Supporting Information for

A polystyrene-based ESIPT fluorescent polymeric probe for highly sensitive detection of chromium (VI) ions and protein staining

Xiaoling Qin, Guoqiang Zhou, Pan Ma, Jiaoyun Xia, Fuchun Gong*, Lusen Chen and Lujie Xu

College of Chemistry and Chemical Engineering, Changsha University of Science and Technology, Changsha, 410114, P. R. China

∗Corresponding authors, Tel: +86-0731-85258733;

E-mail addresses: gongfc139@163.com (F.-C. Gong)

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1. Synthesis and Characterization of f-PP

1.1. Synthesis of acetyl polystyrene

The acetyl polystyrene was synthesized according to the reported method with minor modification [1]. Briefly, dry polystyrene (0.5 g) was placed in a three-neck flask containing 10 mL CS_2 and soaked for 12 h. An appropriate amount of AlCl3 (0.774 g), CS2 (10 mL) and AC (0.585 g) were added to the swollen granules. After mechanical stirring for 10 min, the mixture was circulated and cooled in a oil bath at 80-85 °C for 5 h. Then, the resulting mixture was washed with 3% dilute hydrochloric acid, deionized water and anhydrous ethanol. Finally, the product was dried in a vacuum drying chamber at 50°C to obtain the target compounds. Yield: 74.6%.

1.2. Synthesis of ESIPT fluorescent polymer (f-PP)

ESIPT fluorescent polymer probe f-PP was synthesized according to the reported method in the literature [2]. Briefly, 4-(diethylamino)-2-hydroxybenzaldehyde (1.36g, 10 mM), Acetylated polystyrene (5.6g), malonitrile (0.67g, 10.5 mM) and ammonium acetate (5.4 g, 70 mM) were dissolved in 30 mL ethanol. The mixture reacted by refluxing under stirring for 4 h. After cooling to room temperature, the reaction mixture was filtered and washed with distilled water, acquiring the crude products. Finally, the resulted product is further recrystallization from ethanol and dried at 50 ℃ to afford faint yellow crystal. (3.1 g, 83.2%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.73 (s, 1H), 8.71 (s, 1H), 7.99 (s, 2H), 7.43 (s, 5H), 6.93 (dd, J = 9.8, 2.6 Hz, 2H), 6.74 – 6.64 (m, 3H), 3.76 – 3.30 (m, 39H), 3.13 – 2.72 (m, 9H), 2.58 (d, J = 3.6 Hz, 40H), 1.95 (s, 7H), 1.52 – 1.00 (m, 24H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 197.61, 162.76, 135.12, 40.92, 40.33 (d, J = 21.1 Hz), 40.14 – 39.57 (m), 39.39, 35.46 (d, J = 152.9 Hz), 31.20, 26.86.

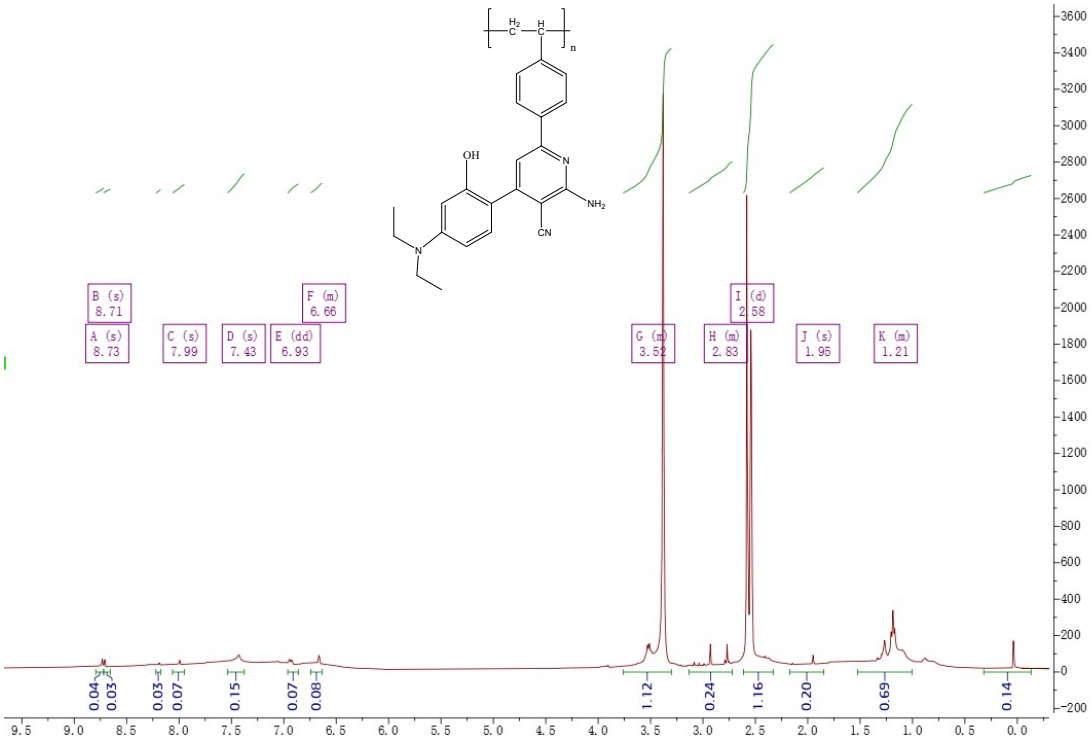

Fig. S1-1 1HNMR characteristic spectra of f-PP

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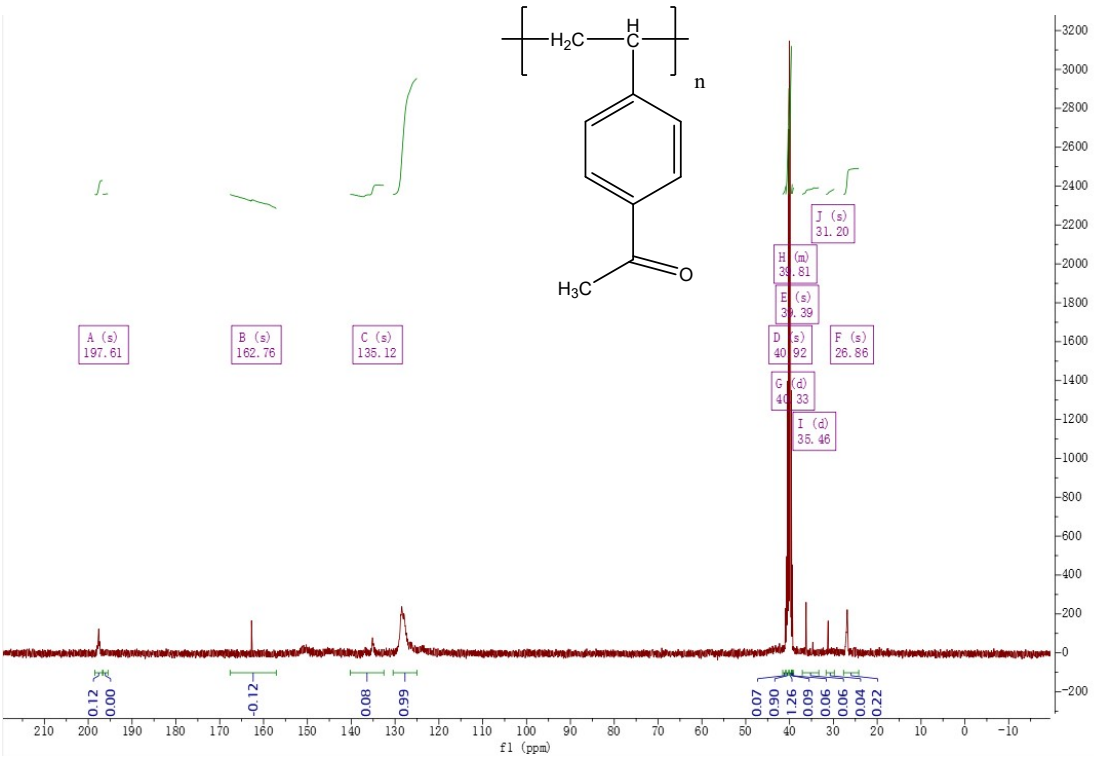

Fig. S1-2 13CNMR characteristic spectra of X-PS

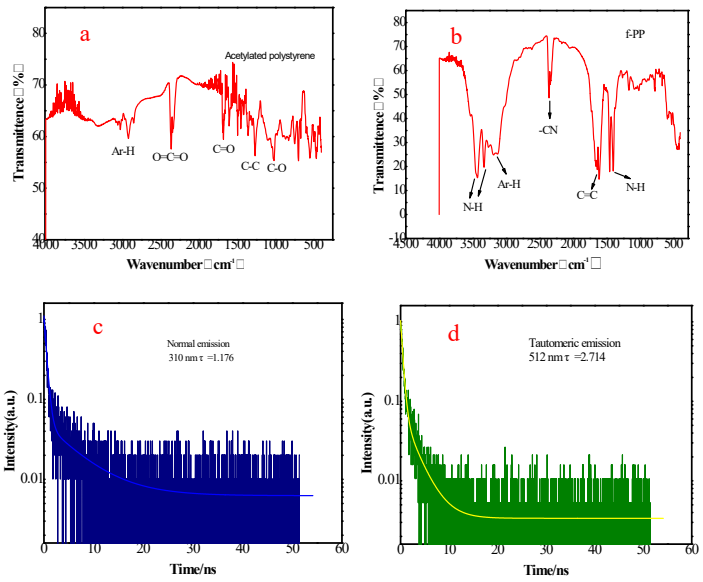

Fig. S2 FTIR spectra and fluorescence decay curves of f-PP. (a), (b) are the FTIR spectra of acetyl polystyrene and f-PP, respectively; (c), (d) are the fluorescence decay times of f-PP at 310 nm and 512 nm, respectively. The concentrations of f-PP were 20 μg.L^{-1}.

UV-visible absorption of f-PP with the addition of competing ions

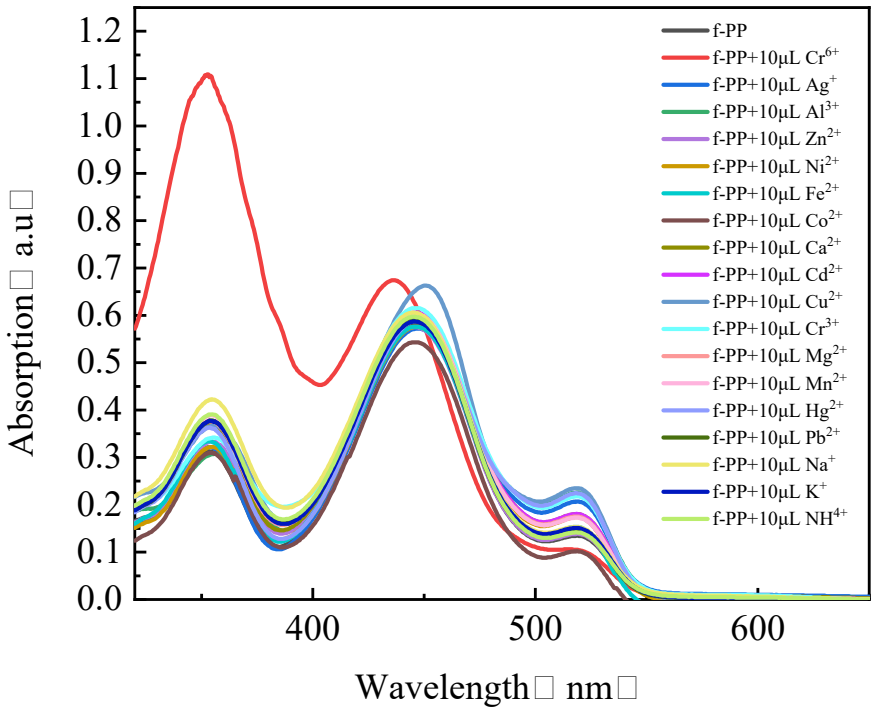

Fig. S3 UV-visible absorption of f-PP with the addition of competing ions in DMF-PBS mixed system(4/6, v/v, pH 7.2)

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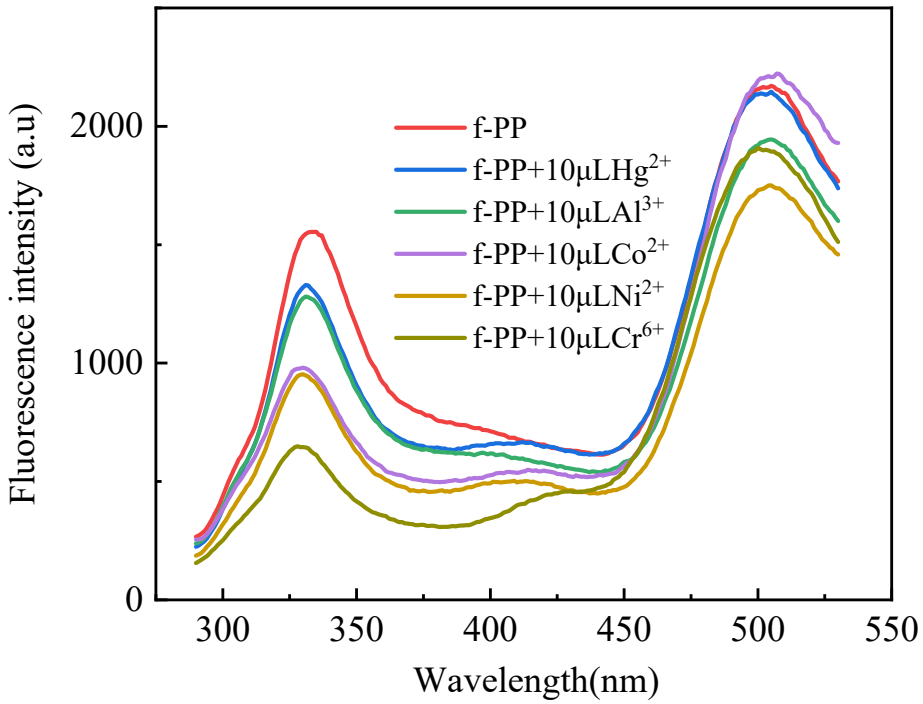

Fig. S4 fluorescence spectra of f-PP with the addition of competing ions in DMF-PBS mixed system(4/6, v/v, pH 7.2)

2. Determination of fluorescence quantum yield

The fluorescence quantum yield (Φ_f) of f-PP in DMF-PBS mixed system (4/6, v/v, pH 7.2) was determined using quinine sulfate (Φ_f =0.55 at 360 nm) in sulfuric acid (0.50 mol.L^{-1}, η =1.47) as the standard substance. The absolute Φ_f values were calculated corresponding to the following equation:

$$\Phi_u=\Phi_s(I_u/I_s)(A_s/A_u)(\eta^2_u/\eta^2_s)$$

Φ is fluorescence quantum yield; I is the measured integrated fluorescence intensity; A is the optical density measured at the selected excitation wavelength; η is the refractive index. The subscript "s" refers to the standard Φ_f of the referenced quinine sulfate. The subscript "u" refers to the unknown Φ_f of the ESIPT fluorescent probe f-PP. In order to minimize re-absorption effect, absorbance in the 1.0 cm fluorescence cuvette was kept under 0.1 at the excitation wavelength of 360 nm.

References

[1] Feng, X.; Yang, X.; Li, M.; Qin, Y.; Li, H.; Xie, Y., Production and method optimization of fluorescent polystyrene. J. Mol. Struct. 2021, 1243, 130746.

[2] Ma, P.; Gong, F.; Zhu, H.; Qian, Y.; He, L.; Xia, J.; Cao, Z., Partnered Excited-State Intermolecular Proton Transfer Fluorescence (P-ESIPT) Signaling for Nitrate Sensing and High-Resolution Cell-Imaging. Molecules 2022, 27 (16), 5164.