Porous cationic polymers: The impact of counteranions and charges on CO_2 capture and conversion

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Supporting Information

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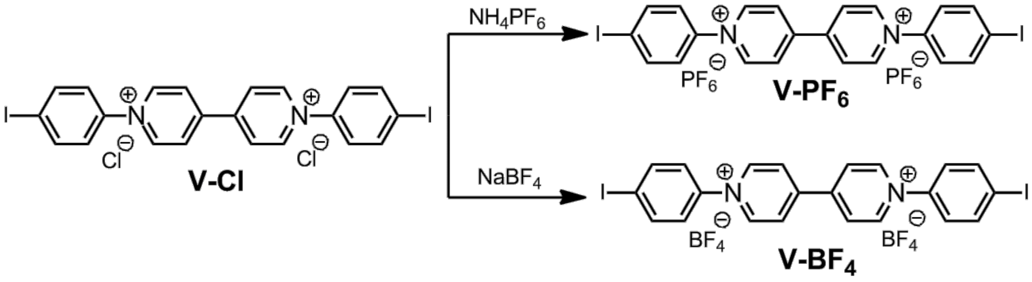
1. General Methods

Materials. Starting materials and reagents were purchased from Aldrich, TCI or ACROS and used as received without further purification. Tetrakis(4-ethynylphenyl)methane[1] and 1,1'-bis(4-iodophenyl)-[4,4'-bipyridine]-1,1'-diium dichloride[2] were prepared following synthetic procedures reported in the literature. All reactions were performed under Ar atmosphere in dry solvents unless otherwise noted. Dry solvents were also purged with Ar gas before its usage. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets, pre-coated with silica gel 60-F_{254} (Merck 5554). Flash chromatography was carried out using silica gel 60 (Silicycle) as the stationary phase.

Characterization Methods. ^{1}H and ^{13}C spectra were recorded on Bruker Avance 300 MHz NMR and Agilent 400 MHz NMR spectrometers at ambient temperature. Solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C, ^{11}B, ^{31}P NMR spectra of polymers were recorded on a Brucker Avance III 400 WB (400 MHz) NMR spectrometer at ambient temperature with a magic angle spinning rate of 7.0 kHz. FT-IR spectra were recorded on ATR mode by using Shimadzu FTIR Spectrometer. Thermogravimetric analysis was performed by using a NETZSCH-TG 209 F3 instrument and the samples were heated to 800^{o}C at a rate of 10^{o}C min^{-1} under air and N_2 atmosphere. The scanning electron microscopy (SEM) and energy dispersive X-ray absorption spectroscopy (EDS) analyses were carried out by using a Hitachi S-4800 FE-SEM at 2.0 - 10 kV. Samples were coated with platinum prior to the analysis. Elemental analysis (C, H, N) were recorded on a FlashEA 2000 [C, H, N, S] Elemental Analyzer. Powder X-ray Diffraction (PXRD) patterns of samples were collected over the 2Θ range 5^{o} to 90^{o} on a Bruker AXS D8 Discover multi-purpose high power X-ray diffractometer. The surface area and pore size distribution of samples were performed with a Micrometrics 3Flex Surface Characterization Analyzer by argon adsorption and desorption at 87 K. The samples were degassed at 100^{o}C for 6 h under vacuum before the analysis. The surface areas of samples were calculated using BET model in the pressure range determined from Rouquerol plot. The pore size distributions of samples were calculated from argon isotherms according to the Nonlocal Density Functional Theory (NLDFT) method using carbon a slit pore model. The low pressure CO_2 and N_2 adsorption isotherms of samples were taken under two different temperatures 273 and 298 K. The samples were also degassed before the adsorption analysis at 100°C under vacuum. The circulator was used to keep the temperature constant during adsorption/desorption analysis. The CO_2/N_2 selectivities were evaluated by using Idea Adsorbed Solution Theory (IAST), which is calculated by means of OriginPro v8.5 and Mathematica v10. Isosteric Heats of absorption (Q_{st}) values were calculated by using the standard calculation routine, that is Clausius-Clapeyron equation, in the data master offline data reduction software (Micrometrics).

2. Synthesis

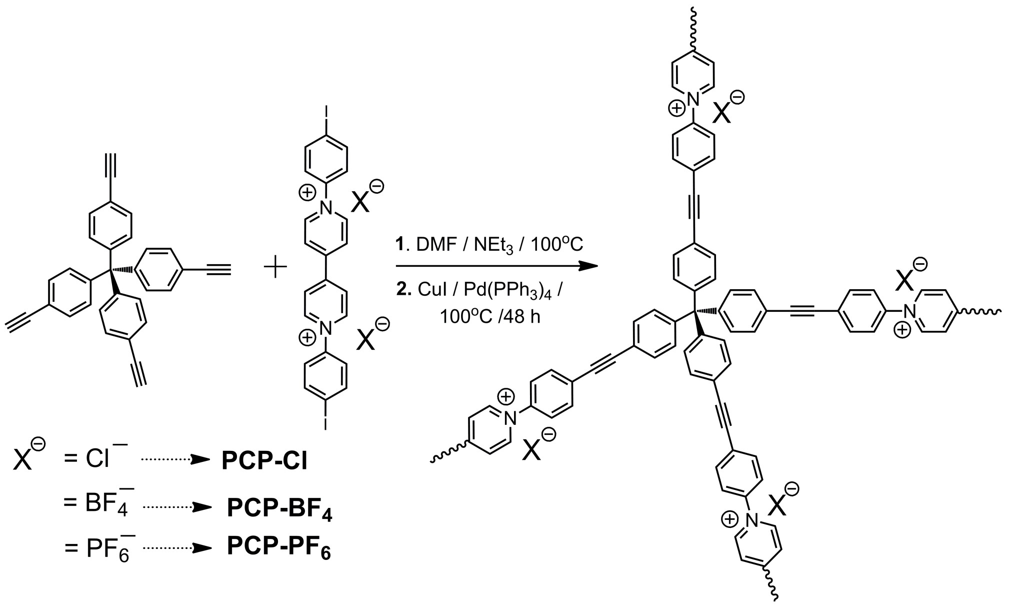
Synthesis of ***V-Cl, V-BF₄ and V-PF₆***



Synthesis of V-Cl : 1,1’-bis(4-iodophenyl)-[4,4’-bipyridine]-1,1’-diium dichloride (**V-Cl**)[2] was prepared following procedures reported in the literature. ^{1}H NMR (300 MHz, D_2O) δ = 9.34 (d, *J* = 7.0 Hz, 4H), 8.73 (d, *J* = 7.0 Hz, 4H), 8.11 (d, *J* = 8.8 Hz, 4H), 7.54 (d, *J* = 8.8 Hz, 4H) ppm. Elemental Analysis for **V-Cl** ($C_{22}H_{16}Cl_2I_2N_2$) [found %, (calcd)] (CHN): 39.61 C% (41.74), 2.32 H% (2.55), 4.13 N% (4.42).

Synthesis of V-BF$_4$: ,1'-bis(4-iodophenyl)-[4,4'-bipyridine]-1,1'-diium dichloride (**V-Cl**) (1.00 g, 1.58 mmol) was dissolved in 100 mL deionized (DI) water. Then, saturated sodium tetrafluoroborate solution was added dropwise to this mixture. The final suspension was stirred at room temperature for 6 h. Afterwards, the resulting precipitate was filtered and washed with excess deionized water. The final solid was dried under vacuum to give the desired product **V-BF$_4$** in quantitative yield. ^{1}H NMR (300 MHz, d_6-DMSO) $\delta = 9.66$ (d, $J =$ 6.8 Hz, 4H), 9.04 (d, $J = 6.8$ Hz, 4H), 8.20 (d, $J = 8.7$ Hz, 4H), 7.75 (d, $J = 8.7$ Hz, 4H) ppm. Elemental Analysis for **V-BF$_4$** ($C_{22}H_{16}B_2F_8I_2N_2$) [found %, (calcd)] (CHN): 35.89 C% (35.91), 2.29 H% (2.19), 3.87 N% (3.81).

Synthesis of V-PF$_6$: 1,1'-bis(4-iodophenyl)-[4,4'-bipyridine]-1,1'-diium dichloride (**V-Cl**) (1.00 g, 1.58 mmol) was dissolved in 100 mL DI water. Then, saturated ammonium hexaphlolorophosphate solution was added to this mixture. The final suspension was stirred at room temperature for 6 h. Afterwards, the resulting precipitate was filtered and washed with excess deionized water. The final solid was dried under vacuum to give the desired product **V-PF$_6$** in quantitative yield. ^{1}H NMR (300 MHz, d_6-DMSO) $\delta = 9.66$ (d, $J = 6.5$ Hz, 4H), 9.04 (d, $J = 6.5$ Hz, 4H), 8.20 (d, $J = 8.7$ Hz, 4H), 7.75 (d, $J = 8.7$ Hz, 4H) ppm. Elemental Analysis for **V-PF$_6$** ($C_{22}H_{16}F_{12}I_2N_2P_2$) [found %, (calcd)] (CHN): 30.41 C% (31.01), 2.01 H% (1.89), 3.48 N% (3.29).



Synthesis of ***PCPs.***

Synthetic Procedures For PCPs:

PCP-Cl : Tetrakis(4-ethynylphenyl)methane (150 mg, 0.36 mmol) and 1,1'-bis(4-iodophenyl)-[4,4'-bipyridine]-1,1'-diium dichloride (**V-Cl**) (304 mg, 0.48 mmol) were added into a 50 mL schlenk flask and dissolved in an anhydrous pre-degassed solvent mixture (20 mL, DMF/ NEt_3 ; 1:1) under Ar atmosphere. Then, the mixture was heated to 100°C. When the reaction mixture reached to the target temperature, a suspension of tetrakis(triphenylphosphine)palladium(0) (22.2 mg, 0.019 mmol) and copper(I) iodide (7.2 mg, 0.038 mmol) in an anhydrous DMF (3 mL) was added. The final reaction mixture was stirred under argon atmosphere for 48 h. After cooling to room temperature, the resulting precipitate was filtered and extensively washed with DMF (3 x 50 mL), THF (3 x 50 mL), methanol (3 x 50 mL), acetone (1 x 50 mL) and diethyl ether (1 x 50 mL). Thereafter, the brown solid was soaked into saturated aqueous sodium chloride solution for 24 h at room temperature in order to eliminate possibility of counteranion exchange during the polymerization reaction. Then, the solid was filtered and washed with H_2O (3 x 50 mL) and methanol (3 x 100 mL), subsequently. The final brown color solid was dried at room temperature under vacuum for 24 h to yield **PCP-Cl** (253 mg, 90 %). ($C_{77}H_{48}Cl_4N_4$) [found %, (calcd)] (CHN): 75.10 %C (78.97), 4.23 %H (4.13), 4.27 %N (4.78).

PCP-BF$_4$: Tetrakis(4-ethynylphenyl)methane (150 mg, 0.36 mmol) and (**V-BF$_4$**) (353 mg, 0.48 mmol) were added into a 50 mL schlenk flask and dissolved in an anhydrous pre-degassed solvent mixture (20 mL, DMF/ NEt_3 ; 1:1) under Ar atmosphere. Then, the mixture was heated to 100°C. When the reaction mixture reached to the target temperature, a suspension of tetrakis(triphenylphosphine)palladium(0) (22.2 mg, 0.019 mmol) and copper(I) iodide (7.2 mg, 0.038 mmol) in an anhydrous DMF (3 mL) was added. The final reaction mixture was stirred under Ar atmosphere for 48 h. After cooling it to room temperature, the resulting precipitate was filtered and extensively washed with DMF (3 x 50 mL), THF (3 x 50 mL), methanol (3 x 50 mL), acetone (1 x 50 mL) and diethyl ether (1 x 50 mL). Thereafter, the brown solid was soaked into saturated aqueous sodium tetrafluoroborate solution for 24 h at room temperature in order to eliminate possibility of counteranion exchange during the polymerization reaction. Then, the solid was filtered and washed with H_2O (3 x 50 mL) and methanol (3 x 100 mL). The final brown color solid was dried at room temperature under vacuum for 24 h to yield **PCP-BF$_4$** (287 mg, 87 %). ($C_{77}H_{48}B_4F_{16}N_4$) [found %, (calcd)] (CHN): 63.62 %C (67.19), 3.57 %H (3.51), 3.69 %N (4.07).

PCP-PF$_6$: Tetrakis(4-ethynylphenyl)methane (150 mg, 0.36 mmol) and (**V- PF$_6$**) (409 mg, 0.48 mmol) were added into a 50 mL schlenk flask and dissolved in an anhydrous pre-degassed solvent mixture (20 mL, DMF/ NEt_3 ; 1:1) under argon atmosphere. Then, the mixture was heated to 100°C. When the reaction mixture reached to the target temperature, a suspension of tetrakis(triphenylphosphine)palladium(0) (22.2 mg, 0.019 mmol) and copper(I) iodide (7.2 mg, 0.038 mmol) in an anhydrous DMF (3 mL) was added. The final reaction mixture was stirred under argon atmosphere for 48 h. After cooling to room temperature, the resulting precipitate was filtered and extensively washed with DMF (3 x 50 mL), THF (3 x 50 mL), methanol (3 x 50 mL), acetone (1 x 50 mL) and diethyl ether (1 x 50 mL). Thereafter, the brown solid was soaked into saturated aqueous ammonium hexafluorophosphate solution for 24 h at room temperature in order to eliminate possibility of counteranion exchange during the polymerization reaction. Then, the solid was filtered and washed with H_2O (3 x 50 mL) and methanol (3 x 100 mL). The final brown color solid was dried at room temperature under vacuum for 24 h to yield **PCP-PF$_6$** (312 mg, 81 %). ($C_{77}H_{48}F_{24}N_4P_4$) [found %, (calcd)] (CHN): 55.82 %C (57.48), 3.23 %H (3.01), 3.21 %N (3.48).

Catalytic conversion of CO_2 to cyclic carbonates:

Catalytic reactions: The catalytic CO_2 conversion reactions have been carried by using a 50 mL glass lined stainless-steel reactor equipped with a magnetic stirrer bar and pressure control system. The reactor was charged with PCP-Cl catalyst (5 wt%) and the corresponding epoxide (5 mmol). Then, the pressure vessel was charged with carbon dioxide (3 MPa). After the reaction mixture was stirred for 12 h at 100^{o}C, the reactor was cooled down to room temperature and the remaining CO_2 was slowly evacuated. Then, the final reaction mixture was filtered and washed with CH_2Cl_2 to ensure the complete removal of the trap unreacted starting material and the desired product. Thereafter, the collected filtrates were combined and concentrated under reduces pressure. The crude samples were directly analyzed by ^{1}H-NMR spectroscopy.

3. Characterization

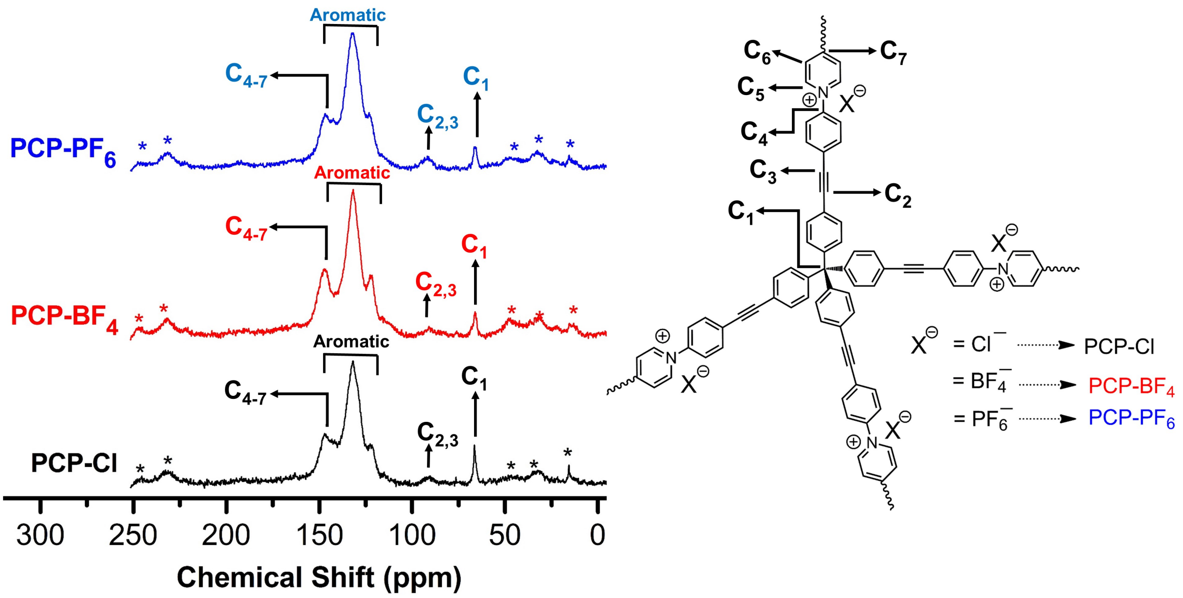


Figure S1. CP/MAS ^{13}C NMR spectra of PCPs and the corresponding peak assignments. The spectra for polymers were measured with a contact time 2 ms, a relaxation of 5 s and at an MAS rate of 7.0 kHz. The carbonyl carbon of glycine was used as an external chemical shift for the ^{13}C-NMR. * denotes spinning side bands.

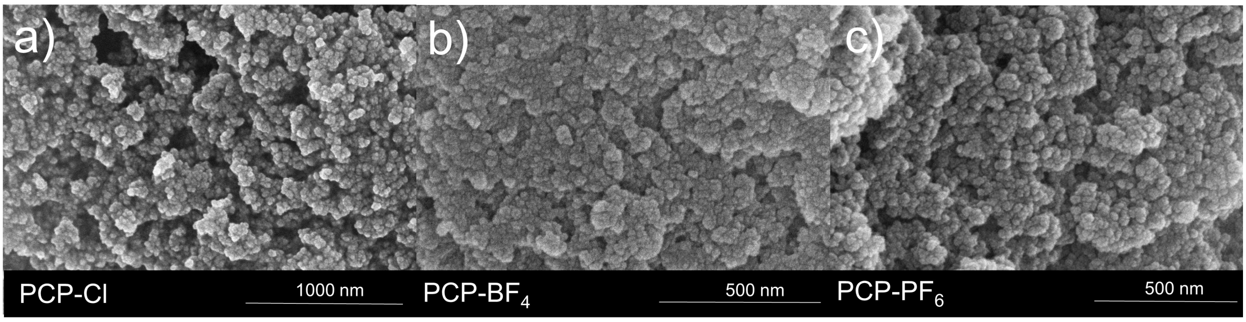


Figure S2. Scanning electron microscopy (SEM) images of PCP-Cl (a), PCP-BF$_4$ (b) and PCP-PF$_6$ (c).

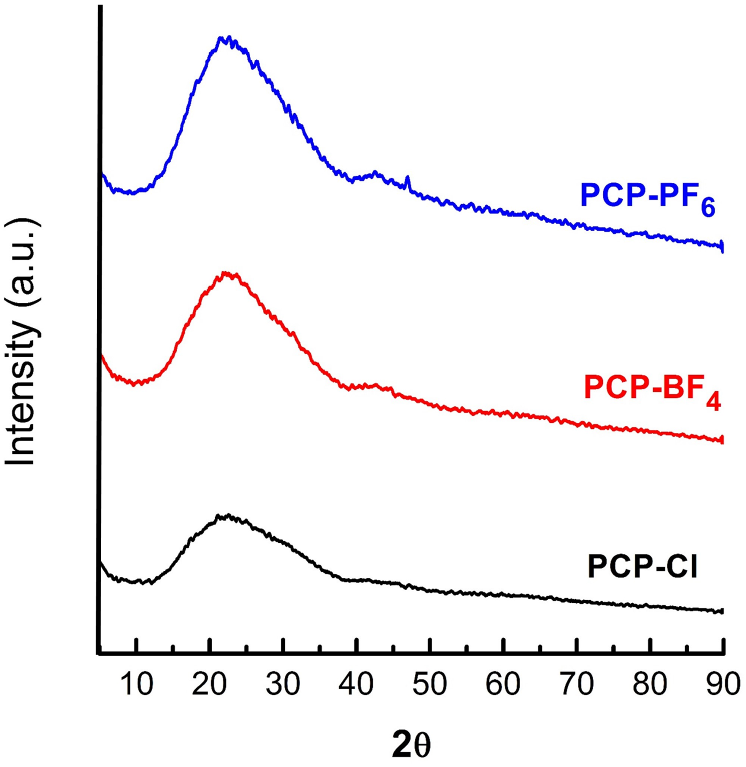


Figure S3. Powder X-ray diffraction patterns of PCPs, indicating the formation of amorphous polymers.

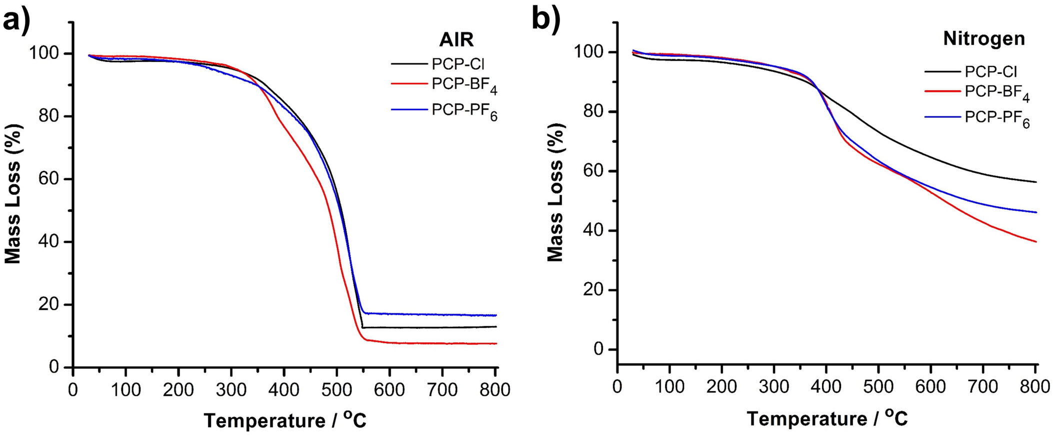


Figure S4. Thermogravimetric analysis (TGA) of PCPs under air (a) and N_2 (b) atmosphere in the range from 30°C to 800°C at a rate of 10°C min^{-1}.

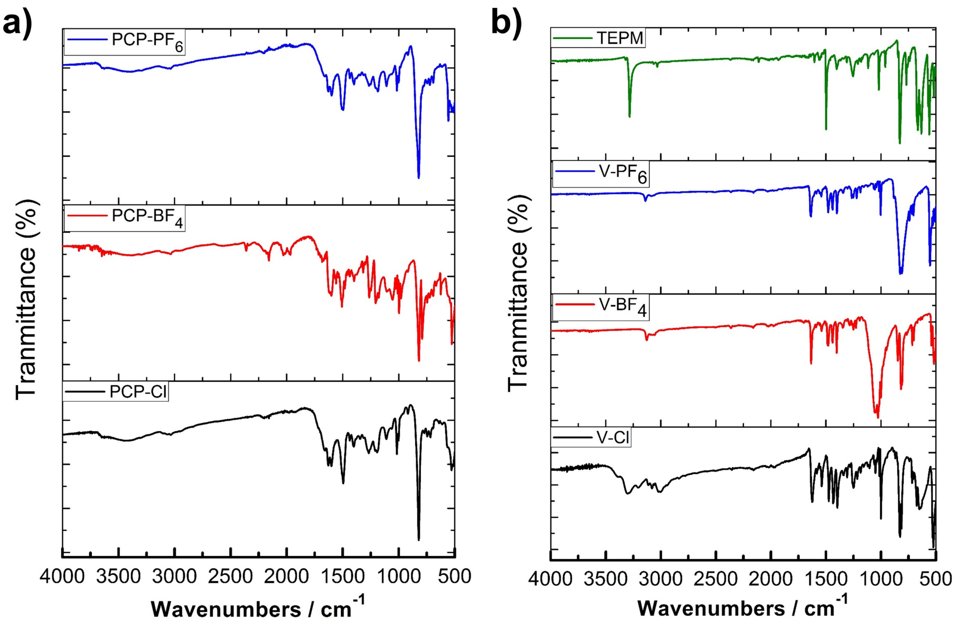


Figure S5. FT-IR spectra of PCPs and their corresponding monomers. The spectra were recorded by using ATR mode under ambient conditions. Abbreviations denoted the monomers, TEPM: tetrakis(4-ethynylphenyl)methane. 1650-1400 cm^{-1} (C=C and C=N, stretching), 3281 cm^{-1} (C≡C-H, stretching), 2111 cm^{-1} (C≡C, stretching).

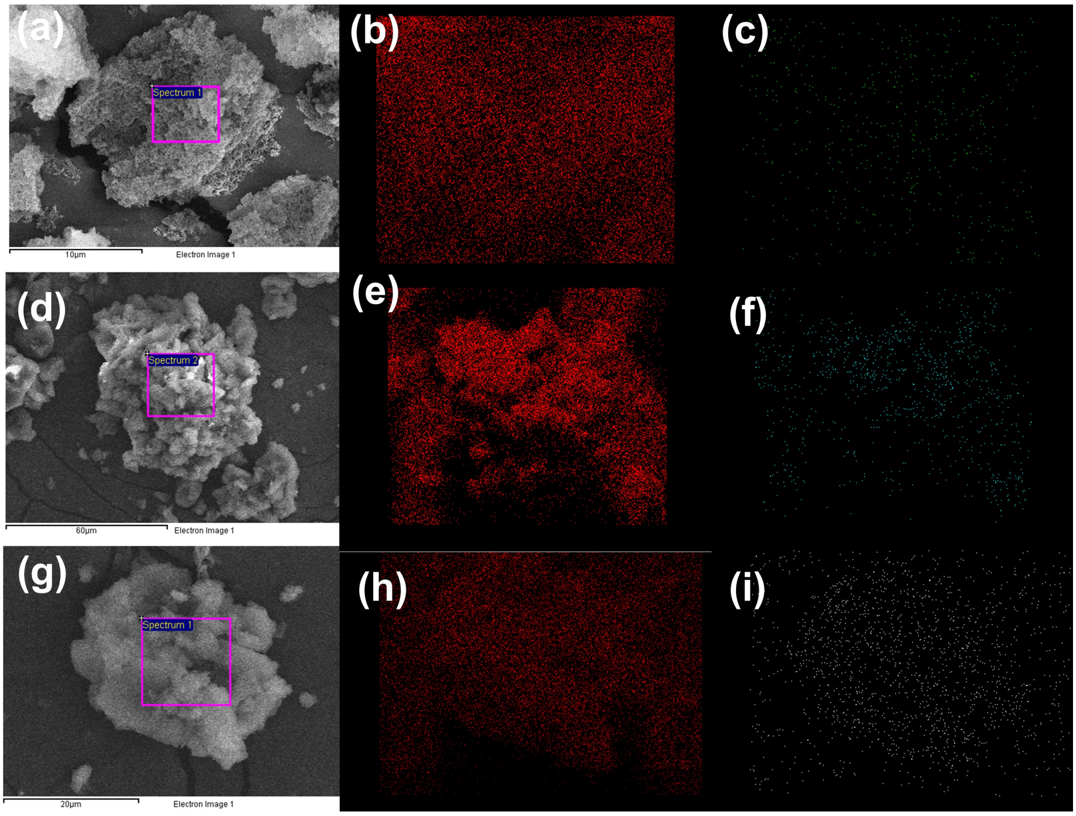


Figure S6. SEM images and energy dispersive X-ray absorption spectroscopy (EDS) of PCPs. The SEM images of PCP-Cl (a), PCP-BF$_4$ (d) and PCP-PF$_6$ (g). The elemental mapping of C/Cl/B/P for PCPs; for Carbon PCP-Cl (b), PCP-BF$_4$ (e), and PCP-PF$_6$ (h); for Chlorine PCP-Cl (c); for Boron PCP-BF$_4$ (f); for Phosphorous PCP-PF$_6$ (i).

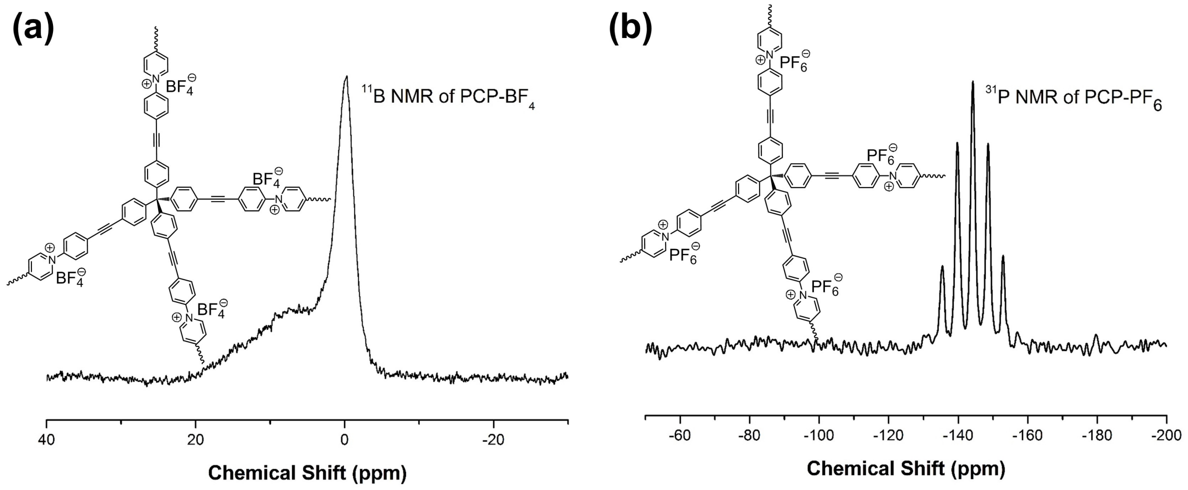
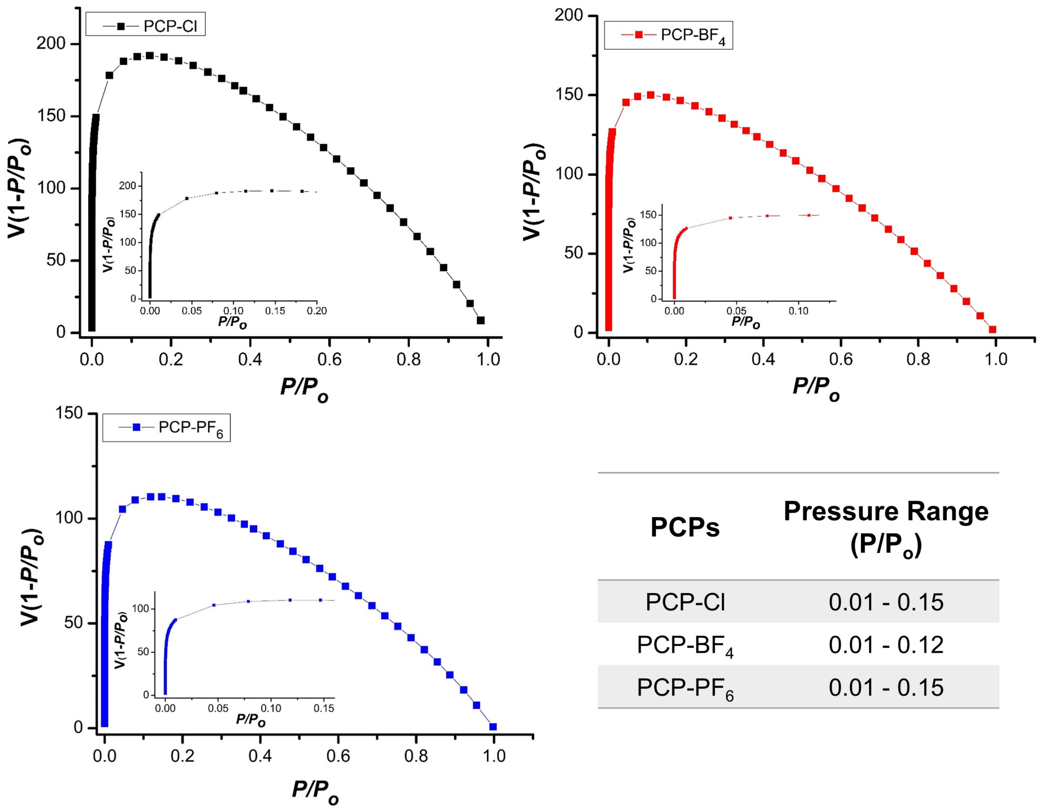
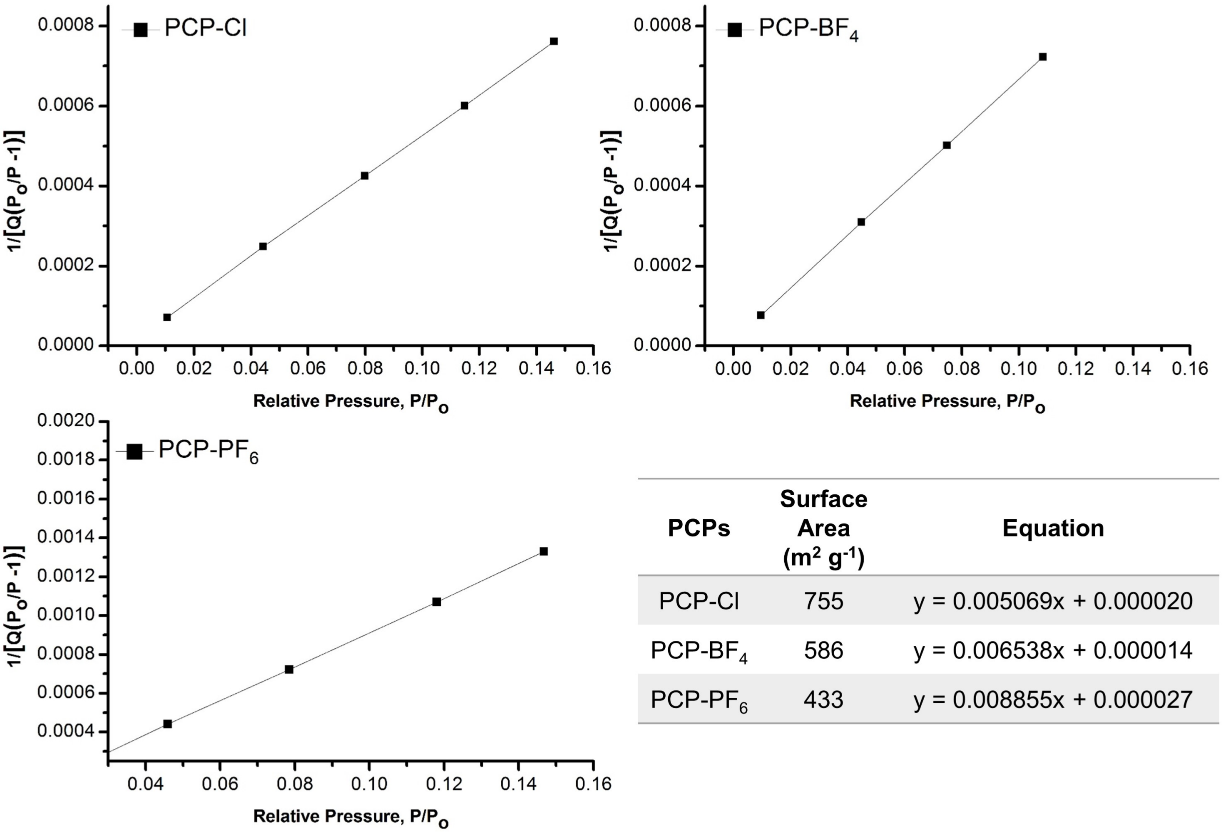


Figure S7. CP/MAS ^{11}B (a) and ^{31}P NMR (b) spectra of PCP-BF_4 and PCP-PF_6, respectively. The spectra for polymers were measured with a contact time 2 ms, a relaxation of 5 s and at a MAS rate of 7.0 kHz.



PCPs	Pressure Range (P/P_o)
PCP-Cl	0.01 - 0.15
PCP-BF_4	0.01 - 0.12
PCP-PF_6	0.01 - 0.15

Figure S8. Calculated Rouquerol plots of PCPs (Inset: Enlarged plot turning part) along with pressure ranges used for BET surface area calculations. The pressure ranges have been used where the term $V(1-P/P_o)$ continuously increases with P/P_o for the surface area calculations.



PCPs	Surface Area (m^2 g^{-1})	Equation
PCP-Cl	755	y = 0.005069x + 0.000020
PCP-BF$_4$	586	y = 0.006538x + 0.000014
PCP-PF$_6$	433	y = 0.008855x + 0.000027

Figure S9. BET plot of PCPs from Ar isotherms at 87 K.

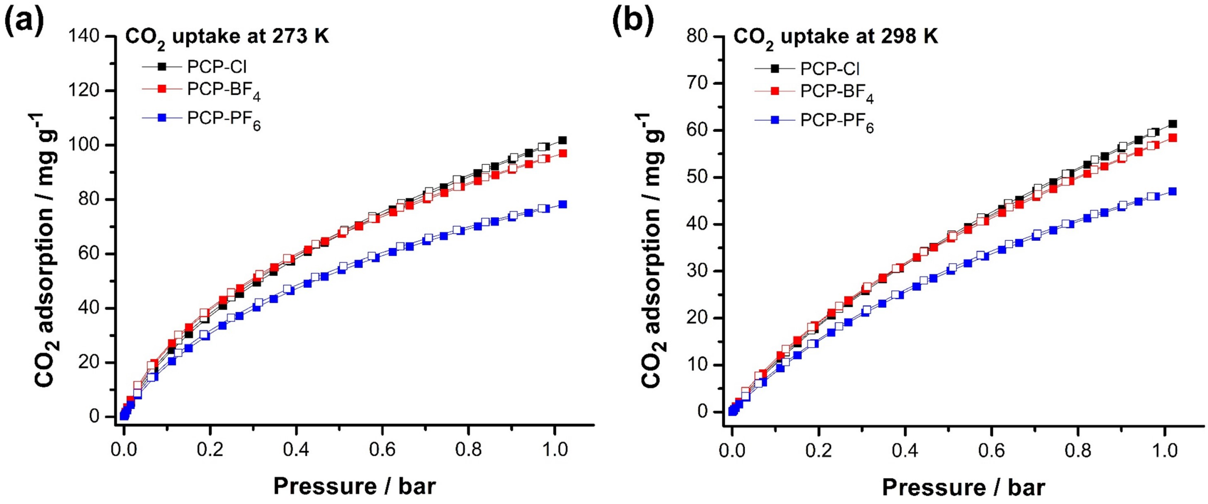


Figure S10. CO$_2$ uptake isotherms of PCPs measured up to 1 bar at 273 K (a) and 298 K (b). Filled and empty symbols represent adsorption and desorption, respectively.

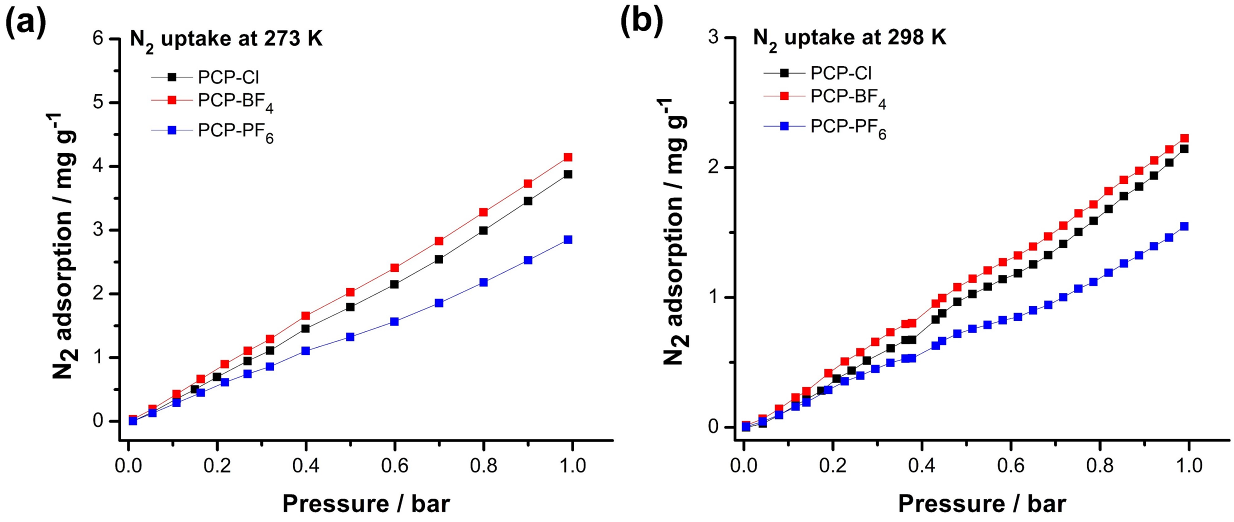


Figure S11. N$_2$ uptake isotherms of PCPs measured up to 1 bar at 273 K (a) and 298 K (b).

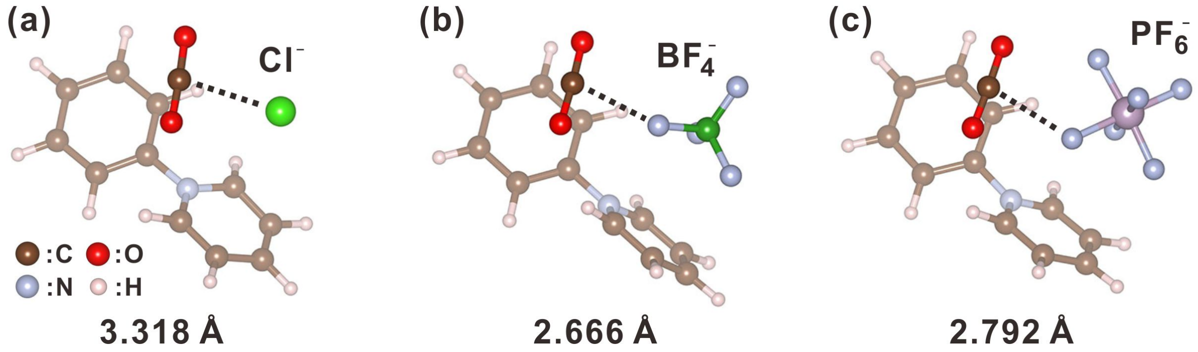


Figure S12. The lowest energy CO$_2$ binding geometries on PCPs (a) with Cl$^-$, (b) with BF$_4^-$, (c) with PF$_6^-$. The numbers at the bottom indicate the distance for specific interactions between the carbon atom of CO$_2$ and chlorine or the fluorine atom of anions (dotted line)

Table S1. Calculated binding energies, population analysis, and the distance between CO_2 and anions for CO_2 adsorption on to the model PCP monomeric unit with different anions.

Anion	Calculated Binding Energy (kJ/mol)	Mulliken Atomic Charge for Anion (e^-)	Distance between Carbon (on CO_2) and Anion (Å)
Cl^-	22.6	- 0.63	3.33
BF_4^-	29.0	- 0.80	2.67
PF_6^-	26.0	- 0.85	2.80

Computational Details

All the calculations were performed using the Q-CHEM quantum chemistry package.[3] The B3LYP functional with the 6-311G* basis was used for all calculations. The atomic partial charges were calculated using the Mulliken population analysis.[4]

Before the CO_2 adsorption, the optimal geometry of the PCPs with the counteranions was obtained. Analogous to the PCP structure, a pyridine and a benzene ring was used as a model monomeric system. In the calculation procedure, first, the pyridine and benzene was placed on the same plane and the counter anions were tested on top of every atom on this double ring model. For all the counter ions, the model system was found to be the most stable when they were placed on top of the carbon linked to the nitrogen in pyridine ring. Next, to find the CO_2 binding sites in our model system, a8x5 grid was scanned for both sides of the double rings. For each grid point the CO_2 molecule was placed either perpendicular or horizontal to the ring. For all counter ions, the most stable structure appeared when the CO_2 molecule was directly interacting with the counter ions. The resulting structures are represented in Figure S12.

Table S2. ICP-MS analysis of PCPs.

Elements Name	**Cu** (wt %)	**Pd** (wt %)
PCP-Cl	0.0005	0.0008
PCP-BF_4	0.0007	0.0007
PCP-PF_6	0.0006	0.0007

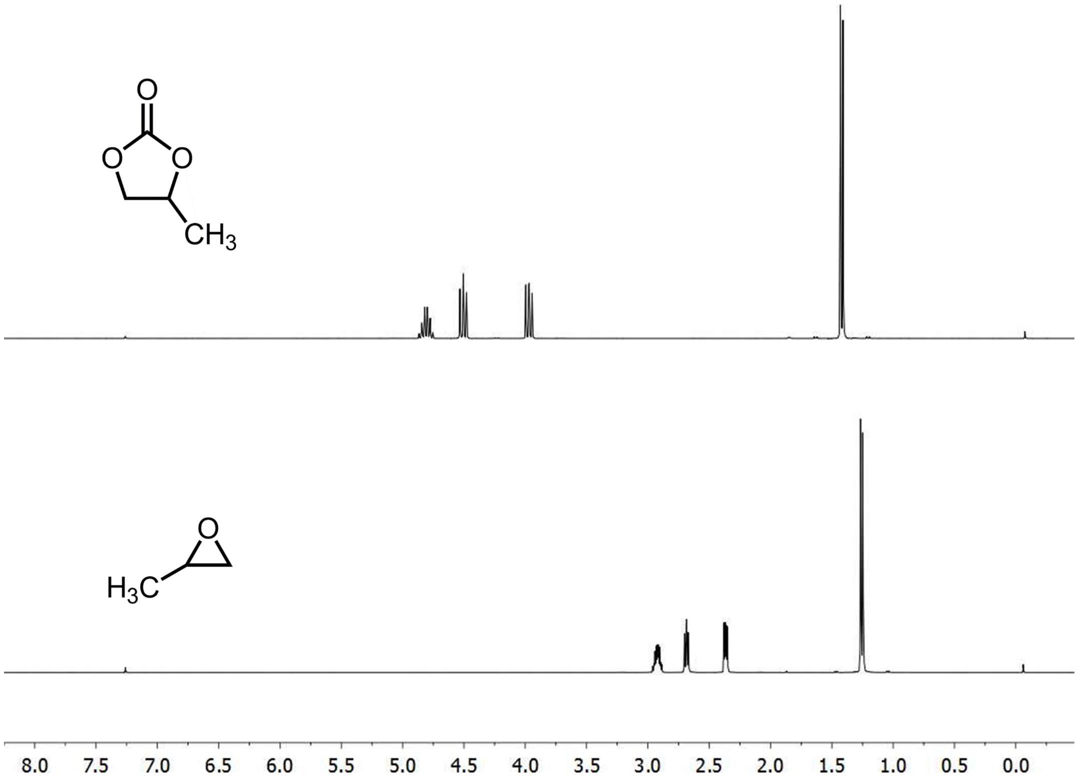


Figure S13. ^1H NMR (300 MHz, $CDCl_3$, 298 K) spectra of (±)-propylene oxide and its corresponding cyclic carbonate (*^1H NMR spectrum was obtained from the crude sample*).

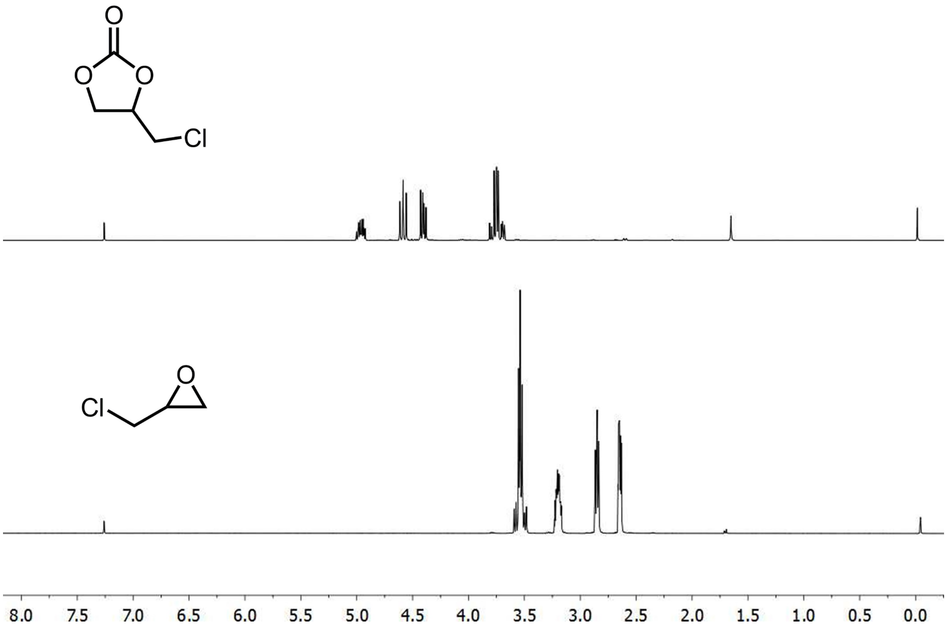


Figure S14. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectrum of (±)-epichlorohydrin and its corresponding cyclic carbonate (*^{1}H NMR spectrum was obtained from the crude sample*).

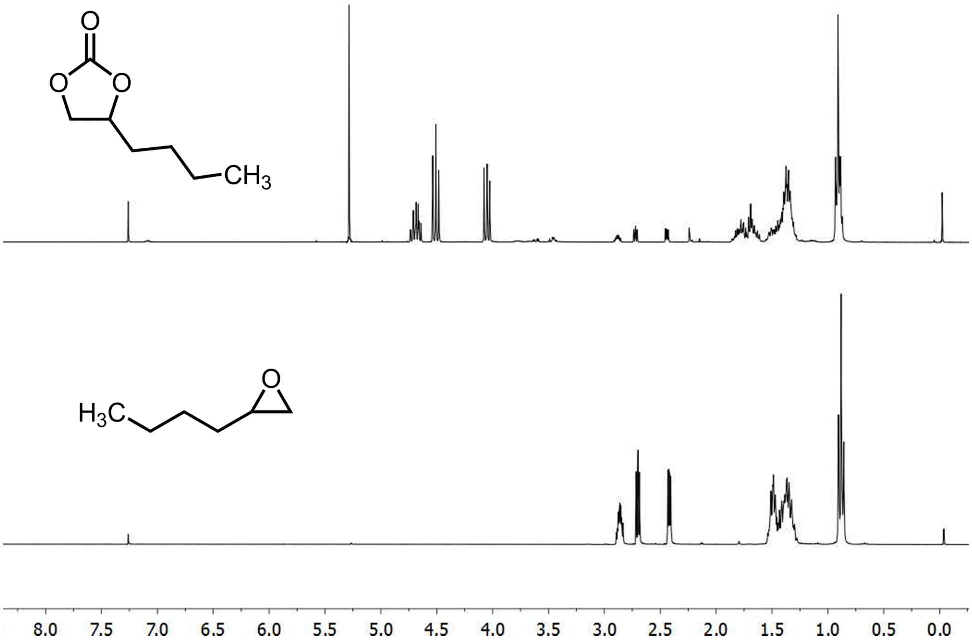


Figure S15. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectrum of 1,2-epoxyhexane and its corresponding cyclic carbonate (*^{1}H NMR spectrum was obtained from the crude sample*).

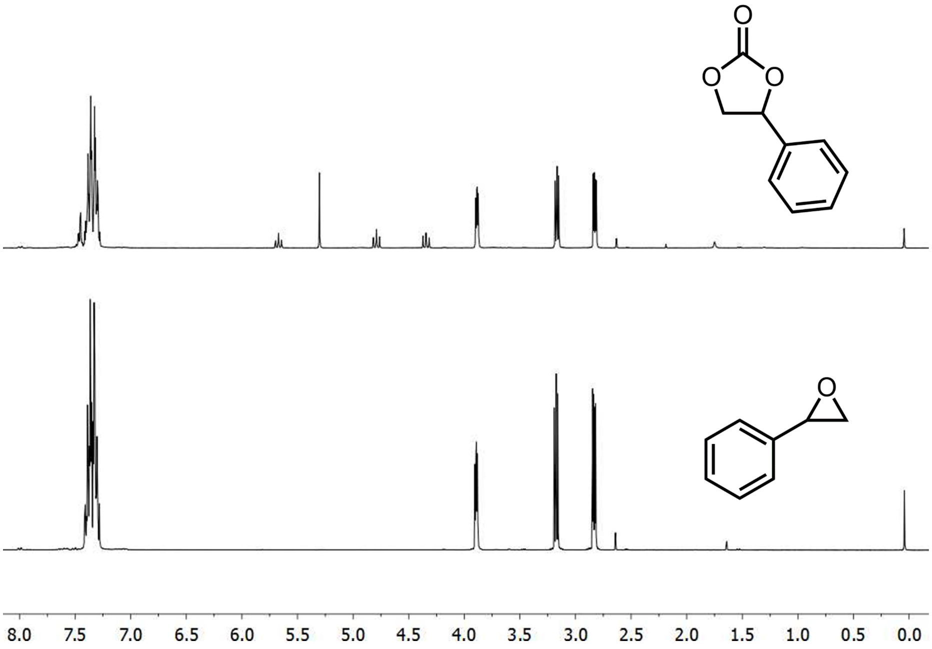


Figure S16. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K) spectrum of styrene oxide and its corresponding reaction mixture (*^{1}H NMR spectrum was obtained from the crude sample*).

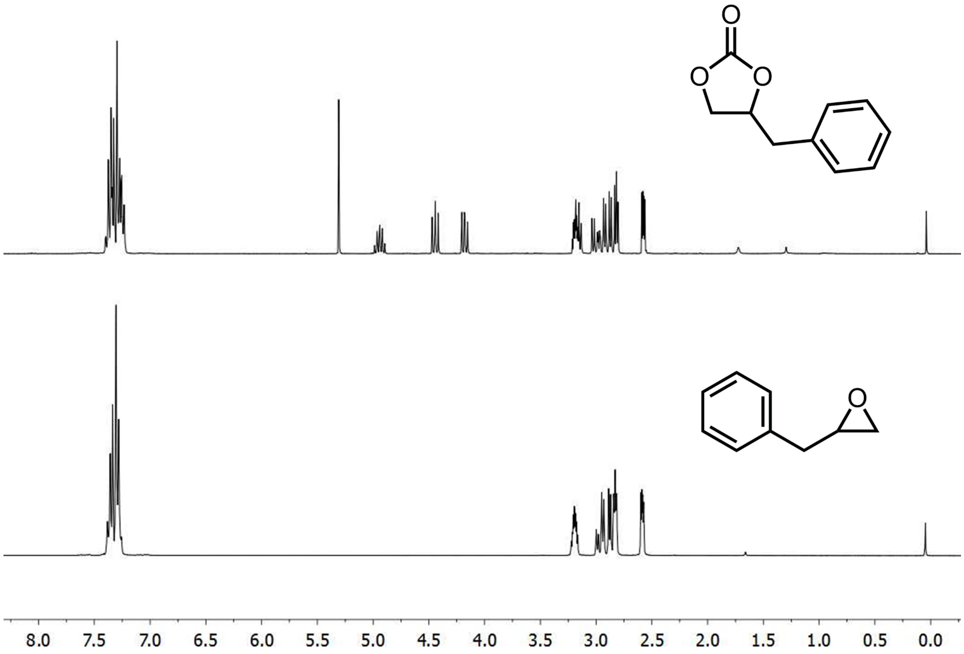


Figure S17. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K) spectrum of epoxypropylene benzene and its corresponding reaction mixture (*^{1}H NMR spectrum was obtained from the crude sample*).

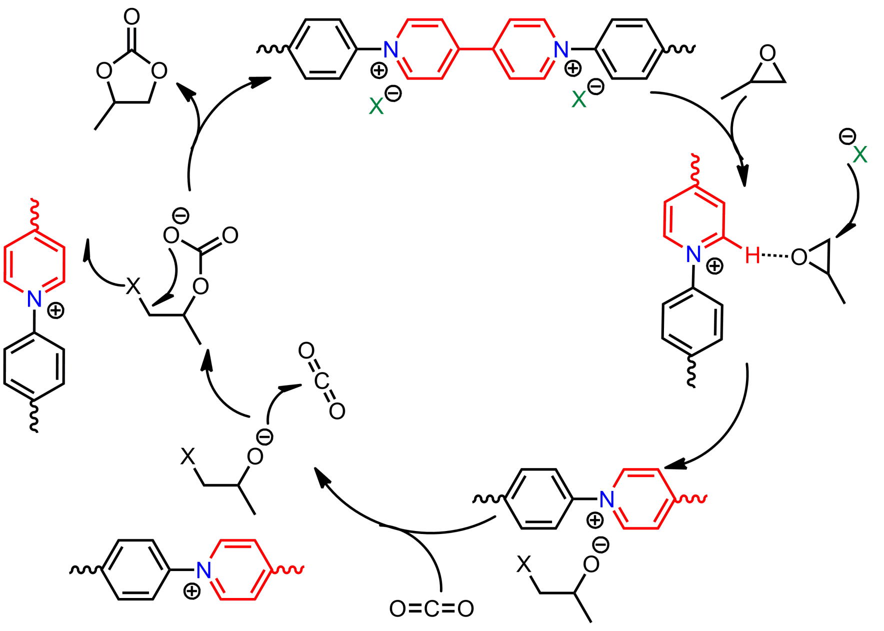


Figure S18. Proposed catalytic reaction pathway for the formation of cyclic carbonates through atom economy reaction between CO_2 and epoxides *via* catalytically active PCP-Cl as a porous organocatalyst.

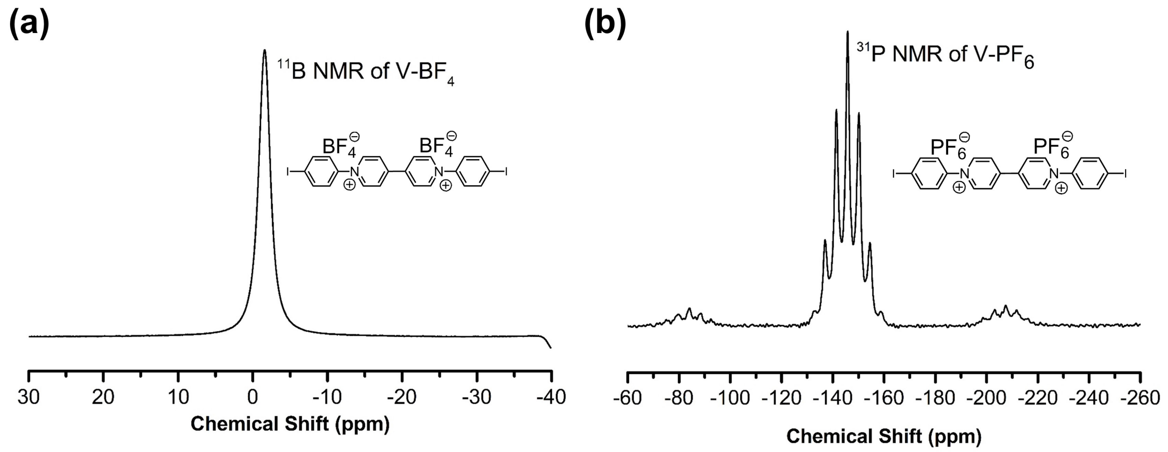


Figure S19. CP/MAS ^{11}B (a) and ^{31}P NMR (b) spectra of V-BF_4 and V-PF_6, respectively. The spectra for polymers were measured with a contact time 2 ms, a relaxation of 5 s and at a MAS rate of 7.0 kHz.

Table S3. SQX result for V-BF_4 calculated from the X-ray fluorescence measurement.

SQX Calculation Result for V-BF_4

No.	Component	Result	Unit	Det. limit	El. line	Intensity	w/o normal
1	F	33.6	mass%	0.23261	F -KA	0.1585	3.7357
2	Na	0.785	mass%	0.01415	Na-KA	0.0830	0.0872
3	Al	0.123	mass%	0.00258	Al-KA	0.2040	0.0136
4	Si	0.206	mass%	0.00065	Si-KA	0.2675	0.0229
5	S	0.0482	mass%	0.00150	S -KA	0.1314	0.0054
6	Cl	0.0119	mass%	0.00533	Cl-KA	0.0099	0.0013
7	Fe	0.144	mass%	0.00502	Fe-KA	0.3753	0.0160
8	Ni	0.176	mass%	0.00395	Ni-KA	0.8756	0.0196
9	Cu	0.0756	mass%	0.00383	Cu-KA	0.4715	0.0084
10	Br	0.136	mass%	0.00302	Br-KA	2.5220	0.0152
11	Sn	0.925	mass%	0.02140	Sn-KA	0.4581	0.1027
12	I	63.4	mass%	0.04152	I -KA	161.9989	7.0492
13	W	0.305	mass%	0.01533	W -LB1	0.7161	0.0339

Table S4. SQX result for V-PF_6 calculated from the X-ray fluorescence measurement.

SQX Calculation Result for V-PF_6

No.	Component	Result	Unit	Det. limit	El. line	Intensity	w/o normal
1	F	44.7	mass%	0.12640	F -KA	0.1266	2.1887
2	Al	0.0480	mass%	0.00077	Al-KA	0.0271	0.0023
3	Si	0.299	mass%	0.00072	Si-KA	0.2018	0.0147
4	P	10.8	mass%	0.00138	P -KA	14.5761	0.5293
5	S	0.103	mass%	0.00153	S -KA	0.1244	0.0050
6	Cl	0.136	mass%	0.00507	Cl-KA	0.0505	0.0067
7	Fe	0.447	mass%	0.00360	Fe-KA	0.7040	0.0219
8	Ni	0.253	mass%	0.00298	Ni-KA	0.7577	0.0124
9	Cu	0.152	mass%	0.00278	Cu-KA	0.5727	0.0074
10	Sn	2.08	mass%	0.01402	Sn-KA	0.6287	0.1018
11	I	40.7	mass%	0.03116	I -KA	96.2699	1.9917
12	Hf	0.274	mass%	0.00892	Hf-LA	0.3269	0.0134
13	W	Trace	mass%	0.23768	W -LB1	0.8287	0.0000
14	Au	Trace	mass%	0.13391	Au-LA	0.5707	0.0000

4. Gas Selectivity Calculations

Ideal Adsorbed Solution Theory (IAST)

The IAST selectivity calculations can be derived from fitting adsorption isotherms with proper Langmuir model, such as a single–site Langmuir model or a dual–site Langmuir model. The calculations of following equations were done using of OriginPro v8.5 and Mathematica.

The equation for the single–site Langmuir model,

$$q = \frac{q_{sat}bp}{1 + bp} \qquad (1)$$

The equation for dual–site Langmuir model,

$$q = q_A + q_B = \frac{q_{sat,A}b_Ap}{1 + b_Ap} + \frac{q_{sat,B}b_Bp}{1 + b_Bp} \qquad (2)$$

where q is molar loading of adsorbate; q_{sat} is saturation loading; b is parameter in the pure component Langmuir adsorption isotherm, A and B is referring to two different sites.

For the CO_2:N_2 (15:85) gas mixtures, the IAST selectivities were calculated by using the following equation in Mathematica v10,

$$S = \frac{q_1/q_2}{p_1/p_2} \qquad (3)$$

Where, S denotes the selectivity factor, q_i shows the mole fraction of component i in the adsorbed phase and p_i denotes the mole fraction of component i in the bulk phase (gas phase).

5. References

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