Aggregation-induced Fluorescent Response of Urea-bearing Polyphenyleneethynylenes toward Anion Sensing

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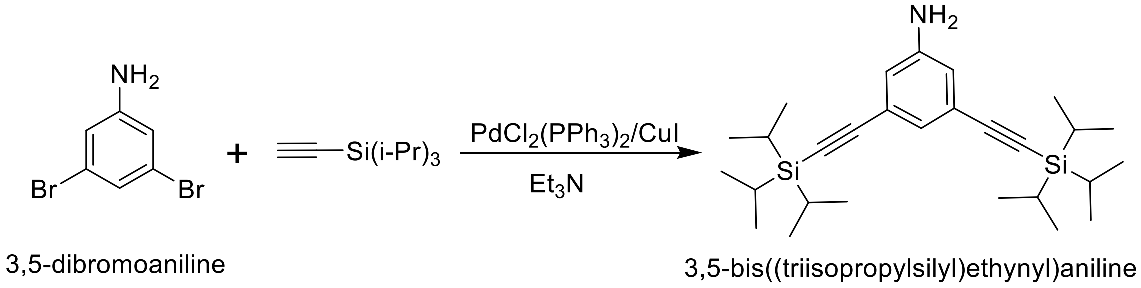
Experimental Section

Materials. Dichloromethane (CH_2Cl_2, >99%), acetone (>98%), deuterated chloroform ($CDCl_3$,>99.8%), acetone-d_6 (CD_3COCD_3,>99.8%), *n*-hexane (98%), tetrahydrofuran (THF,>99%), methanol (MeOH, >98%), toluene (99%), triethylamine (>99.0%), 3,5-dibromoaniline, triisopropylsilylacetylene, trimethylsilylacetylene andsodium hydride (60 wt% in mineral oil) were purchased from TCI Chemicals. Hexyl isocyanate, bis(triphenylphosphine)palladium(II) dichloride were purchased from Aldrich. All other reagents were used as received. Toluene and THF were distilled over Na/benzophenone under an argon atmosphere and degassed by three freeze-pump-thaw cycles prior to use. All other chemicals were purchased from available suppliers and used without further purification.

Measurements. The polymerization was carried out in an MIKROUNA stainless steel glove-box equipped with a gas purification system under a dry argon atmosphere (H_2O, O_2<0.01 ppm). The moisture and oxygen contents in the glove box were monitored by an MB-MO-SE 1 and an MB-OX-SE 1 sensor, respectively. The ^1H and ^{13}C NMR spectroscopy (600 MHz) was recorded using a BRUKER ASCEND TM 600, BrukerBiospin GmbH Rheinstetten, Germany. Size exclusion chromatography (SEC) in DMF was performed at 40 °C at the flow rate of 0.35 mL min^{-1} using a TosohHLC-8320 GPC System equipped with two TSK gel Super Multipore HZ-M columns (4.6 mm I.D. × 15 cm × 2), an EcoSEC GPC System with an RI detector(+,0.5s), a UV-8320 detector(254nm,+0.5s), a GPC Workstation EcoSEC-WS, and an Auto sampler, to which 10μL of sample is injected with the concentration of 0.2wt%.The number-average molecular weight ($M_{n,SEC}$) and polydispersity (M_w/M_n) of the polymers were calculated based on polystyrene standards. The UV-vis absorption spectra of the polymers were measured by a UV-Vis spectrophotometer (Routine UV-Vis, Cary 60, Agilent) and the fluorescence spectra were recorded using a fluorescence spectrophotometer (RF-5301PC, Shimadzu). The particle size distribution and average hydrodynamic diameter were measured by a dynamic light scattering method (NanoBrook 90PlusPALS zeta sizer, Brookhaven Instruments). FT-IR spectra were recorded on a Perkin Elmer Frontier. Samples fashioned into KBr pellet disks were placed into a holder for transmission IR spectral analysis. Spectra of mid infrared from an accumulation of 16 scans in the range of 4000–450 cm^{-1} were recorded.

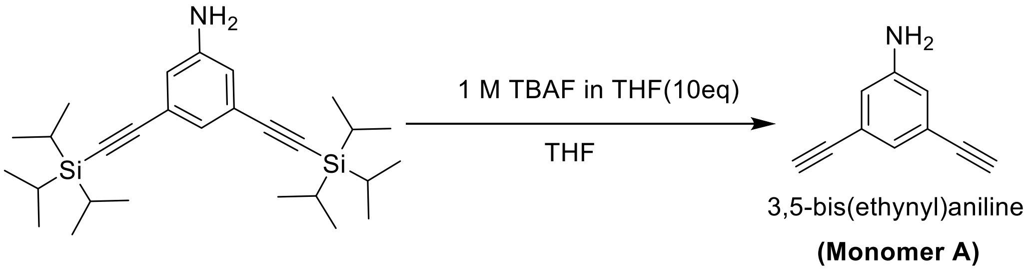
Synthesis of 3,5-bis(triisopropylsilylethynyl)aniline



15.00 g (59.71 mmol) 3,5-dibromoaniline, 3.96 (5.64 mmol) Pd(PPh$_3$)$_2$Cl$_2$ and 2.16 g (11.32 mmol) CuI were dissolved in a mixture of 140 mL triethylamine and 150 mL toluene. The mixture was heated to 80 °C under argon. 21.96 g (117.78 mmol) triisopropylsilyl) acetylene was added dropwise (orange suspension turns dark brown) and the mixture was stirred at 80 °C over night. Water was added to the mixture and the organic phase was washed with satd. NH$_4$Cl (aq), 1 N HCl(aq), 10% Na$_2$CO$_3$ (aq), and dried over MgSO$_4$. After evaporation of the solvent, the crude product was purified by column chromatography using firstly hexane and then a 10:1 mixture of petrol ether and ethyl acetate as eluent to yield 22.71 g (86%) of the pure compound as viscous yellow oil. ^{1}H NMR (500 MHz, CDCl$_3$) d 7.0 (s, 1H, aromatic H), 6.73 (s, 2H, aromatic H), 3.65 (s, 2H, amino H), 1.18 (s, 42H, H from ^{i}Pr). ^{13}C NMR (125 MHz, CDCl$_3$)

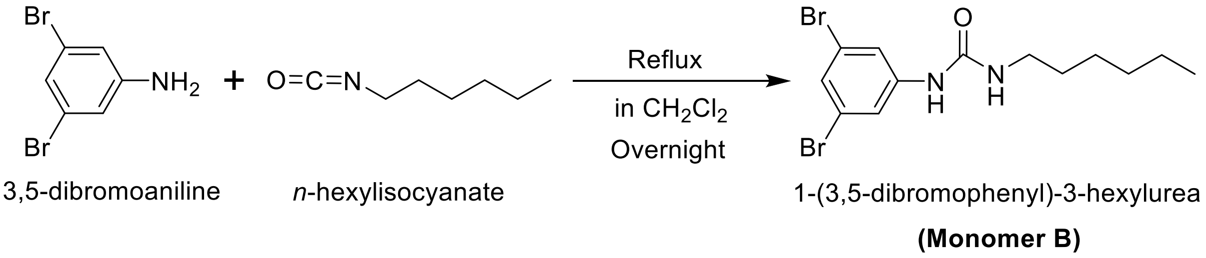
146.95 (aromatic C, 1C), 126.5 (aromatic C, 1C), 124.76 (aromatic C, 2C), 118.0 (aromatic C, 2C), 107 (acetylene C, 2C), 90 (acetylene C, 2C), 19.30 (^{i}Pr C, 6C), 12.45 (^{i}Pr C, 12C).

Deprotection of 3,5-bis((triisopropylsilyl)ethynyl)aniline



Deprotection of 3,5-bis(triisopropylsilylethynyl)aniline was achieved by desilylation using tetra-*n*-butylammonium fluoride (TBAF) in THF promoted by a small amount of CH_3OH. ^{1}H NMR (500 MHz, $CDCl_3$) 6.95 (s, 1H, aromatic H), 6.65 (s, 2H, aromatic H), 3.65 (s, 2H, amino H), 2.95 (s, 2H, acetylene H).

Synthesis of 1-(3, 5-dibromophenyl)-3-hexylurea



Hexyl isocyanate (3.08 g, 24.2 mmol) was added dropwise to the stirring solution of 3, 5-dibromoaniline, 4.12 (20.72 mmol) in 60 mL of dichloromethane at low temperature using ice bath. After complete addition the reaction mixture was then allowed to stir at room temperature for an hour and then reflux for 6 hours, during which time a precipitate appeared. The solvent was then removed by rotavapor and the resulting urea compound was purified by recrystallization from ethanol at low temperature to obtain urea derivative as a white crystalline solid.^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H, urea H), 7.65 (s, 2H, aromatic H), 7.15 (s, 1H, aromatic H), 5.75 (s, 1H, urea H), 3.10 (m, 2H, H from hexyl), 1.4 (m, 2H, H from hexyl), 1.25 (s, 6H, H from hexyl), 0.75 (s, 3H, H from hexyl).

Polymerization procedure of Poly-1 and Poly-2

All polymerizations were carried out in a glass tube equipped with a three-way stopcock under oxygen. DMF (0.4 mL) and Et_3N (0.6 mL) were added to a mixture of monomers (0.05 mmol), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005 mmol), PPh_3 (1.3 mg, 0.005 mmol) and CuI (0.95 mg, 0.005 mmol) under argon, and the resulting solution was kept at 80 °C for 20 h. Then, the reaction mixture was poured into a large volume of diethyl ether to precipitate the polymer. It was separated by filtration using a membrane filter and dried under reduced pressure. ^1H NMR (500 MHz, $CDCl_3$): 6.10-8.65 (m, amide and ring protons), 0.5-1.5 (m, CH_3 and CH_2 protons), 7.60-7.74 (s, 2H, Ar). $M_{n,SEC}$ = 13,500 g mol-1, M_w/M_n = 2.42 for **Poly-1**. Yield >90%. **Poly-2** was sequentially obtained by directly reacting Poly-1 with hexyl isocyanate followed by precipitation in methanol. $M_{n,SEC}$ = 6,090 g mol-1, M_w/M_n = 1.43, almost quantitative yield.

Sample preparation for UV-vis and fluorescent measurements. 4.4 mg polymer (**Poly-1** or **Poly-2**) was first dissolved in 50 mL DMF and then diluted to 100 mL with distilled water to meet the desired stock concentration of 44 mg L^{-1}. The prepared stock solution of anion in DMF/H_2O = 1:1 (v/v) was directly mixed with the polymer solution at 1:1 (v/v) with shaking to ensure the polymer concentration of 22 mg L^{-1} and the anion concentration was adjusted accordingly by dilution from concentrated solution. For the UV-vis and fluorescent analyses, the solution was deposited for several hours (at least 3 h), after which measurements were carried out.

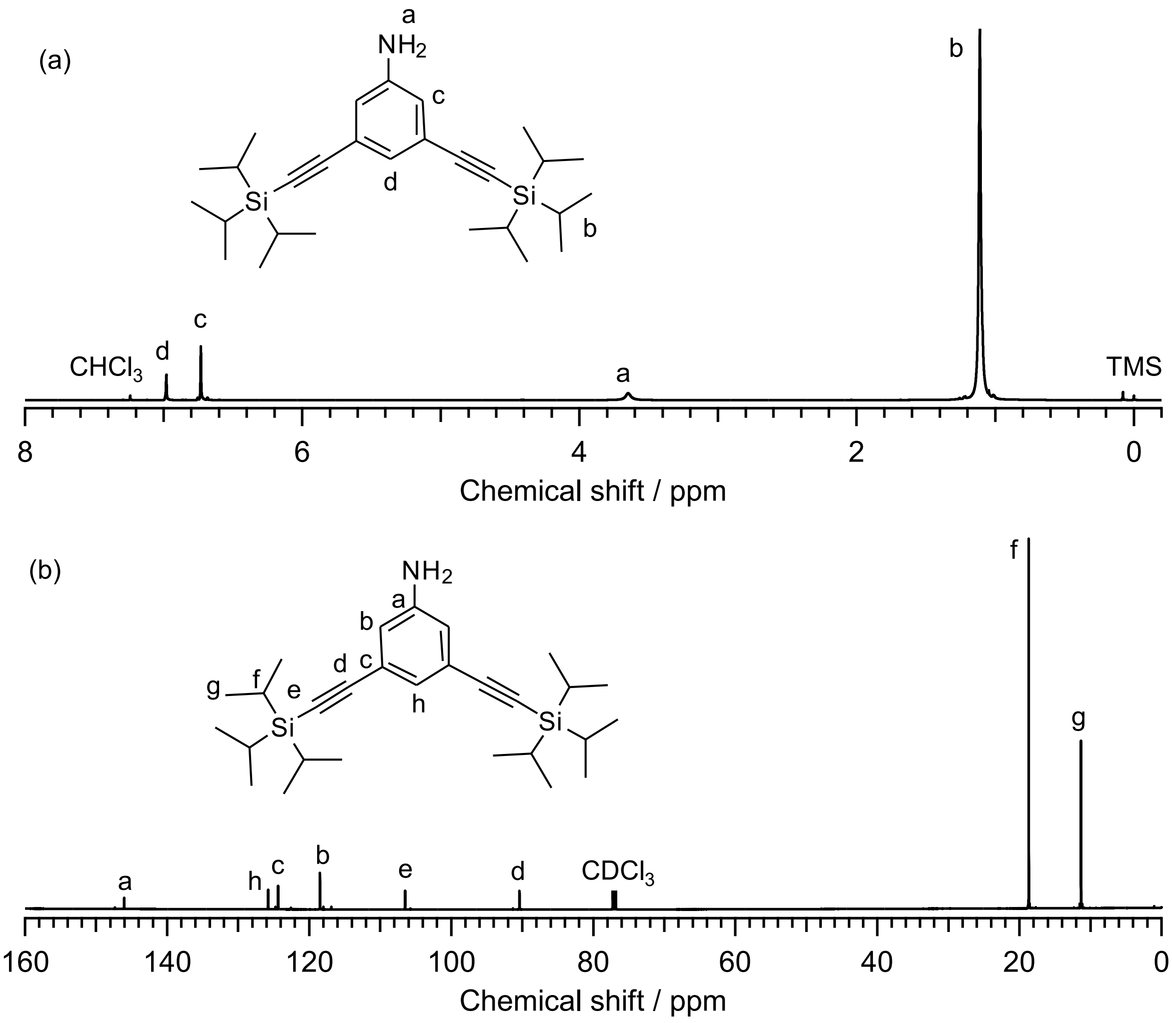


Figure S1. ^{1}H (a) and ^{13}C (b) NMR spectra of 3,5-bis(triisopropylsilylethynyl)aniline in $CDCl_3$.

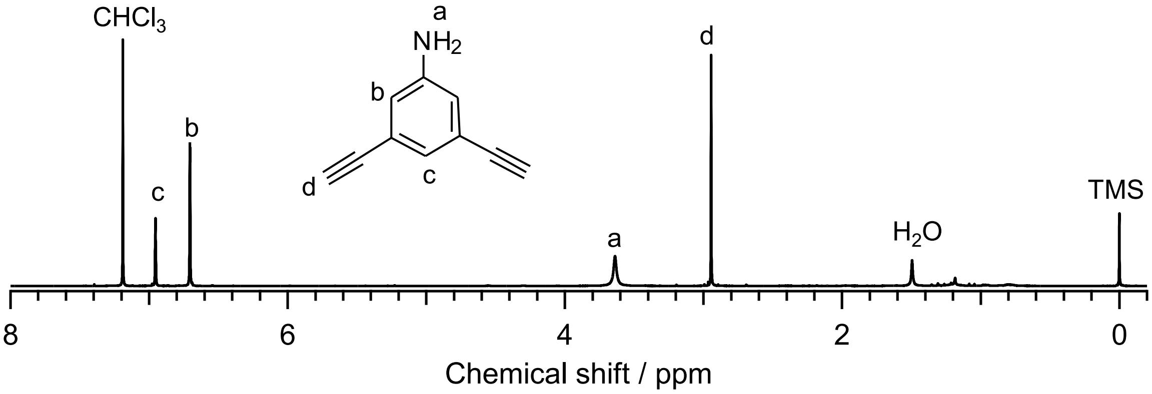


Figure S2. ^{1}H-NMR spectrum of 3,5-diethynylaniline in $CDCl_3$.

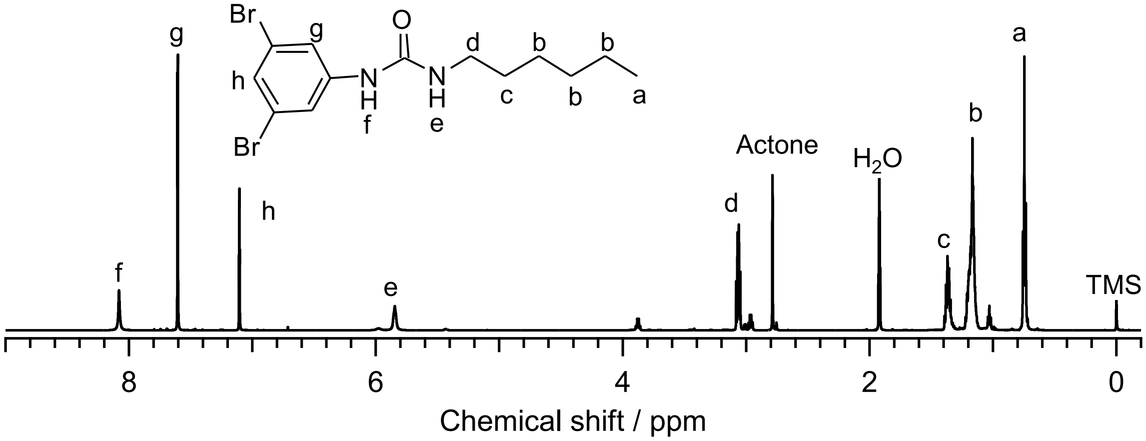


Figure S3. ^{1}HNMR spectrum of 1-(3, 5-dibromophenyl)-3-hexylurea in actone-d_6.

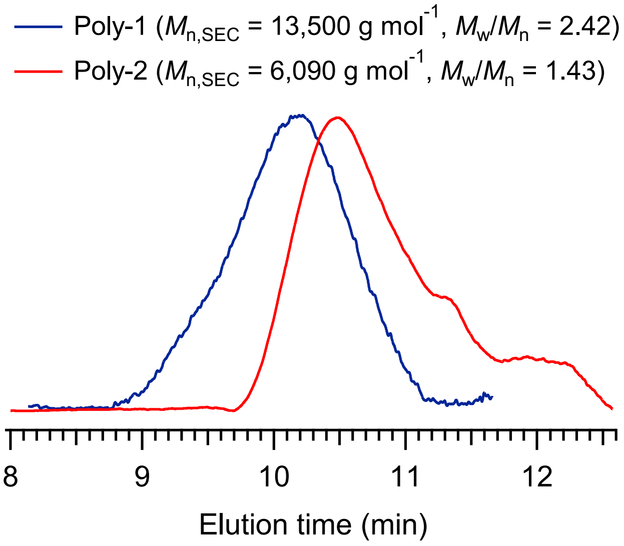


Figure S4. SEC traces of **Poly-1** and **Poly-2** (eluent, 0.01 mol L^{-1} LiBr in DMF; flow rate, 0.35 mL min^{-1}).

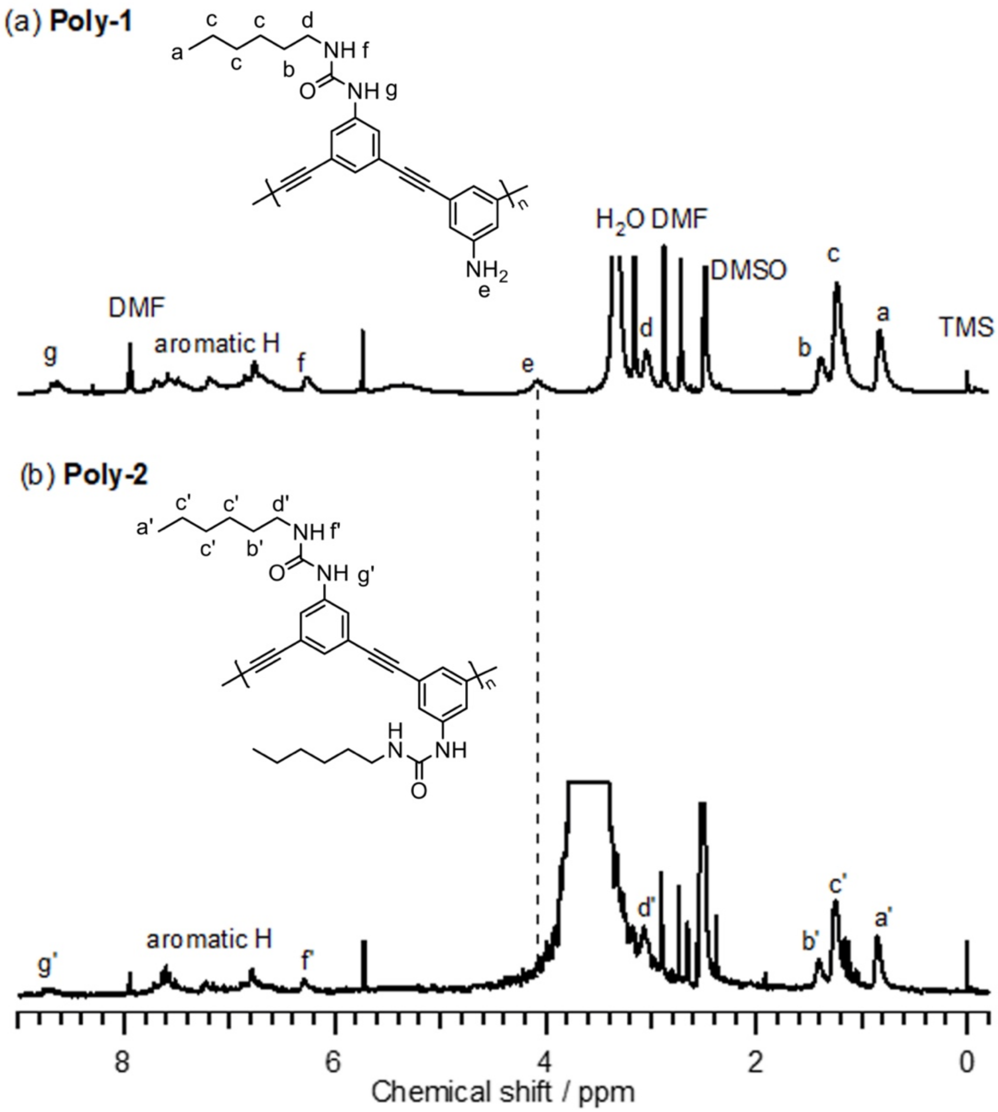


Figure S5. ^{1}H-NMR spectra of **Poly-1** and **Poly-2** determined in DMSO-d_6.

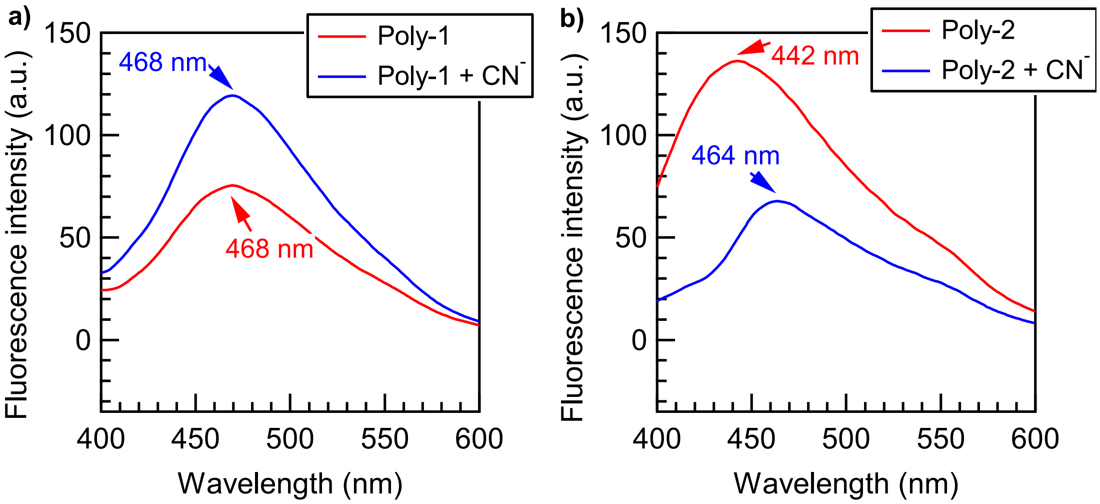


Figure S6. Fluorescence spectra of **Poly-1** and **Poly-2** before (red) and after (blue) addition of CN^- under the condition of 0.01 mM polymer solution and 1.0 mM anion solution in DMF/H_2O (v/v = 1:1).

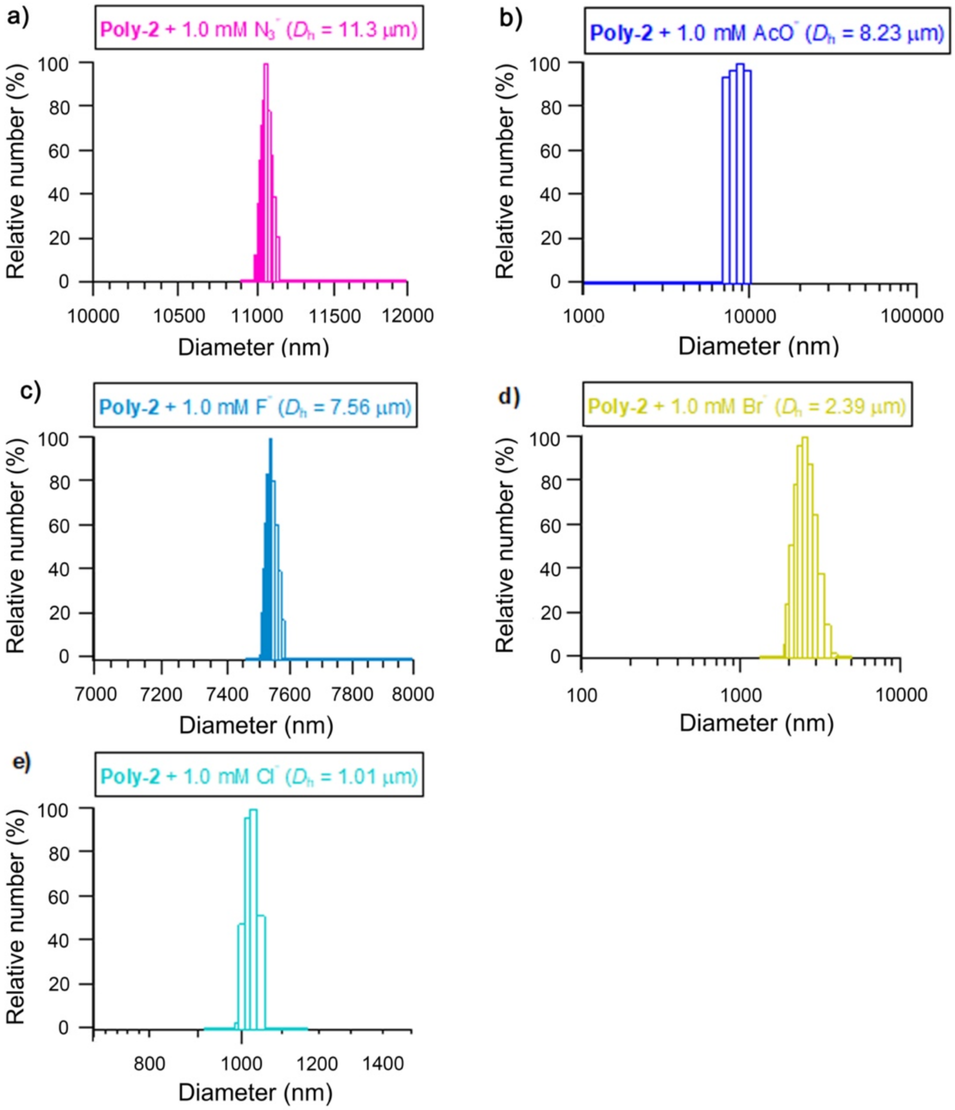


Figure S7. Particle size distribution and average hydrodynamic diameter (D_{h}) of **Poly-2** + anion determined by DLS in DMF/H_2O (v/v = 1:1) mixed solvent at 25 ºC under the weight concentration of 22 mg L^{-1} for **Poly-2** (the concentration of urea group was 91 μM for **Poly-2**) and the anion concentration of 1.0 mM: (a) **Poly-2** + I^-, (b) **Poly-2** + AcO^-, (c) **Poly-2** + F^-, (d) **Poly-2** + Br^-, and (e) **Poly-2** + Cl^-.

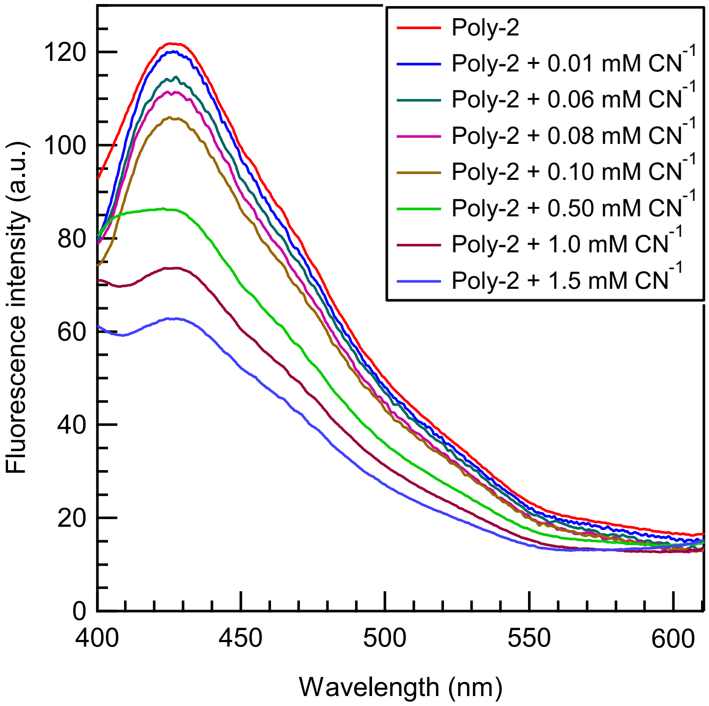


Figure S8. Fluorescence spectra of **Poly-2** with cyanide anion at different concentrations under the conditions of **Poly-2** solution at 22 mg L^{-1} (the concentration of urea group was 91 μM) in DMF/H_2O (v/v = 1:1) at λ_{ex} = 350 nm.

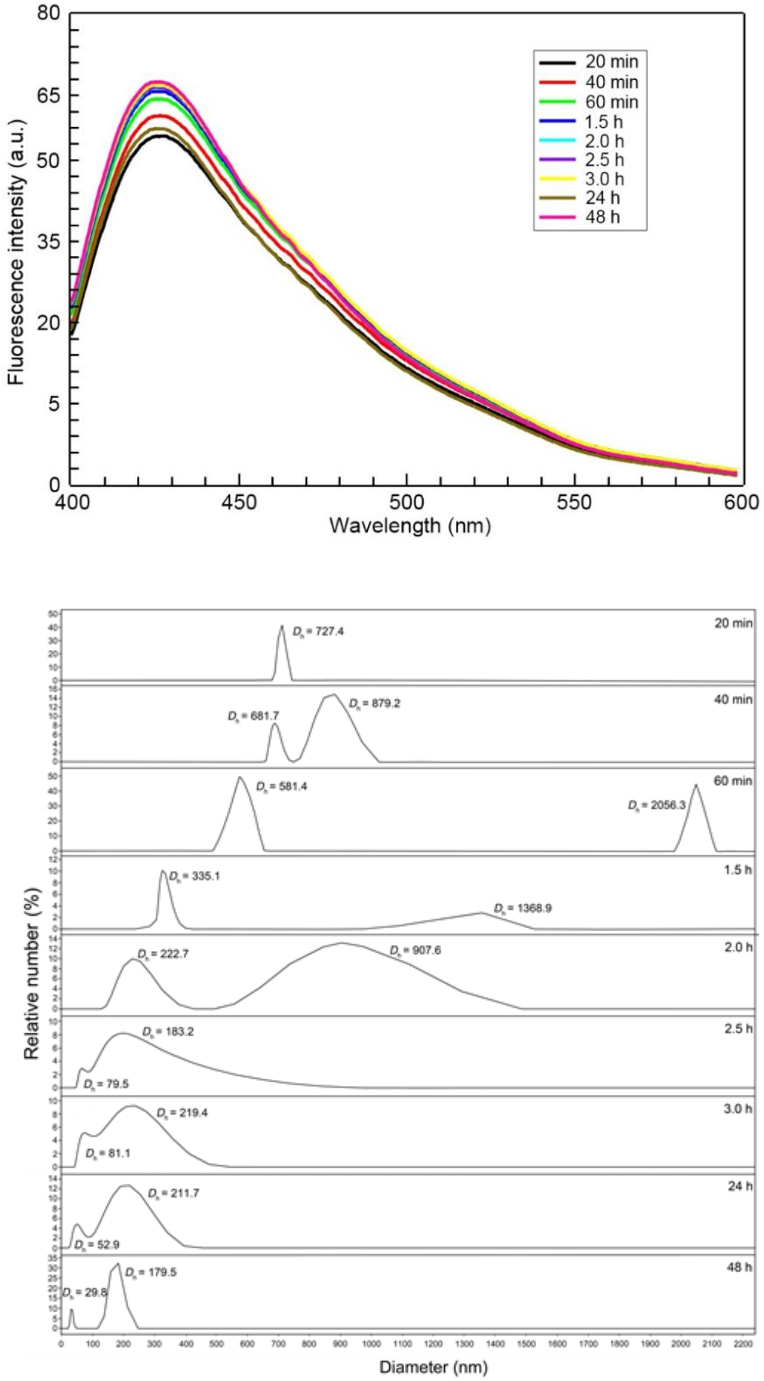


Figure S9. Time-dependent fluorescence spectra (above) and particle size distributions (below) of **Poly-2** with cyanide anion under the conditions of **Poly-2** solution at 22 mg L^{-1} (the concentration of urea group was 91 μM) in DMF/H_2O (v/v = 1:1) at λ_{ex} = 350 nm.