-6100 Fourier transform infrared spectrophotometer. Elemental analyses were carried out on an Elementar model vario EL cube analyzer. Field emission scanning electron microscopy was performed on a SU8020 model HITACHI microscope. High resolution transmission electron microscopy was performed on a FEI Tecnai G2S-Twin instrument with a field emission gun operating at 200 kV. The sample was prepared by drop-casting a methanol suspension of MCTFs onto a copper grid. Powder X-ray diffraction data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from  $2\theta = 1.5^{\circ}$  to  $60^{\circ}$  with 0.02° increment at 25 °C. The Inductive Coupled Plasma (ICP) analysis was measured using a Perkin Elmer Optima 3300DV. Nitrogen sorption isotherms were measured at 77 K with a Bel Japan Inc. model BELSORP-mini II analyzer. Before measurement, the samples were degassed in vacuum at 150 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume, the Saito-Foley (SF) method was applied for the estimation of pore size distribution.

#### Section B. Materials and Synthesis

 $BF_3 \cdot Et_2O$ , *P*-Cyanobenzaldehyde, ZnCl<sub>2</sub> and 1,2,4,5-tetrachloro-benzenquenone were purchased from Aldrich and used as received. Other organic solvents for reactions were distilled over appropriate drying reagents under nitrogen. Deuterated solvents for NMR measurement were obtained from Aldrich.

#### Synthesis of 5,15-Bis(4-cyanophenyl)porphyrin

*P*-Cyanobenzaldehyde (500 mg, 3.42 mmole), dipyrromethane (448 mg, 3.42 mmole), and BF<sub>3</sub>·Et<sub>2</sub>O (0.647 mL) were added to a solution of dry CHCl<sub>3</sub> (500 mL). The reaction mixture was stirred for 2h at room temperature and followed by addition of 1,2,4,5-tetrachloro-benzenquenone (1.04 g, 4.22 mmole). The mixture was stirred for additional 24 h and filtered through silica gel, followed by evaporation of the solvent. The crude reaction mixture was purified by column chromatograph with chloroform as eluent and given purple powder 267 mg (0.52 mmol, 15 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.37 (d, 4H, J = 6.0 Hz, Ar-*H*), 8.51 (d, 4H, J = 6.0 Hz, Ar-*H*), 9.06 (d, 4H, J = 4.0 Hz, pyrrole-*H*), 9.73 (d, 4H, J = 4.0 Hz, pyrrole–*H*), 10.72 (s, 2H,  $H_{meso}$ ). UV/Vis (CHCl<sub>3</sub>, 25 °C):  $\lambda_{max} = 409$ , 504, 538, 579 and 631 nm. MALDI-TOF MS: m/z 512.17, calcd. for C<sub>34</sub>H<sub>20</sub>N<sub>6</sub>; found, [M + H]<sup>+</sup> 512.00. FT-IR (KBr): v 531, 573, 640, 709, 797, 851, 884, 913, 1207, 1309, 1412, 1469, 1568, 2223 cm<sup>-1</sup>.

#### Synthesis of Zinc(II) 5,15-Bis(4-cyanophenyl)porphyrin

5,15-Bis(4-cyanophenyl)porphyrin (0.55 g, 1.07 mmol) was dissolved in dry CHCl<sub>3</sub> (30 mL) and treated with a saturated solution of zinc acetate dihydrate dissolved in CH<sub>3</sub>OH (15 mL). The reaction mixture was stirred for 4h and then solvent was removed under reduced pressure. The residue solid was washed with H<sub>2</sub>O and than dried in vacuum. The powder dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short silica gel column to yield 585 mg (0.101 mmol, 95 %) of a purple solid. <sup>1</sup>H NMR (300 MHz, DMSO-d6):  $\delta$  (ppm) 8.32 (d, 4H, J = 8.0 Hz, Ar-*H*), 8.44 (d, 4H, J = 8.0 Hz, Ar-*H*), 8.94 (d, 4H, J = 4.0 Hz, pyrrole-*H*), 9.58 (d, 4H, J = 4.0 Hz, pyrrole–*H*),

10.45 (s, 2H,  $H_{\text{meso}}$ ). UV/Vis (CHCl<sub>3</sub>, 25 °C):  $\lambda_{\text{max}} = 428$ , 521, 556 and 598 nm. MALDI-TOF MS: m/z 574.09, calcd. for C<sub>34</sub>H<sub>18</sub>N<sub>6</sub>Zn; found, [M + H]<sup>+</sup> 573.82. FT-IR (KBr): v 559, 726, 786, 862, 959, 998, 1059, 1149, 1399, 1498, 1596, 2229 cm<sup>-1</sup>. *Synthesi of s MCTF* 

General synthesis procedure: The monomer and the metal salt  $ZnCl_2$  were transferred into a Pyrex ampoule in the glove box. The ampoule was evacuated, sealed and heated to 300 °C (MCTF@300\* and MCTF@300), 400 °C (MCTF@400) and 500 °C (MCTF@500) for 40 h (Table S1). When the mixture was cooled down to room temperature, the ampoule was opened carefully. The black powder was stirred in the water for 24 h three times to remove ZnCl<sub>2</sub>. Further stirring in acetic acid for 5 h was performed to purify the product. After filtration, the crude products washed with water, methanol, dichloromethane and acetone, respectively. Further purification of the polymers was carried out by Soxhlet extraction with tetrahydrofuran for 24 h. The target product was dried *in vacuo* to give a black powder. MCTFs were isolated in 69-85 % yield.





Figure S1. The IR spectra of MCTF@300\* (black line), MCTF@300 (red line), MCTF@400 (green line), MCTF@500 (blue line) and their monomer (light-blue line).



Section D. The UV spectra of monomer and MCTFs

Figure S2. UV-vis spectra of MCTF@300\* (black line), MCTF@300 (red line), MCTF@400 (green line), MCTF@500 (blue line) and their monomer (light-blue line).

Section E. The stability of MCTF@500



Figure S3. TGA curve of MCTF@500 under nitrogen.





Figure S4. P-XRD curve of MCTF@300\* (a), MCTF@300 (b), MCTF@400 (c) and MCTF@500 (d).

Section G. The SEM images



**Figure S5.** SEM images of MCTF@300\* (a), MCTF@300 (b), MCTF@400 (c) and MCTF@500 (d).

# Section H. Reaction conditions and porous parameters

Entry	Temperature	Time	$ZnCl_2$	Suface area	Total pore volume
	(°C)	(h)	(mol equiv)	$(m^2 g^{-1})$	$(\text{cm}^3 \text{g}^{-1})$
MCTF@300*	300	40	5	264	0.231
MCTF@300	300	40	10	640	0.496
MCTF@400	400	40	10	1060	1.303
MCTF@500	500	40	10	1510	2.674

Table S1. The reaction conditions of MCTFs and their porous parameters.

# Section I. Elemental analysis and ICP of MCTFs

**Table S2.** Elemental analysis and of the MCTFs and Znic contents were determined by ICP.

Entry	C (wt %)	H (wt %)	N (wt %)	Zn (wt %)
MCTF@300*	66.35	2.28	7.27	15.65
MCTF@300	72.94	2.58	6.17	16.34
MCTF@400	73.60	2.62	6.46	13.23
MCTF@500	75.97	2.12	5.50	12.12
Theoretical value	70.90	3.15	14.59	11.35