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Azo-Linked Porous Organic Polymers: Robust and Time-Efficient Synthesis via NaBH₄-Mediated Reductive Homocoupling on Polynitro Monomers and Adsorption towards Aniline in Water

Jin-Xiu Zhou, ^{‡ [a]} Xian-Sheng Luo, ^{‡ [a]} Xiangxiang Liu, ^{* [a,b]} Yan Qiao, ^[c] Pengfei Wang, ^[c] David Mecerreyes, ^[d] Nicolas Bogliotti, ^[e] Shi-Lu Chen^[b], and Mu-Hua Huang^{*[a]}

Time-efficient synthetic methods of porous organic polymers are searched in order to extend the applications of those materials. In this work, we show a robust and time-efficient synthetic method of azo-linked porous organic polymers named Azo-POPs based on a NaBH₄-mediated reductive coupling polymerization on wellknown polynitro monomors. Azo-POPs were found to have high Brunauer–Emmett–Teller (BET) surface area and potential for aniline adsorption. Interestingly, Azo-POP-1 showed adsorption towards aniline as high as 1059.68 mg.g⁻¹ at 293K, which outperformed absorbent materials reported in literature.

Porous Organic Polymers (POPs)¹⁻³ have been attracting much attention owing to their potential applications in many areas, including gas adsorption^{4, 5}, separation⁶, heterogeneous catalysis⁷⁻⁹, drug delivery¹⁰ and water treatment¹¹. The POPs developed in the past two decades include covalent organic frameworks (COFs)^{12, 13}, hypercrosslinked polymers (HCP)², conjugated microporous polymers (CMP)¹⁴, polymers of intrinsic microporosity (PIMs)¹⁵, porous aromatic frameworks (PAFs)¹⁶ and so on. In addition, the introduction of functional groups to porous materials was reported as an efficient way to improve their adsorption capacity and selectivity. For example, the incorporation of sulfonic acid¹⁷, amino group¹⁸ and nitro group¹⁹ were all reported to enhance the CO₂ uptake of POPs. If the functional groups such as triazine^{20, 21}, imide²² ^{23, 24} and urethane²⁵ were involved inside the polymer backbone serving as linkages, interesting functional POPs resulted. The insertion of azo-linkage between two phenyl rings of well known PAF-1²⁶ lead to a new class of azo-linked porous organic polymers gas storage and selective CO₂ capture²⁷. Coskun and Yavuz group found azo group as CO₂-philic and N₂-phobic group in their Azo-COPs²⁸. Zhang group developed Azo-POF-1 and Azo-POF-2 and found them good candidates for selective CO₂ capture²⁹. Liu group developed Azo-MOP-1 for CO₂ adsorption and conversion³⁰. Besides gas uptake, azo-linked POPs were also reported for adsorption of organic pollutants in water³¹, which is a very important topic regarding environmental protection³².

(Scheme 1). Thus, EI-Kaderi group developed ALP-2 and ALP-3 for



Scheme 1 The synthetic methods of azo-linked porous organic polymers reported in literature.

As far as the synthetic method is concerned, azo-linked porous organic polymer usually involve long reaction time (Scheme 1). For instance, ALP-2 was made *via* oxidative coupling on tetra(4-aminophenyl)methane (TPM-4NH₂) in 48 hours²⁷. Azo-POF-1 was prepared via Zinc-mediated reductive coupling on tetra(4-nitrophenyl)methane (TPM-4NO₂) in 36 hours²⁹. Azo-COP-1 was synthesized via condensation between TPM-4NH₂ and TPM-4NO₂ in 24 hours²⁸ (Scheme 1). In this communication, a new time-efficient synthetic method of azo-linked POPs were presented *via* NaBH₄-mediated coupling on four-folded monomers containing nitro

^{a.} School of Materials Science and Engineering, Beijing Institute of Technology No. 5, Zhongguancun South Street, Beijing 100081, China

E-mail: <u>mhhuang@bit.edu.cn</u>

^{b.} School of Chemistry and Chemical Engineering, Beijing Institute of Technology No. 5, Zhongguancun South Street, Beijing 100081, China

E-mail: tdliuxiangxiang@126.com

^c The Biorefinery Research and Engineering Center, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

^{d.} POLYMAT, University of the Basque Country UPV/EHU

Joxe Mari Korta Center, 20018, Donostia-San Sebastián, Spain

^e PPSM, ENS Paris-Saclay, CNRS, Université Paris-Saclay, 94235 Cachan, France
[‡]These authors contributed equally to this work.

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groups (Scheme 1 and Scheme 2). This method was extended to synthesize Azo-POP-1, Azo-POP-2 and Azo-POP-3 by conventional heating. In addition, the adsorption performance of Azo-POP-1 towards aniline in water was tested by nuclear magnetic resonance (NMR) technique.



Scheme 2 Synthesis of Azo-POP-1, Azo-POP-2 and Azo-POP-3 by NaBH₄- mediated reductive coupling on TPM-4NO₂, TPA-4NO₂ and TPE-4NO₂.

The nitro compounds used in this work are usually the precursors to corresponding amino compounds, and thus more easily accessible. In this work, the monomers having four *para*-nitrophenyl moieties were prepared by modifying the known synthetic procedure (see see ESI), such as TPM-4NO₂ with a carbon central unit³³, TPA-4NO₂ with adamantane central unit³⁴ and TPE-4NO₂ with ethene central unit³⁵. It's worth to note that rich chemistry about reductive coupling of nitro aromatics have been developed for small organic molecules³⁶⁻⁴⁰, and versatile compounds containing azo group are available³⁷, which is good model for polymerization.

With this in mind, we tried the reductive coupling with Et₃N·H₂CO₃/Mg/MeOH⁴¹ initially (Entry 1 in Table S1) on TPM-4NO₂. But it was found no reaction took place by thin layer chromatography (TLC) and ¹H-NMR. Then, strong reducing reagent of LiAlH₄ was tested, full conversion of starting materials of TPM-4NO₂ was observed. And a solid product (Azo-POP-1-2) with BET surface area of 25 $\text{m}^2 \cdot \text{g}^{\text{-1}}$ was obtained by drying sample in high vacuo (Entry 2 in Table S1). Interestingly, the try with NaBH₄ as reducing reagent afforded a powdered product (Azo-POP-1-3) with BET surface area (SA) of 279 m²·g⁻¹ (Entry 3 in Table 1 and Figure S1). Encouraged by this result, further optimization was carried out focusing on NaBH₄ by measuring the BET SA of the powder product. Lowering the concentration of monomer from 0.08 M to 0.04 M, BET SA of Azo-POP-1-4 increased to 897 m²·g⁻¹ (Entry 4 in Table S1 and Figure S2). Different from the Zn/NaOH condition²⁹, the combined solvent of DMF/THF did not help increase the BET SA greatly (Entry 5 in Table 1 and Figure S3). Interestingly, when THF was used instead of acetone for the washing solvent in the work-up, the obtained Azo-POP-1-6 has BET SA of 1074 m²·g⁻¹(Entry 6 in Table 1, Figure S4). Further decreasing the concentration from 0.04 M to 0.03 M, gave Azo-POP-1-7 with the BET SA of 1221 m²·g

¹(Entry 7 in Table S1 and Figure S5), using pure DMF as solvent. The similar phenomenon of lower concentration favouring preparation of polymers has been observed previously⁴², possibly ascribed to the improved development of network structure and branched particles in more diluted solution. Finally, the drying way of lyophilisation did increase the BET SA of Azo-POP-1 to 1478 m²·g⁻¹ (Entry 8 in Table S1 and Figure 1).

For the typical procedure, a solution of NaBH₄ in DMF was added dropwise to a hot solution of TPM-4NO₂ in DMF in 15 minutes, the solution was stirred at 85 °C for another 15 minutes. Once the NaBH₄ met polynitro compound in hot DMF, a dark blue mixture was observed, which was supposed to be the formation of polynitroso monomer. The resulting brown solid product was collected by filtration in 94% yield. To our delight, the preparation was carried out in air, and scalable to 5-gram scale (see ESI). With the good result obtained in Azo-POP-1, we immediately tested the generality of our procedure on TPA-4NO₂ and TPE-4NO₂ (Scheme 2). The treatment of TPA-4NO₂ with NaBH₄ gave Azo-POP-2 in 99% yield (Scheme 2). In the case of Azo-POP-3, the yield of 92% was obtained by treating TPE-4NO₂ with NaBH₄ in 30 minutes.

The surface area (SA) and porosity of Azo-POPs were investigated by nitrogen adsorption–desorption isotherms at 77 K (Figure 1).



Figure 1 Nitrogen sorption-desorption isotherms of Azo-POPs at 77 K and their pore size distributions.

The isotherms of Azo-POPs were attributed to a combination of type I and II nitrogen sorption isotherms according to the IUPAC classification. A rapid uptake at low pressure (0–0.1 bar) suggests the presence of permanent micropore, and mesopore shown at high pressure (0.9–1.0 bar). The SA of Azo-POP-1 was found to be 1478 m²g⁻¹ base on BET model. *It's higher than known azo-linked POPs such as ALP-2²⁷, Azo-COP-1²⁸ and Azo-POF-1²⁹(Table 1). It's even higher than ALP-1 (1235 m²g⁻¹)²⁷ and Azo-Trip (510 m²g⁻¹) ⁴³ with triptycene network. However, the reaction time for making Azo-POPs is much shorter than the corresponding azo-linked POPs (Table 1). In the case of Azo-POP-2 and Azo-POP-3, BET SA of 608 and 497 cm².g⁻¹ was obtained respectively (Figure 1a and Table S5-6). The pore size distribution (PSD) based on the HK model has been employed to obtain pore sizes centered at ca. 0.7 nm (Figure 1b).*

Table 1 SA and reaction time required for TPM-based azo-linked POPs

	ALP-2	Azo-COP-1	Azo-POF-1	Azo-POP-1
BET SA (m ² .g ⁻¹) ^a	1065	729	755	1478
Reaction time (h)	48	24	36	0.5
Ref	27	28	29	This work

The chemical structure of the as-prepared Azo-POPs was characterized by multiple spectral methods. The presence of azobond in Azo-POP-1, Azo-POP-2 and Azo-POP-3 was confirmed by Published on 02 March 2018. Downloaded by Fudan University on 03/03/2018 07:44:17.

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the absorption peaks at ca. 1450 cm⁻¹ and 1400 cm⁻¹ in FT-IR spectra (Figure 2), which was ascribed to be asymmetric vibration of azobond.



Figure 2 The Infra Red spectra of Azo-POPs: (a) full spectra and (b) the expanded spectra of Azo-POPs.

The typical $\pi\pi^*(\sim 400 \text{ nm})$ and $n\pi^*(\sim 500 \text{ nm})$ bands of azobenzene was seen in Azo-POP-1's solid UV-vis spectrum⁴⁴ (Figure S6). Interestingly, the azo group in Azo-POP-1 were observed to be cis-N=N as major based on its Raman spectrum⁴⁵ (Figure S23). The strong peak at 1452 cm⁻¹ corresponded to *cis*-N=N, and weak peak at 1403 cm⁻¹ corresponded to *trans*-N=N. In the case of Azo-POP-3, the characteristic peaks of 1446cm⁻¹ and 1397 cm⁻¹ were observed (Figure S24), shifted to shorter wavelength compared with Azo-POP-1. It could be possibly caused by conjugation through C=C bond in TPE subunit. The structure of the polymer is further supported by its ¹³C CP/MS NMR spectrum, showing a characteristic peak at ca. 152 ppm belonging to -C-N=N- for Azo-POPs. Also, the comparison between the ¹³C CP/MAS NMR of Azo-POPs and ¹³C-NMR of corresponding monomers (Figure S20-22) further supported the existence of desired polymer backbone. The above results were confirmed by the elemental analysis data, close to the corresponding theoretical value of Azo-POPs (Table S2). And the spectra of our as-prepared polymers were super similar to the reported data for ALP-2²⁷, azo-POF-1²⁹ and azo-COP-1²⁸, indicating the right materials obtained.

Based on the above experimental phenomenon and structural characterization, the mechanism of reductive homocoupling polymerization was proposed (Scheme S1). The polynitro monomer was reduced quickly by NaBH₄ to give polynitroso monomer, which dimerized to give the azodioxy-linked polymer⁴⁶. And it was further reduced by NaBH₄ to afford Azo-POPs. The *cis*-azo- group could be formed in the dimerization step at 85 °C. Once it was formed to build the network, the *cis*-configuration was locked inside the polymer network.

As adsorbent materials, Azo-POPs showed good thermal stability based on TGA (Figure S7-9). It started to decompose at 241 °C for Azo-POP-1, 227 °C for Azo-POP-2 and 212 °C for Azo-POP-3. And it started to lose weight of ca. 10-15% at above 300 °C, which could correspond to the release of nitrogen (Table S2). The non-ordered and amorphous structure of Azo-POPs was proved by powder X-ray diffraction (PXRD) measurement on them (Figure S31-33).

Considering the azo linkage in the polymer backbone, we wonder if other applications than gas uptake could be performed. And the adsorption of organic pollutants such as aniline has attracted much attention recently⁴⁷⁻⁵⁰. In addition to UV-Vis spectrum and HPLC used in the solution adsorption experiment, NMR could be a powerful tool⁵¹ to quantitatively estimate the accurate contaminant structure and amount. Herein, NMR was employed to quantitatively detect the adsorption of aniline by Azo-POP-1 (Figure S25-S29), with D_2O as solvent and 10 mM sodium acetate as external standard. A control experiment was carried out by measuring the NMR of the aniline in D_2O before and after filtration through filter membrane, which revealed no adsorption of filter toward aniline in water (Figure S30). The adsorption kinetics of adsorption towards aniline was fitted using the pseudo-first (PFO) and pseudo-second order (PSO) kinetic models (Figure 3a-b). From the corresponding correlation coefficients (R^2) and adsorption rate constants given in Table S3, the adsorption kinetics of aniline on Azo-POP-1 were best-fitted by the PFO rate equation, and the aniline rapidly diffused into the high surface area of Azo-POP-1 to achieve equilibrium.



Figure 3 Adsorption behaviour of aniline onto the Azo-POP-1. Adsorption kinetics at 293 K fitted by PFO (a) and PSO (b) kinetics model. Adsorption isotherms at different temperatures fitted by Langmuir (c) and Freundlich (d) isotherm model.

The adsorption activity of Azo-POP-1 was investigated by describing the adsorption isotherm. Langmuir and Freundlich isotherm equations were applied to fit the data (Figure 3c-d), and isotherm parameters were calculated (Table S4). According to the R^2 value, no significant difference suggested the preference of one isotherm model to the other, though it was seen that the Langmuir isotherm might better describe aniline adsorption on Azo-POP-1.



Figure 4 Comparison of Azo-POP-1 with other adsorbent materials for aniline adsorption reported in the literature.

The maximum adsorption capacity was as high as 1059.68 mg/g at 293 K, based on the Langmuir isotherm model as following formula:

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 $\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}}, \text{ where } q_e \text{ is the equilibrium adsorption capacity of aniline; } C_e \text{ is the equilibrium concentration of aniline in the solution; } q_{max} \text{ is the monolayer adsorption capacity; and } K_L \text{ is the equilibrium constant of Langmuir adsorption model (see ESI).}$

It was much higher than other adsorbent materials reported for aniline (Figure 4), such as hypercrosslinked polymers (HCPs, 769.23 mg.g⁻¹)⁴⁷, sawdust- β -CD polymer (SD- β -CD, 84.00 mg.g⁻¹)⁵², molecular imprinted polymers (MIPs, 0.76 mg.g⁻¹)⁴⁸, Graphitic carbon nitride (g-C₃N₄, 93.40 mg.g⁻¹)⁴⁹, and manganese oxide-modified diatomite (Mn-D, 42.90 mg.g⁻¹)⁵⁰.

In addition, the adsorption of aniline onto the Azo-POP-1 was exothermic base on fact that the adsorption capacity decreased along with the temperature increased. The strong adsorption ability of Azo-POP-1 towards aniline, could be a result of the hydrophobic π - π interactions and the potential hydrogen bond interaction between aniline and Azo-POP-1.

In summary, this paper reported a time-efficient and robust preparation of Azo-POPs by reductive coupling polymerization on nitro-containing monomers. The as-prepared Azo-POPs were found to have high BET SA and be good candidates as absorbent materials towards aniline in water. The preparation of more Azo-POPs by our methodology and further applications in removal of organic pollutants from water is now undergoing in our lab. The relevant results will be reported in due course.

There are no conflicts of interest to declare.

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