Supporting Information

Polyamine Functionalized Imidazolyl Poly(ionic liquid)s for the Efficient Conversion of CO_2 into Cyclic Carbonates

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General information

All the epoxide substrates used were of analytical grade, and sourced from Energy Chemical of Anhui Zesheng Technology Co., Ltd. (Shanghai, China). Divinylbenzene (DVB) and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. DVB was treated to remove the polymerization inhibitor before use. All the solvents were used as received without further purification.

Micromeritics ASAP 2460 system was operated to measure nitrogen adsorption and desorption isotherms at the liquid-nitrogen temperature of 77 K, the samples were degassed in vacuum at 120 ℃ for 10 h before analysis , their surface areas and pore size distribution, pore volumes of samples were calculated by the Brunauer−Emmett−Teller (BET) equation and non-local density functional theory (NLDFT) model. Fourier transform infrared spectroscopy (FT-IR) spectrum were obtained from a Nicolet 6700 spectrophotometer ranging from 4000 to 400 cm^{-1} by using KBr pellets. ^{1}H NMR spectra were identified on a Bruker Avance III HD 400 MHz spectrometer with the solvent D_2O and internal reference tetramethylsilane (TMS) at room temperature. Solid-state ^{13}C CP/MAS NMR was registered in a Brucker 400M with 12 kHz spinning rate. The crystal phase of synthesized

samples was identified by X-ray diffraction (XRD, Bruker AXS D8-Focus, Germany) with Cu Kα radiation over the range of 2θ from 5° to 70°. A Netzsch STA 449 F3 thermogravimeter was employed to provide Thermogravimetric analysis (TGA) from 30 to 700 °C at the heating rate of 10 K min^{-1} under dry air. The content of C, H, N elements and their distribution were obtained from a CHN elemental mode of Vario EL cube and elemental mapping in scanning electron microscope (SEM), respectively. SEM was characterized the morphologies and structures of the samples by a SU8010 model Hitachi microscope. The DFT calculations was performed on BIOVIA Materials Studio 2017, the geometry optimizations were conducted by using the GGA-PW91 functional together with the Effective Core Potentials core treatment and DNP basis set.

XRD and TGA of N_4-PIL-2

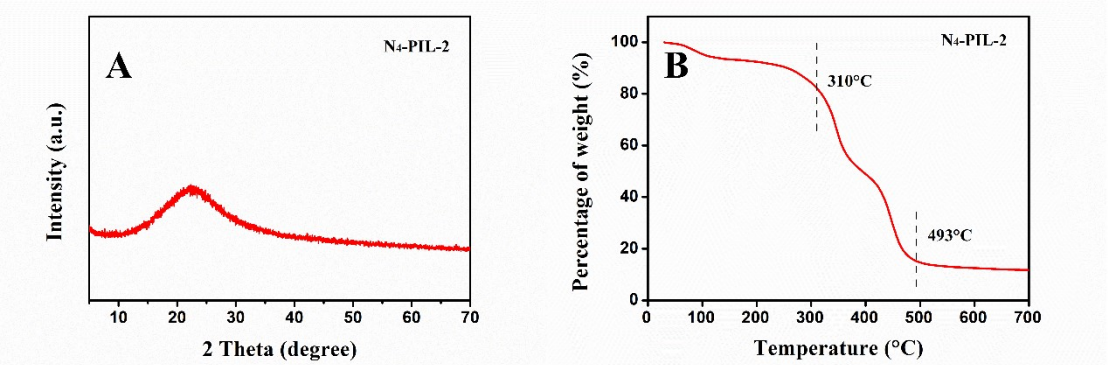
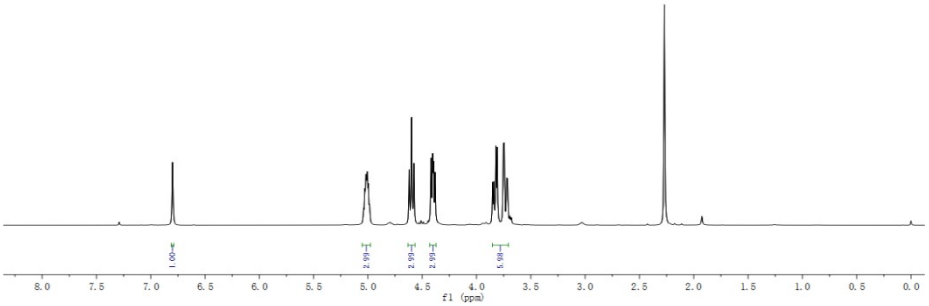


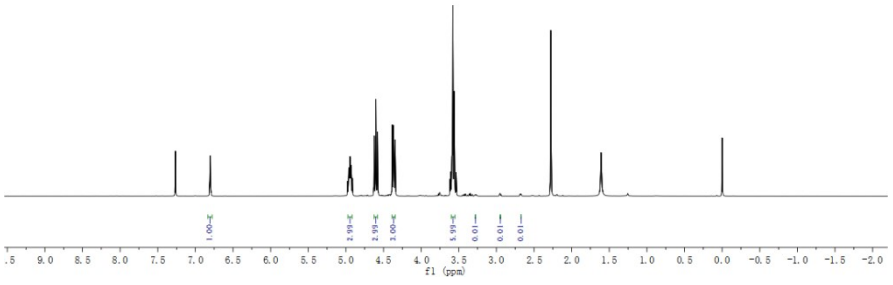
Fig. S1. (A) XRD patterns of the N_4-PIL-2; (B) TGA curves of N_4-PIL-2.

The ^{1}H NMR spectrums

^{1}H NMR of crude product of chloropropene carbonate (containing 10 mol % mesitylene)



^{1}H NMR of crude product of cyclic carbonate from 2-(bromomethyl)oxirane (containing 10 mol % mesitylene)



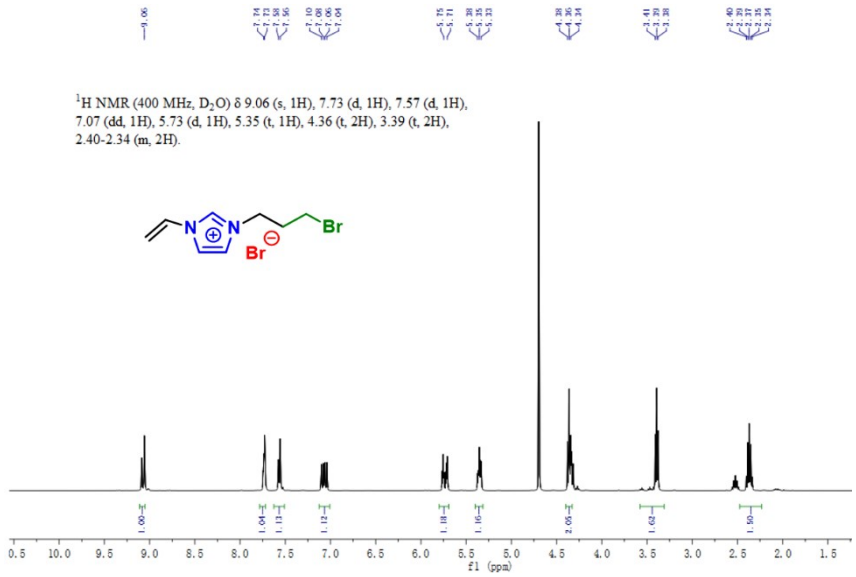


Fig. S2. ^{1}H NMR spectrum of VIMBr in D_2O (Scheme 1).

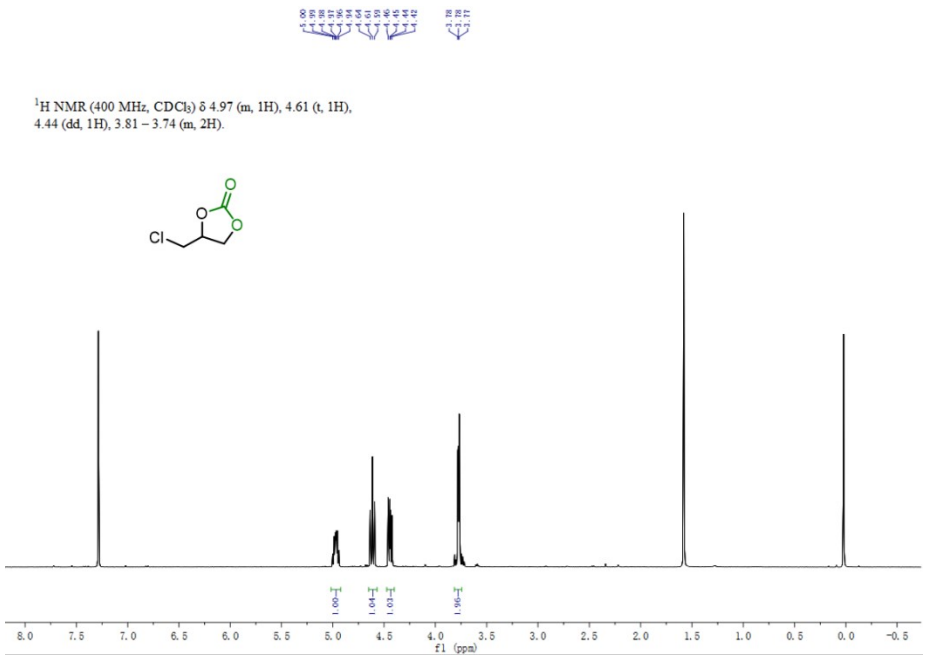


Fig. S3. Crude ^{1}H NMR spectrum of cyclic carbonate from epichlorohydrin in $CDCl_3$ (Table 4, entry 1).

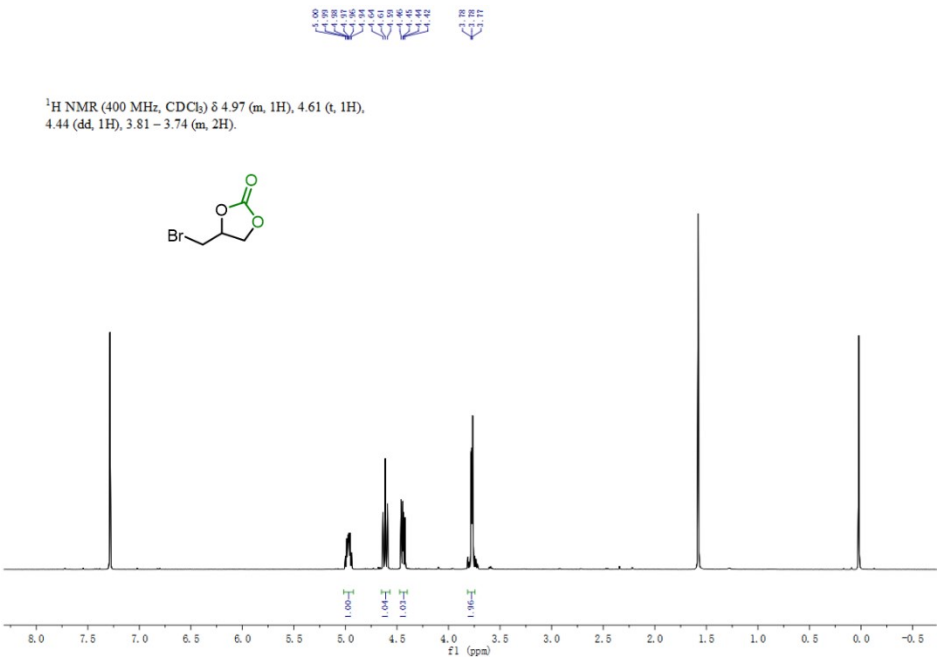


Fig. S4. Crude ^{1}H NMR spectrum of cyclic carbonate from 2-(bromomethyl)oxirane in $CDCl_3$ (Table 4, entry 3).

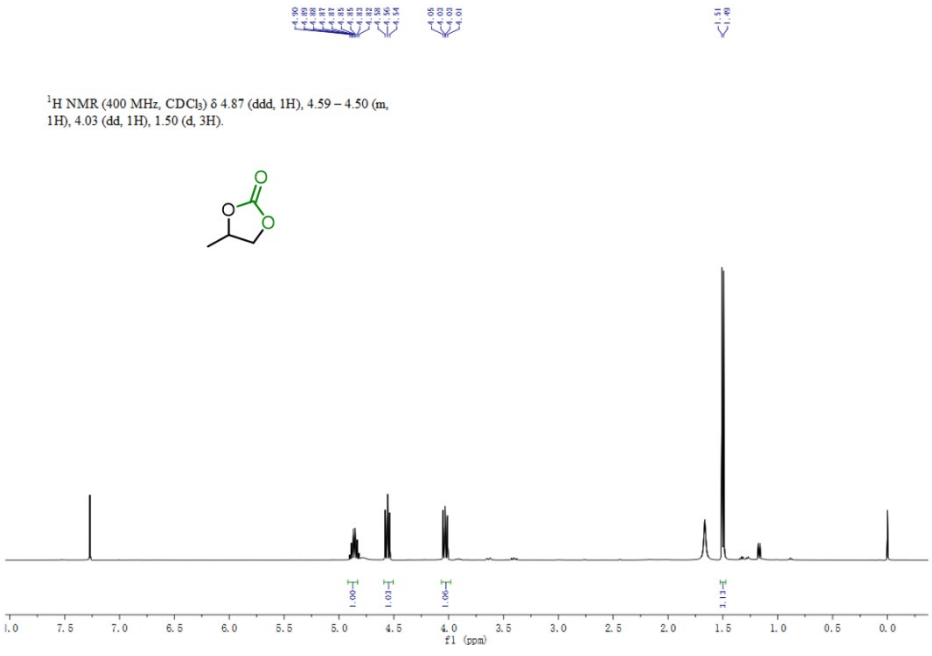


Fig. S5. Crude ^{1}H NMR spectrum of cyclic carbonate from propylene oxide in $CDCl_3$ (Table 4, entry 4).

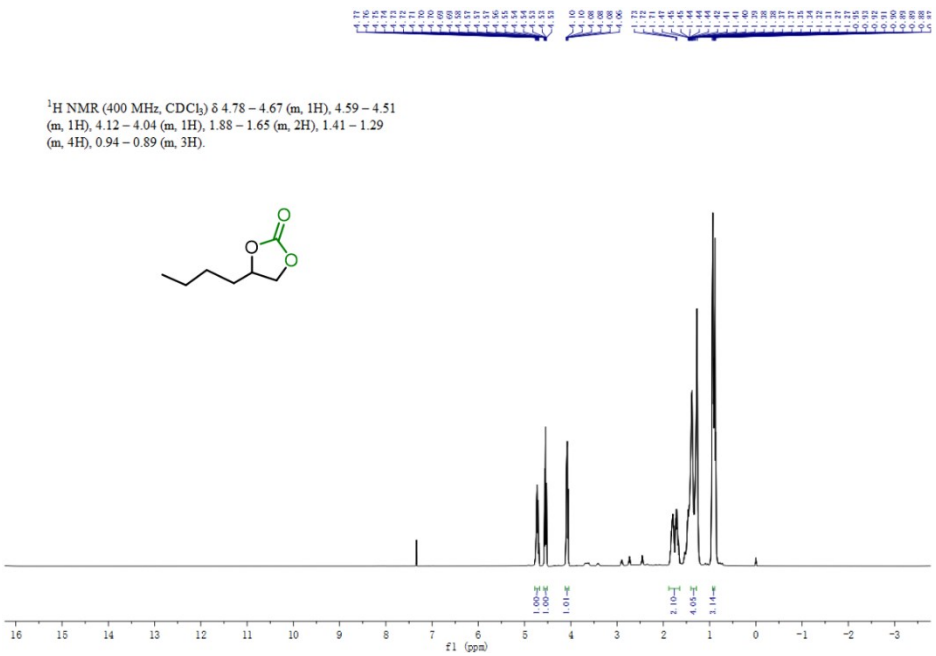


Fig. S6. Crude ^{1}H NMR spectrum of cyclic carbonate from 1,2-epoxyhexane in $CDCl_3$ (Table 4, entry 5).

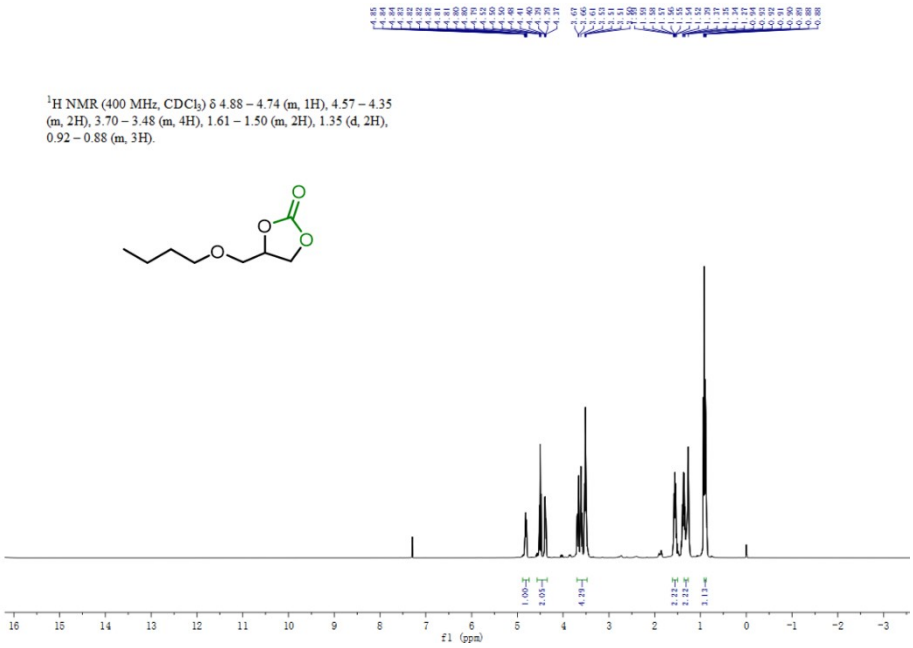


Fig. S7. Crude ^{1}H NMR spectrum of cyclic carbonate from butyl glycidyl ether in $CDCl_3$ (Table 4, entry 6).

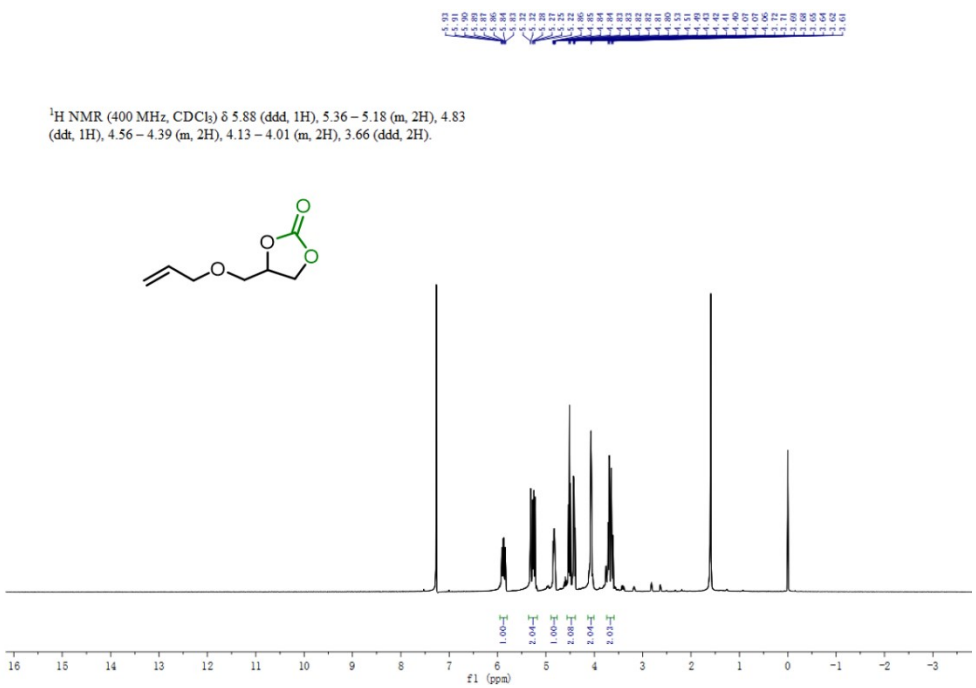


Fig. S8. Crude ^{1}H NMR spectrum of cyclic carbonate from allyl glycidyl ether in $CDCl_3$ (Table 4, entry 7).

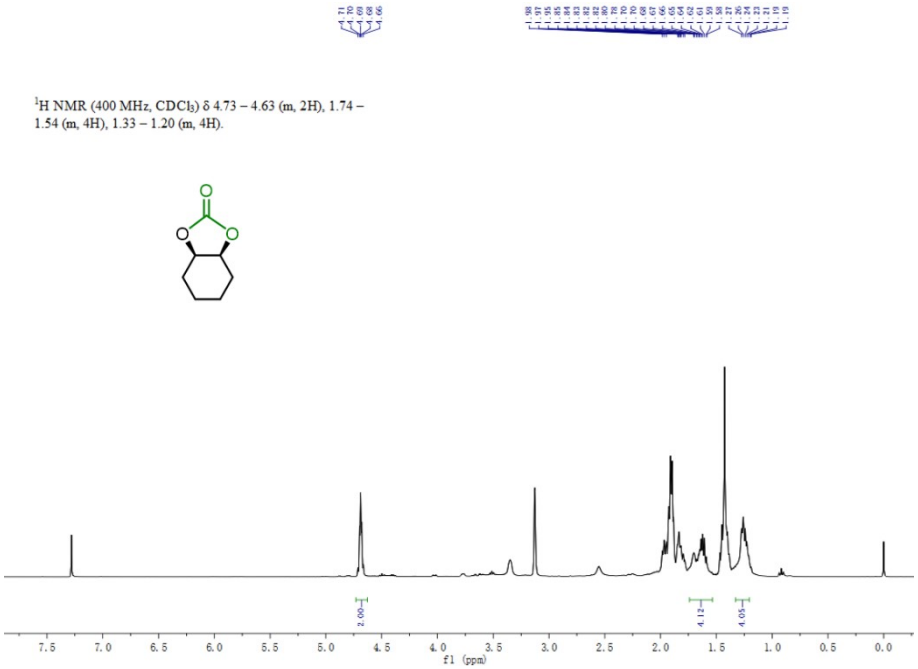


Fig. S9. Crude ^{1}H NMR spectrum of cyclic carbonate from cyclohexene oxide in $CDCl_3$ (Table 4, entry 8).

Comparisons of the catalytic activity of N_4-PIL-2.

Table S1. The heterogeneous catalysts for the cycloaddition reactions of epichlorohydrin and CO_2 at ambient pressure (0.1 MPa).

Catalyst	Catalyst Amount	Epoxide Amount	*T* (°C)	*t* (h)	*P* (MPa)	Con. (TOF)[a] (%)	Ref.
UIIP	0.150 mmol	38.4 mmol	110	21	0.1	98.0 **(11.9)**	S1
IP-1	0.300 mmol	10.0 mmol	100	18	0.1	76.0 **(1.41)**	S2
Ionization imidazole MOF	0.052 mmol	10.0 mmol	120	24	0.1	93.0 **(7.45)**	S3
CCTF-350	10.0 mg	10.0 mmol	120	24	0.1	95.0 **(18.8)**	S4
PEAMCl	100.0 mg	10.0 mmol	120	8	0.1	93.3 **(10.7)**	S5
DB10%- Pa-Tp	0.011 mmol	5.0 mmol	120	96	0.1	99.0 **(4.40)**	S6
PVIm-6-SCD	0.5 mol %	10.0 mmol	50	24	0.1	98.2 **(1.40)**	S7
CPP-IL	30.0 mg	12.7 mmol	100	24	0.1	99.0 **(4.00)**	S8
N_4-PIL-2	**0.012 mmol**	**12.7 mmol**	**100**	**24**	**0.1**	**98.0 (42.4)**	**This work**

[a] parantheses are TOF (h^{-1}) values calculated with the help of reported data.

Table S2. The heterogeneous catalysts for the cycloaddition reactions of epichlorohydrin and CO_2.

Catalyst	Catalyst Amount	Epoxide Amount	*T* (°C)	*t* (h)	*P* (MPa)	Con. (%)	Ref.
P(DMAEMA-EtOH)Br	50 mg	14.3 mmol	110	3	2.0	90.4	S9
PIM2	0.2 mol %	10.0 mmol	130	4	1.0	92.0	S10
V-PCIF-Br	2.9 mol %	5.0 mmol	100	6	1.0	98.0	S11
ZnTPy-BIM4/CNTs-3	Substrate/Catalyst=1450		120	2.5	1.5	98.0	S12
MIL-101(Cr)-$(AIm)_2ZnBr_2$	100 mg	35.7 mmol	120	1	1.0	99.4	S13
3-IPMP-EtI	0.5 mol %	30.0 mmol	90	5	1.0	90	S14
SBA16-PIL-Br	50.0 mg	5 mL	120	4	1.5	90.0	S15
PIL-4	20.0 mg	5.0 mmol	100	12	1.0	99.7	S16
HP-[BZPhIm]Cl-DCX-1	30.0 mg	5.0 mmol	120	5	1.0	99.9	S17
PHUs	[PHU urethane groups]/ [epoxide] = 0.20		120	16	5.2	92.0	S18
PEAMCl	100.0 mg	10 mmol	120	2	1.0	98.7	S5
N_4-PIL-2	**0.012 mmol**	**12.7 mmol**	**100**	**4**	**1.0**	**99.6**	**This work**

Cartesian Coordinates (Å) of the Optimized Structures.

Table S3. Cartesian Coordinates (Å) of the Optimized Structures.

Optimized Structures A

	x	y	z
N	-13.057202	-1.461949	-0.416622
C	-11.686635	-3.618786	0.188701
C	-9.198194	-3.081937	-0.218757
N	-9.051486	-0.612187	-1.052841
C	-11.403086	0.341911	-1.160603
C	-15.711631	-1.096954	-0.294087
C	-17.36152	-2.828852	0.492939
C	-6.750708	0.774275	-1.810972
C	-4.511218	0.387701	-0.032802
C	-2.542894	2.45409	-0.517306
N	-0.19335	2.034275	0.849162
C	1.414514	4.296798	0.719267
C	3.882209	4.037894	2.183051
N	5.861368	2.753066	0.77685
C	8.362429	3.082001	1.880045
C	10.449075	1.939376	0.265153
N	10.464217	-0.823013	0.385918
C	12.521627	-1.939148	-1.095329
C	12.530725	-4.821367	-0.84917
N	10.255129	-6.096997	-1.752778
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H	-19.359104	-2.361059	0.520094
H	-7.285887	2.775296	-1.861309
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H	-2.093265	2.523969	-2.549548
H	-0.593308	1.698775	2.71133
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H	5.472074	0.881036	0.53009
H	8.513128	2.317746	3.832653
H	8.706575	5.125739	2.03975
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H	10.695398	-1.349062	2.233599
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H	12.233852	-1.407809	-3.08752
H	12.810777	-5.317474	1.155794
H	14.174668	-5.584504	-1.858038
H	10.173577	-5.995897	-3.677275
H	8.718044	-5.127005	-1.099893

Optimized Structures B

	x	y	z
N	-7.224333	4.473169	1.746283
C	-6.001194	2.587608	0.385731
C	-3.970545	3.675414	-0.76613
N	-3.953079	6.203324	-0.117945
C	-5.93144	6.658383	1.413634
C	-9.455206	4.24577	3.218247
C	-10.920701	2.197026	3.277716
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C	0.244377	8.139001	0.907162
C	2.236175	9.993393	-0.061428
N	4.504375	9.981441	1.506107
C	6.36285	11.843182	0.584911
C	8.792965	11.888575	2.140132
N	10.682539	10.11054	1.245688
C	13.124706	10.385389	2.478084
C	15.100533	8.583658	1.415456
N	14.571272	5.976657	2.146558
C	16.276179	4.087426	1.07112
C	15.319708	1.421688	1.680652
N	12.818339	0.834116	0.649602
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H	10.058292	8.281084	1.304179
H	13.023655	10.125845	4.564178
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H	11.712486	2.414744	0.837153
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C	6.335164	0.393093	0.40184
Cl	6.301367	0.131785	-3.009015
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H	8.147962	-0.371748	1.052925

Optimized Structures C

	x	**y**	**z**
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C	-14.637417	-1.815036	0.969267
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C	-6.373815	1.084262	-2.146705
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O	3.678694	-2.099575	2.979467

References

S1. M. A. Ziaee, Y. Tang, H. Zhong, D. Tian and R. Wang, *ACS Sustainable Chemistry & Engineering*, 2018, **7**,

2380-2387.

S2. Y. Zhang, E.-S. M. El-Sayed, K. Su, D. Yuan and Z. Han, *Journal of CO_2 Utilization*, 2020, **42**, 101301.

S3. J. Liang, R. P. Chen, X. Y. Wang, T. T. Liu, X. S. Wang, Y. B. Huang and R. Cao, *Chem Sci*, 2017, **8**, 1570-1575.

S4. T. T. Liu, R. Xu, J. D. Yi, J. Liang, X. S. Wang, P. C. Shi, Y. B. Huang and R. Cao, *ChemCatChem*, 2018, **10**, 2036-2040.

S5. X. Wang, Q. Dong, Z. Xu, Y. Wu, D. Gao, Y. Xu, C. Ye, Y. Wen, A. Liu, Z. Long and G. Chen, *Chemical Engineering Journal*, 2021, **403**, 126460.

S6. J. Cao, W. Shan, Q. Wang, X. Ling, G. Li, Y. Lyu, Y. Zhou and J. Wang, *ACS Appl Mater Interfaces*, 2019, **11**, 6031-6041.

S7. Y. Xie, J. Liang, Y. Fu, M. Huang, X. Xu, H. Wang, S. Tu and J. Li, *Journal of Materials Chemistry A*, 2018, **6**, 6660-6666.

S8. C. Cui, R. Sa, Z. Hong, H. Zhong and R. Wang, *ChemSusChem*, 2020, **13**, 180-187.

S9. T. Ying, X. Tan, Q. Su, W. Cheng, L. Dong and S. Zhang, *Green Chemistry*, 2019, **21**, 2352-2361.

S10. Y. Wang, J. Nie, C. Lu, F. Wang, C. Ma, Z. Chen and G. Yang, *Microporous and Mesoporous Materials*, 2020, **292**, 109751.

S11. G. Chen, X. Huang, Y. Zhang, M. Sun, J. Shen, R. Huang, M. Tong, Z. Long and X. Wang, *Chemical Communications*, 2018, **54**, 12174-12177.

S12. S. Jayakumar, H. Li, J. Chen and Q. Yang, *ACS Appl Mater Interfaces*, 2018, **10**, 2546-2555.

S13. M. Zou, W. Dai, P. Mao, B. Li, J. Mao, S. Zhang, L. Yang, S. Luo, X. Luo and J. Zou, *Microporous and Mesoporous Materials*, 2021, **312**, 110750.

S14. W. Zhang, Y. Mei, P. Wu, H.-H. Wu and M.-Y. He, *Catalysis Science & Technology*, 2019, **9**, 1030-1038.

S15. R. Qu, Z. Ren, N. Li, F. Zhang, Z. J. Zhang and H. Zhang, *Journal of CO_2 Utilization*, 2020, **38**, 168-176.

S16. H. Song, Y. Wang, M. Xiao, L. Liu, Y. Liu, X. Liu and H. Gai, *ACS Sustainable Chemistry & Engineering*, 2019, **7**, 9489-9497.

S17. H. Song, Y. Wang, Y. Liu, L. Chen, B. Feng, X. Jin, Y. Zhou, T. Huang, M. Xiao, F. Huang and H. Gai, *ACS Sustainable Chemistry & Engineering*, 2021, **9**, 2115-2128.

S18. S. Motokucho and H. Morikawa, *Chemical Communications*, 2020, **56**, 10678-10681.