Electronic Supplementary Material (ESI) for Polymer Chemistry.
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A fluorescent cross-linked supramolecular network formed by orthogonal metal-coordination and host-guest interactions for multiple ratiometric sensing

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Supporting Information (21 pages)

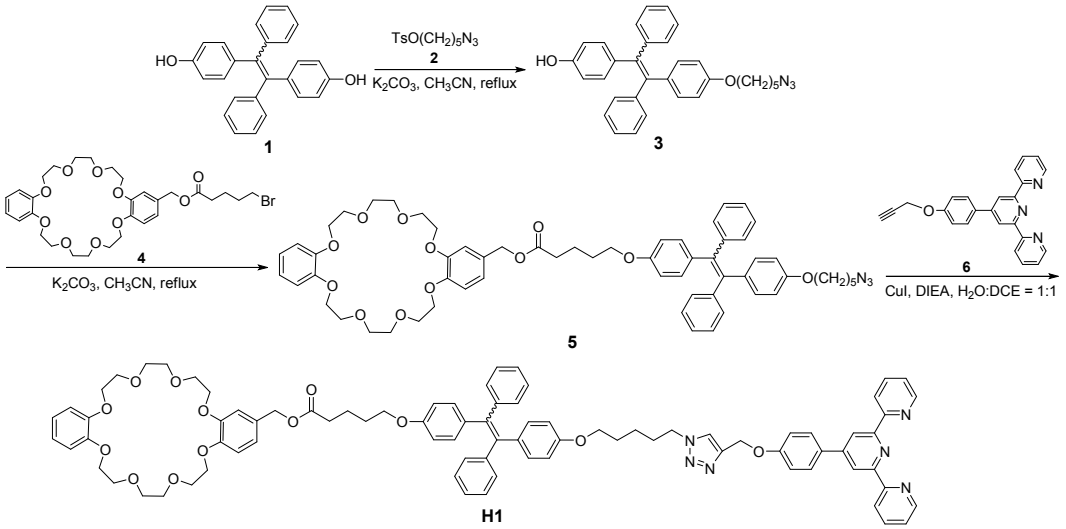
1. Materials and methods

Compounds **1**[S1], **2**[S1], **4**[S2], **6**[S2], **7**[S3]and **9**[S3] were synthesized according to the published procedure. 1D (^{1}H, ^{13}C) and 2D (DOSY, COSY) nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker Avance 500 operating at a frequency of 500 MHz for ^{1}H and 125 MHz for ^{13}C. High-resolution mass data were obtained with an Agilent Technologies 6530 Accurat-Mass Q-TOF LC/MC instrument. Molecular weight and molecular weight distribution of the polymer were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatography equipped with a Waters 510 HPLC pump, a Waters 486 wavelength-tunable UV–vis detector and a Waters 410 differential refractometer. The polymer solutions were prepared in THF (ca. 2.0 mg/mL) and filtered through 0.45-μm PTFE syringe-type filters before being injected into the GPC system. THF was used as the eluent at a flow rate of 1.0 mL/min. The column temperature was maintained at 30°C and the working wavelength of the UV–vis detector was set at 254 nm. A set of monodisperse polystyrene standards (Waters) was used for calibration purposes.

Viscosity measurements were carried out with Ubbelohde dilution viscometers (Julabo Technology Corporation visco-170, 0.47 mm inner diameter) in $CHCl_3$/CH_3CN (1/1, *v*/*v*) containing 0.05 mol/L tetrabutylammonium hexafluorophosphate to exclude the polyelectrolyte effect. Scanning electron microscopy (SEM) investigations were carried out on a Carl Zeiss Jena supra55 sapphire instrument. Rheological data were obtained by using a Physica MCR302 rheometer (Anton Paar) with cone-plate geometry (diameter of 25 mm, 2° cone, truncation height is 0.3 mm). Oscillatory frequency sweep experiments were performed from 0.1 rad/s to 100 rad/s with a strain in the linear region at 4 °C. UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 750 UV/Vis spectrophotometer. The fluorescence spectra were recorded on a HITACHI F7000 fluorescence spectrophotometer. The samples for fluorescent titration measurement were prepared as follows. The host solution and the guest solution ([**H1**] = 100 μM and [**P1**] = 18.6μM in $CHCl_3$/CH_3CN = 1:1) was first prepared. Then different

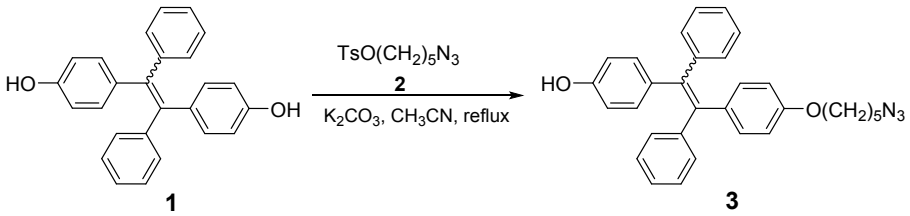
concentrations of Zn^{2+} (0-22 μM) were added into the solution of **H1** and **P1**. The method for other detection was prepared as follows.

2. *Synthesis of compound **H1***



Scheme S1 Synthetic routes of compound **H1**.

2.1. *Synthesis of compound* **3**



1 (364 mg, 1.00 mmol), **2** (283 mg, 1.00 mmol) and K_2CO_3 (1.38 g, 10.0 mmol) were dissolved in CH_3CN (30 mL) and then refluxed for 12 h. After filtration, the solvent was removed with a rotary evaporator and the residue was extracted with H_2O/CH_2Cl_2. The organic phase was collected, dried over anhydrous $MgSO_4$ and then the solvent was removed to give a crude product, which was further purified by flash column chromatography (1:1 CH_2Cl_2/hexane, *v/v*) to afford **3** as a pale yellow liquid (310 mg, 65.3%). ^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ (ppm): 7.14–7.05 (m, J = 7.10 Hz, 10H), 6.98–6.89 (m, 4H), 6.68–6.64 (dd, J_1 = 15.7 Hz, J_2 = 8.7 Hz, 2H), 6.59–6.54 (d, J_1 = 15.4 Hz, J_2 = 8.6 Hz, 2H), 5.16 (s, 1H), 3.93–3.91 (m, 2H), 3.33–3.30 (td, J_1 = 6.8 Hz, J_2 = 1.8 Hz, 2H), 1.82–1.78 (m, 2H), 1.70–1.67 (m, 2H), 1.59–1.54 (m, 2H).

^{13}C NMR (125 MHz,$CDCl_3$, 298K) δ (ppm): 157.4, 154.1, 154.0, 144.3, 144.3, 139.8, 139.8, 139.7, 139.8, 136.6, 136.5, 132.8, 132.7, 132.6, 132.5, 131.5, 127.8, 127.7, 127.6, 126.3, 114.7, 114.6, 113.7, 113.6, 67.5, 51.4, 28.9, 28.7, 23.4. HRMS $[M+Na]^+$: calcd. for $C_{31}H_{29}N_3O_2Na$ 498.2152, found 498.2002.

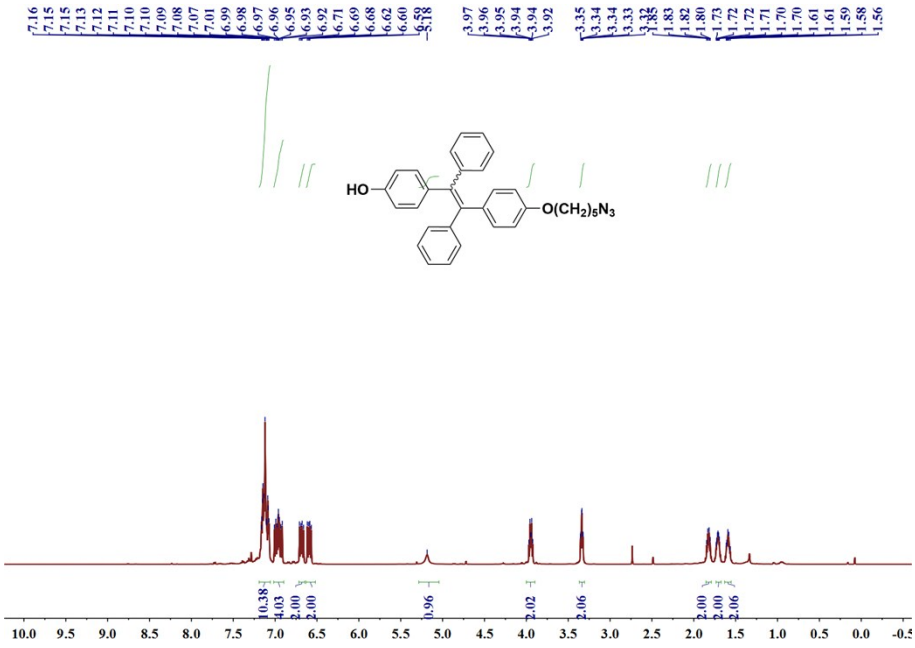


Fig. S1 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of compound **3**.

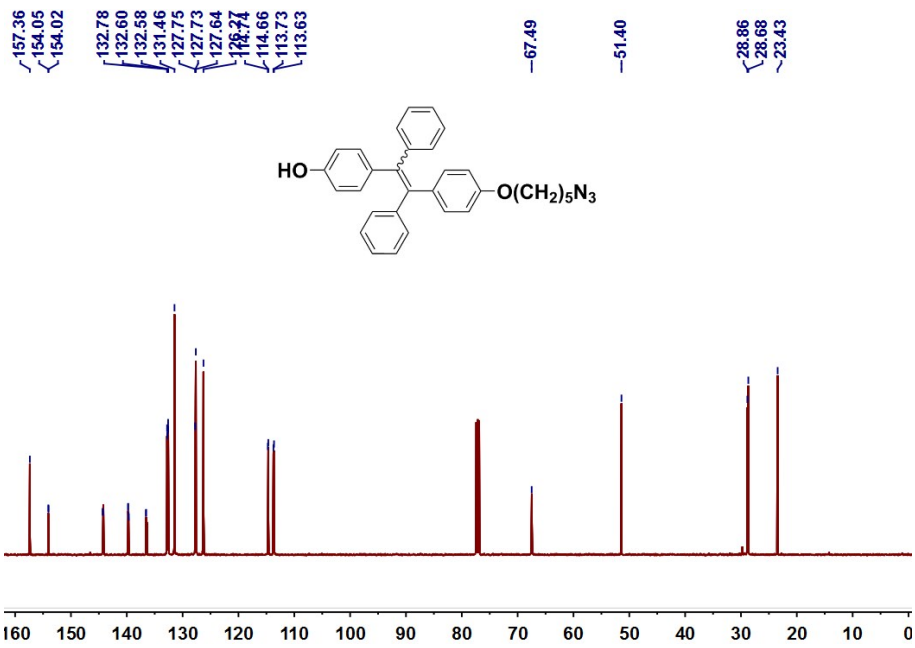
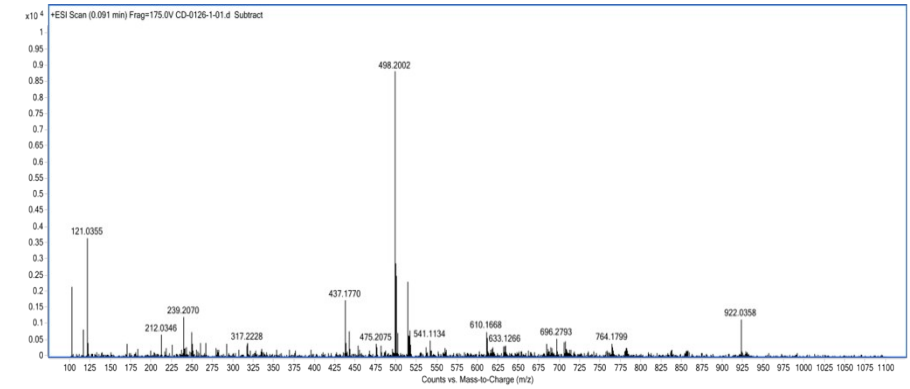


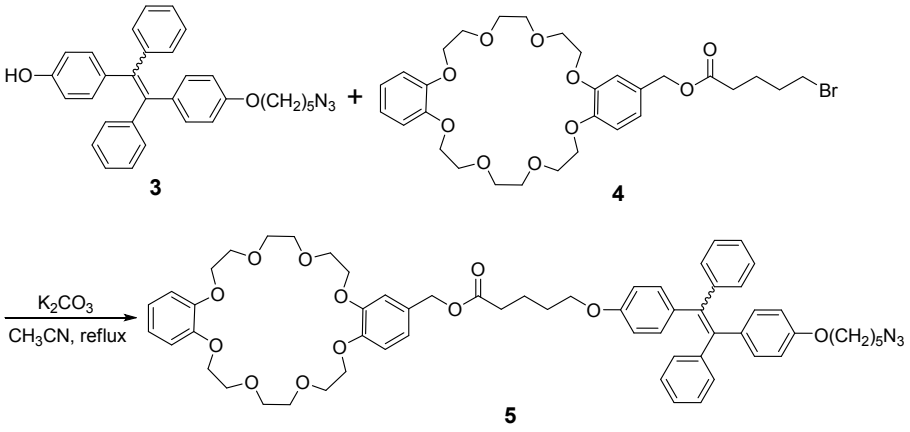
Fig. S2 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298K) of compound **3**.



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C31 H29 N3 O2	99.19	475.211	475.226	498.2152	31.56	19	498.2002

Fig. S3 HRMS spectrum of compound **3**.

2.2. Synthesis of compound **5**



3 (475 mg, 1.00 mmol), **4** (639 mg, 1.00 mmol) and K_2CO_3 (2.76 g, 20.0 mmol) were dissolved in CH_3CN (30 mL) and then refluxed for 12 h. After filtration, the solvent was removed with a rotary evaporator and the residue was extracted with H_2O/CH_2Cl_2. The organic phase was collected, dried over anhydrous $MgSO_4$ and then the solvent was removed to give a crude product, which was further purified by flash column chromatography (1:1 acetic ether/hexane, *v/v*) to afford **5** as a pale cyan liquid (580 mg, 56.0%). ^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ (ppm): 7.09–7.02 (m,10H), 6.94–6.92 (m, 4H), 6.88–6.83 (m, 7H), 6.64–6.58 (m, 4H), 5.00 (s, 2H), 4.15 (s, 8H), 3.91 (m, 12H), 3.83 (s, 8H), 3.29 (s, 2H), 2.41–2.39 (d, J = 6.5 Hz, 2H), 1.80–1.78 (m, 6H), 1.66 (s, 2H), 1.54–1.53 (d, J = 6.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 298K) δ (ppm): 173.4, 157.5, 149.1, 149.1, 149.0, 144.4, 139.8, 132.6, 131.5, 129.2, 127.7, 126.3, 121.9, 121.6, 114.5, 114.2, 113.7, 113.6, 71.4, 70.1, 69.5, 67.5, 67.3, 66.3, 51.5,

34.1, 29.0, 28.9, 28.8, 23.5, 21.8. HRMS $[M+Na]^+$: calcd. for $C_{61}H_{69}N_3O_{12}Na$ 1058.4773, found 1058.3788.

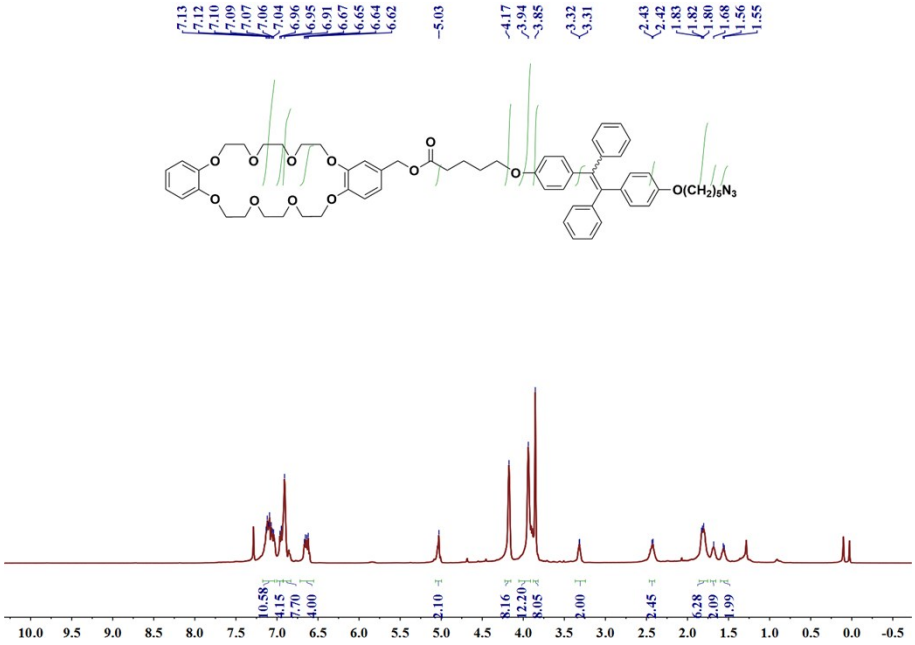


Fig. S4 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of compound **5**.

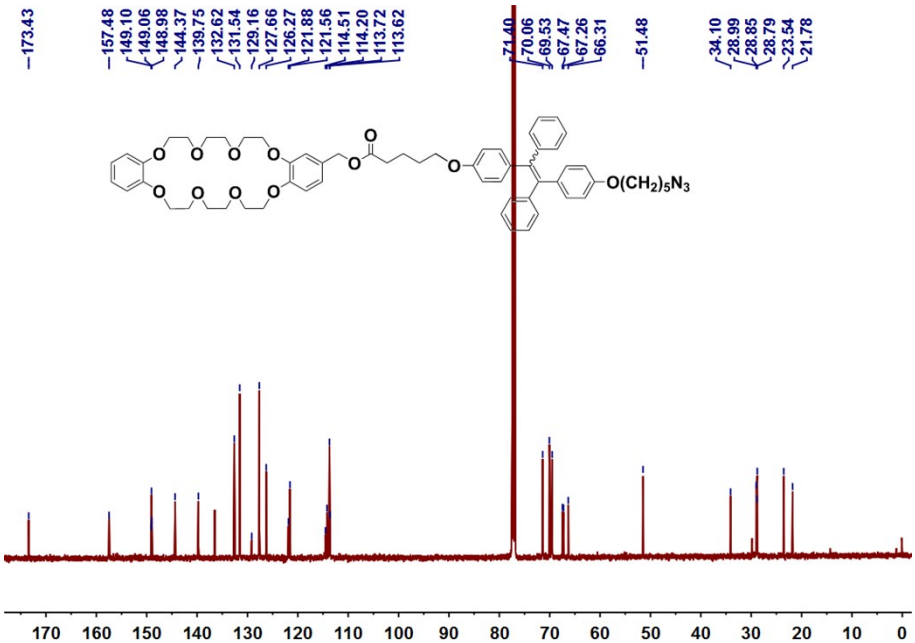
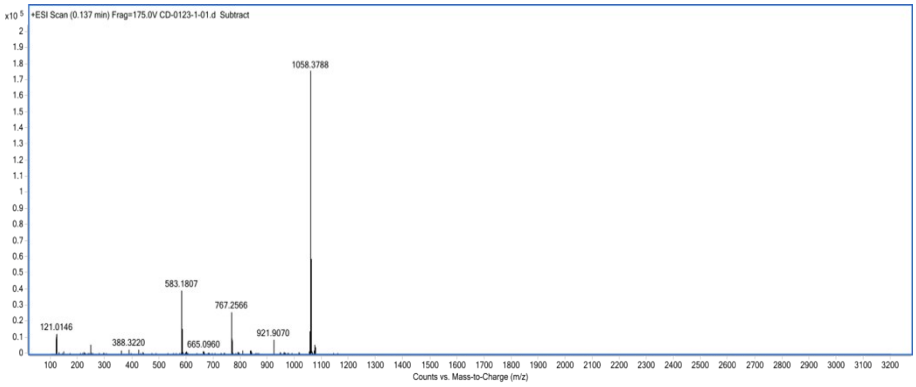


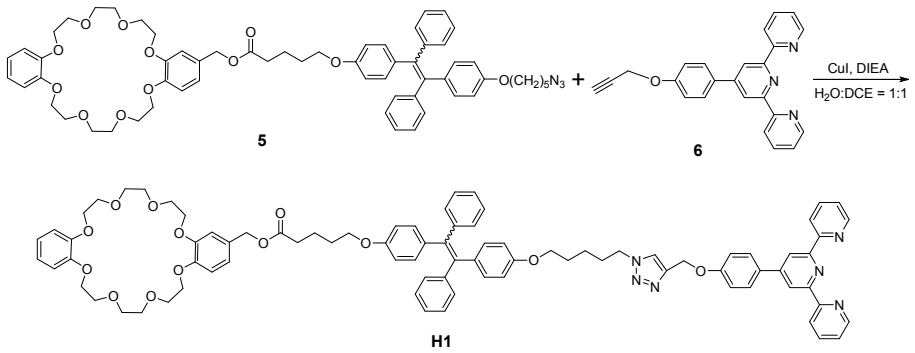
Fig. S5 ^{13}CNMRspectrum (125 MHz, $CDCl_3$, 298K) of compound **5**.



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C61 H69 N3 O12	87.89	1035.3896	1035.4881	1058.4773	95.18	29	1058.3788

Fig. S6 HRMS spectrum of compound **5**.

2.3. Synthesis of compound **H1**



A mixture of **5** (518 mg, 0.50 mmol), **6** (166 mg, 0.50 mmol), CuI (38 mg, 0.20 mmol), DIEA (51 mg, 0.40 mmol) in DCE/H_2O (1:1, 100 mL) was stirred at 50ºC for 24 h. The solvent was removed with a rotary evaporator and the residue was extracted with H_2O/CH_2Cl_2. The organic phase was collected, dried over anhydrous $MgSO_4$ then purified by flash column chromatography(100:1 ethyl acetate/Et_3N, *v*/*v*) to afford the desired product **H1** as a yellow solid (290 mg, 43.3%). ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) δ (ppm): 8.81 (s,2H), 8.78–8.77 (d, J = 4.1 Hz, 4H), 7.98 (s, 2H), 7.95–7.94 (d, J = 8.5 Hz, 2H), 7.64–7.63 (s, 1H), 7.44 (s, 2H), 7.13–6.99 (m, 12H), 6.93–6.82 (m, 11H), 6.62–6.57 (m, 4H), 5.29 (s, 2H), 5.00 (s, 2H), 4.41–4.38 (t, J = 7.2 Hz, 2H), 4.14–4.13 (d, J = 4.5 Hz, 8H), 3.91–3.90 (d, J = 3.3 Hz, 8H), 3.87–3.86 (m, 4H), 3.82–3.82 (m, 8H), 2.40–2.37 (t, J = 6.9 Hz, 2H), 2.01–1.98 (m, 2H), 1.78–1.76 (m, 6H), 1.52–1.50 (m, 2H). ^{13}C NMR (125 MHz, 1:1 $CDCl_3$/CD_3CN, 298K) δ (ppm): 172.2, 158.1, 156.3, 156.2, 155.2, 154.7, 148.6, 148.0, 147.9, 143.3, 143.2,

143.1, 142.9, 138.6, 136.0, 135.4, 135.3, 131.5, 130.3, 127.6, 126.6, 126.5, 125.1, 122.8, 121.6, 120.7, 120.4, 117.4, 114.2, 113.3, 113.0, 112.6, 112.5, 70.3, 70.2, 68.9, 68.8, 68.4, 68.3, 66.0, 65.1, 61.2, 49.3, 32.9, 29.0, 27.7, 27.8, 22.2, 20.6. HRMS $[M+H]^+$: calcd. for $C_{85}H_{87}N_6O_{13}$ 1399.6326, found 1399.6307.

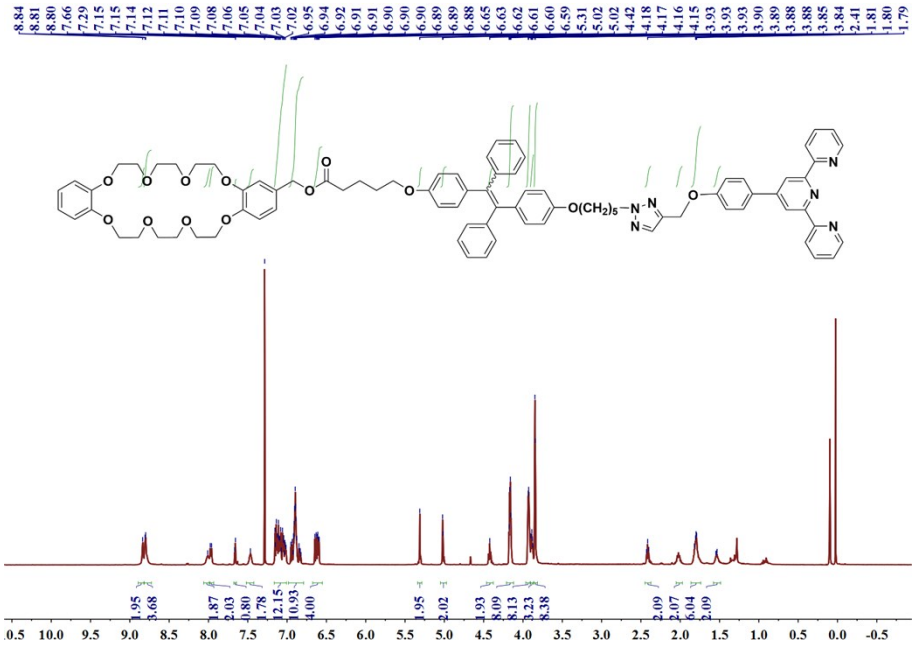


Fig. S7 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of compound **H1**.

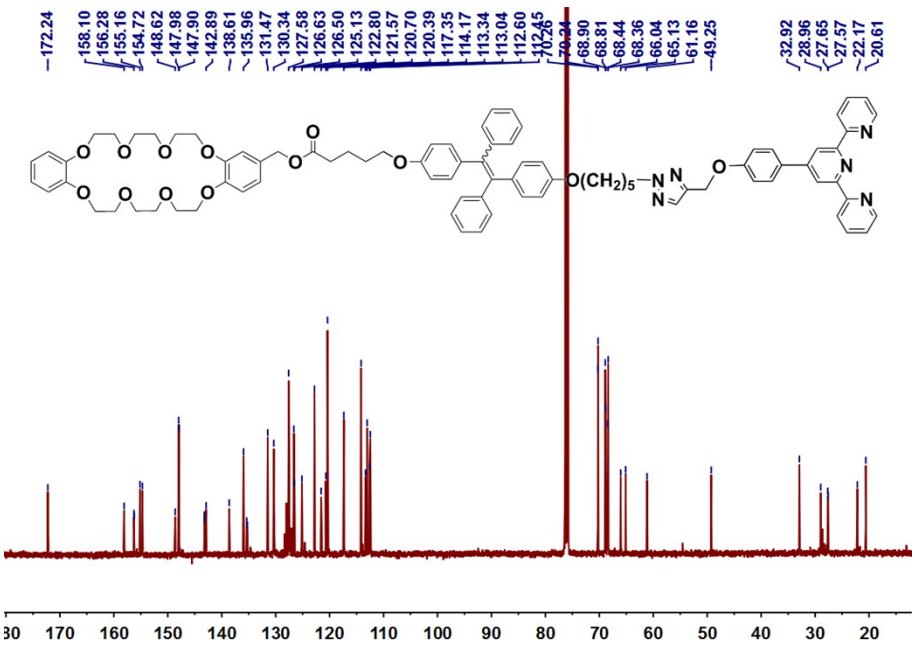
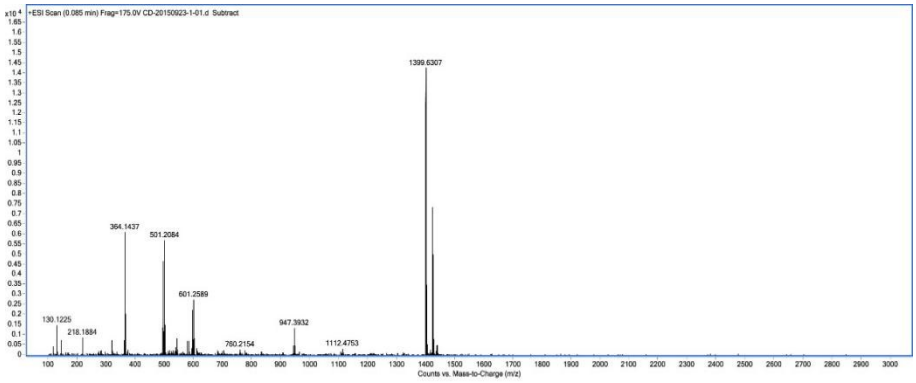


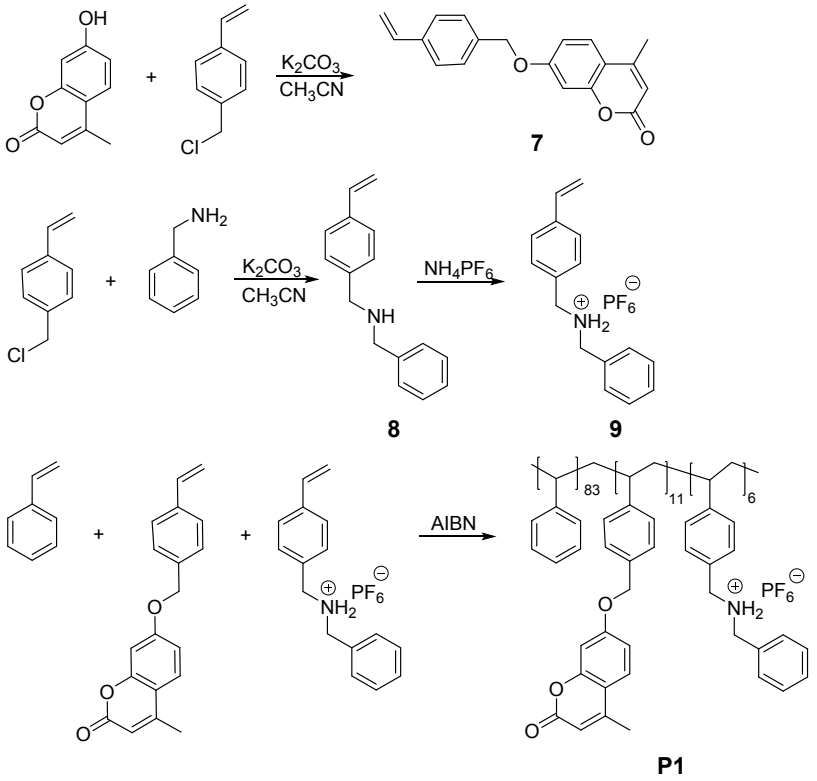
Fig. S8 ^{13}CNMRspectrum (125 MHz, $CDCl_3$, 298K) of compound **H1**.



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C85 H86 N6 O13	100	1398.6234	1398.6253	1399.6326	1.33	46	1399.6307

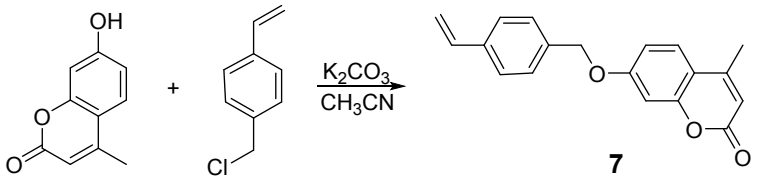
Fig. S9 HRMS spectrum of compound **H1**.

3. *Synthesis of polymer* **P1**



Scheme S2 Synthetic routes of polymer **P1**.

3.1. *Synthesis of compound* **7**



To 50 mL of acetonitrile 4-methylumbelliferone (211.4 mg, 1.20 mmol), 4-vinylbenzylchloride (152.6 mg, 1.00 mmol) and K_2CO_3 (1.38 g, 10.0 mmol) were added, and the mixture were refluxed for 12 h. After filtration, the solvent was removed with a rotary evaporator and the residue was extracted with H_2O/CH_2Cl_2. The organic phase was collected, dried over anhydrous $MgSO_4$ and then the solvent was removed to give a crude product, which was further purified by flash column chromatography (1:1 CH_2Cl_2/hexane, *v/v*) to afford **7** as a pale yellow liquid (240 mg, 82.1%). ^{1}H NMR (500 MHz, $CDCl_3$,298K) δ (ppm): 7.50–7.49 (d, J = 8.8 Hz, 1H), 7.45–7.43 (d, J = 8.2 Hz, 2H), 7.40–7.38 (d, J = 8.2 Hz, 2H), 6.94–6.91 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.88 (d, J = 2.4 Hz, 1H), 6.75–6.69 (m, 1H), 6.13 (s, 1H), 5.79–5.75 (d, J = 17.6 Hz,1H), 5.29–5.26 (d, J = 10.9 Hz, 1H), 5.11 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 298K) δ (ppm): 161.6, 161.3, 155.2, 152.6, 137.7, 136.3, 135.3, 127.8, 126.6, 125.6, 114.5, 113.8, 113.0, 112.1, 102.0, 70.3, 18.7. HRMS $[M+H]^+$: calcd. for $C_{19}H_{17}O_3$ 293.1172, found 293.1141.

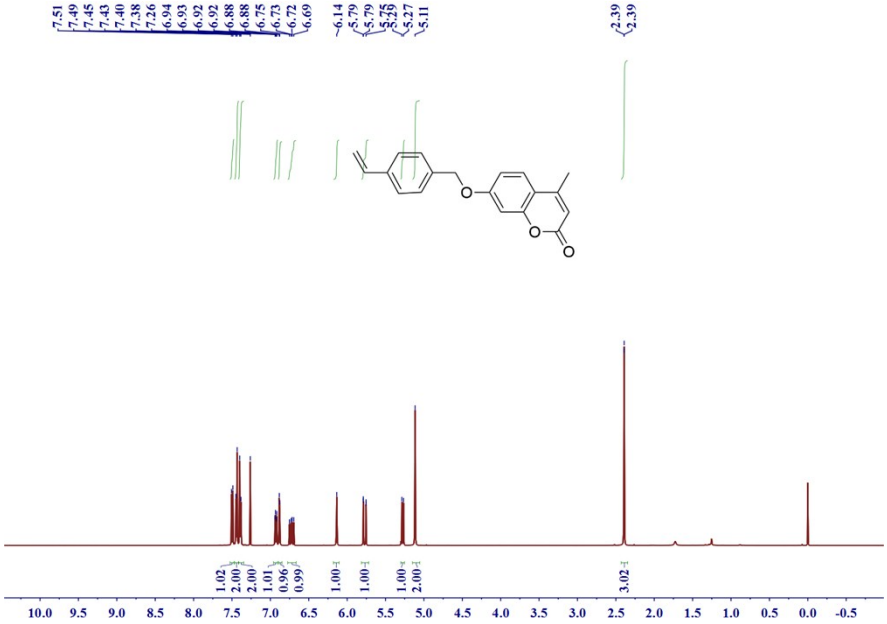


Fig. S10 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of compound **7**.

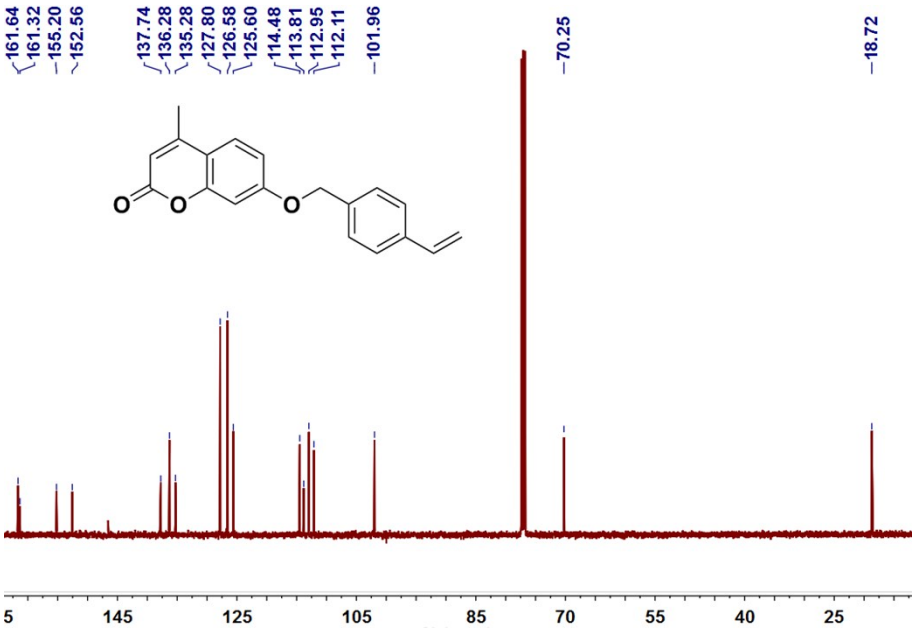
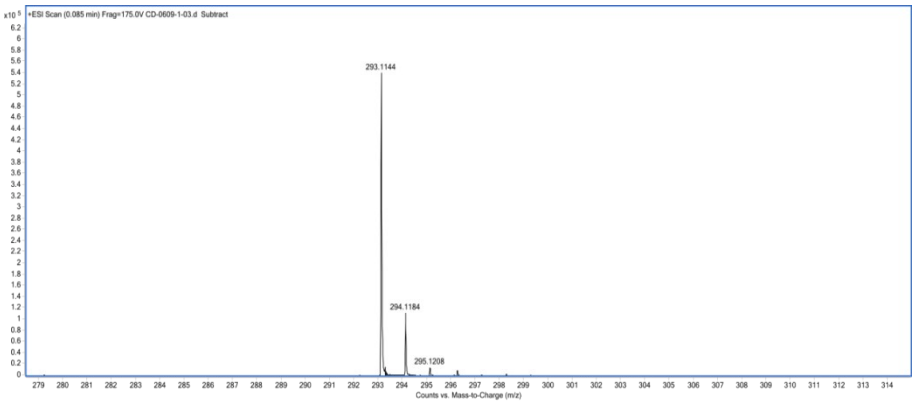


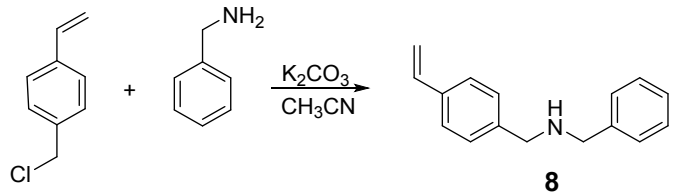
Fig. S11 ^{13}CNMRspectrum (125 MHz, $CDCl_3$, 298K) of compound **7**.



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C19 H16 O3	99.95	292.1068	292.1099	293.1172	10.68	12	293.1141

Fig. S12 HRMS spectrum of compound **7**.

3.2. Synthesis of compound **8**



8

4-Vinylbenzylchloride (5.00 g, 32.8 mmol), benzylamine (35.1 g, 328 mmol) and K_2CO_3 (13.8 g, 100.0 mmol) were dissolved in 250 mL of acetonitrile and then stirred at room temperature for 24 h. The excess of benzylamine was removed in a rotary evaporator. The resulting slurry was dispersed in diethyl ether to precipitate the salt

formed in the reaction, which was then removed by filtration. The organic phase was extracted with H_2O/CH_2Cl_2, dried over anhydrous $MgSO_4$ and the solvent was removed with a rotary evaporator. The crude product was purified by flash column chromatography (first petroleum ether, then ethyl acetate) to afford compound **8** (5.0 g, 65.8%) as a yellow oil. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) δ (ppm): 7.44–7.42 (d, J = 8.1 Hz, 2H), 7.39–7.35 (m, 7H),7.32–7.30 (m, 1H), 6.80–6.74 (dd, J_1 = 17.6 Hz,J_2 = 10.9 Hz 1H), 5.81–5.77 (dd, J_1 = 17.6 Hz, J_2 = 0.8 Hz, 1H), 5.29–5.26 (dd, J_1 = 10.9 Hz, J_2 = 0.7 Hz 1H), 3.80–3.84 (d, J = 2.5 Hz, 4H), 1.66 (s, 1H).

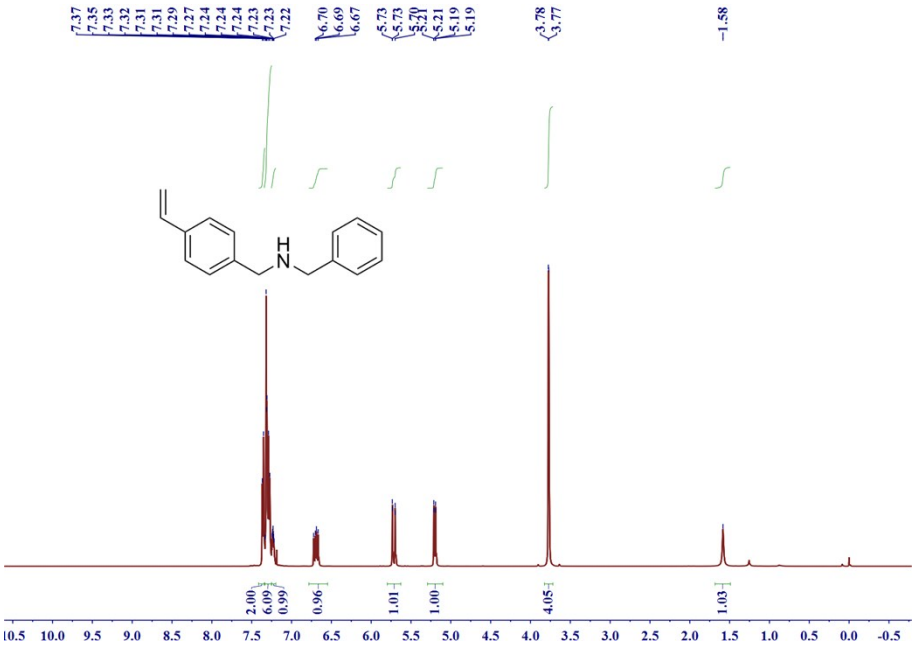
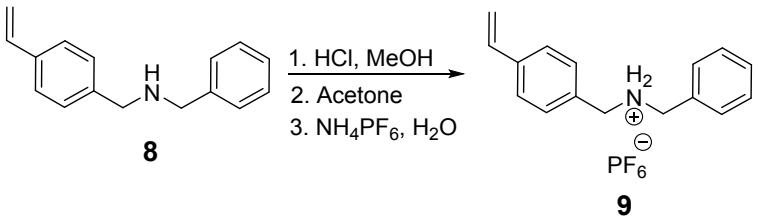


Fig. S13 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of compound **8**.

3.3. Synthesis of compound **9**



Compound **8** (1.0 g, 4.3 mmol) was dissolved in 250 mL of methanol. HCl (1 mol/L) was added to the solution for acidifying the amine and the mixture was stirred at room temperature for 1 h. After removing the solvent by a rotary evaporator, a white solid

will be obtained. The collective white solid was then dissolved in acetone/water (250mL, 5:1, v/v). To this solution, the saturated aqueous solution of NH_4PF_6 was added and stirred at room temperature for 3 h. Acetone was evaporated with a rotary evaporator to afford a yellow brown precipitate, which was filtered off and washed with deionized water to afford compound **9** as a white solid (1.1 g, 69.3%). ^{1}H NMR (500 MHz, DMSO, 298K) δ (ppm): 9.11 (s, 2H), 7.56–7.54 (d, J= 8.1 Hz, 2H), 7.50–7.44 (m, 7H), 6.79–6.74 (dd, J_1 = 17.6 Hz, J_2 = 10.9 Hz, 1H), 5.92–5.88 (d, J= 17.7 Hz, 1H), 5.33–5.31 (d, J = 10.0 Hz, 1H), 4.16 (s, 4H). ^{13}C NMR spectrum (125 MHz, DMSO, 298K) δ (ppm): 138.2, 136.5, 132.7, 132.1, 130.7, 130.4, 129.4, 129.1, 126.8, 115.8, 50.6, 50.4. HRMS $[M\text{-}PF_6]^+$: calcd. for $C_{16}H_{18}N$ 224.1434, found 224.1426.

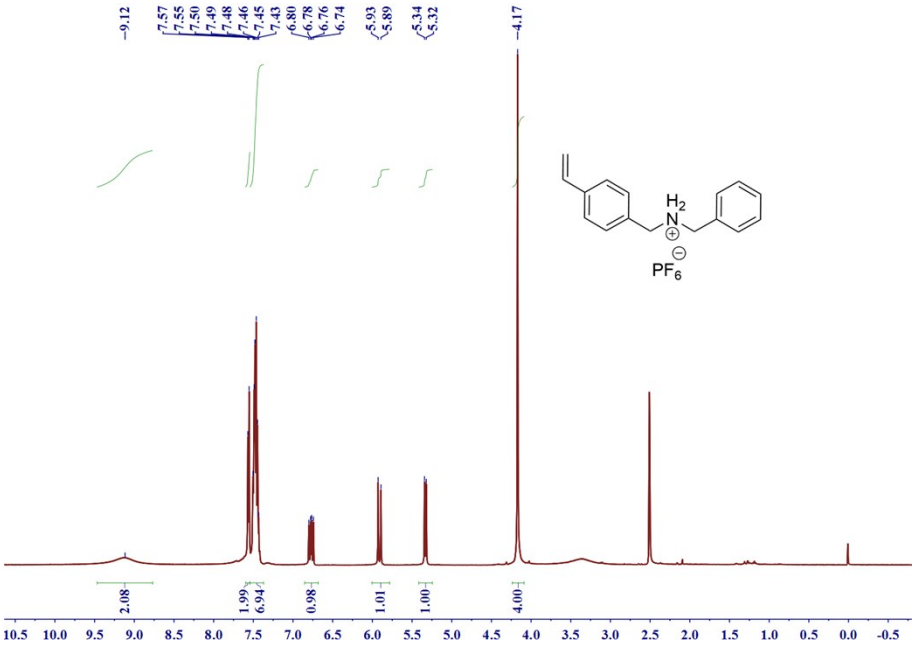


Fig. S14 ^{1}H NMR spectrum (500 MHz, DMSO, 298K) of compound **9**.

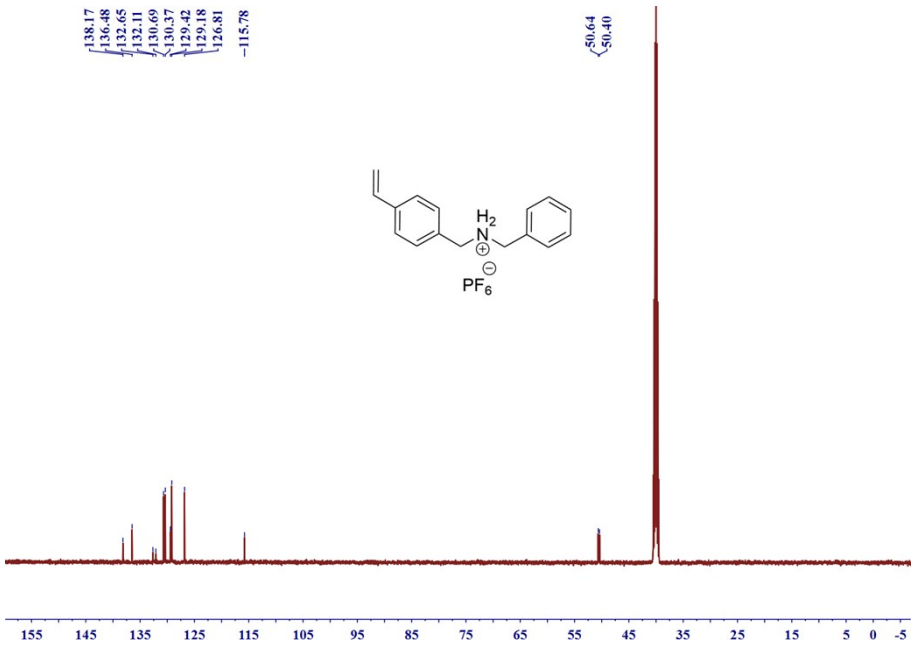
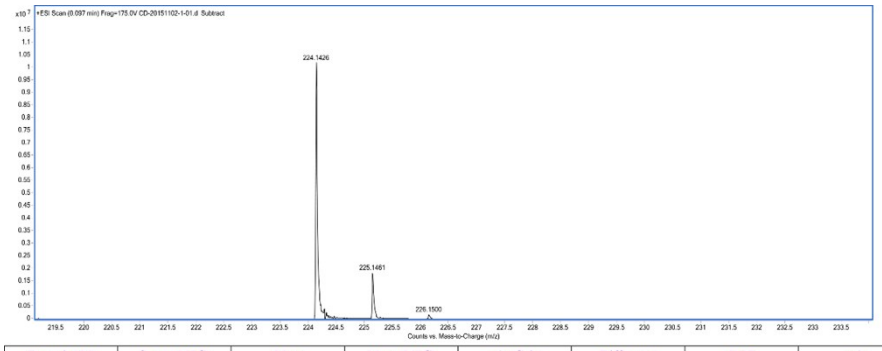


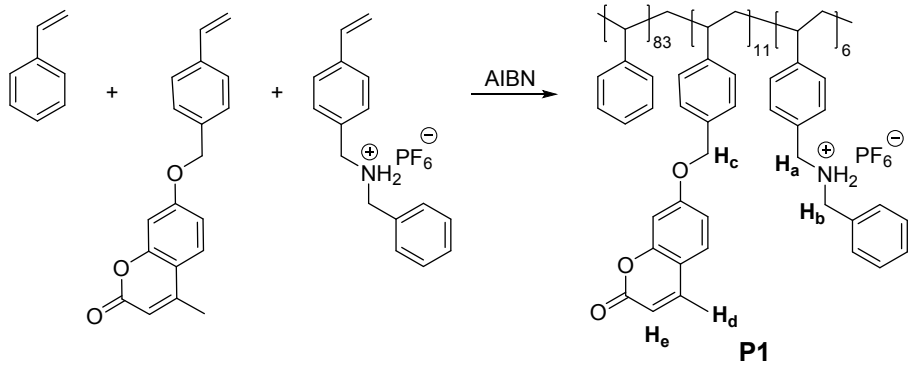
Fig. S15 ^{13}C NMR spectrum (500 MHz, DMSO, 298K) of compound **9**.



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C16 H18 N	100	224.1431	224.1439	224.1434	3.46	8.5	224.1426

Fig. S16 HRMS spectrum of compound **9**.

*3.4. Synthesis of compound **P1***



Styrene (833 mg, 8.00 mmol), compound **7** (292mg, 1.00 mmol), compound **9** (369

mg, 1.00 mmol), AIBN (13 mg, 0.08 mmol) were dissolved in DMF (10 mL). The mixture solution was added into a polymerization tube, and then was degassed by three freeze−pump−thaw cycles. After being sealed under vacuum, the mixture was reacted at 80 °C for 48 h. The reaction mixture was then dropwise added into hot methanol (200 mL). The resulting precipitate was collected and was redissolved in THF. The concentration solution was dropwise added again into hot methanol (200 mL). The dissolution-precipitation process was repeated three times, and the finally isolated precipitant was dried under vacuum at 40 °C to a constant weight. A white powder was obtained (0.83g, yield = 56%). The molar ration of three units were estimated to be x: m: n = 83: 11: 6 according to the NMR spectrum.

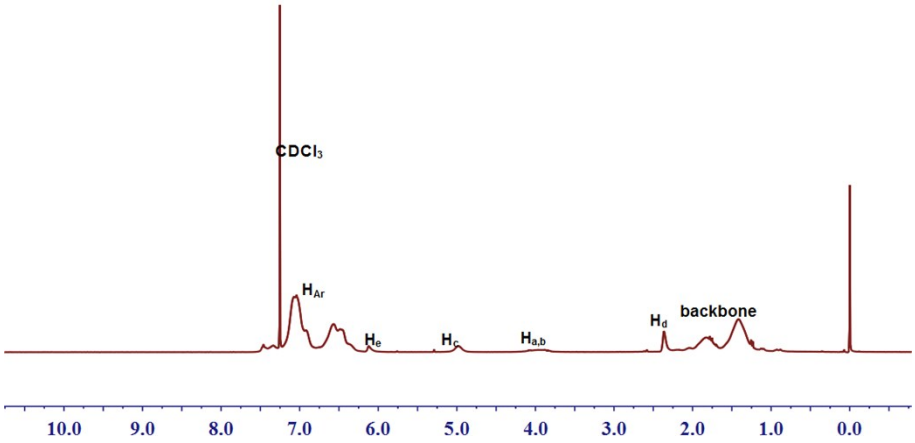
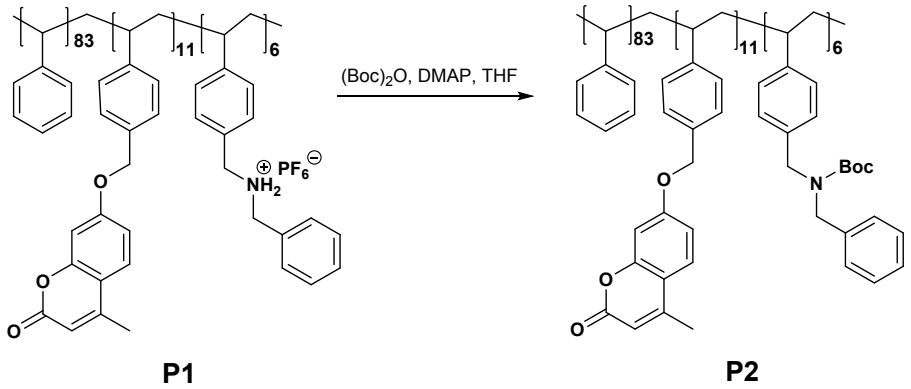


Fig. S17 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of compound **P1**.

*3.5. Synthesis of polymer **P2***



P1 (0.20 g), $(Boc)_2O$ (1.00 g, 4.58 mmol), and 4-dimethylamino pyridine (DMAP, 3 mg, 0.025 mmol) were dissolved in 2 mL of dry THF. After the mixture solution was

stirred at room temperature for 8 h, the solution was concentrated and precipitated in 40 mL of hot methanol. The dissolution-precipitation process was repeated three times to afford copolymer **P2** as a lavender solid (0.15 g, 75%). M_n 8000; M_w/M_n 2.1 (GPC, polystyrene calibration)

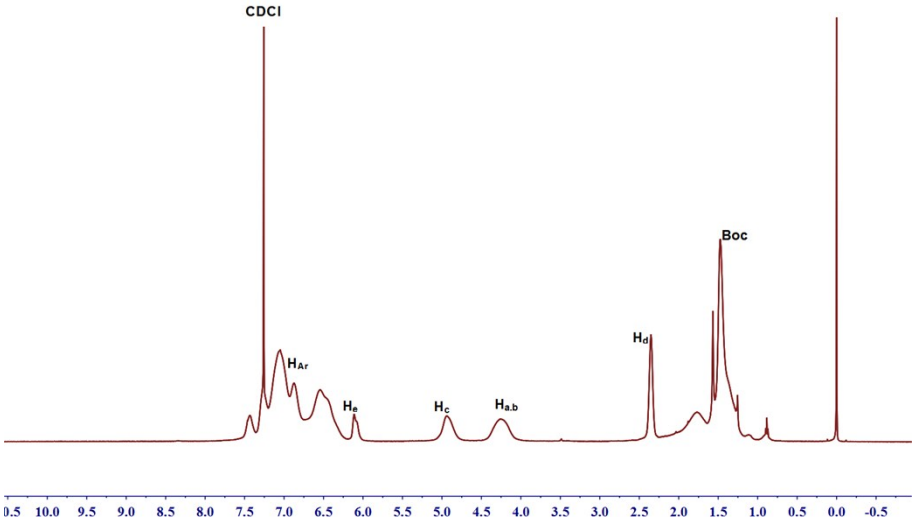


Fig. S18 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298K) of compound **P2**.

4. *UV/Vis absorbance spectra of complexation between **H1** and Zn(OTf)$_2$*

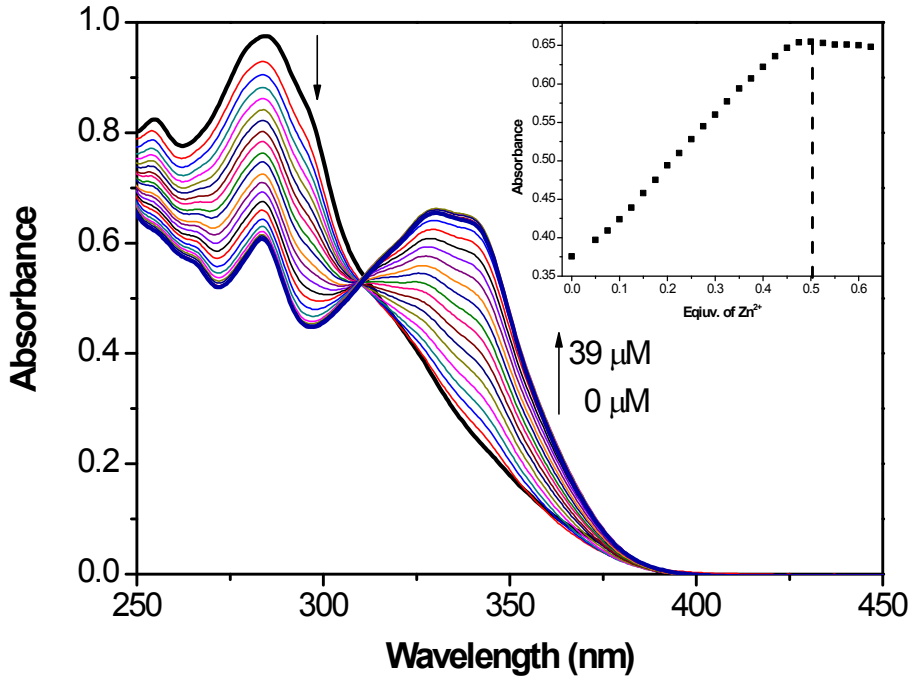


Fig. S19 Change in the UV/Vis absorbance intensity upon stepwise addition of $Zn(OTf)_2$ to **H1** in $CHCl_3/CH_3CN$ (1/1, v/v); Inset: Plot of the absorbance intensity at

327 nm versus the amount of $Zn(OTf)_2$.

5. *COSY spectrum of supramolecular polymer.*

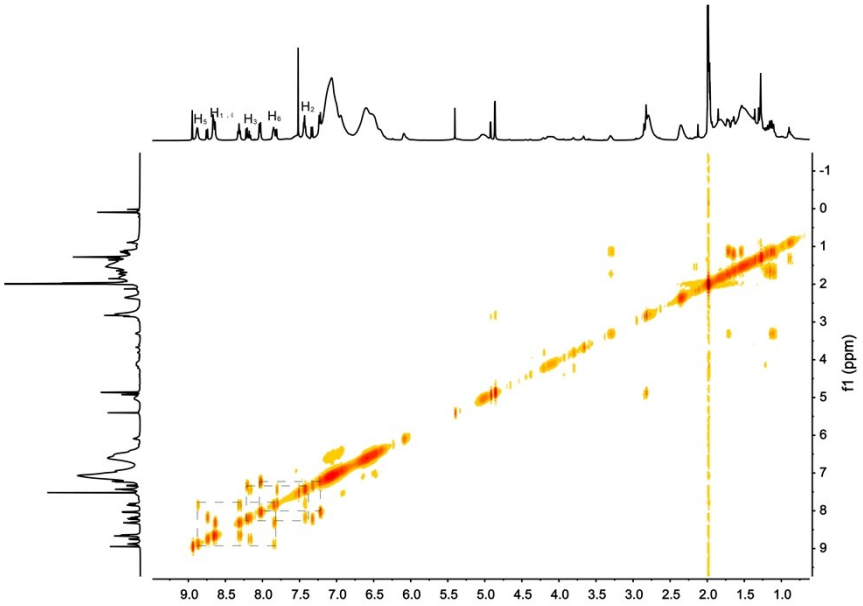


Fig. S20 2D COSY spectrum of supramolecular polymer (500 MHz, $CDCl_3/CD_3CN$ (1/1, v/v), 298K).

6. *^1H NMR spectra of concentration-dependent between **P1** and **H1**+Zn^{2+}*

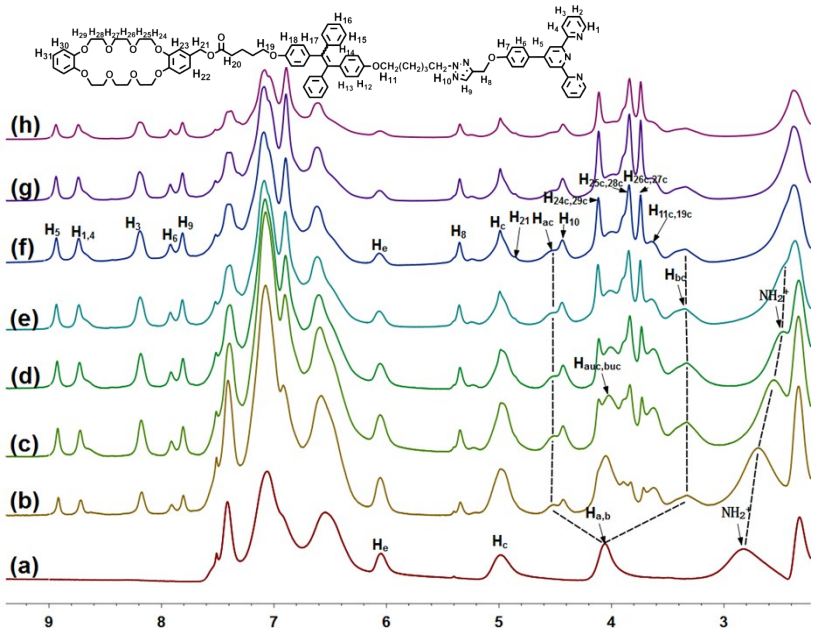


Fig. S21 ^{1}H NMR spectra (500 MHz, $CDCl_3/CD_3CN$ (1/1, v/v), 298 K) of **P1** (5.00 mM) upon addition of (a) 0 mM, (b) 3 mM, (c) 6 mM, (d) 9 mM, (e) 12 mM, (f) 15 mM, (g) 18 mM, and (h) 21 mM of **H1**+Zn^{2+}. Here, c and uc refer to the complexed and uncomplexed species, respectively.

7. *Fluorescence emission spectra of **P1, H1, P1+H1** and **P1+H1**+Zn^{2+} at the different concentrations*

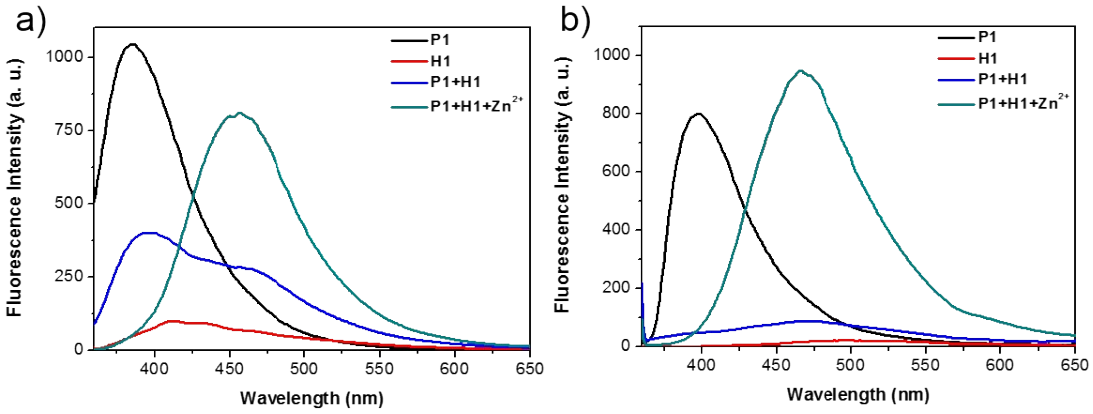


Fig. S22 Fluorescence emission spectra of a) **H1** (red line), **P1** (black line), **P1**+**H1** (blue line) and **P1**+**H1**+Zn^{2+}(dark cyan) (λ_{em}= 355 nm; slit widths: ex. 5 nm, em. 5 nm; 298 K, concentration: [**H1**] = 100 μM, [**P1**] = 18.6 μM, [Zn^{2+}] = 50 μM); b) **H1** (red line), **P1** (black line), **P1**+**H1** (blue line) and **P1**+**H1**+Zn^{2+} (dark cyan)) (λ_{em}= 355 nm; slit widths: ex. 5 nm, em. 5 nm; 298 K, concentration: [**H1**] = 58.4 mM, [**P1**] = 10 mM, [Zn^{2+}] = 28.8 mM).

8. *Fluorescence spectra of H1 or terpyridine derivative solutions (100 μM) with gradual addition of $Zn(OTf)_2$*

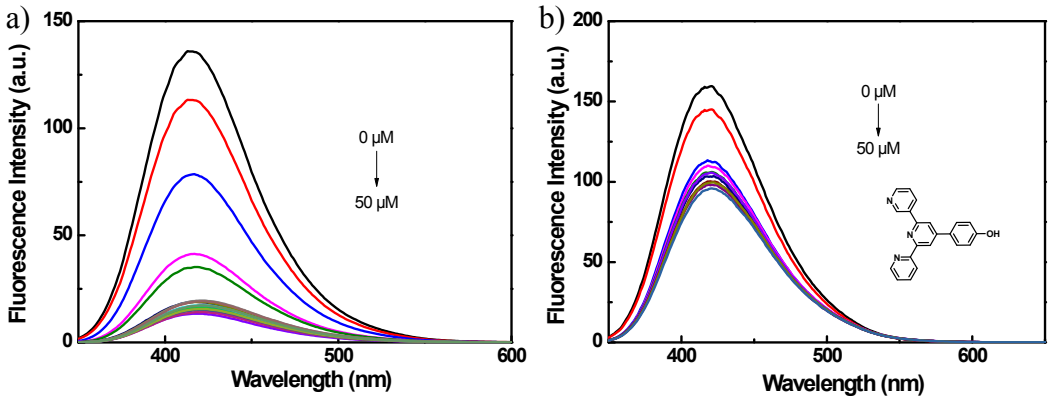


Fig. S23 a) Fluorescence spectra of H1 solution (100 μM) with gradual addition of $Zn(OTf)_2$, b) Fluorescence spectra of terpyridine moiety solution (100 μM) with gradual addition of $Zn(OTf)_2$.

9. Determination of the limit of detection of TBACl, Et_3N and cyclen

According to the literature,[S4] the limit of detection (LOD) was determined on the basis of the fluorescence titration when TBACl, Et_3N and cyclen were added in the **P1**+**H1**+Zn^{2+}. The LOD is calculated using the formula $3\sigma/k$, where σ is the standard deviation of blank (10 sample of I_{460}/I_{390}), and k is the slope between the intensity of I_{460}/I_{390} versus the concentration of TBACl, Et_3N and cyclen. Here,σ was calculated to be 0.32 from 20 blank samples.

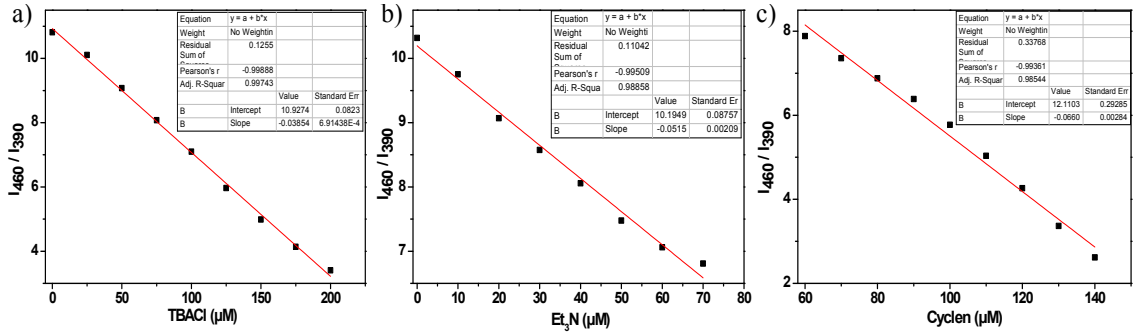


Fig. S24 The linear dynamic fluorescence response for the titration of **P1**+**H1**+Zn^{2+} ([**H1**] = 100 μM, [**P1**] = 18.6 μM, [Zn^{2+}] = 50 μM) with a) TBACl, b) Et_3N and c) cyclen to determine the limit of detection.

10. Photographs and fluorescent graphs of self-healing supramolecular gel

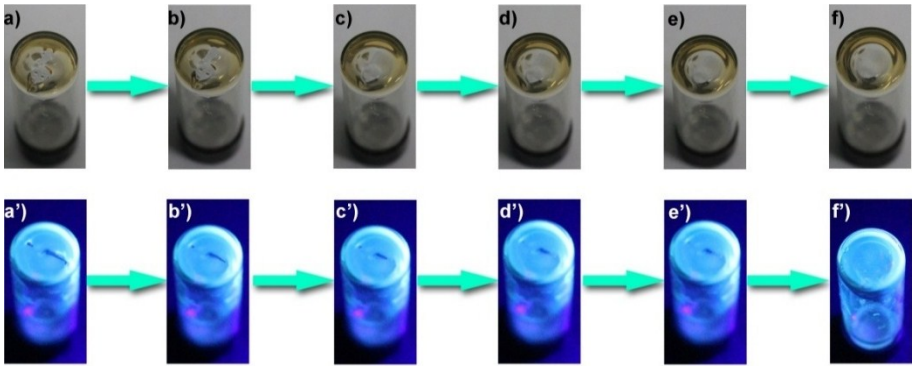


Fig. S25 Photographs and fluorescent graphs of a) supramolecular gel after damage and after free standing for b) 30 s, c) 60 s, d) 90 s, e) 120 s, f) 150 s.

References:

S1. D. Chen, J. Y. Zhan, M. Zhang, J. Zhang, J. Tao, D. Tang, A. Shen, H. Qiu and S. Yin, *Polym. Chem.* 2015, **6**, 25.

S2. J. Zhang, J. Zhu, C. Lu, Z. Gu, T. He, A. Yang, H. Qiu, M. Zhang and S. Yin, *Polym. Chem.* 2016, **7**, 4317.

S3. L. Chen, Y. Tian, Y. Ding, Y-J. Tian and F. Wang, *Macromolecules* 2012, **45**, 8412.

S4. D. Fan, C. Shang, W. Gu, E. Wang and S. Dong, *ACS Appl. Mater. Interfaces* 2017, **9**, 25870.