SUPPLEMENTARY INFORMATION

Description of Synthesis Procedures and Method of Determining Stern –Volmer Coefficients

General.

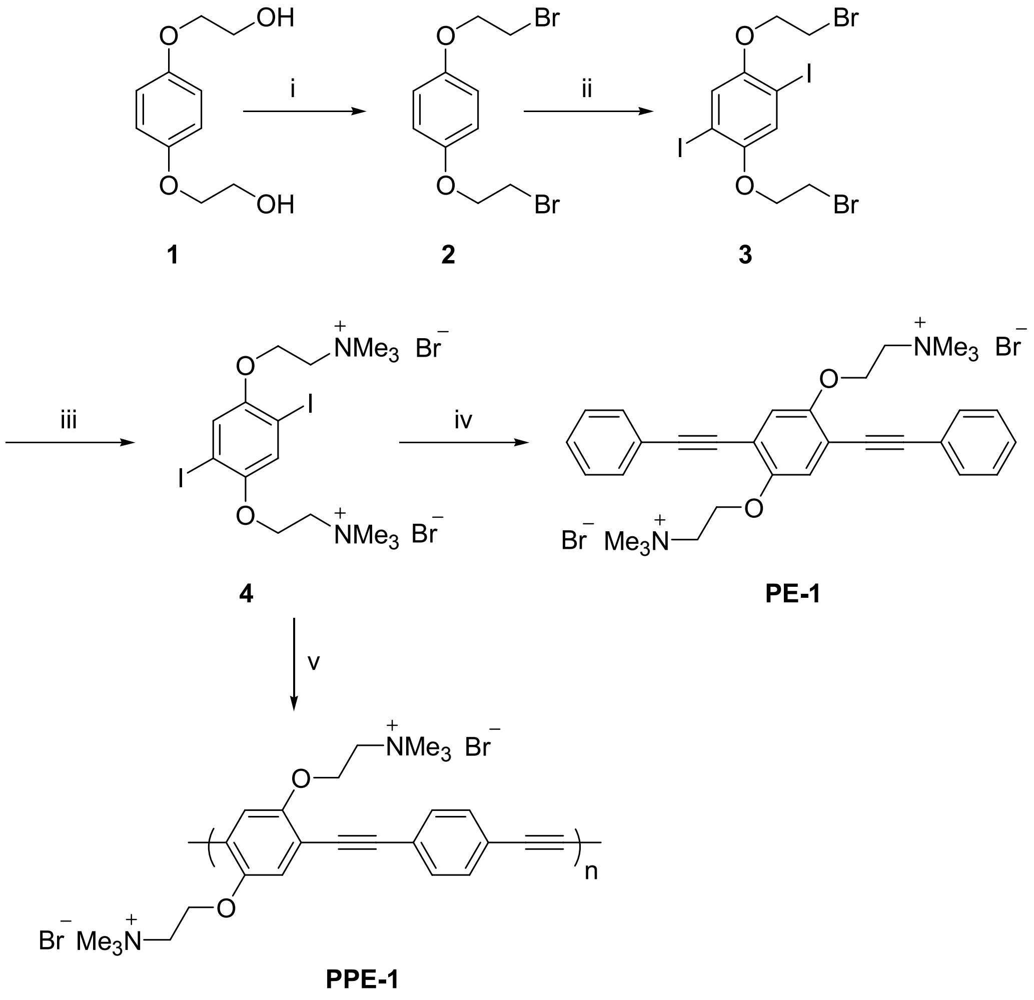
Unless indicated otherwise, all reactions requiring anhydrous conditions were performed using oven-dried glassware and conducted under a nitrogen (99.998 %) or argon (99.998 %) atmosphere and starting materials were obtained from commercial suppliers (Aldrich Chemical Company, Lancaster Synthesis, Avocado, Fisher Scientific, Strem Chemicals) and were used without further purification (in all cases purity was ≥ 98 %). All reaction temperatures recorded indicate the temperature of the bath in contact with the reaction vessel. Anhydrous solvents were prepared in accordance with known protocols; tetrahydrofuran was distilled from Na/Ph_2CO. Methanol was distilled from $CaSO_4$ and acetone from potassium carbonate. Diethyl ether was distilled from K/Na/Ph_2CO. Methylene chloride and acetonitrile were distilled from phosphorus pentoxide. All other reagents were purchased from the Aldrich Chemical Company and used as received. Melting points were obtained using a GallenKamp melting point apparatus and are uncorrected.

^{1}H-NMR and ^{13}C-NMR spectra were recorded in deuterochloroform ($CDCl_3$) on either a Jeol GSX 270 MHz or a Bruker Avance 400 MHz instrument running with a dual resonance BBO probe with z-gradients, using a residual protic solvent ($CHCl_3$, δ_H = 7.26 ppm, or $CDCl_3$, δ_C = 77 ppm, t) as internal reference, unless otherwise indicated. Chemical shifts are expressed in parts per million, (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to the indicated solvent as internal standard. Coupling constants are quoted in Hz. Splitting patterns are designated as s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet; br, broad. Infrared spectra were recorded on a Perkin-Elmer Spectrum RX FT-IR spectrometer. Potassium bromide (KBr) plates were used, and before analysis solids were dissolved in Nujol®. Mass spectra and accurate masses were recorded under CI^+, EI or FAB$^+$ conditions on a Micromass Platform II or a Micromass AUTOSPEC-Q instrument, at the Imperial College Department of Chemistry Mass Spectrometry Service facility.

All intermediates were purified by column chromatography using Kieselgel BDH F_{254} 30-70 μm grade silica gel. Solvents used were ACS grade or GPR grade. Routine monitoring of reactions was performed using analytical thin layer chromatography on pre-coated silica gel $F_{254/366}$ Merck Kieselgel 60 Å, glass-backed plates and visualised using UV light (254 nm) or the following visualisation reagents: Anisaldehyde, Permanganate and Cerium Ammonium Molybdate.

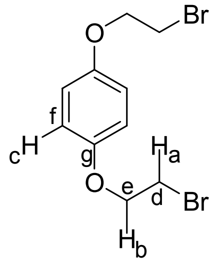
GPC analyses were performed on a Polymer Laboratories PL-GPC 50 Integrated System, running at 1.0 mL/min, equipped with two detectors (refractive and viscosity) using DMF as the eluant and two PL gel 5 μm MIXED-D columns (supplied by Polymer Laboratories) and calibrated using polystyrene standards. Ultraviolet-visible (UV-vis) measurements were conducted on a Perkin-Elmer Lambda 25 UV-vis spectrometer. Fluorescence measurements were conducted on either a Varian Cary-Eclipse Fluorescence Spectrometer with a xenon lamp as a light source or a SPEX Fluoromax-3 Spectrofluorimeter. Both absorbance and emission spectra were measured in quartz cuvettes (1 cm x 1 cm x 4.5 cm); solutions were thoroughly degassed with argon prior to use.

Synthesis of Materials



Scheme S1. **Synthetic route to model compound PE-1 and Polymer PPE-1.** Reagents and Conditions: (i) Br_2, PPh_3, CH_3CN, 20 °C, 4 h, 89%; (ii) $PhI(CF_3CO_2)_2$, I_2, CH_2Cl_2, 20 °C, 6 h, 84%; (iii) 45% NMe_3 in H_2O, EtOH, acetone, reflux, 18 h, 64%; (iv) Phenylacetylene, $Pd(PPh_3)_4$, CuI, $^{i}Pr_2NH$, MeOH/H_2O, reflux, 20 h, 75%; (v) 1,4-diethnylbenzene, $Pd(PPh_3)_4$, CuI, $^{i}Pr_2NH$, DMF, 50 °C, 24 h, 71%.

Figures for Supplementary Information



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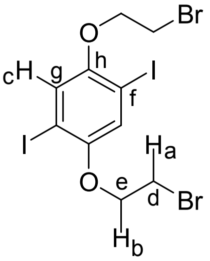

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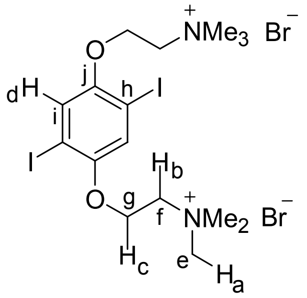

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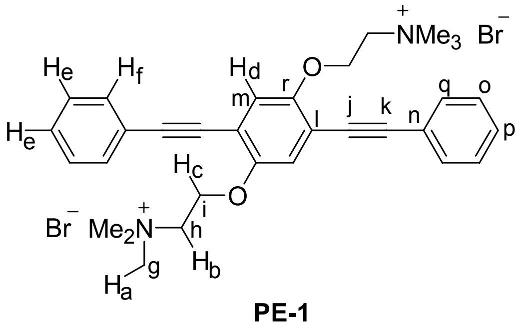
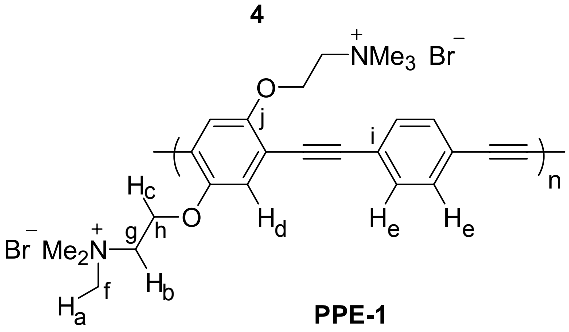


PE-1



PPE-1

1,4-Bis(2-bromoethoxy)benzene (2); procedure adapted from literature precedent.[1]

Carbon tetrabromide (40.2 g, 122 mmol, 2.40 eq) was added slowly to a solution of 1,4-bis(2-hydroxyethoxy)benzene (**1**) (10.0 g, 50.4 mmol, 1.00 eq) and triphenylphosphine (31.5 g, 120.0 mmol, 2.4 eq) in dry acetonitrile (200 mL) at 0 °C with stirring. The reaction mixture was allowed to warm to room temperature and the resulting clear solution was stirred for another 4 hours under argon. Addition of cold (~0 °C) water (200 mL) to the reaction, led to the precipitation of **2** as a white solid. The product was collected by vacuum filtration, thoroughly washed with methanol/water (100 mL, 6:4), and then recrystallised from methanol. The solid was isolated and then dried under vacuum to give **2** (14.7 g, 89%) as white needle-like crystals, m.p. 113 – 114 °C (Lit. 112 – 114 °C);[1] IR (Film) ν_{max}/cm^{-1} 730 (Ar

CH def.), 1231 (CO str.), 1461, 1377 (CH def.), 2924, 2854 (CH str.); δ_H (400 MHz, $CDCl_3$) 3.54 (4H, t, $^3J_{H-H}$ = 6.3 Hz, H_a), 4.18 (4H, t, $^3J_{H-H}$ = 6.3 Hz, H_b), 6.80 (2H, s, H_c); δ_C (100 MHz, $CDCl_3$) 29.3 (C_d), 68.8 (C_e), 116.1 (C_f), 152.9 (C_g); MS (CI, NH_3) *m/z* 326 ([M+H ($^{81}Br_2$)]), 47%, 324 ($[M+H]^+$, (^{79}Br, ^{81}Br), 100%, 322 ([M+H ($^{79}Br_2$)]), 51%. Found: $[M(^{81}Br_2)]^+$, 325.9163. $C_{10}H_{10}{}^{81}Br_2O_2$ requires: $[M(^{81}Br_2)]^+$, 326.2036. Found: $[M(^{81}Br^{79}Br)]^+$, 323.9184. $C_{10}H_{10}{}^{81}Br^{79}BrO_2$ requires: $[M(^{81}Br^{79}Br)]^+$, 324.2036. Found: $[M(^{79}Br_2)]^+$, 321.9204. $C_{10}H_{10}{}^{79}Br_2O_2$ requires: $[M(^{79}Br_2)]^+$, 322.2036.

2,5-Diiodo-1,4-bis(2-bromoethoxy)benzene (3); procedure adapted from literature precedent.[1]

A mixture of **2** (6.98 g, 21.5 mmol, 1.0 eq), bis(trifluoracetoxy)iodobenzene (10.4 g, 24.2 mmol, 1.13 eq), and iodine (5.72 g, 22.5 mmol, 1.05 eq) in dichloromethane (100 mL) was stirred at room temperature for 6 hours at which point the reaction mixture was then diluted with pentane (60 mL) and cooled in an ice/water bath, which promoted the crystallisation of **3**. An off-white crystalline product was obtained after vacuum filtration. The product was washed with cold diethyl ether (30 mL) and crystallised twice from acetone/water 90:10 (100 mL), which furnished pure **3** (10.36 g, 84%) as white needle-like crystals, m. p. 140 – 143 °C (Lit. 140 – 142 °C);[1] IR (Film) ν_{max}/cm^{-1} 722 (Ar CH def.), 1218 (CO str.), 1461, 1377 (CH def.), 2952, 2859 (CH str.); δ_H (400 MHz, $CDCl_3$): 3.59 (4H, t, $^3J_{H-H}$ = 6.4 Hz, H_a), 4.20 (4H, t, $^3J_{H-H}$ = 6.3 Hz, H_b), 7.15 (2H, s, H_c); δ_C (100 MHz, $CDCl_3$) 28.5 (C_d), 70.4 (C_e), 86.7 (C_f), 124.0 (C_g), 153.8 (C_h); MS (CI, NH_3) *m/z* (CI) 578 ([M+H ($^{81}Br_2$)]), 47%, 576 ($[M+H]^+$, (^{79}Br, ^{81}Br) 100%), 574 ([M+H ($^{79}Br_2$)]), 51%. Found: $[M(^{81}Br_2)]^+$, 577.7096. $C_{10}H_{10}{}^{81}Br_2I_2O_2$ requires: $[M(^{81}Br_2)]^+$, 577.9968. Found: $[M(^{81}Br^{79}Br)]^+$, 575.7117. $C_{10}H_{10}{}^{81}Br^{79}BrI_2O_2$ requires: $[M(^{81}Br^{79}Br)]^+$, 575.9968. Found: $[M(^{79}Br_2)]^+$, 573.7137. $C_{10}H_{10}{}^{79}Br_2I_2O_2$ requires: $[M(^{79}Br_2)]^+$, 573.9968.

1,4-Bis-(3-(trimethylammonium)ethoxy)benzene (4); procedure adapted from literature precedent.[2]

3 (5.33 g, 7.66 mmol, 1 eq) was suspended in 45 % trimethylamine in water (50 mL), ethanol (40 mL) and acetone (40 mL). The suspension was heated to 130 °C at which point the suspension clarified giving a pale yellow homogeneous solution which was refluxed for a total of 18 hours. The solution was concentrated on the rotary evaporator to yield a solid, which was recrystallised from ethanol/ether (1:1) to give **4** (5.54 g, 64%) as a white crystalline solid, m.p. 289 – 291 °C; IR (Film) ν_{max}/cm^{-1} 722 (Ar CH def.), 1198 (CO str.), 1305 (CN str.), 1461, 1377 (CH def.), 2922, 2853 (CH str.); δ_H (400 MHz, DMSO-d$_6$) 3.24 (18H, s, H$_a$), 3.84 (4H, m, H$_b$), 4.49 (4H, m, H$_c$), 7.50 (2H, s, H$_d$); δ_C (100 MHz, DMSO-d$_6$) 53.3 (C$_e$), 63.3 (C$_f$), 64.0, (C$_g$), 86.3 (C$_h$), 122.5 (C$_i$), 151.9 (C$_j$); FAB-MS: 615 $[M - {}^{79}Br^-]^+$, 43%, 613 $[M - {}^{81}Br^-]$, 45%; Found: $[M - H - {}^{79}Br^-]^+$, 614.9403. $C_{16}H_{33}{}^{81}BrI_2N_2O_2$ requires: $[M - H - {}^{79}Br^-]^+$, 614.0944; Found: $[M - H - {}^{81}Br^-]^+$, 612.9424. $C_{16}H_{33}{}^{79}BrI_2N_2O_2$ requires: $[M - H - {}^{81}Br^-]^+$, 612.0964; Anal. Calcd for $C_{16}H_{28}Br_2I_2N_2O_2$: C, 27.69; H, 4.07; N, 4.04. Found: C, 27.74; H, 3.98; N, 4.03.

2,5-Bis-(phenyethynyl)-1,4-bis(2-trimethylammonium ethoxy)benzene (PE-1); procedure adapted from literature precedent.[1]

A mixture of **4** (0.70 g, 1.00 mmol, 1.0 eq), phenylacetylene (0.36 mL, 3.32 mmol, 3.32 eq), tetrakis-(triphenylphosphine) palladium(0), Pd(PPh$_3$)$_4$, (104 mg, 90.0 μmol, 0.09 eq), copper (I) iodide (17 mg, 90.0 μmol, 0.09 eq), and diisopropylamine (5 mL) in a methanol/water mixture (40 mL, 4:1), was refluxed for 24 hours under argon with stirring. After this time, the yellow-green reaction mixture was then filtered through a short pad of celite, the solvents removed under reduced pressure, and the remaining solid was crystallised from methanol, to furnish **PE-1** (0.753 g, 75%) as a white crystalline solid, m.p. 303 – 305 °C; IR (Film) ν_{max}/cm^{-1} 722 (Ar CH def.), 1212 (CO str.), 1461, 1377 (CH def.), 1594 (C=N str.), 2959, 2860 (CH str.); δ_H (400 MHz, DMSO-d$_6$) 3.25 (18H, br s, H$_a$), 3.86-3.88 (4H, m, H$_b$), 4.59 (4H, m, H$_c$), 7.38 (2H, s, H$_d$), 7.46-7.47 (6H, m, H$_e$), 7.53-7.55 (4H, m, H$_f$); δ_C (100 MHz, DMSO-d$_6$) 53.2 (C$_g$), 62.8 (C$_h$), 63.9 (C$_i$), 85.5 (C$_j$), 95.0 (C$_k$), 112.8 (C$_l$), 116.7 (C$_m$), 121.9 (C$_n$), 128.8 (C$_o$), 128.9 (C$_p$), 131.1 (C$_q$), 152.1 (C$_r$); FAB-MS: 467 $[M\text{-}Br_2\text{-}Me]^+$, 70%; Anal. Calcd for

$C_{32}H_{38}Br_2N_2O_2 \cdot 9H_2O$: C, 51.21; H, 6.71; N, 3.73. Found: C, 51.21; H, 5.65; N, 3.74. Absorbance λ_{max} (in unbuffered water): 351 nm. Emission λ_{max} (in unbuffered water): 391 nm.

PPE-1; procedure adapted from literature precedent.[3]

Monomer **4** (1.10 g, 1.59 mmol, 1 eq) and 1,4-diethynylbenzene (0.211 g, 1.67 mmol, 1.05 eq) were dissolved in a mixture of water and DMF (16 mL, 1:1) at 50 °C in an argon-purged Schlenk flask with magnetic stirring. The resulting clear solution was deoxygenated by three cycles of the freeze-pump-thaw technique. The catalysts – consisting of tetrakis-(triphenylphosphine) palladium(0), $Pd(PPh_3)_4$, (55.0 mg, 48 μmol, 0.03 eq) and copper (I) iodide (9.0 mg, 48 μmol, 0.03 eq) in a mixture of diisopropylamine and DMF (10 mL, 1:1) – were deoxygenated as described above and quickly added to the former solution by means of a cannula. The final mixture was deoxygenated (as described above) and was then warmed to 50 °C and stirred under a positive pressure of argon for 30 hours. The resulting solution was viscous and bright yellow in colour and exhibited an intense blue fluorescence when illuminated with a near-UV lamp (excitation wavelength at 254 nm). The solution was cooled to room temperature and then slowly added to a cold (~0 °C) solution of methanol (200 mL) which prompted the precipitation of the polymer as a yellow fibre-like material. The product was re-dissolved in water (15 mL), treated with sodium sulfide (0.100 g, 1.28 mmol), and then the solution was filtered through quantitative filter paper, followed by a 10 – 20 μm fritted glass filter, and finally through a 0.8 μm nylon membrane. The polymer was dissolved in water and reprecipitated into methanol twice more to give **PPE-1** (0.637 g, 71%) as a light yellow solid; GPC (DMF, PS Standards): M_n = 7500 Da, (see main text for detail); IR (Film) ν_{max}/cm^{-1} 722 (Ar CH def.), 1155 (CO str.), 1461, 1377 (CH def.), 2924, 2854 (CH str.); δ_H (400 MHz, DMSO-d_6) 3.25 (18H, br s, H_a), 3.82 – 3.85 (4H, m, H_b), 4.49 – 4.61 (4H, m, H_c), 7.31 – 7.36 (6H, m, H_d + H_e); Due to the limited solubility of the compound, only a partial ^{13}C NMR spectrum was acquired; δ_C (100 MHz, DMSO-d_6) 53.3 (C_f), 63.3 (C_g), 64.0 (C_h), 122.5 (C_i), 151.9 (C_j).

Absorbance λ_{max} (in unbuffered water): 374 nm. Emission λ_{max} (in unbuffered water): 430 nm. DSC showed decomposition.

General Procedure for the Measurement of Stern-Volmer constants.

The Stern-Volmer coefficients were determined using the following technique: N_S moles of the sensor (**PPE-1** or **PE-1**) were dissolved into a volume V of solvent which was then divided into two smaller solutions A and B, each of volume $\frac{1}{2}V$. The quencher (dissolved in a small amount of the same solvent) was then added drop-wise to solution B, and the volume of quencher solution required to achieve full quenching (> 95 %) was determined. The same amount again of quencher solution was added to solution B, resulting in a final solution that contained exactly twice the number N_Q of moles required for full quenching of solution B alone (and therefore the appropriate amount for full quenching of the combined solutions A and B). This (double) volume of quencher solution is denoted ΔV. An identical volume ΔV of pure solvent was then added to solution A so that solutions A and B both had the total same volume $V' = \frac{1}{2}V + \Delta V$ after the addition of solvent and quencher solution respectively. Importantly, since solutions A and B contain equal concentrations of sensor (**PPE-1** or **PE-1**), drop-wise addition of B to A does not alter the sensor concentration. Solution A was then transferred to a cuvette and, using an appropriate excitation wavelength, its fluorescence intensity I_0 was measured. Small controlled volumes (V_Q) of solution B were added to solution A using a µL-resolution syringe and, after each addition of B, the fluorescence intensity $I([Q])$ was measured. This process was repeated until all of solution B had been added to solution A. If n is defined as the number of droplets of B added to A, then the quencher concentration $[Q]$ is related to n by the relation

$$[Q] = \frac{nV_Q N_Q}{V'(nV_Q + V')}$$

The Stern-Volmer coefficient may be determined from Eq. 1 using least-squares optimisation. It is common in the literature to use a linearised approach, in which k_{SV} is determined as the best-fit slope obtained from a plot of $I_0/I[Q]$ versus [Q]. This approach, however, does not take into account the existence of measurement errors in both the abscissa [Q] and the ordinate I[Q], and accordingly its use results in biased estimates of k_{SV}.[4] In this paper, we therefore use a total least squares procedure wherein the optimal value of k_{SV} is obtained by minimising the summation:

$$S = \sum_i \left[\frac{(x_i^* - x_i)^2}{\sigma_{xi}^2} + \frac{(y_i^* - y_i)^2}{\sigma_{yi}^2} \right] \tag{3}$$

where x_i and y_i represent the ordinate and abscissa of the individual experimental data points, x_i^* and y_i^* represent the optimal estimators of x_i and y_i, and σ_{xi} and σ_{yi} represent the measurement errors, which were conservatively estimated at 20 % and 5 % respectively. The estimators x_i^* and y_i^* are constrained by the Stern-Volmer relation $y_i^* = y_i^0/(1 + k_{SV} x_i^*)$. The determination of the confidence intervals for k_{SV} is problematic since closed analytical expressions are not generally available for non-linear regression.[4] We therefore used a numerical 'bootstrap' procedure to evaluate the sensitivity of the k_{SV} to random fluctuations in the experimental data.[5] The errors reported in the discussion and figures below correspond to 95 % confidence intervals for k_{SV}. Full experimental details of the procedure we use to determine the Stern-Volmer coefficients and associated confidence intervals will be described in a separate paper.[6]

REFRENCES:

1. Pinto, M. R., Kristal, B. M. & Schanze, K. S. A water-soluble poly(phenylene ethynylene) with pendant phosphonate groups. Synthesis, photophysics, and layer-by-layer self-assembled films. *Langmuir* **19**, 6523-6533 (2003).

2. McQuade, D. T., Hegedus, A. H. & Swager, T. M. Signal amplification of a "turn-on" sensor: Harvesting the light captured by a conjugated polymer. *J. Am. Chem. Soc.* **122**, 12389-12390 (2000).

3. Tan, C. Y., Pinto, M. R. & Schanze, K. S. Photophysics, aggregation and amplified quenching of a water-soluble poly(phenylene ethynylene). *Chem. Commun.*, 446-447 (2002).

4. Lybanon, M. *Am. J. Phys.* **52**, 22-26 (1984).

5. Baumann, K. Regression and calibration for analytical separation techniques. Part II: Validation, weighted and robust regression. *Process Control and Quality* **10**, 75-112 (1997).

6. George, W. N., Steinke, J. H. G. & deMello, J. C. *Manuscript in preparation*.