Supplementary Information

Facile synthesis of water soluble fluorescent metal (Pt, Au，Ag and Cu) quantum clusters for selective detection of Fe^{3+} ions as both fluorescent and colorimetric probe

Shaochen Zhou,[a,b] Mei Zhang,[a,c] Fangyuan Yang,[a,b] Fu Wang[a,*] and Chuanyi Wang[a,*]

[a]Laboratory of Environmental Sciences and Technology, Xinjiang Technical Institute of Physics & Chemistry; Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi, Xinjiang 830011, China

[b]University of Chinese Academy of Sciences, Beijing 100049, China

[c]College of Chemistry and Chemical Engineering, Xinjiang Normal University, Urumuqi 830054, China

Table S1. Preparation of metal (Pt, Au, Ag, Cu) QCs under different conditions

Metal quantum clusters	Solution color after blending of reactants	Solution color after reaction	Fluorescence (excited at 365 nm)	Reaction time (h)	Reaction temperature (^{o}C)
Pt	Colorless	Colorless	Non-luminescent	-	5
		Pale brown	Green light	96	15
		Pale brown	Green light	24	35
		Puce	Green light	4	65
		Puce	Green light	1	80
Au	Brownish yellow	Pale brown	Green light	8	5
		Pale brown	Green light	1	15
		Pale brown	Green light(Blue precipitants were observed)	0.25	35
		Colorless	Blue precipitants	-	65
		Colorless	Precipitants	-	80
Ag	Brown red	Brown	Green light	120	5
		Puce	Green light	48	15
		Puce	Green light	6	35
		Puce	Green light	2.5	65
		Puce	Green light	0.5	80
Cu	Pale blue	Brown	Green light	132	5
		Brown	Green light	40	15
		Brown	Green light	4	35
		Puce	Green light	2	65
		Puce	Green light	0.5	80

Table S2. Excitation and emission peaks ($\lambda_{ex}/\lambda_{em}$), average PL lifetimes (τ_{avg}), QYs, average diameters (d_{avg}) and magic numbers (N) of the as-prepared metal QCs.

Metal QCs	**$\lambda_{ex}/\lambda_{em}$ (nm)**	**τ_{avg} (ns)**	**QY (%)**
Pt	352/480	7.39	2.93
Au	401/495	6.60	13.10
Ag	370/468	4.08	6.97
Cu	375/460	4.59	8.29

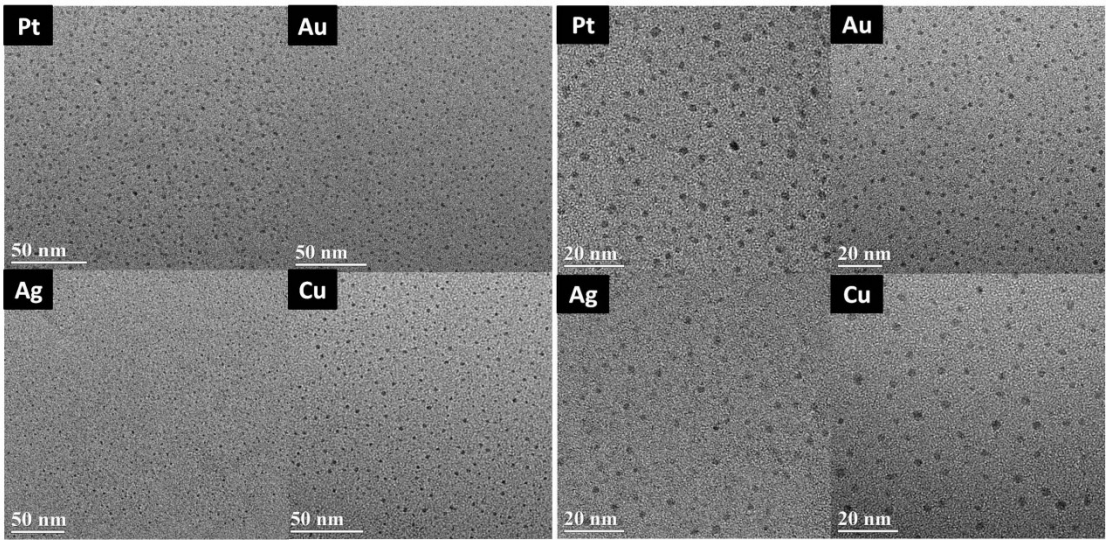

Figure S1. HR-TEM images of the as-synthesized metal (Pt, Au, Ag and Cu) clusters in two different scale bars (50 nm and 20 nm).

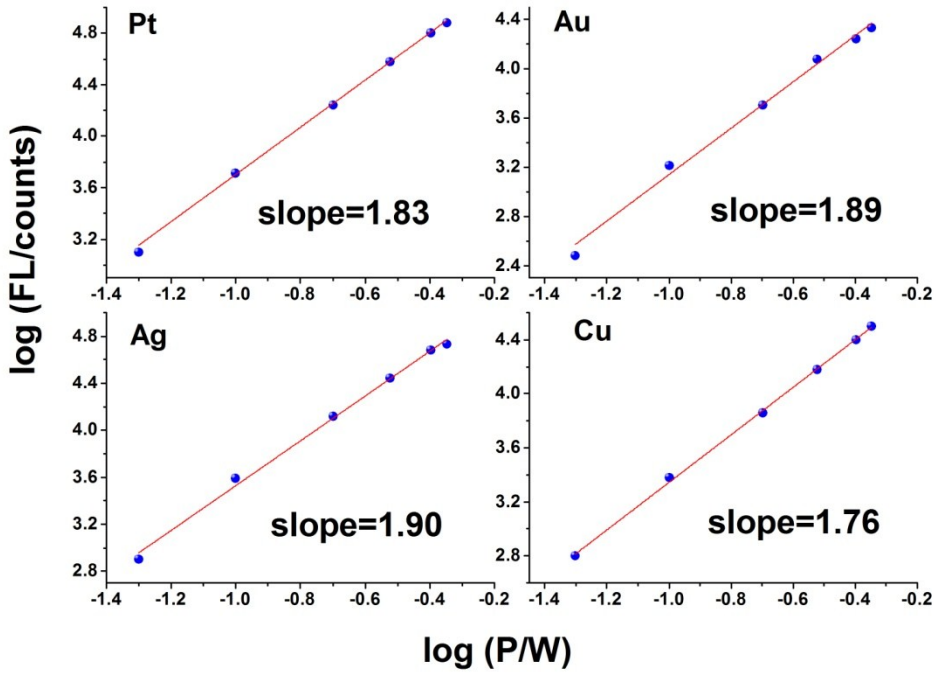

Figure S2. Plots of logarithmic fluorescence intensity (log(FL)) excited by femtosecond laser at 812 nm with the variation in logarithmic pump power (log(P)).

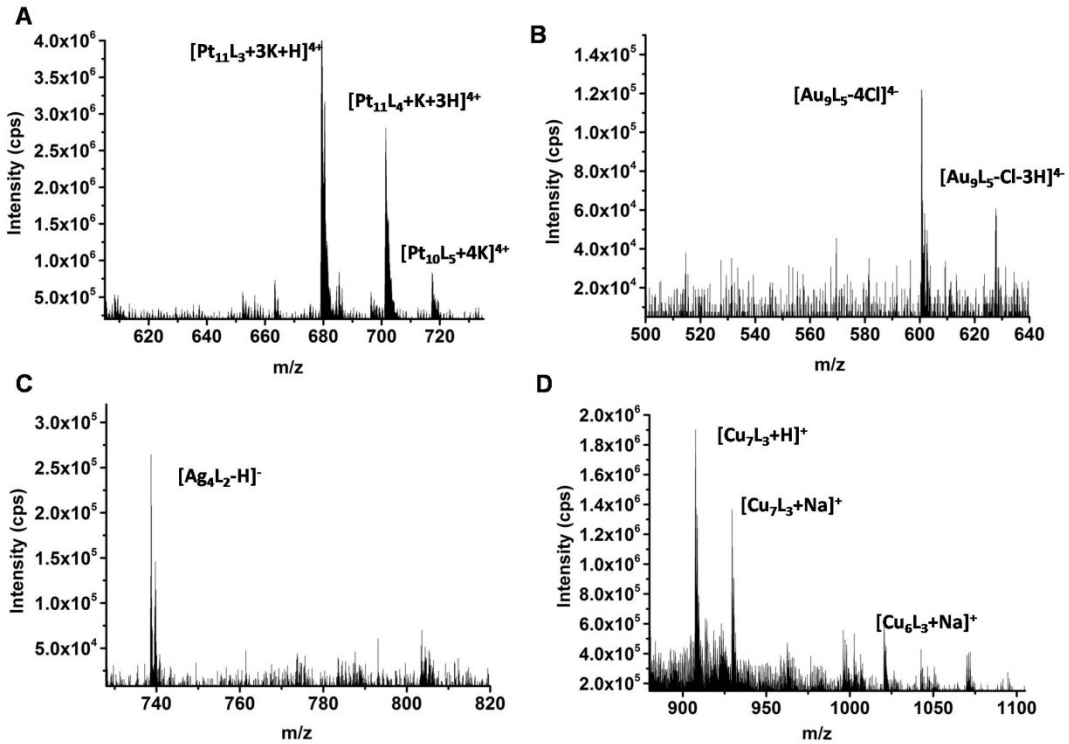

Figure S3. ESI-MS spectra of histidine-capped Pt (A), Au (B), Ag (C) and Cu (D) QCs.

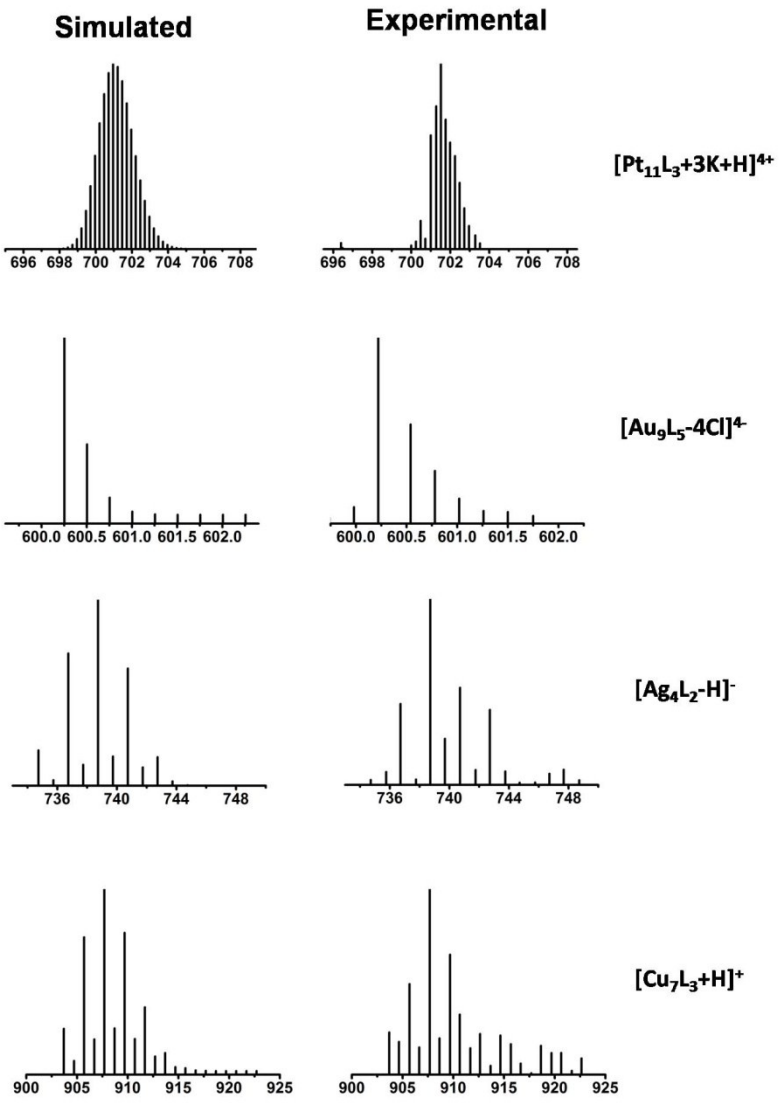

Figure S4. Comparison between experimental and simulated results of ESI-MS spectra

Table S3. Emission energies of the as-prepared metal QCs (E_{em}), Fermi energies of bulk metal (E_f), calculated and actual metal core numbers (N) of metal clusters according to experimental results.

Metal QCs	E_{em} (eV)	E_f (eV)	N (Calculated)	N(experimental)
Pt	2.59	5.65	10.38	11
Au	2.51	5.10	8.39	9
Ag	2.66	4.25	4.08	4
Cu	2.70	4.65	5.11	7

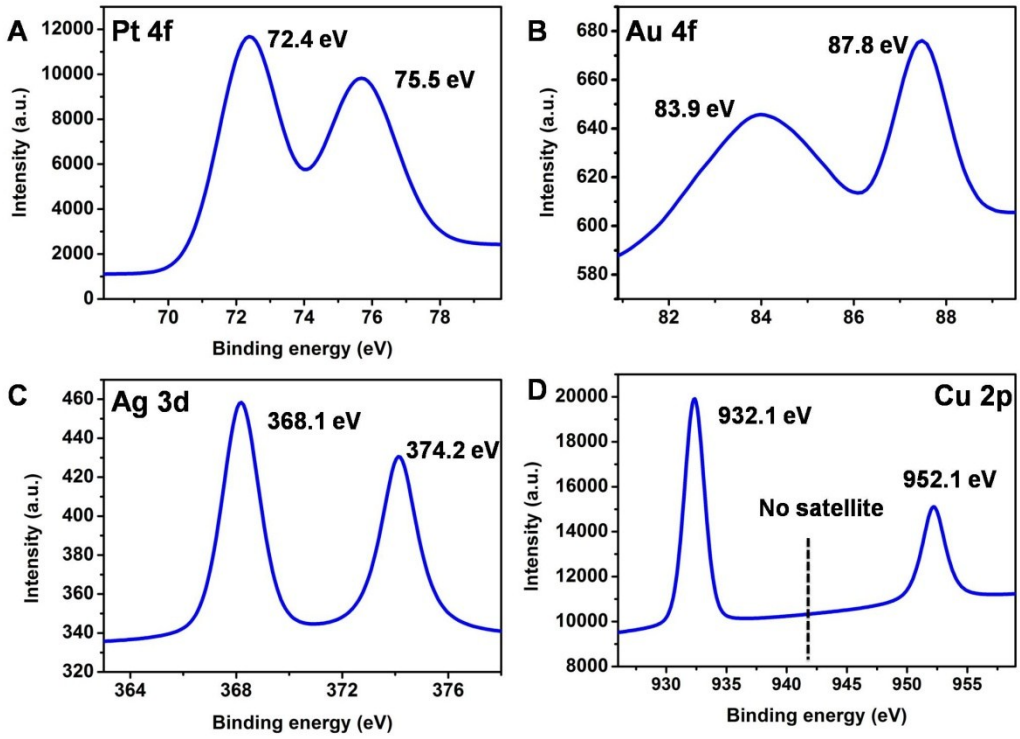

Figure S5. XPS spectra of Pt 4f (A), Au 4f (B), Ag 3d (C) and Cu 2p (D) from the corresponding as-synthesize metal QCs.

Table S4. Binding energies of Pt, Au, Ag and Cu at different valent states

Element	M (0)		M (Ⅰ)		M (Ⅱ)				M (Ⅲ)	
Cu 2p	931.9	951.8	932.7	952.2	932.8	942.1	951.2	956.0	-	-
Au 4f	83.8	87.6	85.1	88.5	85.6		88.9		86.4	89.5
Ag 3d	368.0	374.0	370.0	376.0	-		-		-	-
Pt 4f	71.8	75.1	-	-	74.40		77.60		-	-

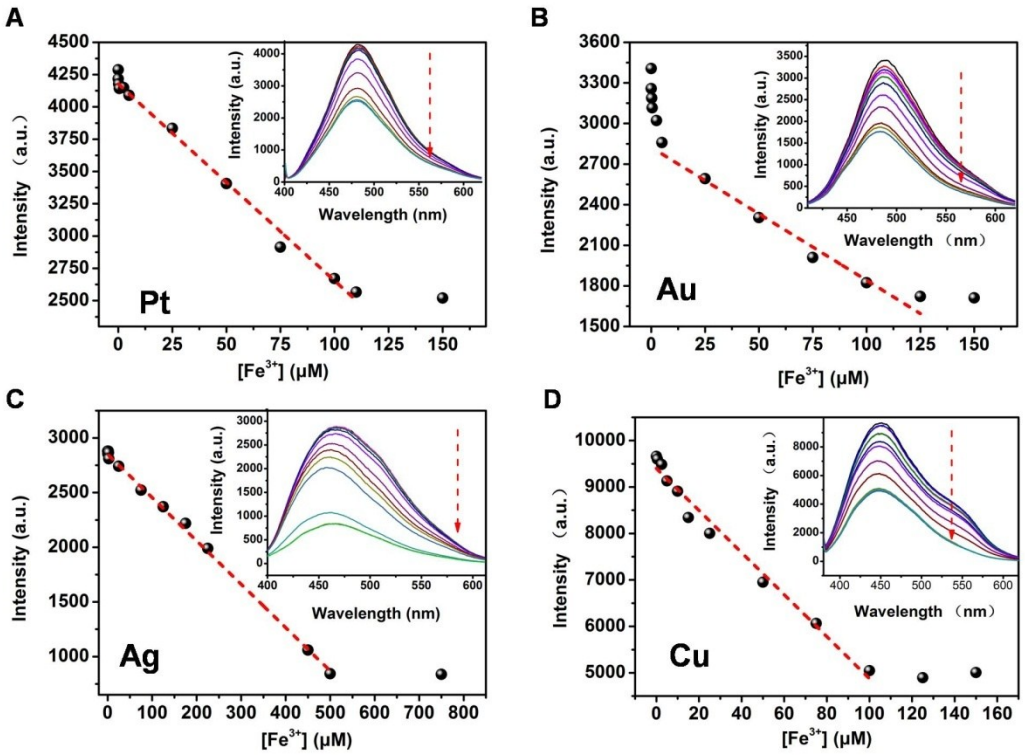

Figure S6. FL spectra of the as-synthesized metal QCs (Pt, Au, Ag, Cu) with the addition of ferric ions.

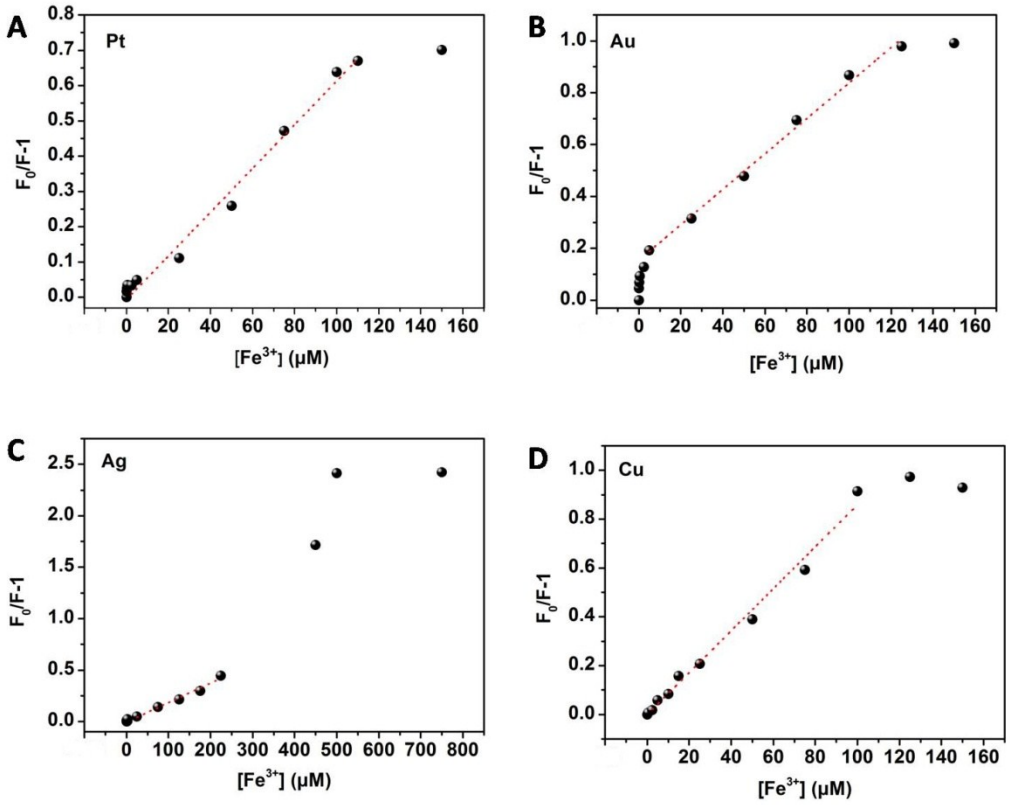

Figure S7. Stern-Volmer plots of the metal (Pt, Au, Ag, Cu) QCs-Fe^{3+} system. K_{sv} values of Pt, Au, Ag, Cu are calculated to be 6.2×10^3, 6.84×10^3, 1.9×10^3 and 8.6×10^3 $L \cdot mol^{-1}$.

Table S5. Quantum yields (QYs) of the metal QCs before and after the addition of ferric ions.

Sample	QY (before)	QY (after)
Pt	2.93 %	1.46 %
Au	13.10 %	5.73 %
Ag	6.97 %	1.76 %
Cu	8.29 %	3.76 %

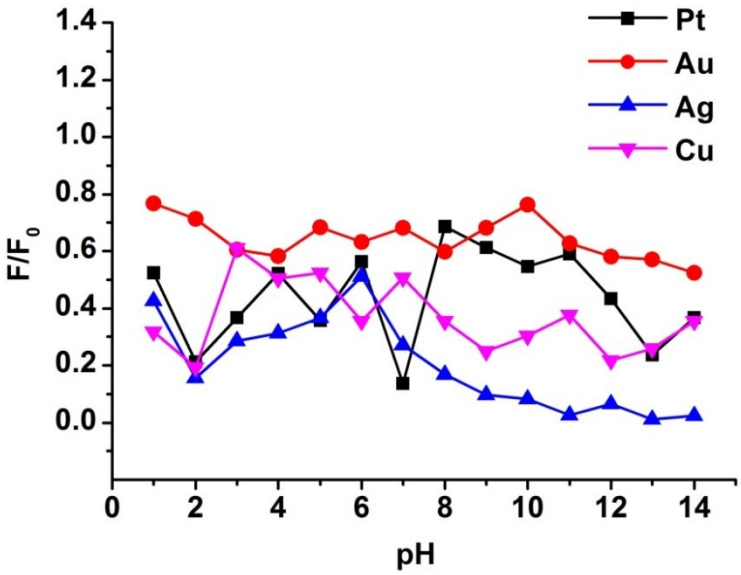

Figure S8. Quenching effect by Fe^{3+} at different pH values. Fe^{3+} ions are added to the metal QCs solution to reach a concetration of 0.5 mM each time. X axis: pH values of the metal QCs-Fe^{3+} system. Y axis: ratio of quenched fluorescence intensity (F) versus initial fluorescence intensity (F_0) at corresponding pH.

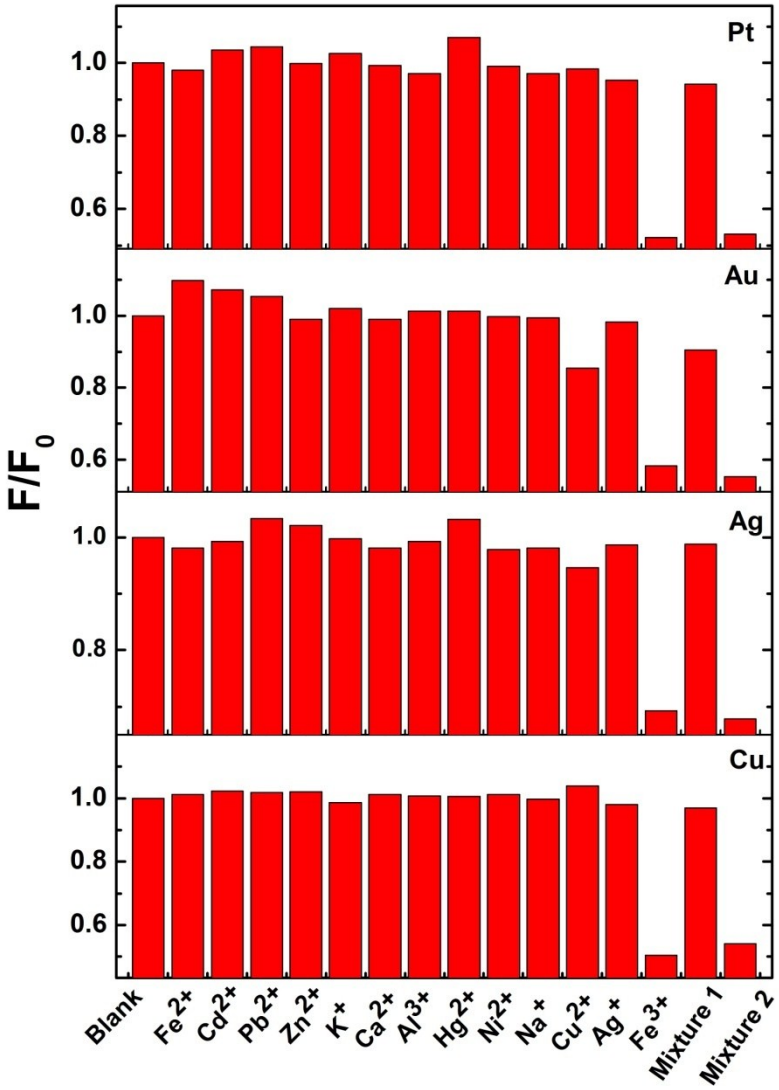

Figure S9. Selectivity and interference tests for the metal (Pt, Au, Ag, Cu) QCs in sensing ferric ions. Mixture 1: system without Fe^{3+} but other metal ions. Mixture 2: system with all of the metal ions. (Concentration for Fe^{3+} is 0.1 mM，and for other metal ions is 1 mM)

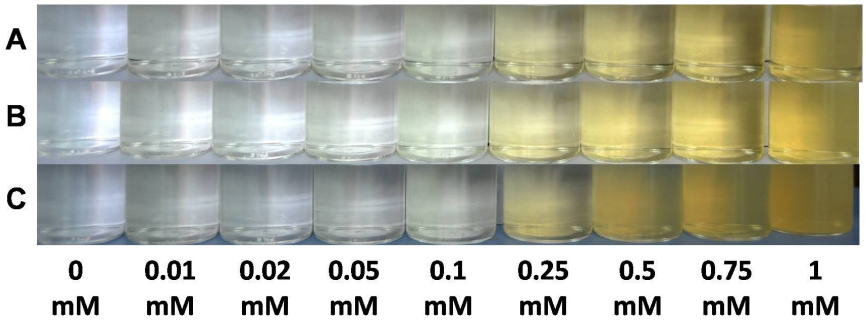

Figure S10. Photographs of the as-synthesized Pt (A), Au (B), Ag (C) QCs solutions with the addition of ferric ions at different concentrations.

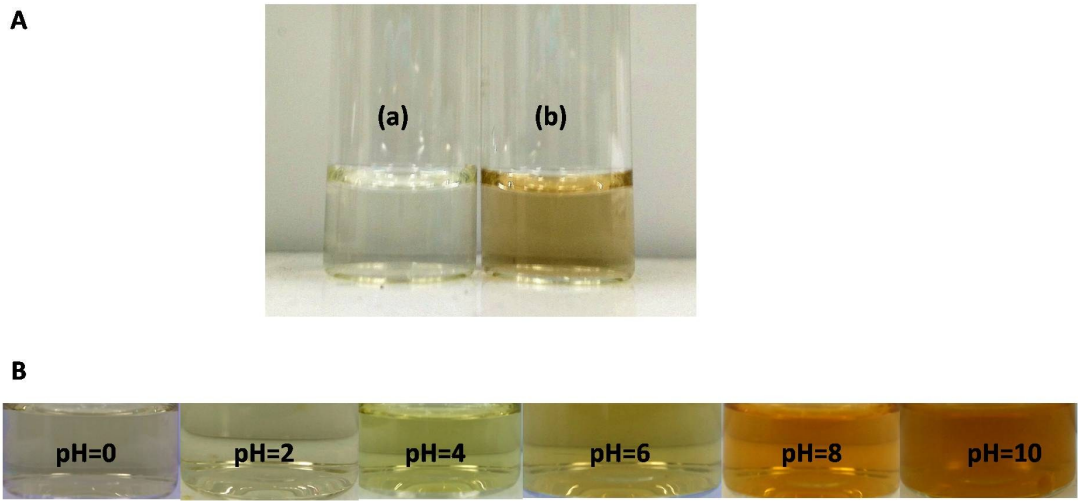

Figure S11. (A) Photographs of Fe^{3+} solutions (0.5 mM, pH=4) without (a) and with (b) metal QCs. (B) Photographs of metal QCs-Fe^{3+} system at different pH values.

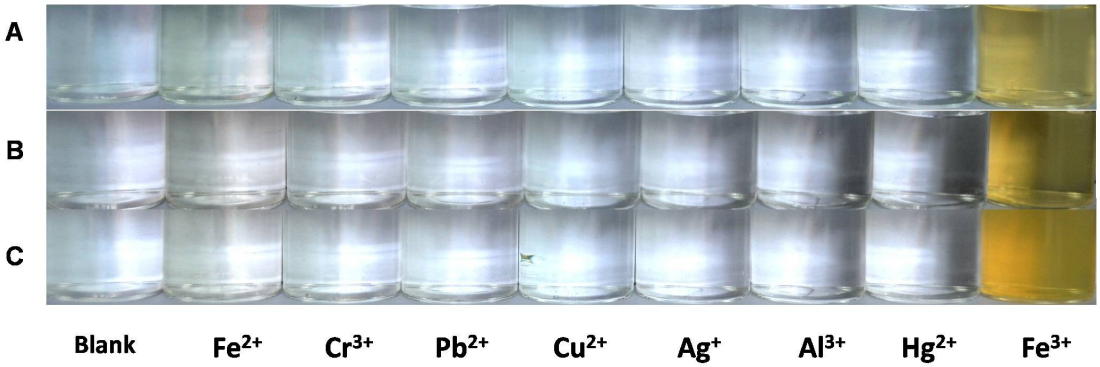

Figure S12. Photographs of the as-synthesized Ag (A), Au (B), Pt (C) QCs solutions with the addition of different metal ions.