Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Novel Imprinted Polyethyleneimine Nano-fluorescent Probes with Controllable Selectivity for Recognizing and Adsorbing Metal Ions

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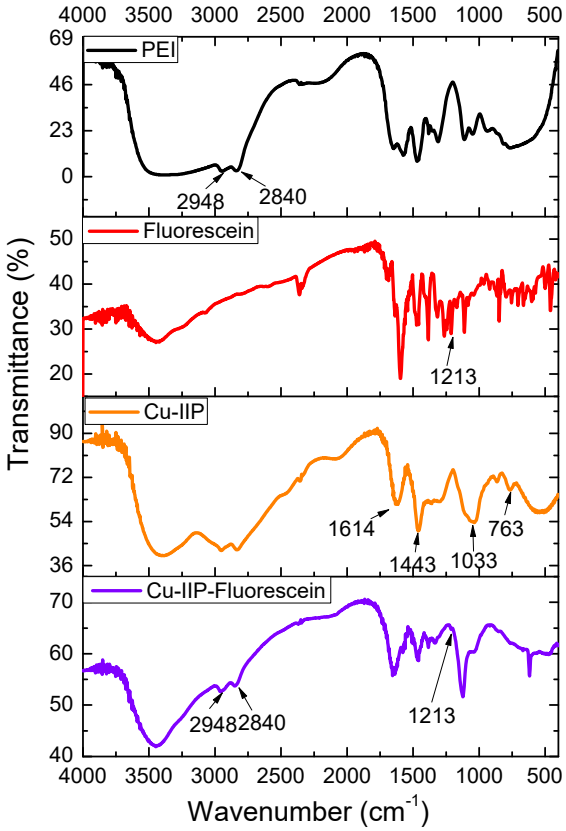


Fig. S1 Infrared spectrum of PEI, fluorescein, Cu-IIP and Cu-IIP-Fluorescein.

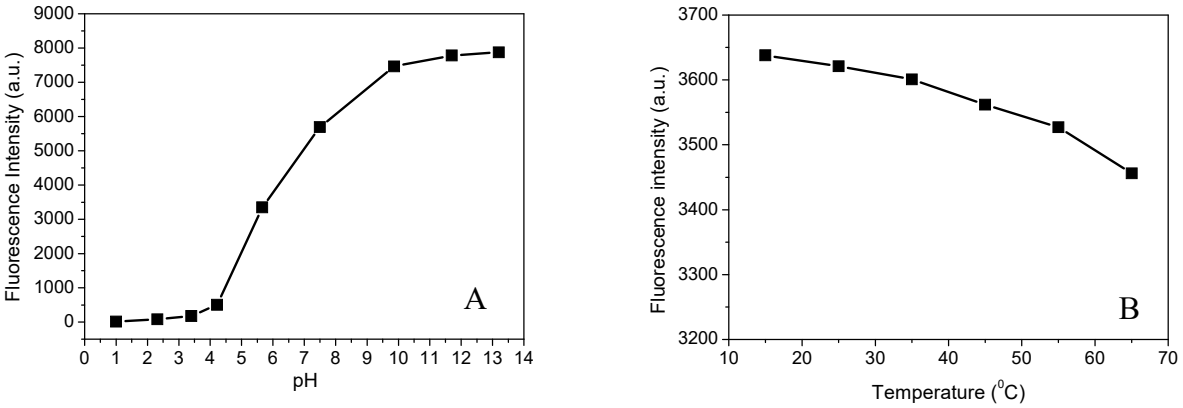


Fig. S2 Fluorescence intensity of fluorescein dependence on pH and temperature. (A) Fluorescein is hydrophobic at low pH of solution. Upon increasing the solution pH, the hydrogen ions on carboxyl and phenolic hydroxyl group of fluorescein are dissociated. The solubility of fluorescein in water increase and charge transfer is enhanced, resulted in the increase of fluorescence intensity. (B) The higher temperature intensifies molecular vibration and collision in solution. The emission energy in electron transition process is easier to dissipation by collision, leading to the decrease of fluorescence intensity.

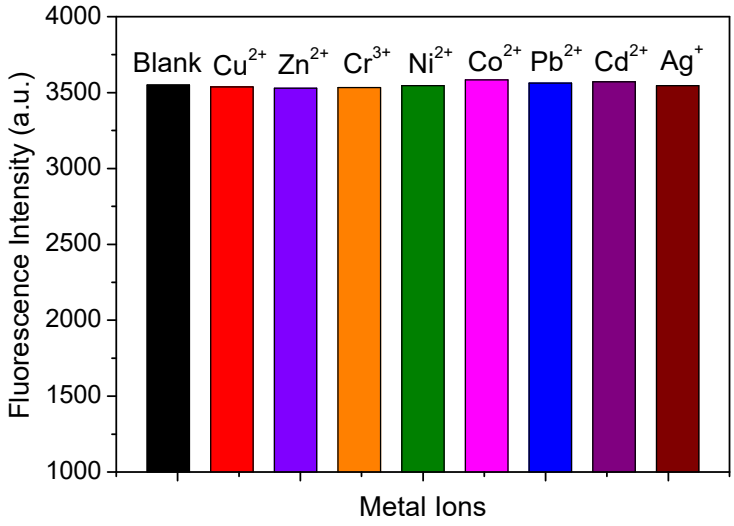
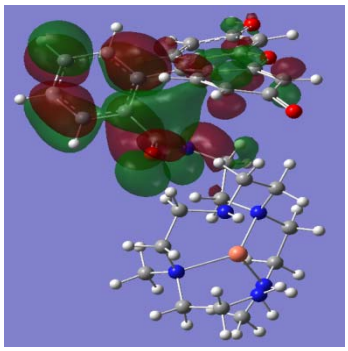
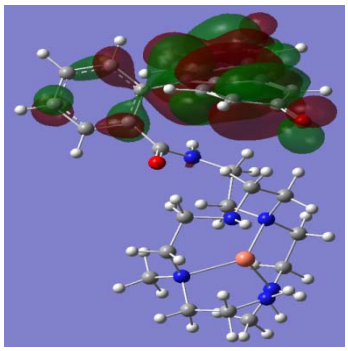


Fig. S3 Fluorescence intensity of fluorescein (0.5μM) with adding of each metal ion (5mg/L).

	Cu-IIP-Fluorescein	Cu-IIP-Fluorescein+ Cu^{2+} (α electron)	Cu-IIP-Fluorescein+ Cu^{2+} (βelectron)
LUMO+1			
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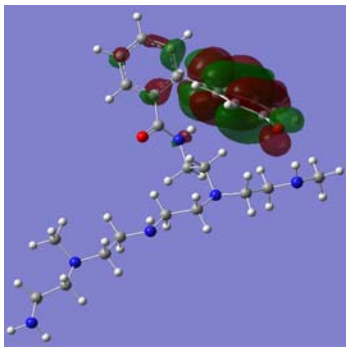
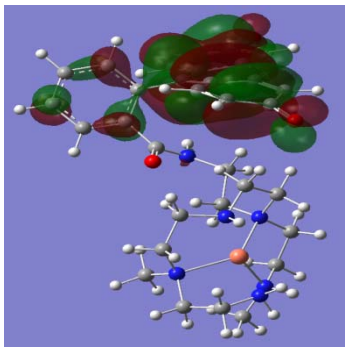
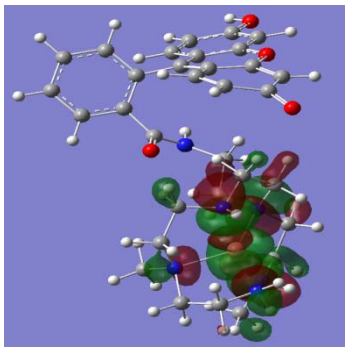
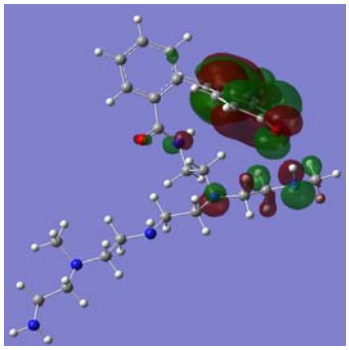
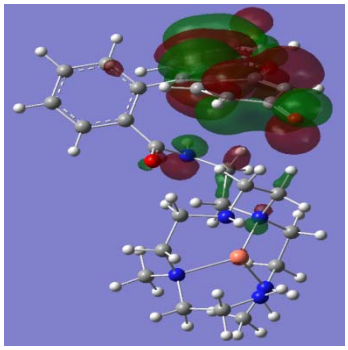
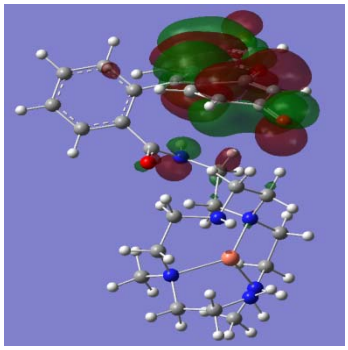
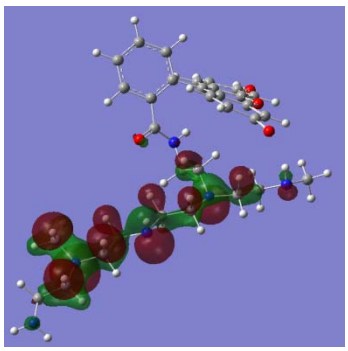
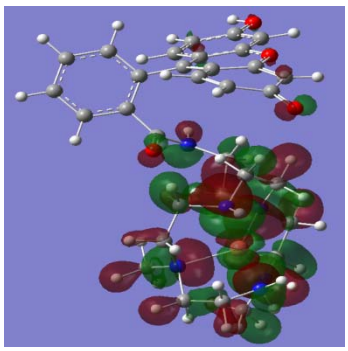
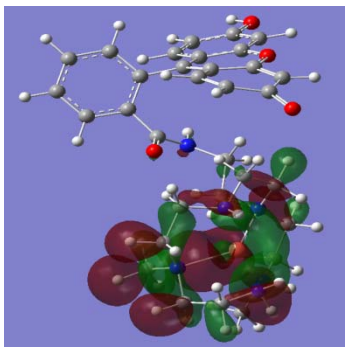
LUMO			
	155 MO -0.09878 a.u.	164 MO -0.09975 a.u.	163 MO -0.11493 a.u.
HOMO			
	154 MO -0.23156 a.u.	163 MO -0.22905 a.u.	162 MO -0.22913 a.u.
HOMO-1			
	153 MO -0.23499 a.u.	162 MO -0.25199 a.u.	161 MO -0.25883 a.u.

Fig. S4 Frontier molecular orbital distributions and energy of Cu-IIP-Fluorescein

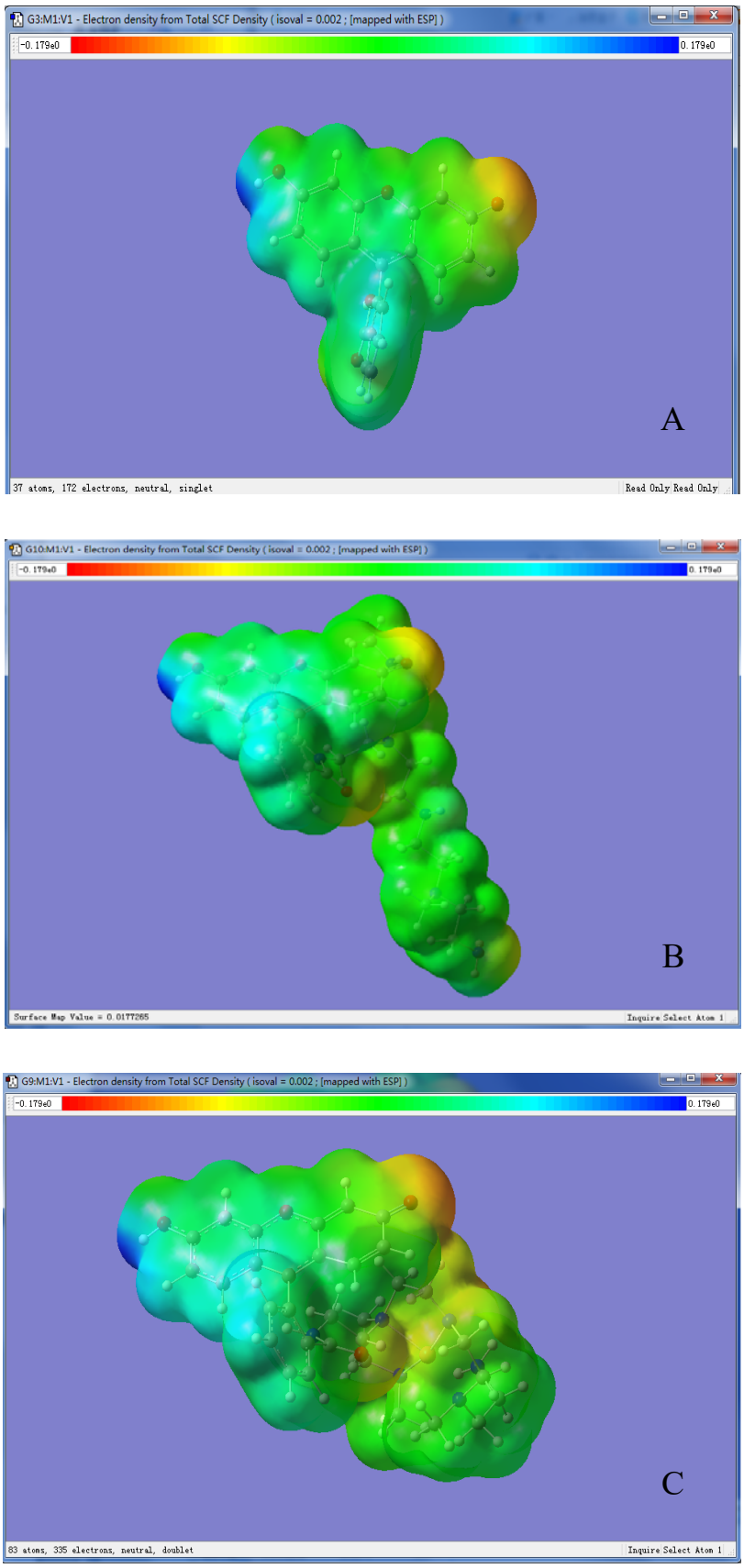
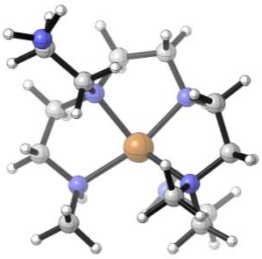
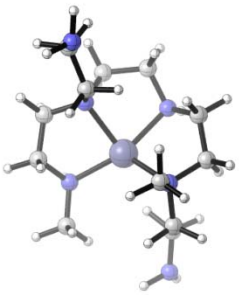


Fig. S5 Electron density distribution of fluorescein (A), probe before (B) and after (C) coordinating with metal ions.



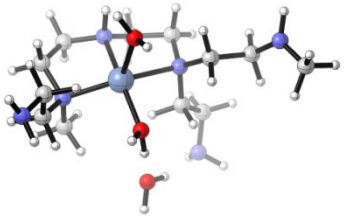
PEI-Cu^{2+}

ΔH = -47.8 kcal/mol



PEI-Zn^{2+}

ΔH = -28.8 kcal/mol

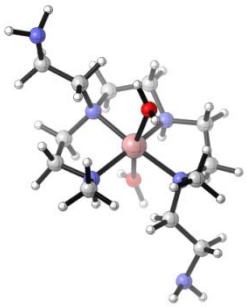


PEI-Cr^{3+}

ΔH = -59.9 kcal/mol

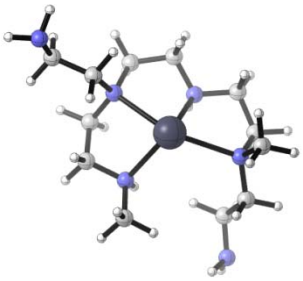
PEI-Ni^{2+}

ΔH = -45.6 kcal/mol



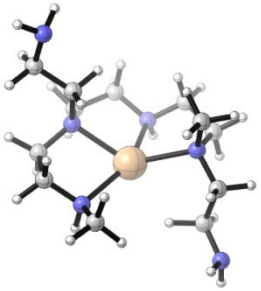
PEI-Co^{2+}

ΔH = -53.2 kcal/mol



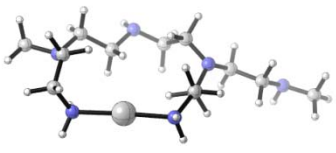
PEI-Pb^{2+}

ΔH = -25.5 kcal/mol



PEI-Cd^{2+}

ΔH = -26.0 kcal/mol



PEI-Ag^{+}

ΔH = -25.4 kcal/mol

Fig. S6 Spatial configuration simulation and enthalpy of PEI coordinated with metal ions. The blue ball

and red ball represent nitrogen atom and oxygen atom, respectively. ΔH means enthalpy changes in coordination process. The higher absolute value indicates the complex is more stable. The PEI-Co^{2+} and PEI-Ni^{2+} have relative higher enthalpy changes, however the adsorption capacities are very low in experiment. The reasonable explanation for PEI-Co^{2+} is that coordination process is under restriction of dynamics with much higher activation energy. The PEI-Ni^{2+} is octahedron structure with 6 amidogen of PEI. However, the PEI polymer chains are hardly to form this compact structure due to intramolecular or intermolecular steric hindrance.

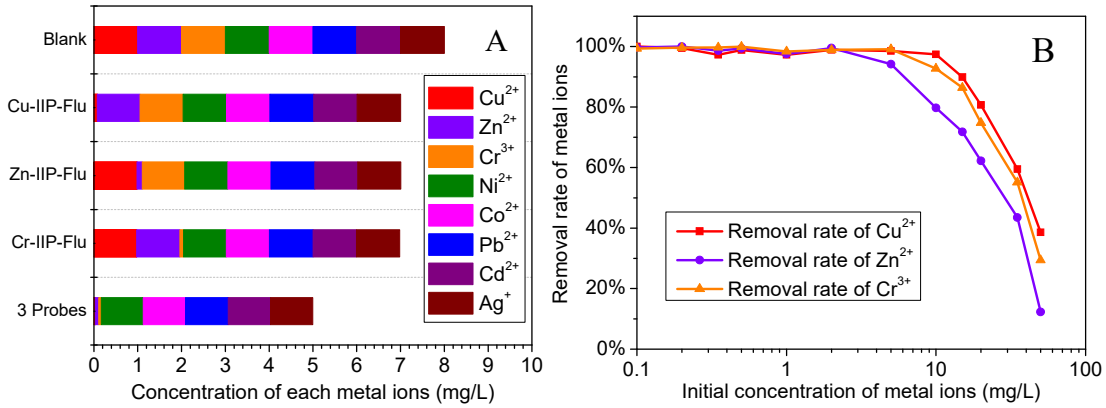


Fig.S7 (A) Concentration distribution histogram of metal ions in river water (added each metal ion of 1 mg/L). Cu-IIP-Flu, Zn-IIP-Flu or Cr-IIP-Flu represents the concentration distribution after treatment by Cu-IIP-Fluorescein, Zn-IIP-Fluorescein or Cr-IIP-Fluorescein, respectively. 3 Probes represents the treatment by three probes together. (B) Removal rate of metal ions with 0.1 μM of each nano-fluorescent probe.

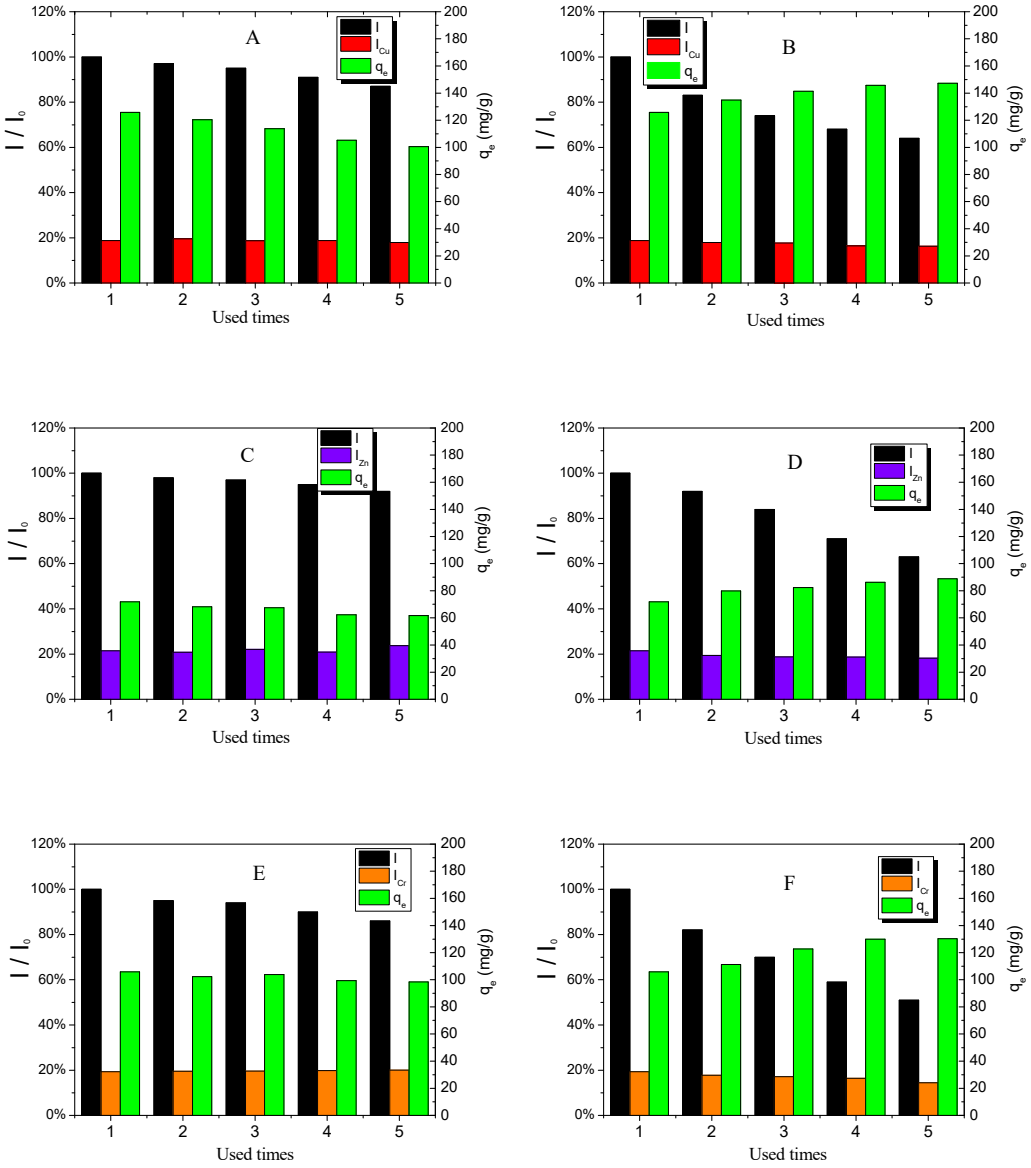


Fig.S8 Relative fluorescence intensity and adsorption capacities of three nano-fluorescent probes to template metal ions (Cu^{2+}, Zn^{2+} or Cr^{3+}) in five times of reuse. The probes were eluted and regenerated with 0.1 M EDTA (A, C and E) or 0.1 M hydrochloric acid (B, D and F). Black bars represent the initial fluorescence intensity of regenerated probes at 523 nm (I) over the original emission at 523 nm (I0). Red, violet or orange bars represent the fluorescence intensities after addition of 10 mg/L Cu^{2+}, Zn^{2+} or Cr^{3+} to a 0.1 μM relevant probe solution, respectively. Green bars represent adsorption capacities to Cu^{2+}, Zn^{2+} or Cr^{3+}, respectively.

Table S1 Particle diameter, Zeta potential and isoelectric point of IIPs and probes

	Particle Diameter (nm) (mean[a] ± SD[b])	Zeta Potential (mV) (mean[a] ± SD[b])	Isoelectric Point (mean[a] ± SD[b])
Cu-IIP	178 ± 12	+ 47.2 ± 0.8	11.24 ± 0.28
Zn-IIP	227 ± 29	+ 68.3 ± 1.8	12.84 ± 0.34
Cr-IIP	208 ± 23	+ 54.6 ± 2.1	11.86 ± 0.53
Cu-IIP-Fluorescein	190 ± 19	+ 32.5 ± 1.2	10.08 ± 0.15
Zn-IIP-Fluorescein	268 ± 44	+ 30.3 ± 3.7	9.54 ± 0.81
Cr-IIP-Fluorescein	241 ± 36	+ 31.8 ± 4.3	9.69 ± 0.26
NIP-Fluorescein	293 ± 109	+22.6 ± 0.2	8.40 ± 0.63
Fluorescein	\	+ 0.4 ± 0.1	5.83 ± 0.12

[a]Mean of three determinations. [b]SD = standard deviation. \ Not nanoparticles.

Table S2 Absorbance and fluorescent peak area of fluorescein and probes

							Slope[a]	R^{2b}
Fluorescein	Concentration (μM)	0.0025	0.005	0.01	0.025	0.05	946249	0.9992
	Absorbance (496 nm)	0.0251	0.0313	0.0422	0.0713	0.111		
	Peak Area	12004	17513	26529	53778	93238		
Cu-IIP-Fluorescein	Concentration (μM)	0.0005	0.001	0.0025	0.005	0.01	857208	0.9999
	Absorbance (496 nm)	0.0273	0.0317	0.0423	0.0606	0.0968		
	Peak Area	4002	7755	17153	32262	63687		
Zn-IIP-Fluorescein	Concentration (μM)	0.0005	0.001	0.0025	0.005	0.01	798111	0.9995
	Absorbance (496 nm)	0.0267	0.0309	0.0401	0.0582	0.0957		
	Peak Area	3437	6427	12875	27873	58191		
Cr-IIP-Fluorescein	Concentration (μM)	0.0005	0.001	0.0025	0.005	0.01	816273	0.9998
	Absorbance (496 nm)	0.0271	0.0319	0.0414	0.0599	0.0989		
	Peak Area	3749	7375	16071	30731	62342		
NIP-Fluorescein	Concentration (μM)	0.0005	0.001	0.0025	0.005	0.01	742295	0.9996
	Absorbance (496 nm)	0.0338	0.0383	0.0495	0.0711	0.1177		
	Peak Area	2780	6278	15563	31345	65239		

[a]Slope of Peak Area (y) dependence on Absorbance (x). The fluorescence quantum yields of probes were calculated through the slope ratio between probes and standard substance (Fluorescein). [b]R^2 = Fitting variance.

Table S3. Determination and removal rate of template metal ions with interferents. (pH = 5.65, 25 °C)

Added Interferent (1 mg/L)	Cu^{2+} (1 mg/L)		Zn^{2+} (1 mg/L)		Cr^{3+} (1 mg/L)	
	Determination	Removal rate	Determination	Removal rate	Determination	Removal rate
$KAl(SO_4)_2 \cdot 12H_2O$	0.735 ± 0.104	95.1%	0.715 ± 0.162	93.4%	0.762 ± 0.128	94.2%
$CaCl_2$	1.013 ± 0.021	96.2%	1.025 ± 0.014	93.1%	1.009 ± 0.023	95.3%
KH_2PO_3	0.994 ± 0.068	95.8%	0.989 ± 0.083	94.4%	1.004 ± 0.059	94.1%
NH_4Ac	0.998 ± 0.013	95.6%	0.108 ± 0.032	94.1%	0.986 ± 0.019	94.8%
Phenol	1.004 ± 0.020	95.9%	1.016 ± 0.036	94.6%	1.042 ± 0.027	95.2%
Methanal	1.022 ± 0.016	96.1%	1.008 ± 0.029	94.3%	0.994 ± 0.034	94.7%
Chloroform	1.016 ± 0.023	95.7%	0.992 ± 0.042	93.2%	1.035 ± 0.039	94.4%
$KMnO_4$	3.156 ± 0.268	95.5%	3.953 ± 0.354	93.3%	3.492 ± 0.468	94.5%