Supporting Information for

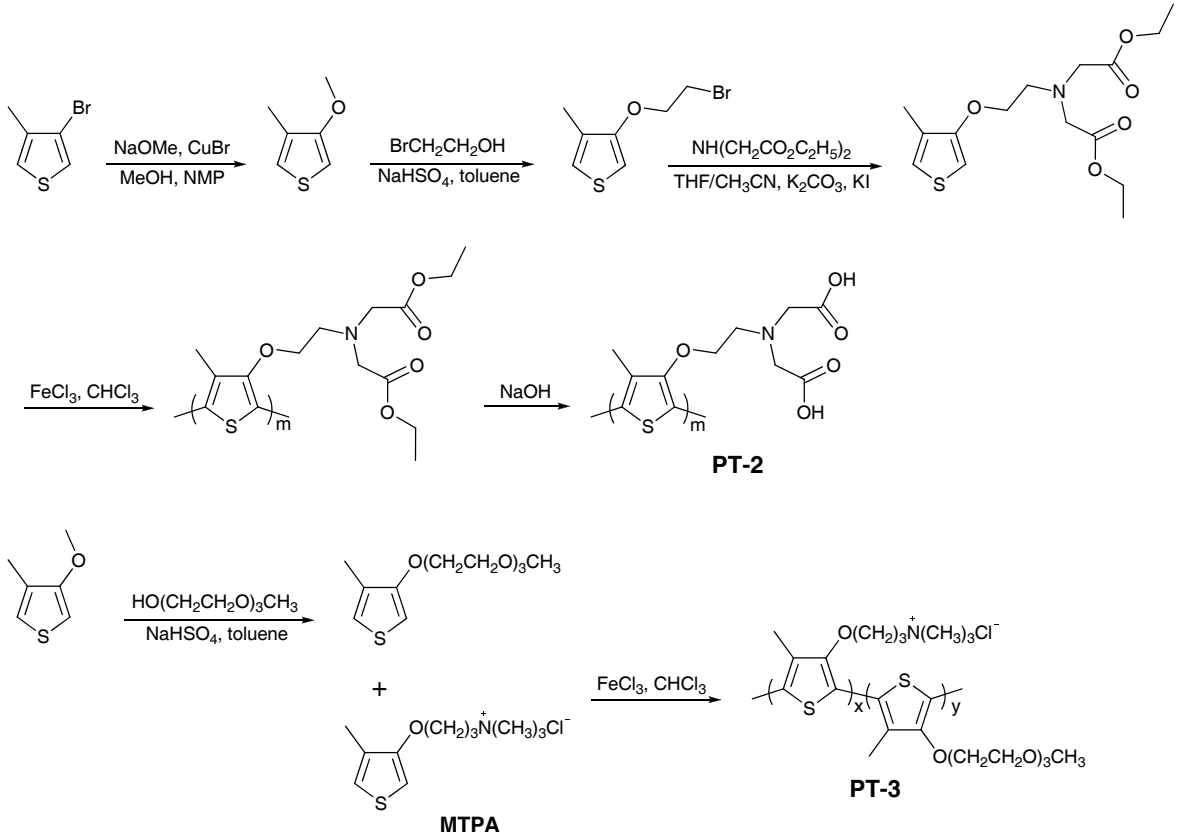
Disassembly of conjugated polyelectrolyte aggregates and their application for colorimetric detection of surfactants in water

Zhiyi Yao, Yugang Li, Chun Li* and Gaoquan Shi,*

Department of Chemistry, Tsinghua University, Beijing 100084, China

Materials. All chemicals were purchased from Aldrich or Beijing Chem. Reagents Co. (Beijing, China) and were used as received. Water-soluble polythiophene derivative, PMTPA, was synthesized and purified as reported previously.[S1]

Synthesis of conjugated polyelectrolytes PT-2 and PT-3.



Synthesis of 3-methoxy-4-methylthiophene (2). 3-Bromo-4-methylthiophene (5.72 g, 32.3 mmol) and CuBr (2.5 g, 17.4 mmol) were added to a mixture of 30 mL sodium methoxide (28% in methanol) and 20 mL NMP, then refluxed for 3 days under N_2 atmosphere. After cooling, the solid

was filtrated, and the filtrate was extracted three times with diethyl ether. The organic phase was dried with magnesium sulfate and then evaporated. The final product was purified by chromatography (silica gel, hexane) (3.69 g, 89%). ^{1}H-NMR ($CDCl_3$, TMS, 300 MHz) δ 6.84 (1H, d), 6.17 (1H, d), 3.86 (3H, s), 2.11(3H, s).

Synthesis of 3-(2-bromo)ethyloxy-4-methylthiophene (3). 3-Methoxy-4-methylthiophene (1.68 g, 13.1 mmol), 2-bromoethanol (5.00 g, 40.0 mmol), and $NaHSO_4$ (246 mg, 2.05 mmol) were added to 24 mL toluene under N_2 atmosphere and heated at 100 ^oC until the produced methanol was distilled off. The reaction mixture was cooled to room temperature and washed three times with water (20 mL each). The collected water phases were extracted with diethyl ether. The organic phase was combined and dried with $MgSO_4$, filtered and evaporated to dryness. The crude product was submitted to column chromatography (silica gel, CH_2Cl_2/hexane (1:1, v/v)) to give 2.06 g (71%) **3** as a colorless oil. ^{1}H-NMR ($CDCl_3$, TMS, 300 MHz) δ 6.84 (1H, d), 6.19 (1H, d), 4.26 (2H, t), 3.65 (2H, t), 2.11 (3H, s).

Synthesis of 3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-4-methylthiophene (4). 3-Methoxy-4-methylthiophene (1.00 g, 7.81mmol), 2-(2-(2-methoxyethoxy)ethoxy)- ethanol(4.0 g, 24.4 mmol), and $NaHSO_4$ (250 mg, 2.02 mmol) were added to 25 mL toluene under N_2 atmosphere and heated at 100 ^oC until the produced methanol was distilled off. The reaction mixture was cooled to room temperature and washed three times with water (20 mL each). The collected water phases were extracted with diethyl ether. The organic phase was combined and dried with $MgSO_4$, filtered and evaporated to dryness. The crude product was submitted to column chromatography (silica gel, CH_2Cl_2/hexane (1:1, v/v)) to give 1.41 g (69%) **4** as colorless oil. ^{1}H-NMR ($CDCl_3$, TMS, 300 MHz) δ 6.82 (1H, d), 6.17 (1H, d), 4.12 (2H, m), 3.86 (2H, m), 3.75 (2H, m), 3.66 (4H, m), 3.56 (2H, m), 3.38 (3H, s), 2.09 (3H, s).

Synthesis of monomer 5. 1.5 g (6.79 mmol) of 3-(2-Bromo)ethyloxy-4-methylthiophene (**3**), 1.568g (8.30 mmol) of diethyl 2,2'-azanediyldiacetate, 1.122 g K_2CO_3 and 0.248 g KI were added to a mixture of 15 mL THF and 15 mL CH_3CN, then refluxed at 85 ^oC for 2 days under N_2 atmosphere. After cooling, the solid was filtrated, and the filtrate was evaporated. The final product was purified by chromatography (silica gel, ethyl acetate/hexane (1:2, v/v)) (0.934 g, 42%).

^{1}H-NMR ($CDCl_3$, TMS, 300 MHz) δ 6.80 (1H, d), 6.15 (1H, d), 4.15 (6H, m), 3.71 (4H, s), 3.23 (2H, t), 2.10 (3H, s), 1.26 (6H, t).

Synthesis of the polymer PT-2. 934 mg (2.84 mmol) of **5** and 1.760g (10.9 mmol) of anhydrous $FeCl_3$ were mixed in 10 mL of dry $CHCl_3$, and stirred for 24 h at room temperature under N_2 atmosphere, then evaporated to dryness. The solid was washed with methanol and filtered. The residue and 0.1 mL hydrazine were mixed in 100 mL methanol and stirred overnight. The solid was washed by methanol and filtered again. The hydrolysis of crude product was performed in 100 mL water with 6.7 g NaOH at 50 ^{o}C for 2 days. The final product was dialyzed through a membrane with a molecular weight cutoff of 3500 for 3 days to yield 90 mg of **PT-2** (12%).

Copolymer PT-3 102 mg (0.41 mmol) of MTPA,[S1] 107 mg (0.41mmol) of 4 and 532 mg (3.28 mmol) of anhydrous $FeCl_3$ were mixed in 25 mL of dry $CHCl_3$, and stirred for 24 h at room temperature under N_2 atmosphere, then evaporated to dryness. The solid was washed by methanol and filtered. The crude product was dissolved in methanol by adding a few drops of hydrazine. The solution was filtered and then evaporated to dryness. The solid was dialyzed through a membrane with a molecular weight cutoff of 500 for 2 days to yield 46 mg of **PT-3** (22%).

Sample Preparation: As a typical procedure, the supramolecular complexes **PT-1** were prepared by adding PMTPA aqueous stock solution (5 mM based on the repeating unit) into a dilute aqueous solution of NSA with the given concentration.

In the experiments of titration with surfactants, stock solutions of SDBS (10 mM), CTAB (10 mM) and Triton X-100 (20 mM) were prepared in HEPES buffer (pH 7.4) and added into a dilute solution of **PT-1**, **PT-2** and **PT-3** in HEPES buffer (pH 7.4) with the given concentration, respectively.

Measurements

Absorption and emission spectra were collected by using a Hitachi 3010 UV-visible spectrometer and a LS 55 fluorescence spectrometer (PerkinElmer), respectively. ^{1}H NMR spectra were carried out on a JNM-ECA300 spectrometer (JEOL).

[S1] C. Li, M. Numata, A.-H. Bae, K. Sakurai, S. Shinkai, *J. Am. Chem. Soc.* 2005, **127**, 4548.

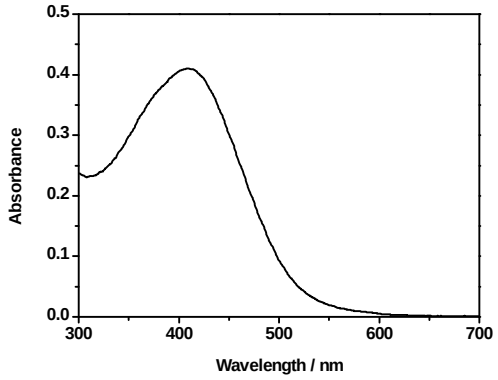


Fig. S1 Absorption spectrum of PMTPA (0.1 mM) in HEPES buffer (10 mM, pH 7.4).

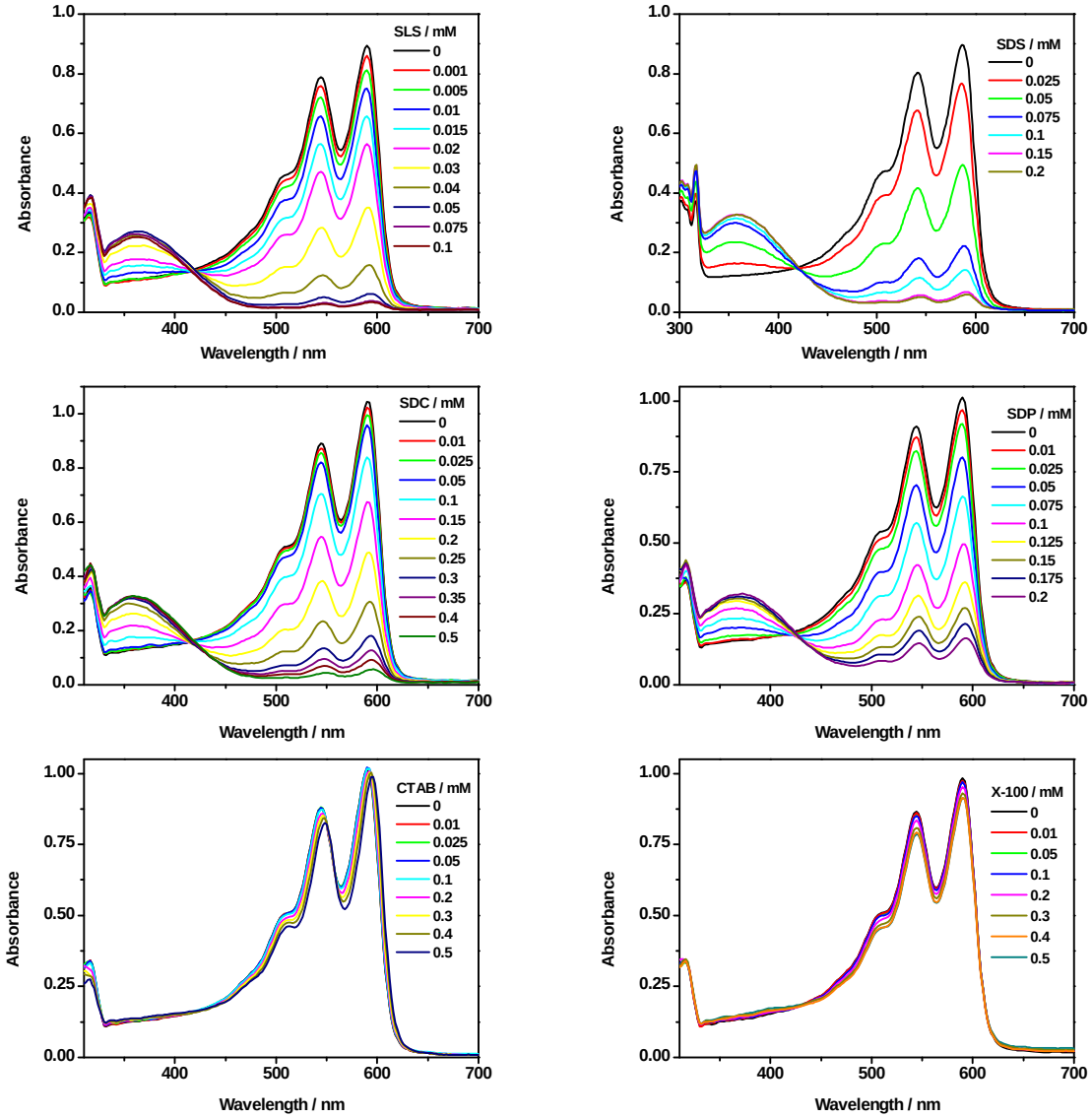


Fig. S2a Variation in the absorption spectra of **PT-1** (0.1 mM) in HEPES buffer (10 mM, pH 7.4) with increasing concentrations of surfactants as indicated.

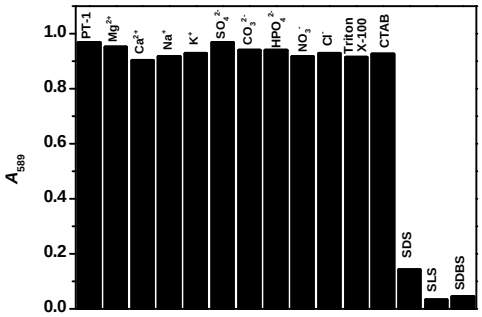


Fig. S2b Relative absorbance of **PT-1** (0.1 mM) in HEPES buffer (10 mM, pH 7.4) in the presence of various analytes.

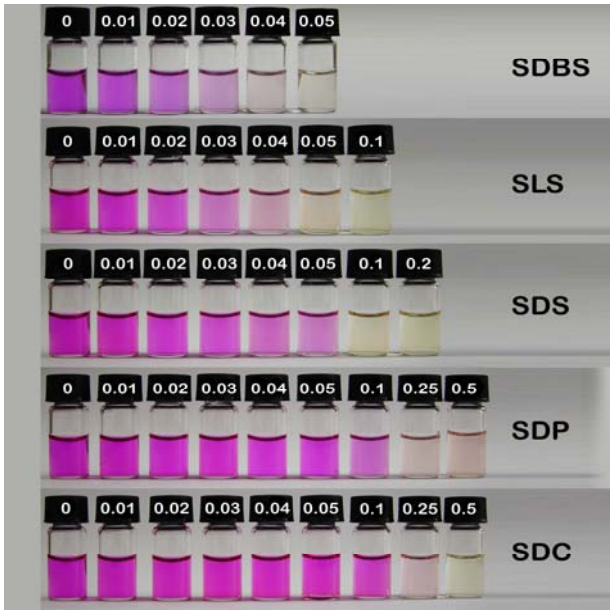


Fig. S3 Colorimetric response of **PT-1** (0.1 mM) in HEPES buffer (10 mM, pH 7.4) induced by the addition of different amounts of anionic surfactants as indicated.

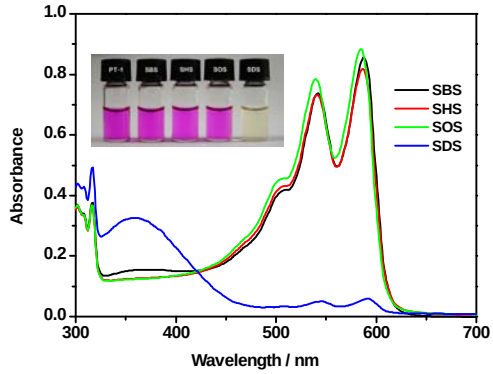


Fig. S4 Absorption spectra of **PT-1** (0.1 mM) in HEPES buffer (10 mM, pH 7.4) upon addition of alkyl sulfonate. [SDS] = 0.2 mM; [SBS] = [SHS] = [SOS] = 0.5 mM. Inset: changes in the color of **PT-1** solution induced by the addition of anionic surfactants as indicated.

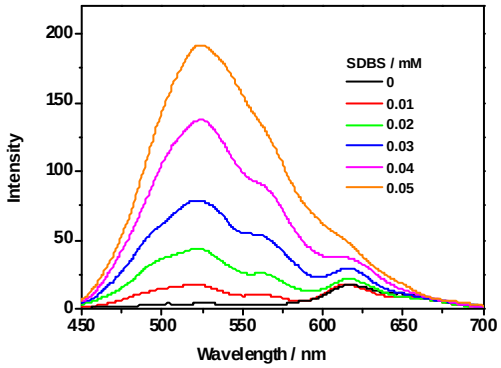


Fig. S5 Emission spectra of **PT-1** (0.1 mM) in HEPES buffer (10 mM, pH 7.4) in the absence and the presence of different amounts of SDBS as indicated. (λ_{ex} = 422 nm)

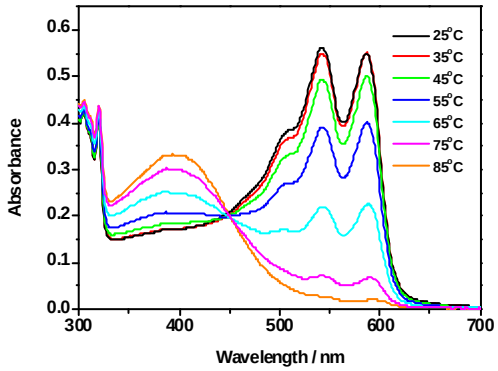


Fig. S6 Temperature-dependent absorption spectra of **PT-1** (0.1 mM) in HEPES buffer (10 mM, pH 7.4).

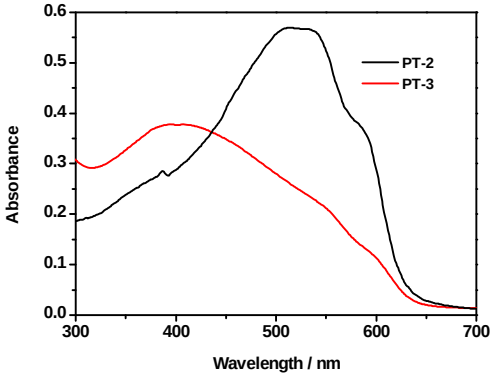


Fig. S7 Absorbance spectra of **PT-2** and **PT-3** in HEPES buffer (10 mM, pH 7.4). [**PT-2**] = 0.1 mM; [**PT-3**] = 0.2 mM.

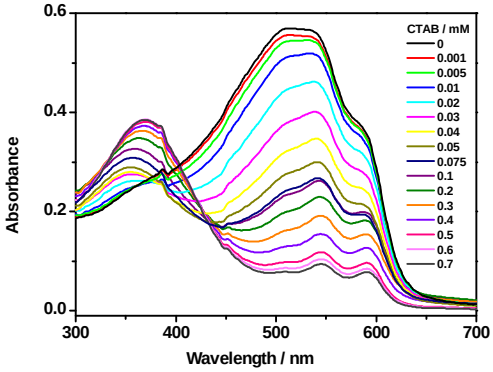


Fig. S8 Variation in the absorption spectra of **PT-2** (0.1 mM) in HEPES buffer (10 mM, pH 7.4) with increasing concentrations of CTAB as indicated.

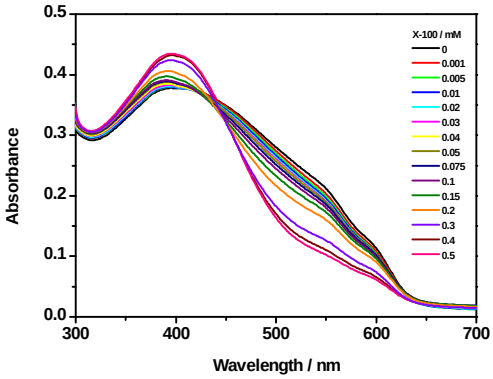


Fig. S9 Variation in the absorption spectra of **PT-3** (0.2 mM) in HEPES buffer (10 mM, pH 7.4) with increasing concentrations of Triton X-100 as indicated.