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Epoxy-functionalized Porous Organic Polymers via Diels-Alder Cycloaddition Reaction for Atmospheric Water Capture**

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Abstract: We report on the synthesis of highly microporous, epoxy-functionalized porous organic polymers (ep-POPs) through one pot, catalyst-free Diels-Alder cycloaddition polymerization. The high oxygen content of ep-POPs offered efficient hydrogen bonding sites for water molecules, thus leading to high water uptake capacities, up to 39.2-42.4%, under a wide temperature range of 5-45°C, covering the climatic conditions and various manufacturing applications. Importantly, ep-POPs demonstrated regeneration temperatures as low as 55°C and excellent water stability, recyclability as well as high specific surface areas (up to 852 m^2 g^{-1}).

Maintaining proper humidity levels is rather significant for human health and comfort. For humidity control, the desiccant driven dehumidification is already being used for wide range of applications such as automotive air conditioning system, marine cargo, pharmaceutical, electronics, product storage and preservation.[1] In addition, the desiccants can also be potentially used for water capture in the countries with high water scarcity provided that the captured water can be recovered with minimum energy penalty. It is, however, important to note that the required temperatures and humidity levels vary greatly depending on the target application. Therefore, it is highly desirable to have desiccants that retain high water uptake capacity under wide range of temperatures. In addition, materials with low regeneration temperatures are preferred for energy efficient capture and release of water. Therefore, it is important to attain heat of adsorption value, which balances the energy required for desorption and the affinity for water molecules over wide range of temperatures and humidity levels.

The most widely used materials for dehumidification include zeolites (22-30 wt% at 90% RH) and activated alumina (19 wt% at 90% RH), in which alkali-metal cations and lattice oxygens act as strong water binding sites. These materials, however, require temperatures as high as 250-350°C during the regeneration step.[2] More recent examples include metal-organic frameworks (MOFs) with water uptake capacities up to 82 wt% at 30% RH[3], regeneration temperatures as low as 105°C[4] and capture performance at wide temperature ranges of 15-45°C.[5] The limited availability of water stable MOFs and their relatively high cost, however, are still important factors to be considered for large scale applications.[6] Along this direction, activated carbons incorporating various oxygen functionalities emerged as promising, low-cost alternatives for water capture. Moreover, these materials showed relatively low regeneration temperatures. N-heterocycle derived carbon cuboids were also reported to have good performance (17.6 wt% at P/P_0=0.2) for atmospheric water capture with a regeneration temperature of 100°C.[7] Other metal-free materials include ordered mesoporous carbons (CMKs)[8] through hydrophobic capillary condensation mechanism with uptake capacity up to 58.3 wt% at 90% RH. The fragile nature of activated carbon-based sorbents along with the high reaction temperatures (>800°C)[7-8] required for their synthesis still present important challenges.

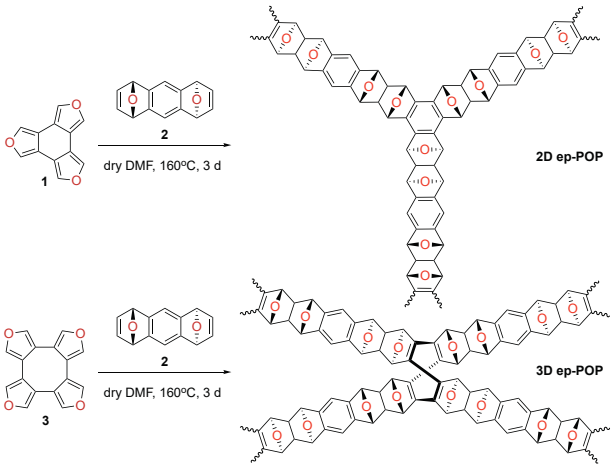

Figure 1. Synthetic scheme for two- and three-dimensional epoxy-functionalized porous organic polymers *via* the Diels-Alder cycloaddition polymerization.

In recent years, porous organic polymers (POPs) have attracted much attention owing to their high physicochemical stability, high surface areas and tunable functionalities. By tailoring their functional groups and textural properties, POPs have already been employed in broad range of applications such as gas sorption and separation, water purification, catalysis, and energy storage.[9] The application of POPs in water capture, however, is still in its infancy.[10] Given the diversity of functional groups introduced to POPs and the modularity of their synthesis, they could potentially offer suitable platforms to achieve optimum binding energy towards water molecules while balancing between uptake capacity and the regeneration temperature. Accordingly, epoxy functionality could be a good alternative considering its high hydrophilicity and the binding enthalpy for water molecules in the range of 44-47 kJ mol^{-1},[11] which could enable low-temperature regeneration. The introduction of epoxy linkages in polymer networks is, however, quite challenging due to their high reactivity in acid or base conditions as well as their low thermal sta bility. Herein, we describe (Figure 1) the synthesis of epoxy-functionalized porous organic polymers (ep-POPs) via catalyst-

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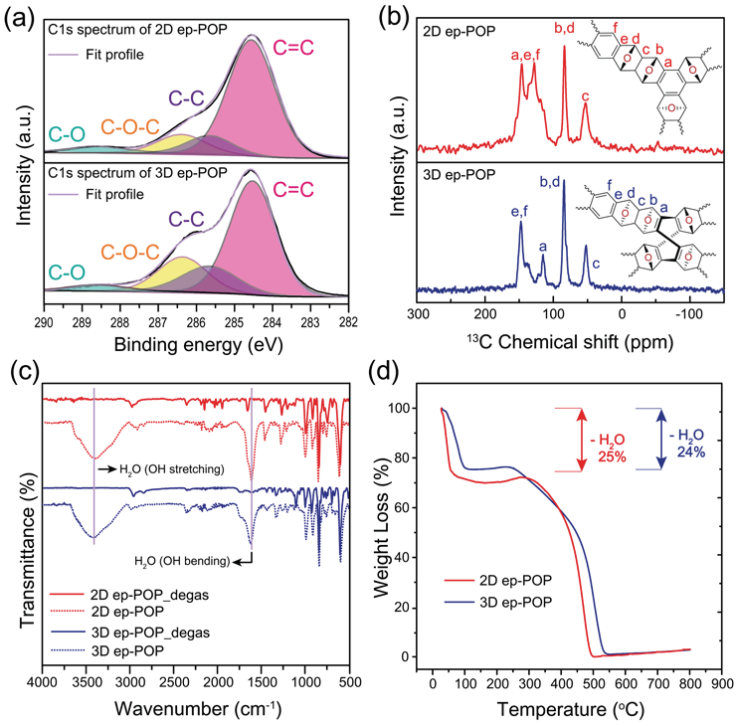

Figure 2. a) C 1s XPS spectra of 2D ep-POP and 3D ep-POP. b) Solid-state CP-MAS ^{13}C NMR spectra of ep-POPs. c) FT-IR spectra of ep-POPs before (dotted lines) and after (solid lines) degassing at 100°C. d) TGA of ep-POPs under air atmosphere.

free, one pot Diels-Alder cycloaddition polymerization. The resulting epoxy-functionalized two (2D) and three-dimensional (3D) ep-POPs are found to be highly microporous and exhibited specific surface areas up to up to 852 m^2 g^{-1}. ep-POPs showed excellent recyclability and high working capacity for water uptake in the range of 39.2-42.4 wt% for 2D ep-POP and 39.9-41.7 wt% for 3D ep-POP. Notably, these uptake capacities were maintained in the wide temperature range of 5-45°C. Importantly, due to relatively low heat of adsorption for 2D ep-POP (48.1 kJ mol^{-1}) and 3D ep-POP (59.6 kJ mol^{-1}), the sorbent regeneration can be performed at temperatures as low as 55°C. In addition, ep-POPs showed high water and thermal stabilities.

The one pot synthesis of ep-POPs was achieved through the Diels-Alder cycloaddition polymerization of cyclofuran-based monomers and diepoxyanthracene (Figure 1). By employing cyclofurans, the bicyclic epoxy groups can be effectively introduced into the resulting polymer networks. While the six membered ring of cyclotrifuran, **1**, with flat geometry results in the formation of a two-dimensional network, the eight membered cyclotetrafuran,[12] **2**, with a boat conformation, leads to the formation of a three-dimensional ep-POP. In addition, as a dienophile, *anti*-diepoxyanthracene is adopted to avoid macrocycle formation, as the *syn*-diepoxyanthracene was shown to promote cyclization.[13] The polymerization reaction was carried out in an anhydrous DMF in a 10 mL Pyrex ampoule at 160°C for 3 days. The resulting powders were washed thoroughly with $CHCl_3$, acetone, MeOH, THF, and H_2O and soxhleted with acetone for 5 days to remove any unreacted reactants and/or oligomers. The obtained ep-POPs were dried under reduced pressure for 6 h at 100°C to yield 2D ep-POP and 3D ep-POP in 53% and 54% yield, respectively.

The formation of ep-POPs was elucidated by the solid-state CP-MAS ^{13}C NMR spectroscopy analysis (Figure 2a). Solid-state CP-MAS ^{13}C NMR spectra of 2D and 3D ep-POPs revealed chemical shifts located in the range of 149 and 129 ppm originating from the aromatic carbons of diepoxyanthracene linkages. In addition, the bridgehead carbon peaks, namely C_b and C_d at 83 ppm and C_c at 53 ppm, point to the successful formation/retention of epoxy linkages. The spectra also revealed distinct differences in chemical shifts between 2D and 3D networks. For 2D network, the trisubstituted benzene core appears at 129 ppm, but the signal appears at a higher field, 115 ppm, for the tetrasubstituted cyclooctatetraene ring in 3D ep-POP.

We also performed X-ray photoelectron spectroscopy (XPS) analysis (Figure 2b and Figure S1) to further investigate the molecular-level connectivity in ep-POPs. The binding energies, corresponding chemical bonds and percentage of atomic concentration are summarized in Table S1 and S2. Notably, the C 1s and O 1s spectra showed almost identical peak shapes and positions, indicating that the molecular-level connectivity of ep-POPs was not affected with changing polymeric dimensions. The strong C 1s peak at 284.6 eV was attributed to sp^2 C=C bonds, originating from benzene and cyclooctatetraene rings. Also, it should be noted that the peaks at 286.4, 288.6 and 532 eV represent ether linkages, deriving from bicyclic epoxy group within the polymers.[14] The high epoxy content resulted in a strong O 1s peak at 533.5 eV.

We also performed FT-IR analyses (Figure 2c and Figure S2) to study the structures of ep-POPs. Before any thermal activation of the polymers, the FT-IR spectra of ep-POPs showed strong peaks centered at 3400 and 1614 cm^{-1}, due to the presence of water molecules within the pores. Notably, these peaks are slightly shifted from the values expected from pure water at 3300 and 1634 cm^{-1} for –OH stretching and bending, respectively. The blue shift for –OH stretching and redshift for –OH bending are strong indication of the hydrogen bonding interactions between ether moieties and water molecules.[15] Upon degassing ep-POPs at 100°C for 6 h, these prominent water peaks completely disappeared. In addition, the disappearance of furan peak (Figure S2) at 1022 cm^{-1} supports the complete consumption of cyclofurans during the polymerization reaction. Notably, in the range of 1150-1070 cm^{-1}, the C-O-C stretching band originating from diepoxyanthracene, **2**, maintained after polymerization reaction, thus further verifying the stability of bicyclic epoxy linkages.

To investigate the thermal stability of ep-POPs, we carried out TGA analysis under air atmosphere up to 800°C (Figure 2d). Both 2D and 3D ep-POPs showed a significant water loss (24-25 wt%) below 100°C, which indicates the dehydration of loosely bound water. Interestingly, the required temperature for complete dehydration is different for 2D and 3D ep-POPs. While 2D ep-POP showed a sharp weight decrease up to 55°C, 3D ep-POP showed a gradual decrease up to 100°C. The low regeneration temperatures represent 2D and 3D ep-POPs as good candidates for energy-efficient desiccation, as compared to the traditional materials[16] with high regeneration temperatures such as zeolites

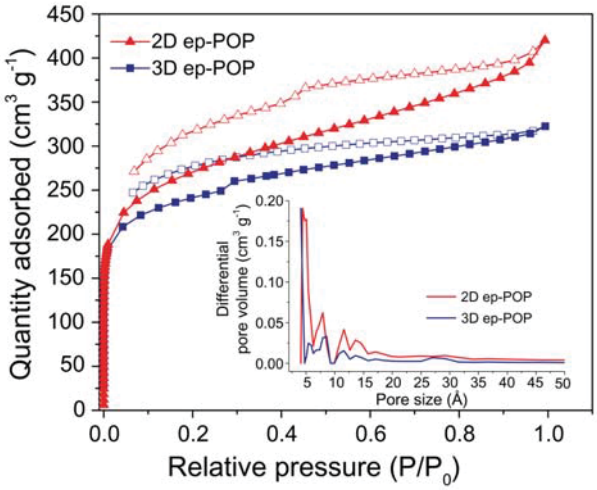

Figure 3. Argon adsorption-desorption isotherms of ep-POPs at 87 K. Filled and empty symbols represent gas adsorption and desorption, respectively. Inset: NLDFT pore-size distributions of ep-POPs.

(350°C), activated alumina (250°C), silica gel (130-150°C), and some commercially available MOFs[6b] such as Basolite A100 (200°C), Basolite F300 (200°C), and Basolite C300 (200°C). Following the loss of water molecules, we observed a slight weight gain in the temperature range of 200-270°C for 2D ep-POP and 200-230°C for 3D ep-POP, which is possibly due to the *retro*-Diels-Alder reaction followed by the oxidation of epoxy groups.[17]

Powder X-ray diffraction (PXRD) analysis was performed in order to study the crystallinity of ep-POPs (Figure S3). The PXRD spectra of ep-POPs revealed strong broad features at 2θ = 18°, revealing that the polymeric networks are mostly amorphous. Field-emission scanning electron microscopy (FE-SEM) analyses revealed bulk scale morphologies of ep-POPs (Figure S4). 2D ep-POP formed flake-like particles and showed horizontal extension during polymerization, whereas 3D ep-POP showed spherical particles, indicating that the morphology of the polymers is somewhat dictated by geometry of monomers.

To evaluate the porosity and textural properties of ep-POPs, we carried out Brunauer-Emmett-Teller (BET) surface area analysis (Figure 3). ep-POPs showed typical type I isotherms, indicating that the materials are predominantly microporous. The BET surface areas were calculated from the pressure ranges determined from the Rouquerol plots (Figure S6). The specific surface areas of 2D and 3D ep-POPs were found to be 852 and 779 m^2 g^{-1}, respectively. The higher surface area of 2D network can be explained from the planarity of 2D rigid benzene core[18], wherein the interpenetration is suppressed. The materials showed comparable micropore surface areas, 464 m^2 g^{-1} for 2D ep-POP and 462 m^2 g^{-1} for 3D ep-POP. The nonlocal density functional theory (NLDFT) pore size distribution plots (Figure 3) showed that the ep-POPs contain ultramicropores (smaller than 0.7 nm). The average pore diameters centered around a primary pore width of 0.47 and 0.40 nm for 2D ep-POP and 3D ep-POP, respectively.

The high surface area with narrow pore-size distribution as well as the hydrophilicity of ep-POPs prompted us investigate their performance for water capture. The volumetric water uptake isotherms of ep-POPs were obtained at 298 K (Figure 4a). Both 2D and 3D ep-POPs showed high sensitivity in the entire pressure range. At low humidity (P/P_0 = 0.1), ep-POPs showed uptake capacities of 2.5 and 6.3 wt% for 2D and 3D ep-POPs, respectively. When the humidity level increased as high as P/P_0 = 0.9, the uptake capacity also reached to the maximum value of 511.7 cm^3 g^{-1} (41.1 wt%) for both 2D and 3D ep-POPs. The high water uptake capacities of ep-POPs attributed to their high surface areas as well as efficient hydrogen bonding interactions between ether moieties and water molecules. To further study the water uptake properties, we also performed water adsorption studies at 313 K (Figure S7). We obtained similar isotherm shapes to the ones collected at 298 K, however, with a slightly decreased maximum uptake. The water adsorption isotherms also clearly reflected the accessibility of pores for each polymer. It should be noted that the pore sizes of 2D and 3D ep-POPs are in the micropore range, but larger than the kinetic diameter of a water molecule (1.3 Å), which enables easy traverse of water molecules in the entire region of relative humidity. Pores of different sizes fill at different levels of relative humidity.[19] At the relative pressure lower than 0.5, pore sizes of 4-10 Å accounts for water uptake. For both ep-POPs, water uptake isotherms appeared rise at P/P_0 < 0.5. 3D ep-POP with an average pore diameter of 4 Å showed a steep rise at 0 < P/P_0 < 0.25. For 2D ep-POP with pore sizes of 4.4 and 5.1 Å, showed successive pore filling through the gradual rise at 0.25 < P/P_0 < 0.4. The pore filling at low pressure also accounts for the presence of hydrophilic surfaces interacting with water molecules.[6b] The water adsorption at P/P_0 > 0.5 originated from the pores larger than 10 Å. The isosteric heats of adsorption (Q_{st}) for water was calculated using the Clausius-Clapeyron equation from the water adsorption data at 298 and 313 K. The Q_{st} values at zero coverage (Figure S8) were found to be 48.1 and 59.6 kJ mol^{-1} for 2D and 3D ep-POP, respectively. The higher Q_{st} value for 3D ep-POP led to a slightly higher temperature required for desorption, as also shown in the TGA analysis, presumably due to the smaller pore diameter of 3D ep-POP. The Q_{st} values of 2D and 3D ep-POPs at zero coverage are well below the Q_{st} values of commercial adsorbents such as zeolite 13X (100.4 kJ mol^{-1}), alumina (~96 kJ mol^{-1}), silica gel (~65 kJ mol^{-1}), allowing ep-POPs to realize lower regeneration temperatures.[20] At high loadings, however, the Q_{st} values fall much below the latent heat of condensation of water vapors (40.8 kJ mol^{-1}), possibly due to the swelling of submicroscopic structure of polymers.[21] The swelling effects were also verified by the presence of hysteresis loop in the water adsorption isotherms.

We also conducted cycle measurements (Figure 4b and S9) for 2D and 3D ep-POPs in order to evaluate the stability and cyclic adsorption/desorption performance. The cycle experiments were performed 40 times in the temperature range of 30-70°C at a relative humidity of 90% RH. Both 2D and 3D ep-POPs showed high cycling stability along with a remarkable working capacity in the range of 36-40 wt%. The capacity differences of ~2% for 2D ep-POP and ~5% for 3D ep-POP between cycles attributed to the remained moisture after degassing at 70°C under 90% RH.

For practical applications, the dehumidification material should retain its high uptake capacity under broad range of temperatures. Therefore, we studied gravimetric water sorption isotherms (Figure 4c) by varying the temperature from 5°C up to 45°C, at a constant relative humidity (RH=90%). Importantly, as depicted in Figure 4b, both 2D and 3D ep-POPs showed almost constant

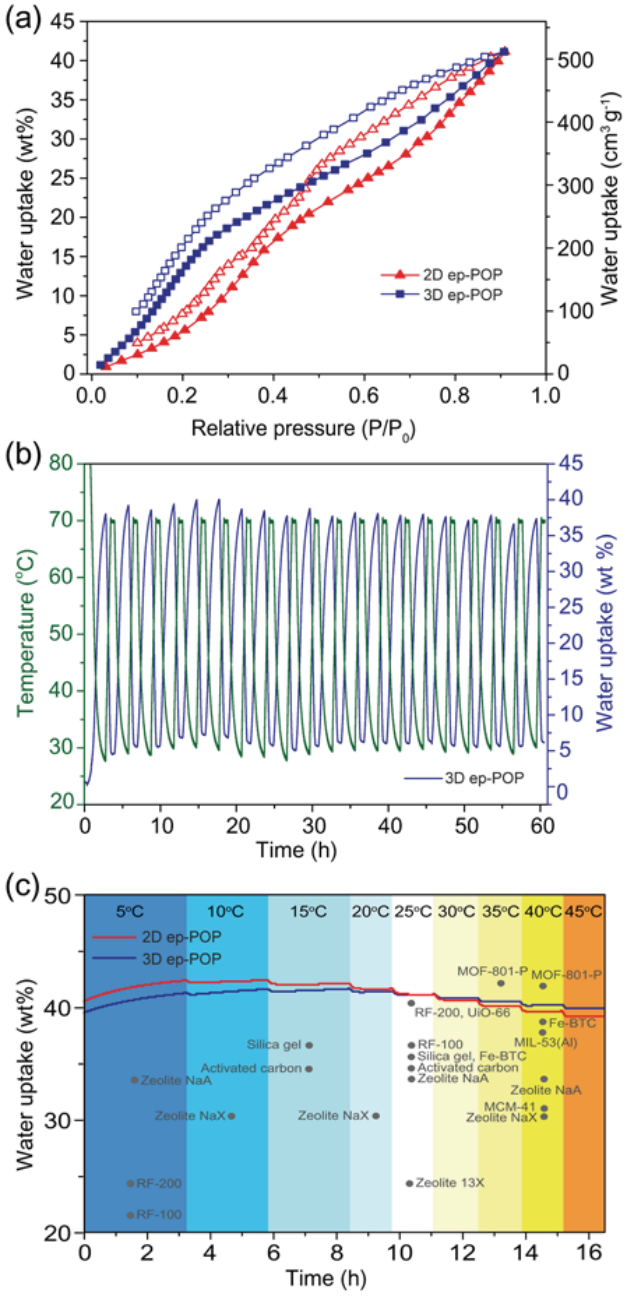

Figure 4. a) Volumetric water adsorption-desorption isotherms of 2D and 3D ep-POPs at 298 K. b) Cycle performance for water uptake using 3D ep-POP over 40 cycles by the continuous change in the temperature between 30 - 70°C at a constant humidity of RH = 90%. c) Gravimetric water uptake experiments of 2D and 3D ep-POPs in the temperature range of 5-45°C, acquired at RH = 90%.

uptake in the entire temperature range. Both 2D and 3D ep-POP showed high working capacities of 39.2-42.4 wt% and 39.9-41.7 wt%, respectively. In order to compare the working capacities of ep-POPs with conventional or previously reported materials, we benchmarked (Figure 4c and Table S4) their uptake capacities as a function of temperature.[5, 22] Carbonaceous materials such as RF-100 and RF-200 showed large dependency on temperature. Since the mesoporosity is the main contributor to their surface area, their uptake capacities decreased significantly with decreasing temperature.[22a] Highly microporous materials such as zeolite NaX, zeolite NaA, activated carbon and silica gel were almost independent towards temperature changes. However, they showed low water uptake capacities and also required high regeneration temperatures. Recently reported[5] MOF-801-P showed almost consistent uptake of water at 25-55°C. ep-POPs were found to be nearly independent of temperature, at 5-45°C, which is attributed to their high microporosity and hydrophilicity.

In summary, we synthesized new type of epoxy-rich porous organic polymers *via* one-pot, catalyst-free Diels-Alder cycloaddition reaction. The high microporosity and hydrophilicity originating from bicyclic epoxy linkages provided the optimum binding enthalpy for water molecules to balance the water uptake capacity and the energy required for the sorbent regeneration. Overall, ep-POPs are highly promising materials for desiccant driven dehumidification and water capture due to their facile synthesis, good cycle performance, high thermal stability, low-cost, low density and low activation temperature as well as high water uptake capacity at a wide temperature range, which shows their broad applicability regardless of geographical regions.

Keywords: water sorption • microporous polymers • Diels-Alder polymerization • dehumidification • porous materials

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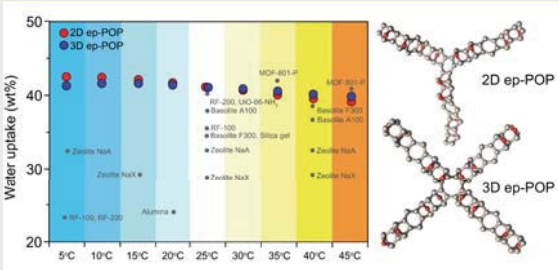

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Page No. – Page No.

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Thirsty polymers: Porous organic polymers incorporating epoxy moieties synthesized through one pot, catalyst-free Diels-Alder cycloaddition polymerization. The hydrogen bonding between epoxy groups and water molecules led to an optimum binding affinity, thus balancing between high water uptake and low regeneration temperature.