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Electronic Supplementary Information

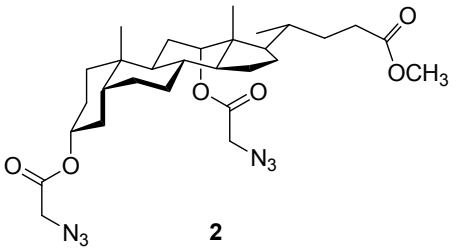
A novel and simple solvent-dependent fluorescent probe based on a click generated 8-aminoquinoline–steroid conjugate for multi-detection of Cu(II), oxalate and pyrophosphate

Zhen Zhang*, Yuan Zou and Chengquan Deng

Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an 710049, China. E-mail: zzlinda@mail.xjtu.edu.cn; Fax: +86 29 82668559; Tel: +86 29 82663914.

Contents

1. ^{1}H NMR spectrum of compound **2**



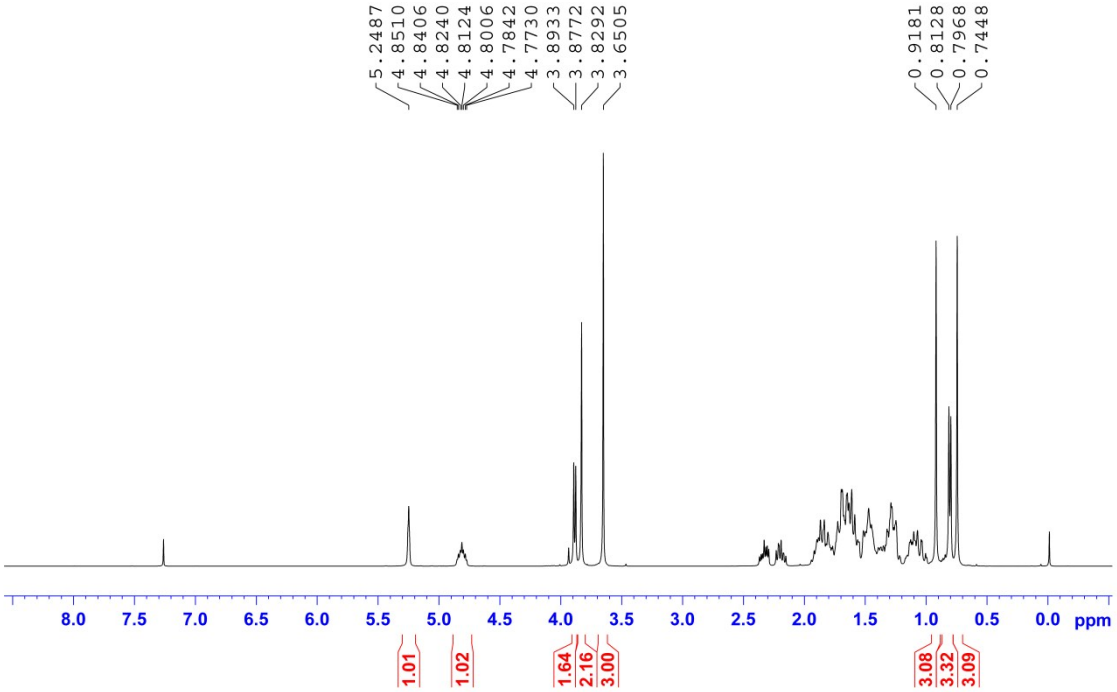
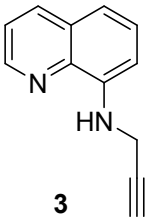


Fig. S1 ^{1}H NMR spectrum of compound **2**.

2. ^{1}H NMR spectrum of compound **3**



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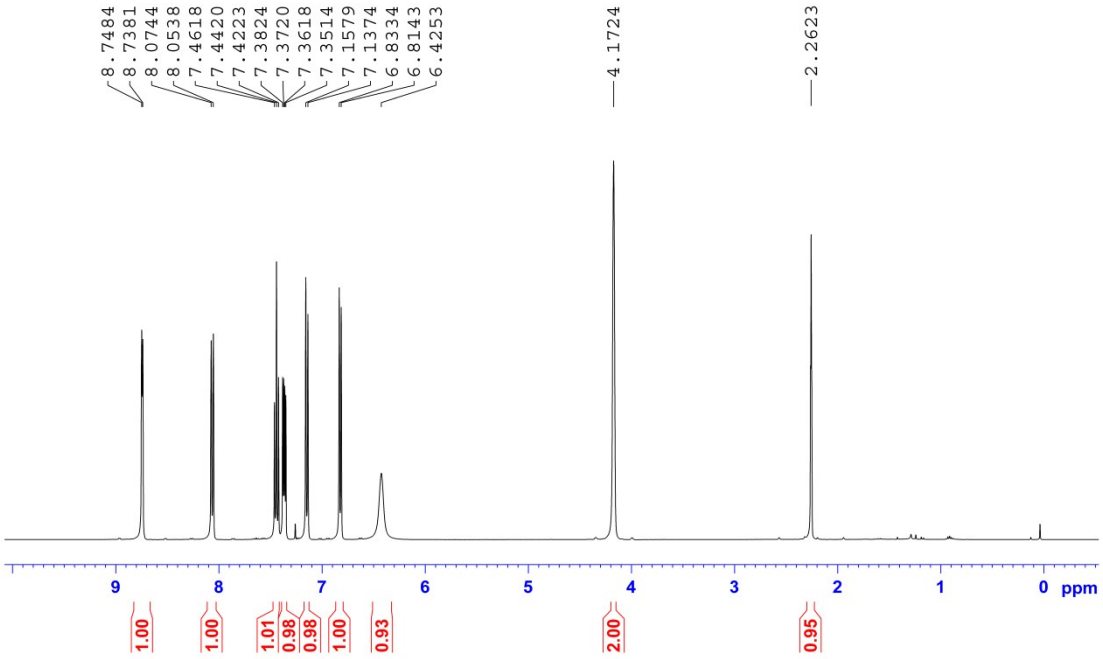
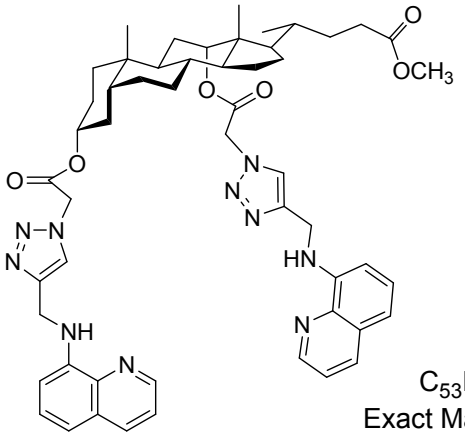


Fig. S2 ^{1}H NMR spectrum of compound **3**.

3. ^{1}H NMR, ^{13}C NMR, and HR-ESI-MS spectra of probe **1**



1
$C_{53}H_{64}N_{10}O_6$
Exact Mass: 936.5010

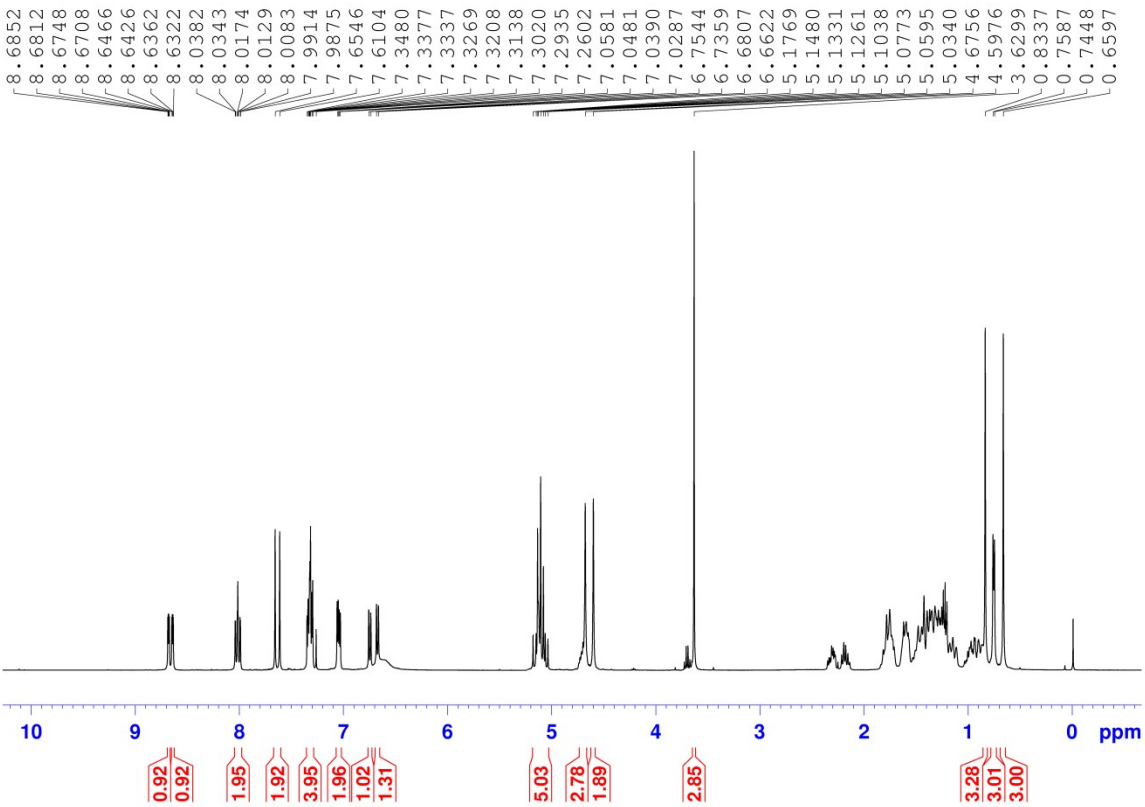


Fig. S3 ^{1}H NMR spectrum of probe **1**.

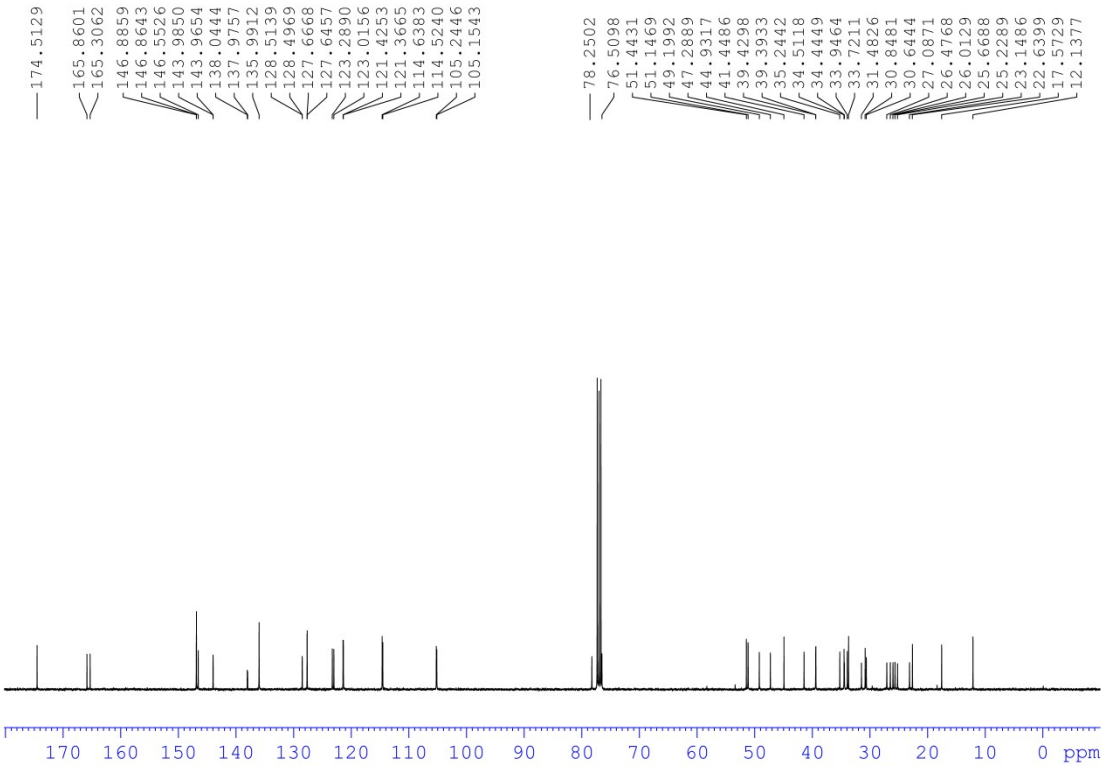


Fig. S4 ^{13}C NMR spectrum of probe **1**.

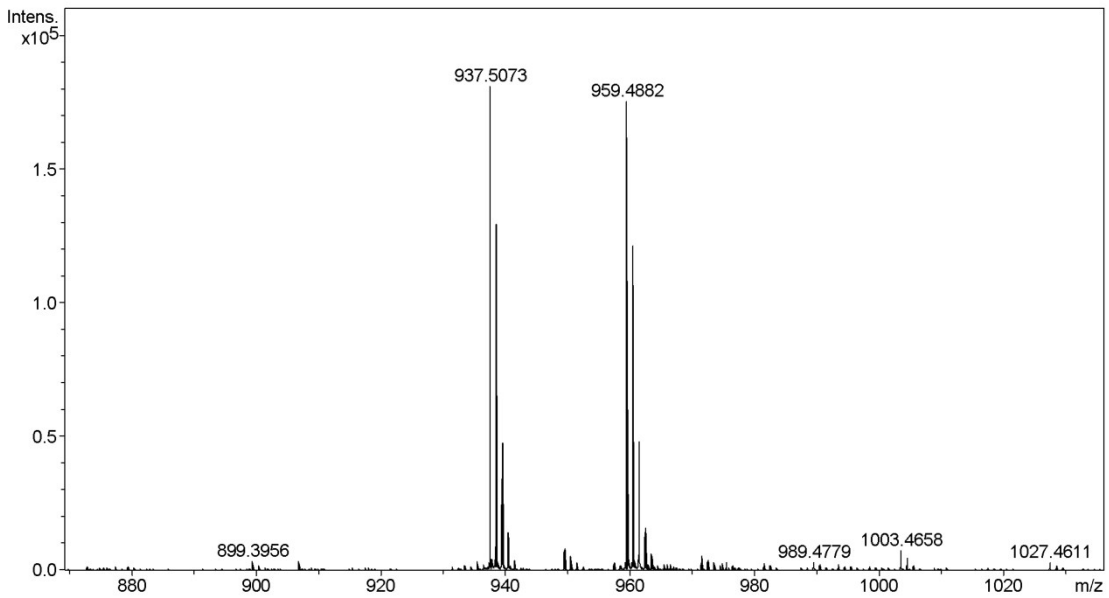


Fig. S5 HR-ESI-MS spectrum of probe **1**.

4. UV-vis absorption spectra of probe **1** with different levels of Cu^{2+}

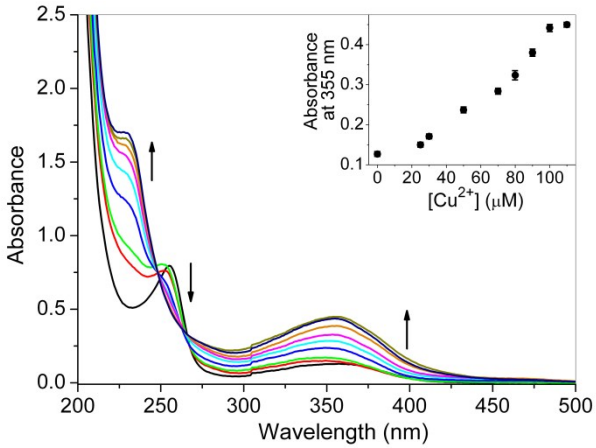


Fig. S6 UV-vis absorption spectra of probe **1** (20 μM) with different levels of Cu^{2+} (from bottom to top: 0, 25, 30, 50, 70, 80, 90, 100 and 110 μM) in $CH_3CN–H_2O$ (99/1, v/v, 10 mM HEPES, pH 7.2). Inset: absorbance changes of probe **1** at 355 nm as a function of Cu^{2+} concentration.

5. UV-vis absorption spectra of probe **1** with different metal ions

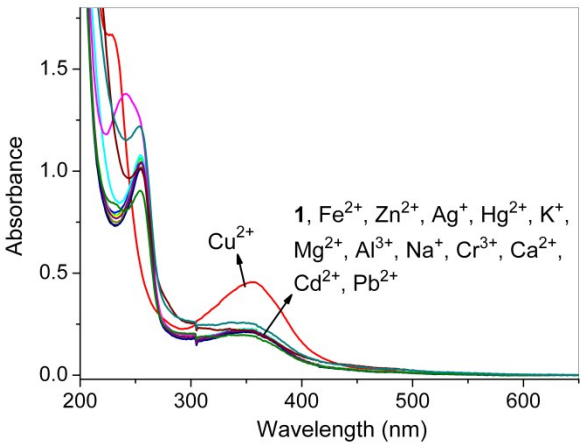


Fig. S7 UV-vis absorption spectra of probe **1** (20 μM) with different metal ions (100 μM) in $CH_3CN–H_2O$ (99/1, v/v, 10 mM HEPES, pH 7.2).

6. Effects of CH_3CN content on the fluorescence response of probe **1** to Cu^{2+}

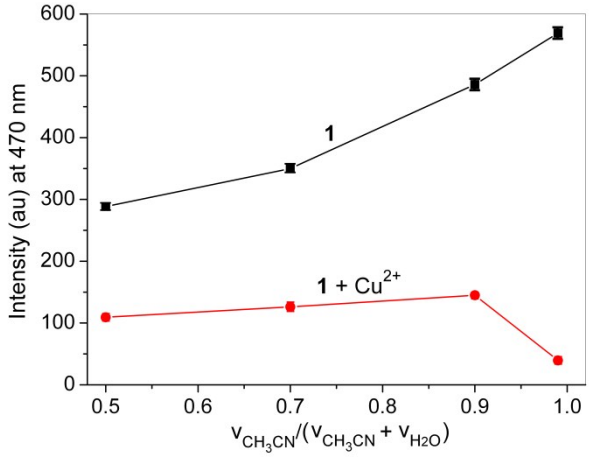


Fig. S8 Effects of CH_3CN content on the fluorescence intensity of probe **1** (20 μM) at 470 nm in the absence and presence of Cu^{2+} (100 μM) in aqueous solution (10 mM HEPES, pH 7.2). λ_{ex} = 350 nm.

7. Effects of pH on the fluorescence response of probe **1** to Cu^{2+}

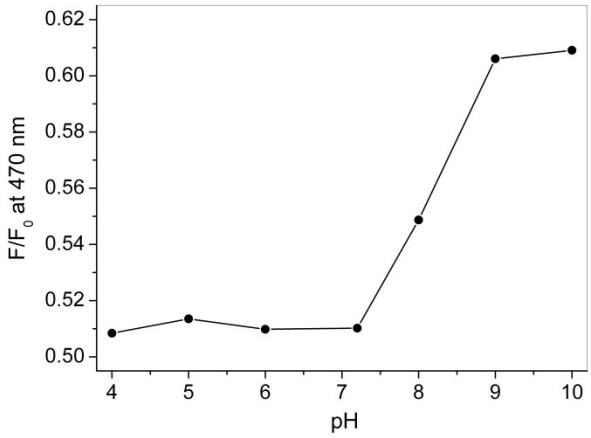


Fig. S9 Fluorescence intensity ratios of probe **1** (20 μM) at 470 nm after (F) and before (F_0) addition of Cu^{2+} (50 μM) in CH_3CN–H_2O (99/1, v/v, 10 mM HEPES) at various pH values (from 4.0 to 10.0). λ_{ex} = 350 nm.

8. Time-dependent fluorescence response of probe **1** upon addition of Cu^{2+}

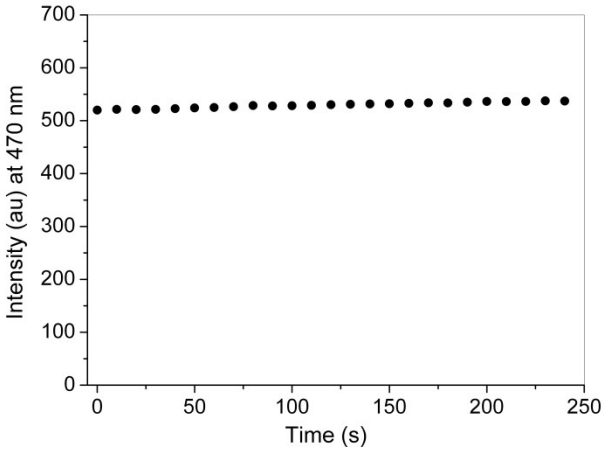


Fig. S10 Time course of the fluorescence intensity changes of probe **1** (20 μM) at 470 nm upon addition of Cu^{2+} (10 μM) in $CH_3CN–H_2O$ (99/1, v/v, 10 mM HEPES, pH 7.2). λ_{ex} = 350 nm.

9. UV-vis absorption spectra of probe **1** with different anion

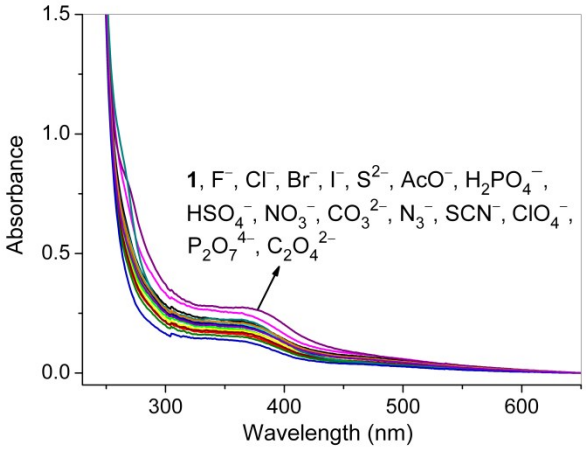


Fig. S11 UV-vis absorption spectra of probe **1** (20 μM) with different anions (30 μM) in DMSO–H_2O (1/1, v/v, 10 mM HEPES, pH 7.2).

10. UV-vis absorption spectra of probe **1** with different levels of $C_2O_4^{2-}/P_2O_7^{4-}$

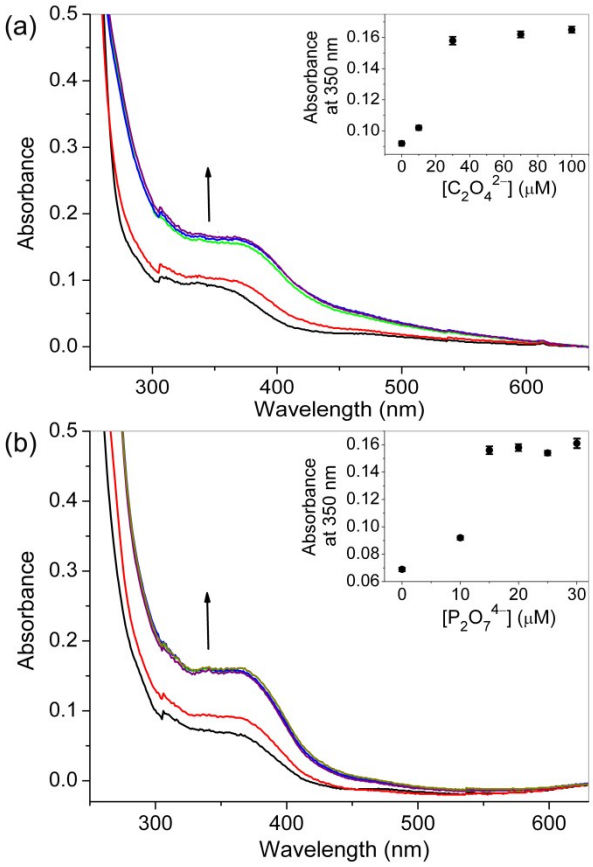


Fig. S12 UV-vis absorption spectra of probe **1** (20 μM) with different levels of (a) $C_2O_4^{2-}$ (from bottom to top: 0, 10, 30, 70 and 100 μM) and (b) $P_2O_7^{4-}$ (from bottom to top: 0, 10, 15, 20, 25 and 30 μM) in DMSO–H_2O (1/1, v/v, 10 mM HEPES, pH 7.2).

11. Effects of DMSO content on the fluorescence response of probe **1** to $C_2O_4^{2-}$/$P_2O_7^{4-}$

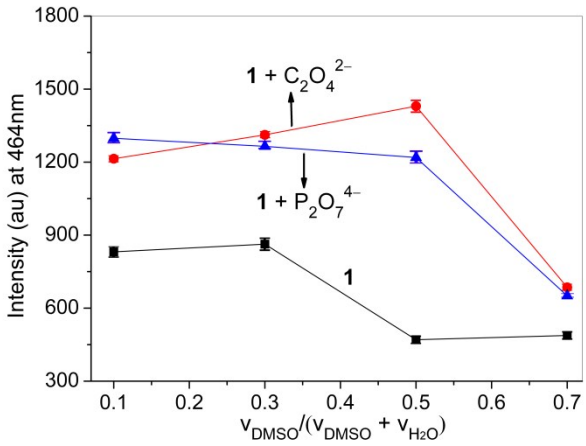


Fig. S13 Effects of DMSO content on the fluorescence intensity of probe **1** (20 μM) at 464 nm in the absence and presence of $C_2O_4^{2-}/P_2O_7^{4-}$ (50 μM) in aqueous solution (10 mM HEPES, pH 7.2). λ_{ex} = 350 nm.

12. Effects of pH on the fluorescence response of probe **1** to $C_2O_4^{2-}/P_2O_7^{4-}$

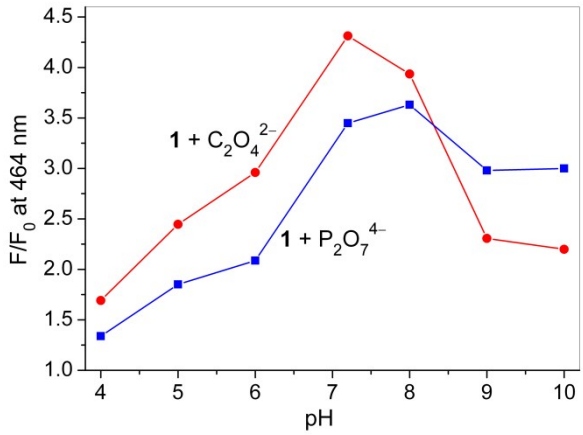


Fig. S14 Fluorescence intensity ratios of probe **1** (20 μM) at 464 nm after (F) and before (F_0) addition of $C_2O_4^{2-}/P_2O_7^{4-}$ (50 μM) in DMSO–H_2O (1/1, v/v, 10 mM HEPES) at various pH values (from 4.0 to 10.0). λ_{ex} = 350 nm.

13. Time-dependent fluorescence response of probe **1** upon addition of $C_2O_4^{2-}/P_2O_7^{4-}$

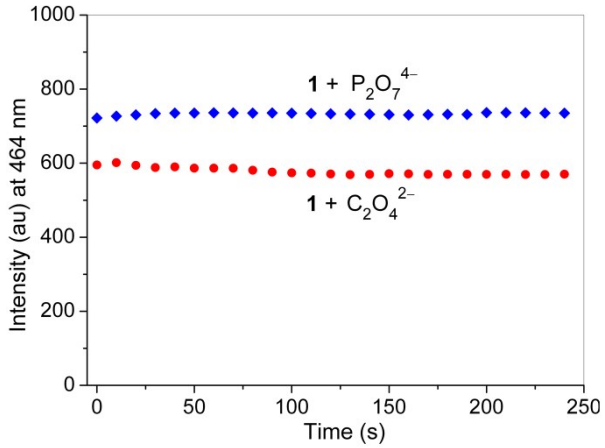


Fig. S15 Time course of the fluorescence intensity changes of probe **1** (20 μM) at 464 nm upon addition of $C_2O_4^{2-}$/$P_2O_7^{4-}$ (10 μM) in DMSO–H_2O (1/1, v/v, 10 mM HEPES, pH 7.2). λ_{ex} = 350 nm.

14. ^{1}H NMR spectra of probe **1** measured before and after addition of Cu^{2+}

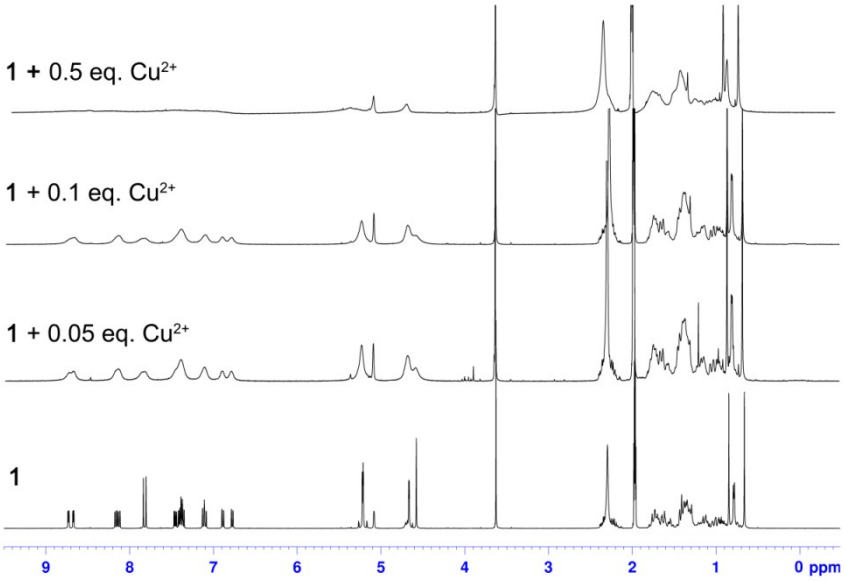


Fig. S16 ^{1}H NMR spectra of probe **1** (10 mM) measured before and after addition of Cu^{2+} (0.05, 0.1 and 0.5 equivalent) in CD_3CN–D_2O (99/1, v/v).

15. The reversibility of probe **1** for Cu^{2+} detection

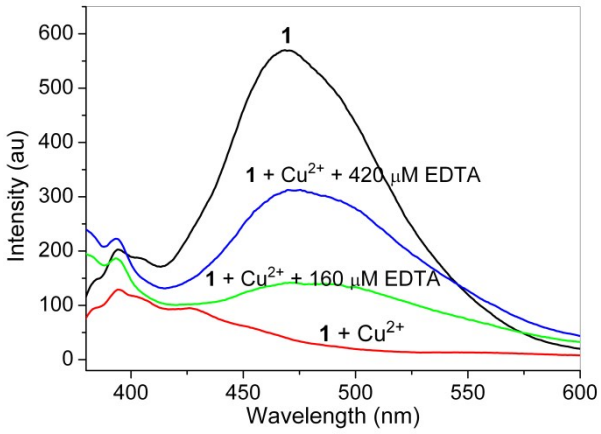


Fig. S17 Fluorescence spectra of probe **1**–Cu^{2+} complex with different levels of EDTA in CH_3CN–H_2O (99/1, v/v, 10 mM HEPES, pH 7.2). Probe **1** (20 M), Cu^{2+} (100 μM). λ_{ex} = 350 nm.

16. The reversibility of probe **1** for $C_2O_4^{2-}$/$P_2O_7^{4-}$ detection

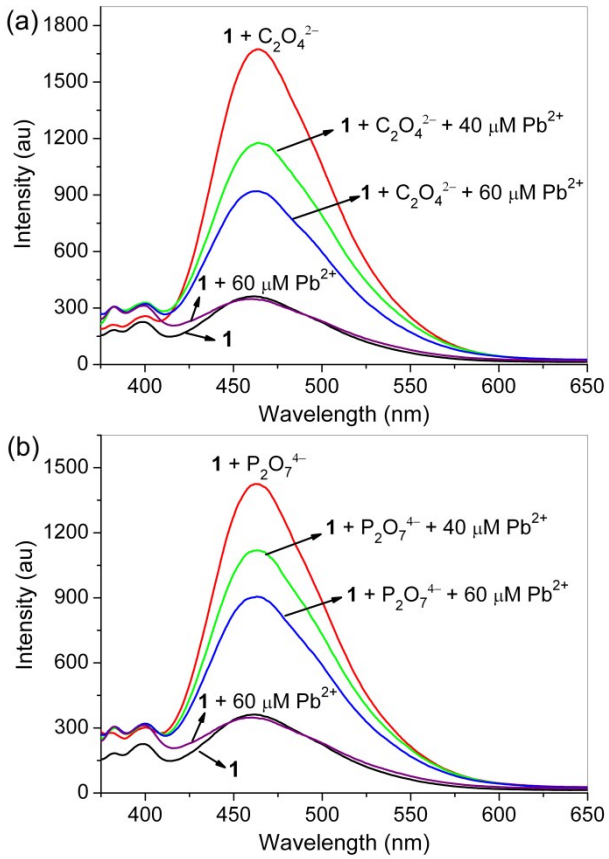
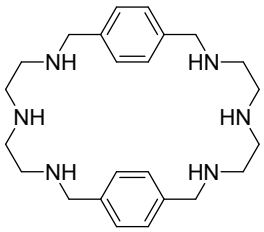
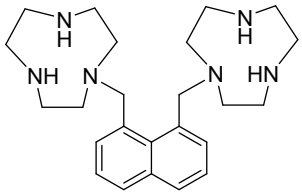
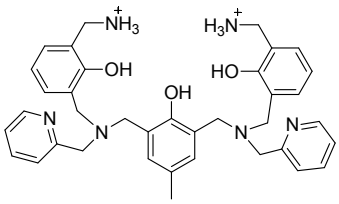
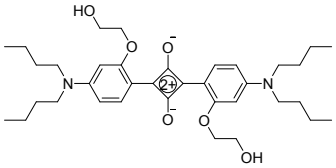
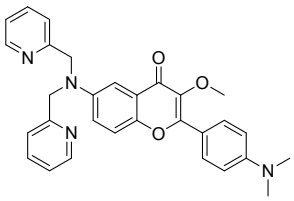
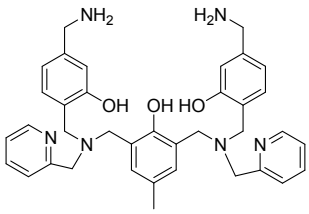
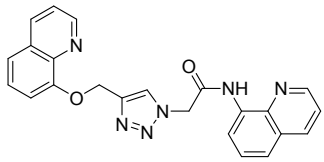
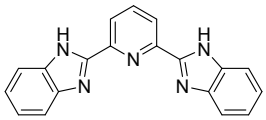
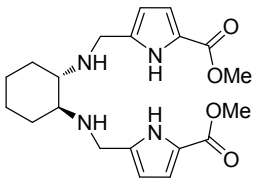
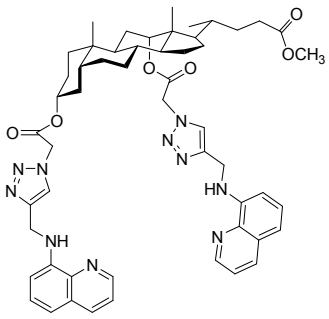


Fig. S18 Fluorescence spectra of (a) probe **1**–$C_2O_4^{2-}$ complex and (b) probe **1**–$P_2O_7^{4-}$ complex with different levels of Pb^{2+} in DMSO–H_2O (1/1, v/v, 10 mM HEPES, pH 7.2). Probe **1** (20 M), $C_2O_4^{2-}$/$P_2O_7^{4-}$ (100 μM). λ_{ex} = 350 nm.

17. **Table S1.** Comparison of the recently reported multi-detection probes for Cu^{2+}, $C_2O_4^{2-}$ and $P_2O_7^{4-}$

Probe	Detection mode and properties	K_a	Detection limit	Response time
carbon dots *Mater. Lett.*, 2014, **115**, 233	fluorescent turn-off/on for sequential detection of Cu^{2+} and $C_2O_4^{2-}$ (based on Cu^{2+} displacement approach) in Tris buffer solution, $\lambda_{ex}/\lambda_{em}$ 470/543 nm, quantitative detection ranged from 10–90 μM for Cu^{2+}, and 10–70 μM for $C_2O_4^{2-}$	no data	1 μM for $C_2O_4^{2-}$	rapid, no data
 *Chem. Commun.*, 2012, **48**, 6951	by fluorescent indicator (fluorescein, $\lambda_{ex}/\lambda_{em}$ 470/510 nm, and eosin Y, $\lambda_{ex}/\lambda_{em}$ 490/540 nm) displacement assays, macrocyclic(L)–Cu^{2+} complex formed an ensemble with $C_2O_4^{2-}$ and showed off-on fluorescent sensing for $C_2O_4^{2-}$ in water at neutral pH with quantitative detection ranged from 0–5 μM using Cu_2L–Eosin Y	$> 10^7$ M^{-1} for $C_2O_4^{2-}$	0.079 μM for $C_2O_4^{2-}$ by Cu_2L–Eosin Y	no data
 *J. Am. Chem. Soc.*, 2008, **130**, 12606	by the fluorescent indicator eosin Y displacement, a dimacrocyclic–Cu^{2+} complex could form an ensemble with $C_2O_4^{2-}$ and showed off-on fluorescent sensing ($\lambda_{ex}/\lambda_{em}$ 524/537 nm) for $C_2O_4^{2-}$ in water at neutral pH	$(1.3 \pm 0.1) \times 10^5$ M^{-1} for $C_2O_4^{2-}$	no data	no data
 *Sens. Actuators B*, 2016, **233**, 591	by indicator (pyrocatechol violet, colorimetric indicator, ratio of A_{655}/A_{444}; esculetine, fluorescent indicator, $\lambda_{ex}/\lambda_{em}$ 380/465 nm) displacement, a dinuclear–Cu^{2+} complex with two ammonium arms formed an ensemble with $P_2O_7^{4-}$, showing color changes and off-on fluorescence in aqueous solution	by the UV indicator, 8.55×10^6 M^{-1} for $P_2O_7^{4-}$	0.15 μM for $P_2O_7^{4-}$ by fluorescence assay	no data

Probe	Detection mode and properties	K_a	Detection limit	Response time
 *Sens. Actuators B*, 2016, **233**, 550	a squaraine-based fluorescent probe chelated Cu^{2+} and showed on-off sensing ($\lambda_{ex}/\lambda_{em}$ 620/670 nm, quantitative detection range 0.5–3.5 μM) in MeCN-H_2O (9/1, v/v). $P_2O_7^{4-}$ extracted Cu^{2+} from the probe-Cu^{2+} complex and restored the spectral signal of free probe (quantitative detection range 0–25 μM)	no data	near 15 nM for Cu^{2+}, and 0.072 μM for $P_2O_7^{4-}$	no data
 *Sens. Actuators B*, 2016, **229**, 131	a flavonoid-based probe exhibited fluorescence quenching ($\lambda_{ex}/\lambda_{em}$ 390/510 nm) to Cu^{2+} with quantitative detection ranged from 0–10 μM in DMSO–H_2O (v/v = 9/1, 0.1 mM PBS, pH 7.4). Moreover, the probe-Cu^{2+} complex could also be used for secondary sensing of $P_2O_7^{4-}$ based on Cu^{2+} displacement approach with fluorescence turn-on behavior	no data	lower than 100 nM for Cu^{2+}	no data
carbon quantum dots with rich carboxyl groups on the surface *Biosens. Bioelectron.*, 2015, **68**, 675	richness of carboxyl on the surface of carbon quantum dots enables aggregation caused fluorescence quenching by Cu^{2+}, and the competitive interaction among carboxyl, Cu^{2+} and $P_2O_7^{4-}$ endows disaggregation induced fluorescence enhancement, $\lambda_{ex}/\lambda_{em}$ 452/525 nm	no data	0.3 μM for $P_2O_7^{4-}$	real-time
 *Org. Lett.*, 2014, **16**, 2220	by colorimetric indicator (pyrocatechol violet, ratio of A_{630}/A_{444}) displacement, a dinuclear–Cu^{2+} complex with ammonium moieties formed an ensemble with $P_2O_7^{4-}$, showing colorimetric changes in aqueous solution	5.75×10^6 M^{-1} for $P_2O_7^{4-}$	no data	no data

Probe	Detection mode and properties	K_a	Detection limit	Response time
 *Tetrahedron Lett.*, 2013, **54**, 5948	a quinoline derivative was used as a fluorescent probe for sequential sensing ($\lambda_{ex}/\lambda_{em}$ 305/412 nm) of Cu^{2+} and $P_2O_7^{4-}$ in DMSO–H_2O (1/1, v/v, 20 mM HEPES, pH 7.4). The probe displayed high selectivity to Cu^{2+} (quantitative detection range 0–20 μM), and the probe-Cu^{2+} showed high selectivity to $P_2O_7^{4-}$ (quantitative detection range 1–20 μM) with emission recovery of the free probe	1.59×10^7 M^{-1} for Cu^{2+}	4.47 μM for Cu^{2+}, and 3.16 μM for $P_2O_7^{4-}$	no data
 *Biosens. Bioelectron.*, 2011, **30**, 282	a turn-on fluorescent probe ($\lambda_{ex}/\lambda_{em}$ 280/395 nm) based on Cu^{2+} complex of 2,6-bis(2-benzimidazolyl) pyridine was developed for $P_2O_7^{4-}$, due to the formation of a ternary complex of probe–Cu^{2+}–$P_2O_7^{4-}$, with quantitative detection range of 3–90 μM at a neutral pH	no data	no data	no data
 *J. Fluoresc.*, 2011, **21**, 701	constructed by a copper complex (receptor) and eosin Y (indicator), an ensemble displayed fluorescent off-on ($\lambda_{ex}/\lambda_{em}$ 523/543 nm) recognition of $P_2O_7^{4-}$ in water at pH 7.4	1.17×10^5 M^{-1} for $P_2O_7^{4-}$	no data	no data
 *This work*	fluorescence quenching ($\lambda_{ex}/\lambda_{em}$ 350/470 nm) upon binding to Cu^{2+} in CH_3CN–H_2O (99/1, v/v, 10 mM HEPES, pH 7.2), and fluorescent enhanced response ($\lambda_{ex}/\lambda_{em}$ 350/464 nm) toward $C_2O_4^{2-}$ and $P_2O_7^{4-}$ in DMSO–H_2O (1/1, v/v, 10 mM HEPES, pH 7.2)	3.28×10^3 M^{-1} for Cu^{2+}, 2.23×10^4 M^{-1} for $C_2O_4^{2-}$ and 4.96×10^4 M^{-1} for $P_2O_7^{4-}$	0.12 μM for Cu^{2+}, 0.28 μM for $C_2O_4^{2-}$ and 0.55 μM for $P_2O_7^{4-}$	completed within several seconds