Supplementary Material (ESI) for Dalton Transactions

Supporting information for

Novel Neutral Octanuclear Copper(I) Complexes Stablized by Pyridine Linked Bispyrazolate Ligands

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Experimental details

All chemicals were of reagent grade quality obtained from commercial sources and used as received, unless stated otherwise. 1,1'-(2,6-pyridyl)bis-1,3-butanedione[1a] and ligand 2,6-bis(5-methyl-1H-pyrazol-3-yl)pyridine[1b,c] (H_2L^1) were prepared according to the reported procedures. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance (400 MHz) spectrometer. Elemental analysis was determined with a Perkin- Elmer 2400C instrument. IR spectra were measured as KBr pellets using a Nicolet 5DX FX-IR spectrophotometer. The photoluminescence study was carried out on powdered samples in the solid state at room temperature using a SHIMADZU RF-540 spectrometer.

1 (*a*) D. E. Fenton, J. R. Tate, U. Casellato, S. Tamburini, P. A. Vigato and M. Vidali, *Inorg. Chim. Acta*, 1984, **83**, 23; (*b*) M. Gal, G. Tarrago, P. J. Steel and C. Marzin, *New J. Chem.*, 1985, **9**, 617; (*c*) Y. Lin and S. A. Lang, *J. Heterocycl. Chem.*, 1977, **14**, 345.

2,6-bis(5-methyl-1H-pyrazol-3-yl)pyridine hemihydrate ($H_2L^1 \cdot 0.5H_2O$).

2,6-bis(5-methyl-1H-pyrazol-3-yl)pyridine was prepared from 2,6-bis(1,3-dioxobutyl)pyridine and hydrazine hydrate. IR data (KBr pellet, cm^{-1}): 3185s, 3127s, 2976s, 2927s, 1574s, 1475s, 1302s, 1160s, 1007s, 804s, 691w. ^{1}HNMR ($CDCl_3$): 12.57 (br., 2H), 7.54 (t, J = 7.6, 1H), 7.25 (d, J = 7.6, 2H), 6.27 (s, 2H), 2.18 (s, 6H). Anal. Calcd for $C_{13}H_{14}N_5O_{0.5}$: C, 62.89; H, 5.68; N, 28.21. Found: C, 73.07; H, 5.81; N, 28.37.

2,6-bis(1'-phenyl-1',3'-dioxopropyl)pyridine.

Under a dinitrogen atmosphere, a 100 cm^3 Schlenk flask was charged with sodium (0.77 g, 33.4 mmol), dry ethanol (15 mL) was added and the mixture was stirred until all sodium was consumed. The ethanol was eliminated in vacuo. To the freshly prepared sodium ethoxide, acetophenone (4.5 mL) in dry toluene (30 mL) was added, followed quickly by dimethyl pyridine-2,6-dicarboxylate (2.50 g, 12.8 mmol). The mixture was stirred for 8 h and a yellowish sodium salt precipitated out of the solution. After stirring at 60 ºC for 4 h, the mixture was filtered and washed with diethyl ether before drying. The dry solid was slowly added to a vigorously stirred solution of acetic acid (15 mL), water (25 mL), and ice (50 g), and the resulting solid collected by filtration. The yellow solid was dissolved in CH_2Cl_2 (150 mL) and filtered. The resulting solution was washed with aqueous sodium bicarbonate solution (6%, 2 × 30 mL) and distilled water (30 mL), then dried over anhydrous magnesium sulphate. A yellow solid was obtained after removal of CH_2Cl_2. Yield: 3.3 g, 69.9%.

Anal. Calcd for $C_{23}H_{17}NO_4$: C, 74.38; H, 4.61; N, 3.77. Found: C, 74.42; H, 4.68; N, 3.75. IR data (KBr pellet, cm^{-1}): 3743w, 3085w, 1610s, 1565s, 1550s, 1485s, 1304m, 1262m, 1230s, 1070s, 837w, 805m, 774s, 685m, 618m. ^{1}H NMR (DMSO-d_6): 16.54 (br.), 16.50 (br.) 8.29-8.21 (m), 8.10-8.07 (m), 7.72 (s), 7.69 (t), 7.61-7.53 (m), 7.19 (s), 4.97 (s), 4.50(s). ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.4, 195.8, 185.5, 183.0, 182.9, 151.5, 151.4, 139.8, 136.2, 134.4, 133.9, 133.4, 129.1, 129.0, 128.4, 127.5, 127.0, 125.6, 124.9, 124.4, 93.9, 92.9, 49.4, 41.2.

2,6-bis(5-phenyl-1H-pyrazol-3-yl)pyridine (H_2L^2).

A mixture of 2,6-bis(1'-phenyl-1',3'-dioxopropyl)pyridine (3.71 g, 10 mmol), hydrazine hydrate (85%, 10 mL), and a few drops of concentrated HCl in methanol (200 mL) was refluxed for 36 h. The resulting solution was concentrated to ca. 20 mL. Addition of H_2O (50 mL) to the above solution resulted in a pale yellow precipitation. The product was purified by recrystallization from CH_3CH_2OH and CH_2Cl_2 (1:1). Yield: 2.1 g, 57.2%. Anal. Calcd for $C_{23}H_{17}N_5$: C, 76.01; H, 4.71; N, 19.27. Found: C, 75.87; H, 4.82; N, 19.32. IR data (KBr pellet, cm^{-1}): 3200s, 3030m, 1602m, 1566s, 1453s, 1313m, 1219m, 1186m, 1156m, 1074m, 810m, 765s, 691s. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.61 (br., 2H), 8.04 (t, J = 7.6, 1H), 7.92 (d, J = 8.0, 4H), 7.82 (d, J = 7.6, 2H), 7.52 (s, 2H), 7.46 (t, J = 7.6, 4H), 7.34 (t, J = 7.6, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.1, 147.5, 143.7, 143.1, 139.4, 133.9, 129.5, 129.2, 128.7, 128.1, 125.6, 118.9, 101.2.

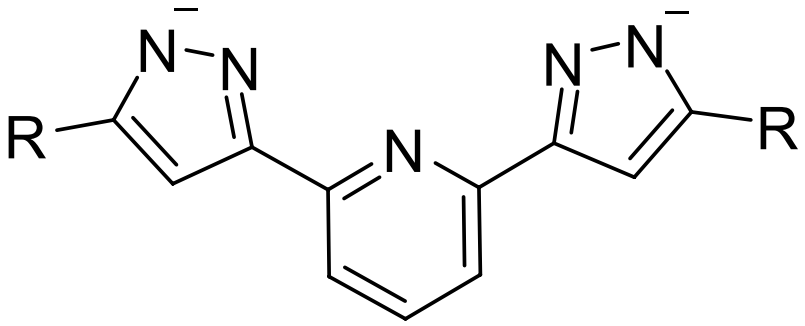
$[Cu_8(L^1)_4]\cdot(CH_3)_2CO$ 1.

A slurry of Cu_2O (71 mg, 0.5 mmol) and 2,6-bis(5-methyl-1H-pyrazol-3-yl)pyridine, H_2L^1 (49 mg, 0.2 mmol) in water (10 mL) and acetone (0.5 mL) was heated at 220 ºC in a sealed tube for 48 hours. The mixture was slowly cooled down to room temperature at a rate of 2 ºC /h. Yellow crystals were isolated. Yield: 35.6%. Anal. Calcd for $C_{55}H_{50}Cu_8N_{20}O$: C, 43.59; H, 3.33; N, 18.48. Found: C, 43.37; H, 3.42; N, 18.57. IR (KBr pellet, cm^{-1}): 3030, 2921, 2852, 1707, 1595, 1568, 1473, 1381, 1343,

1260, 1154, 1077, 1027, 805, 765, 697, 642, 547. ^{1}H NMR (dmso-d_6): 7.42 (t, J = 7.6 Hz, 1H, p-C_5H_3N), 7.15 (d, J = 6.0 Hz, 1H, m-C_5H_3N), 6.77 (d, J = 5.4 Hz, m-C_5H_3N), 6.30 (s, 1H, C_3N_2H), 5.92 (s, 1H, C_3N_2H), 2.34 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.03 (s, 1.5H, CH_3COCH_3). The compound was very slightly soluble in CHCN, DMSO, insoluble in CH_3COCH_3 and ^{13}C NMR spectra could not be recorded.

Synthesis of [$Cu_8(L^2)_4$] 2.

A slurry of Cu_2O (0.40 g, 28 mmol) and 2,6-bis(5-phenyl-1H-pyrazol-3-yl)pyridine, H_2L^2 (0.30 g, 8.3 mmol) in water (20 mL) was heated at 220 ºC in a sealed vessel for 48 hours. After cooled down to room temperature, the precipitate was collected by filtration and washed with acetonitrile. Then the yellow solid was dissolved in 20 mL of DMF and filtered through a short plug of Celite. Slow diffusion of diethyl ether to the DMF solution afforded yellow crystals after a few days. Yield: 76.2%. Anal. Calcd for $C_{92}H_{60}Cu_8N_{20}$: C, 56.55; H, 3.10; N, 14.34. Found: C, 56.38; H, 3.20, N, 14.30. IR (KBr pellet, cm^{-1}): 3062, 2924, 1598, 1567, 1540, 1511, 1455, 1426, 1384, 1338, 1221, 1153, 1123, 1077, 1029, 908, 785, 757, 693, 469, 420. ^{1}H NMR (dmso-d_6): 7.95 (s, 1H, p-C_5H_3N), 7.75 (t, J = 7.6 Hz, 1H, m-C_6H_5), 7.65 (d, J = 6.4 Hz, o-C_6H_5), 7.59 (d, 1H, J = 8.0 Hz, m-C_5H_3N), 7.53 (d, J = 8.0 Hz, 2H, o-C_6H_5), 7.31 (m, 2H, m-C_6H_5), 7.21 (s, 1H, C_3N_2H), 7.17 (d, 1H, J = 7.6 Hz, m-C_5H_3N), 6.93 (t, J = 7.6 Hz, 1H, m-C_5H_3N), 6.79 (t, J = 7.6 Hz, 2H, p-C_6H_5), 6.65 (s, 1H, C_3N_2H). The compound was very slightly soluble in DMSO, and insoluble in CHCN and CH_3COCH_3 and ^{13}C NMR spectra could not be recorded.



$R = CH_3$, Ph

Scheme S1. The bispyrazolate ligands L^1(R = CH_3) and L^2 (R = Ph)

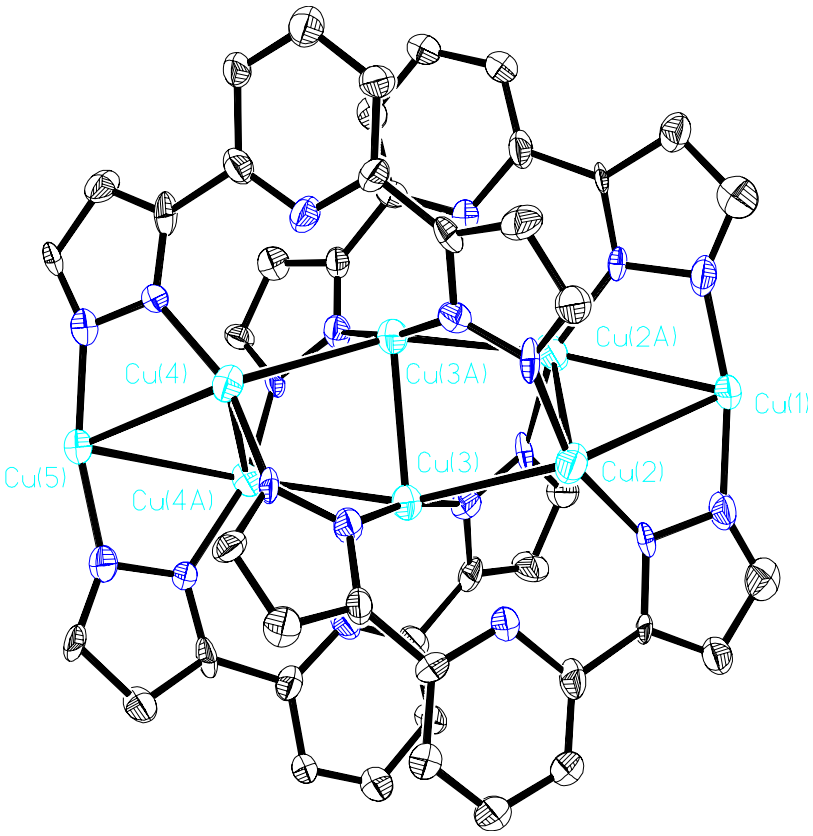


Fig. S1. Molecular structure of $Cu_8L_4^2$ (2) with phenyl rings and hydrogen atoms omitted for clarity.

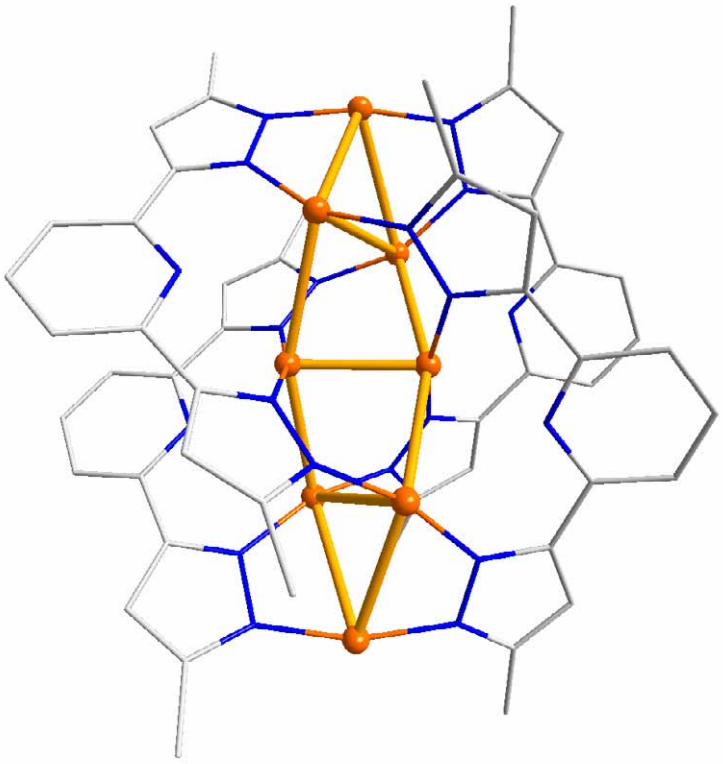


Fig. S2. An X-ray structural drawing of the $[Cu_8L^1_4]$ (1) showing the twisted-boat conformation of copper(I) atoms.

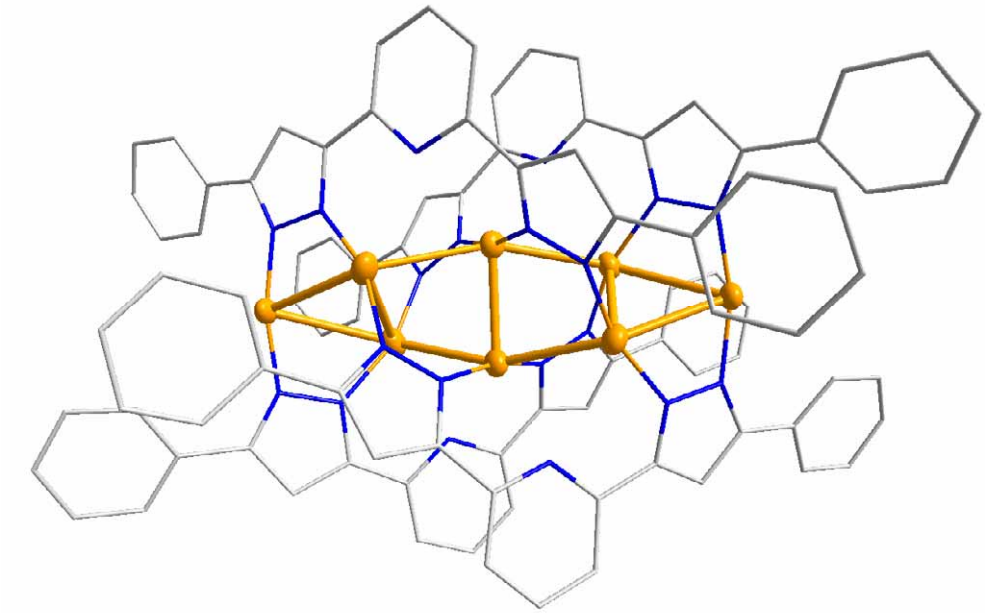


Fig. S3. An X-ray structural drawing of the $[Cu_8L^2_4]$ (2) showing the twisted-boat conformation of copper(I) atoms.

Table S1 Selected bond lengths (Å) and angles (°) of 1 and 2

1		**2**	
Cu(1)-Cu(3)	2.824(1)	Cu(1)-Cu(2)#1	2.996(4)
Cu(1)-Cu(6)	2.897(1)	Cu(1)-Cu(2)	2.996(4)
Cu(1)-Cu(2)	2.616(1)	Cu(2)-Cu(3)	2.854(4)
Cu(2)-Cu(7)	2.870(1)	Cu(2)-Cu(2)#1	3.019(4)
Cu(2)-Cu(4)	2.880(1)	Cu(3)-Cu(3)#1	2.588(4)
Cu(3)-Cu(5)	2.918(1)	Cu(3)-Cu(4)#1	2.848(3)
Cu(3)-Cu(4)	2.990(1)	Cu(4)-Cu(3)#1	2.848(3)
Cu(4)-Cu(5)	2.901(1)	Cu(4)-Cu(4)#1	2.930(4)
Cu(6)-Cu(7)	3.037(1)	Cu(4)-Cu(5)	2.884(4)
Cu(6)-Cu(8)	3.054(1)	Cu(5)-Cu(4)#1	2.884(4)
Cu(7)-Cu(8)	2.968(2)	Cu(1)-N(3)#1	1.845(15)
Cu(1)-N(2)	1.867(5)	Cu(1)-N(3)	1.845(15)
Cu(1)-N(7)	1.882(5)	Cu(2)-N(2)	1.860(13)
Cu(2)-N(17)	1.876(6)	Cu(2)-N(8)	1.883(12)
Cu(2)-N(12)	1.880(6)	Cu(3)-N(7)#1	1.825(13)
Cu(3)-N(18)	1.875(6)	Cu(3)-N(4)	1.881(12)
Cu(3)-N(4)	1.875(6)	Cu(4)-N(5)	1.839(12)
Cu(4)-N(8)	1.865(5)	Cu(4)-N(9)	1.910(13)
Cu(4)-N(14)	1.874(6)	Cu(5)-N(10)	1.859(14)
Cu(5)-N(5)	1.850(6)	Cu(5)-N(10)#1	1.859(14)
Cu(5)-N(15)	1.871(6)		
Cu(6)-N(13)	1.846(6)	N(3)#1-Cu(1)-N(3)	165.8(9)
Cu(6)-N(9)	1.874(6)	N(2)-Cu(2)-N(8)	160.4(5)
Cu(7)-N(3)	1.852(6)	N(7)#1-Cu(3)-N(4)	168.2(5)
Cu(7)-N(19)	1.883(6)	N(5)-Cu(4)-N(9)	163.2(6)
Cu(8)-N(20)	1.853(7)	N(10)-Cu(5)-N(10)#1	165.0(9)
Cu(8)-N(10)	1.854(6)	Cu(2)#1-Cu(1)-Cu(2)	60.49(10)
		Cu(3)-Cu(2)-Cu(2)#1	73.78(7)
N(2)-Cu(1)-N(7)	166.9(2)	Cu(1)-Cu(2)-Cu(2)#1	59.76(5)
N(17)-Cu(2)-N(12)	167.1(2)	Cu(3)-Cu(2)-Cu(3)#1	46.38(8)
N(18)-Cu(3)-N(4)	163.1(3)	Cu(1)-Cu(2)-Cu(3)#1	107.42(8)
N(8)-Cu(4)-N(14)	165.2(3)	Cu(2)#1-Cu(2)-Cu(3)#1	50.96(6)
N(5)-Cu(5)-N(15)	163.9(3)	Cu(3)#1-Cu(3)-Cu(4)#1	79.85(6)
N(13)-Cu(6)-N(9)	160.5(3)	Cu(3)#1-Cu(3)-Cu(2)	80.66(6)
N(3)-Cu(7)-N(19)	155.6(3)	Cu(4)#1-Cu(3)-Cu(2)	160.50(9)
N(20)-Cu(8)-N(10)	166.5(3)	Cu(3)#1-Cu(3)-Cu(4)	53.34(6)
Cu(7)-Cu(8)-Cu(6)	60.55(3)	Cu(2)-Cu(3)-Cu(4)	112.54(8)
Cu(2)-Cu(1)-Cu(6)	79.66(4)	Cu(3)#1-Cu(3)-Cu(2)#1	52.96(6)
Cu(3)-Cu(1)-Cu(6)	159.53(4)	Cu(4)#1-Cu(3)-Cu(2)#1	111.75(9)
Cu(1)-Cu(2)-Cu(7)	80.94(4)	Cu(2)-Cu(3)-Cu(2)#1	55.25(9)
Cu(1)-Cu(2)-Cu(4)	78.90(3)	Cu(4)-Cu(3)-Cu(2)#1	106.30(8)
Cu(7)-Cu(2)-Cu(4)	159.79(4)	Cu(3)#1-Cu(4)-Cu(5)	128.70(9)
Cu(1)-Cu(3)-Cu(5)	127.76(4)	Cu(3)#1-Cu(4)-Cu(4)#1	74.42(6)
Cu(1)-Cu(3)-Cu(4)	73.92(3)	Cu(5)-Cu(4)-Cu(4)#1	59.47(5)
Cu(5)-Cu(3)-Cu(4)	58.81(3)	Cu(3)#1-Cu(4)-Cu(3)	46.80(8)
Cu(2)-Cu(4)-Cu(5)	126.84(4)	Cu(5)-Cu(4)-Cu(3)	107.82(8)
Cu(5)-Cu(4)-Cu(3)	59.36(3)	Cu(4)#1-Cu(4)-Cu(3)	51.72(6)
Cu(4)-Cu(5)-Cu(3)	61.83(3)	Cu(4)#1-Cu(5)-Cu(4)	61.06(11)
Cu(1)-Cu(6)-Cu(7)	73.83(3)		
Cu(1)-Cu(6)-Cu(8)	126.38(4)	Symmetry codes:	
Cu(7)-Cu(6)-Cu(8)	58.33(3)	#1 -x, -y, z	
Cu(2)-Cu(7)-Cu(8)	130.10(4)		
Cu(2)-Cu(7)-Cu(6)	73.54(3)		
Cu(8)-Cu(7)-Cu(6)	61.12(3)		
Cu(2)-Cu(1)-Cu(3)	79.97(4)		

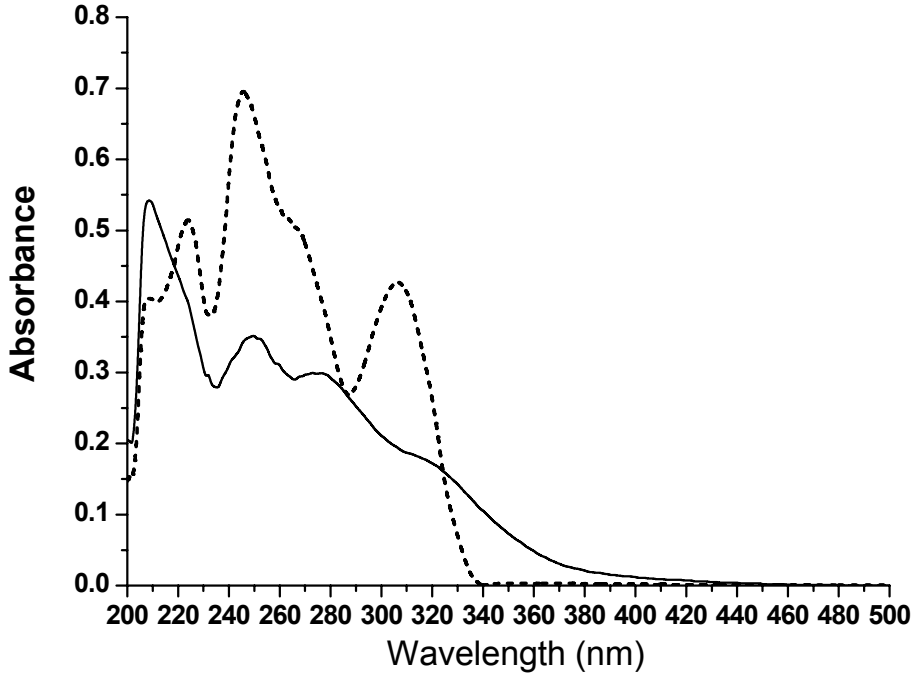


Fig. S4. The UV-vis spectra of H_2L^1 (3.3×10^{-5} M, solid line) and 1 (3.3×10^{-5} M, dashed line) in CH_3CN.

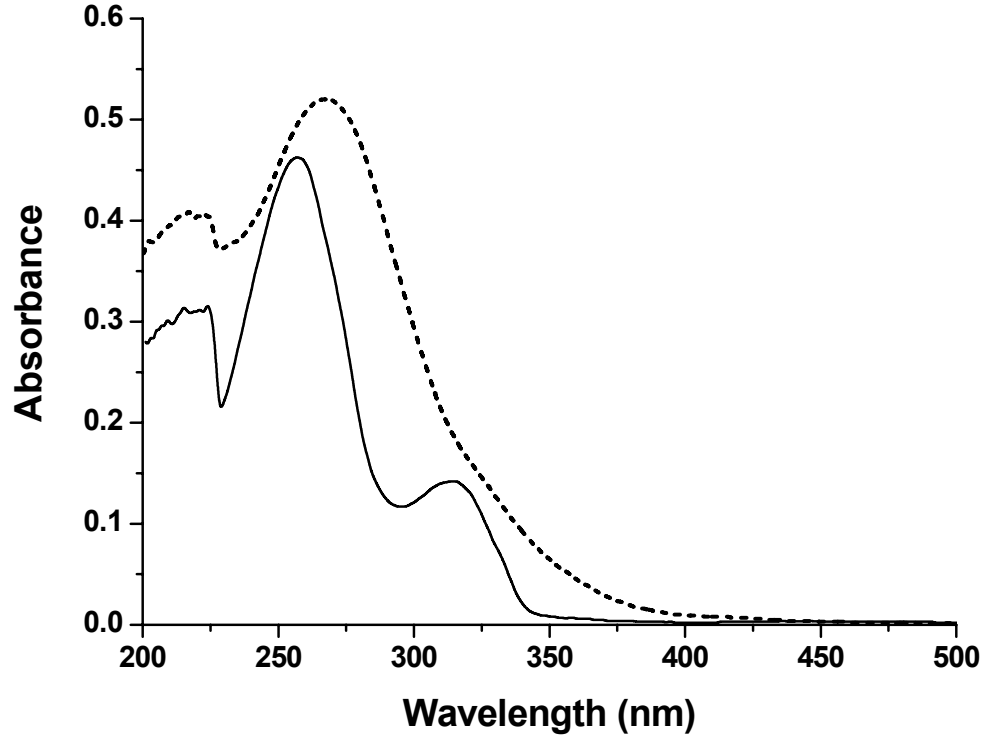


Fig. S5. The UV-vis spectra of H_2L^2 (3.3×10^{-5} M, solid line) and 2 (3.3×10^{-5} M, dashed line) in CH_2Cl_2.

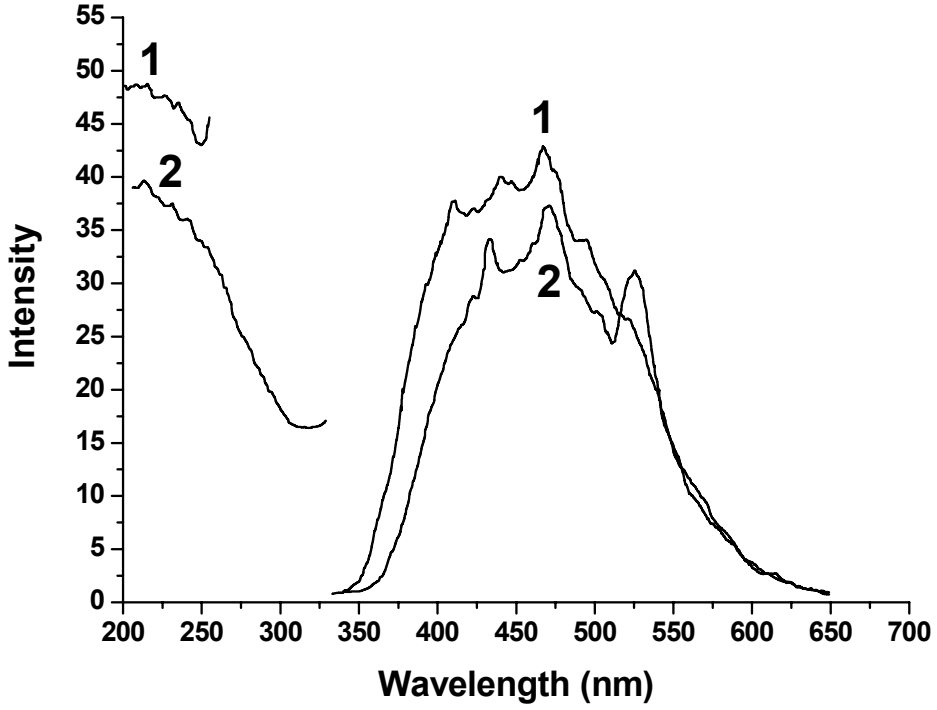


Fig. S6. The emission (right) and excitation (left) spectra of 1 (1.5×10^{-6} M, solid) and 2 (1.0×10^{-6} M, dashed) in CH_2Cl_2.

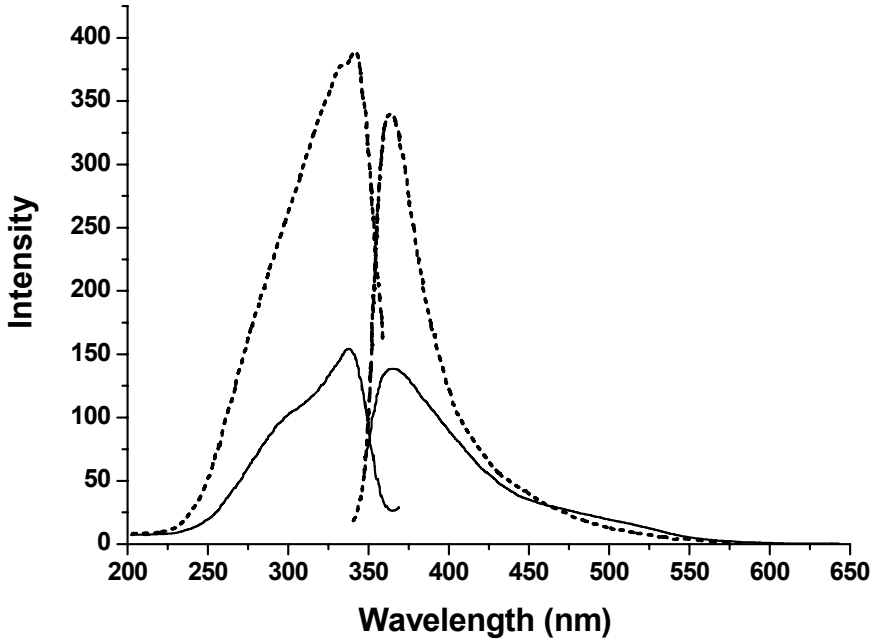


Fig. S7. The solid-state emission (right) and excitation (left) spectra of H_2L^1 (solid line) and H_2L^2 (dashed line).

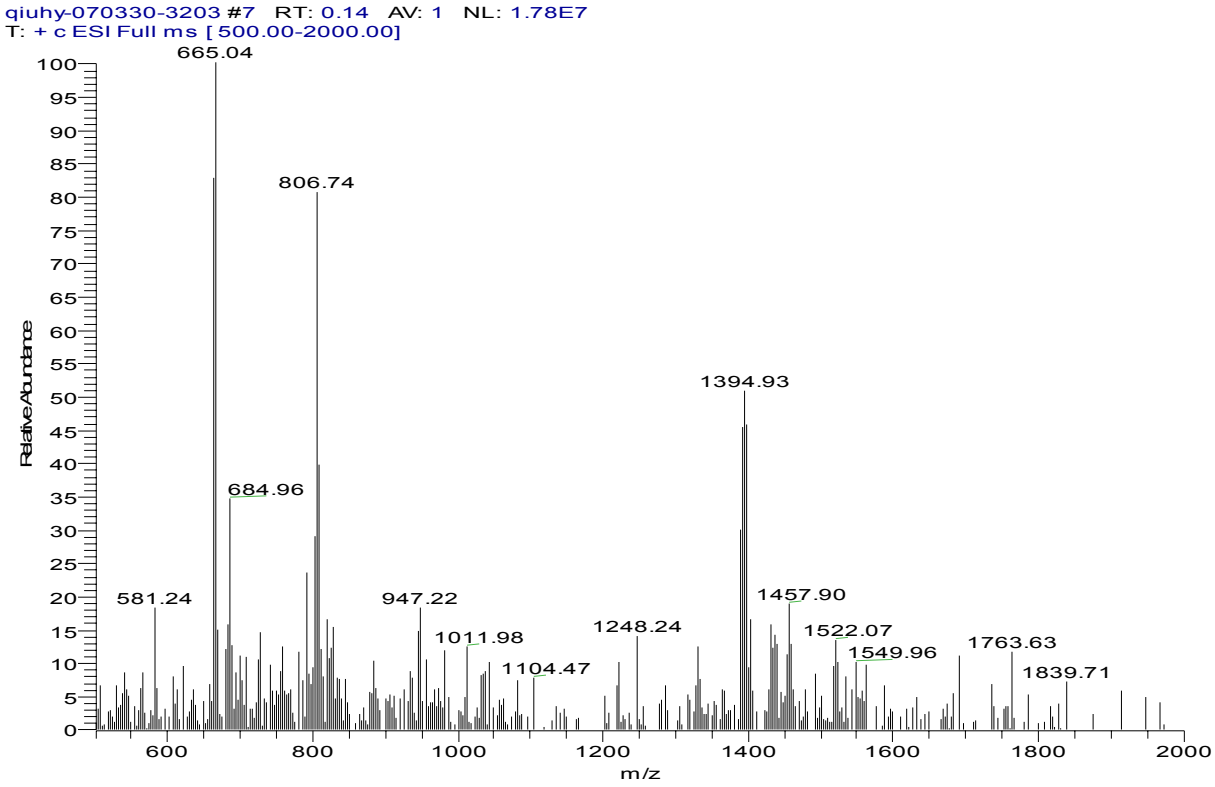


Fig. S8. The ESI-MS (positive ion) spectra of 1 in CH_3CN.

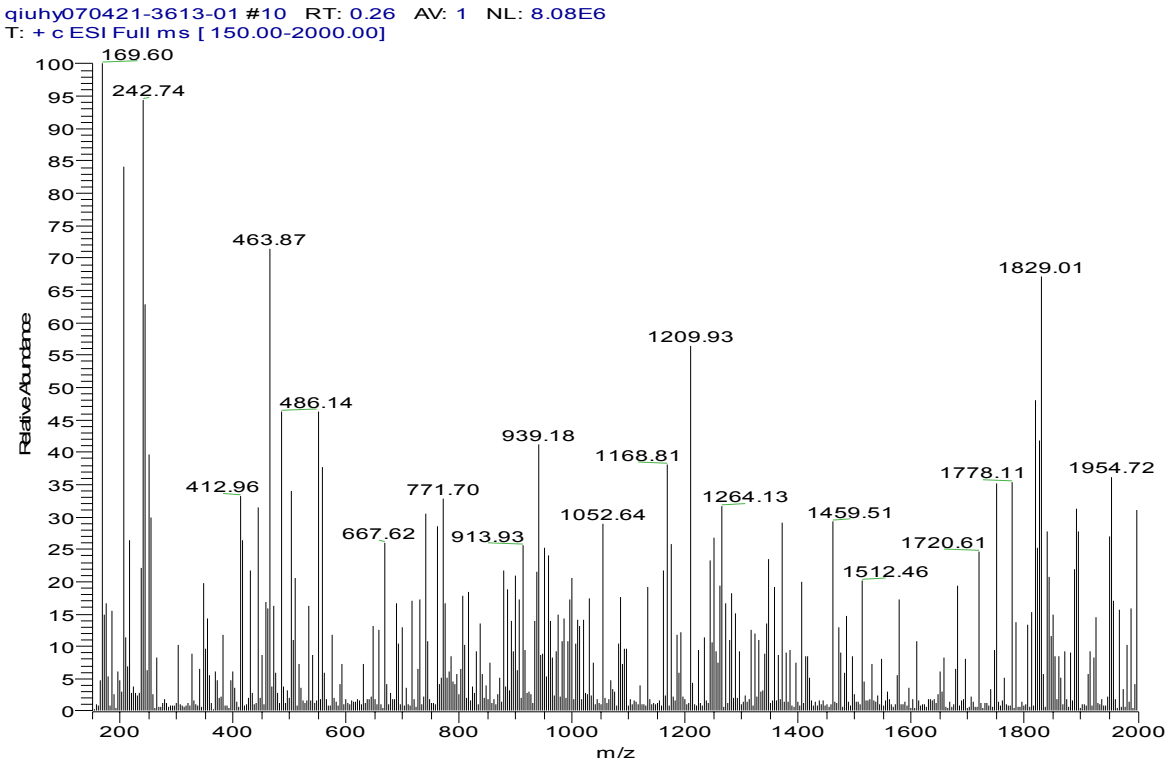


Fig. S9. The ESI-MS (positive ion) spectra of 2 in DMF.