Electronic Supporting Information for

Discrimination of *cis-trans* isomers by dinuclear metal cryptates at physiological pH: selectivity for fumarate *vs.* maleate

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Table S1 Selected bond distances (Å) and angles (°) for **3**·3CH_3CN·H_2O and **4**·3CH_3CN·0.5H_2O.

3·3CH_3CN·H_2O		**4**·3CH_3CN·0.5H_2O	
Cu(1) –Cu(2)	8.769(2)	Cu(1) –Cu(2)	8.773(1)
Cu(1) –O(1)	1.899(5)	Cu(1) –O(1)	1.874(4)
Cu(2) –O(3)	1.896(5)	Cu(2) –O(3)	1.913(4)
Cu(1) –N(1)	2.041(6)	Cu(1) –N(1)	2.034(5)
Cu(1) –N(2)	2.186(6)	Cu(1) –N(2)	2.200(5)
Cu(1) –N(3)	2.131(6)	Cu(1) –N(3)	2.142(5)
Cu(1) –N(4)	2.277(6)	Cu(1) –N(4)	2.264(5)
Cu(2) –N(5)	2.039(6)	Cu(2) –N(5)	2.033(5)
Cu(2) –N(6)	2.168(6)	Cu(2) –N(6)	2.162(4)
Cu(2) –N(7)	2.151(6)	Cu(2) –N(7)	2.163(4)
Cu(2) –N(8)	2.324(6)	Cu(2) –N(8)	2.315(5)
N(1) –Cu(1) –O(1)	178.2(2)	N(1) –Cu(1) –O(1)	178.8(2)
N(1) –Cu(1) –N(2)	83.6(2)	N(1) –Cu(1) –N(2)	83.8(2)

N(1) –Cu(1) –N(3)	84.6(3)	N(1) –Cu(1) –N(3)	84.9(2)
N(1) –Cu(1) –N(4)	82.6(2)	N(1) –Cu(1) –N(4)	83.2(2)
N(2) –Cu(1) –O(1)	97.7(2)	N(2) –Cu(1) –O(1)	97.3(2)
N(2) –Cu(1) –N(3)	125.0(3)	N(2) –Cu(1) –N(3)	125.4(2)
N(2) –Cu(1) –N(4)	114.5(2)	N(2) –Cu(1) –N(4)	113.5(2)
N(3) –Cu(1) –O(1)	95.5(2)	N(3) –Cu(1) –O(1)	95.0(2)
N(3) –Cu(1) –N(4)	116.9(2)	N(3) –Cu(1) –N(4)	117.8(2)
N(4) –Cu(1) –O(1)	95.8(2)	N(4) –Cu(1) –O(1)	95.8(2)
N(5) –Cu(2) –O(3)	176.6(2)	N(5) –Cu(2) –O(3)	175.4(2)
N(5) –Cu(2) –N(6)	84.2(2)	N(5) –Cu(2) –N(6)	84.3(2)
N(5) –Cu(2) –N(7)	83.4(2)	N(5) –Cu(2) –N(7)	82.9(2)
N(5) –Cu(2) –N(8)	81.4(2)	N(5) –Cu(2) –N(8)	81.8(2)
N(6) –Cu(2) –O(3)	94.2(2)	N(6) –Cu(2) –O(3)	95.0(2)
N(6) –Cu(2) –N(7)	138.4(2)	N(6) –Cu(2) –N(7)	139.7(2)
N(6) –Cu(2) –N(8)	107.6(2)	N(6) –Cu(2) –N(8)	106.7(2)
N(7) –Cu(2) –O(3)	95.9(2)	N(7) –Cu(2) –O(3)	94.8(2)
N(7) –Cu(2) –N(8)	109.4(2)	N(7) –Cu(2) –N(8)	109.1(2)
N(8) –Cu(2) –O(3)	101.9(2)	N(8) –Cu(2) –O(3)	102.8(2)
C(50) –C(51)	1.290(10)	C(50) –C(51)	1.505(8)

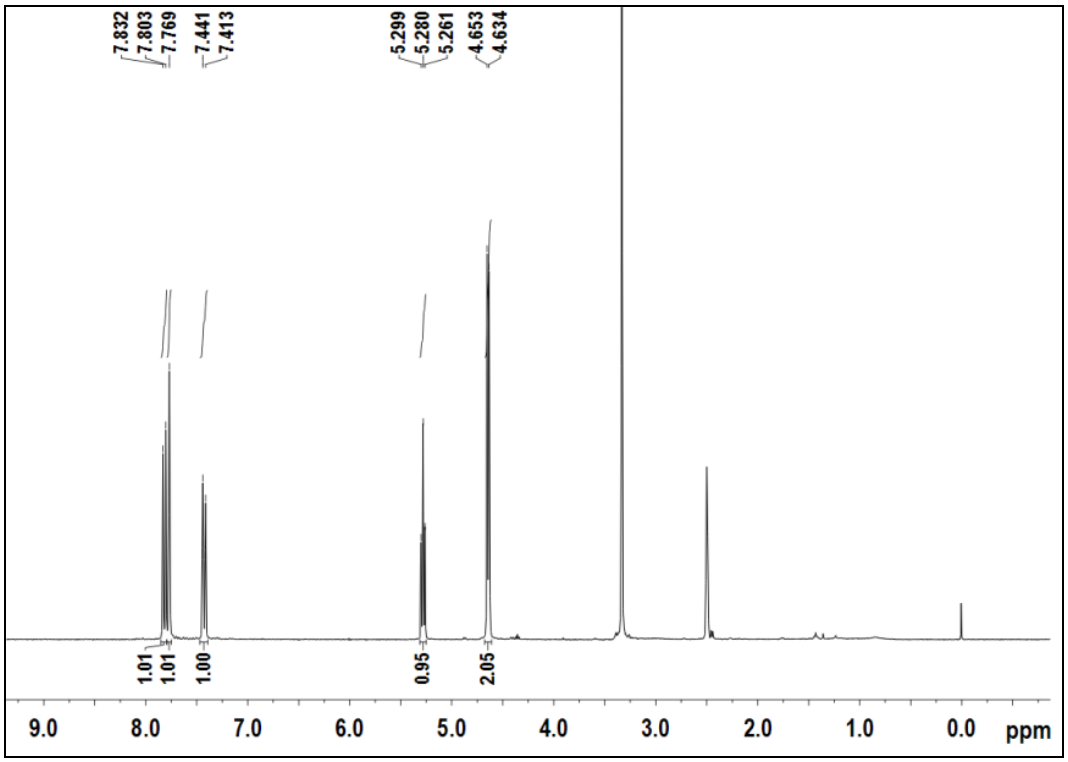

Fig. S1 ^{1}H NMR spectrum of 2,6-bis-hydroxymethyl naphthalene (300 MHz, DMSO-d_6) .

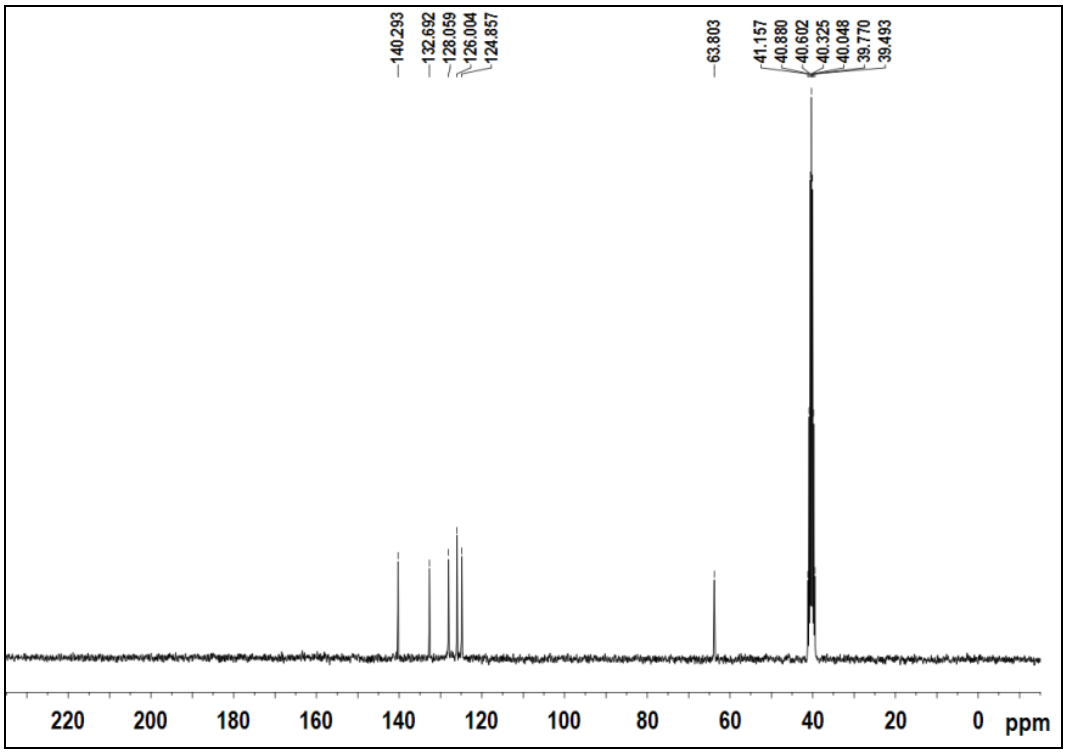

Fig. S2 ^{13}C NMR spectrum of 2,6-bis-hydroxymethyl naphthalene (75 MHz, DMSO-d_6).

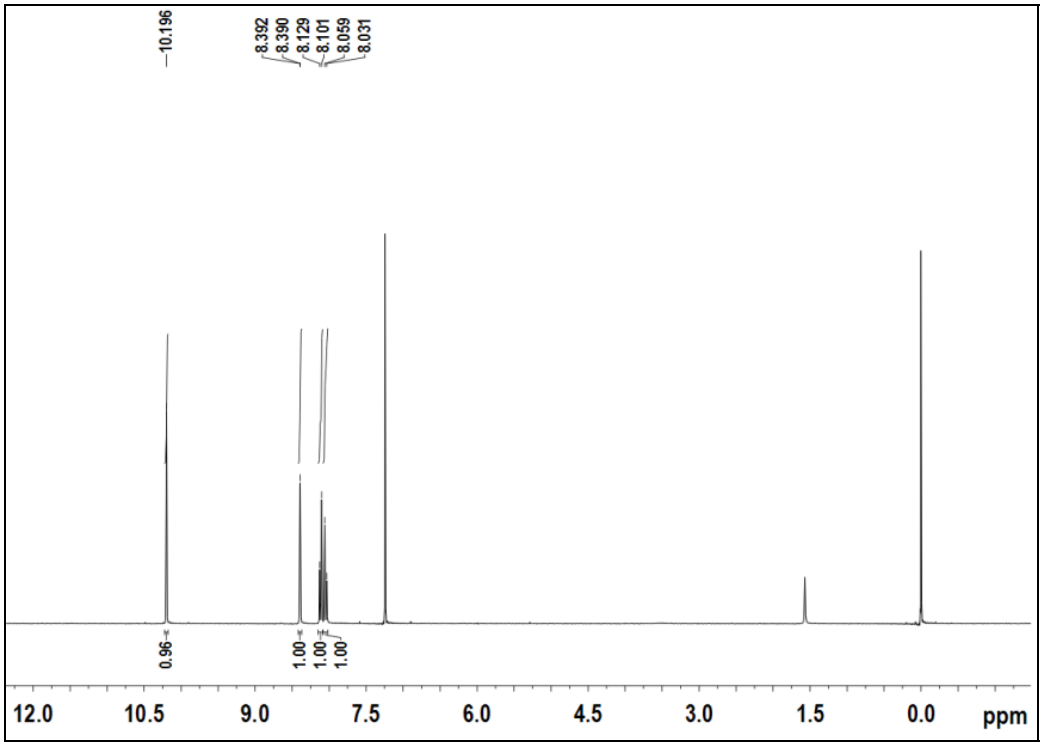

Fig. S3 ^{1}H NMR spectrum of naphthalene-2,6-dicarbaldehyde (300 MHz, $CDCl_3$).

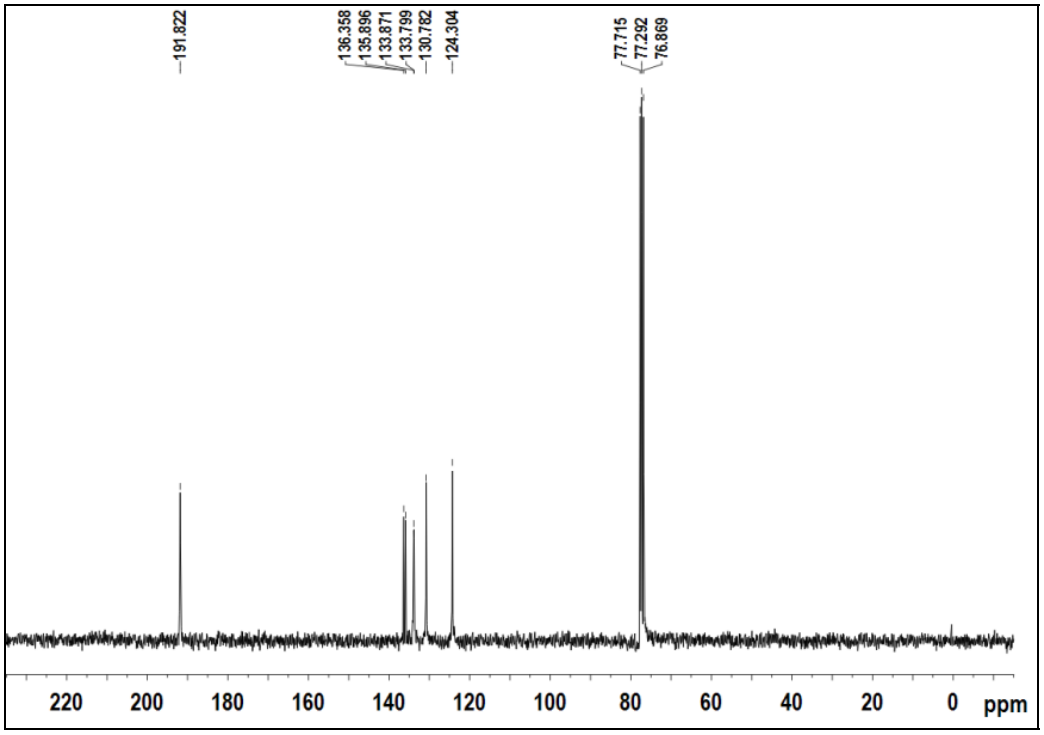

Fig. S4 ^{13}C NMR spectrum of naphthalene-2,6-dicarbaldehyde (75 MHz, $CDCl_3$).

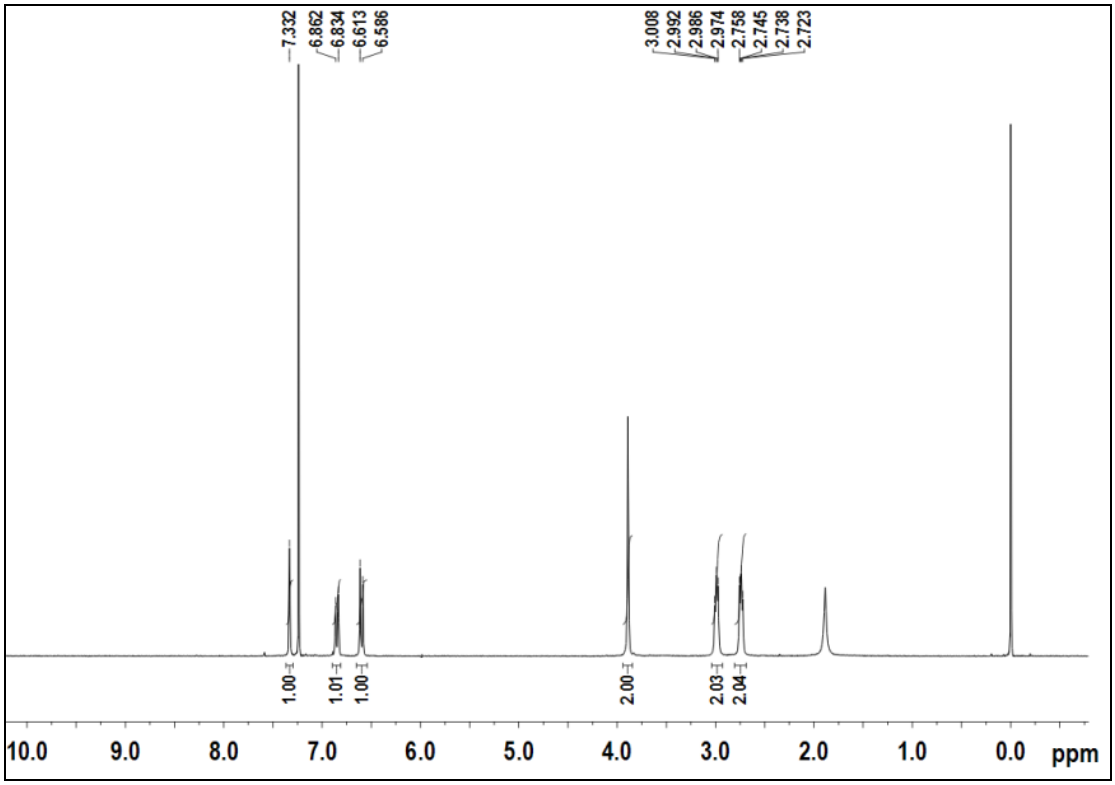

Fig. S5 ^{1}H NMR spectrum of L (300 MHz, $CDCl_3$).

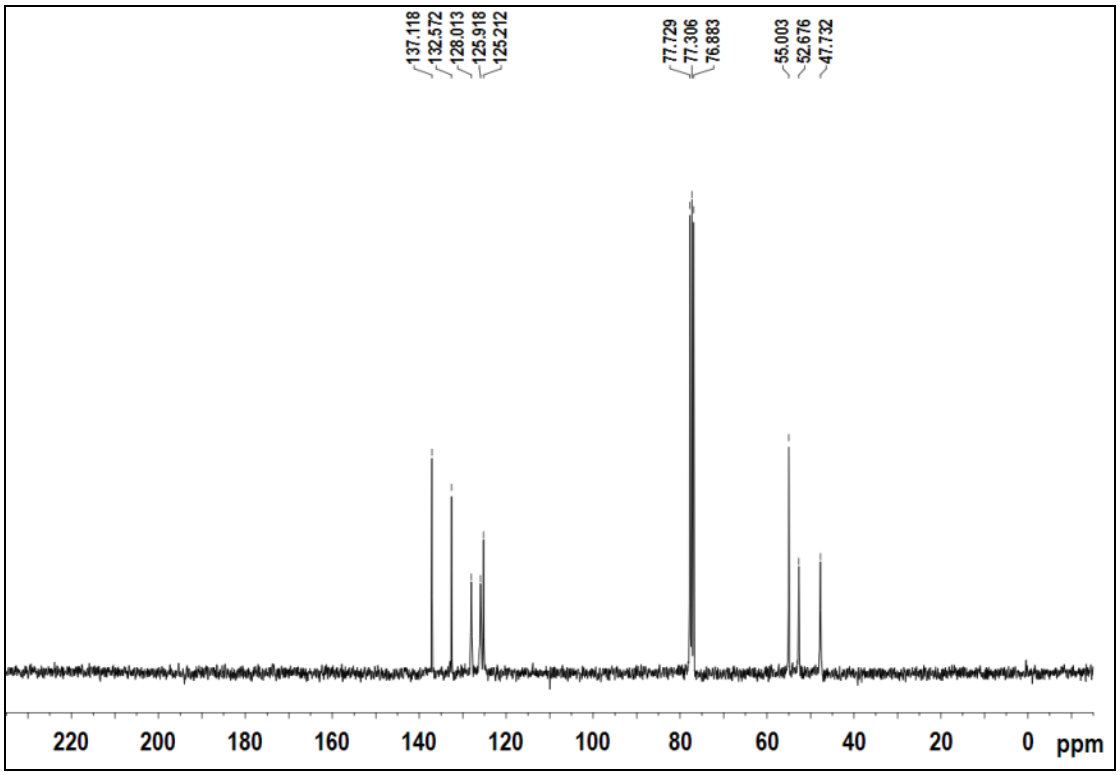

Fig. S6 ^{13}C NMR spectrum of L (75 MHz, $CDCl_3$).

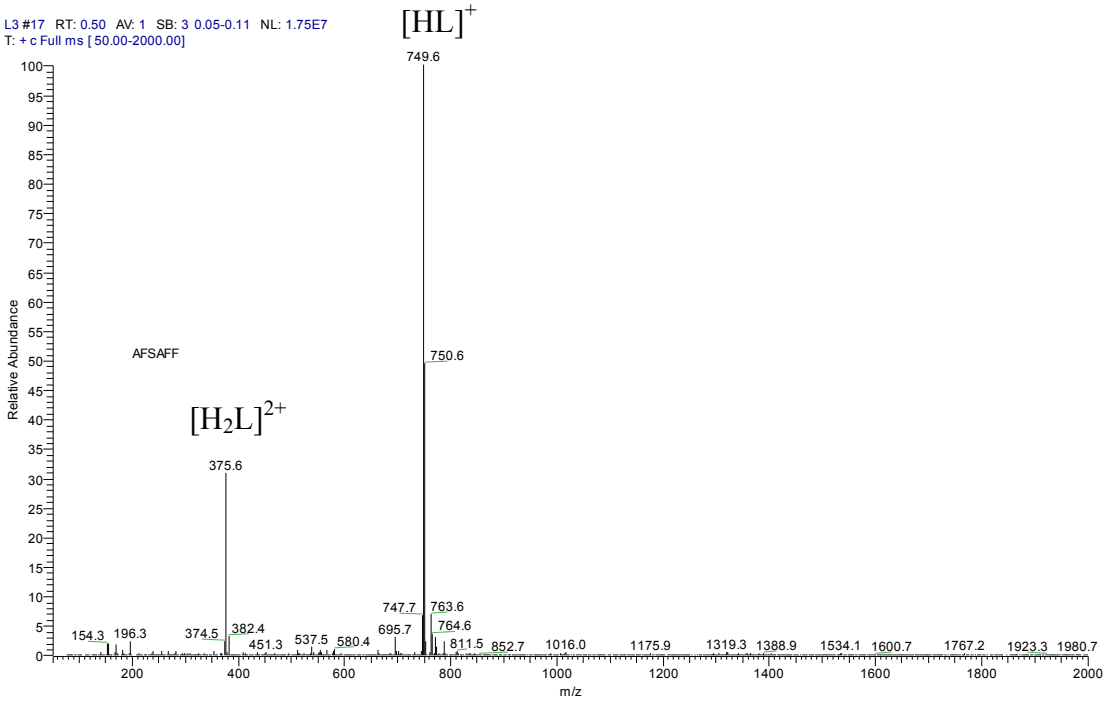

Fig. S7 ESI-MS spectrum of L.

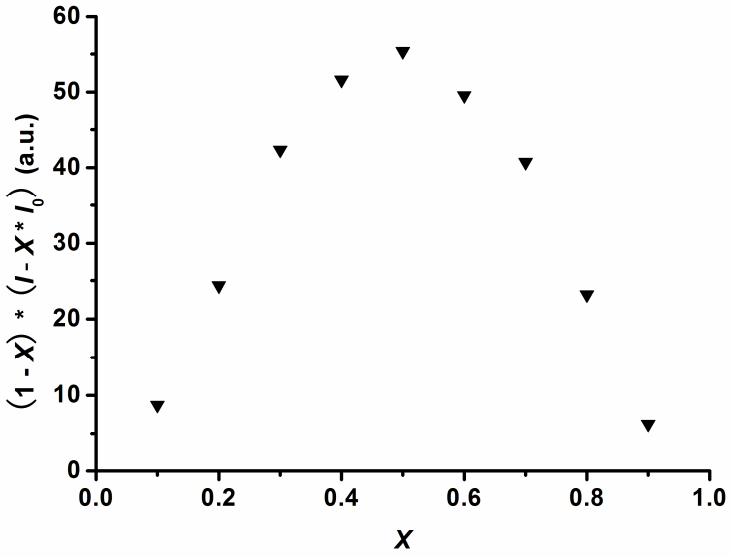

Fig. S8 Job's plot of the complexation between $[Zn_2L]^{4+}$ and suc^{2-} in aqueous solution (HEPES buffer, pH 7.40, 20 mM). Total concentration of $[Zn_2L]^{4+}$ and suc^{2-} was kept constant at 4×10^{-5} M. $X = [Zn_2L]/\{[Zn_2L] + [fum^{2-}]\}$.

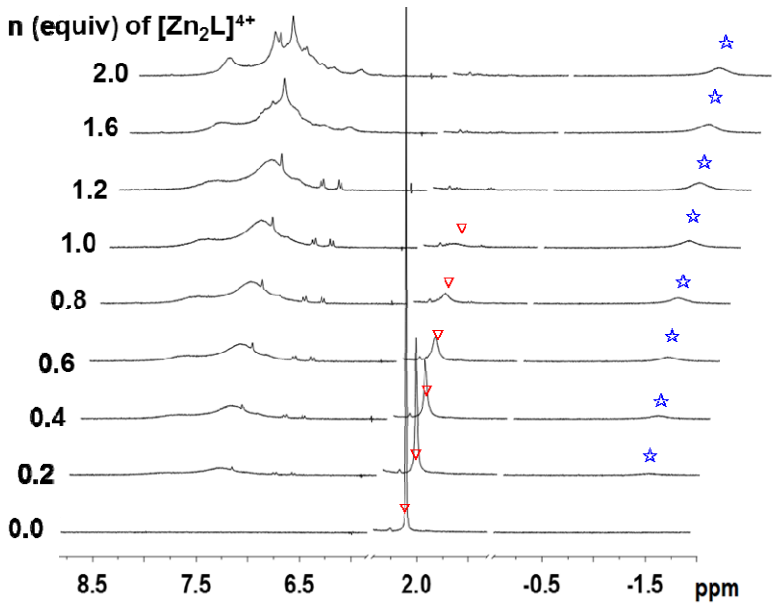

Fig. S9 ^{1}H NMR titration of suc^{2-} (0.011 M) with increasing the concentrations of $[Zn_2L]^{4+}$ in DMSO-d_6 /D_2O (2:1 v/v, pH 7.4). (▽) methylene signals in free suc^{2-}; (☆) methylene signals in bound suc^{2-}.

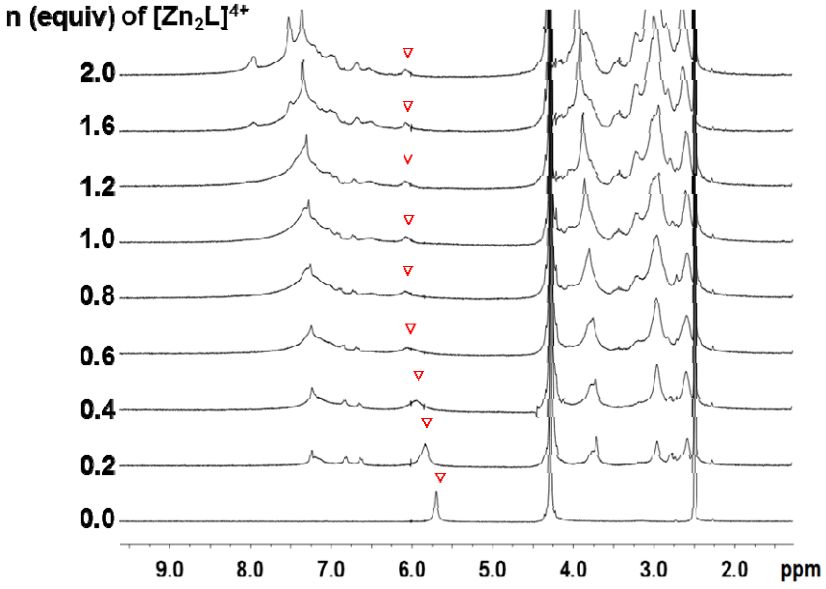

Fig. S10 ^{1}H NMR titration of $male^{2-}$ (0.011 M) with increasing the concentrations of $[Zn_2L]^{4+}$ in DMSO-d_6 /D_2O (2:1 v/v, pH 7.4). (▽) methine signals in free $male^{2-}$.

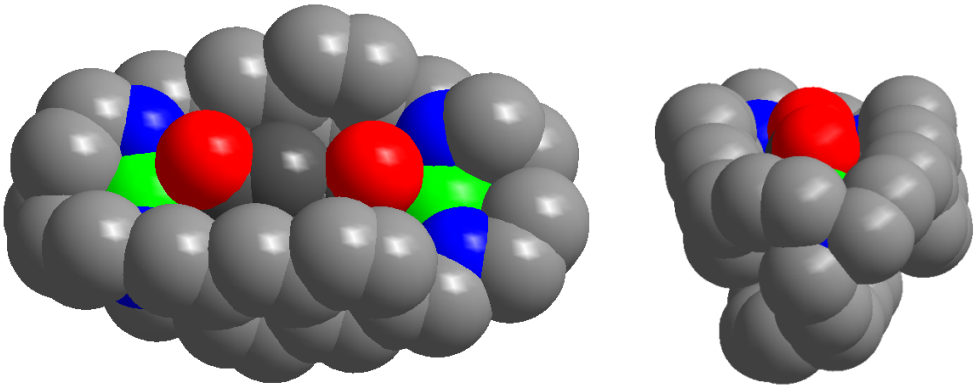

Fig. S11 The space filling model of $[(Cu_2L)(fum)]^{2+}$ cation in **3**.

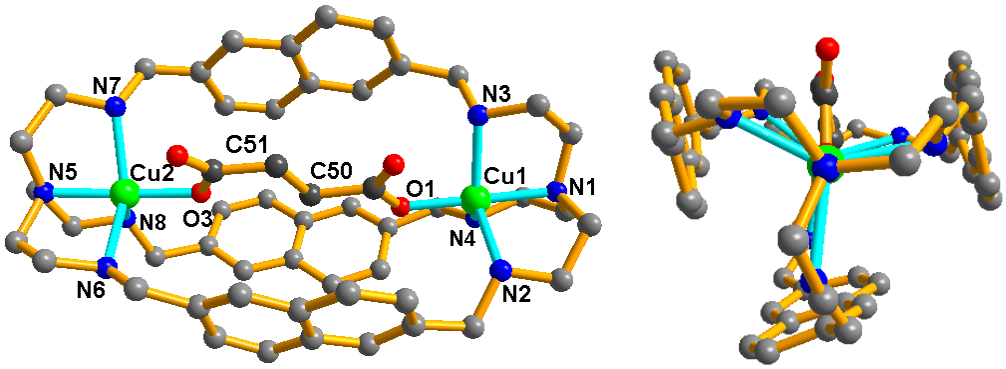

Fig. S12 The structure of $[(Cu_2L)(suc)]^{2+}$ cation in **4**.