Click Functionalized Poly(p-phenylene ethynylene)s as Highly Selective and Sensitive Fluorescence Turn-On Chemosensors for Zn$^{2+}$ and Cd$^{2+}$ Ions

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1. Synthetic Procedures

1.1 Synthesis of PPE-1

The general synthetic route to PPE-1 is outlined in Scheme S-1. Precursors 2, 3, 6, 8, and 9 were prepared according to literature procedures with slight modifications.

**Compound 3.** Compound 2 (3.00 g, 9.26 mmol), I₂ (9.16 g, 36.1 mmol), Hg(OAc)₂ (11.4 g, 35.6 mmol) were added in CH₂Cl₂ (150 mL), and the mixture was stirred at rt overnight. The reaction mixture was then filtered through a short MgSO₄ pad. The resulting solution was sequentially washed with Na₂S₂O₃, H₂O, and dried over MgSO₄. After filtration, the solution was evaporated *in vacuo*, and the residue was recrystallized from EtOH (70 mL) to afford compound 3 as a colorless solid (16.5 g, 28.6 mmol, 56%). ¹H NMR (500 MHz, CDCl₃) δ 7.22 (s, 2 H), 4.27 (t, J = 6.33 Hz, 4 H), 3.66 (t, J = 6.29 Hz, 4 H). ¹³C NMR (75 MHz, CDCl₃) δ 152.8, 123.9, 86.6, 70.3, 28.5.

**Compound 4.** To a mixture of 3 (800 mg, 1.39 mmol), Pd(PPh₃)₂Cl₂ (20 mg, 0.028 mmol), and CuI (26 mg, 0.14 mmol) in dry THF/Et₃N (15 mL, 1:1 v/v) was dropwise added
a solution of trimethylsilylacetylene (TMSA) (408 mg, 4.17 mmol) in THF (2 mL) under constant stirring at rt under a N₂ atmosphere. After addition, the mixture was stirred at rt for 24 h. The solvent was then removed under vacuum, and the resulting solid mass was redissolved in CH₂Cl₂ and washed with H₂O. The organic layer was dried over MgSO₄, filtered, and then column chromatographed (hexanes/EtOAc 6:1) to give compound 4 as an off-white solid (613 mg, 1.19 mmol, 86%). IR (neat) 2956, 2150, 1499, 1396, 1211, 1072, 1025, 902, 840, 756 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.93 (s, 2 H), 4.28 (t, J = 6.46 Hz, 4H), 3.63 (t, J = 6.49 Hz, 4H), 0.26 (s, 18H); ¹³C NMR (75 MHz, CDCl₃) δ 153.8, 118.9, 115.0, 101.5, 100.2, 69.8, 28.8, 0.0; HRMS (EI, +eV) m/z calcd for C₂₂H₃₂Br₂O₂Si₂ 513.9995, found 513.9995 (M⁺).

**Compound 5.** To a solution of compound 4 (600 mg, 1.36 mmol) in DMF (10 mL) was added NaN₃ (486 mg, 7.49 mmol). The reaction mixture was stirred at 40 °C overnight. Cold water (5 mL) and CH₂Cl₂ (15 mL) were then added to the reaction mixture. The organic layer was separated, washed with water and brine, and dried over MgSO₄. The solvent was evaporated in vacuo to furnish 5 as colorless needle-like crystals (533 mg, 1.21 mmol, 89%). IR (neat): 2957, 2153, 2112, 1498, 1396, 1307, 1213, 1062, 1010, 939, 870, 833, 758, 696 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.94 (s, 2 H), 4.14 (t, J = 4.88 Hz, 4H), 3.60 (t, J = 4.88 Hz, 4H), 0.25 (s, 18H). ¹³C NMR (75 MHz, CDCl₃) δ 153.7, 118.1, 114.6, 101.4, 100.2, 68.7, 50.5, 0.0; HRMS (EI, +eV) m/z calcd for C₂₀H₂₈N₆O₂Si₂ 440.1812, found 440.1816 (M⁺).

**Compound 7.**

To a solution of 5 (500 mg, 1.13 mmol) and 6 (403 mg, 2.78 mmole) in dry DMF (10 mL) were added CuI (23 mg, 0.12 mmol) and ¹Pr₂EtN (17 mg, 0.13 mmol). The reaction mixture was stirred at rt for 24 h. The yellow slurry was filtered and the residue was washed with CH₂Cl₂. The filtrate was washed with satd NH₄Cl, water and brine, and then evaporated under vacuum. The residue was purified by flash column chromatography (EtOAc/hexanes, 2:1) to give compound 7 as a pale yellow solid (487 mg, 0.67 mmol, 59%). IR (neat): 2148, 1614, 1559, 1506, 1493, 1399, 1355, 1217, 1033, 942, 893, 845, 788, 754, 699 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.06 (s, 2 H), 7.70 (d, J = 8.89 Hz, 4H), 6.88 (s, 2H), 6.76 (t, J = 8.89 Hz, 4H), 4.81 (t, J = 4.78 Hz, 4H), 4.35 (t, J = 4.88 Hz, 4H), 2.98 (s, 12H), 0.25 (s, 18H); ¹³C NMR (75 MHz, CDCl₃) δ 153.3, 150.5, 148.7, 126.9, 119.7, 119.0, 117.6, 114.3, 112.52, 101.6, 100.4, 68.1, 49.7, 40.6, 0.2; HRMS (EI, +eV) m/z calcd for C₄₆H₅₀N₈O₂Si₂ 730.3595, found 730.3611 (M⁺).

**Compound 1.**

Compound 7 (450 mg, 0.61 mmole) and K₂CO₃ (237 mg, 1.72 mmol) were added to THF/MeOH (15 mL, 2:1 v/v) in a round-bottom flask, and the mixture was stirred at for
1 h. The solvent was then removed in vacuo and the residue was dissolved in CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄ and the solvent was evaporated under vacuum to give compound 1 as a pale yellow solid (275 mg, 0.47 mmol, 77%). IR (neat) 3287, 1612, 1559, 1504, 1446, 1393, 1331, 1270, 1219, 1133, 1041, 941, 865, 805, 737 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆) δ 8.33 (s, 2 H), 7.63 (d, J = 8.72 Hz, 4 H), 7.12, (s, 2 H), 6.78 (t, J = 8.75 Hz, 4 H), 4.75 (t, J = 4.71 Hz, 4 H), 4.48 (s, 2 H), 4.41 (t, J = 4.73 Hz, 4 H), 2.92 (s, 12 H); ¹³C NMR (125 MHz, DMSO-d₆) δ 152.9, 150.0, 146.9, 126.0, 120.2, 118.6, 117.5, 112.7, 112.4, 86.6, 79.4, 67.5, 48.9, 29.0; APCI-MS (+eV) calcd for C₃₄H₃₄N₈O₂ 587.3, found 587.5 (M⁺).

**PPE-1.** Compound 8 (42 mg, 0.06 mmol), compound 1 (43 mg, 0.07 mmol), compound 9 (5.0 mg, 7.5 μmol) as endcapping reagent, Pd(PPh₃)₂Cl₂ (4.0 mg, 5.7 μmole), and CuI (5.0 mg, 26.3 μmol) were dissolved in dry THF/piperidine (40 mL, 5:3 v/v). After two freeze-pump-thaw cycles to completely deoxygenate, the mixture was heated up to 60 °C and stirred at this temperature for 24 h. Afterwards the content was cooled to rt, and the solvent was evaporated off under vacuum. The residual solid mass was redissolved in CH₂Cl₂ and washed sequentially with water and brine to give a deep-red organic layer, which was concentrated to dryness and dissolved again in CH₂Cl₂. To the solution was added MeOH, and **PPE-1** was precipitated out (36 mg, 37 μmol, 56%) as a yellow-orange solid. IR (neat) 2921, 2850, 1614, 1561, 1501, 1455, 1357, 1269, 1207, 1040, 938, 858, 811, 722 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.26 (m, 2 H), 7.38 (m, 6 H), 6.98 (m, 4 H), 6.48 (m, 4 H), 4.82 (m, 4 H), 4.39 (m, 4 H), 3.91 (m, 6 H), 2.94 (m, 12 H), 1.74 (m, 2 H), 1.21 (m, 42 H), 0.85 (m, 11 H), 0.07 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 150.2, 148.6, 126.5, 112.3, 112.3, 90.1, 90.1, 69.8, 50.0, 49.6, 40.6, 40.3, 31.9, 29.6, 29.5, 29.4, 29.3, 22.7, 22.7, 14.2.

**1.2 Synthesis of PPE-2**

The general synthetic route towards **PPE-2** is described in Scheme S-2.
Scheme S-2

**Compound 11.** To a mixture of phenylacetylene (10) (255 mg, 2.50 mmol), CuI (28 mg, 0.15 mmol), and iPr₂EtN (21 mg, 0.16 mmol) in dry THF (15 mL) was dropwise added a solution of compound 5 (500 mg, 1.13 mmol) in THF (5 mL). After addition the reaction mixture was stirred at 50 °C for 24 h. The white slurry was filtered and the residue was washed with EtOAc. The filtrate was washed with satd NH₄Cl, water and brine, and then evaporated under vacuum. The resulting solid was washed with hexanes, and dried in vacuo to afford compound 11 as a pale yellow fine powder (670 mg, 1.04 mmol, 92%). IR (neat) 2961, 2142, 1498, 1402, 1260, 1214, 1023, 932, 864, 797, 756, 691 cm⁻¹; ¹H NMR (300 MHz, CD₂Cl₂) δ 8.13 (s, 2 H), 7.74 (d, J = 7.78 Hz, 4 H), 7.33 (t, J = 7.39 Hz, 4 H), 7.24 (t, J = 7.49 Hz, 2 H), 6.83 (s, 2 H), 4.75 (t, J = 4.76 Hz, 4 H), 4.28 (t, J = 4.77 Hz, 4 H), 0.15 (s, 18 H); ¹³C NMR (75 MHz, CD₂Cl₂) δ 153.6, 148.2, 131.3, 129.2, 128.5, 126.1, 121.6, 117.9, 114.6, 101.9, 100.8, 68.4, 50.3, 1.2; HRMS (EI, +eV) m/z calc C₃₆H₄₀N₆O₂Si₂ 644.2751, found 644.2753 (M⁺).

**Compound 12.** Compound 11 (600 mg, 0.93 mmol) and K₂CO₃ (629 mg, 4.56 mmol) were mixed in THF/MeOH (15 mL, 1:1 v/v) and stirred for 0.5 h. The solvent was removed in vacuo and the residue was dissolved in EtOAc and washed with water. The organic layer was dried over MgSO₄ and the solvent was evaporated under vacuum to give 12 as a pale yellow solid (433 mg, 0.860 mmol, 93%). IR (neat) 3290, 1666, 1565, 1496, 1396, 1353, 1269, 1224, 1156, 1041, 925, 869, 803, 759, 698 cm⁻¹; ¹H NMR (300 MHz, CD₂Cl₂) δ 8.14 (s, 2 H), 7.74 (d, J = 7.14 Hz, 4 H), 7.34 (t, J = 7.03 Hz, 4 H), 7.24 (t, J = 7.22 Hz, 2 H), 6.88 (s,
2H), 4.74 (t, J = 4.74 Hz, 4H), 4.27 (t, J = 4.97 Hz, 4H), 3.38 (s, 2H); $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) δ 153.9, 147.9, 131.3, 129.2, 128.4, 125.9, 122.0, 118.2, 113.9, 83.8, 79.6, 68.3, 50.1; APCI-MS (+eV) m/z calcd for C$_{30}$H$_{24}$N$_6$O$_2$ 500.2, found 501.4 (M + H)$^+$.  

**PPE-2.** Compound 8 (70 mg, 0.11 mmol), compound 12 (60 mg, 0.12 mmol), compound 9 (6.5 mg, 0.02 mmol) as endcapping reagent, Pd(PPh$_3$)$_2$Cl$_2$ (1.5 mg, 0.01 mmol), and CuI (6 mg, 0.03 mmol) were dissolved in dry THF/piperidine (40 mL, 5:3 v/v). After two freeze-pump-thaw cycles to deoxygenate, the content was heated up to 60 °C. The reaction mixture was stirred for 24 h at this temperature, and then cooled down to rt. The solvent was evaporated off under vacuum and the residual solid mass was dissolved in CH$_2$Cl$_2$ and washed sequentially with 1% HCl and satd NH$_4$Cl solution to give a deep-red organic layer, which was concentrated to dryness and dissolved again in CH$_2$Cl$_2$. To the organic solution was added MeOH to precipitate out PPE-2 (69 mg, 0.08 mmol, 65%) as a deep-yellow solid. IR (neat) 2921, 2851, 1562, 1498, 1459, 1423, 1369, 1269, 1210, 1040, 920, 857, 761, 693 cm$^{-1}$; $^1$H NMR (300 MHz, CD$_2$Cl$_2$) δ 8.34 (m, 2 H), 7.79 (m, 2 H), 4.77 (m, 4 H), 4.33 (m, 4 H), 3.86 (m, 6 H), 1.68 (m, 9 H), 1.13 (m, 42 H), 0.76 (m, 12 H), 0.19 (m, 1 H); $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) δ 148.0, 148.0, 129.0, 128.2, 126.1, 125.8, 125.7, 125.7, 122.3, 122.2, 70.3, 70.1, 50.2, 32.3, 32.3, 30.03, 29.99, 29.74, 29.73, 26.5, 23.11, 23.08, 14.3.  

1.3 Synthesis of PPE-3

The general synthetic route towards PPE-3 is described in Scheme S-3. Precursor 16 was prepared according to the literature procedure.
**Supporting Information**  
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**Compound 15.** 4-(\(N,N\)-dimethylamino)benzoic acid (13) (902 mg, 5.47 mmol), 2,5-diiodohydroquinone (14) (900 mg, 2.47 mmol) were dissolved in pyridine (15 mL) and the mixture was cooled down to 0 °C. To the mixture, a solution of SOCl₂ (650 mg, 5.47 mmol) dissolved in pyridine (5 mL) was slowly added. The reaction mixture was stirred at rt overnight and then a large amount of cold water was added. White precipitate was formed and collected through vacuum filtration. The resulting solid mass was washed several times with MeOH to give compound 15 (729 mg, 1.11 mmol, 45%) as an off-white solid. IR (neat) 1725, 1605, 1537, 1451, 1378, 1269, 1160, 1040, 991, 945, 823, 755, 692 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.12-8.09 (d, \(J = 9.06\) Hz, 4H), 7.71 (s, 2H), 6.74-6.71 (d, \(J = 9.10\) Hz, 4H), 3.10 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 164.2, 154.0, 149.6, 132.7, 132.4, 115.0, 110.9, 90.1, 40.1; HRMS (EI, +eV) \(m/z\) calcd for C₂₄H₂₂I₂N₂O₄ 655.9669, found 655.9665 (M⁺).

**PPE-3.** Compound 15 (80 mg, 0.12 mmol), compound 16 (61 mg, 0.13 mmol), compound 9 (9.0 mg, 0.01 mmol) as endcapping reagent, Pd(PPh₃)₂Cl₂ (8.0 mg, 0.011 mmol), and CuI (5.0 mg, 0.026 mmol) were dissolved in dry THF/piperidine (50 mL, 5:3 v/v). After deoxygenation by two freeze-pump-thaw cycles, the content was heated up to 50 °C and stirred for 24 h at this temperature. Aterwards, the reaction mixture was cooled down to rt, and the solvent was evaporated off under vacuum. The residual solid mass was dissolved in CH₂Cl₂ and washed sequentially with water and brine to give a deep-red organic layer, which was concentrated to dryness and redissolved in CH₂Cl₂. To the resulting solution was added MeOH to precipitate out PPE-3 (97 mg, 0.08 mmol, 72%) as a green-orange solid. IR (neat): 2923, 2853, 1722, 1603, 1539, 1500, 1458, 1426, 1374, 1269, 1211, 1160, 945, 854 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.97 (m, 8 H), 6.70 (m, 4 H), 4.00 (m, 32 H), 3.09 (m, 12 H), 2.04 (m, 18H), 1.27 (m, 196 H), 0.86 (m, 45 H), 0.26 (m, 5 H).

**1.4 Synthesis of PPE-4**

The general synthetic route towards PPE-4 is described in Scheme S-4. Precursor 17 was prepared according to the literature procedure.

**Scheme S-4**
PPE-4. Compound 17 (108 mg, 0.17 mmol), compound 1 (98 mg, 0.17 mmol), Pd(PPh₃)₂Cl₂ (15 mg, 0.021 mmol) and CuI (7 mg, 0.04 mmol) were suspended in a mixture solvent of DMF/H₂O/i-Pr₂EtN (10 mL, 3:2:1 v/v) under nitrogen atmosphere. The mixture was stirred at 50 °C for 12 h, and then the reaction mixture was cooled down to rt and slowly added to MeOH/acetone/ether (100 mL, 1:4:5 v/v). The formed precipitate was isolated by centrifugation and then redissolved in water/MeOH (20 mL, 7:3 v/v). To the solution was added Na₂S (100 mg, 1.82 mmol), and the mixture was filtered. To the filtrate was slowly added MeOH/acetone/Et₂O (200 mL, 1:4:5 v/v). The precipitate was collected by centrifugation to afford PPE-4 (147 mg, 0.12 mmol, 70%) as a deep red powder. IR (neat) 2922, 2850, 1659, 1613, 1500, 1360, 1325, 1204, 1040, 942, 815, 783 cm⁻¹. ¹H NMR (500 MHz, DMSO-d₆) δ 7.70-7.36 (m, 10H), 7.31 (s, 2H), 6.60-6.47 (m 2H), 4.98-4.69 (m, 4H), 4.63-4.40 (m, 4H), 4.19-3.92 (m, 8H), 2.91-2.83 (m, 12H), 2.35-2.24 (m, 4H). Meaningful ¹³C NMR spectrum was not obtained due to limited solubility in water and other organic solvents.

1.5 Synthesis of 4-(1-decyl-1 H-1,2,3-triazol-4-yl-N,N-dimethylaniline (18)

![Chemical Structure](image)

4-Ethynyl-N,N-dimethylaniline 6 (157 mg, 1.08 mmol) and n-decylazide (198 mg, 1.08 mmol) were dissolved in dry DMF (5 mL) under nitrogen protection. CuI (25 mg, 0.12 mmol) and i-Pr₂EtN (21 mg, 0.16 mmol) were added to the mixture. The reaction mixture stirred at 50 °C for 12 h. The reaction mixture was filtered and the residue was washed with ethyl acetate. The filtrate was washed with water and brine, and then dried under vacuum. Flash column chromatography with ethyl acetate/hexanes (2:3) as eluent gave 18 as a light brown solid (228 mg, 0.70 mmol, 65%). ¹H NMR (300 MHz, CDCl₃) δ 7.71 (d, J = 8.81 Hz, 2H), 7.60, (s, 1H), 6.78 (t, J = 8.82 Hz, 2H), 4.36 (t, J = 7.19 Hz, 2H), 1.95-1.90 (m, 2H), 1.34-1.25 (m, 14H), 0.87 (t, J = 6.38 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 150.4, 130.5, 126.6, 117.9, 112.5, 110.6, 50.4, 40.5, 31.9, 30.4, 29.5, 29.4, 29.3, 29.1, 26.6, 22.7, 14.1.
2. UV-Vis and Fluorescence Spectroscopic Analyses

2.1 UV/Vis and fluorescence spectroscopic data for polymers and model compound 18

Fig. S – 1: UV-Vis absorption of spectra of PPE-1, PPE-2, and PPE-3 (concentration: 100 μg/mL) measured in THF at 298 ± 2 K.

Fig. S – 2: UV-Vis absorption (left) and fluorescence (right, λ<sub>ex</sub> = 280 nm) spectra of 4-(1-decyl-1 H)-1,2,3-triazol-4-yl-N,N-dimethylaniline (18) at concentration of 5.9 × 10<sup>-5</sup> M in THF at 298 ± 2 K.
**Supporting Information**

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**Fig. S – 3:** Fluorescence titration of **PPE-2** (concentration: 100 µg/mL) with model compound, 4-(1-decyl-1 H-1,2,3-triazol-4-yl-N,N-dimethylanilinein (18), in THF at 298 ± 2 K. λ<sub>ex</sub> = 400 nm. Concentrations of model compound **18**: 0.0, 0.08, 0.48, 1.68, 2.08, 2.48, 2.88, 3.28, 6.48, and 9.28 mM. The arrow indicates the direction of spectral response to increasing addition of **18**. Inset: Stern-Volmer plot calculated from emission titration at λ = 469 nm.

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**Fig. S – 4:** UV-Vis absorption spectral changes of **PPE-2** (concentration: 100 µg/mL) upon addition of model compound, 4-(1-decyl-1 H-1,2,3-triazol-4-yl-N,N-dimethylanilinein (18), in THF at 298 ± 2 K. Concentrations of model compound **18**: 0.0, 0.08, 0.48, 1.68, 2.08, 2.48, 2.88, 3.28, 6.48, and 9.28 mM. The arrows indicate the direction of spectral response to increasing addition of **18**.

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2.2 UV/Vis and fluorescence titrations of PPE-1 with various cationic species

Fig. S-5: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-1 (100 μg/mL) obtained simultaneously as a function of increasing aliquots of Ba(OTf)₂ in THF at 298 ± 2 K. Concentrations of Ba(OTf)₂: 0.0, 1.0 × 10⁻⁴, 2.0 × 10⁻⁴, 3.7 × 10⁻⁴, 5.3 × 10⁻⁴, 8.0 × 10⁻⁴, 1.1 × 10⁻³, 1.6 × 10⁻³ M. λₑₓ = 380 nm. The arrows indicate the direction of spectral response to increasing addition of analyte. Inset: Stern-Volmer plot calculated from emission titration at λ = 475 nm.
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Fig. S – 6: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-1 (100 μg/mL) obtained simultaneously as a function of increasing aliquots of Cd(ClO₄)₂ in THF at 298 ± 2 K. Concentrations of Cd(ClO₄)₂: 0.0, 3.3 × 10⁻⁶, 1.0 × 10⁻⁵, 3.0 × 10⁻⁵, 9.0 × 10⁻⁵, 4.3 × 10⁻⁵, 6.3 × 10⁻⁵ M. λₑₓ = 380 nm. The arrows indicate the direction of spectral response to increasing addition of analyte. Inset: Stern-Volmer plot calculated from emission titration at λ = 475 nm.

Fig. S – 7: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-1 (100 μg/mL) obtained simultaneously as a function of increasing aliquots of Cu(OTf)₂ in THF at 298 ± 2 K. Concentrations of Cu(OTf)₂: 0.0, 1.0 × 10⁻⁵, 2.7 × 10⁻⁵, 4.7 × 10⁻⁵, 7.3 × 10⁻⁵ M. λₑₓ = 380 nm. The arrows indicate the direction of spectral response to increasing addition of analyte. Inset: Stern-Volmer plot calculated from emission titration at λ = 475 nm.
Fig. S - 8: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-1 (100 µg/mL) obtained simultaneously as a function of increasing aliquots of TFA in THF at 298 ± 2 K. Concentrations of TFA: 0.0, 6.7 x 10^{-6}, 1.7 x 10^{-5}, 2.7 x 10^{-5}, 6.0 x 10^{-5}, 7.7 x 10^{-5}, 1.0 x 10^{-4}, 1.4 x 10^{-4}, 1.7 x 10^{-4}, 2.1 x 10^{-4} M. λ_{ex} = 380 nm. The arrows indicate the direction of spectral response to increasing addition of analyte. Inset: Stern-Volmer plot calculated from emission titration at λ = 475 nm.

Fig. S - 9: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-1 (100 µg/mL) obtained simultaneously as a function of increasing aliquots of NaClO₄ in THF at 298 ± 2 K. Concentrations of NaClO₄: 0.0, 3.3 x 10^{-5}, 1.7 x 10^{-4}, 3.0 x 10^{-4}, 5.7 x 10^{-4}, 9.7 x 10^{-4} M. λ_{ex} = 380 nm. The arrows indicate the direction of spectral response to increasing addition of analyte. Inset: Stern-Volmer plot calculated from emission titration at λ = 475 nm.
Fig. S - 10: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-1 (100 µg/mL) obtained simultaneously as a function of increasing aliquots of LiOTf in THF at 298 ± 2 K. Concentrations of LiOTf: 0.0, 3.3 × 10^{-5}, 1.3 × 10^{-4}, 2.6 × 10^{-4}, 4.7 × 10^{-4}, 6.7 × 10^{-4}, 1.53 × 10^{-3}, 2.13 × 10^{-3}, 4.68 × 10^{-3} M. λ_{ex} = 380 nm. The arrows indicate the direction of spectral response to increasing addition of analyte. Inset: Stern-Volmer plot calculated from emission titration at λ = 475 nm.

Fig. S - 11: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-1 (100 µg/mL) obtained simultaneously as a function of increasing aliquots of Zn(OTf)_{2} in THF at 298 ± 2 K. Concentrations of Zn(OTf)_{2}: 0.0, 3.3 × 10^{-6}, 1.0 × 10^{-5}, 3.0 × 10^{-5}, 1.7 × 10^{-4}, 8.3 × 10^{-4}, 1.1 × 10^{-3}, 1.5 × 10^{-3}, 3.4 × 10^{-3}, 6.2 × 10^{-3} M. λ_{ex} = 380 nm. The arrows indicate the direction of spectral response to increasing addition of analyte. Inset: Stern-Volmer plot calculated from emission titration at λ = 475 nm.
2.3 Fluorescence titrations of PPE-1/SDS with Cd\(^{2+}\) in water

![Fluorescence spectra graph](image)

Fig. S - 12: Fluorescence spectra of PPE-1 (100 µg/mL) obtained simultaneously as a function of increasing aliquots of Cd(ClO\(_4\))\(_2\) in DMSO/water (1:1, v/v) and in the presence of SDS (0.5 mg/mL) at 298 ± 2 K. Concentrations of Cd(OTF)\(_2\): 0.0, 2.4 × 10\(^{-3}\), 4.4 × 10\(^{-3}\), 8.4 × 10\(^{-3}\), 1.6 × 10\(^{-2}\), 3.0 × 10\(^{-2}\), 5.0 × 10\(^{-2}\) M. \(\lambda_{ex} = 425\) nm. The arrow indicates the direction of spectral response to increasing addition of analyte.
2.4 UV/Vis and fluorescence titrations of PPE-4 with various cation species in water

![UV-Vis absorption and fluorescence spectra of PPE-4](image)

Fig. S-13: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-4 (100 µg/mL) obtained simultaneously as a function of increasing aliquots of TFA in water at 298 ± 2 K. Concentrations of TFA: 0.0, 1.2 x10^{-4}, 1.6 x10^{-4}, 1.8 x10^{-4}, 2.4 x10^{-4}, 3.2 x10^{-4}, 4.0 x10^{-4}, 4.4 x10^{-4}, 4.8 x10^{-4}, 5.2 x10^{-4}, 5.6 x10^{-4}, 6.4 x10^{-4}, 8.0 x10^{-4}, 8.0 x10^{-3}, 1.0 x10^{-3}, 1.5 x10^{-3}, and 2.0 x10^{-3} M. λ_{ex} = 400 nm. The arrows indicate the direction of spectral response to increasing addition of analyte. Inset: Stern-Volmer plot calculated from emission titration at λ = 490 nm.
Fig. S – 14: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-4 (100 µg/mL) obtained simultaneously as a function of increasing aliquots of Cd(ClO₄)₂ in water at 298 ± 2 K. Concentrations of Cd(ClO₄)₂: 0.0, 2.0 × 10⁻³, 2.4 × 10⁻³, 2.8 × 10⁻³, 3.2 × 10⁻³, 3.6 × 10⁻³, 4.0 × 10⁻³, 4.8 × 10⁻³, 6.0 × 10⁻³, 8.0 × 10⁻³, 1.2 × 10⁻², 2.0 × 10⁻², and 2.8 × 10⁻² M. λ<sub>ex</sub> = 400 nm. The arrows indicate the direction of spectral response to increasing addition of analyte. Inset: Stern-Volmer plot calculated from emission titration at λ = 490 nm.

Fig. S – 15: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-4 (100 µg/mL) obtained simultaneously as a function of increasing aliquots of Cu(OTf)₂ in water at 298 ± 2 K. Concentrations of Cu(OTf)₂: 0.0, 8.0 × 10⁻⁴, 2.4 × 10⁻³, 5.6 × 10⁻³, 1.2 × 10⁻², 2.5 × 10⁻², 5.0 × 10⁻², and 0.1 M. λ<sub>ex</sub> = 400 nm. The arrows indicate the direction of spectral response to increasing addition of analyte.
Fig. S–16: UV-Vis Absorption (left) and fluorescence (right) spectra of PPE-4 (100 µg/mL) obtained simultaneously as a function of increasing aliquots of LiOTf in water at 298 ± 2 K. Concentrations of LiOTf: 0.0, 8.0 x 10^{-4}, 2.4 x 10^{-3}, 5.6 x 10^{-3}, 1.2 x 10^{-2}, 2.5 x 10^{-2}, 5.0 x 10^{-2} M. \( \lambda_{ex} = 400 \) nm. The arrows indicate the direction of spectral response to increasing addition of analyte.

Fig. S–17: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-4 (100 µg/mL) obtained simultaneously as a function of increasing aliquots of Zn(OTf)\(_2\) in water at 298 ± 2 K. Concentrations of Zn(OTf)\(_2\): 0.0, 8.0 x 10^{-4}, 2.4 x 10^{-3}, 5.6 x 10^{-3}, 1.2 x 10^{-2}, 2.6 x 10^{-2} M. \( \lambda_{ex} = 400 \) nm. The arrows indicate the direction of spectral response to increasing addition of analyte.
Fig. S – 18: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-4 (100 μg/mL) obtained simultaneously as a function of increasing aliquots of Ba(OTf)$_2$ in water at 298 ± 2 K. Concentrations of Ba(OTf)$_2$: 0.0, 8.0 ×10$^{-4}$, 2.4 ×10$^{-3}$, 5.6 ×10$^{-3}$, 1.2 ×10$^{-2}$, 2.5 ×10$^{-2}$, 5.0 ×10$^{-2}$ M. $\lambda_{\text{ex}} = 400$ nm. The arrows indicate the direction of spectral response to increasing addition of analyte.

Fig. S – 19: UV-Vis absorption (left) and fluorescence (right) spectra of PPE-4 (100 μg/mL) obtained simultaneously as a function of increasing aliquots of NaOTf in water at 298 ± 2 K. Concentrations of NaOTf: 0.0, 6.5 ×10$^{-3}$, 1.3 ×10$^{-2}$, 2.8 ×10$^{-2}$, 6.0 ×10$^{-2}$, 0.12, 0.18, and 0.38 M. $\lambda_{\text{ex}} = 400$ nm. The arrows indicate the direction of spectral response to increasing addition of analyte.
3. UV-Vis, Fluorescence Spectroscopic Data and SPECFIT analysis for Compound 1

Fig. S - 20: UV-Vis absorption (left) and fluorescence (right, $\lambda_{ex} = 375$ nm) spectra of compound 1 ($1.5 \times 10^{-5}$M) measured in DMSO at 298 ± 2 K.
Fig. S-21: (A) Concentration profiles of colorful species extracted from the global fit (SPECFIT) using 1:[Cd$^{2+}$]$_4$ model of binding. (B) Deconvoluted absorption spectra of prevailing colorful species at different stages of titration. (C) Change in absorbance at $\lambda = 292$ nm after each addition of [Cd(ClO$_4$)$_2$] and the corresponding fit.
4. Proposed Fluorescence Quenching Mechanism for PPE-1

The substantial fluorescence quenching observed for PPE-1 is rationalized by the following photophysical mechanism.

The proposed mechanism is consistent with the observation that PPE-1 shows a very weak charge-transfer (CT) emission band at $\lambda_{em} = 462$ nm and $\Phi = 0.038$ (see Figure 1A of the paper). Similar CI emission bands are observed in the fluorescence spectra of model compound 1 (Figure S-20) and 18 (Figure S-2), the structures of which contain both dimethylamino and triazole groups. Furthermore, a Stern-Volmer quenching study was conducted between another reference polymer, PPE-2, with compound 18 as quencher (Q). The data shown in Figure S-2 clearly indicate that there is dynamic and static quenching with increasing [Q]. UV-Vis absorption spectra taken over the course of the quenching experiment (Figure S-4) also reveal a low energy transition assigned to an outer sphere CT adduct, between PPE-2 and compound 18. Based on these experimental data, the above proposed photophysical mechanism is believed to be reasonable. Detailed photophysical investigations are currently underway and will be reported in due course.
5. NMR Spectra for New Compounds
Fig. S – 22: $^1$H NMR (300 MHz, CDCl$_3$) spectrum of compound 4.
Fig. S - 23: $^{13}$C NMR (75 MHz, CDCl$_3$) spectrum of compound 4.
Fig. S - 24: $^1$H NMR (300 MHz, CDCl$_3$) spectrum of compound 5.
Fig. S - 25: $^{13}$C NMR (75 MHz, CDCl$_3$) spectrum of compound 5.
Fig. S - 26: $^1$H NMR (300 MHz, CDCl$_3$) spectrum of compound 7.
Fig. S - 27: $^{13}$C NMR (75 MHz, CDCl$_3$) spectrum of compound 7.
Fig. S - 28: $^1$H NMR (300 MHz, CDCl$_3$) spectrum of compound 11.
Fig. S - 29: $^{13}$C NMR (75 MHz, CDCl$_3$) spectrum of compound 11.
Fig. S – 30: $^1$H NMR (300 MHz, CD$_2$Cl$_2$) spectrum of compound 12.
Fig. S-31: $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) spectrum of compound 12.
Fig. S – 32: $^1$H NMR (500 MHz, DMSO-$d_6$) spectrum of compound 1.
Fig. S - 33: $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectrum of compound 1.
Fig. S - 34: $^1$H NMR (300 MHz, CDCl$_3$) spectrum of compound PPE-1.
Fig. S - 35: $^{13}$C NMR (75 MHz, CDCl$_3$) spectrum of compound PPE-1.
Fig. S – 36: $^1$H NMR (300 MHz, CD$_2$Cl$_2$) spectrum of compound PPE-2.
Fig. S-37: $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) spectrum of compound PPE-2.
Fig. S-38: $^1$H NMR (300 MHz, CDCl$_3$) spectrum of compound PPE-3.
Fig. S - 39: $^1$H NMR (500 MHz, DMSO-$d_6$) spectrum of compound PPE-4.