

Electronic Supporting Information Available

Multiring-Induced Multicolor Emission: Hyperbranched Polysiloxane with Silicon Bridge for Data Encryption

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Supporting information

Materials and methods

All chemicals were purchased from Sigma-Aldrich and used directly without further purification. Molecular weight and distribution within the medium were measured using an ultimate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA). Tetrahydrofuran (THF) was used as the mobile phase and the measurement was performed at a flow rate of 1 ml/min. ^{13}C NMR (101MHz) and ^1H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer in CDCl_3 or DMSO-d_6 solvent, using TMS as an internal standard. Fourier transform infrared (FTIR) spectra of the oligomers and distillates were collected using a NICOLET 5700 FTIR spectrometer ranging from 4000 to 400 cm^{-1} . UV-vis absorption spectra for EtOH solution of **P1** and **P2** were measured by a Shimadzu UV-2500 spectrophotometer. Fluorescent excitation/emission spectra for EtOH solution of **P1** and **P2** were measured on a Hitachi F-4600 fluorescence spectrophotometer. Fluorescence lifetime and absolute fluorescence quantum yield for pure **P1** and **P2** was measured on a steady/transient-state fluorescence spectrometer coupled with an integrating sphere (FLS980, Edinburgh

Instruments). Transmission electron microscopy (TEM) images were obtained via a FEI Tecnai G2 F20 microscopy. Particle size distributions of the solutions were measured using dynamic light scattering (DLS) by a Zetasizer Nano (Malvern Inst. Ltd., UK) equipped with either a four-side clear cuvette. Theoretical calculations were performed by using the density functional theory (DFT) or time-dependent density functional theory (TD-DFT) with B3LYP/6-31G(d). The security paper was fabricated by wetting the commercial available filter paper with **P1** ethanol solution (100 mg/ml).

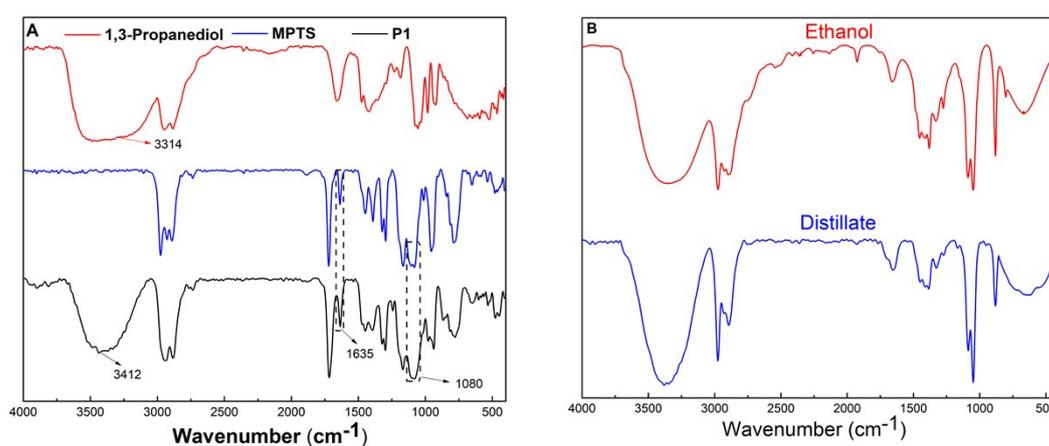
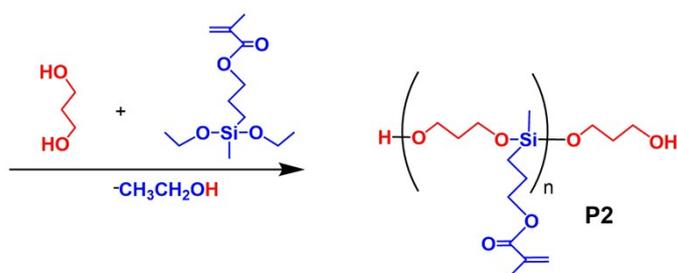


Figure S1 A) FT-IR spectra of 1,3-propanediol, MPTS and **P1**; B) FT-IR spectra of the distillate of **P1** and ethanol.

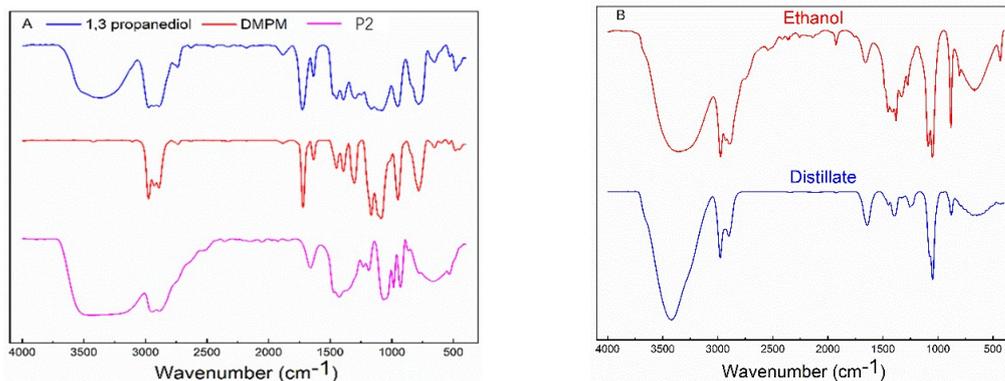


Figure S2 A) FT-IR spectra of **P2**, DMPM and 1,3-propanediol; B) FT-IR spectra of the distillate of **P2** and ethanol.

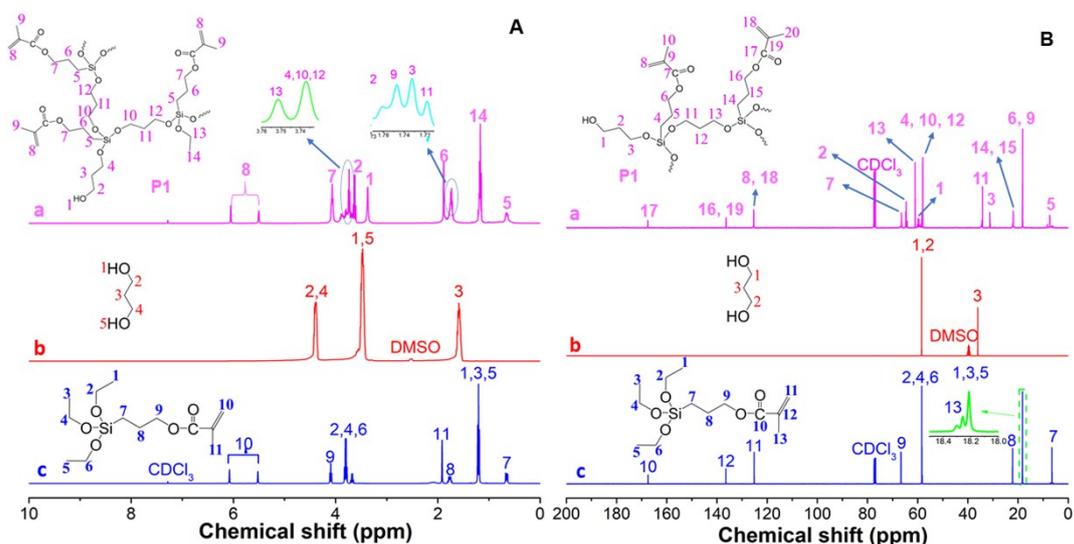


Figure S3 ^1H NMR spectrum of a) **P1**, b) 1,3-propanediol, c) MPTS (A) and ^{13}C NMR spectrum of a) **P1**, b) 1,3-propanediol, c) MPTS (B).

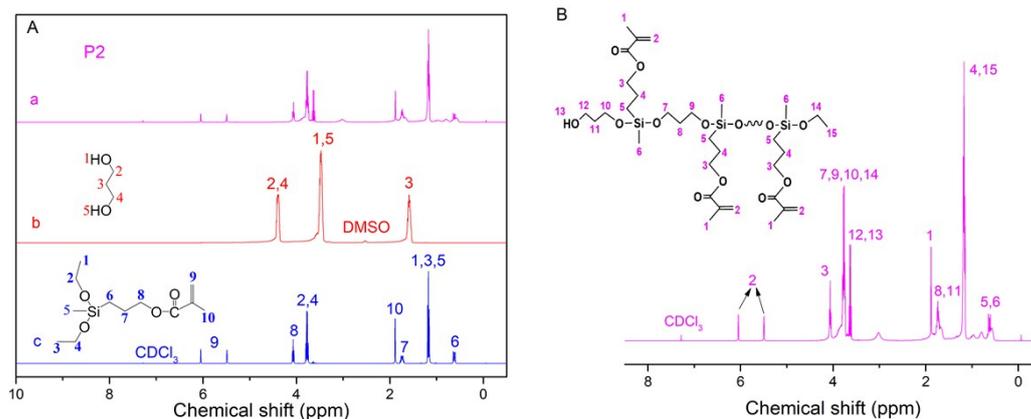


Figure S4 A) ^1H NMR spectrum of a) **P2**, b) 1,3-propanediol, c) DMPM; B) solitary ^1H NMR spectrum of **P2**.

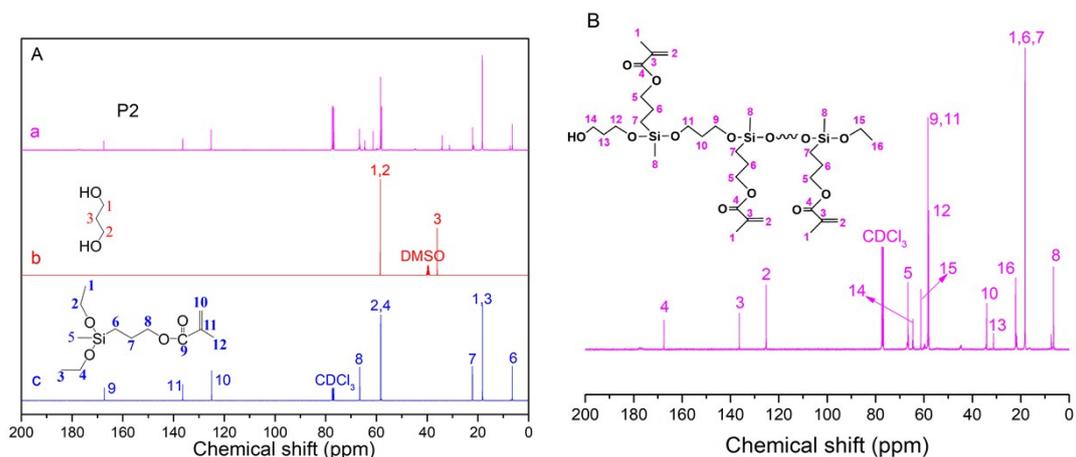


Figure S5 A) ^{13}C NMR spectrum of a) **P2**, b) 1,3-propanediol, c) DMPM; B) solitary ^{13}C NMR spectrum of **P2**.

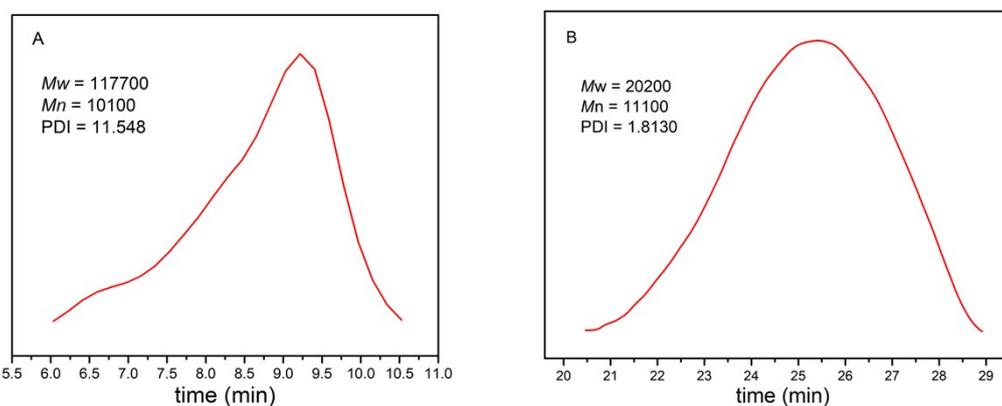


Figure S6 A) GPC curve of **P1**; B) GPC curve of **P2**.

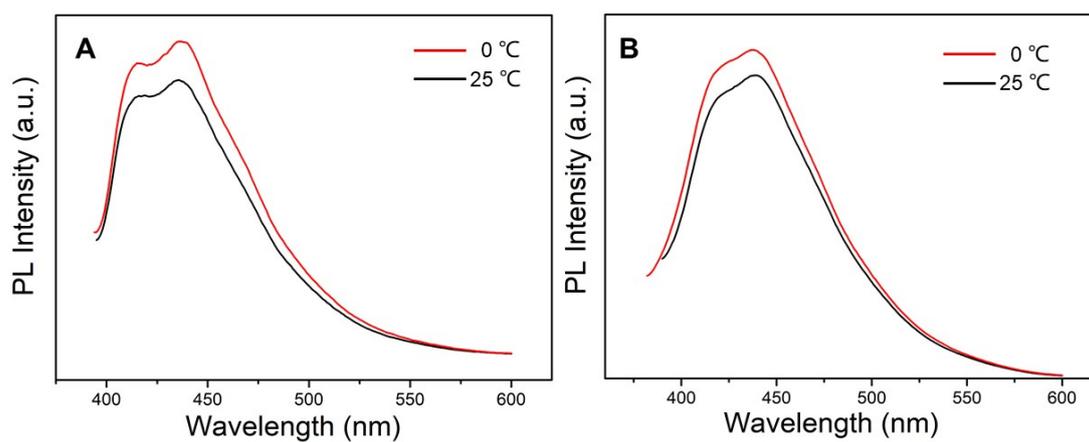


Figure S7 A) The emission spectra of **P1** in ethanol solution (100 mg/ml) at 25 °C and 0 °C; B) The emission spectra of pure **P1** at 25 °C and 0 °C.

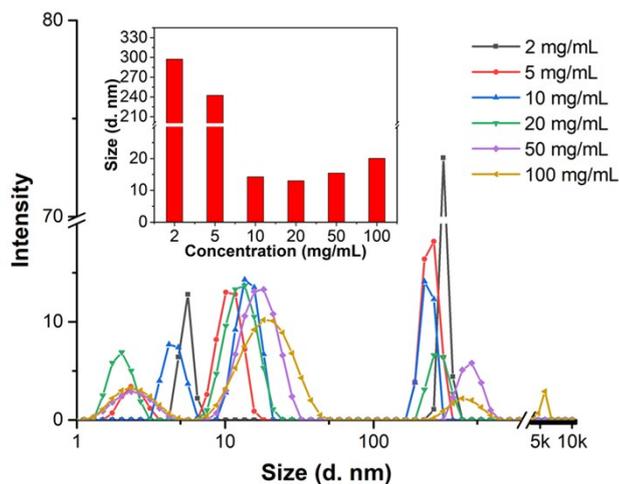


Figure S8 Particle size distribution of **P1** at different concentrations and Particle size of high proportion aggregates of **P1** at different concentrations.

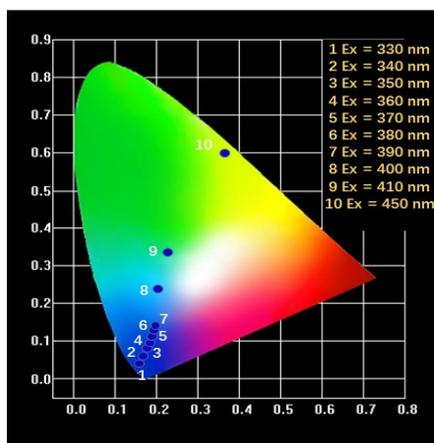


Figure S9 CIE chromaticity coordinates obtained from the emission spectra of **P1** at a concentration of 100 mg/mL in ethanol solution.

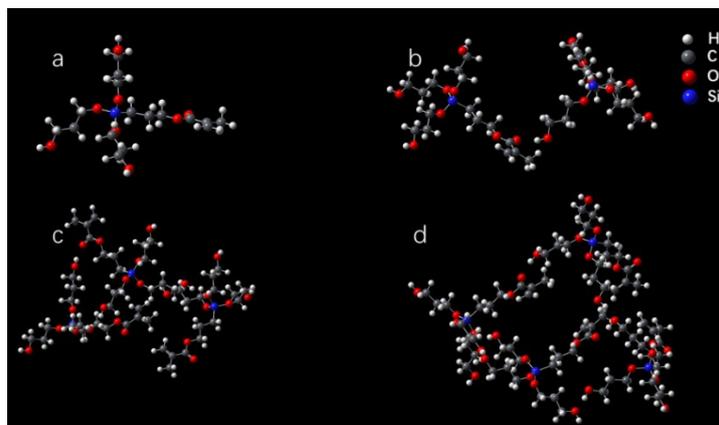


Figure S10 Optimized conformations of the first generation **P1** molecules increased from 1 to 4 (a-d).

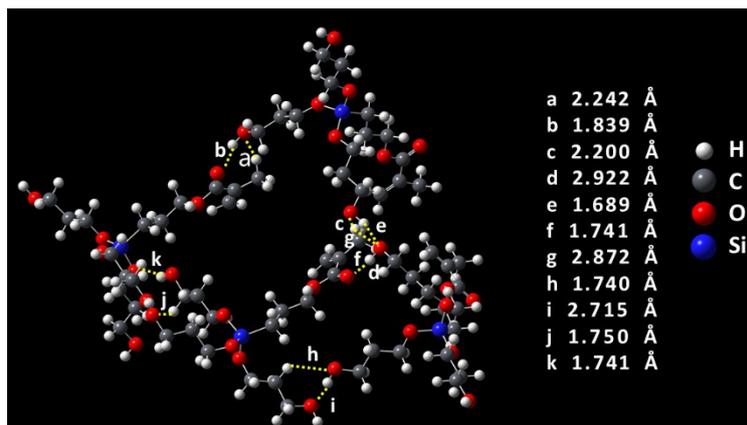


Figure S11 The accumulation of four P1 first generation molecules induced by H...O strong intermolecular interactions and their distance.

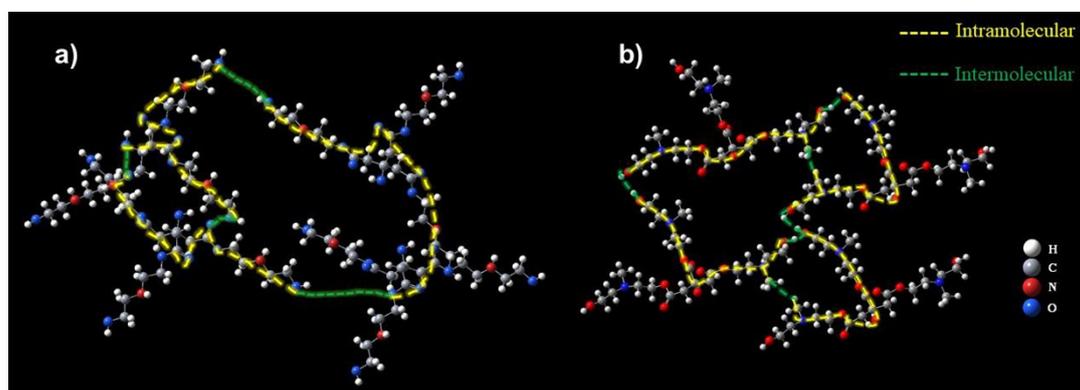


Figure S12 The accumulation of four first generation molecules and the “silicon-bridge” promoted multiring through-space conjugation of hyperbranched poly(amino ester)s we synthesized from a) CA and NMDEA^[1] or b) TEC and DEA via DFT calculation.^[2]

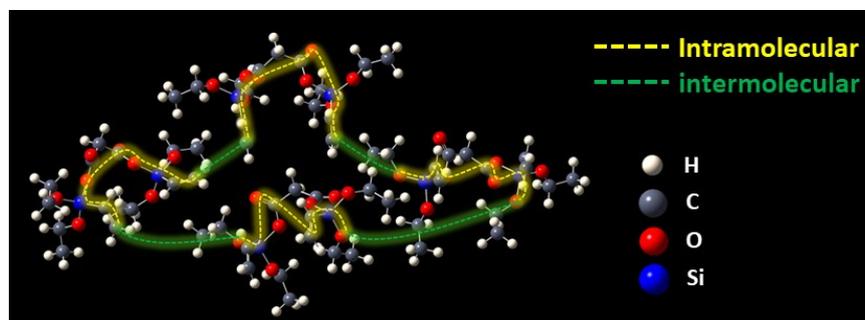


Figure S13 The accumulation of four first generation molecules and the “silicon-bridge” promoted single ring through-space conjugation of hyperbranched polysiloxane.^[3]

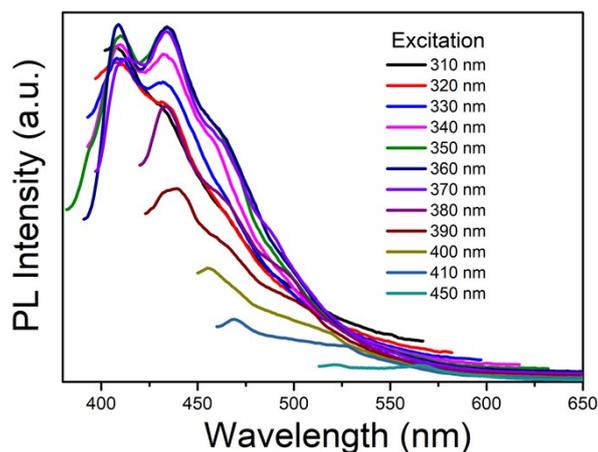


Figure S14 Emission spectra of **P1** in ethanol with the concentration of 200 mg/ml upon different excitation wavelength.

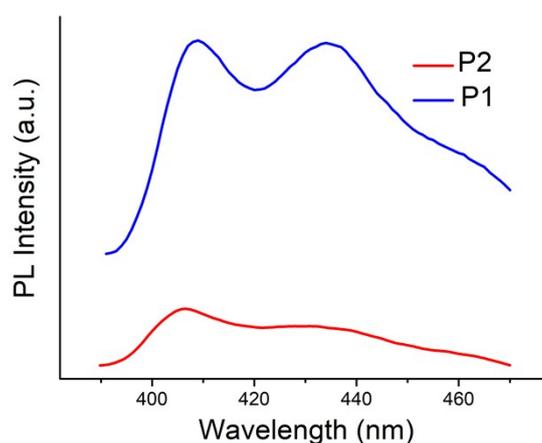


Figure S15 Fluorescence spectra of **P1** and **P2** ethanol solution (100 mg/mL, $\lambda_{\text{ex}} = 360$ nm).

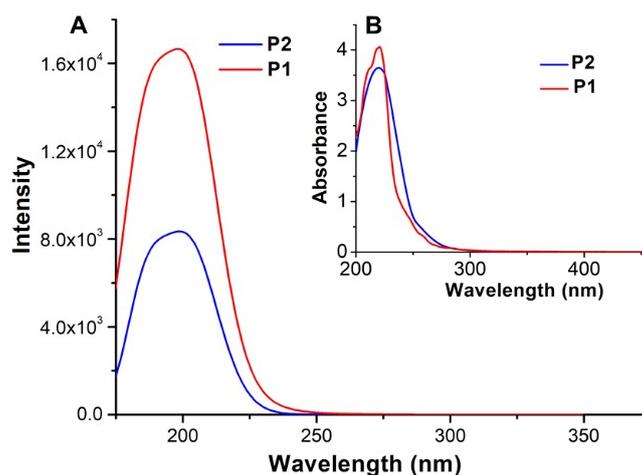


Figure S16 (A) UV-Vis spectra for **P1** and **P2** first generation molecules obtained from theoretical calculation; (B) UV-vis absorption spectra of **P1** and **P2** (100 mg/mL ethanol solution).

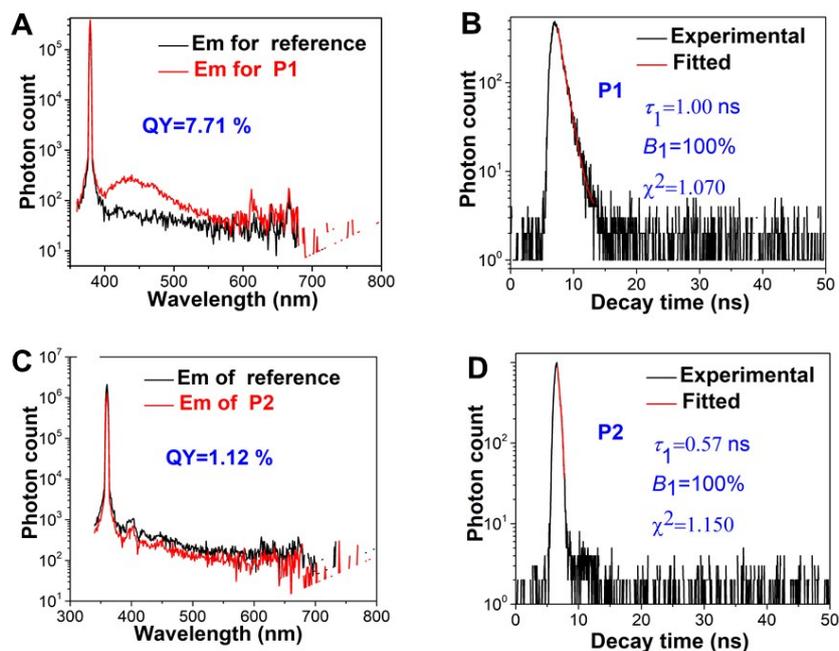


Figure S17 The absolute fluorescence quantum yield of the pure **P1** (A) and **P2** (C) ($\lambda_{\text{ex}} = 360$ nm); The transient photo luminescence temperature decay curve of the pure **P1** (B) and **P2** (D) at 406 nm ($\lambda_{\text{ex}} = 360$ nm).

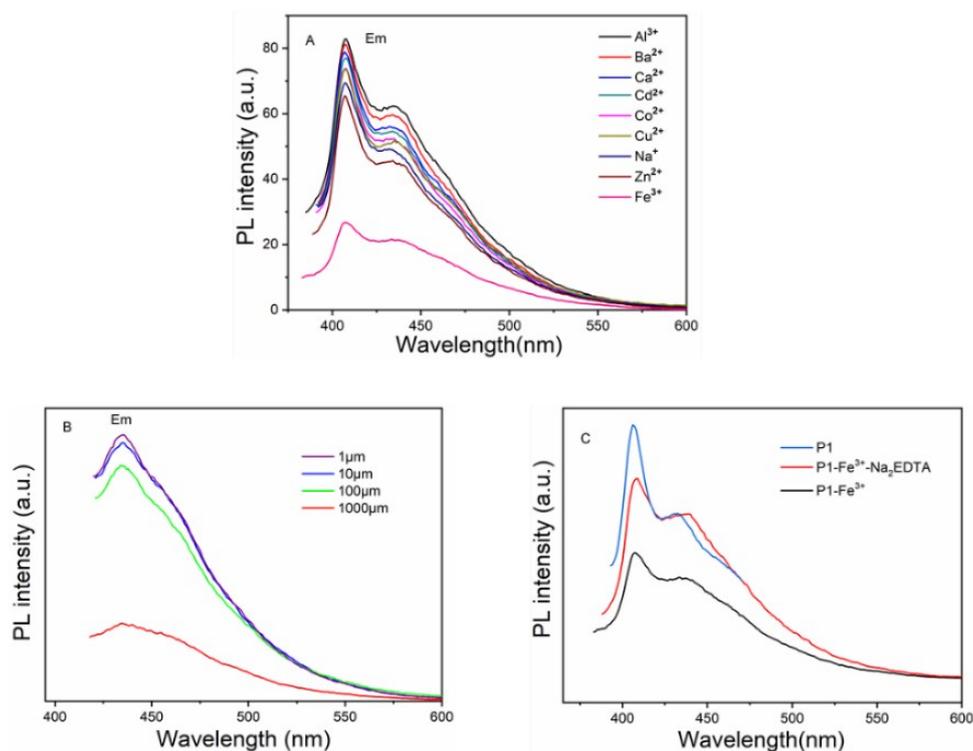


Figure S18 A) Emission spectra of **P1** water-ethanol solution (15 mg/mL) with the presence of different metal ions (1×10^{-3} mol/L, $\lambda_{\text{ex}} = 360$ nm); B) The emission spectra of **P1** water-ethanol solution (15 mg/mL) with the presence of Fe^{3+} at different concentrations; C) The emission spectra of **P1**, **P1-Fe³⁺**, **P1-Fe³⁺-Na₂EDTA** water-ethanol solution (15 mg/mL).

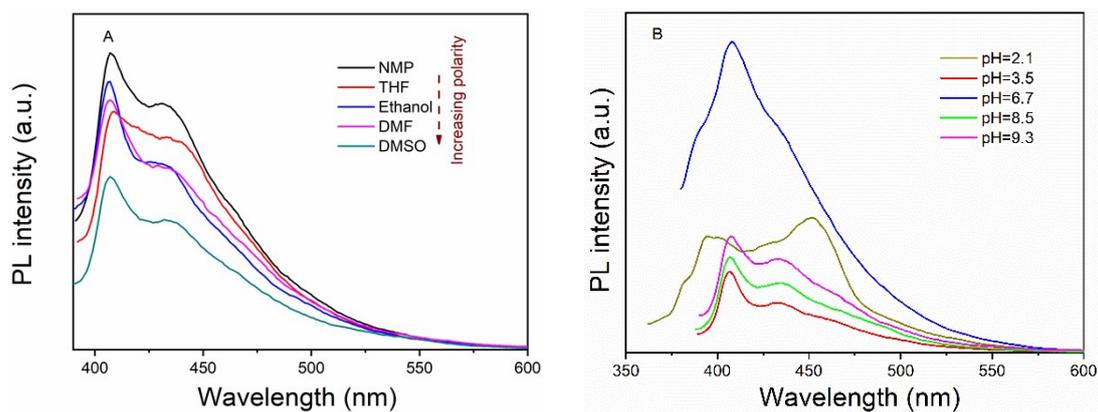


Figure S19 A) The emission spectra of **P1** in various solvents at the concentration of 15 mg/mL; B) The emission spectra of **P1** water-ethanol solution (15 mg/mL) at different pH.

Table S1 GPC data for **P1** and **P2**.

Polymer	<i>M_n</i>	<i>M_w</i>	<i>M_z</i>	<i>M_z+1</i>	PDI
P1	10100	117700	990800	1794800	11.548
P2	11100	20200	36100	55600	1.8130

Table S2 DFT and TD-DFT calculation results of four first generation **P1** and **P2** molecules.

Polyme r	E(HOMO)/a.u.	E(LUMO)/a.u.	Energy gap/a.u.	Energy gap/ev	Excitation Energy (nm)	Oscillato r strengths
P1	-0.237	-0.053	0.184	5.018	203.5	0.1323
P2	-0.267	-0.039	0.229	6.218	204.3	0.1074

Table S3 Particle size and proportion of **P1** assembly with different concentrations.

Concentration (mg/mL)	PEAK 1 (d.nm)/	PEAK 2 (d.nm)/	PEAK 3 (d.nm)/
	Intensity (%)	Intensity (%)	Intensity (%)
2	297.4/78.5	5.476/21.5	0.000/0.0
5	242.4/44.9	10.83/44.7	2.399/10.4
10	14.26/46.5	230.9/30.4	4.556/23.1
20	13.02/59.2	2.012/22.1	275.5/18.7
50	15.43/59.9	288.3/26.6	1.910/13.6

References:

- [1] Y. Du, T. Bai, H. Yan, Y. Zhao, W. Feng, W. Li, *Polymer*, **2019**, 185, 121771.
- [2] L. Y. Yuan, H. X. Yan, L. H. Bai, T. Bai, Y. Zhao, L. L. Wang and Y. B. Feng, *Macromol. Rapid Commun.*, **2019**, 40, 1800658.
- [3] Y. B. Feng, T. Bai, H. X. Yan, F. Ding, L. H. Bai and W. X. Feng, *Macromolecules*, **2019**, 52, 3075-3082.