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Elucidating the role of non-covalent interactions in unexpectedly high and selective CO\textsubscript{2} uptake and catalytic conversion of porphyrin-based ionic organic polymers

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Abstract

Here, we present the viologen-porphyrin based ionic covalent organic polymers (H\textsubscript{2}-ICOP and Zn-ICOP) with multiple CO\textsubscript{2}-philic sites. The specific surface areas of H\textsubscript{2}-ICOP and Zn-ICOP were found to be 9 m\textsuperscript{2}.g\textsuperscript{-1} and 20 m\textsuperscript{2}.g\textsuperscript{-1}, respectively. The CO\textsubscript{2} uptake analyses reveal that H\textsubscript{2}-ICOP exhibits very high CO\textsubscript{2} capture uptake (62.9 mg.g\textsuperscript{-1}), which is one of the highest values among the previously reported ICOPs. The results indicate very efficient non-covalent interactions between H\textsubscript{2}-ICOP and CO\textsubscript{2}. The possible non-covalent interactions hydrogen (O\textsubscript{CO2}···H-N), tetrel (C\textsubscript{CO2}···N, C\textsubscript{CO2}···Cl\textsuperscript{-}), pnicogen (O\textsubscript{CO2}···N\textsuperscript{+}), and spodium bonds (O\textsubscript{CO2}···Zn) between CO\textsubscript{2} and H\textsubscript{2}-ICOP and Zn-ICOP are investigated via the symmetry adapted perturbation theory (SAPT)
analysis and the electrostatic potential maps (MEP). The strength of non-covalent interactions in 
H2-ICOP and Zn-ICOP is decreasing in the following order $\Delta E_{C\cdots N} > \Delta E_{C\cdots Cl} > \Delta E_{O\cdots N^+}$ and $\Delta E_{Zn\cdots O} > \Delta E_{C\cdots Cl} > \Delta E_{C\cdots N} > \Delta E_{O\cdots N^+}$ respectively. The major CO$_2$ uptake contribution comes from C$_{CO2}\cdots N$ tetrel bonding ($-22.02$ kJ.mol$^{-1}$) interaction for H2-ICOP, whereas O$_{CO2}\cdots Zn$ spodium bonding ($-21.065$ kJ.mol$^{-1}$) interaction for Zn-ICOP. The H2-ICOP has more CO$_2$-philic moieties with powerful non-covalent interactions compared to Zn-ICOP, which is in good agreement with experimental results. Furthermore, CO$_2$ catalytic conversion performances of Zn-ICOP and H2-ICOP gave good yields of 83% and 54%, respectively. Surprisingly, Zn-ICOP, despite having significantly lower CO$_2$ uptake capacity, displayed better catalytic activity than H2-ICOP, owing to a higher number of the counter anion (Cl$^-$) on its surface, which shows the crucial role of the counter anion (Cl$^-$) in the mechanism of this catalytic reaction.

1. Introduction

The rise of atmospheric carbon dioxide (CO$_2$) concentration has become a widespread concern due to its link to the greenhouse effect and threat to the environment.$^1$ Therefore, viable solutions to efficiently capture and utilization of CO$_2$ (CCU) have received much attention in the past decades.$^{2,3}$ Among various CO$_2$ removal technologies, physical adsorbents such as zeolites, metal-organic frameworks (MOFs), covalent organic frameworks (COFs) and porous covalent organic polymers (COPs) came into focus owing to their high CO$_2$ capture capacities, catalytic transformation, and low energy requirements for regeneration.$^4-^8$ Especially COPs have evolved for CCU due to their high specific surface areas, easily tunable pore structures, good chemical and thermal stabilities, tailored surface manipulation with polar groups, and variation in the synthesis.$^9-^{13}$
The high selective uptake of CO$_2$ is known to arise from large surface areas and non-covalent interactions between CO$_2$ and surfaces of materials. In the past decade, significant effort has been mainly focused on increasing surface areas of materials and the non-covalent interactions between CO$_2$ and surfaces of materials have not attracted enough attention.$^{14}$ One should note that large surface area is one of the parameters, but not the only one, that allows for high CO$_2$ capture. However, materials with the low surface area may still exhibit large CO$_2$ capture capacity with efficient non-covalent interactions with CO$_2$. Therefore, it is vitally important to identify and estimate the strength of these non-covalent interactions in terms of contribution to CO$_2$ capture capacity.$^{15,16}$ The CO$_2$ is known to be able to form simultaneous non-covalent interactions via its electron-rich terminal oxygen atoms and its electron-deficient central carbon atom.$^{16,17}$ The electron-deficient central carbon atom acts as a Lewis acid (LA) and can form tetrel bonding interaction with anions or lone-pair-possessing atoms such as N, O, S, and F.$^{18-21}$ On the other hand, the electron-rich terminal oxygen atom acts as a Lewis base (LB) and can form hydrogen bonding with hydrogen atoms and, as recently reported, halogen bonding with halogen atoms (I, Br, Cl) containing moieties.$^{22-29}$

In particular, the electron-rich nitrogen-based functional groups, such as amines, triazoles, triazine cores, imines, tetrazoles, benzimidazoles, azo linkages, and viologens, continues to be a dominant polar functional group to enhance CO$_2$ adsorption capacity and CO$_2$/N$_2$ selectivity thanks to their multiple non-covalent interactions with CO$_2$.$^{20,27,30-38}$ Among nitrogen based adsorbents, viologen linked ionic covalent organic polymers (ICOPs) are of particular importance in CCU technologies because they not only have all
the advantages of COPs but also possess charged cationic skeletons paired with counterions which provide additional CO₂ affinity owing to their electrostatic interactions with CO₂ molecules.\textsuperscript{35,39–42} Consequently, the CO₂ uptake capacity of viologen linked ICOPs is found to be significantly higher compared to their neutral counterparts.\textsuperscript{34,43,44} Moreover, unlike other porous materials, selective recognition of viologen linked ICOPs can be manipulated by simply controlling the redox state of viologen or the nature of counter-ions for the desired application.\textsuperscript{39,41}

In recent years, several cationic viologen linked ICOPs with good surface areas has been reported for CCU.\textsuperscript{34,39,43–49} The general understanding of these studies is that the high CO₂ capture capacity of viologen linked ICOPs is credited mostly to tetrel bonding interaction between counter anions and CO₂.\textsuperscript{50} Commonly, nitrogen-based groups in CCU applications are preferred for their Lewis basic characters to form non-covalent interactions with electron-deficient central carbon (Lewis acid) of CO₂. However, in the case of viologen, the quaternary nitrogen (N\textsuperscript{+}) atom lacks lone electron pairs, hence acts as Lewis acid, consequently, the formation of efficient interaction between cation (N\textsuperscript{+}) nitrogen and the electron-rich terminal oxygen atoms of CO₂, commonly referred to as pnicogen bonds, is highly possible.\textsuperscript{19,51} Yet, the pnicogen (O\textsubscript{CO₂}···N\textsuperscript{+}) interaction is often disregarded, and its contribution to CO₂ capture has not been reported.

However, despite their attractive features for CCU applications, only a limited number of viologen linked ICOPs has been reported in the literature mainly due to their low physicochemical stability. This drawback can be overcome by the incorporation of
viologens into polymeric systems with suitable rigid and symmetric macrocycles such as porphyrin.\textsuperscript{52} The incorporation of porphyrin brings three advantages, first, unstable cationic species get stabilized by extended delocalized polymeric structures. Second, porphyrin is another excellent N containing molecular building block, which can increase CO\textsubscript{2} uptake and selectivity through CO\textsubscript{2} interaction with pyrroles (-C=N, -NH). Third, the metalation of porphyrin core with Lewis acidic metal such as zinc (II) can promote additional non-covalent interaction with electron-rich terminal oxygen atoms of CO\textsubscript{2}, known as spodium bonding.\textsuperscript{53} In addition to their multiple CO\textsubscript{2}-philic functional sides, both viologen and porphyrin are also known to exhibit effective CO\textsubscript{2} catalytic conversion, which makes them very promising bifunctional materials in CCU applications.\textsuperscript{46–48,54–56}

Herein, based on the above considerations, we report viologen-linked porphyrin ICOPs (H\textsubscript{2}-ICOP and Zn-ICOP) synthesized through the Zincke reaction of H2 and Zn(II) tetrakis (4-aminophenyl) porphyrin with viologen Zincke salt, as presented in Scheme 1.
**Scheme 1.** Schematic representation of the synthesis of the viologen-linked porphyrin ICOPs via Zincke reaction under solvothermal conditions.

The resultant ICOPs were characterized with various experimental analyses including FTIR spectroscopy, solid-state $^{13}$C NMR spectroscopy, energy-dispersive X-ray spectroscopy (EDX), diffuse reflectance spectroscopy (DRS), thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), field emission scanning electron microscopy (SEM), transmission electron microscopy (TEM) and dynamic light scattering (DLS). Furthermore, their CO$_2$ capture capacity, CO$_2$/N$_2$ selectivity, and CO$_2$ catalytic conversion performances were explored. The Brunauer–Emmett–Teller (BET) surface area analyses reveal that both **H2-ICOP** (9 m$^2$.g$^{-1}$) and **Zn-ICOP** (20 m$^2$.g$^{-1}$) possess very low surface area. Yet, despite their nearly non-porous surfaces, especially **H2-ICOP** exhibits very large CO$_2$ capture capacity (62.9 mg.g$^{-1}$) and CO$_2$/N$_2$ selectivity, which indicates powerful non-covalent interactions with CO$_2$. The detailed theoretical analyses have been conducted
to decode insights into these unexpected large CO₂ capture capacities and CO₂/N₂ selectivity. The strength of possible non-covalent interactions, such as hydrogen, tetrel, pnicogen, and spodium bonding, between CO₂ molecules and H2-ICOP and Zn-ICOP surfaces, were calculated, in terms of contribution to CO₂ capture capacity. Additionally, CO₂ catalytic conversion performances of Zn-ICOP and H2-ICOP gave good yields of 83% and 54% in the mild conditions, respectively.

2. Results and Discussion

2.1. Synthesis and characterization

The synthesis of ionic covalent organic polymers (H2-ICOP, Zn-ICOP) was carried out under solvothermal conditions by Zincke reaction of 1,1'-bis(2,4-dinitrophenyl)-[4,4'-bipyridine]-1,1'-diium dichloride (Vio) with either 5,10,15,20-tetrakis (4-aminophenyl) porphyrin (H2-Porph) or 5,10,15,20-tetrakis (4-aminophenyl) porphyrinato zinc(II) (Zn-Porph) in a mixture of 1,4-dioxane: water (4:1,v/v) or DMF:water (4:1,v/v) (Scheme 1, for details see ESI). A gel-like material was obtained in DMF:water mixture whereas powder was obtained in 1,4-dioxane:water mixture (Figure S1). Washing the solids with the appropriate solvents is found to be crucial to remove unreacted starting materials and any smaller oligomers that may have formed. Therefore, the solids were washed with ethanol and DMSO several times until a colourless solution was obtained. The purification procedure was completed by washing with water and acetone. Complementary methods were used for the detailed structural characterization of ICOPs. The formation of ICOPs is confirmed by Fourier-transform infrared (FTIR) spectroscopy and solid-state ¹³C NMR. In FTIR (Figure 1), the decline of the characteristic –NH₂ peak at 3345 cm⁻¹ and –NO₂ peak at 1343 cm⁻¹ and the appearance of the characteristic pyridinium C=N peak at 1628
cm\(^{-1}\) for H2-ICOP and 1656 cm\(^{-1}\) for Zn-ICOP indicate the loss of 2,4-dinitroaniline group and the formation of viologen-linked ICOPs. Besides, the peaks belonging to the porphyrin ring at 964, 790 cm\(^{-1}\) for H2-ICOP and at 993, and 794 cm\(^{-1}\) for Zn-ICOP confirm the formation of the expected materials. The same structures are obtained for H2-ICOP-dx and Zn-ICOP-dx with identical FTIR as can be shown in Figure S2. The solid-state \(^{13}\)C NMR spectra (Figure S3) of materials show broad multi-peaks between \(\delta = 100-170\) ppm. The peaks at 151 ppm for H2-ICOP and 152 ppm for Zn-ICOP can be attributed to the carbon signals in the bipyridinium moieties whereas the peaks at 122 ppm for H2-ICOP and Zn-ICOP correspond to phenyl carbons of the porphyrin subunit.

Figure 1. FTIR spectra of H2-ICOP and Zn-ICOP in comparison with the corresponding monomers (H2-Porph, Zn-Porph and Vio).
The diffuse reflectance spectroscopy (DRS) of H2-ICOP and Zn-ICOP display the characteristic Soret and Q bands of the porphyrin at 436 nm, 535 nm for H2-ICOP, and 447 nm, 538 nm for Zn-ICOP (Figure 2a). Moreover, characteristics of viologen radical bands were observed at 627 nm for H2-ICOP and 586 nm for Zn-ICOP. The H2-ICOP and Zn-ICOP exhibit an electron paramagnetic resonance (EPR) signal (Figure 2b). The radical character of these ICOPs is the result of a charge transfer from the aromatic porphyrin core to the viologen unit and is an indication of the highly conjugated structures.57

![Figure 2](image-url). DR spectra (a) EPR signals (b) and TGA curves (c) of H2-ICOP and Zn-ICOP.

Thermogravimetric analysis (TGA) shows that H2-ICOP and Zn-ICOP exhibit thermal stability up to 300 °C with slight weight losses (Figure 2c). However, it is noteworthy to mention that both materials retain about 60% of their initial mass even at 900 °C, indicating good thermal-stability. H2-ICOP and Zn-ICOP have similar experimental PXRD profiles with low angle diffraction peaks in vicinities of 2θ values of 5°, which is characteristic for expected large unit-cell parameters (Figure S4). However, the broadening of peaks on both profiles in combination with a large peak at ca. 22.5° indicate semi-crystalline nature of the studied materials. To determine the structures of H2-ICOP and Zn-ICOP, the geometry optimization of constructed models
having the eclipsed (AA) and staggered (AB) topology were performed by an ABINIT code using
the following unit cell parameters: \(a = b = 35.563\), \(c = 4.09\) (7.8 for staggered structure) Å, \(\alpha = \beta = \gamma = 90^\circ\), space group P1. The comparison of both experimental and calculated PXRD profiles
based on relaxed models are presented in Figure S4a for H2-ICOP and in Figure S4b for Zn-
ICOP. The experimental PXRD profiles of both ICOPs are in a good agreement with the simulated
staggered AB-stacking model (Figure S4d). Since PXRD patterns of H2-ICOP-dx and Zn-
ICOP-dx showed amorphous nature rather than semi-crystalline structure, H2-ICOP and Zn-
ICOP were used for further investigations. Elemental mapping by energy dispersive spectroscopy
(EDS) exhibits the elements C, N, and Cl for H2-ICOP and C, N, Cl, and Zn for Zn-ICOP (Figure
S5), which is consistent with compositions of our ICOPs. Dynamic light scattering (DLS) analyses
showed two particle populations with average colloidal particle size in the range between 1-10 μm
for both ICOP, suggesting a polydisperse nature (Figure S6). The stability of colloidal systems of
H2-ICOP and Zn-ICOP were evaluated with zeta potential measurement in water (pH=7.4)
(Figure S7). Interestingly, the zeta potential values of the H2-ICOP shows a positive zeta potential
value (+25), whereas Zn-ICOP shows a negative zeta potential value (-21.6). These high absolute
values of zeta potential of H2-ICOP and Zn-ICOP indicate a stable state of their colloidal
systems, which is also confirmed by observation of Tyndall effect (Figure S8). Furthermore, zeta
potential data not only reflect the stability of colloidal systems of H2-ICOP and Zn-ICOP
dispersion in water but also can be used to explain the adsorption and conversion mechanisms of
CO\(_2\), which we will discuss in related sections.

Depending on the solvent mixture used, structures with different morphologies were obtained.
Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies reveal
that the ICOPs obtained by using DMF:water mixture (H2-ICOP and Zn-ICOP) exhibit sheet-like morphology whereas the ICOPs obtained by using 1,4-dioxane:water mixture (H2-ICOP-dx and Zn-ICOP-dx) exhibit spherical morphology (Figure 3). Uniform spheres with an average diameter of 1.4 µm for H2-ICOP-dx and 0.65 µm for Zn-ICOP-dx were observed by both SEM (Figure 3b, d, and Figure S9) and TEM analysis (Figure 3f, h).

![Figure 3](image)

**Figure 3.** Microscopic characterization [SEM (top row) and TEM (bottom row)] of H2-ICOP(a, e) and Zn-ICOP(c, g) prepared in DMF:water (4:1, v/v) and obtained as plates; H2-ICOP-dx (b, f) and Zn-ICOP-dx (d, h) prepared in 1,4-dioxane:water (4:1, v/v) and obtained as spheres.

### 2.2. CO2 Uptake and CO2/N2 Selectivity performance

To investigate the permanent porosity of H2-ICOP and Zn-ICOP, Krypton (Kr) adsorption–desorption isotherms were measured via Brunauer–Emmett–Teller (BET) model, at 77 K (for details see ESI). As shown in Figure 4b, both H2-ICOP and Zn-ICOP show typical type-II reversible adsorption isotherms and their porosities are found to be mesoporous in the range...
of 3-20 nm, whereas nitrogen (N\textsubscript{2}) adsorption–desorption isotherms show non-porous surfaces. The specific surface areas of \textbf{H2-ICOP} and \textbf{Zn-ICOP} were found to be 9 m\textsuperscript{2}.g\textsuperscript{-1} and 20 m\textsuperscript{2}.g\textsuperscript{-1}, respectively (Figure 4a). This difference in the BET surface areas can be explained by zeta potential values of \textbf{H2-ICOP} (+25) and \textbf{Zn-ICOP} (-21.6) (Figure S7). The positive zeta potential value suggests that pores are occupied by nearly all of chloride counter ions and do not remain on the surface of \textbf{H2-ICOP}, whereas the negative zeta potential value indicates some chloride counter-ions remain on the surface of \textbf{Zn-ICOP}. Notably, the surface areas of both ICOPs are one of the lowest values reported to date for any ICOP. These relatively low values are likely due to the pores of the materials being occupied by chloride counterions and their semi-crystalline state and staggered morphology with an AB stacking sequence (Figure S4d).

Owing to their multiple CO\textsubscript{2}-philic sides, despite their low surface areas, we explored the affinity of \textbf{H2-ICOP} and \textbf{Zn-ICOP} toward CO\textsubscript{2} and N\textsubscript{2}. To evaluate their performance for CO\textsubscript{2} capture, we carried out temperature-dependent CO\textsubscript{2} uptake measurements at 273, 298, and 323 K up to 1 bar (Figure 4c, d). The CO\textsubscript{2} capture capacity of \textbf{H2-ICOP}, despite the lower BET surface area, is found to be up to 26 (42.4 mg.g\textsuperscript{-1}, 273 K), 44 (62.9 mg.g\textsuperscript{-1}, 298 K), and 13 cm\textsuperscript{3}.g\textsuperscript{-1} (17.3 mg.g\textsuperscript{-1}, 323 K) at 1 bar, which is much higher than that of \textbf{Zn-ICOP} 25 (39.3 mg.g\textsuperscript{-1}, 273 K), 16.7 (24 mg.g\textsuperscript{-1}, 298 K) and 10.2 cm\textsuperscript{3}.g\textsuperscript{-1} (13.9 mg.g\textsuperscript{-1}, 323 K) at 1 bar, respectively. Notably, the CO\textsubscript{2} uptake capacities are not saturated for \textbf{H2-ICOP} within the pressure range, suggesting that the CO\textsubscript{2} uptake capacities can be further improved with increased pressure. Remarkably, CO\textsubscript{2} capture capacities of \textbf{H2-ICOP} and \textbf{Zn-ICOP} are one of the highest values reported among the previously reported viologen based ICOF and ICOP with much larger surface areas (Table 1). The CO\textsubscript{2} capture capacity of these viologen linked ICOF and ICOPs is attributed mainly to tetrel
bonding interaction between counter anions and CO$_2$. However, as the positive zeta potential value of H$_2$-ICOP shows that pores are occupied by nearly all of chloride counter ions and do not remain on the surface, yet H$_2$-ICOP has very high CO$_2$ capture capacity. The results indicate that H$_2$-ICOP, due to our molecular design, possess much stronger non-covalent interactions with CO$_2$ than counter anions.

Figure 4. (a) Kr adsorption/desorption isotherms of H$_2$-ICOP and Zn-ICOP measured at 77 K, filled and empty symbols represent adsorption and desorption, respectively. (b) Pore size distribution of H$_2$-ICOP and Zn-ICOP calculated from Kr isotherms calculated using NLDFT. CO$_2$ adsorption isotherms of H$_2$-ICOP(c) and Zn-ICOP(d) collected up to 1 bar at 273, 298, and 323 K. (e) CO$_2$/N$_2$ (IAST method) selectivity H$_2$-ICOP and Zn-ICOP at 273 K, 298 K, and 323 K (f) The isosteric heat of adsorption ($Q_m$) plots of CO$_2$ for H$_2$-ICOP and Zn-ICOP.
To gain further insights from the non-covalent interactions between materials and CO$_2$ molecules, the CO$_2$ isosteric heat of adsorption (Q$_{st}$) of H$_2$-ICOP and Zn-ICOP was obtained with the Clausius–Clapeyron equation from the CO$_2$ uptake isotherms recorded (Figure 4f). The Q$_{st}$ values for CO$_2$ were found to be 39 and 36 kJ.mol$^{-1}$ for H$_2$-ICOP and Zn-ICOP, respectively, at zero coverage. This difference of Q$_{st}$ value for the two polymers shows that the non-covalent interactions of the CO$_2$ molecules with the skeleton of H$_2$-ICOP is more efficient than with Zn-ICOP, which may explain the higher CO$_2$ capture capacity of H$_2$-ICOP compare to Zn-ICOP. It is also worth mentioning that the Q$_{st}$ values of the polymers are moderate, not exceeding 50 kJ.mol$^{-1}$, which implies that CO$_2$ is physically adsorbed by both ICOPs and the recyclability of the adsorbent at a low energy penalty.

Table 1. BET surface area, CO$_2$ uptake, selectivity, and heat adsorptions (Q$_{st}$) of ICOPs

| ICOP     | BET surface area (m$^2$.g$^{-1}$) | CO$_2$ adsorption (mg.g$^{-1}$) | CO$_2$/N$_2$: selectivity (15/85) | Pressure (bar) | Q$_{st}$ (kJ.mol$^{-1}$) |
|----------|----------------------------------|---------------------------------|----------------------------------|---------------|------------------------|
| H$_2$-ICOP | 9                                | 42.4                            | 62.9 17.3                        | 1             | 39                     |
| Zn-ICOP   | 20                               | 39.3                            | 24 13.9                          | 1             | 36                     |
| PCP-C1    | 755                              | 101                             | 61.4 -                            | 1             | 28.5                   |
| V-PCIF-C1 | 174                              | 86.7                            | 62.4 -                            | 1             | 56.6                   |
| POV-V1    | 812                              | -                               | 40.5 -                            | 1             | 25                     |
| POV-V2    | 960                              | -                               | 55.9 -                            | 1             | 24                     |
| c-CTF-400 | 744                              | 126                             | 83 52                             | 1             | 49                     |
| c-CTF-450 | 861                              | 99                              | 62 38                             | 1             | 46                     |
| c-CTF-500 | 1247                             | 133                             | 80 47                             | 1             | 43                     |
| SYSU-Zn@IL1 | 38                            | 68                              | 40 -                              | 1             | 27.2                   |

Additionally, to assess the potential in separation CO$_2$ from flue gas (>70% N$_2$), the adsorption selectivity of CO$_2$ over N$_2$ (15/85) of H$_2$-ICOP and Zn-ICOP were calculated with Myers and Prausnitz's ideal adsorbed solution theory (IAST) at three different temperatures (273, 298, and 320 K) up to 1 bar (Figure 4e, Table 1). The selectivity of CO$_2$ from CO$_2$ / N$_2$ (15/85) of H$_2$-ICOP and Zn-ICOP are 55.7 and 5.5 at 273 K, 35.1, and 7.2 at 298 K, and 5.1 and 2.55 at 323 K,
respectively. As expected, the H2-ICOP exhibits much higher selectivity compared to Zn-ICOP, which also indicates a powerful CO2 affinity of H2-ICOP.

2.3. Computational analysis of non-covalent bonds

The high CO2 capture and selectivity capacities of H2-ICOP and Zn-ICOP, despite their low surface areas, clearly show the powerful non-covalent interactions between CO2 molecules and multiple CO2-philic moieties of H2-ICOP and Zn-ICOP. The theoretical analyses (for details of computational methodology see ESI) have been performed to get insights into possible non-covalent interactions between CO2 molecules and surfaces of H2-ICOP and Zn-ICOP, and their contribution to selective CO2 uptake of these compounds.

**Figure 5.** Electrostatic potentials mapped on the molecular surfaces of CO2, H2-ICOP and Zn-ICOP. The values of MEPs lie in the intervals -7.794, +7.794 kcal.mol⁻¹ for CO2 and -18.825, +18.825 kcal.mol⁻¹ for H2-ICOP and Zn-ICOP.
To model the mentioned non-covalent interactions the fragments H2-ICOP and Zn-ICOP were ‘cut off’ from polymeric chains and linkers were replaced by hydrogen atoms. H2-ICOP and Zn-ICOP contain two porphyrin cores, chlorine counterion, and positively charged viologen linker. The σ-hole formation on the surface of H2-ICOP, Zn-ICOP, and CO2 have been visualized using the electrostatic potential maps (MEP) and results are displayed in Figure 5 along with the corresponding electrostatic potential values. The calculated MEP surfaces show that a maximum of positive potential (σ-hole) involves a region along with the cationic viologen subunits and Zn-ICOP porphyrin core (Zn) as well as in the carbon atom C_{CO2}, which show Lewis acidic character of these regions. The negative electrostatic potential is located in the vicinity of oxygen O_{CO2}, chlorine atoms, and nitrogen atoms in H2-ICOP porphyrin core (Figure 6). Thus, positive and negative MEPs distributions of H2-ICOP, Zn-ICOP, and CO2 indicate that attractive interactions are favourable for the formation of the above mentioned non-covalent bonds.

Figure 6. Scheme of possible non-covalent interactions between CO2 and H2-ICOP and Zn-ICOP.
The MEPs analyses have revealed possible non-covalent interactions, such as hydrogen, tetrel, pnicogen, and spodium bonds formed between CO$_2$ molecules and surfaces of H2-ICOP and Zn-ICOP, and their contribution to selective CO$_2$ uptake of these compounds (Figure 6).

These noncovalent interactions can be uniformly defined based on the positive electrostatic region present on an atom due to the anisotropic distribution of the electron density. The positive electrostatic region presents on an atom along a σ- polymer is called σ-hole. The size and magnitude of σ-holes dependent on both the nature of its atom and the electron-withdrawing ability of groups attached to this atom. These σ-holes can have an attractive interaction with electron donors such as Lewis base, anions or radicals. Depending on the σ-holes origins, these interactions are called tetrel bonding (group IV), pnicogen bonding (group V), chalcogen bonding (group VI), halogen bonding (group VII) or spodium bonding (group XII).\(^{59}\)

The symmetry adapted perturbation theory (SAPT) analysis, which partitions the attractive forces into electrostatic ($E_{\text{elst}}$), exchange-repulsion ($E_{\text{exch}}$), induction ($E_{\text{ind}}$), and dispersion ($E_{\text{disp}}$) terms, has been carried out to calculate the interaction energy of hydrogen (O$_{\text{CO}_2}$···H), tetrel (C$_{\text{CO}_2}$···N, C$_{\text{CO}_2}$···Cl$^-$), pnicogen (O$_{\text{CO}_2}$···N$^+$), and spodium bonds (O$_{\text{CO}_2}$···Zn) in H2-ICOP and Zn-ICOP and estimate the preferable binding sites to capture the CO$_2$ molecules on their surfaces (Table 3). For all studied non-covalent interactions, the calculated attractive components $E_{\text{elst}}$, $E_{\text{ind}}$, and $E_{\text{disp}}$ provide sufficient stabilization to overcome the repulsive exchange component $E_{\text{exch}}$, and the resultant interactions energy
(E_{int}) values are negative, except hydrogen bonding. The value of E_{exch} for hydrogen bonds in H2-ICOP is very large and suppresses other attractive components, therefore the resulting interaction energy is positive which indicates that the formation of H-bonds between CO_{2} and -NH (porp) is not favourable (Table 2, Figure 7d). The dispersion forces (E_{disp}) is found to be dominant in attractive binding energies of pnicogen (O_{CO_{2}}···N^{+}) and C_{CO_{2}}···N tetrel bonds and spodium bond (O_{CO_{2}}···Zn), while the electrostatic interactions (E_{elest}) dominate in C_{CO_{2}}···Cl⁻ tetrel bonds in both compounds. The percentage contribution of dispersion term in overall attractive forces for pnicogen bonds consists of 73% in CO_{2}-H2-ICOP and CO_{2}-Zn-ICOP, while for C_{CO_{2}}···N tetrel bonds in these systems it is equal to 58% and 66% respectively. For spodium bond dispersion term constitutes 53%. For C_{CO_{2}}···Cl⁻ tetrel bonds in both compounds the percentage contribution of electrostatic interactions in overall attractive forces consists of 58%.

**Table 2.** Summary of SAPT results (kJ.mol⁻¹) for pnicogen (O_{CO_{2}}···N^{+}), tetrel (C_{CO_{2}}···N, C_{CO_{2}}···Cl⁻), hydrogen (H···O_{CO_{2}}) and spodium (Zn···O_{CO_{2}}) bonds in CO_{2}-H2-ICOP and CO_{2}-Zn-ICOP. R is the bond length (Å). "The D-H···A angel for both CO_{2} are 125.8 and 118.7°."
The strength of non-covalent interactions in \(	ext{CO}_2\text{-H}_2\text{-ICOP}\) and \(\text{CO}_2\text{-Zn-ICOP}\) is decreasing in the following order \(\Delta E_{\text{C} \cdots \text{N}} > \Delta E_{\text{C} \cdots \text{Cl}^-} > \Delta E_{\text{O} \cdots \text{N}^+}\) and \(\Delta E_{\text{Zn} \cdots \text{O}} > \Delta E_{\text{C} \cdots \text{Cl}^-} > \Delta E_{\text{C} \cdots \text{N}} > \Delta E_{\text{O} \cdots \text{N}^+}\) respectively (Table 2, Figure 7 a-h). The binding energy of \(\text{C}_{\text{CO}_2\cdots\text{N}}\) tetrel bonds in \(\text{CO}_2\text{-H}_2\text{-ICOP}\) is -22.02 kJ.mol\(^{-1}\) and strongest among studied non-covalent interactions. Interestingly, upon Zn metalation in porphyrin core, the binding energy of \(\text{C}_{\text{CO}_2\cdots\text{N}}\) tetrel bonds in \(\text{CO}_2\text{-Zn-ICOP}\) is decreased to -15.163 kJ.mol\(^{-1}\), probably due to an increase of positive electrostatic potential around nitrogen atoms (Figure 6) in porphyrin core, which resulted in the formation of weaker tetrel bond (\(\text{C}_{\text{CO}_2\cdots\text{N}}\)) with \(\text{CO}_2\). In addition, further analyses were performed to calculate binding energy of the simultaneous presence, on the same porphyrin core, of two \(\text{C}_{\text{CO}_2\cdots\text{N}}\) tetrel bonds in \(\text{H}_2\text{-ICOP}\) and spodium and \(\text{C}_{\text{CO}_2\cdots\text{N}}\) tetrel bonds in \(\text{Zn-ICOP}\). The analyses reveal that the simultaneous presence of spodium and \(\text{C}_{\text{CO}_2\cdots\text{N}}\) tetrel bonds are impossible on the same porphyrin core in \(\text{Zn-ICOP}\) because of the strong repulsion between two \(\text{CO}_2\) molecules (Table S1, Figure S10), while two tetrel bonds may form in \(\text{H}_2\text{-ICOP}\) porphyrin core because of negligible repulsion between \(\text{CO}_2\) molecules (Figure S11, Table S1). Overall, in our fragment model, \(\text{H}_2\text{-ICOP}\) can potentially form two pnicogen, two \(\text{C}_{\text{CO}_2\cdots\text{Cl}^-}\) and four \(\text{C}_{\text{CO}_2\cdots\text{N}}\) tetrel bonds with \(\text{CO}_2\), while \(\text{Zn-ICOP}\) can form two pnicogen, two \(\text{C}_{\text{CO}_2\cdots\text{Cl}^-}\) tetrel, and two spodium bonds with \(\text{CO}_2\). The major \(\text{CO}_2\) uptake contribution comes from four \(\text{C}_{\text{CO}_2\cdots\text{N}}\) tetrel bonding interactions for \(\text{H}_2\text{-ICOP}\), whereas two spodium bonding interactions for \(\text{Zn-ICOP}\). In conclusion, \(\text{H}_2\text{-ICOP}\) has more binding sites with more powerful non-covalent interactions that lead to an enhancement of the \(\text{CO}_2\) uptake compared to \(\text{Zn-ICOP}\), which is in good agreement with experimental results.
2.4. The catalytic performance in CO₂ conversion into cyclic carbonates

To evaluate catalytic activities of viologen-linked porphyrin H₂-ICOP and Zn-ICOP, the cycloaddition of CO₂ to propylene oxide was chosen as a model reaction and the results were listed in Table 3. The reactions were conducted under 1.0 MPa CO₂ pressure and solvent and co-catalyst free condition at 80 °C (for details see ESI).

The compared catalyst Zn-ICOP and H₂-ICOP gave the yields of 83% and 54%, respectively. Surprisingly, Zn-ICOP, despite having significantly lower CO₂ uptake...
capacity, displayed better catalytic activity than H2-ICOP. The high activity of Zn-ICOP can be attributed to the synergistic effect of Lewis acid Zn site and a nucleophile counter anion (Cl\(^-\)). As the zeta potential data revealed that Zn-ICOP possess counter anion (Cl\(^-\)) on its surface, whereas H2-ICOP does not, which indicates the crucial role of the counter anion (Cl\(^-\)) in the mechanism of this catalytic reaction.\(^{46,47}\) Notably, the catalytic activity of Zn-ICOP was achieved with lowered temperature and CO\(_2\) pressure, in the solvent-free reaction system, and comparable to that of most of the reported examples (Table 3).

**Table 3.** The cycloaddition of CO\(_2\) with propylene Oxide (PO) catalysed by various ICOPs

*This work (Yields are determined by \(^1\)H NMR)

| Catalyst         | Loading | T(°C) | P\(_{CO2}\) (bar) | t (h) | Yield(%) | Ref. |
|------------------|---------|-------|-------------------|-------|----------|------|
| CTF-P-HSA        | 0.1 g   | 130   | 6.9               | 4     | 83       | 60   |
| cCTF             | 4 wt%   | 90    | 10                | 12    | 99       | 34   |
| PCP-Cl           | 5 wt%   | 100   | 30                | 12    | 99       | 39   |
| Zn-CIF2-C\(_3\)H\(_5\) | 0.18mol% | 120   | 25                | 5     | 98       | 61   |
| TBB-Bpy-a        | 0.08 g  | 120   | 10                | 4     | 99       | 48   |
| COF-salen-Zn     | 0.1 mol % | 100  | 20                | 3     | 90       | 62   |
| SYSU-Zn@IL1      | 0.16mol% | 80   | 10                | 12    | 62       | 47   |
| H2-ICOP          | 0.16mol% | 80   | 10                | 12    | 54 \(\ast\) |      |
| Zn-ICOP          | 0.16mol% | 80   | 10                | 12    | 83 \(\ast\) |      |

The catalytic performance of Zn-ICOP was compared with that of the corresponding polymer SYSU-Zn@IL1(Br\(^-\)) since both structures based on Zn-porphyrin and viologen. SYSU-Zn@IL1, with a BET surface area of 38 m\(^2\).g\(^{-1}\), has a nearly identical chemical composition to Zn-ICOP. Under similar conditions, Zn-ICOP had 83% conversion of PO, whereas SYSU-Zn@IL1 (Br\(^-\)) could only afford a PO conversion of 62%. The higher
activity of Zn-ICOP (Cl⁻) is mainly attributed to the higher nucleophility of its counter anions (Cl⁻ > Br⁻).

Under the optimized reaction conditions, the catalytic activity of Zn-ICOP was further studied over a variety of epoxides. As shown in Table 4, various epoxides are efficiently converted into desired products with moderate yields under mild conditions by the Zn-ICOP. With the increase of the size of epoxides, a steady decrease in the yield of cyclic carbonates was observed from PO (83%), 1,2-epoxybutane (42%) to styrene oxide (4%), likely owing to their increasing steric hindrances, except for epichlorohydrin (77%) (Table 4). The deviation of epichlorohydrin’s yield from the trend, despite its larger size, is probably due to additional non-covalent interaction between chlorine functional group and CO₂.

Table 4. The addition of CO₂ to various epoxide by Zn-ICOP catalyst. Reaction conditions: epoxide (1 mL), catalyst (0.16 mol%), 80 °C, 1 MPa, 12 h.

| Epoxide       | Product     | Conversion (%) |
|---------------|-------------|----------------|
|               |             | 83             |
| α-CD          | O            | 42             |
| 1,2-epoxybutane| Cl-O        | 77             |
| Styrene oxide | O-CO₂       | 4              |

3.Conclusion

Two viologen-porphyrin based ionic covalent organic polymers were constructed by a one-pot facile Zincke reaction. The BET surface area analyses reveal that both H2-ICOP (9 m².g⁻¹) and Zn-ICOP (20 m².g⁻¹) possess a very low surface area. Yet, despite their
nearly non-porous surfaces, especially **H2-ICOP** exhibits very large CO$_2$ capture capacity and CO$_2$/N$_2$ selectivity, which indicates efficient non-covalent interactions with CO$_2$. The theoretical analyses show that **H2-ICOP** can potentially form two pnicogen, two C$_{CO2}$$\cdots$Cl$^-$ and four C$_{CO2}$$\cdots$N tetrel bonds with CO$_2$, while **Zn-ICOP** can form two pnicogen, two C$_{CO2}$$\cdots$Cl$^-$ tetrel, and two spodium bonds with CO$_2$. The strength of non-covalent interactions in **H2-ICOP** and **Zn-ICOP** is decreasing in the following order \( \Delta E_{C\cdots N} > \Delta E_{C\cdots Cl} > \Delta E_{O\cdots N}^+ \) and \( \Delta E_{Zn\cdots O} > \Delta E_{C\cdots Cl} > \Delta E_{C\cdots N} > \Delta E_{O\cdots N}^+ \) respectively. The binding energy of C$_{CO2}$$\cdots$N tetrel bonds in CO$_2$-H$_2$-ICOP is -22.02 kJ.mol$^{-1}$ and strongest among studied non-covalent interactions. The major CO$_2$ uptake contribution comes from four C$_{CO2}$$\cdots$N tetrel bonding interaction for **H2-ICOP**, whereas two spodium bonding interaction for **Zn-ICOP**. Furthermore, CO$_2$ catalytic conversion performances of **Zn-ICOP** and **H2-ICOP** gave encouraging yields of 83% and 54%, respectively. Surprisingly, **Zn-ICOP**, even with significantly lower CO$_2$ uptake capacity, displayed better catalytic activity than **H2-ICOP**, probably due to the crucial role of the counter anion (Cl$^-$) in the mechanism of this catalytic reaction.

Overall, we have demonstrated here that ICOP with multiple CO$_2$-philic sites can indeed exhibit very large CO$_2$ capture capacity, CO$_2$/N$_2$ selectivity, and highly efficient catalytic activity of CO$_2$ cycloaddition of epoxides, owing to efficient non-covalent interactions with CO$_2$, in spite of low surface areas. These results set a useful example for the importance of non-covalent interactions with CO$_2$ for the capture and conversion of CO$_2$ into value-added products. Therefore, we believe that these findings will prove to be of key importance to the design of bifunctional charged materials for CCU applications.
Associated Content

**Supporting Information.** Synthesis and analysis details; photographs of gel-like or powder ICOPs; FTIR of H2-ICOP-dx and Zn-ICOP-dx; CP/MAS $^{13}$C-NMR; PXRD with simulated patterns, EDS, DLS and Zeta potentials for H2-ICOP and Zn-ICOP; SEM images of H2-ICOP-dx and Zn-ICOP-dx; formation of simultaneous tetrel bonds in H2-ICOP and Zn-ICOP; SAPT results for interaction between two CO$_2$ molecules placed at the same porphyrin fragments in H2-ICOP and Zn-ICOP.

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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