Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A Cu(II) Complex-based Fluorescence Chemosensor for Cyanide in Aqueous Media

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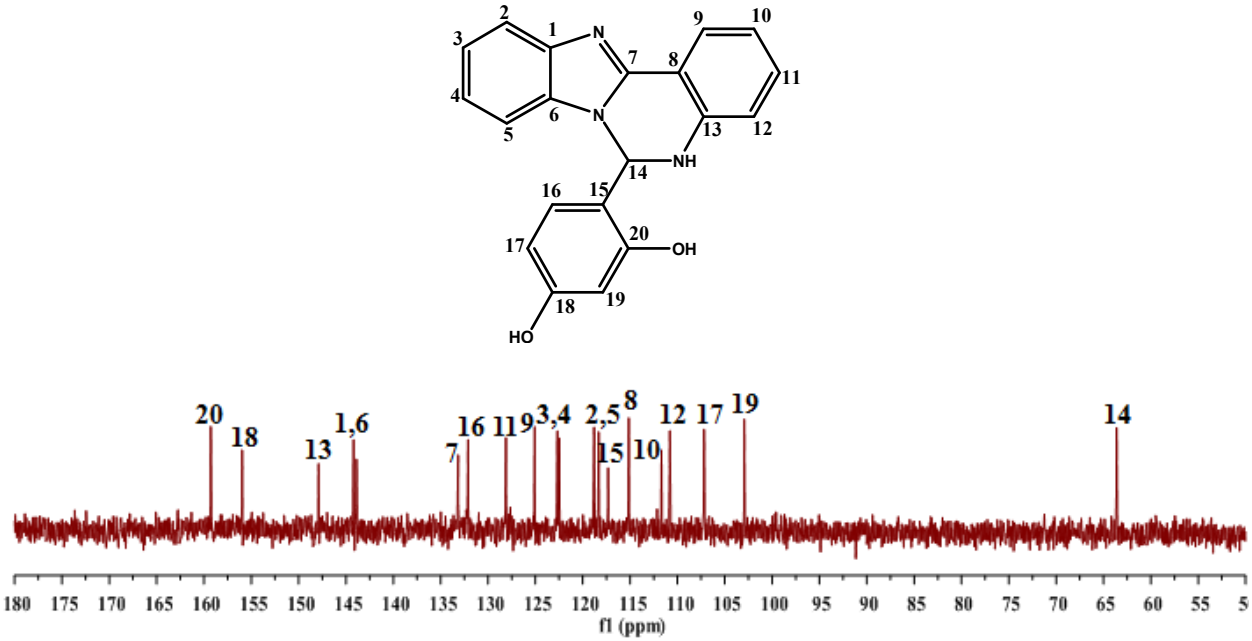


Fig. S1 ^{13}C NMR spectra of **H_2L** in DMSO-d_6.

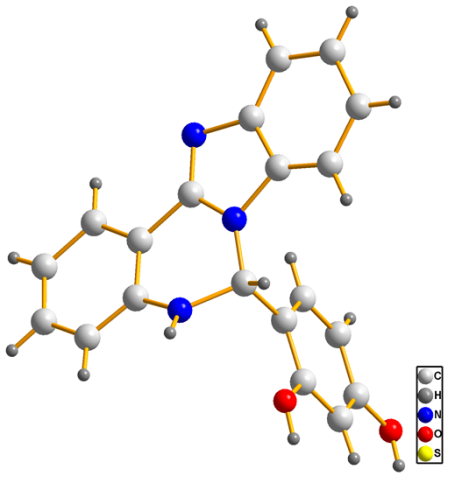
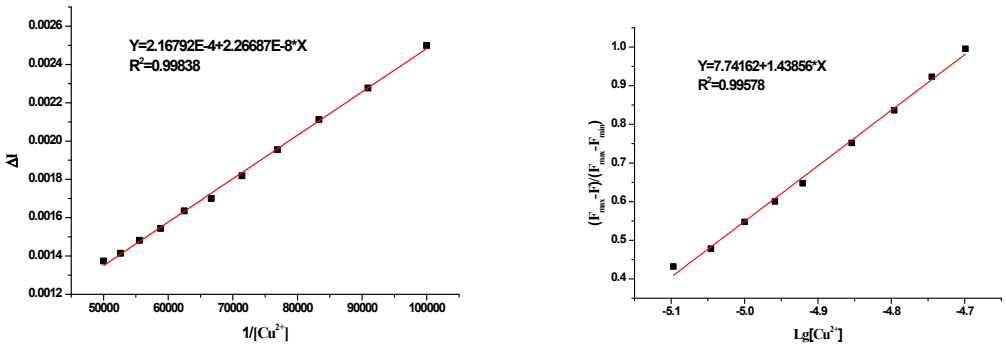


Fig. S2 Molecular structures with an atom labeling schemes for the ligand **H_2L**.



(a) (b)

Fig. S3 (a) Estimation of association constant by Benesi-Hildebrand (B-H) plot for 1:1 stoichiometry for the complexation between H_2L and Cu^{2+} in DMSO/H_2O (1:1, v/v). (b) Normalized response of fluorescence signal at 432 nm to changing Cu^{2+} concentrations.

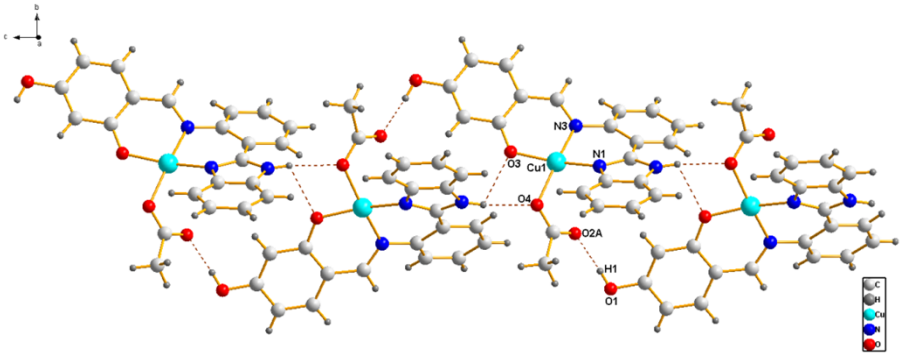


Fig. S4 The intermolecular hydrogen bond in **1**.

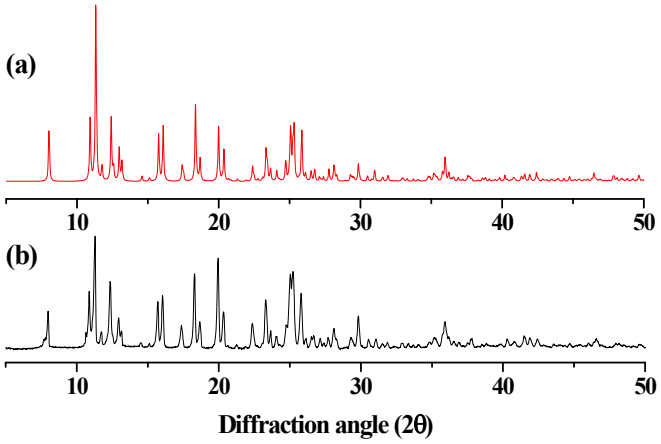


Fig. S5 PXRD patterns of [Cu(HL^1)(Ac)]: (a) simulated from 1 single-crystal X-ray diffraction data, (b) PXRD patterns of **1'** as-synthesized.

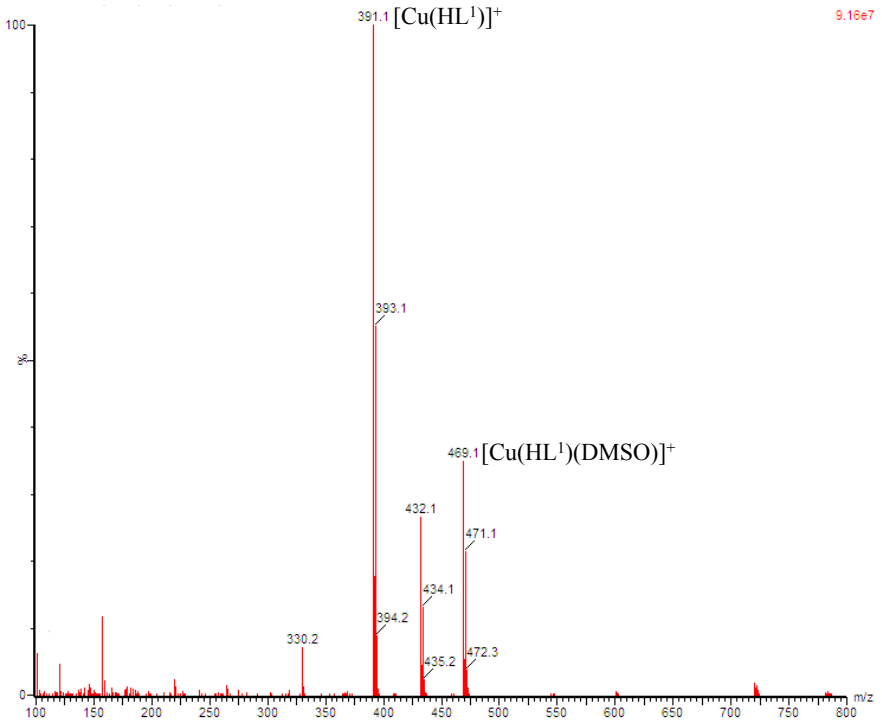
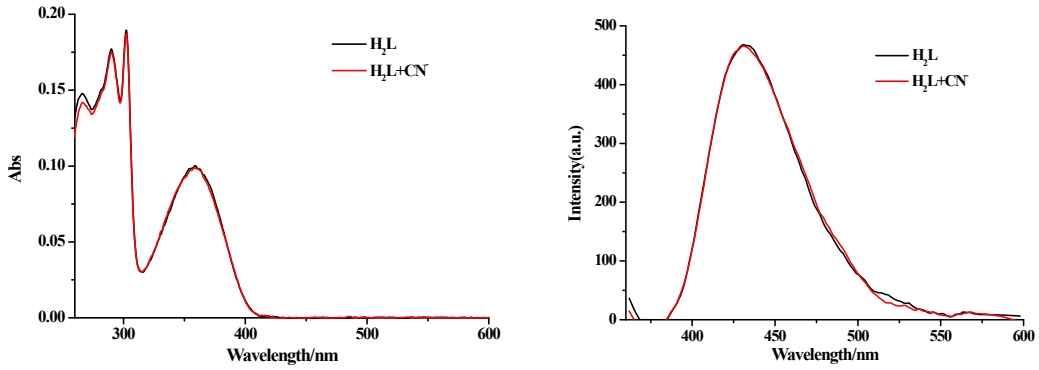


Fig. S6 ESI-MS spectrum of H_2L (50 μM) after treatment with an equal amount of Cu^{2+}.



(a) (b)

Fig. S7 (a) UV-vis spectra of H_2L (10 μM) in DMSO/H_2O (1:1, v/v) with 1.0 equiv. of CN^- ions. (b) Fluorescence spectra of H_2L (10 μM) in DMSO/H_2O (1:1, v/v) with 1.0 equiv. of CN^- ions. λ_{ex}=358 nm.

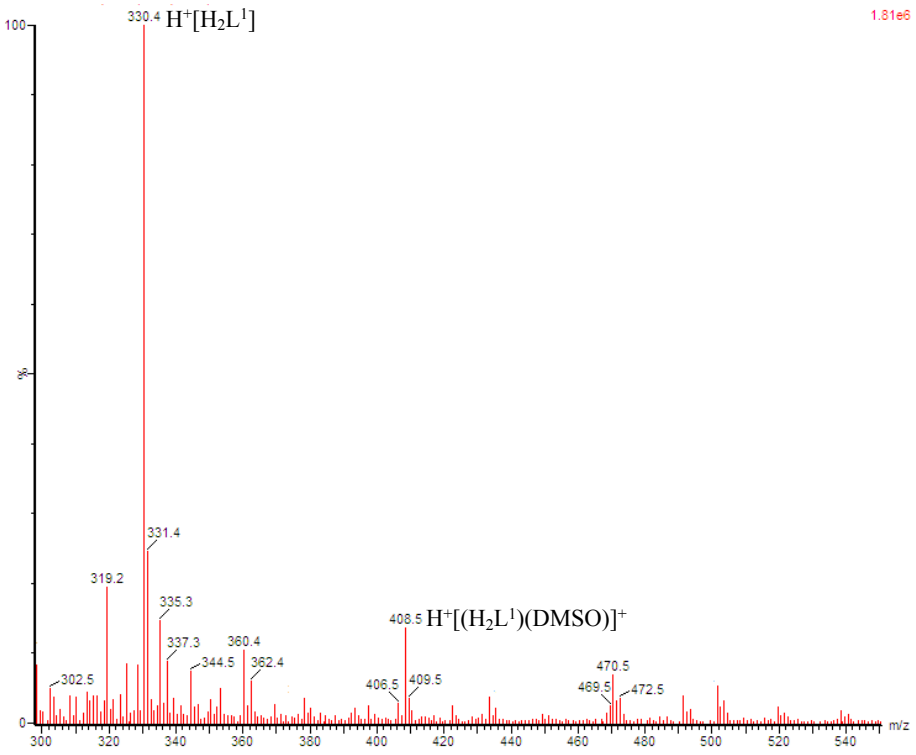


Fig. S8 ESI-MS spectrum of **1** (10 μM) after treatment with 4.0 equiv. CN^-.

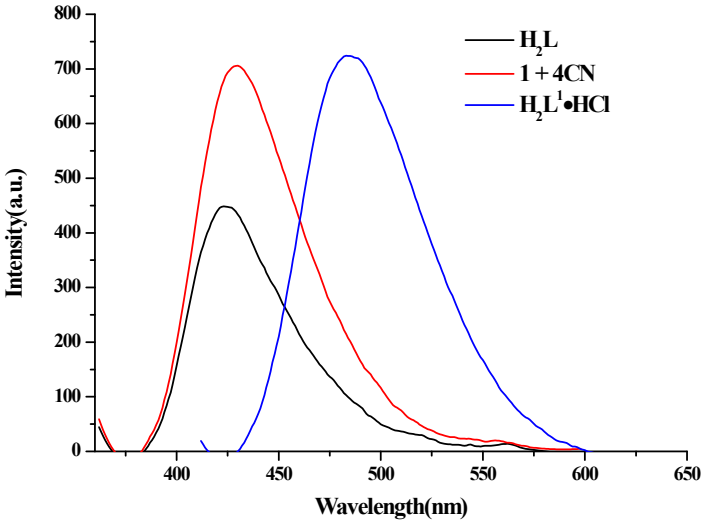
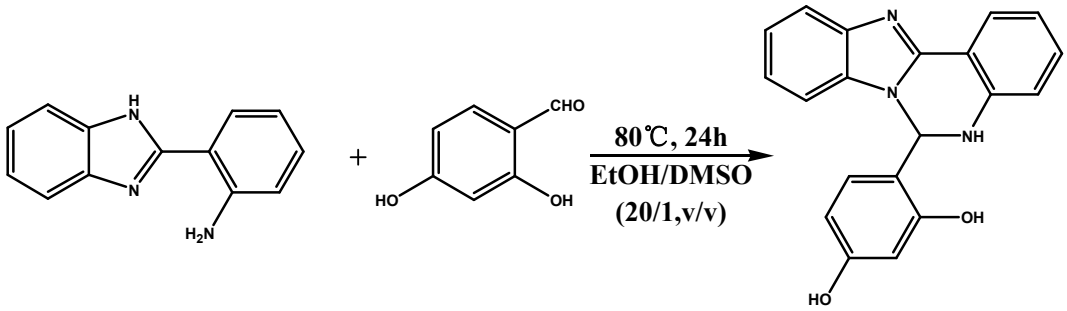


Fig. S9 Fluorescence spectra of **H_2L** (λ_{ex}=358 nm), **1** upon the addition of 4 equiv. CN^- (λ_{ex}=358 nm) and **H_2L^1•HCl** (λ_{ex}=408 nm) in DMSO/H_2O (1:1, v/v).



Scheme S1 Reaction scheme for the synthesis of the ligand $\mathbf{H_2L}$.

Table S1 Crystal data and structure refinement parameters of $\mathbf{H_2L}$.

Compound	$\mathbf{H_2L}$
Formula	$C_{22}H_{21}N_3O_3S$
Fw	407.49
Crystal system	Orthorhombic
Space group	*P*bca
a (Å)	10.0302(11)
b (Å)	16.5489(19)
c (Å)	23.691(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3932.4(8)
Z	8
calculated density (g/cm^3)	1.377
F (000)	1712
Reflections collected/unique	25333 / 4522 [R(int) = 0.0934]
Goodness-of-fit on F^2	1.353
Final R indices [$I>2\sigma(I)$]	R_1 = 0.1262, wR_2 = 0.3705
R indices (all data)	R_1 = 0.2072, wR_2 = 0.4269

$R_1 = \Sigma(|F_o| - |F_c|)/|F_o|$; $wR_2 = \{\Sigma[(w|F^2_o| - |F^2_c|)^2/\Sigma w(F^2_o)^2]\}^{1/2}$.

Table S2 Selected Bond Distances (Å) and Angles (deg) for **H_2L** and**1**.

H_2L			
C(1)-C(2)	1.385(8)	C(10)-C(11)	1.353(11)
C(1)-C(6)	1.385(7)	C(11)-C(12)	1.431(11)
C(2)-O(2)	1.365(6)	C(12)-C(13)	1.417(10)
C(2)-C(3)	1.398(7)	C(13)-C(14)	1.512(9)
C(3)-C(4)	1.355(7)	C(14)-N(3)	1.274(8)
C(4)-C(5)	1.385(7)	C(14)-N(2)	1.323(7)
C(5)-C(6)	1.412(7)	C(15)-C(20)	1.357(10)
C(5)-C(7)	1.513(7)	C(15)-C(16)	1.375(9)
C(6)-O(1)	1.360(6)	C(15)-N(3)	1.463(9)
C(7)-N(2)	1.413(7)	C(16)-C(17)	1.368(12)
C(7)-N(1)	1.500(8)	C(17)-C(18)	1.458(12)
C(8)-C(9)	1.348(10)	C(18)-C(19)	1.358(11)
C(8)-C(13)	1.373(9)	C(19)-C(20)	1.317(10)
C(8)-N(1)	1.406(8)	C(20)-N(2)	1.463(8)
C(9)-C(10)	1.360(11)		
C(2)-C(1)-C(6)	119.5(5)	C(8)-C(13)-C(12)	120.3(6)
O(2)-C(2)-C(1)	122.2(5)	C(8)-C(13)-C(14)	119.6(6)
O(2)-C(2)-C(3)	118.0(5)	C(12)-C(13)-C(14)	120.0(6)
C(1)-C(2)-C(3)	119.8(5)	N(3)-C(14)-N(2)	118.9(7)
C(4)-C(3)-C(2)	120.0(5)	N(3)-C(14)-C(13)	127.4(6)
C(3)-C(4)-C(5)	122.1(5)	N(2)-C(14)-C(13)	113.6(6)
C(4)-C(5)-C(6)	117.7(5)	C(20)-C(15)-C(16)	120.3(7)
C(4)-C(5)-C(7)	124.9(4)	C(20)-C(15)-N(3)	113.6(6)
C(6)-C(5)-C(7)	117.5(5)	C(16)-C(15)-N(3)	126.1(7)
O(1)-C(6)-C(1)	123.3(4)	C(17)-C(16)-C(15)	117.9(7)
O(1)-C(6)-C(5)	115.8(4)	C(16)-C(17)-C(18)	119.4(6)
C(1)-C(6)-C(5)	120.8(5)	C(19)-C(18)-C(17)	119.6(7)
N(2)-C(7)-N(1)	104.1(5)	C(20)-C(19)-C(18)	118.1(7)

N(2)-C(7)-C(5)	113.1(5)	C(19)-C(20)-C(15)	124.6(6)
N(1)-C(7)-C(5)	112.7(5)	C(19)-C(20)-N(2)	133.9(7)
C(9)-C(8)-C(13)	120.7(6)	C(15)-C(20)-N(2)	101.5(6)
C(9)-C(8)-N(1)	121.6(7)	C(8)-N(1)-C(7)	119.7(5)
C(13)-C(8)-N(1)	117.3(6)	C(14)-N(2)-C(7)	130.4(6)
C(8)-C(9)-C(10)	119.5(7)	C(14)-N(2)-C(20)	106.0(5)
C(11)-C(10)-C(9)	124.1(8)	C(7)-N(2)-C(20)	123.3(6)
C(10)-C(11)-C(12)	117.4(7)	C(14)-N(3)-C(15)	99.9(6)
C(13)-C(12)-C(11)	118.0(7)		

1

Cu(1)-N(1)	1.953(2)	Cu(1)-O(3)	1.8839(19)
Cu(1)-N(3)	1.9574(19)	Cu(1)-O(4)	1.9851(19)
O(3)-Cu(1)-N(1)	162.18(9)	C(7)-N(1)-Cu(1)	124.68(16)
O(3)-Cu(1)-N(3)	94.48(8)	C(6)-N(1)-Cu(1)	129.00(16)
N(1)-Cu(1)-N(3)	91.03(8)	C(14)-N(3)-Cu(1)	120.41(15)
O(3)-Cu(1)-O(4)	84.31(8)	C(13)-N(3)-Cu(1)	122.57(15)
N(1)-Cu(1)-O(4)	94.11(8)	C(20)-O(3)-Cu(1)	126.28(15)
N(3)-Cu(1)-O(4)	166.64(8)	C(2A)-O(4)-Cu(1)	114.97(15)