Electronic Supplementary Information

Azo-Linked Porous Organic Polymers: Robust and Time-Efficient Preparation 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]}

^{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>

E-mail: tdliuxiangxiang@126.com

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

^{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.

Table of Contents

General Information for materials and measurements:	1
Syntheses of monomers and Azo-POPs:	2
Synthesis of Azo-POP-1	2
Synthesis of Azo-POP-2.	3
Synthesis of Azo-POP-3.	5
Adsorption of Azo-POPs towards aniline	7
Kinetic adsorption studies on aniline	7
Isotherm adsorption studies on aniline	8
Tables in ESI	9
Table S1 The optimization on the preparation and Brunauer-Emmett-Teller (BET) sur	face
area of Azo-POP-1	9
Table S2 Elemental analysis of Azo-POPs	9
Table S3 Kinetic parameters for aniline adsorption onto the azo-POP-1	10
Table S4 Adsorption isotherm model parameters for aniline adsorption onto azo-POP-1	10
Table S5 SA and reaction time required for making azo-linked POPs based on TPA	10
Table S6 SA and reaction time required for making azo-linked POPs based on TPE	10
Figures in ESI	11
Figure S1 Nitrogen sorption-desorption isotherm and pore size distribution of Azo-POP	-1-3
$(BET SA = 279 cm^2.g^{-1})$	11
Figure S2 Nitrogen sorption-desorption isotherm and pore size distribution of Azo-POP	-1-4
$(BET SA = 897 cm^2.g^{-1})$	12
Figure S3 Nitrogen sorption-desorption isotherm and pore size distribution of Azo-POP	-1-5
$(BET SA = 955 cm^2.g^{-1})$	13
Figure S4 Nitrogen sorption-desorption isotherm and pore size distribution of Azo-POP	-1-6
$(BET SA = 1074 cm^2.g^{-1})$	14
Figure S5 Nitrogen sorption-desorption isotherm and pore size distribution of Azo-POP	-1-7
$(BET SA = 1221 cm^2.g^{-1})$	15
Figure S6 Solid UV-Vis of Azo-POP-1	16
Figure S7 TGA of Azo-POP-1	16
Figure S8 TGA of Azo-POP-2	17
Figure S9 TGA of Azo-POP-3	17
Figure S12 The FT-IR spectrum of TPE-4NO ₂	20
Figure S13 ¹ H-NMR spectrum of TPM-4NO ₂ in DMSO-d6	21
Figure S14 The ¹³ C-NMR spectrum of TPM-4NO ₂ in DMSO-d6	22
Figure S15 The ¹ H-NMR spectrum of TPA-4NO ₂ in DMSO-d6	23
Figure S16 The ¹³ C-NMR spectrum of TPA-4NO ₂ in DMSO-d6	24
Figure S17 The ¹ H-NMR spectrum of TPE-4NO ₂ in CDCl ₃	25
Figure S18 The ¹³ C-NMR spectrum of TPE-4NO ₂ in CDCl ₃	26
Figure S22 The comparison between ¹³ C-NMR of TPE-4NO ₂ and ¹³ C-CP/MS NMR of A	Azo-
POP-3	30
Figure S23 Raman spectrum of Azo-POP-1	31
Figure S24 Raman spectrum of Azo-POP-3	32
- •	

Figure S25 Aniline standard curve using quantitative NMR.	.33
Figure S26 ¹ H-NMR spectra of aniline unabsorbed onto azo-POP-1 at different time	.34
Figure S27 ¹ H-NMR spectra of aniline unadsorbed onto azo-POP-1 with different ini	tial
concentrations at 293 K	.35
Figure S28 ¹ H-NMR spectra of aniline adsorption onto azo-POP-1 with different ini	tial
concentrations at 303 K.	.35
Figure S29 ¹ H-NMR spectra of aniline unadsorbed onto azo-POP-1 with different ini	tial
concentrations at 313 K.	.36
Figure S30 ¹ H-NMR spectra of aniline before and after filter (control experiment)	.36
Figure S31 XRD of Azo-POP-1.	.37
Figure S32 XRD of Azo-POP-2.	.37
Figure S33 XRD of Azo-POP-3.	.38
Schemes in ESI	.39

General Information for materials and measurements:

All chemicals were purchased from commercial suppliers (Sinopharm Chemical Regent Co.) and used without further purification, unless otherwise noted. The monomer of tetra(4-nitrophenyl)methane (TPM-4NO₂), tetra(4-nitrophenyl)adamantane (TPA-4NO₂) and tetra(4-nitrophenyl)ethene (TPE-4NO₂) were synthesized by modifying the reported methods.

Solution ¹H NMR spectra were taken by Varian Mercury-400 MHz or Bruker AV400 NMR spectrometer (1H at 400 MHz, 13C at 100 MHz). Solid-state 13C crosspolarization 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 4 mm MAS probe and ZrO₂ motor were used, and spin rates at 9000 Hz. Infrared spectra were recorded on a PerkinElmer Spectrum Two Fourier transform spectrometer. Raman spectra were recorded on a Micro Raman Imaging spectrometer by using a laser of 532 nm. 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 Q600 SDT (TA, US) Thermogravimetric Analyzer, heated from 25 °C to 800 °C at a rate of 5 °C/minute under N2 atmosphere. Solid UV-Vis measurement: A mixture of Azo-POP-1 and NaCl (ratio Azo-POP-1: NaCl = ca. 1 : 50 w/w) was finely powdered in a mortar. The resulting solid solution was placed between two microscope glass plates held together using adhesive tape. The absorption spectrum of the resulting sample was analyzed using an integration sphere linked to Cary 5000 absorption spectrometer from Agilent Technologies.

The specific surface areas of as-prepared Azo-POPs were screened using a GAPP V-Sorb 2800P BET surface area and pore volume analyser with a 5-point BET measurement between the pressure range of 0.05-0.35 P/P0. Polymer pore size distributions were measured by nitrogen adsorption and desorption at 77 K using a GAPP V-Sorb 2800P BET surface area and pore volume analyzer. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the HK pore model for pillared clay with cylindrical pore geometry. Samples were degassed at 130°C for over 12 h under vacuum before all gas analysis.

Syntheses of monomers and Azo-POPs:

Synthesis of Azo-POP-1.



Tetraphenylmethane (TPM). To a 500 ml flask was added triphenylchloromethane (65 g), aniline (194.7ml) and magnetic stirrer, the mixture was heated to 200°C for 3h. Then cool down to 90°C followed by the addition of methanol (194.7 ml) and conc. HCl (97 ml). The flask was stirred at 90°C for another 5 h. The mixture was filtered after cooling down to room temperature, washed by water (5×1000 ml) and ethanol (3×200 ml) to get light purples solid (75g, yield 86.5%). The 2000 ml beaker was added tetraphenylmethane aniline (hydrochloride) (75 g), acetonitrile (500 ml) and magnetic stirrer. Conc. HCl (275ml) and hypophosphite (187.5 ml) were added upon stirring. The mixture was heated to 40°C. Subsequently, sodium nitrite (10 M) aqueous solution was slowly dropped upon vigorous stirring. After the reaction was stirred for 6h, the mixture was filtered, and washed by water (5×1000 ml) and ethanol (3×200 ml). White solid was obtained after vacuum drying.

¹H-NMR(400MHz, CDCl₃) δ (ppm): 7.17-7.30 (m, 20H, Ar-H).

¹³C-NMR(100MHz, CDCl₃): 146.8; 131.2; 127.5; 125.9; 65.0.

Tetra (4-nitrophenyl)methane (TPM-4NO₂)^{1, 2}. Prepared by modifying a known procedure. To a cooled fuming nitric acid (270 ml) in a round bottom flask at -40 °C, was added Tetraphenylmethane (50 g, 156 mmol) portion-wise within 1.5 h. After the reaction mixture was stirred for 0.5 h at that temperature, acetic anhydride (85 ml) and glacial acetic acid (170 ml) were added. After another 1.5 h, the solid was washed by glacial acetic acid (2×150ml), followed by water (3×500 ml) and THF (2×250 ml). The title compound was obtained as a yellow solid (34.5 g, yield 44%).

¹H-NMR(400 MHz, DMSO-d6) δ (ppm): 8.20 (d, J = 8.9 Hz, 8H); 7.57 (d, J = 8.9 Hz,

8H).

¹³C-NMR(100 MHz, DMSO-d6) δ (ppm): 151.5; 146.5; 131.9; 124.3; 65.7.

FT-IR (cm⁻¹): 3111 (vw), 3081 (vw), 1606(w), 1591 (w), 1514 (s), 1494 (m), 1340 (vs), 1301 (m), 1109 (m), 1012 (w), 838 (s), 758 (w), 744 (s), 710 (s).

Azo-POP-1: To a solution of tetra (4-nitrophenyl)methane (5.0 g, 10 mmol) in DMF(300 ml) was added a solution of NaBH₄ (1.5 g, 40 mmol) in DMF(200 ml) portion-wise in 15 min. The resulting mixture was stirred under an air atmosphere at 85 °C for 15 min. Afterwards, the mixture was filtered and washed with DMF, HCl and water. The resulting swelling polymer was further washed with THF. After freezing drying, brown powder (3.5 g, yield 94%) was obtained.

¹³C CP/MS NMR, δ (ppm): 151.11, 147.21, 131.39, 122.12, 116.15, 65.20.

FT-IR (cm⁻¹): 3378 (vw), 3039 (vw), 1598 (w), 1492 (m), 1453 (m), 1403 (w), 1347 (w), 1289 (w), 1113 (w), 1011 (m), 831 (vs), 724 (m), 586 (s), 523(m).

EA: C (75.75%), N (14.41%), H (4.63%).

Synthesis of Azo-POP-2.



Tetra(4-nitrophenyl)adamantine (**TPA-4NO**₂)³ 1-Bromoadadamantane (50g) and AlCl₃ (2.5g) were added into 1000ml three neck flask. A condenser, funnel and magnetic stirrer was added. t-BuBr (52ml) was dissolved in benzene (500ml), the solvent was then slowly dropped under ice bath in 2h. NaOH aqueous solution was employed to absorb the emitted HCl. The mixture was then refluxed for 5h. The mixture was cooled to room temperature, filtered, and the residue was washed with acetone, chloroformed. The insoluble residue was dried, affording pure tetraphenyladamantane as a white solid (129.3g, yield 60%).

To a cooled fuming nitric acid (60 ml) in a round bottom flask at -40 °C, was added tetraphenyladamantane (8.4 g, 191 mmol) portion-wise within 1 h. After the reaction mixture was stirred for another 0.5 h at that temperature, a mixture of acetic anhydride (75 ml) and glacial acetic acid (100 ml) were added. After another 15 min, the solid resulted from the reaction mixture was washed by glacial acetic acid (2×50ml), followed by DMSO (2×70 ml) and ethanol (2×50 ml). The title compound was obtained as a yellow solid (34.5 g, yield 29.1%).

¹H-NMR(400 MHz, DMSO-d6) δ (ppm): 8.20 (d, *J* = 9.0 Hz, 8H); 7.91 (d, *J* = 9.0Hz, 8H).

¹³C-NMR(100 MHz, DMSO-d6) δ (ppm): 157.1; 146.3; 127.41; 123.75; 45.1. FT-IR (cm⁻¹): 3109 (vw), 2931 (vw), 2853 (vw), 1603 (m), 1592 (m), 1514 (s), 1494 (vs), 1113 (w), 1054 (w), 857 (m), 783 (w), 746 (m), 701 (m).

Azo-POP-2: To a solution of tetra (4-nitrophenyl)adamantane (6.2 g, 10 mmol) in DMF(300 ml) was added a solution of NaBH₄ (1.5 g, 40 mmol) in DMF(200 ml) 4 portion-wise in 15 min. The resulting mixture was stirred under an air atmosphere at 85 °C for 15 min. Afterward, the mixture was filtered and washed with DMF, HCl and water. The resulting swelling polymer was further washed with THF. After freezing drying, brown powder (4.9 g, yield 99%) was obtained. ¹³C CP/MS NMR, δ (ppm): 151.11, 147.21, 131.39, 122.12, 116.15, 65.20.

FT-IR (cm⁻¹): 3370 (w), 2928 (w), 2851 (w), 1599 (m), 1517 (s), 1450 (m), 1344 (vs), 1290 (w), 1112 (w), 1011 (w), 832 (s), 779 (m), 747 (m), 695 (m), 558 (s). EA: C (73.07%), N(9.82%), H (5.93%).

Synthesis of Azo-POP-3.



1,1,2,2-tetrakis(4-nitrophenyl)ethene (TPE-4NO₂)⁴ A suspension of zinc (7.18 g, 0.1098 mol) in dry THF (80 ml) was stirred under nitrogen at 0°C for 10 mins. TiCl₄ (6 ml, 0.0549 mol) was injected slowly over a period of 30 mins, the ice-salt-water bath was removed and the reaction mixture was heated under reflux for about 2h. After, a solution of benzophenone (5.00 g, 0.0274mol) in dry THF (20 ml) was added slowly using a needle/syringe and refluxed overnight. The reaction mixture was quenched with 5% aqueous solution of ammonium chloride (150ml, 5%w/v) and extracted with ethyl acetate (2×200 ml). The organic extracts were combined, washed with water, dried (MgSO₄), filtered and the solvent removed using a rotary evaporator. The crude product was washed with ethanol and filtered to yield a white crystalline solid (4.43 g, 97 %).

¹H-NMR(400 MHz, DMSO-d6) δ (ppm): 7.05-7.15 (m, 20H).

¹³C-NMR(100 MHz, DMSO-d6) δ (ppm): 140.7; 141.0; 131.3; 127.7; 126.4.

To a cooled fuming nitric acid (20 ml) and acetic acid (20 ml) in a round bottom flask at -40 °C, was added tetraphenylethene (2.0 g, 6.0 mmol) portion-wise within 0.5 h. After the reaction mixture was stirred for 0.5 h at that temperature. After the reaction temperature reached to 10 °C, the whole mixture was poured into ice, the solid was collected by filtration, washed with water and then dried, to give the title compound as a yellow solid (2.93 g, yield 95%).

¹H-NMR(400 MHz, CDCl₃) δ (ppm): 8.06 (d, J = 8.8 Hz, 8H); 7.20 (d, J = 8.8 Hz,

8H).

¹³C-NMR(100 MHz, DMSO-d6) δ (ppm): 147.6; 146.6; 140.9; 132.0; 123.6.

FT-IR (cm⁻¹): 3080 (vw), 2919 (vw), 2851 (vw), 1593 (m), 1515 (vs), 1408(vw), 1385 (vs), 1108 (w), 1014 (w), 837 (m), 810 (w), 748 (m), 705 (m).

Azo-POP-3: To a solution of tetra (4-nitrophenyl)ethene (5.1 g, 10 mmol) in DMF(300 ml) was added a solution of NaBH₄ (1.5 g, 40 mmol) in DMF(200 ml) portion-wise in 15 min. The resulting mixture was stirred under an air atmosphere at 85 °C for 15 min. Afterward, the mixture was filtered and washed with DMF, HCl and water. The resulting swelling polymer was further washed with THF. After freezing drying, brown powder (3.5 g, yield 92%) was obtained.

¹³C CP/MS NMR, δ (ppm): 151.1, 146.0, 131.4, 122.0.

FT-IR (cm⁻¹): 3368 (w), 3032 (w), 2921 (w), 1600 (s), 1510 (s), 1401 (m), 1279 (m), 1179 (m), 1106 (m), 1009 (w), 830 (vs), 789 (s), 744 (m), 572 (s), 504 (s).

EA: C (75.44%), N (12.52%), H (5.14%).

Adsorption of Azo-POPs towards aniline

The control experiment was carried out before all the adsorption experiments as following: A 1.5 mg/ml aniline aqueous was filtered by commercial Polyvinylidene Fluoride (PVDF) syringe filter with 0.22 um pore size and 13 mm diameter, which has negligible adsorption of aniline. The ¹H-NMR spectra of aniline before and after filtration is shown in Figure S30.

Kinetic adsorption studies on aniline

The batch kinetic adsorption experiments were performed with magnetic stirring at room temperature. 20 mg Azo-POP-1 was added to a 5 mL amber vial with 2 mL deuterium oxide (D₂O) to yield a 10 mg/mL suspension. The suspension was sonicated for 3 min to disperse evenly. After this procedure the suspension was added into the D₂O solution of aniline to form the final mixture contains 1 mg/mL Azo-POP-1 and 3 mg/mL aniline. Samples with volume of 0.5 mL were collected at certain time intervals and filtered with a 0.22 μ m syring filter (ANPEL). The residual aniline in D₂O was analyzed by ¹H-NMR (400MHz) using sodium acetate (NaAc) as external standard. The concentration of the residual aniline was calculated by the standard curve. The amount of adsorbed aniline (q_t) at time t was calculated using the following formula:

$$q_t = (C_0 - C_t)/V \tag{1}$$

where C_0 and C_t (mg/L) represent the concentrations of aniline at the initial and time *t*, respectively; *V* is the volume of aniline solution; q_t is the amount of adsorbed aniline at time *t*.

The amount of aniline adsorbed at different times were fitted by the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic mechanism models.

The formula of PFO kinetic model is expressed as follows:

$$q_t = q_e \left(1 - e^{\kappa_1 t} \right) \tag{2}$$

where k_1 (min⁻¹) is the rate constant of PFO model; q_e is the equilibrium adsorption capacity of aniline; q_t is the amount of adsorbed aniline at time t.

The formula of PSO kinetic model is expressed as follows:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_{ek_2 t}}$$
(3)

where k_2 (g/(mg·min⁻¹) is the rate constant of PSO model; q_e is the equilibrium adsorption capacity of aniline; q_t is the amount of adsorbed aniline at time t.

Isotherm adsorption studies on aniline

The isotherm experiments were conducted with magnetic stirring at 293, 303 and 313 K in thermostatic water bath for 18 h. 1.07 mg Azo-POP-1 and aniline stock solution was spiked to generate initial concentrations of 0.60, 1.35, 2.10, 2.85, 3.60, 4.35 and 5.10 mg/mL. The suspensions were stirred for 18 h to reach the equilibrium, then filtered by 0.22 μ m syring filter (ANPEL), and the filtrate was analyzed by ¹H-NMR (400 MHz) using NaOAc as external standard. The concentration of aniline was calculated by aniline standard curve. The equilibrium adsorption amount of aniline (q_e) was calculated using the formula (1). The isotherm data were fitted by the Langmuir and Freundlich isotherm models, and the formula of Langmuir isotherm model is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{4}$$

where q_e is the equilibrium adsorption capacity of aniline; C_e is the equilibrium concentration of aniline in the solution; q_{max} is the monolayer adsorption capacity; and K_L is the equilibrium constant of Langmuir adsorption model.

The formula of Freundlich isotherm model is expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

Where K_F is Freundlich adsorption model constant; 1/n is the heterogeneity factor. The Freundlich constant K_F and the affinity constant n are empirical constants that depend on several environmental factors.

Tables in ESI

		NO ₂ NO ₂ M-4NO ₂	$\xrightarrow{s^{s}}_{s^{s}} \xrightarrow{N=N}_{N=N} \xrightarrow{s^{s}}_{N=N} \xrightarrow{s^{s}}_{Azo-POP-1}$		
Entry	Reaction condition	[TPM-4NO ₂] ^c	Work-up method	Samples	$S_{BET}/m^2\!\cdot\!g^{\text{-}1}$
1	EtN·H ₂ CO ₂ , Mg, MeOH, 65min	0.08 M	b	b	b
2	LiAlH ₄ , THF, 65 °C ^a , 45 min	0.08 M	Acetone, vacuum dried@150 °Cd	Azo-POP-1-2	25
3	NaBH ₄ , DMF, 85 °C ^a , 30 min	0.08 M	Acetone, vacuum dried@150 °Cd	Azo-POP-1-3	279
4	NaBH ₄ , DMF, 85 °C ^a , 30 min	0.04 M	Acetone, vacuum dried@150 °Cd	Azo-POP-1-4	897
5	NaBH ₄ , DMF/THF, 85 °C ^a , 30 min	0.04 M	Acetone, vacuum dried@150 °Cd	Azo-POP-1-5	955
6	NaBH ₄ , DMF/THF, 85 °C ^a , 30 min	0.04 M	THF, vacuum dried@150 °C ^d	Azo-POP-1-6	1074
7	NaBH ₄ , DMF, 85 °C ^a , 30 min	0.03 M	THF, vacuum dried@150 °Cd	Azo-POP-1-7	1221
8 ª,oil bath te	NaBH ₄ , DMF, 85 °C ^a , 30 min mperature; ^b no any product insoluble i	0.03 M n DMF, and ¹ H-NM	THF, Freeze drying R showed no reaction took place; ^{c.} th	Azo-POP-1 ne molar concentra	1478 tion of monomer
tetra(4-nitro	phenyl)methane (TPM-4NO ₂); ^d carried	out at that temperatu	ire for 12 hours.		

Table S1 The optimization on the preparation and Brunauer-Emmett-Teller (BET) surface area of Azo-POP-1

Table	S2	Elemental	analysis	of A	zo-POPs
			5		

			Q	uality Perc	entage (%)			
Sample		Fou	ınd			Theoreti	cal ^a	
	Ν	С	Н	C/N	Ν	С	Н	C/N
Azo-POP-1	14.41	75.75	4.63	5.26	15.04	80.63	4.33	5.36
Azo-POP-2	9.82	73.07	5.93	7.44	11.37	82.90	5.73	7.29
Azo-POP-3	12.52	75.44	5.14	6.03	14.57	81.23	4.20	5.58

[a] Theoretical values were calculated assuming an ideal structure of Azo-POPs for the elemental analysis.

$C /(m \sigma/L)$	Pse	udo-first-ord	er	Pseudo-s	econd-order	
$C_0/(\text{Img/L})$	K ₁ (min ⁻¹)	q _e (mg/g)	R ²	$K_2(g/(mg \times min^{-1}))$	q _e (mg/g)	R ²
3769.82	5.398	622.10	0.979	-2.074×10 ⁴⁴	614.20	0.950

Table S3 Kinetic parameters for aniline adsorption onto the azo-POP-1.

Table S4 Adsorption isotherm model parameters for aniline adsorption onto azo-POP-1.

Tama anotara (V)	L	angmuir constants		Freu	ndlich const	ants
Temperature(K)	q _{max} (mg/g)	K _L (L/mol 10 ⁻⁴)	R ²	K _F (L/g)	n	R ²
293	1059.68	2.567	0.991	1.749	1.442	0.995
303	1059.57	2.175	0.992	1.066	1.346	0.993
313	847.46	2.117	0.993	1.123	1.415	0.989

Table S5 SA and reaction time required for making azo-linked POPs based on TPA.

	ALP-3	Azo-POP-2
BET SA (m ² .g ⁻¹) ^a	975	608
Reaction time (h)	48	0.5
Ref	5	This work

Table S6 SA and reaction time required for making azo-linked POPs based on TPE.

	Azo-POF-2	Azo-POP-3
BET SA (m ² .g ⁻¹) ^a	439	497
Reaction time (h)	36	0.5
Ref	6	This work

Figures in ESI



Figure S1 Nitrogen sorption–desorption isotherm and pore size distribution of Azo-POP-1-3 (BET SA = $279 \text{ cm}^2.\text{g}^{-1}$)



Figure S2 Nitrogen sorption–desorption isotherm and pore size distribution of Azo-POP-1-4 (BET SA = $897 \text{ cm}^2.\text{g}^{-1}$)



Figure S3 Nitrogen sorption–desorption isotherm and pore size distribution of Azo-POP-1-5 (BET SA = $955 \text{ cm}^2.\text{g}^{-1}$)



Figure S4 Nitrogen sorption–desorption isotherm and pore size distribution of Azo-POP-1-6 (BET SA = $1074 \text{ cm}^2.\text{g}^{-1}$)



Figure S5 Nitrogen sorption–desorption isotherm and pore size distribution of Azo-POP-1-7 (BET SA = $1221 \text{ cm}^2.\text{g}^{-1}$)



Figure S6 Solid UV-Vis of Azo-POP-1.



Figure S7 TGA of Azo-POP-1



Figure S8 TGA of Azo-POP-2



Figure S9 TGA of Azo-POP-3



Figure S10 The FT-IR spectrum of TPM-4NO₂



Figure S11 The FT-IR spectrum of TPA-4NO₂



Figure S12 The FT-IR spectrum of TPE-4NO₂



Figure S13 ¹H-NMR spectrum of TPM-4NO₂ in DMSO-d6



Figure S14 The ¹³C-NMR spectrum of TPM-4NO₂ in DMSO-d6



Figure S15 The ¹H-NMR spectrum of TPA-4NO₂ in DMSO-d6



Figure S16 The ¹³C-NMR spectrum of TPA-4NO₂ in DMSO-d6



Figure S17 The ¹H-NMR spectrum of TPE-4NO₂ in CDCl₃



Figure S18 The ¹³C-NMR spectrum of TPE-4NO₂ in CDCl₃



Figure S19 The ¹³C CP/MS NMR of Azo-POP-1.



Figure S20 The comparison between ¹³C-NMR of TPM-4NO₂ and ¹³C-CP/MS NMR of Azo-POP-1



Figure S21 The comparison between ¹³C-NMR of TPA-4NO₂ and ¹³C-CP/MS NMR of Azo-POP-2



Figure S22 The comparison between ¹³C-NMR of TPE-4NO₂ and ¹³C-CP/MS NMR of Azo-POP-3



Figure S23 Raman spectrum of Azo-POP-1





Figure S25 Aniline standard curve using quantitative NMR.

		/01.10	11				
t=0.34min	M		MM			1	
7.0 7.4 7.3	7.2 7.1	7.0 6.9	6.8 6.7 f1 (ppm)	6.6	1.9	1.8 1.7	1.6
t=0.69min	- M	100.01	M.			100.00	
7.5 7.4 7.3	7.2 7.1	7,0 6.9	6.8 6.7	• • • • •	11 1 1.9	1.8 1.7	1.6
t=1.08min		529.54	rt (ppm)			100.00	
	, M				··· · ·		
t=2.20min	7.2 7.1	7.0 6.9 10.62	6.8 6.7 f1 (pps)	6.6	1.9		1. 6
	'_M_'		M				
t=3 28min	7.2 7.1	7.0 6.9 98.83	6.8 6.7 f1 (ppm)	6.6	1, 9	1.8 1.7	1.6
t=3.20mm	- the		J.			-100.00	
· <u>····</u> ·······························		· · · ·		·	11 . 10		
t=4.41min	14	93.48	ri (ppm)			100.00	
			, <u></u>		11		
	14	96.31	tt (ppm)	6, 6	1.4		1.6
t=5.48min	· M				-		
. 7.4 7.3	7.2 7.1 A 15	0 6.9	6.8 6.7 ±1 (AA)	6.6	1.9	1.8 1.7	1.6
10.17min	M		Jun			100.00	
.5 7.4 7.3	7.2 7.1 15	03.74	6.8 6.7 f1 (ppn)	6.0	1.9	1.8 1.7	1.6
14.82min		03.74	6.8 6.7 f1 (ppn)	6, 0	1.9	1.8 1.7 	1.6
-14.82min		0 6.9	6.8 6.7 ft (pps)	6.0	· · · · · · · · · · · · · · · · · · ·	1.8 1.7 —100.00	1.6
.a 7.4 7.3 ■14.82min ■ 7.4 7.3	1.2 7.2 7.2 7.1 15	03.74 03.74	6.8 6.7 f1 (ppn) 6.8 6.7 f1 (ppn)	6,0		1.8 1.7 	1,6
:		03.74 03.74	6.8 6.7 f1 (ppa) 6.8 6.7 f1 (ppa)	6.0 6.6		1.8 1.7 	1.6 1.6
14.82min 14.82min 14.82min 1=30min		03.74 03.14 03.14	6.8 6.7 6.8 6.7 6.8 6.7 6.8 6.7	6, 0 1, 0 6, 6		1.8 1.7 	1. 6 L. 6
ta da da =14.82min = da da t=30min = da da	7.2 7.1 15 7.2 7.1 15	0.000000000000000000000000000000000000	6.8 0.7 6.8 0.7 6.8 0.7 6.8 0.7 6.8 0.7 6.7 6.7 6.7 6.7	6, 6		1.8 1.7 	1.6
t=30min t=60min	7.2 7.1 15 7.2 7.1 15	03.74 03.74 03.14	0.8 0.7 1 (rps] 0.8 0.7 1 (rps] 0.8 0.7 1 (rps] 0.7 1 (rps]	6,0		L8 L7 	1, 0 1, 0 1, 6
5 24 23 14.82min 5 24 25 t=30min 5 24 25 t=60min 74 7.8		03.74 03.74 03.14 0.9 08.65	6.8 6.7 1 (rps) 6.8 6.7 1 (rps) 6.8 6.7 1 (rps) 6.7 6.7 6.7	6, 6 6, 6	1.9 1.9 1.9	L8 L7 	1,0 1,0 1,0
14.82min 14.82min t=30min t=60min	7.2 7.2 7.2 7.2 7.2 7.1 15 7 15 15 15 15 15	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	6.8 6.7 1 (rps) 6.8 6.7 1 (rps) 6.7 6.7 6.7 6.7 6.7 6.7 6.7 6.7	6.6 6.6 6.6		L8 L7 	1,0 1,0 1,6
t=30min t=30min t=60min t=90min	7.2 7.1 15 7.2 7.1 15 7.2 7.1 15 7.2 7.1 15	1.0 1.9 003.74 0.3.14 0.9 08.65 08.65	6.8 6.7 1 (rps) 6.8 6.7 1 (rps) 6.8 6.7 1 (rps) 6.8 6.7 1 (rps) 6.7 1 (rps) 1	6.0		Ls L7 	1.6 L.6
5 24 23 14.82min 2 24 28 t=30min 5 24 28 t=60min 74 78 t=90min 24 23	7.2 7.1 7. 7.2 7.1 7.1 7.1 7. 7.2 7.1 7.1 7.1 7.1 7. 7.2 7.1 7.1 7.1 7.1 7.1 7.1 7.1 7.1 7.1 7.1	1.0 6.9 003.74 2.3.14 6.9 0.08.65	6.8 6.7 1. (ppa) 6.8 1. (ppa) 6.8 1. (ppa) 6.8 1. (ppa) 6.8 1. (ppa) 6.7 1. (ppa) 6.8 0.7 6.7 1. (ppa) 6.7 1. (ppa) 6.	0.0 10.0 10.0	1.9 1.9 1.9	L8 L7 	1.6 1.6 1.6
t=30min t=30min t=60min t=90min t=120min	1/2 1/1 1 1/2 1/1 1 1/2 1/1 1 1/2 1/1 1 1/2 1/1 1 1/2 1/1 1	0. 6.9 03.74 0.3.14 0.9 08.65 0.38 0.9 0.38	6.8 6.7 1. (spa) 6.8 1. (spa) 6.8 1. (spa) 6.8 1. (spa) 6.8 1. (spa) 6.7 6.8 1. (spa) 6.7 6.7 6.7 6.7 6.7 6.7 6.7 6.7	0,6		Ls L7 	1.6 1.6 1.6 1.6
t=30min t=30min t=60min t=90min t=120min	7.2 7.1 15 7.2 7.1 15 7.2 7.1 15 7.2 7.1 15	0.03.74 0.03.74 0.03.74 0.03.14 0.00.65 0.00.65 0.00.65 0.00 0.08.65 0.00 0.08.65 0.00 0.08.65	6.8 6.7 1 (rps) 6.8 6.7 1 (rps) 6.8 6.7 1 (rps) 6.8 6.7 6.8 6.7 6.8 6.7 6.8 6.7 6.8 6.7 6.8 6.7 6.7 6.7		1.9 1.9 1.9 1.9 1.9 1.9 1.9 1.9	Ls L7 	1.6 1.6
t=30min t=30min t=60min t=90min t=120min		0. 6.9 0. 74 0. 9 0.	6.8 6.7 1 (rps) 6.8 6.7 1 (rps) 6.8 6.7 6.8 6.7 6.8 6.7 6.8 6.7 6.8 6.7 6.8 6.7 6.8 6.7 6.7 (rps) 6.7 (rps)	6.0 0.6 0.6	1.9 1.9 1.9 1.9 1.9 1.9 1.9	L8 L7 -100.00 - L8 L7 -100.00 -	1.6 1.6
t=30min t=30min t=60min t=90min t=120min t=300min		0. 6.9 03.74 03.14 0.9 08.65 0.9 08.65 0.9 08.65 0.9 0.37 0.9 0.37	6.8 6.7 1 (real) 6.8 71 (real) 6.8 71 (real) 6.7 71 (real) 6.7 71 (real) 71 (real) 6.7 71 (real) 71 (r	6.0 0.0 0.0 0.0 0.0 0.0	1.9 1.9 1.9 1.9 1.9 1.9 1.9 1.9	L8 L7 	1.6 1.6
 t. t. t. t. t. t. <lit.< li=""> t. t.</lit.<>		1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	6.8 6.7 1. (pps) 6.8 1. (pps) 6.8 1. (pps) 6.8 1. (pps) 6.8 1. (pps) 6.8 1. (pps) 6.8 1. (pps) 6.7 1. (pps		1.9 1.9 1.9 1.9 1.9	L8 L7 	1.6 1.6 1.6
5 14.82min		1.0 6.9 003.74 	6.8 6.7 1. (pps) 6.8 1. (pps) 6.8 1. (pps) 6.8 0.7 1. (pps) 6.8 1. (pps) 6.8 1. (pps) 6.8 1. (pps) 6.7 6.8 1. (pps) 6.7 6.7 6.7 6.7 6.7 6.7 6.7 6.7	6.6 1 0.0 1 1 1 1 1 1 1 1 1 1 1 1 1	1.9 1.9 1.9 1.9 1.9	L8 L7 100.00 -	1.6 1.6 1.6

Figure S26 ¹H-NMR spectra of aniline unabsorbed onto azo-POP-1 at different time.



Figure S27 ¹H-NMR spectra of aniline unadsorbed onto azo-POP-1 with different initial concentrations at 293 K



Figure S28 ¹H-NMR spectra of aniline adsorption onto azo-POP-1 with different initial concentrations at 303 K.



Figure S29 ¹H-NMR spectra of aniline unadsorbed onto azo-POP-1 with different initial concentrations at 313 K.



Figure S30 ¹H-NMR spectra of aniline before and after filter (control experiment).



Figure S31 XRD of Azo-POP-1.



Figure S32 XRD of Azo-POP-2.



Figure S33 XRD of Azo-POP-3.

Schemes in ESI



Scheme S1 The plausible mechanism for the reductive homocoupling to form Azo-POPs.

References:

1. G. Li and Z. Wang, *Macromolecules*, 2013, 46, 3058-3066.

2. P. Ganesan, X. Yang, J. Loos, T. J. Savenije, R. D. Abellon, H. Zuilhof and E. J. R. Sudhoelter, *J Am Chem Soc*, 2005, **127**, 14530-14531.

3. O. Plietzsch, C. I. Schilling, M. Tolev, M. Nieger, C. Richert, T. Muller and S. Brase, *Org Biomol Chem*, 2009, **7**, 4734-4743.

- 4. J. H. Gorvin, J. Chem. Soc., 1959, 678-682.
- 5. P. Arab, M. G. Rabbani, A. K. Sekizkardes, T. Islamoglu and H. M. El-Kaderi, *Chem Mater*, 2014, **26**, 1385-1392.
- 6. J. Lu and J. Zhang, J Mater Chem a, 2014, 2, 13831-13834.