

Supplementary information for

Polymer nanoparticles integrated with ESIPT modules for sensing cysteine based on modulation of their tautomeric emission

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Section 1. Synthesis and characterization of ESIPT-exhibiting polymer quantum dots (e-PNPs)

The e-PNPs were synthesized by condensation polymerization using 2,6-diformyl-4-methylphenol and guanidine hydrochloride as monomers. The procedure is as follows: Firstly, 2,6-diformyl-4-methylphenol and guanidine hydrochloride were added into a certain volume of ethanol and stirred to dissolve. 1.0 mL piperidine was added into the mixture and reacted in the range of 60-80 °C for 2-4 h. Secondly, the solvent was removed by vacuum evaporation and the residue was dissolved in distilled water. The assemblies of fluorescent polymers were then purified by extraction with n-butylalcohol (3×10 mL). The aqueous solution was collected by removing the large dots through centrifugation at 8000-12000 rpm for 10-30 min and then dialyzing against ultrapure water through a dialysis membrane for 24 h. Finally, after vacuum-freeze drying, a cinnamon-colored solid residue was obtained.

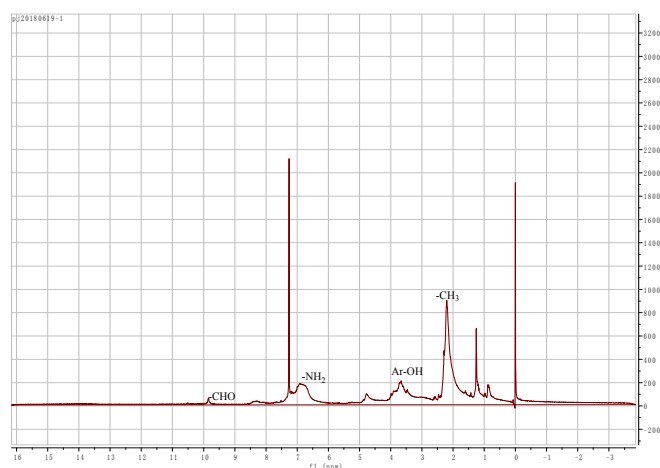


Fig. S1 ¹H-NMR spectra of e-PNPs

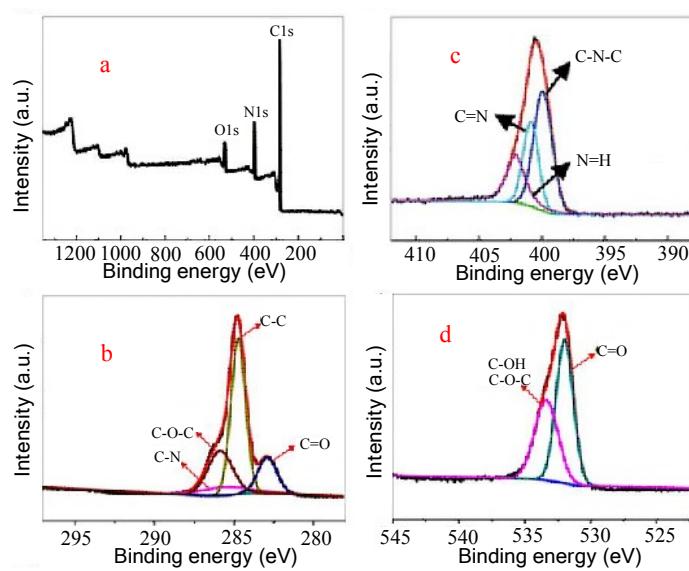


Fig. S2 (a) XPS survey, (b), (c) and (d) are deconvoluted C1s, N1s and O1s spectra of e-PNPs, respectively.

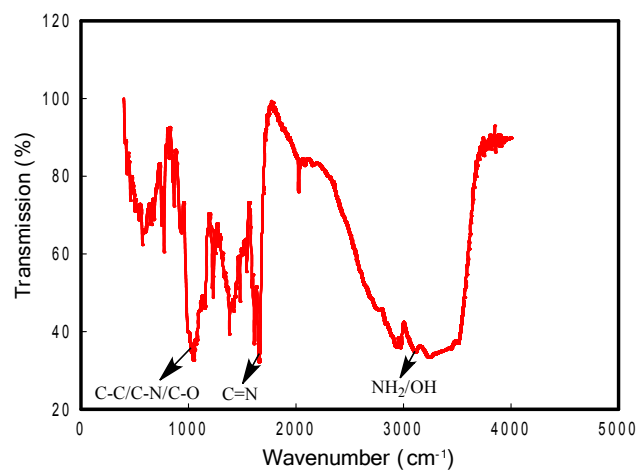


Fig. S3 FTIR spectrum of e-PNPs

Section 2. Optimization of synthesis conditions and determination of fluorescence quantum yield (FQY)

We have also investigated the influence of different reaction conditions (e.g., the ratio of 2,6-diformyl-4-methylphenol to guanidine hydrochloride, reaction time and temperature) on t-FL performance of the resulting e-PNPs. The results showed that when the mole ratio of 2,6-diformyl-4-methylphenol to guanidine hydrochloride is 1:1, the reaction temperature is 75°C and the reaction time reaches 3.5, e-PNPs with excellent performance can be obtained (**datas not shown**).

The fluorescence quantum yield (FQY) of the prepared e-PNPs were determined using quinine sulfate in sulfuric acid solution (0.1 mol/L, $\eta = 1.33$, FQY=0.54 at 360 nm) as the standard. The absolute FQY values were calculated corresponding to the following equation:

$$\Phi_u = \Phi_s (I_u / I_s) (A_s / A_u) (\eta_u^2 / \eta_s^2)$$

Φ is FQY; I is the measured integrated e-FL emission intensity; A is the optical density tested at the excitation wavelength; η is the refractive index. The subscript “s” represents the standard FQY of reference quinine sulfate. The subscript “u” refers to the unknown FQY of e-PNPs. In order to minimize re-absorption effects, absorbance in the 1 cm fluorescence cuvette were kept under 0.1 at the excitation wavelength of 345 nm. The fluorescence quantum yield of the tautomeric fluorescence is 0.87.

Section 3. ESIPT-fluorescence properties of e-PNPs

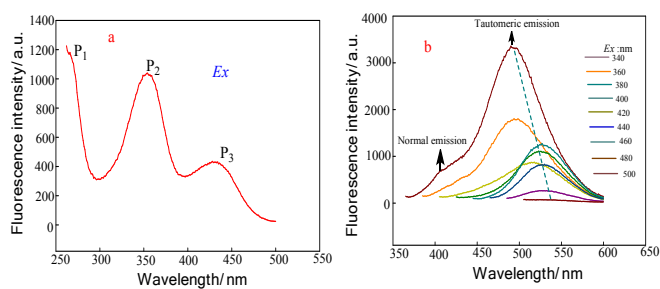


Fig. S4 (a) Excitation spectrum of e-PNPs (Em :510 nm); Fluorescence emission spectra of e-PNPs in a HEPES buffer solution (10 mM, pH 7.4) with increasing excitation wavelength from 380 nm on the shift with 20 nm increments. The slit widths of emission and excitation were 5 nm.

Section 4. Optimization of e-PNPs-Cu²⁺ complex-based nanoprobe for sensing Cys

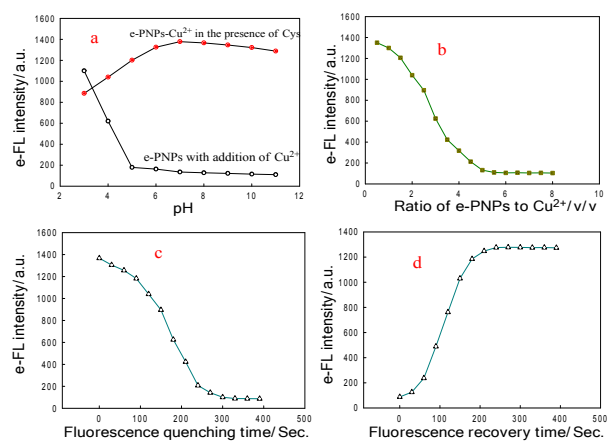


Fig. S5. t-FL responses of e-PNPs and e-PNPs-Cu²⁺ complexes at different pH values (a); The ratio of e-PNPs to Cu²⁺ (b); The t-FL quenching time of e-PNPs quenched by Cu²⁺ (c) and recovery time of the nanoprobe with Cys (d).