Supporting information

Photophysical properties of a D-π-A Schiff base and its applications in detection of metal ions

Yang Kang, Zhuang Liao, Min Wu, Sai Li, De-Cai Fang, Xiang-Jun Zheng* and Lin-Pei Jin

Table S1. Crystal Data and Structure Refinement Parameters of [CuL']·THF

	H_2L(New)	**[CuL']·THF**
Empirical formula	$C_{15}H_{17}N_5O$	$C_{30}H_{36}CuN_6O_3$
Formula weight	283.33	592.19
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n
Temperature (K)	100	100
a (Å)	9.3825(2)	14.3591(3)
b (Å)	7.1727(2)	8.3292(2)
c (Å)	21.5510(5)	23.2265(7)
α (°)	90	90
β (°)	90.853(2)	98.326(2)
γ (°)	90	90
V(Å^3)	1450.18(6)	2748.61(12)
Z	4	4
D_c (g cm^{-3})	1.298	1.431
μ (mm-1)	0.697	1.476
F(000)	600	1244
θ range(°)	4.10 to 73.30	3.41 to 73.49
R(int)	0.0196	0.0268
R_1, wR_2[I > 2(I)]	0.0415, 0.1151	0.0387, 0.0969
R_1, wR_2 (all data)	0.0450, 0.1189	0.0457, 0.1015

[a] $R_1 = \Sigma(|F_o| - |F_c|)/|Fo|$; $wR_2 = \{\Sigma[(w|F_o^2| - |F_c^2|)^2/Pw(F_o^2)^2]\}^{1/2}$

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

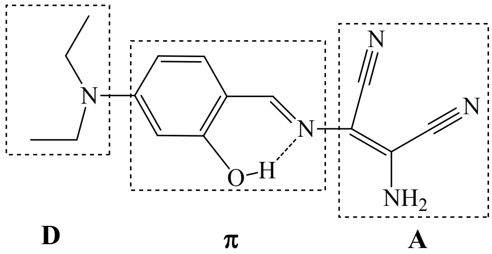
C1-C2	1.3704(17)	C7-C8	1.3829(17)
C1-C4	1.4425(17)	C7-O1	1.3544(15)
C1-N2	1.3548(17)	C8-C9	1.4111(17)
C2-C3	1.4397(18)	C9-C10	1.4242(19)
C2-N1	1.3901(15)	C9-N5	1.3679(16)
C3-N3	1.1471(18)	C10-C11	1.3632(18)
C4-N4	1.1431(17)	C12-C13	1.5235(19)
C5-C6	1.4249(17)	C12-N5	1.4642(16)
C5-N1	1.3052(16)	C14-C15	1.513(2)
C6-C7	1.4198(18)	C14-N5	1.4605(17)
C6-C11	1.4080(17)		
C2-C1-C4	119.34(11)	O1-C7-C8	117.63(11)
N2-C1-C2	124.47(11)	C7-C8-C9	121.06(12)
N2-C1-C4	116.14(11)	C8-C9-C10	117.34(11)
C1-C2-C3	119.47(11)	N5-C9-C8	122.29(12)
C1-C2-N1	119.63(11)	N5-C9-C10	120.35(11)
N1-C2-C3	120.87(11)	C11-C10-C9	120.85(12)
N3-C3-C2	175.28(14)	C10-C11-C6	122.52(12)
N4-C4-C1	177.36(14)	N5-C12-C13	114.93(11)
N1-C5-C6	123.25(12)	N5-C14-C15	113.36(11)
C7-C6-C5	123.69(11)	C5-N1-C2	119.78(11)
C11-C6-C5	119.59(12)	C9-N5-C12	121.05(11)
C11-C6-C7	116.70(11)	C9-N5-C14	122.28(11)
C8-C7-C6	121.39(11)	C14-N5-C12	116.60(10)
O1-C7-C6	120.98(11)		

Table S3. Selected Bond Distances (Å) and Angles (deg) for [Cu(L')(THF)]

Cu1-O1	1.9027(14)	C4-C5	1.354(3)
Cu1-O2	1.8913(14)	C5-C6	1.427(3)
Cu1-N1	1.9537(16)	C6-C7	1.396(3)
Cu1-N2	1.9475(16)	C8-C9	1.519(5)
O1-C1	1.306(2)	C8A-C9A	1.497(19)
O2-C14	1.306(2)	C10-C11	1.518(3)
N1-C20	1.323(3)	C12-C13	1.440(3)
N1-C25	1.389(2)	C12-C25	1.371(3)
N2-C7	1.322(3)	C14-C15	1.401(3)
N2-C12	1.381(3)	C14-C19	1.441(3)
N3-C26	1.146(3)	C15-C16	1.401(3)
N4-C13	1.147(3)	C16-C17	1.440(3)
N5-C16	1.359(3)	C17-C18	1.360(3)

N5-C21	1.467(3)	C18-C19	1.425(3)
N5-C23	1.489(3)	C19-C20	1.402(3)
N6-C3	1.363(3)	C21-C22	1.521(3)
N6-C8	1.485(4)	C23-C24	1.515(3)
N6-C8A	1.572(14)	C25-C26	1.432(3)
N6-C10	1.461(3)	O3-C27	1.411(4)
C1-C2	1.402(3)	O3-C30	1.424(5)
C1-C6	1.445(3)	C27-C28	1.525(4)
C2-C3	1.403(3)	C28-C29	1.495(4)
C3-C4	1.438(3)	C29-C30	1.437(5)
O1-Cu1-N1	176.70(6)	C7-C6-C5	117.79(18)
O1-Cu1-N2	93.74(6)	N2-C7-C6	124.60(18)
O2-Cu1-O1	89.40(6)	N6-C8-C9	111.9(3)
O2-Cu1-N1	93.03(7)	C9A-C8A-N6	100.6(11)
O2-Cu1-N2	176.72(7)	N6-C10-C11	114.1(2)
N2-Cu1-N1	83.80(7)	N2-C12-C13	122.15(18)
C1-O1-Cu1	127.52(12)	C25-C12-N2	116.66(17)
C14-O2-Cu1	128.42(13)	C25-C12-C13	121.17(18)
C20-N1-Cu1	126.32(14)	N4-C13-12	179.0(2)
C20-N1-C25	122.18(17)	O2-C14-C15	117.68(18)
C25-N1-Cu1	111.50(13)	O2-C14-C19	123.88(17)
C7-N2-Cu1	125.65(14)	C15-C14-C19	118.43(18)
C7-N2-C12	122.41(17)	C16-C15-C14	123.12(19)
C12-N2-Cu1	111.78(13)	N5-C16-C15	121.12(19)
C16-N5-C21	122.67(18)	N5-C16-C17	121.17(19)
C16-N5-C23	119.80(18)	C15-C16-C17	117.70(18)
C21-N5-C23	116.24(17)	C18-C17-C16	119.93(19)
C3-N6-C8	121.41(19)	C17-C18-C19	122.98(19)
C3-N6-C8A	115.6(4)	C18-C19-C14	117.69(18)
C3-N6-C10	121.74(19)	C20-C19-C14	124.01(18)
C10-N6-C8	116.81(19)	C20-C19-C18	118.28(18)
C10-N6-C8A	112.4(4)	N1-C20-C19	124.32(18)
O1-C1-C2	118.06(17)	N5-C21-C22	111.93(19)
O1-C1-C6	123.65(18)	N5-C23-C24	112.1(2)
C2-C1-C6	118.29(18)	N1-C25-C26	121.75(18)
C1-C2-C3	123.10(18)	C12-C25-N1	116.24(17)
N6-C3-C2	122.39(19)	C12-C25-C26	121.98(18)
N6-C3-C4	119.76(19)	N3-C26-C25	177.2(2)
C2-C3-C4	117.82(18)	C27-O3-C30	108.9(3)
C5-C4-C3	120.02(18)	O3-C27-C28	107.7(2)
C4-C5-C6	123.14(18)	C29-C28-C27	102.5(2)
C5-C6-C1	117.61(18)	C30-C29-C28	106.1(3)
C7-C6-C1	124.56(18)	O3-C30-C29	106.9(3)

Table S4. The calculated excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) and their oscillator strengths (f_{ex} and f_{em}) for studied species



	D-π-A	π-A	D-π-A-H_2O
LUMO-HOMO(eV)	3.04	3.44	3.06
λ_{ex}(nm)	429	390	428
f_{ex}	1.077	0.480	1.065
λ_{em} (nm)	497	460	496
f_{em}	1.005	0.512	1.162

Table S5. The optimized Cartesian Coordinates (in Å) of species studied.

Species	Cartesian coordinates	Species	Cartesian coordinates
D-π-A (ground state)	C -1.41523 -0.82974 -0.16485	**D-π-A** (excited state)	C 1.42329 0.97787 -0.17455
	H -1.70468 -1.86932 -0.35849		H 1.69798 2.02544 -0.32928
	N -2.33005 0.09267 0.00658		N 2.33196 0.04384 -0.05149
	C -0.01185 -0.56891 -0.11592		C 0.00134 0.66732 -0.12172
	C 0.91005 -1.61609 -0.35429		C -0.94666 1.67021 -0.40629
	C 0.53634 0.71704 0.17364		C -0.50194 -0.63010 0.22286
	C 2.27217 -1.42810 -0.32141		C -2.30875 1.43657 -0.36733
	C 1.91025 0.91905 0.20914		C -1.86788 -0.87768 0.26346
	C 2.81961 -0.13790 -0.03663		C -2.80855 0.13900 -0.02983
	H 0.51898 -2.60903 -0.56690		H -0.58942 2.66523 -0.66029
	H 2.92019 -2.27731 -0.49441		H -2.98377 2.25611 -0.57618
	H 2.24969 1.92615 0.41403		H -2.17366 -1.88552 0.51275
	O -0.26267 1.77677 0.41980		O 0.33248 -1.64515 0.51963
	H -1.19994 1.45977 0.35440		H 1.26059 -1.29891 0.42277
	N 4.17491 0.06469 0.00014		N -4.16017 -0.10489 0.01388
	C 4.75677 1.34933 0.39974		C -4.70247 -1.38889 0.46911
	H 4.15068 1.78668 1.19878		H -4.07911 -1.77452 1.27992
	H 5.73445 1.13654 0.84520		H -5.68673 -1.18459 0.90247
	C 4.92092 2.33840 -0.76027		C -4.83585 -2.42199 -0.65909
	H 3.95521 2.58446 -1.21298		H -3.86242 -2.65710 -1.09985
	H 5.56477 1.92094 -1.54235		H -5.49234 -2.05288 -1.45406
	H 5.37987 3.26724 -0.40284		H -5.26840 -3.34608 -0.26074
	C 5.13133 -0.98619 -0.36199		C -5.15365 0.89513 -0.39354
	H 4.72346 -1.57982 -1.18527		H -4.76039 1.47544 -1.23169

	H	6.02033	-0.48808	-0.76349		H	-6.01878	0.34529	-0.77795
	C	5.52951	-1.88754	0.81238		C	-5.59083	1.81488	0.75500
	H	4.66158	-2.41584	1.21979		H	-4.74637	2.39215	1.14401
	H	5.97852	-1.30100	1.62158		H	-6.01978	1.23735	1.58060
	H	6.26377	-2.63265	0.48549		H	-6.35330	2.51443	0.39579
	C	-3.68024	-0.23023	-0.00937		C	3.68711	0.29751	-0.06475
	C	-4.62806	0.77582	0.01762		C	4.59440	-0.80751	-0.07899
	C	-4.11471	-1.59353	-0.05672		C	4.17737	1.62482	-0.06408
	N	-4.39527	-2.72466	-0.09073		N	4.52368	2.74407	-0.05253
	C	-6.01987	0.43854	0.05270		C	5.96088	-0.62619	0.19866
	N	-7.15787	0.19797	0.09411		N	7.10355	-0.48880	0.44422
	N	-4.32926	2.11054	-0.05088		N	4.17412	-2.06865	-0.45673
	H	-3.35538	2.35998	0.08113		H	3.16887	-2.19315	-0.52021
	H	-4.99941	2.76896	0.33064		H	4.66845	-2.86219	-0.06014
π-A (ground state)	C	0.43634	0.75869	0.06463	**π-A** (excited state)	C	0.45165	0.89736	0.09160
	H	0.20144	1.82703	0.13586		H	0.23004	1.96378	0.16238
	N	-0.51361	-0.12897	0.00406		N	-0.51627	-0.00995	0.05065
	C	1.84086	0.42022	0.04277		C	1.84291	0.50127	0.05514
	C	2.79331	1.45621	0.16700		C	2.86524	1.43194	0.24010
	C	2.30503	-0.91626	-0.10716		C	2.24584	-0.87075	-0.18698
	C	4.15329	1.19139	0.15236		C	4.22026	1.05598	0.20527
	C	3.68132	-1.17736	-0.12438		C	3.60916	-1.24120	-0.21250
	C	4.59132	-0.13443	0.00632		C	4.59296	-0.28249	-0.01840
	H	2.43526	2.47758	0.27790		H	2.60346	2.47171	0.41856
	H	4.87146	1.99956	0.25179		H	4.98486	1.81255	0.35587
	H	4.01096	-2.20549	-0.24082		H	3.84898	-2.28398	-0.39742
	O	1.45783	-1.95612	-0.24229		O	1.33784	-1.81174	-0.41049
	H	0.53603	-1.59578	-0.21495		H	0.42581	-1.37408	-0.32030
	C	-1.85260	0.25245	-0.00936		C	-1.83812	0.30241	0.02552
	C	-2.83687	-0.71523	0.08585		C	-2.82195	-0.72509	0.15929
	C	-2.22806	1.62761	-0.11529		C	-2.26686	1.65396	-0.11219
	N	-2.45929	2.76656	-0.20834		N	-2.55863	2.77779	-0.23878
	C	-4.21668	-0.32319	0.01963		C	-4.18661	-0.44805	-0.05082
	N	-5.34224	-0.03780	-0.04137		N	-5.32757	-0.23472	-0.22915
	N	-2.60026	-2.03720	0.29051		N	-2.47539	-1.99141	0.56381
	H	-1.64290	-2.36515	0.23888		H	-1.48717	-2.21799	0.58026
	H	-3.32671	-2.71380	0.08826		H	-3.09239	-2.76015	0.32308
	H	5.65601	-0.35367	-0.00678		H	5.64177	-0.56182	-0.04044

D-π-A-H_2O (ground state)	C	1.26636	1.15202	-0.02971	**D-π-A-H_2O** (excited state)	C	-1.27740	-1.25711	-0.04526
	H	1.53457	2.21194	0.05027		H	-1.54163	-2.31425	0.02926
	N	2.19065	0.22966	-0.10130		N	-2.20590	-0.31531	-0.10227
	C	-0.13199	0.84312	-0.04749		C	0.12275	-0.91028	-0.06347
	C	-1.09758	1.86652	0.08423		C	1.11476	-1.91021	0.06880
	C	-0.62415	-0.48540	-0.19660		C	0.58683	0.43909	-0.21346
	C	-2.45113	1.61208	0.08713		C	2.46463	-1.62218	0.06055
	C	-1.98385	-0.75771	-0.20032		C	1.93784	0.74216	-0.21987
	C	-2.94074	0.27742	-0.05331		C	2.91936	-0.27353	-0.08320
	H	-0.75233	2.89182	0.20055		H	0.79572	-2.94180	0.18983
	H	-3.13584	2.43995	0.21746		H	3.17050	-2.43227	0.18621
	H	-2.27870	-1.78905	-0.34522		H	2.20997	1.77975	-0.36145
	O	0.23824	-1.52401	-0.35818		O	-0.30069	1.45821	-0.36074
	H	1.15834	-1.13005	-0.39247		H	-1.21418	1.03395	-0.38395
	N	-4.28560	0.00830	-0.04801		N	4.25901	0.02494	-0.08699
	C	-4.80279	-1.36270	-0.07516		C	4.74762	1.40726	-0.10115
	H	-4.14460	-2.00810	0.51438		H	4.07501	2.03139	0.49237
	H	-5.76496	-1.35577	0.44821		H	5.71192	1.41020	0.41625
	C	-4.98788	-1.92380	-1.49007		C	4.91687	1.97677	-1.51687
	H	-4.03718	-1.96085	-2.03139		H	3.96313	2.00247	-2.05246
	H	-5.68229	-1.30455	-2.06866		H	5.62135	1.37433	-2.09981
	H	-5.39708	-2.93946	-1.44361		H	5.30854	2.99787	-1.45695
	C	-5.29333	1.07271	-0.01466		C	5.29378	-1.01513	-0.08309
	H	-4.94347	1.92206	-0.60874		H	4.95076	-1.86751	-0.67420
	H	-6.18134	0.69196	-0.53053		H	6.16005	-0.60302	-0.60963
	C	-5.67043	1.51974	1.40249		C	5.70606	-1.45573	1.32802
	H	-4.80441	1.92596	1.93483		H	4.86206	-1.89251	1.87057
	H	-6.06251	0.67977	1.98659		H	6.08477	-0.60836	1.90900
	H	-6.44395	2.29508	1.36159		H	6.50093	-2.20629	1.26085
	C	3.54217	0.54641	-0.12188		C	-3.54448	-0.55992	-0.09601
	C	4.48782	-0.45781	0.01490		C	-4.46631	0.53683	-0.05478
	C	3.97466	1.89850	-0.28552		C	-4.04567	-1.88984	-0.12196
	N	4.24829	3.02451	-0.42091		N	-4.39356	-3.00611	-0.14657
	C	5.87841	-0.10962	-0.07945		C	-5.83849	0.32065	-0.29010
	N	7.01410	0.13321	-0.15141		N	-6.98715	0.15849	-0.48512
	N	4.20941	-1.77452	0.20041		N	-4.03288	1.82033	0.16067
	H	3.29623	-2.08517	0.55698		H	-3.19314	1.99026	0.73062
	H	4.98480	-2.39354	0.40430		H	-4.75049	2.52733	0.26172
	O	1.89313	-3.09480	1.30619		O	-1.73015	2.74648	1.71407
	H	1.06541	-2.68175	0.99074		H	-0.98967	2.43515	1.15612
	H	1.90711	-3.95687	0.85146		H	-1.78438	3.69638	1.52225

Table S6. Reported LODs data for Cu^{2+} and Mn^{2+} ions

Targeted metal ion	LODs	References
Cu^{2+}	8.86×10^{-8} M	(1)
	3.7×10^{-7} M	(2)
	2.2×10^{-7} M	(3)
	7.29×10^{-7} M	
	1.69×10^{-6} M	(4)
	57.8×10^{-9} M	(5)
	1.35×10^{-7} M	(6)
	8.10×10^{-7} M	(7)
	2.84×10^{-6} M	(8)
	1.8×10^{-7} M	(9)
	9.72×10^{-7} M	(10)
Mn^{2+}	1.80×10^{-7} M	(11)
	2.65×10^{-7} M	
	2.13×10^{-7} M	
	6.03×10^{-6} M	(12)
	5×10^{-6} M	(13)
	4.6×10^{-5} M	(14)
	3.75×10^{-7} M	(15)
Cu^{2+}	1.55×10^{-7} M	This work
Mn^{2+}	2.58×10^{-7} M	This work

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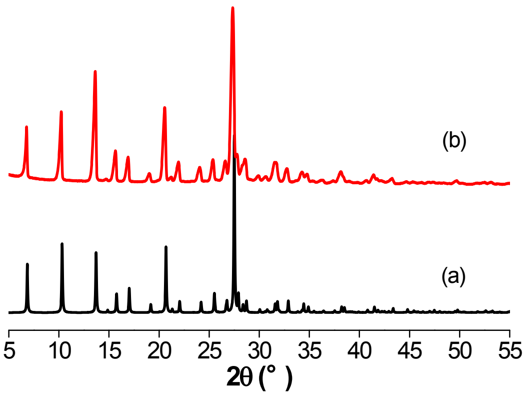


Fig. S1 PXRD patterns of (a) simulated H_2L^R based on the data from ref. 52 and (b) synthesized H_2L^R.

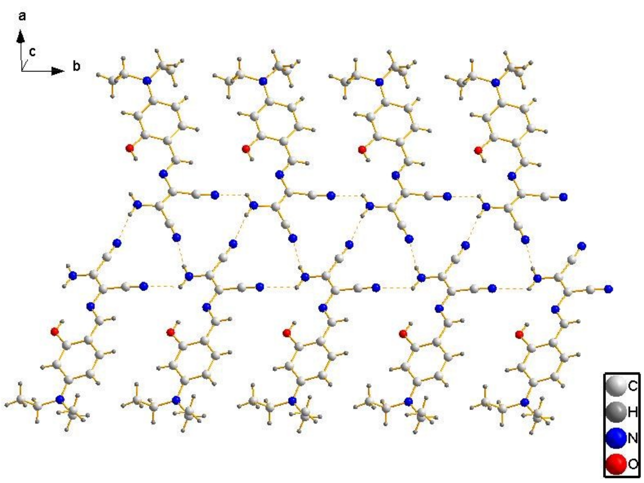


Fig. S2 2D hydrogen-bond network via intermolecular hydrogen bonds.

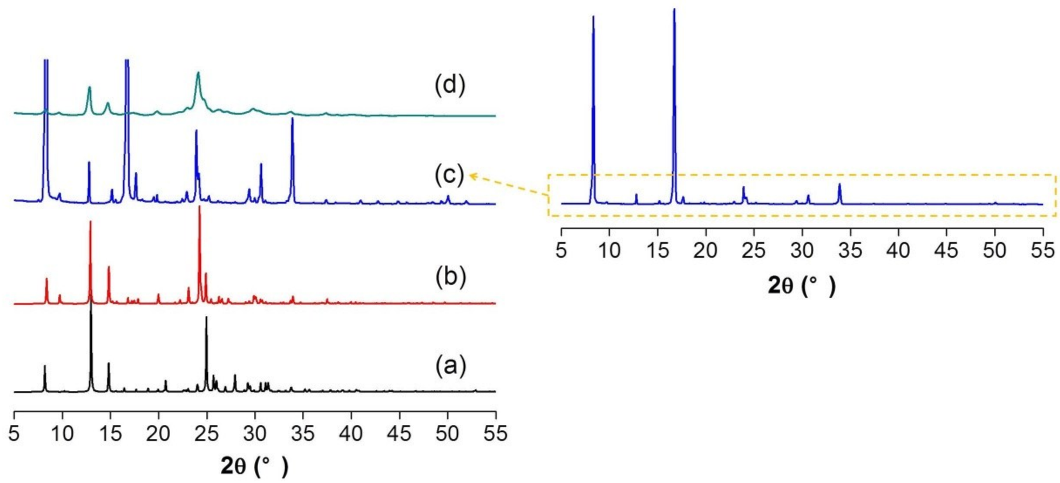


Fig. S3 PXRD patterns of (a) simulated H_2L based on the data in this paper, (b) simulated H_2L based on the data from ref. 53, (c) recrystallized H_2L before grinding and (d) recrystallized H_2L after grinding. Right insert: the whole pattern of (c).

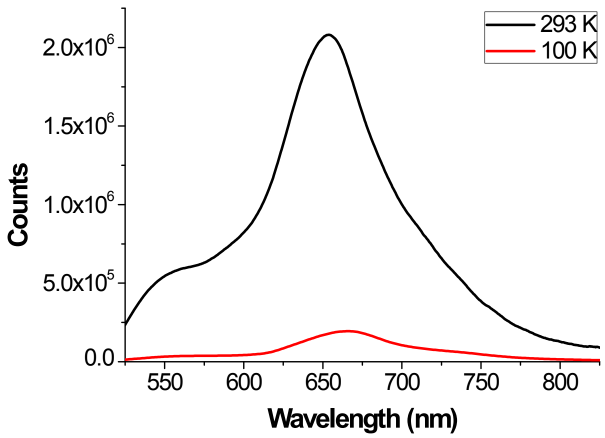


Fig. S4 Fluorescence emission spectra of H_2L solid under 293 K (black) and 100 K(red), excited by 514 nm.

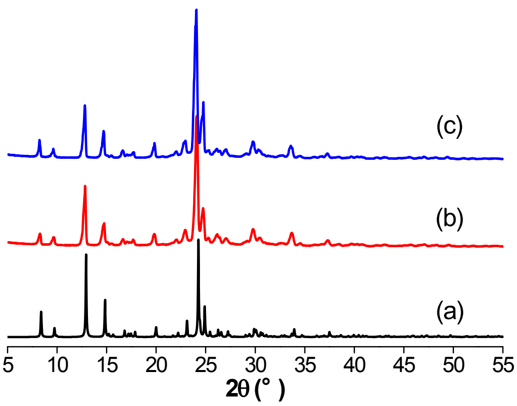


Fig. S5 PXRD patterns of (a) simulated H_2L based on the data from ref. 53, (b) aggregates separated from THF/H_2O (v/v: 2:8) and (c) aggregates separated from THF/H_2O (v/v: 1:9).

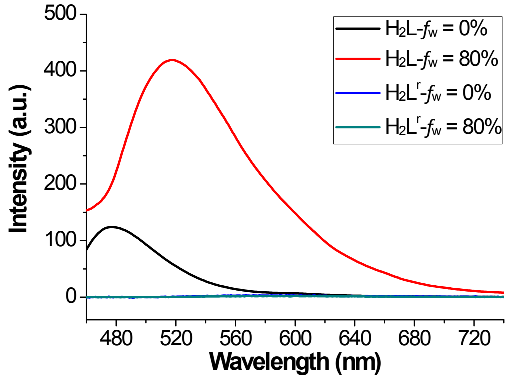


Fig. S6 Fluorescence emission spectra of H_2L (λ_{ex} = 450 nm) and H_2L^R (λ_{ex} = 415 nm) in THF and THF/H_2O. Concentration: 1x10^{-5} M. f_w: the volumetric fraction of water.

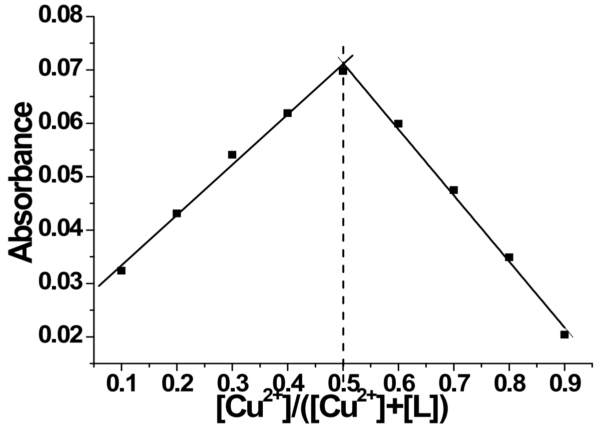


Fig. S7 Job-plot for determination of stoichiometry between H_2L and Cu^{2+} in THF/H_2O (v/v: 2/8).

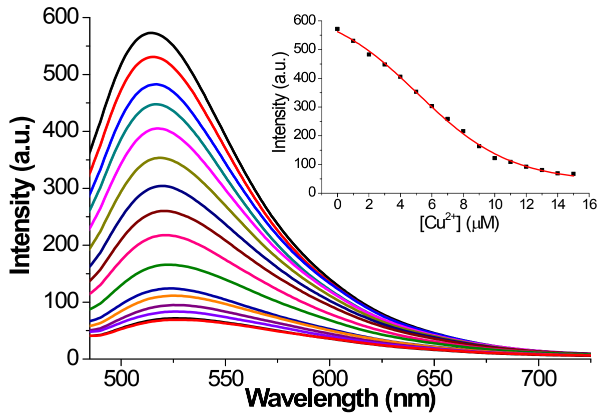


Fig. S8 Fluorescence titration of H_2L (1×10^{-5} M) with different concentration of Cu^{2+} in THF/H_2O (v/v: 2/8). Insert: fluorescent emission intensity at 517 nm with Cu^{2+} increasing.

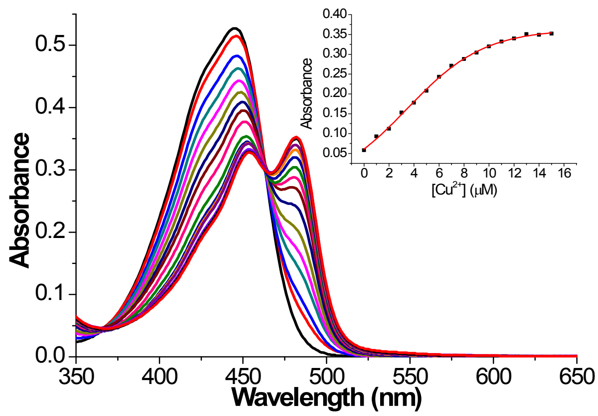


Fig. S9 UV-Vis absorption titration of H_2L (1×10^{-5} M) with different concentration of Cu^{2+} in THF/H_2O (v/v: 2/8). Insert: absorption value at 482 nm with Cu^{2+} increasing.

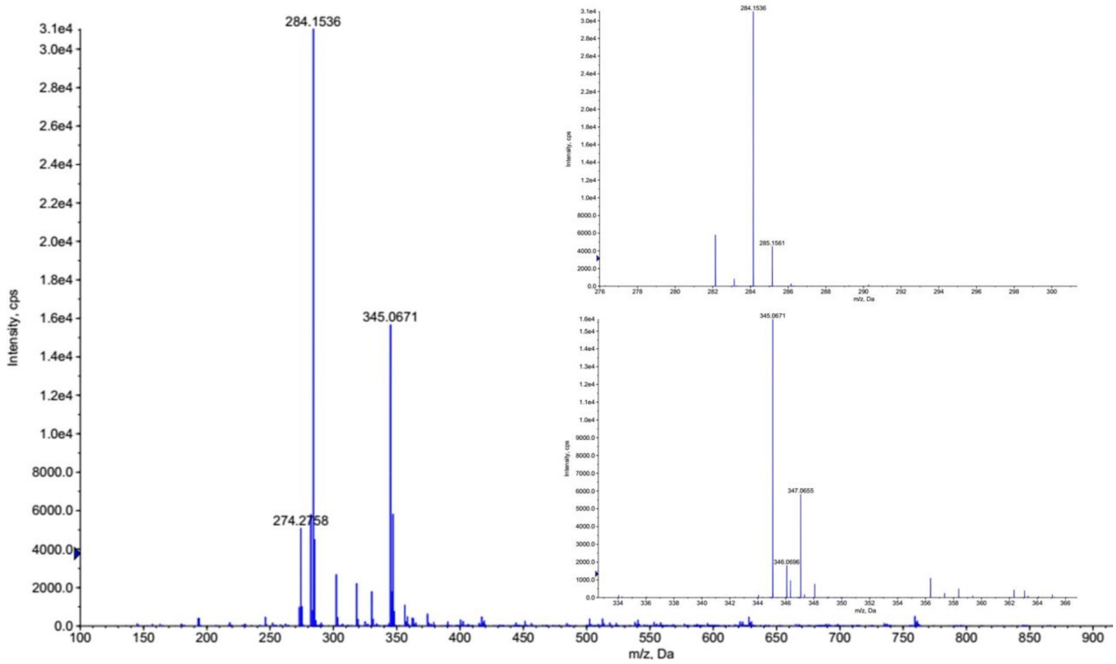


Fig. S10 High resolution ESI-MS spectrum of H_2L with 1.0 equiv. Cu^{2+} ion in THF/H_2O (v/v: 2/8) diluted with MeOH. Insert: the isotopic peak distribution of $[H_2L]H^+$ (up) and $[CuL]H^+$ (down).

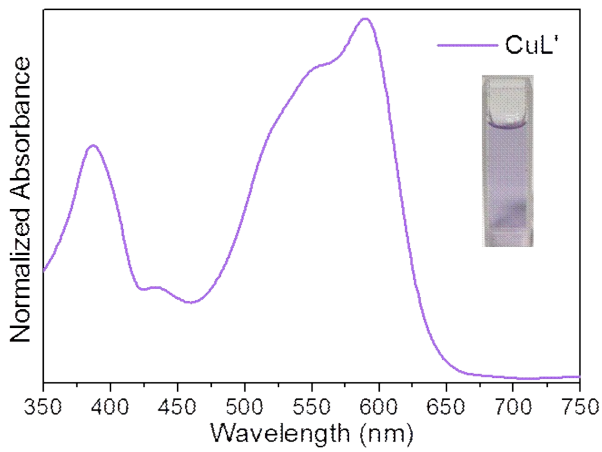


Fig. S11 Normalized UV-Vis absorption spectrum of [CuL’]·THF in THF/H_2O (v/v: 2/8) (insert: the image of measured sample).

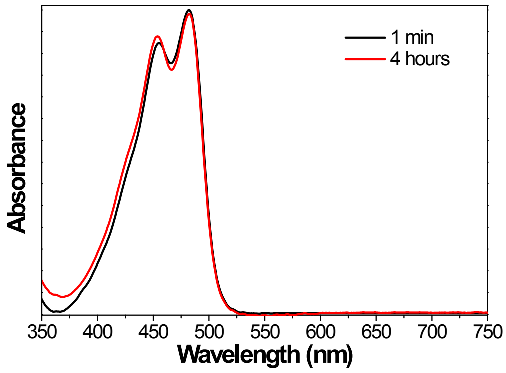


Fig. S12 The UV-VIS absorption spectra of H_2L with equal Cu^{2+} in THF/HEPES buffer (*p*H 8.00) (v/v: 2/8) kept for 1 min. and 4 hs, respectively.

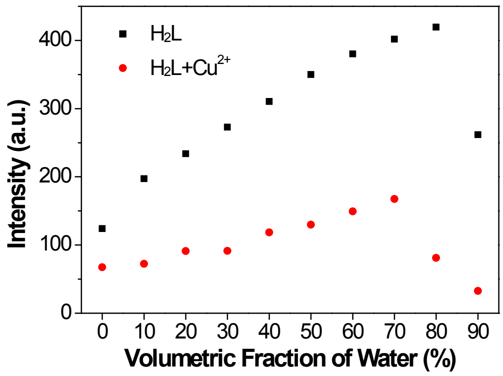
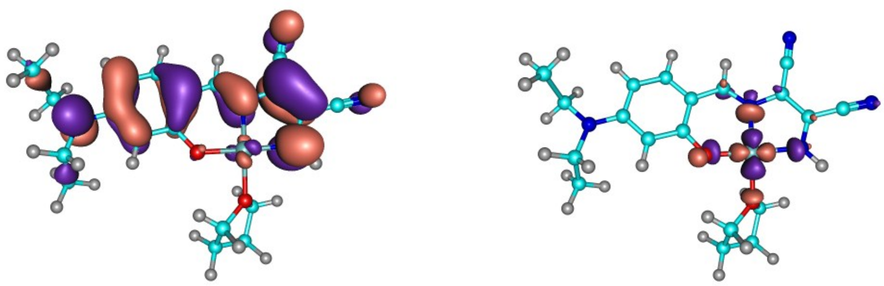


Fig. S13 Fluorescence intensity of H_2L and H_2L with 1.0 equiv. Cu^{2+} in THF/HEPES buffer (*p*H: 8.00) with different ratio.



(a) HOMO(e=-4.899eV) (b) LUMO(e=-2.138eV)

Fig. S14 HOMO and LUMO orbitals for [CuL(THF)].

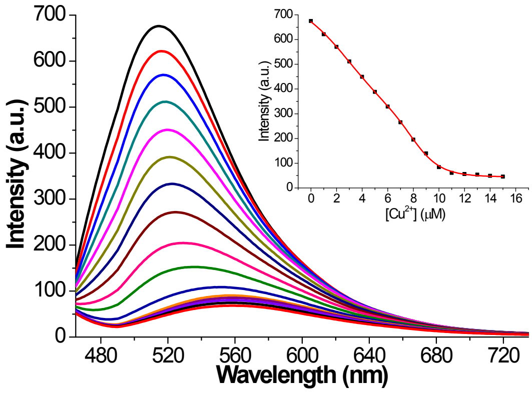


Fig. S15 Fluorescence titration of H_2L (1×10^{-5} M) with different concentration of Cu^{2+} in THF/HEPES buffer (*p*H 8.00) (v/v: 2:8). Inset: intensity of fluorescent emission at 515 nm with Cu^{2+} ions increasing.

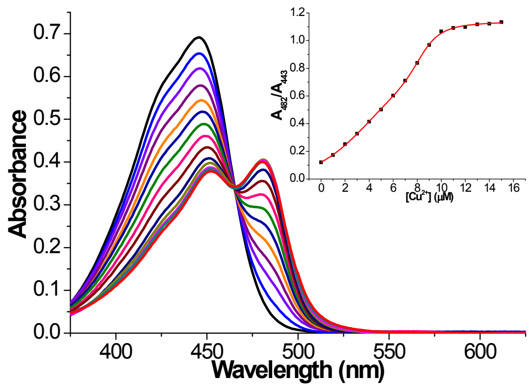


Fig. S16 UV-Vis absorption titration of H_2L (1×10^{-5} M) with different concentration of Cu^{2+} in THF/HEPES buffer (*p*H 8.00) (v/v: 2:8). Inset: value of A_{482}/A_{443} with Cu^{2+} ions increasing.

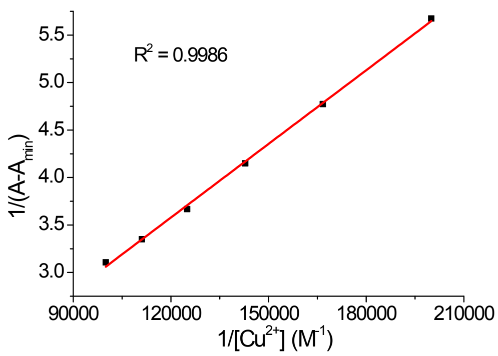


Fig. S17 Benesi-Hildebrand plots of H_2L with Cu^{2+} in THF/HEPES buffer (*p*H 8.00) (v/v: 2:8) based on data from UV-Vis absorption spectra.

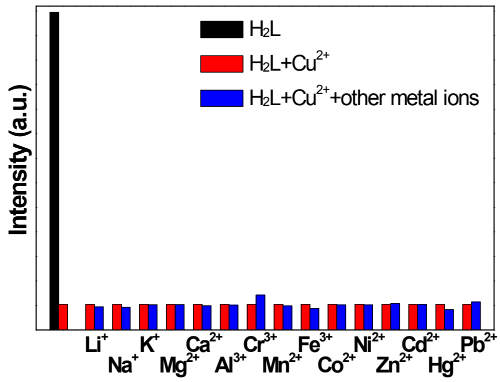


Fig. S18 Fluorescence emission intensity at 515 nm of H_2L (black), H_2L with 2.0 equiv. Cu^{2+} ion (red) and H_2L with 2.0 equiv. Cu^{2+} in the presence of equal other metal ions (blue) in THF/HEPES buffer (*p*H 8.00) (v/v: 2:8), excited by 450 nm.

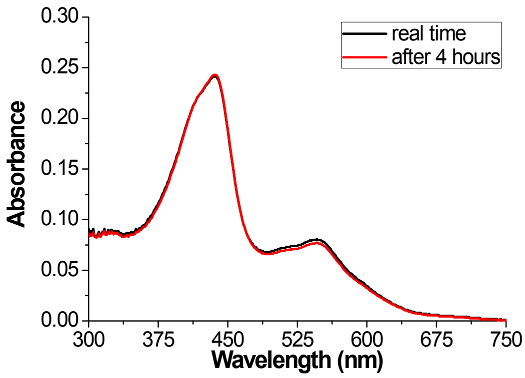


Fig. S19 UV-Vis absorption spectra of H_2L (1×10^{-5} M) with equal Mn^{2+} ions in ACN measured real time and after 4 hours.

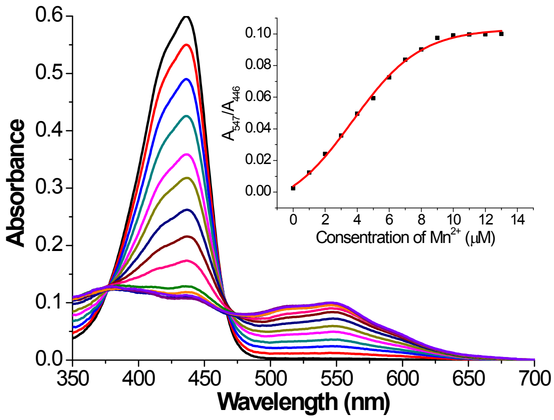


Fig. S20 UV-Vis absorption titration of H_2L (1×10^{-5} M) with different concentration of Mn^{2+} in ACN. Inset: value of A_{547}/A_{443} with Mn^{2+} increasing.

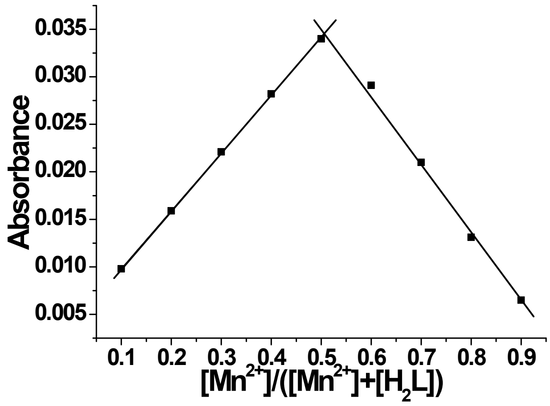


Fig. S21 Job-plot for determination of stoichiometry between H_2L and Mn^{2+} in ACN based on data from UV-Vis absorption spectra.

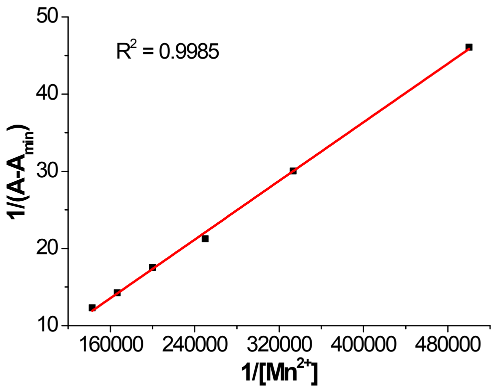
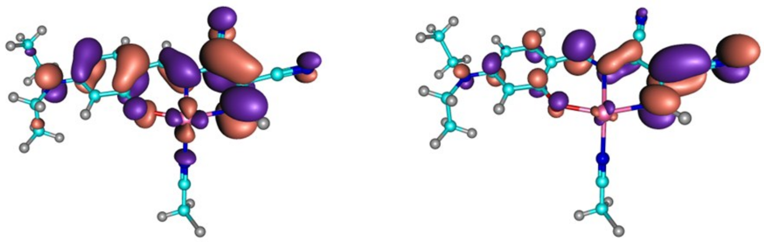


Fig. S22 Benesi-Hildebrand plot of H_2L with Mn^{2+} in ACN based on data from UV-Vis absorption spectra.



(a) HOMO(e=-4.572eV) (b) LUMO(e=-1.787eV)

Fig. S23 HOMO and LUMO orbitals for $[MnL(CH_3CN)]$.