Supporting Information

Amino-Functionalized Cerium based MOF for Sustainable CO_2 Fixation into Cyclic Carbonates

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Table of Contents

Instrumentation:

General Remarks:

PXRD measurements were collected in 2θ range of 5 to 50º using Bruker D8 DISCOVER X-ray diffractometer with Cu Kα radiation. The microstructures of the specimens were analyzed using SIGMA, Carl Zeiss FESEM fitted with an energy dispersive spectrometer (EDX, Oxford Instruments, UK) at 20 kV with a 10 mm working distance. NMR spectra were recorded on a Bruker Ascend NMR spectrometer (400 MHz). Temperature-Programmed Desorption (TPD) measurements were performed using a microtrac BELCAT II instrument. 50 mg sample was pre-treated to remove adsorbed impurities. After cooling to room temperature, the sample was exposed to adsorbate gas, CO_2, NH_3 for adsorption. Desorption was conducted by heating the sample from 100 to 700 °C at 30 mL/min. Chemical shifts were reported in parts per million (ppm) taking about the appropriate solvent peak or 0 ppm for TMS. FT-IR spectra were done using Bruker, Alpha II spectrometer using a powder-pressed KBr pellet in the 400 to 4000 cm^{-1} range. Thermo gravimetric measurements were carried out using STA 8000 Lab System model at a heating rate of 10º C/min in a nitrogen atmosphere.

Crystallography

Various temperature single crystal x-ray diffraction data for **Ce-TPTC-NH_2** was collected on Bruker Smart Apex Duo diffractometer using MoKα radiation (λ = 0.71073 Å). Crystal structures of various temperatures were solved by direct method and refined using the full-matrix least-squares method against F^2 on all data using SHELX-2014/7 built in the APEX-3

program and Olex2 software.[1, 2] All the non-hydrogen atoms were refined anisotropically.[3] The structural parameters were retrieved by using DIAMOND-3.1 software.

Table S1. Details of crystallographic data of **Ce-TPTC-NH_2**.

Compound	**Ce-TPTC-NH_2** (150 K)
Chemical formula	C_{17} $H_{19.8}$ Ce N_4 O_{11}
Formula weight	596.29
Temperature	150(2) K
Crystal system	monoclinic
Space group	*C2/c*
a(Å); α(°)	25.226(2); 90
b(Å); β(°)	13.9949(12); 100.896(2)
c (Å); γ (°)	15.0352(12); 90
V(Å^3); Z	5212.3(7); 8
P(calc.) Mg m^{-3}	1.520
μ(Mo Kα)mm^{-1}	1.802
2θmax (°)	49.77
R (int)	0.0623
Completeness to θ (%)	995
Data/param.	4511 / 225
GOF	1.057
R1[F>4σ(F)]	0.0564
wR2 (all data)	0.1623
max. peak/hole (e.Å^{-3})	2.31/ -1.30

Table S2. Selected bond lengths [Å] and angles [°] for compound **Ce-TPTC-NH_2**.

Compound	Bond Length		Bond Angle	
Ce-TPTC-NH_2	Ce(1)-O(3)^1	2.453(6)	O(3)^1-Ce(1)-O(5)^2	67.7(2)
150 K	Ce(1)-O(5)^2	2.835(5)	O(3)^1-Ce(1)-O(5)^3	73.0(2)
	Ce(1)-O(5)^3	2.485(5)	O(3)^1-Ce(1)-O(2)	131.5(2)
	Ce(1)-O(2)	2.481(5)	O(3)^1-Ce(1)-O(4)^2	74.2(2)
	Ce(1)-O(4)^2	2.521(5)	O(3)^1-Ce(1)-O(8)^2	69.0(2)
	Ce(1)-O(10)	2.554(7)	O(3)^1-Ce(1)-O(10)	138.6(2)
	Ce(1)-O(9)	2.537(7)	O(3)^1-Ce(1)-O(9)	138.9(2)
	Ce(1)-O(6)	2.601(8)	O(3)^1-Ce(1)-O(6)	73.2(3)
	Ce(1)-O(7)	2.553(8)	O(3)^1-Ce(1)-O(7)	77.6(3)
	Ce(1)-O(7A)	2.56(2)	O(3)^1-Ce(1)-O(7A)	9.8(12)
	Ce(1)-O(6A)	2.626(18)	O(3)^1-Ce(1)-O(6A)	64.8(8)
			O(5)^3-Ce(1)-O(5)^2	75.31(16)
			O(5)^3-Ce(1)-O(4)^2	122.20(16)

		$O(5)^3$-Ce(1)-O(10)	147.3(2)
		$O(5)^2$-Ce(1)-O(9)	85.4(3)
		$O(5)^3$-Ce(1)-O(7)	137.7(2)
		$O(5)^3$-Ce(1)-O(7A)	65.7(13)
		$O(5)^3$-Ce(1)-O(6A)	72.2(10)
		O(2)-Ce(1)-$O(5)^2$	68.26(16)
		O(2)-Ce(1)-$O(5)^3$	77.16(17)
		O(2)-Ce(1)-$O(4)^2$	91.21(19)
		O(2)-Ce(1)-$O(8)^2$	79.15(19)
		O(2)-Ce(1)-O(10)	73.3(2)
		O(2)-Ce(1)-O(9)	73.5(2)
		O(2)-Ce(1)-O(6)	140.5(3)
		O(2)-Ce(1)-O(7)	144.3(3)
		O(2)-Ce(1)-O(7A)	131.6(12)
		O(2)-Ce(1)-O(6A)	137.7(9)
		$O(4)^2$-Ce(1)-$O(5)^2$	48.44(15)
		$O(4)^2$-Ce(1)-$O(8)^2$	24.02(17)
		$O(4)^2$-Ce(1)-O(10)	72.7(2)
		$O(4)^2$-Ce(1)-O(9)	145.2(2)
		$O(4)^2$-Ce(1)-O(6)	127.8(2)
		$O(4)^2$-Ce(1)-O(7)	76.2(2)
		$O(4)^2$-Ce(1)-O(7A)	146.8(13)
		$O(4)^2$-Ce(1)-O(6A)	123.3(10)
		O(10)-Ce(1)-$O(5)^2$	105.9(2)
		O(10)-Ce(1)-$O(8)^2$	89.2(2)
		O(10)-Ce(1)-O(6)	109.7(3)
		O(10)-Ce(1)-O(7A)	146.8(13)
		O(10)-Ce(1)-O(6A)	123.3(10)
		O(9)-Ce(1)-$O(5)^2$	105.9(2)
		O(9)-Ce(1)-$O(8)^2$	150.6(2)
		O(9)-Ce(1)-O(10)	73.0(3)
		O(9)-Ce(1)-O(6)	70.4(3)
		O(9)-Ce(1)-O(7)	98.0(3)
		O(9)-Ce(1)-O(7A)	129.7(10)
		O(9)-Ce(1)-O(6A)	75.6(8)
		O(6)-Ce(1)-$O(5)^2$	139.7(3)
		O(6)-Ce(1)-$O(8)^2$	138.8(3)
		O(7)-Ce(1)-$O(5)^2$	119.9(2)
		O(7)-Ce(1)-$O(8)^2$	98.0(2)
		O(7)-Ce(1)-O(10)	71.0(3)
		O(7)-Ce(1)-O(6)	57.8(3)
		O(7A)-Ce(1)-$O(5)^2$	73.0(9)

		O(7A)-Ce(1)-O(6A)	57.2(7)
		O(6A)-Ce(1)-O(5)[2]	128.1(9)
		O(7A)-Ce(1)-O(8)[2]	133.5(8)

Symmetry transformations used to generate equivalent atoms:
[1]1/2-x, 3/2-y, 1-z; [2]+x, 1-y, -1/2+z; [3]1/2-x, 1/2+y, 3/2-z

[1]H NMR Spectroscopic Data of Cyclic Carbonate Derivatives:

1. 4-(chloromethyl)-1,3-dioxolan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00-4.97 (m, 1H), 4.67-4.54 (m, 1H), 4.42 (dd, J = 11.4, 3.2 Hz, 1H), 3.75 (dd, J = 5.0, 0.6 Hz, 2H) ppm.
2. 4-methyl-1,3-dioxolan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91-4.83 (m, 1H), 4.55 (dt, J = 7.9, 5.3 Hz, 1H), 4.03-3.98 (m, 1H), 1.49 (d, J = 6.4 Hz, 3H) ppm.
3. 4-ethyl-1,3-dioxolan-2-one: ^{1}H NMR (400MHz, $CDCl_3$) δ 4.66-4.53 (m, 1H), 4.53-4.44 (m, 1H), 4.06-3.97 (m, 1H), 1.79-1.70 (m, 2H), 0.96 (dt, J = 10.11, 5.5 Hz, 3H) ppm.
4. 4-Phenyl-1,3-dioxolan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.40-7.37 (m, 3H), 7.31-7.26 (m, 2H), 5.59 (t, J=7.9 Hz, 1H), 4.77 (dd, J=8.3, 7.9 Hz, 1H), 4.30 (dd, J=8.3, 7.9 Hz, 1H).
5. hexahydrobenzo[1,3]dioxol-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (s, 2H), 1.88 (d, J = 5.4 Hz, 4H), 1.76-1.66 (m, 2H), 1.51-1.33 (m, 2H) ppm.
6. 4,5-Tetramethylene-1,3-dioxolan-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.63-4.67 (m, 2 H), 1.87-1.80 (m, 4 H), 1.61-1.54 (m, 2 H), 1.40-1.34 (m, 2H).

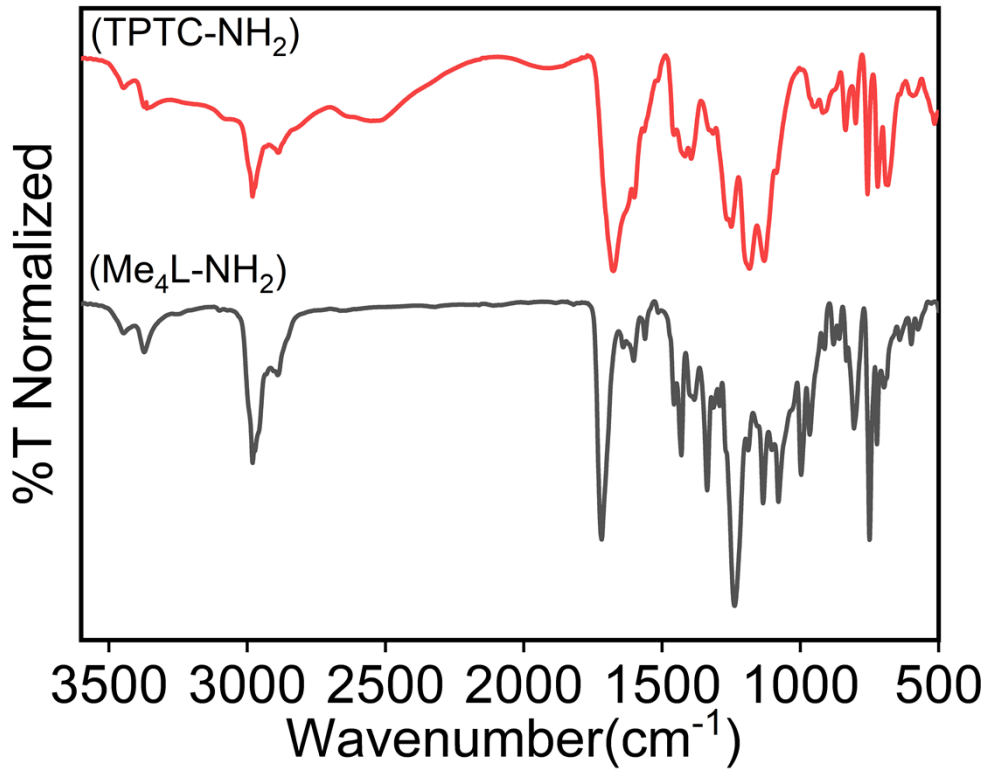

Figure S1. FT-IR data of synthesized TPTC-NH_2 (red) and Me_4L-NH_2 (black) ligand.[4]

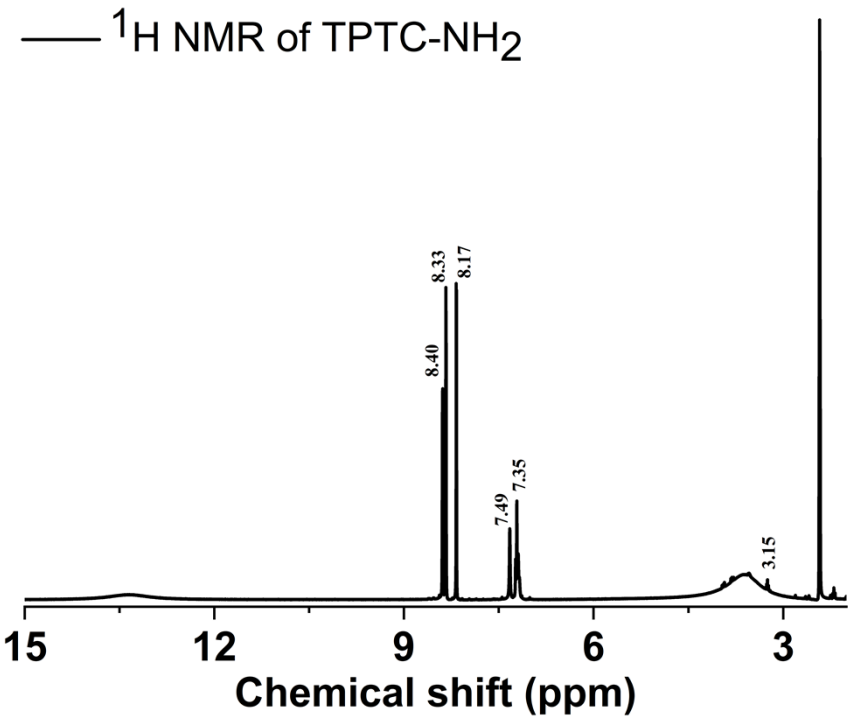

Figure S2. ^{1}H NMR spectra of TPTC-NH_2 ligand.

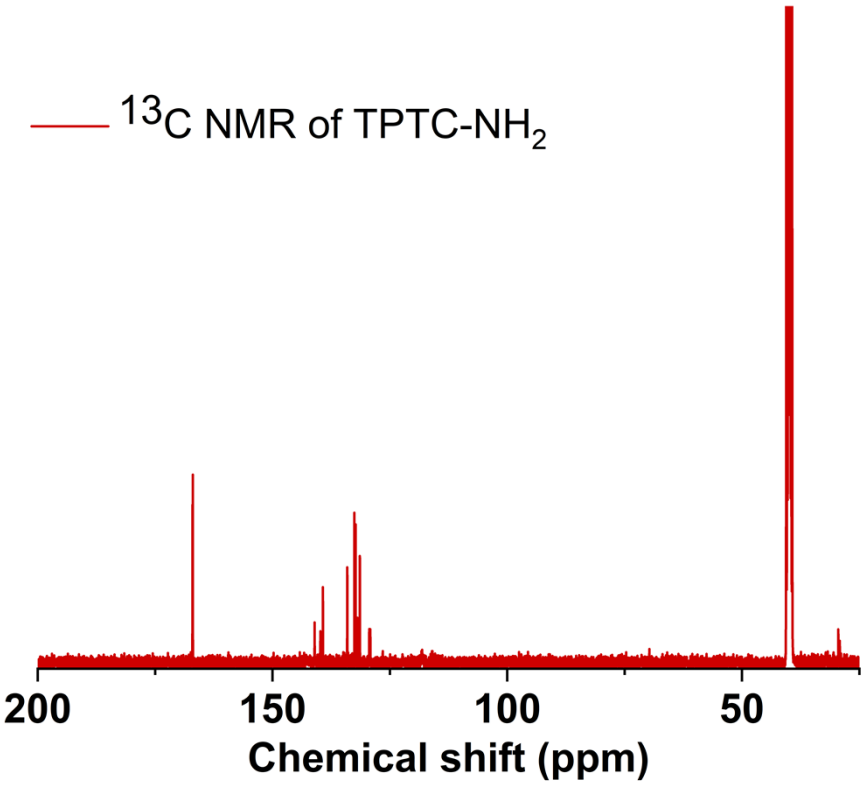

Figure S3. ^{13}C NMR spectra of TPTC-NH_2 ligand.

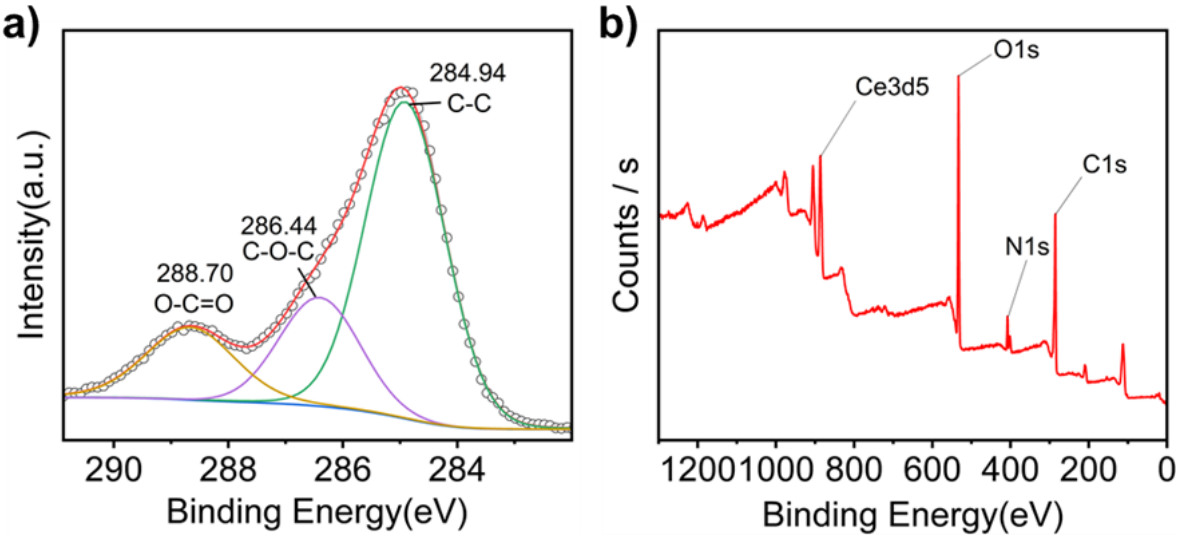

Figure S4. XPS deconvolution spectra of (a) C1s (b) XPS survey of **Ce-TPTC-NH_2** MOF.

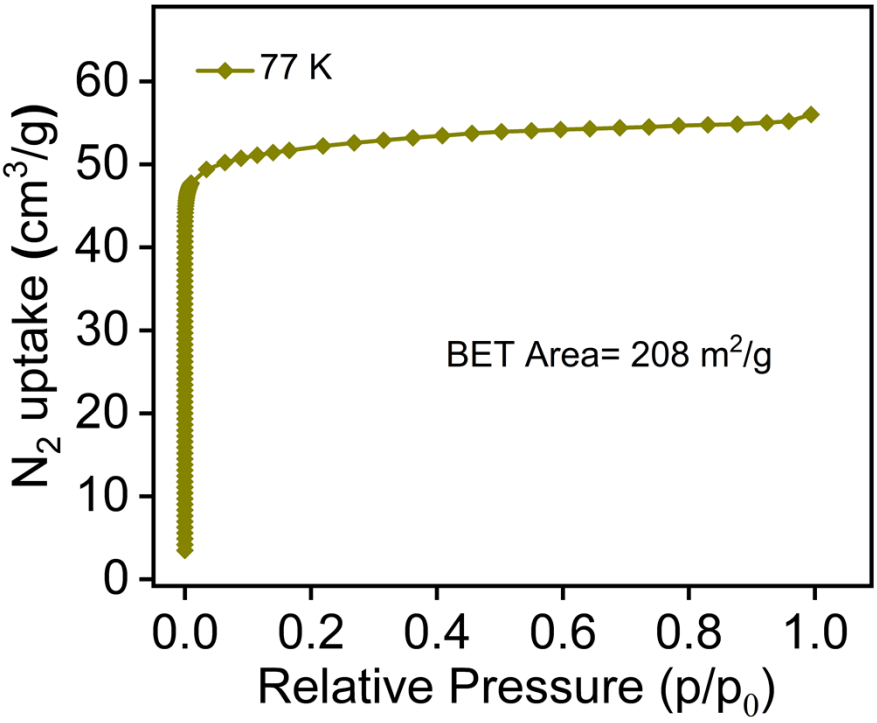

Figure S5. N_2 adsorption−desorption isotherms collected at 77 K for activated **Ce-TPTC-NH_2** MOF.

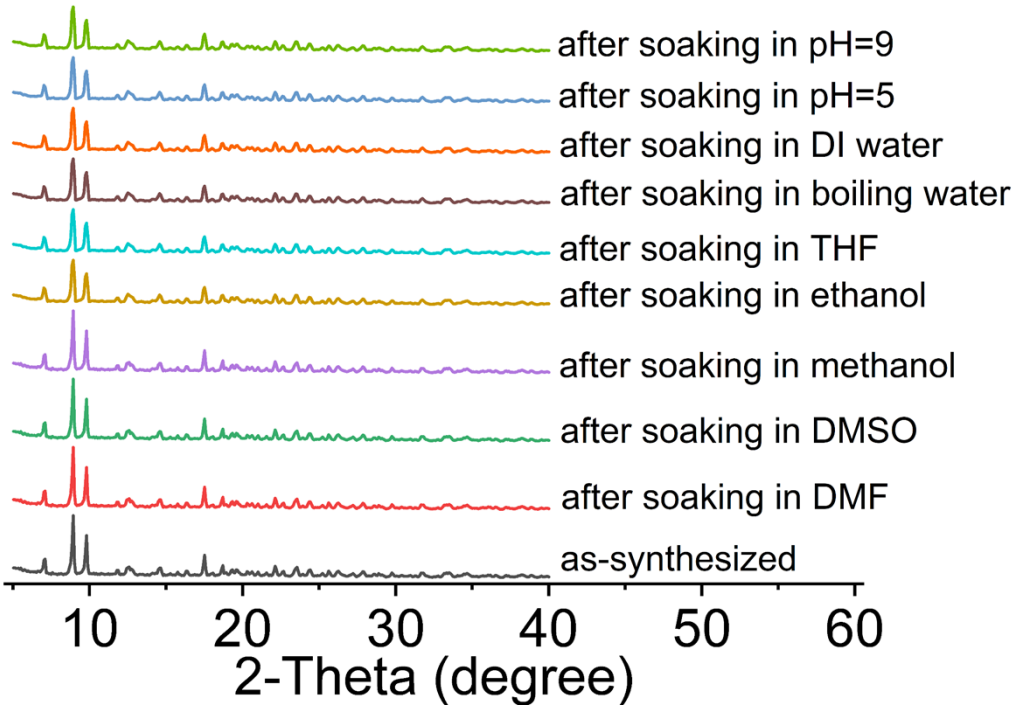

Figure S6. PXRD pattern of **Ce-TPTC-NH_2** MOF after solvent stability test for 24 h.

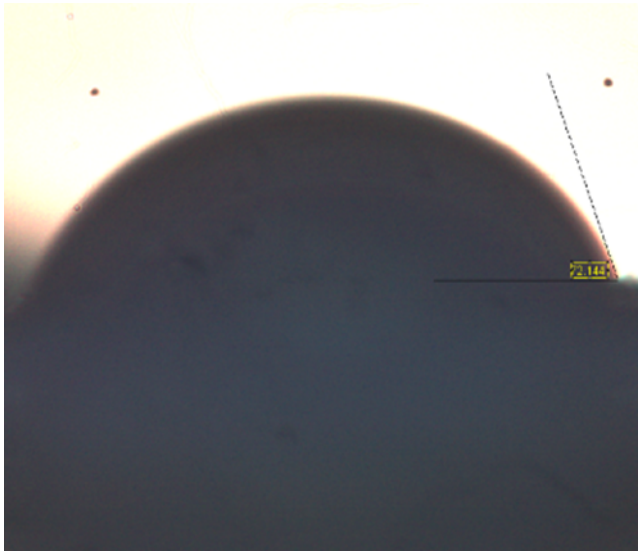

Figure S7. Representative contact angle measurement for **Ce-TPTC-NH_2** MOF.

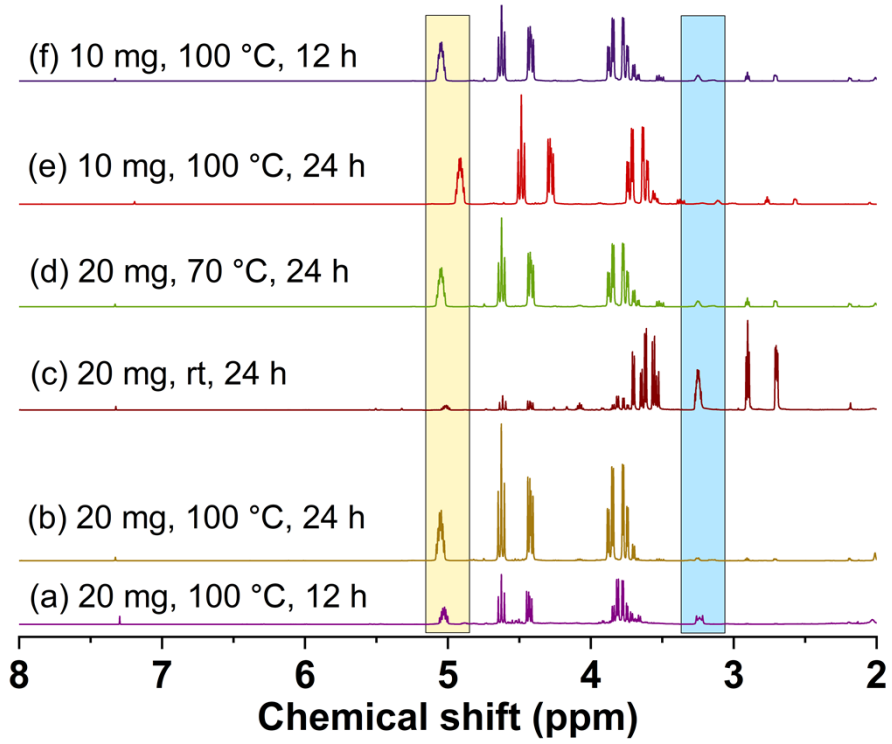

Figure S8. Comparative ^{1}H-NMR data of the conversion of Epichlorohydrin into cyclic carbonates.

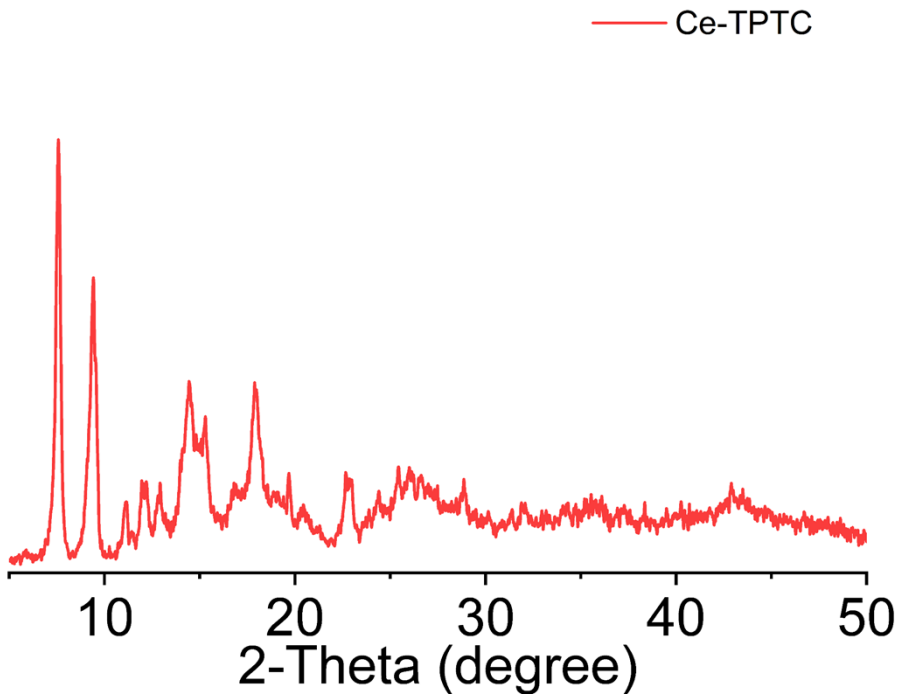

Figure S9. PXRD pattern of **Ce-TPTC** MOF.

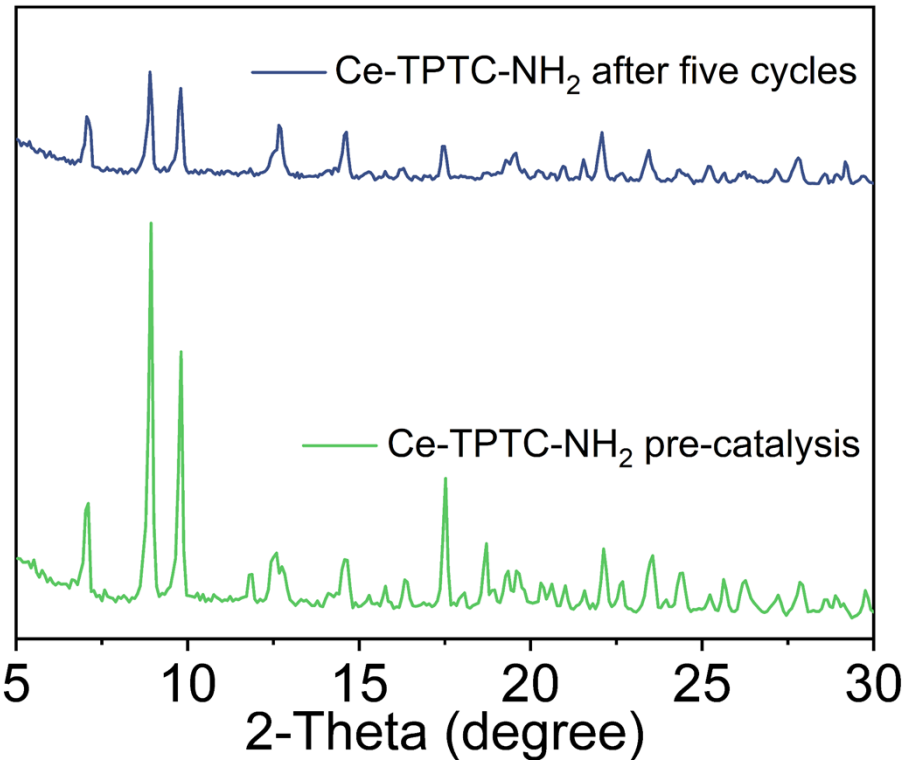

Figure S10. PXRD patterns of **Ce-TPTC-NH_2** before and after five reaction cycles in the cycloaddition reaction.

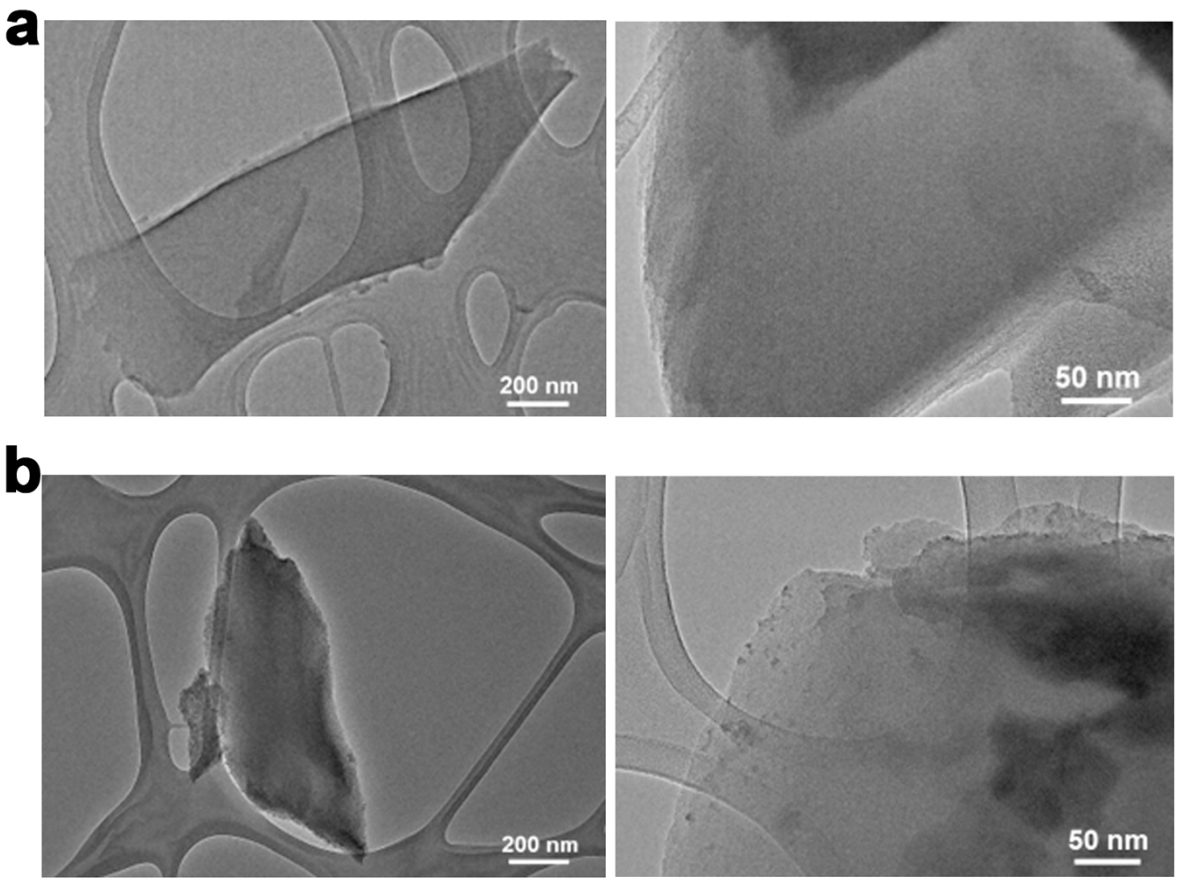

Figure S11. HR-TEM images of **Ce-TPTC-NH_2** (a) before and, (b) after five reaction cycles in cycloaddition reaction.

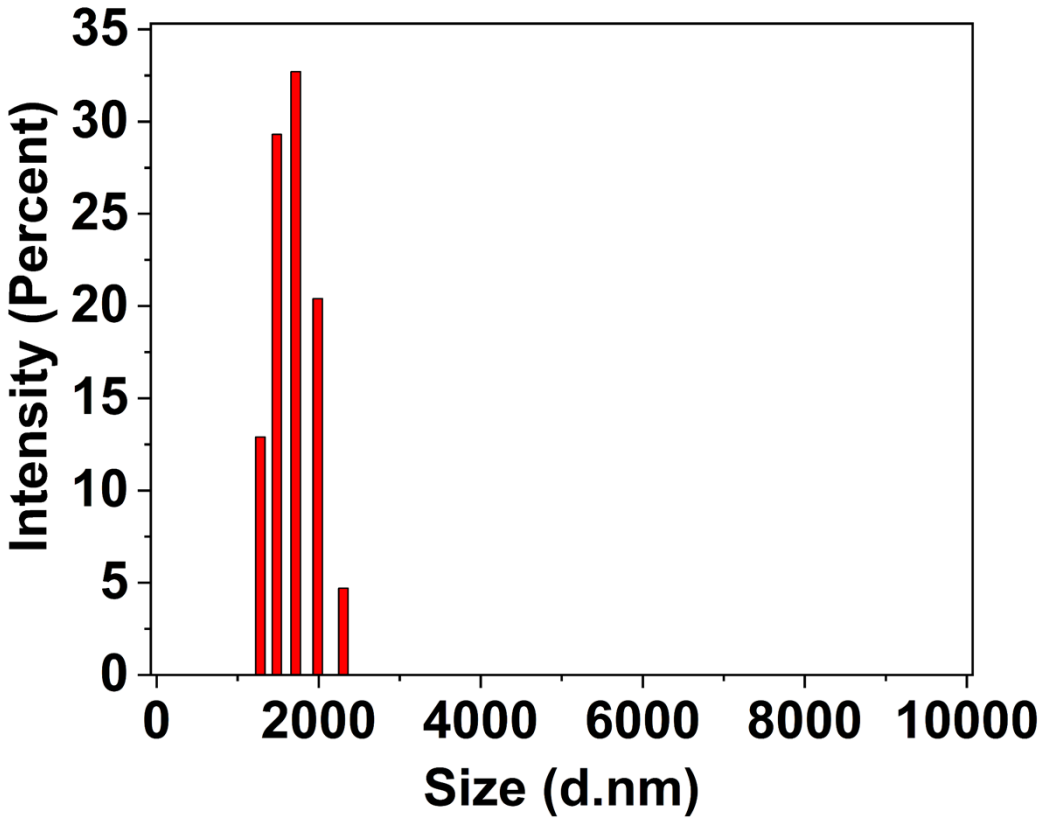

Figure S12. Dynamic light scattering measurement for **Ce-TPTC-NH_2** MOF.

References

1. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2015, **71**, 3-8.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
3. A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2009, **65**, 148-155.
4. J. Cai, H. Wang, H. Wang, X. Duan, Z. Wang, Y. Cui, Y. Yang, B. Chen and G. Qian, *RSC Adv.*, 2015, **5**, 77417-77422.
5. K. M. Bhin, J. Tharun, K. R. Roshan, D.-W. Kim, Y. Chung and D.-W. Park, *J. CO_2 Util.*, 2017, **17**, 112-118.
6. A. Bavykina, N. Kolobov, I. S. Khan, J. A. Bau, A. Ramirez and J. Gascon, *Chem. Rev.*, 2020, **120**, 8468-8535.
7. Q. Yang, C. C. Yang, C. H. Lin and H. L. Jiang, *Angew. Chem. Int. Ed.*, 2019, **131**, 3549-3553.
8. J. F. Kurisingal, Y. Rachuri, Y. Gu, R. K. Chitumalla, S. Vuppala, J. Jang, K. K. Bisht, E. Suresh and D.-W. Park, *ACS Sustainable Chem. Eng.*, 2020, **8**, 10822-10832.
9. Y. Hu, R. Abazari, S. Sanati, M. Nadafan, C. L. Carpenter-Warren, A. M. Slawin, Y. Zhou and A. M. Kirillov, *ACS Appl. Mater. Interfaces*, 2023, **15**, 37300-37311.
10. W.-L. Bao, J. Kuai, H.-Y. Gao, M.-Q. Zheng, Z.-H. Sun, M.-Y. He, Q. Chen and Z.-H. Zhang, *Dalton Trans.*, 2024, **53**, 6215-6223.
11. C.-Y. Gao, J. Ai, H.-R. Tian, D. Wu and Z.-M. Sun, *Chem. Commun.*, 2017, **53**, 1293-1296.