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# Functional Porous Organic Polymers Comprising Triaminotriphenylazobenzene Subunit as a Platform for Copper Catalyzed Aerobic C-H Oxidation

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**ABSTRACT:** To develop functional porous materials as a platform for heterogeneous catalytic oxidation reaction provides good way to solve the high environmental issues resulted by traditional oxidation processes in industry. This article reported a design and facile synthesis of N-rich functional porous organic polymers with mesopores such as Azo-POP-4, Azo-POP-5 and Azo-POP-6 based on triaminotriphenylazobenzene subunit for the first time. The nitrogen-rich POPs with triaminotriphenylazobenzene subunit was found to remove 85% of copper ions from water within 30 mins. The as-synthesized Cu@Azo-POP-4 demonstrated high catalytic reactivity and selectivity in aerobic C-H bond oxidation to afford the desired ketones in high yield. In addition, the catalyst could be reused easily for 5 times without decreasing the reactivity, which will help design catalysts reducing environmental pollution and advance the chemical technology.

## **1. INTRODUCTION**

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Chemical industry created lots of products beneficial to human being, although it also produced pollution to the society, which need seek the solution from advanced functional materials. Oxidation reaction is one of the most important chemical processes in industry and plays a central role in the manufacture of high-value-added products<sup>1</sup>. Many traditional oxidants based on Mn or Cr<sup>2</sup> typically required stoichiometric quantities and generated toxic and hazardous waste chemicals. In order to achieve high atomic economic efficiency3 and low environmental factor4 for the oxidation reactions, heterogeneous catalysis for aerobic C-H bond oxidation with high selectivity has been considered as an important strategy<sup>5</sup>. Plenty of nanomaterials including Pd, Pt, Cu, Co, Ru, and Rh have been designed to catalyze organic oxidation reactions<sup>6</sup>. Functional carbon materials including N-doped graphene7 and N-doped nanotube8 has been considered as good supports to immobilize metal for heterogeneous catalysis. As a new generation of functional porous materials, porous organic polymers (POPs) showed great potential for immobilization of metals9, due to their structural designability, rich functionality and good chemical stability. Actually, functional POPs could merge multiple functions into one catalyst<sup>10</sup>. They incorporated coordination sites into the polymer backbone, provided location of the high specific surface area to promote the catalytic reactions, and grasped metal species tightly to avoid the metal loss and product contamination. Cu has attracted much attention in the heterogeneous catalysis<sup>11</sup>, due to its low cost and easy availability. And polymeric ionic liquid complex (PILC) with mesopores containing nitrogen-rich pendant imidazolium salt had been developed as a platform for Cu catalyst in C-H bond oxidation reaction by Yuan group<sup>12</sup>. The orthohydroxyl-aminobenzene moiety in HAzo-POP-1 with mesopores was reported by Liu group<sup>13</sup> to capture Cu<sup>2+</sup> efficiently. The above mentioned examples as well as Ndoped carbons14 showed clearly that the mesopores did contribute to the excellent performance. Considering amino group was more Cu<sup>2+</sup>-philic than hydroxyl group, we designed the porous Azo-POP-4 containing triaminotriphenylazobenzene subunit, by replacing all hydroxyl groups in HAzo-POP-1 with amino groups. Furthermore, polyamine-functionalized porous materials have been interesting targets for application-oriented synthesis15-18.



**Figure 1** The chemical structure of Azo-POP-4, Azo-POP-5, Azo-POP-6 and Cu@Azo-POP-4

The polyamines were usually synthesized by reduction of polynitro compounds, which were made from nitration of aromatics. The conventional post-functionalization strategy was unsuitable for Functional POPs comprising triaminotriphenylazobenzene subunit.

In this regard, a facile synthesis of polyamine-functionalized POPs (Azo-POP-4, Azo-POP-5 and Azo-POP-6, **Figure 1**) was designed and carried out based on a triple azo-coupling polymerization. In addition, their applications in fast removal of  $Cu^{2+}$  from water, as well as Cu@Azo-POP-4 for the efficient aerobic C-H bond oxidation will be discussed in detail.

## 2. EXPERIMENTAL SECTION

## 2.1. Chemicals and Materials

1,3,5-triaminobenzene was prepared by modifying a known procedure<sup>19</sup> (see ESI). Aniline, p-methyl aniline, p-methoxy aniline, 4,4'-diaminobiphenyl, 4,4'-diaminobiphenylmethane, 4,4'-diaminobiphenylether, concentrated HCl, sodium nitrite, sodium carbonate, copper acetate, methanol, ethanol, DMF, de-ionized water were purchased from Sinopharm chemical reagent Beijing Co. Ltd. Diphenylmethane, fluorene, xanthene, phthalan, benzyl methyl ether, difluorodiphenylmethane, deteurated solvents such as  $D_2O$ ,  $CD_3CN$  and DMSO- $D_6$  were ordered from Energy chemical company in China. The chemicals were used as received.

## 2.2. Instrumentation

Solution NMR spectra were measured in D<sub>2</sub>O (with TMS as internal standard) CD<sub>2</sub>CN or DMSO-D<sub>6</sub> on a Varian INOVA-400M (1H at 400 MHz, 13C at 100 MHz) magnetic resonance spectrometer. Solid-state <sup>13</sup>C cross-polarization magic angle spinning (CP-MAS) NMR spectra of solid samples were obtained using a Bruker Avance III 600 MHz Wide Bore spectrometer (14.2 T). A 3.2 mm MAS probe and ZrO<sub>2</sub> motor were used, and spin rates at 12 kHz. Chemical shifts ( $\delta$ ) are reported in ppm, and coupling constants (J) are in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m =multiplet. Fourier Transform Infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum Two Fourier transform spectrometer from 500-4000 cm<sup>-1</sup>. High-resolution EI mass spectra (HR-EI-MS) were recorded on a GCT CA127 Micronass UK mass spectrometer. Elemental analysis was measured in the analytical instrumentation center of Beijing University, Beijing, China, by using Elementar Vario EL CUBE. Thermogravimetric analysis (TGA) was carried out on a Q6oo SDT (TA, US) thermogravimetric analyzer, heated from 25 °C to 800 °C at a rate of 20 °C/minute under N2 atmosphere. The specific surface areas of as-prepared Azo-POPs were screened using a BEL-SORP MAX II analyzer by nitrogen adsorption and desorption at 77 K, BET surface area were analyzed by at-least 5-point measurement between the pressure range of 0.05-0.35  $P/P_0$ . The Barrett-Joyner-Halenda (BJH) method was used to determine the distribution of pore sizes. Samples were degassed at 100°C for over 12 h under vacuum before all gas analysis. The Scanning Electron Microscopy (SEM) images were taken by a Hitachi SU-70 Scanning Electron Microscope. A Tecnai G<sup>2</sup> F<sub>3</sub>o transmission

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electron microscope (FEI) equipped with an energydispersive X-ray spectrometer system and HAADF detector was used at 300 kV for high-resolution electron microscopy imaging and HAADF imaging. Inductively coupled plasmaatomic emission spectroscopy (ICP-AES) was performed on a SPECTRO ARCOS EOP Axial View Inductively Coupled Plasma Spectrometer after acidic digestion or dilution. Quantitative and qualitative analyses of oxidized products were performed by GC-MS QP2010 ultra (Shimadzu, Kyoto, Japan) equipped with DB-5MS capillary column (Agilent, J&W Scientific, 30 m  $\times$  0.25 mm i.d.; 0.25  $\mu$ m film thickness) using helium as the carrier gas (1 mL/min) and the split ratio of 10:1. The conditions were as follows: column initial temperature (40 °C, 2 min); temperature rate (10 °C /min); column final temperature (320 °C , 5 min); injector temperature (250 °C). Electron paramagnetic resonance (EPR) spectra were recorded at ambient (~293 K) temperature with a Bruker EMX-plus spectrometer working in the X-band: microwave power was 5 microwatts; the field was swept 800 G in 150 s and modulated at 100 kHz with 5 G amplitude. Xray photoelectron spectroscopy (XPS) was performed on a PHI Quantera II spectrometer at a pressure of 1.9×10<sup>-9</sup> mtorr (1 torr = 133.329 Pa) using Al Ka as the excitation source (hn = 1486.6 eV) and operated at 15 kV and 25 W.

2.3. Synthesis of Azo-POP-4 and Cu@Azo-POP-4

26 A suspension of 4,4'-diaminobiphenyl (3.317 g, 18 mmol) in 27 water (50 ml) was treated with con. HCl (8 ml) at 0 °C. After stirring for 15 min, aqueous sodium nitrite (36.1 mmol) was 28 added and stirred for 30 min to afford the dual-diazonium 29 reagent 2. Subsequently, the mixture was neutralized with 30 aqueous Na<sub>2</sub>CO<sub>3</sub> solution, and then mixed with aqueous 31 solution of 1,3,5-triaminobenzene (1.478 g, 12 mmol) at 0 °C. 32 After 12 h, the resulted solid was filtered, washed successively 33 with water, methanol, DMF, methanol, and water, then 34 freeze-dried to give the title porous polymer Azo-POP-4 35 (4.57 g, yield 88%). 36

FT-IR (cm<sup>-1</sup>): 3429 (w), 3377 (w), 3028 (w),1571 (s), 1522 (m), 1481 (m), 1403(w), 1342(vs), 1301 (m) ,1201 (m), 1115 (m), 1001 (m), 963 (w), 823 (s), 779 (w), 763 (w), 721 (w), 696 (w), 506 (m), 479 (m).

<sup>13</sup>C CP/MS NMR, δ (ppm): 151.93, 140.35, 127.46, 115.67.

41 Elemental Analysis: found N24.21%, C67.44%, H4.56%.

The preparation of Azo-POP-4 loaded with copper (II) salt (Cu@Azo-POP-4) was carried out in ethanol. Azo-POP-4 (1 g) was loaded into flask charged with 100 ml of absolute ethanol and Cu(OAc)2 (230 mg; 8 wt.%). After refluxing for 12 h, the Cu@Azo-POP-4 was obtained by filtration, washed using ethanol three times and dried in vacuum till constant weight.

2.4. Cu@Azo-POP-4 catalyzed aerobic CH oxidation

A typical C-H oxidation reaction was carried out with substrate (2.5 mmol) in CD<sub>3</sub>CN (5 ml) in a 25 ml of round bottom flask using O<sub>2</sub> balloon. The reaction was performed at 80 °C under magnetic stirring for special period of time. Then, the catalyst of Cu@Azo-POP-4 was filtered, the filtrate was analyzed by 'H-NMR directly. The conversion was calculated based on the integration of the peak of desired product and the corresponding substrate. For the experiments using recycled catalyst, Cu@Azo-POP-4 was filtered, washed with ethanol for 3 times, dried in a vacuum oven, and used directly in the next run's C-H oxidation reaction.

## 3. RESULTS AND DISCUSSIONS

Functionalization of POPs has been an important research topic since it is crucial to their performances. In fact, the introduction of sulfonate<sup>20</sup>, hydroxyl group<sup>21</sup>, amino group<sup>22</sup>, nitro group<sup>23</sup>, tetrazole<sup>24</sup> and amidoxime<sup>25</sup> into the polymer backbone were all reported to enhance their performances of POPs such as adsorption capacity and selectivity, by the conventional post-functionalization strategy (Scheme S1). However, it became challenging in the cases of denselyfunctionalized POPs with well-defined structure, owing to the reaction efficiency issue of polymer. As an alternative, the pre-functionalization<sup>26,</sup> and in-situ-functionalization<sup>27-30</sup> strategy possessed some advantages, including making use of functional group<sup>31</sup> as directing group<sup>26</sup>. In this paper, we would like show the powerful pre- and in-situfunctionalization strategy make to triaminotriphenylazobenzene-functionalized POPs, which could serve as a support for heterogeneous catalysis.

# 3.1. Design principles for synthesis of Azo-POP-4, Azo-POP-5 and Azo-POP-6

Although metal catalyzed C-H oxidation has been studied broadly, the high selectivity and high conversion remained as an important issue<sup>32, 33</sup>. As far as heterogeneous Cu catalyzed C-H bond oxidation is concerned, POPs with high N% content and well-defined chelating sites will help, basically<sup>12</sup>. Knowing HAzo-POP-1 was good for Cu<sup>2+</sup> capture, we wonder if it will further improve the performance the copper catalyst by replacing the three hydroxyl groups in HAzo-POP-1 with three amino groups. Thus, polyamine-functionalized POPs such as Azo-POP-4, Azo-POP-5 and Azo-POP-6 came into our mind (Figure 1). Amino group was usually protected owing to its poor tolerance with polymerization conditions<sup>34</sup>, though the protecting group-free strategy will be ideal in materials development in the atomic economy' point of view<sup>3</sup>. Interestingly, the specific situation of three amino groups of 1,3,5-triaminobenzene (1) made it very attractive for the direct C-modification<sup>35</sup> possible at 2,4,6-positions, including C-azocoupling, C-thiocyanation. In addition, the well-developed polyimide industry offered aryldiamines widely36, and the aryldiamine-derived dual-diazonium reagent will be easily available<sup>37</sup>. We would like to develop nitrogen-rich functional POPs based on the azo-coupling polymerization between 1,3,5-triaminobenzene (1) and aryldiamine-derived dual-diazonium reagent 6-8 (Scheme 1).

# 3.2. Synthesis and characterization of Azo-POP-4, Azo-POP-5 and Azo-POP-6

Azo-POP-4, Azo-POP-5 and Azo-POP-6 with the crosslinking polymer structure were supposed to have very poor solubility, which made the characterization difficult. And the model compounds with the same subunit would be very helpful for the structure elucidation of Azo-POPs by simple comparison of their spectra.



**Scheme 1** The synthesis of model compounds **5a**, **5b** and **5c** and Azo-POP-4, Azo-POP-5 and Azo-POP-6

Having developed a facile synthesis of 1,3,5-triaminobenzene (1) recently<sup>38</sup> (See ESI), we synthesized the model compounds **5a-5c** by coupling 1 with diazonium salt **2-4** in 64-97% yield (**Scheme 1** and **Figure S7-24**).

3.2.1. Synthesis and careful characterization of model compounds 5a-5c

The structure of compound 5a was well characterized, by showing a peak of 436.1996 for [M+H]+ (Figure S9) in the high-resolution Mass Spectrum (HR-MS) and 28.47 N %, 65.57 C % and 4.80 H% in the elemental analysis (EA) (Figure S10). Furthermore, compound 1 showed one sharp singlet peak at 5.15 ppm for the aromatic CH, and broad singlet peak at 4.31 ppm for NH<sub>2</sub> in its <sup>1</sup>H-NMR spectra (Figure S4 and S11). The triply coupling of 1 with diazonium salt 2 afforded the triaminotriphenylazobenzene (5a, abbr. TATPAB). It showed a broad peak at 9.62 ppm for NH<sub>2</sub> in its <sup>1</sup>H-NMR spectra, which was in much lower field compared with 1, possibly owing to the intramolecular hydrogen bonding between the NH<sub>2</sub> and neighboring -N=N- bond. The phenyl ring attached to azo group showed doublet, triplet and triplet peaks at 7.88, 7.50, 7.34 ppm respectively, which moved to high field compared with diazonium salt derived from aniline (8.66, 8.26, 7.98 ppm) (Figure S7 and S11). The peaks at 149.3 and 90.9 ppm for C-NH<sub>2</sub> and C-H of 1 were observed in its <sup>13</sup>C-NMR spectra (Figure S13), while the peak of 149.1 and 114.2 ppm was found for C-NH<sub>2</sub> and C-N=N- in 5a (Figure S13-14), after 1 triply coupled with diazonium salt. The peak at 153.5 ppm was observed for C-N=N- in phenylazo

(Ph-N=N-) group, as well as peaks at 129.3, 128.1 and 121.5 ppm for other carbons of phenyl (Figure S14). From the FT-IR spectra (Figure S10-11), the characteristic adsorption peaks were seen at 3331 and 3400 cm<sup>-1</sup> for the primary amino group in aniline, which shifted to higher wave numbers of 3383 and 3427 cm<sup>-1</sup> in 5a (Figure S11). This could be the evidence for the formation of intramolecular hydrogen bonding between H and nitrogen of its neighboring -N=Nbond, being consistent with the <sup>1</sup>H-NMR data. Compound **5**b and 5c were synthesized and well characterized (Figure S12-19) by using diazonium salt 3 and 4. In order to get further understanding on the high reactivity of the triply azocoupling reaction,, we looked at the electrostatic potential (ESP) mapping of 1,3,5-triaminobenzene 1 and model compound 5a (Figure S61). It showed much more electro-rich aromatic ring in 1 compared 5a, which favored the aromatic electronic substitution. With the clear idea of how the FT-IR and <sup>13</sup>C-NMR spectra looked like for the core structure of 5, we moved to the synthesis of the Azo-POP-4 immediately.

## 3.2.2. Optimization on the Synthesis of Azo-POP-4

By taking BET surface area, isolated yield and N% content as key parameters, we carried out a careful optimization of the azo-coupling polymerization (Table S1-3 and Figure S27-28). Considering the pH value, the molar ratio of two components and addition ways might affect the property of the resulted porous polymer, we firstly tried the coupling polymerization at pH of 7.0 using 1 mmol of 1,3,5triaminobenzene, by varying the quantities of dualdiazonium reagent 6a derived from 4,4'-benzidine. In order to convert 1,3,5-triaminobenzene fully, the excess of 6 (6 mmol) was used initially. However, the polymer with BET SA of 57 m<sup>2</sup>.g<sup>-1</sup> was obtained (Entry 1, Table S1). With the decrease of 6 from 6 mmol to 2 mmol, the BET SA increased, as well as the yield (Entry 2-3, Table S1). However, when 1 mmol of 6 was used, the yield dropped to 72%, although the BET surface area remained high (Entry 4, Table S1). The try with the ideal ratio of 6 to 1 of 1.5:1 gave the polymer in 96% yield, showing BET surface area as high as 368 m<sup>2</sup>.g<sup>-1</sup>, and the N% content as high as 24.21% (Entry 5, Table S1). By adding 6 into the solution of 1 also afforded the polymer in low yield (Entry 6, Table S1). It is also found that the polymerization at pH 6 gave low yield and N% content (Entry 7, Table S1). Using the condition listed in entry 5 as best condition, 4.57 grams of Azo-POP-4 were easily synthesized in one batch (Figure S29).

## 3.2.3 Characterization and basic properties of Azo-POP-4, Azo-POP-5 and Azo-POP-6

Similar to the synthesis of Azo-POP-4, Azo-POP-5 and Azo-POP-6 were obtained in 86% and 83% yield respectively, by using the dual-diazonium reagent 7 and 8 derived from 4,4'-diaminodiphenylmethylene and 4,4'-diaminodiphenylether (Scheme 1). Azo-POP-5 and Azo-POP-6 showed BET SA of 196 and 210 m<sup>2</sup>.g<sup>-1</sup>, as well as 22.54 N% and 22.35N% (Table S<sub>3</sub>) in elemental analysis. The chemical structure of Azo-POP-4 and Azo-POP-5 were characterized based on comparisons between their CP-MS-<sup>13</sup>C-NMR and the solution <sup>13</sup>C-NMR spectra of model compound 5b (Figure 2a). The common chemical shifts of *c.a.*150 and 115 ppm the C<sub>Ph</sub>-N=N-

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and  $C_{TATPAB}$ -N=N- were observed in their NMR, as well as c.a.140 ppm for  $C_{TATPAB}$ -NH<sub>2</sub>. The chemical shifts for  $C_{TATPAB}$ -NH<sub>2</sub> varied a little bit with compound **5**c and Azo-POP-6 due to the presence of ether linkage (**Figure 2a** and **S20-21**).



**Figure 2** (a) <sup>13</sup>C-NMR of model compound **5b** in DMF-D<sub>7</sub> and <sup>13</sup>C-CP/MAS NMR of Azo-POPs. (b) FT-IR spectra of model compound **5b** and Azo-POPs.

The primary NH<sub>2</sub> groups were observed in all the Azo-POPs based on the peaks in the region of 3500-3300 cm<sup>-1</sup> in their FT-IR spectra (**Figure 2b**), although sharper peaks were seen in model compound **5b**. Otherwise, they had similar FT-IR spectra in the region of 1300-1700 cm<sup>-1</sup> owing to the common subunit structure. The strong peak at 1232 cm<sup>-1</sup> for ether bond was shown for Azo-POP-6.

The adsorption-desorption isotherms of aforementioned Azo-POPs were recorded at 77 K under N<sub>2</sub> (**Figure 3a**), which showed a composite of the type I and type II adsorption isotherms, indicative of mixed micropores and mesopores in the polymers. They had high pore volume of 1.8 cm<sup>3</sup>.g<sup>-1</sup> mainly from mesopores, only <2.4% pore volume contributed from micropores (**Table S4**). BJH model showed the average pore width (4V/A) of 25.7 nm, 38.2 nm and 35.0 nm for Azo-POP-4, Azo-POP-5 and Azo-POP-6 respectively (**Figure 3b**).



Figure 3 (a) Adsorption (filled symbols) and desorption (empty symbols) isotherms recorded at 77 K under  $N_2$  and (b) pore-size-distribution of Azo-POP-4, Azo-POP-5 and Azo-POP-6 based on BJH model.

It is worth mentioning that the preparation of mesoporous organic polymer usually required template such as silica and surfactants<sup>40</sup>. To our delight, the porous Azo-POPs with mesopores containing densely-functionality were obtained without any template. The mesoporosity and morphology of Azo-POPs were also investigated by SEM and HR-TEM (**Figure 4**).



**Figure 4** Typical images for Azo-POP-4 (a-c), Azo-POP-5 (d-f) and Azo-POP-6 (g-i): SEM image(a, d, g), TEM image(b, e, h), and HR-TEM image(c, f, i).

The typical SEM images of Azo-POP-4 (Figure 4a) showed that the as-prepared Azo-POPs were composed of irregularly tiny particles (<50 nm). And it had massive irregular holes among the particles (Figure 4b). The enlarged TEM images revealed the amorphous structure of polymers cross-linked with each other to form mesopores with different pore shapes and sizes. The similar situation was seen in Azo-POP-5 (Figure 4d-4f) and Azo-POP-6 (Figure 4g-4i). The stacked particle sizes of Azo-POP-5 and Azo-POP-6 were a little larger than Azo-POP-4, and the percent of micro-pore decreased, so did the specific surface area and the pore volume. But the pore sizes of them increased, which were consistent with the porosity analysis in Table S<sub>3</sub> and Figure 3. However, the amorphous structure of Azo-POP-4, Azo-POP-5 and Azo-POP-6 was confirmed by the broad peaks in the Powder-XRD measurement (Figure S<sub>30</sub>).

The high thermal stability of Azo-POP-4, Azo-POP-5 and Azo-POP-6 was investigated by TGA (**Figure S<sub>31</sub>**), which showed decomposition (5% weight loss) started at 284, 289 and 309 °C respectively, and maximum decomposition temperature occurred at *c. a.* 350 °C to give the char in higher than 40% yield. Compared with the very popular imine-based COFs, the azo-linked POPs possessed higher chemical stability towards acid and aqueous media, by replacing the CH=N bond with N=N bond. It was found that all the three Azo-POPs were stable upon treating with 1% aqueous HCl for 24 h (**Figure S<sub>32</sub>**), and no mass decrease of the materials was observed. This is really important when the

real application of the porous materials is concerned, especially in the cases requiring exposure to water or moisture.

## 3.3. Fast removal of Cu<sup>2+</sup> from water by Azo-POP-4

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It is well known that Cu2+ in drinking water has been considered a very important health-related issue for human body. Thus the fast removal of Cu<sup>2+</sup> from water with high efficiency became a hot research topic in recent years<sup>41, 42</sup>, where high-performance porous materials were highly desirable. Realizing the densely-functionalized POPs with triaminotriphenylazobenzene subunit structure could be helpful to chelate with Cu2+, we evaluated the removal of Cu<sup>2+</sup> from water using Azo-POP-4. The removal efficiency of Cu<sup>2+</sup> was found to be influenced by the pH value of the medium (Figure S32), and pH 5.0 was set for the experiments. A removal efficiency of 61% for Cu2+ was observed within only 3 min (initial  $Cu^{2+}$  concentration = 10 ppm) in the removal kinetics experiments (Figure 5a), comparable with highly efficient adsorbents reported very recently such as N-doped graphene nanosheets43 and mesoporous silica44. The curve fitted very well with pseudosecond-order (PSO) model (Figure 5b, Table S5), indicating the rate-limiting step of the chemo-sorption process owing to the chelating of Cu2+ with amino-azo group. It was confirmed by comparison between FT-IR spectra of Azo-POP-4 before and after adsorption (Figure S<sub>34</sub>). An obvious shift from 1574 cm<sup>-1</sup> to 1596 cm<sup>-1</sup> was seen for aromatic ring vibration, as well as from 1196 cm<sup>-1</sup> to 1265 cm<sup>-1</sup> for C-N bond after Cu<sup>2+</sup> was loaded onto Azo-POP-4. Besides, the removal efficiency reached 85% within the first 30 min, which is much faster than some reported adsorbent materials, including biocomposite hydrogel (TP-PS4 Hydrogel, 60 min)45, sugar cane bagasse cellulose and gelatin based composite hydrogels (CPGTCB Hydrogel, 80 min)<sup>46</sup>, drinking water treatment solids (DWTS, 300 min), geopolymer/alginate hybrid spheres (GAS-4, 1600 min)47 and magnetic beads based on modified gum tragacanth/graphene oxide (Magnetic Beads, 5400 min)<sup>48</sup> (Figure 5c).



**Figure 5** Removal of Cu<sup>2+</sup> by Azo-POP-4. (a) Effect of contact time on the removal efficiency of Cu<sup>2+</sup> from water. (b) Adsorption kinetics fitted by PSO kinetics model. (c) Comparisons of Cu<sup>2+</sup> removal time required with 85% removal efficiency among Azo-POP-4 and

reported adsorbent materials. (d) Removal efficiency of  $Cu^{2*}$  over adsorption-elution-regeneration cycles.

The adsorption isotherms of Azo-POP-4 toward Cu<sup>2+</sup> (Figure **S35, Table S6**) showed the adsorption fitted Langmuir model well, and the adsorption capacity increased along with the temperature increased, indicating that the adsorption process was an endothermic adsorption reaction. To examine the reusability of Azo-POP-4, adsorption-elution-regeneration cycles were evaluated and the data are shown in **Figure 5d**. The EDTA-2Na solution (o.1 M) followed by water was used for successful elution and simultaneous regeneration. It was found that the removal efficiency of Cu<sup>2+</sup> by Azo-POP-4 remained 95% after 5 cycles. This made the Azo-POPs very promising for the purification of drinking water in the future.

## 3.4. Aerobic C-H bond oxidation by Cu@Azo-POP-4

Realizing the fast removal of  $Cu^{2+}$  could be due to chelation between  $Cu^{2+}$  and the ortho-amino-azo moiety, we tried loading more of  $Cu^{2+}$  onto the backbone of the Azo-POPs. The resulted catalyst could serve as efficient solid catalyst for aerobic C-H bond oxidation.

#### 3.4.1. Synthesis and characterization of Cu@Azo-POP-4

The solid catalyst Cu@Azo-POP-4 was prepared by refluxing the as-synthesized Azo-POP-4 with Cu(OAc)<sub>2</sub> in ethanol for 12 h, with slightly decrease of the surface area and pore volume (**Figure S36**). The loading of Cu<sup>2+</sup> was measured to be as high as 61.7 mg/g by ICP-AES. The FT-IR spectra of catalyst Cu@Azo-POP-4 was also showed in **Figure S34**. It appeared the similar peak shifts for aromatic ring vibration and C-N to the FT-IR spectra of the Cu<sup>2+</sup> adsorption from water by Azo-POP-4, both of which illustrated the chelation between Cu and the ortho-amino-azo moiety on the backbone of the Azo-POP-4. The morphology of Cu@Azo-POP-4 was observed by TEM image (**Figure 6a**), the porous structure remained unchanged.



**Figure 6** The morphology of the catalyst Cu@Azo-POP-4. TEM images of (a) the catalyst and (c) the catalyst after reuse for 5 times. Dispersion of different elements in the catalyst of Cu@Azo-POP-4 (b) and (d) after 5 times' recycling.

XPS measurements were performed to investigate the coordination site and oxidation state of N and Cu species (**Figure S52-53**). The majority of N in the Azo-POP-4 were stable azo nitrogen, the binding energy (BE) at 397.9 eV, and the other peak with the BE of 400.6 eV for N 1s were associated with aryl amino group<sup>49, 50</sup>. The BE of N 1s in Cu@Azo-POP-4 catalyst exhibited a slightly higher value of 398.8 eV (azo nitrogen) and 401.2 eV (aryl amino) than that

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in Azo-POP-4, while the BE of P 2p showed no difference. This implied that Cu were coordinated at the azo and aryl amino sites in the polymer. Cu 2p3/2 of the catalyst exhibited a sharp peak at 934.2 ± 0.1 eV and a strong satellite peak on the higher BE site, which indicated the presence of divalent Cu species<sup>51</sup>. Additionally, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was used to investigate the dispersion of carbon, nitrogen and copper elements in catalyst Cu@Azo-POP-4 (**Figure 6b**). It showed that all the three elements dispersed highly uniformly within the Azo-POP-4, which corresponded to the specific attachment sites for precisely controlled Cu<sup>2+</sup> distribution within the frameworks. Such uniform dispersion mode could lead to a high catalytic activity of the Cu@Azo-POP-4.

## 3.4.2. Cu@Azo-POP-4 catalyzed C-H bond oxidation reaction

17 Metal-catalyzed C-H oxidation reaction has been developed 18 as one of the most important organic transformations in 19 chemical industry, owing to the serious pollution by 20 stoichometirc oxidants such as permanganate, pyridinium 21 chlorochromate and Dess-Martin periodinanes<sup>52</sup>. Various 22 oxidants such as hydrogen peroxide, *tert*-butyl 23 hydroperoxide (TBHP), oxygen and ozone have been used for the oxidation of C-H bond. Among them, oxygen was 24 obviously one of the most environmentally friendly and 25 cheap oxidants. And N-hydroxyphthalimide (NHPI) has been 26 proved as efficient co-catalyst53 owing to the formation of 27 phthalimide-*N*-oxyl reactive radical species (PINO)<sup>54</sup>, which 28 helped abstract a hydrogen atom in the C-H oxidation 29 reaction<sup>55</sup>. The metal used to generate PINO included Pb<sup>56</sup>, 30 Co<sup>57, 58</sup>, Cu<sup>59</sup> and so on. Catalytic tests in our work were 31 performed for the oxidation of various hydrocarbons with a 32 balloon of oxygen, using Cu@Azo-POP-4 (3 mol% based on 33 Cu) as catalyst and N-hydroxyphthalimide (NHPI) (10 mol%) 34 as co-catalyst. The reaction temperature and time were 35 optimized to be 80 °C and 12 h based on C-H oxidation on 36 diphenylmethane (Table S<sub>7</sub>), by monitoring the reaction 37 with TLC (Figure S65) and crude <sup>1</sup>H-NMR spectra (Figure **S49-50**). The yield was calculated to be 96% based on the 38 products isolated by flash column chromatography 39 purification. The selectivity of the C-H oxidation were 40 determined to be 99% by the ratio of desired ketone product 41 to the corresponding secondary alcohol and other related by-42 products based on GC-MS (Figure S59). Similar situation 43 was found for indane, when indane in CD<sub>3</sub>CN was subjected 44 to the aforementioned oxidation condition for 12 h. It gave 45 the desired indanone in a yield of 91% after column 46 chromatography. Based on the GC-MS, c.a. 92% selectivity 47 was obtained (Figure S58 and Entry 2 of Table 1). Besides, the TOF value was as high as 479 h<sup>-1</sup>, which were measured 48 after the first 3 h of reaction (Table **S**9). 49

As control experiments, the above aerobic C-H oxidation
gave much lower isolated yield without NHPI, without
Cu@Azo-POP-4, or without Cu loading and NHPI (Entries 3of Table 1 and Figure S38-40). The aerobic C-H oxidation
reaction with combination of Cu(OAc)<sub>2</sub> (3 mol%) and NHPI
gave 86% yield, lower than 91% yield by using the same
molar amount of copper catalyst. It revealed that the

combination of Cu@Azo-POP-4 and NHPI did play as an efficient catalyst system.

 Table 1
 NHPI/Cu@Azo-POP-4 catalyzed aerobic C-H

 oxidation of organic compounds



Cu@Azo-POP-4 was also used to catalyze the C-H oxidation of many hydrocarbons with benzylic methylene. It showed that the electro-donating substrates such as diphenylmethane, fluorene, xanthene, phthalan and benzyl methyl ether gave 94-97% yield (Entries 5-9 of Table 1 and Figure S42-46). However, the electro-deficient hydrocarbons such as difluorodiphenylmethane gave lower yield of 84% (Entry 10 of Table 1 and Figure S47) under the same condition, owing to the lower conversion of 92% based on GC-MS. Interestingly, crude NMR and GC-MS showed no other products than the desired ketone, meaning very good selectivity in the C-H oxidation within 12 h.

3.4.3. Recyclability of Cu@Azo-POP-4 for aerobic C-H bond oxidation

The stability and reusability of heterogeneous catalyst systems are crucial parameters for their practical applications. The recycling test of Cu@Azo-POP-4 for above aerobic C-H bond oxidation was conducted and the results showed in the **Table S8**. The Cu@Azo-POP-4 can be easily recovered by

filtration and reused for the next-run of C-H oxidation reaction. The C-H oxidation on indane with the recycled catalyst gave 85% isolated yield after 5 cycles, i.e. without significant loss of reactivity. The remaining Cu species in the crude product was measured to be 240-616 ppm by ICP-AES, which was about 1/30 of the case when Cu(OAc)<sub>2</sub> was used as catalyst (**Figure 7a and S43**).



**Figure 7** The Cu leaching of Cu@Azo-POP-4 during the recycling experiments. (a) The residual Cu<sup>2+</sup> in crude product of C-H oxidation on indane, catalyzed by recycled Cu@Azo-POP-4 and by Cu(OAc)<sub>2</sub> (3 mol% based on Cu<sup>2+</sup>). (b) The change of Cu<sup>2+</sup> loading in Cu@Azo-POP-4 after recycle test.

In addition, the copper content of Cu@Azo-POP-4 catalyst dropped 12% from 61.7 mg to 54.1 mg after 5 cycles. i.e., c.a. 2.5% copper loss for each cycle averagely. This corresponded to the low copper contamination of the crude product, much lower than the case of Cu(OAc)<sub>2</sub> catalyst. This also meant tight grasping of Cu by Azo-POP-4, which was especially crucial for heterogeneous catalysts for continuous operation without reactivation of recovered catalyst. TEM characterization confirmed that uniformly elemental distribution of Cu@Azo-POP-4 remained unchanged after 5 times' recycling (Figure 6c). The elemental mapping image (Figure 6d) showed the Cu still uniformly dispersed in the catalyst. Active Cu2+ species in the Cu@Azo-POP-4 catalyst were observed before and after catalysis based on EPR measurements (Figure S51), which showed two (instead of one) features were found at high field at 3470 and 3521 G<sup>60</sup>. In addition, XPS measurements were performed to further investigate the state of Cu (Figure S53-54). The BE of Cu on the catalyst after catalysis showed no difference from the freshly catalyst, indicating the stability of catalyst.

## 4. CONCLUSIONS

In conclusion, the triaminotriphenylazobenzene functionalized porous organic polymers (Azo-POP-4, Azo-POP-5 and Azo-POP-6) were designed and synthesized by pre- and in-situ-functionalization strategy. The key azocoupling polymerization between aryldiamine-derived dualdiazonium reagents and 1,3,5-triaminobenzene (1) worked well. Azo-POP-4 was found to remove Cu2+ very fast from water with high efficiency. Cu@Azo-POP-4 was developed as an efficient catalyst to catalyze the C-H bond oxidation of organic compounds. It gave excellent isolated yield and selectivity, as well as good reusability and low product contamination. The protocol reported in this paper will lead to fast access of densely-functionalized polymer materials with well-defined structure, which will attract interests in near future. Further application of Cu@Azo-POPs in transformations such as click reaction and ATRP

polymerization are undergoing, the relevant results will be reported in due course.

## ASSOCIATED CONTENT

#### Supporting Information

Additional FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, HR-MS for model compounds **5a-5c**, tables for optimization of synthetic conditions of Azo-POP-4, EA, TGA and PXRD for Azo-POP-4, Azo-POP-5 and Azo-POP-6, adsorption isotherms of Cu<sup>2+</sup> onto the Azo-POP-4, as well as the crude <sup>1</sup>H-NMR spectra for the key C-H oxidation reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interests.

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## REFERENCES

1. Sun, M.; Zhang, J.; Putaj, P.; Caps, V.; Lefebvre, F.; Pelletier, J.; Basset, J., Catalytic Oxidation of Light Alkanes (C1-C4) by Heteropoly Compounds. *Chem. Rev.* **2014**, 114, (2), 981-1019.

2. Marshall, C. W.; Ray, R. E.; Laos, I.; Riegel, B., 7-Oxo steroids. II. Steroidal  $3\beta$ -hydroxy- $\Delta$ 5-7-ones and  $\Delta$ 3,5-7-ones. *J. Am. Chem. Soc.* **1957**, 79, 6308-13.

3. Trost, B. M., The atom economy--a search for synthetic efficiency. *Science* **1991**, **2**54, (5037), 1471-7.

4. Sheldon, R. A., Atom efficiency and catalysis in organic synthesis. *Pure Appl. Chem.* **2000**, *72*, (7), 1233-1246.

5. Latimer, A. A.; Kulkarni, A. R.; Aljama, H.; Montoya, J. H.; Yoo, J. S.; Tsai, C.; Abild-Pedersen, F.; Studt, F.; Noerskov, J. K., Understanding trends in C-H bond activation in heterogeneous catalysis. *Nat. Mater.* **2017**, *16*, (2), 225-229.

6. Zaera, F., Nanostructured materials for applications in heterogeneous catalysis. *Chem. Soc. Rev.* **2013**, 42, (7), 2746-2762.

7. Shi, R.; Zhao, J.; Liu, S.; Sun, W.; Li, H.; Hao, P.; Li, Z.; Ren, J., Nitrogen-doped graphene supported copper catalysts for methanol oxidative carbonylation: Enhancement of catalytic activity and stability by nitrogen species. *Carbon* **2018**, 130, 185-195.

8. Li, J.; Liu, G.; Shi, L.; Xing, Q.; Li, F., Cobalt modified Ndoped carbon nanotubes for catalytic C=C bond formation via dehydrogenative coupling of benzyl alcohols and DMSO. *Green Chem.* 2017, 19, (24), 5782-5788.

9. Sun, Q.; Dai, Z.; Meng, X.; Wang, L.; Xiao, F., Task-Specific Design of Porous Polymer Heterogeneous Catalysts beyond Homogeneous Counterparts. *ACS Catal.* **2015**, *5*, (8), 4556-4567.

10. Wu, J.; Xu, F.; Li, S.; Ma, P.; Zhang, X.; Liu, Q.; Fu, R.; Wu, D., Porous Polymers as Multifunctional Material Platforms toward Task-Specific Applications. *Adv. Mater.* **2019**, **31**, **201802922**.

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58 59

60

11. Gawande, M. B.; Goswami, A.; Felpin, F.; Asefa, T.; Huang, X.; Silva, R.; Zou, X.; Zboril, R.; Varma, R. S., Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis. *Chem. Rev.* **2016**, 116, (6), 3722-3811.

12. Zhao, Q.; Zhang, P.; Antonietti, M.; Yuan, J., Poly(ionic liquid) Complex with Spontaneous Micro-/Mesoporosity: Template-Free Synthesis and Application as Catalyst Support. J. Am. Chem. Soc. 2012, 134, (29), 11852-11855.

13. Ji, G.; Yang, Z.; Zhang, H.; Zhao, Y.; Yu, B.; Ma, Z.; Liu, Z., Hierarchically Mesoporous o-Hydroxyazobenzene Polymers: Synthesis and Their Applications in CO<sub>2</sub> Capture and Conversion. *Angew. Chem., Int. Ed.* **2016**, 55, (33), 9685-9689.

Wang, G.; Cao, Z.; Gu, D.; Pfänder, N.; Swertz, A.;
 Spliethoff, B.; Bongard, H.; Weidenthaler, C.; Schmidt, W.; Rinaldi,
 R.; Schüth, F., Nitrogen-Doped Ordered Mesoporous Carbon
 Supported Bimetallic PtCo Nanoparticles for Upgrading of
 Biophenolics. Angew. Chem., Int. Ed. 2016, 55, (31), 8850-8855.

Madrid, E.; Rong, Y.; Carta, M.; McKeown, N. B.; MalpassEvans, R.; Attard, G. A.; Clarke, T. J.; Taylor, S. H.; Long, Y.; Marken,
F., Metastable Ionic Diodes Derived from an Amine-Based Polymer
of Intrinsic Microporosity. *Angew. Chem. Int. Ed.* 2014, 53, (40),
10751-10754.
16 Thao, D.; Liu, X.; Guo, J.; Xu, H.; Zhao, Y.; Lu, Y.; Sun, W.

19 16. Zhao, D.; Liu, X.; Guo, J.; Xu, H.; Zhao, Y.; Lu, Y.; Sun, W.,
20 Porous Metal-Organic Frameworks with Chelating Multiamine Sites
21 for Selective Adsorption and Chemical Conversion of Carbon
22 Dioxide. *Inorg. Chem.* 2018, 57, (5), 2695-2704.

17. Van Humbeck, J. F.; McDonald, T. M.; Jing, X.; Wiers, B. M.; Zhu, G.; Long, J. R., Ammonia Capture in Porous Organic Polymers Densely Functionalized with Brønsted Acid Groups. *J. Am. Chem. Soc.* **2014**, 136, (6), 2432-2440.

Chem. Soc. 2014, 136, (6), 2432-2440.
Mondal, J.; Kundu, S. K.; Hung Ng, W. K.; Singuru, R.;
Borah, P.; Hirao, H.; Zhao, Y.; Bhaumik, A., Fabrication of Ruthenium Nanoparticles in Porous Organic Polymers: Towards
Advanced Heterogeneous Catalytic Nanoreactors. Chem. - Eur. J.
2015, 21, (52), 19016-19027.

19. Arai, I.; Sei, Y.; Muramatsu, I., Preparation of 1,3,5triaminobenzene by reduction of phloroglucinol trioxime. *J. Org. Chem.* **1981**, 46, (22), 4597-4599.

20. Lu, W.; Yuan, D.; Sculley, J.; Zhao, D.; Krishna, R.; Zhou, H., Sulfonate-Grafted Porous Polymer Networks for Preferential CO2 Adsorption at Low Pressure. *J. Am. Chem. Soc.* **2011**, 133, (45), 18126-18129.

21. Zhang, X.; Lv, Y.; Liu, X.; Du, G.; Yan, S.; Liu, J.; Zhao, Z., A hydroxyl-functionalized microporous organic polymer for capture and catalytic conversion of CO<sub>2</sub>. *RSC Adv.* **2016**, 6, (80), 76957-76963.

22. Mason, C. R.; Maynard-Atem, L.; Heard, K. W. J.; Satilmis, B.; Budd, P. M.; Friess, K.; Lanc, M.; Bernardo, P.; Clarizia, G.; Jansen, J. C., Enhancement of CO<sub>2</sub> Affinity in a Polymer of Intrinsic Microporosity by Amine Modification. *Macromolecules* **2014**, 47, (3), 1021-1029.

43 23. Hei, Z.; Huang, M.; Luo, Y.; Wang, Y., A well-defined nitro-functionalized aromatic framework (NO2-PAF-1) with high CO2 adsorption: synthesis via the copper-mediated Ullmann homo-coupling polymerization of a nitro-containing monomer. *Polym.*46 *Chem.* 2016, 7, (4), 770-774.

24. Du, N.; Park, H. B.; Robertson, G. P.; Dal-Cin, M. M.; Visser, T.; Scoles, L.; Guiver, M. D., Polymer nanosieve membranes for CO2-capture applications. *Nat. Mater.* **2011**, 10, (5), 372-375.

49 25. Yue, Y.; Zhang, C.; Tang, Q.; Mayes, R. T.; Liao, W.; Liao,
50 C.; Tsouris, C.; Stankovich, J. J.; Chen, J.; Hensley, D. K.; Abney, C.
51 W.; Jiang, D.; Brown, S.; Dai, S., A Poly(acrylonitrile)-Functionalized
52 Porous Aromatic Framework Synthesized by Atom-Transfer Radical
53 Polymerization for the Extraction of Uranium from Seawater. *Ind.*54 26 Hei, Z.; Huang, M.; Luo, Y.; Wang, Y. A. well-defined

54 26. Hei, Z.; Huang, M.; Luo, Y.; Wang, Y., A well-defined
55 nitro-functionalized aromatic framework (NO2-PAF-1) with high
56 CO2 adsorption: synthesis via the copper-mediated Ullmann homo57 coupling polymerization of a nitro-containing monomer. *Polym.*

Chem. 2016, 7, (4), 770-774.

27. Zhou, J.; Luo, X.; Liu, X.; Qiao, Y.; Wang, P.; Mecerreyes, D.; Bogliotti, N.; Chen, S.; Huang, M., Azo-linked porous organic polymers: robust and time-efficient synthesis via NaBH4-mediated reductive homocoupling on polynitro monomers and adsorption capacity towards aniline in water. *J. Mater. Chem. A* 2018, 6, (14), 5608-5612.

28. Yoon, K.; Dong, G., Modular In Situ Functionalization Strategy: Multicomponent Polymerization by Palladium/Norbornene Cooperative Catalysis. *Angew. Chem., Int. Ed.* **2018**, *57*, (28), 8592-8596.

29. Yu, S.; Mahmood, J.; Noh, H.; Seo, J.; Jung, S.; Shin, S.; Im, Y.; Jeon, I.; Baek, J., Direct Synthesis of a Covalent Triazine-Based Framework from Aromatic Amides. *Angew. Chem., Int. Ed.* **2018**, 57, (28), 8438-8442.

Patel, H. A.; Je, S. H.; Park, J.; Chen, D. P.; Jung, Y.; Yavuz,
C. T.; Coskun, A., Unprecedented high-temperature CO2 selectivity in N2-phobic nanoporous covalent organic polymers. *Nat. Commun.* 2013, 4, 1357.

31. Chen, Q.; Luo, M.; Hammershoej, P.; Zhou, D.; Han, Y.; Laursen, B. W.; Yan, C.; Han, B., Microporous Polycarbazole with High Specific Surface Area for Gas Storage and Separation. *J. Am. Chem. Soc.* **2012**, 134, (14), 6084-6087.

32. Chen, G.; Wang, J.; Jin, F.; Liu, M.; Zhao, C.; Li, Y.; Dong, Y., Pd@Cu(II)-MOF-Catalyzed Aerobic Oxidation of Benzylic Alcohols in Air with High Conversion and Selectivity. *Inorg. Chem.* **2016**, 55, (6), 3058-3064.

33. Liu, Y.; Gao, T.; Chen, X.; Li, K.; Ma, Y.; Xiong, H.; Qiao, Z., Mesoporous Metal Oxide Encapsulated Gold Nanocatalysts: Enhanced Activity for Catalyst Application to Solvent-Free Aerobic Oxidation of Hydrocarbons. *Inorg. Chem.* **2018**, 57, (20), 12953-12960. 34. Chen, J.; Li, M.; He, W.; Tao, Y.; Wang, X., Facile Organocatalyzed Synthesis of Poly(ε-lysine) under Mild Conditions. *Macromolecules* **2017**, 50, (23), 9128-9134.

35. Thomaides, J.; Maslak, P.; Breslow, R., Electron-rich hexasubstituted benzene derivatives and their oxidized cation radicals, dications with potential triplet ground states, and polycations. *J. Am. Chem. Soc.* **1988**, 110, (12), 3970-9.

36. Hasegawa, M.; Horie, K., Photophysics, photochemistry, and optical properties of polyimides. *Prog. Polym. Sci.* 2001, 26, (2), 259-335.

37. Ma, D.; Zhang, J.; Zhang, C.; Men, Y.; Sun, H.; Li, L.; Yi, L.; Xi, Z., A highly efficient dual-diazonium reagent for protein crosslinking and construction of a virus-based gel. *Org. Biomol. Chem.* **2018**, 16, (18), 3353-3357.

38. Huang, M.; Deng, H.; Posson, P.; Liu, X.; Luo, X., New preparation of 1,3,5-triaminobenzene. *Chinese Inventory Patent* **2018**, 101718474.

39. Chaoui, N.; Trunk, M.; Dawson, R.; Schmidt, J.; Thomas, A., Trends and challenges for microporous polymers. *Chem. Soc. Rev.* **2017**, 46, (11), 3302-3321.

40. Chakraborty, S.; Colon, Y. J.; Snurr, R. Q.; Nguyen, S. T., Hierarchically porous organic polymers: highly enhanced gas uptake and transport through templated synthesis. *Chem. Sci.* 2015, 6, (1), 384-389.

41. Wang, X.; Wang, Z.; Chen, H.; Wu, Z., Removal of Cu(II) ions from contaminated waters using a conducting microfiltration membrane. *J. Hazard. Mater.* **2017**, 339, 182-190.

42. Tang, S.; Qiu, Y., Removal of copper(II) ions from aqueous solutions by complexation-ultrafiltration using rotating disk membrane and the shear stability of PAA-Cu complex. *Chem. Eng. Res. Des.* **2018**, 136, 712-720.

43. Liu, L.; Guo, X.; Tallon, R.; Huang, X.; Chen, J., Highly porous N-doped graphene nanosheets for rapid removal of heavy metals from water by capacitive deionization. *Chem. Commun.* 2017, 53, (5), 881-884.

44. Awual, M. R., New type mesoporous conjugate material for selective optical copper(II) ions monitoring & removal from polluted waters. *Chem. Eng. J.* **2017**, 307, 85-94.

45. Maity, J.; Ray, S. K., Competitive Removal of Cu(II) and Cd(II) from Water Using a Biocomposite Hydrogel. *J. Phys. Chem. B* **2017**, 121, (48), 10988-11001.

46. Maity, J.; Ray, S. K., Removal of Cu (II) ion from water using sugar cane bagasse cellulose and gelatin based composite hydrogels. *Int. J. Biol. Macromol.* **2017**, **97**, 238-248.

47. Ge, Y.; Cui, X.; Liao, C.; Li, Z., Facile fabrication of green geopolymer/alginate hybrid spheres for efficient removal of Cu(II) in water: Batch and column studies. *Chem. Eng. J.* **2017**, 311, 126-134.

48. Sahraei, R.; Sekhavat Pour, Z.; Ghaemy, M., Novel magnetic bio-sorbent hydrogel beads based on modified gum tragacanth/graphene oxide: Removal of heavy metals and dyes from water. *J. Clean. Prod.* **2017**, 142, 2973-2984.

49. Bera, R.; Ansari, M.; Alam, A.; Das, N., Triptycene, Phenolic-OH and Azo-functionalized Porous Organic Polymers: Efficient and Selective CO<sub>2</sub> capture. *ACS Appl. Mater. Interfaces* **2019,1, 959-968**.

50. Meng, N.; Ren, J.; Liu, Y.; Huang, Y.; Petit, T.; Zhang, B., Engineering oxygen-containing and amino groups into twodimensional atomically-thin porous polymeric carbon nitrogen for enhanced photocatalytic hydrogen production. *Energ. Environ. Sci.* **2018**, 11, (3), 566-571.

51. Puthiaraj, P.; Pitchumani, K., Triazine-Based Mesoporous Covalent Imine Polymers as Solid Supports for Copper - Mediated Chan–Lam Cross-Coupling N-Arylation Reactions. *Chem.–A Eur. J.* **2014**, 20, (28), 8761-8770.

52. Dess, D. B.; Martin, J. C., Readily accessible 12-I-5 oxidant for the conversion of primary and secondary alcohols to aldehydes and ketones. *J. Org. Chem.* **1983**, 48, (22), 4155-6.

53. Gaster, E.; Kozuch, S.; Pappo, D., Selective Aerobic Oxidation of Methylarenes to Benzaldehydes Catalyzed by N-Hydroxyphthalimide and Cobalt(II) Acetate in Hexafluoropropan-2-ol. *Angew. Chem., Int. Ed.* **2017**, 56, (21), 5912-5915.

54. Hruszkewycz, D. P.; Miles, K. C.; Thiel, O. R.; Stahl, S. S.,
Co/NHPI-mediated aerobic oxygenation of benzylic C-H bonds in
pharmaceutically relevant molecules. *Chem. Sci.* 2017, 8, (2), 12821287.

31 1207.
32 55. Mo, Y.; Jensen, K. F., Continuous N-Hydroxyphthalimide (NHPI)-Mediated Electrochemical Aerobic Oxidation of Benzylic C-H Bonds. *Chem. - Eur. J.* 2018, 24, (40), 10260-10265.

56. Coseri, S., N-Hydroxyphthalimide (NHPI)/lead
tetraacetate reactions with cyclic and acyclic alkenes. J. Phys. Org. *Chem.* 2009, 22, (5), 397-402.
Patil M. B.: Dedhia, N. P.: Kandi, A. B.: Kumar, A. V.

50 57. Patil, M. R.; Dedhia, N. P.; Kapdi, A. R.; Kumar, A. V.,
37 Cobalt(II)/N-Hydroxyphthalimide-Catalyzed Cross-Dehydrogenative
38 Coupling Reaction at Room Temperature under Aerobic Condition.
39 J. Org. Chem. 2018, 83, (8), 4477-4490.

J. Org. Chem. 2018, 83, (8), 4477-4490.
Zhang, P.; Wang, C.; Chen, Z.; Li, H., Acetylacetone-metal catalyst modified by pyridinium salt group applied to the NHPI-catalyzed oxidation of cholesteryl acetate. *Catal. Sci. Technol.* 2011, 1, (7), 1133-1137.

43 59. Arzumanyan, A. V.; Goncharova, I. K.; Novikov, R. A.;
44 Milenin, S. A.; Boldyrev, K. L.; Solyev, P. N.; Tkachev, Y. V.; Volodin,
45 A. D.; Smol'Yakov, A. F.; Korlyukov, A. A.; Muzafarov, A. M., Aerobic
46 siloxanols. *Green Chem.* 2018, 20, (7), 1467-1471.

60. Gao, F.; Walter, E. D.; Karp, E. M.; Luo, J.; Tonkyn, R. G.; Kwak, J. H.; Szanyi, J.; Peden, C. H., Structure–activity relationships in NH3-SCR over Cu-SSZ-13 as probed by reaction kinetics and EPR studies. *J. Catal.* **2013**, 300, 20-29.

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This paper reported the design and facile synthesis of well-defined functional porous organic polymers comprising triaminotriphenylazobenzene subunit. Their application for the fast removal of copper ions from water and copper catalyzed heterogeneous aerobic C-H bond oxidation were investigated. The Cu@Azo-POP-4 showed high catalytic reactivity, high selectivity, good reusability and low metal contamination on the product.

