Electronic Supplementary Information

Sulphur-containing nonaromatic polymers: clustering-triggered emission and luminescence regulation by oxidation

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Fig. S8 Schematic illustration of possible intra- and intermolecular interactions within the clusters of P**2** molecules at aggregated state.

Fig. S9 Schematic illustration of possible intra- and intermolecular interactions within the clusters of P**3** molecules at aggregated state.

Experimental

Materials and methods

Materials. 1,4-butanedithiol (BDT) was purchased from Sigma-Aldrich, Co., Ltd. 1,4-butanediol diacrylate (BDDA), superdry *N*,*N*-dimethylformamide (DMF), and $CDCl_3$ were obtained from J&K Scientific Chemical Co., Ltd. Triethylamine was provided by TCI Development Co., Ltd. Ethyl thioglycolate (ETG) was purchased from Shanghai Macklin Biochemical Co., Ltd. Sulfamic acid (SA) was bought from Adamas-Reagent Co., Ltd. Anhydrous diethyl ether, ethanol, hydrogen peroxide (H_2O_2) and picric acid (PA) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). PA was recrystallized from ethanol before use. Other reagents were directly used without further purification.

Instruments. ^1H and ^{13}C NMR spectra were obtained on a Bruker ARX-500 NMR spectrometer using $CDCl_3$ as solvents. FTIR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer. Absorption spectra were taken on a Lambda 35 UV/vis spectrometer (Perkin Elmer, USA). Emission spectra were collected on a Perkin-Elmer LS 55 fluorescence spectrometer. Lifetimes ($<\tau>$) were acquired with a QM/TM/IM steady-state & time-resolved fluorescence spectrofluorometer (ns scale, PTI, USA), while quantum yields (Φ) were measured on them with a SPEKTRON-R98 coated integrating sphere (φ 80 mm) (Everfine, China). Molecular weights (M_w and M_n) and polydispersity indexes (M_w/M_n) of the polymers were estimated in DMF using an HLC-8320GPC instrument and calibrated with standard polyethylene glycol, at a constant column temperature of 30 °C. All photographs were captured by Sony α 7s digital camera. P**1**/DMF solutions at different concentrations were placed into the NMR tubes before graphing.

Synthetic procedures

General procedure for the synthesis of P1. The target polymer P**1** was synthesized via a Michael polyaddition. Briefly, in a reaction tube, 0.24 mL of BDT was dissolved in 1 mL of DMF, and then 0.56 mL of triethylamine was added. Afterwards, 0.42 mL of BDDA was dissolved in 1mL of DMF and added into the system dropwise under stirring. The system was degassed by three freeze-pump-thaw cycles to remove air and moisture. The tube was sealed under vacuum and placed in an oil bath at 50 °C. 12 h later, 0.44 mL of ETG was added and stirred for another 12 h for end capping. After cooling to room temperature, the product was precipitated by pouring the solution into anhydrous diethyl ether while stirring vigorously. The precipitates were collected and dissolved into a small amount of DMF. Then the solution was added into anhydrous diethyl ether under vigorous stirring to get sediment. This cycle was repeated for three times to get the purified product. After filtration and drying in vacuum at 40 °C overnight, the final product was acquired. White powders were obtained in 89.1% yield. M_w: 5 100; M_w/M_n: 1.48. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.20 (q, J = 7.1 Hz, 2H), 4.13 (s, 15H), 2.92 (t, J = 7.2 Hz, 2H), 2.78 (t, J = 7.3 Hz, 15H), 2.66 (t, J = 7.2 Hz, 3H), 2.61 (t, J = 7.4 Hz, 15H), 2.55 (s, 15H), 1.94–1.71 (m, 19H), 1.71–1.64 (m, 15H), 1.61 (s, 8H), 1.29 (t, J = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.94, 64.22, 64.14, 61.46, 34.80, 34.26, 33.69, 31.66, 28.47, 27.53, 26.95, 25.26, 14.17.

General procedure for the synthesis of P2. P**2** was synthesized via a simple oxidation. In a reaction tube, 160 mg of P**1** and 4.9 mg of SA was dissolved into 4.5 mL of DMF, then 1.2 equivalent H_2O_2 was added under stirring. After reaction for 50 min at room temperature, the product was precipitated by pouring the solution into anhydrous diethyl ether under vigorous stirring. The precipitates were dissolved in a small amount of DMF and then poured into anhydrous diethyl ether under vigorous stirring to get sediment. This cycle was repeated for three times to get the purified product. After filtration and drying in vacuum at 40 °C overnight, white powders were obtained in 85.6% yield. M_w: 5300; M_w/M_n: 1.55. ^1H NMR (500 MHz, $CDCl_3$) δ 4.20 (q, J = 7.2 Hz, 2H), 4.13 (s, 15H), 2.92 (t, J = 7.1 Hz, 2H), 2.78 (s, 14H), 2.61 (t, J = 7.3 Hz, 17H), 2.55 (s, 14H), 1.72 (s, 18H), 1.69 (s, 17H), 1.29 (t, J = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.94, 77.28, 77.03, 76.78, 64.15, 34.81, 31.65, 28.48, 26.94, 25.26.

General procedure for the synthesis of P3. P**3** was synthesized via the similar oxidation procedure for the preparation of P**2** described above, but with different amount of oxidant. Briefly, in a reaction tube, 160 mg of P**1** and 38.8 mg of SA was dissolved into 4.5 mL of DMF, then 3.6 equivalent H_2O_2 was added under stirring. After stirring for 2 h at 80 °C, the solution was poured into anhydrous diethyl ether under vigorous stirring. The precipitates were dissolved in a small amount of DMF and then poured into anhydrous diethyl ether under vigorous stirring to get sediment. This cycle was repeated for three times. After filtration and drying in vacuum at 40 °C overnight, white powders were obtained in 95.7% yield. M_w: 5600; M_w/M_n: 2.10. ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (s, ^1H), 4.16 (s, 2H), 2.89–2.83 (m, 3H), 2.85–2.77 (m, 2H), 2.03–1.97 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.30, 77.30, 77.05, 76.79, 64.67, 27.06, 25.17, 22.18, 21.84.

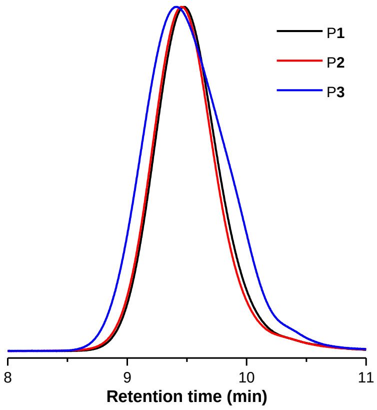


Fig. S1 GPC chromatograms of P**1**, P**2** and P**3**.

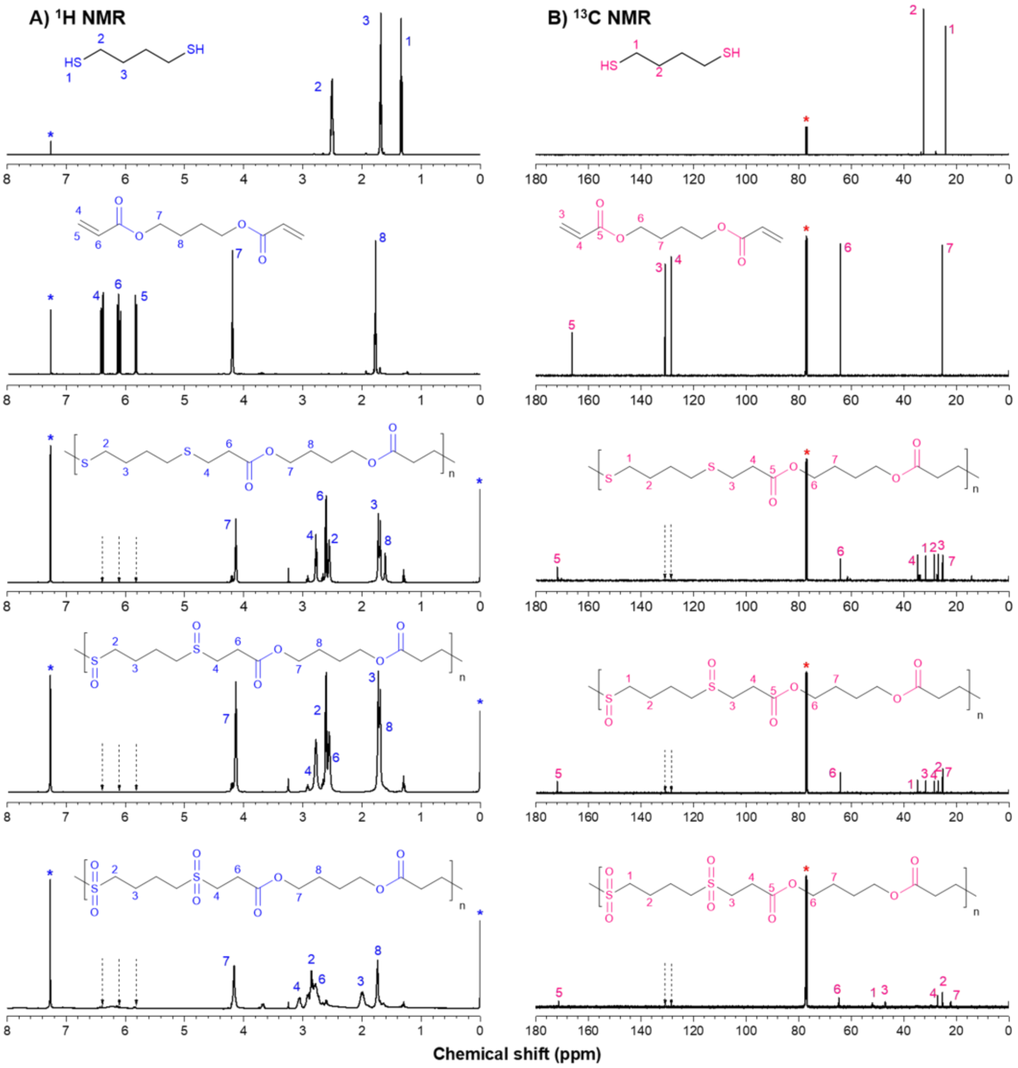


Fig. S2 (A) ^{1}H and (B) ^{13}C NMR spectra of the monomers and corresponding polymers. The solvent peaks are marked with asterisks.

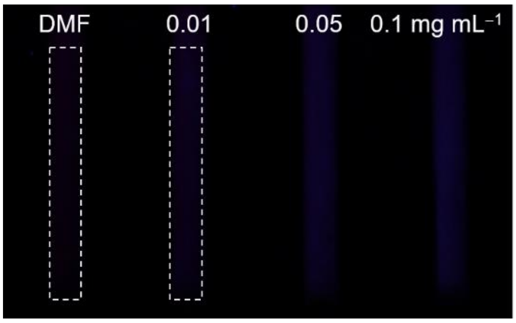


Fig. S3 Luminescent photograph of varying dilute P**1**/DMF solutions at 77 K under 365 nm UV light.

To check the overlap concentration, we observed the solution emission at cryogenic temperatures (i.e. 77 K), which can afford rigidified conformation for the possible clusters. As can be seen from Fig. S3, the solution gets emissive when the concentration is 0.05 mg mL^{-1} at 77 K. Therefore, the overlap concentration is supposed to be between 0.01 and 0.05 mg mL^{-1}.

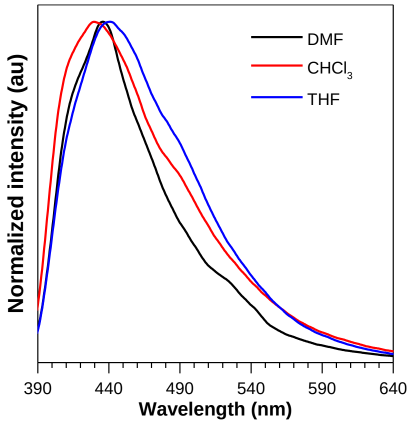


Fig. S4 Emission spectra of P**1** in DMF, $CHCl_3$ and THF (10 mg mL^{-1}) with λ_{ex} of 365 nm.

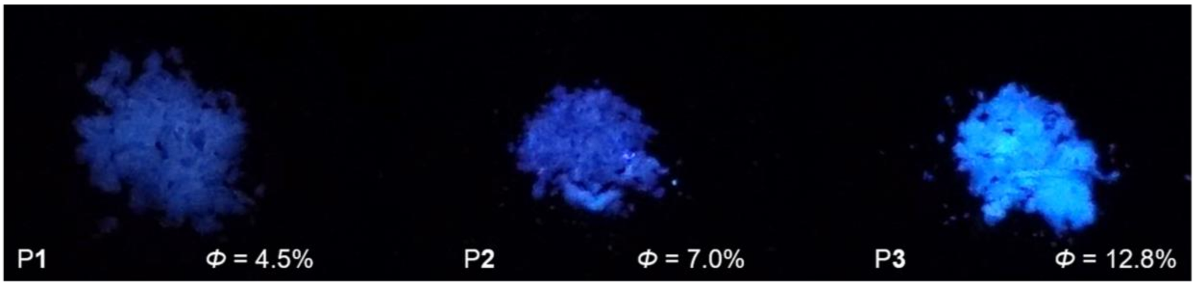


Fig. S5 Photographs of P**1**, P**2** and P**3** solid taken at room temperature under 365 nm UV light.

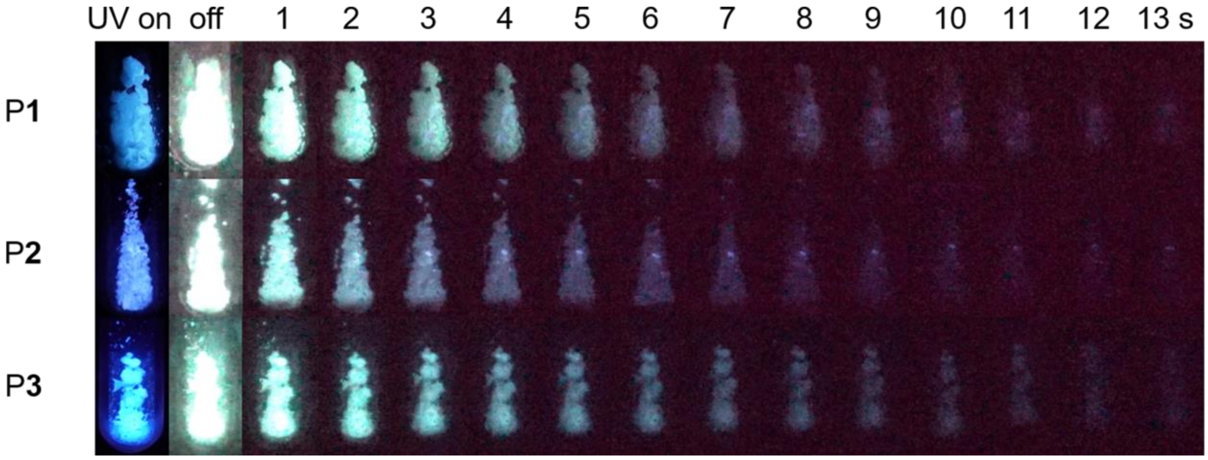


Fig. S6 Photographs of P**1**, P**2** and P**3** solid taken at 77 K by seconds under or after ceasing the 365 nm UV irradiation.

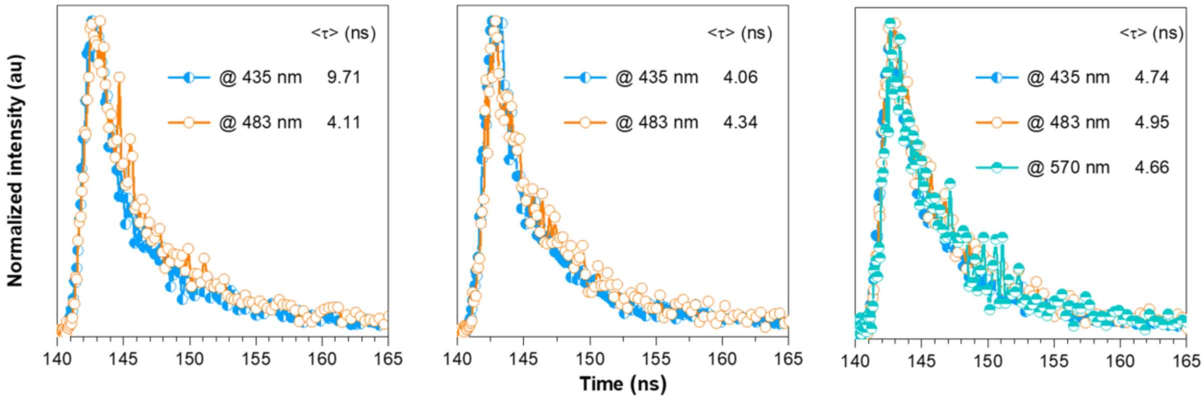
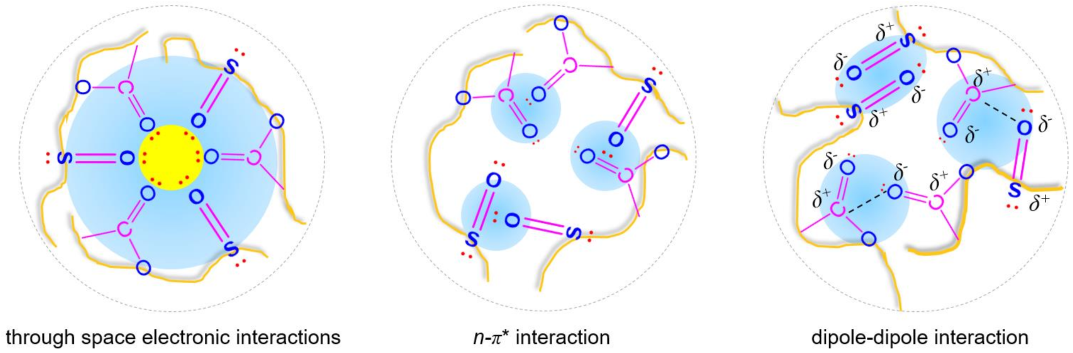


Fig. S7 Lifetimes of 31 mM P**1**/DMF, P**2**/DMF and P**3**/DMF solutions monitored at different wavelengths (λ_{ex} = 365 nm).

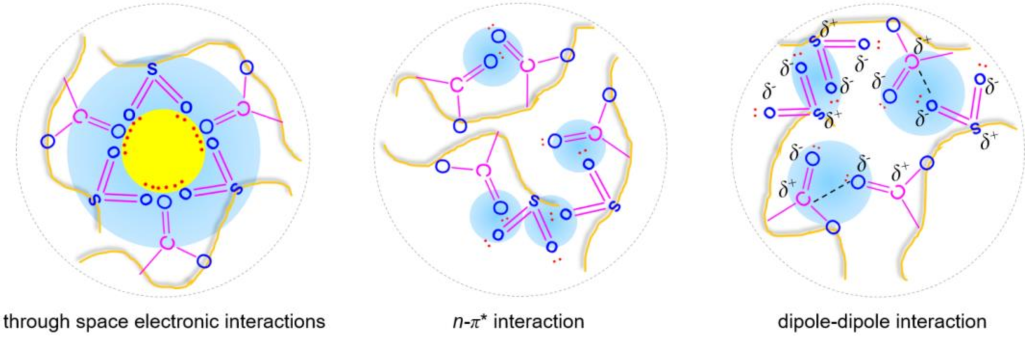


through space electronic interactions

n-*π** interaction

dipole-dipole interaction

Fig. S8 Schematic illustration of possible intra- and intermolecular interactions within the clusters of P**2** molecules at aggregated state.



through space electronic interactions

n-*π** interaction

dipole-dipole interaction

Fig. S9 Schematic illustration of possible intra- and intermolecular interactions within the clusters of P**3** molecules at aggregated state.