Electronic Supplementary Material for

Redox modulation of polydopamine surface chemistry: a facile strategy to enhance the intrinsic fluorescence of polydopamine nanoparticles for sensitive and selective detection of Fe³⁺

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1. Quantum yield measurement

The quantum yield of PDANPs was measured by a relative method. Quinine sulfate in $0.1 \text{ M H}_2\text{SO}_4$ (quantum yield is 0.54 at 360 nm) was chose as a standard. The quantum yield of a sample was then calculated according to the following equation:

$$\varphi_x = \varphi_{st} \times \frac{\eta_x^2}{\eta_{st}^2} \times \frac{m_x}{m_{st}}$$

where the subscripts "st" and "x" denote the standards and samples respectively, φ is the fluorescence quantum yield, m is the slop determined by the curves of integrated fluorescence intensity vs absorbance, and η is the refractive index with 1.33 as the default for both quinine sulfate and samples. To minimize reabsorption effects, the absorbance values in the 10 mm fluorescence cuvette were kept under 0.1 at the excitation wavelength (360 nm).

2. Additional Results



Fig. S1 Effect of pH values (A, B) and reaction time (C, D) on the optical properties of PDA solutions (DA concentration was 1 mg/mL during the reaction but diluted 40-fold before the spectral analysis). The UV-visible spectra (A, C) and fluorescence intensity (B, D) of various PDA solutions were recorded at different pH values (the pH values was controlled by different buffers, including sodium acetate buffers with different pH (50 mM, pH 3-7) and Tris-HCl buffer (50 mM, pH 8)) and different reaction time, respectively.



Fig. S2 TEM images of o-PDANPs synthesized in the presence of 10 mM (A), 40 mM (B) and 60 mM (C) SP; (D, E, F) The corresponding size distribution of o-PDANPs measured by TEM.



Fig. S3 The fluorescence spectra of the PDA solution synthesized by SP-induced oxidation (a) and successive oxidization and reduction induced by SP and NaBH₄ (b).



Fig. S4 The effects of NaBH₄ concentration and reduction reaction time on the quantum yields of r-PDANPs.



Fig. S5 (A) Fluorescence spectra of r-PDANPs aqueous solution upon excitation at different wavelengths. (B) The fluorescence intensity of r-PDANPs at different pH values. (C) Effect of NaCl concentration on the fluorescence intensity of r-PDANPs. (D) Photostability of r-PDANPs irradiated by xenon lamp for different amounts of time.



Fig. S6 Reversible investigation of r-PDANPs (100 μ g/mL) through the alternate addition of Fe³⁺ (20 μ M) and PPi (60 μ M).

Fluorescent probe types	Sensing system	detection limit (μM)	Ref.
Fluorescent dyes	Azaindole derivative	0.56	[1]
	pyrazoline derivative	1.4	[2]
Carbon dots	DA-derived carbon dots	0.32	[3]
	Citric acid-derived carbon dots	17.9	[4]
FONs	polyepinephrine-based FONs	0.67	[5]
	glutathione-integrated PDANPs	0.66	[6]
	H ₂ O ₂ -induced PDA dots	0.3	[7]
	r-PDANPs	0.15	This work

Table S1. Comparison of the present method with other luminescent nanosensors about the detection of Fe^{3+} .

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