Novel functionalized conjugated polypyrene with polyacrylate: synthesis, electrochemistry, luminescence, and chemical sensing properties

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The fluorescence quantum yield ($\Phi$) of soluble Py-PAA, PPy-AA and PPy-PAA were measured and calculated according to the well-known method given as:

$$\Phi = \Phi_{ref} \frac{n^2 A_{ref} I}{n_{ref}^2 A_{ref}}$$

(1)

where $\Phi_{ref}$ denotes the reference, $n$ is the refractive index of the solvent, $A$ is the absorbance at the excitation wavelength, and $I$ is the intensity of the emission spectrum. Here, we use anthracene in acetonitrile ($\Phi_{ref} = 0.27$) as the reference [1]. It is worth mentioning that absorbance of the sample and the reference should be similar and small (<0.10) [2].

The fluorescence quantum efficiency of Py-PAA, PPy-AA and PPy-PAA-2 in THF were measured to be 0.39, 0.55 and 0.66 respectively according to Eq.(1).

The molecular weight measurements of PPy-AA and PPy-PAA-2 were determined by gel permeation chromatography (GPC) with tetrahydrofuran as the solvent. From GPC results, PPy-AA showed its number-average molar mass ($M_n$) of about 4211 and weight-average molar mass ($M_w$) of 7582 ($M_w/M_n$=1.80) in tetrahydrofuran. The PPy-PAA-2 showed $M_n$=11366 and $M_w$=16902 ($M_w/M_n$=1.48).
Fig. S1. IR spectra of 6-bromo-1-(pyren-1-yl)hexan-1-one (a) and 1-(6-Bromohexyl) pyrene (b).
Fig. S2. CVs of PPy-AA (A) and PPy-PAA-1 (B) films prepared from DCM containing Bu$_4$NPF$_6$ (0.1 M) in concentrated sulfuric acid at potential scan rates of (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, and (f) 300 mV s$^{-1}$. Inset: plots of redox peak current densities vs. potential scan rates. $j_p$ is the peak current density: $j_{p,a}$ and $j_{p,c}$ denote the anodic and cathodic peak current densities, respectively.
Fig. S3. Solid-state UV–vis spectra and emission spectra of PPy-PAA-1 deposited on the ITO electrode. Inset: Photograph of PPy-PAA-1 under 365 nm UV irradiation.
Fig. S4 Fluorescence emission spectra of PPy-PAA-2 ($1 \times 10^{-6}$ M) in THF in the presence of different amounts of metal ions. Excitation wavelength: 363 nm.
Fig. S5 Fluorescence Emission spectra of PPy-PAA-2 (1×10⁻⁶ M) in THF in the presence of different metal ions (5.67×10⁻⁷ mol/L), A: PPy-PAA-2, B: PPy-PAA-2 + cation without Fe³⁺, C: PPy-PAA-2 + all cation. Excitation wavelength (nm): 363.
Fig. S6 Fluorescence emission response profiles of PPy-PAA-2 + Fe$^{3+}$ in THF after added Fe$^{3+}$ ($5.67 \times 10^{-7}$ mol L$^{-1}$), and turned on by different anions ($3.5 \times 10^{-5}$ mol L$^{-1}$). Insert: fluorescence images in the presence of different metal anions. A) PPy-PAA, B) PPy-PAA-2 + Fe$^{3+}$, C) Pi, D) NO$_2^-$, E) SO$_3^{2-}$, F) S$_2$O$_3^{2-}$, G) I$^-$, H) Cl$^-$, I) SO$_4^{2-}$, J) CO$_3^{2-}$, K) F$^-$, L) HCO$_3^-$, M) NO$_3^-$, N) Br$^-$. The polymer concentration was $1.0 \times 10^{-6}$ mol L$^{-1}$. Excitation wavelength (nm): 363.
Fig. S7 Fluorescence emission spectra of PPy (1 × 10⁻⁶ M, figure A) and PPy-AA (5 × 10⁻⁶ M, figure B) in THF in the presence of different amounts of Fe³⁺. Inset: fluorescence response of PPy and PPy-AA to Fe³⁺. Excitation wavelength (nm): 317 for PPy and 355 for PPy-AA.

The quenching efficiency of PPy, PPy-AA and PPy-PAA-2 were nearly fit to the Stern–Volmer equation, \( I_0/I = K_{SV}[A] + 1 \), which related the fluorescence intensity, I,
at different concentrations of analyte quencher, [A], where \( I_0 \) was the intensity at [A] = 0, and \( K_{SV} \) was the Stern–Volmer constant. According to the fluorescence titration of PPy, PPy-AA and PPy-PAA in THF solutions with Fe\(^{3+}\), \( K_{SV} \) were determined to be \( 8.6 \times 10^3 \) M\(^{-1}\) for PPy, \( 8.0 \times 10^4 \) M\(^{-1}\) for PPy-AA and \( 4.7 \times 10^5 \) M\(^{-1}\) for PPy-PAA-2, respectively.

Reference:
