Electronic Supplementary Material (ESI) for Analyst

Novel pyrene-pyridine oligomer nanorods for super-sensitive fluorescent detection of Pd^{2+}

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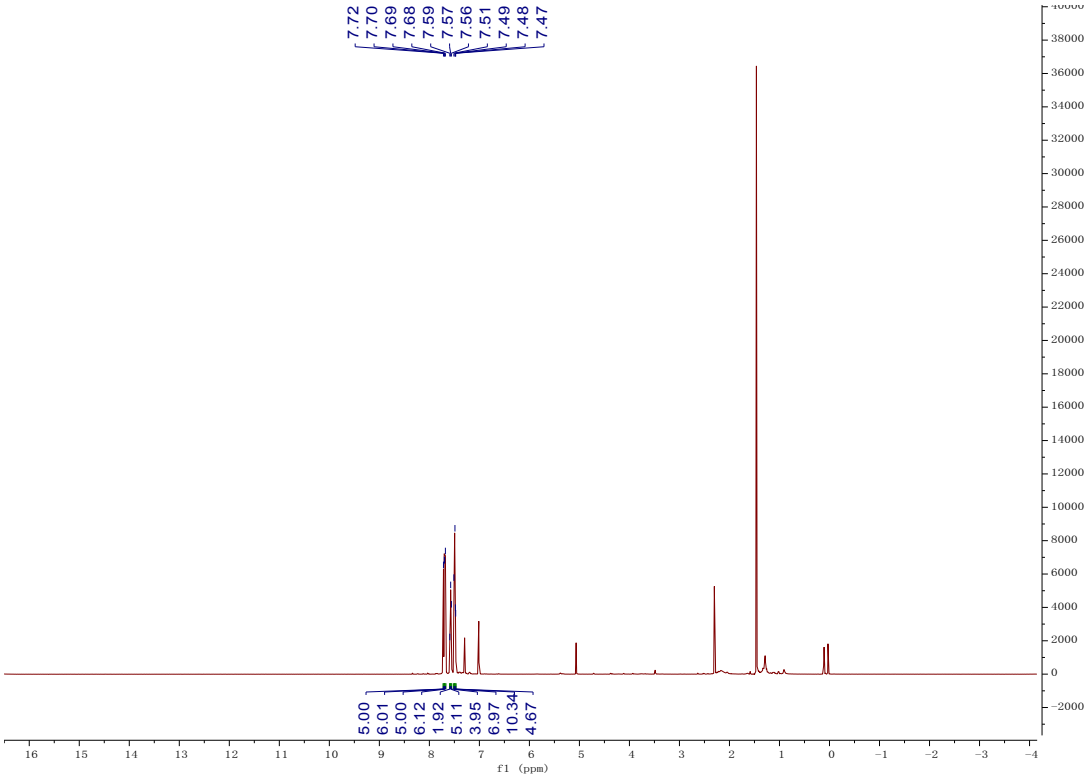
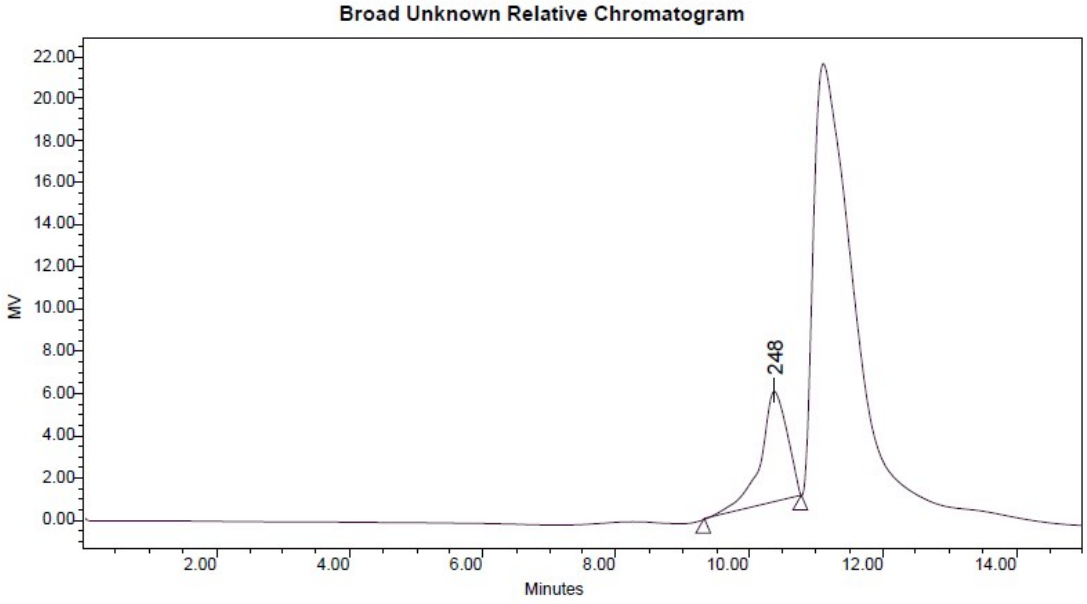
P1 ^{1}H NMR:



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 1.2 Hz, 5H), 7.70 (d, *J* = 1.6 Hz, 6H), 7.69 (d, *J* = 1.2 Hz, 5H), 7.68 (d, *J* = 1.6 Hz, 6H), 7.59 (q, *J* = 1.5 Hz, 2H), 7.58 (d, *J* = 1.9 Hz, 5H), 7.56 (q, *J* = 1.6 Hz, 4H), 7.51 (d, *J* = 2.9 Hz, 7H), 7.49 (d, *J* = 2.9 Hz, 10H), 7.48 – 7.46 (m, 5H)

P1 GPC: Mw = 310 Mn = 249 Mz = 431

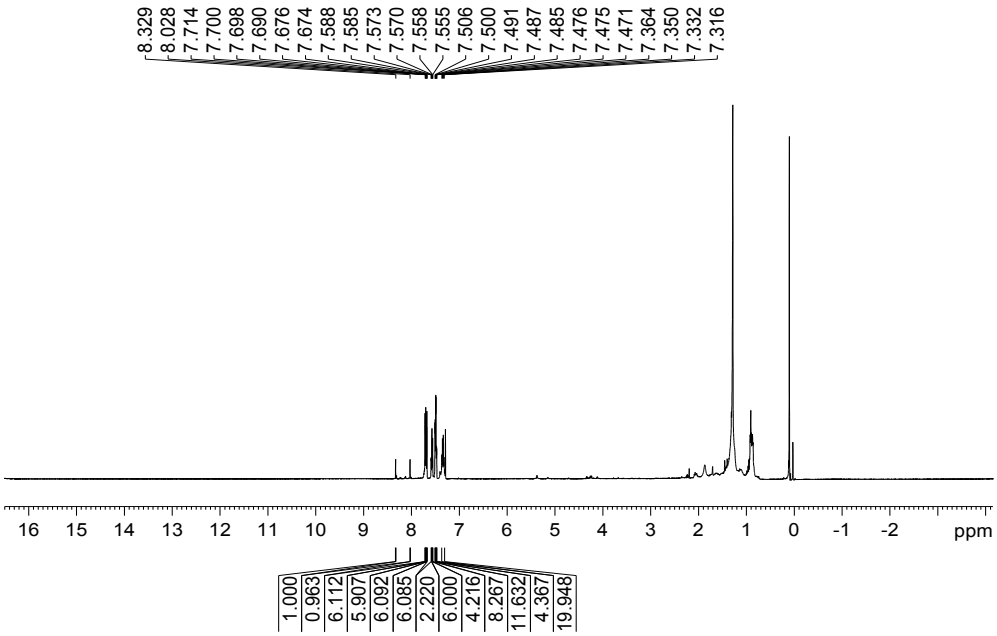


Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		249	310	248	431	641	1.244893	1.391313	2.067493

Fig. S1 Molecular weights of P1 indicated by GPC.

P2 ^{1}H NMR:



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (s, 1H), 8.00 (s, 1H), 7.69 (s, 6H), 7.67 (d, *J* = 1.5 Hz, 6H), 7.66 (s, 6H), 7.65 (d, *J* = 1.5 Hz, 6H), 7.56 (d, *J* = 1.5 Hz, 2H), 7.54 (d, *J* = 1.5 Hz, 6H), 7.53 (d, *J* = 1.5 Hz, 4H), 7.48 (d, *J* = 3.0 Hz, 8H), 7.47 – 7.45 (m, 12H), 7.45 (d, *J* = 3.0 Hz, 4H), 7.34 (s, 2H), 7.32 (s, 4H), 7.31 (s, 8H), 7.29 (s, 2H).

P2 GPC: Mw = 520 Mn = 469 Mz = 580

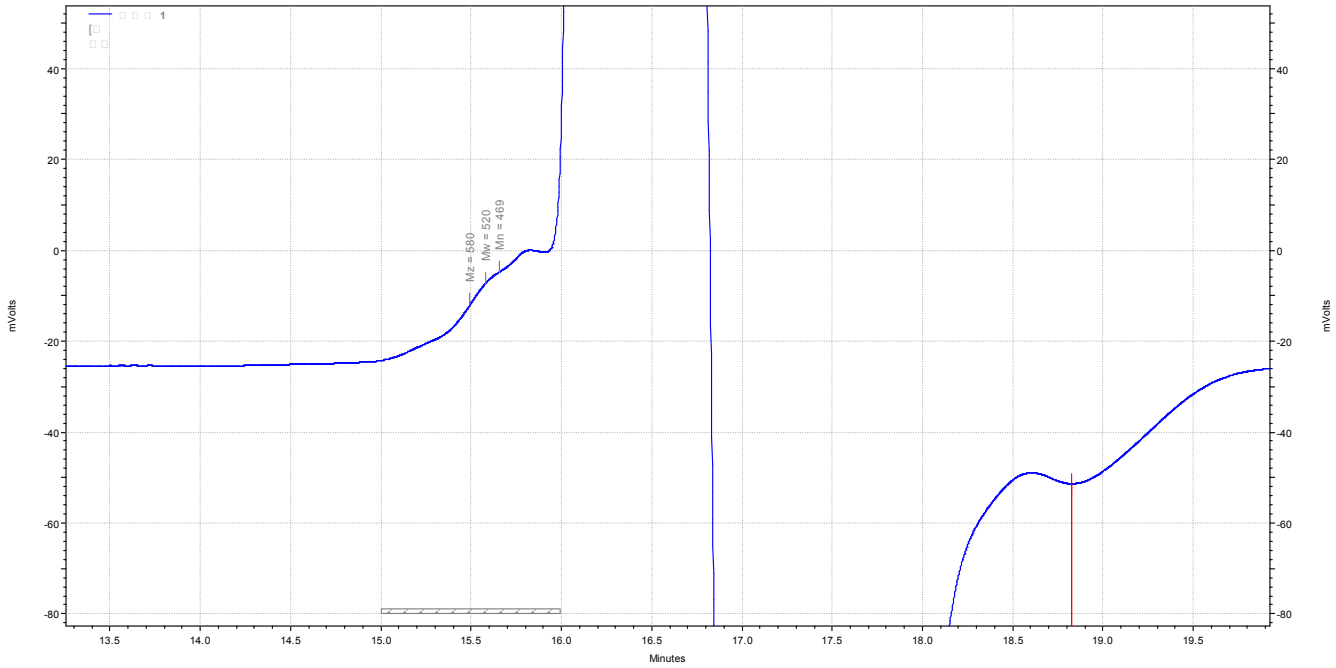
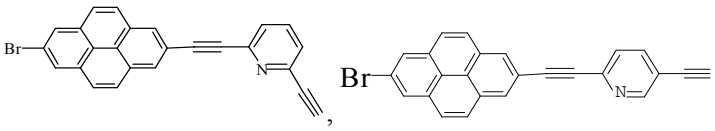
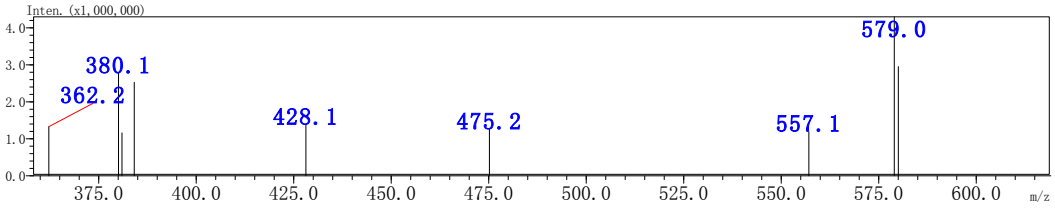


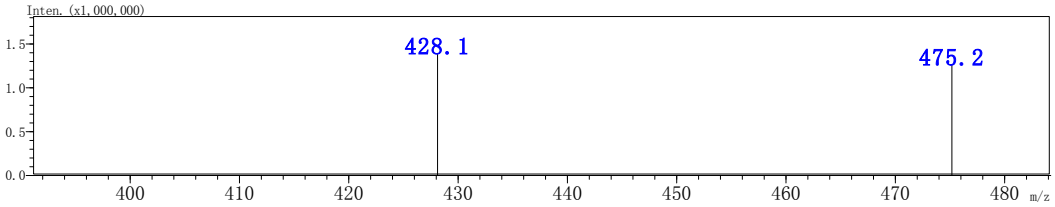
Fig. S2 Molecular weights of P2 indicated by GPC.

S1: Possible structures of **P1** and **P2** indicated by **LC-MS**

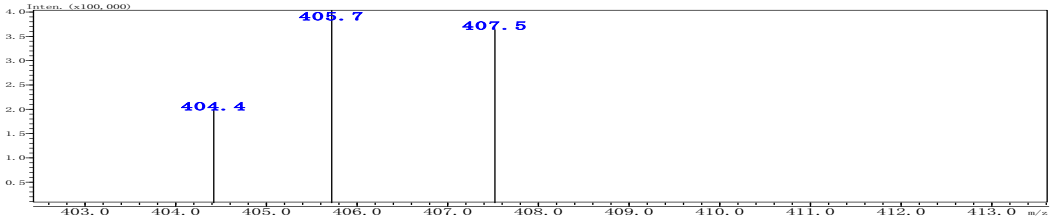


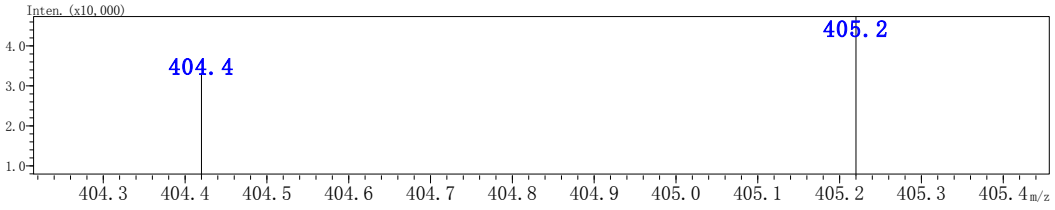
m/z 428 $[M+Na]^+$

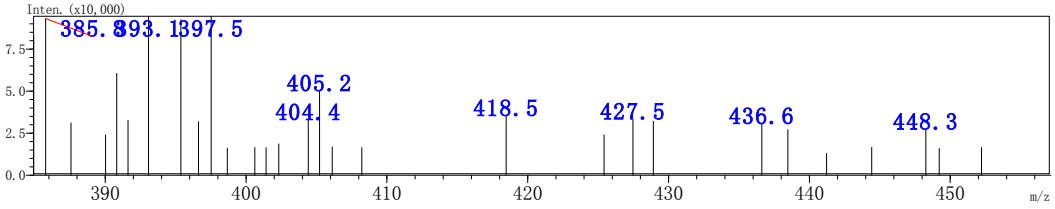


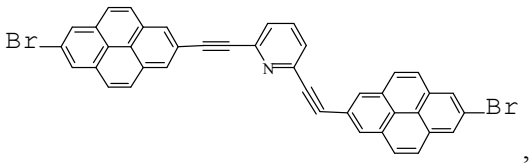


m/z 404 $[M-H]^-$









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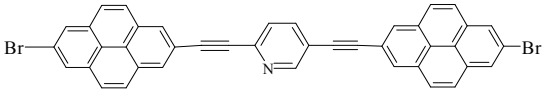
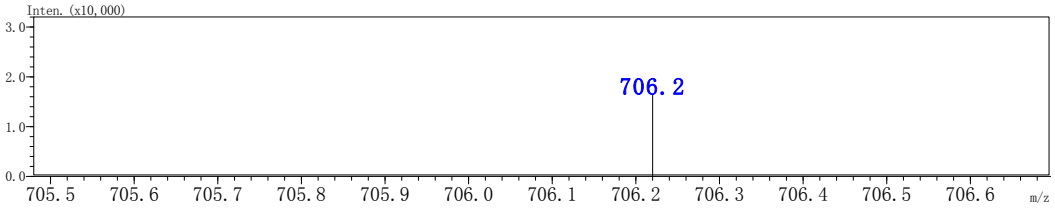
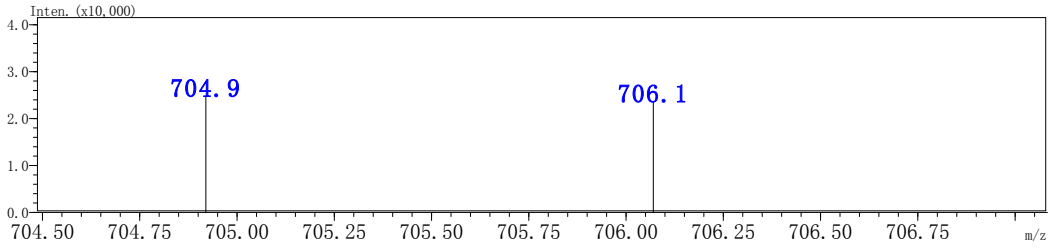
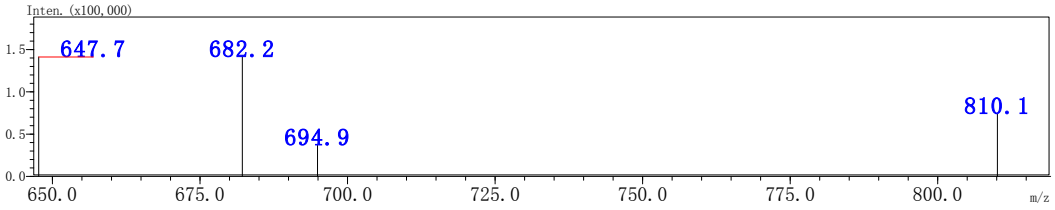


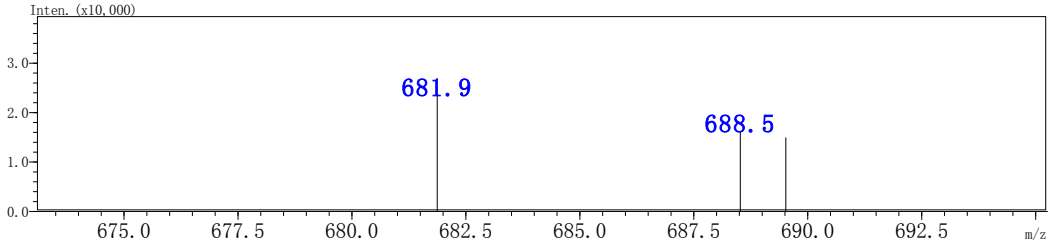
m/z 706.2 $[M+Na]^+$

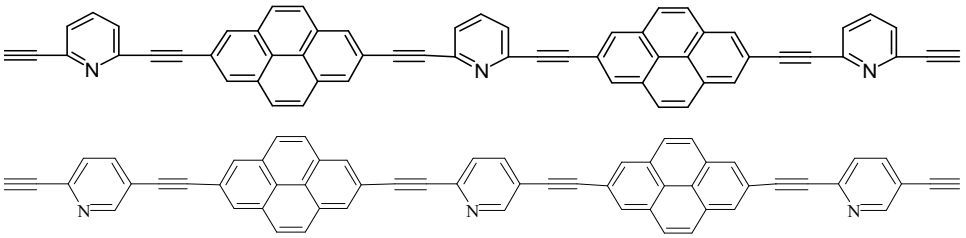




m/z 682 $[M-H]^-$

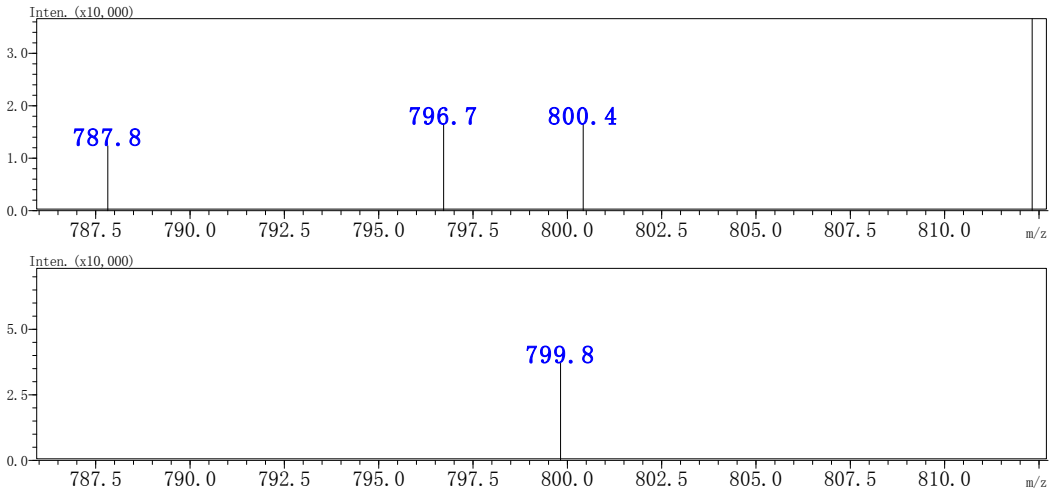




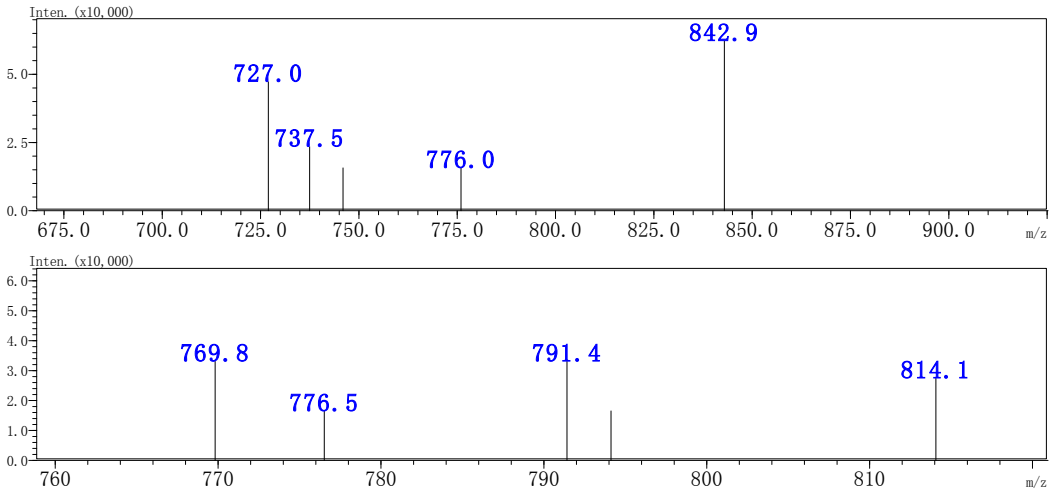


,

m/z 800.2 $[M+Na]^+$



m/z 776.2 $[M-H]^-$



S2: Calculation of Quantum Yield

Calculation of quantum yield: The quantum yield (QY) of P1NRs or P2NRs was calculated using quinine sulfate (QY = 0.55) in sulfuric acid (0.1 M, $\eta = 1.33$) as the standard and 360 nm as the excitation wavelength as reference. For calculation of quantum yield, five concentrations of each compound were made, all of which had absorbance less than 0.1. The P1NRs or P2NRs sample was dissolved in water ($\eta = 1.33$). Their fluorescence spectra were recorded at excitation of 340 or 324 nm. Then by comparing the integrated fluorescence intensities (excited at 340 or 324 nm) and the absorbency values (at 231 or 239 nm) of the P1NRs or P2NRs sample with the reference of quinine sulfate, QY of the P1NRs or P2NRs sample was determined. The quantum yield was estimated with the equation:

$$\Phi_x = \Phi_{std}(F_x A_{std} \eta_x)/(F_{std} A_x \eta_{std})$$

Where Φ, F, A, and η are the quantum yield of the standard sample, integrated fluorescence intensity, absorbance, and refractive index, respectively. The subscript "std" refers to the standard fluorophore of known quantum yield, for an example, quinine sulfate used in present work.

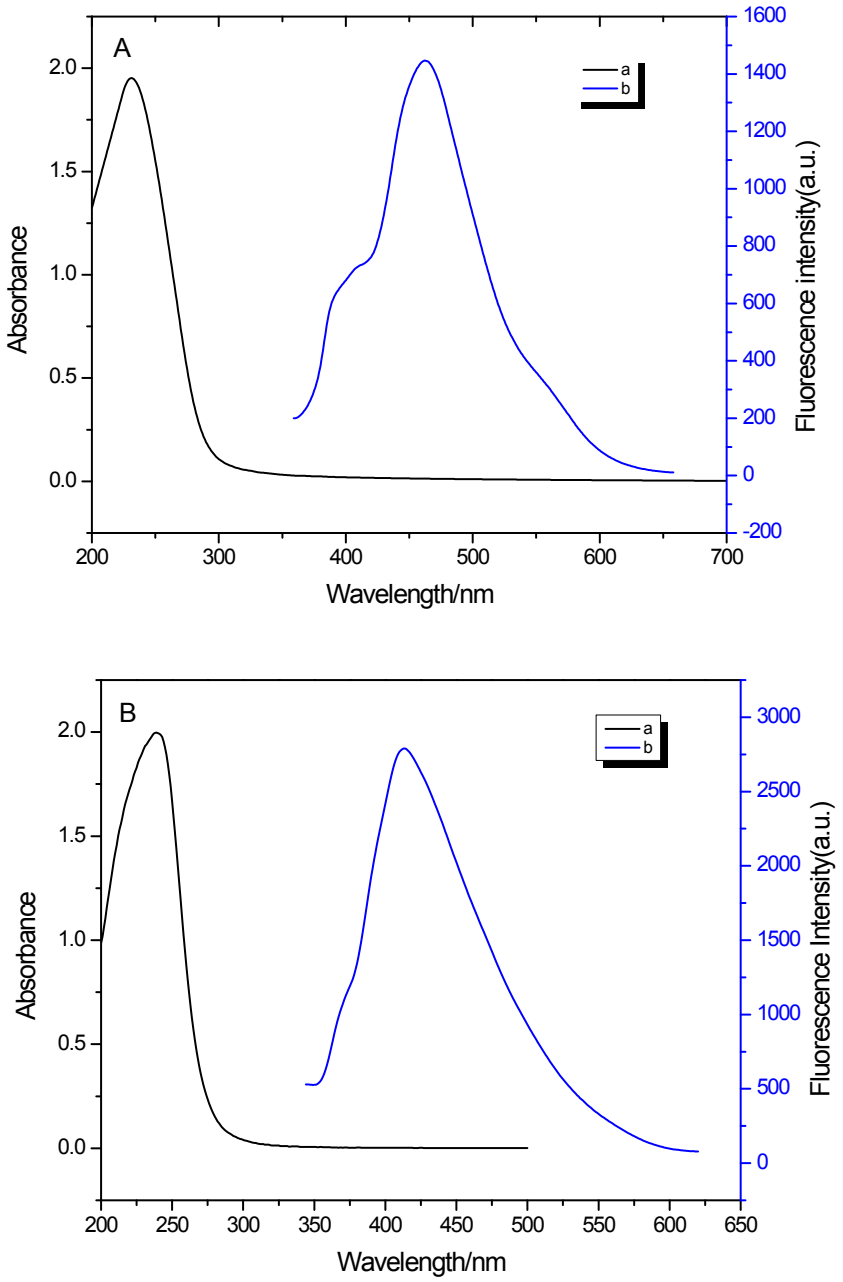


Fig. S3 (**A**) UV-visible spectrum (**a**) and fluorescence spectrum (λ_{ex} = 340 nm, λ_{em} = 468 nm) (**b**) of P1NRs. (**B**) UV-visible spectrum (**a**) and fluorescence spectrum (λ_{ex} = 324 nm, λ_{em} = 413 nm) (**b**) of P2NRs. [P1NRs] = [P2NRs] = 50 μg mL^{-1}.

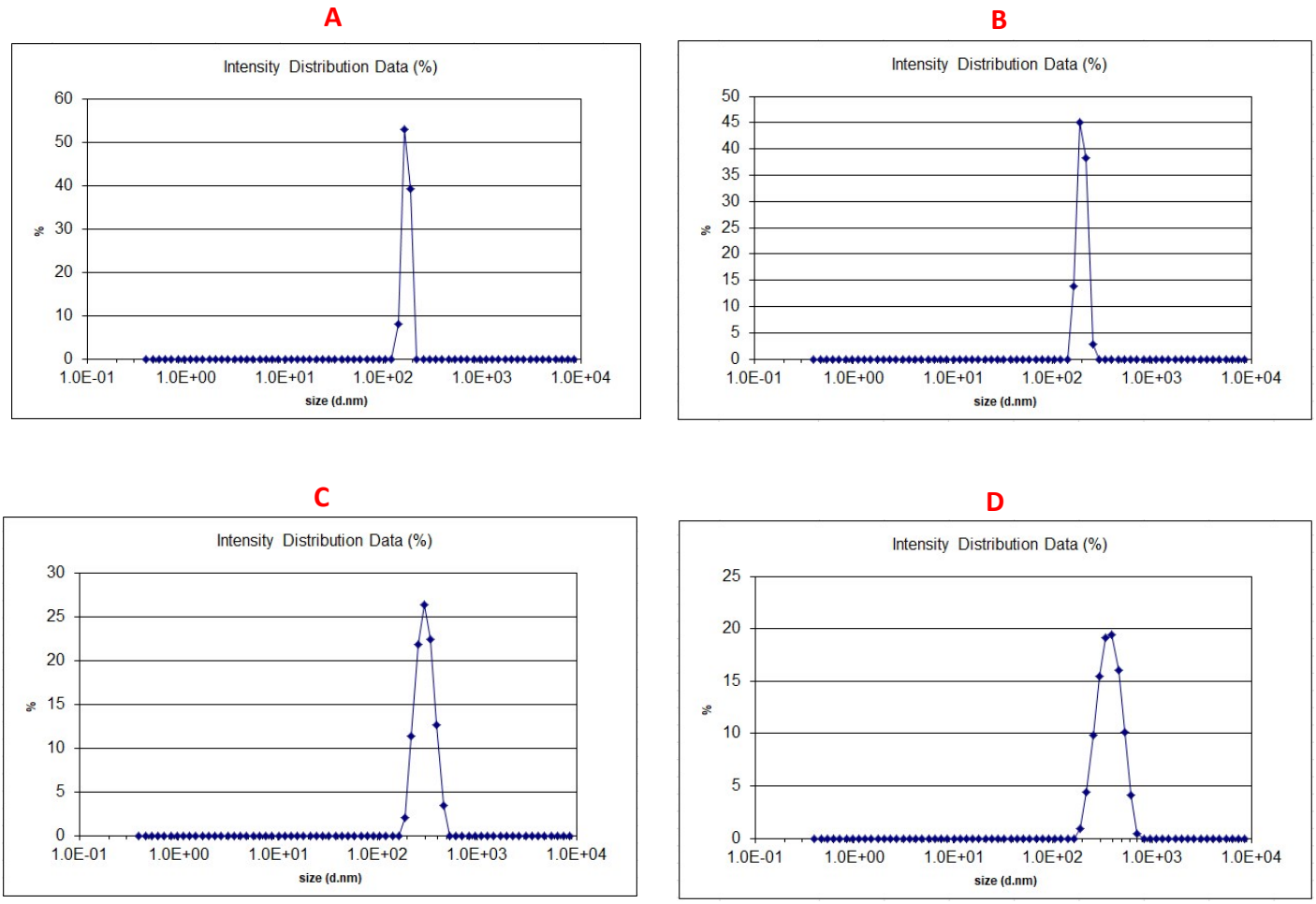


Fig. S4 Size distribution of the PINRs or P2NRs nanorods examined by DLS in H_3Cit-Na_2HPO_4 buffer solution. Average hydrodynamic diameter of PINRs (pH = 2.2) or P2NRs (pH = 3.0) nanorods increased from around 160 (**A**) or 190 nm (**B**) to ~300 (**C**) or 400 nm (**D**) after adding Pd^{2+}.

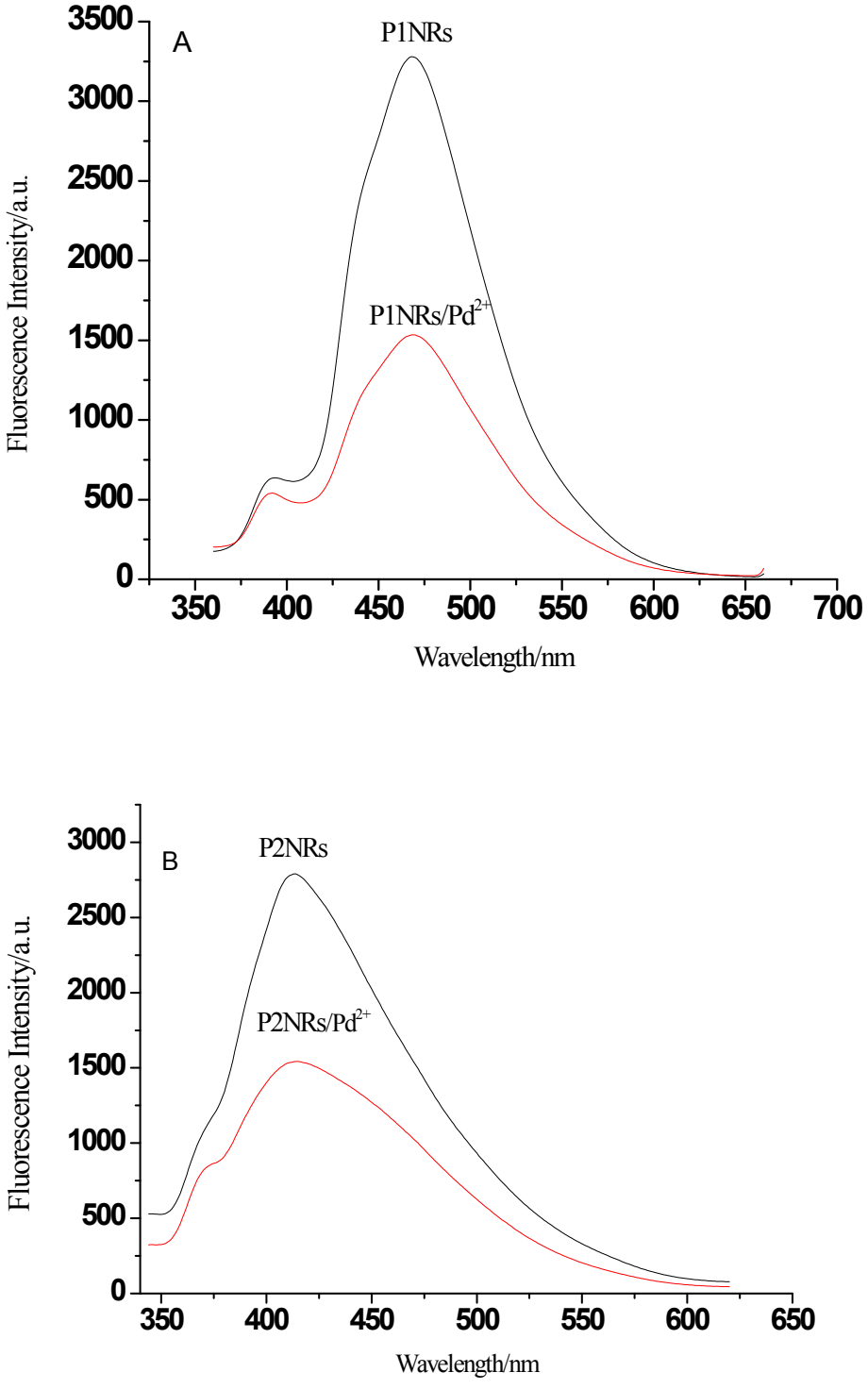


Fig. S5 (**A**) Fluorescence emission spectra (λ_{ex} = 340 nm) of P1NRs and P1NRs/Pd^{2+} in H_3Cit-Na_2HPO_4 buffer solution (pH = 2.2). [P1NRs] = 22.5 μg mL^{-1}, [Pd^{2+}] = 100 μM. (**B**) Fluorescence emission spectra (λ_{ex} = 324 nm) of P2NRs and P2NRs/Pd^{2+} in H_3Cit-Na_2HPO_4 buffer solution (pH = 3.0). [P2NRs] = 17.5 μg mL^{-1}, [Pd^{2+}] = 10 μM.

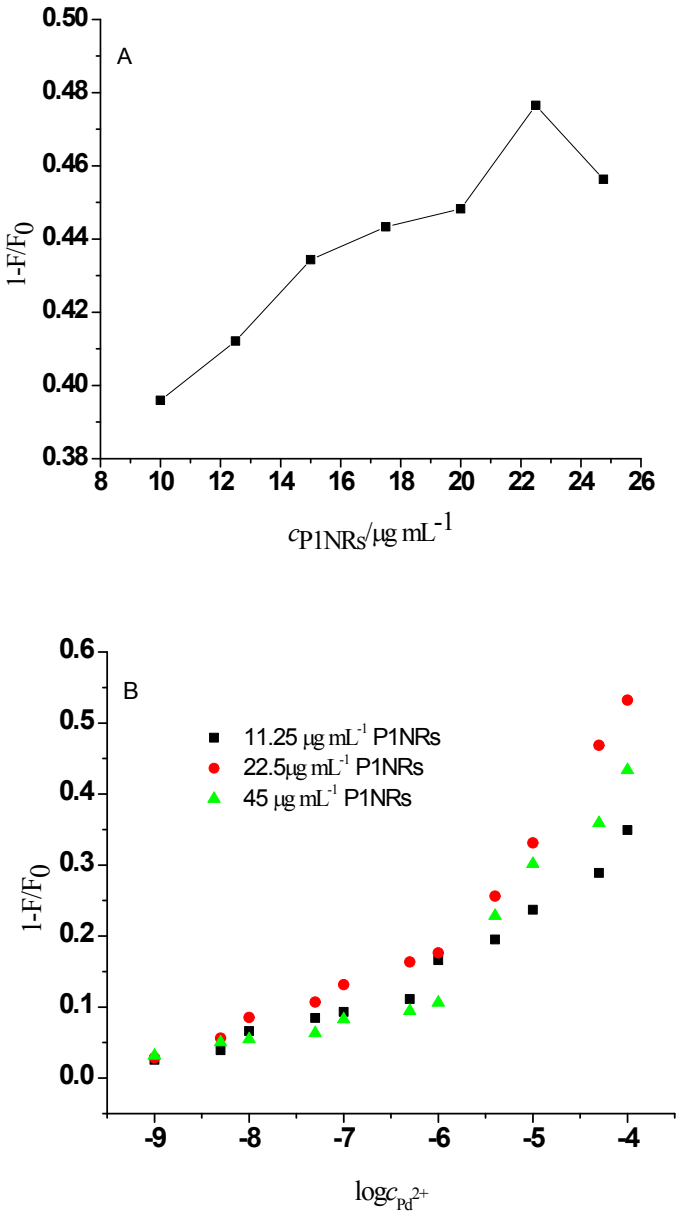


Fig. S6 (A) Effect of nanoparticle concentration on fluorescence detection of Pd^{2+}, [Pd^{2+}] = 50 μM. (B) Fluorenscence response of different concentrations of P1NRs to Pd^{2+} in pH 2.2 buffer solution. [Pd^{2+}] = 1 nM, 5 nM, 10 nM, 50 nM, 100 nM, 500 nM, 1 μM, 4 μM, 10 μM, 50 μM and 100 μM.

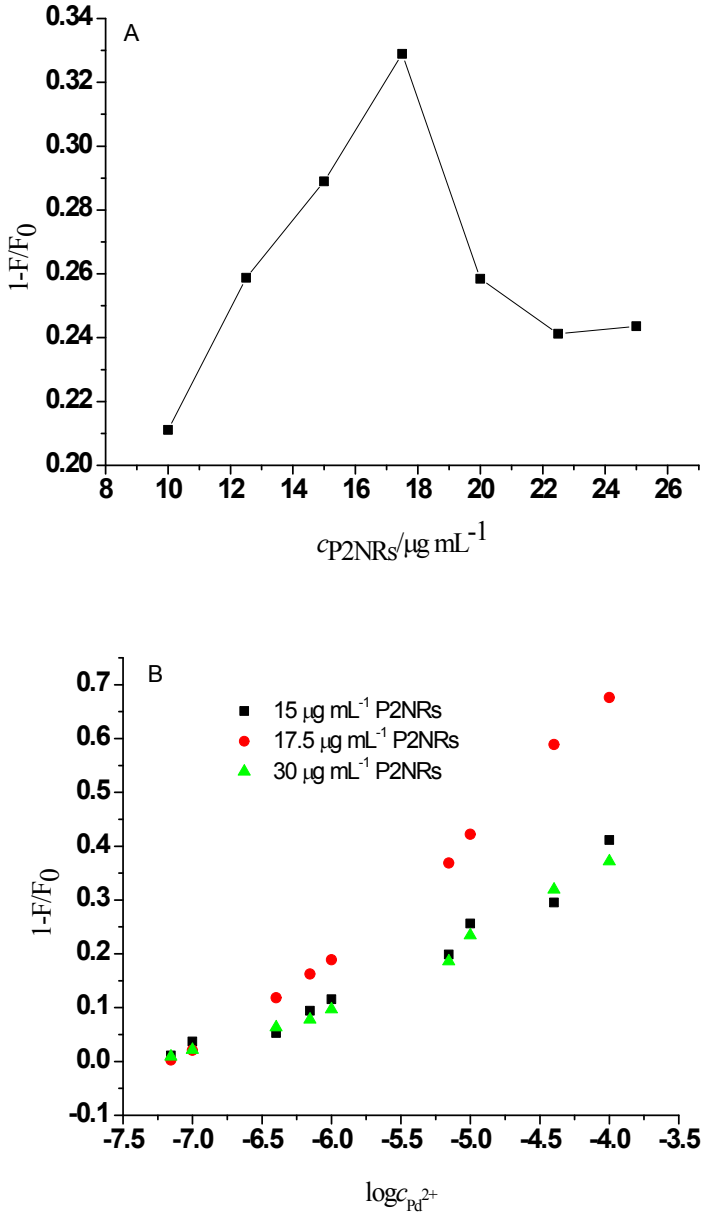


Fig. S7 (A) Effect of nanoparticle concentration on fluorescence detection of Pd^{2+}, [Pd^{2+}] = 4 μM. (B) Fluorenscence response of different concentrations of P2NRs to Pd^{2+} in pH 3.0 buffer solution. [Pd^{2+}]: 70 nM, 100 nM, 500 nM, 700 nM, 1 μM, 7 μM, 10 μM, 50 μM and 100 μM.

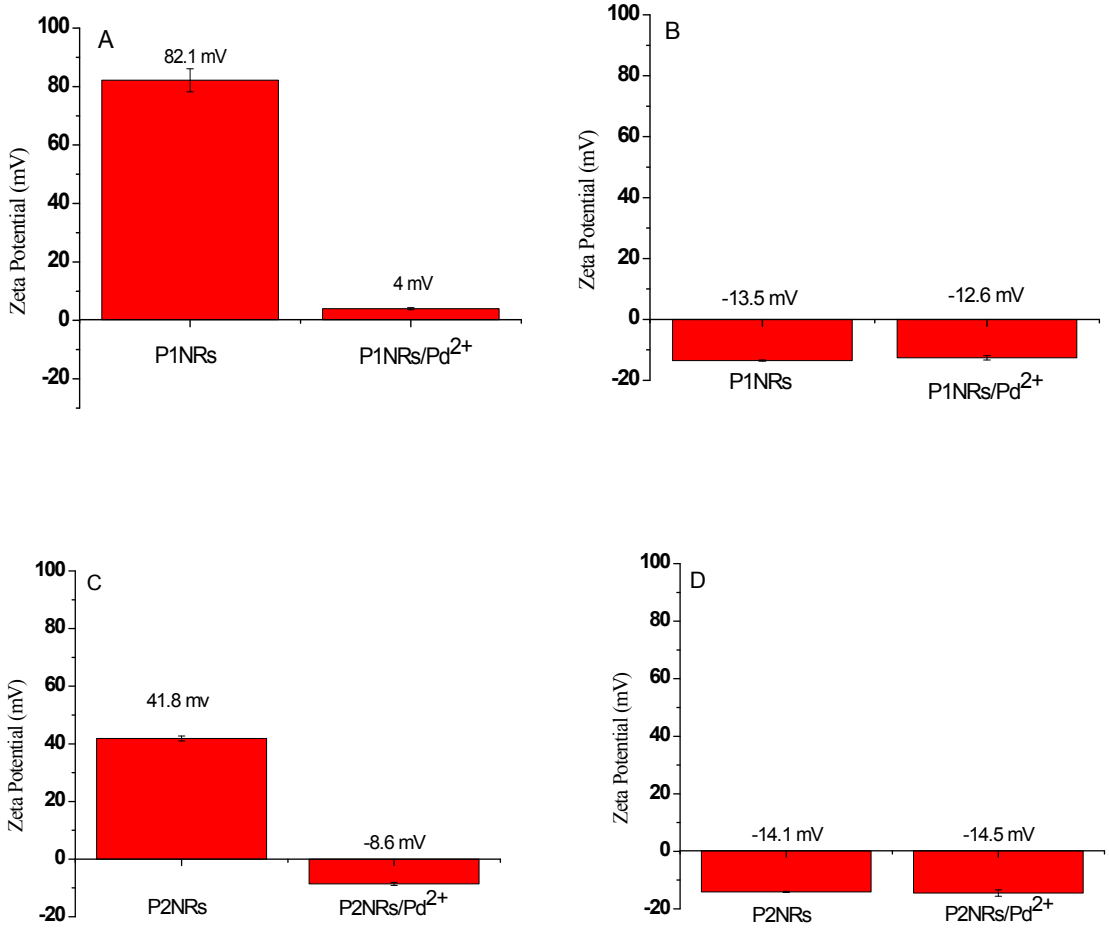


Fig. S8 Zeta potential of P1NRs or P2NRs under different conditions. (A) [P1NRs] = 22.5 μg mL^{-1}, [Pd^{2+}] = 100 μM, pH = 2.2. (B) [P1NRs] = 22.5 μg mL^{-1}, [Pd^{2+}] = 100 μM, pH = 6.0. (C) [P2NRs] = 17.5 μg mL^{-1}, [Pd^{2+}] = 100 μM, pH = 3.0. (D) [P2NRs] = 17.5 μg mL^{-1}, [Pd^{2+}] = 100 μM, pH = 6.0.

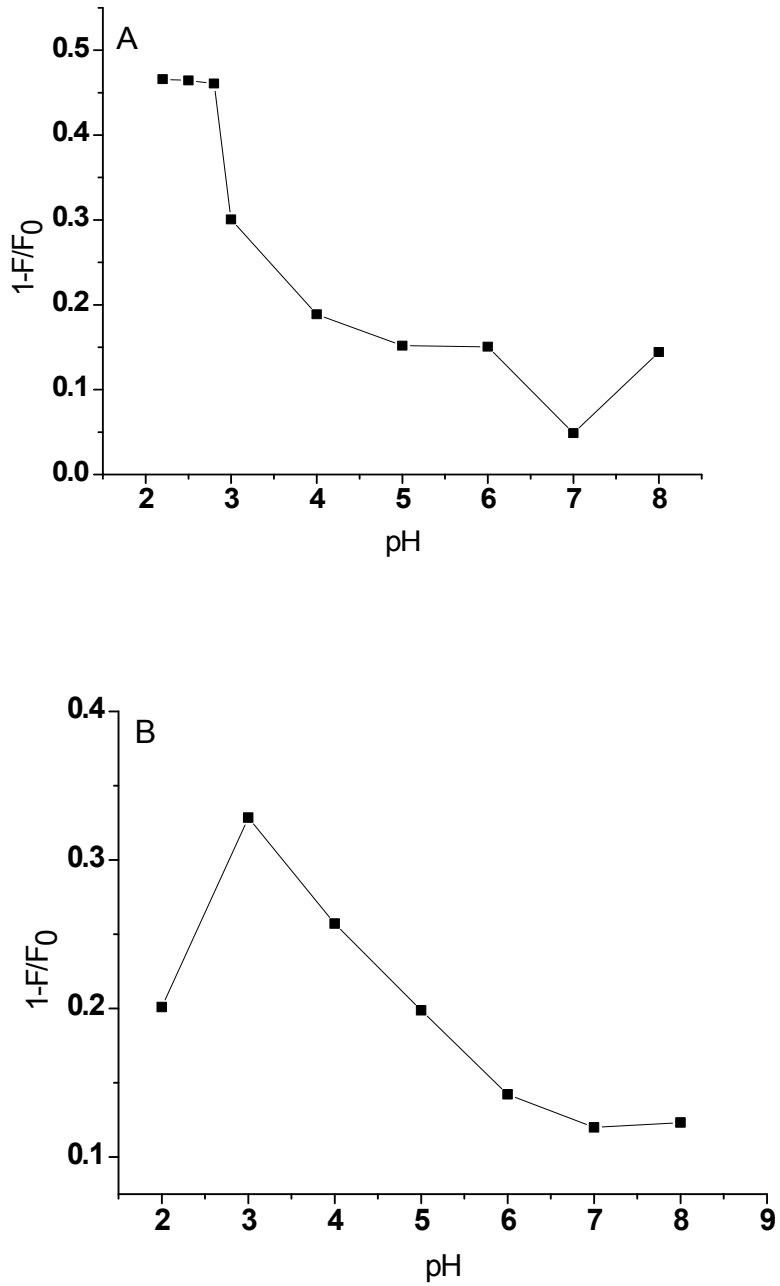


Fig. S9 (A) Effect of solution pH on the fluorescence response to Pd^{2+} (50 μM). Buffer solution: H_3Cit-Na_2HPO_4 (pH 2.0 to 8.0). [P1NRs] = 22.5 μg mL^{-1}. (B) Effect of solution pH on the fluorescence response to Pd^{2+} (4 μM). Buffer solution: H_3Cit-Na_2HPO_4 (pH 2.0 to 8.0). [P2NRs] = 17.5 μg mL^{-1}.

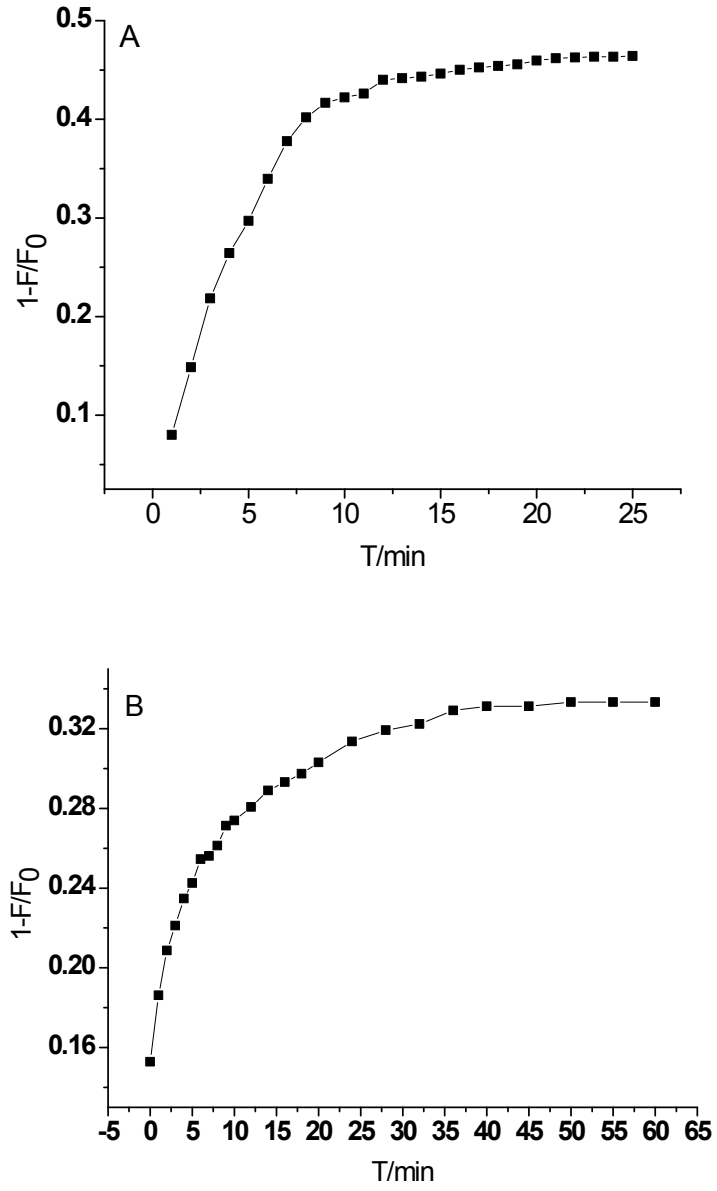


Fig. S10 (A) Effect of reaction time on the detection of Pd^{2+}, [P1NRs] = 22.5 μg mL^{-1}, [Pd^{2+}] = 50 μM, pH = 2.2. (B) Effect of reaction time on the detection of Pd^{2+}, [P2NRs] = 17.5 μg mL^{-1}, [Pd^{2+}] = 4 μM, pH = 3.0.

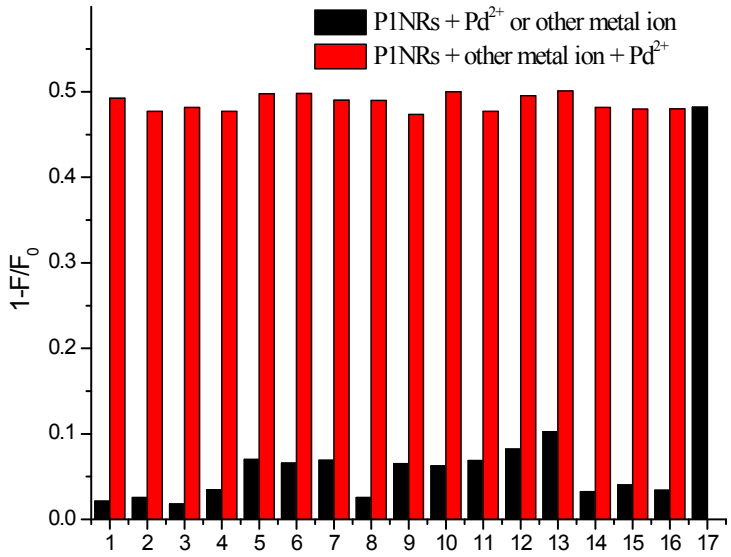


Fig. S11 Fluorescence response of P1NRs for Pd^{2+} in the presence of other ions. Analyte 1 to 17: Ca^{2+}, Pb^{2+}, Ni^{2+}, Ce^{3+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Ba^{2+}, Ag^{+}, Fe^{2+}, Na^{+}, NH_4^{+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Cd^{2+} and Pd^{2+}. c_{P1NRs} = 22.5 μg mL^{-1}, pH = 2.2, [cation] = 50 μM.

Table S1

Comparison of different fluorescent probes for Pd^{2+} analysis.

Ref.	Detection method	System	Linear range (nM)	LOD (nM)
[20]	Ratiometric fluorescence	Naphthylamine-rhodamine hybrid	0- 2×10^3	45.9
[21]	Fluorescent probe	Rhodamine B hydrazide derivative	-	57
[22]	Fluorescent probe	Ferrocene–rhodamine conjugate	-	8.46
[23]	Fluorescent probe	Boron-dipyrromethene derivative	0- 1.2×10^4	290
[24]	Fluorescent nanoprobe	Carbon nanoparticles	3.5×10^4- 1.0×10^5	58
[26]	Fluorescent polymer	2,6-Bis(2-thienyl)pyridine-based CP	-	2×10^3
[60]	Fluorescent probe	Pyridine-linked anthracene	-	9.55
[61]	Fluorescent probe	Rhodamine-based derivative	0- 1×10^4	190
This work	Fluorescence nanoprobe	P1NRs	1- 1×10^3, 1×10^3- 1×10^5	1
This work	Fluorescence nanoprobe	P2NRs	70- 1×10^5	70