Electronic Supporting Information

Development of Fluorescence Sensors with Copper-based Nanoclusters via Förster Resonance Energy Transfer and the Quenching Effect for Vanillin Detection

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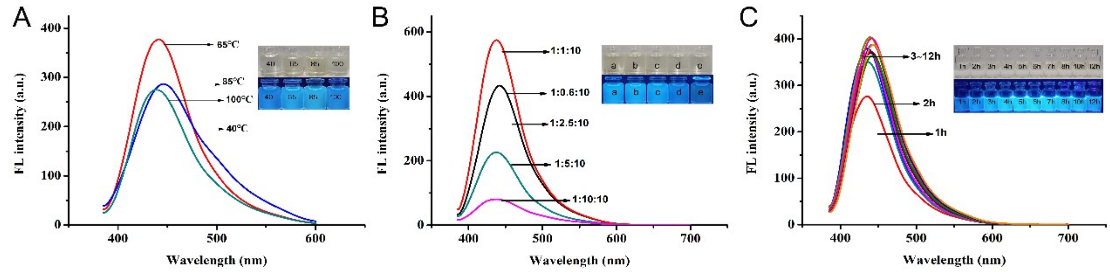

Fig. S1 Optimization of synthesis conditions of CuNCs. (A) temperature (B) molar ratio (Cu^{2+}:SH-β-CD:AA) (C) time.

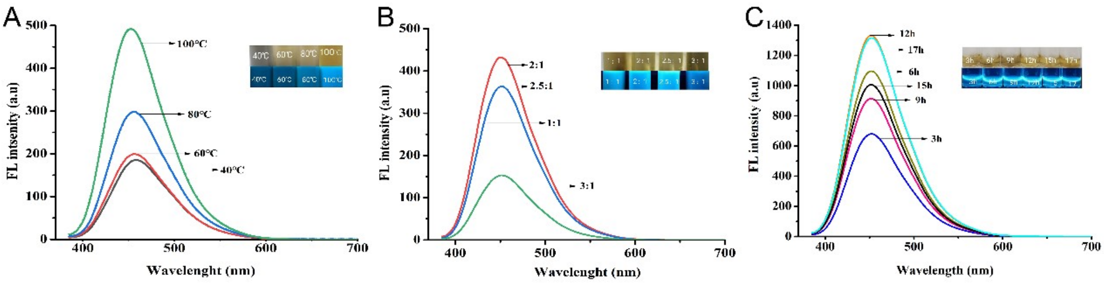

Fig. S2 Optimization of synthesis conditions of CuAuNCs. (A) temperature (B) molar ratio (copper ion :chloroauric acid) (C) time.

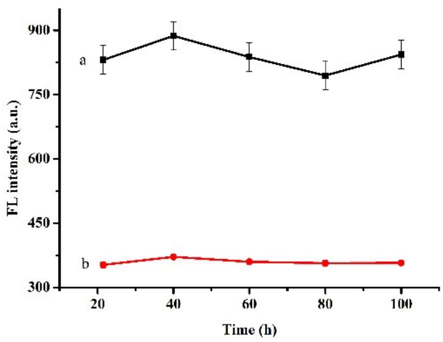

Fig. S3 Fluorescent stability with time (a: CuNCs, b: CuAuNCs)

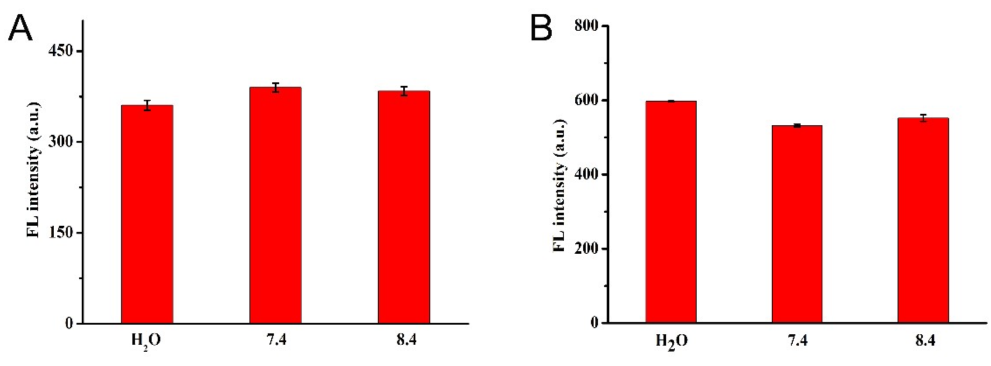

Fig. S4 Fluorescent stability in H_2O and 0.01 M PBS buffers (pH 7.4, 8.4) (A) CuNCs (B) CuAuNCs.

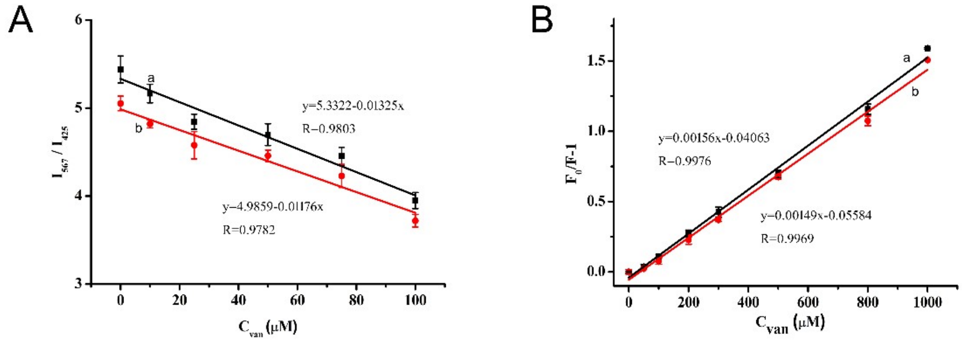

Fig. S5 Linear curve fitting of vanillin by (A) FRET system between CuNCs and NR, (B) CuAuNCs (a: Regression curves of vanillin standard series solutions, b: Spiked recovery curve of milk pretreatment solution).

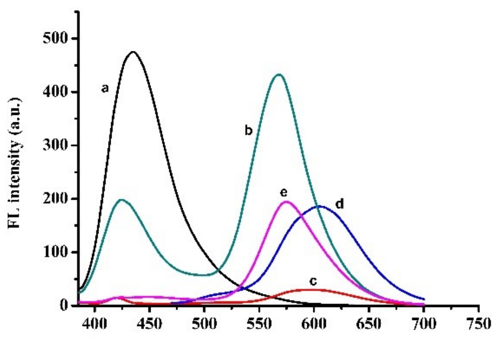

Fig. S6 Fluorescence spectra. (a) CuNCs (100 μL). (b) CuNCs (100 μL) + NR (10^{-4} M). (c) NR (10^{-4} M, λex=365 nm). (d) NR (10^{-4} M, λex=450 nm). (e) β-CD (4 mM) + NR (10^{-4} M).

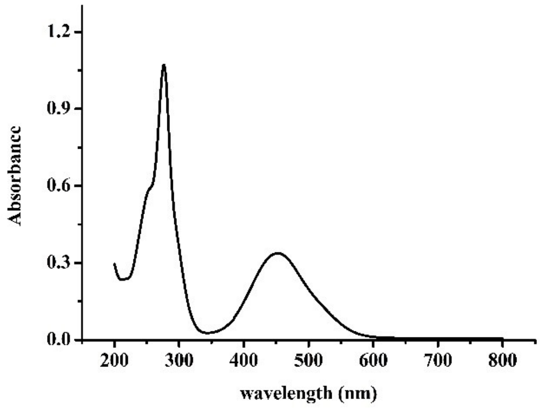

Fig. S7 UV Spectrum of NR

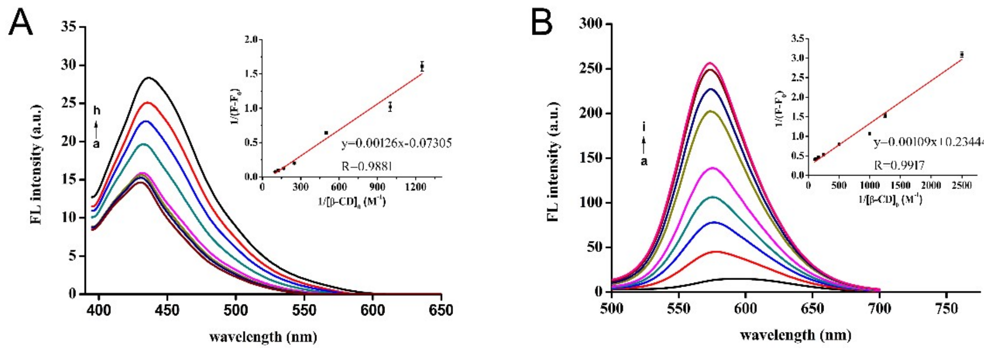

Fig. S8 (A) Fluorescence spectra of vanillin (2×10^{-6} M) at pH 8.4 containing (1) 0, (2) 0.8, (3) 1.0, (4) 2.0, (5) 4.0, (6) 6.0, (7) 7.0, and (8) 10 mM β-CD. (B) Fluorescence spectra of NR (1.0×10^{-5} M) at pH 8.4 containing (1) 0, (2) 0.4, (3) 0.8, (4) 1.0, (5) 2.0, (6) 4.0, (7) 6.0, (8) 7.0, and (9) 10 mM β-CD. Inset: Double reciprocal plot of M/β-CD complex, $1/(F-F_0)$ vs $1/[CD]_0$.

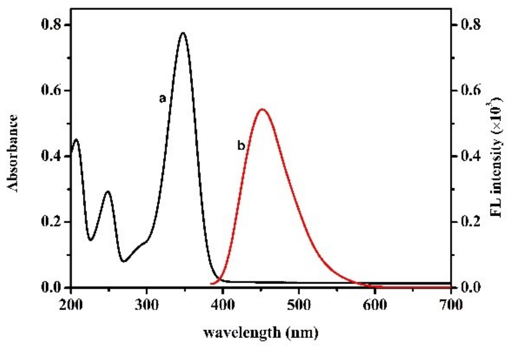

Fig. S9 UV spectrum of vanillin (a) and fluorescence spectrum of CuAuNCs (b)

Tab. S1 Comparison of various fluorescence sensors and their analytical parameters for determination of vanillin

materials	Linear ranges (μM)	LOD(μM)	Ref.
Cd(II) coordination polymer	0~10	1.41	1
Zr(IV)-MOF	12.5~45	0.38	2
N-doped carbon dots (NCDs)	0.43~264	0.10	3
Graphene quantum dots	0~10	0.025	4
CdSe/ZnS quantum dots	13~130	6.51	5
CuNCs	10~100	8.08	This work
CuAuNCs	50~1000	10.17	

Table S2. Determination of vanillin in real samples (n=3).

sample	Method Proposed	Added (μM)	Total found (μM)	Recovery (%)	RSD (%)
milk	FRET between CuNCs and NR Quenching by CuAuNCs	30	31.2	103.9	3.43
		80	79.8	99.7	2.15
		250	253.6	101.4	4.39
		700	719.6	102.8	0.78

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