CO_2 Capture

International Edition: DOI: 10.1002/anie.201602667
German Edition: DOI: 10.1002/ange.201602667

Hierarchically Mesoporous *o*-Hydroxyazobenzene Polymers: Synthesis and Their Applications in CO_2 Capture and Conversion

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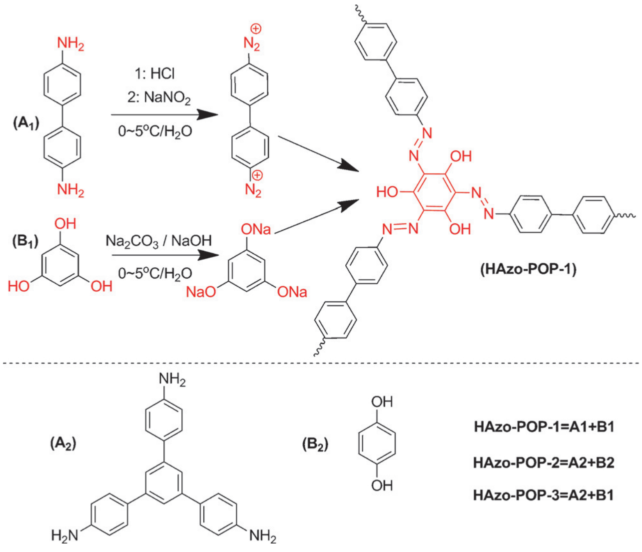
Abstract: *The synthesis of hierarchically mesoporous polymers with multiple functionalities is challenging. Herein we reported a template-free strategy for synthesis of phenolic azo-polymers with hierarchical porous structures based on diazo-coupling reaction in aqueous solution under mild conditions. The resultant polymers have surface areas up to 593 $m^2 g^{-1}$ with the mesopore ratio of $>80\,\%$, and a good ability to complex with metal ions, such as Cu^{2+}, Zn^{2+},Ni^{2+}, achieving a metal loading up to 26.24 wt%. Moreover, the polymers complexed with Zn showed excellent performance for catalyzing the reaction of CO_2 with epoxide, affording a TOF of 2570 h^{-1} in the presence of tetrabutyl ammonium bromide (7.2 mol%). The polymer complexed with Cu could catalyze the oxidation of alcohol with high efficiency.*

Benefiting from the diversity of the organic reactions, porous organic polymers (POPs) can be designed to integrate multiple functionalities, the resulting POPs therefore have promise for applications in adsorption,[1] separation,[2] catalysis,[3] light harvesting, electric energy storage, sensors, and have developed rapidly in recent years. To date, coupling reactions, such as Suzuki reaction,[4] Yamamoto reaction,[5] Sonogashira–Hagihara reaction,[6] dibenzodioxane reaction,[7] cyclotrimerzation reaction,[8] free-radical polymerization,[3c] knitting polymerization,[9] have been adopted for the synthesis of POPs. In most cases, noble-metal catalysts and high temperature are required, and the synthetic methods are environmentally unfriendly. Owing to the limitation of the solubility of the organic monomers, the synthesis of POPs is generally carried out in organic solvents, and rarely in aqueous solutions.

Though POPs have exhibited promising performance in areas such as light harvesting, energy storage, and sensors, the researches still focus on gas selective adsorption and heterogeneous catalysis. The POPs for CO_2 capture and conversion have been widely investigated because CO_2 emission is considered as a primary factor for the global climate change. For example, the POPs with nitrogen-rich functionalities, such as azo,[10] triazine,[11] tetrazole,[7a] imidazole[12] and amine[13] species have been developed, showing "CO_2-philic" properties and superior capacity to CO_2 uptake due to the enhanced CO_2-framework interactions.[14] Moreover, some metalated POPs showed high catalytic activities for CO_2 conversion due to the synergistic effects between the polymer and the metal species.[3c,10d,15] To meet requirements for CO_2 capture and conversion, the POPs should have CO_2-philic properties and/or catalytically active sites together with high surface areas. Mesoporous structures are especially desirable because they are favorable to the mass transfer of reactants.[16] For the synthesis of the mesoporous POPs, templates (e.g., SiO_2[17]) or surfactants (e.g., F127[18]) are usually required, which are generally hard to remove completely. More recently, Xiao and co-workers reported a solvent-mediated approach for the synthesis of mesoporous POPs based on divinylbenzene polymerization without any template.[19] Though such progress has been made, the synthesis of POPs with mesoporous structures is still challenging.

Herein we present a novel approach to synthesize *o*-hydroxyazobenzene POPs with mesoporous structures. The polymers were synthesized based on diazo-coupling reaction of aryl tri/diamines with tri/diphenols in aqueous solution without any template under mild conditions (Scheme 1). The resulting polymers have surface areas up to



Scheme 1. Synthetic process of *o*-hydroxy azo-hierarchical porous organic polymers (HAzo-POPs) through diazo-coupling reaction between diazonium salts and multihydroxy benzene. Red: polar regions; black: non-polar regions.

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Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201602667.

593 $m^2 g^{-1}$ with about 80 % contribution from the mesopores, and showed high selectivity of CO_2/N_2 up to 106, comparable to the highest value (110) reported.[10c] The integration of azo and phenolic -OH gave the polymer the ability to chelate with metal ions, such as Cu^{2+}, Zn^{2+}, Ni^{2+}, achieving a high metal loading (e.g., up to 26.24 % for Cu^{2+}). The presence of plenty of phenolic -OH gave the polymers the ability to form hydrogen bonds. Served as catalysts, the Zn^{2+}-coordinated polymers showed very high activity for catalyzing the reaction of CO_2 with epoxide with a very high TOF of 2570 h^{-1}, resulting from the joint effects of the metal active species and the hydrogen bonding. In addition, the resultant metal-coordinated polymeric catalysts exhibited good stability and recyclability.

As illustrated in Scheme 1, three polymer samples (denoted as HAzo-POPs) were synthesized via diazo-coupling reactions carried out in aqueous solutions at 0–5 °C, and their solid yields reached 86–97 %. The resultant samples were in the form of loose powders with colors from brown to black depending on the starting materials. All the samples showed excellent dispersity in water, polar, and apolar organic solvents, such as *N*,*N*-dimethylformamide (DMF), methanol, toluene (Figure S1a in the Supporting Information), and maintained good dispersity without any coagulation in most solvents even after kept for 7 days (Figure S1b). This might be ascribed to their unique chemical structures with polar (Scheme 1, red) and non-polar (Scheme 1, black) regions in their frameworks.

The formation the resultant HAzo-POPs was verified by the solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C NMR and fourier-transform infrared (FT-IR) spectra. Only signals in the range from $\delta = 116$ to 178 ppm were observed in the CP/MAS ^{13}C NMR spectra, ascribing to the aromatic carbons in the frameworks of the polymers (Figure S2). In the FT-IR spectrum of each HAzo-POP sample, the peaks around 1400 cm^{-1} were attributed to the asymmetric vibration of the -N=N- bond (Figure S3),[10b] and the broad peaks around 3430 cm^{-1} was assigned to the Ar-OH groups. The presence of Ar-OH groups in the frameworks of HAzo-POPs were also comfirmed via intense adsorption of methylene blue (MB) dye that can selectively interact with phenolic -OH groups through strong hydrogen bonding.[20] The MB adsorption capacity of the polymers was in the order: HAzo-POP-3 > HAzo-POP-1 > HAzo-POP-2, which might reflect the contents of phenolic -OH group in the HAzo-POPs (Figure S4, Table S1). The elemental analysis indicated that the N contents in HAzo-POP-1 (15.11 %) and HAzo-POP-3 (12.31 %) were much higher than that in HAzo-POP-2 (2.62 %). This may indicate that 1,3,5-triphenol was more active than *p*-diphenol under the experimental conditions, and more aryl amines involved the formation of the polymers via the azo bonds. Thermogravimetric analysis (TGA) was employed to study the thermal stability of the HAzo-POPs, showing no obvious decomposition occurred below 200 °C under air atmosphere (Figure S5). Notably, HAzo-POPs exhibated strong and broad optical adsorption in the UV/Vis adsorption range from 200 to 800 nm (see Figure 2 a), implying their potential applications in photocatalysis.

The morphology of the polymers were observed by SEM and HR-TEM (Figure S6). From the typical images of HAzo-POP-1, it is obvious that the as-prepared HAzo-POPs were composed of irregularly tiny particles (< 100 nm) and had massive irregular holes among the particles (Figure 1 a). The enlarged image of TEM images clearly showed the microporous structure of the polymer matrix (Figure 1 c), which crosslinked with each other to form mesopores with different pore sizes (Figure 1 b).

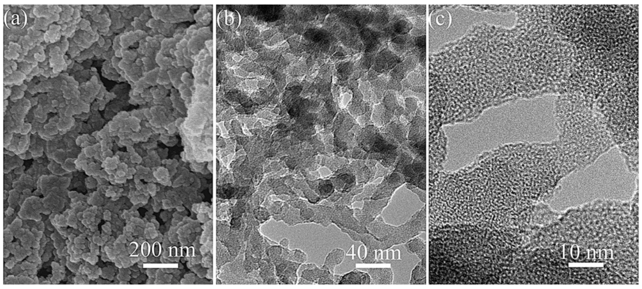


Figure 1. Typical images for HAzo-POP-1: a) SEM image. b) TEM image. c) HR-TEM image.

Textural information of the polymers was obtained from N_2-sorption isotherms achieved at 77 K. As illustrated in Figure 2 b, the resultant polymers exhibited IV isotherms, indicative of mesoporous characteristics. The hysteresis at high pressures (> 0.6) and relatively low adsorption at low pressures (< 0.1) indicated that the polymers mainly pos-

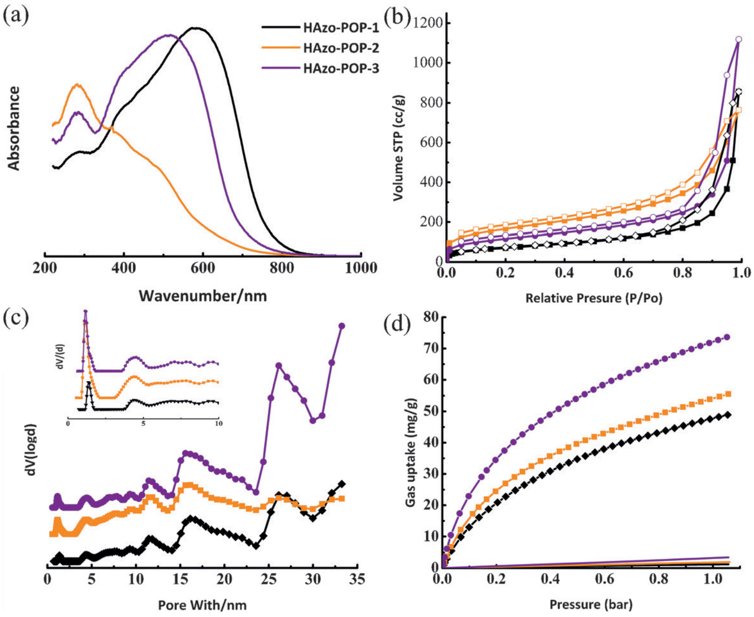


Figure 2. a) Solid state UV/Vis spectrum of HAzo-POPs. b) Adsorption (filled symbols) and desorption (empty symbols) isotherms of N_2 at 77 K. c) Pore size distribution curve; d) Adsorption of CO_2 (line with symbols) and N_2 (line) at 273 K.

sessed mesopores (Figure 2b). The pore size distributions estimated by the Brunauer–Emmett–Teller (BET) surface areas determined from the isotherms are listed in Table 1 and Figure S7, which indicated that all the HAzo-POP samples showed high BET surface areas dominated from mesopores. HAzo-POP-2 showed the highest surface area of 593 m^2g^{-1} with over 80 % from mesopores. HAzo-POP-3 showed higher surface area than HAzo-POP-1, probably due to the larger extended geometry of A2 than that of A1. Notably, only < 2 % surface area of HAzo-POP-1 was from the micropores, meaning that HAzo-POP-1 was almost mesoporous. In addition, note that the drying way for the polymers impacted their porous structures. The freeze-dried polymers were fluffy, while the thermally dried polymers were hard blocks (Figure S8), suggesting that the freezing drying way was favorable to keeping inherent porous structures in polymers. This implies that during the process of the polymer synthesis the water molecules might form hydrogen bonds with phenolic -OH and induce the porous structures of the HAzo-POPs. Similar phonomenon was also observed by zhang et al.[21]

Table 1: BET surface areas of HAzo-POPs.

Polymer	S_{total}[a] $[m^2g^{-1}]$	S_{micro}[b] $[m^2g^{-1}]$	S_{meso}[c] $[m^2g^{-1}]$	PV[d] $[cm^2g^{-1}]$
HAzo-POP-1	256.48	3.92	252.56	1.325
HAzo-POP-2	593.48	110.29	483.19	1.182
HAzo-POP-3	417.66	49.02	368.64	1.730

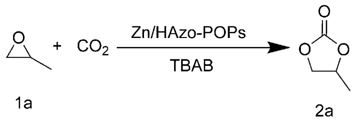
[a] Total surface area. [b] Microporous surface area calculated from the t-plots method. [c] Mesoporous surface area. [d] Total pore volume.

It was reported that the azo-containing porous polymer could adsorb CO_2 with high capacity.[10b–d] As expected, the HAzo-POPs prepared in this work, which have both azo- and phenolic groups, showed high CO_2 adsorption capacity. For example, HAzo-POP-3 afforded a 7.5 wt % CO_2 adsorption capacity at 273 K and 1.0 bar, comparable to those of the reported azo-containing POPs with similar surface areas.[10b–d] Furthermore, the N_2 adsorption capacity of the HAzo-POPs was determined at 273 K as well (Figure 2d), and it indicated that HAzo-POPs showed the selectivity of CO_2/N_2 in the range of 83–106, much higher than those obtained from most of the reported POPs with azo[10] or Ar-OH[20] groups. Especially, the CO_2/N_2 selectivity of HAzo-POP-1 reached 106, comparable to the highest selectivity (110) obtained over azo-COP-2 reported by Patel et al. (Figure S9).[10c] The high CO_2/N_2 selectivity of HAzo-POPs might attribute to massive CO_2-philic groups (i.e., azo groups) in the frameworks and their porous structures. In contrast, HAzo-POP-2 and HAzo-POP-3 had lower CO_2/N_2 selectivity than HAzo-POP-1, probably suggesting that the presence of micropores in polymers may be more favorable to the N_2 adsorption, which therefore resulted in their lower CO_2/N_2 selectivity.

Besides the good CO_2 adsorption capacity, HAzo-POPs was found to be capable of efficiently adsorbing metal ions (such as Cu^{2+}, Zn^{2+}, Ni^{2+}). As listed in Table S3, the metal contents reached 26.24 wt % for Cu, 23.47 wt % for Zn, and 20.65 wt % for Ni, respectively, as HAzo-POP-1 was treated in the ethanol solutions of corresponding metal salts with high concentrations (Table S2). This implied that the metal ions might coordinate with the functional groups in the polymers. Moreover, it was indicated that the Zn loading capacity of the polymers was in the order: HAzo-POP-3 > HAzo-POP-1 > HAzo-POP-2 (Table S3), which was consistent with that for MB adsorption (Figure S4). In addition, as $ZnCl_2$ was used as the precursor instead of $Zn(OAc)_2$, the Zn loading content decreased to 4.48 wt %, implying that OAc^{-1} maybe involved in the coordination of metal to the polymer and was favorable to the coordination. To explore whether and how the metal coordinated with the polymer, Zn/HAzo-POP-1 (4.54 wt % Zn), HAzo-POP-1 and $Zn(OAc)_2$ were examined by X-ray photoelectron spectroscopy (XPS) (Figure S10). The peak at 289 eV in the C1s XPS spectrum of Zn/HAzo-POP-1 was assigned to -C=O, indicating the presence of OAc^{-1}. The new peak at 530.68 eV in the O1s XPS spectrum of Zn/HAzo-POP-1 may be assigned to -O-Zn, implying that Zn^{2+} might coordinate with the phenolic -OH. Importantly, the binding energy (BE) of $Zn2p_{3/2}$ (1022.87 eV) shifted to higher value, compared to that of $Zn(OAc)_2$ (1022.37 eV), indicating that Zn species had less electrons, thus resulting in higher complexing ability. In addition, the BE of N1s changed little, implying that -N=N- might not involve coordination with metal ions. In addition, no obvious peak ascribing to C=O of $Zn(OAc)_2$ was observed in the FT-IR spectrum of Zn/HAzo-POP-1 (Figure S11), indicating that $Zn(OAc)_2$ was not simply physically adsorbed, while a new peak appeared at 1280 cm^{-1}, possibly assigning to the C−O vibration of Ar-OZn, which indicated Zn^{2+} was complexed. A blue shift from 584 to 563 nm was observed in the solid UV/Vis spectrum of Zn/HAzo-POP-1 (Figure S12), also suggesting the coordination between Zn and phenolic -OH. Based on the above analysis, it can be deduced that $Zn(OAc)_2$ may chelate with Ar-OH to form Ar-O-Zn-OAc moieties during the metallization process, as illustrated in Scheme S1.

Based on the above results, Zn/HAzo-POPs were examined for catalyzing cycloaddition of epoxides with CO_2 that is an important kind of reactions of CO_2 transformation.[15,22] All Zn/HAzo-POPs showed excellent performances for catalyzing cyclization of propylene oxide (PO) with CO_2 in the presence of tetrabutyl ammonium bromide (TBAB; Table 2). Zn/HAzo-POP-2 displayed the highest TOF, probably ascribing to its highest surface area from mesopores (Table 2, Entry 2). Compared to the salen-based Co-CMP catalyst that was the best heterogeneous catalyst reported for this reaction,[15b] all the Zn/HAzo-POPs showed over ten-fold higher TOFs under the similar conditions (Table 2, Entry 1–3,6,7), probably resulting from their unique chemical structures. It was reported that hydrogen bonding could promote the catalytic reaction of epoxides with CO_2.[23] The as-prepared Zn/HAzo-POPs had large amount of phenolic -OH groups that can form hydrogen bonding with the epoxide, which may promote the cyclization of epoxide with CO_2 (Table 2, compare entries 1–3 with entries 4,5). On the other hand, the mesoporous structure and excellent dispersity of Zn/HAzo-POPs in solvent were favorable to the contact of the reactants with the catalytically active sites, thus resulting in high catalytic performance. In addition, the Zn species

Table 2: Cyclic carboxylic reaction between propylene oxide (**1a**) with CO_2.[a]



Entry	Catalysts	*t* [h]	Yield[b] [%]	TOF[c] [h^{-1}]
1	Zn/HAzo-POP-1	0.5	90	2888
2	Zn/HAzo-POP-2	0.5	83	3330
3	Zn/HAzo-POP-3	0.5	86	2393
4	TBAB	1	40	–
5[d]	HAzo-POP-1	1	56	–
6	Zn/HAzo-POP-1	0.8	98	2041
7[e]	Co-CMP	1	98	201
8[f]	Zn/HAzo-POP-1	1	78	2570
9[g]	Zn/HAzo-POP-1	48	>99	4.2

[a] Reaction conditions: **1a** (20 mmol), TBAB (7.2 mol%), 100 °C, $CO_2 = 3$ MPa, Zn/HAzo-POPs = 18 mg. [b] Determined by ^1H NMR spectroscopy ($CDCl_3$, 400 MHz) using 1,1,2,2-tetrachloroethaneas an internal standard. [c] TOF = [moles of product]/[(total moles of metal)*(reaction time)] in the presence of TBAB. [d] HAzo-POP-1 (18 mg). [e] Data was obtained from Ref. [15b]. [f] **1a** (40 mmol). [g] **1a** (12.5 mmol), CO_2 (0.1 MPa), 25 °C.

might activate epoxide due to the high complexing ability of Zn. It was worth noting that the cycloaddition of epoxides bearing different substituents with CO_2 could be catalyzed by Zn/HAzo-POP-1 under atmospheric pressure and room temperature (Scheme S2), and propylene oxide exhibited the best product yield >99%. As far as we know, Zn/HAzo-POP-1 showed the highest TOF under similar conditions among the very few POP-based heterogeneous catalysts that could catalyze the cycloaddition of propylene oxide with CO_2 under atmospheric pressure and room temperature.[15b,22a,c]

To further demonstrate the universality of the HAzo-POPs as a useful platform for heterogeneous catalysts, Cu/HAzo-POP-2, (6.03 wt %) was used to catalyze the oxidation of benzyl alcohols with the co-catalyst TEMPO under O_2 atmosphere at 75 °C (Table S4), which showed very high activity for catalyzing these reactions, comparable to the mesoporous metal–organic framework (MOF) of $Cu_3(BTC)_2$.[24]

To test the recyclability, the used Zn/HAzo-POP-1 and Cu/HAzo-POP-2 were washed with methanol for 3 times, dried at 120 °C under vacuum and reused for the next run. As shown in Figure S13, the product yields of these two reactions showed no obvious decrease after 5 runs, indicating that the catalysts had good recyclability and stability. However, the ICP-OES analysis on the used Zn/HAzo-POP-1 for 5 runs indicated slight leaching of Zn species from the initial amount of 4.54 to 4.26 wt %. Similar phenomena were also observed by Deng et al.[15b] Since the polymer can be easily metalized again, the leaching of metal may not affect the use of the catalyst.

In summary, a novel kind of mesoporous *o*-hydroxyazobenzene POP was developed, which have high surface areas, excellent dispersity in common solvents, and very high CO_2/N_2 selectivity. Moreover, the HAzo-POPs have a good ability to coordinate with metal ions, and the resultant Zn/HAzo-POP-1 and Cu/HAzo-POP-2 exhibited high catalytic activity and recyclability for the cycloaddition of CO_2 with epoxides and the oxidation of benzyl alcohols under mild conditions, respectively. These POPs may find promising applications in many areas, such as photocatalysis, owing to their unique structures and functions. The exploration of their applications in catalysis is under way.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 21125314, 21402208, 21533011).

Keywords: CO_2 conversion · diazo-coupling reaction · *o*-hydroxyazobenzene · porous organic polymers

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 9685–9689
Angew. Chem. **2016**, *128*, 9837–9841

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Received: March 16, 2016