Dual-Mode Fluorescence Switching Induced by Self-Assembly of Well-Defined Poly(arylene ether sulfone)s Containing Pyrene and Amide Moieties.

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Supporting Information

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1 Experimental

1.1 Materials

All chemicals were purchased from Sigma-Aldrich. 1-Pyrenemethylamine hydrochloride, 4-fluoro-3-(trifluoromethyl)benzoyl chloride, 5-aminoisophthalic acid, 3,5-diaminobenzoic acid, 1-hydroxybenzotriazole, 1-ethyl-3-(3-dimethylaminopropyl) carbodiamide, and 18-crown-6 were used without further purification. Triethylamine (TEA), methylene chloride (MC), and tetrahydrofurane (THF) were purchased with anhydrous grade and used without further purification. *N*,*N*-Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), sulfolane, and toluene were distilled under reduced pressure before use.

1.2 Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Fourier Transform AC 400 (400 MHz) spectrometer. Chemical shift of NMR was reported in part per million (ppm) using residual proton resonance of solvent as internal reference. Gel permeation chromatography (GPC) traces were obtained with Younglin 9200 equipped with UV detector (set at 270 nm) and packing column (Shodex, GF-HQ columns). *N*, *N*-Dimethyl formamide (DMF) containing 50 mmol of lithium bromide was used as an eluent at 40 ^{o}C. The number and weight average molecular weights of the polymers were calculated by using linear polystyrene standards. UV-vis absorption experiments were performed on a OPTIZEN POP (Mecasys Co., Ltd) spectrometer. Fluorescence spectra were recorded on a SHIMADZU RF-5301pc. Field-emission scanning electron microscopy (FE-SEM) study was conducted with Nova 230 FE-SEM or Magellan 400 FE-SEM after the osmium sputtering. Field-emission transmission electron microscopy (FE-TEM) study was performed on a Tecnai F20 FE-TEM (200 kV). Specimens were prepared by stamping formvar/carbon-coated copper grid on the top of the diluted gel and investigated without staining. FT-IR spectra were obtained with a Bruker EQUINOX-55 spectrometer. Powder X-ray diffraction (XRD) pattern was obtained on a Rigaku D/MAX III diffractometer with sampling width of 0.01 ^{o} and sampling rate of 0.5 ^{o}/min, using CuK$_\alpha$ ($\lambda = 0.1541$ nm) as a light source.

1.3 Synthesis

4-Fluoro-*N*-(pyren-1-ylmethyl)-3-(trifluoromethyl)benzamide (Pyr1-1). 1-Pyrenemethylamine hydrochloride (1.30 g, 4.86 mmol) dissolved in MC (15 mL) was stirred in one-neck round bottomed flask. 4-Fluoro-3-(trifluoromethyl)benzoyl chloride (1.21 g, 5.34 mmol) and triethylamine (1.03 g, 10.2 mmol) dissolved in MC (5 mL) were portionwise added to the above solution. After 12 h, the reaction mixture was washed with water, 1N HCl solution, 5% $NaHCO_3$ solution, and water again. The organic layer was dried over $MgSO_4$ and filtered. After removing the solvent, the solid was purified by recrystalization from chloroform and hexane (1.23 g, 60.1%). mp 182 °C. ESI-MASS: 444.10 for $[M+Na]^+$ (Calcd: 444.10). δ_H (400 MHz; DMSO-d_6; Me_4Si) 9.47 (1H, t, J = 5.58Hz, NHCO), 8.46-8.00 (11H, m, Ar), 7.58 (1H, m, Ar), 5.23 (2H, d, J = 5.55Hz, CH_2NH). δ_C (100 MHz; DMSO-d_6; Me_4Si) 163.77, 160.6 (dd, J_1 = 257.98 Hz, J_2 = 2.34 Hz), 134.67 (d, J = 9.68 Hz), 132.36, 130.96 (d, J = 3.42 Hz), 130.74, 130.25, 130.17, 128.15, 127.60, 127.31, 127.03, 126.84, 126.52 (m), 126.18, 125.22, 125.12, 124.68, 124.03, 123.90, 123.12, 122.36 (q, J = 271Hz), 117.43 (d, J = 20.89Hz), 116.51 (qd, J_1 = 32.72Hz, J_2 = 12.73Hz), 41.28. Anal. Calcd for $C_{25}H_{15}F_4NO$: C, 71.26; H, 3.59; F, 18.03; N, 3.32; O, 3.80. Found: C, 71.31; H, 3.54; N, 2.97.

5-(4-Fluoro-3-(trifluoromethyl)benzamido)-*N*^{1},*N*^{3}-bis(pyren-1-ylmethyl)isophthalamide (Pyr2-1). 5-Aminoisophthalic acid (1.00 g, 5.52 mmol) dissolved in DMF (4 mL) and THF (5 mL) was placed and stirred in one-neck round bottomed flask. The solution was cooled down in ice/water bath, then 4-fluoro-3-(trifluoromethyl)benzoyl chloride (1.38 g, 6.07 mmol) dissolved in DMF (1mL) and THF (3mL) was added slowly to the solution. After removing the ice bath, the solution was stirred for additional 2 h. Triethylamine (0.838 g, 8.28 mmol) dissolved in THF (2 mL) was added to the reaction mixture dropwise. After 6 h, the reaction mixture was acidified by adding excess amount of acetic acid. The reaction mixture was poured into deionized water, and the precipitated solid was filtered off. The solid was purified by washing with MC and hot EA/MeOH to remove any unreacted 4-fluoro-3-(trifluoromethyl)benzoic acid. This solid identified as 5-(4-fluoro-3-(trimethyl)benzamido)isophthalic acid was used for next step without further purification (1.44 g, 70%).

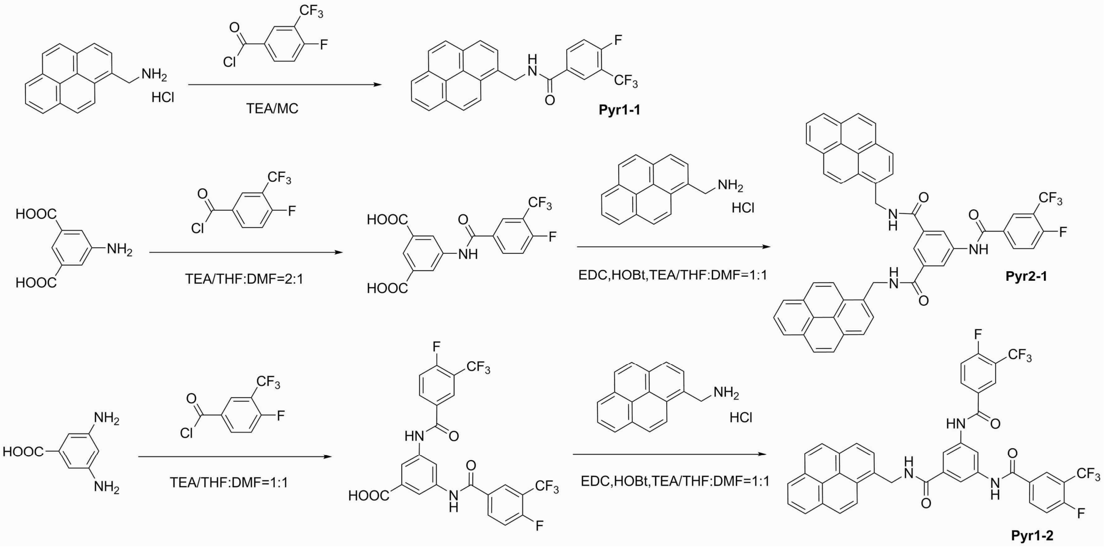
5-(4-Fluoro-3-(trimethyl)benzamido)isophthalic acid (0.719 g, 1.94 mmol), 1-pyrenemethylamine hydrochloride (1.09 g, 4.07 mmol), and 1-hydroxybenzotriazole (0.549 g, 4.07 mmol) dissolved in DMF (15 mL) and THF (15 mL) was stirred in one-neck round bottomed flask. After 30 min, 1-ethyl-3-(3-dimethylaminopropyl) carbodiamide (0.779 g, 4.07 mmol) and triethylamine (0.784g, 7.75 mmol) were added to the solution. Then, the solution was stirred for 12 h at 60 °C. The reaction mixture was poured into a saturated NaCl aqeuous solution and extracted with THF. The organic phase was dried over $MgSO_4$. After removing the solvent, the solid was purified by recrytalization from acetone (0.841g, 54.4%). mp 221 °C. ESI-MASS: 820.22 for $[M+Na]^+$ (Calcd: 820.22). δ_H (400 MHz; DMSO-d_6; Me_4Si) 10.72 (1H, s, NHCO), 9.31 (2H, t, J = 5.75, NHCO), 8.49 (1H, s, Ar), 8.47 (2H, m, Ar), 8.39 (1H, dd, J_1 = 6.95Hz, J_2 = 2.26Hz, Ar), 8.34 (1H, ddd, J_1 = 8.44Hz, J_2 = 4.85Hz, J_3 = 2.29Hz, Ar), 8.23 (10H, m, Ar), 8.09 (6H, m, Ar), 8.02 (2H, t, J = 7.63Hz, Ar), 7.66 (1H, dd, J_1 = 10.52Hz, J_2 = 8.80Hz, Ar), 5.23 (4H, d, J = 5.65Hz, C*H2*NH). δ_C (100 MHz; DMSO-d_6; Me_4Si) 165.86, 163.10, 160.73(dd, J_1 = 259.01Hz, J_2 = 2.13Hz), 138.95, 135.31, 135.16 (d, J = 9.84Hz), 132.72, 131.09 (d, J = 3.40Hz), 130.75, 130.26, 130.09, 128.12, 127.54, 127.32, 126.99, 126.92 (m), 126.73, 126.18, 125.20, 125.11, 124.65, 124.02, 123.91, 123.21, 122.45, 122.34 (q, J = 271Hz), 121.60, 117.63 (d, J = 20.99Hz), 116.58 (qd, J_1 = 32.81Hz, J_2 = 12.91Hz), 41.14. Anal. Calcd for $C_{50}H_{31}F_4N_3O_3$: C, 75.27; H, 3.92; F, 9.53; N, 5.27; O, 6.02. Found: C, 75.17; H, 3.89; N, 4.82.

***N,N'*-(5-Pyren-1-ylmethylcarbamoyl)-1,3-phenylene)bis(4-fluoro-3-(trifluoromethyl)benzamide) (Pyr1-2).** 3,5-Diaminobenzoic acid (0.500 g, 3.29 mmol) dissoled in DMF (15 mL) and THF (15 mL) was placed and stirred in one-neck round bottomed flask. The solution was cooled down in ice/water bath. 4-Fluoro-3-(trifluoromethyl)benzoyl chloride (1.56 g, 6.90 mmol) dissolved in DMF (10 mL) and THF (10 mL) was added slowly to the solution. After removing the ice bath, the solution was stirred for additional 2 h. Triethylamine (0.689 g, 6.90 mmol) dissoled in THF (2 mL) was dropwise added to the reaction mixture. After 6 h, the reaction mixture was acidified by adding excess amount of acetic acid. The reaction mixture was poured into deionized water, and the precipitated solid was filtered off. The product was purified by washing with MC and EA/MeOH to remove any unreacted 4-fluoro-3-(trifluoromethyl)benzoic acid. Other side products were removed by column chromatography with 1:1 ratio of THF and Hx. This solid identified as 3,5-bis(4-fluoro-3-(trifluoromethyl)benzamido)benzoic acid was used for next step without further purification (0.642 g, 36.7%).

3,5-Bis(4-fluoro-3-(trifluoromethyl)benzamido)benzoic acid (0.355 g, 1.33 mmol), 1-pyrenemethylamine hydrochloride (0.642 g, 1.21 mmol), and 1-hydroxybenzotriazole (0.245 g, 1.810 mmol) dissolved in DMF (15 mL) and THF (15 mL) were stirred in one-neck round bottomed flask. After 30 min, 1-ethyl-3-(3-dimethylaminopropyl) carbodiamide (0.347 g, 1.81 mmol) and triethylamine (0.183 g, 1.81 mmol) were added to the solution. Then, the solution was stirred for 12 h at 60 ^{o}C. The reaction mixture was poured into a saturated NaCl aqueous solution and extracted with THF. The organic phase was dried over $MgSO_4$. After removing the excess solvent, the solid was purified by recrytalization from MeOH (0.456g, 46.0%). mp 265 ^{o}C. ESI-MASS: 768.15 for $[M+Na]^+$ (Calcd: 768.15). δ_H (400 MHz; DMSO-d_6; Me_4Si) 10.66 (2H, s, NHCO), 9.25 (1H, t, J = 5.75Hz, NH), 8.53 (1H, t, J = 1.98Hz, Ar), 8.50 (1H, d, J = 9.28Hz, Ar), 8.17 (14H, m, Ar), 7.65 (2H, m, Ar), 5.23 (2H, d, J = 5.69Hz, C*H2*NH). δ_C (100 MHz; DMSO-d_6; Me_4Si) 166.25, 163.10, 160.68 (d, J = 257.61Hz), 138.98, 135.61, 135.15 (d, J = 9.92Hz), 132.92, 131.30 (d, J = 3.45Hz), 130.75, 130.28, 130.08, 128.13, 127.53, 127.33, 126.94 (m), 126.71, 126.17, 125.19, 125.10, 124.64, 124.04, 123.92, 123.25, 122.33 (q, J = 272.58Hz), 117.54 (d, J = 20.99Hz), 116.53 (qd, J_1 = 32.84Hz, J_2 = 12.88Hz), 115.66, 115.57, 41.10. Anal. Calcd for $C_{40}H_{23}F_8N_3O_3$: C, 64.43; H, 3.11; F, 20.38; N, 5.64; O, 6.44. Found: C, 64.36; H, 3.19; N, 5.37.

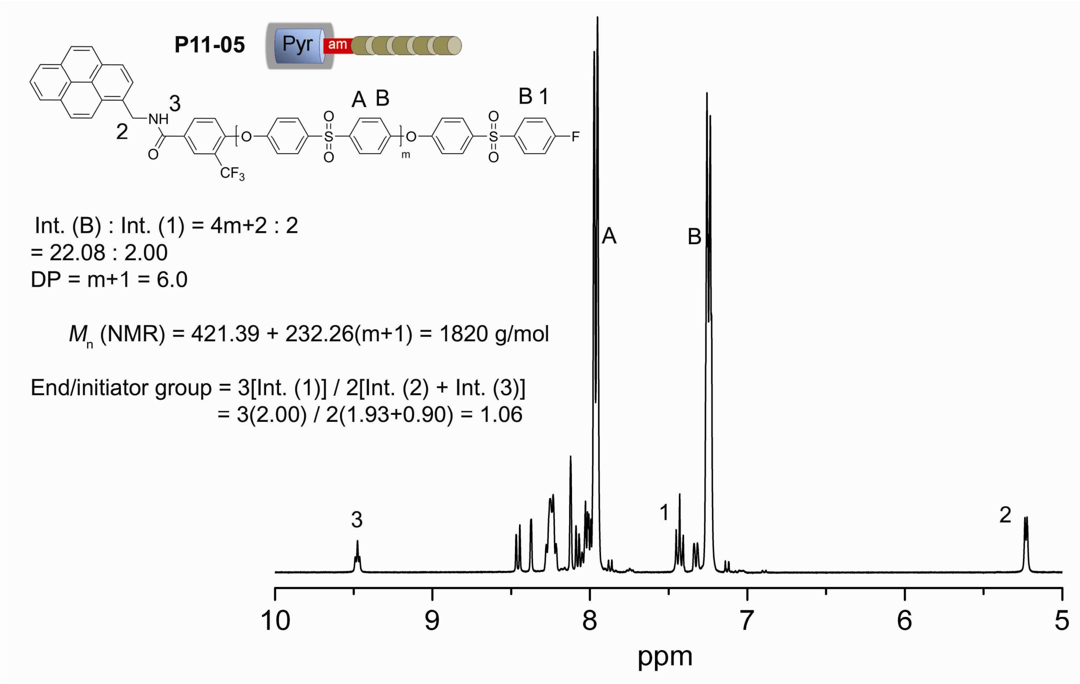
4-Fluoro-4’-hydroxydiphenyl sulfone potassium salt (1). 4-Fluoro-4’-hydroxydiphenyl sulfone potassium salt was prepared according to the literature procedure.[1]

Polymerization. CGCP of **1** were conducted similarly according to the literature procedures.[1-2] A dried Schlenk flask charged with initiator (**Pyr1-1**, **Pyr2-1**, or **Pyr1-2**), monomer **1**, and 18-crown-6 (1 eq to monomer) was dried *in vacuo* for 6 h at 50 ^{o}C. The feed ratio of the monomer to the initiator was varied to control the molecular weights of polymers. Sulfolane (5 wt% to monomer contents) was added to a flask *via* gas-tight syringe under dry nitrogen atmosphere. The mixture was degassed three times by "freeze-pump-thaw" cycles. Then, the reaction mixture was heated at 115 °C for 48~96 h (time depended on initial feed ratio). After polymerization, the reaction mixture was cooled to room temperature and precipitated into methanol (900 mL) containing acetic acid (9 mL). The solid was filtered off and washed with deionized water and methanol. The polymer was dried *in vacuo* at 60 °C for overnight.



Scheme S1 Synthesis of the initiators.

(a)

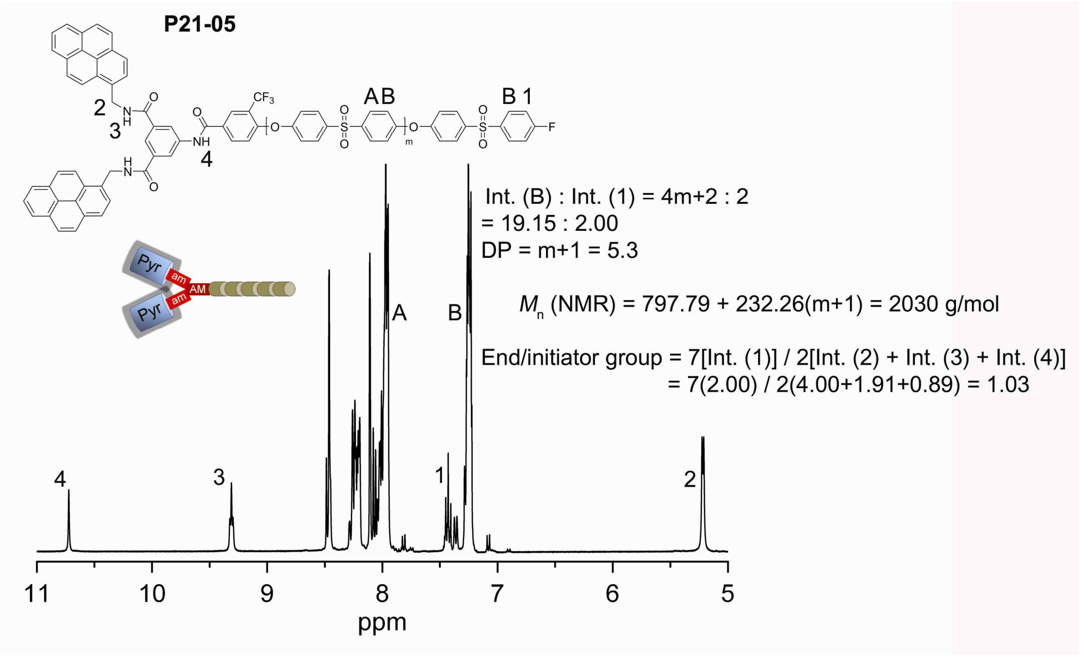


Int. (B) : Int. (1) = 4m+2 : 2
= 22.08 : 2.00
DP = m+1 = 6.0

M_n (NMR) = 421.39 + 232.26(m+1) = 1820 g/mol

End/initiator group = 3[Int. (1)] / 2[Int. (2) + Int. (3)]
= 3(2.00) / 2(1.93+0.90) = 1.06

(b)



Int. (B) : Int. (1) = 4m+2 : 2
= 19.15 : 2.00
DP = m+1 = 5.3

M_n (NMR) = 797.79 + 232.26(m+1) = 2030 g/mol

End/initiator group = 7[Int. (1)] / 2[Int. (2) + Int. (3) + Int. (4)]
= 7(2.00) / 2(4.00+1.91+0.89) = 1.03

(c)

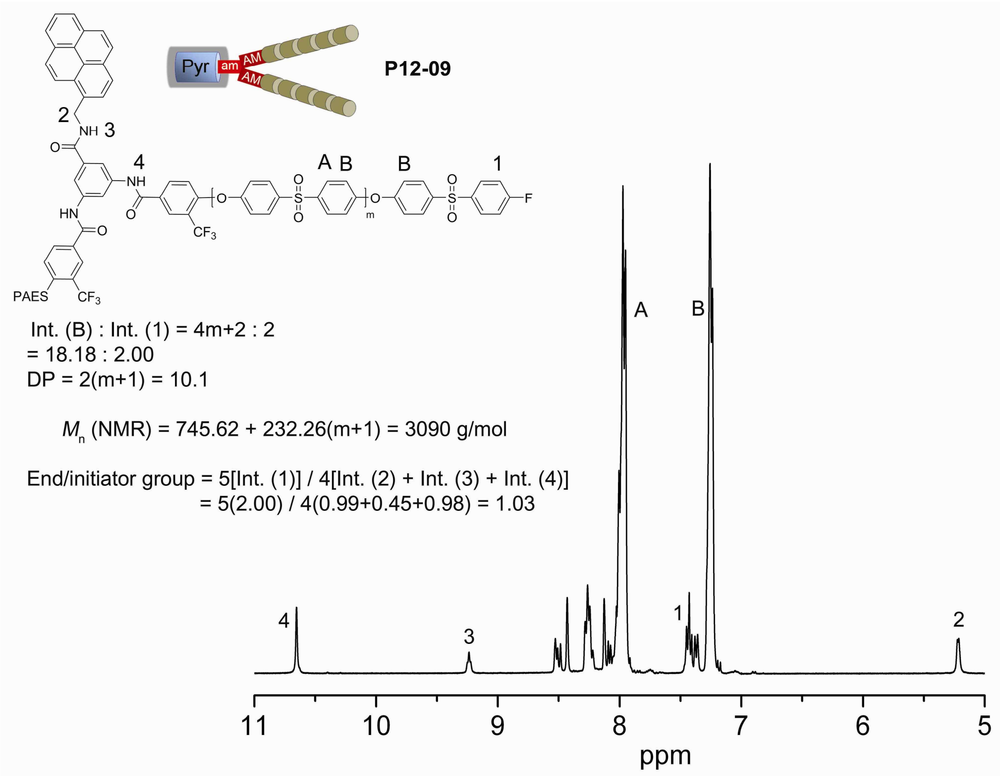


Fig. S1 ^{1}H NMR spectra and calculation of molecular weights of (a) **P11-05**, (c) **P21-05**, and (c) **P12-09** (DMSO-d_6, 400 MHz).

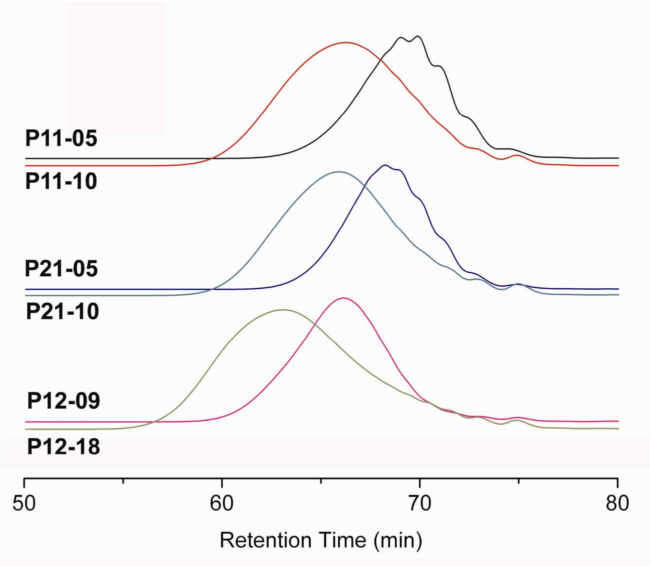


Fig. S2 DMF-GPC profiles of the synthesized polymers (50 mmol of LiBr, UV detector, polystyrene standard).

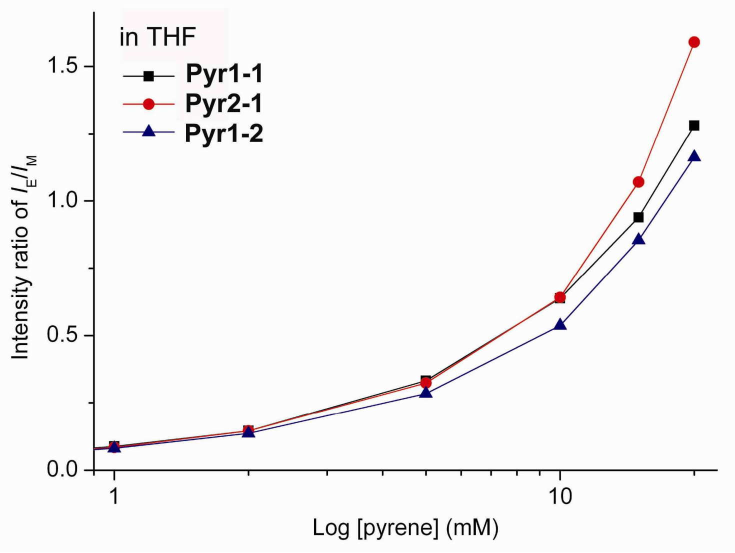


Fig. S3 A plot of I_E/I_M as a function of the pyrene concentration in the initiators in THF (λ_{ex} = 345 nm).

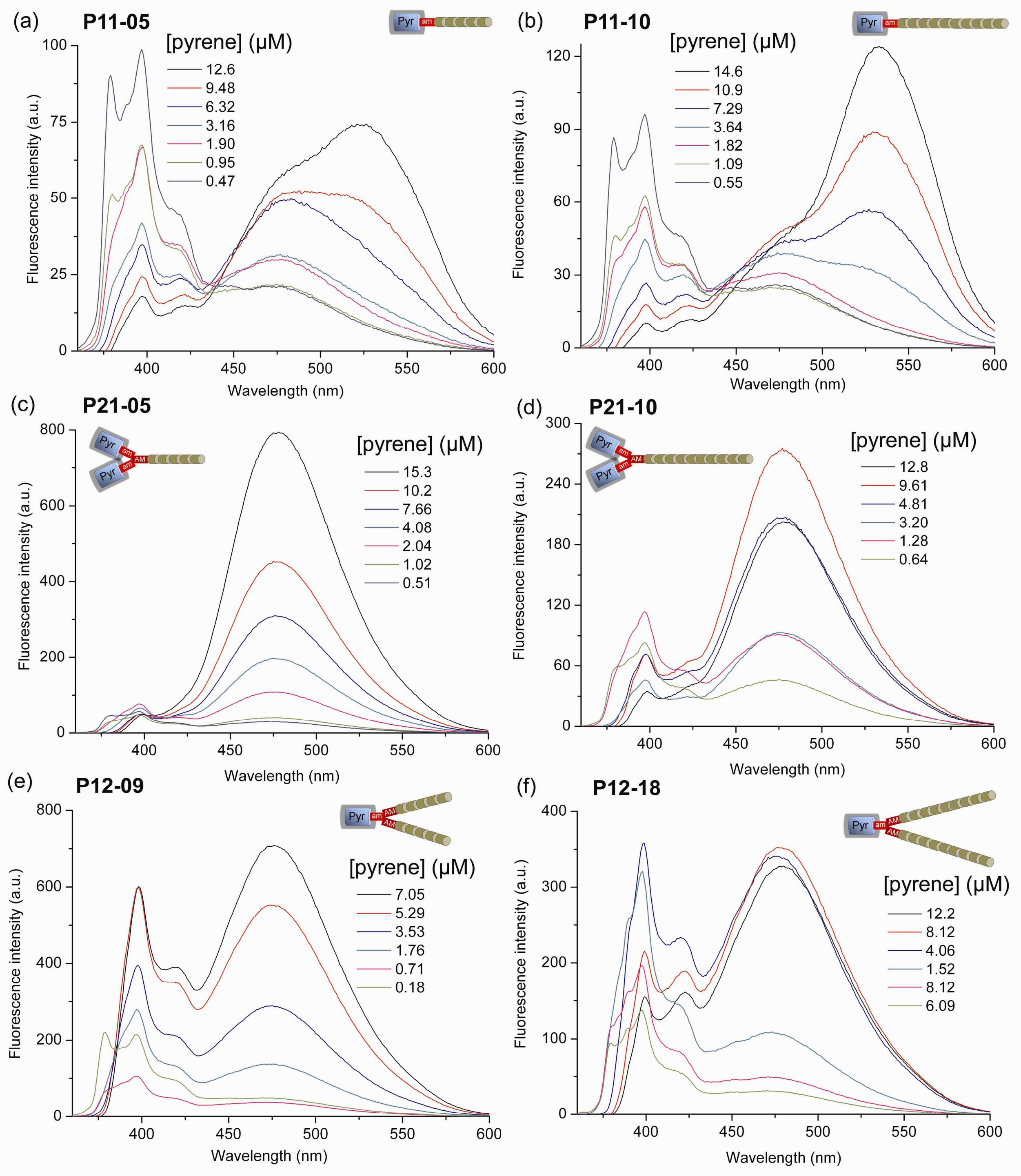


Fig. S4 Representative fluorescence spectra of (a) **P11-05**, (b) **P11-10**, (c) **P21-05**, (d) **P21-10**, (e) **P12-09**, and (f) **P12-18** in different pyrene concentration in MC (λ_{ex} = 345 nm).

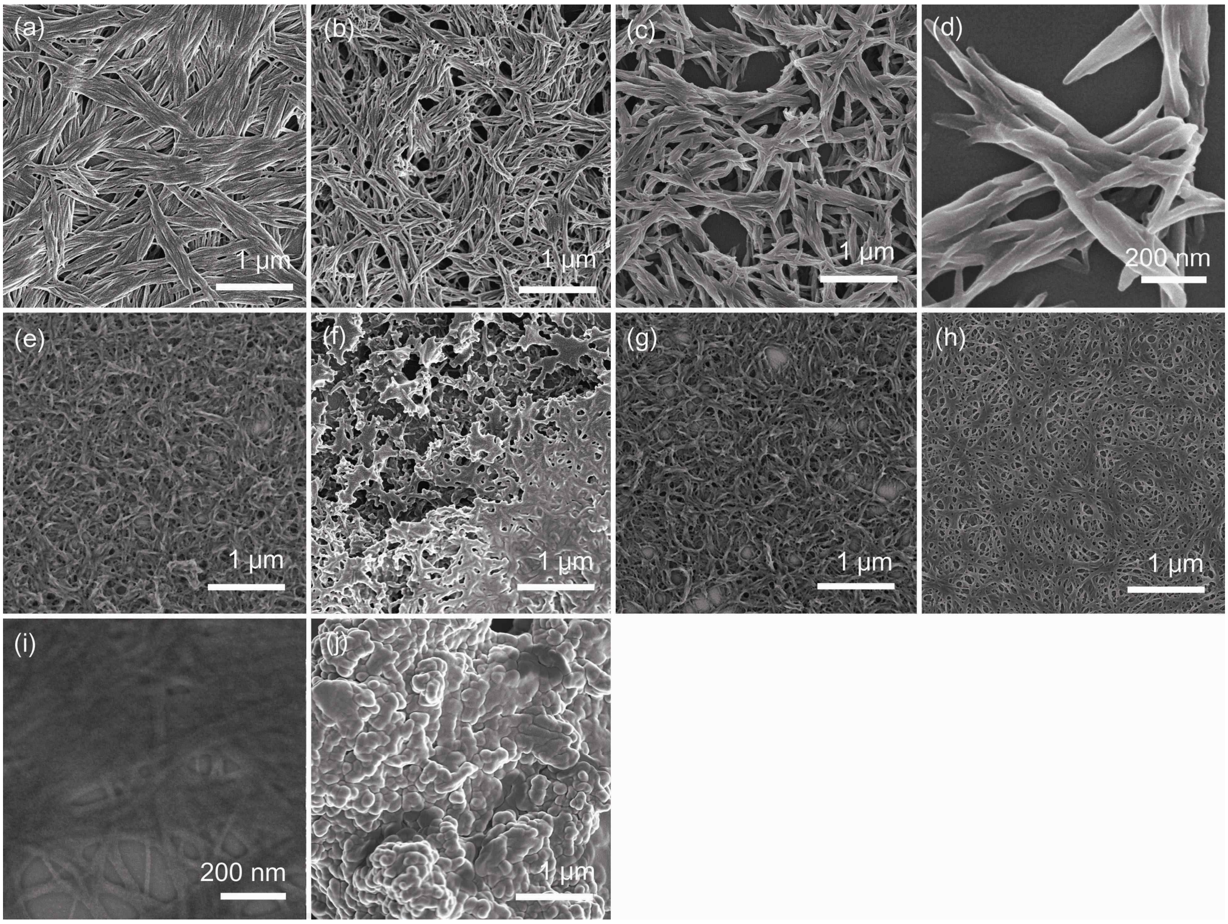


Fig. S5 FE-SEM images of the xerogel of (a) **P11-05**, (b) **P11-10**, (c-d) **P21-05**, (e) **P21-10**, (f) **P12-09**, and (g) **P12-18** gelled in THF. FE-SEM images of the xerogel of (h) **P12-18** gelled in THF (10% DMSO). FE-SEM images of xerogel of (i) **P21-05** and (j) **P21-10** gelled in MC.

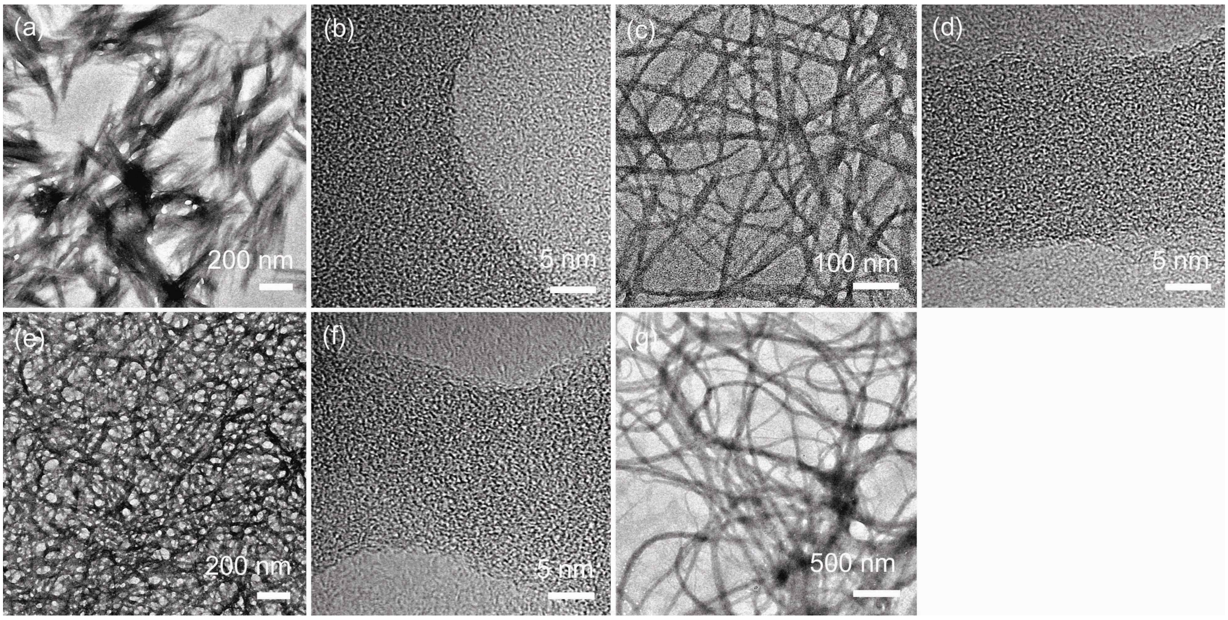


Fig. S6 FE-TEM images of the xerogel (gel-like precipitate) of (a-b) **P21-05** gelled in THF. FE-TEM images of the xerogel of (c-d) **P21-05** gelled in MC, (e-f) **P21-10** gelled in THF (10% DMSO), and (g) **P21-10** gelled in MC.

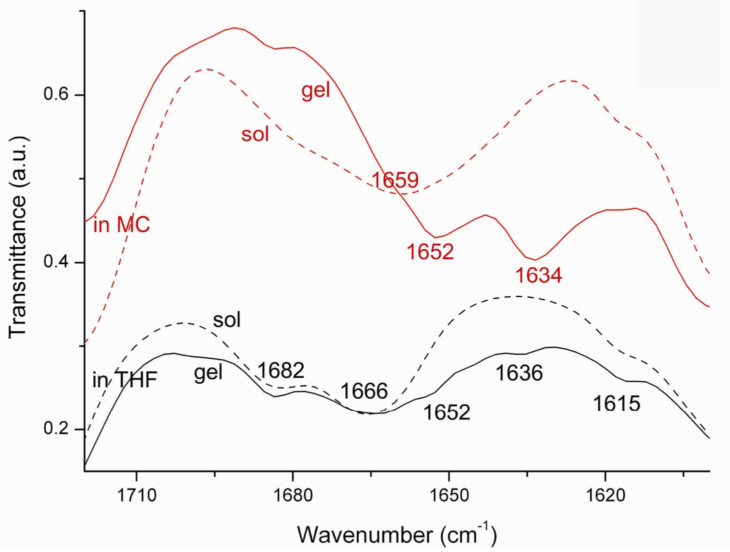


Fig. S7 FT-IR spectra of **P21-05** in THF (black dashed line: sol, black straight line: gel), and in MC (red dashed line: sol, red straight line: gel) (10 g L–1).

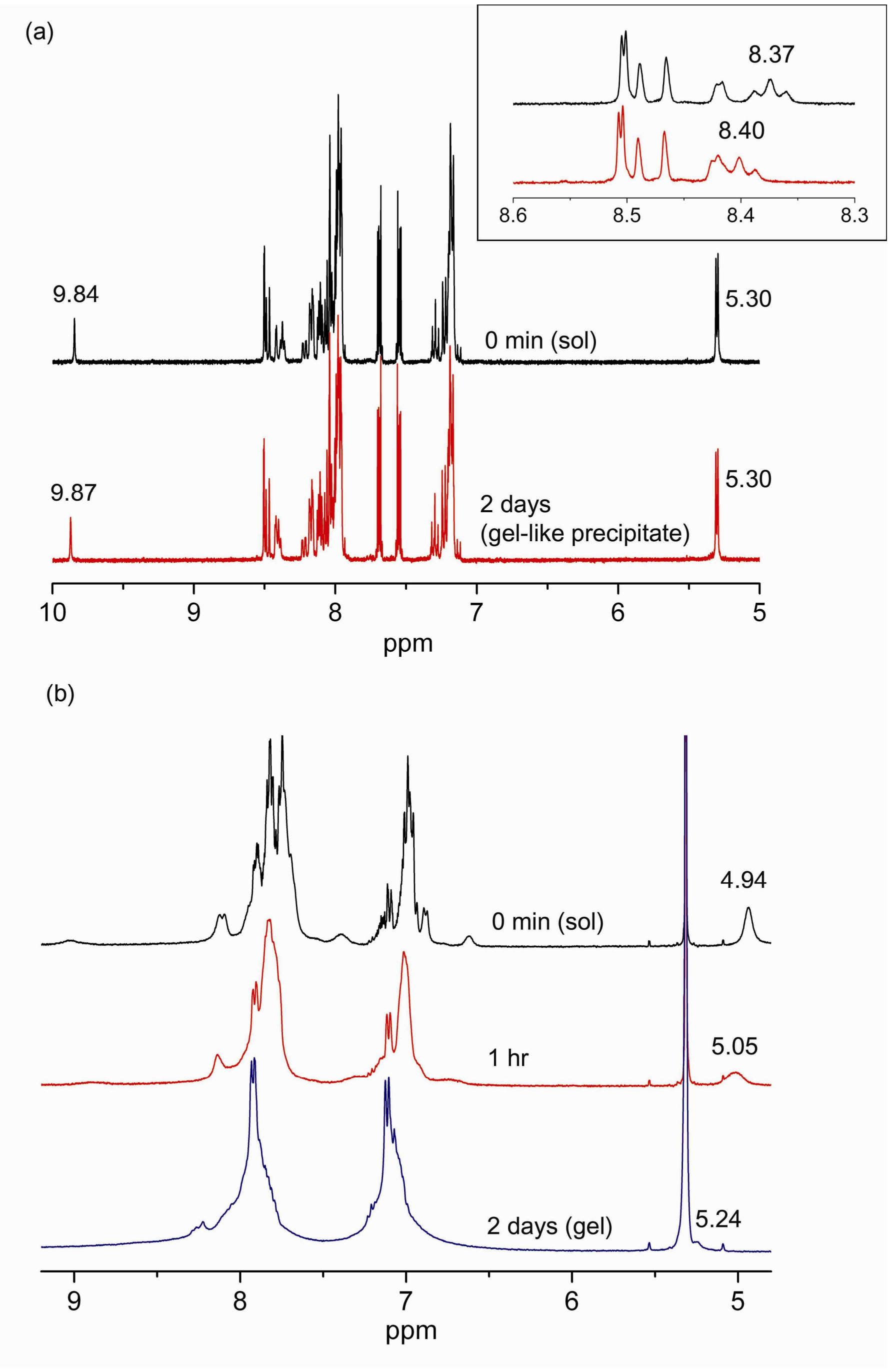


Fig. S8 Time-dependent ^{1}H NMR spectra of **P21-05** from (a) THF-d_8, and (b) MC-d_2 (400 MHz).

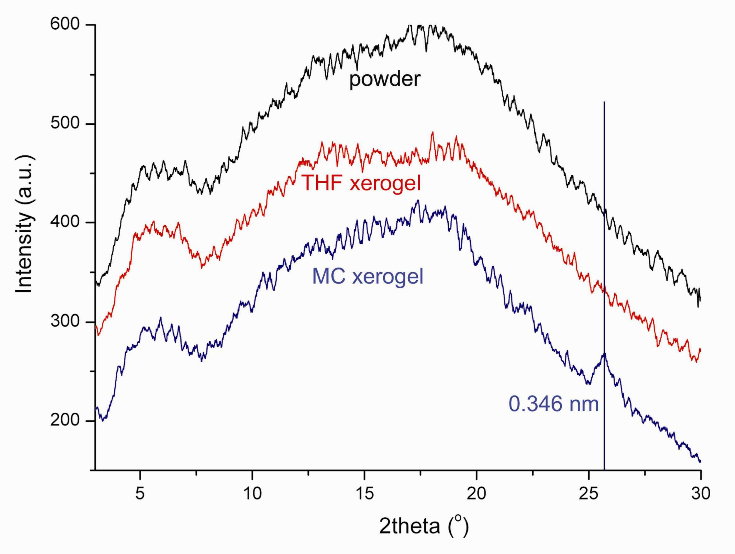


Fig. S9 Wide-angle powder XRD patterns of **P21-05** in powder (black line), the THF xerogel (red line), and the MC xerogel (blue line).

References

1. J. Park, M. Moon, M. Seo, H. Choi and S. Y. Kim, *Macromolecules*, 2010, **43**, 8304-8313.

2. T. Yokozawa, T. Taniguchi, Y. Suzuki and A. Yokoyama, *J. Polym. Sci. Part A: Polym. Chem.*, 2002, **40**, 3460-3464.