**Supporting Information (SI)**

# Highly Sensitive and Selective Fluorescent Sensor for $Zn^{2+}$/$Cu^{2+}$ and New Approach for Sensing $Cu^{2+}$ by Central Metal Displacement

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## Contents

## 1. Materials and methods

All chemicals were purchased from commercial suppliers and used without further purification. All reactions were performed under an argon atmosphere with the solvents purified with standard methods.

$^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane (TMS) as the internal standard. Mass spectra were obtained on high resolution mass spectrometer (IonSpec4.7 Tesla FTMS-MALDI/DHB).

All spectral characterizations were carried out in HPLC-grade solvents at 20 °C within a 10 mm quartz cell. UV-Vis absorption spectra were measured with a TU-1901 double-beam UV-Vis Spectrophotometer, and fluorescence spectra were determined on a Hitachi F-4500 spectrometer.

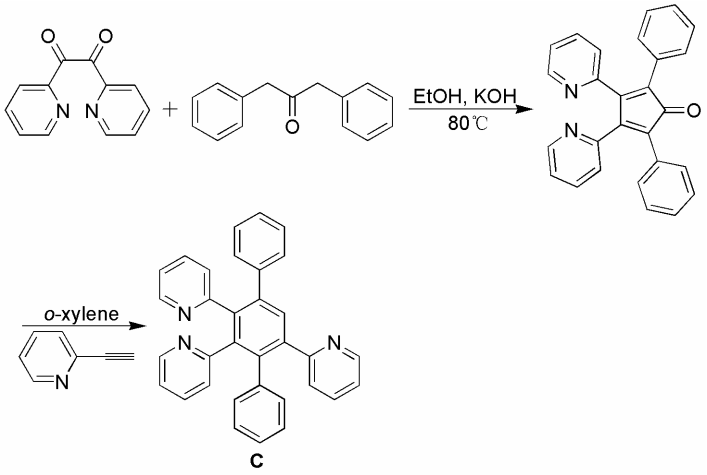
## 2. Synthetic procedure and characterization of compound C

### Synthesis of 2,5-diphenyl-3,4-dipyridyl-cyclopentenone

1,3-diphenyl-cyclopentenone (630.84 mg, 3 mmol) and 2,2'-pyridyl-ketone were dissolved in ethanol (5 mL). Under refluxing and stirring, the ethanol solution of KOH (94.08 mg KOH and 2 mL ethanol) was dropwised in the above mixture. After reacting 5 min., the product was obtained after the above solution was cold for 12 hours and was filtrated. The yield was 73.86 %. Characterization of 2,5-diphenyl-3,4-dipyridyl-cyclopentenone: $^{1}H$-NMR: $\delta_H$ (400 MHz, $CDCl_3$, $Me_4Si$) 8.45 (m, 1H), 8.32 (m, 1H), 7.72 (m, 2H), 7.64 (m, 5H), 7.39 (m, 3H), 7.27 (m, 1H), 7.10 (m, 4H), 6.65 (m, 1H). $^{13}C$-NMR: $\delta_C$ (100 MHz, $CDCl_3$): 205.82, 164.10, 163.59, 154.01, 148.86, 141.58, 136.43, 136.27, 134.60, 130.64, 129.89, 129.50, 128.78, 128.71, 128.50, 128.02, 127.55, 127.29, 125.80, 123.41, 121.80, and 120.94. Elemental analysis (%) calcd for $C_{27}H_{18}N_2O$ (386.44): C 83.92, H 4.69, N 7.25; found: C 83.50, H 4.71, N 7.20.

### Synthesis of compound C

2,5-diphenyl-3,4-dipyridyl-cyclopentenone (772.96 mg, 2 mmol) and 2-ethynyl- pyridine (0.24 mL) were dissolved in *o*-xylene in argon atmosphere. After refluxing 15 hours, the cooled petroleum ether was added into the above solution. After cooling 2 hours, the product was obtained after filtrating the mixture. The yield was 68.75%. Characterization of compound **C**: HRMS (EI) calcd. for $C_{33}H_{24}N_3$ [$M^+$], 461.1892; found, 461.1951. $^{1}H$-NMR: $\delta_H$ (400 MHz, $CDCl_3$, $Me_4Si$) 8.62 (m, 1H), 8.60 (m, 2H), 8.21 (s, 1H, phenyl), 7.35 (m, 1H), 7.30 (m, 2H), 7.28 (m, 6H), 7.20 (m, 1H), 7.06 (m, 7H), 6.86 (m, 2H), 6.78(m, 1H). $^{13}C$-NMR: $\delta_C$ (100 MHz, $CDCl_3$): 158.93, 158.88, 158.70, 149.23, 148.09, 147.75, 141.00, 140.96, 140.88, 140.44, 139.38, 139.26, 138.80, 134.99, 134.71, 134.44, 131.99, 129.80, 127.63, 127.25, 126.89, 126.79, 126.46, 126.11, 125.47, 121.28, 120.59, 120.38.




**Scheme S1.** Synthetic route of compound **C**.

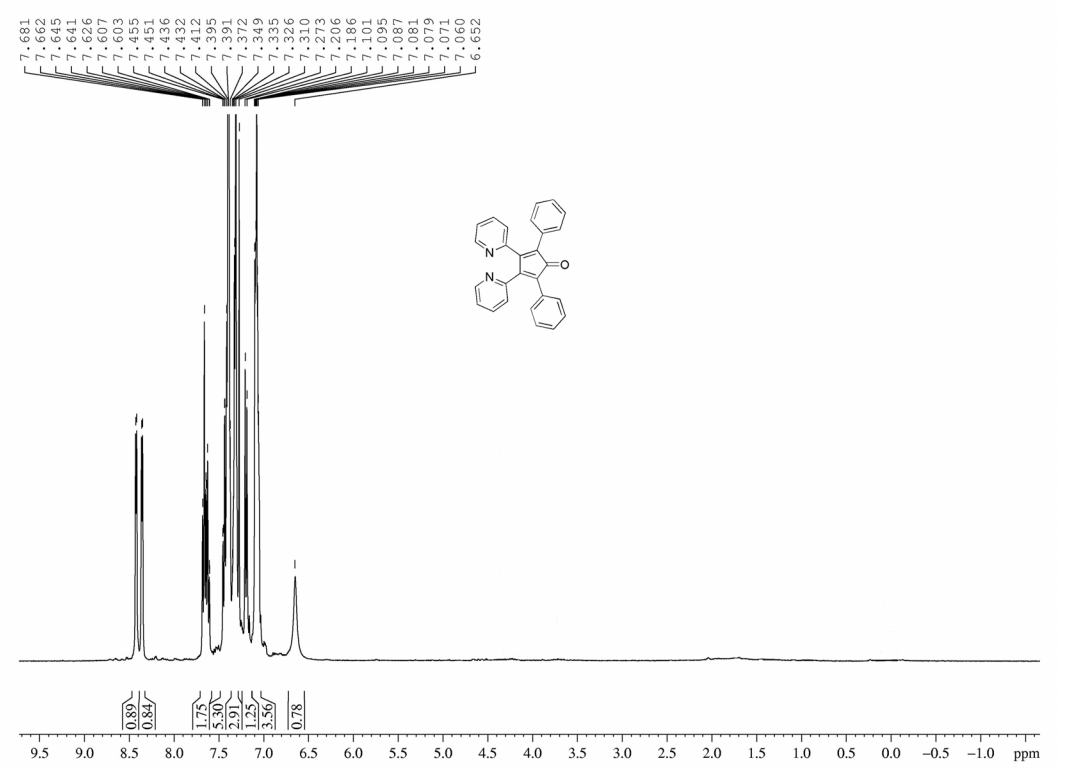



**Fig. S1.** $^{1}$H NMR ($CDCl_3$, 400 MHz) spectrum of 2,5-diphenyl-3,4-dipyridyl-cyclopentenone.

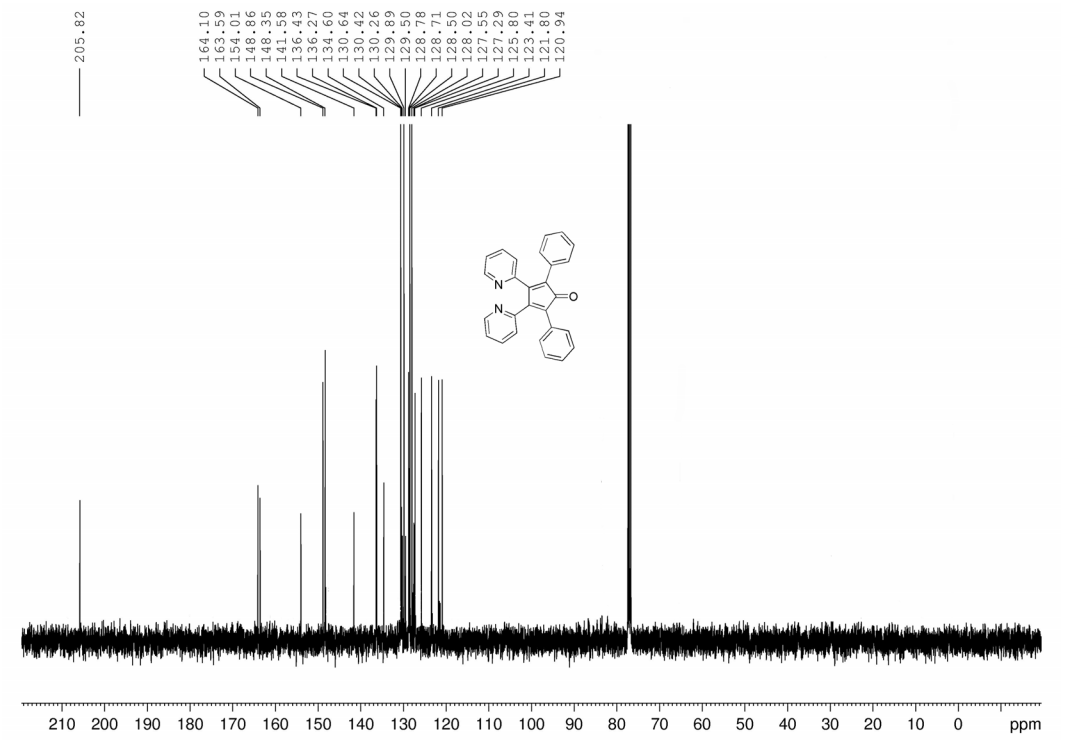



**Fig. S2.** $^{13}C$ NMR ($CDCl_3$, 100 MHz) spectrum of 2,5-diphenyl-3,4-dipyridyl-cyclopentenone.

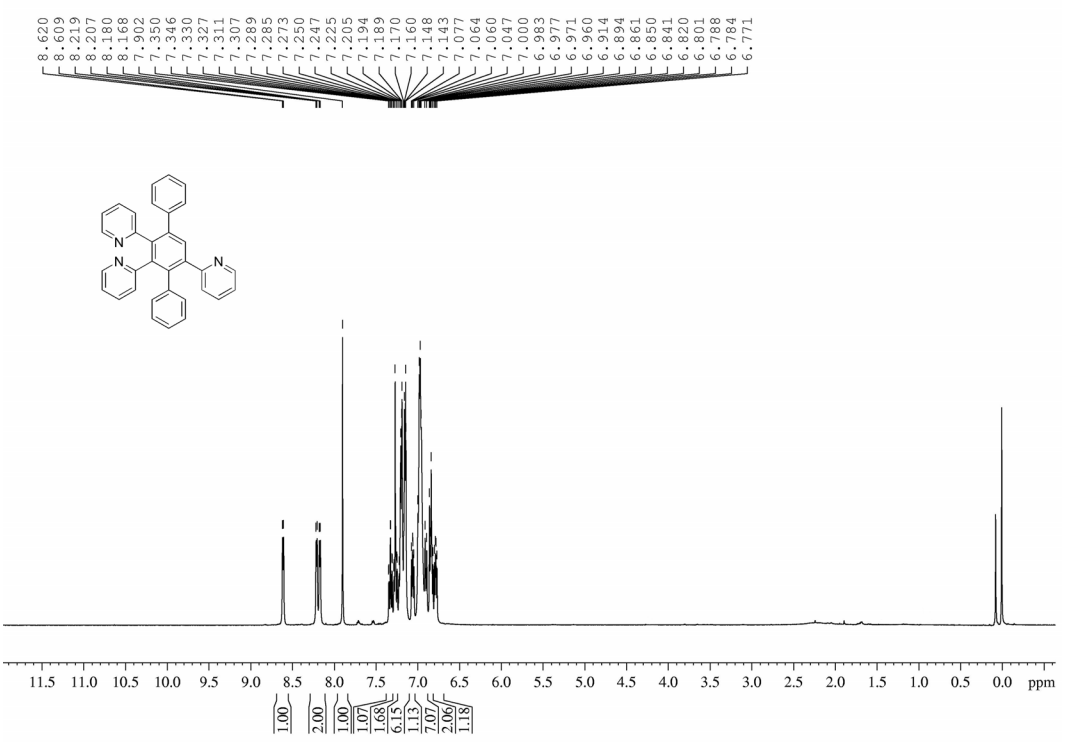



**Fig. S3.** $^{1}H$ NMR ($CDCl_3$, 400 MHz) spectrum of **C**.

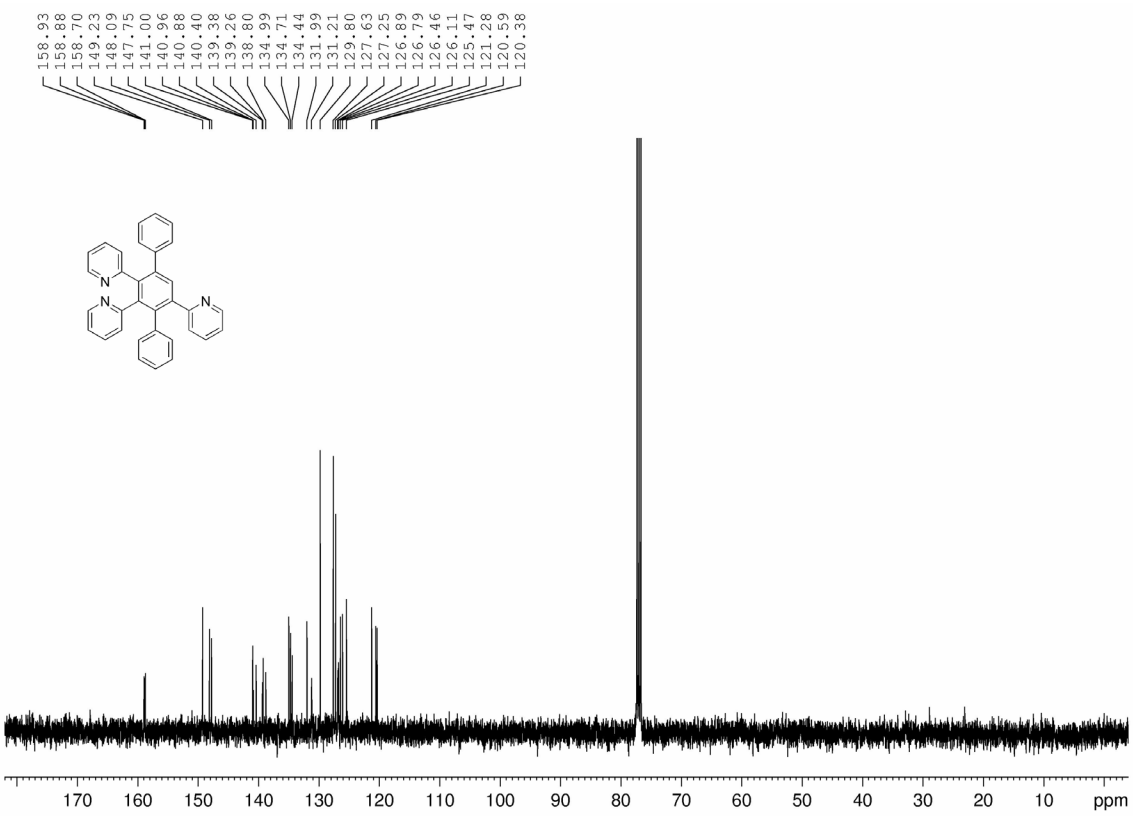



**Fig. S4.** $^{13}C$ NMR ($CDCl_3$, 100 MHz) spectrum of **C**.

## 3. Supplementary spectra data (Fig. S5 ~ S13)

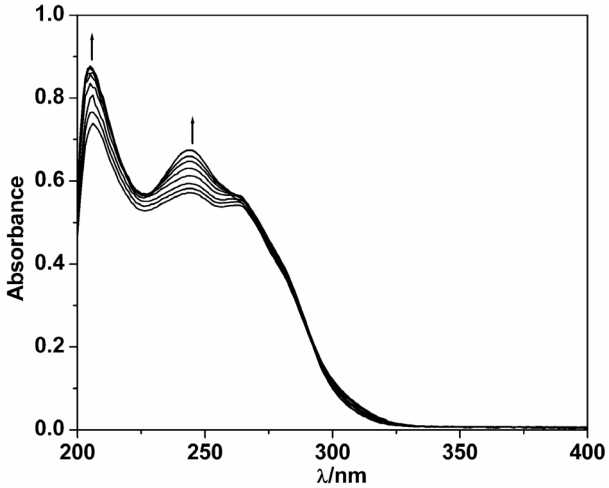



**Fig. S5.** Changes in absorption spectra of **C** ($2.0 \times 10^{-5}$ M) in ethanol upon addition of $Zn^{2+}$. The final ratio of $Zn^{2+}$ to **C** is 4:1 equiv.

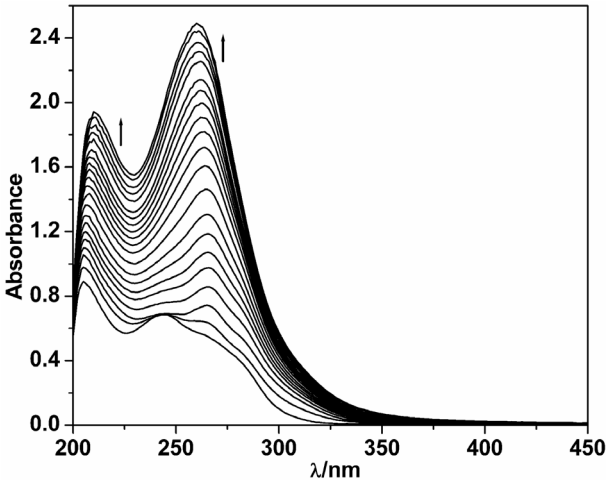



**Fig. S6.** Changes in absorption spectra of **C** ($2.0 \times 10^{-5}$ M) in ethanol upon addition of $Cu^{2+}$. The final ratio of $Cu^{2+}$ to **C** is 1:1 equiv.

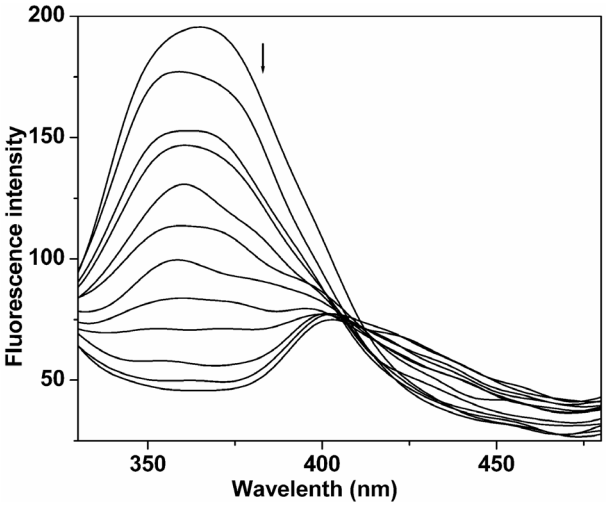



**Fig. S7.** Changes in fluorescence emission spectra of **C** ($2.0 \times 10^{-5}$ M) in ethanol upon addition of $Cu^{2+}$. The final ratio of $Cu^{2+}$ to **C** is 1:1 equiv.

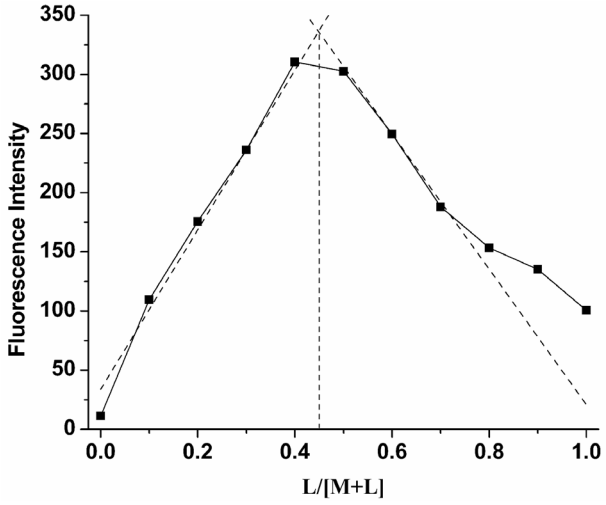



**Fig. S8.** Molar ratio-extinction curve of $Zn^{2+}$.

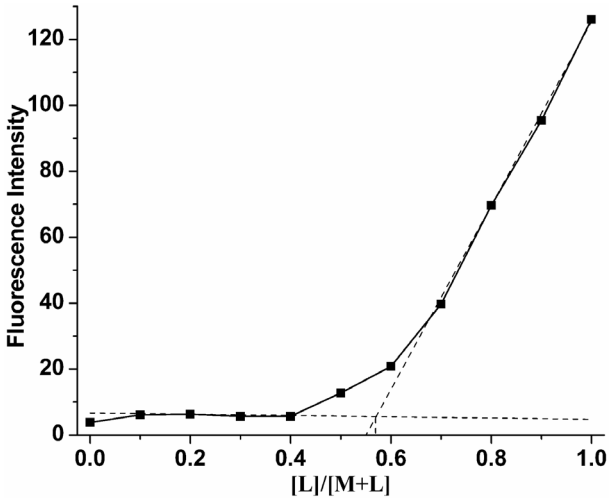



**Fig. S9.** Molar ratio-extinction curve of $Cu^{2+}$.

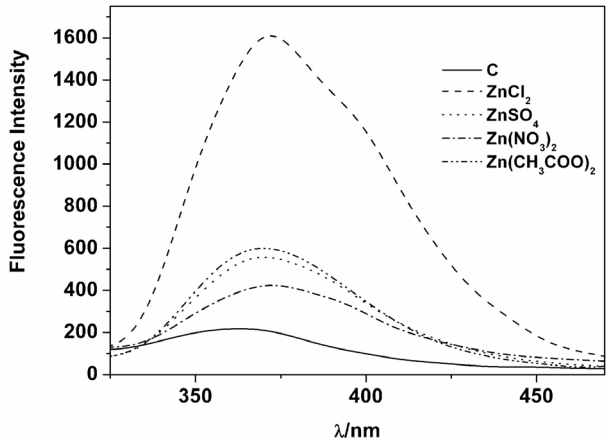



**Fig. S10.** Emission spectra of compound **C** upon excitation at 246 nm in ethanol upon addition of different zinc salts.

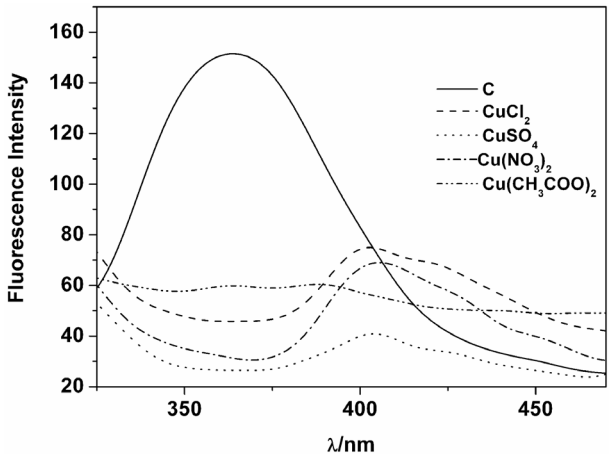



**Fig. S11.** Emission spectra of compound **C** upon excitation at 246 nm in ethanol upon addition of different copper salts.

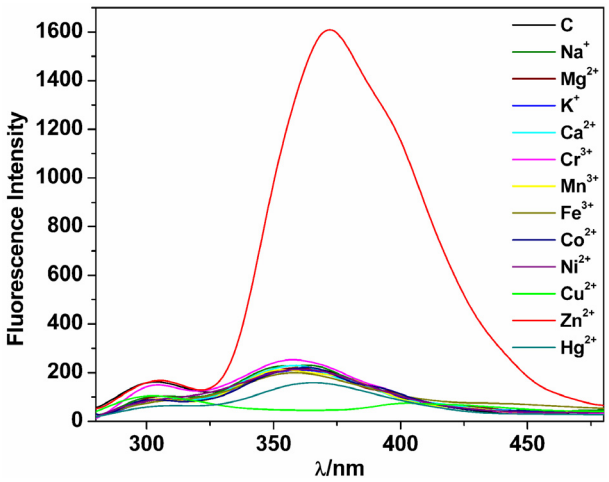



**Fig. S12.** Emission spectra of compound **C** upon excitation at 246 nm in ethanol upon addition of different metal ions.

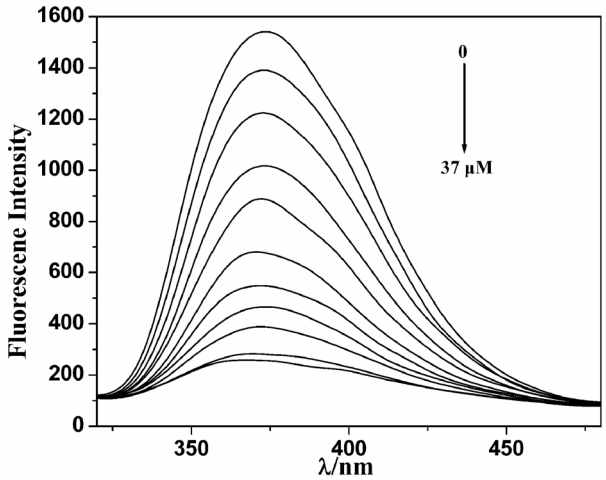



**Fig. S13.** Changes in fluorescence emission spectra of **C** ($2.0 \times 10^{-5}$ M) and $Zn^{2+}$ ($8.0 \times 10^{-5}$ M) in ethanol upon addition of EDTA disodium in aqueous solution. The excitation wavelength was 246 nm.

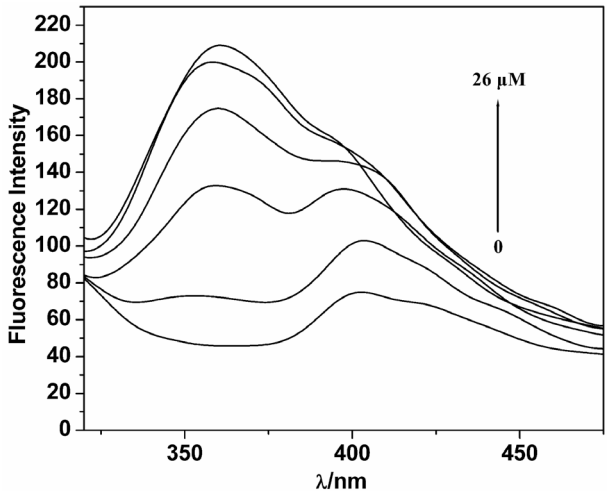



**Fig. S14.** Fluorescent responses of **C** ($2.0 \times 10^{-5}$ M) and $Cu^{2+}$ ($2.0 \times 10^{-5}$ M) in ethanol solution upon addition of EDTA disodium in aqueous solution. The excitation wavelength was 246 nm.

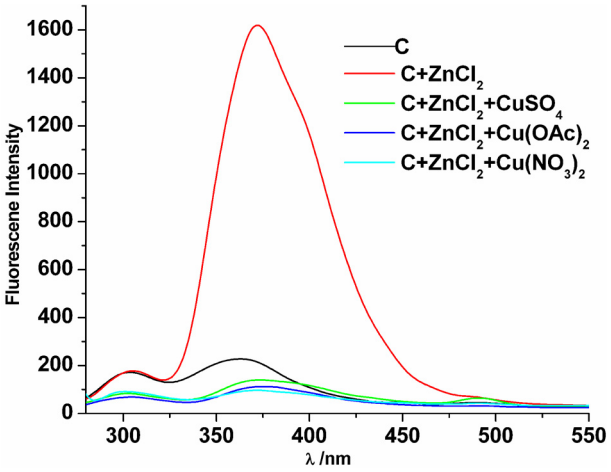



**Fig. S15.** Fluorescence spectra of **C** ($2.0 \times 10^{-5}$ M) + 4 equiv of $Zn^{2+}$ upon the addition of different copper salts (1 equiv) in ethanol solution with excitation at 246 nm.