A Novel Supramolecular Polymer π-gel Based on Bis-Naphthalimide Functionalized-Pillar[5]arene for Fluorescence Detection and Separation of Aromatic Acid Isomers

Qi Lin,*[a] Xiao-Wen Guan,[a] Shan-Shan Song, [a] Haiyan Fan,[b] Hong Yao,[a] You-Ming Zhang,[a] Tai-Bao Wei*[a]

[a] *Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu, 730070, P. R. China. E-mail: linqi2004@126.com; weitaibao@126.com.*

[b] *Chemistry Department, School of Science and Technology, Nazarbayev University Astana 010000, Kazakhstan.*

Contents

1. Experimental section

Materials and methods. All reagents were analytical purification, which were purchased from Alfa Aesar and used as received. Fresh double distilled water was used throughout the experiment. Nuclear magnetic resonance (NMR) spectra were recorded on Varian Mercury 400 and Varian Inova 600 instruments. Mass spectra were recorded on a Bruker Esquire 6000 MS instrument. The X-ray diffraction analysis (XRD) was performed in a transmission mode with a Rigaku RINT2000 diffractometer equipped with graphite monochromated CuKa radiation (λ = 1.54073 Å). The morphologies and sizes of the xerogels were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8 kV. The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Absorbance values were recorded on Shimadzu UV-2550 spectrometer.

Xerogel preperation: The compounds **BPN** (5.0 mg) was added into cyclohexanol (0.20 mL), the **BPN** was heated to dissolve, then the hot was dumped on the glass plate and aired at room temperature, obtaining the xerogel.

2. Characterization Spectra of compounds **M**, **PB**, **NA**, **BPN**, **FPN** and **ZPN**.

Synthesis of compound PZ: Compound **PZ** was prepared according to the published procedures.[S1]

Synthesis of compound M: The mixture of 1,10-dibromodecane (1.20 g, 4.0 mmol) and KI (0.66 g, 4.0 mmol) was added to a solution of K_2CO_3 (0.14 g, 1.0 mmol) and hydroquinone (0.11 g, 1.0 mmol) in acetone (200 mL). The mixture was heated and refluxed under nitrogen atmosphere for 72 h. The solid was filtered and the solvent was removed. The residue was recrystallized in dichloromethane and petroleum ethers. The white solid product M was collected by filtration, and dried under vacuum (0.45 g, 82 %). M.p: 83-85 °C. The ^{1}H NMR spectrum of **M** is shown in Fig. S1. ^{1}H NMR (600 MHz, $CDCl_3$). δ 6.81 (s, 4H), 3.89 (t, J = 4.4 Hz, 4H), 3.40 (t, J = 4.4 Hz, 4H), 1.87-1.82 (m, 4H), 1.77-1.72 (m, 4H), 1.46-1.30 (m, 24H).

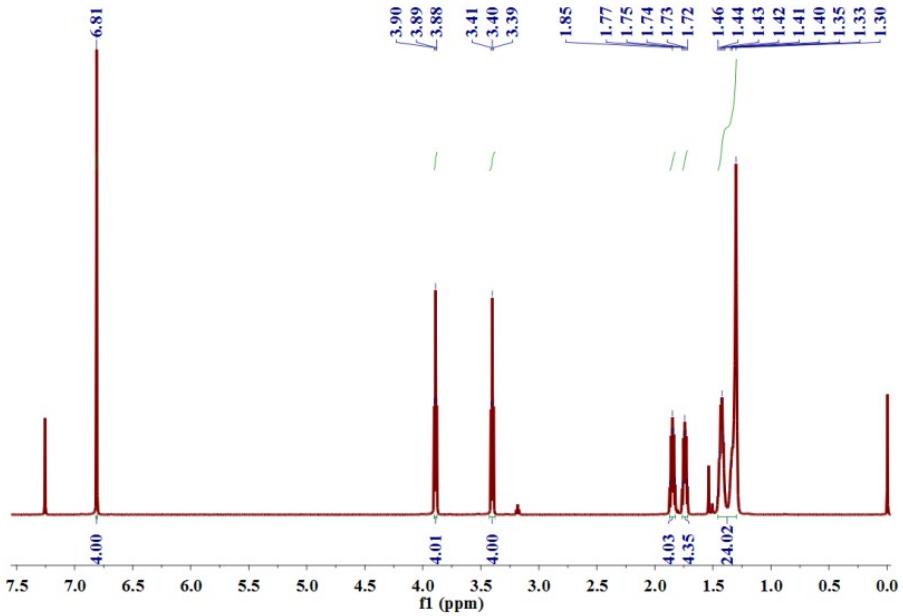

Fig. S1. ^{1}H NMR spectrum of compound **M** ($CDCl_3$, 600 MHz, 298 K).

Synthesis of the pillar[5]arene PB: Paraformaldehyde (0.75 g, 25.0 mmol) was added to a solution of 1,4-dimethoxybenzene (3.36 g, 24.0 mmol) and the compound **M** (1.60 g, 3.0 mmol) in 1,2-dichloroethane (200 mL). Then, boron trifluoride diethyl etherate ($BF_3O(C_2H_5)_2$, 4.5 ml) was added to the solution, and the mixture was stirred at 30 °C for 15-30 min. The solution was poured into water (100 mL) to quench the reaction. The mixture was filtered and the solvent was removed. The residue was dissolved in dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was isolated by column chromatography using ethyl acetate/petroleum ether (v/v, 1:40) to give **PB** as a white solid (1.39 g, 40 %). M.p: 111-113 °C. The ^{1}H NMR spectrum of **PB** is shown in Fig. S2. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 6.95-6.86 (m, 10H), 3.94 (t, J = 4.4 Hz, 4H), 3.79 (s, 10H), 3.77-3.76 (m, 28H), 1.87-1.82 (m, 6H), 1.54-1.50 (m, 7H), 1.33 (m, 7H), 1.17 (s, 6H), 0.88-0.86 (m, 6H). The ^{13}C NMR spectrum of **PB** is shown in Fig. S3. ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 150.27, 150.19, 150.16, 149.51, 128.10, 128.07, 127.95, 114.06, 113.47, 113.03, 112.98, 112.93, 67.86, 55.46, 55.25, 55.21, 33.85, 32.16, 29.21, 29.09, 28.07, 27.73. ESI-MS is shown in Fig. S4: m/z $[M + NH_4]^+$ calcd. for $C_{63}H_{88}Br_2NO_{10}$ 1178.4769, found 1178.4758.

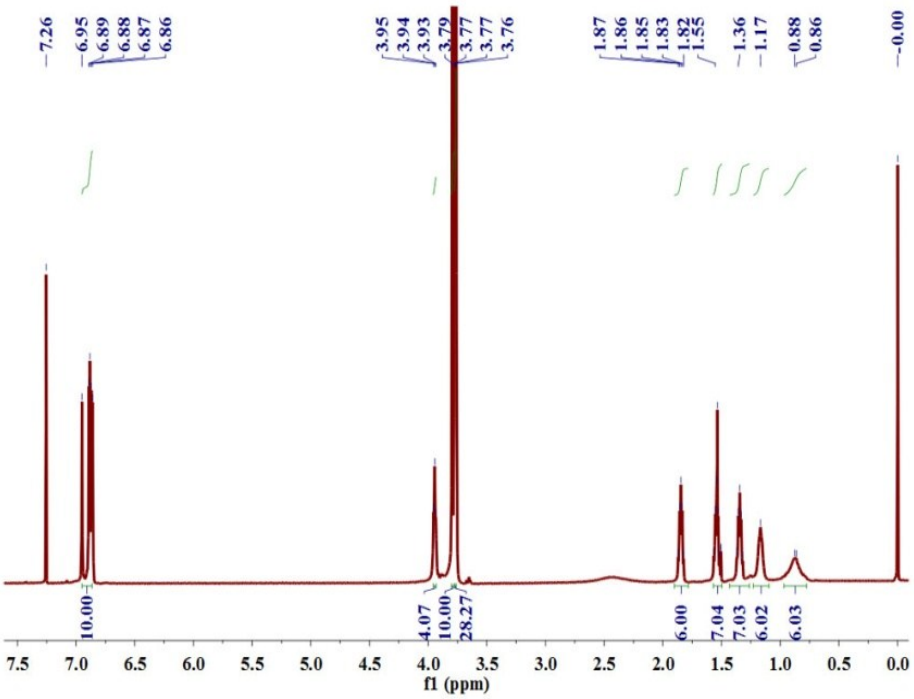

Fig. S2. ^{1}H NMR spectrum of compound **PB** ($CDCl_3$, 600 MHz, 298 K).

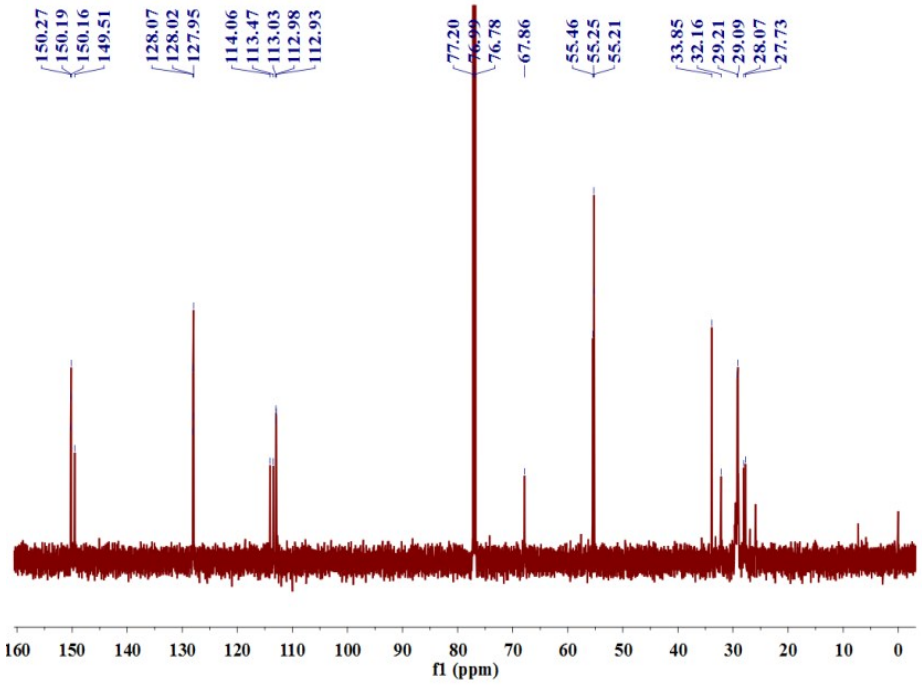

Fig. S3. ^{13}C NMR spectrum of compound **PB** ($CDCl_3$, 150 MHz, 298 K).

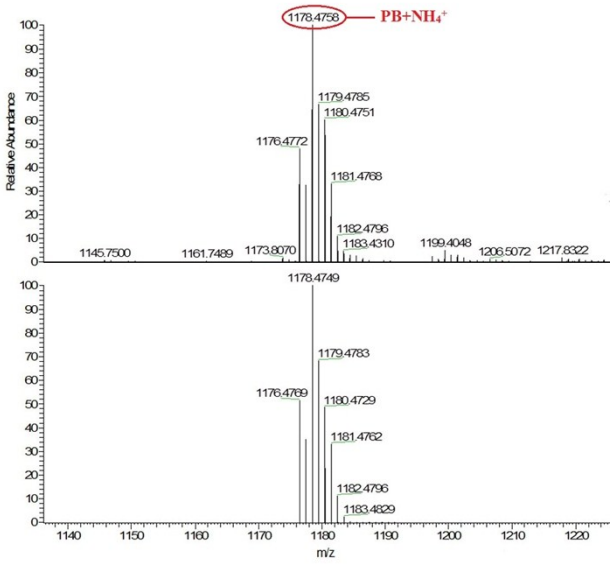

Fig. S4. Mass spectrum of **PB**

Synthesis of compound NA: The mixture of 1,8-naphthalic anhydride (0.19 g, 1.0 mmol) and 4-aminophenol (0.22 g, 2.0 mmol) was added into C_2H_5OH (60 mL). Then, the reaction mixture was stirred and refluxed for 48 h. After reaction was finished, the solvent was filtered under reduced pressure. The crude product was washed with ethanol to give **NA** as a white solid (0.28 g, 96 %). M.p: > 290 °C. The proton NMR spectrum of **NA** is showed in Fig. S5. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 9.65 (s, 1H), 8.47-8.46 (t, J = 5.2 Hz, 4H), 7.86 (t, J = 5.2 Hz, 2H), 7.15-7.13 (d, J = 5.6 Hz, 2H), 6.88-6.87 (d, J = 5.6 Hz, 2H). The ^{13}C NMR spectrum of **NA** is showed in Fig. S6. ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm): 164.28, 157.55, 134.72, 130.34, 127.32, 123.07, 115.82.

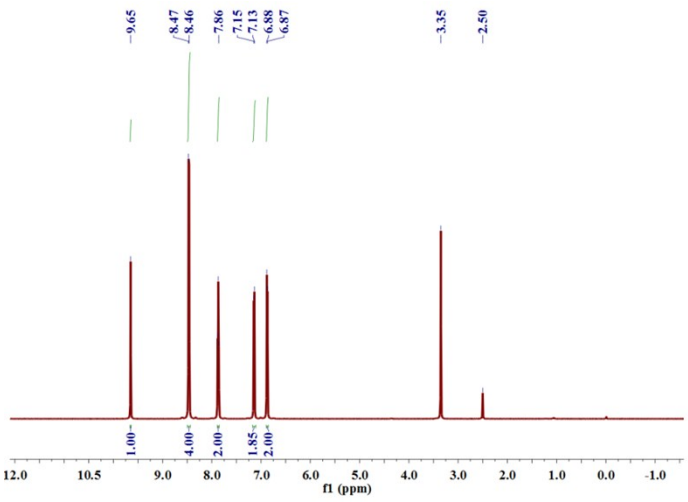

Fig. S5. ^{1}H NMR spectrum of compound **NA** (DMSO–d_6, 600 MHz, 298 K).

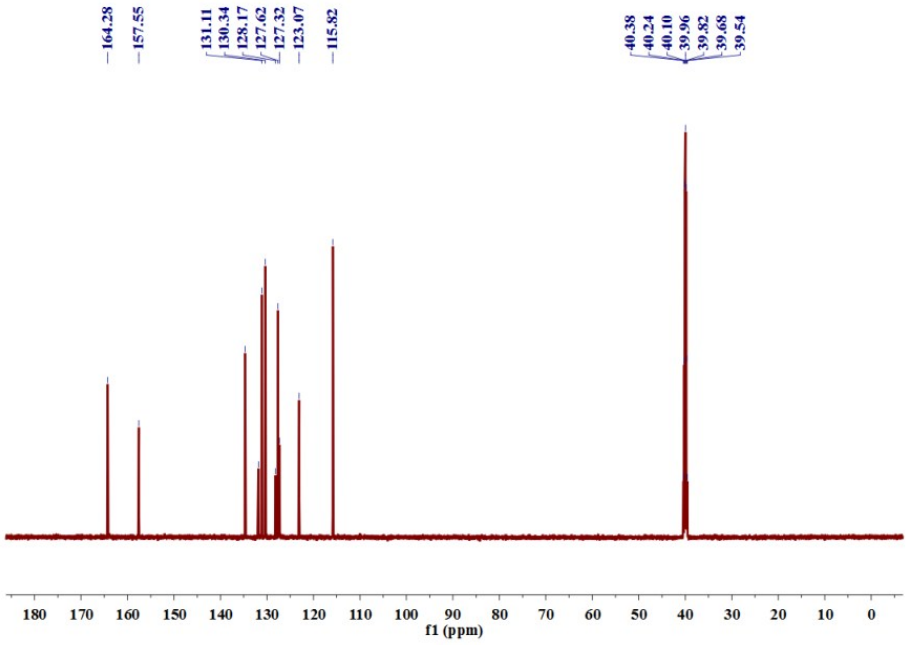

Fig. S6. ^{13}C NMR spectrum of compound **NA** (DMSO–d_6, 150 MHz, 298 K).

Synthesis of compound BPN: Compound **PB** (1.16 g, 1.0 mmol) was added to a mixture of compound **NA** (0.64 g, 2.2 mmol) and K_2CO_3 (0.42 g, 3.0 mmol) in acetonitrile (50 mL), and the resulting mixture was stirred and refluxed for 48 h. After reaction was finished, the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel. Elution with a mixture of dichloromethane/ethyl acetate (v/v, 50:1) afforded **BPN** as a yellow solid (1.29 g, 82 %). M.p: 102-103 °C. The ^{1}H NMR spectrum of **BPN** is shown in Fig. S7. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.65 (d, J = 7.2 Hz, 4H), 8.27-8.26 (d, J = 7.2 Hz, 4H), 7.79 (t, J = 7.6 Hz, 4H), 7.22-7.21 (d, J = 8.7 Hz, 4H), 7.03-7.02 (d, J = 8.7 Hz, 4H), 6.87-6.80 (m, 10H), 3.91-3.86 (m, 8H), 3.82-3.72 (m, 10H), 3.72-3.69 (m, 24H), 1.82-1.76 (m, 3H), 1.54-1.21 (m, 19H), 1.05 (s, 3H),0.89-0.85 (m, 7H). The ^{13}C NMR spectrum of **BPN** is shown in Fig. S8. ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.56, 159.20, 150.65, 134.16, 131.73, 131.55, 129.43, 128.10, 126.99, 122.91, 115.11, 68.29, 55.71, 55.68, 55.55, 29.08, 29.03. ESI-MS is shown in Fig. S9: m/z $[M]^+$ calcd. for $C_{99}H_{104}N_2O_{16}$ 1577.7419, found 1577.7498.

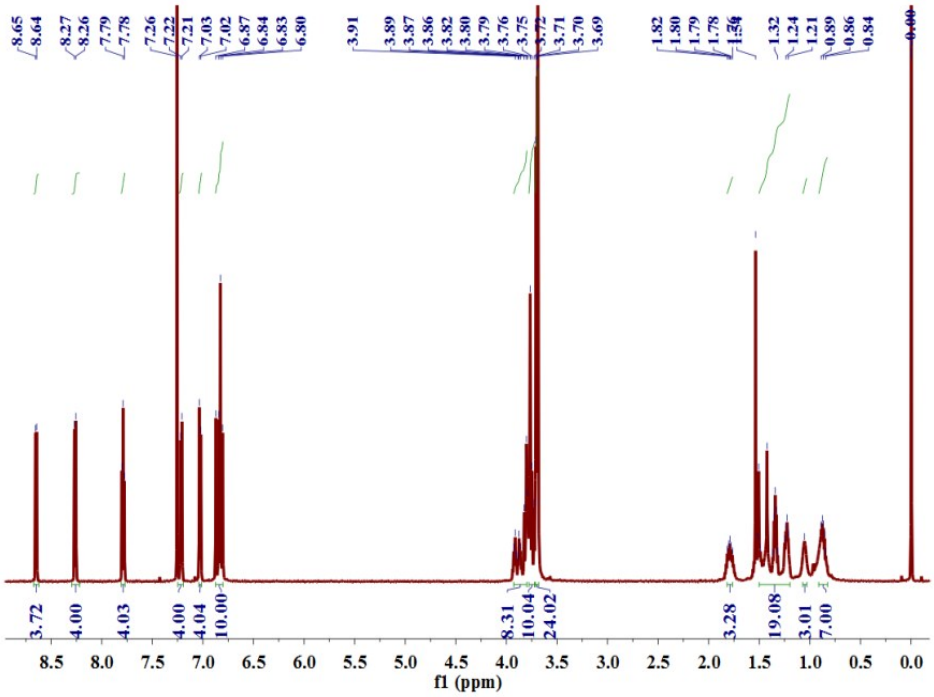

Fig. S7. ^{1}H NMR spectrum of compound **BPN** ($CDCl_3$, 600 MHz, 298 K).

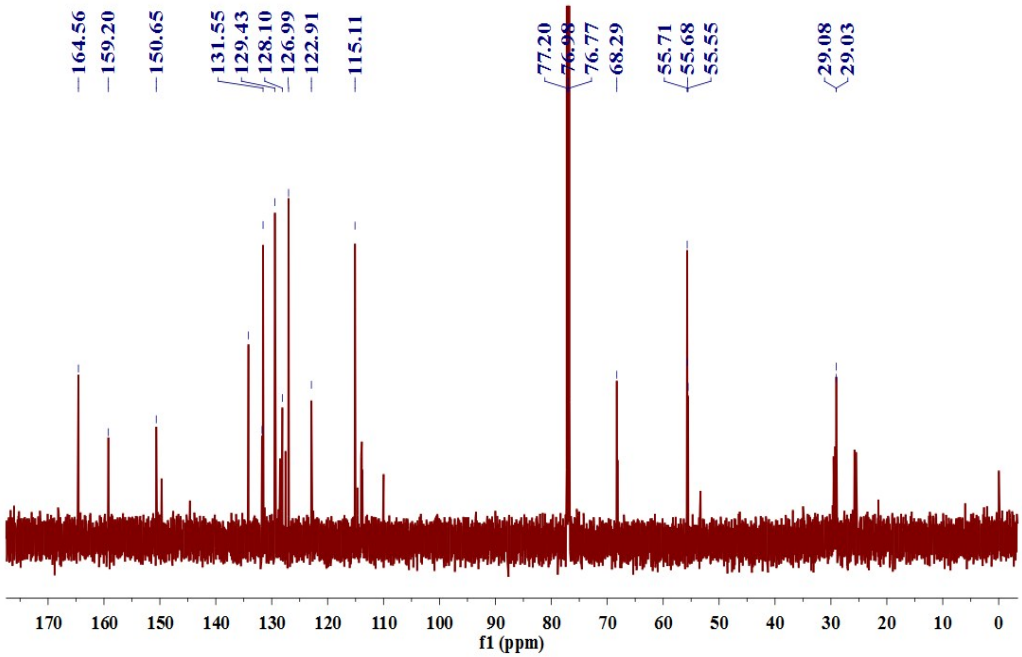

Fig. S8. ^{13}C NMR spectrum of compound **BPN** ($CDCl_3$, 150 MHz, 298 K).

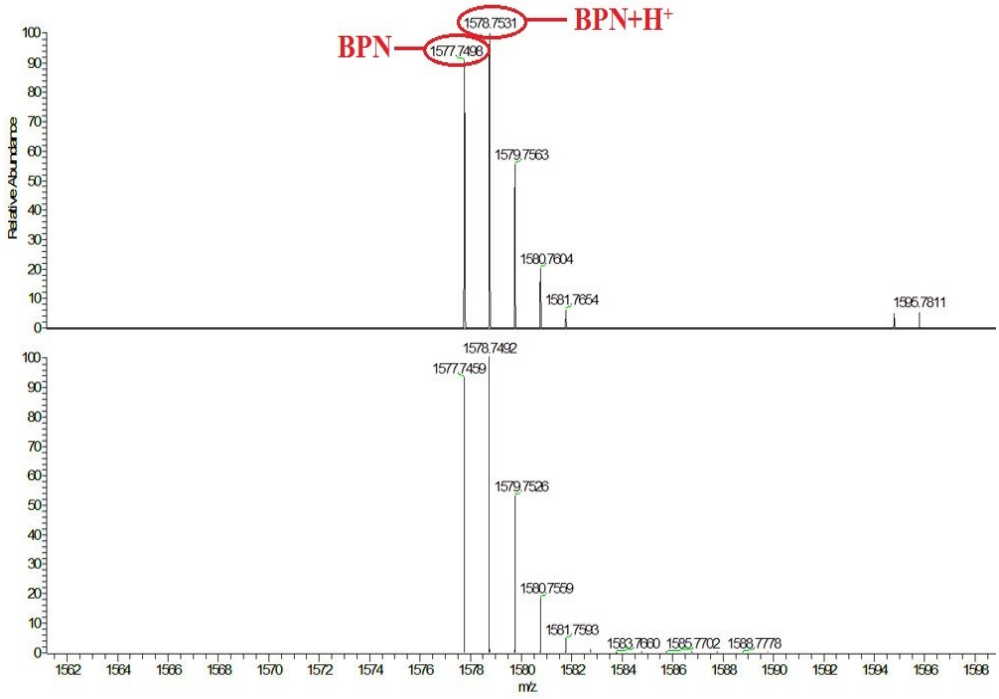

Fig. S9. Mass spectrum of **BPN**.

Synthesis of compound FPN: Compound **PB** (1.16 g, 1.0 mmol) was added to a mixture of compound **NA** (0.29 g, 1.0 mmol) and K_2CO_3 (0.42 g, 3.0 mmol) in acetonitrile (50 mL), and the resulting mixture was stirred and refluxed for 48 h. After reaction was finished, the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel. Elution with a mixture of dichloromethane/ethyl acetate (v/v, 50:1) afforded **FPN** as a yellow solid (0.79 g, 58 %). M.p: 94-96 °C. The proton NMR spectrum of **FPN** is shown in Fig. S10. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.65 (d, J = 7.4 Hz, 2H), 8.27-8.25 (d, J = 8.3 Hz, 2H), 7.79 (t, J = 7.4 Hz, 2H), 7.22-7.21 (d, J = 8.8 Hz, 2H), 7.03-7.02 (d, J = 8.8 Hz, 2H), 6.93-6.84 (m, 10H), 3.95-3.94 (m, 8H), 3.81-3.80 (m, 12H), 3.78-3.74 (m, 24H), 1.87-1.69 (m, 6H), 1.54-1.53 (m, 5H), 1.41-1.15 (m, 19H), 0.87-0.85 (m, 2H). The ^{13}C NMR spectrum of **FPN** is shown in Fig. S11. ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.55, 159.16, 150.21, 150.12, 131.55, 128.13, 128.01, 127.91, 122.90, 115.20, 112.93, 68.20, 67.87, 55.42, 55.39, 55.29, 33.09, 31.85, 29.78, 29.48, 29.32, 29.21, 29.14, 29.05, 26.24, 25.95. ESI-MS is shown in Fig. S12: m/z $[M+NH_4]^+$ calcd. for $C_{81}H_{98}BrN_2O_{13}$ 1387.6247, found 1387.6190.

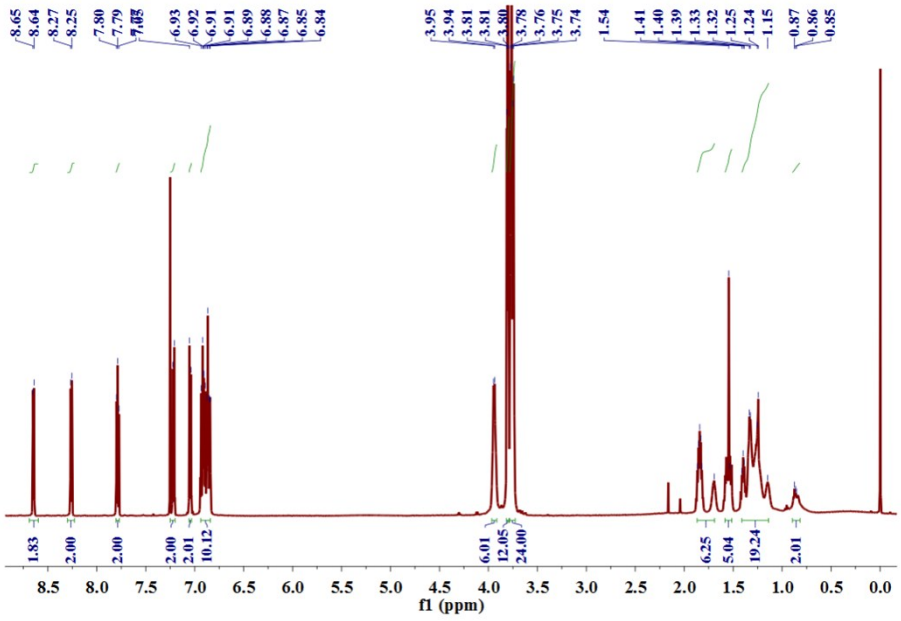

Fig. S10. ^{1}H NMR spectrum of compound **FPN** ($CDCl_3$, 600 MHz, 298 K).

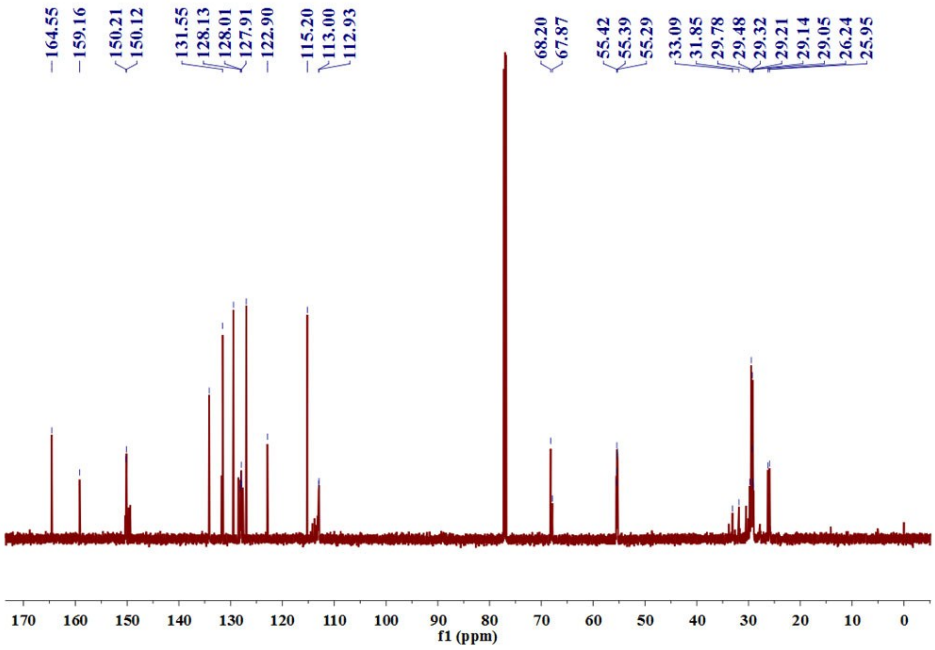

Fig. S11. ^{13}C NMR spectrum of compound **FPN** ($CDCl_3$, 150 MHz, 298 K).

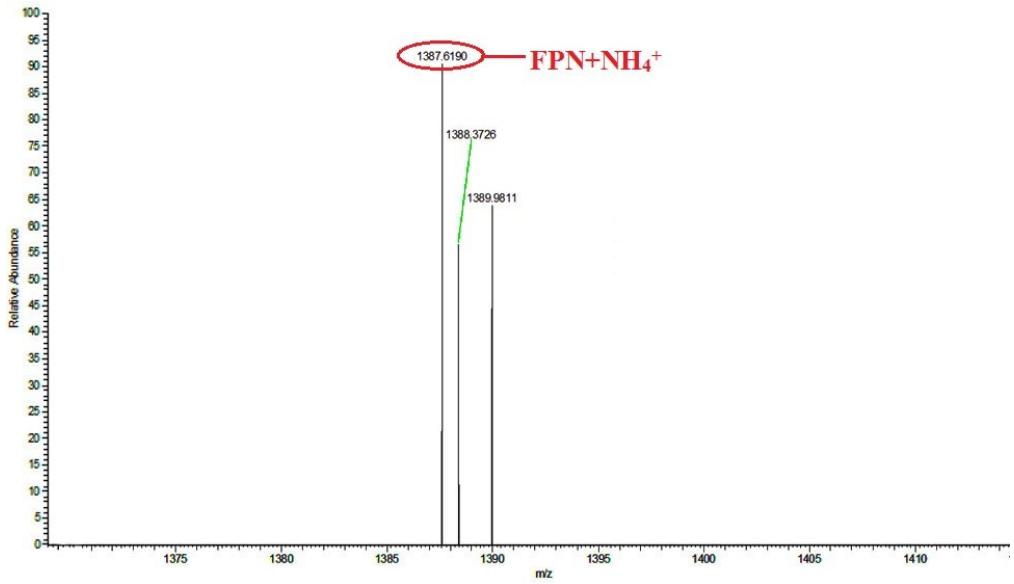

Fig. S12. Mass spectrum of **FPN**.

Synthesis of compound ZPN: Compound **PZ** (0.95 g, 1.0 mmol) was added to a mixture of compound **NA** (0.29 g, 1.0 mmol) and K_2CO_3 (0.42 g, 3.0 mmol) in acetonitrile (50 mL), and the resulting mixture was stirred and refluxed for 48 h. After reaction was finished, the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel. Elution with a mixture of petroleum ethers/ethyl acetate (v/v, 30:1) afforded **ZPN** as a yellow solid (1.02 g, 86 %). M.p: 86-88 °C. The ^{1}H NMR spectrum of **ZPN** is shown in Fig. S13. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.67-8.65 (d, J = 7.2 Hz, 2H), 8.29-8.27 (d, J = 8.3 Hz, 2H), 7.82-7.78 (t, J = 7.2 Hz, 2H), 7.24-7.22 (d, J = 8.7 Hz, 2H), 7.05-7.03 (d, J = 8.8 Hz, 2H), 6.83-6.77 (m, 10H), 3.92-3.77 (m, 13H), 3.68-3.66 (m, 28H), 1.35-1.19 (m, 11H), 0.88-0.86 (m, 5H). The ^{13}C NMR spectrum of **ZPN** is shown in Fig. S14. ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.59, 159.28, 150.67, 150.48, 149.86, 134.19, 131.54, 129.51, 129.50, 127.00, 122.91, 114.56, 114.17, 114.10, 113.98, 113.96, 113.78, 113.70, 68.38, 68.10, 55.73, 55.64, 55.63, 55.52, 29.70, 29.59, 29.54, 29.48, 29.46, 28.95, 28.78, 25.61, 25.34. ESI-MS is shown in Fig. S15: m/z $[M+NH_4]^+$ calcd. for $C_{72}H_{81}N_2O_{13}$ 1181.5733, found 1181.5702.

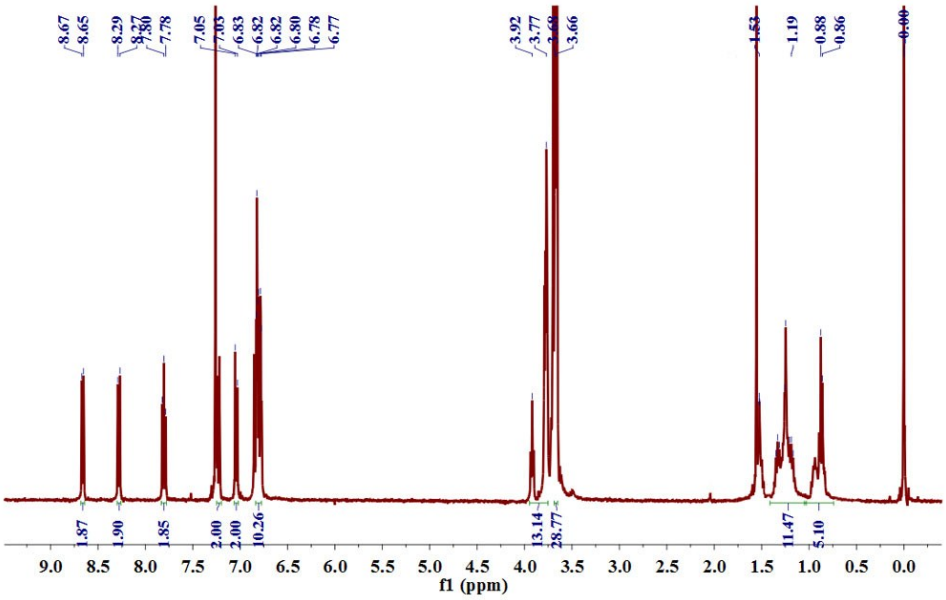

Fig. S13. ^{1}H NMR spectrum of compound **ZPN** ($CDCl_3$, 400 MHz, 298 K).

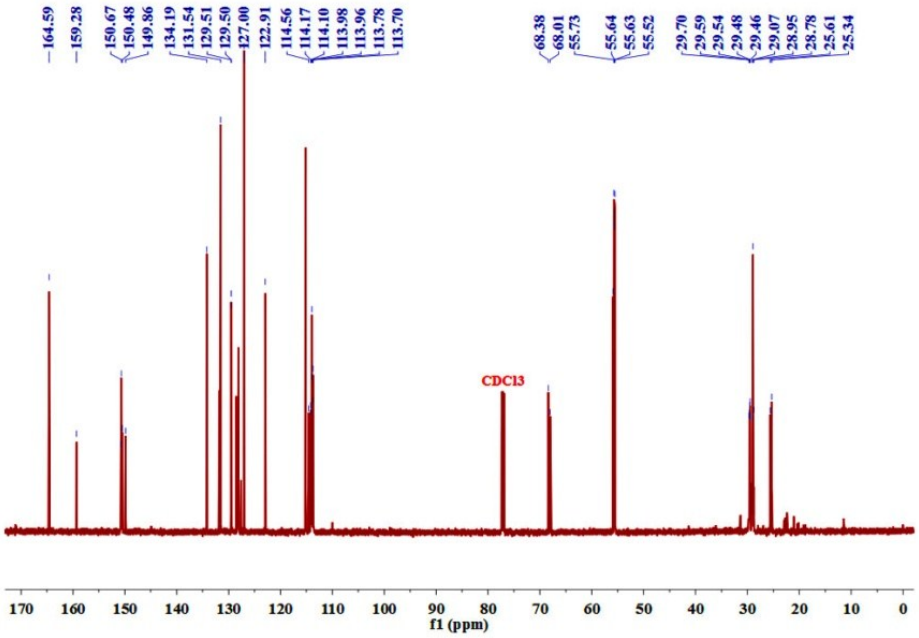

Fig. S14. ^{13}C NMR spectrum of compound **ZPN** ($CDCl_3$, 150 MHz, 298 K).

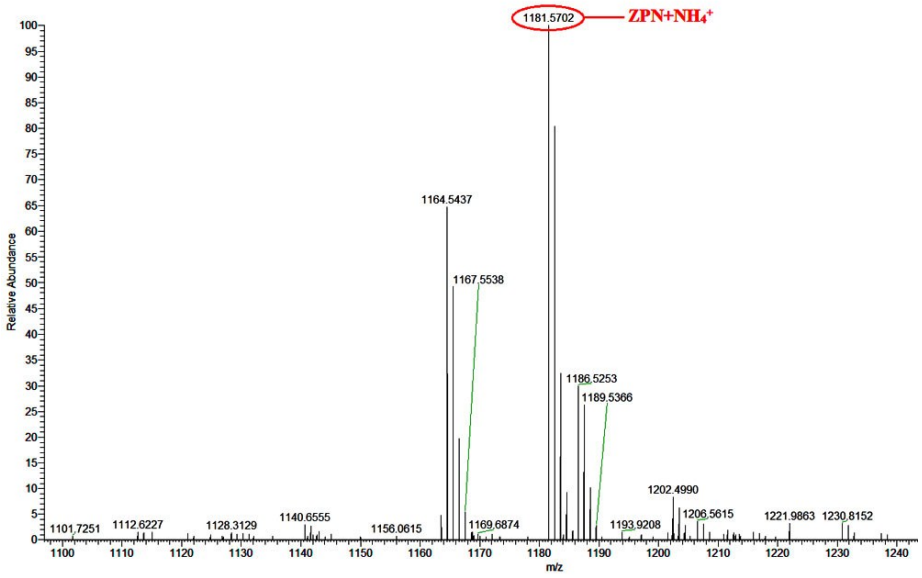

Fig. S15. Mass spectrum of **ZPN**

3. Gelation property of supramolecular monomer molecule **BPN**

***Table S1*.** Gelation property of supramolecular monomer molecule **BPN.**

Entry	Solvent	Statea	CGC_b(%)	Tgelc (°C, wt%)
1	Water	P	\	\
2	Acetone	S	\	\
3	Methanol	P	\	\
4	Ethanol	P	\	\
5	Isopropanol	P	\	\
6	Isopentanol	P	\	\
7	Acetonitrile	S	\	\
8	THF	S	\	\
9	DMF	S	\	\
10	DMSO	S	\	\
11	CCl_4	S	\	\
12	n-Hexane	S	\	\
13	Ethanediol	G	5	23 ~ 28 (5 %)
14	Benzene	S	\	\
15	CH_2Cl_2	S	\	\
16	$CHCl_3$	S	\	\
17	CH_2ClCH_2Cl	S	\	\
18	Petroleum Ether	P	\	\
19	Ethyl Acetate	S	\	\
20	n-Butyl Alcohol	P	\	\
21	n-Amyl Alcohol	P	\	\
22	Cyclohexanol	G	5	41 ~ 43 (5 %)
23	n-Hexanol	G	7	33 ~ 36 (7 %)

a G, P and S denote gelation, precipitation and solution, respectively, c = A %.

b The critical gelation concentration (wt%, 10mg/ml = 1.0 %).

c The gelation temperature(°C).

Fig. S16. (a) Photograph of compound **BPN** form stable supramolecular π-gel; (b) **FPN** and (c) **ZPN** would not form gel in cyclohexanol under the same conditions (5%，w/v, 10 mg/mL = 1%).

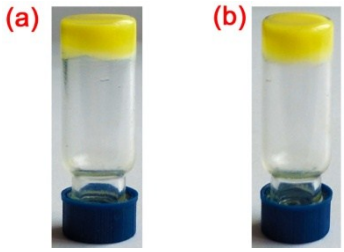

Fig. S17. Photograph of (a) **FPN** and (b) **ZPN** form stable supramolecular π-gel in cyclohexanol, the lowest critical gelation concentration (CGC) were 12% and 15.5% (w/v, 10 mg/mL = 1%),respectively.

4. Characterization of **BPN** and **BPN-G**

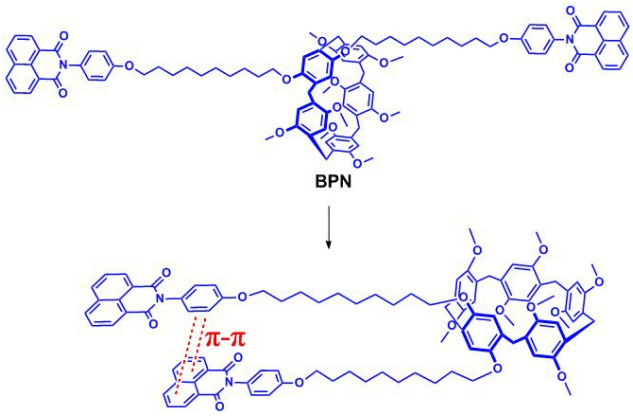

Fig. S18. The proposed interaction in **BPN** at low concentrations (c = 1 mM).

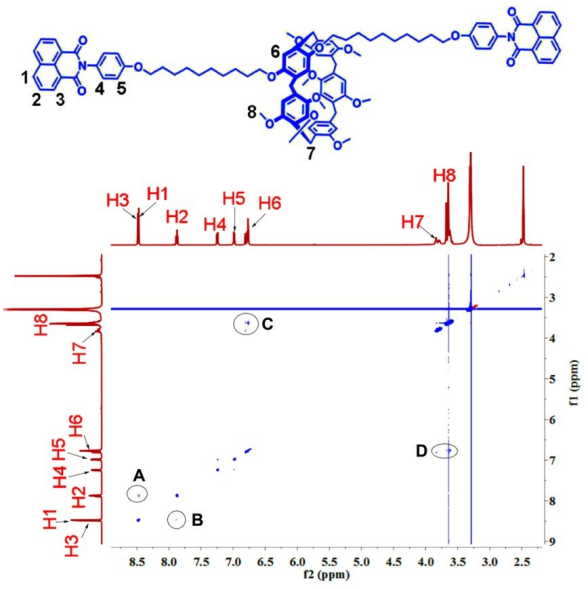

Fig. S19. 2D NOESY spectrum of **BPN** 6mM in DMSO-d_6 solution.

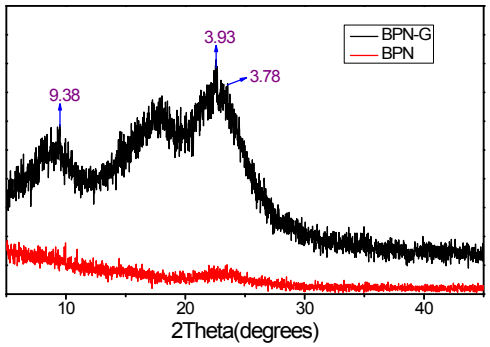

Fig. S20. Powder XRD patterns of monomer **BPN** and xerogel of **BPN-G**.

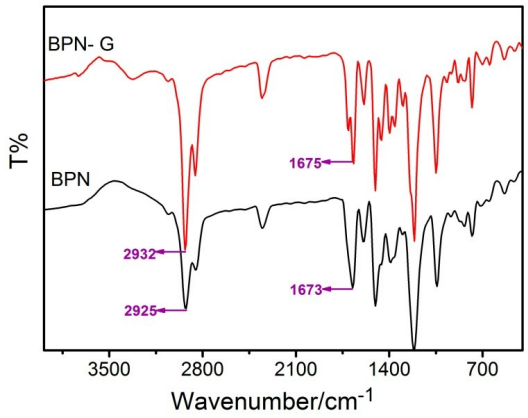

Fig. S21. FT-IR Spectra of xerogel of **BPN-G** and monomer **BPN**.

5. Interaction study of **BPN-G** and aromatic acids

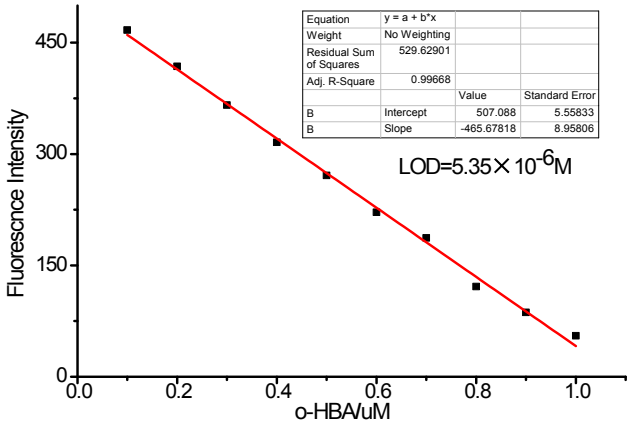

Fig. S22. The photograph of the linear range **BPN-G** for *o*-HBA.

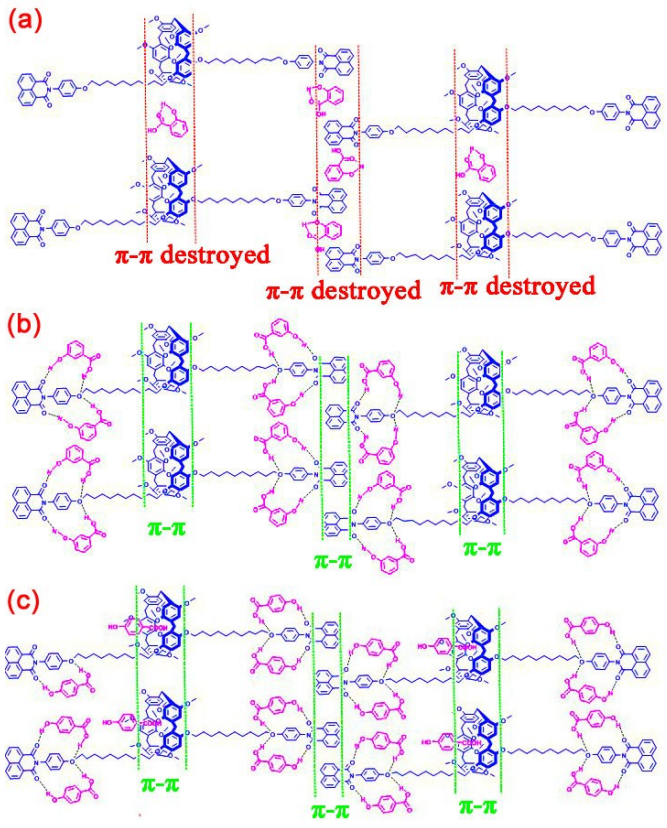

Fig. S23. Proposed response mechanism of **BPN-G** to (a) *o*-HBA; (b) *m*-HBA; (c) *p*-HBA.

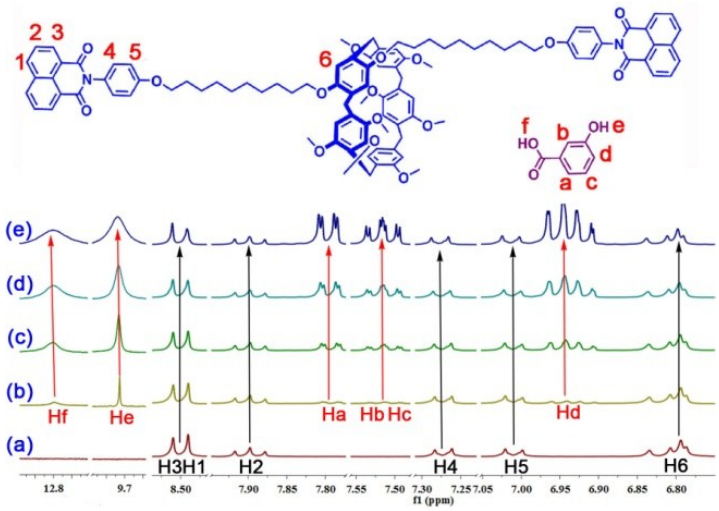

Fig. S24. Partial ^{1}H NMR spectra of **BPN** in DMSO-d_6 with increasing amounts of *m*-HBA. (a) **BPN**; (b) 2.36; (c) 4.72; (d) 7.08; (e) 9.44 equiv.

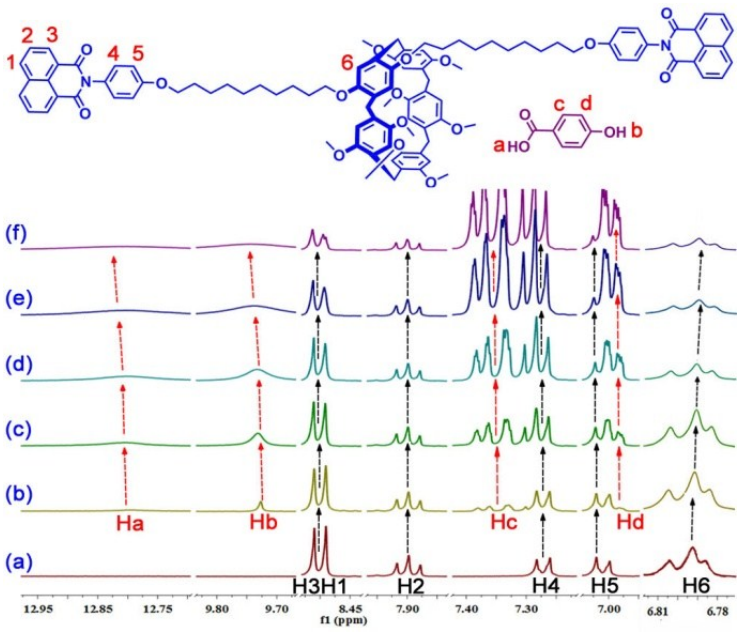

Fig. S25. Partial ^{1}H NMR spectra of **BPN** in DMSO-d_6 with increasing amounts of *p*-HBA. (a) **BPN**; (b) 2.36; (c) 4.72; (d) 7.08; (e) 9.44; (f) 11.8 equiv.

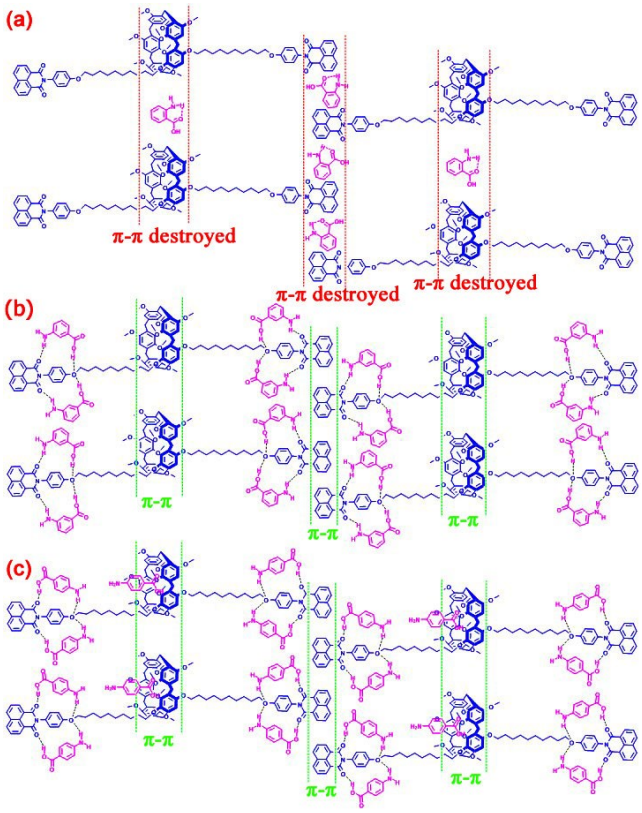

Fig. S26. Proposed response mechanism of (a) *p*-ABA and **BPN-G**; (b) *m*-ABA and **BPN-G**; (c) *o*-ABA and **BPN-G**.

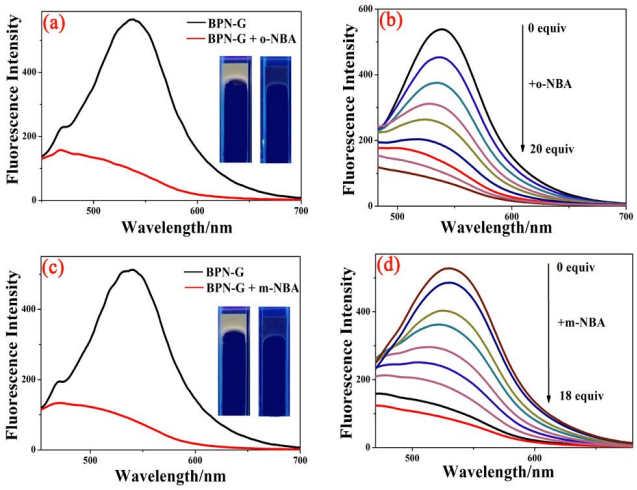

Fig. S27. Fluorescence spectra of (a) **BPN-G** and **BPN-G**@*o*-NBA; (b) The fluorescent titrations of **BPN-G** for *o*-NBA; (c) **BPN-G** and **BPN-G**@*m*-HBA; (d) The fluorescent titrations of **BPN-G** for *m*-HBA (λ_{ex} = 400 nm).

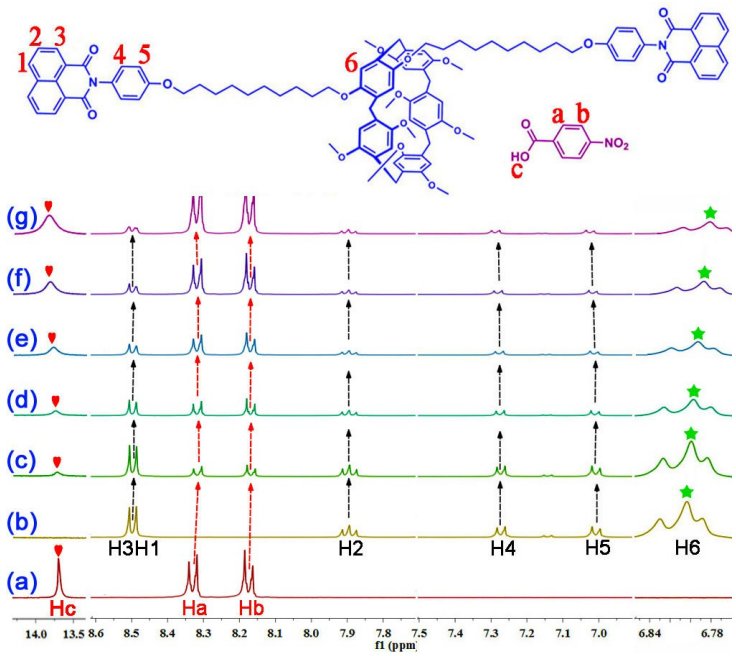

Fig. S28. Partial ^{1}H NMR spectra of **BPN** with various equivalents of *p*-NBA in DMSO-d_6. (a) *p*-NBA; (b) **BPN**; (c) 2.0; (d) 4.0; (e) 8.0; (f) 12.0; (g) 16.0 equiv.

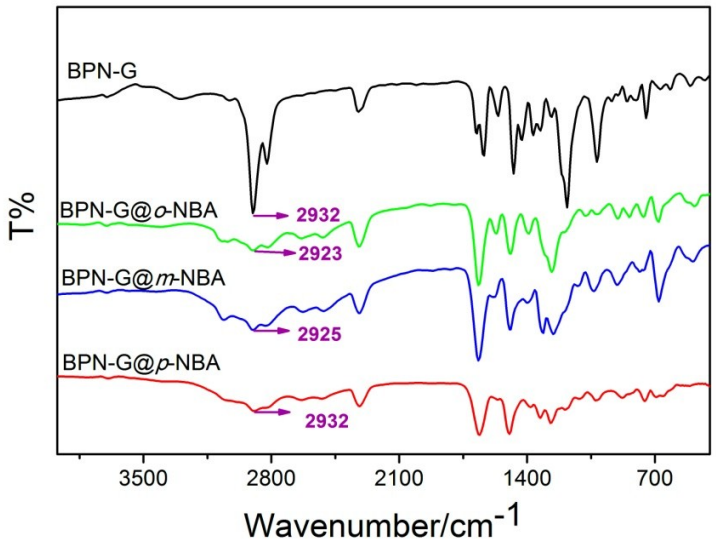

Fig. S29. FT-IR Spectra of xerogel **BPN-G** and **BPN-G**@*o*-NBA, BPN-G@*m*-NBA, BPN-G@*p*-NBA.

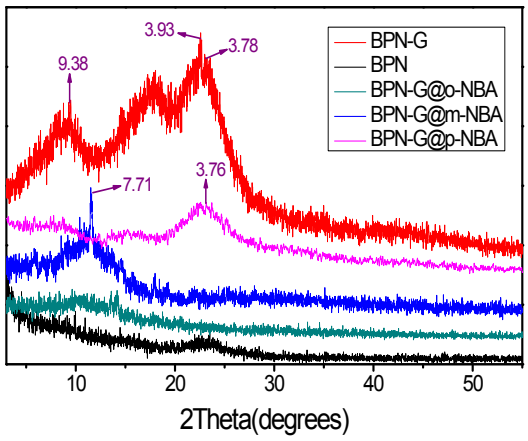

Fig. S30. Powder XRD patterns of powder **BPN-G** and **BPN-G@***o*-NBA, **BPN-G@***m*-NBA, **BPN-G@***p*-NBA xerogel.

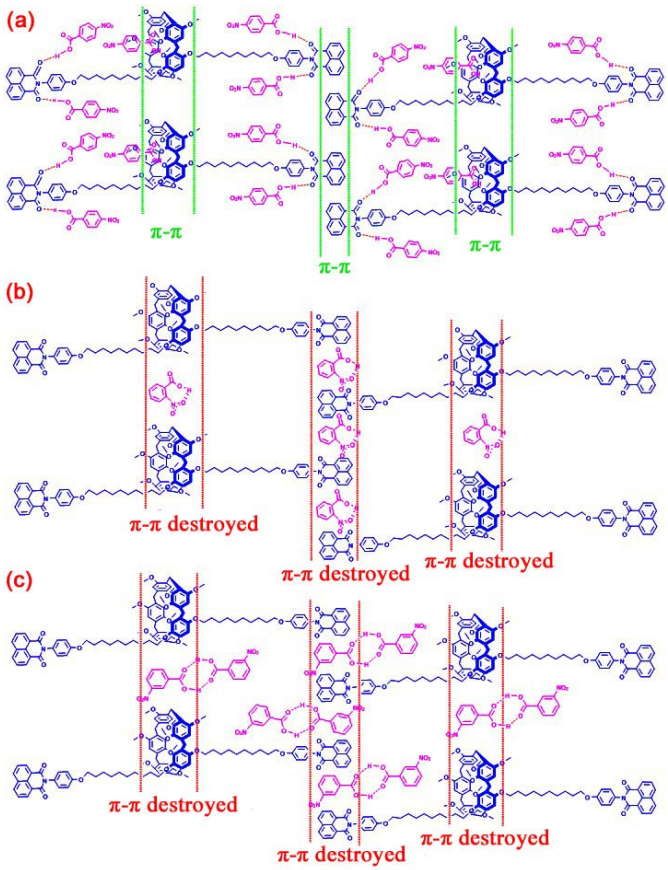

Fig. S31. Proposed response mechanism of (a) *p*-NBA and **BPN-G**; (b) *o*-NBA and **BPN-G**; (c) *m*-NBA and **BPN-G**.

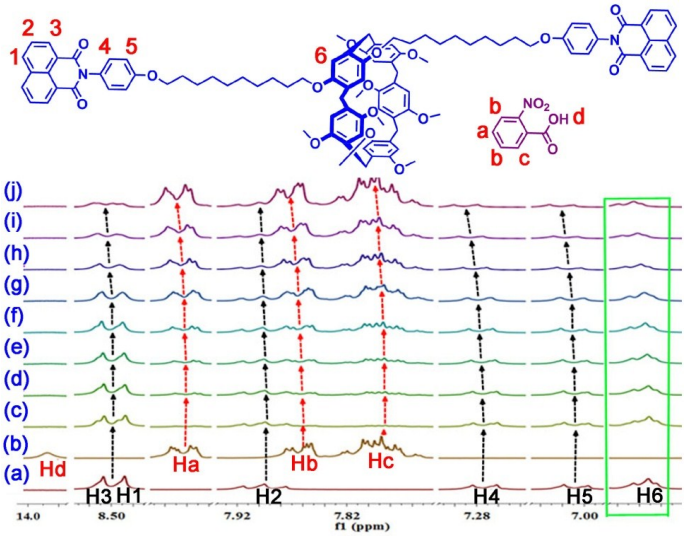

Fig. S32. Partial ^{1}H NMR spectra of **BPN** with various equivalents of *o*-NBA in DMSO-d_6. (a) **BPN**; (b) *o*-NBA; (c) 2.36; (d) 4.72; (e) 7.08; (f) 9.44; (g) 11.8; (h) 14.16; (i) 16.52; (j) 18.8 equiv.

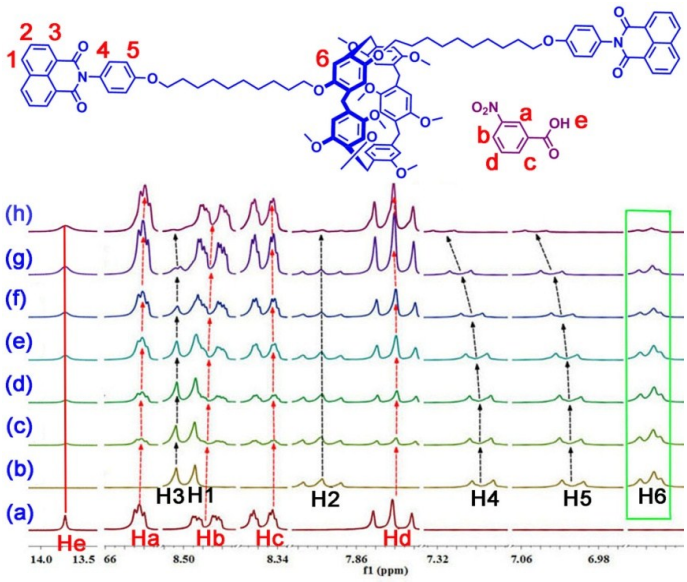

Fig. S33. Partial ^{1}H NMR spectra of **BPN** with various equivalents of *m*-NBA in DMSO-d_6. (a) *m*-NBA; (b) **BPN**; (c) 2.36; (d) 4.72; (e) 7.08; (f) 9.44; (g) 11.8; (h) 14.16 equiv.

6. Adsorption experiment

Standard curve made:

Table S2 *P*-NBA at different concentrations of absorbance.

Concentration	0.002mM	0.004 mM	0.006 mM	0.008 mM	0.01 mM	0.012 mM
Absorbance	0.052	0.087	0.128	0.164	0.205	0.242

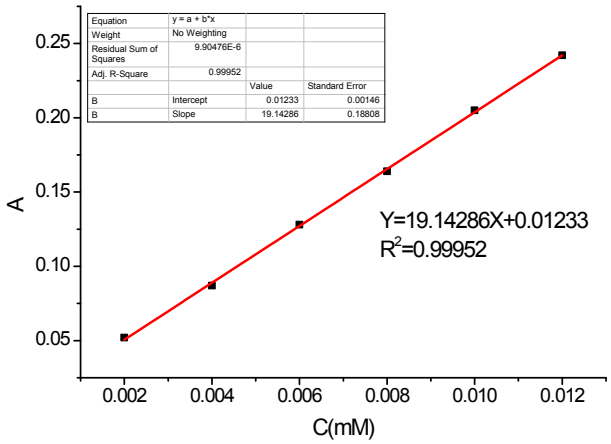

Fig. S34. Standard curve for *p*-NBA measurements (aqueous solution) on UV spectrophotometer.

General procedure

Firstly, xerogel (0.29 mg) was suspended in a dilute aqueous solution of *p*-NBA ($C_0 = 7 \times 10^{-5}$ M in 10 mL) and stirred for 12 h. Then, the suspension was centrifuged at 8000 r/min for 5 min, the precipitate was removed by the way of filtration. Finally, we analysis the *p*-NBA residual absorbance of filtrate by the way of UV spectrophotometer.

Standard equation: $Y = 19.14286\ X + 0.01233$ $R^2 = 0.99952$

The absorbance of the *p*-NBA residual solution after adsorption: $A = 0.103$

Calculated by standard equation: $C_E = 4.7 \times 10^{-6}$ M

Percentage of adsorption formula: $E = (C_0 - C_E)/C_0 \times 100\ \%$ $E = 93.2\ \%$

Description: C_E is the solution concentration after adsorption; C_0 is the original solution concentration; E is the percentage of adsorption.

References

S1. C. Li, K. Han, J. Li, H. Zhang, J. Ma, X. Shu, Z. Chen, L. Weng, X. Jia, *Org. Lett.* 2012, **14**, 42.