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Electronic Supplementary Information

Facile Synthesis of Porous polynorbornene with azobenzene subunit: Selective adsorption of 4-nitrophenol over 4-aminophenol in water

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1. General Information for characterization and measurements

All chemicals were purchased from commercial suppliers (Sinopharm Chemical Regent Co.) and used without further purification, unless otherwise noted. The monomer of were synthesized by modifying the reported methods[1]. Solution ^{1}H-NMR spectra were taken by Varian Mercury-400 MHz (^{1}H at 400 MHz, ^{13}C at 100 MHz). 2D ^{1}H DOSY-NMR spectra were taken by Varian Mercury-400 MHz under constant temperature of 20 °C. The pulse sequence named 'Dbppste' was used for DOSY experiment with parameters as 'ss=-8', 'il='y'', 'bs=4', delflag='y', del=0.15s and gt1=0.004s. The concentration of the test samples was maintained at 1 mg/0.4ml, *N*, *N*-Dimethylformamide-d7 and Chloroform-*d* were used as solvent. Diffusion coefficients (*D*) of polystyrene samples with known molecular weights (*Mw*) were obtained by DOSY. Thus, linear relationship between diffusion coefficients and molecular weights was fitted and calculated as Lg(*D*) = -0.5900*Lg(*Mw*)-3.4411 and Lg(*D*) = -0.5344*Lg(*Mw*)-3.2315. The diffusion coefficient of endo-PNBNPE, exo-PNBNPE and L-Azo-POP were measured by DOSY. And its molecular weight (*Mw*) was calculated through the linear relationship between diffusion coefficients and molecular weights. Solid-state cross-polarization magic angle spinning (CP-MAS) ^{13}C-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 ZrO_2 motor were used, and spin rates at 151 MHz. Infrared spectra were recorded on a PerkinElmer Spectrum Two Fourier transform 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 Q600 SDT (TA, US) thermogravimetric analyzer, heated from 25 ℃ to 800 ℃ at a rate of 10 ℃/minute under N_2 atmosphere. Solution UV-vis spectra were recorded on a Milton Roy Spectronic 3000 Array spectrophotometer. The morphologies of polymers were studied using a Hitachi S4800 scanning electron microscope (SEM) and FEIT Tecnai G2 F30 transmission electron microscope (TEM) working at 300 kV. N_2 adsorption/desorption studies were carried out at 77K using the BELSORP-MAX-II (BEL, Japan, Inc., Japan). BET surface area and pore volume were obtained by Brunauer-Emmett-Teller (BET) method between the pressure of 0.05-0.35 P/P_0. Polymer pore size distributions were calculated from the adsorption branches using non-local density functional theory (NLDFT) methods.

To obtain the binding energies to understand the selective adsorption towards 4-NP over 4-AP, various complexes between model compounds (see Table S10) and 4-nitrophenol (4-NP) /4-aminophenol (4-AP) were optimized. Many initial

configurations were tested and the optimized ones with the lowest energies (see Figure S30) were taken into the calculations of binding energies.

All calculations presented in this paper were performed using density functional theory (DFT) with the hybrid functional B3LYP[1–3] as implemented in Gaussian 09 package.[4] Geometry optimizations were carried out with the 6-31G(d,p) basis set. On the basis of the optimized geometries, more accurate energies were obtained by performing single-point calculations with a larger 6-311+G (2d,2p) basis set. Using an empirical formula by Grimme et al,[5-8] dispersion effects were taken into account throughout geometry optimizations and single-point calculations. Frequency calculations were performed at the same level of theory as in the optimizations to further confirm the nature of stationary points and to obtain zero-point energies (ZPE). The binding energies reported in this paper (given in Table S10) have been corrected for dispersion and ZPE effects.

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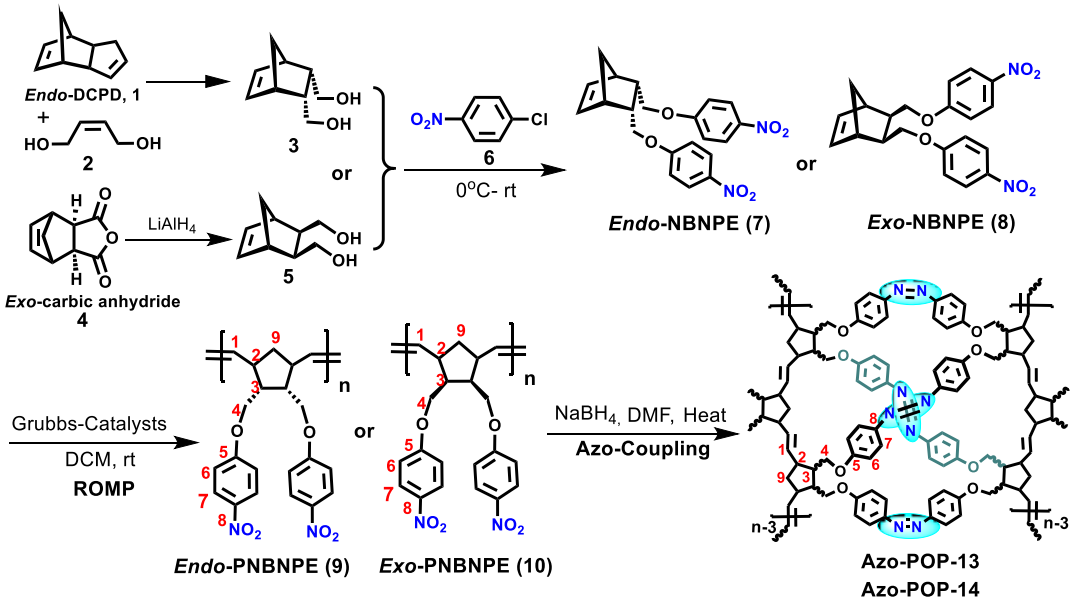
2. General Synthetic Procedures

The monomers endo-NBNPE (7), exo-NBNPE (8), linear polymers endo-PNBNPE (9) exo-PNBNPE (10), Azo-POP-13 and Azo-POP-14 were synthesized by the following scheme.

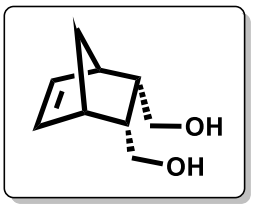


Scheme 1. The synthetic routes for Azo-POP-13 and Azo-POP-14

2.1 Synthesis of Azo-POP-13

2.1.1 Synthesis of *endo*-norbornene-dimethanol (3)

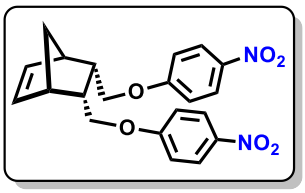
According to the previous reported synthetic procedure[1]: The dicyclopentadiene **1** (DCPD, 30 mL, 0.35 mol) was heated at 200 °C to give fresh cyclopentadiene (25 mL, 0.30 mol), which was mixed with *cis*-1,4-but-2-ene-diol **2** (18 mL, 0.2 mol) in a 250 mL of sealed tube. The whole mixture was heated at 210 °C (heating block) for 6 h. Upon cooling, the crystalline (14 g, 45%) was filtered off, the filtrate was dissolved in hot water (100 ml, 80 °C) and separated with funnel. The aqueous phase was dried on vacuum and heating, upon cooling, another crystalline (7.0 g, 23%) was obtained, with a total isolated yield of 68%.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.00 (t, J = 1.9 Hz, 2H), 4.27 (d, J = 4.5 Hz, 2H), 3.58 (dd, J = 9.6, 5.8 Hz, 2H), 3.32 (t, J = 10.4 Hz, 2H), 2.76 (h, J = 1.8 Hz, 2H), 2.55 – 2.40 (m, 2H), 1.36 (qt, J = 8.2, 1.7 Hz, 2H).

2.1.2 Synthesis of *endo*-NBNPE (7)

To a solution of *endo*-norbornene-dimethanol **3** (6.2 g, 40 mmol, 1.0 equiv.) in DMF (300 mL) were slowly added NaH (60 wt%, 3.4 g, 84 mmol，2.1equiv.) in the ice bath, and continue to stir for about 30min. Then 4-chloronitrobenzene **6** (15.6 g, 100 mmol, 2.5 equiv.) was added to above mixtures. The reaction mixture was stirred at room temperature overnight, then the reaction was quenched and diluted with ice-water. The crude material was poured into 400 mL of H_2O/EtOH (2: 1) to afford the title *endo*-NBNPE **7** as a precipitate, which was filtered, washed with water, and dried (13.8 g, 87%).

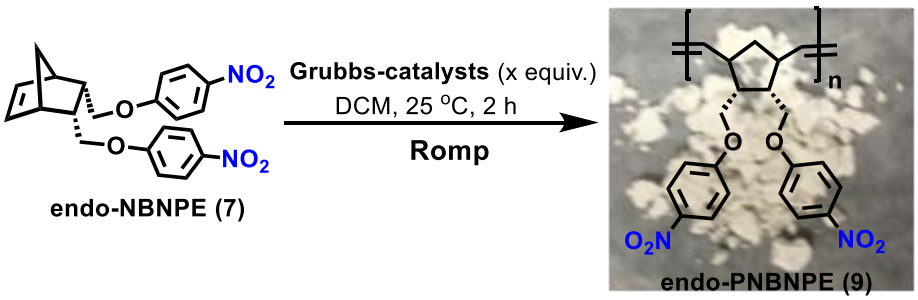


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 – 8.05 (m, 4H), 7.01 – 6.78 (m, 4H), 6.23 (t, J = 1.9 Hz, 2H), 4.01 – 3.91 (m, 2H), 3.80 (ddd, J = 9.2, 6.6, 2.2 Hz, 2H), 3.11 (p, J = 1.7 Hz, 2H), 2.84 (q, J = 6.3, 4.6 Hz, 2H), 1.64 (dt, J = 8.5, 2.0 Hz, 1H), 1.49 (dt, J = 8.5, 1.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 163.5, 141.3, 135.4, 125.7, 114.1, 68.8, 49.2, 45.4, 40.9.

HRMS (ESI): m/z calcd for $C_{21}H_{20}N_2O_6Na^+$ $[M+Na]^+$ 419.1214, found 419.1205.

FIT-IR (cm^{-1}): 2977 (vw), 2932 (vw), 1593 (vs), 1499 (vs), 1461 (w), 1331 (vs), 1250 (vs), 1174 (s), 1108 (ms), 1003 (ms), 837 (ms), 743 (ms), 688 (s), 643 (ms).

2.1.3 Synthesis of *endo*-PNBNPE (9)



Scheme 2. ROMP for Synthesis of *endo*-PNBNPE (9)

The synthetic procedure: To a solution of ***endo*-NBNPE** (**7**, 12.0 g, 30 mmol, 1.0 equiv.) in DCM (300 mL) were added Grubbs-II (240 mg, 0.3 mmol，0.01 equiv.) and stirred at room temperature about 2 hours, and then ethyl vinyl ether (1 mL, excess) was added to above solution. The reaction mixture was stirred for further 30min, and the mixture was dissolved in hot DMF (300 mL, 80°C). The above solution poured into 500 mL of water to yield a white precipitate, which was filtered, washed with water, and freeze-dried for ***endo*-PNBNPE** (**9**, 11.8 g, 96% yield).

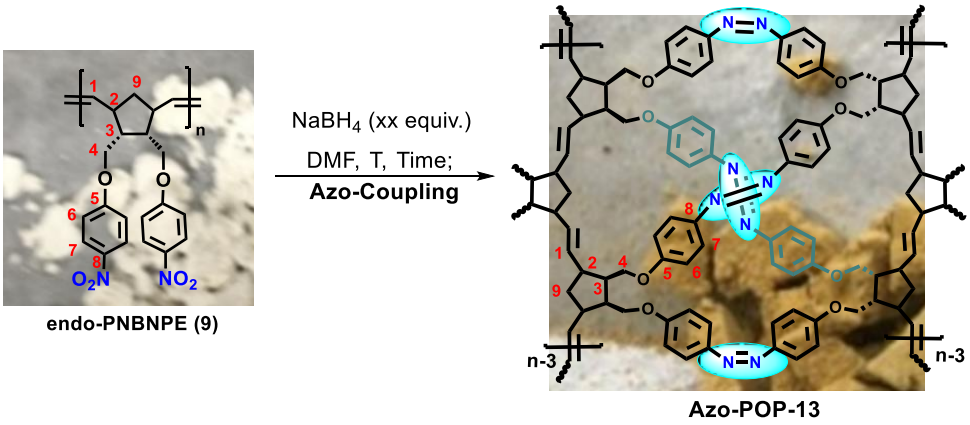
^{1}H NMR (400 MHz, DMF-d_7) δ (ppm): 8.34 – 8.07 (m, 4H), 7.33 – 7.09 (m, 4H), 5.98 – 5.60 (m, 2H), 4.37 (m, 4H), 3.69 (m, 2H), 3.14 – 2.73 (m, 2H), 2.46 – 2.07 (m, 1H), 1.75 (s, 1H); **^{13}C NMR** (100 MHz, DMF-d_7) δ (ppm): 164.2, 141.3, 132.4, 125.9, 114.9, 67.8, 45.4, 40.2, 38.5.

FT-IR (cm^{-1}): 3083 (vw), 2935 (ms), 2890 (ms), 1587 (vs), 1499 (vs), 1497 (vs), 1337 (vs), 1253 (vs), 1170 (s), 1112 (vs), 978 (s), 837 (ms), 743 (ms), 688 (s), 643 (ms).

Elemental Analysis: C (63.61%), N (6.99%), H (5.09%).

2D ^{1}H DOSY-NMR: molecular weight (*Mw*) = 105300 g.mol^{-1}.

2.1.4 Synthesis of Azo-POP-13



Scheme 3. Synthesis of Azo-POP-13 by azo-coupling polymerization

The Synthetic Procedure: To a solution of ***endo*-PNBNPE** (**9**, 4 g, 1.0 equiv.) in DMF (150 mL) was added a solution of $NaBH_4$ (7.6 g, 10 equiv.) in DMF (50 mL) dropwise in 15 min. The resulting mixture was stirred for about 6 hours. The resulting solid was filtered, washed with hot DMF (50-100 mL) and 100ml of H_2O, and then dried via lyophilization to give **Azo-POP-13** (3.4 g, 86% yield).

^{13}C CP/MS NMR, δ (ppm): 160.6, 152.1, 147.5, 132.9, 114.9, 68.5, 43.6, 32.4.

FT-IR (cm^{-1}): 2935 (w), 2877 (w), 1600 (s), 1509 (vs), 1465 (w), 1401 (vw), 1305(m) 1234 (vs), 1151 (m), 1099 (w), 1016 (s), 823 (s), 753 (vw), 727 (vw), 522 (w);

Elemental Analysis: C (72.98%), N (7.15%), H (6.95%).

2.2 Synthesis of Azo-POP-14

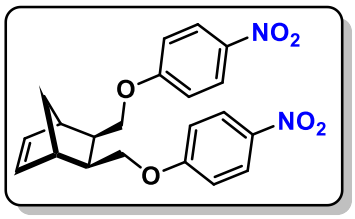
2.2.1 Synthesis of *exo*-norbornene-dimethanol (5)

According to the previous reported synthetic procedure [2]: To a solution of *exo*-carbic anhydride **4** (1.64 g, 10 mmol, 1.0 equiv.) in THF (50 mL) were added $LiAlH_4$ (1.2 g, 30 mmol，3 equiv.) under the ice bath, stirred about 30min, and the reaction mixture

was stirred for 12 hours at room temperature. The reaction mixture was cooled into ice bath, quenched with 2mL of ice-water and 10%NaOH (aq). The filtrate was removed by distillation under reduced pressure, after the mixture was dissolved in AcOEt (3 x 50 mL) and brine (15 mL), The organic phase was dried with $MgSO_4$, and then removed the AcOEt to afford the desired product (**5**, 1.2 g) without purified.

2.2.2 Synthesis of *exo*-NBNPE (8)

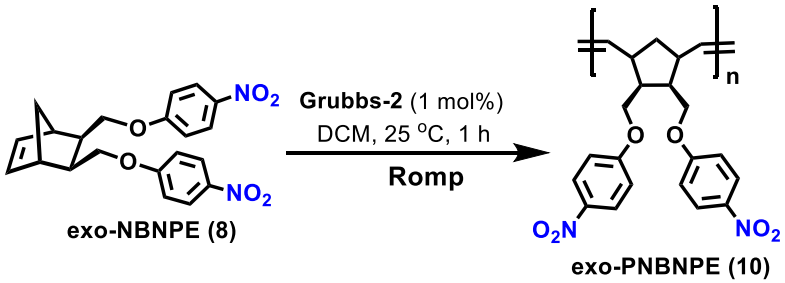
To a solution of *exo*-norbornene-dimethanol **5** (1.3 g, 8.8 mmol, 1.0 equiv.) prepared above in DMF (50 mL) were added NaH (0.8 g, 18.5 mmol，2.1 equiv.) under the ice bath, stired about 30min, and then compound **6** (3.45 g, 22 mmol, 2.5 equiv.) was added to above solution. The reaction mixture was stirred for 12 hours at room temperature and cooled to room temperature, diluted and washed with ice-water. The crude material was poured into 100ml of H_2O/ EtOH (1:1) to yield a precipitate, which was filtered, washed with water, and dried for *exo*-NBNPE (**8**, 3.1g).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.13 (m, 4H), 6.96 – 6.89 (m, 4H), 6.28 (t, J = 1.9 Hz, 2H), 4.27 (ddd, J = 9.4, 4.2, 1.7 Hz, 2H), 4.07 (ddd, J = 9.3, 5.1, 2.3 Hz, 2H), 2.92 (t, J = 1.8 Hz, 2H), 2.15 (td, J = 5.2, 1.8 Hz, 2H), 1.65 (dd, J = 9.2, 1.6 Hz, 1H), 1.48 (dt, J = 9.3, 1.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.4, 141.3, 137.2, 125.7, 114.1, 69.8, 44.8, 43.0, 40.0; **HRMS (ESI)**: m/z calcd for $C_{21}H_{20}N_2O_6Na^+$ $[M+Na]^+$ 419.1214, found 419.1209.

FIT-IR (cm^{-1})： 3117 (vw), 2985 (vw), 2940 (w), 1592 (ms), 1509 (vs), 1397 (vw), 1332 (vs), 1256 (vs), 1173 (s), 1108 (ms), 1007 (ms), 836 (ms), 748 (s), 712 (s), 642 (s), 500 (w).

2.2.3 Synthesis of *exo*-PNBNPE (10)



Scheme 4. ROMP for Synthesis of *exo*-PNBNPE (10)

The synthetic procedure: To a solution of *exo*-NBNPE (**8**, 12.0 g, 30 mmol, 1.0 equiv.) in DCM (300 mL) were added Grubbs-II (240 mg, 0.3 mmol，0.01 equiv.) and

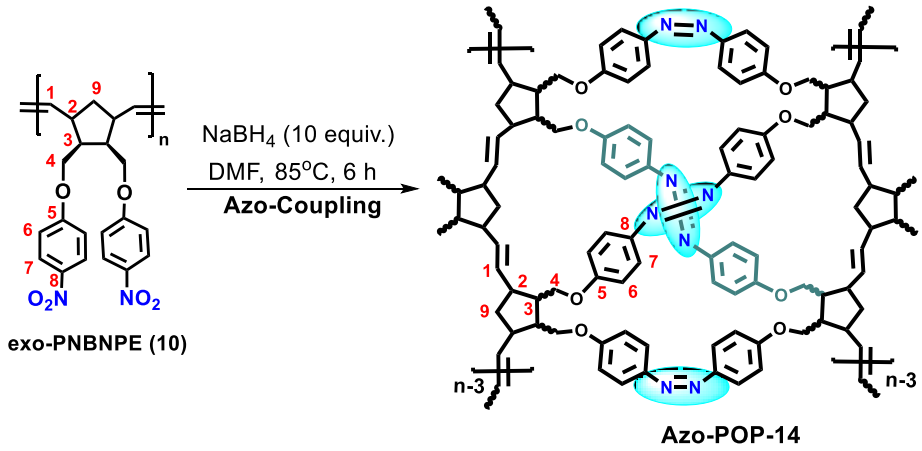
stirred at room temperature about 1 hours, and then ethyl vinyl ether (1 mL, excess) was added to above solution. The reaction mixture was stirred for further 30min, and the mixture was dissolved in hot DMF (300 mL, 80°C). The above solution poured into 500 mL of water to yield a white precipitate, which was filtered, washed with water, and freeze-dried for ***exo*-PNBNPE** (**10**, 11.9 g, 98% yield).

^{1}H NMR (400 MHz, DMF-d_7) δ (ppm): 8.33 – 8.00 (m, 4H), 7.38 – 6.90 (m, 4H), 5.76 – 5.55 (m, 2H), 4.36 (m, 4H), 3.81 – 3.21 (m, 2H), 2.19 – 2.05 (m, 2H), 2.19 – 2.03 (m, 1H), 1.57-1.44 (s, 1H); **^{13}C NMR** (100 MHz, DMF-d_7) δ (ppm): 164.3, 141.1, 133.4, 125.6, 114.7, 68.9, 47.2, 46.1, 39.8.

FT-IR (cm^{-1}): 3117 (vw), 3078 (vw), 2991 (ms), 2922 (ms), 1592 (vs), 1493 (vs), 1402 (ms), 1333 (vs), 1301 (ms), 1247 (vs), 1172 (s), 1116 (vs), 994 (s), 845 (ms), 748 (ms), 691 (s).

2D ^{1}H DOSY-NMR: molecular weight (*Mw*) = 71300 g.mol^{-1}.

2.2.4 Synthesis of Azo-POP-14

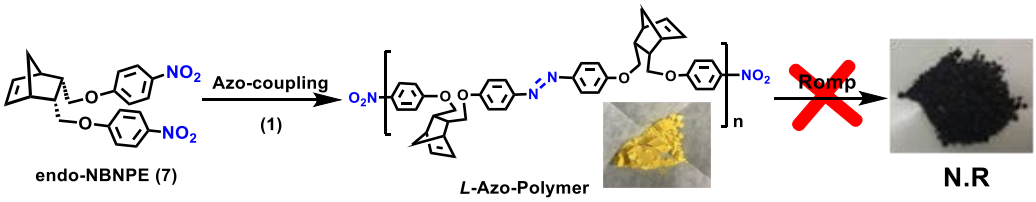


Scheme 5. Synthesis of Azo-POP-14 by azo-coupling polymerization

The Synthetic Procedure: To a solution of *exo*-PNBNPE (**10**, 4.0 g, 1.0 equiv.) in DMF (150 mL) was added a solution of $NaBH_4$ (7.6 g, 10 equiv.) in DMF (50 mL) dropwise in 15 min. The resulting mixture was stirred for about 6 hours. The resulting solid was filtered, washed with hot DMF (50-100 mL) and 100ml of H_2O, and then dried via lyophilization to give **Azo-POP-14** (3.2 g, 83% yield).

FT-IR (cm^{-1}): 3071 (vw), 2934 (w), 2871 (w), 1597 (s), 1511 (vs), 1465 (s), 1402 (w), 1345(s) 1253 (vs), 1116 (m), 1018 (w), 972 (s), 835 (s), 754 (vw);
Elemental Analysis: C (57.1%), N (7.5%), H (6.1%).

2.3 Another strategy for Synthesis of Porous polynorbornene with azobenzene subunit



Scheme 6. The other synthetic route for Porous polynorbornene with azobenzene subunit.

2.3.1 Synthesis of Linear Azo-polymer

To a solution of *endo*-NBNPE (**7**, 0.8 g, 1.0 equiv.) in DMF (50 mL) was added a solution of $NaBH_4$ (0.4 g, 10 equiv.) in DMF (20 mL) or DMSO (20 mL) dropwise in 15 min. The resulting mixture was stirred for about 3 hours. The reaction mixture was filtrated and the residue washed with DMF and water, then dried to get the yellow powder (***L*- Azo-polymer**, 0.56 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.26 – 8.20 (m, 3H), 6.90 (m, 3H), 6.22 (m, 2H), 3.95-3.87 (m, 2H), 3.75-3.66 (m, 2H), 2.83 – 2.80 (m, 2H), 1.61 (m, 1H), 1.47 (m, 1H);

FT-IR (cm^{-1}): 3059 (vw), 2966 (w), 2925 (s), 2861 (w), 1671 (w), 1595 (vs), 1501 (vs), 1466 (s), 1408 (w), 1303 (s) 1245 (vs), 1152 (vs), 1082 (s), 1024 (vs), 918 (s), 837 (vs), 726 (s).

2D ^{1}H DOSY-NMR ($CDCl_3$): molecular weight (*Mw*) = 9400 $g.mol^{-1}$ (DMF); molecular weight (*Mw*) = 4000 $g.mol^{-1}$ (DMSO).

2.3.2 ROMP on the Linear Azo-polymer

To a solution of L-Azo-POP (40 mg) in $CDCl_3$ (2 mL) were added Grubbs-I (4.0 mg,), and Grubbs-II (4.0 mg,) respectively at room temperature. The mixture was stirred about 24 hours. The progress of the reaction was monitored by ^{1}H NMR. Unfortunately, the L-Azo-POP remained unchanged.

3 Selective Adsorption of 4-Nitrophenol

3.1 Azo-POP-13 for Selective Adsorption of 4-Nitrophenol

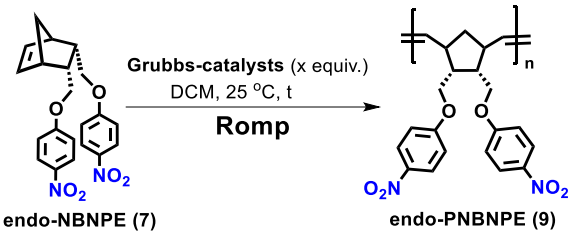
The solution of 4-nitrophenol (0.01 mmol or 0.02 mmol) and 4-aminophenol (0.01 mmol or 0.02 mmol) in deuterated water (2 mL) was prepared. The initial ratio of 4-NP and 4-AP (around 1/1) was detected by ^{1}H NMR before they were treated with Azo-POP-13 (10 mg) at room temperature for some time. Then the mixture was passed through 0.22 μm syring filter (ANPEL), and the filtrate was analyzed by ^{1}H-NMR (400 MHz). The Azo-POP-13 can be reused after removing the residues through washed with EtOH and water, activated by freeze drying.

3.2 The selective adsorption of 4-nitrophenol by using activated carbon

To compare with newly developed Azo-POP-13, the commercially available activated carbon (S_{BET}=1450 m^2/g) was used for the selective adsorption. The procedure of adsorption on 4-nitrophenol was according to the above mentioned methods. The solution of 4-nitrophenol (0.01 mmol or 0.02 mmol) and 4-aminophenol (0.01 mmol or 0.02 mmol) in deuterated water (2 mL) was prepared. The initial ratio of 4-NP and 4-AP (around 1/1) was detected by ^{1}H NMR before they were treated with activated carbon (10 mg) at room temperature for some time. Then the mixture was passed through 0.22 μm syring filter (ANPEL), and the filtrate was analyzed by ^{1}H-NMR (400 MHz).

4 Tables in ESI

Table S1. The optimization on the synthesis of **endo-PNBNPE (9)**



endo-NBNPE (7) endo-PNBNPE (9)

Entry	monomer	Conditions[a]	Polymers	Conversion (%)	Theoretical *Mw*	*Mw*[b]
1	**endo-NBNPE**	Grubbs-I (5 mol%)	**endo-PNBNPE -1**	~15	7920	16600
2	**endo-NBNPE**	Grubbs-II (5 mol%)	**endo-PNBNPE -2**	> 99	7920	63300
3	**endo-NBNPE**	Grubbs-II (1 mol%)	**endo-PNBNPE -3**	> 99	39600	105300

[a]**The General Procedure**: endo-NBNPE (**7,** 396 mg, 1.0 mmol, 1.0 equiv.), Grubbs-I (5 mol%) or Grubbs-II (1 or 5 mol%), DCM (0.1 M), rt, 2h. [b] Mw determined by 2D ^{1}H DOSY (400MHz, DMF-d7).

Table S2. The standard working curve for calculating macromolecule's weight

Sample[a]	PS-1	PS-2	PS-3	PS-4	PS-5
M_w	2870	6480	9000	42300	79000
PDI	1.05	1.04	1.07	1.03	1.03
D^b ($\times10^{-6}$cm^2/s)	3.86	1.73	1.50	0.719	0.469

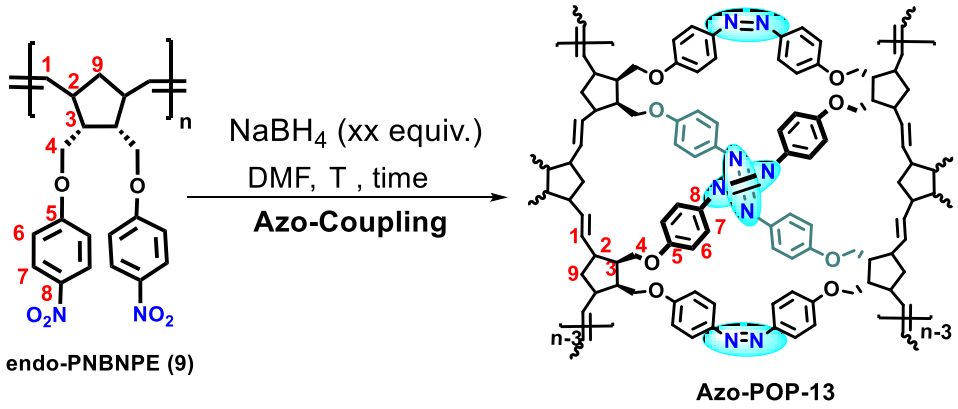
[a] All of polystyrene (PS) samples (1.0 mg) are dissolved in DMF-d7 (0.4 mL), T= 20 °C; [b] The Diffusion value determined by 2D ^{1}H DOSY (400MHz, DMF-d7).

Table S3. The standard working curve for calculating macromolecule's weight

Sample[a]	PS-1	PS-2	PS-3	PS-4	PS-5
M_w	2870	6480	9000	42300	79000
PDI	1.05	1.04	1.07	1.03	1.03
D^b ($\times10^{-6}$cm^2/s)	7.3	5.8	4.7	2.6	1.1

[a] All of polystyrene (PS) samples (1.0 mg) are dissolved in $CDCl_3$ (0.4 mL), T= 20 °C; [b] The Diffusion value determined by 2D ^{1}H DOSY (400MHz, $CDCl_3$).

Table S4. The optimization on the preparation of Azo-POP-13



Entry	Reaction Condition[a]	PNBNBE[f]	Work-up method[g]	Samples	*BET* (m^2/g)[h]
1[b]	Et_3N H_2CO_2(5 equiv.), Mg (10 equiv.), MeOH, rt, 8h	0.02 g/mL	/	/	/
2[c]	$LiAlH_4$ (1.1 equiv.), THF, 65 °C, 1h	0.02 g/mL	/	/	/
3[d]	Zn (4 equiv.), NaOH (8 equiv.), DMF/THF(4/1), 100°C, 24h	0.02 g/mL	/	/	/
4[e]	Zn /NaOH/ $NaBH_4$ (1: 4: 8), DMF/THF(4/1), 100°C, 24h	0.02 g/mL	DMF, EtOH, H_2O Freeze drying	**Azo-POP-13-1**	49
5	$NaBH_4$ (5 equiv.), DMF, 85°C, 6h	0.02 g/mL	HCl (aq), EtOH, H_2O, Freeze drying	**Azo-POP-13-2**	59
6	$NaBH_4$ (10 equiv.), DMF, 85°C, 6h	0.02 g/mL	HCl (aq), EtOH, H_2O, Freeze drying	**Azo-POP-13-3**	106
7	$NaBH_4$ (20 equiv.), DMF, 85°C, 6h	0.02 g/mL	HCl (aq), EtOH, H_2O, Freeze drying	**Azo-POP-13-4**	119
8	$NaBH_4$ (10 equiv.), DMF, 85°C, 6h	0.04 g/mL	HCl (aq), EtOH, H_2O, Freeze drying	**Azo-POP-13-5**	92
9	$NaBH_4$ (10 equiv.), DMF, 85°C, 6h	0.02 g/mL	THF, H_2O, Freeze drying	**Azo-POP-13-6**	26
10	$NaBH_4$ (10 equiv.), DMF, 100°C, 6h	0.02 g/mL	HCl (aq), EtOH, H_2O, Freeze drying	**Azo-POP-13-7**	125
11	$NaBH_4$ (10 equiv.), DMF, 150°C, 6h	0.02 g/mL	HCl (aq), EtOH, H_2O, Freeze drying	**Azo-POP-13-8**	98
12	**$NaBH_4$ (10 equiv.), DMF, 85°C, 6h**	**0.02 g/mL**	**DMF, EtOH, H_2O Freeze drying**	**Azo-POP-13**	**225**

Standard Condition: [a] $NaBH_4$ (10 equiv.), DMF (0.02 g/mL), 85°C; [b, c, d] FT-IR showed no reaction took place; [e] partial conversion determined by FT-IR; [f] the concentration of ***endo*-PNBNPE**; [g] carried out at that temperature for 12 hours; [h] N_2 isotherm at 77 K.

Table S5. The elemental analysis of **endo-PNBNPE (9), exo-PNBNPE (10), Azo-POP-13** and **Azo-POP-14**

Sample	Quality Percentage (%)							
	Found				Theoretical[a]			
	C	H	N	C/N	C	H	N	C/N
endo-PNBNPE	63.61	5.09	6.99	10.6	63.63	5.09	7.07	10.5
exo-PNBNPE	63.60	5.10	6.96	10.6	63.63	5.09	7.07	10.5
Azo-POP-13	72.98	6.95	7.15	11.9	75.88	6.06	8.43	10.5
Azo-POP-14	71.91	7.02	7.13	11.8	75.88	6.06	8.43	10.5

[a] Theoretical values were calculated assuming an ideal structure of **endo-PNBNPE (9), exo-PNBNPE (10), Azo-POP-13** and **Azo-POP-14** for the elemental analysis.

Table S6. Solubility of **endo-PNBNPE (9), exo-PNBNPE (10), Azo-POP-13** and **Azo-POP-14** in different solvent

Solvents	Solubility of endo/exo-PNBNPE	Solubility of Azo-POP-13/14
DMF	Soluble	Insoluble
NMP	Soluble	Insoluble
DMSO	Insoluble	Insoluble
Acetone	Insoluble	Insoluble
THF	Insoluble	Insoluble
Ethyl acetate	Insoluble	Insoluble
MeCN	Insoluble	Insoluble
CH_2Cl_2	Insoluble	Insoluble
$CHCl_3$	Insoluble	Insoluble
1,4-Dioxane	Insoluble	Insoluble
Methanol	Insoluble	Insoluble
Ethanol	Insoluble	Insoluble

Table S7. Porosity Parameters for **Azo-POP-13** and **Azo-POP-14**

Samples	SA_{BET} ($m^2.g^{-1}$)	V_{total} ($cm^3.g^{-1}$) [a]
Azo-POP-13	225	1.22
Azo-POP-14	176	0.69

[a]. Calculated from the N_2 adsorbed at P/P_0 = 0.99.

Table S8. The **Azo-POP-13 (10 mg)** for selective adsorption of 4-NP and 4-AP.

Entry	4-NP (mg/mmol)	4-AP (mg/mmol)	D_2O (mL)	Time (mins)	Removal efficiency (%) 4-NP: 4-AP[a]
1	1.4 / 0.01	1.1/ 0.01	2	5	83 / 8
2	2.8 / 0.02	2.2 / 0.02	2	5	73 / 5
3	1.4 / 0.01	1.1/ 0.01	2	30	83 / 10
4	2.8 / 0.02	2.2 / 0.02	2	30	73 / 6

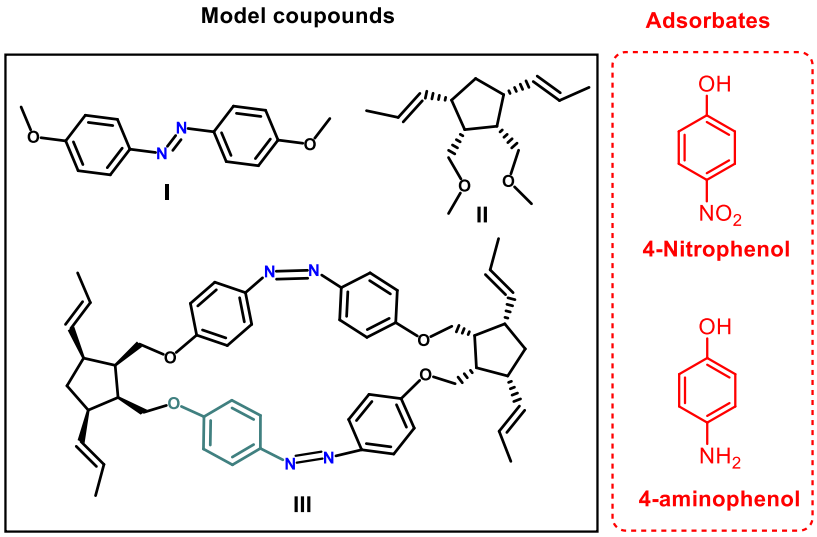
[a] The removal efficiency of 4-NP and 4-AP was calculated based on the concentration decrease after 5 min and 30 min by the ^{1}H NMR (400 MHz).

Table S9. The **activated carbon (10 mg)** for selective adsorption of 4-NP and 4-AP.

Entry	4-NP (mg/mmol)	4-AP (mg/mmol)	D_2O (mL)	Time (min)	Removal efficiency (%) 4-NP: 4-AP[a]
1	1.4 / 0.01	1.1/ 0.01	2	5	95 / 72
2	2.8 / 0.02	2.2 / 0.02	2	5	95 / 80
3	1.4 / 0.01	1.1/ 0.01	2	30	92 / 67
4	2.8 / 0.02	2.2 / 0.02	2	30	93 / 71

[a] The removal efficiency of 4-NP and 4-AP was calculated based on the concentration decrease after 5 min and 30 min by the ^{1}H NMR (400 MHz).

Table S10. Comparison of binding energy between model compounds and adsorbates



Model Compounds[a]	Adsorbates	Binding energy (kcal/mol)
I	**4-Nitrophenol (4-NP)**	**-14.2**
I	**4-Aminophenol (4-AP)**	**-10.0**
II	**4-Nitrophenol (4-NP)**	**-13.2**
II	**4-Aminophenol (4-AP)**	**-11.4**
III	**4-Nitrophenol (4-NP)**	**-25.3**
III	**4-Aminophenol (4-AP)**	**-16.0**

[a]The models are shown below, which represent 4,4'-dialkoxyl-azobenzene, dialkoxyl-nobornene, and 4,4'-dialkoxyl-azobenzene-norbornene subunit in Azo-POP-13, respectively

5 Figures in ESI

Utilizing DOSY NMR allows us to determine the diffusion coefficient and thus the *Mw* of the product thanks to a standard curve with different known *Mw* of polystyrene with this equation:

Lg (*D*) = slope x Lg (*Mw*) + intercept

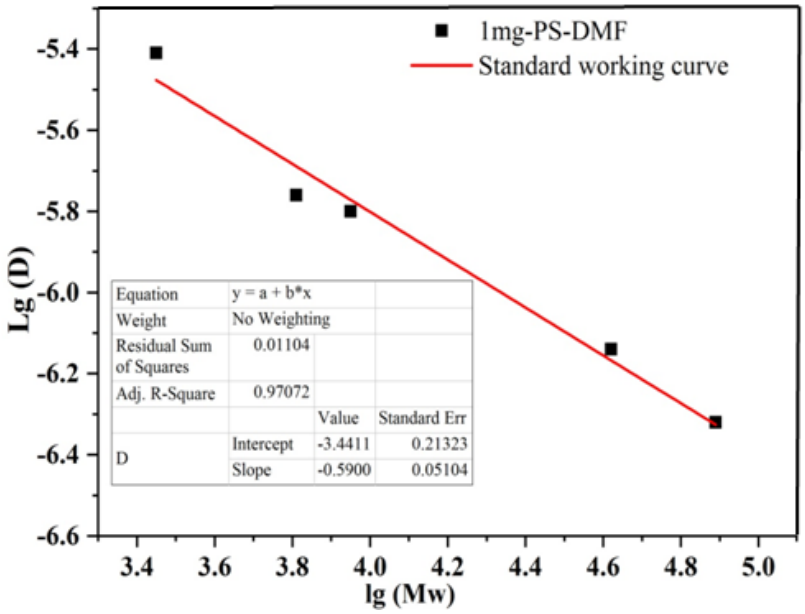


Figure S1 Polystyrene (PS, 1.0 mg/0.4 mL) working curve using 2D-^{1}HDOSY-NMR (DMF-d7, 293K).

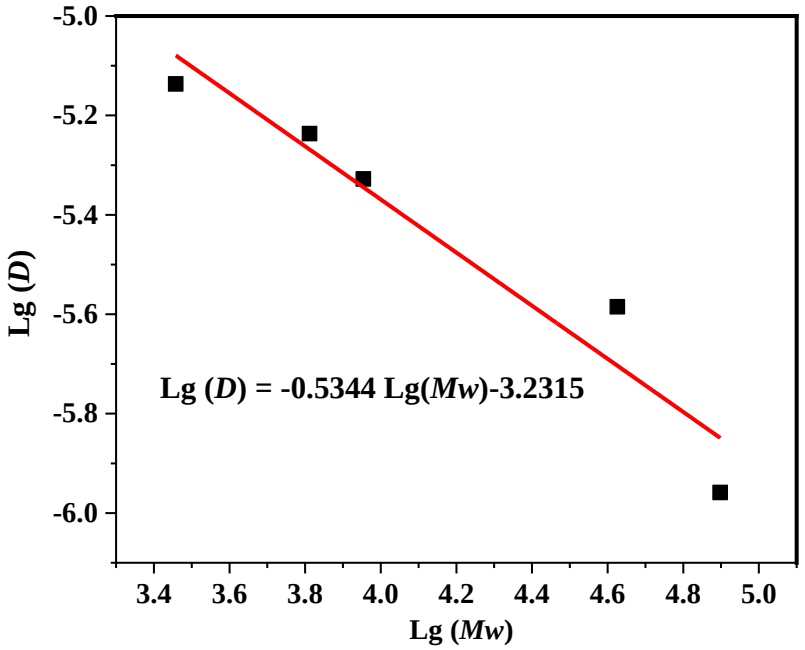


Figure S2 Standard curve of polystyrene (PS, 1.0 mg/0.4 mL) for determination of *Mw* by 2D-^{1}HDOSY-NMR ($CDCl_3$, 293K).

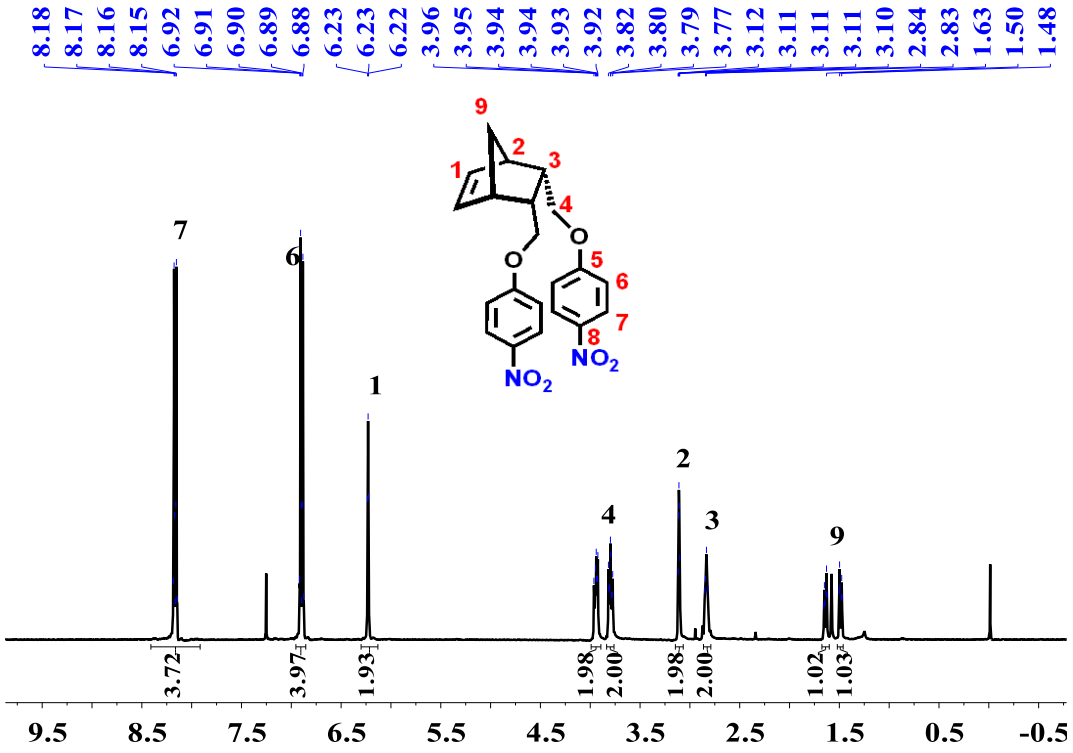


Figure S3 The ^{1}H-NMR spectrum of endo-NBNPE (7) in $CDCl_3$ (400 MHz, 298 K)

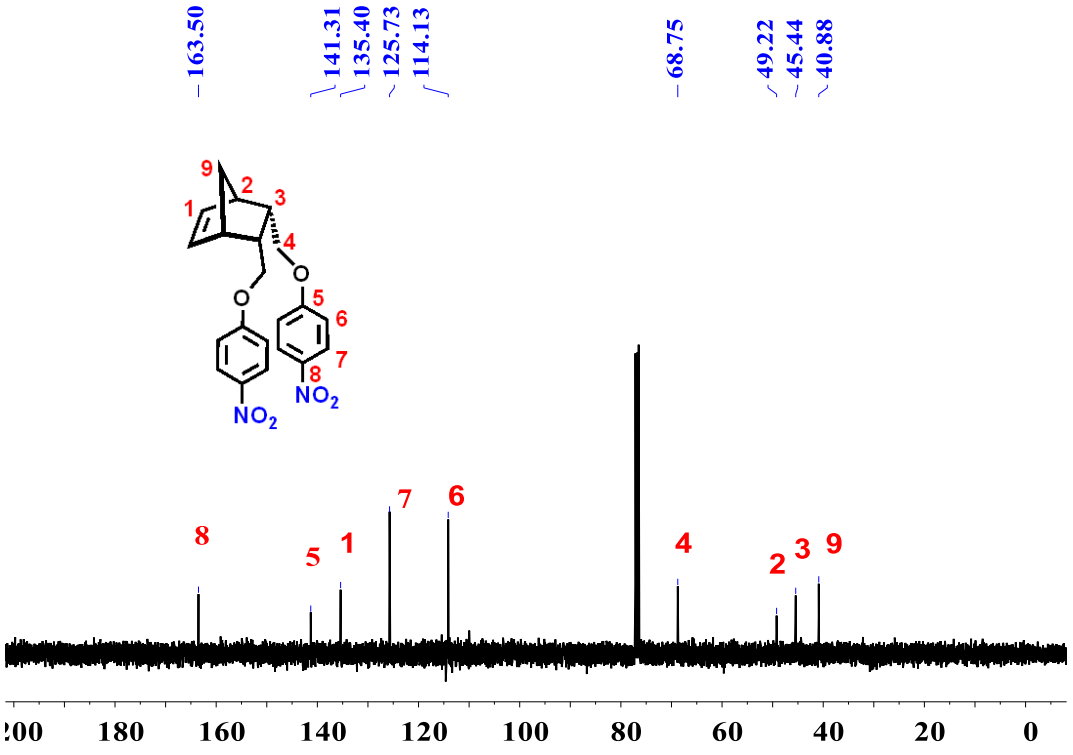


Figure S4 The ^{13}C-NMR spectrum of endo-NBNPE (7) in $CDCl_3$ (100 MHz, 298 K)

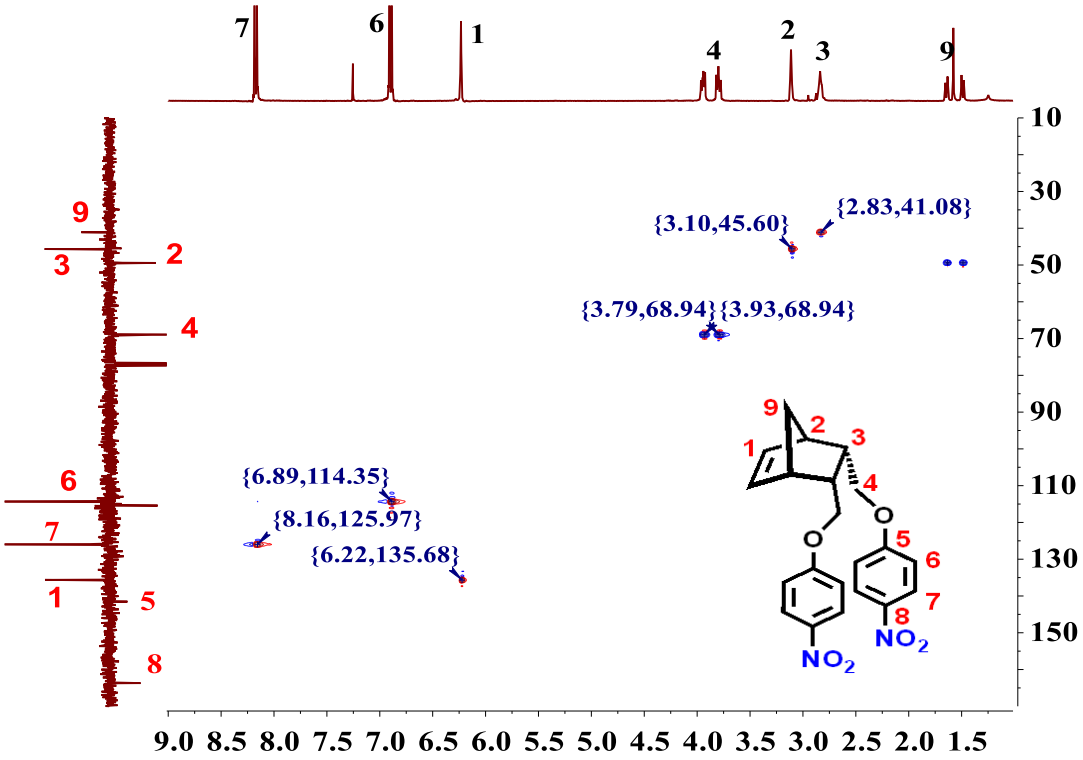


Figure S5 The ^{13}C-^{1}H gHSQC-NMR spectrum of endo-NBNPE (7) in $CDCl_3$

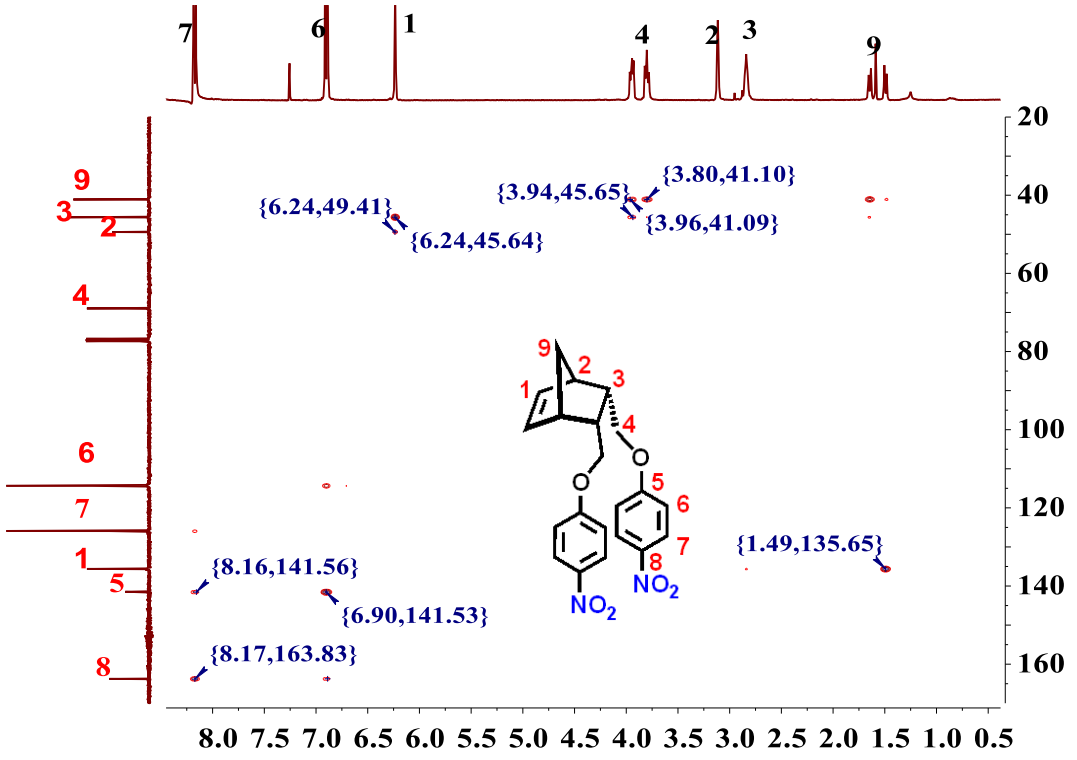


Figure S6 The ^{13}C-^{1}H gHMBC-NMR spectrum of endo-NBNPE (7) in $CDCl_3$

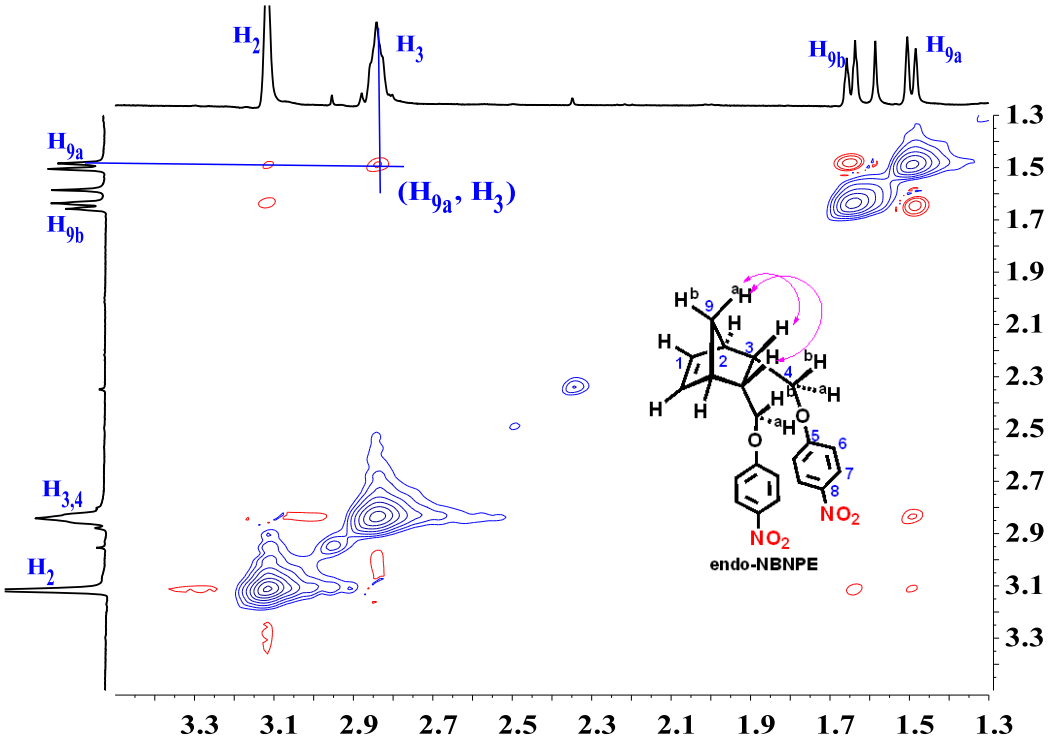


Figure S7 The NOESY-NMR spectrum of endo-NBNPE (7) in $CDCl_3$ (400 MHz, 298K)

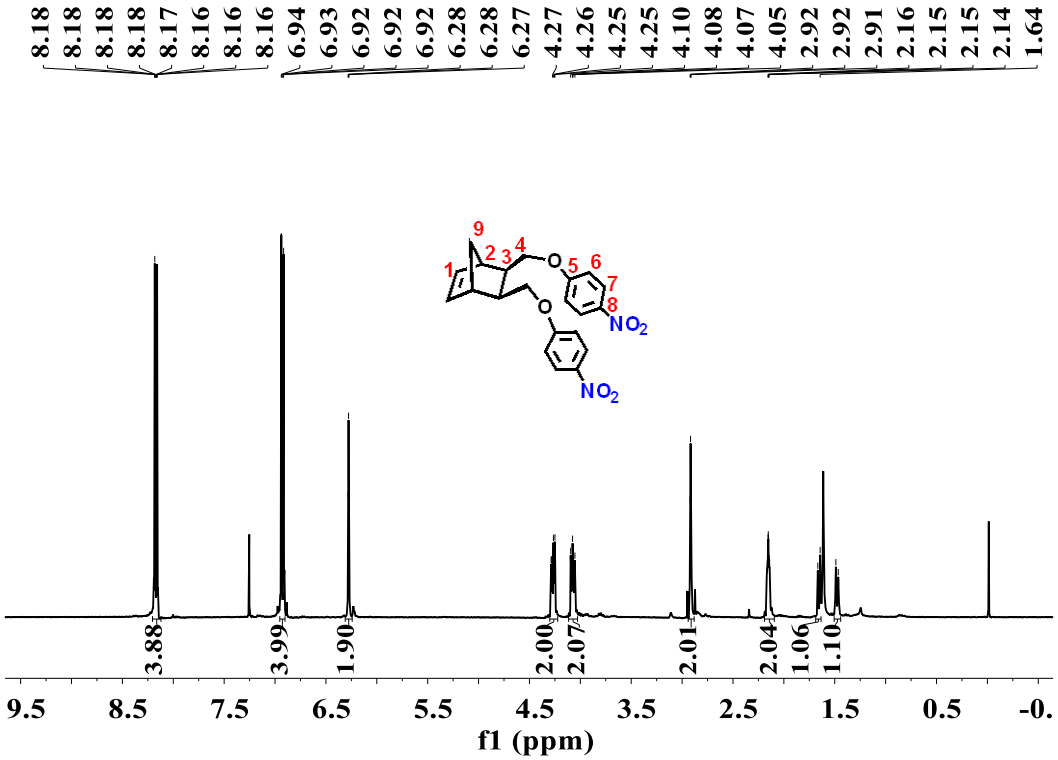


Figure S8 The ^{1}H-NMR spectrum of exo-NBNPE (8) in $CDCl_3$ (400 MHz, 298 K)

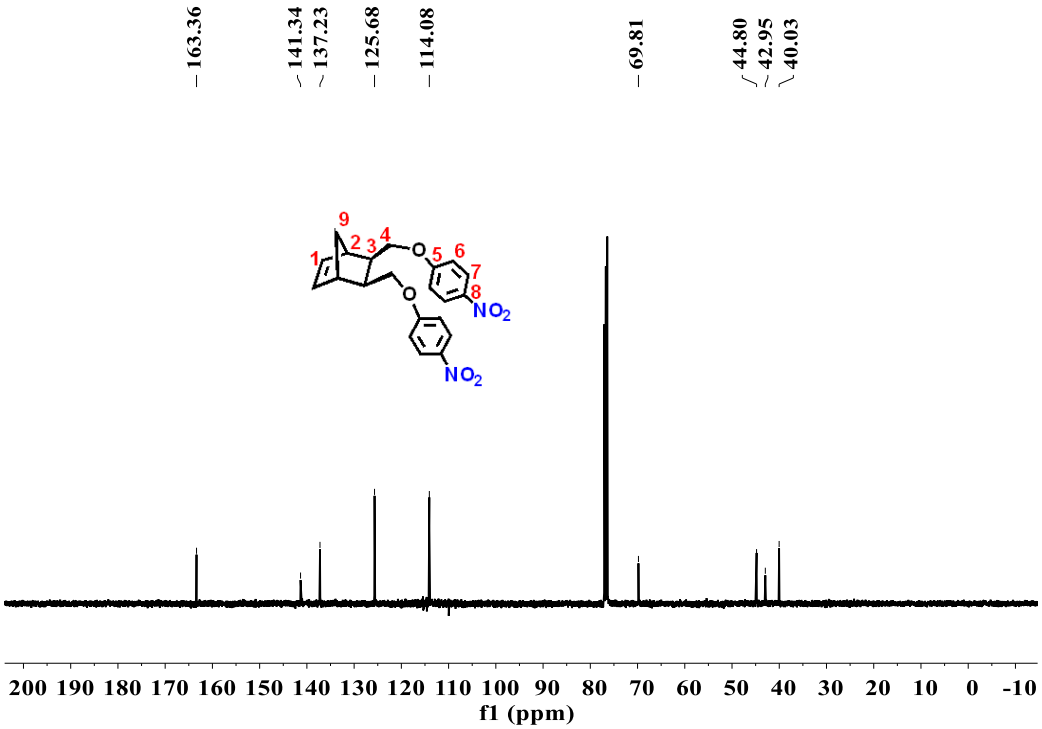


Figure S9 The ^{13}C-NMR spectrum of exo-NBNPE (8) in $CDCl_3$ (100 MHz, 298 K)

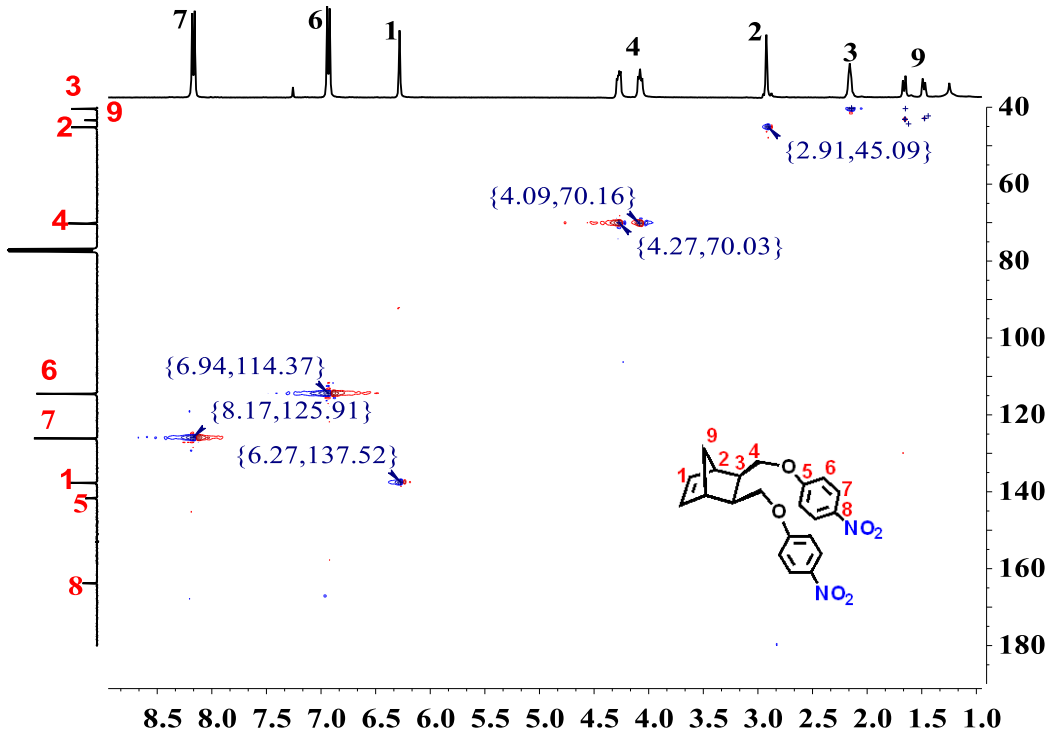


Figure S10 The ^{13}C-^{1}H gHSQC-NMR spectrum of exo-NBNPE (8) in $CDCl_3$

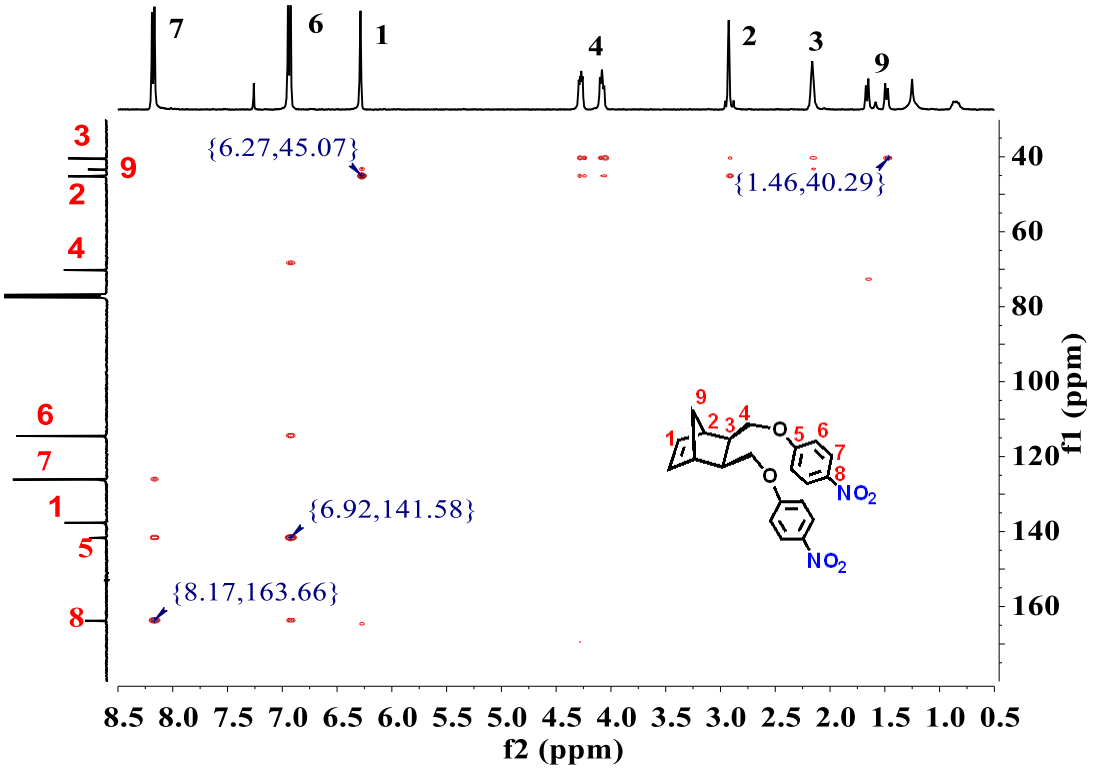


Figure S11 The ^{13}C-^{1}H gHMBC-NMR spectrum of exo-NBNPE (8) in $CDCl_3$

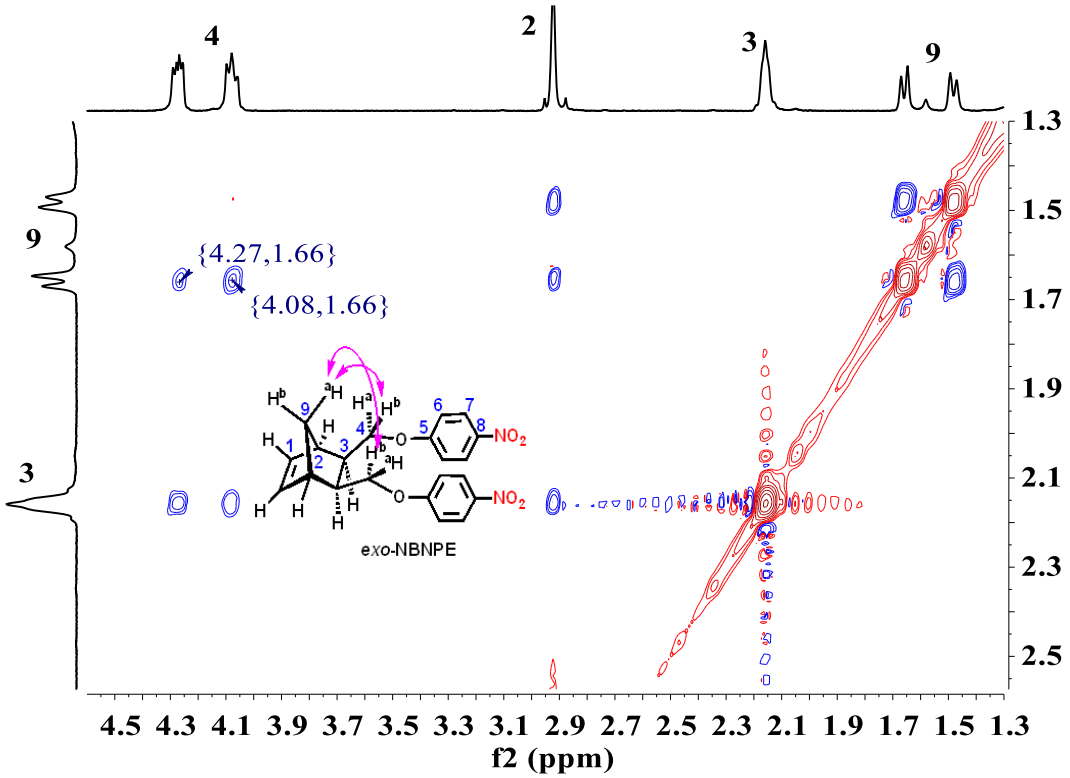


Figure S12 The NOESY-NMR spectrum of exo-NBNPE (8) in $CDCl_3$ (400 MHz, 298K)

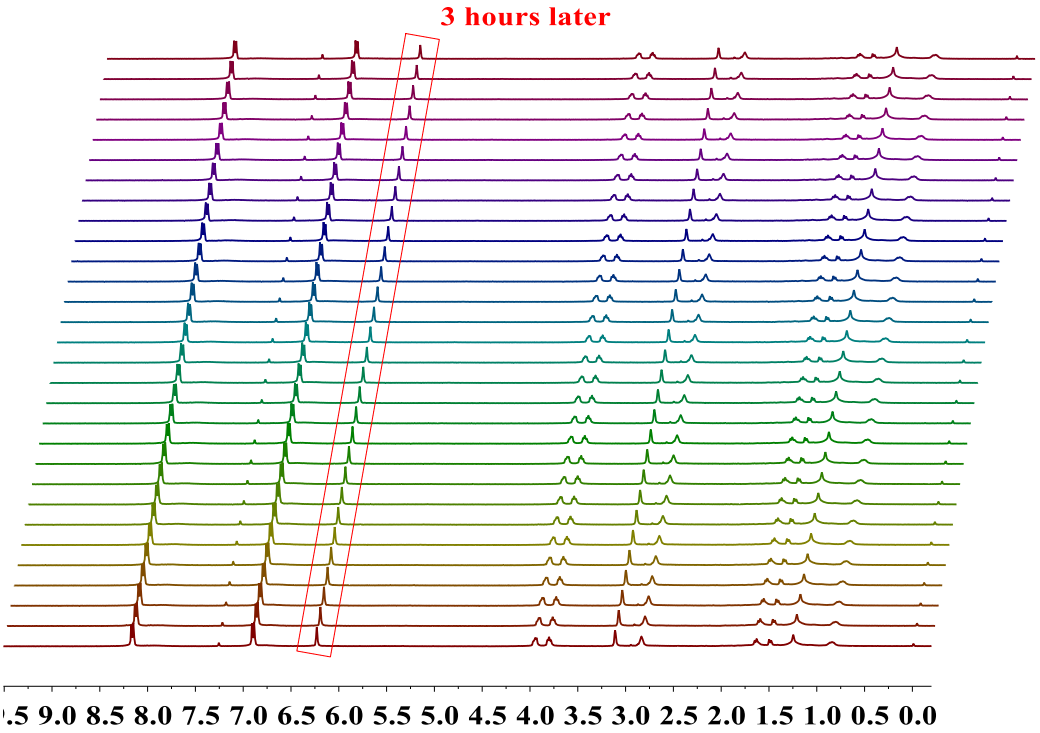


Figure S13 The array ^{1}H-NMR spectra on ROMP reaction (endo-NBNPE, by G-I, 5 mol%) in $CDCl_3$ (400 MHz, 298K).

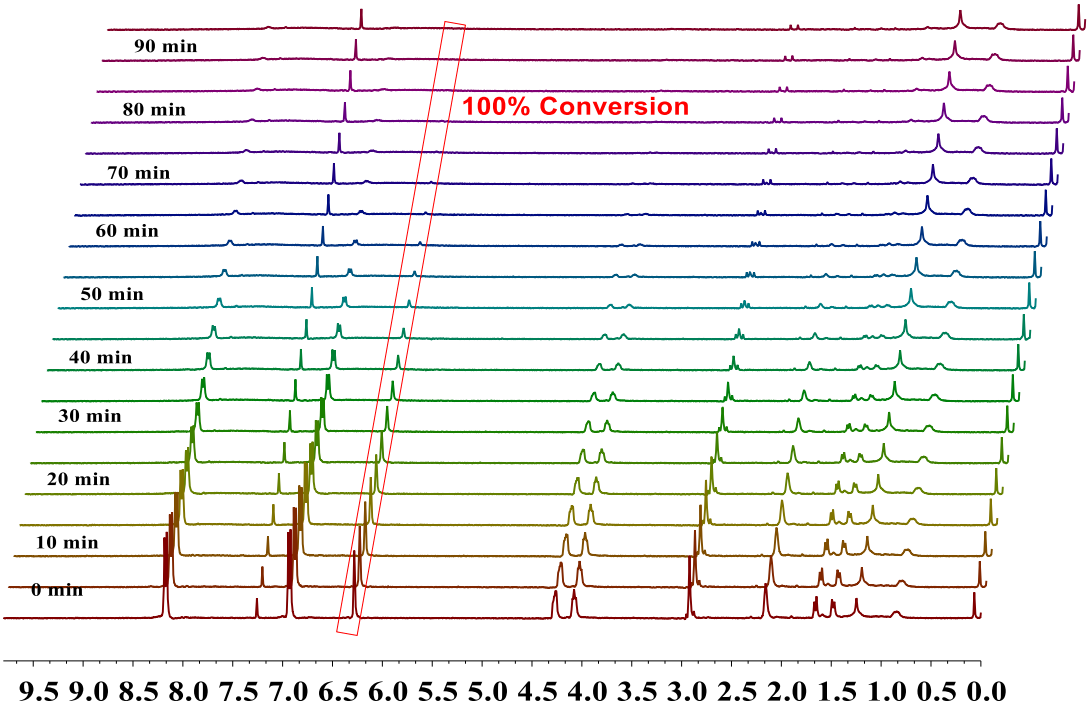


Figure S14 The array ^{1}H-NMR spectra on ROMP reaction (endo-NBNPE, by G-II, 5 mol%) in $CDCl_3$ (400 MHz, 298K

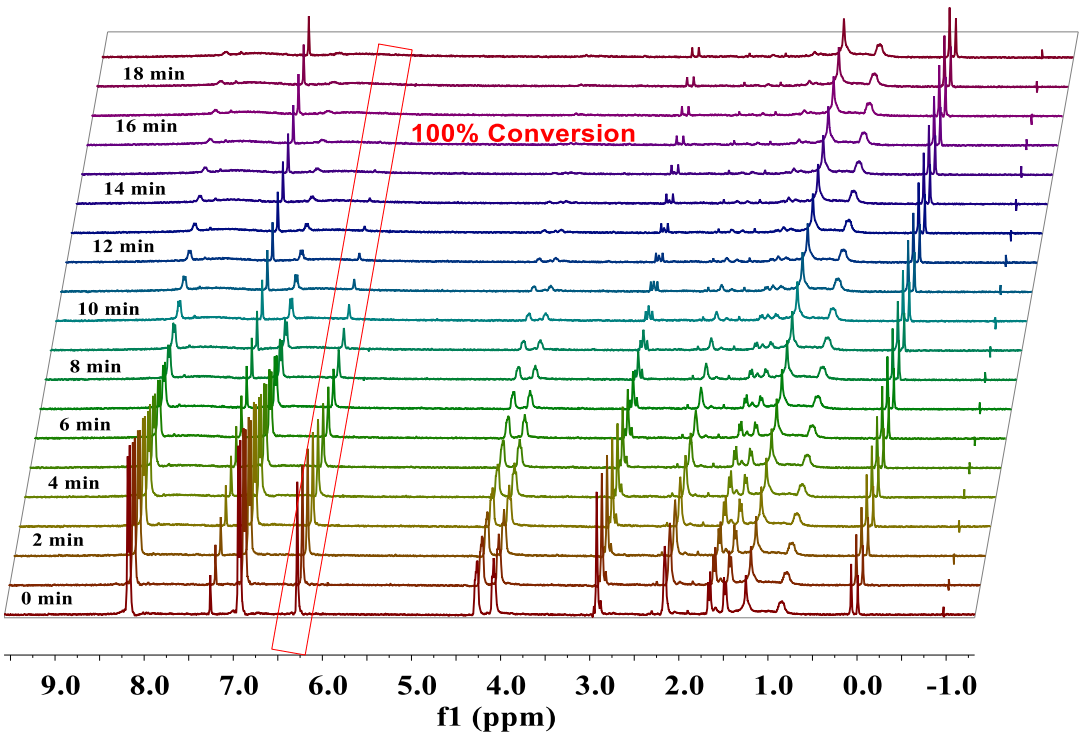


Figure S15 The array ^{1}H-NMR spectra on ROMP reaction (exo-NBNPE, by G-II, 5 mol%) in $CDCl_3$

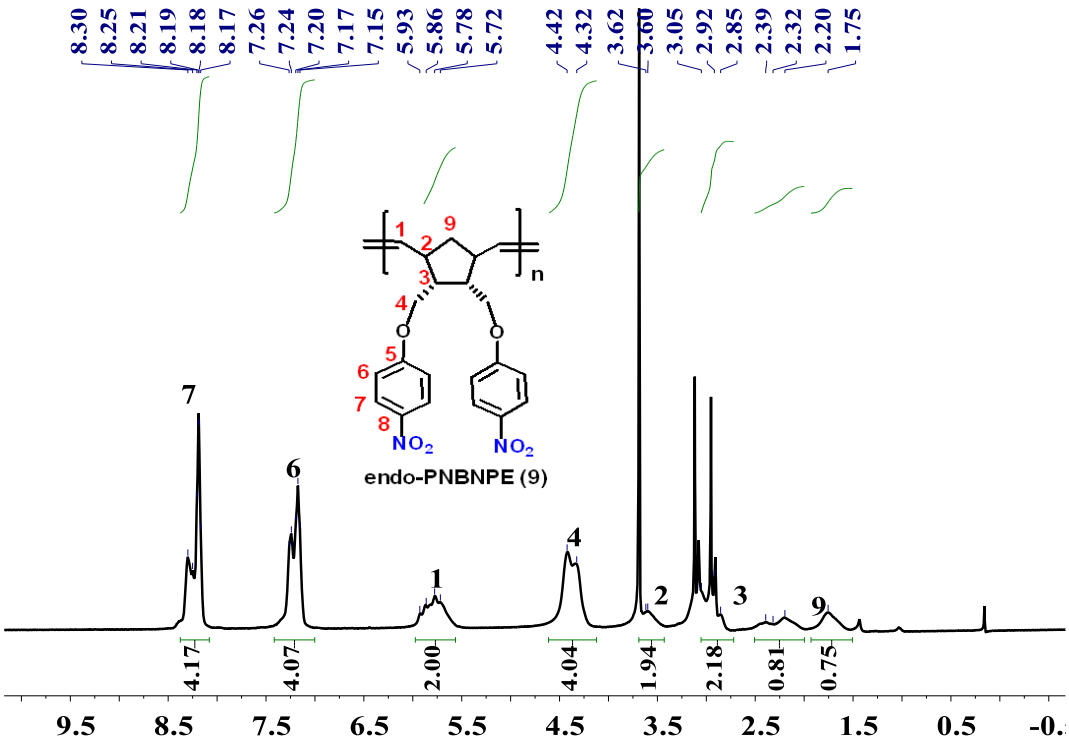


Figure S16 The ^{1}H-NMR spectrum of endo-PNBNPE (9) in DMF-d7 (400 MHz, 298K)

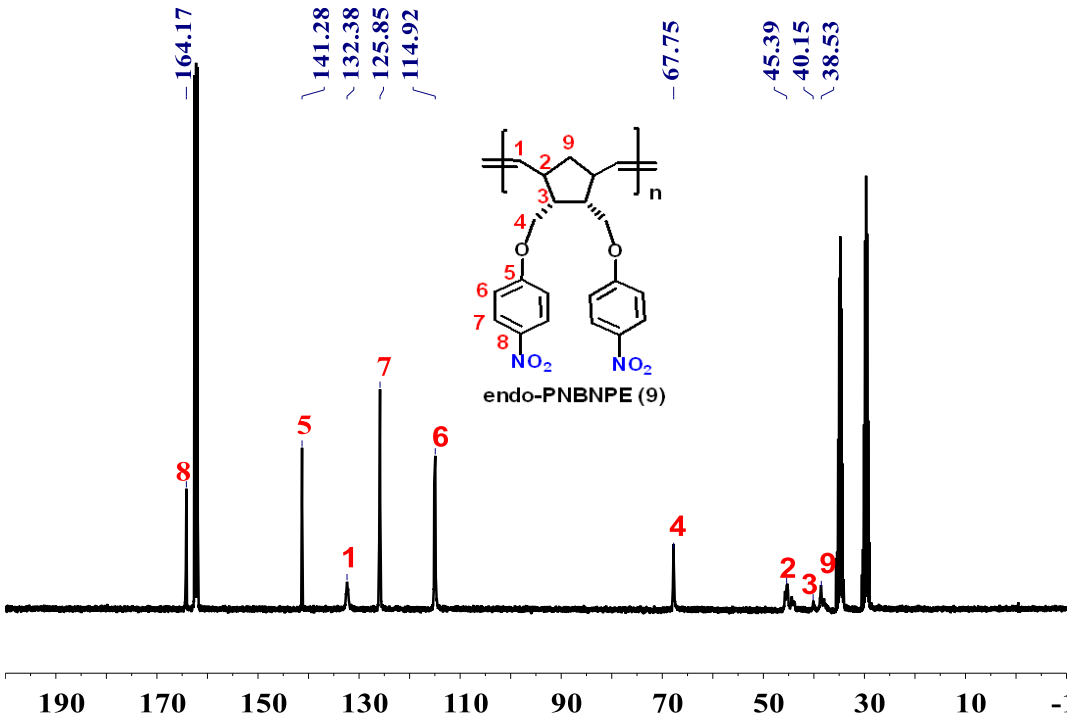


Figure S17 The ^{13}C-NMR spectrum of endo-PNBNPE (9) in DMF-d7 (100 MHz, 298K)

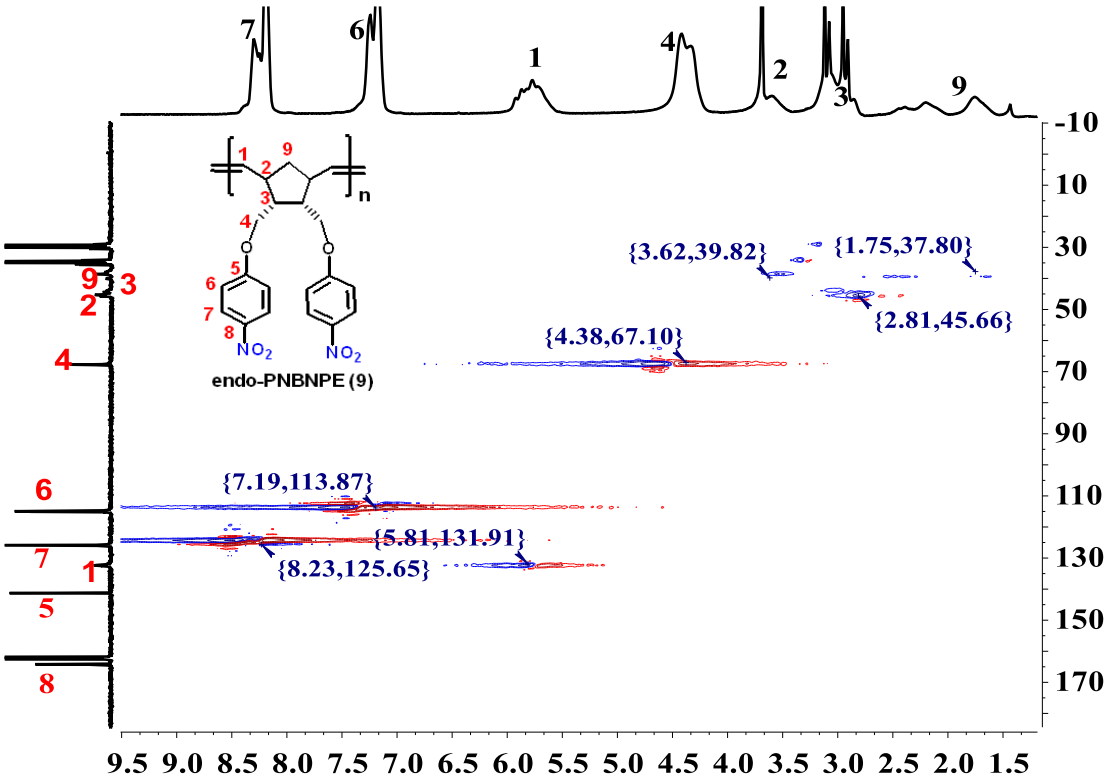


Figure S18 The gHSQC-NMR spectrum of endo-PNBNPE (9) in DMF-d7

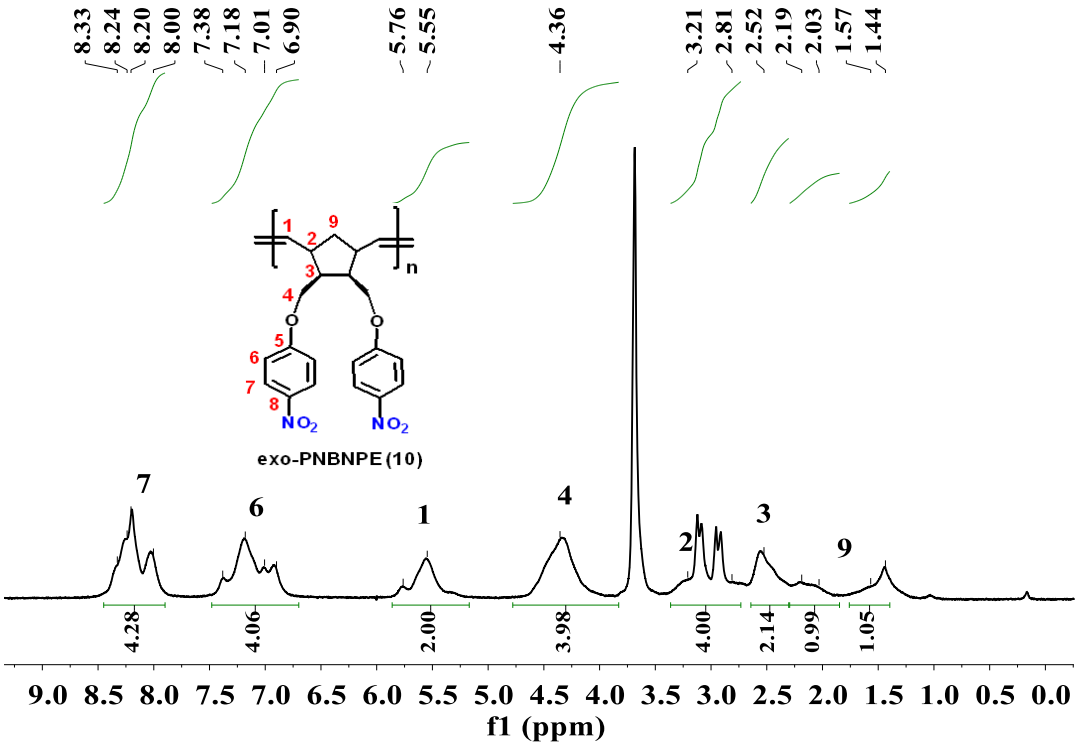


Figure S19 The [1]H-NMR spectrum of exo-PNBNPE (10) in DMF-d7 (400 MHz, 298K)

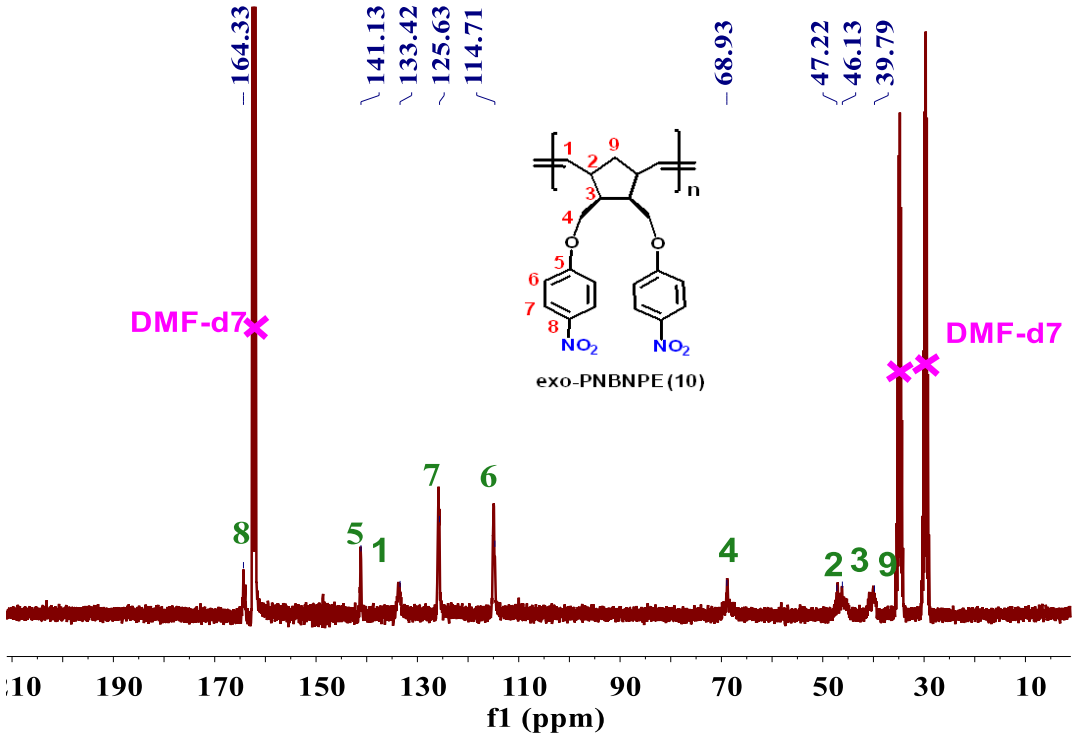


Figure S20 The [13]C-NMR spectrum of exo-PNBNPE (10) in DMF-d7 (100 MHz, 298K)

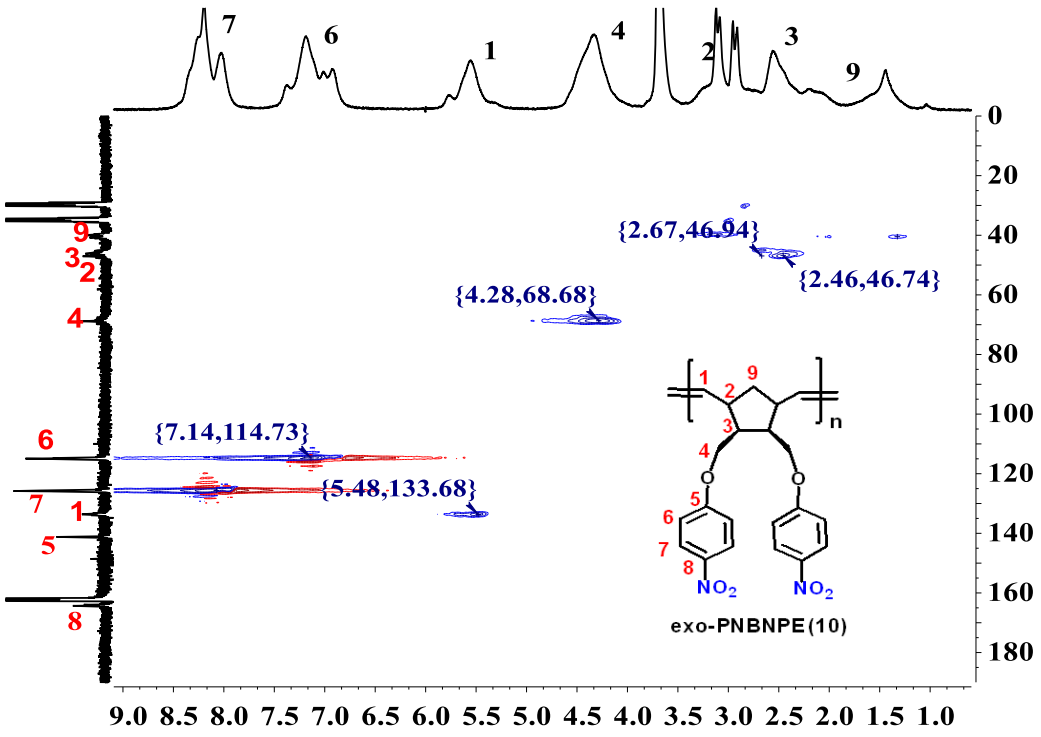


Figure S21 The gHSQC-NMR spectrum of exo-PNBNPE (10) in DMF-d7

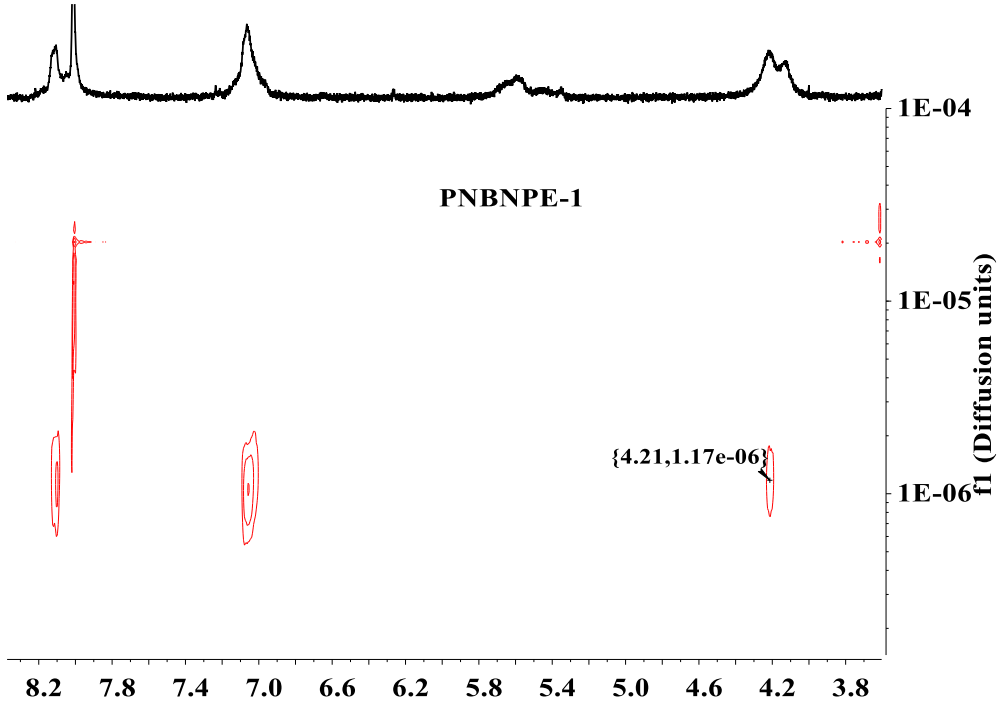


Figure S22 The 2D-^{1}HDOSY-NMR spectrum (DMF-d7, 293K) of endo-PNBNP E-1

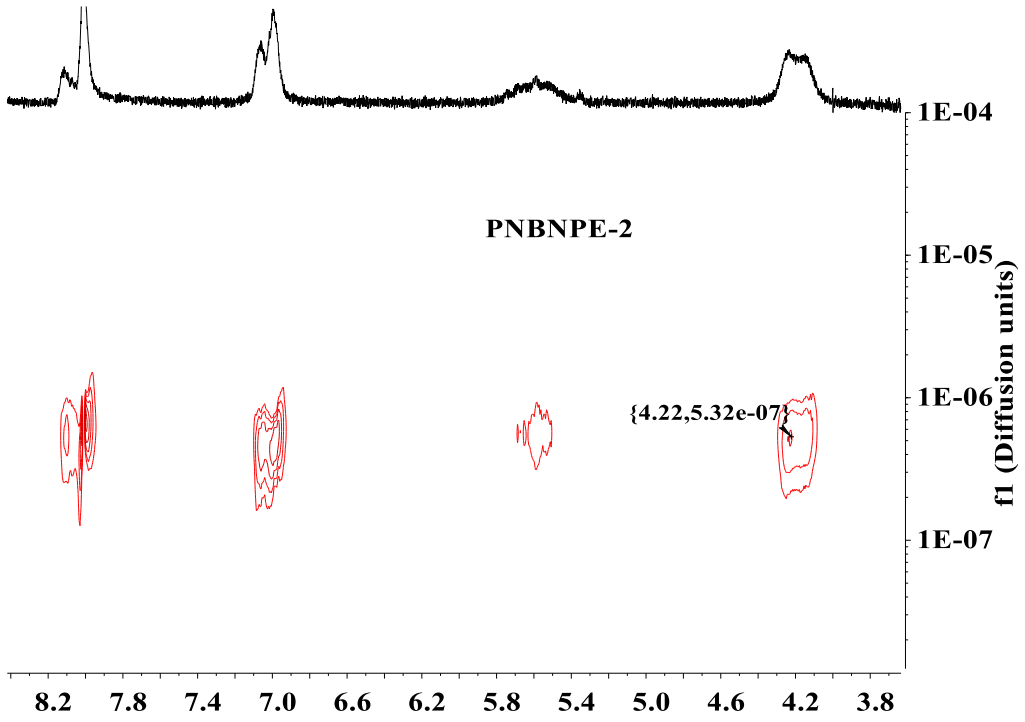


Figure S23 The 2D-^{1}HDOSY-NMR spectrum (DMF-d7, 293K) of endo-PNBNP E-2.

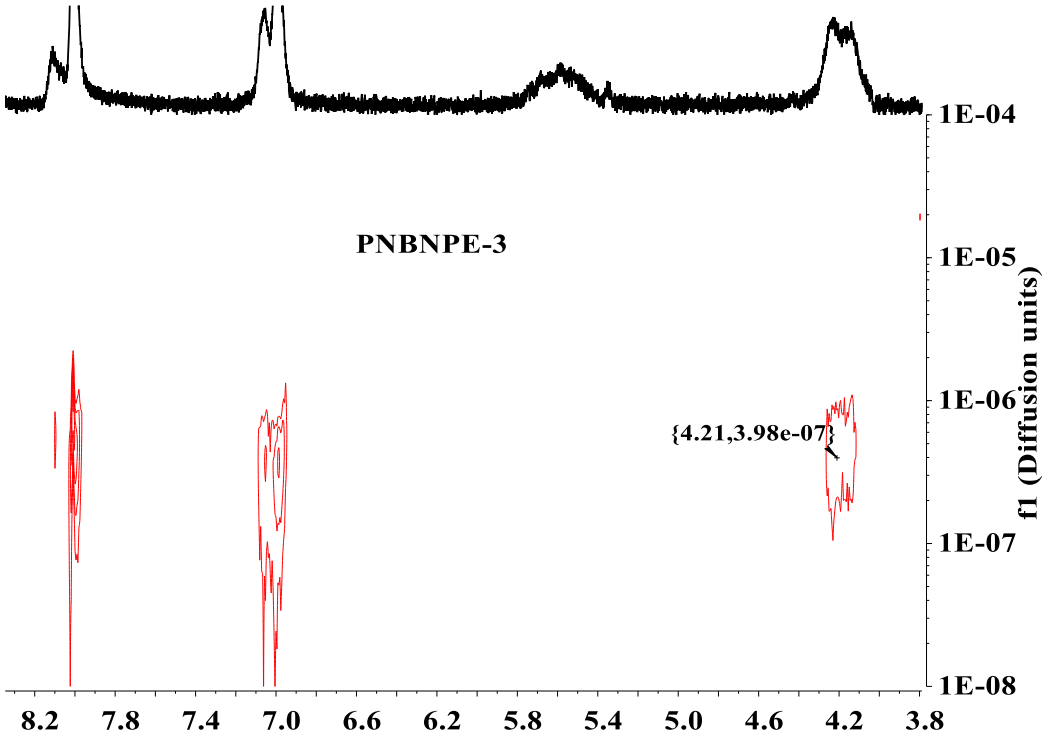


Figure S24 The 2D-^{1}HDOSY-NMR spectrum (DMF-d7, 293K) of endo-PNBNP E-3

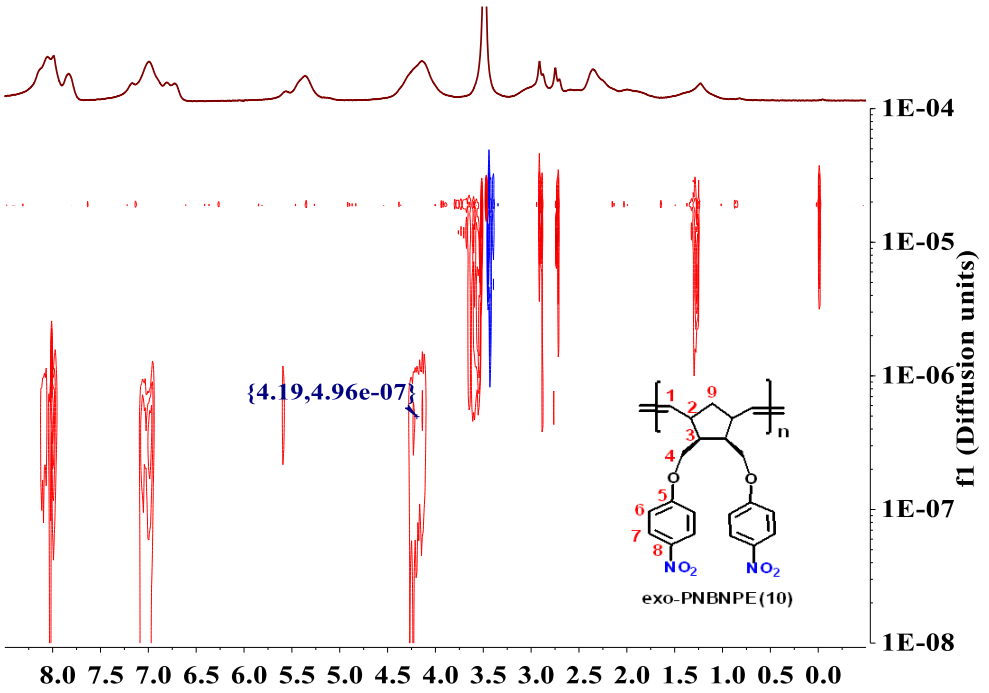


Figure S25 The 2D-^{1}HDOSY-NMR spectrum (DMF-d7, 293K) of exo-PNBNPE (10)

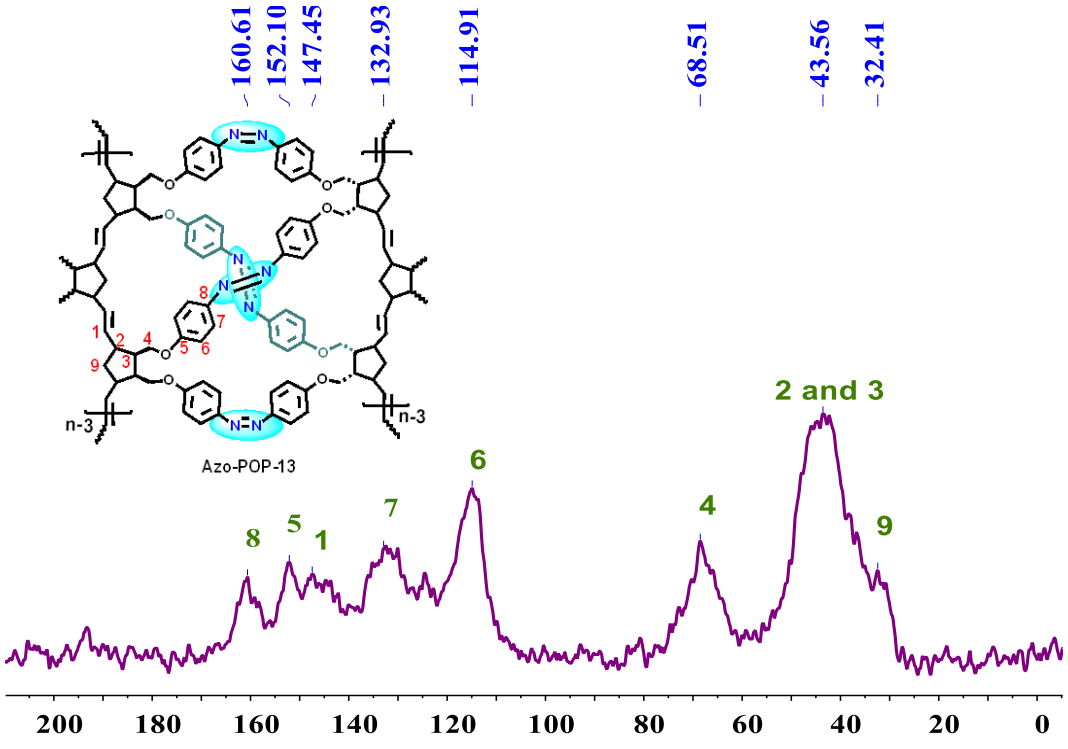


Figure S26 Characterization of Azo-POP-13 by CP-MS-^{13}C-NMR

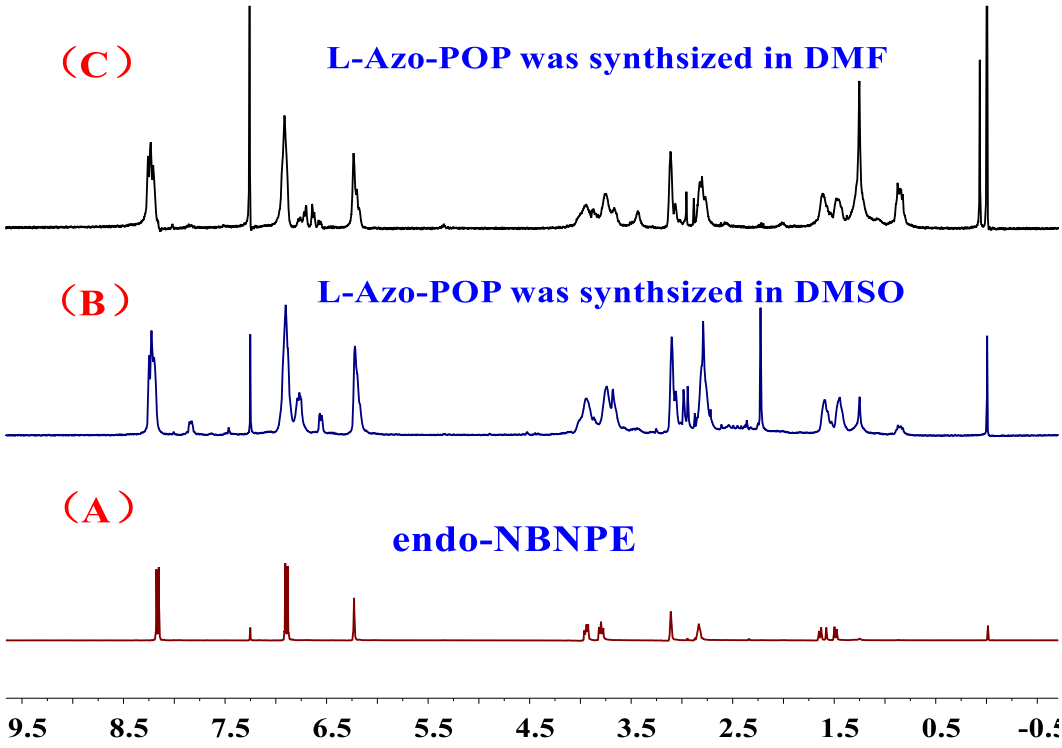


Figure S27 Comparison between the ^{1}H-NMR (400 MHz) of endo-NBNPE (A) and L-Azo-POP (B and C) in $CDCl_3$

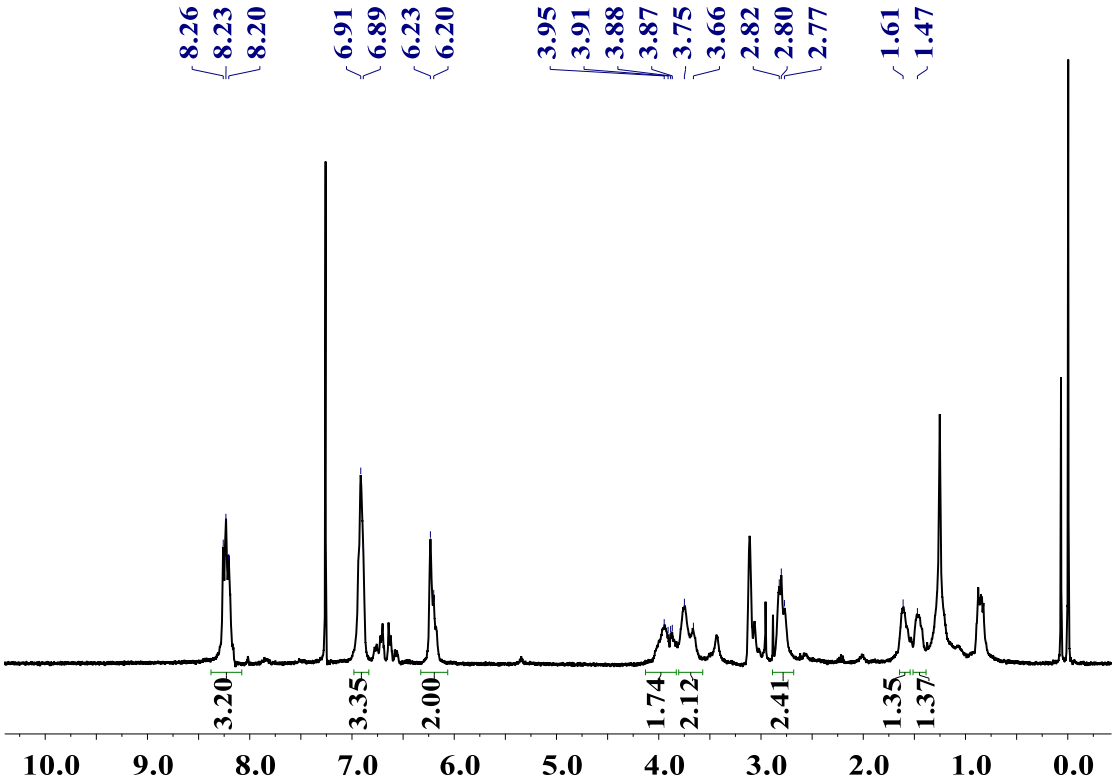


Figure S28 The ^{1}H-NMR spectrum of L-Azo-POP in $CDCl_3$ (400 MHz, 298K)

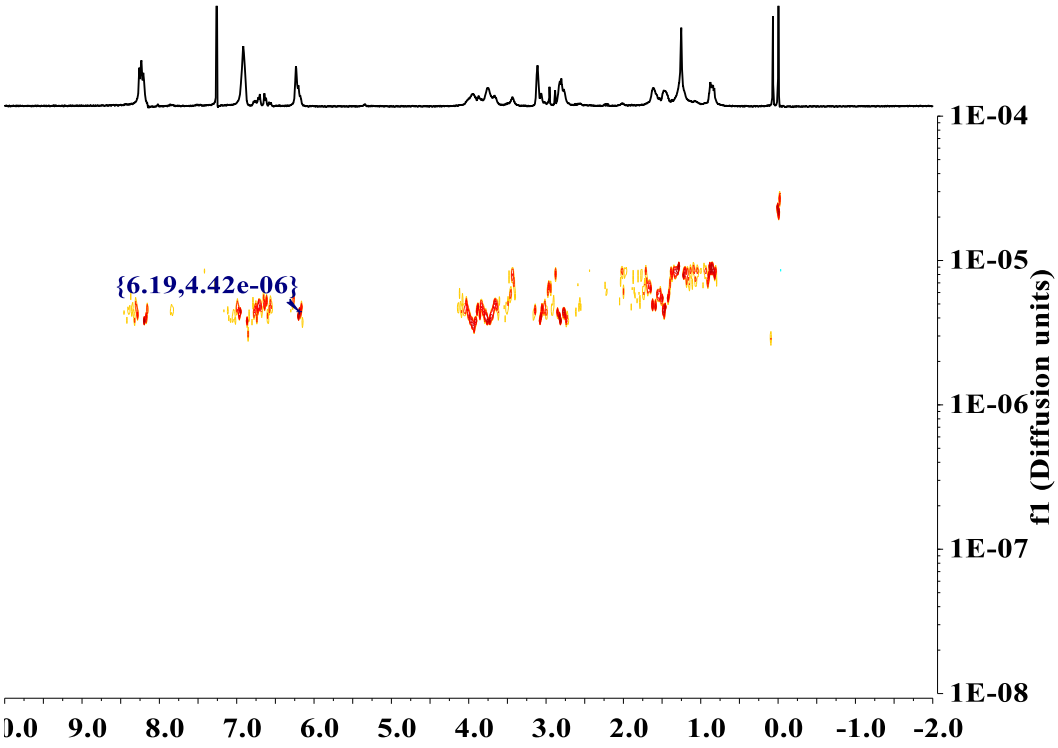


Figure S29 The 2D-^{1}HDOSY-NMR spectrum ($CDCl_3$, 293K) of L-Azo-POP, which was synthesized in DMF.

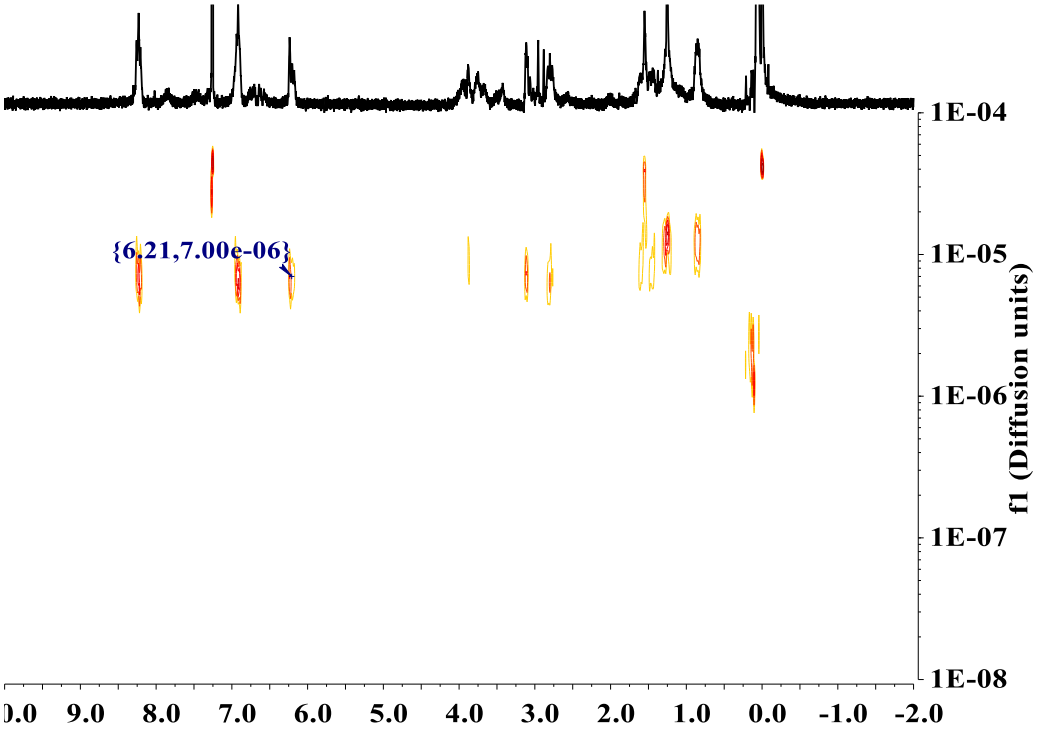


Figure S30 The 2D-^{1}HDOSY-NMR spectrum ($CDCl_3$, 293K) of L-Azo-POP, which was synthesized in DMSO.

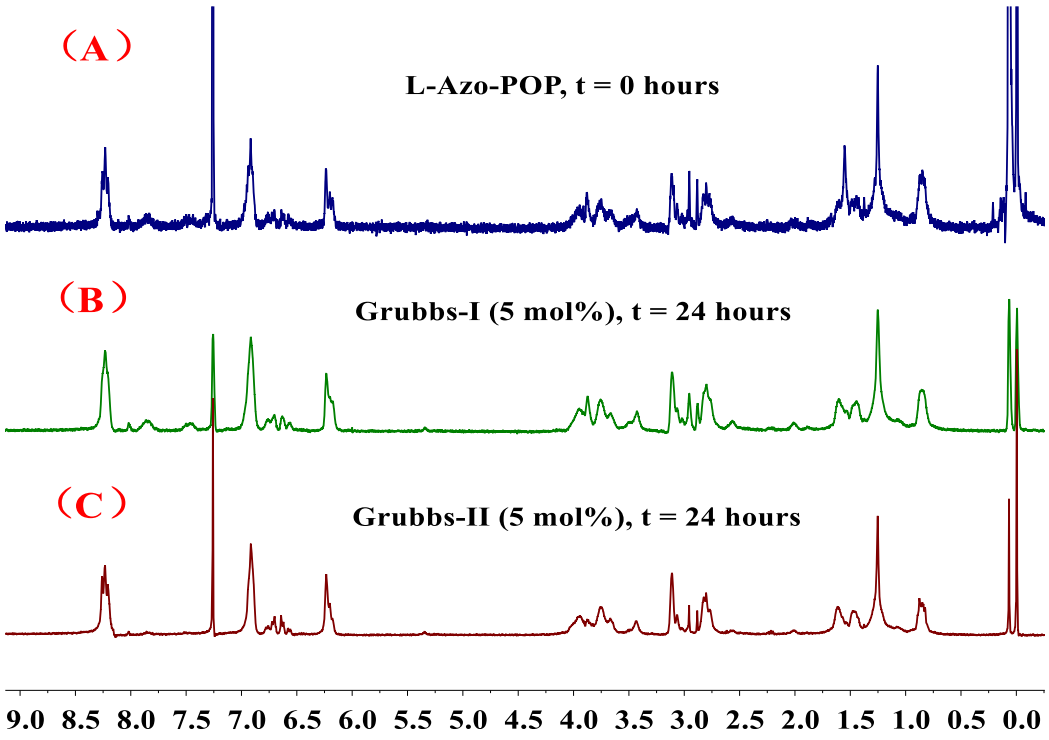


Figure S31 Comparison between the ^{1}H-NMR (400 MHz, $CDCl_3$) of L-Azo-POP (A), ROMP on L-Azo-POP (by G-I, 5 mol%, B) and L-Azo-POP (by G-II, 5 mol%, C)

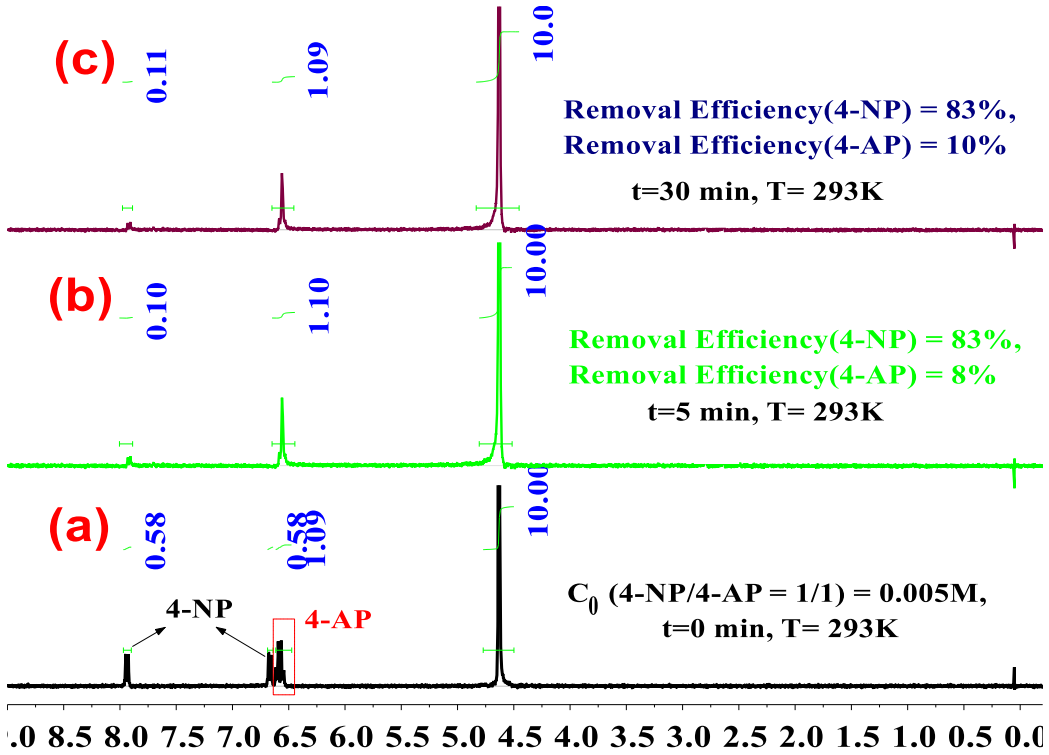


Figure S32 The selective adsorption of 4-NP (0.01 mmol) and 4-AP (0.01 mmol) in D_2O (2 mL) with absorbents: Azo-POP-13 (10 mg), t=0 min (a); t=5 min (b); t=30 min (c) detection on ^{1}H NMR spectra.

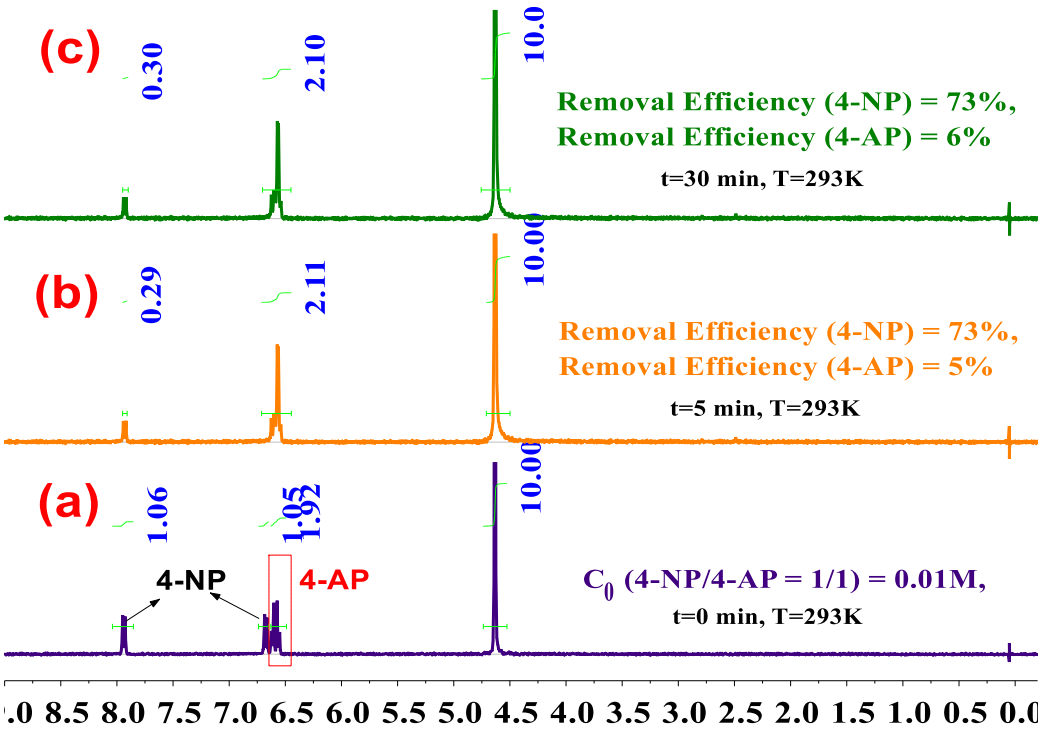


Figure S33 The selective adsorption of 4-NP (0.02 mmol) and 4-AP (0.02 mmol) in D_2O (2 mL) with absorbents: Azo-POP-13 (10 mg), t=0 min (a); t=5 min (b); t=30 min (c) detection on ^1H NMR spectra.

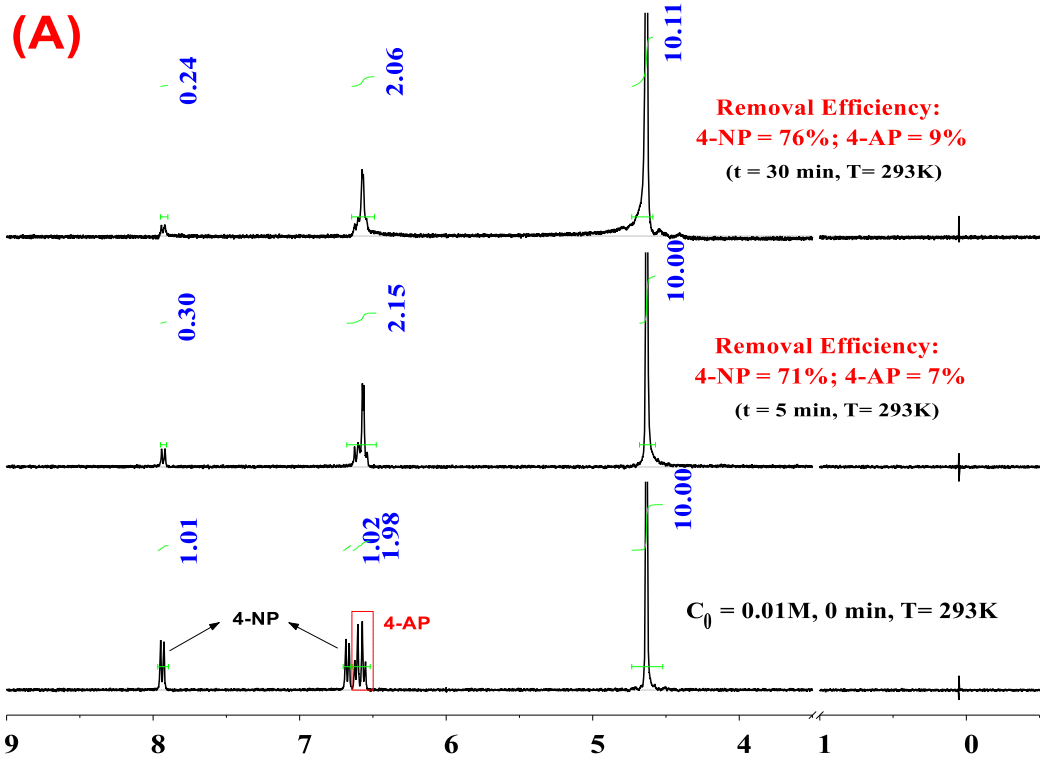


Figure S34 The selective adsorption of 4-NP (0.02 mmol) and 4-AP (0.02 mmol) in D_2O (2 mL) with absorbents: recycled Azo-POP-13 (10 mg), t=0 min (a); t=5 min (b); t=30 min (c) detection on ^1H NMR spectra.

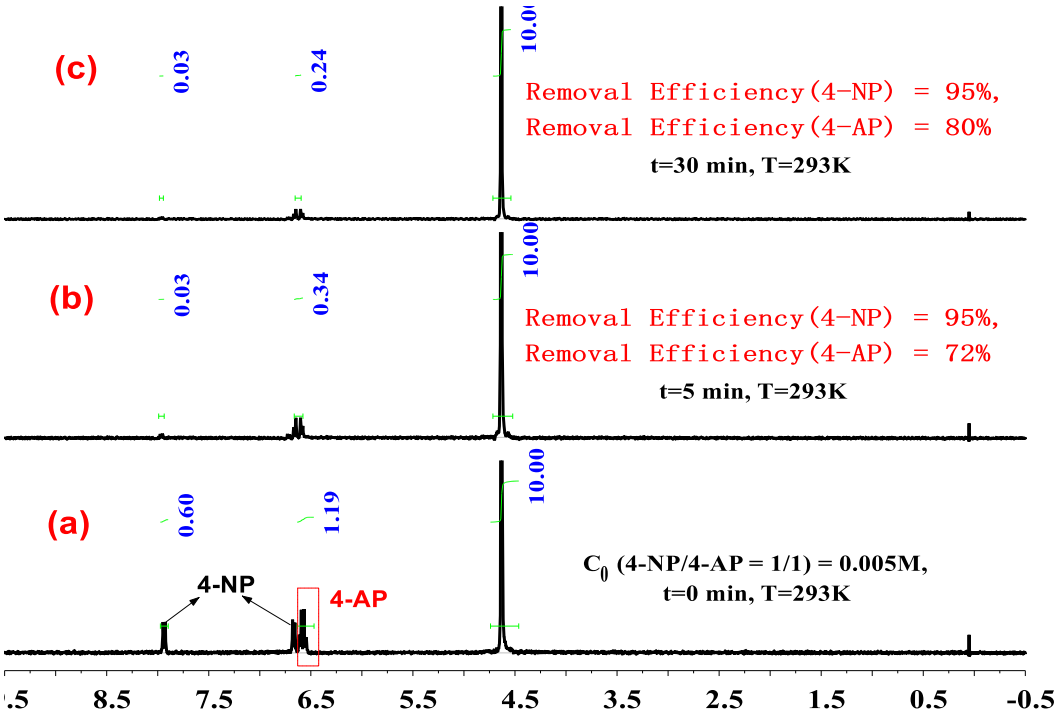


Figure S35 The selective adsorption of 4-NP (0.01 mmol) and 4-AP (0.01 mmol) in D_2O (2 mL) with absorbents: Activated Carbon (10 mg), t=0 min (a); t=5 min (b); t=30 min (c) detection on ^1H NMR spectra.

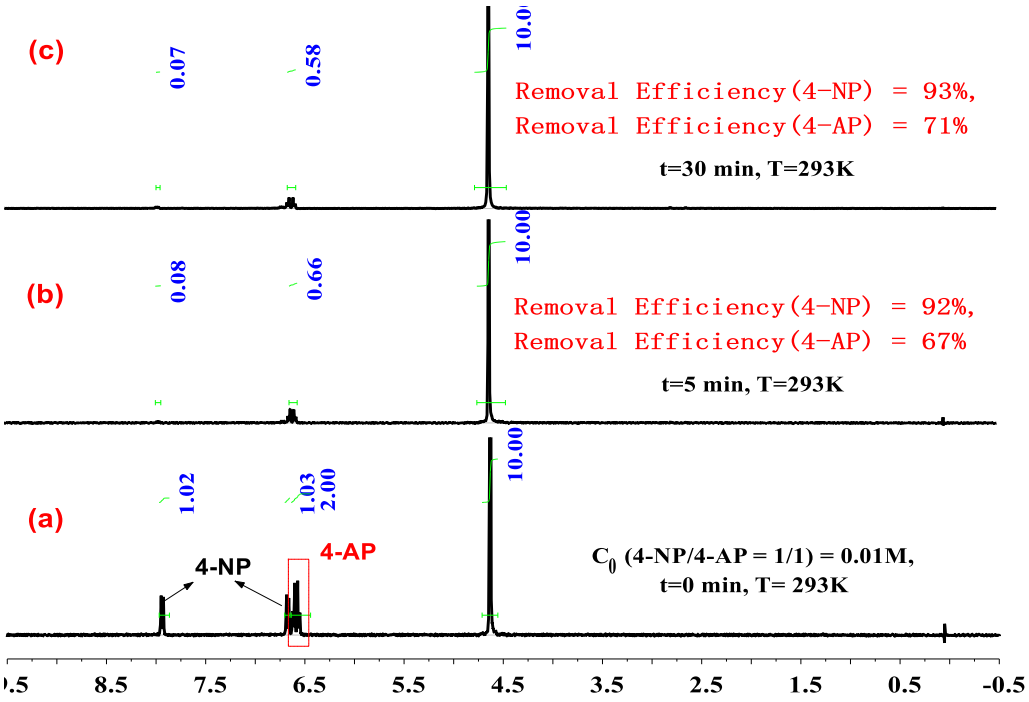


Figure S36 The selective adsorption of 4-NP (0.02 mmol) and 4-AP (0.02 mmol) in D_2O (2 mL) with absorbents: Activated Carbon (10 mg), t=0 min (a); t=5 min (b); t=30 min (c) detection on ^1H NMR spectra.

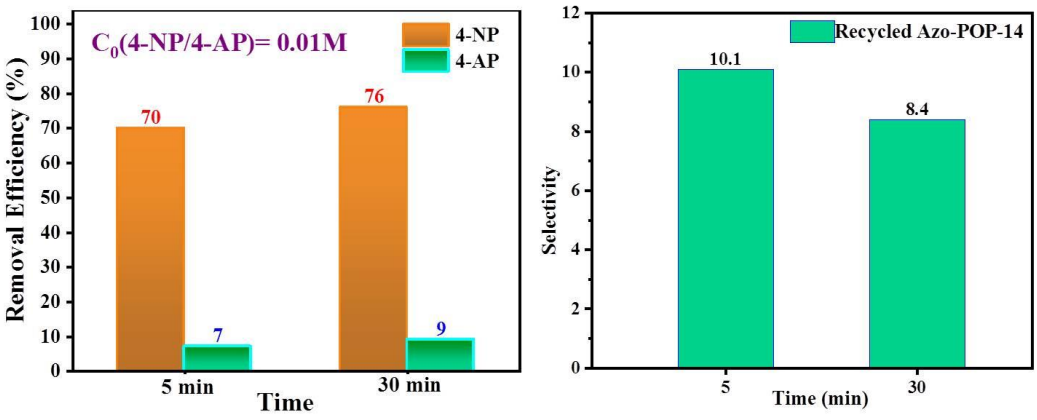


Figure S37 Comparison of removal efficiency and adsorption selectivity at different time with C_0 (4-NP/4-AP) = 0.01 M (b) by recycled Azo-Pop-13.

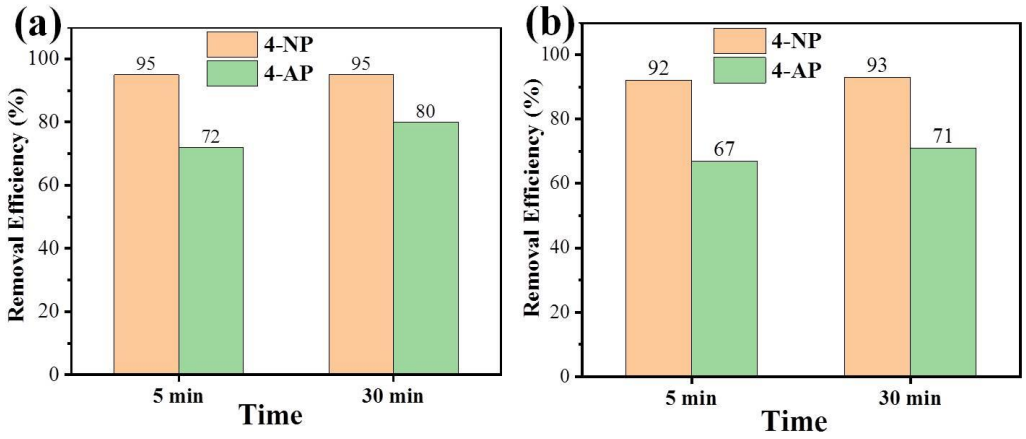


Figure S38 Comparison of removal efficiency at different time with C_0 (4-NP/4-AP) = 0.005 M (a) and C_0 (4-NP/4-AP) = 0.01 M (b) by activated carbon.

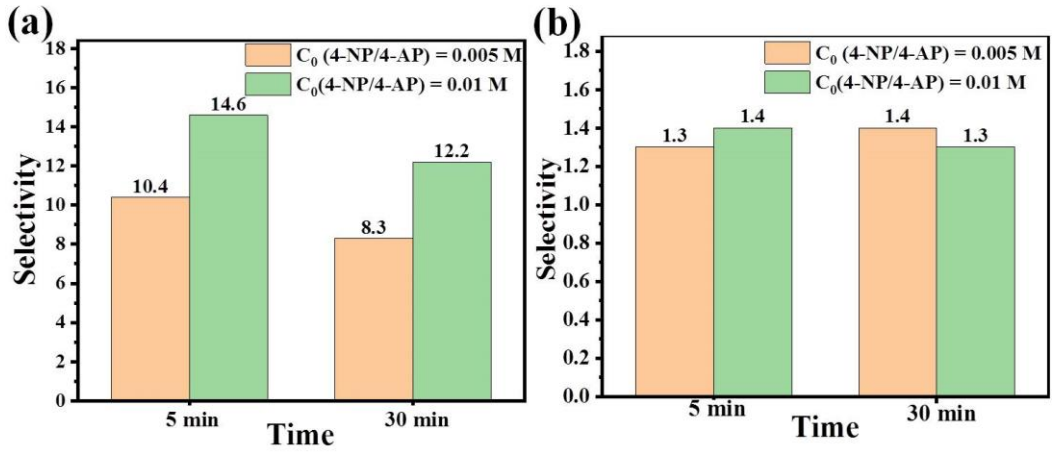


Figure S39 Comparison of adsorption selectivity towards 4-NP over 4-AP at different time with C_0 (4-NP/4-AP) = 0.005 M and 0.01 M by Azo-POP-13 (a) and activated carbon (b).

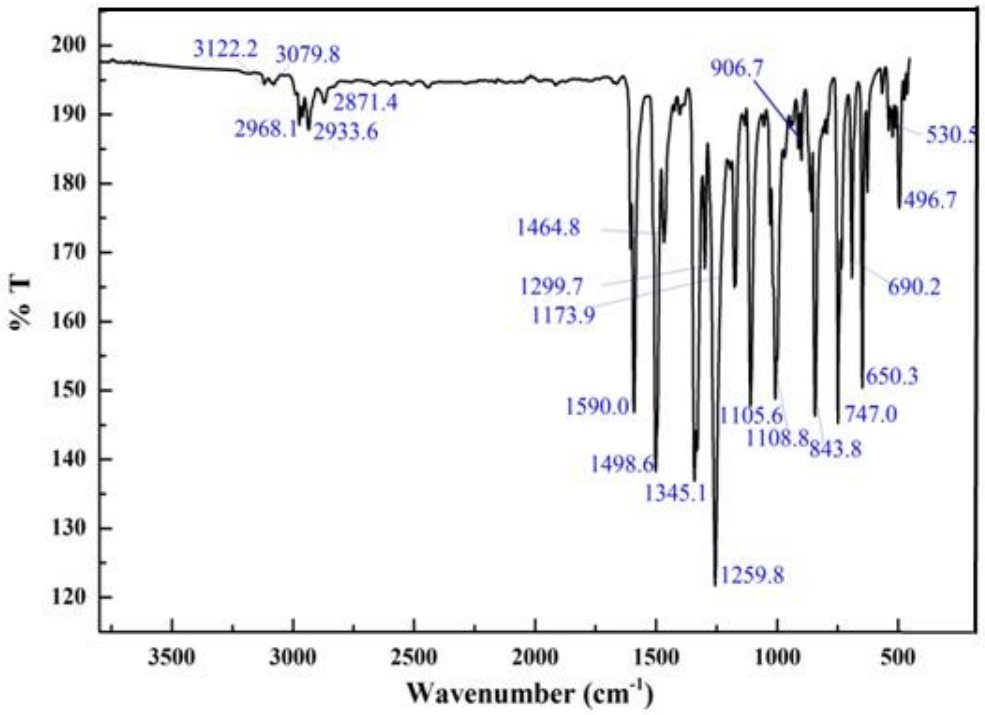


Figure S40 The FT-IR spectrum of endo-NBNPE (7)

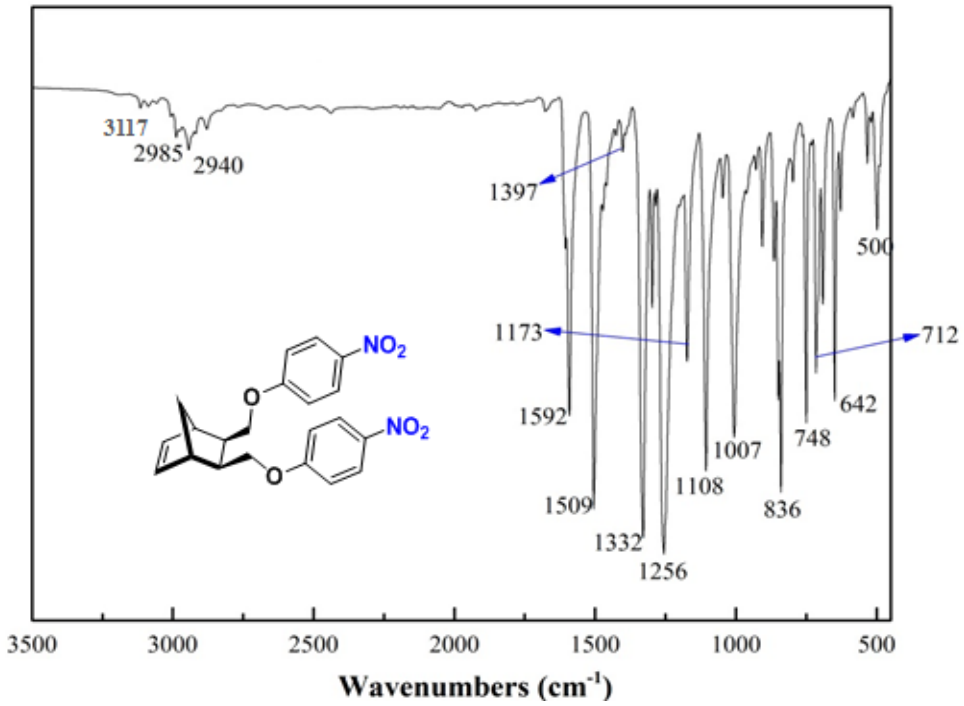


Figure S41 The FT-IR spectrum of exo-NBNPE (8)

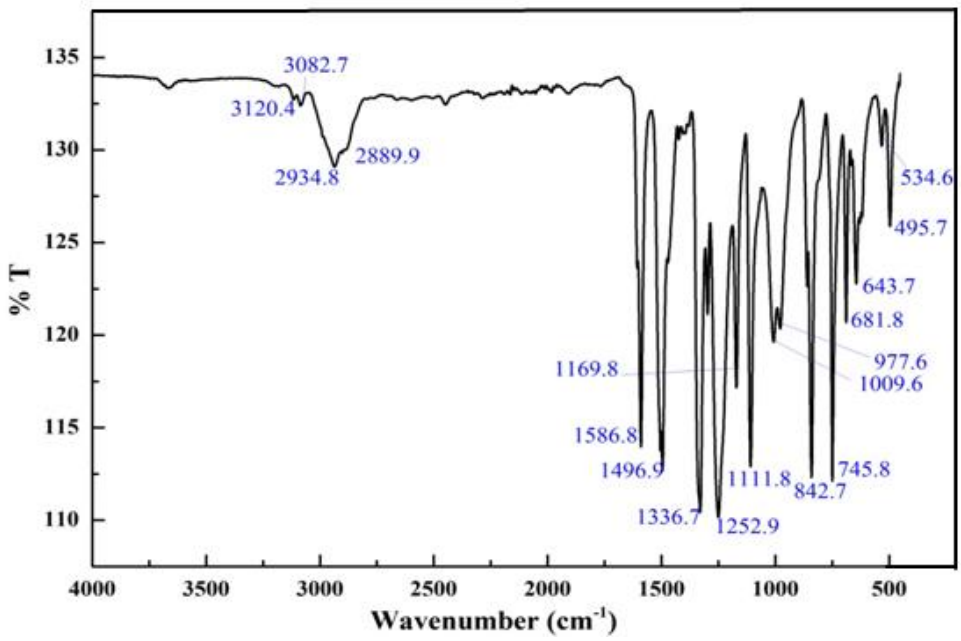


Figure S42 The FT-IR spectrum of endo-PNBNPE (9)

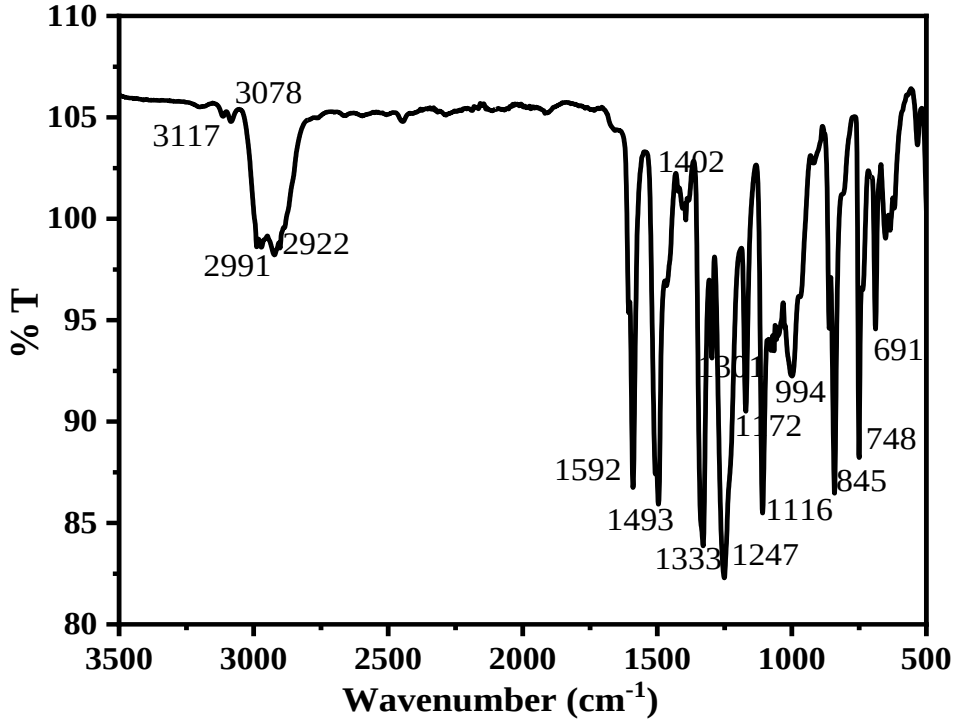


Figure S43 The FT-IR spectrum of exo-PNBNPE (10)

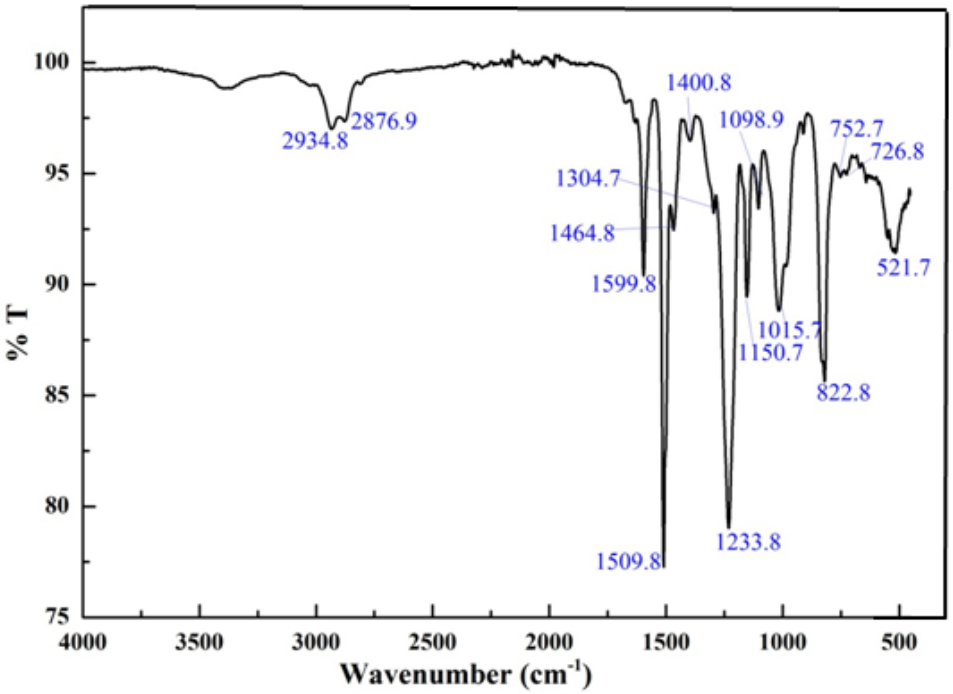


Figure S44 The FT-IR spectrum of Azo-POP-13

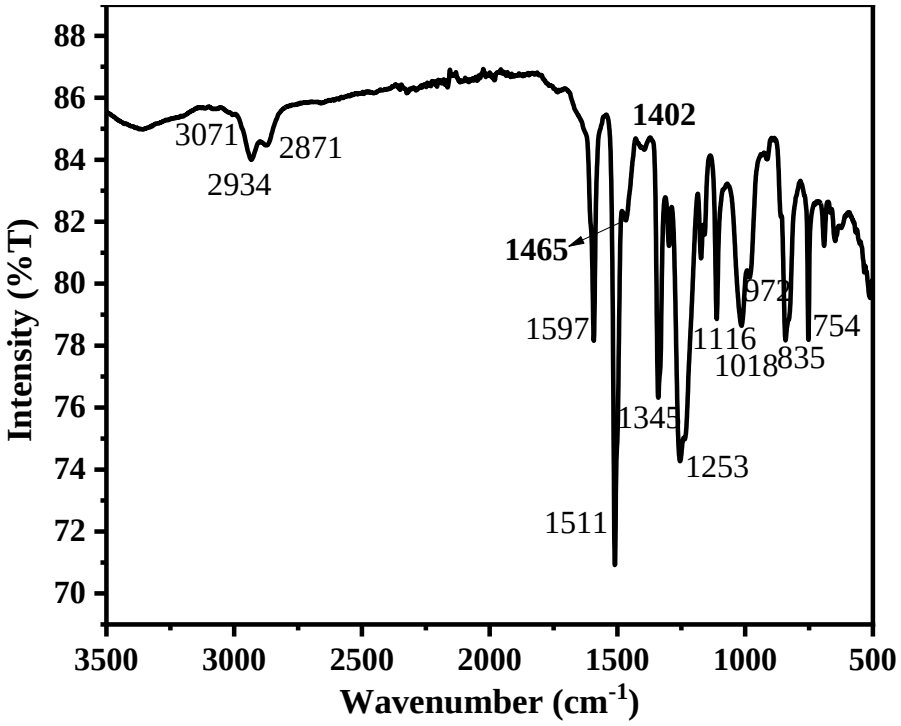


Figure S45 The FT-IR spectrum of Azo-POP-14

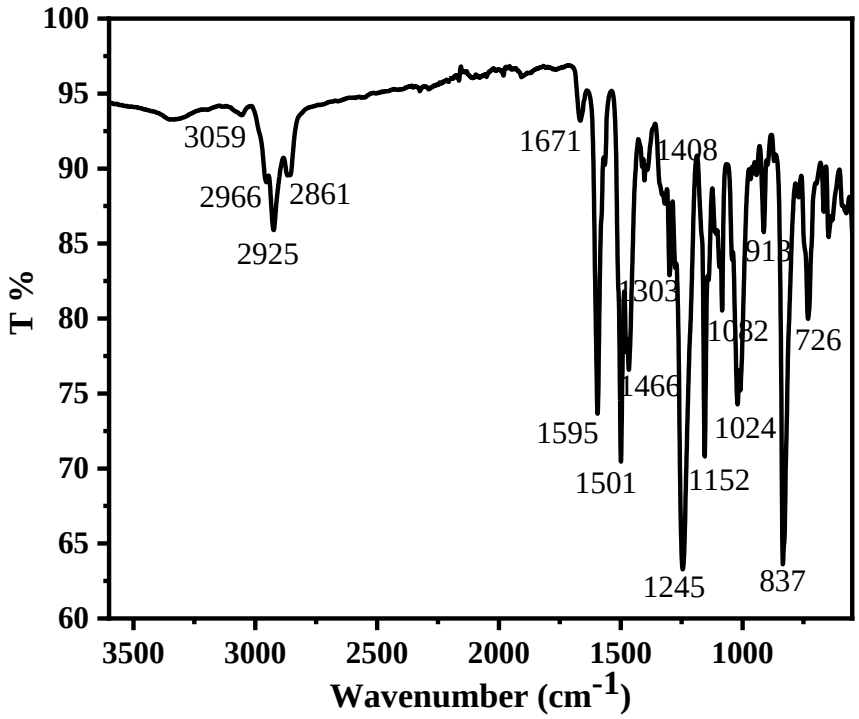


Figure S46 The FT-IR spectrum of L-Azo-Polymer

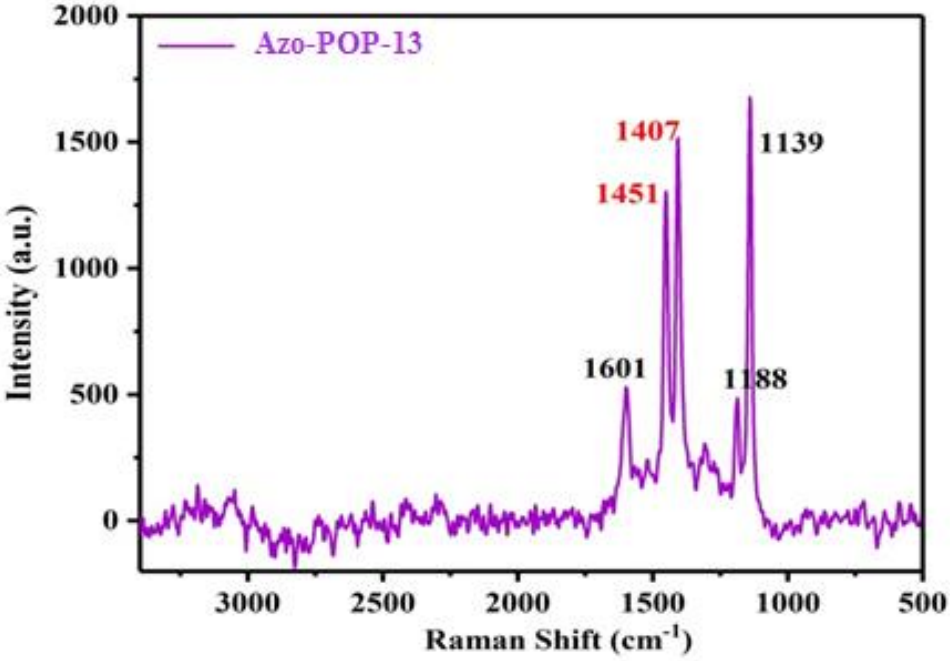


Figure S47 The Ramman spectrum of Azo-POP-13

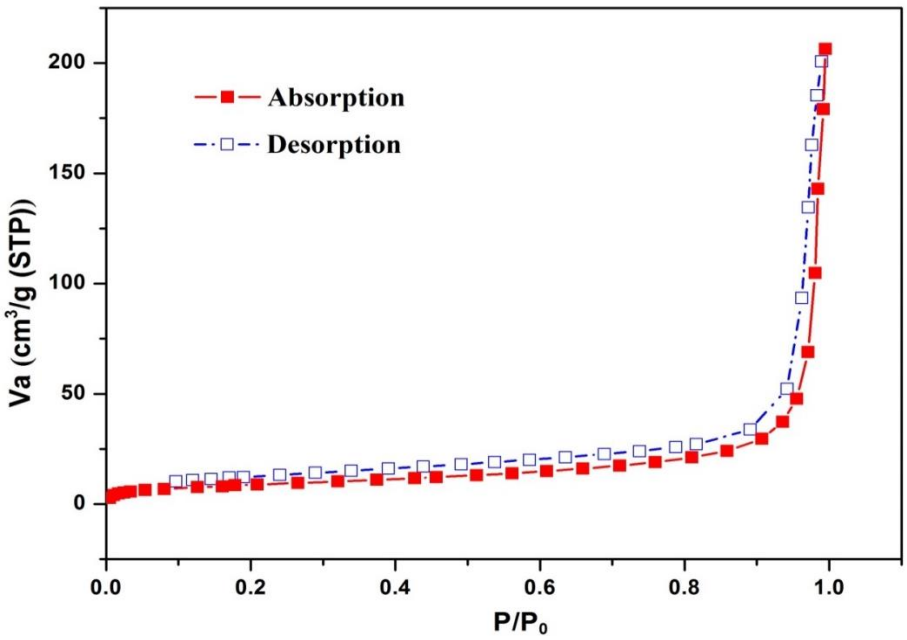


Figure S48 Nitrogen sorption–desorption isotherm of endo-PNBNPE (SA_{BET} = 32 $m^2.g^{-1}$)

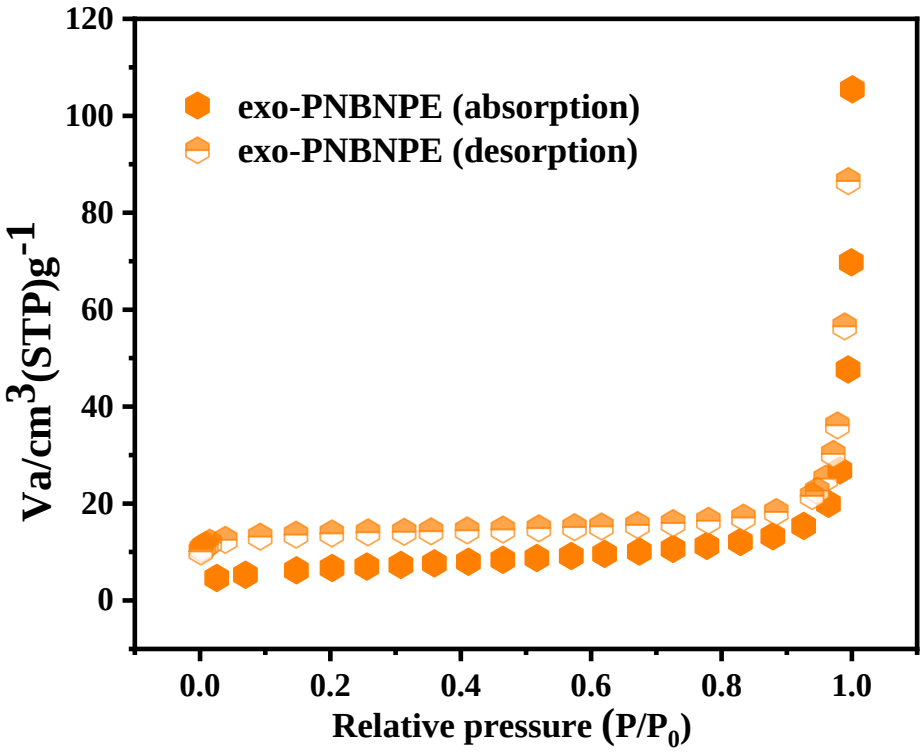


Figure S49 Nitrogen sorption–desorption isotherm of exo-PNBNPE (SA_{BET} = 25 $m^2.g^{-1}$)

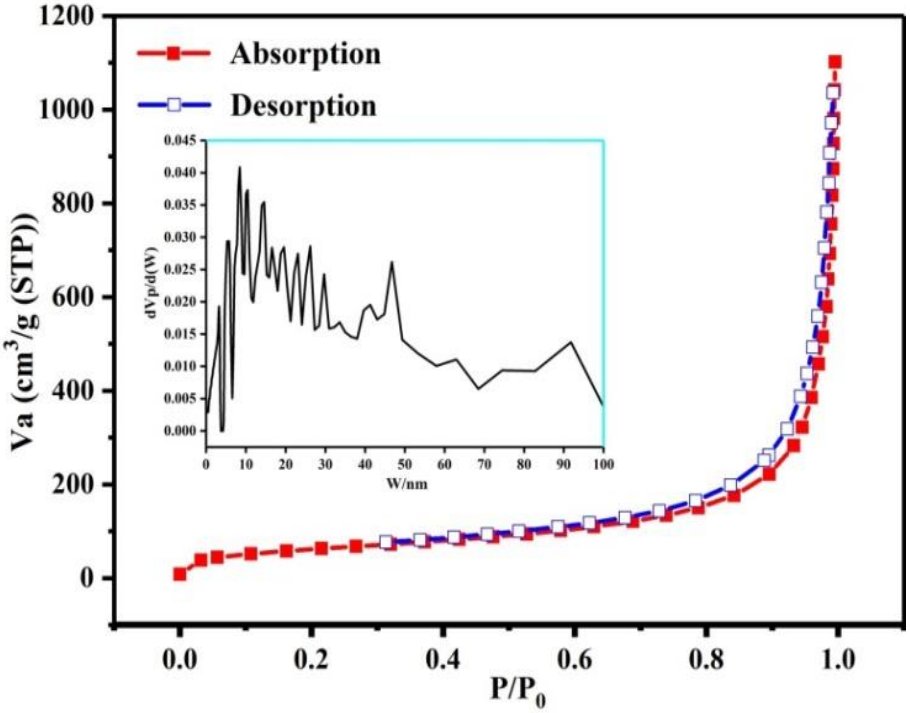


Figure S50 Nitrogen absorption–desorption isotherm and pore size distribution of Azo-POP-13 (SA_{BET} = 225 $m^2.g^{-1}$)

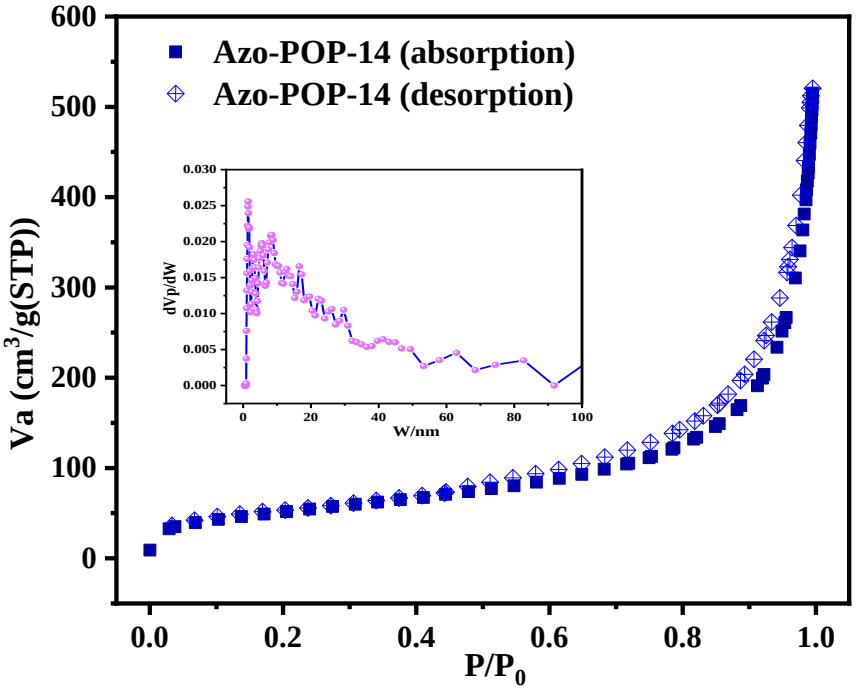


Figure S51 Nitrogen absorption–desorption isotherm and pore size distribution of Azo-POP-14 (SA_{BET} = 176 $m^2.g^{-1}$)

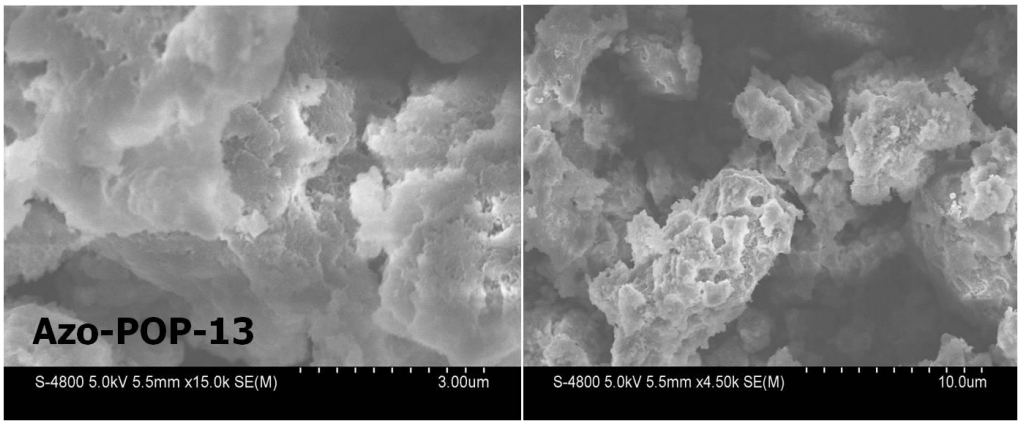


Figure S52 SEM images of Azo-POP-13

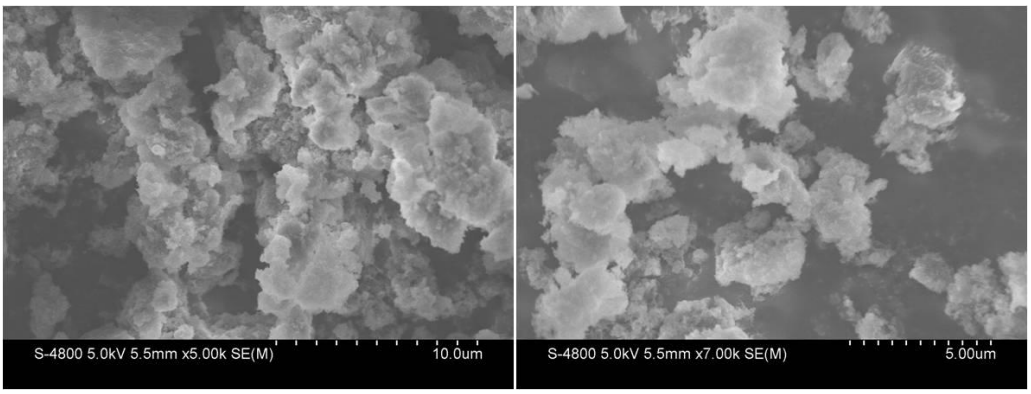


Figure S53 SEM images of Azo-POP-14

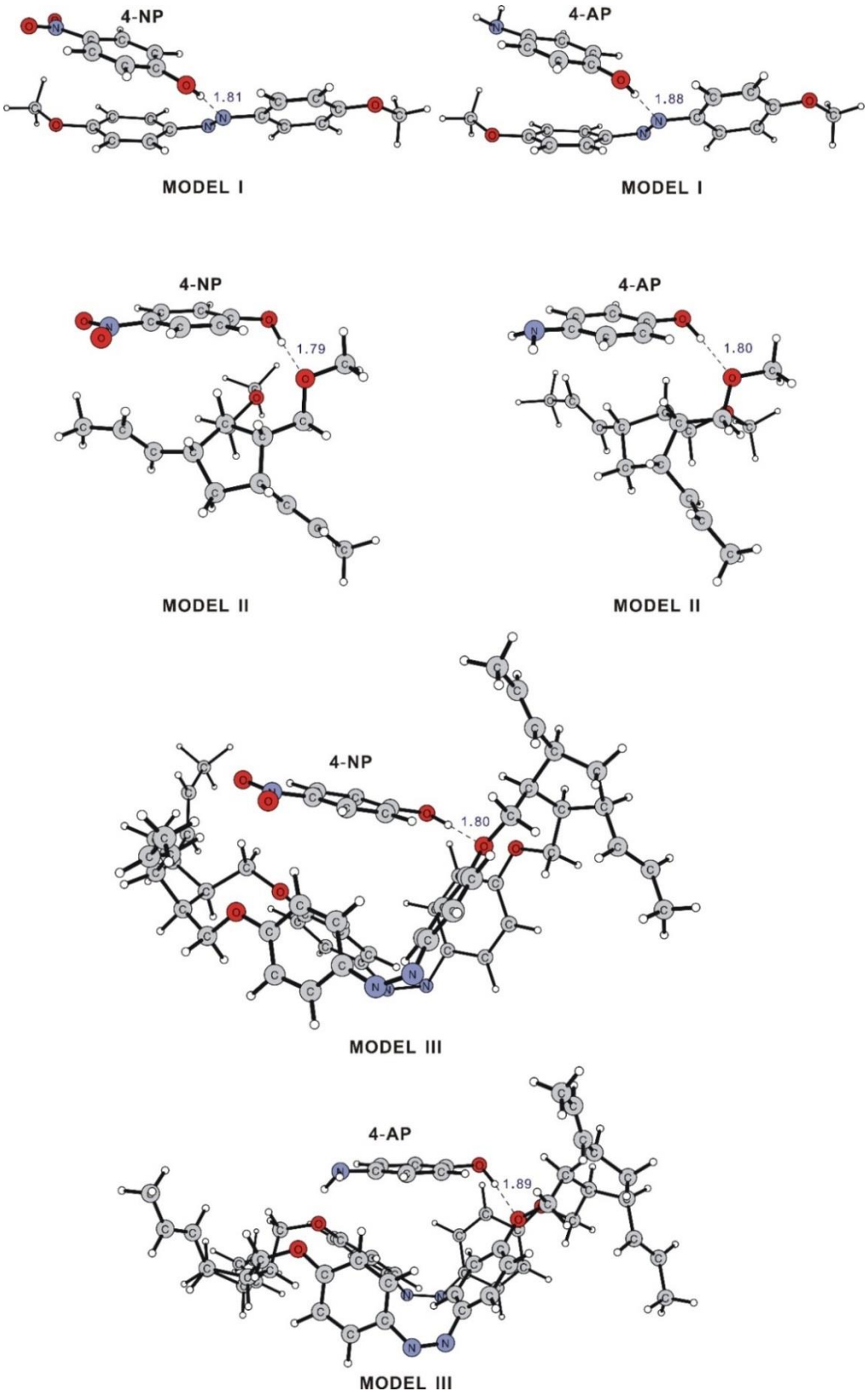


Figure S54 DFT-optimized complexes' structure between models and 4-NP/4- 4-AP The models (also shown in Table S10) represent 4,4'-dialkoxyl-azobenzene, dialkoxyl-nobornene and 4,4'-dialkoxyl-azobenzene-norbornene subunit in Azo-POP-13, respectively. The distances are shown in angstrom (Å).

6 References:

1. K. Jiang, H.-L. Deng, Q. Zhang, S. Wang, H. Wu, Y. Liu, C. Chai and M.-H. Huang, *Green Chemistry*, 2018, **20**, 2813-2820.
2. T. R. Long, P. K. Maity, T. B. Samarakoon and P. R. Hanson, *Org. Lett.*, 2010, **12**, 2904-2907.