

Supporting Information for

**A Stable Nanotubular Metal–Organic Framework as Heterogeneous
Catalyst for Efficient Chemical Fixation of CO₂**

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Materials and Characterizations

Unless otherwise specified, all reagents and solvents are AR grade and do not need further purification when used. 4,4',4''-tricarboxyltriphenylamine (H₃tca) was synthesized according to the literature methods.^{S1} Cd(NO₃)₂·4H₂O was purchased from Shanghai Fourth Chemical Reagent Company (China). The epoxides (epichlorohydrin, epibromohydrin, glycidol, allyl glycidyl ether, butyl glycidyl ether, glycol diglycidyl ether, 2-(phenoxyethyl) oxirane, 2-((4-nitrophenoxy)methyl) oxirane, 2-((4-methoxyphenoxy)methyl)oxirane, 1,3-bis(oxiran-2-ylmethoxy)benzene) and Tetrabutylammonium Bromide (TBABr) were purchased from Beijing Innochem Science & Technology Co., Ltd.

JASCO FT/IR-430 machine was used to test FT-IR spectra of the sample KBr pellets. Rigaku D/max-2400 X-ray powder diffractometer (Japan) was used to test X-Ray powder diffraction (XRD) patterns of the samples, its radiation wavelength was Cu-K α ($\lambda = 1.5405 \text{ \AA}$). Bruker-400 spectrometer was used to test ¹H NMR spectra, its internal standard was Me₄Si. The C, H and N elemental analyses were tested on a Vario EL III elemental analyzer. Hitachi SU8010 was used to test the morphologies of the prepared samples treated by Pt sputtering for 90 s by a Field Emission Scanning Electron Microscopy (SEM). FT-IR spectra were recorded as KBr pellets on JASCO FT/IR-430. X-ray photoelectron spectroscopy (XPS) experiments were performed with a PHI QUANTUM2000 surface analysis instrument. Rigaku Thermo plus TG-8120 instrument was used to test thermogravimetric analysis (TGA), its ramp rate was 5 °C/min and its flow was static air. Leeman PROFILE

SPEC inductively coupled plasma mass spectrometry (ICP-MS) was used to test the contents of metal ions.

Synthesis of Cd-TCA'

Cd-TCA was firstly soaked in a methanol solution, and exchanged with the fresh methanol every 20 minutes. The removal of DMA molecules was confirmed through FT-IR. Then the compound was further desolvated under vacuum at 423 K for 12 h to afford the activated samples Cd-TCA'.

Crystallographic studies

A suitable single crystal was mounted on a Bruker APEX II CCD diffractometer, whose monochromator is graphite and radiation is Mo-K α ($\lambda = 0.71073 \text{ \AA}$). The direct methods was used for the solution of the structure and full-matrix least-squares cycles was used for the refinement in SHELXTL version 6.1. A riding model was used for the refinement of hydrogen atoms. SQUEEZE program within PLATON was used to remove disorder solvent molecules.

Table S1. Crystallographic data for Cd-TCA

Cd-TCA	
formula	C ₃₇ H ₄₈ N ₅ O ₁₀ Cd _{1.5}
formula weight	891.40
crystal system	trigonal
space group	<i>R</i> -3 <i>c</i>
<i>a</i> /Å	41.5946(11)
<i>b</i> /Å	41.5946(11)
<i>c</i> /Å	28.0270(11)
γ (°)	120
<i>V</i> /Å ³	41993(3)
<i>Z</i>	36
ρ_{calcd} /g cm ⁻³	1.269
μ /mm ⁻¹	5.959
Collected reflections	8233
unique reflections	6820
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.1074
<i>wR</i> ₂ (all data)	0.3543
CCDC	2193251

Table S2 Selected bond lengths (Å) and angles (°) for Cd-TCA.

Cd(1)–O(5A)	2.239(4)	Cd(1)–O(5B)	2.239(4)
Cd(1)–O(4C)	2.257(3)	Cd(1)–O(4D)	2.257(3)
Cd(1)–O(2E)	2.274(4)	Cd(1)–O(2)	2.274(4)
Cd(2)–O(6)	1.936(4)	Cd(2)–O(1F)	1.938(4)
Cd(2)–O(7)	1.982(5)	Cd(2)–O(3G)	2.032(3)
Cd(2)–O(4G)	2.416(4)	Cd(2)–C(1G)	2.540(5)
O(5A)–Cd(1)–O(5B)	179.989(1)	O(5A)–Cd(1)–O(4C)	87.06(15)
O(5B)–Cd(1)–O(4C)	92.95(14)	O(5A)–Cd(1)–O(4D)	92.94(14)
O(5B)–Cd(1)–O(4D)	87.05(15)	O(4C)–Cd(1)–O(4D)	180.0
O(5A)–Cd(1)–O(2E)	92.19(15)	O(5B)–Cd(1)–O(2E)	87.81(15)
O(4C)–Cd(1)–O(2E)	89.15(14)	O(4D)–Cd(1)–O(2E)	90.85(14)
O(5A)–Cd(1)–O(2)	87.81(15)	O(5B)–Cd(1)–O(2)	92.19(15)
O(4C)–Cd(1)–O(2)	90.85(14)	O(4D)–Cd(1)–O(2)	89.14(14)
O(2E)–Cd(1)–O(2)	180.0	O(6)–Cd(2)–O(1F)	135.76(16)
O(6)–Cd(2)–O(7)	96.09(19)	O(1F)–Cd(2)–O(7)	94.6(2)
O(6)–Cd(2)–O(3G)	108.92(16)	O(1F)–Cd(2)–O(3G)	108.35(16)
O(7)–Cd(2)–O(3G)	107.6(2)	O(6)–Cd(2)–O(4G)	89.35(16)
O(1F)–Cd(2)–O(4G)	90.68(17)	O(7)–Cd(2)–O(4G)	165.65(19)
O(3G)–Cd(2)–O(4G)	58.04(14)	O(6)–Cd(2)–C(1G)	99.18(16)
O(1F)–Cd(2)–C(1G)	101.98(18)	O(7)–Cd(2)–C(1G)	136.5(2)
O(3G)–Cd(2)–C(1G)	28.94(17)	O(4G)–Cd(2)–C(1G)	29.16(16)

Symmetry code A: $2/3+x-y$, $4/3-y$, $-1/6-z$; B: $1-x+y$, y , $-1/2+z$; C: $2-x$, $1-x+y$, $-1/2-z$; D: $-1/3+x$, $1/3+x-y$, $-1/6+z$; E: $5/3-x$, $4/3-y$, $-2/3-z$; F: $5/3-y$, $1/3+x-y$, $1/3+z$; G: $1-x+y$, y , $1/2+z$.

Figure S1. The asymmetric unit of Cd-TCA. Atomic scheme: Cd, green; O, red; C, gray; N, blue; H, light green.

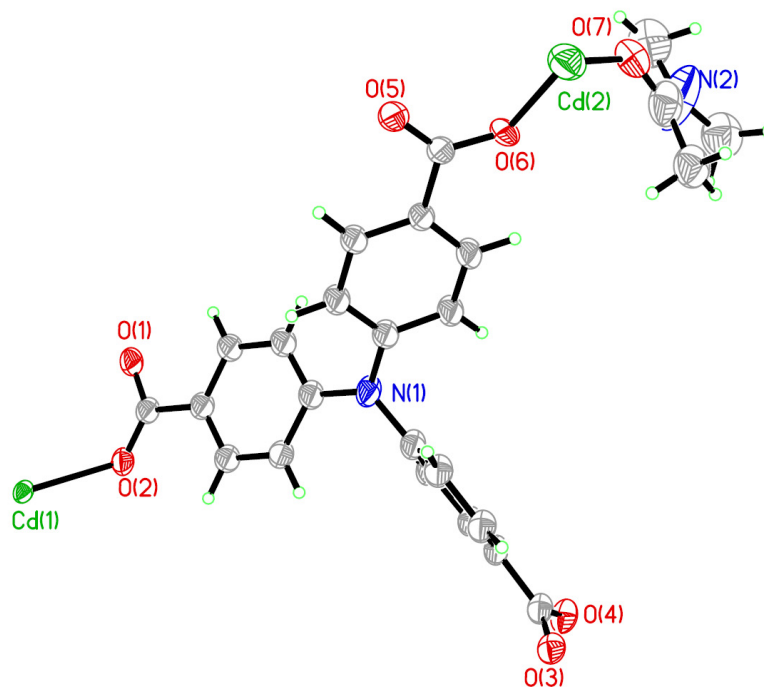


Figure S2. (a) The Cd coordination environment in Cd-TCA. (b) The $\mu_6\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^2$ coordination mode of the tca^{3-} ligand.

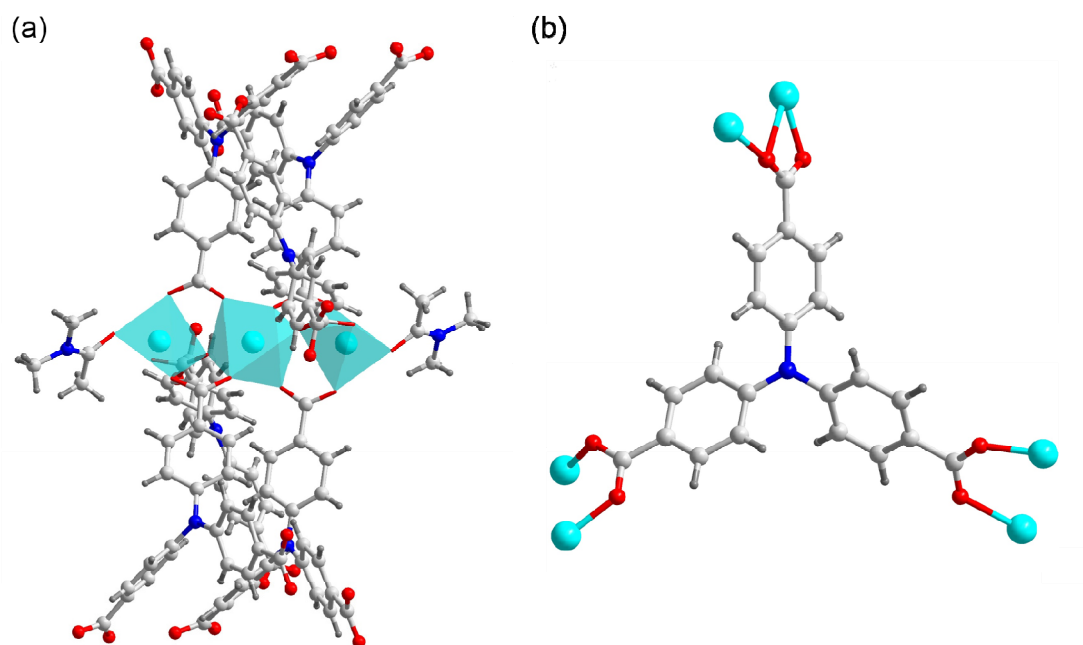


Figure S3. The “crown ether”-like hexagonal metallo-macrocycles extend infinitely along the ab plane with adjacent channels sharing the corrugated walls.

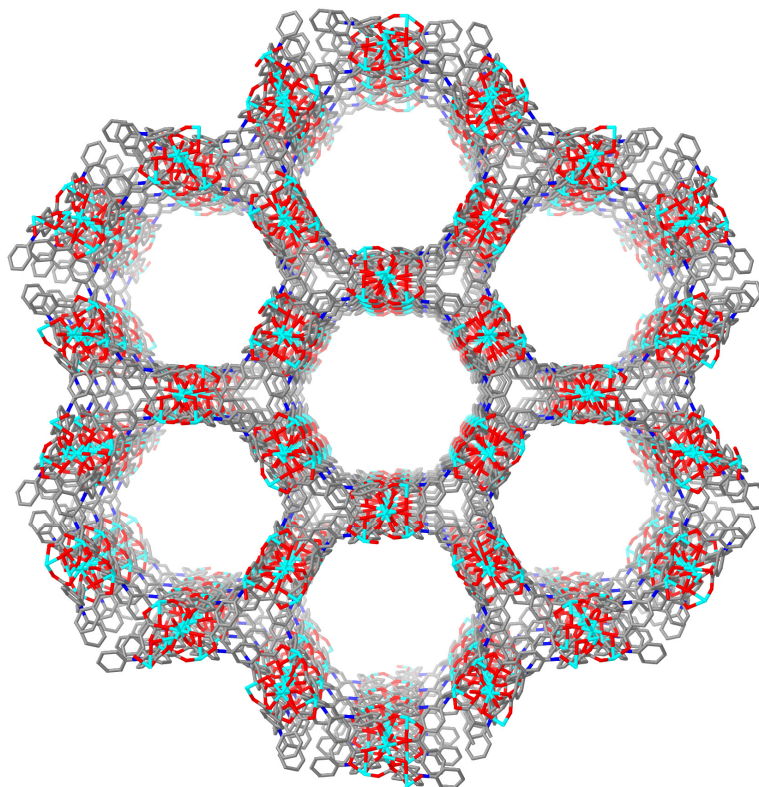


Figure S4. FT-IR of Cd-TCA and Cd-TCA'.

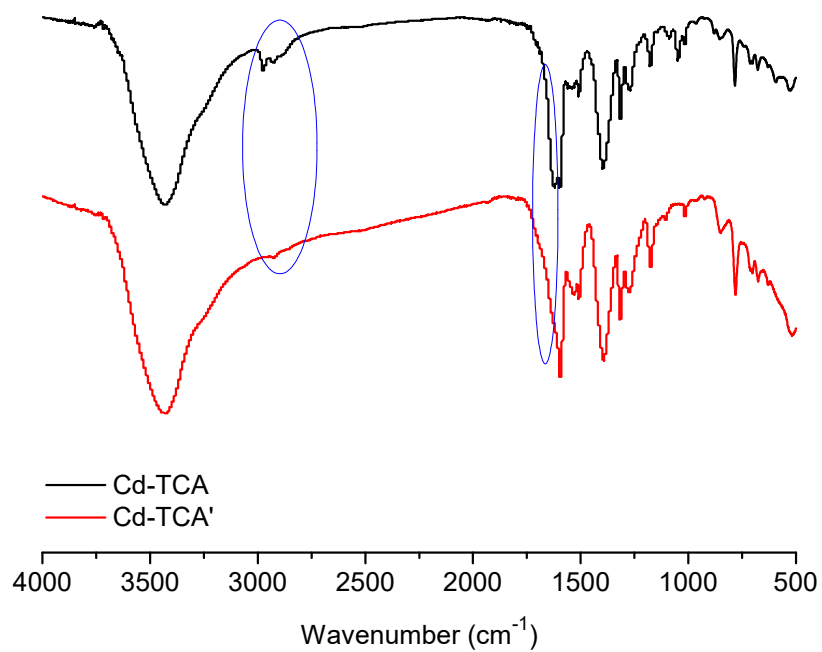


Figure S5. Optimized catalyst dosage and reaction temperature experiments of coupling of epichlorohydrin with CO₂.

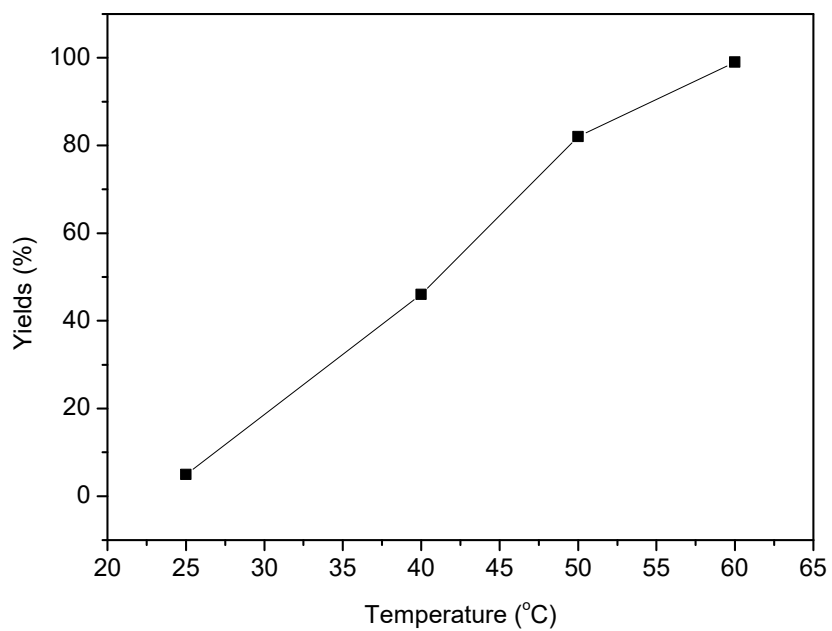
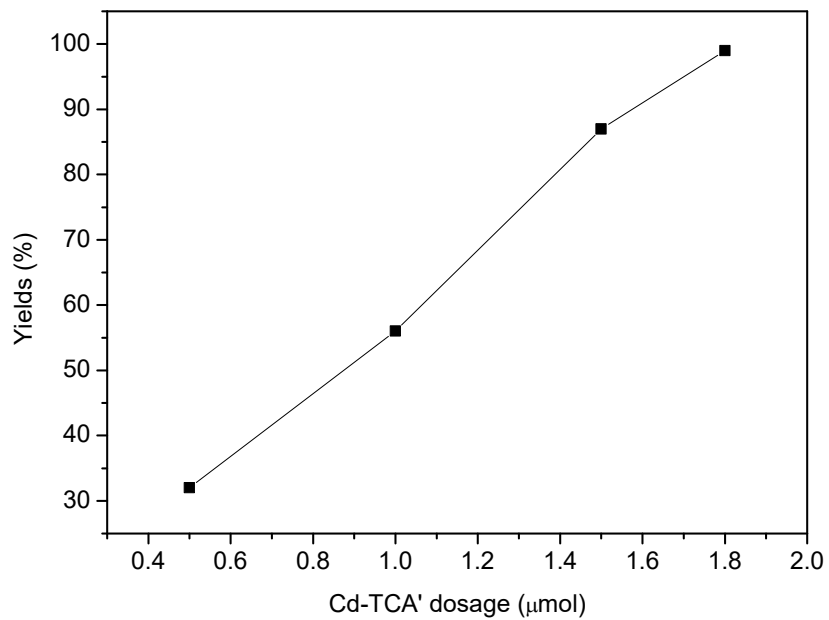


Figure S6. SEM image of Cd-TCA' (left) and Cd-TCA' after 5 cycles of catalysis (right).

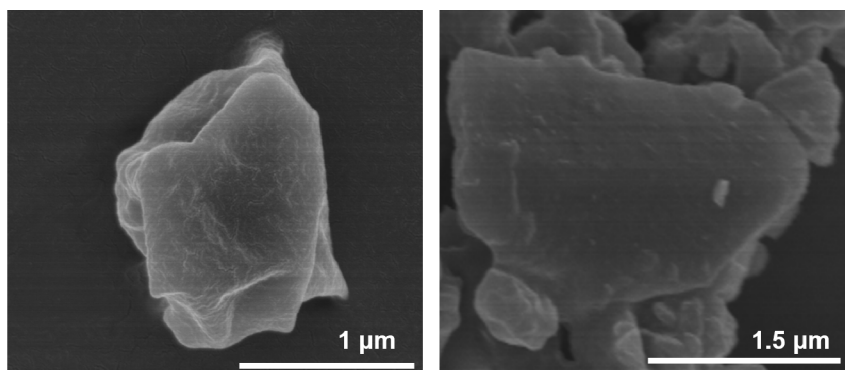


Figure S7. FT-IR spectra of Cd-TCA' (black), Cd-TCA' impregnated with epichlorohydrin (red) and epichlorohydrin (green).

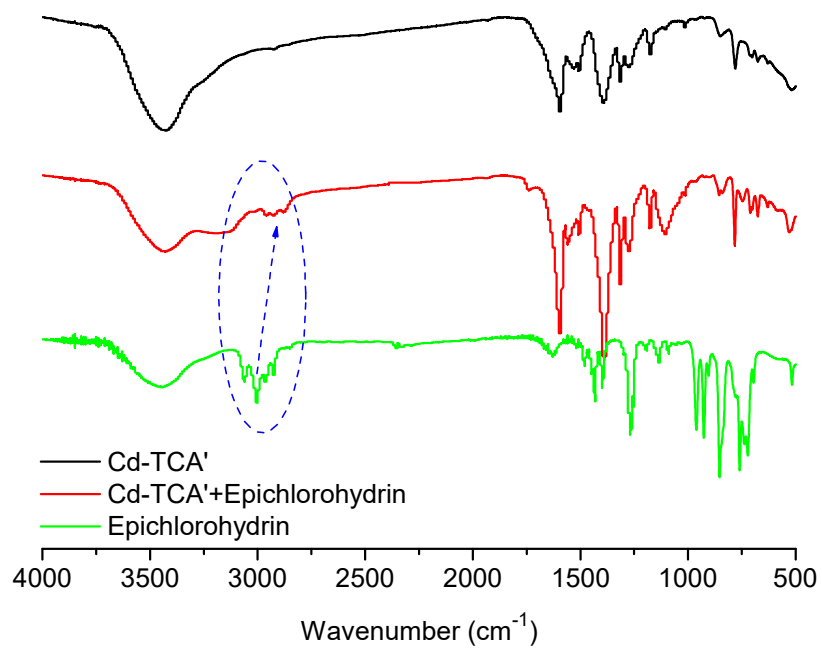
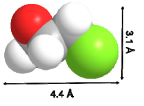
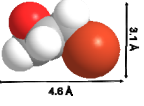
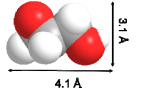
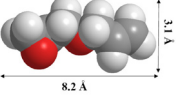
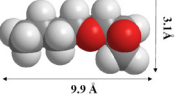
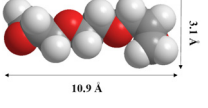
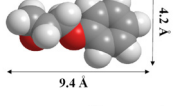
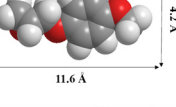
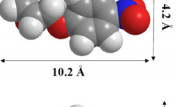
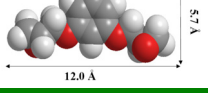


Table S3. Comparison with different MOFs catalysts in the cyclic addition of CO₂ and epichlorohydrin under similar conditions (0.1 MPa CO₂).

Entry	Catalyst	T (K)	T (hr)	Yield(%)	TON	TOF	Ref.
1	ZIF-8-HS	363	24	98	/	/	S2
2	PNU-25-NH ₂	338	18	92	1380	76.7	S3
3	IL@MIL-101-SO ₃ H	363	48	98	/	/	S4
4	polyILs@MIL-101	343	24	94	/	/	S5
5	UiO-67-IL	363	3	99	/	/	S6
6	Meim-UiO-66	393	24	100	192	8	S7
7	1	343	15	99	200	13	S8
8	Co(II)-MOF	353	9	99	/	/	S9
9	Cu(II)-MOF	343	16	99	4	0.25	S10
10	Ni-MOF-1a	333	6	97	38.8	6.5	S11
11	1	343	15	100	200	13.3	S12
12	1	333	10	97	194	19.4	S13
13	1	343	12	100	80	6.7	S14
14	FJI-C10	333	24	87	494	20.6	S15
15	1	323	12	98	19.6	1.63	S16
16	F-NH ₂ -Zr(H ₂ L)	333	48	85	850	17.7	S17
17	1	333	12	99	247.5	20.6	S18
18	Cd-TCA'	333	6	100	1833	306	This work

Table S4. The molecular size of selected substrates.

Entry	Epoxides	Molecular Size
1	<chem>ClCC1OC1</chem>	
2	<chem>BrCC1OC1</chem>	
3	<chem>OCC1OC1</chem>	
4	<chem>C=CCOC1OC1</chem>	
5	<chem>CCCCOC1OC1</chem>	
6	<chem>C1OC1CCOC2OC2</chem>	
7	<chem>c1ccc(cc1)OCC1OC1</chem>	
8	<chem>COc1ccc(cc1)OCC1OC1</chem>	
9	<chem>[O-][N+](=O)c1ccc(cc1)OCC1OC1</chem>	
10	<chem>OCC1OC1c2ccc(OCC1OC1)cc2</chem>	

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