Supporting Information

Highly efficient Aggregation-induced emission fluorescent sensor for Copper (II) in aqueous media

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Materials and Methods

Materials. All reagents and solvents were chemical pure (CP) grade or analytical reagent (AR) grade and were used as received.

Measurements

^{1}H and ^{13}C NMR were measured on 400 MHz Bruker Advanced III. Mass spectrum was measured on Waters instrument. IR was measured on Bruker VERTEX70. Fluorescent spectra were collected on Hitachi F-4500 spectrophotometer. UV-Vis scanning were measured on Hitachi U-3010 spectrophotometer. Dynamic light scattering (DLC) was measured on a particle size analyzer. Fluorescence lifetimes were measured on Edinburgh Instruments FLS 980. Fluorescence quantum yield were measured on Hamamatsu Quantaurus-QY C11347-11.

Synthesis of 3

To the flask were added (*E*)-α-(*p*-aminophenyl)-β-(*p*-hydroxyphenyl) acrylonitrile (2.36 g, 10 mmol), salicylic aldehyde (1.22 g, 10 mmol), dry ethanol (30 ml) and acetic acid (0.12 g, 2 mmol) in order. The mixture was refluxed for about 2 h . After cooling to room temperature, the formed yellow precipitate was filtered. Then, the crude product was recrystallized in methanol to get **3** as yellow powder (3.10 g, 91 %). Mp 216.4–218.6 ^{o}C; IR (KBr) ν 3346, 3278, 2212, 1615, 1593, 1510, 1282, 1172, 837, 761 cm^{-1}; ^{1}H NMR (400 MHz, DMSO) δ 12.99 (s, 1H), 10.30 (s, 1H), 9.03 (s, 1H), 7.96 (s, 1H), 7.88 (d, J = 6.4 Hz, 2H), 7.80 (d, J = 6.0 Hz, 2H), 7.68 (d, J = 6.0 Hz, 1H), 7.55 (d, J = 6.8 Hz, 2H), 7.43 (s, 1H), 6.98 (d, J = 7.6 Hz, 2H), 6.92 (d, J = 6.8 Hz, 2H) ppm; ^{13}CNMR (100 MHz, DMSO) δ: 163.6, 160.3, 160.1, 148.0, 142.5, 133.5, 132.9, 132.6, 131.5, 126.4, 124.8, 122.2, 119.3, 119.2, 118.5, 116.6, 115.9, 105.2, 105.1 ppm; MS m/z calcd for $C_{22}H_{16}N_2O_2$ 340.1 [M], found 340.15 [M].

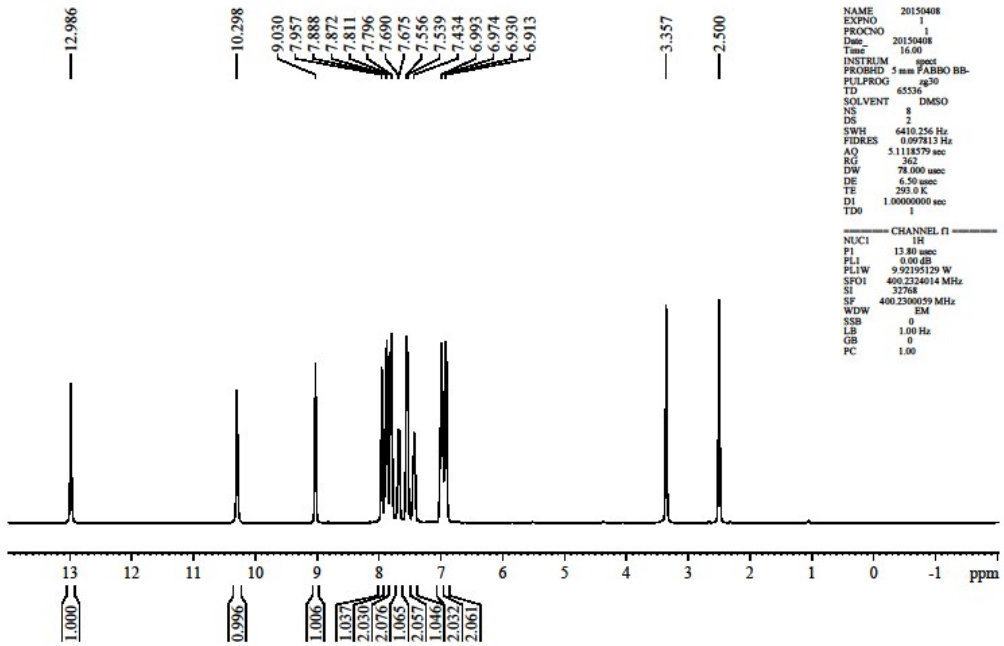

Fig. S1. [1]H NMR spectrum of **3** in DMSO.

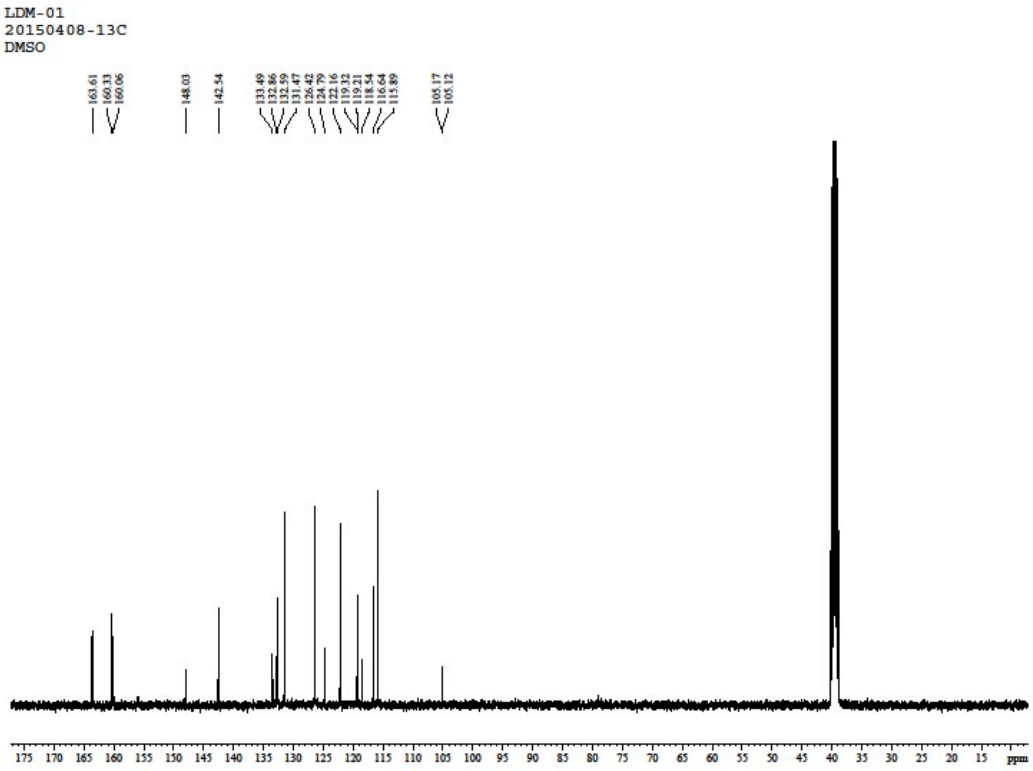

Fig. S2. [13]C NMR spectrum of **3** in DMSO.

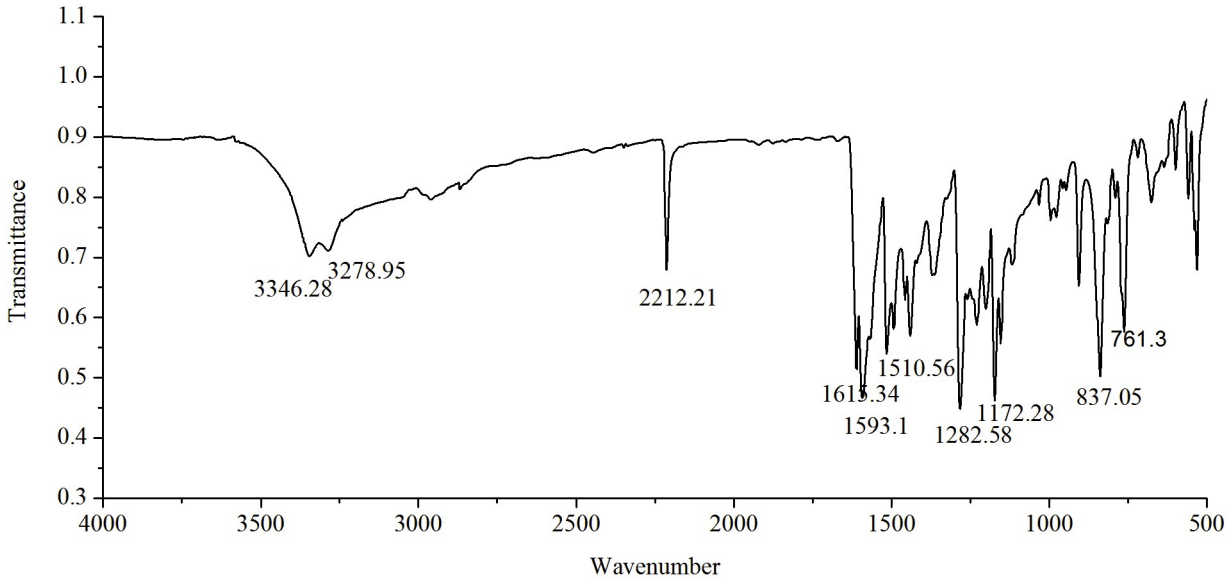

Fig. S3. IR spectrum of **3**.

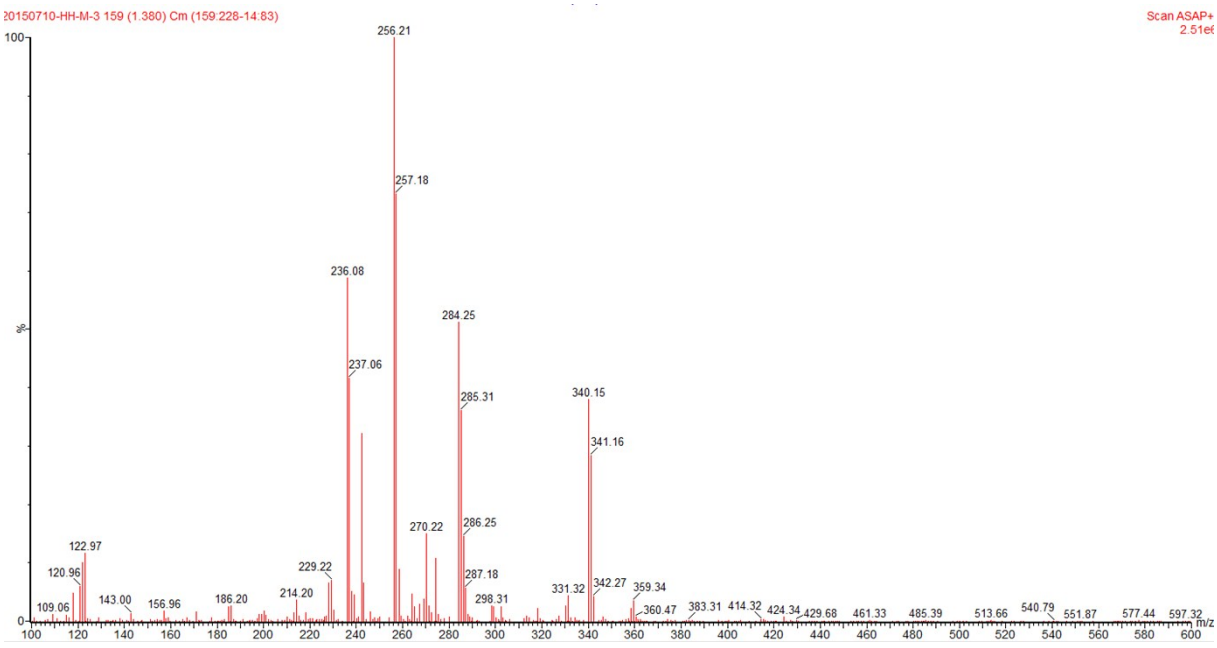

Fig. S4. MS spectrum of **3**.

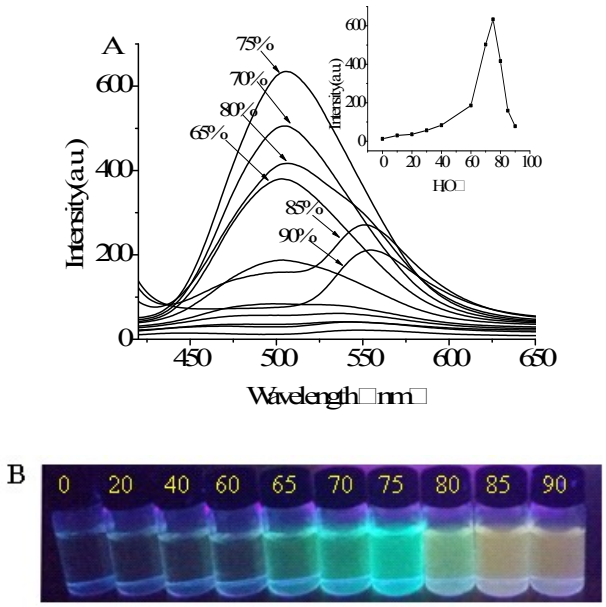

Fig. S5. (A) Fluorescence spectra of **3** (5.0 ×10^{-5} M) with a change of the water fraction in THF. Inset: fluorescence intensity of **3** at 508 nm vs. water fraction; (B) Images of compound **3** (5.0 ×10^{-5} M) with a change of the water fraction in THF under UV light.

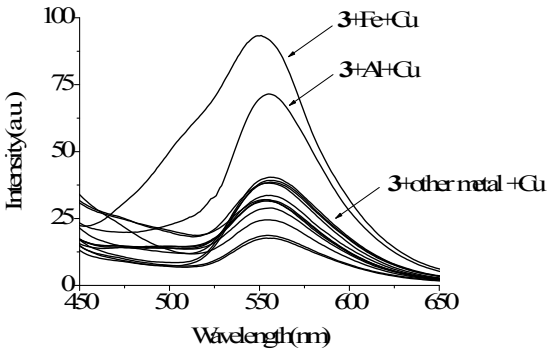

Fig. S6. Fluorescence spectrum of **3** in the mixture of Cu^{2+} and other metal ions, solvent: H_2O : THF = 9 : 1, [**3**] = [metal] = 2×10^{-5} M.

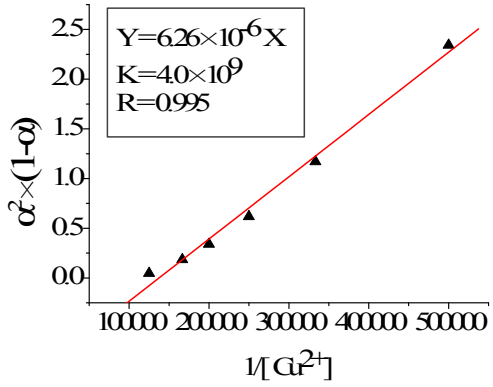

Fig. S7. The plot of $a^2/(1-a)$ vs. $1/[Cu^{2+}]$ at 555 nm, solvent: H_2O : THF = 9 : 1, [**3**] = 2×10^{-5} M; $[Cu^{2+}]$ = 0–4×10^{-5} M.

Calculation of binding constant: The binding constant of 2 : 1 complexes were evaluated by the equation:[1-2] $a^2/(1-a) = 1/(2K_aC_F[M])$, where a is defined as $[F-F_0]/[F_1-F_0]$, C_F is the total concentration of probe **3**, F is fluorescence intensity of probe **3** in the presence of Cu^{2+}, F_1 is fluorescence intensity of probe **3** in the absence of metal; F_0 is fluorescence intensity of probe **3** completely complexed with the metal ion. The plot $a^2/(1-a)$ vs. $1/[Cu^{2+}]$ was a straight line, and the binding constant of **3**–Cu^{2+} was found to be $4\times10^9\ M^{-2}$.

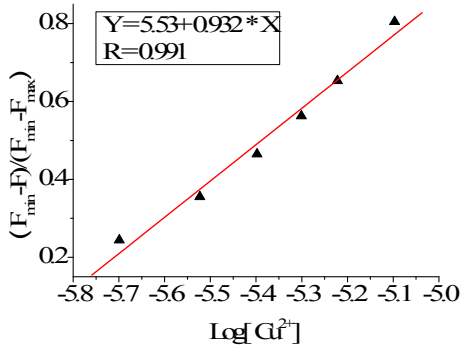

Fig. S8. The detection limit of probe **3** for copper Cu^{2+}

Calculation of detection limit: The detection limit was calculated based on a reported method.[3] According to the fluorescence titration experiment, the fluorescent intensity of **3** decreases with the increase of the content of copper ion in the range of 0-10 um. A linear was then fitted between $Log[Cu^{2+}]$ and $(F_{min}-F)/(F_{min}-F_{max})$, and the point at which this line crossed the axis was considered as the detection limit (1.5×10^{-6} M).

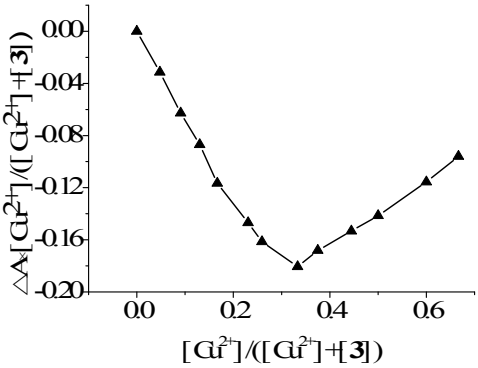

Fig. S9. The Job plot of compound **3** (2×10^{-5} M) with Cu^{2+} at 370 nm, solvent: H_2O : THF = 2:1; [**3**] = 2.5×10^{-5} M; $[Cu^{2+}] = 0–5\times10^{-5}$ M.

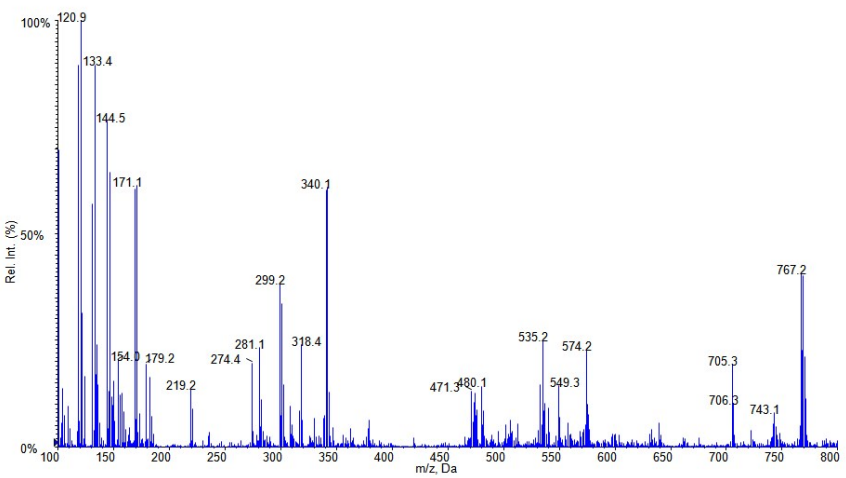

Fig. S10. MS spectrum of compound **3** in the presence of Cu^{2+}, the peak at m/z 767.2 correspond to [2· **3**+ Cu^{2+} + Na^+].

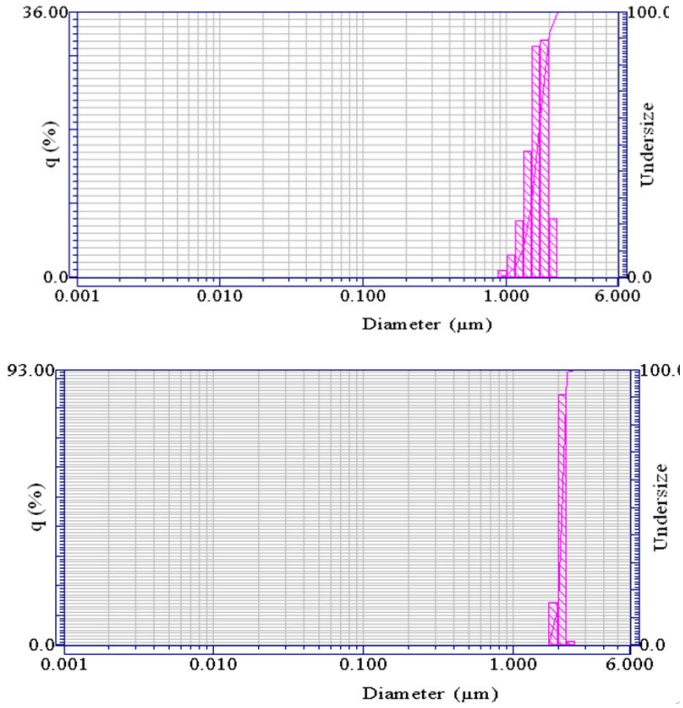

Fig. S11. (A) Dynamic light scattering (DLS) diagram of compound **3,** (B) DLS diagram of compound **3** and **Cu^{2+}.** solvent: H_2O : THF = 9:1; [**3**] = 2×10^{-5} M; [Cu^{2+}] = 1×10^{-5} M.

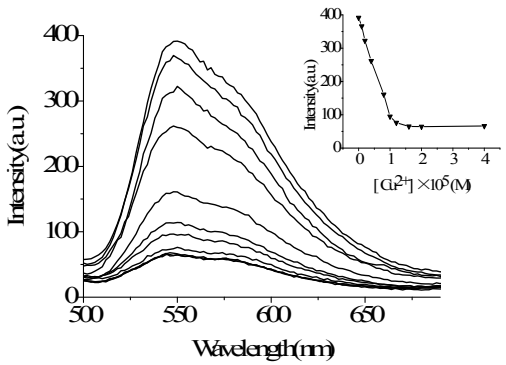

Fig. S12. Fluorescence spectra of compound **3** with different amounts of Cu^{2+}. Solvent: lake water: THF = 9 : 1; [**3**] = 2×10^{-5} M; [Cu^{2+}] = 0–4×10^{-5} M; Inset: the fluorescence change of compound **3** with Cu^{2+} at 550 nm; (B) The Job plot of compound **3** (2×10^{-5} M) with Cu^{2+} at 550 nm.

References:

1. V. S. Jisha, A. J. Thomas and D. Ramaiah, *J. Org. Chem.*, 2009, **74**, 6667-6673.

2. J.-T. Yeh, W.-C. Chen, S.-R. Liu and S.-P. Wu, *New J. Chem.*, 2014, **38**, 4434-4439.

3. Y. Fu, Q.-C. Feng, X.-J. Jiang, H. Xu, M. Li and S.-Q. Zang, *Dalton Trans.*, 2014, **43**, 5815-5822.