Supplementary Information

for

Multifunctional ionic porous frameworks for CO$_2$ conversion and combating microbes

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I. Instrumentation and methods

**Nuclear magnetic resonance (NMR) spectroscopy:** Bruker Avance III 500 MHz NMR spectrometer was used to check the solution state $^1$H NMR spectra. The residual solvent signals were used as internal standard, and chemical shifts (δ) were reported in parts per million (ppm). The yields of the cyclic carbonates during catalysis were calculated using 1,1,2,2-tetrachloroethane as an external NMR standard. The solid-state $^{13}$C cross-polarization magic angle spinning (CP/MAS) NMR experiments were carried out on JEOL ECX2 400 MHz (field 9.4 T) standard bore spectrometer equipped with 4 mm solid-state MAS probe. The samples were packed into a 4 mm Zirconia rotor and spun at 8 kHz at the magic angle.

**Fourier transform infrared spectroscopy (FTIR):** Perkin-Elmer Model 2000 FTIR was used to measure the FTIR spectra of the samples using KBr pellet. Twenty scans were signal-averaged, with a resolution of 8 cm$^{-1}$ at ambient temperature.

**Thermogravimetric analysis (TGA):** Perkin Elmer TGA-6000 instrument was used to carry out TGA of the samples. The sample was heated from 30 °C to 900 °C under the nitrogen atmosphere at a scan rate of 10 °C min$^{-1}$.

**Powder X-ray diffraction (PXRD):** PANalytical Empyrean XRD instrument was used to carry out the PXRD experiment. Data was collected for 2θ values ranging from 5° to 60°.

**Field emission scanning electron microscopy (FESEM):** The surface morphology of all polymers was examined using a Carl Zeiss (Ultraplus) field emission scanning electron microscope. Samples for microscopy were prepared by dispersing ~ 0.5 mg of the sample in 2 mL of MeOH and drop-casting the dispersion on to a silicon wafer covered with adhesive carbon tape. All samples were coated with a thin layer of sputtered gold before imaging. FESEM was carried out using an accelerating voltage of 5 kV and 10 kV.

**Transmission electron microscopy (TEM):** The morphology of the polymers was examined using FEI TALOS 200S instrument at a working voltage of 200 kV. The samples for TEM analysis were prepared by drop-casting a homogeneous dilute MeOH dispersion of the polymers over a carbon-coated 400 mesh Cu grid.

**Energy dispersive X-ray spectroscopy (EDS):** was carried out at a working voltage of 200kV using Cu as a reference.

**Gas adsorption studies:** All the gas adsorption measurements were performed on Quantachrome Autosorb QUA211011 equipment. The temperature was maintained using liq. N$_2$ for measurements.
at 77 K and chiller bath for measurements at 273 K and 298 K. Isotherms were analyzed using ASIQwin software. All the samples were treated at 100 °C for 24 h under high vacuum for the degassing before the analysis.

**X-ray photo electron spectroscopy (XPS):** The XPS experiment was performed using PHI 5000 Versa Prob II, FIE Inc on a sample holder with a vacuum-dried powder sample drop of the size 1.5 mm radius. The scan time was set for 1 h per element for core level scan (energy band: 20 eV) with a pass setting of 23.5 eV. 0.025 eV step and 100 ms time per step for 5 cycles were followed.

**Inductively coupled plasma optical emission spectrometry (ICP-OES):** Zn/POF2 before and after catalytic conversion of CO₂ and epoxide into cyclic organic carbonates was subjected to ICP-OES analysis to quantify the metal leaching. 10 mg of each sample digested in conc. HCl (diluted to 10³-fold), and were analysed for the amount of Zn present in the catalyst.
II. Fabrication of POFs and Zn/POFs

(a) Chemicals

All the chemicals were used as received unless stated otherwise. Guanidine hydrochloride (≥99%), hydrazine hydrate (50-60%), benzene-1,3,5-tricarboxaldehyde (97%), terephthalaldehyde (99%), 1,2-dichlorobenzene (99%), 1-butanol (99.8), acetic acid (≥99%), tetrabutylammonium bromide (≥99%), (±)-propylene oxide (≥99.5%), zinc acetate dihydrate (≥98%) were received from Sigma-Aldrich. 1,1,2,2-Tetrachloroethane was received from Sigma-Aldrich and used as an external standard for the % yield calculations.

(b) Synthesis of triaminoguanidium chloride (TAG)

The monomer TAG was synthesized following a reported procedure (Scheme S1).\(^1\) Typically, guanidium chloride (1 mmol) was taken in 30 mL of isopropanol in a 100 mL round bottom flask. To the above-stirred solution, 50-60% hydrazine hydrate (4.5 mmol) was added and stirred to reflux for 6 h. After the reaction, the formed precipitate was filtered and washed with 50 mL of isopropanol to yield 97% of triaminoguanidium chloride.

\[
\begin{align*}
\text{H}_2\text{N} & \underset{\oplus}{\text{NH}_2} \text{Cl} \quad \text{H}_2\text{N} & \underset{\oplus}{\text{NH}_2} \text{H}_2\text{O} \\
\quad \text{Isopropanol, reflux} & \\
\text{H}_2\text{N} & \underset{\oplus}{\text{NH}_2} \text{N} & \underset{\oplus}{\text{NH}_2} \text{Cl}
\end{align*}
\]

Scheme S1 Synthetic protocol of TAG.

MALDI-TOF: Calculated m/z for C\(_1\)N\(_6\)H\(_{10}\) [M\(^+\)] 140.57, found [M+5H\(^+\)]145.68.

We checked the crystal structure of TAG to confirm the formation of the product. The molecular structure obtained from the crystal structure [space group: \(P6_3/m\), unit cell dimensions: \(a = 7.4862(9) \, \text{Å}, b = 7.4862(9) \, \text{Å}, c = 6.2347(8) \, \text{Å}, \alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ\)] analysis was found to be similar to the reported one.\(^2\)

![ORTEP diagram of TAG](image)

Fig. S1 ORTEP diagram of TAG at 50% ellipsoid probability level crystallized in the \(P6_3/m\) space group.
(c) Fabrication of POFs

(i) Fabrication of POF1

In a typical synthesis (Scheme S2), a mixture of TAG (0.31 mmol) and terephthalaldehyde (0.53 mmol) was degassed in a Schlenk tube. A mixture of o-dichlobenzene (5 mL), n-butanol (5 mL), and acetic acid (1 mL) was degassed using 3 cycles of freeze-pump-thaw and was added to the reaction mixture under an inert atmosphere of argon. The reaction was allowed to continue for 72 h. Later, the reaction mixture was washed with MeOH (excess) and then filtered. The collected residue was further subjected to Soxhlet extraction using methanol, acetone, and chloroform each for 24 h. A yellowish solid was collected and subjected to extensive drying. Yield: 95%.

![Scheme S2 Synthetic protocol of POF1 and Zn/POF1 (crystallite/particle size of ZnO is not to scale as per the pore sizes of the frameworks in the pictorial depiction).](image)

(ii) Fabrication of POF2

A mixture of TAG (0.31 mmol), 1,3,5-benzene-tricaboxaldehyde (0.31 mmol) was degassed in a Schlenk tube. A mixture of o-dichlobenzene (5 mL), n-butanol (5 mL), and acetic acid (1 mL) was degassed using 3 cycles of freeze-pump-thaw and was added to the reaction mixture under an inert atmosphere of argon. The reaction was allowed to continue for 72 h. Later, the reaction mixture was washed with MeOH (excess) and then filtered. The collected residue was further subjected to Soxhlet extraction using methanol, acetone, and chloroform each for 24 h. A greenish-yellow solid was collected and subjected to extensive drying (Fig. 1a). Yield: 92%.

(d) Fabrication of Zn/POFs

(i) Fabrication of Zn/POF1

In a typical synthesis (Scheme S2), 50 mg of POF1 was added to Zn(OAc)₂ solution in EtOH (10 wt.% in EtOH) and was degassed with vacuum-argon cycles for 3 times. The reaction mixture was allowed to stir at 90 °C for 12 h under argon atmosphere. The solid was collected
through filtration and subjected to Soxhlet purification using MeOH and CHCl₃ each for 24 h. The yellow color solid was dried at 100 °C in a glass-oven under vacuum.

(ii) Fabrication of Zn/POF₂

A similar procedure was followed for the fabrication of Zn/POF₂ (Fig. 1a), as mentioned above, for Zn/POF₁.

(e) Synthesis of MTAG

The synthesis of the model compound based on TAG was carried out following the procedure mentioned below (Scheme S3). To the solution of benzaldehyde (1.06 mmol) in 10 mL of EtOH, few drops of conc. HCl was added and stirred for 2 mins at room temperature. Then 0.35 mmol of TAG was added to the above solution and allowed to stir at 70 °C for 12 h. After the reaction, the solvent was evaporated, and the resultant solid was washed with diethyl ether and then dried under the vacuum. Yield 90%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 11.39 (3 H, s), 8.68 (3 H, s), 7.92 (6 H, s), 7.42 (9 H, s). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 151.46, 147.99, 132.78, 130.99, 128.76, 128.65. MALDI-TOF: Calculated m/z for C₂₂H₂₂N₆ [M+] 369.45, found 369.14.

Scheme S3 Synthetic protocol for the model compound of POF₂ (MTAG).

Crystallographic details of MTAG: Crystals of MTAG were obtained by slow evaporation from acetonitrile solution. The structural details are mentioned below (Table S1, CCDC No. 1966910).

Fig. S2 The crystal structure packing of the model compound for POF₂ (MTAG) (C: grey, N: blue, Cl: green, H: white).
| **Table S1** Crystal data and structure refinement for MTAG (CCDC No. 1966910) |
|--------------------------------------------------|
| **Empirical formula** | C\textsubscript{22}H\textsubscript{21}N\textsubscript{6}Cl, C\textsubscript{2}H\textsubscript{3}N, H\textsubscript{2}O |
| **Formula weight** | 505.0283 |
| **Temperature** | 296(2) K |
| **Wavelength** | 0.71073 Å |
| **Crystal system** | Monoclinic |
| **Space group** | P\textit{2}_1/c |
| **Unit cell dimensions** | \(a = 8.6917(2)\) Å, \(b = 15.6895(5)\) Å, \(c = 17.8706(6)\) Å, \(\alpha = 90^\circ\), \(\beta = 101.494(2)^\circ\) and \(\gamma = 90^\circ\) |
| **Volume** | 2388.11(12) Å\(^3\) |
| **Z** | 4 |
| **Density (calculated)** | 1.405 mg/m\(^3\) |
| **Absorption coefficient** | 0.211 mm\(^{-1}\) |
| **F(000)** | 1088 |
| **Crystal size** | 0.22 x 0.18 x 0.12 mm\(^3\) |
| **Theta range for data collection** | 1.743 to 30.741° |
| **Index ranges** | \(-11 \leq h \leq 12, -22 \leq k \leq 22, -23 \leq l \leq 25\) |
| **Reflections collected** | 27187 |
| **Independent reflections** | 7340 [R(int) = 0.0501] |
| **Completeness to theta = 25.242°** | 99.9 % |
| **Absorption correction** | None |
| **Refinement method** | Full-matrix least-squares on \(F^2\) |
| **Data / restraints / parameters** | 7340 / 0 / 302 |
| **Goodness-of-fit on \(F^2\)** | 1.056 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0671, wR2 = 0.1643 |
| **R indices (all data)** | R1 = 0.1170, wR2 = 0.1923 |
| **Largest diff. peak and hole** | 0.737 and -0.298 e.Å\(^{-3}\) |
III. Characterization of POFs and Zn/POFs

(a) Fourier transform infrared spectroscopic (FTIR) analysis

![FTIR spectra of TAG (blue), terephthalaldehyde (brown), and POF1 (green).](image1)

**Fig. S3** FTIR spectra of TAG (blue), terephthalaldehyde (brown), and POF1 (green).

The FTIR spectra of respective monomers along with that of POF1 and POF2 are shown in Fig. S3 and S4, respectively. The C=N stretching at 1632 cm$^{-1}$ indicates the cross-condensation between the monomers. The peak at 1102 cm$^{-1}$ can be assignable to the C-N stretching of the TAG unit. Further, a new peak appears at 462 cm$^{-1}$ that refers to the formation of ZnO in Zn/POF2 (Fig. 1b). The shift of the peak at 1632 cm$^{-1}$ in pristine POFs to 1566 cm$^{-1}$ in Zn/POFs refers to the decrease in the bond length of C=N after the ZnO loading suggesting the metal coordination in the polymer framework (Fig. S5, 1b).

![FTIR spectra of TAG (blue), trimesaldehyde (benzene-1,3,5-tricarboxaldehyde, brown), and POF2 (green).](image2)

**Fig. S4** FTIR spectra of TAG (blue), trimesaldehyde (benzene-1,3,5-tricarboxaldehyde, brown), and POF2 (green).
The thermogravimetric analysis of POFs revealed that the POFs were stable up to ~250 °C. The amount of the ZnO loading in Zn/POFs was further confirmed by the TGA analysis (Fig. 1c, S6). The variation of the ZnO loading in Zn/POFs, in samples obtained through different batches of fabrication was examined (Fig. S6) and ZnO amount in Zn/POF2 was found to be 57.3 ± 1.2 wt%. Further, the TGA of the sample after the hot filtration experiment was performed to confirm no significant metal leaching (Fig. S7).

![FTIR spectra of Zn/POF1 (blue), and POF1 (green).](image)

**Fig. S5** FTIR spectra of Zn/POF1 (blue), and POF1 (green).

**Fig. S6** The thermogravimetric analysis of Zn/POF2 obtained through different batches of synthesis, indicating the high loading of ZnO.

(b) Thermogravimetric analysis (TGA)

The thermogravimetric analysis of POFs revealed that the POFs were stable up to ~250 °C. The amount of the ZnO loading in Zn/POFs was further confirmed by the TGA analysis (Fig. 1c, S6). The variation of the ZnO loading in Zn/POFs, in samples obtained through different batches of fabrication was examined (Fig. S6) and ZnO amount in Zn/POF2 was found to be 57.3 ± 1.2 wt%. Further, the TGA of the sample after the hot filtration experiment was performed to confirm no significant metal leaching (Fig. S7).
The structure modelling of the POFs was performed using the Reflex module implemented in Materials Studio 6.1 software package (Fig. S8a, S8b). The unit cell dimension was first determined by the observed powder X-ray diffraction peak positions. Further, the cell was optimized using Pawley refinement constructed in the module until the Rwp value converges (Rwp

![Graph](image)

**Fig. S7** Thermogravimetric analysis of Zn/POF2 before (brown) and after the hot water treatment (blue).

(c) **Powder X-ray diffraction (PXRD) analysis**

The structure modelling of the POFs was performed using the Reflex module implemented in Materials Studio 6.1 software package (Fig. S8a, S8b). The unit cell dimension was first determined by the observed powder X-ray diffraction peak positions. Further, the cell was optimized using Pawley refinement constructed in the module until the Rwp value converges (Rwp

![Image](image)

**Fig. S8** Modelled structures of POF2 in (a) eclipsed and (b) staggered conformation. (c) The simulated PXRD (blue), experimental PXRD pattern (red) as well as the observed peaks (green) for POF2 using Materials Studio 6.1. (d) The comparative analysis of powder X-ray diffraction patterns of POF2 with the modelled PXRD patterns (eclipsed as well as staggered forms).
The experimental PXRD indexing for POF2 revealed a tetragonal system with the lattice parameters $a = 18.18$, $b = 18.18$, $c = 5.17$, $\alpha = 90^\circ$, $\beta = 90^\circ$ and $\gamma = 90^\circ$ (Fig. S8c). The conformations (eclipsed as well as staggered) of POFs were modelled in the Materials Studio with an interplanar spacing of 3.6 Å with a $P4$ space group that showed similarity with the experimental PXRD data. The results suggested the presence of both eclipsed as well as staggered conformations that led to the broadening of the PXRD pattern (Fig. S8d). The low crystallinity of TAG-based POFs is likely due to the electrostatic repulsion between the two layers of cationic triaminoguanidinium units and intercalated chloride ions leading to the poor $\pi$-$\pi$ stacking.$^{2,3}$

The powder X-ray diffraction analysis was carried out, collecting the data at a $2\theta$ range of 5° to 60°. The broad pattern of the peak signifies the amorphous nature of the polymer. The incorporation of ZnO in Zn/POF2 was further confirmed by the peaks at 2$\theta$ equals to 31.7°, 34.3°, 36.2°, 47.4°, and 56.5° that correspond to the planes (100), (020), (101), (102) and (110) of ZnO,

**Fig. S9** The PXRD of POF1 (green), Zn(OAc)$_2$ (brown), and Zn/POF1 (blue).

**Fig. S10** The PXRD analysis of the samples after refluxing Zn(OAc)$_2$ with only ethanol (brown), in the presence of TAG (Zn/TAG, green), and POF2 (Zn/POF2, blue) in ethanol indicating the role of triaminoguanidinium core (TAG) for the formation of ZnO.
respectively in the wurtzite form (Fig. 1d). Owing to the heterogeneous nature of the reaction medium, it is difficult to examine the exact reaction mechanism for the formation of ZnO from the precursor Zn(OAc)$_2$. However, for the qualitative elucidation of the mechanism, we performed a number of control experiments. We carried out a similar reaction in the absence of POFs, where we observed, there was no formation of ZnO (Fig. S10). It is obvious because in the absence of base/acid, the hydrolysis of Zn(OAc)$_2$ is not possible to occur.$^4$ Similarly, taking triaminoguanidinium chloride (TAG-Cl) in the reaction mixture instead of POF, we observed the formation of ZnO, as proved by PXRD analysis (Fig. S10). These results indicate that there is a profound role of triaminoguanidinium-based POFs and more precisely the $N$-rich guanidinium core for the formation of ZnO. The PXRD analysis of Zn/POFs indicated the crystallite size in the range of 11-15 nm. The ZnO particles were impregnated with the network. Even though we could observe the fringe pattern from the TEM images, but the discrimination of ZnO from the network was not possible.

Based on the above experimental evidence, we proposed a plausible mechanism for the in situ formation of ZnO from Zn(OAc)$_2$ facilitated by the $N$-rich network (Fig. S11). The following mechanism illustrates that in the steps (i), (ii) and (iii), the intermediate species of mono and disubstituted Zn-complex are formed. A similar mode of complexation of triaminoguanidinium-based ligands with different metal ions (e.g., Zn$^{2+}$) was also anticipated by us as well as reported in previous literature.$^1,4$ In the final step (i.e., step iv), a condensation between intermediate Zn(II)-complexes (step ii, iii) leading to the elimination of water and formation of polymeric -O-Zn-O-Zn-O- species is presumed. The mechanism of formation of ZnO infused POFs was proposed considering the mechanistic illustration presented in the earlier literature.$^5$ Here, the POFs not only act as the catalyst but also as the template. However, the validity of the mechanism of the in situ formation of ZnO is intriguing and can be a subject of further experimental exploration.
Fig. S11 The plausible mechanism depicting the in situ formation of ZnO infused triaminoguanidinium framework (dotted lines between N and Zn atoms represent stabilizing interaction(s).
(d) Microscopic characterizations

The field emission scanning electron microscopy (FESEM) image of POF2 (Fig. S12a) illustrates the formation of granular morphology like microstructures (composed of small spherical aggregates). Whereas, the formation of agglomerates of the irregular granular morphology was observed in the case of Zn/POF2 (Fig. S12b). The transmission electron microscopy (TEM) images revealed the porous nature of POF2 and Zn/POF2 (Fig. S14a, S14b, respectively). The EDS analysis was carried out for POF2 and Zn/POF2 (Fig. S15). Further, the uniform distribution of ZnO in Zn/POF2 was confirmed by the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) elemental mapping (Fig. S16).

Fig. S12 FESEM images of (a) POF2 and (b) Zn/POF2.

Fig. S13 FESEM images of (a) POF1 and (b) Zn/POF1.
Fig. S14 TEM images of (a) POF2 and (b) Zn/POF2 (scale bar = 20 nm); inset: the fringe pattern in Zn/POF2 due to the infused ZnO matrix (scale bar = 5 nm).

Fig. S15 The EDS analysis of (a) POF2 and (b) Zn/POF2 showing the elemental distribution.
(e) X-ray photoelectron spectroscopic (XPS) analysis

The XPS analysis of POFs and Zn/POFs are shown in Fig. S17-S19. The peak at 530.2 eV in the O1s XPS spectrum was taken as the reference for the calculation of the amount of ZnO loading in Zn/POFs (Fig. S18d). All the nitrogen atoms of triaminoguanidinium in POFs are in a similar chemical environment due to the extensive resonating structure. It is evident by the single peak of N1s (B.E. = 398.44 eV, before metal loading) in the X-ray photoelectron spectroscopy (XPS) (Fig. S17b). After the metal loading, the N1s XPS showed a single peak at 398.01 eV in Zn/POF2 (Fig. S18b). Even though the N1s XPS spectrum revealed a slight shift due to the interaction with ZnO, no splitting was observed, presumably due to the conjugation. Similar kinds of results were observed in the recent reports for the N1s high-resolution XPS spectra of POFct-1 before and after adsorbing Hg(II) and Cu(II),\textsuperscript{6a} and also for N1s in PFe\textsubscript{3}O\textsubscript{4}@NH\textsubscript{2}-MIL-125 before and after Pb(II) adsorption.\textsuperscript{6b} Inward contraction of N-valence electrons takes place due to the metal-N coordination. Thereby N1s core electron experiences more screening compared to the pristine N, and consequently, resulting in the smaller binding energy of the N1s core level.\textsuperscript{6c} It is to be noted that an upfield shift of the aldimine protons of the triaminoguanidinium Schiff base in the solution-state \textsuperscript{1}H NMR spectra while titration with Zn\textsuperscript{2+}/Cd\textsuperscript{2+} was observed in earlier work asserting coordination of Zn(II) with triaminoguanidinium core.\textsuperscript{1,6d}
However, a clear distinction was observed in the guanidinium C, imine C and phenylic C of POFs and Zn/POFs. The C1s XPS spectra of POFs revealed the presence of three types of C (phenylic: 282.8 eV; imine: 284.0 eV; guanidinium: 286.6 eV) with distinct distributions (Fig. S17a). Whereas, in Zn/POFs, a significant change in XPS spectra was observed due to the interaction with ZnO [POF2: 59.6% (phenylic-C); 31.3% (imine-C); 8.9% (guanidinum-C), Zn/POF2: 63.5% (283.1 eV, phenylic-C); 31.3% (283.9 eV, imine-C); 5.0% (287.1 eV, guanidinium-C), Fig. 1i, S17a, S18a]. Furthermore, the shift of the peak at 1632 cm⁻¹ in POFs to 1566 cm⁻¹ in Zn/POFs indicates the increase of C=N bond length due to the ZnO loading, signifying the coordination with the framework (Fig. 1b, S5). The stability and recyclability of Zn/POFs in catalysis further support the same (vide infra).

![XPS analysis](image)

Fig. S17 The XPS analysis of POF2 for (a) C1s, (b) N1s, and (c) Cl2p, respectively.

**Table S2** Atomic (at.) % of carbon, nitrogen, zinc, and oxygen, acquired from XPS analysis.

| Substance  | C   | N   | Zn   | O   |
|------------|-----|-----|------|-----|
| POF1       | 81.1| 17.4| -    | -   |
| Zn/POF1    | 47.4| 12.2| 17.4*| 17.4|   |
| POF2       | 70.9| 26.9| -    | -   |
| Zn/POF2    | 47.6| 14.9| 16.5*| 16.5|   |

*Percentage of Zn calculated by taking the O1s XPS analysis.
Fig. S18 The XPS analysis of Zn/POF2 for (a) C1s, (b) N1s, (c) Cl2p, and (d) O1s, respectively.

Fig. S19 The XPS analysis of POF1 for (a) C1s, (b) N1s, and (c) Cl2p, respectively.
(f) Gas adsorption studies of POFs and Zn/POFs

(i) Nitrogen gas sorption and porosity

The nitrogen sorption isotherms of POFs and Zn/POFs indicate type II isotherms (Fig. 1j, S20). The pore size distribution plots were estimated using the nonlocal density functional theory (NLDFT) method, confirming the hierarchical porosity from micro to mesoporous region (Fig. 1k). The specific BET surface area plots of POF2, as well as Zn/POF2, are shown in Fig. S21. The plot is obtained by fitting the BET equation given below.

\[
\frac{P}{P_0} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} \left( \frac{P}{P_0} \right)
\]

Where \( P/P_0 \) refers to the relative pressure, \( n_m \) refers to the specific monolayer capacity, \( n \) is the specific amount adsorbed at \( P/P_0 \), and \( C \) is the BET constant. The low value of the BET constant of Zn/POF2 (\( C = 10.8 \)) refers to the decrease in the micropore regime as compared to POF2 (\( C = 70.8 \)), which suggests the blocking of micropores through the impregnation of ZnO with the network.\(^7\)

Fig. S20 (a) Nitrogen sorption profile of POF1 and (b) the specific BET surface area plot of POF1.
(ii) CO₂ sorption and selectivity

The CO₂ adsorption isotherms of POFs and Zn/POFs collected at 273 K along with the CO₂/N₂ selectivity are shown in Fig. S22-S24. The CO₂ interaction with the POFs can be estimated by the enthalpy of adsorption (Fig. S25) following the Clausius-Clapeyron equation given below.⁷

\[
\ln \left( \frac{P_1}{P_2} \right) = \frac{\Delta H_{ads}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

The CO₂/N₂ selectivity was further evaluated by employing Ideal Adsorbed Solutions Theory (IAST) for the pure components.⁸ A flue gas composition of 15% CO₂ and 85% N₂ was taken according to IAST for the calculation of selectivities.⁸

\[
\text{Selectivity, (S)} = \frac{q_1/q_2}{p_1/p_2}
\]

Where, \( q_1 \) and \( q_2 \) are the amount of adsorbate at pressure \( p_1 \) and \( p_2 \), respectively. The hysteresis loops present in the CO₂ adsorption-desorption isotherms (Fig. S22a, S23a, S24a) of POFs and Zn/POFs indicate the flexibility of the network as well as the kinetic trapping of CO₂ inside the N-rich pores of the frameworks during the sorption experiment.⁹
Fig. S22 (a) CO₂ sorption and (b) CO₂ over N₂ selectivity of POF2 measured at 273 K and 1 bar.

Fig. S23 (a) CO₂ sorption and (b) CO₂ over N₂ selectivity of POF1 measured at 273 K and 1 bar.

Fig. S24 (a) CO₂ sorption and (b) CO₂ over N₂ selectivity of Zn/POF2 measured at 273 K and 1 bar.
**Fig. S25** The CO$_2$ isosteric heat of adsorption profiles of POF1 (blue) and POF2 (green).
IV. CO$_2$ conversion catalyzed by POFs and Zn/POFs

All the CO$_2$ conversion experiments were performed with 17.2 mmol of the epoxide and a CO$_2$ pressure of 2.5 bar. Briefly, TBAB (2.5 mol%) and catalyst (POF or Zn/POF, 20 mg) were taken in a Schlenk-sealed tube and deaerated and filled with CO$_2$. Under ice-cold conditions, epoxides of particular interest were added, and the CO$_2$ pressure was set at 2.5 bar and was further stirred at 90 °C. Then, the reaction mixture was allowed to cool, and 1,1,2,2-tetrachloroethane was added as an external NMR standard for the calculation of % of conversion (Table S3). The product formed was isolated by column chromatography using 20% EtOAc/hexane as eluent.

Table S3 Catalytic conversion of propylene oxide to propylene carbonate.

| S. No. | Substance     | Pressure (bar) | Reaction time (h) | Conversion# |
|--------|---------------|----------------|-------------------|-------------|
| 1.     | TBAB          | 2.5            | 9                 | 17%         |
| 2.     | MTAG          | 2.5            | 9                 | 28%         |
| 3.     | POF1/POF2*    | 2.5            | 9                 | < 2%        |
| 4.     | POF1          | 2.5            | 9                 | 51%         |
| 5.     | POF2          | 2.5            | 9                 | 42%         |
| 6.     | Zn/POF1       | 2.5            | 9                 | 94%         |
| 7.     | Zn/POF2       | 2.5            | 2                 | 40%         |
| 8.     | Zn/POF2       | 2.5            | 6                 | 85%         |
| 9.     | Zn/POF2       | 2.5            | 9                 | 92%         |
| 10.    | ZnO bulk†$\ddagger$ | 2.5        | 9                 | 65%         |
| 11.    | ZnO NPs$\ddagger$ | 2.5        | 9                 | 86%         |

*% conversion calculated by the $^1$H NMR using 1,1,2,2-tetrachloroethane as an external standard. The results were cross-verified by calculating the GC yields using the same external standard. †In the absence of cocatalyst (TBAB). ‡The amount used is identical with ZnO present in Zn/POF2 (57 wt%). §nonrecyclable.

Fig. S26 A plausible mechanism of CO$_2$ conversion depicting the synergistic effect of Lewis-acidic ZnO and –NH functionality present in the framework (crystallite/particle size of ZnO is not to scale as per the pore sizes of the frameworks in the pictorial depiction).
A decrease in the percentage of conversion of cyclic carbonate was observed in subsequent cycles (Fig. S27a). However, the systematic analysis revealed that the decrease in conversion was due to the loss of catalyst amount during the filtration and was not due to the diminished catalyst activity (Fig. 2b, 2c, S27b, S27c).

We performed the control experiment with bulk ZnO for the catalytic conversion of epoxide (propylene oxide) into cyclic organic carbonates that showed ~65% conversion in the optimized reaction conditions (Fig. S49). We found with ZnO nanoparticles (size < 100 nm), ~85% conversion under identical conditions (Fig. S50). However, the catalyst was not recoverable after the reaction (from 20 mg catalyst, ~6 mg could be recovered: eventually, the catalytic conversion during the second cycle reduced to ~20%). The conversion of styrene oxide using ZnO nanoparticles was found to be 66% (Fig. S51). On the other hand, Zn/POFs showed excellent catalytic activity (92-99% conversion) with easy recyclability in identical reaction conditions. The high catalytic efficiency of Zn/POFs suggests the importance of N-rich CO2-philic ionic frameworks for the activation of epoxides in addition to the Lewis acidic metal centres (Fig. S26).

Table S4 The quantitative analysis of metal leaching from Zn/POF2 through ICP-OES analysis.

| S. No. | Name of the samples                     | Amount of Zn²⁺ (wt %) |
|--------|-----------------------------------------|-----------------------|
| 1.     | Zn/POF2 (Before reaction)                | 49.98                 |
| 2.     | Zn/POF2 (After 4th cycle)               | 47.97                 |
V. Antibacterial and antiviral studies with POFs and Zn/POFs

Bacterial strains and culture conditions:

The Gram-positive *Staphylococcus aureus* (*S. aureus* ATCC® 6538P™) and Gram-negative *Escherichia coli* (*E. coli* ATCC® 8739™) were obtained from HiMedia Laboratories. Both the bacterial strains were grown in Luria-Bertani (LB) broth medium (DIFCO™ LB Broth, Miller, Lot-8079540). Both bacterial strains were cultured overnight, aerobically at 37 °C in a culture tube/flask with shaking at 200 rpm in a shaker incubator (INFORS HT, Ecotron). In order to investigate the antimicrobial activity of nanoporous frameworks, an estimation of bacterial growth was carried out using a spectrophotometer (Eppendorf, Germany) and the plating assay was performed as the measure of bacterial growth and viability. All the measurements were performed with three replicates (n = 3), and the error bars represent standard deviation from the mean.

(a) **Antibacterial activity analysis:**

We cultured both Gram-positive, and Gram-negative bacteria in LB supplemented with the nanoporous frameworks. Culture lacking nanoporous frameworks served as control and nanoporous frameworks containing media having no bacteria was taken as a blank control to eliminate the optical interference. The overnight grown culture was inoculated in the respective media for the experiment in a 12 well format at initial cell OD600 of 0.05-0.06 as measured in a

![Fig. S28](image)

**Fig. S28** The antibacterial activity of the model compound of POF2 (MTAG, 500 µg/mL) against (a) Gram-positive bacteria (*Staphylococcus aureus*) and (b) Gram-negative bacteria (*Escherichia coli*) indicating the antibacterial activity of N-rich pristine ionic core.
spectrophotometer (Eppendorf, Germany). After incubating the culture for 12-15 h, the optical density (OD) was measured and diluted further (x1000) for LB agar plating.

(i) Colony-forming unit (CFU) analysis:

The CFU assay was used to deduce the antibacterial activity of the porous materials.\textsuperscript{11} The bacterial suspensions containing various doses of POF2 or Zn/POF2 (100, 200, 500 µg/mL) were incubated for 12 h at 37 °C. The living cells were taken from the suspension, diluted 1000-fold, and were allowed to grow on agar plates overnight at 37 °C for the assessment of the colony-forming units (CFU). The suspension without POF2 or Zn/POF2 served as control. The images of the representative agar plates were captured using a DSLR D5300 camera.

(ii) Growth curve analysis:

The growth dynamics of the bacteria containing POF2 and Zn/POF2 were observed by using the diluted bacterial culture (OD 0.05) maintained in 24 well plate. Bacterial growth curves measurements were obtained in triplicates using plate reader SpectraMax i3X (Molecular Devices, USA). LB containing respective frameworks was taken as blank control. The bacterial suspension without porous frameworks was taken as control. Readings were captured in a span of 2 h in kinetics mode.

(iii) TEM analysis of bacteria:

For the TEM analysis, bacteria (both control and treated) were captured in the mid-log phase and then pellets of bacteria obtained by centrifugation (6000xg for 3 minutes) and washed with 0.1 M phosphate buffer solution (PBS). Afterwards, the pellets were fixed with 0.5 mL of 2.5 % glutaraldehyde solution for 20 minutes following a reported protocol,\textsuperscript{12} and then were subjected to a series of alcohol dehydration process for 1 minute each (using 30%, 50%, 70% aq. EtOH solution) followed by 0.1 M PBS washing. Finally, the pellets were dispersed in 1 mL of absolute ethanol, and 10 µL sample was drop cast on the TEM grids.

(iii) AlamarBlue cytotoxicity assay:

The AlamarBlue (HiMedia TC235) assay was performed as per the reported protocol with a slight modification.\textsuperscript{13} In this assay, a blue colored resazurin (nonfluorescent) dye gets converted to a pink colored resorufin (fluorescent) dye in the presence of live cells (Fig. S29-S30).
**Fig. S29** (a) The alamarBlue cell viability fluorescence-based assay for Gram-negative (*E. coli*) bacteria showing reduced fluorescence intensity indicating the decrease in the bacterial population with increasing the amount of Zn/POF2. (b) Comparative study against the Gram-negative bacteria (*E. coli*) showing percentage viability with increasing concentration of POF2, Zn/POF2, ZnO nanoparticles (NPs), and bulk ZnO powder.

**Fig. S30** Schematic illustration of bacterial reduction mechanism of nonfluorescent resazurin to fluorescent resorufin in the alamarBlue-based assay.

**Fig. S31** Analysis of cell integrity upon treatment of POF2 using transmission electron microscopy (TEM): (a, b) Gram-positive bacteria (*S. aureus*) and (c, d) Gram-negative bacteria (*E. coli*).
(b) **Bacterial biofilm formation:**

The bacterial biofilm formation assay was performed following a reported protocol. Briefly, a single colony was maintained till the mid-log phase, and a 50 µL of 100-fold diluted in LB medium culture was incubated aerobically in 96-well format for 24 h. The post incubated wells were washed with water several times to remove the unbounded bacteria. The wells were further stained with 0.1% crystal violet (Sigma Aldrich) and washed after 5 minutes of staining with water, and the plate was air-dried overnight. Further, the biofilm was treated for 2 h with POF2 and Zn/POF2. Post-treated biofilm was captured using a digital camera for visual assessment (Fig. S32) and further quantitatively by measuring absorbance at 570 nm by dissolving crystal violet in 33% acetic acid (Fig. 5a, 5b).

![Image](image)

**Fig. S32** Bactericidal effects of POF2 and Zn/POF2 confirmed by their action on the biofilm disruption with increasing concentration (µg/mL).

(c) **Antibacterial film coating:**

The antibacterial coatings employing Zn/POF2 were made using a 2% poly(vinylalcohol) in water solution. The effective concentration of Zn/POF2 was maintained as 500 µg/mL, and the corresponding dispersion was coated on a glass slide using a spin coater. The coated slides were dried in an oven at 90 °C for 6 h before the antibacterial studies. The bacterial solution (~ 10^5 CFU/mL) was incubated in static conditions over the slide coated with Zn/POF2 in a Petri dish for 6, and 12 h at 37 °C. The bacterial growth was monitored by measuring OD at 600 nm (Fig. S33) and the percentage cell viability was plotted with respect to the control (only PVA coated slide).
SYBR Green-I and propidium iodide (PI) staining:

To determine the fraction of non-living cells against the living cells, the staining was performed with the nucleic acid stains like propidium iodide (PI) and SYBR Green-I.\textsuperscript{15} The fluorophore stock solution of SYBR Green-I and PI were prepared following a standard protocol, filtered with 0.22 µM membrane filters (Cole Parmer), and stored in the dark at -20 and 4 °C, respectively.\textsuperscript{16} A single colony of \textit{E. coli} was inoculated and grown until the mid-log phase (the fastest bacterial growth phase, 7-8 h). The bacterial concentration was calculated by measuring optical density at 600 nm, and a bacterial stock of $10^8$ CFU/mL was prepared by dissolving it in LB media. The Bacterial culture (2 mL) was mixed with the 500 µg/mL of porous organic frameworks and maintained for 4 h at 37 °C in a continuous agitation in a shaker incubator. The cells were pelleted down and washed multiple times with the Hanks' balanced salt solution (HBSS) (Lonza, Switzerland) and finally resuspended in the same. Later, the cells were treated with 10x concentration of SYBR Green-I (Molecular Probes, Thermo Scientific, USA) and 2.5 µM propidium iodide (Sigma Aldrich) solution in HBSS for 20 minutes. The post incubated cells were washed multiple times with HBSS, and 20 µL resuspended cells were mounted on a glass slide with the help of ProLong\textsuperscript{TM} Glass Antifade Mountant (Invitrogen, Thermo Scientific, USA) and kept for drying for 4 h. The fluorescent microscopic images were captured using a Zeiss Apotome fluorescence microscope (Carl Zeiss, Germany) using a 63x objective lens (Fig. 5c).
SYBR Green-I is a bacterial cell membrane permeable, nonspecific dye that can stain the live as well as the dead-cell. Whereas, propidium iodide (PI), the red-emitting fluorescent dye can only stain the dead cell. In the control bacterial cell (E. coli), the abundance of green fluorescence was found to be more than that of the red, suggesting the presence of a greater extent of the live cells. Whereas in both the POF2 and Zn/POF2 treated cells (E. coli), the abundancy of red fluorescence was observed to a greater extent (indicative of dead cell population). The merged images depicting both red and green fluorescence (column 3, Fig. 5c) reflect the extent of the presence of live/dead cells. The study revealed that the cell membrane was intact (indicative of live population) as reflected by the green fluorescence signal from the SYBR Green-I in control (without porous frameworks). Whereas, the POF2 or Zn/POF2 treated cells showed a high red fluorescence due to possible rupture of the cell membrane and hence PI stained specifically the dead cell and SYBR Green-I penetrated nonspecifically to both the cells (live/dead) to result in a merged signal. Thus, it is confirmed that POF, as well as Zn/POF, rupture the bacterial cell membrane (Fig. 5c, S34).

![Diagram of antibacterial activity](image)

**Fig. S34** The mechanism of antibacterial activity of Zn/POFs against *Escherichia coli* (Gram-negative) bacteria (dimension of bacteria and ZnO-infused framework is not to scale in the pictorial depiction).
(e) Water purification

The columns for the purification of water were prepared using a Pasteur pipette (Fig. S35). First, polystyrene beads of weight ~50 mg were loaded into the Pasteur pipette for packing the thin neck followed by a cotton plug of equal weight (~16 mg) in control and the test column. The Zn/POF2 of ~50 mg was loaded for the column-based purification of water. As a control, an equal amount of agarose was loaded, and the bacteria-contaminated water was allowed to pass through the packed column (flow rate: ~1 mL/12 min without any external pressure, 0.5 cm column bed width). The bacteria-contaminated water was prepared by spiking a known concentration of *E. coli* (~10⁸ CFU/mL) in ultra-pure water. The bactericidal effect of Zn/POF2 was examined by the CFU plating studies (Fig. S35), SYBR Green-I/PI live/dead cell assay (Fig. S36), as well as the DNA leaching assay followed by agarose gel electrophoresis (Fig. S37).

A complementary experiment involving the analysis of released DNA from the Zn/POF2 column-treated water, as a function of bacterial lysis, was performed next. A 0.7% agarose gel was made in 1x tris-acetate-EDTA (TAE) buffer. The DNA was visualized on the gel using the SYBR Safe-DNA gel stain (Invitrogen, Thermo Scientific). In order to compare the size of the DNA, the 1 KB plus DNA ladder (Fermentas) was used. The input contaminated water was heated

![Figure S35](image_url)

**Fig. S35** (a) The clearance of bacteria-contaminated water by passing through the columns packed with Zn/POF2 in comparison with the agarose-loaded column (control). Bacterial load after filtration was quantified by calculating (b) CFU/mL using agar plating method, and (c) percentage bacterial viability assessment (based on absorbance (OD) @ 600 nm). The bars represent the standard deviation from the mean (n = 3, mean ± s.d).
at 90 °C to get a positive control for lysis. The flow-through from the respective columns (20 µL each) was mixed with 6x DNA loading dye and was loaded on the agarose gel for electrophoresis (Fig. S37). The presence of more DNA content on the agarose gel in the case of Zn/POF2 (lane 4, Fig. S37) as compared to the background (lane 3) indicated its high bactericidal activity.

(f) **Bradford assay:**

Further to validate bacterial lysis, we performed Bradford protein quantification assay on the filtered water following a standard protocol. Precisely, 100 µL of filtrate after centrifugation...
(removal of live bacteria) was mixed with 3 mL of Bradford reagent (Sigma Aldrich) in a glass tube and was incubated for five minutes at room temperature. Post-incubation, 200 μL of the reaction mixture in triplicates was transferred into 96 well plate, and the absorbance was measured at 595 nm. Bradford reagent having no filtrate was used as blank. The high value of absorbance (presence of more protein) obtained in flow-through from the Zn/POF2-packed column as compared to the agarose-packed column is indicative of more lysis-associated intracellular protein release. Data was represented as bar plot (Fig. 5e).

**Antiviral activity**

**Cell lines:** The TZM-GFP and HEK293T cell lines described previously,18 were maintained in Dulbecco's Modified Eagle Medium with L-glutamine containing 10% heat-inactivated fetal bovine serum (FBS) (Gibco, Thermo Scientific USA, Cat. No. 10082147, lot no. 2097440). The cells were incubated at 37°C in a humidified 5% CO2 incubator (NuAire, USA). Cell monolayers were maintained at a split ratio of 1:10 by treatment with 0.25% trypsin, 1 mM EDTA (Invitrogen, Thermo Scientific, USA). All the measurements were performed with four replicates (n = 4), and the error bars represent standard deviation from the mean.

**(g) Virus production:**

A replication-defective single cycle NL4-3 (carrying a defect in Env and Nef open reading frame) was trans-complemented with HXB2 envelope coding plasmids, and was co-transfected in HEK293T cells using a calcium phosphate method.18 The virus-containing culture supernatants were collected after 48 h of transfection, clarified by centrifugation at 300xg for about 5 minutes, and passed through filters of 0.45-μm pores (Cole-Parmer) as described previously.19 For lentiviral pseudoparticles generation, we used ZS-Green reporter expressed through pScalps,20 psPAX2 (Addgene#12260), and pMD2.G (Addgene#12259, kind gift from Didier Trono), and were cotransfected in HEK293T cells using calcium phosphate method. Subsequent steps were the same as described for the HIV-1 virus.

**(i) Virus quantification:**

The quantification of retroviral reverse transcriptase (RT) activity in retrovirus containing filtered supernatant by quantitative reverse transcription polymerase chain reaction (qRT-PCR) as a method for the titration of lentiviral/retrovirus vector was followed.21
(ii) Infectivity assay:

The virus was five-fold diluted in a series of four steps while adding in target cells (TZM-GFP). The TZM-GFP cells (seeded one day before infection) were infected for 48 h in 96 well format (Eppendorf, Germany). Further, the infectivity was assayed as a function of green cells scored using CellInsight CX7 High-Content Screening (HCS) Platform (Thermo Fisher Scientific, USA) after counter staining the nuclei of total cells using Hoechst 33258 (Sigma Aldrich). The percentage of infectivity was represented (Fig. 6a, 6b). The representative images were captured using both CellInsight CX7 High-Content Screening (HCS) Platform (Fig. 6g) and SpectraMax i3x multimode microplate (Molecular Devices, USA) reader as shown in Fig. S38.

(iii) Virus fusion assay:

We employed the nlsCre delivery assay in order to evaluate the fusion of viruses in the target cells. The Cre delivery upon virus fusion activates the RFP in the TZM lox RFP target cells. For this assay, virus production was carried out using p8.9 Cre and pMD2.G (Addgene plasmid #12259) in HEK293T cells. Virus was subsequently quantified as described earlier, diluted and added to the TZM lox RFP cells seeded one day before in 96 well format in the absence and

Fig. S38 The fluorescence microscopy images of the single-cycle HIV-1 (top panel) and VSV-G pseudotyped lentiviral vector (bottom panel) infectivity against both POF2 and Zn/POF2 with respect to the control.
presence of porous frameworks (20 µg/mL). After 48 h of incubation, the red cells were scored and imaged using CellInsight CX7 High-Content Screening (HCS) Platform (Fig. 6c, 6d).

(h) Cytotoxicity analysis using cell counting and alamarBlue assay:

In order to analyze the cytotoxicity associated with the porous frameworks along with a comparative analysis using ZnO and ZnO nanoparticles, we performed total cell counting assay by nuclear staining using Hoechst 33258 (Sigma-Aldrich).22 We incubated porous frameworks with TZM-GFP target cell lines for 48 h. Post-incubation, cells were fixed using 4% paraformaldehyde (Sigma-Aldrich) and washed thrice with 1x PBS (Amresco), reconstituted using PBS tablets in Milli-Q water. Finally, cells were stained using Hoechst for 15 minutes at room temperature. Further, the staining was terminated by transferring the plate at 4 °C. Later, the cells were imaged and counted using CellInsight CX7 High-Content Screening (HCS) Platform (Thermo Fisher Scientific). The cell number represented in bar plots is shown in Fig. S39.

To check the cytotoxicity associated with the porous frameworks (POFs and Zn/POFs) in the host cells, firstly, TZM-GFP cells were incubated with the various doses of porous frameworks for 48 h.18 Post incubation, 1x alamarBlue (diluted from the 100x stock solution, i.e., 0.5 g in 100 mL 1x PBS) was added to the respective wells, and the fluorescence was recorded using SpectraMax i3x multimode plate reader (Molecular Devices, USA) and the corresponding bar plots showing cell viability were represented.13

![Figure S39](image_url)

Fig. S39 Comparative study of POF2, Zn/POF2 with ZnO nanoparticles (NPs), as well as bulk ZnO with varying doses showing (a) target cell viability (TZM-GFP) analysis, and (b) infectivity analysis using HIV-1.
Cell counting based cell viability assay (Hoechst based nuclear staining) indicates that the ZnO nanoparticles are toxic to the human cells in comparison to Zn/POF2, as shown in Fig. S39a. On the other hand, the antiviral activity of Zn/POF2 (20 μg/mL) is better than that of the bulk ZnO powder and comparable to the ZnO nanoparticles. In fact, the antimicrobial activity of pristine ZnO nanoparticles is further contributed by the cytotoxicity associated with ZnO nanoparticles (Fig. S39b). These data clearly ascertain that the developed materials are highly effective against the microbes with minimal cytotoxicity to the human cells.

(i) Virus lysis assay:

Virus particles containing supernatant were incubated for 2 h with the various doses of porous frameworks (5, 10, 20 μg/mL). After incubation, frameworks were removed using centrifugation at 500xg and 5 μL supernatants were taken to quantify the virus particles using SG-PERT assay with the SG-PERT lysis buffer as a control for effective lysis. The frameworks lyse the viruses and release the reverse transcriptase (RT) from the viral core, as reflected in the SG-PERT assay (Fig. 6e, 6f, S40).

![Diagram](image)

*Fig. S40* The plausible mechanism of antiviral activity of Zn/POFs against HIV.
VI. Comparative tables

We studied the reports of some of the well-known composite materials where the metal loading was found to be significantly high (Table S5). The metal loading was highlighted as a key feature of the composite materials for the enhanced performance in some of the said applications, as listed below.

**Table S5** Comparative accounts of metal/metal oxide loading capacities (wt%) of triaminoguanidinium based porous ionic frameworks developed in the present study with other representative porous materials, like porous organic polymers (POPs), covalent organic frameworks (COFs), porous carbons (PCs), and metal organic frameworks (MOFs) for catalysis and biomedical applications.

| Material                  | Metal loading | Application                                                      | Reference                        |
|---------------------------|---------------|------------------------------------------------------------------|-----------------------------------|
| **Zn/POF2**               | ZnO           | CO₂ conversion to cyclic carbonates, antibacterial (biofilm disruption, water treatment) and antiviral agent | Present work                     |
|                           | (57.3 ± 1.2 wt%; Zn (47.2 wt%) |                                                                      |                                   |
| **Porous Organic Polymers (POPs)** |               |                                                                  |                                   |
| HAz0-POP-1                | Cu (26.2 wt%), Zn (23.5 wt%), Ni (20.6 wt%) | CO₂ conversion to cyclic organic carbonates, oxidation of benzyl alcohols | Angew. Chem. Int. Ed., 2016, 55, 9685.23 |
| PAF-50                    | Ag (39.9 wt%) | Antibacterial polymer coatings                                   | Adv. Mater., 2013, 25, 6619.24     |
| Co-CMP                    | Co (7.3 wt%), Al (3.5 wt%) | CO₂ conversion to cyclic organic carbonates                       | Nat. Commun., 2013, 4, 1960.25     |
| Al-CMP                    |               |                                                                  |                                   |
| PP3-ILBr-ZnBr2@POPs      | Zn (4.6 wt%) | Conversion of CO₂ to cyclic carbonates                           | ACS Catal., 2016, 6, 6091.26      |
| Poly-(PPh3)-azo-Ag,      | Ag (0.2 wt%), Ru (3.7 wt%) | Carboxylative cyclization of propargyl alcohol with CO₂            | ACS Catal., 2016, 6, 1268.27      |
| Poly-(PPh3)-azo-Ru       |               |                                                                  |                                   |
| POPs Bp-Zn@MA            | Zn (1.9 wt%) | Synthesis of cyclic carbonates from flue gas                      | Green Chem., 2016, 18, 6493.28    |
| Ag-SN1-CMP               | Ag (12.3 wt%) | Effective antimicrobial carriers                                  | ACS Appl. Bio Mater., 2018, 1, 473.29 |
| **Covalent Organic Frameworks (COFs)** |           |                                                                  |                                   |
| Pd/COF-LZU1              | Pd (7.1 ± 0.5 wt%) | Suzuki–Miyaura coupling reaction                                 | J. Am. Chem. Soc., 2011, 133, 19816.30 |
| PdNPs@COF                | Pd (26.3 wt %) | Nitrophenol reduction and Suzuki–Miyaura coupling reaction        | J. Am. Chem. Soc., 2017, 139, 17082.31 |
| PtNPs@COF                | Pt (34.4 wt %) |                                                                  |                                   |
| Cu@COF                   | Cu (7.0 wt%) | Synthesis of unsymmetrical diynes via Glaser–Hay coupling         | ACS Appl. Mater. Interfaces, 2019, 11, 15670.32 |
| Material                        | Metal (%) | Reaction                                                                 | Journal/Year |
|--------------------------------|-----------|--------------------------------------------------------------------------|--------------|
| COF–Co/Co(OH)$_2$              | Co (16.0 wt%) | Hydrogen evolution and one-pot organic reductions                       | Small, 2018, 14, 1801233 |
| **Porous Carbons (PCs)**       |           |                                                                          |              |
| ZnO@polymer                    | Zn (10.9 wt%), (1.5 wt%) | Selective hydrogenation of phenylacetylene to phenylethylene          | Adv. Funct. Mater., 2018, 28, 1801737 |
| ZnO@carbon                     |           |                                                                         |              |
| ZnO@NC/S-1(0.0)                | Zn (2.8 wt%), (2.0 wt%) | Propane dehydrogenation                                                | iScience, 2019, 13, 269 |
| ZnO@NC/S-1(1.0)                |           |                                                                         |              |
| **Metal Organic Frameworks (MOFs)** |           |                                                                          |              |
| Cu@MOF-5                       | Cu (13.8 wt%) | Methanol synthesis                                                        | Angew. Chem. Int. Ed., 2005, 44, 6237 |
| Pd@MOF-5                       | Pd (35.6 wt%) |                                                                         |              |
| Au@MOF-5                       | Au (48.0 wt%) |                                                                         |              |
| Cu@MOF-5                       | Cu (11.2 wt%) | Methanol synthesis                                                        | Chem. Mater., 2008, 20, 4576 |
| Cu/ZnO@MOF-5                   | Zn (47.6 wt%) |                                                                         |              |
| Cu–Pd@MIL-101                  | Cu-Pd (10.4 wt%) | Homocoupling reaction of phenylacetylene                               | ACS Cent. Sci., 2019, 5, 176 |
| 3c-ZnO/SiO$_2$                 | ZnO (45.1 wt%) | Atomic layer deposition of ZnO on mesoporous silica                     | Nanomaterials, 2020, 10, 981 |

* Determined by TGA, ICP-OES, ICP-MS, XRF, or elemental analysis.
Table S6: A comparative account of CO₂ conversion to cyclic organic carbonates by POFs and Zn/POFs in comparison with the other reported catalysts including homogeneous catalysts, inorganic catalysts, MOFs, ionic liquids, cage compounds, porous silica-based materials, metal loaded frameworks (M-POFs), and porous organic polymers.

| S. No. | Substance | Pressure (bar) | Temp. (°C) | TBAB | Conversion (%) | Reference |
|-------|-----------|----------------|-------------|------|---------------|-----------|
| 1.    | Zn/POF1   | 2.5            | 90          |      | 94 (9)        | Present work |
| 1.    | Zn/POF2   | 2.5            | 90          | 2.5 mol% | 99 (9)        | Present work |

**Homogeneous catalysts**
(Solvent-mediated catalysis, post-synthetic purification needed, entry 2, 3: inorganic catalysts)

| S. No. | Substance | Pressure (bar) | Temp. (°C) | TBAB | Conversion (%) | Reference |
|-------|-----------|----------------|-------------|------|---------------|-----------|
| 2.    | Al-catalyst C* | 10          | 25          | 5 mol% | 99 (14)       | Angew. Chem. Int. Ed., 2016, 55, 3972.³⁹ |
| 3.    | Co(salen) (3g)* | 1           | 25          | Phosphorane | 97 (36)       | Green Chem., 2017, 19, 3908.⁴⁰ |
| 4.    | Squaramide-5*  | 10          | 45          | 5 mol% (TBAI) | 74 (18)       | ACS Catal. 2017, 7, 3532.⁴¹ |

**Metal organic frameworks (MOFs)**

| S. No. | Substance | Pressure (bar) | Temp. (°C) | TBAB | Conversion (%) | Reference |
|-------|-----------|----------------|-------------|------|---------------|-----------|
| 5.    | ZIF-8/CN  | 10            | 80          |      | 99 (24)³⁵     | Adv. Funct. Mater., 2017, 27, 1700706.⁴² |
| 6.    | Acrylamide-containing MOF | 10 | 100          | 0.3 mmol | 99 (2)           | Nat. Commun., 2019, 10, 4362.⁴³ |
| 7.    | Zn-DPA    | 1 atm         | 30-40       | 1 mol% | 99 (24)       | Chem. Eur. J. 2020, 26, 788.⁴⁵ |

**Ionic liquids**

| S. No. | Substance | Pressure (bar) | Temp. (°C) | TBAB | Conversion (%) | Reference |
|-------|-----------|----------------|-------------|------|---------------|-----------|
| 9.    | PDMBr (ionic liquid) | 10          | 110         |      | 99 (4)       | Chem. Sci., 2015, 6, 6916.⁴⁶ |
| 10.   | KCC-1/IL/HPW NPs | 10          | 90          |      | 98 (1.5)     | Green Chem., 2015, 17, 3059.⁴⁷ |

**Cage Compounds**

| S. No. | Substance | Pressure (bar) | Temp. (°C) | TBAB | Conversion (%) | Reference |
|-------|-----------|----------------|-------------|------|---------------|-----------|
| 11.   | Co(III)@cage | 10          | 25          | 10 mol% | 58 (48)       | Chem. Sci., 2019, 10, 1549.⁴⁸ |
| 12.   | Cg-Am*   | 2.5          | 90          | 2.5 mol% | 95 (9)        | Sustainable Energy Fuels, 2019, 3, 2567.⁴⁹ |

**Porous Silica / Si-based materials**

| S. No. | Substance | Pressure (bar) | Temp. (°C) | TBAB | Conversion (%) | Reference |
|-------|-----------|----------------|-------------|------|---------------|-----------|
| 13.   | I-POSS1a (Silsesquioxane) | 7.5          | 110         |      | 88 (6)        | ACS Appl. Mater. Interfaces, 2017, 9, 3616.⁵⁰ |
Most of the catalysts required drastic reaction conditions (≥ 10 bar of CO₂ pressure with 100-120 °C temperature) or otherwise milder conditions with longer reaction time (24 to 48 h). We could achieve 90-99% conversion for a range of substituted epoxides with milder reaction conditions (2.5 bar of CO₂ pressure at 90 °C) and reasonably lesser reaction time (9 h). However, we must emphasize that the catalytic conversion of CO₂ and epoxides into cyclic carbonates can certainly be improved further. Currently, the focus is to achieve the catalytic conversion at ambient conditions (1 atm, room temperature) in a shorter time. To the best of our knowledge, Zn/POFs hold a prominent place among the porous materials-based recyclable, heterogeneous catalysts for the conversion of a range of epoxides and CO₂ into cyclic carbonates. In this context, we also refer to a recent review article on imidazolium-functionalized organic cationic polymers for the conversion of CO₂ into cyclic carbonates justifying the ingenuity in our report.

| 14. | 0.2 EmimBr@mSiO₂ | 20 | 120 | - | 87 (3) | Green Chem., 2018, 20, 3232.51 |
| 15. | Supported POSS based material (5b) | 40 | 150 | - | 55 (3) | ChemCatChem, 2019, 11, 560.52 |

### Metal loaded porous organic frameworks (M-POFs)

| 16. | Co-CMP | 30 | 100 | 1.8 mol% | 98 (1) | Nat. Commun., 2013, 4, 1960.53 |
| 17. | Zn(OAc)₂ loaded o-hydroxyazo POPs | 30 | 100 | 7.2 mol% | 90 (0.8) | Angew. Chem. Int. Ed., 2016, 55, 9685.23 |
| 18. | Co/Zn R@HMTA | 10 | 100 | 7.2 mol% | 99 (1.5) | Adv. Mater., 2017, 29, 1700445.54 |
| 19. | Zn/RN4-Az-OH | 1 | 35 | 0.25 mmol | 92 (24)⁵ | Chem. Mater., 2019, 31, 8440.55 |

### Porous organic frameworks (POFs)

| 20. | N-Heterocyclic carbenes polymers | 1 | 120 | 10 mol% | 98 (24) | Chem. Mater., 2015, 27, 6818.56 |
| 21. | Porphyrin-based POPs | 15 | 100 | 1 mol% | 99 (5) | Green Chem., 2018, 20, 903.57 |
| 22. | COP-222 | 1 | 100 | - | 99 (24) | Chem, 2019, 5, 3232.58 |
| 23. | N-rich click-based POP (CPP) | 1 | 100 | - | 99 (24) | ChemSusChem, 2020, 13, 180.59 |

⁵ Propylene oxide or styrene oxide used as the substrate, unless stated otherwise; *Nonrecyclable
⁵ Epichlorohydrin used as substrate, catalysis further assisted by the anchimeric assistance of –Cl group

# Propylene oxide or styrene oxide used as the substrate, unless stated otherwise; *Nonrecyclable

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Table S7 Comparison of multifunctional applications, including CO$_2$ conversion, antibacterial, and antiviral activities of POF2 and Zn/POF2 with some of the representative porous materials.

| S. No. | Adsorbent          | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | CO$_2$ conv. | Antibacterial | Antiviral (HIV-1, VSV) | Reference                                      |
|-------|--------------------|----------------------------------|--------------|---------------|------------------------|------------------------------------------------|
| 1.    | POF2               | 490                              | ✓            | ✓             | ✓                      | Present work                                   |
|       | Zn/POF2            | 104                              | ✓            | ✓             | ✓                      |                                                 |
| 2.    | PZP-nanocomposites | -                                | -            | ✓             | -                      | Adv. Mater. Interfaces, 2018, 5, 1800167.61     |
| 3.    | TpTG$_{\text{Br}}$ | 305                              | -            | ✓             | ✓                      | J. Am. Chem. Soc., 2016, 138, 2823.2            |
|       | TpTG$_{\text{Cl}}$ | 267                              | -            | ✓             | ✓                      |                                                 |
| 4.    | MOF-525/PCL MMMs   | -                                | -            | ✓             | -                      | ACS Appl. Mater. Interfaces, 2017, 9, 41512.62  |
| 5.    | ZIF-8/GO           | -                                | -            | ✓             | -                      | ACS Appl. Mater. Interfaces, 2016, 8, 25508.63  |
| 6.    | SURGEL             | -                                | -            | ✓             | -                      | ACS Appl. Mater. Interfaces, 2018, 10, 1528.64  |
| 7.    | PAF-50             | 384                              | -            | ✓             | -                      | Adv. Mater., 2013, 25, 6619.24                 |
| 8.    | AgCl-PAF-50        | -                                | -            | ✓             | -                      |                                                 |
| 9.    | PDMBr (ionic liquid) | -                              | ✓            | -             | -                      | J. Mater. Chem. A, 2015, 3, 18696.65           |
| 10.   | cCTF-500           | 1247                             | ✓            | -             | -                      | ACS Appl. Mater. Interfaces, 2017, 9, 7209.66   |
| 11.   | POF-Zn$_{2+}$-I$^-$ | 298                              | ✓            | -             | -                      | Green Chem., 2018, 20, 5285.67                 |
| 12.   | PPS⊂COF-TpBpy-Cu   | 496                              | ✓            | -             | -                      | J. Am. Chem. Soc., 2016, 138, 15790.68         |
| 13.   | Cu-BTTri MOF       | -                                | -            | -             | $P$. aeruginosa         | Adv. Funct. Mater., 2017, 27, 1702255.69       |
| 14.   | PCN-224-Ag-HA      | 1898                             | -            | ✓             | ✓                      | Adv. Funct. Mater., 2019, 29, 1808594.70       |
| 15.   | GO-Ag-MOF          | 1-32                             | -            | $B$. subtilis | ✓                      | Adv. Mater. Interfaces, 2018, 5, 1701365.71     |
| 16.   | NU-1008            | 1400                             | ✓            | -             | -                      | Chem. Sci., 2019, 10, 1186.72                  |
Table S8 Comparative account of biofilm disruption by POF2 and Zn/POF2 with some of the representative polymeric materials, MOFs, metal nanoparticles, and composite materials.

| Entry | Materials | Structure | Surface area (m² g⁻¹) | Biofilm disruption | Reference |
|-------|-----------|-----------|----------------------|--------------------|-----------|
|       | POF2      | ![POF2](image) | 490                  | ×                  | *E. coli* |
| 1     | Zn/POF2   | ![Zn/POF2](image) | 104                  | ×                  | *E. coli* |
|       | **Organic polymer-based materials**          |                       |                     |                    |           |
| 2     | Quaternary-ammonium compounds tethered on hyperbranched polyurea (Si-HB-PEI⁺) | ![Polymeric material](image) | -                   | ×                  | *P. aeruginosa* | *Adv. Funct. Mater.*, 2014, 24, 346.73 |
| 3     | Poly-{[(9,9-bis(6′-N,N,N-trimethylammonium)hexyl)fluorenylene]dibromide} (PFP) | ![Polymeric material](image) | -                   | S. aureus         | ×          | *ACS Appl. Mater. Interfaces* 2017, 9, 16933.74 |
| 4     | Copolymerization of N-acryloyl-3-aminophenylboronic acid glucose ester with N-vinyl-2-pyrrolidone and N-isopropylacrylamide | ![Polymeric material](image) | -                   | E. coli          | ×          | *Chem. Eur. J.*, 2017, 23, 14883.75 |
| 5     | Cationic homopolymer PE₀ and copolymer PE₃₁ containing 31 mol % of ethyl methacrylate | ![Polymeric material](image) | -                   | S. mutans        | ×          | *Biomacromolecules* 2017, 18, 257.76 |
| No. | Method                                                                 | Compound                                                                 | Organism     | Result  |
|-----|------------------------------------------------------------------------|--------------------------------------------------------------------------|--------------|---------|
| 7   | Silicon(IV) phthalocyanine anchored poly(vinyl alcohol)                |                                                                          | E. coli      | ×       |
| 8   | Nitric oxide-loaded antimicrobial polymer                               |                                                                          | P. aeruginosa| ×       |
| 9   | Porphyrin-based POP                                                    |                                                                          | S. aureus    | ×       |
| 10  | Quaternary polyethylenimine (QPEI) polymers with an amide or ester group in their pendant alkyl chain |                                                                          | S. aureus    | E. coli |
| 11  | Fluorescent-conjugated polymer nanoparticles (PFPPBA)                  |                                                                          | P. aeruginosa| ×       |

**Metal organic frameworks, composite materials and metal nanoparticles**

| No. | Method                                                                 | Compound                                                                 | Organism     | Result  |
|-----|------------------------------------------------------------------------|--------------------------------------------------------------------------|--------------|---------|
| 12  | Graphitic carbon nitride by embedded Ag nanoparticles                  |                                                                          | S. aureus    | E. coli |
| 13  | Fe-terephthalate MIL-88B(Fe)                                           |                                                                          | S. typhimurium| ×       |
| 14  | Surface-adaptive gold nanoparticles (AuNPs)                           |                                                                          | S. aureus    | ×       |
|   | Material System                                                                 | Minimal (pM) | Maximum (nM) | Bacterium     | Reference                                      |
|---|---------------------------------------------------------------------------------|--------------|--------------|---------------|-----------------------------------------------|
| 16| ZIF-8 nanoparticles, polyvinylidene fluoride (PVDF) perfluoroctyltriethoxysilane (POTS) composite PVDF/ZIF-8/POTS (PZP) | -            | -            | E. coli      | *Adv. Mater. Interfaces* 2018, 5, 1800167.85 |
| 17| PVA/CeO$_{2-x}$ NR composites                                                   | -            | -            | E. coli      | *ACS Appl. Mater. Interfaces* 2018, 10, 44722.86 |
| 18| MOF/Ce-based nanozymes                                                          | -            | -            | S. aureus    | *Biomaterials* 2019, 208, 21.87                |
| 19| CeO$_2$-decorated porphyrin-based MOF                                          | -            | ~2600        | S. aureus    | *Small* 2019, 15, 1902522.88                  |
VII. Nuclear magnetic resonance (NMR) spectroscopy

i. Solid-state $^{13}$C CP-MAS NMR spectroscopic analysis of POF and Zn/POF

Fig. S41 The solid-state $^{13}$C NMR spectrum of POF2; *denotes the unassigned peaks.

Fig. S42 The solid-state $^{13}$C NMR spectrum of Zn/POF2; *denotes the unassigned peaks.
ii. NMR spectroscopic analysis of model compound (MTAG)

**Fig. S43** $^1$H (top) and $^{13}$C (bottom) NMR spectra (CDCl$_3$) of the model compound (MTAG).
Fig. S44 $^1$H NMR spectrum of the reaction mixture (in CDCl$_3$) for the conversion of propylene oxide with Zn/POF2 as catalyst using $1,1,2,2$-tetrachloroethane as external NMR standard.

Fig. S45 $^1$H NMR spectrum of the reaction mixture (in CDCl$_3$) for the conversion of epichlorohydrin with Zn/POF2 as catalyst using $1,1,2,2$-tetrachloroethane as external NMR standard.
Fig. S46 $^1$H NMR spectrum of the reaction mixture (in CDCl$_3$) for the conversion of styrene oxide with Zn/POF2 as catalyst using 1,1,2,2-tetrachloroethane as external NMR standard.

Fig. S47 $^1$H NMR spectrum of the reaction mixture (in CDCl$_3$) for the conversion of cyclohexene oxide with Zn/POF2 as catalyst using 1,1,2,2-tetrachloroethane as external NMR standard.
Fig. S48 $^1$H NMR spectrum of the reaction mixture (in CDCl$_3$) for the conversion of 1,2-epoxy-3-phenoxypropane with Zn/POF2 as catalyst using $1,1,2,2$-tetrachloroethane as external NMR standard.

Fig. S49 $^1$H NMR spectrum of the reaction mixture (in CDCl$_3$) for the conversion of propylene oxide with bulk ZnO using $1,1,2,2$-tetrachloroethane as external NMR standard (indicating 65% conversion).
Fig. S50 $^1$H NMR spectrum of the reaction mixture (in CDCl$_3$) for the conversion of propylene oxide with ZnO nanoparticles using $1,1,2,2$-tetrachloroethane as external NMR standard (indicating 85% conversion).

Fig. S51 $^1$H NMR spectrum of the reaction mixture (in CDCl$_3$) for the conversion of styrene oxide with ZnO nanoparticles using $1,1,2,2$-tetrachloroethane as external NMR standard (indicating 66% conversion).
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