Supporting Information 1

I$_2$ catalyzed access of spiro[indoline-3,4'-pyridine] appended amine dyad: 
New ON-OFF chemosensors for Cu$^{2+}$ and imaging in living cells

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Figure S1. ESI-MS spectra of compound 5a−5f, 5h−5l and in copper complexes:

ESI-MS compound 5a

ESI-MS of compound 5b
ESI-MS of compound 5h

ESI-MS of compound 5i
ESI-MS of compound 5j

ESI-MS of compound 5k
ESI-MS of compound 5l

ESI-MS of compound 5a+Cu
ESI-MS of compound 5b+Cu

ESI-MS of compound 5c+Cu
ESI-MS of compound 5d+Cu

ESI-MS of compound 5e+Cu
ESI-MS of compound 5f+Cu

ESI-MS of compound 5h+Cu
ESI-MS of compound 5i+Cu

ESI-MS of compound 5j+Cu
ESI-MS of compound 5k+Cu

ESI-MS of compound 5l+Cu
Figure S2. UV-vis spectra of 5a (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) ×10^{-6} M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to 5a solution.

Figure S3. UV-vis spectra of 5b (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) ×10^{-6} M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to 5b solution.
Figure S4. UV-vis spectra of 5c (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) ×10^{-6} M. Inset: visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to 5c solution.

Figure S5. UV-vis spectra of 5d (5×10^{-6} M) in DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) ×10^{-6} M. Inset: visual color change (green to colorless) observed with addition of Cu^{2+} ion to 5d solution.
Figure S6. UV-vis spectra of 5e (5×10⁻⁶ M) in DMSO/H₂O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu²⁺ (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) ×10⁻⁶ M. Inset: visual color change (yellow to colorless) observed with addition of Cu²⁺ ion to 5e solution.

Figure S7. UV-vis spectra of 5f (5×10⁻⁶ M) in DMSO/H₂O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu²⁺ (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) ×10⁻⁶ M. Inset: visual color change (yellow to colorless) observed with addition of Cu²⁺ ion to 5f solution.
Figure S8. UV-vis spectra of 5h (5×10⁻⁶ M) in DMSO/H₂O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu²⁺ (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) ×10⁻⁶ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu²⁺ ion to 5h solution.

Figure S9. UV-vis spectra of 5i (5×10⁻⁶ M) in DMSO/H₂O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu²⁺ (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) ×10⁻⁶ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu²⁺ ion to 5i solution.
**Figure S10.** UV-vis spectra of 5j (5×10⁻⁶ M) in DMSO/H₂O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu²⁺ (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) ×10⁻⁶ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu²⁺ ion to 5j solution.

**Figure S11.** UV-vis spectra of 5k (5×10⁻⁶ M) in DMSO/H₂O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu²⁺ (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) ×10⁻⁶ M. **Inset:** visual color change (yellow to colorless) observed with addition of Cu²⁺ ion to 5k solution.
Figure S12. UV-vis spectra of 5l (5×10^{-6} M) in DMSO/H_{2}O (1:9, v/v) HEPES buffer (pH = 7.4) solution in the presence of various concentrations of Cu^{2+} (0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10) ×10^{-6} M. Inset: visual color change (yellow to colorless) observed with addition of Cu^{2+} ion to 5l solution.
Figure S13. Fluorescence Quenching Efficiency (FQE), \(\{(F_0 - F)/F_0\} \times 100\) of 5d \((5 \times 10^{-6} \text{ M})\) in the presence of 4 equiv. of different cations except 2 equiv. of Cu\(^{2+}\) in solution [the green bar portion]. Fluorescence Quenching Efficiency (FQE) of a mixture of 5d \((5 \times 10^{-6} \text{ M})\) with other metal ions \((20 \times 10^{-6} \text{ M})\) followed by the addition of Cu\(^{2+}\) \((10 \times 10^{-6} \text{ M})\) to the DMSO/H\(_2\)O \((1:9, \text{ v/v})\) HEPES buffer \((\text{pH} = 7.4)\) solution [the red bar portion] \((\lambda_{\text{ex}} = 375.7 \text{ nm}, \lambda_{\text{em}} = 493.5 \text{ nm})\).

Figure S14. Fluorescence Quenching Efficiency (FQE), \(\{(F_0 - F)/F_0\} \times 100\) of 5f \((5 \times 10^{-6} \text{ M})\) in the presence of 4 equiv. of different cations except 2 equiv. of Cu\(^{2+}\) in solution [the green bar portion]. Fluorescence Quenching Efficiency (FQE) of a mixture of 5f \((5 \times 10^{-6} \text{ M})\) with other metal ions \((20 \times 10^{-6} \text{ M})\) followed by the addition of Cu\(^{2+}\) \((10 \times 10^{-6} \text{ M})\) to the DMSO/H\(_2\)O \((1:9, \text{ v/v})\) HEPES buffer \((\text{pH} = 7.4)\) solution [the pink bar portion] \((\lambda_{\text{ex}} = 310.9 \text{ nm}, \lambda_{\text{em}} = 491.7 \text{ nm})\).
Figure S15. Fluorescence Quenching Efficiency (FQE), \([\{(F_0 - F)/F_0\} \times 100]\) of 5h (5 \times 10^{-6} M) in the presence of 4 equiv. of different cations except 2 equiv. of Cu^{2+} in solution [the green bar portion]. Fluorescence Quenching Efficiency (FQE) of a mixture of 5h (5 \times 10^{-6} M) with other metal ions (20 \times 10^{-6} M) followed by the addition of Cu^{2+} (10 \times 10^{-6} M) to the DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution [the red bar portion] (\(\lambda_{ex} = 308.5\) nm, \(\lambda_{em} = 498.7\) nm).

Figure S16. Fluorescence Quenching Efficiency (FQE), \([\{(F_0 - F)/F_0\} \times 100]\) of 5j (5 \times 10^{-6} M) in the presence of 4 equiv. of different cations except 2 equiv. of Cu^{2+} in solution [the green bar portion]. Fluorescence Quenching Efficiency (FQE) of a mixture of 5j (5 \times 10^{-6} M) with other metal ions (20 \times 10^{-6} M) followed by the addition of Cu^{2+} (10 \times 10^{-6} M) to the DMSO/H_2O (1:9, v/v) HEPES buffer (pH = 7.4) solution [the pink bar portion] (\(\lambda_{ex} = 302.4\) nm, \(\lambda_{em} = 497.8\) nm).
Figure S17. Fluorescence Quenching Efficiency (FQE), \[\{(F_0 - F)/F_0\} \times 100\] of 5k (5 × 10^{-6} M) in the presence of 4 equiv. of different cations except 2 equiv. of Cu^{2+} in solution [the cyan bar portion]. Fluorescence Quenching Efficiency (FQE) of a mixture of 5k (5 × 10^{-6} M) with other metal ions (20 × 10^{-6} M) followed by the addition of Cu^{2+} (10 × 10^{-6} M) to the DMSO/H_{2}O (1:9, v/v) HEPES buffer (pH = 7.4) solution [the red bar portion] (\(\lambda_{\text{ex}} = 312.5\) nm, \(\lambda_{\text{em}} = 503.5\) nm).
Figure S18. Job's plot for determination of stoichiometry of Cu$^{2+}$: 5a complex in solution.

Figure S19. Job's plot for determination of stoichiometry of Cu$^{2+}$: 5b complex in solution.
Figure S20. Job's plot for determination of stoichiometry of Cu$^{2+}$ : 5c complex in solution.

Figure S21. Job's plot for determination of stoichiometry of Cu$^{2+}$ : 5d complex in solution.
Figure S22. Job's plot for determination of stoichiometry of Cu$^{2+}$ : 5e complex in solution.

Figure S23. Job's plot for determination of stoichiometry of Cu$^{2+}$ : 5f complex in solution.
Figure S24. Job’s plot for determination of stoichiometry of Cu$^{2+}$ : 5h complex in solution.

Figure S25. Job’s plot for determination of stoichiometry of Cu$^{2+}$ : 5i complex in solution.
Figure S26. Job’s plot for determination of stoichiometry of Cu$^{2+}$ : 5j complex in solution.

Figure S27. Job’s plot for determination of stoichiometry of Cu$^{2+}$ : 5k complex in solution.
Figure S28. Job’s plot for determination of stoichiometry of Cu$^{2+}$ : 5l complex in solution.
Figure S29. Benesi-Hildebrand plot $1 / (F_0 - F)$ vs. $1/\left[\text{Cu}^{2+}\right]$ for complexation between 5d and Cu$^{2+}$ derived from emission titration curve.

Figure S30. Benesi-Hildebrand plot $1 / (F_0 - F)$ vs. $1/\left[\text{Cu}^{2+}\right]$ for complexation between 5f and Cu$^{2+}$ derived from emission titration curve.
Figure S31. Benesi-Hildebrand plot \( \frac{1}{(F_0 - F)} \) vs. \( \frac{1}{[Cu^{2+}]} \) for complexation between \(5h\) and \(Cu^{2+}\) derived from emission titration curve.

Figure S32. Benesi-Hildebrand plot \( \frac{1}{(F_0 - F)} \) vs. \( \frac{1}{[Cu^{2+}]} \) for complexation between \(5j\) and \(Cu^{2+}\) derived from emission titration curve.
Figure S33. Benesi-Hildebrand plot $\frac{1}{(F_0 - F)}$ vs. $\frac{1}{[\text{Cu}^{2+}]}$ for complexation between $5k$ and Cu$^{2+}$ derived from emission titration curve.
Detection limit calculation in emission spectroscopy:

The limit of detection (LOD) of compounds (5d, 5f, 5h, 5j, 5k) with Cu\(^{2+}\) was measured on the basis of fluorescence titration measurement. The detection limit was calculated using the following equation:

\[
DL = K \times \frac{\sigma}{S}
\]

where \(K = 2\) or 3 (we take 3 in this case), ‘\(\sigma\)’ is the standard deviation of the blank solution and ‘\(S\)’ is the slope between the ratio of emission intensity versus \([\text{Cu}^{2+}]\).

Figure S34. The limit of detection (LOD) of 5d for Cu\(^{2+}\) as a function of \([\text{Cu}^{2+}]\).
**Figure S35.** The limit of detection (LOD) of 5f for Cu$^{2+}$ as a function of [Cu$^{2+}$].

**Figure S36.** The limit of detection (LOD) of 5h for Cu$^{2+}$ as a function of [Cu$^{2+}$].
Figure S37. The limit of detection (LOD) of 5j for Cu^{2+} as a function of [Cu^{2+}].

Figure S38. The limit of detection (LOD) of 5k for Cu^{2+} as a function of [Cu^{2+}].
Figure S39. Fluorescence emission spectra of chemosensor (5d) in the presence of Cu$^{2+}$ ion followed by addition of EDTA.

Figure S40. Fluorescence emission spectra of chemosensor (5f) in the presence of Cu$^{2+}$ ion followed by addition of EDTA.
Figure S41. Fluorescence emission spectra of chemosensor (5h) in the presence of Cu$^{2+}$ ion followed by addition of EDTA.

Figure S42. Fluorescence emission spectra of chemosensor (5j) in the presence of Cu$^{2+}$ ion followed by addition of EDTA.
Figure S43. Fluorescence emission spectra of chemosensor (5k) in the presence of Cu\(^{2+}\) ion followed by addition of EDTA.
Figure S44. Emission intensity of 5d (5×10^-6 M) in absence and in presence of Cu^{2+} as a function of pH values in aqueous DMSO solution at 493.5 nm.

Figure S45. Emission intensity of 5f (5×10^-6 M) in absence and in presence of Cu^{2+} as a function of pH values in aqueous DMSO solution at 491.7 nm.
Figure S46. Emission intensity of $5h$ ($5 \times 10^{-6}$ M) in absence and in presence of $Cu^{2+}$ as a function of pH values in aqueous DMSO solution at 498.7 nm.

Figure S47. Emission intensity of $5j$ ($5 \times 10^{-6}$ M) in absence and in presence of $Cu^{2+}$ as a function of pH values in aqueous DMSO solution at 497.8 nm.
Figure S48. Emission intensity of 5k (5×10^{-6} M) in absence and in presence of Cu^{2+} as a function of pH values in aqueous DMSO solution at 503.5 nm.