Supporting Information *for*

Bonding-Induced Emission of Silyl-Protected Copper Nanoclusters for Luminescence Turn-on Detection of Trace Water in Organic Solvents

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amount of water in organic solvents

1. Experimental Section

1.1 Materials and Reagents.

Triple-distilled water was used throughout the experimental process. Copper nitrate ($Cu(NO_3)_2$) was obtained from Aladdin Company (Shanghai, China). (3-Mercaptopropyl)trimethoxysilane (MPTMS) was purchased from J&K Chemical Company (Shanghai, China). Acetonitrile (CH_3CN), N,N-dimethylformamide (DMF), ethanol (CH_3CH_2OH), 1,4-dioxane (Diox) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich (Shanghai, USA). All of the solvents were purified using a VTI organic solvent purification system, and the water content of purified organic solvents was controlled at ppm level.

1.2 Synthesis of Silyl-Protected CuNCs.

In a typical procedure, $Cu(NO_3)_2$ (0.006 g) was added into 20 mL of anhydrous acetonitrile in a 100-mL round-bottom flask, and then 25 μL of (3-mercaptopropyl)-trimethoxysilane (MPTMS) was added into the solution. The solution was vigorously stirred at room temperature for 30 min. A colorless and transparent solution was obtained, which was preserved at low-temperature conditions for the further experiment.

1.3 Luminescence Turn-on Quantitation of Trace Amount of Water in Organic Solvents.

For optimization of incubation time of emission enhancement of silyl-protected CuNCs by trace water, 9.0 μL of water was added into 3.00 mL of silyl-protected CuNCs acetonitrile solution, and then the luminescence of mixed solution was monitored with different incubation times of 0-40 min where the interval is 2 min. To examine the temperature effect on the optimum incubation time, three temperatures including 25, 35 and 45 ℃ were tested in the similar way. A dilution of water in acetonitrile was first prepared as the stock solution by mixing 100.0 μL of water and 900.0 μL anhydrous acetonitrile. Under the optimum incubation time (30 min), the luminescence of silyl-protected CuNCs solution (3.00 mL) was recorded with continuous addition of different volumes of water dilution in acetonitrile after 30 min of incubation. The same procedure was also performed for detection of water in DMF, THF, 1,4-dioxane and CH_3CH_2OH. All experiments were conducted at 25 ℃.

1.4 Characterization Methods.

Transmission electron microscopy (TEM) was conducted on a JEOL-Model 2100F instrument with an accelerating voltage of 200 kV. A Kratos Axis ULTRA X-ray photoelectron spectroscopy was used for the X-ray photoelectron spectroscopy analyses. The UV-vis spectra were recorded on a Perkin-Elmer Lambda 950 spectrometer. The luminescence spectra and time-resolved luminescence decay tests were performed using Edinburgh Instruments Model FLS980 fluorescence spectrophotometer.

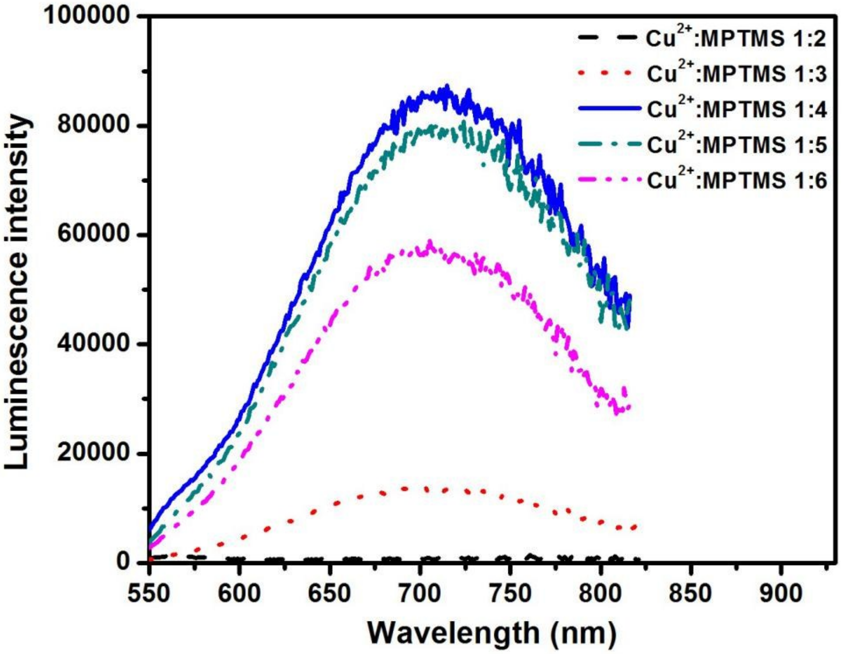

Figure S1. Change in luminescence spectra of the mixtures containing $Cu(NO_3)_2$ (2.5 mM) and different amounts of (3-mercaptopropyl)trimethoxysilane (5.0, 7.5, 10.0, 12.5, 15.0 mM) in CH_3CN.

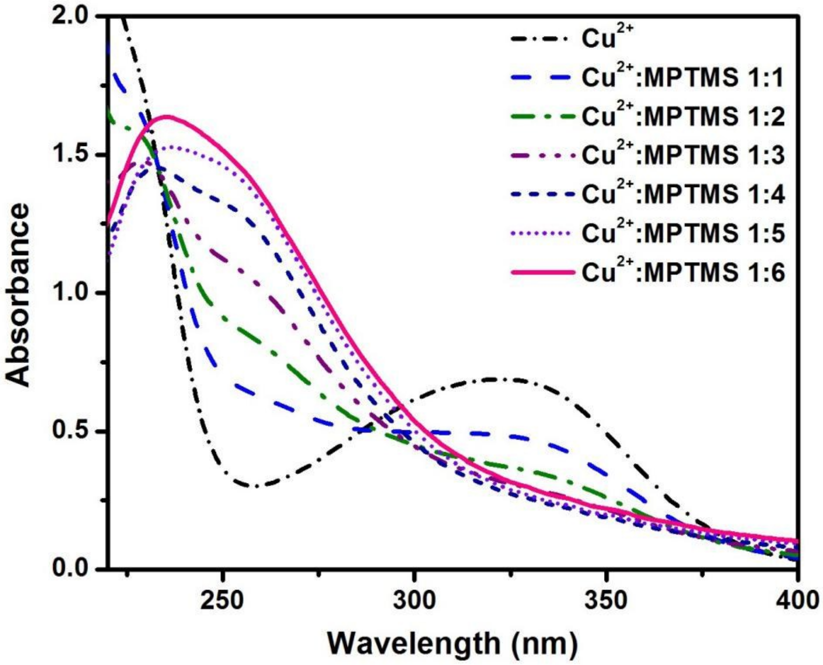

Figure S2. Change in UV-visible spectra of the mixtures containing $Cu(NO_3)_2$ (2.5 mM) and different amounts of (3-mercaptopropyl)trimethoxysilane (0.0, 2.5, 5.0, 7.5, 10.0, 12.5, 15.0 mM) in CH_3CN.

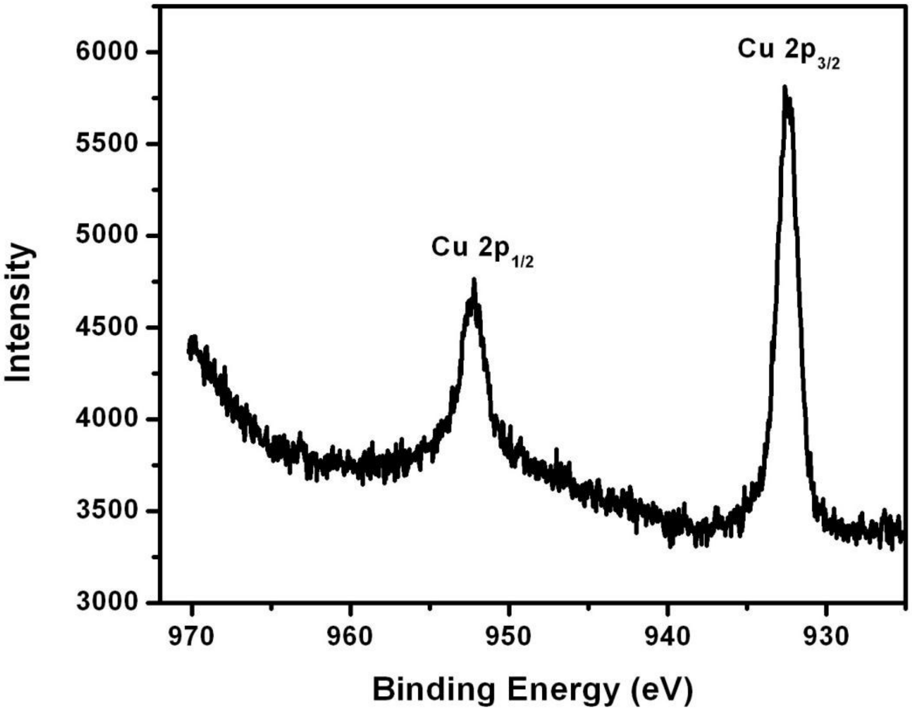

Figure S3. High-resolution X-ray photoelectron spectrum of Cu 2p electrons in CuNCs.

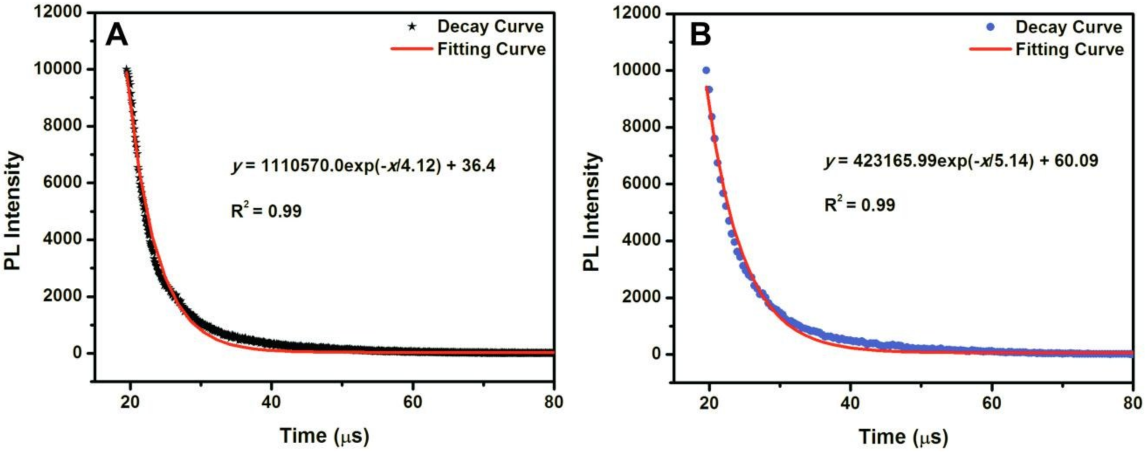

Figure S4. Time-resolved luminescence decay curves of CuNCs solution (A) and CuNCs powder (B). Their lifetimes are determined to 4.12 and 5.14 μs, respectively.

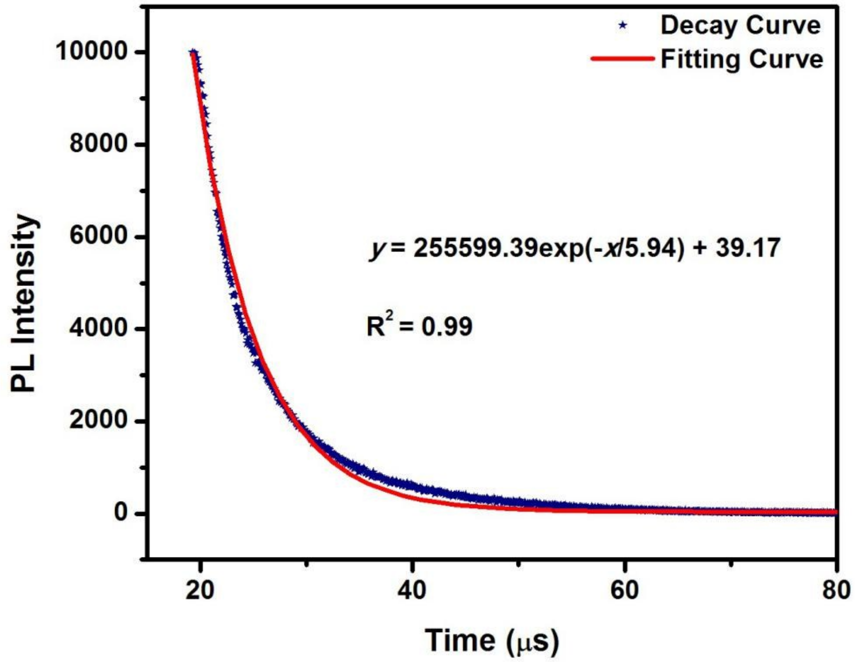

Figure S5. Time-resolved luminescence decay curve of CuSiNPs solution in acetonitrile. The lifetime of CuSiNPs is determined to be 5.94 μs.

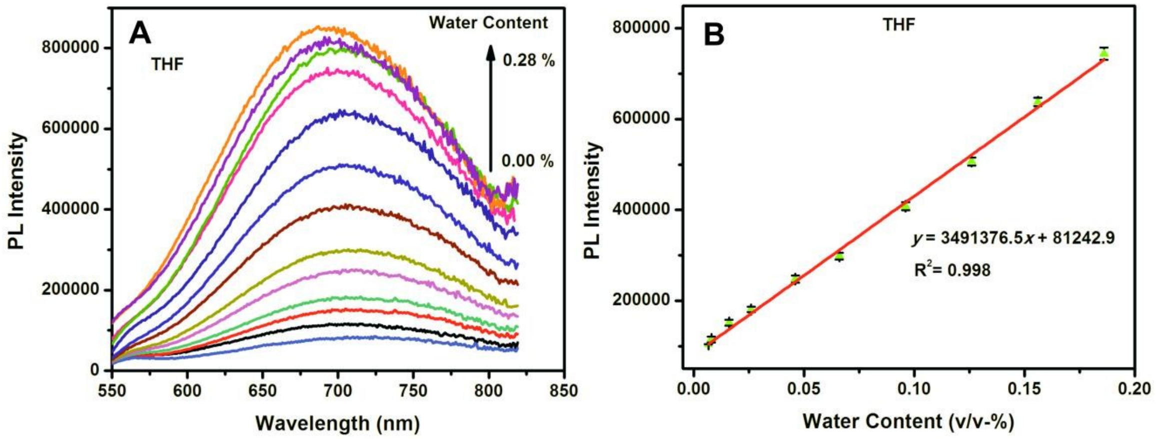

Figure S6. (A) The change in luminescence spectrum of CuNCs in THF as the function of water content in the range of 0.0 v/v% – 0.28 v/v%. (D) Calibration curve between PL intensity and water content ranging from 0.0% to 0.19 v/v%.

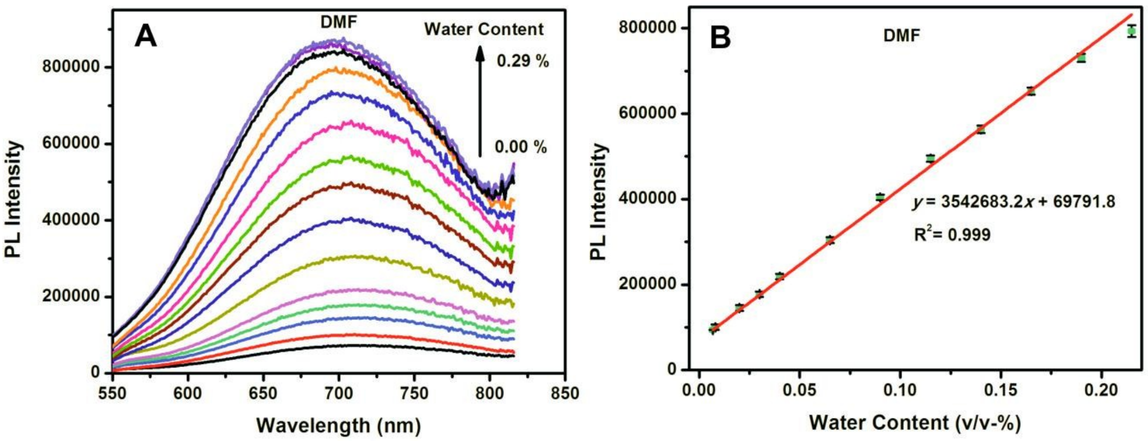

Figure S7. (A) The change in luminescence spectrum of CuNCs in DMF as the function of water content in the range of 0.0 v/v% – 0.29 v/v%. (D) Calibration curve between PL intensity and water content ranging from 0.0% to 0.22 v/v%.

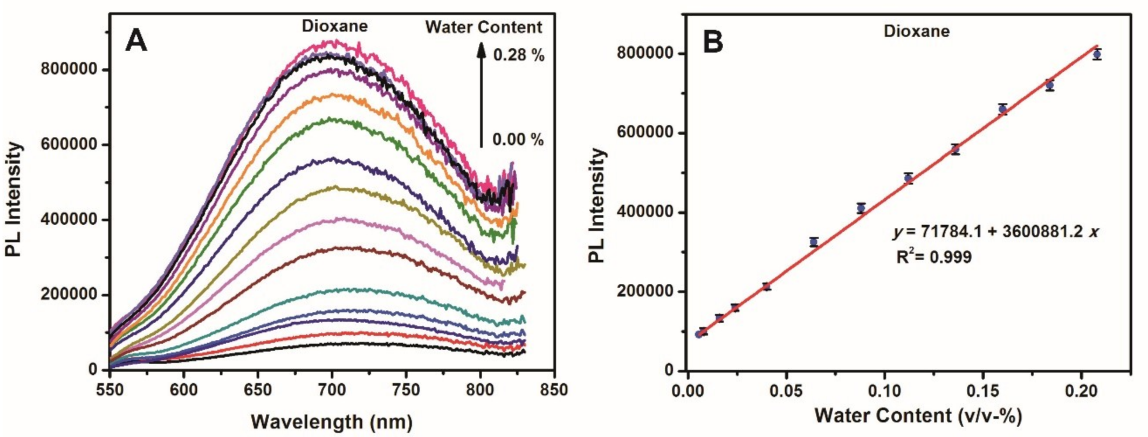

Figure S8. (A) The change in luminescence spectrum of CuNCs in dioxane as the function of water content in the range of 0.0 v/v% – 0.28 v/v%. (D) Calibration curve between PL intensity and water content ranging from 0.0% to 0.21 v/v%.

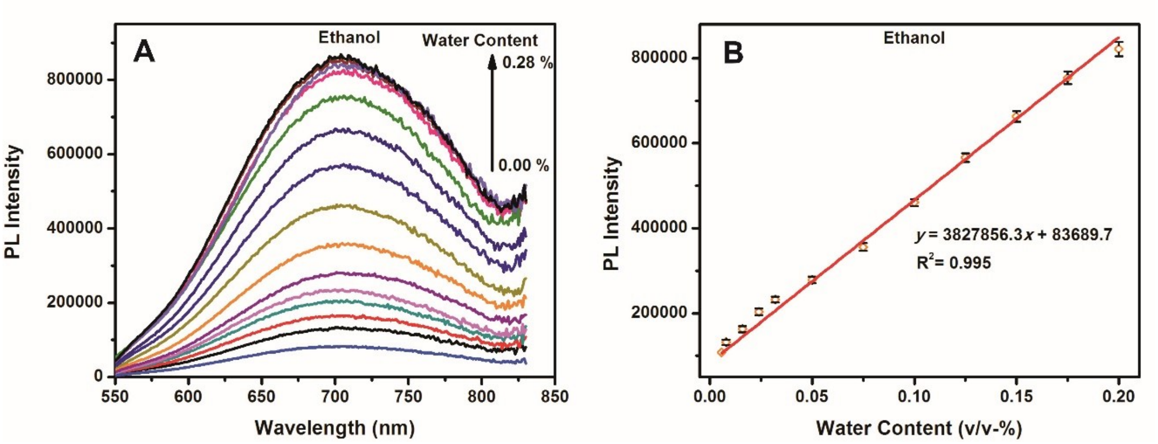

Figure S9. (A) The change in luminescence spectrum of CuNCs in ethanol as the function of water content in the range of 0.0 v/v% – 0.28 v/v%. (D) Calibration curve between PL intensity and water content ranging from 0.0% to 0.20 v/v%.

Table S1. Analytical performance of the sensing system in water detection of five chosen organic solvents.

Solvent	Detection limit (v/v-%)	Linear Range (v/v-%)
Acetonitrile	1.8×10^{-3}	6.2×10^{-3}~1.9×10^{-1}
THF	1.9×10^{-3}	6.6×10^{-3}~1.9×10^{-1}
DMF	2.0×10^{-3}	6.8×10^{-3}~2.2×10^{-1}
Dioxane	1.1×10^{-3}	5.6×10^{-3}~2.1×10^{-1}
Ethanol	1.8×10^{-3}	5.9×10^{-3}~2.0×10^{-1}

Table S2. Comparison of existing methods and our assay for the quantitation of trace amount of water in organic solvents

Luminescent probe	Signaling mode	solvents	Detection limit (v/v %)	Linear scope (v/v %)	Ref.
Anthracene-boronic acid ester	Turn on	Acetonitrile	0.0320	<1.04	3
		1,4-Dioxane	0.2100	<1.36	
		Ethanol	0.0310	<1.03	
		THF	0.1800	<1.17	
Anthracene-boronic acid ester	Turn on	Acetonitrile	0.0104	<0.8	4
		1,4-Dioxane	0.0190	<1.0	
		THF	0.0120	< 0.89	
		Ethanol	0.0055	0.024–0.19	
Acridinyl dyes	Turn off	THF	0.0020	0–1.0	5
		ethyl acetate	0.0030	0–1.0	
		CH_2Cl_2	0.0040	0–1.0	
Salicylic acid/PVA film	Turn off	1,4-Dioxane	0.2000	1.0–60.0	7
Thioxanthone-base probe	Turn off	THF	0.0025	0–1.0	9
		1,4-Dioxane	0.0019	0–0.6	
		DMF	0.0028	0–0.9	
		Acetonitrile	0.0034	0.2–0.8	
TPE-derivatives	Turn off	THF	0.0056	0–1.0	10
Copper complex	Turn on	THF	0.0027	0–1.15	11
		Acetone	0.0420	0–2.13	
		Acetonitrile	0.3900	0–1.54	
		Methanol	0.0260	0–2.85	
Coumarin-based Schiff base	Turn on	DMSO	0.1800	0–1.0	12
BODIPY-based probe	Ratio	Acetonitrile	0.0030	0–20.0	13
		THF	0.0030	0–20.0	
		acetone	0.0060	0–20.0	
		DMSO	0.0070	0–20.0	
		1,4-Dioxane	0.0080	0–20.0	
Iridium complex	Turn on	Dichloromethane	0.0006	0.001 – 0.05	14
		Acetonitrile	0.0016	0.003 – 1.0	
		Acetone	0.0065	0.01 – 1.0	
		DMF	0.0053	0.01 – 1.0	
Mg^{2+} metal-organic framework	Turn on	THF	0.0500	0–5.0	15
		Acetonitrile	0.0500	0.05–5.0	

		Ethanol	0.0500	0.05–3.0	
Lanthanide metal-organic framework	Ratiometric	DMF	0.0300	0.05–4.0	16
GSH-capped CuNCs	Turn off	DMSO	0.00032	0.001–0.01	17
		DMF	0.00042	0.0014–0.01	
		Acetonitrile	0.00020	0.0007–0.01	
		THF	0.00016	0.0005–0.01	
Silyl-protected CuNCs	Turn on	Acetonitrile	0.0018	0.0062–0.19	This work
		THF	0.0019	0.0066–0.19	
		DMF	0.0020	0.0068–0.22	
		1,4-Dioxane	0.0011	0.0056–0.21	
		Ethanol	0.0018	0.0059–0.20	