Analyte-Induced Aggregation of Conjugated Polyelectrolyte: Role of the Charged Moieties and Its Sensing Application

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

Sample Preparation. The \textit{in situ} premodification reaction of taurine and OPA was performed as the following procedures: stock solutions of taurine and OPA were mixed at 25 °C to give a mixture with the molar ratio of OPA to taurine, 1.5:1, in 20 mM borate buffer (pH = 9.0).

Control experiments for addressing the specificity of PMTPA toward taurine were carried out under the identical conditions. Sulfur-containing amino acids, Met, Cys, Hcy, Cyt, and aromatic acids, Trp and Tyr were premodified by reacting with OPA for 3 min, respectively, and then the probe PMTPA was added into the OPA/analyte mixture to give a solution containing 0.1 mM PMTPA, 0.5 mM analyte and 0.75 mM OPA. After 5 min, the sample was measured by UV-visible spectrometer.

For NMR measurements, equimolar amount of taurine or β-Ala and OPA (1.0 × 10\textsuperscript{-3} M) was reacted for 48 h at 25°C in 20 mM borate buffer (pH = 9.0). Then the reaction mixture
was sent to be freezing-dried and the obtained powder was dissolved in deuterated water for NMR measurements. PI-taurine: $^1$H NMR (D$_2$O, 300 MHz) ($\delta$): 7.37-7.59 (m, 4H), 4.49 (s, 2H), 3.86 (t, 2H), 3.13 (t, 2H); PI-$\beta$-Ala: $^1$H NMR (D$_2$O, 300 MHz) ($\delta$): 7.42-7.63 (m, 4H), 4.47 (s, 2H), 3.74 (t, 2H), 2.45 (t, 2H).

**Measurements.** Absorption spectra were collected by using a Hitachi 3010 UV-visible spectrometer. $^1$H-NMR spectra were carried out on a JNM-ECA300 spectrometer (JEOL).

Reference


**Fig. S1** Variation in the absorption spectra of PMTPA (1.0 × 10$^{-4}$ M) in 20 mM borate buffer (pH = 9.0) with increasing concentrations of taurine as indicated.
Fig. S2 $^1$H-NMR spectra of the phthalimidine derivative of taurine (PI-taurine). Solvent: D$_2$O.

Fig. S3 Absorption spectra of PMTPA ($1.0 \times 10^{-4}$ M) in 20 mM borate buffer (pH = 9.0) in the absence and the presence of sulfur-containing amino acids as indicated.
Fig. S4 $^1$H-NMR spectra of the phthalimidine derivative of β-Ala (PI-β-Ala). Solvent: D$_2$O.

Fig. S5 Absorption spectra of PMTPA (1.0 × 10$^{-4}$ M) in borate buffer in the absence and the presence of PI-taurine and PI-β-Ala. [OPA] = 1.0 × 10$^{-4}$ M, [β-Ala] = [taurine] = 5.0 × 10$^{-4}$ M.
**Fig. S6** Relative absorbance of PMTPA (1.0 × 10⁻⁴ M) in the presence of OPA (7.5 × 10⁻⁴ M) and Met, Cys, Hcy, Cyt, Trp, Tyr and taurine in borate buffer (pH = 9.0). [amino acids] = 5.0 × 10⁻⁴ M.

**Fig. S7** Fluorescence quenching of PMTPA (1.0 × 10⁻⁵ M) by PI-taurine at various concentrations. The fluorescence quenching \( QI = [(I_0 - I)/I_0] \times 100\% \); \( I_0 \) is the fluorescence intensity at 552 nm of a solution of PMTPA (1.0 × 10⁻⁵ M); \( I \) is the fluorescence intensity at 552 nm of a solution of PMTPA (1.0×10⁻⁵ M) in the presence of different amounts of taurine. Inset: plot of \( QI \) vs taurine concentration at lower concentration. Excitated wavelength \( \lambda_{ex} = 450 \) nm.