Porous cationic polymers (PCPs) with surface areas up to 755 m$^2$ g$^{-1}$ bearing positively charged viologen units in their backbones and different counteranions have been prepared. We have demonstrated that by simply varying counteranions both gas sorption and catalytic properties of PCPs can be tuned for metal-free capture and conversion of CO$_2$ into value-added products such as cyclic carbonates with excellent yields.

Porous polymers have emerged as promising solid-sorbents in recent years due to their simple synthesis, structural tunability, high surface area combined with high physical and chemical stability for applications including gas/liquid separation, gas storage, catalysis, sensors and charge carriers. The burning of fossil fuels is the major source of anthropogenic CO$_2$ emissions and there is an urgent need for porous sorbents, which can selectively capture CO$_2$ from a flue gas mixture and preferentially convert it into value-added products to not only mitigate CO$_2$ emissions, but also create incentives for research efforts in this area. To date, a great number of porous polymers have been prepared and utilized in the context of CO$_2$ capture and separation. These investigations revealed that the nature of chemical functionality along with the textural properties of polymers is an important parameter to tailor CO$_2$ affinity of these frameworks. In particular, polar functional groups such as amines, triazoles, carboxylic acids, triazine cores, imines, tetrazoles, benzimidazoles, and azo linkages were shown to enhance the CO$_2$-philicity of polymers via dipole–quadruple interactions between CO$_2$ and the polar functional groups. In recent years, charged porous polymers have also been investigated for gas storage applications. However, rather a limited number of charged porous polymers are reported in the literature mainly due to the difficulties associated with their synthesis and low physicochemical stability of these materials. In spite of these obstacles, however, there is still a great motivation to design new charged porous networks as organic zeolites due to their promising gas-adsorption properties and exchangeable counterions, which introduce new catalytic abilities such as CO$_2$ conversion to them. In addition, unlike other porous materials, properties of cationic frameworks could be altered by simply changing the nature of counterions for the desired application. Herein, we report the synthesis of three structurally similar charged porous polymers incorporating different counteranions (Cl$^-$, BF$_4^-$ and PF$_6^-$) via Sonogashira–Hagihara palladium catalyzed cross coupling reaction. The porous cationic polymers (PCPs) showed high affinity towards CO$_2$ ($Q_{st}$ = 28.5–31.6 kJ mol$^{-1}$, 78.1–101.7 mg g$^{-1}$ at 273 K, 1 bar) and good CO$_2$/N$_2$ selectivity (42–48). The cationic nature of the framework allowed us to tune the gas sorption and catalytic properties of PCPs by simply varying counteranions rather than changing the structure for the desired application. While PCPs incorporating BF$_4^-$ (PCP-BF$_4^-$) and PF$_6^-$...
(PCP-PF6) counteranions showed high-affinity towards CO2, PCP-Cl as a porous organocatalyst showed excellent catalytic activity for CO2 capture and conversion into cyclic carbonates using epoxides with high product yields up to 99% and excellent product and substrate selectivity.

The synthesis of PCPs was achieved by the Pd-catalyzed Sonogashira–Hagihara coupling reaction between tetrakis(4-ethylphenyl)methane and 1,1′-bis(4-iodophenyl)-4,4′-bipyridine-1,1′-diium salts, namely, dichloride (Cl−), difluoroborate (BF4−) and dihexafluorophosphate (PF6−), in a 1:1 solvent mixture of DMF : NEt3 at 100°C. The reaction mixture was kept at 100°C for 48 h to yield desired PCPs (see the synthesis section for details, ESI†).

PCPs were extensively characterized using solid-state cross-polarization magic-angle spinning (CP-MAS) 13C, 31P and 14N NMR, scanning electron microscopy (SEM), powder X-ray diffraction (PXRD), FTIR spectroscopy, thermogravimetric analysis (TGA), and elemental analysis (EA) (for details, see the ESI†). First, the structural integrity of polymers was verified by using CP-MAS 13C NMR (see Fig. S1, ESI†). The broad chemical shifts appearing in the region between 120 and 150 ppm are associated with the aromatic carbon atoms of the framework. The peaks located at 90 ppm and 60 ppm, which were attributed to the ethynyl carbons and the quaternary carbon core of tetraphenylmethane, respectively, also verified the successful synthesis of PCPs. The scanning electron microscopy (SEM) analysis was performed in order to investigate the bulk scale morphology of PCPs (see Fig. S2, ESI†). PCPs formed uniform spherical particles with a particle size ranging from 20 to 50 nm. The broad featureless PXRD patterns of PCPs indicate that they have amorphous character (see Fig. S3, ESI†).

As the lack of thermal stability even during the polymerization reaction is an important issue for cationic polymers, we have also investigated the thermal stability of PCPs (see Fig. S4, ESI†). PCPs exhibited exceptional thermal stability and remained stable up to 390°C in air and up to 420°C under an N2 atmosphere presumably due to well-spaced charged groups within a three-dimensional network. The slight weight loss below 200°C was mostly associated with the trapped moisture and solvent molecules in the pores. The structural integrity of PCPs was further verified using FTIR analysis. The bands located at 1650, 1400 cm⁻¹ (C=C and C=N, stretching) and 2111 cm⁻¹ (C≡C, stretching) along with the absence of a C≡C–H stretching band at 3281 cm⁻¹ confirmed the successful coupling reaction between the monomers (see Fig. S5, ESI†). The counteranion content of PCPs was verified by using energy dispersive X-ray absorption spectroscopy (EDS) to monitor chlorine, boron and phosphorous atoms for PCP-Cl, PCP-BF4 and PCP-PF6, respectively (see Fig. S6, ESI†). Furthermore, the chemical shift located at −0.5 ppm in the solid-state 13B MAS-NMR spectrum of PCP-BF4 and the multiplet peak at −145 ppm in the 31P MAS-NMR spectrum of PCP-PF6 in which multiplicity originated from 31P–19F coupling, further indicated the successful incorporation of positive charges into the framework along with their respective counteranions (see Fig. S7, ESI†).

Argon adsorption/desorption isotherms collected (Fig. 2, Table 1) at 87 K were used to evaluate the porosity of PCPs. As depicted in Fig. 2a, PCPs exhibit reversible type I isotherms (in combination with type II for PCP-Cl). The observed rapid gas sorption at a relatively low-pressure range (below P/P0 0.05) indicates the permanent microporous nature of polymers. The increase in the adsorption trend at a higher relative pressure range along with the H4 hysteresis for desorption could be attributed to the presence of mesopores. The Brunauer–Emmett–Teller (BET) surface areas of PCPs were calculated (Table 1) from the argon adsorption/desorption isotherms by determining the linear BET range from the Rouquerol plots16 (see Fig. S8 and S9, ESI†). The BET surface areas of PCP-Cl, BF4− and PF6− were found to be 755, 586 and 433 m² g⁻¹, respectively. We observed a decrease in surface areas of PCPs with increasing ionic radius of counteranions from Cl− (2.70 Å) to BF4− (3.44 Å) and PF6− (3.70 Å). The pore size distributions of PCPs were estimated from the argon adsorption/desorption isotherms (Fig. 2b) by using nonlocal density functional theory (NLDFT). All polymers exhibited similar pore size distribution patterns with varying intensities. The major peaks located below 2 nm agree well with the microporosity of PCPs. The CO2 and N2 adsorption isotherms of PCPs were measured (Fig. 3, Fig. S10 and S11, ESI†) up to 1 bar at 273 K and 298 K, and the corresponding data are presented in Table 1. Due to the higher surface area of PCP-Cl compared to the other PCPs, it exhibited the highest CO2 adsorption capacity of 101.7 mg g⁻¹ and 61.4 mg g⁻¹ at 273 K and 298 K, respectively. This comparably high CO2 uptake capacity of PCP-Cl (SA_BET = 755 m² g⁻¹, 6.2 wt% CO2 at 298 K)17 can be attributed to increased electrostatic interactions between CO2 molecules and charged units along with the counteranions within the framework. PCP-BF4 also showed significant CO2 uptake (97.0 mg g⁻¹ at 273 K), although its surface area is much lower compared to PCP-Cl. This increase in CO2 adsorption indicates the enhanced CO2 binding affinity due to Lewis acid–base interaction between BF4− ions and CO2 molecules.18 The same interaction was also observed for PCP-PF6, which showed a CO2 uptake capacity of 78.1 mg g⁻¹ at 273 K. Furthermore, the corresponding isosteric heat of adsorption (Qst) values of PCPs for CO2 at zero coverage was found to be in the range of
28.5–31.6 kJ mol\(^{-1}\), which is much higher than the values reported\(^{19}\) for structurally similar non-charged porous polymers (26 and 22 kJ mol\(^{-1}\) for MOP-1 and -3, respectively). The high CO\(_2\) affinity of PCP-BF\(_4\) and PCP-PF\(_6\) can also be further verified by probing their \(Q_{st}\) values, which were found to be about 4 kJ mol\(^{-1}\) higher than that of PCP-Cl. These anion-dependent isosteric heat of adsorption values were investigated further using density functional calculations. We first obtained the anion binding geometry to the cationic monomeric unit and all the counteranions were found (see Fig. S12, ESI\(^{†}\)) to be the most stable when placed on top of the carbon linked to the charged nitrogen atom of the pyridine unit. The calculated Mulliken charges followed the expected trend, that is, larger and softer anions are capable of retaining more charges than smaller and harder ones. The absolute binding energies were slightly underestimated (see Table S1, ESI\(^{†}\)) compared to the experimental \(Q_{st}\) values, presumably due to the interpenetrated structure of PCPs, which could allow interaction of CO\(_2\) with multiple binding sites. It is, however, important to note that the trend across the different anions is in good agreement with the multiple binding sites. It is, however, important to note that the distance between the carbon atom of CO\(_2\) and halide atoms of anions (Cl\(^-\), or F of BF\(_4^–\) and PF\(_6^–\)) follows well the binding strength trend. In other words, a specific CO\(_2\)-halide interaction via a proper choice of counteranions appears to play an important role in tuning the binding strength of CO\(_2\) even for the same cationic units.

The selectivity ability of PCPs for CO\(_2\)/N\(_2\) separation from post combustion flue gas was calculated (Fig. 3) using Ideal adsorbed solution theory (IAST) from CO\(_2\) and N\(_2\) adsorption isotherms measured at 273 K and 298 K, which are summarized in Table 1. The CO\(_2\)/N\(_2\) selectivities of PCPs at 273 K and 1 bar were found to be in the range of 42–48 and the selectivities decreased to 30–36 upon increasing the temperature to 298 K.

The usage of CO\(_2\) as a C1 building block for making value added products is an alternative approach to tackle with the increasing CO\(_2\) emissions.\(^{20}\) The conversion of CO\(_2\) into cyclic carbonates is one of the promising routes, which is an important chemical feedstock not only in the production of polycarbonates but also organic solvents.\(^{21}\) Although ionic liquids based on pyridinium salts and polymer/nanoparticle-supported pyridinium catalysts have been well-documented for CO\(_2\) conversion,\(^{22}\) to the best of our knowledge, this is the first demonstration of a porous heterogeneous organocatalyst, in which bipyridinium moieties work as active centres in a porous network. In order to demonstrate the performance of PCP-Cl as a porous organocatalyst for CO\(_2\) capture and conversion, we first investigated (Table 2) its catalytic activity in the conversion of CO\(_2\) using (+)-propylene oxide to form the corresponding cyclic carbonate at 100 \(^\circ\)C under 3 MPa of CO\(_2\). The conversion yields were calculated according to \(^1\)H NMR analysis (see Fig. S13–S17, ESI\(^{†}\)). We observed an impressive 99% yield for the formation of propylene carbonate, indicating the importance of the CO\(_2\)-philic porous network for CO\(_2\) capture and conversion. In full consistency with the literature,\(^{23}\) PCP-Cl showed the best performance due to high nucleophilicity and leaving ability of Cl\(^-\) (see for the proposed mechanism Fig. S18, ESI\(^{†}\)) whereas PCP-BF\(_4\) and PCP-PF\(_6\) showed lower catalytic activity. In order to test the recyclability of PCP-Cl, we recycled the catalyst four times, in which we observed no change in activity and product yields. This indicates that the catalyst is highly stable and can be reused for multiple cycles. Once establishing PCP-Cl as an excellent porous organocatalyst for the CO\(_2\) conversion, we have also investigated various challenging epoxide substrates. Interestingly, we observed a decrease in product yields (from 99% to 16%) with increasing

### Table 1 CO\(_2\) and N\(_2\) uptakes at 1 bar, CO\(_2\)/N\(_2\) selectivities, heat of adsorption values of CO\(_2\) for PCPs

<table>
<thead>
<tr>
<th>Polymers</th>
<th>BET(^a) (m(^2) g(^{-1}))</th>
<th>CO(_2) adsorption (mg g(^{-1}))</th>
<th>N(_2) adsorption (mg g(^{-1}))</th>
<th>CO(_2)/N(_2) (15 : 85) at 1 bar(^b)</th>
<th>(Q_{st}) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCP-Cl</td>
<td>755</td>
<td>101.7</td>
<td>61.4</td>
<td>42</td>
<td>28.5 (22.6)</td>
</tr>
<tr>
<td>PCP-BF(_4)</td>
<td>586</td>
<td>97.0</td>
<td>58.4</td>
<td>44</td>
<td>31.6 (26.2)</td>
</tr>
<tr>
<td>PCP-PF(_6)</td>
<td>433</td>
<td>78.1</td>
<td>47.0</td>
<td>48</td>
<td>30.8 (25.5)</td>
</tr>
</tbody>
</table>

\(a\) Calculated according to Rouquerol plots from argon isotherms. \(b\) From IAST at a CO\(_2\) : N\(_2\) ratio of 0.15 : 0.85 at 1 bar. 

\(Q_{st}\) for different anions with the same cationic backbone, we particularly note that the distance between the carbon atom of CO\(_2\) and halide atoms of anions (Cl\(^-\), or F of BF\(_4^–\) and PF\(_6^–\)) follows well the binding strength trend. In other words, a specific CO\(_2\)-halide interaction via a proper choice of counteranions appears to play an important role in tuning the binding strength of CO\(_2\) even for the same cationic units.

### Fig. 3 CO\(_2\) and N\(_2\) uptake isotherms of PCPs measured up to 1 bar at 273 K (a) and 298 K (b). (c) CO\(_2\)/N\(_2\) selectivity of PCPs calculated from the IAST technique for a molar ratio of 15 : 85 gas mixtures of CO\(_2\)/N\(_2\) at 273 K and 298 K. (d) Isosteric heats of adsorption (\(Q_{st}\)) of CO\(_2\) for PCPs.
Table 2  Catalytic activity of PCP-Cl for the conversion of CO₂ to cyclic carbonates with different epoxides (1–5) to cyclic carbonates

<table>
<thead>
<tr>
<th>Entry</th>
<th>Epoxides</th>
<th>Cyclic carbonate</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂C</td>
<td>CO₂/PCP-Cl (5 W, 3 MPa, 100°C)</td>
<td>12</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>Cl</td>
<td></td>
<td>12</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>C₂</td>
<td></td>
<td>12</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>C₃</td>
<td></td>
<td>12</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>C₄</td>
<td></td>
<td>12</td>
<td>41</td>
</tr>
</tbody>
</table>

"The products were characterized by ^1H NMR and the yields refer to isolated products.

kinetic diameter of the substrates presumably due to the presence of well-developed micropores in PCP-Cl, thus leading to substrate selectivity. It is important to note that such substrate selectivity is rather difficult to achieve using homogeneous organocatalysts.

In conclusion, we have introduced highly stable cationic organic zeolites incorporating bipyridinium subunits. We have demonstrated that by simply varying counteranions within the porous network structure both gas sorption properties and catalytic activity of porous polymers could be altered. PCPs are also shown to be excellent porous organocatalysts for the conversion of CO₂ into cyclic carbonates. These results indicate the promising aspect of cationic polymers for metal-free, capture and conversion of CO₂ into value-added products, thus utilizing CO₂ as a renewable and environmentally friendly C1 building block.

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Notes and references