‘Connecting the dots’: knitting C-phenylresorcin[4]arenes with aromatic linkers for task-specific porous organic polymers

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ABSTRACT: Macroyclic cavitands having aesthetically appealing architecture and excellent host-guest complexation ability exhibit a broad range of applications from molecular separation, catalysis, sensing to drug delivery. However, the close packing of the zero dimensional (0D) porous cavitands reduces the guest-responsive properties in the solid state. Knitting the macrocyclic cavitands using suitable aromatic linkers may lead to a new generation of porous organic polymers (POPs) where the intrinsic properties of the cavitands can be augmented through interconnected pores in the solid state. Herein, we demonstrate the design strategy of linking the 0D-discrete pores by connecting C-phenylresorcin[4]arene (RN4), through three different aromatic linkers. The flexible azo linkers generate highly dispersible hierarchically mesoporous POP (RN4-Az-OH) exhibiting a remarkable catalytic activity towards metal-free cycloaddition of CO$_2$ with epoxides under mild reaction conditions. Alkyne-based rigid linkers lead to microporous polymer (RN4-OH) which show significant CO$_2$ and H$_2$ uptake at low pressure. The fluorine-rich linkers produce ultramicroporous hydrophobic POP (RN4-F) exhibiting high efficiency towards the charge-specific size-selective removal of organic micropollutants from water. Resorcin[4]arene-derived POPs show superior performance compared to the pristine 0D-porous building units. Thus, ‘connecting the dots’ (0D pores) gives rise to a new interface between supramolecular chemistry and porous organic materials which can be explored further to address the challenging problems related to green energy and environmental remediation.

KEYWORDS: Cavitand, resorcin[4]arene, porous organic polymer, CO$_2$ conversion, micropollutant removal

INTRODUCTION:

Applications of porous materials depend primarily on (i) accessibility of the pores and (ii) permeability of the probe molecule through the pores. Based on the two parameters, porous materials can be categorized as, having (a) open porosity, and (b) closed porosity. Open porosity refers to the pores where the probe molecules can easily permeate from one pore to another, and closed porosity refers to zero-dimensional (0D) pores where molecular occupants cannot flow. Macrocyclic cavitands like cyclodextrins, calix[n]arenes, pillar[n]arenes possess well-defined cavities and excellent guest recognition properties which trigger an avalanche of applications ranging from molecular separation, sensing, catalysis, mimicking enzyme activity, drug delivery to the development of artificial molecular machines. These interesting features of the cavitands are mostly demonstrated in the solution state. However, in the solid state, the closed packing of the macrocyclic cavitands mostly reduces the open channels or void space leading to the 0D-discrete pores. Thus, the cavities are buried inside the solid matrix and are largely inaccessible to the molecular species. The narrow channels restrict facile mass transfer.
At the same time, due to the noncovalent interactions in the supramolecular assembly of the macrocycles, it is challenging to maintain the permanent porosity upon guest removal.

On the other hand, zeolites, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), polymers of intrinsic microporosity (PIMs), porous organic polymers (POPs) possess open, continuous two-dimensional (2D) or three-dimensional (3D) rigid networks. These materials are highly porous because of effective polymeric connection (covalent or coordinate bonds) leading to shape-persistent interconnected pores. A possible avenue to retain the guest-responsive properties of 0D-macrocyclic cavitands in the solid state is to convert them into 2D/3D frameworks through suitable linkers. The fruits of integrating macrocyclic cavitands have been realized in the recent reports of macrocycle-based porous polymers.

Dichtel and coworkers first developed the well-known macrocyclic cavand, β-cyclodextrin-based POP (P-CDP, S_{BET} 263 m^2 g^{-1}) for rapid removal of organic micropollutants from water. Coskun and coworkers employed pillar[5]arene for the development of conjugated microporous polymers (CMPs, S_{BET} 400 m^2 g^{-1}) for propane/methane separation. Trabolsi and coworkers developed calix[4]arene-based POPs (S_{BET} 596 m^2 g^{-1}) for water purification. Yuan and coworkers recently reported calix[4]resorcinarene-based POPs (S_{BET} 303 m^2 g^{-1}) for iodine adsorption. A similar approach of ‘macrocycle/cage-to-framework’ was demonstrated by Zhang and coworkers. Such frameworks were shown to exhibit high gas uptake with excellent selectivity.

Resorcin[n]arenes are known for the cationic guest encapsulation and also as catalysts for various chemical reactions owing to their intrinsic porosity. We employed C-phenylresorcin[4]arene (RN4) as a new 0D porous macrocyclic building block in order to augment the guest-responsive properties in the form of 3D porous solid. We connected RN4 with a series of diverse functional linkers, and could tune the surface area of the POPs from 340 m^2 g^{-1} to 1229 m^2 g^{-1}, much higher than that of p-hydroxyphenylresorcin[4]arene (HRN4, 156 m^2 g^{-1}). We observed that the linker length and functionality governed the physicochemical properties of the RN4-based POPs. The flexible and long linkers containing CO\(_2\)-philic diazo groups provide hierarchically porous well-dispersible POP, RN4-Az-OH. It turned out to be a promising heterogeneous catalyst facilitating a remarkable metal-free conversion of CO\(_2\) and epoxide into cyclic organic carbonates under solvent-free reaction conditions. The rigid and short alkyne linkers impart microporosity in RN4-OH suitable for gas uptake at low pressure. The fluorine-rich linkers endow hydrophobicity in the resultant polymer, RN4-F, which exhibits charge-specific size-selective removal of organic micropollutants from water. Thus, the objective of enhanced solid-state applications of macrocyclic cavitand-based POPs compared to pristine cavitand was unequivocally demonstrated through selective gas uptake, CO\(_2\) conversion and micropollutant separation. In view of the existing literature, the environmentally benign applications exhibited by the RN4-based POPs as well as the detailed structure-activity relationship established in the present study are unique and would contribute to the development of the task-specific POPs.

**RESULTS AND DISCUSSION**

Resorcin[n]arenes (n = 4, 6, 8) are structurally quite distinct compared to highly investigated macrocyclic hosts like crown ethers, cyclodextrins, cucurbit[n]urils, calix[n]arenes, pillar[n]arenes. Resorcin[n]arenes can easily be prepared from inexpensive starting materials such as resorcinol and corresponding aromatic/aliphatic aldehyde. The
presence of p-substituted phenyl groups in the lower rims deepen the cavity and facilitates the polycondensation. Thus, C-phenylresorcin[4]arenes is a versatile, functional building block compared to pristine resorcin[4]arenes. p-Hydroxyphenyl (HRN4) and p-bromophenylresorcin[4]arene cores were synthesized through Brønsted acid-catalyzed condensation reaction of resorcinol with p-hydroxyphenylresorcin[4]arene and tetrafluoroterephthalonitrile (digital photographs of the respective POPs in the form of powder). (b) FTIR spectra, (c) solid state 13C-(CP/MAS) NMR spectra and (d) thermogravimetric analysis of the POPs: RN4-Az-OH, RN4-OH, and RN4-F.

Synthesis and characterization of the POPs

The POPs were synthesized through the functionalization of upper and lower rims and utilizing phenolic hydroxyl groups of RN4 employing three different fabrication procedures (Figure 1a). Liu and coworkers developed a facile route of making azo-linked POPs through simple diazo coupling reaction between aryl amines and phenols. Envisioning the wider scope of the methodology and scalability, we chose p-hydroxyphenylresorcin[4]arene (HRN4) as the polyphenolic core and benzidine as an aromatic diamine linker for the fabrication of azo-linked POP, RN4-Az-OH in an aqueous medium (yield: 90-95%). Another scalable synthetic protocol, aromatic nucleophilic substitution reaction between p-hydroxyphenylresorcin[4]arene (HRN4) and tetrafluoroterephthalonitrile, was employed for the fabrication of fluorine-rich POP, RN4-F (yield: 60-70%). Alkyne-linked POP, RN4-OH, was developed through Pd(II)-catalyzed A3-B2 type Sonogashira cross-coupling
polycondensation between \( p \)-bromophenylresorcin[4]arene and 1,4-diethynylbenzene (yield ~ 50\%). All the POPs are insoluble in water and common organic solvents, and are highly stable upon exposure to acids and bases providing a facile heterogeneous platform.

The structural characterizations of POPs were carried out through detailed spectroscopic and microscopic analysis. The broad peak around 3300-3400 cm\(^{-1}\) in the FTIR spectra of all the POPs was due to the aromatic-OH stretching of resorcin[4]arene core (Figure 1b). In the case of RN4-Az-OH, the characteristic peaks at 1160 cm\(^{-1}\) and 1400 cm\(^{-1}\) were attributed to the symmetric and asymmetric vibrations of the -N=N- linkages respectively, indicating the formation of the azo-POP. C=C-H stretching of 1,4-diethynylbenzene near 2100 cm\(^{-1}\) was completely vanished in RN4-OH and a new peak appeared at 2200 cm\(^{-1}\) due to the C=C-C stretching confirming the C-C bond formation (Figure 1b). RN4-F showed a peak around 2246 cm\(^{-1}\) due to the C=N stretching (Figure 1b). The peaks at 1304 and 1052 cm\(^{-1}\) were attributed to the C-F stretching and the C-O-C stretching, respectively which further confirmed the formation of RN4-F.

The solid-state \(^{13}\)C NMR spectra of POPs revealed the peaks in the range of 100-165 ppm corresponding to the aromatic carbons present in the macrocyclic core as well as in the linkers (Figure 1c). The peak at 40-45 ppm attributed to the aliphatic carbon (C-H) of the C-phenylresorcin[4]arene core. The aromatic carbons linked with the azo-groups in RN4-Az-OH appeared at 150 ppm (Figure 1c). The presence of C=C in RN4-OH was confirmed by the peaks near 80 ppm (Figure 1c). The carbons with ether linkages (C-O-C) in RN4-F resonated at 140 ppm (Figure 1c). Thermogravimetric analysis (TGA) profiles of the POPs revealed that the RN4-Az-OH was stable up to 250 °C whereas thermal stability of RN4-OH and RN4-F was found to be up to 350 °C (Figure 1d). The broad powder X-ray diffraction patterns (PXRD) suggested the amorphous nature of the POPs as expected due to the kinetically driven irreversible polymerization conditions (Figure S1).\(^{27}\)

The field emission scanning electron microscopy (FESEM) images revealed distinct morphologies of the POPs obtained through different fabrication methods (Figure 2a-2c). The high-resolution transmission electron microscopy (HRTEM) images of the POPs showed the irregular distribution of pores (Figure 2a-2c, inset) further suggesting the amorphous nature.\(^{27}\) The size and functionality of the linkers not only affect the morphology but also influence the dispersibility of the POPs. RN4-OH and RN4-F are hydrophobic due to the presence of alkyne and fluorne-rich linkers, respectively as seen from the photographs where particles are floating on the upper meniscus of water (Figure 1d).\(^{19,24}\)

**Nitrogen sorption isotherms**

The surface area and porosity of POPs were estimated by nitrogen adsorption-desorption isotherms at 77 K (Figure 2e). \( p \)-Hydroxyphenylresorcin[4]arene (HRN4) showed Type III isotherms indicating weak adsorbate-adsorbent interaction.\(^{28,29}\) Interestingly, no steep uptake at the lower pressure, \( P/P_0 < 0.1 \) indicates the absence of micropores. It also infers that the deep-seated cavities of the macrocycles are inaccessible. The Brunauer–Emmett–Teller (BET) specific surface area of the monomer HRN4 was found to be 156 m\(^2\) g\(^{-1}\) arising due to the interparticle void space.\(^{29}\) After knitting with aromatic linkers, the connectivity among the pores was established, and a clear trend of increase in the surface areas was observed. The BET specific surface areas of RN4-Az-OH, RN4-OH, and RN4-F were found to be 340, 720 and
1229 m$^2$ g$^{-1}$, respectively. RN4-F shows one of the high values of the surface area obtained from the cavitand-based POPs. The high surface area of RN4-F is due to the smaller length and rigidity of the F-rich linker as well as a highly cross-linkable polymerization condition.

The pore size distributions of POPs were estimated by non-local density functional theory (NLDFT) analysis (Figure 2f). The average pore width of RN4-Az-OH was in the mesoporous region (2.8 nm) due to the larger azo-linker. Additionally, RN4-Az-OH exhibited hierarchical pore size distribution (Figure 2f). In contrast, RN4-OH possess the pores in the microporous region (1.4 nm). In the case of RN4-F, the narrow bimodal pore size distribution was observed in the microporous regime at 0.7 nm (ultramicroporous) and 1.4 nm (Figure 2f). Interestingly, the peaks at 1.4-1.6 nm present in the POPs are not observed in HRN4. The peaks observed for the POPs in the microporous regime are likely to be contributed by the intrinsic pores of resorcinarene-based building blocks (Figure S2). The pore size distribution results indicate the deep seated 0D-cavities of HRN4 are inaccessible to the gas molecules in the solid state. The total pore volumes of RN4-Az-OH, RN4-OH, and RN4-F at P/P$_0$ = 0.95 were found to be 0.55, 0.71 and 0.95 cm$^3$ g$^{-1}$, respectively indicating the promising scope of the POPs as sorbents. We demonstrated three mutually connected applications, namely selective gas uptake, catalytic conversion of CO$_2$, and removal of organic micropollutants from water to substantiate the benefits of interconnected pores in macrocyclic cavitand-based POPs.

**Selective CO$_2$ uptake**

The heteroatom (O, N, F)-rich networks along with high surface area prompted us to measure the CO$_2$ and H$_2$ uptake capacity of the POPs (Table 1, Figure 2g, S3). CO$_2$ uptake by RN4-F, RN4-OH and RN4-Az-OH was found to be respectively, 11.4 wt% (2.6 mmol g$^{-1}$),
9.9 wt% (2.25 mmol g\(^{-1}\)) and 9 wt% (2.1 mmol g\(^{-1}\)) at 273 K, 1 bar which are comparable to some of the well-known porous materials with similar surface areas.\(^{31,32}\) The surface area of RN4-OH is almost double than that of RN4-Az-OH. But both the POPs exhibit almost similar CO\(_2\) uptake capacity. This interesting observation led us to estimate the isosteric heat of adsorption (\(Q_{st}\)) for probing the interactions between CO\(_2\) and POPs (Figure S3b). Among the POPs, RN4-Az-OH possesses the highest \(Q_{st}\) of 30.8 kJ mol\(^{-1}\) at the onset of adsorption. Such a high \(Q_{st}\) value is quite significant compared to many other reported POPs (25–33 kJ mol\(^{-1}\)).\(^{32,33}\) The highly decorated pore walls with CO\(_2\)-philic functionalities like -N=N-, -OH lead to favorable interactions between RN4-Az-OH and CO\(_2\). RN4-F and RN4-OH have an initial \(Q_{st}\) of 29.5 kJ mol\(^{-1}\) and 28.5 kJ mol\(^{-1}\), respectively. Employing the ideal adsorbed solution theory (IAST) model,\(^{34,35}\) the selectivity of CO\(_2\) over N\(_2\) uptake for RN4-Az-OH, RN4-OH and RN4-F was found to be respectively, 19, 20 and 35, respectively. Being ultramicroporous, RN4-F exhibits a high selectivity towards CO\(_2\) over N\(_2\).\(^{36,37}\)

### H\(_2\) uptake

The H\(_2\) uptake measurement was carried out at 77 K and 1 atm. A high uptake of 1.4 wt% (6.9 mmol g\(^{-1}\)), 2 wt %, (10 mmol g\(^{-1}\)) and 1.1 wt% (5.5 mmol g\(^{-1}\)) was observed for RN4-F, RN4-OH, and RN4-Az-OH, respectively (Figure S3c). The uptake capacity of the POPs is quite significant compared to many of the reported POPs, COFs, MOFs and porous carbons. In spite of having the highest surface area and ultrimicropores, RN4-F shows less H\(_2\) uptake than that of RN4-OH. The PXRD pattern of RN4-OH includes a small peak around \(2\theta = 40^\circ\) corresponding to (111) plane of Pd (Figure S1).\(^{38}\) The EDS and HRTEM data also indicate the presence of Pd nanoparticles. The phenolic -OH groups in the RN4-OH polymer can effectively stabilize palladium nanoparticles formed during the Sonogashira cross-polycondensation.\(^{39}\) Hence, the presence of a trace amount of residual palladium in RN4-OH enhances the H\(_2\) uptake capacity.

### Cycloaddition of CO\(_2\) with epoxides

Macrocyclic molecular containers possessing binding pockets like natural enzymes have emerged as promising materials in catalysis.\(^{6,40}\) The catalysis inside the molecular container has several advantages over that of the bulk solution. The restricted internal volume of the cavitand provides size-selective substrate encapsulation.\(^{41}\) On the other hand, a large number

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**Table 1** The summary of gas sorption properties of resorcinarene-based POPs and macrocyclic core.

<table>
<thead>
<tr>
<th>POP</th>
<th>(S_{BET}) (m(^2) g(^{-1}))</th>
<th>Pore size (nm)</th>
<th>(^{a})Pore volume (cm(^3) g(^{-1}))</th>
<th>(^{b})CO(_2) uptake (wt%)</th>
<th>(^{c})H(_2) uptake (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRN4</td>
<td>156</td>
<td>2.8</td>
<td>0.28</td>
<td>6.1</td>
<td>0.3</td>
</tr>
<tr>
<td>RN4-Az-OH</td>
<td>340</td>
<td>2.8</td>
<td>0.55</td>
<td>9.0</td>
<td>1.1</td>
</tr>
<tr>
<td>RN4-OH</td>
<td>720</td>
<td>1.4</td>
<td>0.71</td>
<td>9.9</td>
<td>2.0</td>
</tr>
<tr>
<td>RN4-F</td>
<td>1229</td>
<td>0.7</td>
<td>0.95</td>
<td>11.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

\(^{a}\)Pore volumes calculated at \(P/P_0 = 0.95\), \(^{b}\)CO\(_2\) uptake measured at 273 K, \(^{c}\)H\(_2\) uptake measured at 77 K.
of phenolic -OH groups in resorcin[n]arenes can activate various substrates through H-bonding. Thus, the incorporation of resorcin[n]arenes in the porous framework is likely to provide a new testbed for heterogeneous catalysis with high recyclability. As cavitand-based POPs exhibit preferential adsorption of CO₂, we have chosen catalytic fixation of CO₂ with epoxide for the synthesis of cyclic carbonates. The above reaction has drawn significant attention due to the high atom economy as well as the versatile utility of cyclic organic carbonates as polycarbonate precursors, fuel additives, electrolytes for Li-ion battery, drug precursors, and polar aprotic solvents.

A large number of catalysts are reported for the cycloaddition of CO₂ with epoxides. Although most of the reactions require harsh conditions of pressure (>10 bar) and temperature (>100 °C) as well as transition metal catalysts. Thus, development of a metal-free heterogeneous catalyst for the conversion of CO₂ in mild reaction conditions is of high demand. Resorcin[4]arenes having a large number of phenolic-OH groups can catalyze the reaction. However, the degradation of the cavitand in the reaction condition prevents its activity as well as reusability. We optimized the catalytic conversion of CO₂ to cyclic carbonates by taking styrene oxide as the model substrate, cavitand-based POPs as catalysts and tetra-n-butylammonium bromide (TBAB) as a cocatalyst at 2.5 bar of CO₂ pressure at 90 °C under solvent-free conditions. RN4-Az-OH showed excellent conversion up to 95% within 12 h, while RN4-OH and RN4-F exhibited the conversion up to 86% and 75%, respectively under the similar reaction conditions (Table 2).

The reverse trend of catalytic performance with respect to the specific surface area of the POPs (RN4-Az-OH: 340 m² g⁻¹, RN4-OH: 740 m² g⁻¹, RN4-F: 1229 m² g⁻¹) can be explained considering the following aspects: (a) porosity, (b) availability of phenolic -OH groups, (c) interaction of CO₂ with the pore-wall and finally, (d) dispersibility of the catalyst in the reaction medium. The hierarchical mesoporosity of RN4-Az-OH improves the mass transfer while ultramicropores of RN4-F poses a restriction for the easy permeation of the reagents and products through the pores. The lesser number of phenolic -OH groups in RN4-OH (in monomeric core, p-bromophenylresorcin[4]arene) and RN4-F (formation of ether linkages) compared to RN4-Az-OH further reduce the epoxide activation sites. Additionally, the high value of the heat of adsorption of RN4-Az-OH (30.8 kJ mol⁻¹) indicates the facile interaction of CO₂ with the diazo and phenolic -OH functionalized pore walls which further facilitates the CO₂ insertion. The high dispersibility of RN4-Az-OH in polar solvents as well as in the reaction medium makes the catalytically active centers more expose to the substrates. The high negative zeta potential of -32.5 mV in water at neutral pH reaffirms the stability of the dispersion.
It has been reported that the \( \pi \)-electron-rich aromatic cavity of resorcin[4]arene provides facile interaction with cationic guests (e.g., tetra-n-butylammonium bromide, tetraethylammonium tetrafluoroborate). The cationic tetra-n-butylammonium ion was effectively trapped through cation-\( \pi \) interaction inside the \( \pi \)-electron-rich cavity of the macrocyclic core of the POPs. As a result, the nucleophilic attack to the epoxide carbon by the counter bromide anion becomes more facile leading to the increase in the catalytic efficiency. We protected the -OH groups through post-synthetic modification of RN4-Az-OH with epichlorohydrin to obtain RN4-Az-OR. It showed only 34% conversion in the same catalytic conditions (Table 2, entry 5). The reduced efficiency of RN4-Az-OR compared to RN4-Az-OH and other POPs suggests the importance of -OH groups in the reaction. RN4-Az-OH also showed excellent catalytic conversion (84%) for epichlorohydrin under ambient conditions like 35 °C and 1 bar of \( \text{CO}_2 \) pressure in 24 h (Table 2, entry 7).

The catalytic conversion of various epoxides to corresponding cyclic carbonates depicts the broad applicability of RN4-Az-OH (Table 3). A faster conversion was observed for the smaller-sized epoxides like propylene oxide and epichlorohydrin. A clear trend based on the molecular size was observed when the reactions were carried out at a large-scale (20 mmol) with low cocatalyst amount (TBAB, 0.12 mmol) for the fixed time (12 h). For the smallest substrate, propylene oxide, the conversion was 98% (Table S1, entry 1). Whereas, for the larger substrates like 1,2-epoxyhexane, the conversion was 65% under identical conditions (Table S1, entry 4). The hindrance to diffusion of large-sized substrate molecules through the pores may decrease the efficiency of the reaction leading to the low conversion. The percentage of conversion of epoxide to the corresponding cyclic carbonate was found to be 92% even in the 10th cycle employing RN4-Az-OH demonstrating the reusability of the catalyst. The efficiency of RN4-Az-OH was further enhanced through the metalation with Zn(OAc)$_2$, (Zn/RN4-Az-OH, Table 2, entry 6, 8, Table S1). The composite material Zn/RN4-Az-OH consisting of sub-micron sized spherical ZnO particles anchored to the polymeric network boosts the activation of

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>TBAB</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>RN4-Az-OH</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>RN4-OH</td>
<td>86</td>
</tr>
<tr>
<td>4</td>
<td>RN4-F</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>RN4-Az-OR</td>
<td>34</td>
</tr>
<tr>
<td>6</td>
<td>Zn/RN4-Az-OH</td>
<td>98</td>
</tr>
<tr>
<td>7</td>
<td>RN4-Az-OH</td>
<td>84</td>
</tr>
<tr>
<td>8</td>
<td>Zn/RN4-Az-OH</td>
<td>92</td>
</tr>
</tbody>
</table>

Reaction conditions: Styrene oxide (10 mmol, 1.2 g), TBAB (0.25 mmol), \( \text{CO}_2 \) (2.5 bar), 90 °C and 12 h. a Catalyst (POP: 30 mg). b Zn/RN4-Az-OH (30 mg), 6 h. c Catalyst (POP: 30 mg), epichlorohydrin (2.5 mmol), TBAB (0.5 mmol), 24 h, \( \text{CO}_2 \) (1 bar), 35 °C. #% of conversion calculated through \( ^1 \text{H} \) NMR analysis.
epoxides through Lewis acidic sites along with the hydroxyl-functionalized framework (Table 3).

Analysing the trend of CO$_2$ fixation by different POPs, a plausible reaction mechanism considering the previous literature reports can be proposed.$^{53,54}$ The epoxides are effectively activated by the H-bond donating phenolic-OH groups of the macrocyclic cores.$^{47,53}$ At the first step, the H-bonding between the -OH groups and the epoxide oxygen takes place. Subsequently, the nucleophile, Br- of the cocatalyst TBAB, selectively attacks the less sterically hindered carbon of the epoxide which leads to the ring opening. This step is considered to be the rate-determining step of the reaction.$^{53}$ The oxide anion of the open ring epoxide attacks the carbon atom of CO$_2$ resulting in a carbonate intermediate. The intermediate carbonate can effectively H-bonded with the -OH groups and as a consequence reduces the energy barrier of the forward reaction. Finally, the intramolecular ring closure leads to the cyclic carbonate as a product and the regeneration of the cocatalyst takes place. In case of Zn/RN4-Az-OH, both the Brønsted acidic phenolic -OH groups of C-phenylresorcin[4]arene core as well as the Lewis acidic Zn(II) metal centers act synergistically lowering down the activation energy barrier of the forward path.

**Removal of organic micropollutants from water**

Resorcin[n]arenes-based cavitands are well-known hosts for a large number of organic molecules. We have noticed that the POPs developed in the present study have a strong affinity towards the cationic quaternary ammonium salt. The size selectivity in the CO$_2$ conversion by the RN4-based POPs has also been demonstrated (vide supra). These observations inspired us to investigate their potential for charge-specific size-selective uptake of organic micropollutants from water. We employed a large variety of organic dyes based on solubility in water, different sizes and charges including cationic, e.g., methylene blue (MB), rhodamine B (RhB), rhodamine 101 (Rh101), cresyl violet (CV) and anionic dyes, e.g., methyl blue.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Epoxide</th>
<th>Product</th>
<th>% Conversiona</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>RN4-Az-OH</td>
</tr>
<tr>
<td>1</td>
<td><img src="epoxide1.png" alt="Epoxide" /></td>
<td><img src="product1.png" alt="Product" /></td>
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</tr>
<tr>
<td>2</td>
<td><img src="epoxide2.png" alt="Epoxide" /></td>
<td><img src="product2.png" alt="Product" /></td>
<td>96 (6h)</td>
</tr>
<tr>
<td>3</td>
<td><img src="epoxide3.png" alt="Epoxide" /></td>
<td><img src="product3.png" alt="Product" /></td>
<td>95 (12h)</td>
</tr>
<tr>
<td>4</td>
<td><img src="epoxide4.png" alt="Epoxide" /></td>
<td><img src="product4.png" alt="Product" /></td>
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<tr>
<td>5</td>
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<td><img src="product5.png" alt="Product" /></td>
<td>99 (12h)</td>
</tr>
</tbody>
</table>

*Reaction conditions:* Epoxide (10 mmol), TBAB (0.25 mmol), CO$_2$ (2.5 bar), 90°C, catalyst (RN4-Az-OH or, Zn/RN4-Az-OH: 30 mg). a% of conversion calculated through $^1$H NMR analysis.

Table 3. RN4-Az-OH catalyzed CO$_2$ fixation with various epoxide derivatives to cyclic organic carbonates
10 (MeB), Congo red (CR), methyl orange (MO), rose bengal (RB) for the study. The decrease in the absorbance at the \( \lambda_{\text{max}} \) of the corresponding cationic/anionic dye was monitored over time (Figure 3a, 3b). The RN4-based POPs adsorbed the cationic dyes even without any mechanical agitation. Considering methylene blue (MB) as the model micropollutant,\textsuperscript{55,56} we checked the % removal efficiency for all the POPs in 30 min (Figure 3a, 3c). RN4-based POPs exhibited much higher dye adsorption capacity compared to that of the pristine \( p \)-hydroxyphenylresorcin[4]arene (HRN4) monomer in 30 min; (d) the percentage removal efficiency of various cationic dyes: methylene blue (MB), rhodamine B (RhB), rhodamine 101 (Rh101), cresyl violet (CV) and anionic dyes: methyl blue (MeB), Congo red (CR), methyl orange (MO) and rose Bengal (RB) employing RN4-F for 30 min; the error bars represent the standard deviation of three independent measurements. (e) The time-dependent adsorption of aqueous solutions of CV, MB, RhB, and Rh101 (0.1 mM) by RN4-F (1 mg mL\(^{-1}\)). (f) The pore size distribution obtained from NLDFT analysis of BET adsorption isotherms of RN4-F before and after adsorption with MB; inset: the calculated size of MB molecule in X and Y directions (using density functional theory (DFT) and Material Studio version 6.1, space-filled model) depicting close similarity with pore size distribution of pristine RN4-F. (g) UV-vis absorption spectra of 1:1 (v/v) mixed dye solution (MB: cationic dye, 0.1 mM and MO: anionic dye, 0.1 mM) at a different time interval in the presence of RN4-F (1 mg mL\(^{-1}\)); inset: digital photographs further suggesting the charge-specific dye separation.

(MeB), Congo red (CR), methyl orange (MO), rose bengal (RB) for the study. The decrease in the absorbance at the \( \lambda_{\text{max}} \) of the corresponding cationic/anionic dye was monitored over time (Figure 3a, 3b). The RN4-based POPs adsorbed the cationic dyes even without any mechanical agitation. Considering methylene blue (MB) as the model micropollutant,\textsuperscript{55,56} we checked the % removal efficiency for all the POPs in 30 min (Figure 3a, 3c). RN4-based POPs exhibited much higher dye adsorption capacity compared to that of the pristine \( p \)-hydroxyphenylresorcin[4]arene (Figure 3c). RN4-F was found to be the best adsorbent due to the high pore volume, presence of a large number of electronegative fluorine atoms (facilitating fluorine-cation interaction), \( \pi \)-electron rich cavity (facilitating cation-\( \pi \) interaction) with polar phenolic -OH groups as well as the hydrophobic nature of the polymer (Figure 3c).\textsuperscript{24} Albeit of low surface area, RN4-Az-OH showed better dye adsorption capacity than that of RN4-OH due to the presence of a greater number of phenolic -OH groups and azo linkages in the POP (Figure 3c).
Subsequently, we considered RN4-F as the model adsorbent to demonstrate the selective dye uptake. RN4-F effectively adsorbed unipositive dyes, e.g., cresyl violet, methylene blue, rhodamine B, rhodamine 101 with a removal efficiency of 99 ± 0.1%, 95.4 ± 4.1%, 90.9 ± 3.5% and 96.8 ± 2.2%, respectively (Figure 3d, 3e). On the other hand, neutral molecules like p-nitrophenol and 2-naphthol (0.1 mM) were removed up to 80% and 76%, respectively by RN4-F (1 mg mL⁻¹). To explain the fast adsorption kinetics of the cationic species, we estimated the size of the micropollutants by the density functional theory (DFT) calculations.⁵⁷ The molecular dimension was measured from the geometry optimized structure using Materials Studio version 6.1.⁵⁸ The computed molecular dimensions of CV, MB, RhB, Rh 101, p-nitrophenol, and 2-naphthol are 1.48 × 0.83, 1.55 × 0.73, 1.50 × 1.44, 1.54 × 1.33, 0.79 × 0.55 and 0.82 × 0.62 nm, respectively. Thus, the pores around 0.7 and 1.4 nm as revealed through the pore size distribution of RN4-F are easily accessible to the dyes leading to the excellent uptake capacity (Figure 3d, 3f). The complete disappearance of the peaks at 0.7 and 1.4 nm of MB-adsorbed RN4-F indicates that the pores are occupied by the dye molecules of similar sizes (Figure 3f). CV being the smallest among the cationic dyes was adsorbed much faster than RhB and MB (Figure 3e).

A negligible uptake of 13.9 ± 0.4% and 17 ± 1.1% was observed for the anionic dyes with multiple charges, like methyl blue (MeB) and Congo red (CR), respectively. The larger size of MeB (2.41 nm × 1.76 nm) and CR (2.74 nm × 0.87 nm) than that of the pores of RN4-F are responsible for the poor uptake capacity (Figure 3b, 3d). On the other hand, anionic dyes with unit charge, e.g., methyl orange (MO) and rose bengal (RB) were adsorbed moderately up to 33.2 ± 1.5 and 38.4 ± 0.6 %, respectively (Figure 3d). This can be attributed to the comparable size of MO (1.59 nm × 0.55 nm) and RB (1.31 nm × 1.33 nm) as that of the pores. Dyes having similar molecular dimensions but opposite charges, e.g., cationic CV, MB, and anionic MO, showed different uptake by RN4-F. Nearly 99% CV, 96% MB whereas only 33% of MO were sequestered by RN4-F. This finding indicates that a positive charge on the guest assists predominantly in the selective uptake when molecular size is comparable to the dimension of the pore. We further carried out the dye adsorption measurement employing a 1:1 v/v mixed dye solution (cationic dye methylene blue: 0.1 mM, anionic dye methyl orange: 0.1 mM). A clear visual color change from green to orange was observed within 15 min indicating the selective adsorption of cationic dye (Figure 3g). We performed the batch-adsorption kinetic measurements to investigate the mechanistic insight of dye adsorption by RN4-F. The experimental data were fitted quite well with the pseudo-second order model (MB: $R^2 \sim 0.99$; RhB: $R^2 \sim 0.98$, Figure S4-S5).⁵⁹-⁶¹

CONCLUSION

Taking C-phenylresorcin[4]arene as a model zero-dimensional porous molecular solid, we demonstrated that connecting the 0D porous-cores through aromatic linkers led to the 3D-POPs with the drastic improvement in the surface area from 156 to 1229 m² g⁻¹. The inherent guest-responsive properties of the 0D porous building blocks were not only retained but also enhanced many folds in the 3D porous framework. We developed hierarchically mesoporous to ultramicroporous POP by tuning the length and functionality of aromatic linkers. Three environmentally relevant issues, namely, selective gas uptake, catalytic conversion of CO₂ to value-added chemicals and removal of micropollutant from water were demonstrated to substantiate the advantage of interconnected pores originating through crosslinking of
macrocyclic cavitands. Azo-linked RN4-Az-OH was found to be a remarkable metal-free recyclable catalyst for cycloaddition of CO₂ with several substituted epoxides under solvent-free reaction conditions. Alkyne-linked microporous POP, RN4-OH having a high surface area (720 m² g⁻¹) and residual palladium showed considerable H₂ uptake (10 mmol g⁻¹) at 1 atm. Fluorinated small linkers led to hydrophobic ultramicroporous POP, RN4-F (S_{BET}: 1229 m² g⁻¹), a highly robust and efficient material for charge-specific size-selective separation of organic dyes from water. Thus, the approach of ‘connecting the dots’, paves the way for the development of multifunctional macrocycle-based 3D-POPs for targeting several environmental remediation problems like catalytic conversion of greenhouse gases, selective separation of micropollutants from a complex aqueous mixture, and water desalination.

**Experimental section**

**General methods**

Solution-state ¹H and ¹³C NMR spectra were acquired from Bruker Avance III 500 MHz NMR spectrometers. The solid-state ¹³C NMR (CP/MAS) experiments were carried out on JEOL ECX2 400 MHz (field 9.4 T, 4 mm probe) standard bore spectrometer. Infrared spectra were obtained in KBr discs on a PerkinElmer Model 2000 FTIR spectrometer in the 400-4000 cm⁻¹ region. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream using a PerkinElmer TGA-6000 instrument at a heating rate of 10 °C min⁻¹. The powder X-ray diffraction (PXRD) data were recorded on the PANalytical Empyrean XRD instrument. The surface morphologies of the POPs were examined using a Carl Zeiss (Ultraplus) field emission scanning electron microscope (FESEM). Energy dispersive X-ray spectroscopy (EDS) was performed using Oxford Instruments X-MaxN spectrometer attached to FESEM. The morphology of all the POPs was further studied using FEI TALOS 200S instrument at a working voltage of 200 kV. Gas sorption studies were performed on Quantachrome Autosorb QUA211011 equipment. POP samples were degassed at 80-100 °C for 12 h before the measurements. Isotherms were analyzed using ASIQwin software. The pore size distribution was obtained through non-local density functional theory (NLDFT) analysis. UV/visible absorption spectra were recorded by Cary 100 spectrophotometer.

**Synthesis of monomers**

p-Hydroxyphenylresorcin[4]arene (HRN4) was synthesized following the procedure given below. Resorcinol (4.1 mmol, 1 equiv.) and concentrated HCl (3.5 mL) were dissolved in anhydrous ethanol (25 mL) and stirred at 0 °C for a few minutes. An ethanolic solution of p-hydroxybenzaldehyde (4.1 mmol, 1 equiv.) was added dropwise to the cold solution and refluxed (85 °C) for 12 h. After cooling down to room temperature, the pink color precipitate was filtered out and purified via reprecipitation in deionized water. The reprecipitated purple colored solid was washed with methanol, ethanol, acetone, diethyl ether and dried under vacuum for 12 h at 50 °C (Yield: 45%). Following the same protocol, p-bromophenylresorcin[4]arene was synthesized using resorcinol and p-bromobenzaldehyde (Yield: 42 %).

**Synthesis of RN4-Az-OH**

Benzidine (0.7 mmol, 2 equiv.) was taken in a 100 mL round bottom flask and was charged with 30 mL of deionized water and 2 mL of concentrated HCl. The solution was stirred for 30
min in an ice bath. Then 20 mL of aqueous sodium nitrite (1.4 mmol, 4 equiv.) was added dropwise and stirred for 30 min maintaining the temperature at 2-3 °C. The solution was neutralized with dilute sodium carbonate solution. Then it was added to the 30 mL aqueous solution of \( p \)-hydroxyphenylresorcin[4]arene (0.35 mmol, 1 equiv.) and sodium carbonate (4.2 mmol, 12 equiv.) and stirred for 12 h at 2-3 °C. Solid sample was separated from the reaction mixture by filtration and washed with dilute HCl solution. The dark grey colored solid was thoroughly washed by multiple Soxhlet extractions with methanol, THF, ethanol, respectively followed by freeze-drying (Yield: 90-95%).

**Synthesis of RN4-OH**

In a typical procedure, \( p \)-bromophenylresorcin[4]arene (0.18 mmol, 1 equiv.), copper(I) iodide, bis(triphenylphosphine)palladium(II) chloride were taken in 5 mL degassed THF/DMF (1:1). Diisopropylamine (0.72 mmol, 4 equiv.), 1,4-diethynylbenzene were dissolved in a 5 mL dry, degassed THF. The solution containing the ethynyl linker (0.36 mmol, 2 equiv.) was added dropwise to the solution containing the \( p \)-bromophenylresorcin[4]arene with stirring to afford a dark grey reaction mixture. The mixture was heated at 65 °C under N\(_2\) for 48 h. After cooling to room temperature, the reaction mixture was quenched with cold acidified methanol. The precipitate was collected through gravimetric filtration. Then it was washed with THF, methanol and followed by thorough washing by Soxhlet extraction for 24 h each in methanol, THF, chloroform, and ethanol, respectively. The resulting yellowish-brown solid was dried under vacuum at 80 °C for 12h (Yield ∼50%).

**Synthesis of RN4-F**

\( p \)-Hydroxyphenylresorcin[4]arene (0.35 mmol, 1 equiv.) and potassium carbonate (2.8 mmol, 8 equiv.) were taken to a Schlenk tube, and 1.5 mL of dry DMF was added. A solution of tetrafluoroterephthalonitrile (1 mmol, 3 equiv.) in anhydrous THF (13 mL) was added to the above mixture dropwise while stirring under N\(_2\) atmosphere. The stirring was continued for 48 h at 85 °C. Then, the light brown suspension was cooled. The residual K\(_2\)CO\(_3\) was quenched by washing with 1N HCl until CO\(_2\) evolution stopped. The solid was filtered followed by soaking for 15 min each in H\(_2\)O, THF, and DCM, respectively. Then the POP was dried through freeze-drying (Yield: 60-70%).

**ACKNOWLEDGMENT**

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REFERENCES


Supporting information

for

‘Connecting the dots’: knitting C-phenylresorcin[4]arenes with aromatic linkers for task-specific porous organic polymers

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Contents

<table>
<thead>
<tr>
<th></th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PXRD analysis of porous organic polymers (POPs)</td>
</tr>
<tr>
<td>2</td>
<td>Non-local density functional theory (NLDFT) analysis</td>
</tr>
<tr>
<td>3</td>
<td>CO₂ and H₂ uptake</td>
</tr>
<tr>
<td>4</td>
<td>CO₂ conversion</td>
</tr>
<tr>
<td>5</td>
<td>Micropollutant removal</td>
</tr>
<tr>
<td>6</td>
<td>MALDI-TOF, ¹H and ¹³C NMR analysis of compounds</td>
</tr>
</tbody>
</table>
1. PXRD pattern

The broad PXRD profiles signify the amorphous nature of the POPs. In the case of RN4-OH, a small peak at $2\theta = 40^\circ$ was attributed to the presence of residual palladium [(111) Miller plane] in the porous network (Figure S1b).

![Figure S1](image)

**Figure S1** The PXRD patterns of (a) RN4-Az-OH, (b) RN4-OH, and (c) RN4-F.

2. Non-local density functional theory (NLDFT) analysis

The pore size distribution (PSD) profiles were estimated through (NLDFT, using carbon slit pore model) method (Figure 3f). We found that the pristine macrocycles showed the pores 2.4 to 6 nm. These are the extrinsic voids originated from the packing of the resorcin[4]arene monomers in the solid state. However, from the crystal structure analysis of $p$-hydroxyphenylresorcin[4]arene, we found the size of the cavity is of $\sim 1.25$ nm width and $\sim 1.17$ nm deep (inner ring diameter $\sim 0.72$ nm, *Chem. Eur. J.* 2016, 22, 15202). The nearly similar size of the cavity of metal-coordinated calix[4]resorcinarene cavitands was also reported in literature (cavity diameters:1.62-1.83 nm, *J. Am. Chem. Soc.* 2017, 139, 7648). In the solid state, the cavities of the pristine macrocycles remain inaccessible, and only the extrinsic voids are contributing to the PSD. On the other hand, connecting the macrocycles with aromatic linkers leads to the interconnected porous 3D networks. The interconnectivity between the pores in the network makes the intrinsic cavity of the macrocyclic building blocks accessible to the guests. The peaks emerging around 1.4 – 1.6 nm in the PSD profiles of RN4-Az-OH, RN4-OH, and RN4-F are clearly noticeable, which are contributed to the intrinsic pores of resorcinarene. As a consequence, a large increase in the specific surface area was observed.
Figure S2 The NLDFT pore size distribution profiles of (a) RN4-F, RN4-OH, RN4-Az-OH and monomer HRN4 (Carbon slit pore model). (b-e) Crystal structure of HRN4 analyzed using the software package in Mercury 4.1.2 revealing the dimension of p-hydroxyphenylresorcin[4]arene (CCDC No. 1477373, Chem. Eur. J. 2016, 22, 15202).

3. CO₂ and H₂ uptake

The carbon dioxide sorption isotherms of the POPs were measured at 273 K as well as 298 K to calculate the isosteric heat of adsorption (Q_st). The isotherms at 298 K are shown in Figure S3a. The hydrogen sorption isotherms for all the POPs were measured at 77 K (Figure S3c). The microporous nature (type Ib H₂ sorption isotherm), as well as high surface area, facilitate the high H₂ uptake in RN4-F and RN4-OH over that of RN4-Az-OH. H₂ having small kinetic diameters (2.89 Å) are effectively adsorbed by smaller pores.

Figure S3. (a) CO₂ sorption isotherms at 298 K and (b) isosteric heat of adsorption (Q_st) profile of RN4-F, RN4-OH, RN4-Az-OH, and HRN4. (c) H₂ sorption isotherm of RN4-F, RN4-OH, RN4-Az-OH, and HRN4 at 77 K.
4. CO₂ conversion to cyclic carbonates

The % of conversion of various epoxides to carbonates catalyzed by POPs was calculated from the ¹H NMR spectra by integrating the epoxide versus cyclic carbonate peaks (Figure S22-S36). We have chosen styrene oxide (boiling point: 194 °C) as the model substrate to optimize the reaction conditions for the CO₂ fixation to cyclic carbonates. The macrocycle-based POPs in the absence of cocatalyst (TBAB) did not show any catalytic activity justifying the role of cocatalyst (nucleophile, Br⁻). Again, by employing only the TBAB (0.15, 0.25, 0.5 mmol), the catalytic conversion of styrene oxide (10 mmol) in 12 h (2.5 bar CO₂ and 90 °C) was found to be very low (15, 25 and 40, respectively) indicating the importance of POPs as catalysts. Again, metalation of RN₄-Az-OH with Zn(OAc)₂ enhance the catalytic performance (% of conversion of styrene oxide was increased from 76% to 98% in 6 h, Figure S36). The isolated yields of cyclic carbonates were determined after silica gel column purification (Figure S12-S21).

Table S1 CO₂ fixation with various epoxide derivatives to cyclic carbonates in a larger scale.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Epoxide</th>
<th>Product</th>
<th>% Conversion</th>
<th>RN₄-Az-OH</th>
<th>Zn/RN₄-Az-OH</th>
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<tr>
<td>1</td>
<td></td>
<td></td>
<td>98 (90)ˢ</td>
<td>99 (90)⁴</td>
<td>99 ˢᵈ</td>
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<td>99 (88)⁴</td>
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<td></td>
<td>65 (60)ˢ</td>
<td>99 (92)⁴</td>
<td>99 ˢ</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>71 (67)ˢ</td>
<td>86 (80)⁴</td>
<td>99 ˢ</td>
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</tbody>
</table>

**Reaction conditions:** Epoxide (20 mmol), TBAB (0.12 mmol), CO₂ (2.5 bar), 90 °C, catalyst (RN₄-Az-OH or, Zn/RN₄-Az-OH: 30 mg). Reaction time: ᵃ12 h, ᵄ4 h, ᵇ6 h, ᵆ3h. ᵇEpoxide (10 mmol). TBAB (0.25 mmol), CO₂ (2.5 bar), 90 °C. ᵏ% of conversion calculated through ¹H NMR analysis. Isolated yields were estimated after silica gel column purification and reported inside the parentheses.
5. Kinetic analysis of micropollutant uptake

**Figure S4** UV/Vis absorption spectra of cationic dyes (a) methylene blue (0.1 mM), (b) rhodamine B (0.1 mM) at different time (min) interval in the presence of RN4-F (1 mg mL⁻¹) in water. The pseudo second-order fitting for the kinetics of adsorption of (c) methylene blue and (d) rhodamine B by RN4-F.

**Figure S5** Pseudo first order fitting of (a) methylene blue (0.1 mM, $R^2 = 0.92$), (b) rhodamine B (0.1 mM, $R^2 = 0.91$) at different time interval in the presence of RN4-F (1 mg mL⁻¹).
6. $^1$H, $^{13}$C NMR and MALDI-TOF spectra of compounds

![NMR spectra](image1)

**Figure S6** $^1$H NMR spectrum of $p$-hydroxyphenylresorcin[4]arene.

![NMR spectra](image2)

**Figure S7** $^{13}$C NMR spectrum of $p$-hydroxyphenylresorcin[4]arene.
Figure S8 $^1$H NMR spectrum of $p$-bromophenylresorcin[4]arene.

Figure S9 $^{13}$C NMR spectrum of $p$-bromophenylresorcin[4]arene.
Figure S10 MALDI-TOF analysis of \( p \)-hydroxyphenylresorcin[4]arene.

Figure S11 MALDI-TOF analysis of \( p \)-bromophenylresorcin[4]arene.
Figure S12 $^1$H NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one.

Figure S13 $^{13}$C NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one.
Figure S14 $^1$H NMR spectrum of 4-methyl-1,3-dioxolan-2-one.

Figure S15 $^{13}$C NMR spectrum of 4-methyl-1,3-dioxolan-2-one.
Figure S16 $^1$H NMR spectrum of 4-butyl-1,3-dioxolan-2-one.

Figure S17 $^{13}$C NMR spectrum of 4-butyl-1,3-dioxolan-2-one.
Figure S18 $^1$H NMR spectrum of 4-phenyl-1,3-dioxolan-2-one.

Figure S19 $^{13}$C NMR spectrum of 4-phenyl-1,3-dioxolan-2-one.
Figure S20 $^1$H NMR spectrum of 4-(phenoxy methyl)-1,3-dioxolan-2-one.

Figure S21 $^{13}$C NMR spectrum of 4-(phenoxy methyl)-1,3-dioxolan-2-one.
Figure S22 $^1$H NMR conversion of styrene oxide in presence of TBAB (Conversion: 25%, Table 2, entry 1).

Figure S23 $^1$H NMR conversion of styrene oxide in presence of RN4-OH (Conversion: 86 %, Table 2, entry 3).
Figure S24 $^1$H NMR conversion of styrene oxide in presence of RN4-F (Conversion: 75%, Table 2, entry 4).

Figure S25 $^1$H NMR conversion of styrene oxide in presence of RN4-Az-OR (Conversion: 34%, Table 2, entry 5).
Figure S26 $^1$H NMR conversion of propylene oxide in presence of RN4-Az-OH (Conversion: 98%, Table 3, entry 1).

Figure S27 $^1$H NMR conversion of epichlorohydrin in presence of RN4-Az-OH (Conversion: 96%, Table 3, entry 2).
Figure S28 $^1$H NMR conversion of styrene oxide in presence of RN4-Az-OH (Conversion: 95%, Table 3, entry 3).

Figure S29 $^1$H NMR conversion of epoxyhexane in presence of RN4-Az-OH (Conversion: 99%, Table 3, entry 4).

Figure S30 $^1$H NMR conversion of 1,2-epoxy-3-phenoxypropane in presence of RN4-Az-OH (Conversion: 99%, Table 3, entry 5).

Figure S31 $^1$H NMR conversion of propylene oxide in presence of Zn/RN4-Az-OH (Conversion: 99 %, Table S1).
Figure S32 $^1$H NMR conversion of epichlorohydrin in presence of Zn/RN4-Az-OH (Conversion: 99%, Table S1).

Figure S33 $^1$H NMR conversion of styrene oxide in presence of Zn/RN4-Az-OH (Conversion: 98%, Table S1).
Figure S34 $^1$H NMR conversion of epoxyhexane in presence of Zn/RN4-Az-OH (Conversion: 99 %, Table S1).

Figure S35 $^1$H NMR conversion of 1,2-epoxy-3-phenoxypropane in presence of Zn/RN4-Az-OH (Conversion: 99 %, Table S1).
Figure S36 $^1$H NMR conversion of styrene oxide in presence of RN4-Az-OH (Conversion: 76%).