

Supporting Information

A Well-defined Alternating Copolymer Based on Salicylaldimine Schiff Base for Highly Sensitive Zinc(II) Detection and pH Sensing in Aqueous Solution

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Synthesis of cumyl dithiobenzoate (CDB)

CDB was prepared according to the literature¹. ¹H NMR (400 MHz, CDCl₃, δ): 2.00 (s, 6H, CH₃), 7.21 (t, 1H, ArH), 7.30 (m, 4H, ArH), 7.43 (t, 1H, ArH), 7.54 (d, 2H, ArH), 7.84 (d, 2H, ArH) (**Figure S1**).

Synthesis of *para*-Methoxydiethylene glycol-substituted Styrene 5 (VBCDEG)

The macromonomers VBCDEG was prepared according to the literature². Typical procedure as following: 2-(2-Methoxyethoxy)ethanol (2.0 g, 16.6 mmol) was added into a Schlenk flask containing toluene (50 mL), and the mixture was refluxed at 110 °C overnight. After toluene was removed by distillation, THF (15 mL) and NaH (0.8 g, 33.3 mmol) were added under N₂. After the mixture was stirred in an ice bath under N₂ for 1 h, the solution of 4-vinylbenzyl chloride (1.83 g, 12 mmol) in anhydrous THF (10 mL) was added dropwise. The reaction was carried out at room temperature for 24 h. Then THF was evaporated and brine (200 mL) was added into the residue. The aqueous phase was extracted with CH₂Cl₂ (50 mL) four times, and the organic phase were dried over anhydrous Na₂SO₄ overnight. The solvent was concentrated and further purified by silica gel column chromatography using EtOAc/petroleum ether (1:4, v/v) as the eluent. The product was dried at room temperature in a vacuum oven for 12 h to obtain a yellowish oil (yield: 2.0 g, 71%). ¹H NMR (400 MHz, CDCl₃, δ): 3.39 (s, 3H, OCH₃), 3.55-3.69 (m, 8H, OCH₂CH₂O), 4.55 (s, 2H, ArCH₂O); 5.23 (d, 1H, CH₂=CH), 5.74 (d, 1H, CH₂=CH), 6.71 (dd, 1H, CH₂=CH), 7.30 (d, 2H, ArH), 7.38 (d, 2H, ArH) (**Figure S2**). MS (EI, *m/z*): calculated for C₁₄H₂₀O₃, 236.1; found, 236.1.

Ordinary radical polymerization of VBCDEG and SaAEMI without RAFT agent

In a typical experiment, maleimide monomer 4 (11.5 mg, 0.047 mmol), VBCDEG (10 mg, 0.045 mmol), AIBN (0.25 mg, 0.0015 mmol), and 0.25 mL dried THF were charged into a glass flask equipped with a magnetic stirring bar. The flask was degassed by three freeze-evacuate-thaw cycles and then sealed under vacuum. The polymerization was carried out in an oil bath at 65 °C for 24 h, and then quenched into liquid nitrogen. The tube was opened, and the solution was precipitated into an excess of cold diethyl ether. The above dissolution-

precipitation was repeated for three times. The alternating copolymer was obtained as a yellowish powder after drying at room temperature in a vacuum oven overnight ($M_n = 8\,900$, $M_w = 17\,600$, $M_w/M_n = 1.98$).

Synthesis of *N*-(2-(*t*-Boc)-Aminoethyl)butanethiolsuccinimide **7**

Compound **2** (961 mg, 4 mmol) and 1-butanethiol (430 μ L, 4 mmol) were firstly dissolved in 10 mL of DCM. The catalytic amount of 1-butylamine was added into above solution, and then stirred for 24 h at room temperature. The solution was concentrated and further purified by silica gel column chromatography using EtOAc/petroleum (1:3, v/v) as the eluent. A colorless oil was obtained (yield: 1.0 g, 75%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 0.92 (t, 3H, CH_2CH_3), 1.44 (m, 11H, CCH_3 , $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.61 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.50 (q, 1H, SCHCH_2CON), 2.75, 2.88 (m, 2H, SCHCH_2CON), 3.12 (q, 1H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.34 (q, 2H, $\text{CH}_2\text{CH}_2\text{NH}$), 3.59-3.75 (m, 3H, $\text{CH}_2\text{CH}_2\text{NH}$, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.78 (br s, 1H, NH).

Synthesis of *N*-(2-Aminoethyl)butanethiolsuccinimide Trifluoroacetate Salt **8.** Compound **6** was prepared as a white solid according to the similar procedure as compound **3** (yield: 603 mg, 60%).

Synthesis of *N*-(2-Salicylaldehyde-Aminoethyl)butanethiolsuccinimide **9 (SaAE-BtSI).**

Compound **7** was obtained as a yellow oil according to the similar procedure as compound **4** (yield: 456 mg, 78%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 0.89 (t, 3H, CH_2CH_3), 1.35 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.52 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.47, 2.52 (dd, 1H, SCHCH_2CON), 2.60, 2.80 (m, 2H, SCHCH_2CON), 3.11 (q, 1H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.69 (q, 1H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.85 (m, 4H, $\text{CH}_2\text{CH}_2\text{N}$), 6.86 (t, 1H, ArH), 6.94 (d, 1H, ArH), 7.22 (q, 1H, ArH), 7.29 (m, 1H, ArH), 8.32 (s, 1H, CHNCH_2), 12.73 (s, 1H, OH). FTIR (KBr, cm^{-1}): 3417, 3000-2800, 1777, 1701, 1349, 1279, 1178, 1152, 758.

Kinetic Fitting of Time-dependent Fluorescence

The fluorescence data were analyzed with a pseudo-first-order kinetic expression as follow:

$$F_t = F_e[1 - \exp(-kt)]$$

where F_t is the fluorescence intensity of P(VBCDEG-*alt*-SaAEMI)-30 at set pH value at time t , F_e is the equilibrium fluorescence intensity of P(VBCDEG-*alt*-SaAEMI)-30 at set pH value at long equilibrium times, and k is the pseudo-first-order rate constant for the hydrolysis of succinimide moieties in P(VBCDEG-*alt*-SaAEMI)-30.

Table S1. Conditions and results of the RAFT alternating copolymerization of VBCDEG with SaAEMI using CDB as the RAFT agent

Samples ^a	[VBCDEG]/[SaAEMI] /[CDB]/[AIBN] ^b	M_n (g/mol) ^c	M_w (g/mol) ^c	M_w/M_n ^c
P(VBCDEG- <i>alt</i> -SaAEMI)-10	10:10.5:1:0.1	4 600	5 500	1.18
P(VBCDEG- <i>alt</i> -SaAEMI)-20	20:21:1:0.1	6 500	8 500	1.32
P(VBCDEG- <i>alt</i> -SaAEMI)-30	30:30.15:1:0.1	9 550	12 900	1.35

^a the numbers correspond to the value of [VBCDEG]/[CDB].

^b the polymerization reaction performed in THF at 65 °C for 24 h, CDB as the chain transfer agent, AIBN as the initiator.

^c determined by GPC with polystyrene standards.

Scheme 1. Synthesis of SaAE-BtMI.

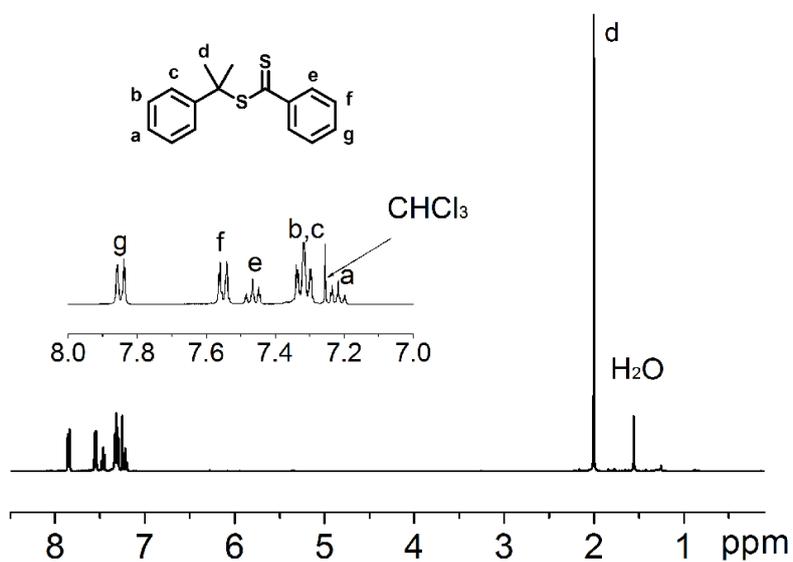
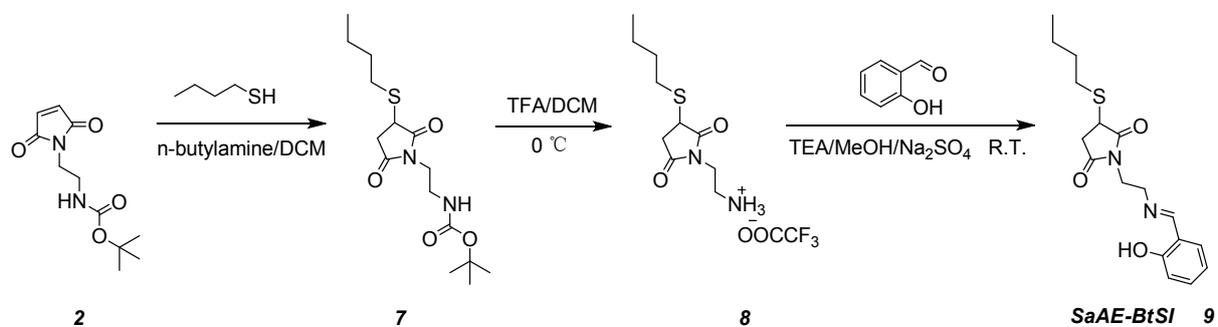


Figure S1. ¹H NMR spectrum of CDB in CDCl₃.

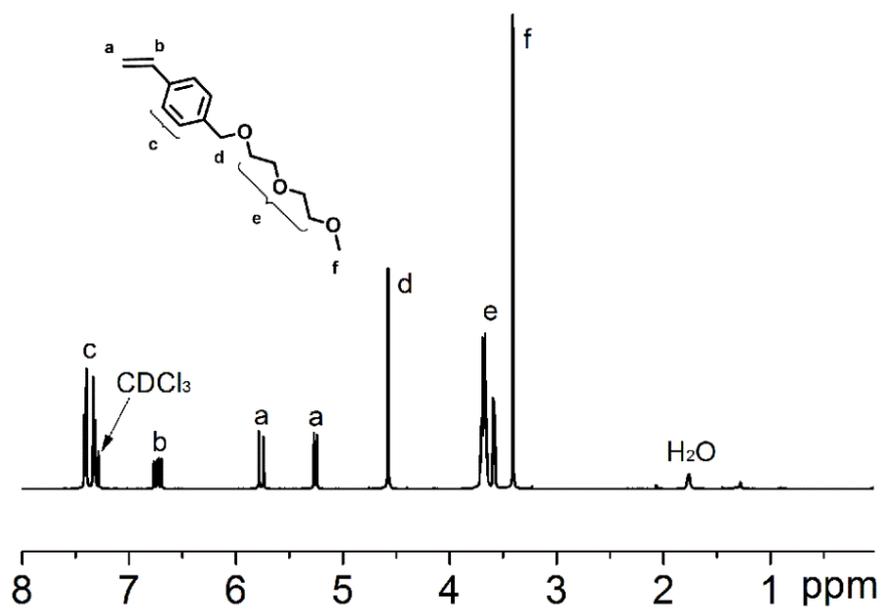


Figure S2. ^1H NMR spectrum of VBCDEG in CDCl_3 .

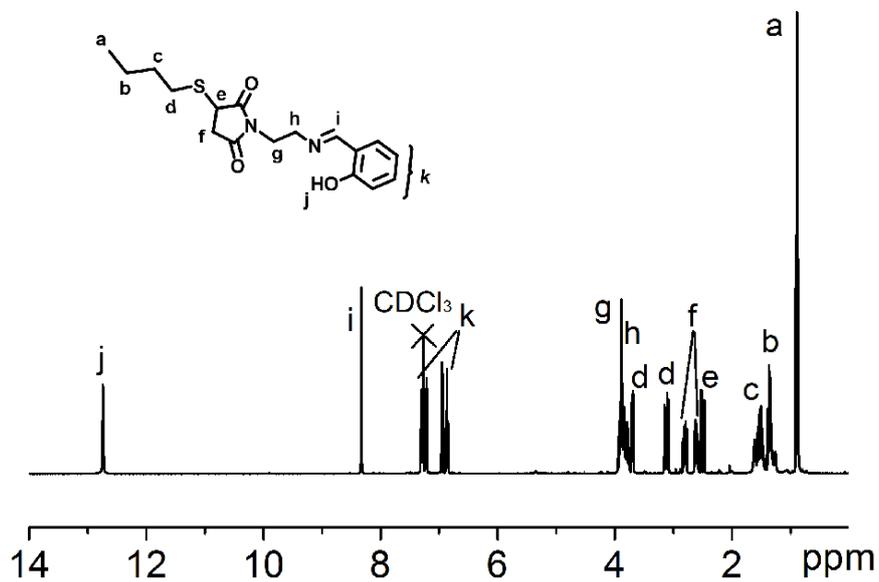


Figure S3. ^1H NMR spectrum of SaAE-BtSI in CDCl_3 .

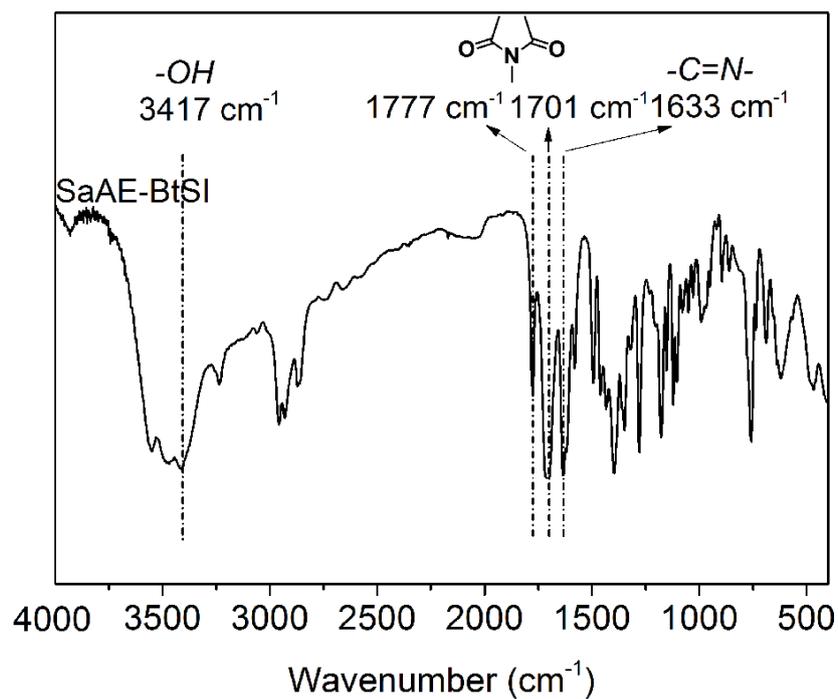


Figure S4. FT-IR spectrum of SaAE-BtSI.

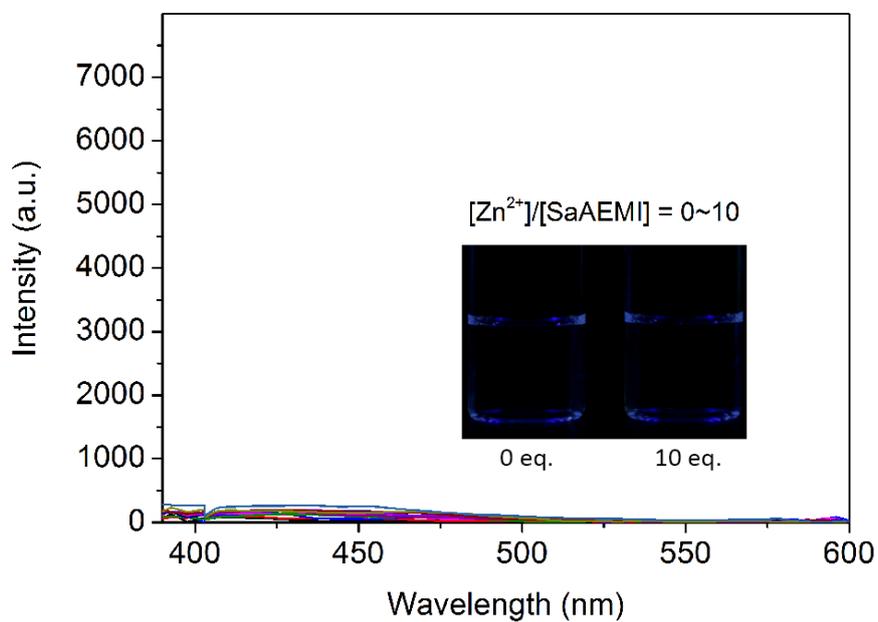


Figure S5. Fluorescence spectra ($\lambda_{\text{ex}} = 368 \text{ nm}$) of SaAEMI ($20 \mu\text{M}$) with different concentration of (0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 equiv.) Zn^{2+} in MeCN/HEPES mixture (8/2, v/v; 20 mM; $\text{pH} = 7.2$).

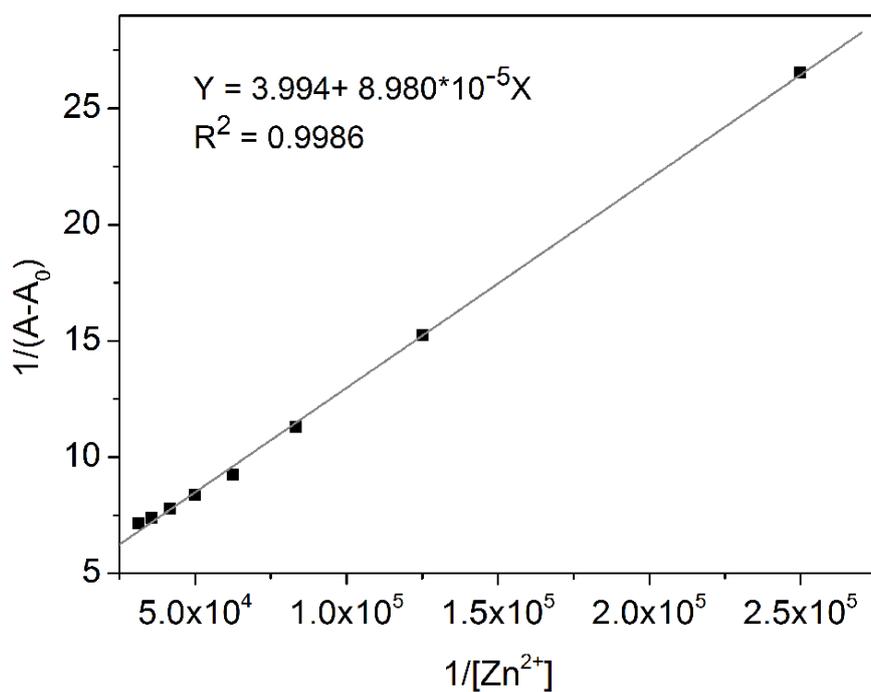


Figure S6. Benesi–Hildebrand plot of P(VBCDEG-*alt*-SaAEMI)-30 with Zn²⁺.

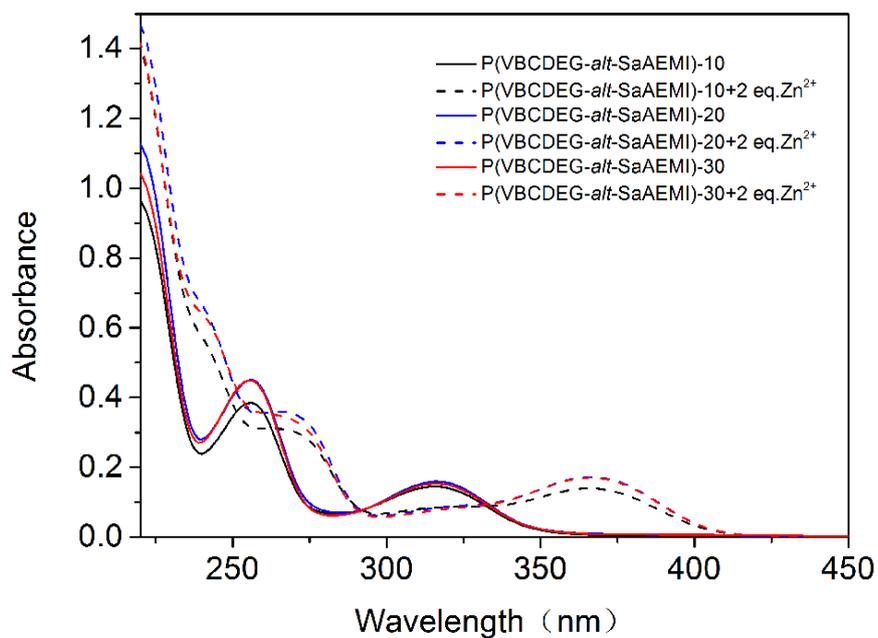


Figure S7. Absorbance spectra of P(VBCDEG-*alt*-SaAEMI) (40 μM) with and without 2.0 equiv. Zn²⁺ in MeCN/HEPES mixture (8/2, v/v; 20 mM; pH = 7.2).

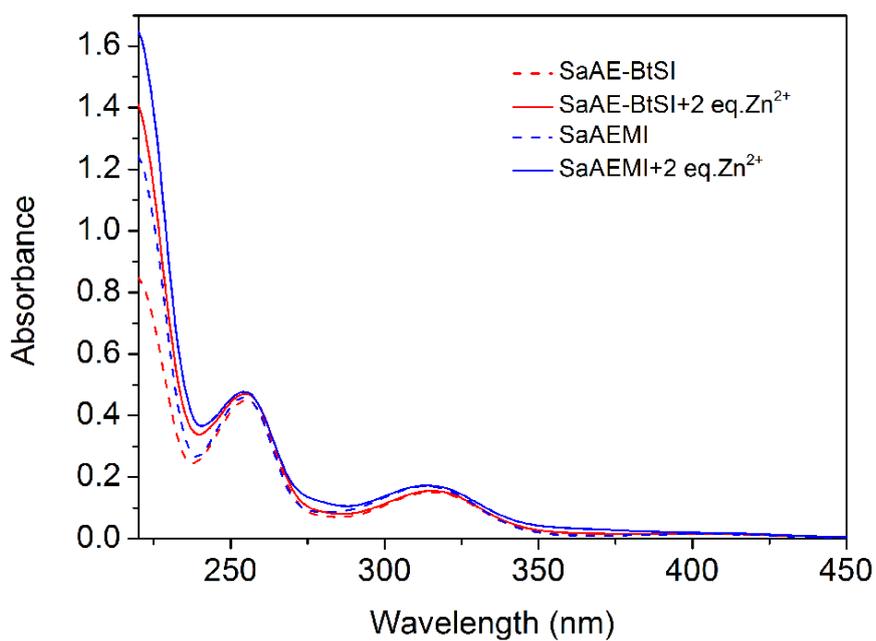


Figure S8. Absorbance spectra of SaAE-BtSI, SaAEMI (40 μM) with and without 2.0 equiv. Zn^{2+} in MeCN/HEPES mixture (8/2, v/v; 20 mM; pH = 7.2).

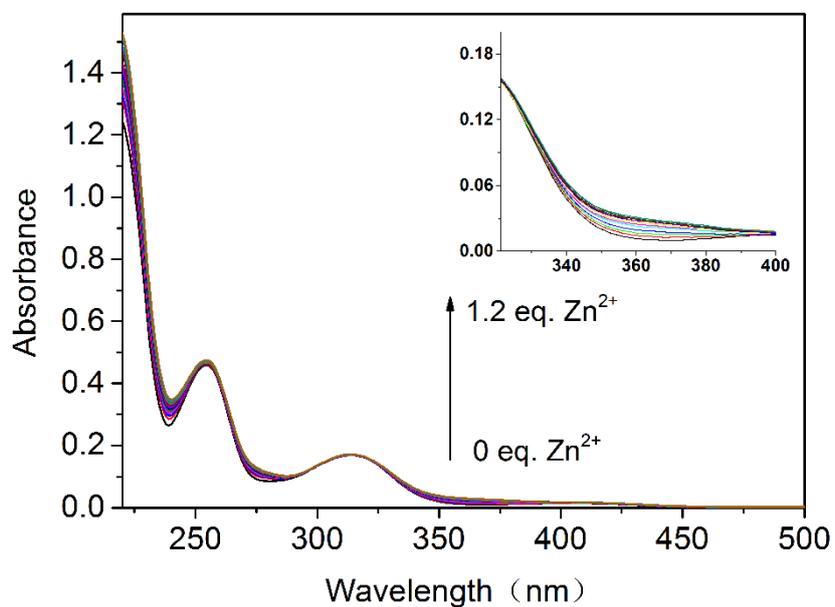


Figure S9. UV-Vis titration of SaAEMI (40 μM) with Zn^{2+} (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2 equiv.) in MeCN/HEPES mixture (8/2 v/v; 20 mM; pH = 7.2). The inset shows the magnification of the region between 320 and 400 nm.

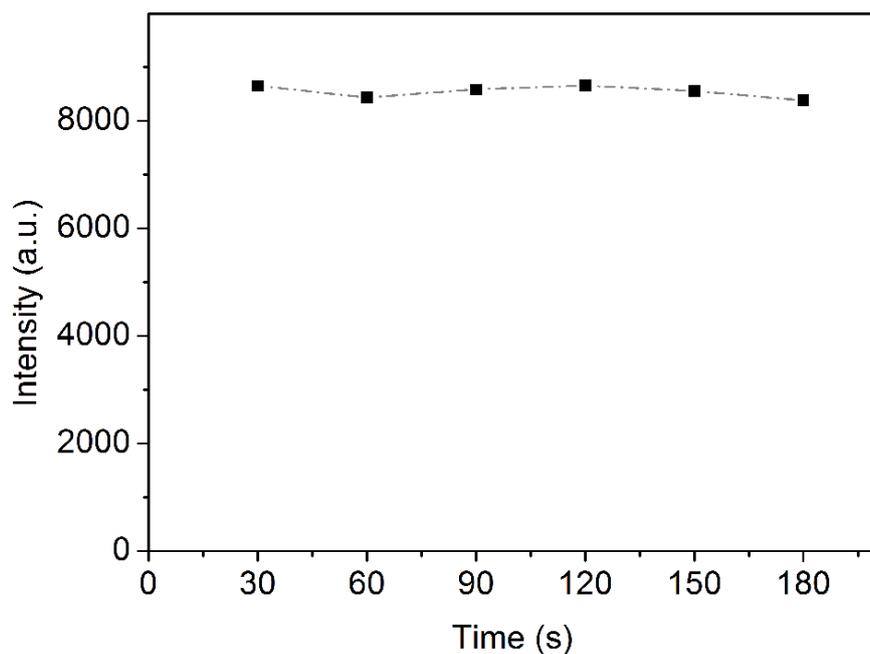


Figure S10. Time-dependent fluorescence intensity of P(VBCDEG-*alt*-SaAEMI)-30 (20 μM) upon addition of Zn^{2+} .

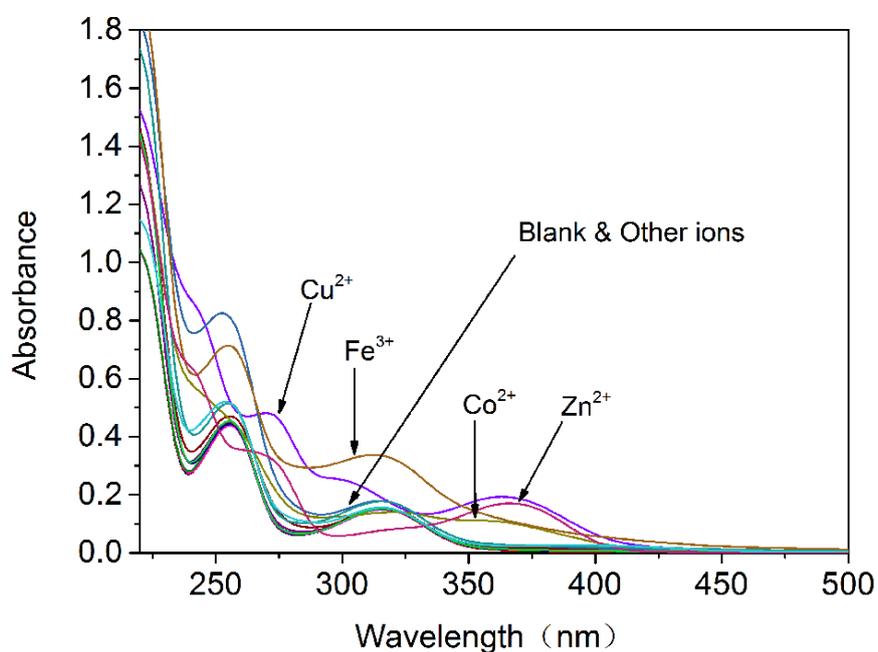


Figure S11. Absorbance spectra of P(VBCDEG-*alt*-SaAEMI)-30 (40 μM) in MeCN/HEPES mixture (8/2 v/v; 20 mM; pH = 7.2) with and without addition of 2.0 equiv. of various metal ions.

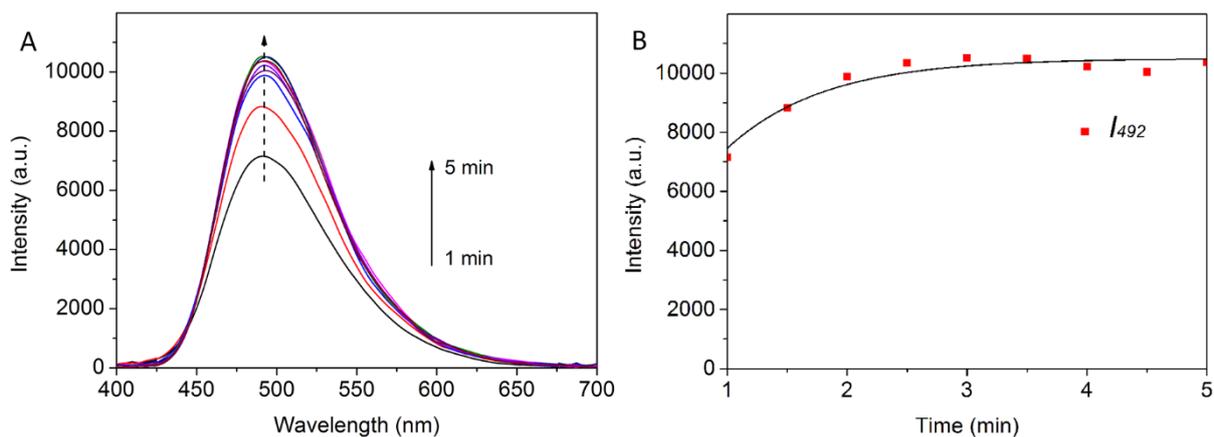


Figure S12. (A) Time-dependent fluorescence spectra of P(VBCDEG-*alt*-SaAEMI)-30 (20 μ M) in MeCN/HEPES mixture (8/2 v/v; 20 mM; pH = 13). (B) Time-dependent fluorescence intensity ($\lambda_{em} = 492$ nm) as a function of time. Solid line is a nonlinear least-squares fit to pseudo-first-order equation.

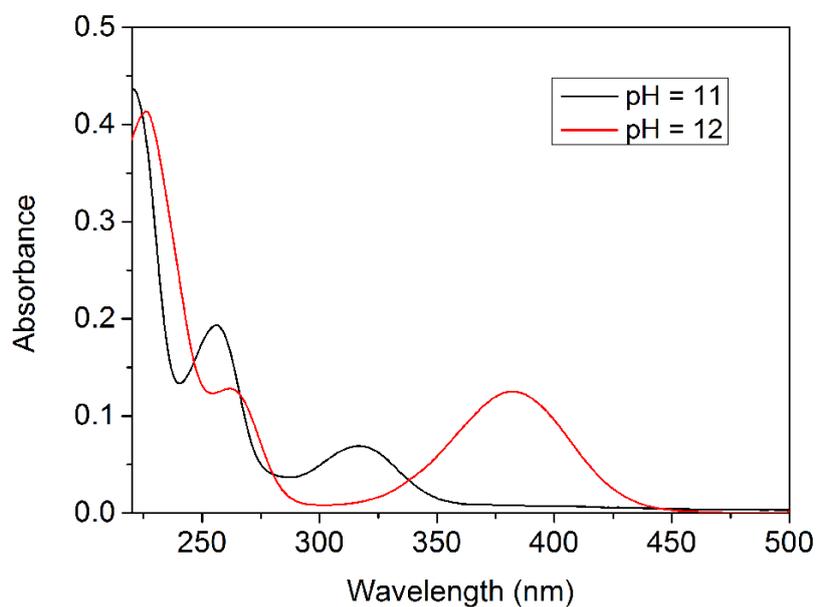


Figure S13. Absorbance spectra of P(VBCDEG-*alt*-SaAEMI)-30 (20 μ M) in MeCN/HEPES mixture (8/2 v/v; 20 mM; pH = 11 and pH = 12).

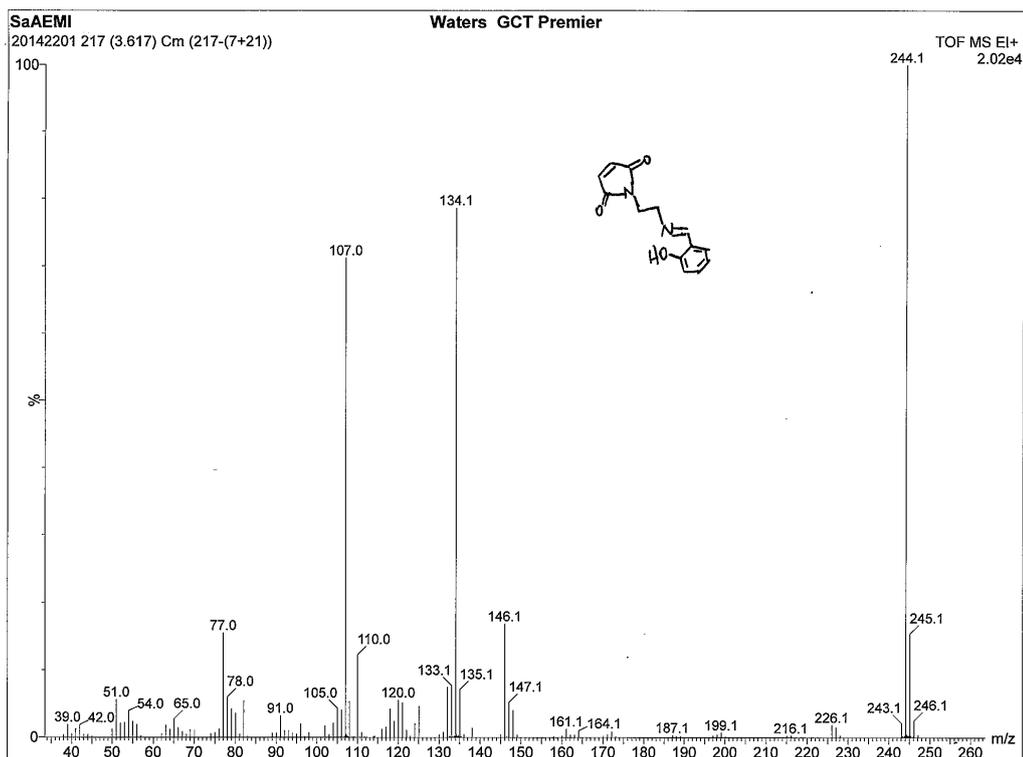


Figure S14. EI-MS spectrum of SaAEMI.

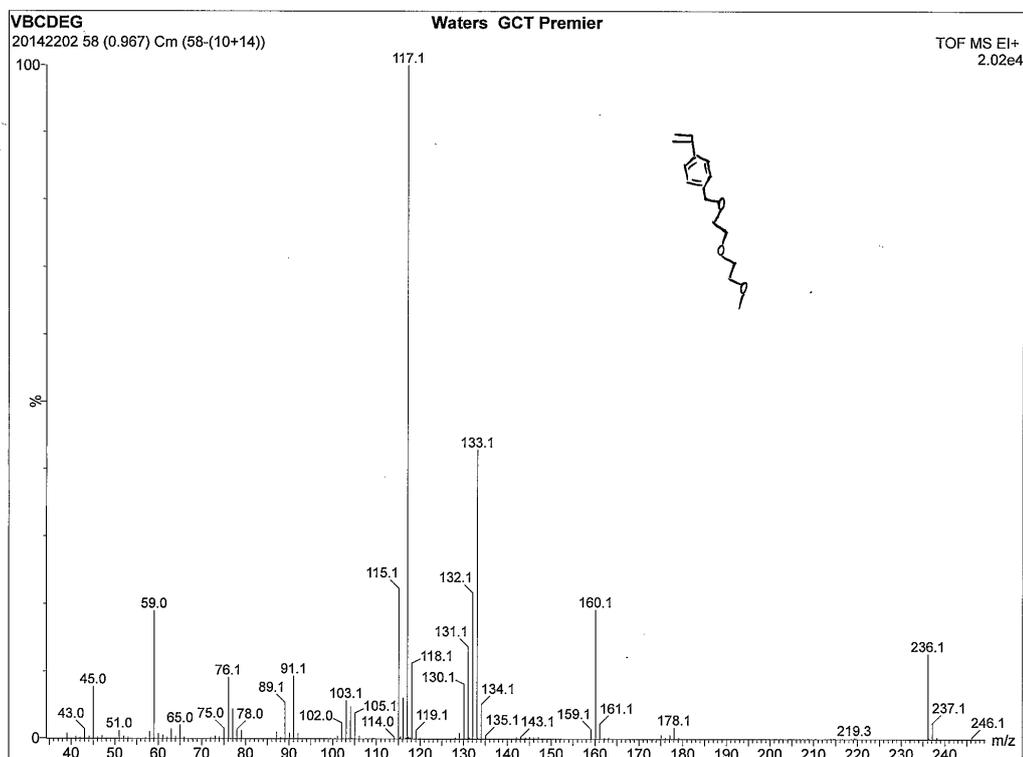


Figure S15. EI-MS spectrum of VBCDEG.

References

1. Y. Liu, J. He, J. Xu, D. Fan, W. Tang and Y. Yang, *Macromolecules*, 2005, **38**, 10332-10335.
2. H. Zhu, G. Deng and Y. Chen, *Polymer*, 2008, **49**, 405-411.