Electronic Supplementary Information for

A new water-soluble copper(II) complex as a selective fluorescent sensor for azide ion

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Experimental section

Materials and physical methods: All reagents and chemicals were purchased from Sigma and used without further purification. Solvents used for spectroscopic studies were purified and dried by standard procedures before use. FT-IR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Elemental analysis was carried out in a 2400 Series-II CHN analyzer, Perkin Elmer, USA. Fluorescence spectra were performed using a Perkin Elmer LS 55 Luminescence Spectrometer. Fluorescence life times were determined from time-resolved intensity decay by the method of time-correlated single-photon counting using a picosecond diode laser at 462 nm as light source.

CAUTION: Perchlorate salts with organic ligands are potentially explosive. Only a small amount of material should be prepared and handled with caution.

Synthasis of ligand H_3L: 4-methyl-2,6-diformylphenol was synthesized starting from *p*-cresol following a published procedure [1]. To a solution of 4-methyl-2,6-diformylphenol (0.328 g, 2 mmol) in 25 mL of methanol was added 2-amino-2-methyl-1-propanol (0.356 g, 4 mmol) in 10 mL acetonitrile. The reaction mixture was refluxed for 3 h. The solution was filtered and kept overnight at 4°C for few days. Yellow colored crystalline compound, H_3L, was obtained in a good yield. (0.57 g, 94%). Anal. Calcd. for $C_{17}H_{26}N_2O_3$: C 66.63, H 8.55, N 9.14; Found: C 66.23, H 8.15, N 9.89 %; FT-IR (KBr phase) (υ_{max}/cm^{-1}): 1640s, 1605s.

Synthesis of $\{[Cu_2(H_2L)(OH)(H_2O)]\cdot(ClO_4)_2(H_2O)\}$ (**1**): A 25 mL of methanolic solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.27 g, 0.72 mmol) was added slowly to a stirred 20 mL methanolic solution of the ligand (H_3L) (0.11 g, 0.36 mmol) followed by the addition of a 10 mL methanolic solution of KOH (0.02, 0.36 mmol). The mixture is stirred for 30 min whereby a dark green colour solution was formed. X-ray quality single crystals were obtained on slow evaporation of the solution at ambient temperature after few days (0.20 g, 82%). Anal. Calc. for $C_{17}H_{30}N_2O_{14}Cl_2Cu_2$: C 29.83, H 4.42, N 4.09; Found: C 29.54, H 4.29, N 4.12 %. FT-IR (KBr phase) (υ_{max}/cm^{-1}): 3433br, 3215br, 1617vs, 1556vs, 1452m, 1323m, 1238w, 1113vs, 625s.

Synthesis of $[Cu_6(HL)_2(\mu_{1,1}\text{-}N_3)_8]$ (**2**): Addition of 30 mL aqueous solution of **1** (0.30 g, 0.44 mmol) to the aqueous solution of NaN_3 (0.12g, 1.76 mmol) gives rise to the formation of dark brown solution. Single crystals of **2** suitable for X-ray crystallography were obtained on evaporation at room temperature within couple of weeks (0.22 g, 74%). Anal. Calc. for $C_{34}H_{48}N_{28}O_6Cu_6$: C 30.79, H 3.62, N 29.56; Found: C 30.10, H 3.09, N 28.92 %. FT-IR (KBr phase) (υ_{max}/cm^{-1}): 3384br, 2114vs, 2077vs, 2048vs, 1641vs, 1556vs, 1454m, 1396m, 1315m.

X-ray Data Collection and Structure Determination: Crystal data for **1** and **2** are summarised in Table S4 (below). The diffraction experiments were carried out with a Bruker SMART CCD area detector diffractometer at 293 K for complexes **1** and at 150 K for **2** using Mo Kα radiation (λ = 0.71073) with a graphite crystal monochromator in the incident beam. No crystal decay was observed, so that no time decay correction was needed. The collected frames were processed with the software SAINT,[2] and an empirical absorption correction was applied (SADABS)[3] to the collected reflections. The calculations of **1** and **2** were performed by using SHELX-97 and Personal Structure Determination Package[4] and the physical constants tabulated therein[5] respectively. The structures were solved by direct methods (SHELXS)[6] and refined by full-matrix least squares by using all reflections and minimizing the function $\Sigma w(F_o^2 - kF_c^2)^2$ (refinement on F^2). All the non-hydrogen atoms were refined with anisotropic thermal factors. The five hydrogen atoms (H1, H25, H26, H27 and H28) in **1** were refined with isotropic thermal parameters and except these, all the hydrogen atoms were placed in their ideal positions (C–H 0.97 Å), with the thermal parameter *U* 1.10 times that of the atom to which they are attached, and not refined. The hydrogen atoms of the coordinated water O5 could not be located from the Difference fourier map of **1**. In case of **2** The four hydrogen atoms H1 (bonded to O3), and H2, H3, H4 (bonded to C14) were refined with isotropic thermal parameters. All the other hydrogen atoms were placed in their ideal positions (C-H = 0.97 Å), with the thermal parameter *U* being 1.10 times that of the atom to which they are attached, and not refined. In the final Fourier map the maximum and minimum residuals were +1.11(35) e$\cdot$Å^{-3} at 0.06 Å from Cu3, and –0.85(35) e$\cdot$Å^{-3}. CCDC 739898 (**1**) and 732702 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Fluorimetric Analysis: Fluorescence spectroscopic studies were performed with a Perkin Elmer LS 55 Luminescence Spectrometer. Fluorescence quantum yields (*Φ*) were estimated by integrating the area under the fluorescence curves with the equation:

$$\phi_{\text{sample}} = \frac{\text{OD}_{\text{standard}} \times A_{\text{sample}}}{\text{OD}_{\text{sample}} \times A_{\text{standard}}} \times \phi_{\text{standard}}$$

where *A* is the area under the fluorescence spectral curve and OD is optical density of the compound at the excitation wavelength.[7] The standard used for the measurement of fluorescence quantum yield was tris(2,2'-bipyridyl)ruthenium(II) ($\Phi = 0.042$ in water).[8]

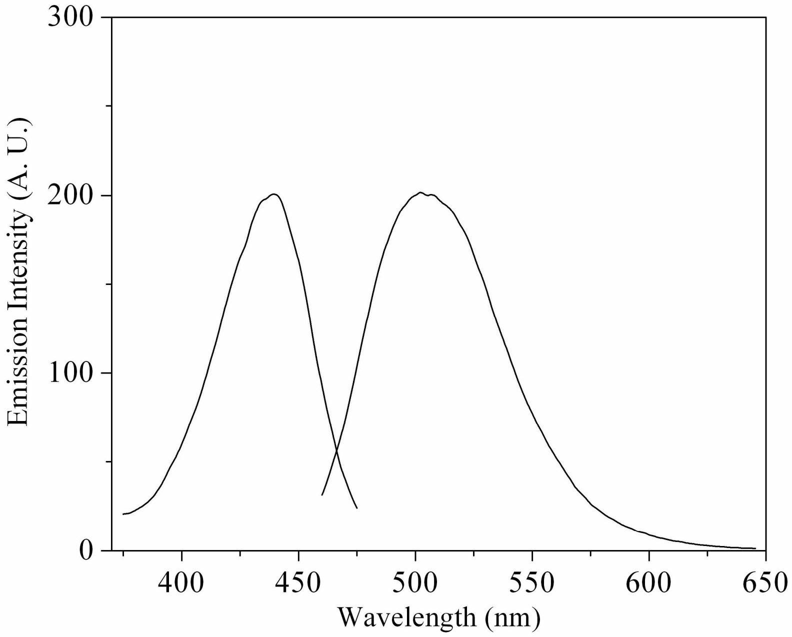

Fig. S1 Excitation and emission spectra of **1** (50 μM).

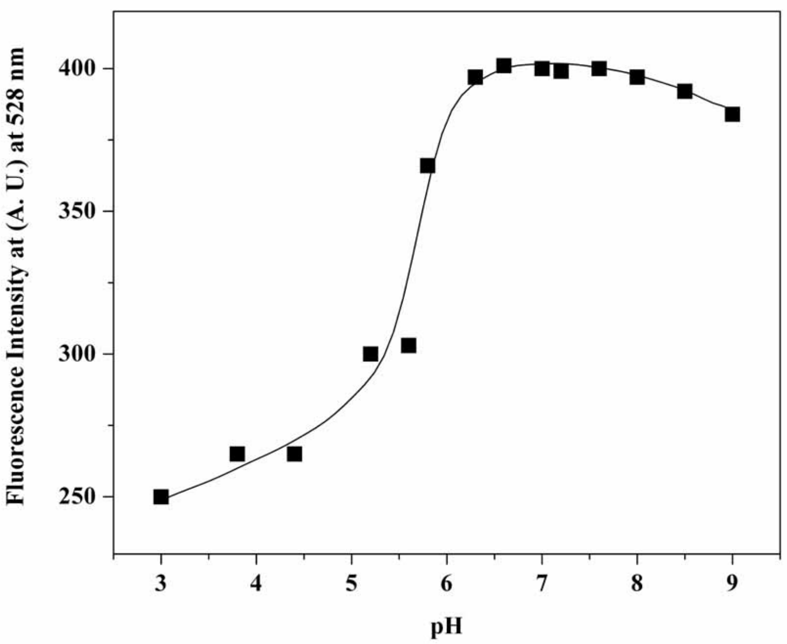

Fig. S2 Effect of pH on the fluorescence intensity of **1** (50 μM) in presence of azide ions (200 μM).

Equation (1)[10]

$$\mathbf{Y} = \mathbf{Y}_0 + \frac{(Y_{\mathrm{lim}} - Y_0)}{2}\{1 + \frac{C_M}{C_L} + \frac{1}{K_a C_L} - [(1 + \frac{C_M}{C_L} + \frac{1}{K_a C_L})^2 - 4\frac{C_M}{C_L}]^{1/2}\}$$

Y was the recorded fluorescence intensity, Y_0 was the fluorescence intensity without the addition of N_3^-, Y_{lim} was the limiting value, C_M was the target molecule concentration, and C_L was the sensor (**1**) concentration. The following equation was used for the nonlinear least squares analysis to determine the association constant, K_a (Fig. S3, below) and the vale of K_a was 2.77 (±0.13) × 10^3 mol^{-1} L^{-1}.

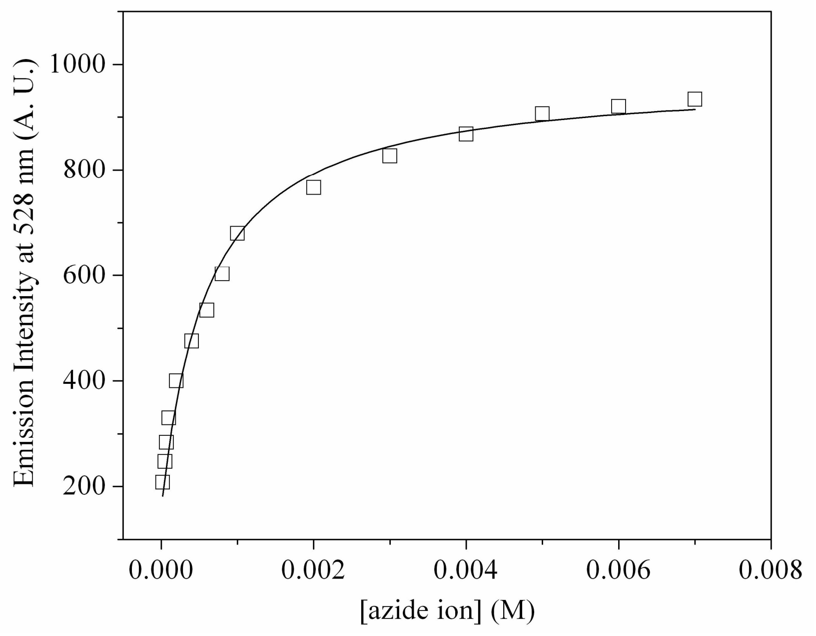

Fig. S3 Determination of association constant, K_a

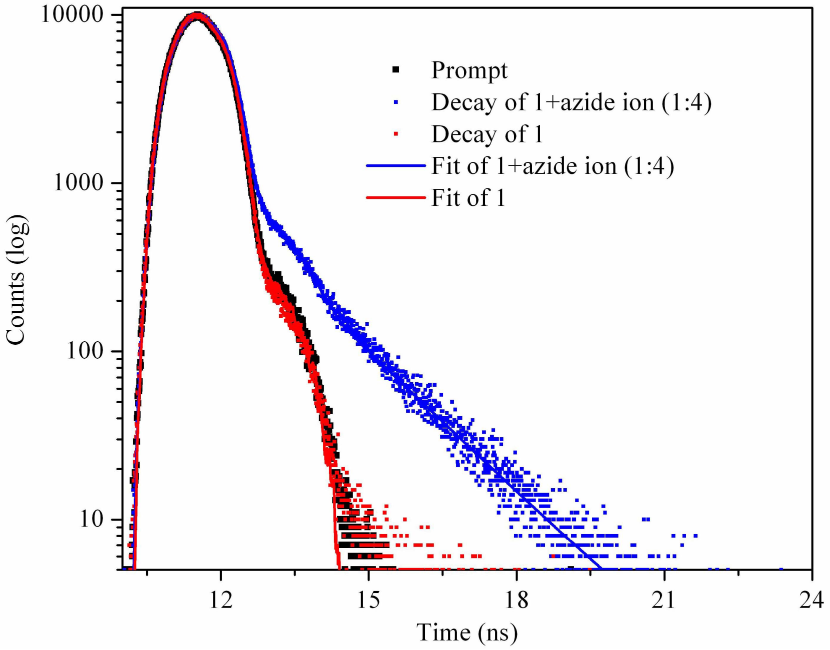

Fig. S4 Time-resolved fluorescence decay of **1** (50 μM in aqueous medium) in the absence and presence of added N_3^- (200 μM) (λ_{ex} = 462 nm).

Table S1 Radiative and the total nonradiative rate data.

	τ_f(ps)	Φ_f	k_r ($10^9 s^{-1)}$	k_{nr} (10^9 s^{-1})	χ^2
1	12.6	19.8×10^{-3}	1.5	77.9	1.244
1 + N_3^- mol ratio (1: 4)	140.1	130.0×10^{-3}	0.9	6.2	0.845

Table S2 Selected bond lengths [Å] and angles [°] for complex **1**

Cu2−O2	1.911(3)	Cu1−O2	1.915(3)
Cu2−O3	1.915(3)	Cu1−N1	1.927(3)
Cu2−N2	1.929(3)	Cu1−O4	1.943(3)
Cu2−O4	1.963(3)	Cu1−O1	1.972(3)
Cu2−O5	2.359(5)		
O2−Cu2−O3	177.26(15)	O4−Cu2−O5	97.59(15)
O2−Cu2−N2	93.15(12)	O2−Cu1−N1	92.32(13)
O3−Cu2−N2	86.15(14)	O2−Cu1−O4	82.13(12)
O2−Cu2−O4	81.68(12)	N1−Cu1−O4	174.01(13)
O3−Cu2−O4	98.82(13)	O2−Cu1−O1	176.05(14)
N2−Cu2−O4	173.26(14)	N1−Cu1−O1	85.67(14)
O2−Cu2−O5	92.43(16)	O4−Cu1−O1	99.73(12)
O3−Cu2−O5	90.17(18)	Cu1−O4−Cu2	96.71(12
N2−Cu2−O5	86.90(16)	Cu2−O2−Cu1	99.42(12)

Table S3 Selected bond lengths [Å] and angles [°] for complex **2**

Cu1−O1	1.917(2)	Cu2−N2	1.930(2)
Cu1−O2	1.947(2)	Cu2−N3	1.968(2)
Cu1−N1	1.933(2)	Cu2−N12	2.475(2)
Cu1−N3	1.960(2)	Cu3−N6	1.995(2)
Cu1−N9	2.450(2)	Cu3−N9	1.969(2)
Cu2 O2	1.957(2)	Cu3−N12	1.955(2)
Cu2−O3	1.932(2)		
O3–H1---O1	1.42(3), 174(3)		
O1−Cu1−O2	167.9(1)	O3−Cu2−N3	101.7(1)
O1−Cu1−N1	86.7(1)	O3−Cu2−N12	98.2(1)
O1−Cu1−N3	99.4(1)	N2−Cu2−N3	170.8(1)
O1−Cu1−N9	105.1(1)	N2−Cu2−N12	95.1(1)
O2−Cu1−N1	92.4(1)	N3−Cu2−N12	88.1(1)
O2−Cu1−N3	79.6(1)	N6−Cu3−N6	76.9(1)
O2−Cu1−N9	86.9(1)	N6−Cu3−N9	96.5(1)
N1−Cu1−N3	168.3(1)	N6−Cu3−N12	168.5(1)
N1−Cu1−N9	97.0(1)	N6−Cu3−N9	173.2(1)
N3−Cu1−N9	91.1(1)	N6−Cu3−N12	91.9(1)
O2−Cu2−O3	170.9(1)	N9−Cu3−N12	94.6(1)
O2−Cu2−N2	92.2(1)	Cu1−O2−Cu2	101.1(1)
O2−Cu2−N3	79.1(1)	Cu1−N3−Cu2	100.2(1)
O2−Cu2−N12	90.9(1)	Cu1−N9−Cu3	106.1(1)
O3−Cu2−N2	86.4(1)	Cu2−N12−Cu3	101.1(1)

Table S4 Crystallographic informations for **1** and **2**.

	$C_{17}H_{30}N_2O_{14}Cl_2Cu_2$ (**1**)	$C_{34}H_{48}N_{28}O_6Cu_6$(**2**)
Formula weight	684.43	1326.18
Crystal system	triclinic	triclinic
Space group	P−1 (No. 2)	P−1 (No. 2)
A (Å)	6.9798(4)	10.005(1)
B (Å)	12.3990(7)	10.063(1)
C (Å)	15.5894(8)	13.026(1)
α (°)	100.199(2)	72.91(1)
β (°)	101.453(2)	86.75(1)
γ (°)	96.492(2)	86.52(1)°
V (Å^3)	1285.93(12)	1250.2(2)
Z	2	1
$D_{\text{calcd.}}$ (g cm^{-3})	1.762	1.761
T (K)	293	150
μ (Mo-Kα) (mm^{-1})	1.929	2.59
F (000)	696	670
λ (Mo-Kα)	0.71073	0.71073
θ-range	1.36-30.63	3.00-27.00
No. of reflections (total; independent)	22664, 7624	15808, 6295
R_{int}	0.036	0.0297
R1 (wR2 for all data)	0.0603 (0.1629)	0.033 (0.062)
GOF	1.055	0.985

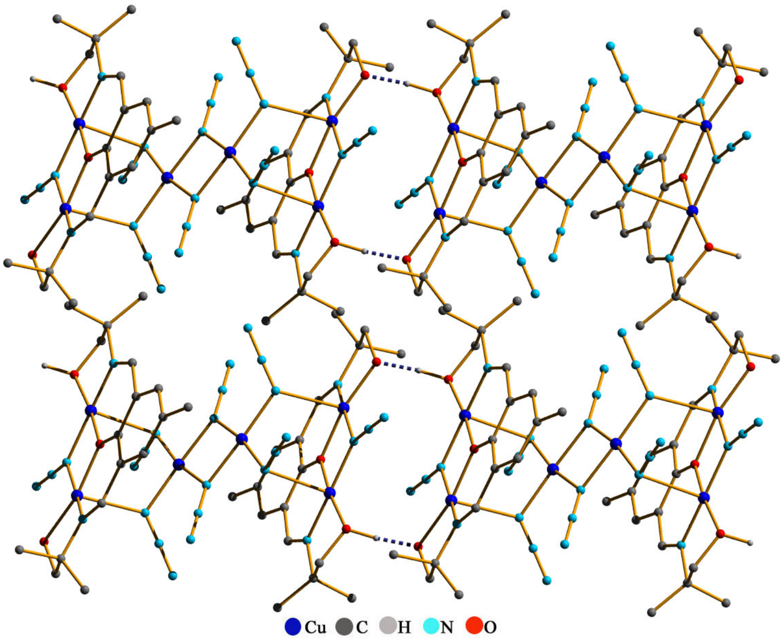

Fig. S5 Crystal packing of **2** illustrates the intermolecular O–H---O hydrogen bonding interactions to form a 1D chain-like structure along crystallographic *c*-axis.

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