Functional ionic porous frameworks based on triaminoguanidinium for CO₂ conversion and combating microbes


Abstract: Porous organic frameworks (POFs) with heteroatom rich ionic backbone have emerged as advanced materials for catalysis, charge-specific molecular separation and antibacterial activity. The loading of metal ions further enhances Lewis acidity augmenting the activity associated with the frameworks. Metal-loaded ionic POFs however often suffer from physicochemical instability, limiting their scope for diverse applications. Herein, we report the fabrication of triaminoguanidinium-based ionic POFs through Schiff base condensation in a cost-effective and scalable manner. The resultant N-rich ionic frameworks facilitate selective CO₂ uptake and provide high metal (ZnO, 57.3 ± 1.2%) loading capacity. The hierarchically mesoporous ZnO-rich metalated frameworks (Zn/POFs) show remarkable catalytic activity in the cycloaddition of CO₂ and epoxides into cyclic organic carbonates under solvent-free condition with high catalyst recyclability. In addition, both ionic POFs and Zn/POFs exhibit robust antibacterial (Gram-positive, S. aureus and Gram-negative, E. coli) and antiviral activity targeting HIV and VSV-G enveloped lentiviral particles. The enhanced catalytic, as well as broad-spectrum antimicrobial activity, are likely due to the synergistic effect of triaminoguanidinium ions and ZnO infused with the frameworks. We thus establish triaminoguanidinium-based POFs and Zn/POFs as a new class of multifunctional materials for environmental remediation and biomedical applications.

The scientific community is engaged in developing advanced materials for addressing some of the major challenges of 21st century. Challenges like steady increase of the CO₂ concentration in the atmosphere with rapid urbanization and its consequence in global warming and climate change are at the forefront and require urgent attention.[1] In addition to this, growing number of mortality due to the antimicrobial resistance pose a formidable threat to the mankind.[2] One of the emerging and worthy areas of materials science research for addressing some of these major concerns is the identification of materials possessing multifunctional properties. Such multifunctional materials if generated can serve to tackle today’s environmental and biomedical challenges, provided the economic viability is duly considered.[3,4]

Selective CO₂ adsorption and conversion to counteract increased concentration is now being tackled by employing porous materials, starting from porous carbons, zeolites and metal-organic frameworks (MOFs).[5] The aforementioned strategy is expected to provide the vast stock of CO₂ as a low-cost, nontoxic, renewable C1 source for the synthesis of useful chemicals. In this context, the catalytic fixation of CO₂ with epoxides into cyclic organic carbonates have gained considerable interest due to the high atom economy of the reaction and the extensive commercial use of materials derived from cyclic carbonates.[6] Heteroatoms decorated, hierarchically porous polymers like, porous organic polymers (POPs) have emerged as a promising heterogeneous platform for catalytic conversion of CO₂.[7,8] Flexibility in the design and fabrication, the ease of post-synthetic modification along with high thermal and hydrothermal stability are added advantages of these materials rendering for multifunctional applications.[9,10]

N-rich ionic porous organic frameworks (POFs)-a subclass of POPs having a certain degree of ordered network,[9] promote the catalytic conversion of CO₂ due to the exchangeable counter ions acting as a nucleophile for epoxide ring opening.[10] At the same time, similar to antimicrobial peptides (AMPs), ionic POFs can disrupt the growth of the microbes through electrostatic interactions with their charged membranes.[11,12] Recently, Banerjee and coworkers, employed triaminoguanidinium-based ionic frameworks for antibacterial applications.[13] Zhu and coworkers reported pyridinium-based porous aromatic frameworks and their AgCl-loaded counterparts as effective antimicrobial coatings.[14] The incorporation of metal coordination in the porous frameworks provide additional Lewis-acidic sites that may enhance both catalytic conversion of CO₂ and antimicrobial activity.[15,16]

In the quest of multifunctional materials for CO₂ conversion and efficient antimicrobial action, we developed triaminoguanidinium-based ionic porous frameworks (POFs) through Schiff base condensation. N-rich ionic frameworks enable chelation with Zn(II) in the form of ZnO. The high loading of ZnO resulting in Zn/POFs, remarkably enhance the catalytic as well as antimicrobial activities. Zn/POFs can be reusable for multiple cycles retaining high catalytic activity. Systematic studies on bacterial growth dynamics, cell viability, lysis evidenced using transmission electron microscopy (TEM) and fluorescence imaging with Gram-positive bacteria (S. aureus), Gram-negative bacteria (E. coli) and viral strains with distinct entry mechanisms including human immunodeficiency virus-1 (HIV-1) and vesicular stomatitis virus glycoprotein (VSV-G)-pseudotyped lentiviral vectors, unequivocally establish Zn/POFs as robust antimicrobial agents. The catalytic CO₂ conversion and antimicrobial action including first time demonstration of antiviral activity by porous framework materials demonstrated in the present study paves the way for the development of multifunctional materials combating global issues of environmental protection and antimicrobial resistance.

The emerging arena of ionic POFs for catalysis and antibacterial activity,[10,12,14] motivated us to use the triaminoguanidinium (TAG) cation as a triangular building block for the development of ionic nanoporous frameworks. The N-rich guanidinium core is known for antibacterial activity and suitable for anchoring metal ions.[11,15] The incorporation of Lewis acidic metal centre in POF is likely to enhance the catalytic activity and imparts specific interactions with microbial membranes. In this context, the loading of ZnO, ‘generally recognized as safe’ (GRAS) material as per the U.S. Food and Drug Administration,[16] into the framework can be a viable option. We envisioned that the

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ZnO-coordinated ionic network involving TAG might lead to multifunctional materials for heterogeneous catalysis and combating microbes. So, we set out to fabricate the ionic POFs via Schiff base polycondensation reaction between triaminoguanidinium chloride (TAG-Cl) and terephthalaldehyde (A3 + B2 polycondensation: POF1), and benzene-1,3,5-tricarboxaldehyde (A3 + B3 polycondensation: POF2) (Figure 1a).

The metalation of pristine frameworks (POF1 and POF2) were carried out upon refluxing with 10 wt% of Zn(OAc)$_2$ in EtOH. The fabrication method is highly scalable and does not require any costly catalysts. The POFs and the corresponding Zn/POFs were purified through Soxhlet extractions using MeOH and CHCl$_3$ each for 24 h.

The Fourier transform infrared spectroscopy (FTIR) analysis of POFs revealed a C=N stretching at 1632 cm$^{-1}$, indicating the cross-condensation between the monomers (Figure 1b).

Figure 1. (a) Synthetic schemes of triaminoguanidinium-based ionic porous organic framework (POF2) and ZnO-loaded framework (Zn/POF2). (b) The Fourier transform infrared (FTIR) spectra of POF2 and Zn/POF2. (c) The thermogravimetric analysis (TGA) of POF2 (green) and Zn/POF2 (blue) demonstrating the high loading of ZnO in Zn/POF2. (d) The comparative analysis of powder X-ray diffraction pattern of POF2, Zn/POF2, and ZnO illustrating the coordination of ZnO in Zn/POF2. (e) The crystal structure and packing of the model compound based on triaminoguanidinium chloride and benzaldehyde (MTAG) depicting Cl$^-$ ions sandwiched between the layers; (f) The PXRD analysis of POF2: simulated PXRD pattern (blue), experimental PXRD pattern (red), observed peaks (green) and the eclipsed structure model of POF2 (top view); grey: carbon, blue: nitrogen, green: chlorine. The FESEM and TEM (inset) images of (g) POF2 and (h) Zn/POF2, respectively. (i) The C1s XPS analysis of Zn/POF2. (j) The nitrogen sorption isotherms of POF2 (green) and Zn/POF2 (blue) measured at 77 K; solid circles represent adsorption and open circles represent desorption. (k) The pore size distribution estimated by non-local density functional theory (NLDFT) method depicting hierarchical porosity in POF2 and Zn/POF2.
peak at 1102 cm\(^{-1}\) is assignable to the C-N stretching of the TAG unit. A new peak at 462 cm\(^{-1}\) (Zn–O stretching) in Zn/POFs refers to the formation of ZnO (Figure 1b). 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, further signifying the metal coordination in the polymer framework (Figure 1b). The solid-state \(^{13}\)C cross-polarization magic angle spinning (CP/MAS) NMR spectra of POFs showed a peak resonating at 198 ppm due to the chloride ions which are sandwiched between the successive layers with interplanar distance of 3.6 Å (Figure 1d). The low crystallinity of TAG-based POFs is likely to be due to the electrostatic repulsion between the two layers of cationic triaminoguanidinium units leading to the poor π-π stacking, and is also consistent with the previous literature report.\(^{[12,17]}\) Interestingly, the packing of the model compound, MTAG, based on TAG-Cl and benzaldehyde depicts the chloride ions which are sandwiched between the successive layers with interplanar distance of 3.6 Å (Figure 1d). Accordingly, we modelled the framework structure and simulated the PXRD patterns (Figure 1e). Considering the broad PXRD pattern of the framework, it is challenging to unambiguously ascertain the conformation as eclipsed or staggered (Figure 1f). However, the eclipsed stacked structures (unit cell parameters: \(a = 18.18\) Å, \(b = 18.18\) Å, and \(c = 5.17\) Å) correspond to the best agreement between the experimental and the simulated PXRD patterns. The well-defined sharp peaks were observed for Zn/POFs (Figure 1d) in addition to the broad peak of POFs. The Miller planes \((100), (020), (101), (102)\) and \((110)\) suggest the presence of ZnO in the wurtzite form (JCPDS 36-1451).\(^{[18]}\) No peaks of Zn(OAc)\(_2\) were obtained in Zn/POFs. Thus, PXRD analysis coupled with FTIR and TGA unambiguously ascertain the loading of ZnO in Zn/POFs.

The field emission scanning electron microscopy (FESEM) images of POF1 and POF2 show a network-like and a granular morphology, respectively (Figure 2g). Whereas, the agglomerate structures are noticeable in the case of Zn/POF1 and Zn/POF2 (Figure 2h). The transmission electron microscopy (TEM) images of POF2 and Zn/POF2 also revealed the porous nature of the frameworks (Figure 2g, h). The high-angle annular dark-field imaging (HAADF) of Zn/POF2 indicates the homogeneous distribution of ZnO in the framework. The C1s X-ray photoelectron spectroscopy (XPS) analysis of POFs and Zn/POFs demonstrates the presence of phenyllic-C (282.8 eV), guanidinium-C (287.1 eV), and the imine-C (284.0 eV). The decrease in the guanidinium-C and increase in the imine-C distributions in Zn/POFs compared to that in the pristine POFs is due to the coordination with ZnO (Figure 1i). The percentage Zn(II) loading was found to be 47.2 wt% (Zn/POF2) as obtained from the XPS analysis, consistent with the TGA data. The Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis of Zn/POF2 also corroborates with the values obtained from the XPS analysis.

The porosity and the surface area of the POFs were estimated using nitrogen gas sorption analysis at 77 K (Figure 1j). POFs exhibit type II sorption isotherms (Figure 1j), indicative of mesoporous characteristics.\(^{[19]}\) The Brunauer–Emmett–Teller (BET) specific surface area of POF1 and POF2 was found to be

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\begin{array}{|c|c|c|}
\hline
\text{Entry} & \text{Catalyst} & \% \text{Conversion} \\
\hline
1 & TBAB & 17 \\
2 & POF1 & 51 \\
3 & POF2 & 46 \\
4 & Zn/POF1 & 94 \\
5 & Zn/POF2 & 92 \\
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Figure 2. (a) Catalytic performance of ionic POFs in the cycloaddition of CO\(_2\) and propylene oxide: the substrate scope, percentage of conversion and isolated yields are indicated. Epoxide (17.2 mmol), TBAB (cocatalyst, 2.5 mol%, 0.43 mmol), catalyst (POF or Zn/POF: 2 wt%, 20 mg), CO\(_2\) (2.5 bar), 90 °C and 9 h. The substrate scope was explored employing Zn/POF2 (20 mg) as catalyst. % of conversion was determined by the \(^1\)H NMR analysis of the reaction mixture with 1,1,2,2-tetrachloroethane as an external standard. (b) Recyclability of Zn/POF2 after catalytic cycloaddition reaction between propylene oxide and CO\(_2\) by maintaining the fixed amount of the catalyst to 20 mg circumventing the weight loss (1-1.5 mg per cycle) during the recovery process; more than 90% conversion for multiple cycles ascertain no loss in catalytic efficiency. (c) The PXRD profiles and (d) FTIR spectra of the pristine and regenerated catalyst demonstrating the robustness of Zn/POF2 in catalytic CO\(_2\) conversion. (e) The FESEM image depicting no change in the morphology of Zn/POF2 after four catalytic cycles in comparison with the pristine one (Figure 1h).
200 ± 20 and 470 ± 30 m² g⁻¹ with a total pore volume of 0.30 and 0.22 cm³ g⁻¹, respectively at P/0.9. Upon ZnO loading, the specific BET surface area was decreased; it was found to be 40 ± 5 and 104 ± 20 m² g⁻¹ for Zn/POF1 and Zn/POF2, respectively (Figure 1). The pore size distribution analysis revealed pore dimension ranging from 1.5 – 20 nm both for POF2 and Zn/POF2 (Figure 1k). Such hierarchical pore size distribution in microporous as well as mesoporous regime facilitate the mass transfer and suitable for catalytic applications. The CO₂ uptake by POF2 and Zn/POF2 was 7.4 and 6.2 wt%, respectively at 273 K and 1 bar. The isosteric heat of adsorption (Qₑ) value of pristine POF2 was 20.6 kJ mol⁻¹ (CO₂/N₂ selectivity: 48). The strong dipole-quadrupole interaction between N-rich triaminoguanidinium core and CO₂ leads to the high Qₑ value. The high affinity of POFs and Zn/POFs with CO₂ prompted us to investigate the catalytic performance of the frameworks in the conversion of CO₂ and epoxides into cyclic carbonates. The multifarious applications of cyclic organic carbonates such as polar aprotic solvents, fuel additives, electrolytes for Li-ion battery and polycarbonate precursors place the cycloaddition of CO₂ and epoxides as an industrially relevant reaction. The reaction was carried out using porous frameworks (POFs as well as Zn/POFs) as catalyst, tetra-n-butylammonium bromide (TBAB, 2.5 mol%) as cocatalyst under the optimized reaction conditions of 90 °C and 2.5 bar pressure of CO₂ (Figure 2a). Without the cocatalyst, the catalyst (POFs as well as Zn/POFs) afforded a very low conversion of < 2%. Whereas, the cyclic carbonate obtained using only the cocatalyst (TBAB) was ~ 17% (Figure 2a). POFs and Zn/POFs yielded ~ 46-51% and 92-94% conversion to propylene carbonate, respectively with TBAB (2.5 mol%, Figure 2a). The high catalytic efficiency of Zn/POFs over that of the pristine POFs suggests the importance of the Lewis acidic metal centres for the activation of epoxides in addition to N-rich CO₂-philic ionic frameworks.

The plausible mechanism for the conversion of epoxide to the corresponding cyclic carbonates involves the activation of epoxide by the pristine frameworks through H-bonding interactions. The process is further facilitated by Lewis acidic Zn(II) centers in Zn/POFs. The nucleophilic attack of Br⁻ (TBAB) opens up the epoxide to an oxoanion species stabilized

Figure 3. Antibacterial activity analysis of POF2 and Zn/POF2 by real-time growth curve analysis and systematic colony forming unit (CFU) imaging. Action against Gram-positive bacteria (Staphylococcus aureus): growth curves (a) POF2, (b) Zn/POF2, (c) percentage viability with increasing concentration of POF2, Zn/POF2 and (d) the comparative CFU images with increasing concentration of POF2, Zn/POF2 (100, 200, 500 µg/mL) with respect to the control. Action against Gram-negative bacteria (Escherichia coli): growth curves (e) POF2, (f) Zn/POF2, (g) percentage viability with increasing concentration of POF2, Zn/POF2 and (h) the comparative CFU images with increasing concentration of POF2, Zn/POF2 (100, 200, 500 µg/mL) with respect to the control. The error bars represent the standard deviation of mean from three measurements.

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through H-bonding interaction. The corresponding oxoanion attacks the CO$_2$ molecules, preferentially adsorbed by the N-rich ionic framework as indicated by the Qst values. Subsequently, the cyclization leads to the formation of desired cyclic carbonates with the removal of Br$^-$.

The broad applicability of the catalyst (Zn/POF2) in the conversion of substituted epoxides to their corresponding cyclic organic carbonates is shown in Figure 2a; the high percentage of conversion is noticeable for varieties of substrates (Figure 2a).

Zn/POF2 showed excellent recyclability and more than 90% conversion was observed even after eight cycles (circumventing the weight loss of 1-1.5 mg in each cycle, Figure 2b). The chemical stability of the recovered Zn/POF2 after multiple cycles of use was ascertained through PXRD (Figure 2e) and FTIR (Figure 2d) analysis. The morphology of the reused catalyst was also found to be similar to that of the pristine one (Figure 2e, 1h). The hot-filtration test followed by TGA suggested no significant weight loss due to the metal-leaching. The ICP-OES analysis of Zn/POF2 after four cycles of catalysis indicated less than 2% loss of ZnO signifying the robustness of the catalyst. Thus, ZnO-impregnated triaminoguanidium-based ionic porous organic frameworks are promising for heterogeneous catalytic fixation of CO$_2$ under solvent-free reaction conditions.

The ionic frameworks with guanidinium core and high loading of ZnO encouraged us further to explore the ability of the materials to affect the microbial growth. Towards this, we performed the growth curve analysis with and without the porous framework using representative strains of Gram-positive (Staphylococcus aureus) and Gram-negative (Escherichia coli) bacterium (Figure 3). The bacterial growth dynamics for both E. coli and S. aureus was carried out in a 24 well plate format with $10^5$ CFU/mL in LB (Luria-Bertani) broth with the increasing doses (100, 200 and 500 µg/mL) of the porous frameworks (Figure 3d, 3h). The growth was monitored in a real-time manner and the values obtained were plotted considering the absorbance at 600 nm versus the incubation time. The relatively slow growth rate of S. aureus against POF2 compared to that of E. coli suggests the more effective interaction of the cationic framework with the former (Figure 3a, 3e). This can be due to the presence of loosely packed glycan chains in the peptidoglycan lattice in the case of S. aureus unlike E. coli with additional bilayer phospholipid structure. The sluggish growth dynamics of S. aureus compared to that of E. coli in the presence of Zn/POF2 further suggests the stronger interactions with the former (Figure 3b, 3f). The relatively higher activity of Zn/POF2 over that of POF2 is plausibly due to the synergistic effect of ZnO and the cationic triaminoguanidinium framework. This observation also corroborates with the percentage viability plots (Figure 3c, 3g).

The Alamar blue cell viability fluorescence-based assay against Gram-negative (E. coli) bacteria showed reduced fluorescence.
Further, the bacterial cell-viability assay against both *S. aureus* and *E. coli* with different concentrations of the POF2 and Zn/POF2 was visualized by a classical agar plating method. The respective bacterial suspensions with POF2 or Zn/POF2 were incubated for 12 h at 37 °C and the live cells were taken from the suspension and allowed to grow on agar plates for overnight at 37 °C for the assessment of the colony forming units (CFU). The suspension without POF2 or Zn/POF2 served as control. The results of photographic representation over the agar plate are shown in Figure 3d, 3h, as CFU relative to increasing concentrations (100–500 µg/mL) of POF2 and Zn/POF2 with respect to the control. As a function of bacterial cell growth, the concentration-dependent reduction of the bacterial colonies, indicating the high antibacterial activity of both POF2 and Zn/POF2 (Figure 3d and 3h). Zn/POF2 exhibited a strong activity against both the bacteria (*S. aureus* and *E. coli*) demonstrating that the incorporation of ZnO in Zn/POF2 enhanced the antibacterial activity.\(^{[2b,16b]}\) We further probed the antibacterial action of the porous frameworks (POFs and Zn/POFs) using the transmission electron microscopy (TEM) imaging. The untreated (control) and post-treated bacterial samples with the porous frameworks (POFs as well as Zn/POFs) were first fixed using glutaraldehyde prior to imaging (Figure 4). The untreated *S. aureus* was observed to be in sphere-like morphology with intact cell membranes (Figure 4a, 4b). Whereas, the treated bacteria (*S. aureus*) with POF2 (Figure 4e, 4f) and Zn/POF2 (Figure 4i, 4j) showed the presence of ruptured cell morphology as evident from the TEM imaging. Similar kind of observations were also found in the case of *E. coli* where the untreated bacterial sample depicted a regular rod-like structure (Figure 4c, 4d).\(^{[12,24]}\) The treatment with POF2 (Figure 4g, 4h) and Zn/POF2 (Figure 4k, 4l) revealed shrunken and skewed morphology indicating the possible rupture of cells.

Interestingly, the antibacterial activity of POFs as well as Zn/POFs was found to be not limited for liquid bacterial culture but even was applicable to the disruption of the biofilm formed by *E. coli* (Figure 5a, 5b). Again, Zn/POF2 showed robust performance in biofilm disruption (Figure 5b). To further explore the effect of porous frameworks (POFs and Zn/POFs) on the bacterial cells (*E. coli*), we performed the “live-dead” cell staining using the mixture of SYBR Green I and propidium iodide (PI) dyes (Figure 5c).\(^{[25]}\) Briefly, the treated bacterial cells were incubated with the dye mixture (SYBR Green I and PI). SYBR Green-I can diffuse through the lipid membrane of both the live as well as the dead bacteria. Whereas, PI specifically enters when membrane integrity is compromised as the case with dead bacterial cells. The pristine POFs containing positively charged guanidinium backbone possibly interact with the negatively charged lipid membrane of the bacterial cell-wall and rupture the bacterial cells exhibiting moderate antibacterial activity.\(^{[26]}\) In comparison, the ZnO-coordinated Zn/POFs with additional Lewis-acidic metal sites show enhanced bactericidal activity.\(^{[20]}\) As a proof of concept, we employed Zn/POF matrix for clearing bacterial load from the water sample. Reduction in the CFU coupled with the analysis of the released DNA in the presence of Zn/POF2 in flow-through suggest promising application for obtaining potable water by clearing the live bacterial load.

Apart from the antibacterial activity of the porous framework, owing to the presence of the guanidinium functional group, we further anticipated the antiviral activity for POFs as well as Zn/POFs. To ascertain, we evaluated antiviral activities in TZM-GFP cell line against HIV-1 and vesicular stomatitis virus glycoprotein (VSV-G) pseudotyped GFP-encoded lentiviral vectors (LV VSV-G).\(^{[27]}\) Virus was produced from Human embryonic kidney (HEK293T) cells by cotransfecting helper plasmids.\(^{[28]}\) The virus containing supernatant was added in the TZM-GFP cell line (as target cells) pre-incubated for 4 h with different doses of POF2 and Zn/POF2. Virus infectivity was calculated after counting the fluorescent green cells as a function of successful virus entry. As shown in Figure 6a and 6b, Zn/POF2 showed enhanced antiviral activity against both HIV-1 and VSV-G pseudoparticles plausibly due to the synergistic effect of ZnO and the triaminoguanidinium framework. Whereas, a relatively lower inhibition of viral infectivity was observed with POF2 because of the presence of triaminoguanidinium framework only.\(^{[15a]}\) Interestingly, the effective doses of POFs and Zn/POFs were found to be non-toxic to the mammalian cells used in viral infectivity assay. However, an equivalent amount of free ZnO in comparison to that infused with the framework (Zn/POF2) is toxic to the target cells.

A high-content imaging analysis of infected cells revealed reduced infected cell counts upon the use of POF2 or Zn/POF2 at an effective concentration of 20 µg/mL suggestive of an antiviral action that plausibly target an early step in virus infection. The action of Zn/POF on virus life cycle was therefore tested next to get the mechanistic insights into the framework action. Towards this, we employed an assay that reports viral-mediated delivery of
Investigate the antimicrobial activity of nanoporous frameworks, we used optical measurements. The S. aureus and E. coli were cultured aerobically at 37 °C in LB medium. The antibacterial activity was measured using the disc diffusion assay. The frameworks were cultured with the bacterial strains for 24 h and the inhibition zone was measured.

In summary, we developed triaminoguanidinium-basedionic POFs employing a scalable protocol using Schiff base condensations. The N-rich frameworks facilitated complexation with ZnO with a high loading. Both the POFs as well as ZnO-rich, Zn/POFs showed the catalytic conversion of CO2 to cyclic organic carbonates under solvent-free reaction conditions. Remarkably, more than 90% conversion of a range of substituted epoxides to the corresponding cyclic carbonates was observed. Zn/POFs also exhibited robust antibacterial and antiviral activity due to the synergistic effect of ZnO and guanidinium-based ionic framework. An investigation comprising complementary assays coupled with electron and optical fluorescence microscopy imaging, asserted Zn/POFs as broad-spectrum antimicrobial agents. Such multifunctional applications ranging from catalysis to combating microbes as diverse as bacteria and viruses by POFs, to the best of our knowledge, are unique in the field of porous materials. Crucial observations including bactericidal effect promising for water purification and the antiviral activity of porous frameworks, we adopted the second virucidal assay to complement the RT release assay according to the standard protocol with slight modifications. Precisely, we incubated the virus along with the various doses (5, 10, 20 µg/mL) of Zn/POF2 (Figure 6g). After incubation, instead of diluting, the virus containing frameworks were removed by centrifugation and the supernatant having viruses were added to the TZM-GFP cell line (reporter cell line). The reduced virus infectivity showed the virucidal activity of the porous framework (Figure 6g). The lack of recovery of the virus infectivity upon removal of the frameworks further ascertains the virucidal effect over virustatic. The presence of the guanidinium core in the porous frameworks as well as ZnO in Zn/POFs thus determine the broad antimicrobial activity, including bactericidal and virucidal efficacy.

Experimental Section: The triaminoguanidinium chloride was synthesized using guanidine hydrochloride following a reported procedure. The antibacterial studies were performed on Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli) obtained from Himedia. Both the bacterial strains were grown in Luria-Bertani (LB) medium (DIFCO cultured aerobiocally at 37 °C in glass culture tube with shaking at 200 rpm in a shaker incubator (Infor HT). In order to investigate the antiviral activity of nanoporous frameworks, we used optical
density and plating assay as the measure of bacterial growth and viability. For the antiviral studies, single cycle Env-defective and nef-defective NL4-3 and envelop coding pHXB2 plasmids were co-transfected in HEK293T using a calcium phosphate method.

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