Supporting Information

Remarkable Photophysics and Amplified Quenching of Conjugated Polyelectrolyte Oligomers

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Experimental

Ester-type oligomer stock solutions (0.5 mM) were prepared in chloroform. The stock solutions of CPE-Os (0.5 mM) were prepared in water (pH 9.0). Water (pH 8.0) was used for all of experiments unless special notation was mentioned. UV/vis absorption spectra were recorded on a Shimadzu 1800 photospectrometer. Steady state emission spectra were collected on a PTI (Photon Technology International) fluorometer. Lifetime experiments were performed on PicoHarp300 equipped with light source by excitation at 370 nm. Transient absorption measurements were conducted on a home-built apparatus using a Continuum Surelite Ii Nd:YAG laser for excitation (6 ~ 7 mJ/pulse) and PI-Max intensified CCD camera coupled with spectrograph as a detector, and the probe source was a Perkin-Elmer LS1130-3 pulsed xenon lamp. The optical density (355 nm) of samples was adjusted to 0.7 and samples were purged with argon for 20 minutes prior to transient absorption measurements. The solutions of methyl viologen (MV^{2+}) and 3,3´-diethyloxacarbocyanine iodide (DOC) were freshly prepared in water (pH 8.0) for quenching experiments. The solutions of sodium chloride and calcium chloride were freshly prepared in water (pH 8.0) for ionic effect experiments.

FCS measurements were taken on a homemade setup using a 405 nm diode laser (Coherent, CUBE) as the excitation light. Fluorescein (30 nM in 10 mM phosphate buffer, pH = 8) was used as the calibration for the system. The concentrations of oligomer and polymer samples are 5 uM for both pH-dependent and salt-dependent experiments. For pH-dependent studies, pH 2.5, pH 8.0 and pH 11.0 aqueous solutions were chosen. For salt-dependent investigation, 0, 1.0 and 10 mM CaCl2 was chosen to study the diffusion behaviors.(see the next paragraph)

Principal component analysis (PCA) was done following the procedure previously reported.[1] In brief, PCA was performed on a personal computer with a macro written in Matlab. A non-orthogonal target transformation was applied to obtain the real eigenvectors which correspond to the absorption spectra of the principal components. Figure 2c (see main paper) illustrates the principal component

spectra, and Figure 2d (see main paper) shows the factor loadings which correspond to the principal component spectra. The normalized factor loadings are proportional to the fraction of each conformer present in the mixture as a function of Ca^{2+} concentration.

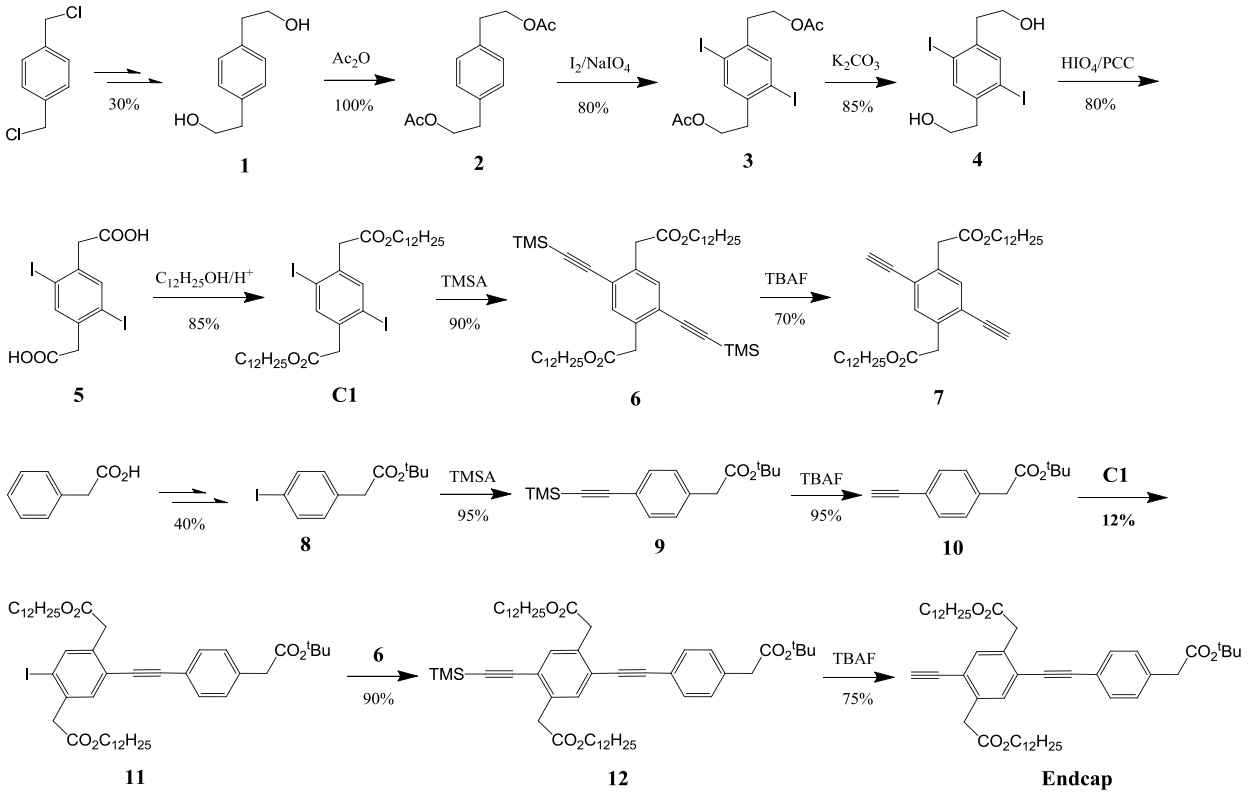

Figure S1. Synthetic scheme of **C1**, **7** and **Endcap**.

Compound **1** was prepared from *p*-xylene dichloride in four-steps including cyano substitution, acid-catalyzed hydrolysis, esterization and reduction by lithium aluminum hydride. [2,3]

Synthesis of **2**: Compound **1** (10 g, 60 mmol), acetic anhydride (50 mL), pyridine (200 mL) and 4-dimethylamino pyridine (catalytic amount) were mixed and stirred at room temperature for overnight. The solvent and excess acetic anhydride were removed under vacuum. The residue was subject to silica column to give **2** as a white solid (15 g, 100%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (s, 4H), 4.26 (t, 4H, *J* = 7.2 Hz), 2.91 (t, 4H, *J* = 7.2 Hz), 2.03 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.19, 136.28, 129.24, 65.12, 34.89, 21.18. MS (ESI) *m/z* ($[M + Na]^+$) 273.1283.

Synthesis of **3,** following a reported iodination procedure [4]: Sodium periodate (7.3 g, 34 mmol, 40% excess) and iodine (26.2 g, 104 mmol, 40% excess) were stirred into a mixture of glacial acetic acid (129 mL) and acetic anhydride (64.5 mL) at 0~5ºC. Concentrated sulfuric acid (43 mL, 860 mmol) was then added slowly to the stirring suspension. Compound **2** (21.5 g, 86 mmol) was added to this solution and stirred continuously for 6 h at room temperature. The reaction mixture was then poured into an ice-water mixture containing previously dissolved Na_2SO_3. The precipitate was collected and recrystallized in ethanol to give compound **3** as a white solid (34.5 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (s, 2H), 4.24 (t, 4H, *J* = 6.9 Hz), 3.00 (t, 4H, *J* = 6.9 Hz), 2.06 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.13, 141.26, 140.57, 100.43, 63.34, 38.89, 21.16. MS (ESI) *m/z* ($[M]^+$) 502.9225.

Synthesis of **4**: To the solution of **3** (8.4g, 16.7 mmol) in dichloromethane (50 mL) and methanol (200 mL) was added potassium carbonate (25 g, 181 mmol) stirred at room temperature overnight. The solvent was removed under vacuum. Water (300 mL) was added and the suspension was strongly stirred at room temperature for 2 h. The solid was collected to give **4** as a white solid (5.9 g, 85%). ^{1}H NMR (300 MHz, Acetone-d6) δ 7.71 (s, 2H), 3.86 (m, 4H), 2.94 (t, 4H, *J* = 6.9 Hz), 1.38 (t, 2H, *J* = 5.7 Hz). ^{13}C NMR (75 MHz, Acetone-d6) δ 142.26, 140.50, 100.25, 61.15, 42.84. MS (ESI) *m/z* ($[M + Na]^+$) 440.8827.

Synthesis of **5**, following a reported procedure with minor modifications [5]: To acetonitrile (80 mL) was added periodic acid (4.8 g, 21 mmol) and the mixture was stirred at room temperature for 15 min. The mixture was cooled down to 0 ºC, and compound **4** (2.0 g, 4.8 mmol)was then added, followed by addition of freshly prepared pyridinium chlorochromate (44 mg, 2 mol%) in acetonitrile (10 mL). The reaction mixture was stirred at room temperature for 6 h. After removal of most solvent under vacuum, the residue was added into water (100 mL). The precipitate was collected and recrystallized in toluene to afford **5** as a white solid (1.7 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.50 (s, 2H), 7.80 (s, 2H), 3.68 (4, 2H). ^{13}C NMR (75 MHz, DMSO-d6) δ 171.98, 141.33, 139.99, 102.18, 45.12. MS (ESI) *m/z* ($[M + Na]^+$) 468.8404.

Synthesis of **C1**: A mixture of **5** (9.0 g, 20 mmol), dodecyl alcohol (80.0 g, 465 mmol) and 85% phosphoric acid (0.5 mL) was heated at 150 °C in a flask equipped with a Dean-Stark trap. After reaction over 6 h, the solvent was removed under vacuum. The residue was recrystallized in isopropanol to give **6** as an off-white solid (13.4 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (s, 2H), 4.12 (t, 4H, *J* = 6.6 Hz), 3.71 (s, 4H), 1.63 (m, 4H), 1.26 (m, 36H), 0.88 (t, 6H, *J* = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.09, 140.84, 138.85, 100.81, 65.64, 45.31, 32.14, 29.88, 29.81, 29.59, 29.43, 28.75, 26.12, 22.93, 14.36. MS (ESI) *m/z* ($[M + Na]^+$) 805.2160.

Synthesis of **6**: Compound **C1** (3.9 g, 5 mmol) was dissolved in a mixture of THF (40 mL) and isopropylamine (120 mL), and combined with $Pd(PPh_3)_2Cl_2$ (14 mg, 0.2 mmol) and CuI (7.5 mg, 0.4 mmol). After a complete degas, trimethylsilylacetylene (1.4 g, 15 mmol) was added, and reacted overnight at room temperature. The solvent was removed and the residue was extracted with dichloromethane/water. The organic layer was washed with saturated ammonium chloride, water and brine, and then dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the crude product was purified by silica chromatography (hexane/dichloromethane, 2/1) to give compound **6** as light yellow oil (3.2 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (s, 2H), 4.10 (t, 4H, *J* = 6.9 Hz), 3.75 (s, 4H) 1.59 (m, 4H), 1.26 (m, 36H), 0.88 (t, 6H, *J* = 6.9 Hz), 0.23 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.88, 135.59, 133.63, 123.92, 102.68, 101.05, 65.32, 39.60, 32.14, 29.88, 29.86, 29.80, 29.74, 29.58, 29.45, 28.78, 26.07, 22.91, 14.34, 0.08. MS (ESI) *m/z* ($[M + Na]^+$) 745.5018.

Synthesis of **7**: To the solution of compound **6** (2.0 g, 2.8 mmol) in chloroform (50 mL) was added tetra-n-butylammonium floride (TBAF, 6.7 mL, 6.7 mmol, 1 M in THF). After reaction over 1 h, the reaction mixture was passed through a silica column and gave **6** as white solid (1.1 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (s, 2H), 4.10 (t, 4H, *J* = 6.6 Hz), 3.78 (s, 4H), 3.33 (s, 2H), 1.61 (m, 4H), 1.26 (m, 36H), 0.88 (t, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.16, 135.67, 134.17, 123.34, 83.56, 81.06, 63.15, 52.34, 39.15, 32.98, 32.12, 29.84, 29.66, 29.56, 25.97, 22.89, 14.31. MS (ESI) *m/z* ($[M + Na]^+$) 601.4227.

Synthesis of **9**: Compound **8** [6,7] (6.4 g, 20 mmol) was dissolved in a mixture of THF (50 mL) and isopropylamine (150 mL), and combined with $Pd(PPh_3)_2Cl_2$ (28 mg, 0.4 mmol) and CuI (15 mg, 0.8

mmol). After a complete degas, trimethylsilylacetylene (4.8 g, 50 mmol) was added, and reacted overnight at room temperature. The solvent was removed and the residue was extracted with dichloromethane/water. The organic layer was washed with saturated ammonium chloride, water and brine, and then dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the crude product was purified by silica chromatography (hexane/dichloromethane, 2/1) to give compound **9** as light yellow solid (5.5 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, 2H, *J* = 8.1 Hz), 7.21 (d, 2H, J = 8.1 Hz), 3.50 (s, 2H), 1.43 (s, 9H), 0.24 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.45, 135.45, 132.28, 129.33, 42.87, 28.23, 0.24. MS (ESI) *m/z* ($[M + Na]^+$) 311.1448.

Synthesis of **10**: To the solution of compound **9** (2.9 g, 10 mmol) in chloroform (50 mL) was added tetra-n-butylammonium floride (TBAF, 12 mL, 12 mmol, 1M in THF). After reaction over 1 h, the reaction mixture was passed through a silica column and gave **10** as light yellow solid (2.0 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, 2H, *J* = 8.1 Hz), 7.24 (d, 2H, *J* = 8.1 Hz), 3.52 (s, 2H), 3.06 (s, 1H), 1.43 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.55, 135.71, 132.38, 129.40, 83.69, 81.29, 42.77, 28.22. MS (ESI) *m/z* ($[M + Na]^+$) 239.1043.

Synthesis of **11**: Compound **6** (3.6 g, 5 mmol) was dissolved in a mixture of THF (50 mL) and isopropylamine (150 mL), and combined with $Pd(PPh_3)_2Cl_2$ (14 mg, 0.2 mmol) and CuI (7.5 mg, 0.4 mmol). After a complete degas, **10** (0.2 g, 1 mmol) was added, and reacted overnight at room temperature. The solvent was removed and the residue was extracted with dichloromethane/water. The organic layer was washed with saturated ammonium chloride, water and brine, and then dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the crude product was purified by silica chromatography (hexane/dichloromethane, 3/2) to give compound **11** as light yellow solid (0.1 g, 12%).

%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.41 (m, 2H), 7.22 (d, 2H, *J* = 8.1 Hz), 4.09 (m, 4H), 3.77 (s, 2H), 3.73 (s, 2H), 3.49 (s, 2H), 1.60 (m, 4H), 1.40 (s, 9H), 1.22 (m, 36H), 0.87 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.71, 170.47, 170.32, 140.75, 137.11, 136.78, 135.59, 133.54, 131.80, 129.47, 124.23, 121.54, 100.97, 95.24, 86.72, 81.24, 65.53, 65.48, 45.95, 42.82, 39.52, 32.15, 29.88, 29.81, 29.76, 29.59, 29.44, 28.78, 28.23, 26.12, 26.09, 22.93, 14.37. MS (ESI) *m/z* ($[M + Na]^+$) 893.4191.

Synthesis of **12**: Compound **11** (0.15 g, 0.17 mmol) was dissolved in a mixture of THF (5 mL) and isopropylamine (15 mL), and combined with $Pd(PPh_3)_2Cl_2$ (2.8 mg, 0.04 mmol) and CuI (1.5 mg, 0.08 mmol). After a complete degas, trimethylsilylacetylene (0.19 g, 2 mmol) was added, and reacted overnight at room temperature. The solvent was removed and the residue was extracted with dichloromethane/water. The organic layer was washed with saturated ammonium chloride, water and brine, and then dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the crude product was purified by silica chromatography (hexane/dichloromethane, 2/1) to give compound **12** as light yellow solid (0.13 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (m, 4H), 7.23 (d, 2H, *J* = 8.1 Hz), 4.08 (m, 4H), 3.81 (s, 2H), 3.77 (s, 2H), 3.51 (s, 2H), 1.60 (m, 4H), 1.42 (s, 9H), 1.23 (m, 36H), 0.88 (t, 6H, *J* = 6.6 Hz), 0.24 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.99, 170.89, 170.52, 135.75, 135.56, 135.24, 133.78, 133.30, 131.86, 129.49, 124.11, 123.68, 121.69, 102.80, 101.00, 95.66, 87.36, 81.22, 65.38, 65.31, 42.82, 39.93, 39.65, 32.14, 29.88, 29.80, 29.75, 29.72, 29.58, 29.45, 29.42, 28.80, 28.22, 26.10, 26.06, 22.91, 14.34, 0.10. MS (ESI) *m/z* ($[M + Na]^+$) 863.5601.

Synthesis of **Endcap**: To the solution of compound **12** (0.12 g, 0.14 mmol) in chloroform (10 mL) was added tetra-n-butylammonium floride (TBAF, 0.2 mL, 0.2 mmol, 1 M in THF). After reaction over 1 h, the reaction mixture was passed through a silica column and gave **13** as light yellow solid (82 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (m, 4H), 7.24 (d, 2H, *J* = 8.1 Hz) 4.11 (m, 4H), 3.83(s, 2H), 3.81 (s, 2H), 3.53 (s, 2H), 3.34 (s, 1H), 1.60 (m, 4H), 1.44 (s, 9H), 1.25 (m, 36H), 0.88 (t, 6H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.92, 170.86, 170.50, 135.86, 135.59, 135.30, 134.22, 133.34, 131.85, 129.48, 124.51, 122.60, 121.56, 95.75, 87.13, 83.19, 81.50, 81.26, 65.42, 65.38, 42.82, 39.92, 39.51, 32.15, 29.88, 29.81, 29.60, 29.44, 28.78, 28.23, 26.08, 22.93, 14.37. MS (ESI) *m/z* ($[M + H]^+$) 769.5419.

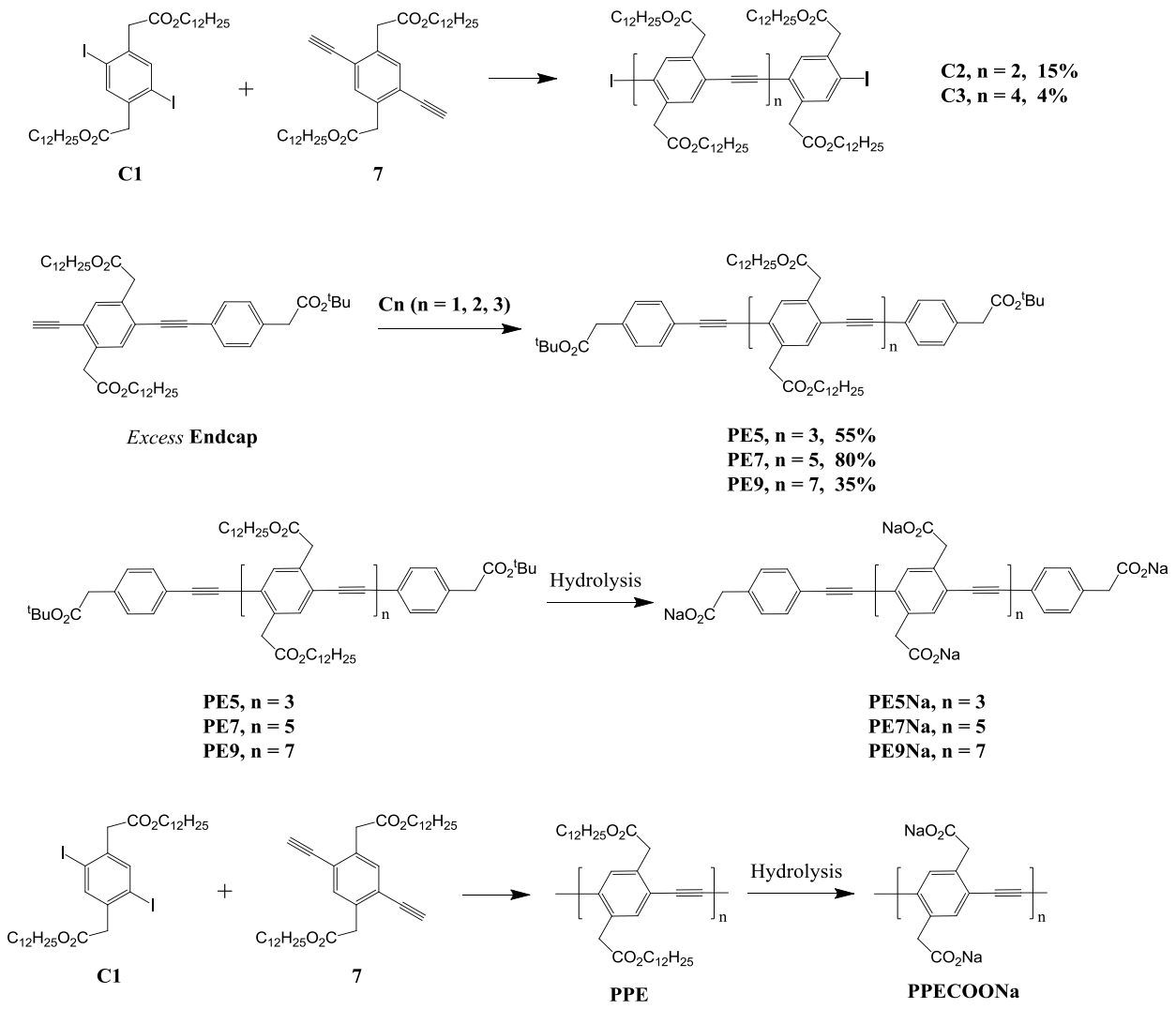

Figure S2. Synthetic scheme of oligomers.

Synthesis of **C2** and **C3**: Compound **C1** (1.8 g, 2.3 mmol) was dissolved in a mixture of THF (150 mL) and isopropylamine (150 mL), and combined with $Pd(PPh_3)_2Cl_2$ (14 mg, 0.2 mmol) and CuI (7.5 mg, 0.4 mmol). After a complete degassing procedure, compound **7** (0.38 g, 0.65 mmol) was added, and reacted overnight at room temperature. The solvent was removed under vacuum and the residue was extracted with chloroform/water. The organic layer was washed with saturated ammonium chloride, water and brine, and then dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the crude product was purified by silica chromatography to give **C2** (190 mg, 15%) and **C3** (80 mg, 4%).

C2: ^{1}H NMR (500M Hz) δ 7.83 (s, 2H), 7.48 (s, 2H), 7.43 (s, 2H), 4.10 (m, 12H), 3.84 (s, 4H), 3.82 (s, 4H), 3.77 (s, 4H), 1.60 (m, 12H), 1.26 (m, 108H), 0.88 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.78, 170.61, 170.28, 140.83, 137.30, 136.66, 135.32, 133.98, 133.83, 123.89, 123.84, 101.70, 92.86, 92.82, 65.63, 65.57, 65.53, 45.95, 39.77, 39.32, 32.18, 32.17, 29.94, 29.92, 29.91, 29.89, 29.88, 29.86, 29.84, 29.80, 29.79, 29.62, 29.60, 29.52, 29.51, 29.47, 28.84, 28.83, 28.81, 26.14, 26.11, 26.09, 22.94, 14.37. MS (MALDI-TOF) *m/z* ($[M]^+$) 1888.166.

C3: ^{1}H NMR (500M Hz) δ 7.84 (s, 2H), 7.50 (m, 6H), 7.44 (2H), 4.10 (m, 20H), 3.87 (s, 8H), 3.85 (s, 4H), 3.82 (s, 4H), 3.77 (s, 4H), 1.60 (m, 20H), 1.26 (m, 180H), 0.88 (m, 30H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.76, 170.59, 170.25, 140.81, 137.28, 136.64, 135.31, 133.96, 133.88, 133.77, 123.94, 123.83, 101.67, 93.45, 92.85, 65.60, 65.54, 65.51, 45.94, 39.73, 39.30, 32.15, 29.91, 29.89, 29.86, 29.82, 29.79, 29.60, 29.50, 29.45, 28.83, 26.12, 26.08, 22.92, 14.34. MS (MALDI-TOF) *m/z* ($[M]^+$) 2993.283.

Synthesis of polymer **PPE** and oligomers **PEn**s (n = 5, 7, 9): The solution of **Cn** (1.0 eq, n = 1, 2, 3 for oligomers and n = 1 for polymer) in THF/isopropylamine (1/2, v/v) was degassed 40 min at room temperature before $Pd(dba)_2$ (0.02 eq) and CuI (0.04 eq) were added. The mixture was degassed at 50℃ for additional 30 min, followed by dropwise adding degassed solution of **Endcap** (4.0 eq) for oligomers or **7** (1.0 eq) for polymer in THF. After reaction under argon atmosphere at 50℃ for 2 days, the solvent was removed and the residue was extracted with chloroform/water. The organic layer was washed with saturated ammonium chloride, water and brine, and dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the crude product was purified by silica chromatography.

PE5 (80 mg, 55%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 10H), 7.27 (d, 4H, *J* = 8.5 Hz), 4.10 (m, 12H), 3.87 (s, 8H), 3.86 (s, 4H), 3.54 (s, 4H), 1.60 (m, 12H), 1.44 (s, 18H), 1.23 (m, 108H), 0.88 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.01, 170.94, 170.86, 170.60, 135.64, 135.45, 135.31, 135.27, 133.90, 133.85, 133.43, 131.92, 129.54, 124.43, 123.96, 123.42, 121.69, 95.96, 93.57, 93.25, 87.40, 81.33, 65.54, 65.50, 42.88, 40.03, 39.79, 39.77, 32.17, 29.94, 29.93, 29.92, 29.92, 29.91, 29.90, 29.89, 29.86, 29.84,

29.81, 29.80, 29.77, 29.62, 29.62, 29.61, 29.54, 29.51, 29.48, 28.86, 28.84, 28.83, 28.26, 26.11, 26.09, 22.94, 14.36. MS (MALDI-TOF) *m/z* ($[M]^+$) 2064.614.

PE7 (80 mg, 80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 14H), 7.28 (d, 4H, *J* = 8.5 Hz), 4.12 (m, 20 Hz), 3.88 (s, 16H), 3.86 (s, 4H), 3.53 (s, 4Hz), 1.61 (m, 20H), 1.45 (s, 18H), 1.24 (m, 180H), 0.88 (m, 30H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.00, 170.93, 170.84, 170.82, 170.81, 170.59, 135.65, 135.46, 135.34, 135.32, 135.27, 133.91, 133.89, 133.87, 133.83, 133.43, 131.92, 129.54, 124.45, 124.04, 123.96, 123.88, 123.41, 121.68, 95.98, 93.62, 93.53, 93.48, 93.24, 87.40, 81.32, 65.54, 65.50, 42.88, 40.03, 39.77, 32.18, 29.94, 29.92, 29.92, 29.91, 29.90, 29.88, 29.86, 29.84, 29.82, 29.80, 29.77, 29.62, 29.53, 29.51, 29.48, 28.86, 28.85, 28.83, 28.26, 26.11, 22.94, 14.36. MS (MALDI-TOF) *m/z* ($[M]^+$) 3168.058.

PE9 (35 mg, 35%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 18H), 7.28 (d, 4H, *J* = 8.5 Hz), 4.12 (m, 28H), 3.88 (s, 24H), 3.86 (s, 4H), 3.54 (s, 4H), 1.61 (m, 28H), 1.45 (s, 18H), 1.24 (m, 252H), 0.88 (m, 42H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.01, 170.93, 170.85, 170.83, 170.81, 170.61, 135.66, 135.65, 135.63, 135.45, 135.33, 135.32, 135.27, 133.91, 133.90, 133.88, 133.83, 133.43, 131.92, 129.54, 124.45, 124.04, 123.97, 123.96, 123.95, 123.88, 123.40, 121.68, 95.97, 93.61, 93.52, 93.47, 93.22, 87.40, 81.33, 70.80, 65.55, 65.51, 42.88, 40.02, 39.77, 32.18, 29.94, 29.92, 29.91, 29.90, 29.88, 29.86, 29.84, 29.82, 29.81, 29.77, 29.62, 29.53, 29.51, 29.48, 28.86, 28.26, 26.10, 22.94, 14.36. MS (MALDI-TOF) *m/z* ($[M]^+$) 4273.837.

PPE (160 mg, 80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 0.1H), 7.51 (m, 2H), 4.10 (m, 4H), 3.87 (m, 4H), 1.60 (m, 4H), 1.24 (m, 36H), 0.87 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.79, 170.77, 170.75, 170.65, 170.63, 170.60, 170.57, 170.27, 135.44, 135.43, 135.40, 135.38, 135.37, 135.36, 135.34, 135.32, 133.91, 133.90, 133.88, 133.87, 133.86, 133.85, 133.84, 123.98, 123.95, 123.94, 123.79, 93.53, 93.48, 93.47, 93.46, 93.44, 65.62, 65.60, 65.57, 65.53, 42.86, 39.76, 39.75, 32.18, 29.94, 29.92, 29.89, 29.88, 29.84, 29.82, 29.79, 29.62, 29.61, 29.53, 29.51, 29.47, 28.85, 28.84, 28.81, 26.14, 26.13, 26.10, 22.94, 14.36.

General synthesis of **PPECOONa** and oligomers **PEnNa** (n = 5, 7, 9): The precursor **PEn** (~ 40 mg) or **PPE** was dissolved in chloroform (3 mL) and treated by excess TFA (3 mL) over 5 hours at ambient temperature. The solvents were completely removed under vacuum. The residue was dissolved in THF (20 mL) and then a solution of sodium hydroxide (10 equivalents to ester group) in methanol/water (3 mL, 2/1, v/v) was added. The mixture was stirred at 50 ℃ overnight. The solvents THF and methanol were removed under vacuum, and water (10 mL) was added to the residue, followed by additional reaction at 50 ℃ for 5 hours. The mixture was concentrated to about 2 mL, precipitated in acetone (25 mL), and centrifuged. The precipitate was dissolved again in water (pH 9, 2 mL). Multiple precipitation was repeated 3 ~ 5 times in acetone (containing 5 ~ 20% methanol). Any insoluble in water was removed by centrifuge before precipitation operation. After filtration on a membrane filter with a 0.45 μm pore size and complete dryness under vacuum, the solid was completely dissolved in water and subjected to dialysis using dialysis tube (molecular weight cutoff 500 Da for **PEn**s and 12,000 Da for **PPECOONa**) against water (pH 8) over 3 days. Light yellow solid was obtained in a yield of 80 ~ 90% after water was removed under vacuum.

PE5Na: ^{1}H NMR (300 MHz, D_2O) δ 7.2 ~ 7.6 (m), 3.4 ~ 3.9 (m).

PE7Na: ^{1}H NMR (500 MHz, D_2O) δ 7.15 ~ 7.4 (m), 3.4 ~ 3.9 (m).

PE9Na: ^{1}H NMR (500 MHz, D_2O) δ 7.25 ~ 7.6 (m), 3.5 ~ 3.9 (m).

PPECOONa: ^{1}H NMR (500 MHz, D_2O) δ 7.85 (s), 7.25 ~ 7.6 (m), 3.3 ~ 3.9 (m).

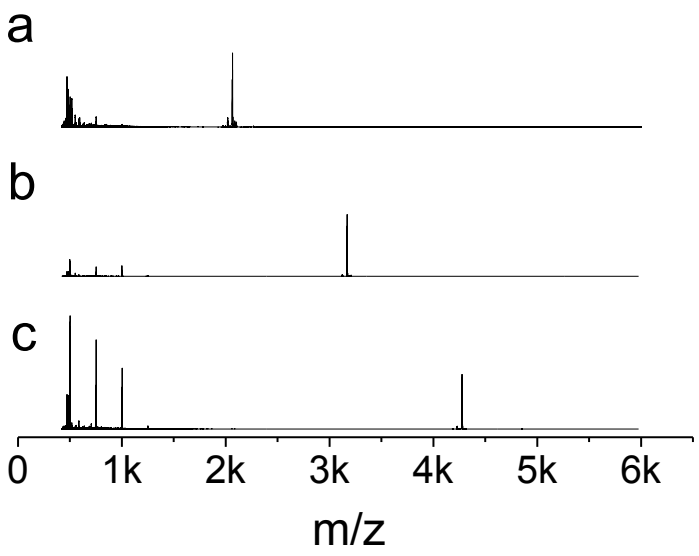

Figure S3. MALDI-TOF analysis of a) **PE5**, b) **PE7** and c) **PE9**.

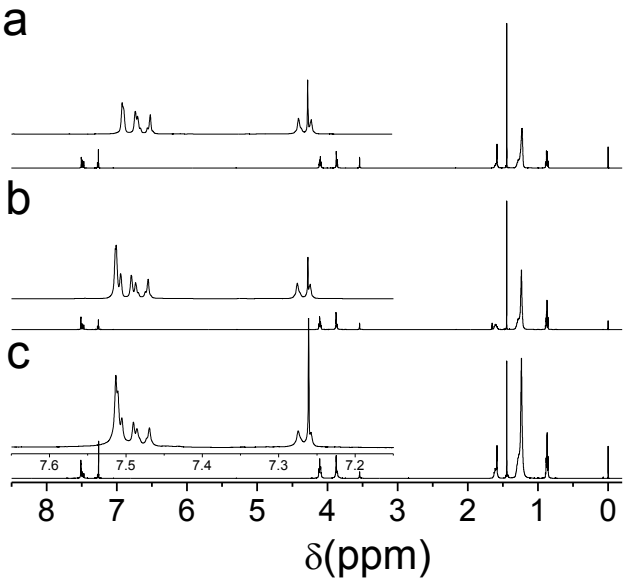

Figure S4. ^{1}HNMR analysis of a) **PE5**, b) **PE7** and c) **PE9** in $CDCl_3$.

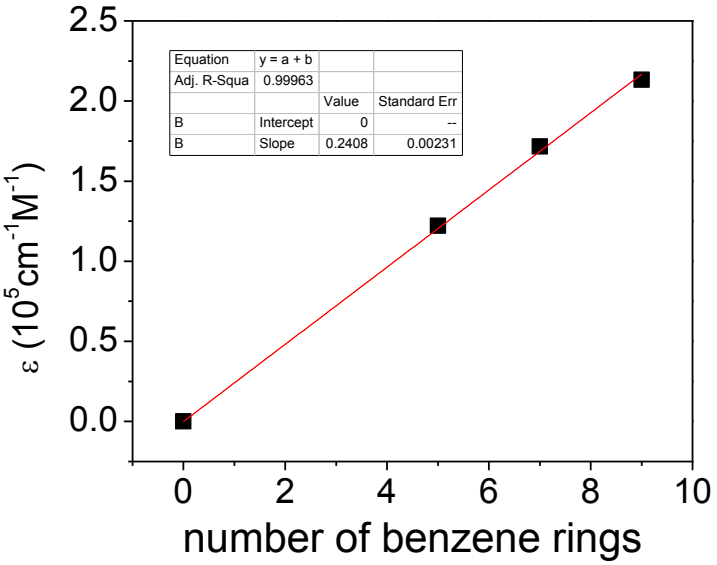

Figure S5. Plot of extinction coefficient as a function of number of absorbing unit.

Table S1. Correlation time from fluorescence anisotropy decay

	$CHCl_3$			H_2O		
	PE5	**PE7**	**PE9**	**PE5Na**	**PE7Na**	**PE9Na**
$\theta_{400\ nm}$, ns	1.00	---[a]	---[a]	1.39	---[a]	---[a]
$\theta_{420\ nm}$, ns	1.18	1.27	1.41	1.36	1.75	1.64
$\theta_{450\ nm}$, ns	1.10	1.31	1.43	1.40	1.88	1.76
$\theta_{500\ nm}$, ns	1.12	1.33	1.58	1.39	1.86	1.75
R_H, nm	1.27	1.34	1.40	1.15	1.26	1.24
V, nm^3	8.7	10.2	11.7	6.5	8.5	7.9

[a]Measurements were not available as the emission intensity is too weak.

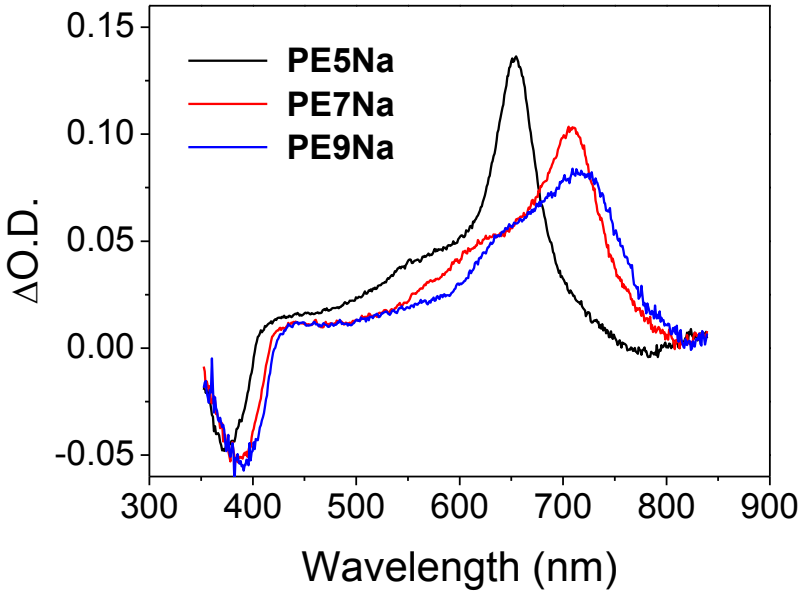

Figure S6. Transient absorption spectra of **PEnNa**s (n = 5, 7, 9) in MeOH containing 10 mM NaOH. The optical density at 355 nm is 0.7.

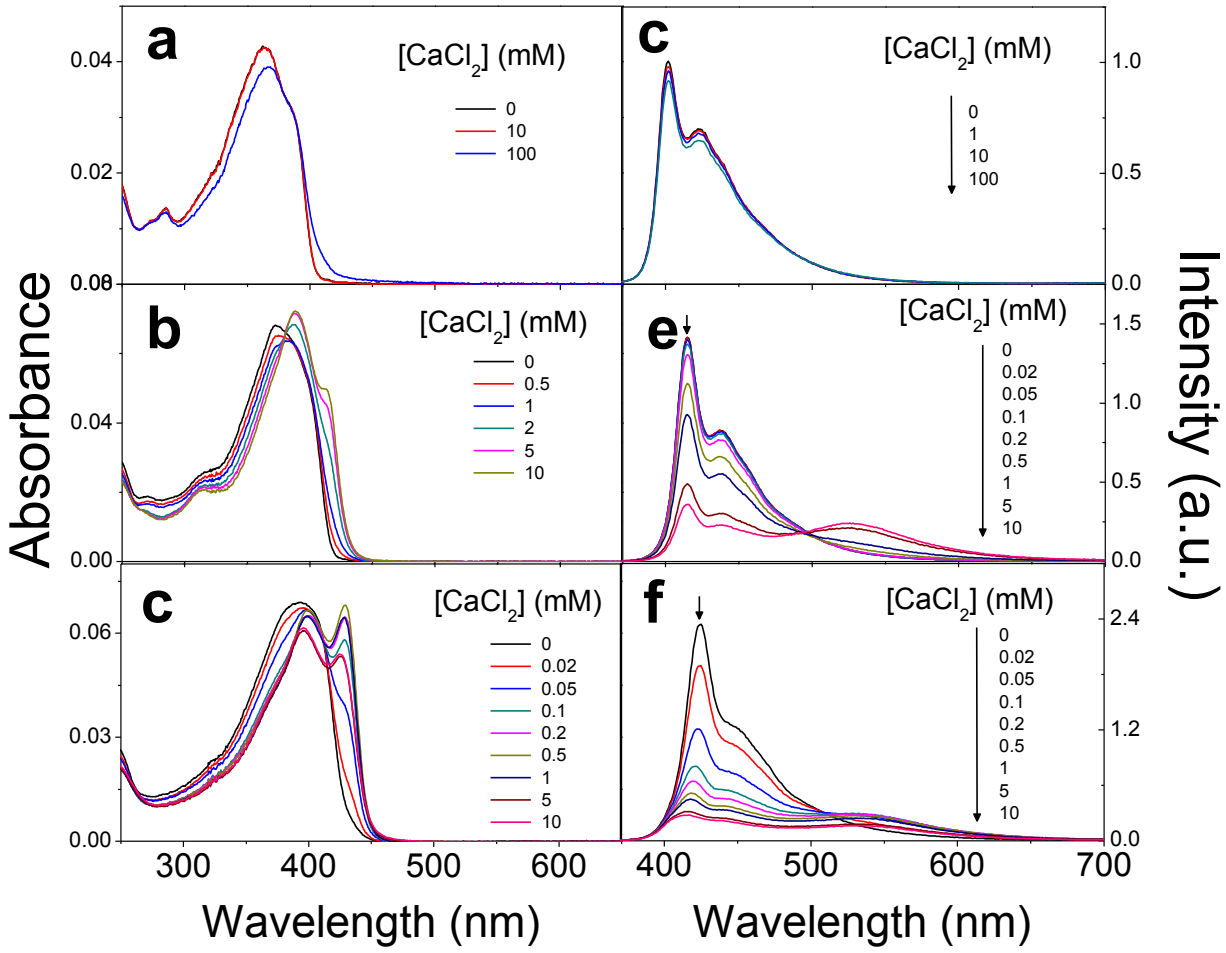

Figure S7. Absorption spectra of a) **PE5Na**, b) **PE7Na**, c) **PPECOONa** in water upon adding $CaCl_2$; fluorescence spectra of d) **PE5Na**, e) **PE7Na**, f) **PPECOONa** in water upon adding $CaCl_2$, λ_{ex} = 360 nm. [**PEnNa**] (n 5, 7, 9) = 1.0 μM, [**PPECOONa**] = 5 μM in repeat unit.

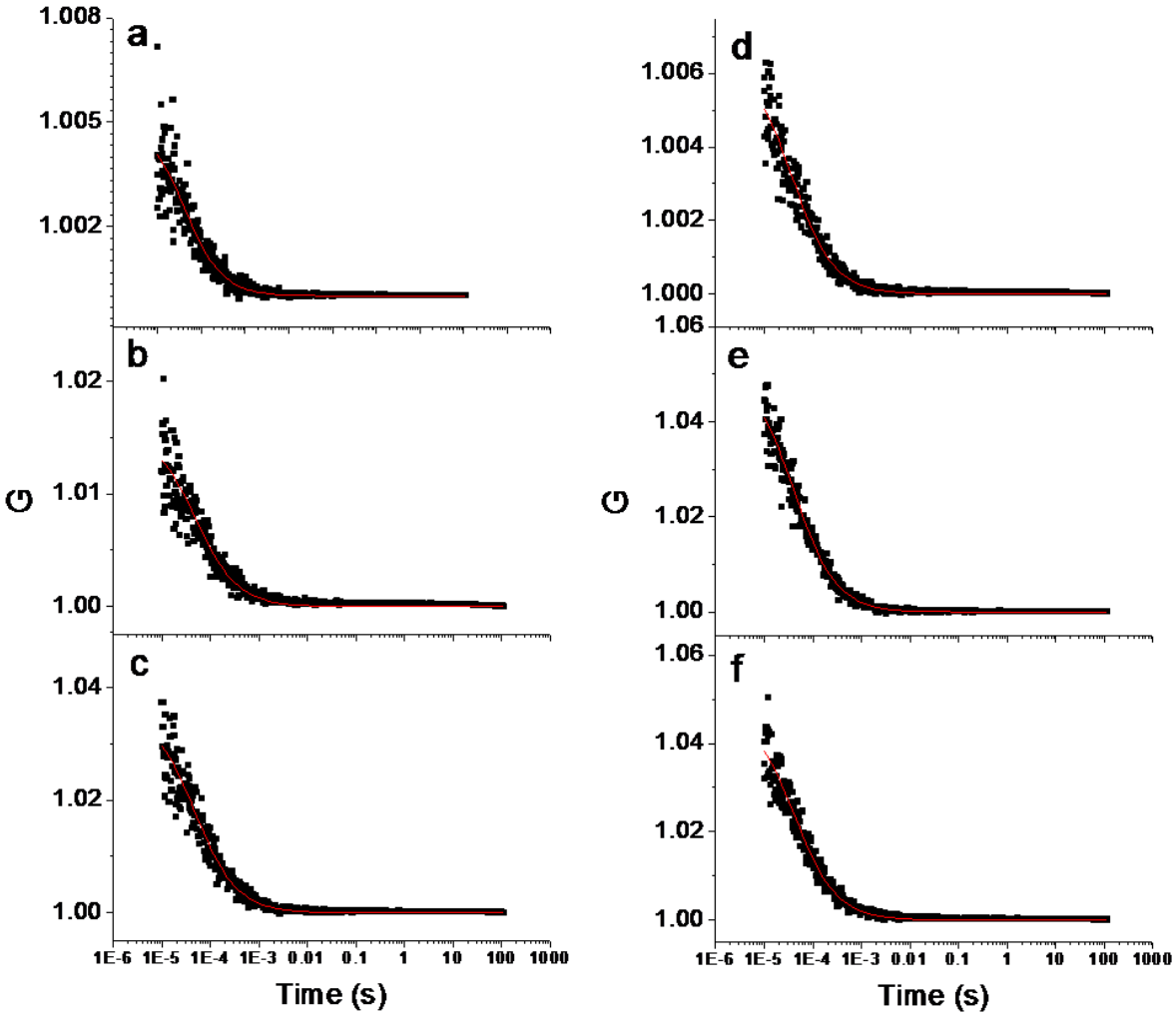

Figure S8. FCS trace of a-c) **PE7Na** in the presence of 0, 1.0 and 10.0 mM $CaCl_2$ respectively; d-f) **PE9Na** in the presence of 0, 1.0 and 10.0 mM $CaCl_2$ respectively.

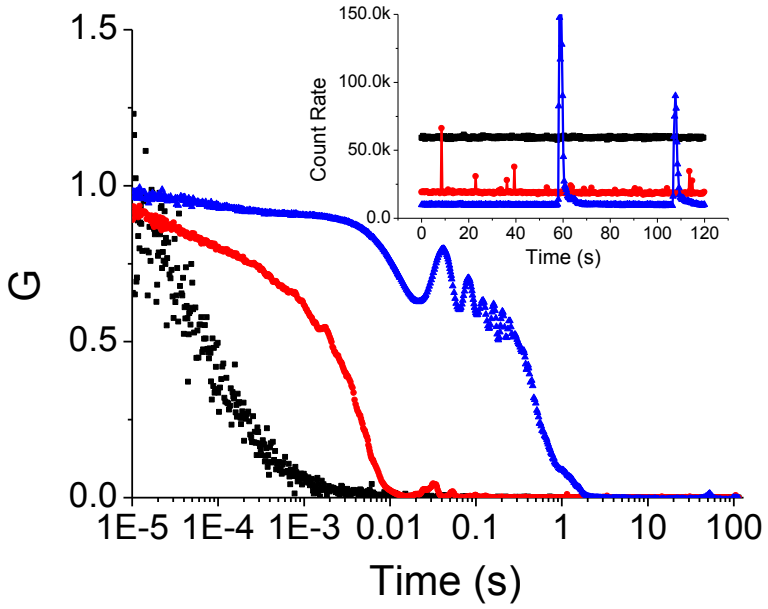

Figure S9. FCS trace of **PPECOONa** (5 mM in water) in the presence of 0 mM $CaCl_2$ (black), 1.0 mM $CaCl_2$ (red, measured at t = 24 h after $CaCl_2$ was added.) and 10.0 mM $CaCl_2$ (blue, measured at t = 24 h after $CaCl_2$ was added.) respectively. The inset was the corresponding count rate diagram.

Table S2. Diffusion time (τ_D) determined by FCS

		PE5Na	**PE7Na**	**PE9Na**	**PPECOONa**
τ_D, 10^{-5} s	[$CaCl_2$] = 0	4.4 ± 0.4	4.5 ± 0.4	5.0 ± 0.2	6.2 ± 0.4
	[$CaCl_2$] = 10 mM	5.5 ± 0.4	5.2 ± 0.3	5.4 ± 0.5	--------[a]

[a] First order fitting is not available.

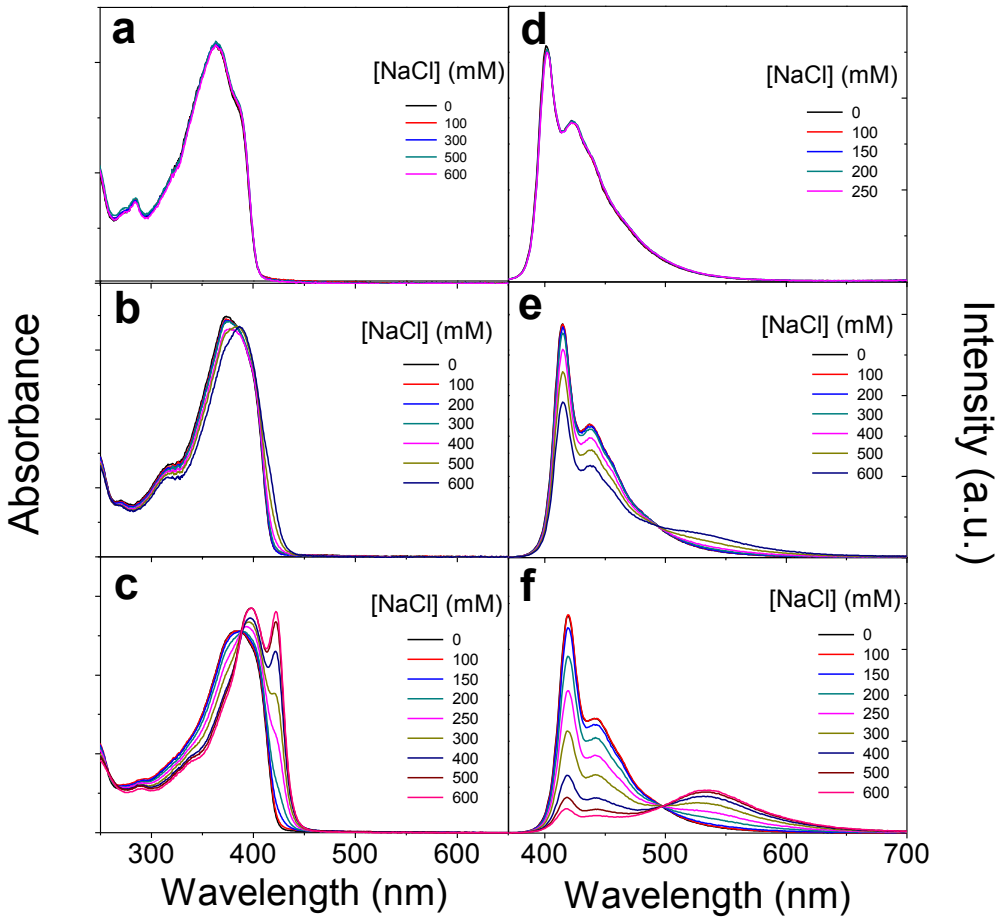

Figure S10. Absorption spectra of a) **PE5Na**, b) **PE7Na** and c) **PE9a** in water containing varying NaCl concentrations; fluorescence spectra of d) **PE5Na**, e) **PE7Na** and f) **PE9a** in water containing varying NaCl concentrations, λ_{ex} = 360 nm. [**PEnNa**] (n = 5, 7, 9)= 1.0 μM.

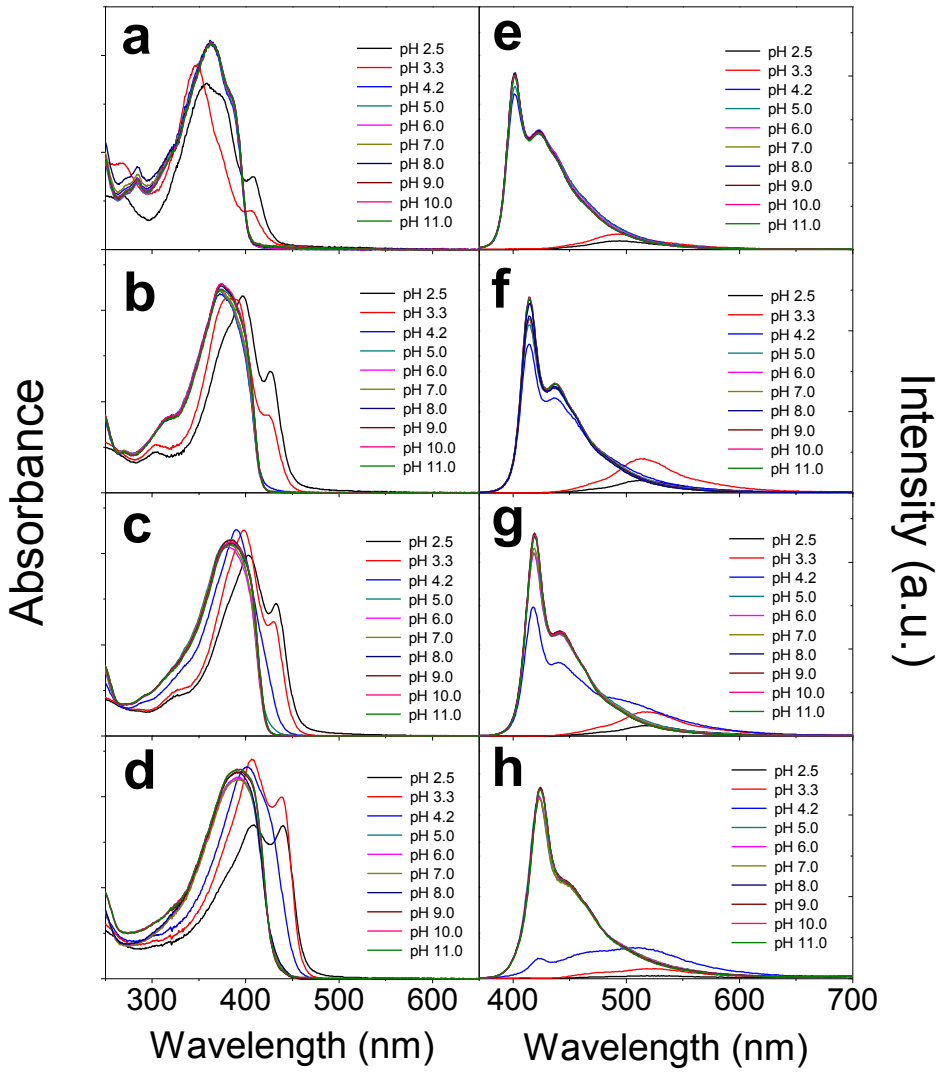

Figure S11. Absorption spectra of a) **PE5Na**, b) **PE7Na**, c) **PE9a** and d) **PPECOONa** in water upon changing pH; fluorescence spectra of e) **PE5Na**, f) **PE7Na**, g) **PE9a** and h) **PPECOONa** in water upon changing pH, λ_{ex} = 360 nm. [**PEnNa**] (n = 5, 7, 9) = 1.0 μM, [**PPECOONa**] = 5 μM in repeat unit.

Table S3. Diffusion time (τ_D) determined by FCS

		PE5Na	PE7Na	PE9Na	PPECOONa
τ_D, 10^{-5} s	pH 11	5.1 ± 0.1	5.0 ± 0.4	5.2 ± 0.2	7.9 ± 0.6
	pH 2.5	4.3 ± 0.1	4.9 ± 0.2	4.9 ± 0.4	--------[a]

[a] First order fitting is not available.

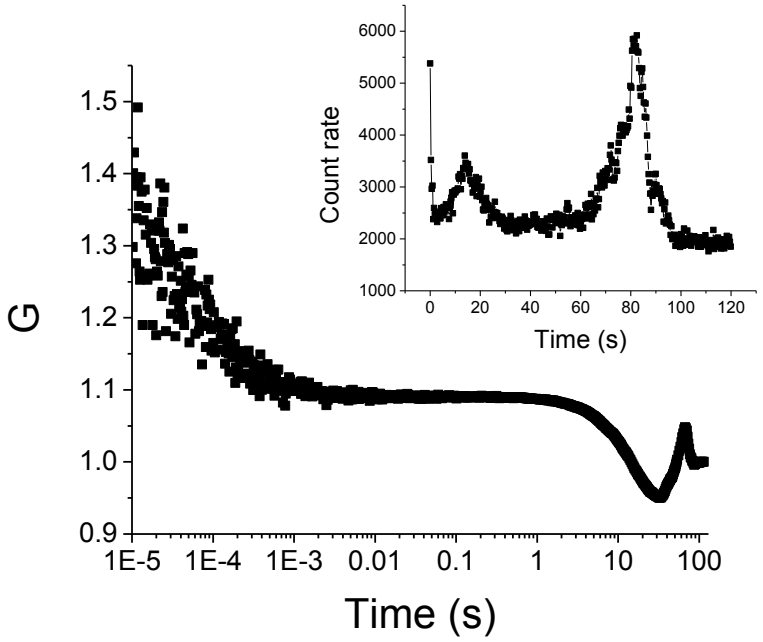

Figure S12. FCS trace of **PPECOONa** at pH 2.5. [**PPECOONa**] = 5 μM. The inset is count rate history recorded under the same condition.

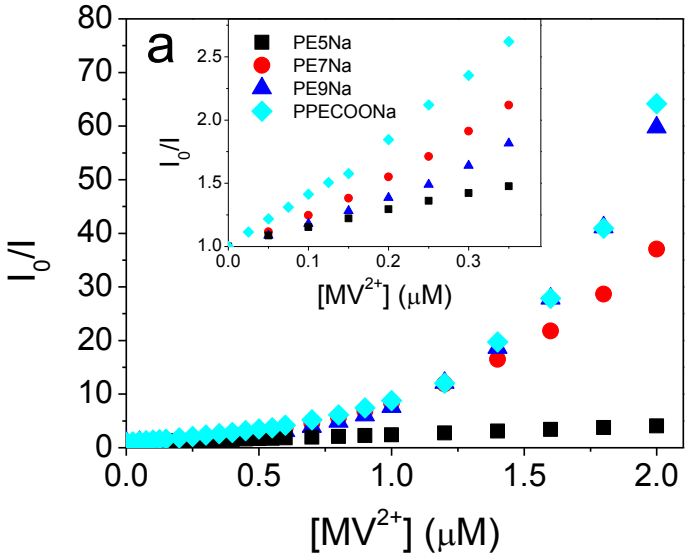

Figure S13. Stern-Volmer plot of I_0/I as a function of MV^{2+} concentration. [**PEnNa**] (n = 5, 7, 9) = 1.0 μM, [**PPECOONa**] = 5.0 μM in repeat unit. λ_{ex} = 360 nm.

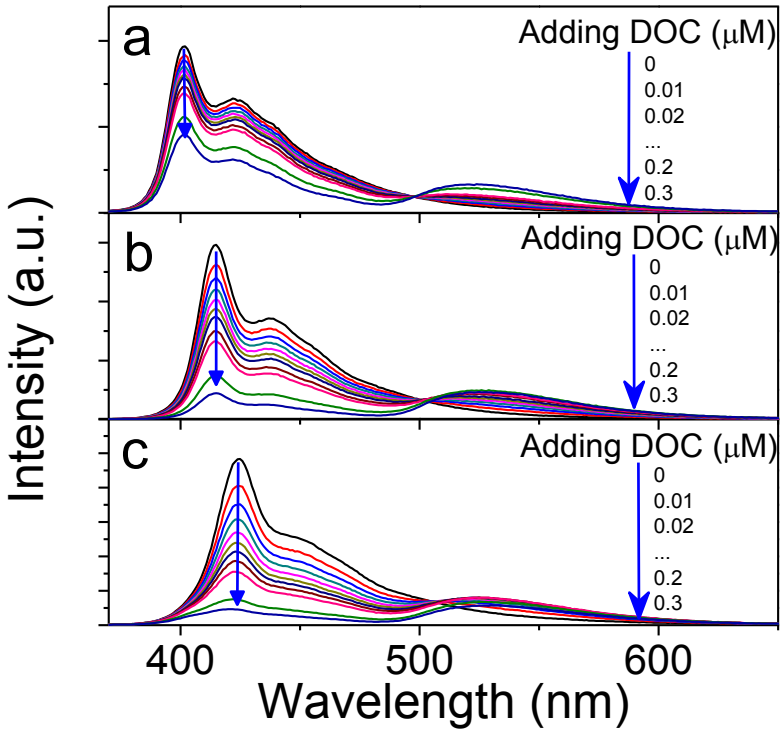

Figure S14. Fluorescence spectra of a) **PE5Na**, b) **PE7Na**, c) **PPECOONa** upon adding DOC, λ_{ex} = 360 nm. [**PEnNa**] (n = 5, 7) = 1.0 μM, [**PPECOONa**] = 5 μM in repeat unit.

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