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 CI11347-11.

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 °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 caled for C$_{22}$H$_{16}$N$_2$O$_2$ 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_{2}O : 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_{2}O : 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:  
\[ a^2/(1-a) = 1/(2K_aC_F[M]), \]
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 \( 4 \times 10^{-9} \) 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. 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 \( \mu \)m. 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 \( \times \) 10\(^{-6} \) M).

Fig. S9. The Job plot of compound 3 (2\( \times \)10\(^{-5} \) M) with \( Cu^{2+} \) at 370 nm, solvent: H\(_2\)O : THF = 2:1; [3] = 2.5 \( \times \) 10\(^{-5} \) M; [Cu\(^{2+}\)] = 0–5 \( \times \) 10\(^{-5} \) M.

Fig. S10. MS spectrum of compound 3 in the presence of \( Cu^{2+} \); the peak at m/z 767.2 correspond to [2\( \cdot \)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$_2$O : 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: