

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

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

$$\Phi = \Phi_{\text{ref}}(n^2 A_{\text{ref}} I / n_{\text{ref}}^2 A I_{\text{ref}}) \quad (1)$$

where 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 ($\Phi_{\text{ref}} = 0.27$) 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 $M_w=16902$ ($M_w/M_n=1.48$).

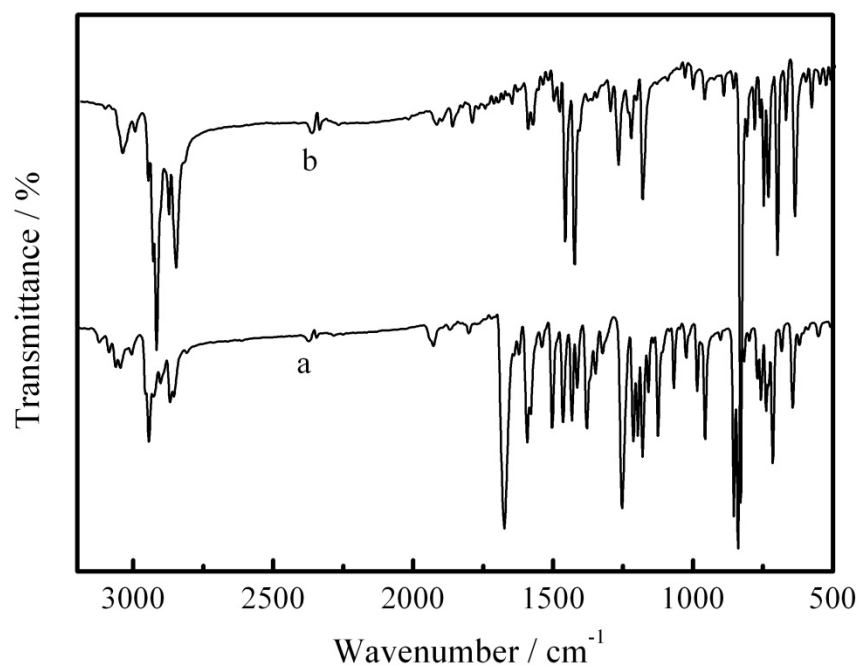


Fig. S1. IR spectra of 6-bromo-1-(pyren-1-yl)hexan-1-one (a) and 1-(6-Bromohexyl)pyrene (b).

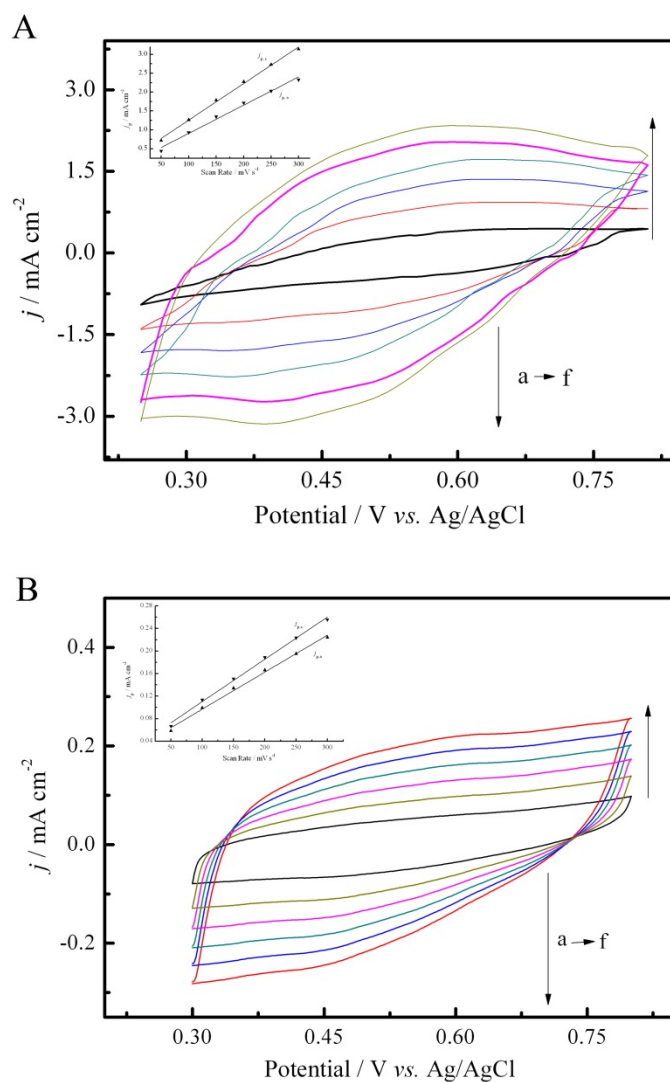


Fig. S2. CVs of PPy-AA (A) and PPy-PAA-1 (B) films prepared from DCM containing Bu_4NPF_6 (0.1 M) in concentrated sulfuric acid at potential scan rates of (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, and (f) 300 mV s^{-1} . Inset: plots of redox peak current densities vs. potential scan rates. j_p is the peak current density: $j_{p,a}$ and $j_{p,c}$ denote the anodic and cathodic peak current densities, respectively.

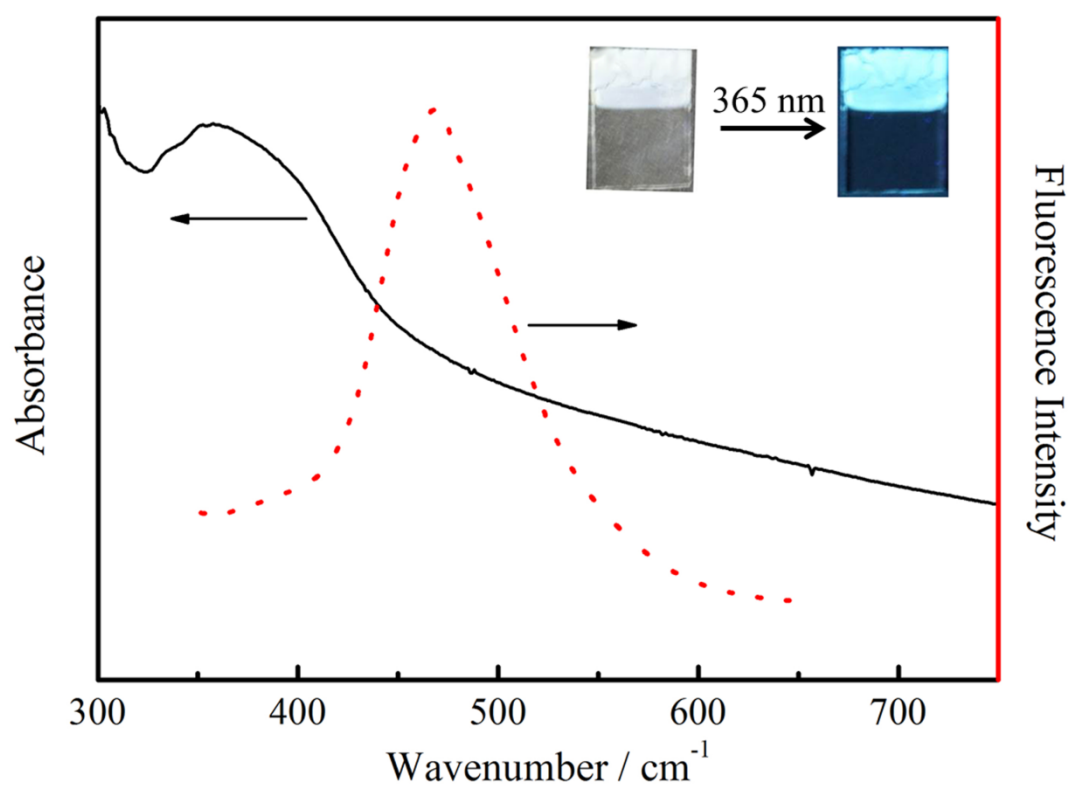


Fig. S3. Solid-state UV-vis spectra and emission spectra of PPy-PAA-1 deposited on the ITO electrode. Inset: Photograph of PPy-PAA-1 under 365 nm UV irradiation.

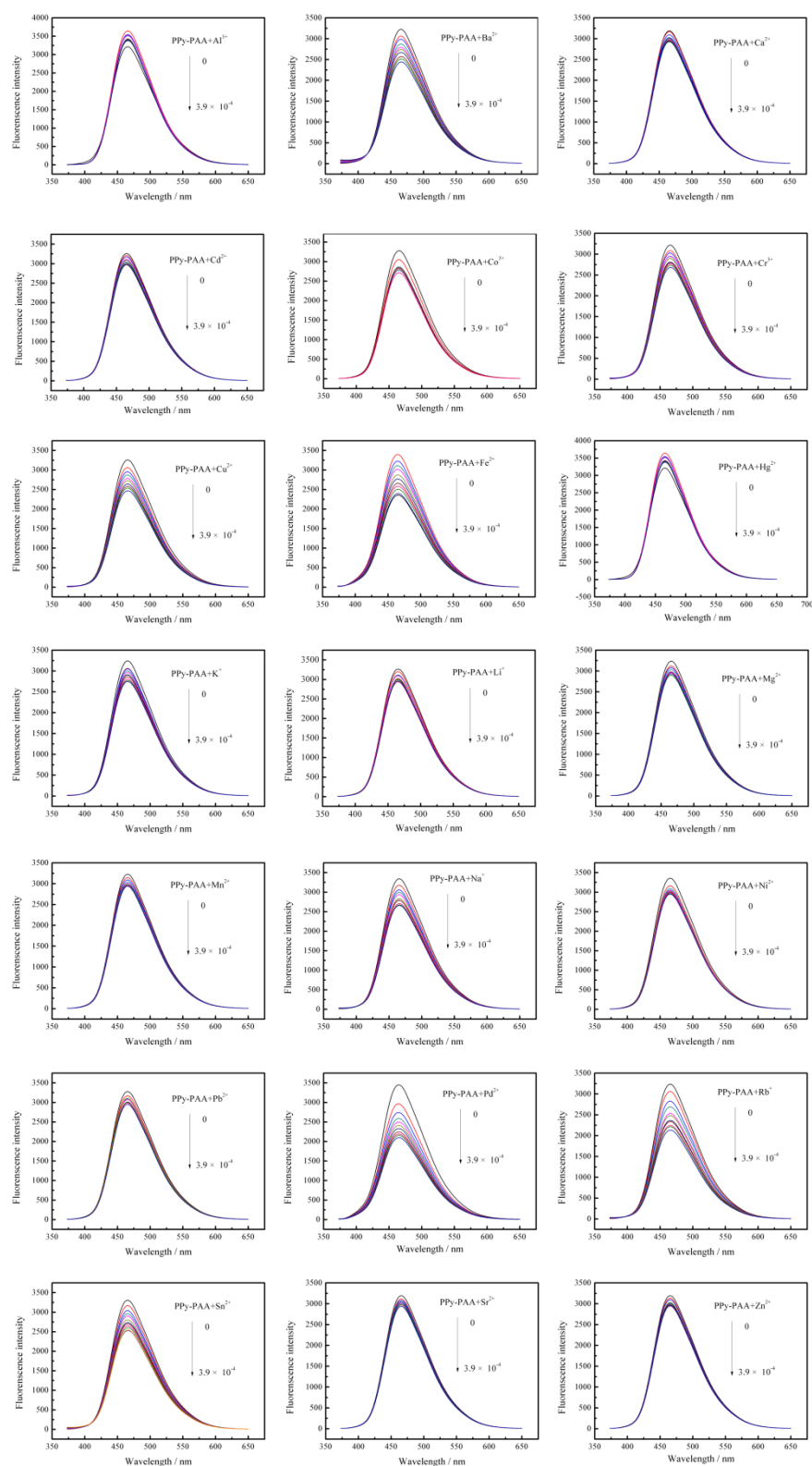


Fig. S4 Fluorescence emission spectra of PPy-PAA-2 (1×10^{-6} M) in THF in the presence of different amounts of metal ions. Excitation wavelength: 363 nm.

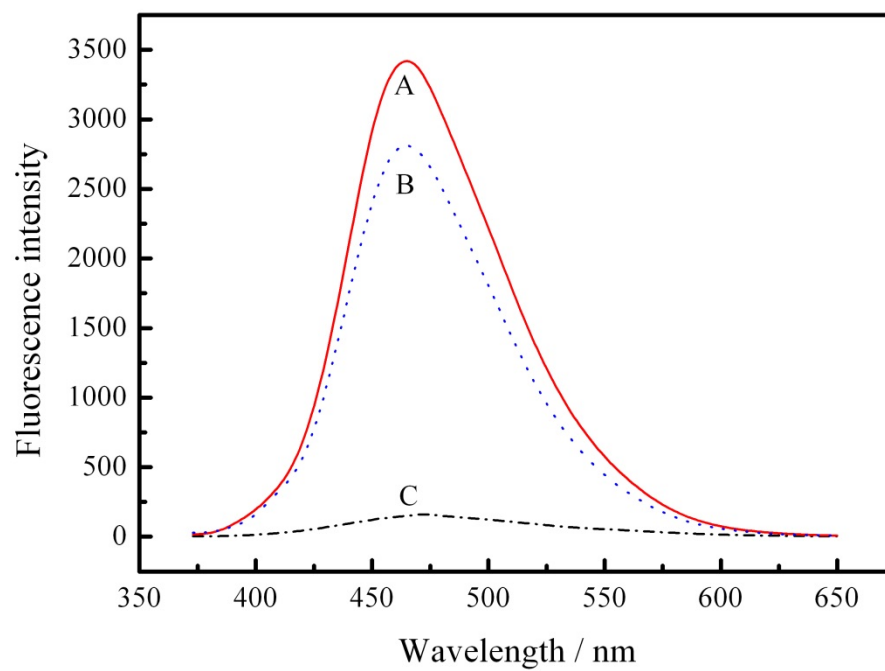


Fig. S5 Fluorescence Emission spectra of PPy-PAA-2 (1×10^{-6} M) in THF in the presence of different metal ions (5.67×10^{-7} mol/L), A: PPy-PAA-2, B: PPy-PAA-2 + cation without Fe^{3+} , C: PPy-PAA-2 + all cation. Excitation wavelength (nm): 363.

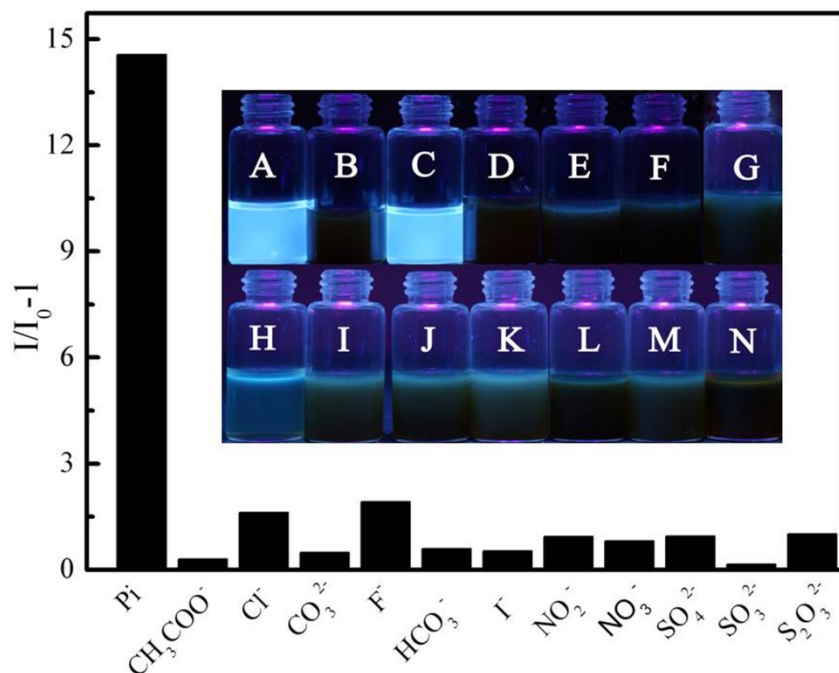


Fig. S6 Fluorescence emission response profiles of PPy-PAA-2 + Fe³⁺ in THF after added Fe³⁺ ($5.67 \times 10^{-7} \text{ mol L}^{-1}$), and turned on by different anions ($3.5 \times 10^{-5} \text{ mol L}^{-1}$). Insert: fluorescence images in the presence of different metal anions. A) PPy-PAA, B) PPy-PAA-2 + Fe³⁺, C) Pi, D) NO₂⁻, E) SO₃²⁻, F) S₂O₃²⁻, G) I⁻, H) Cl⁻, I) SO₄²⁻, J) CO₃²⁻, K) F⁻, L) HCO₃⁻, M) NO₃⁻, N) Br⁻. The polymer concentration was $1.0 \times 10^{-6} \text{ mol L}^{-1}$. Excitation wavelength (nm): 363.

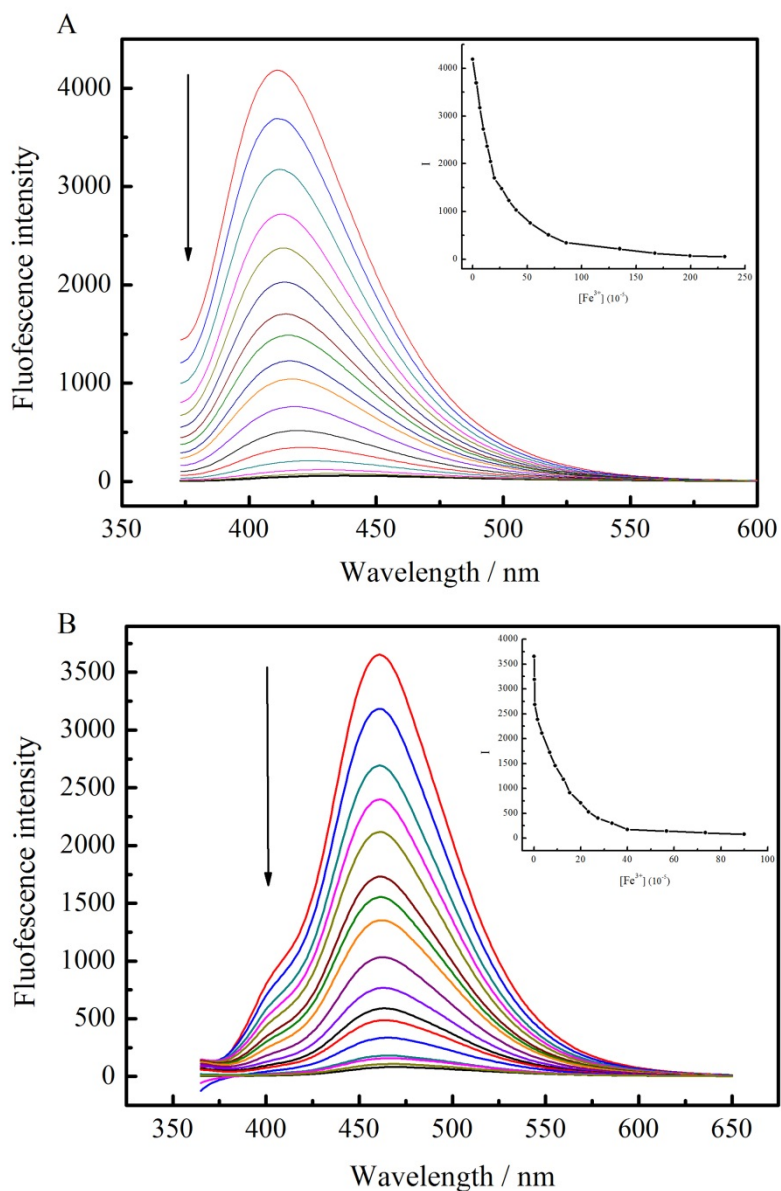


Fig. S7 Fluorescence emission spectra of PPy (1×10^{-6} M, figure A) and PPy-AA (5×10^{-6} M, figure B) in THF in the presence of different amounts of Fe^{3+} . Inset: fluorescence response of PPy and PPy-AA to Fe^{3+} . Excitation wavelength (nm): 317 for PPy and 355 for PPy-AA.

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 $8.6 \times 10^3 \text{ M}^{-1}$ for PPy, $8.0 \times 10^4 \text{ M}^{-1}$ for PPy-AA and $4.7 \times 10^5 \text{ M}^{-1}$ for PPy-PAA-2, respectively.

Reference:

1. C. Zimmermann, M. Mohr, H. Zipse, R. Eichberger, W. Schnabel, J. Photochem. Photobiol. A. Chem., 1999, 125, 47.
- [2] F. C. Tasi, C. C. Chang, C. L. Liu, W. C. Chen, S. A. Jenekhe, Macromolecules, 2005, 38, 1958.