Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information

A novel supramolecular organogel based on acylhydrazone functionalized pillar[5]arene acts as I^- responsive smart material

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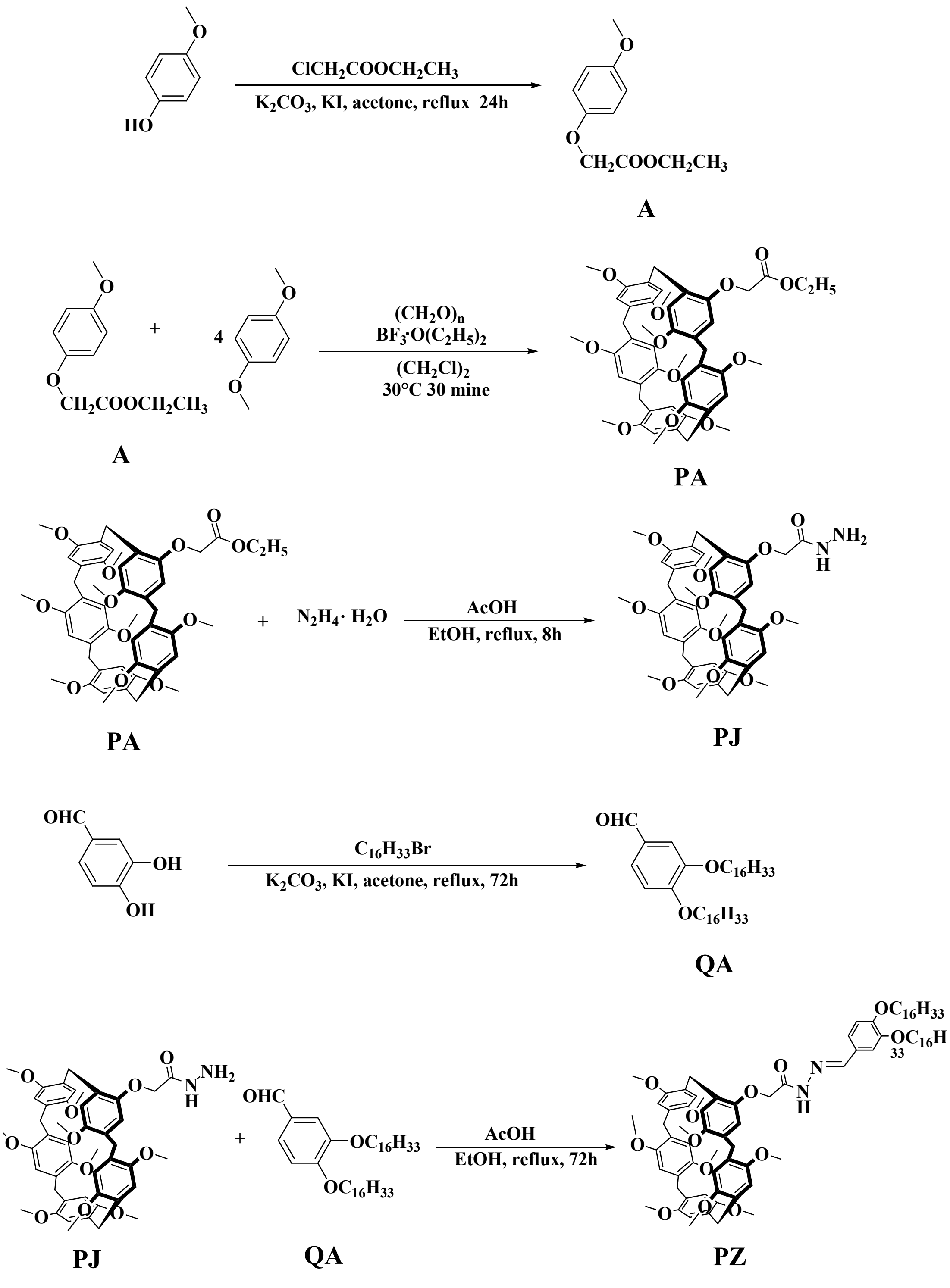
Materials and instruments

All reagents we used were analytical and commercial grade without doing anything. All the anions were added in the form of tetrabutylammonium (TBA) salts. They were all purchased from Sigma-Aldrich Chemical and were stored in a vacuum desiccator. Melting points were measured by an X-4 digital melting point apparatus. Fluorescence spectra was recorded on a Shimadzu RF-5310. ^{1}H NMR spectra was recorded on a Mercury-600BB spectrometer at 600 MHz and ^{13}C NMR spectra was recorded on a Mercury-600BB spectrometer at 150 MHz with $CDCl_3$ as solvent. Mass spectra was performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. 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 infrared spectra was performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer.

Synthesis and characterizations of compound PZ.



Scheme S1. The Synthesis of **PZ.**

Synthesis of gelator PZ

1. Compound **A**

4-methoxyphenol (12.4 g, 100 mmol), K_2CO_3 (13.8 g, 100 mmol), KI (3.3 g, 20 mmol), ethyl chloroacetate (12.2 g, 100 mmol) and acetone (400 mL) were added into a 500 mL round-bottom flask, the mixture was stirred at reflux for 24h. The solvent was evaporated after adding moderate silica gel. Finally the column chromatography (silica gel, petroleum ether : ethyl acetate = 50:1) afforded a Light yellow liquid (20.16g, 96%). ^1H NMR (600MHz, $CDCl_3$), δ 6.82 (q, *J*=9 Hz, 4H, ArH), 4.53 (s, 2H, OCH_2CO), 4.22 (q, *J*=7.2 Hz, 2H, OCH_2), 3.73 (s, 3H, OCH_3), 1.26 (t, *J*=7.2 Hz, 3H, CH_3).

2. Compound **PA**

1,4-dimethoxybenzene (2.76 g, 20 mmol), compound **A** (1.05 g, 5 mmol), 1,2-dichloroethane (80 mL), paraformaldehyde (0.75 g, 25 mmol), were added into a round-bottomed flask. Then, boron trifluoride diethyl etherate (2.7 mL, 25 mmol) was added, the mixture was stirred under the protection of nitrogen at 30℃ temperature for 30 minutes, the solution was poured into Distilled water and the resulting precipitate was washed by chloroform, the filtrate was poured into solution and washed twice using water, the organic layer was dried by anhydrous Na_2SO_4. Then, evaporated to afford the crude product, which was separated by flash column chromatography using petroleum ether/ dichloromethane (3:1). Finally we could get a kind of white solid (1.03g, 25 %) after the concentration under vacuum. m.p. 209-210℃. ^1H NNR (600 MHZ, $CDCl_3$), δ 6.93-6.58 (m, 10H, ArH), 4.50 (s, 2H,

OCH_2CO), 3.82-3.62 (m, 37H, 27OCH_3, 10CH_2), 2.19 (q, J=6.6 Hz, 2H, OCH_2), -1.45 (t, *J*=7.0 Hz, 3H, CH_3).

3. Compound **PJ**

Compound **PA** (2.91 g, 5 mmol), hydrazine hydrate (1.25 g, 25 mmol), two drops of glacial acetic acid, Anhydrous ethanol (100 mL) were added into a round-bottomed flask, reflux for eight hours, then kept the round-bottomed flask standing still for about 30 minutes, then, filtrated the precipitation, at the same time, washed the precipitation using cold hydrazine hydrate, we could get white solid. (2.78 g, 98%), m.p. 213-214℃ ^{1}H NNR (600 MHZ, $CDCl_3$), δ 6.89-6.26(m, 10H, ArH), 4.19 (s, 2H, OCH_2CO), 3.83-3.48 (m, 37H, 27OCH_3, 10CH_2), 1.63 (s, 2H, NH_2), 1.17 (t, *J*=7.2 Hz, 1H, NH).

4. Compound **QA** was synthesized according to the literature methods[1].

5. Comound **PZ**

Compound **PJ** (1.616 g, 2 mmol), Compound **QA** (1.172 g, 2 mmol), two drops of glacial acetic acid, Anhydrous ethanol (100 mL) were added into a round-bottomed flask reflux for 72 hours, then, evaporated to afford the crude product, which was separated by flash column chromatography using petroleum ether/ ethyl acetate (10:1), we could get white solid (1.79 g, 65%), after the concentration under vacuum, m.p. 79-80℃, ^{1}H NNR (600 MHZ, $CDCl_3$), δ 9.64 (s, 1H, NH), 8.05 (s, 1H, CH=N), 7.47 (s, 1H, ArH), 7.09 (d, 1H, *J*=6.6 Hz, ArH), 6.88-6.63 (m, 11H, ArH), 4.49 (s, 2H, OCHCO), 4.04-4.00 (m, 4H, OCH_2), 3.87-3.52 (m, 37H, 10 ArH, 27 OCH_3), 1.81-

1.25 (m, 56H, CH_2), 0.86 (s, 6H, CH_3). ESI-MS m/z: [**PZ**+Na]$^+$ calcd for 1399.8577; Found 1399.8739.

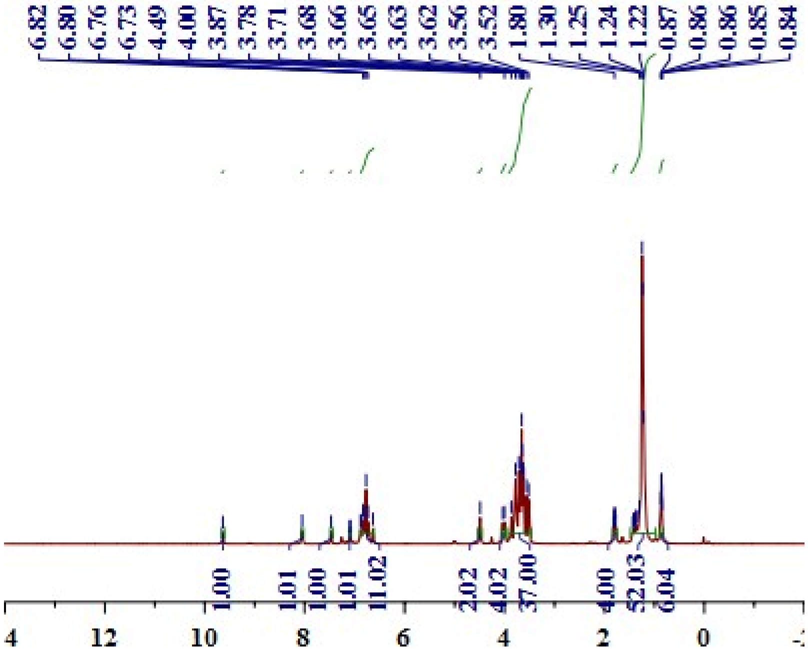


Figure S1. ^{1}H NMR Spectrum of **PZ**

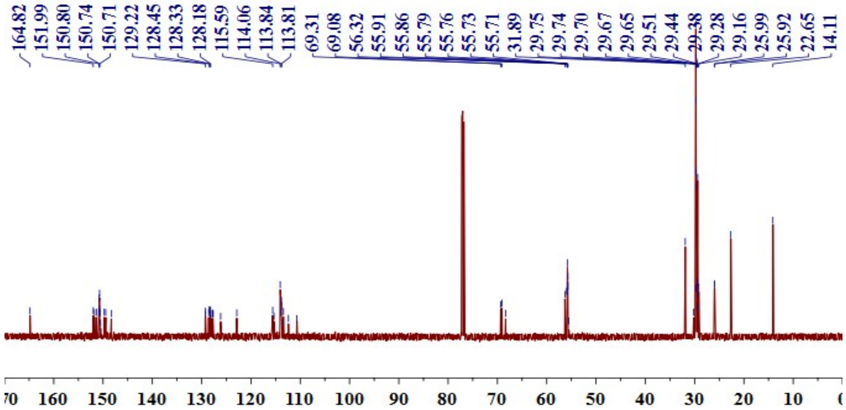


Figure S2. ^{13}C NMR Spectrum of **PZ**

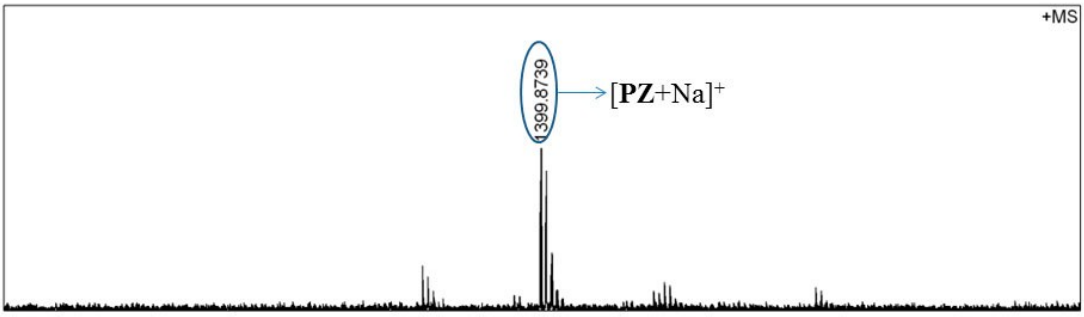


Figure S3. Mass Spectrum of **PZ**

Table S1. Gelation Property of organogelator **OPZ**

Entry	Solvent	State[a]	CGC[b](%)	Tgel[c](°C, wt%)
1	Acetone	S	\	\
2	n-Hexanoic acid	S	\	\
3	Xylene	S	\	\
4	Tetrahydrofurane	S	\	\
5	CH_2Cl_2	S	\	\
6	$CHCl_3$	S	\	\
7	CCl_4	S	\	\
8	$N_2H_4{\cdot}H_2O$	P	\	\
9	HCl	P	\	\
10	Ethylene glycol	P	\	\
11	Acetic acid	P	\	\
12	Isopropyl alcohol	P	\	\
13	Water	P	\	\
14	DMSO	P	\	\
15	Methanol	G	30	\
16	Ethanol	WG	30	\
17	Tert-butanol	WG	50	\
18	Cyclohexanol	G	1.25	48°C (5%)

[a] G P and S denote gelation, precipitation and solution, respectively, c= 0.8%.

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

[c] The gelation temperature(°C).

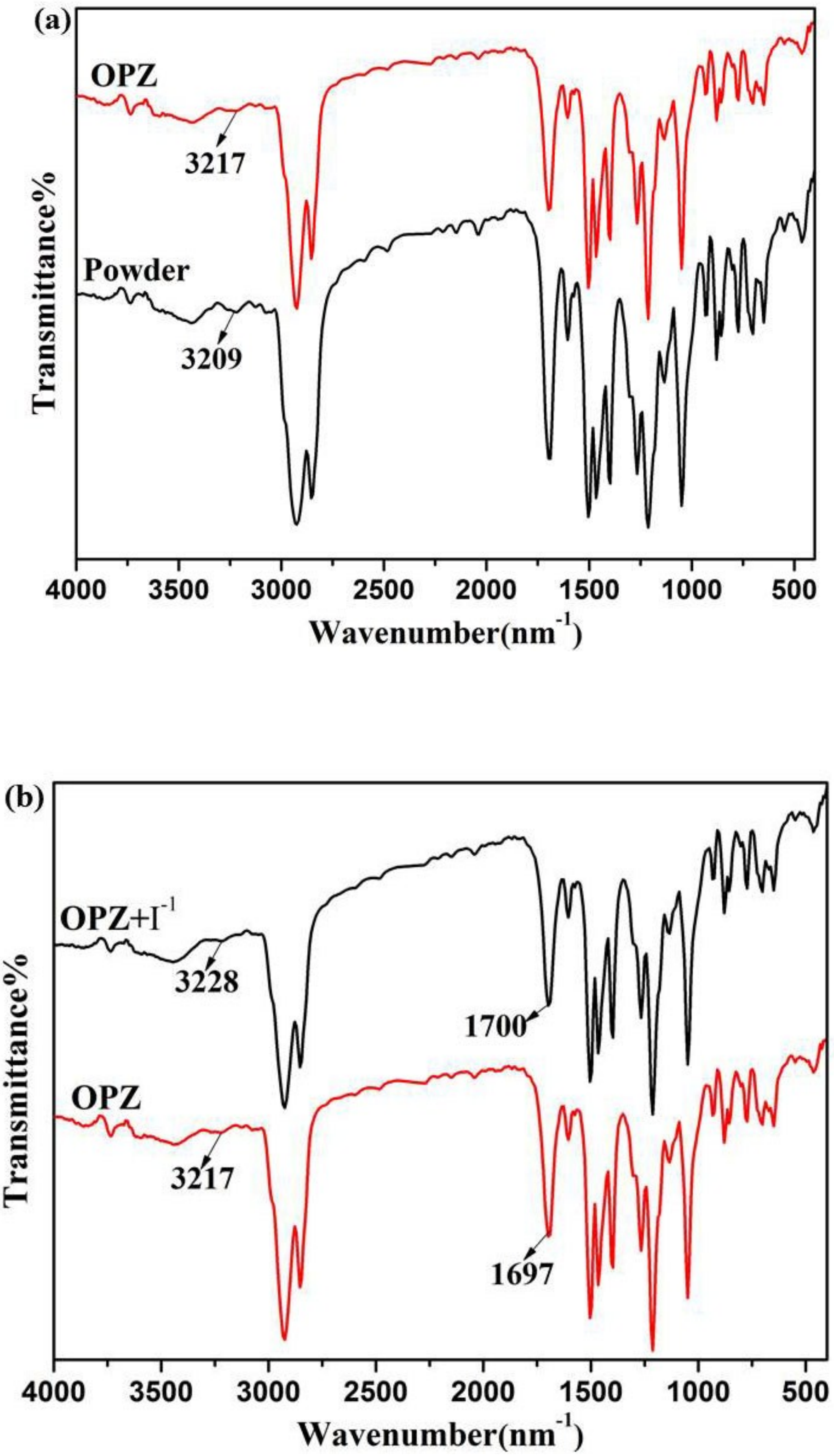
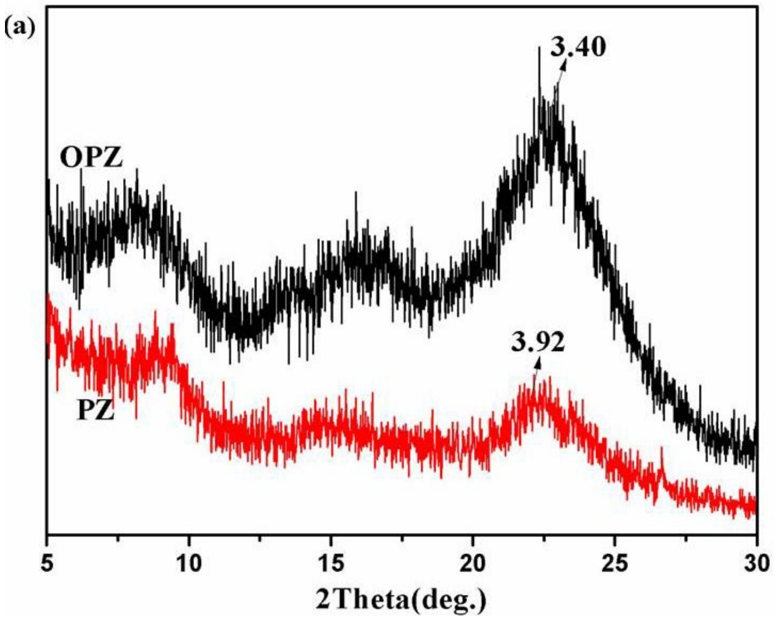


Figure S4. FT-IR spectra of (a) powder **PZ** and xerogel of organogel **OPZ** (b) xerogel of **OPZ**, and xerogel **OPZ**+I^-.



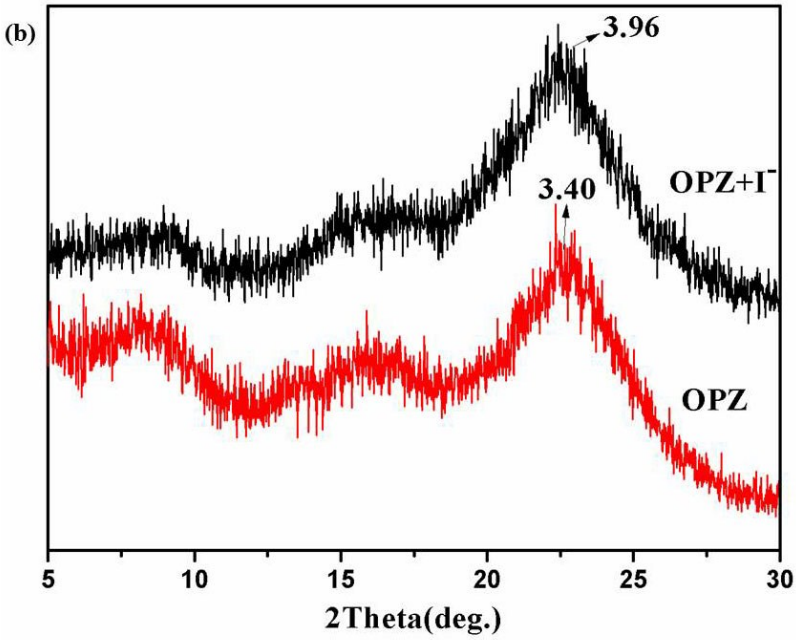


Figure S5. Powder XRD patterns (a) powder **PZ** and xerogel of organogel **OPZ** (b) xerogel of **OPZ**, and xerogel **OPZ**+I^-.

Table S2. Comparative result of I^- chemosensors

Entry	Compounds of probe	LOD for I^-	Ref.
1	**OPZ**	9.4×10^{-8}	\
2	**CS**	1.1×10^{-6}	16(a)
3	**ZnG**	1.0×10^{-6}	17(g)
4	**CdG**	1×10^{-7}	17(d)

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[1] Q. Lin, T. T. Lu, J. C. Lou, G. Y. Wu, T. B. Wei, Y. M. Zhang, *Chem. Commun.*, 2015, **51**, 12224-12227.