Role of the conformational twists brought in the arms of 1,3-Di-capped conjugate of calix[4]arene (L) in turning on the fluorescence of L by Hg^{2+}

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Electronic Supplementary Information

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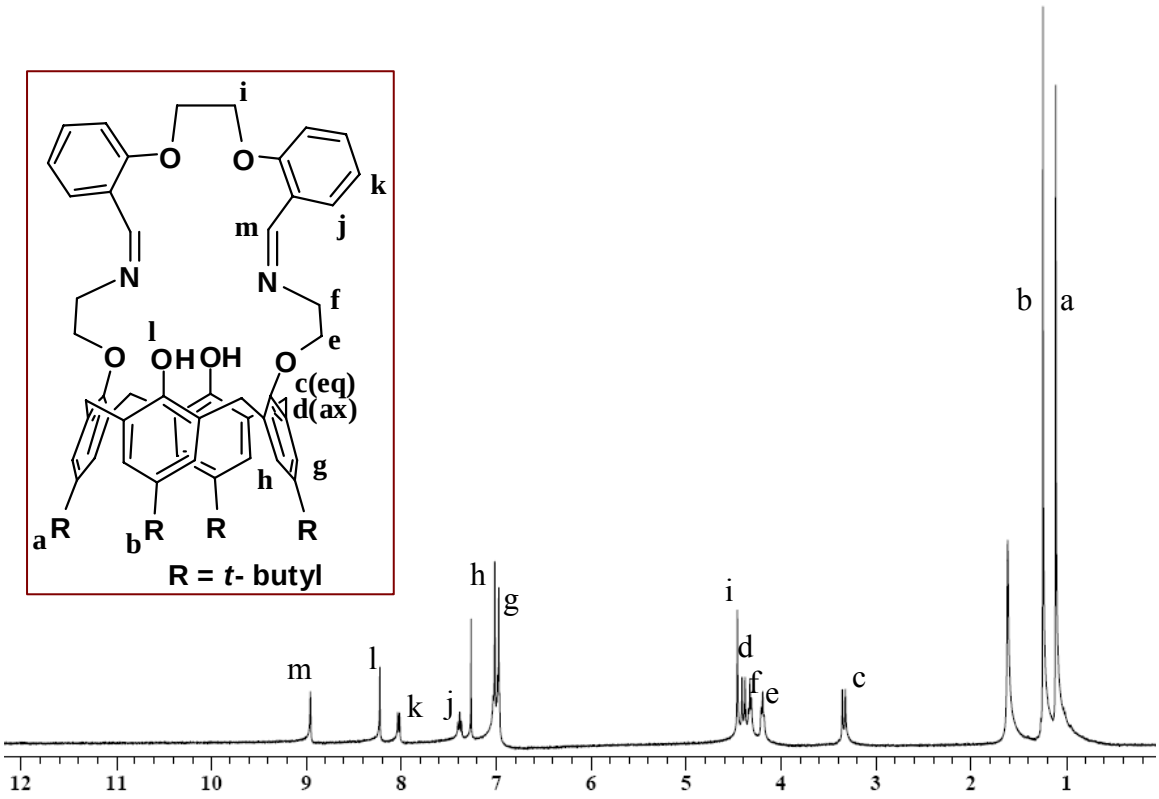
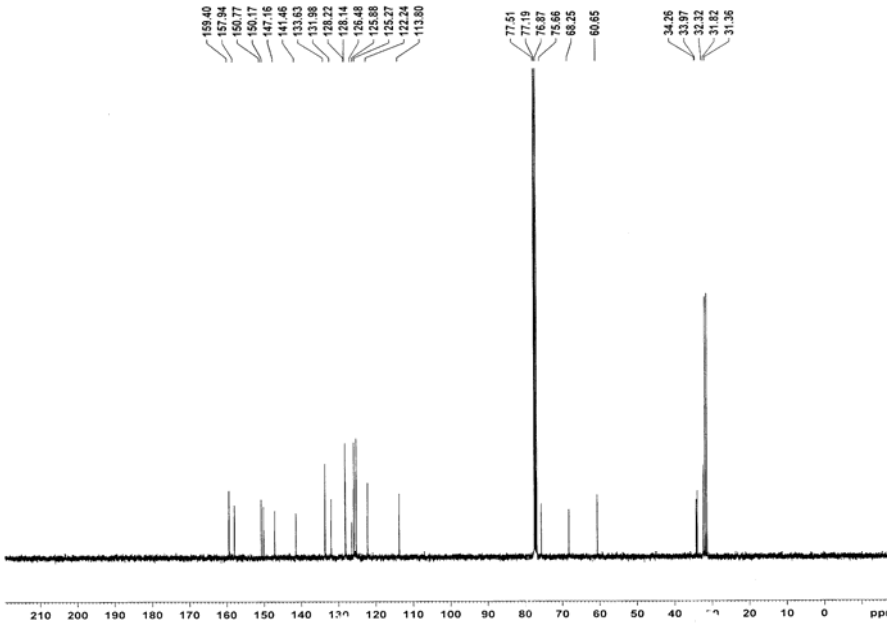
S01. Synthesis and Chracterization of L and 4:

(a). Synthesis and Characterization Data for the receptor molecule L: To a mixture of **3** (0.5g, 1.02mmol) in dry methanol, 2,2'-(ethane-1,2-diylbis(oxy))dibenzaldehyde (0.5g, 2.55 mmol) was added with stirring and was heated at reflux for 2h. The product settled after cooling reaction mixture was filtered, seperated and dried. Yield (0.635 g, 64 %). ^{1}H NMR ($CDCl_3$, δ ppm): 1.11 (s, 18H, C(C**H**$_3$)$_3$), 1.24(s, 18H each, C(C**H**$_3$)$_3$), 3.33 (d, 4H, Ar-C**H**$_2$-Ar, *J* = 13.33 Hz), 4.41 (t, 4H, C**H**$_2$-CH$_3$ *J* = 5.95 Hz), 4.32 (t, 4H, C**H**$_2$-CH$_3$ *J* = 6.6 Hz), 4.39 (d, 4H, Ar-C**H**$_2$-Ar J = 13.19 Hz), 4.45 (s, 4H, O-C**H**$_2$-C**H**$_2$-O), 6.97 (s, 4H, Ar-**H**), 7.01(s, 4H, Ar-**H**), 7.37 (t, 2H, Ar-**H**), 8.01(d, 2H, Ar-**H**)8.22 (s, 2H, Ar-O**H**), 8.95 (s, 2H, Ar-C**H**-N). ^{13}C NMR ($CDCl_3$, 400 MHz δ ppm): 31.3, 31.8 (C(***C***H3)3), 32.3 (Ar-***C***H2-Ar), 34.2, 34.2 (***C***(CH3)3), 60.6 (OCH2***C***H2N), 68.2 (Ar-O***C***H2CH2), 75.6 (Ar-O***C***H2), 113.8, 122.2, 125.3, 125.9, 126.5, 128.1, 128.2, 131.9, 133.6, 141.5, 147.2, 150.2, 150.8, 157.9, 159.4 (Imine ***C***, Ar-***C***). ESI-MS: *m/z* = 969, 100%. Anal. (% found) C 75.88, H 8.67, N 2.65, $C_{64}H_{76}N_2O_6.2CH_3OH.H_2O$ (% Calculated) C 75.52, H 8.57, N 2.59.

(b) ^{1}H-NMR spectrum of L in $CDCl_3$



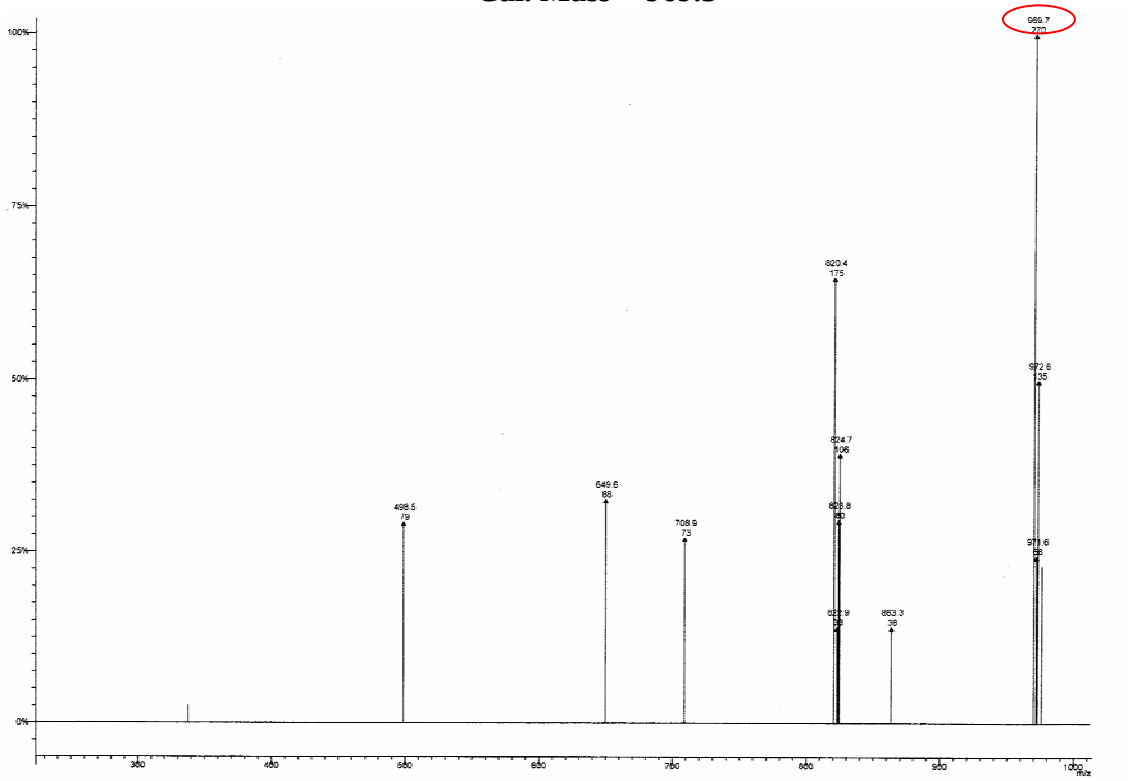
(c) ^{13}C-NMR spectrum of L



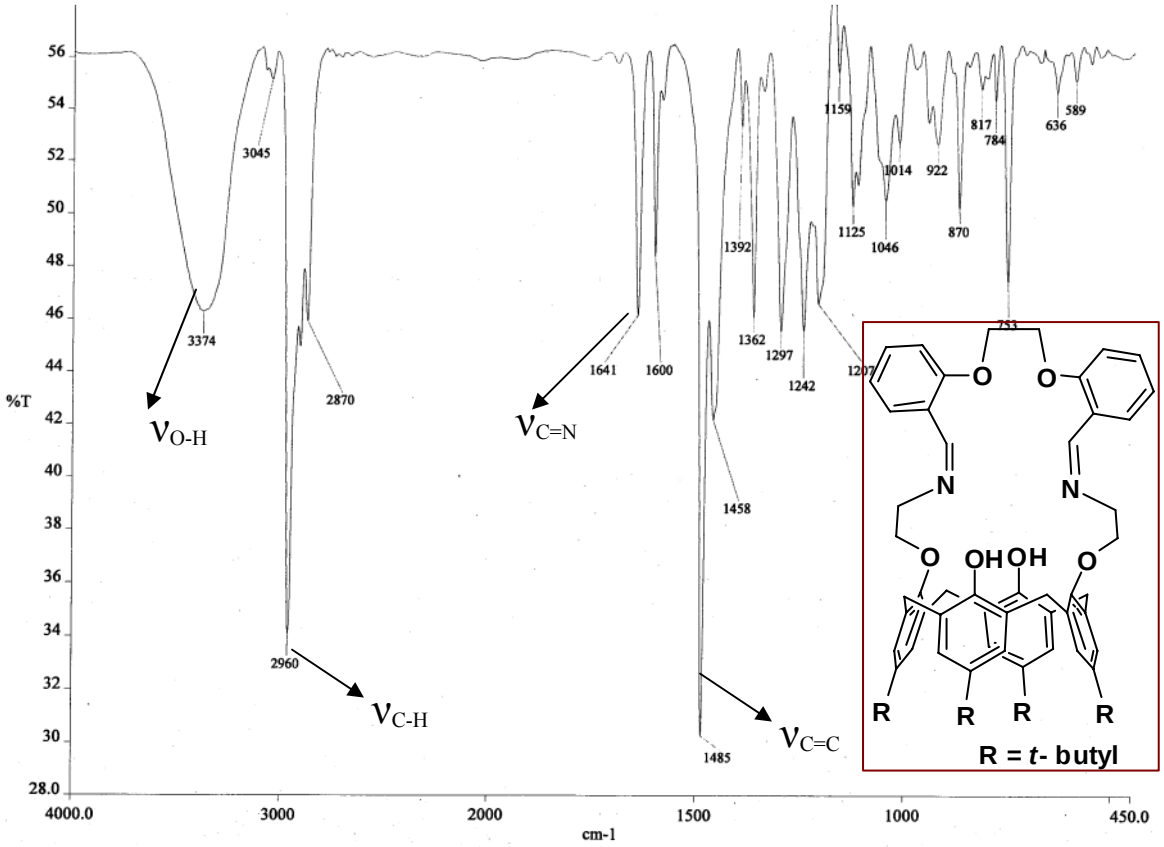
(d). ESI-MS spectrum of L (Positive ion mode)

Cal. Mass = 969.3

969.7



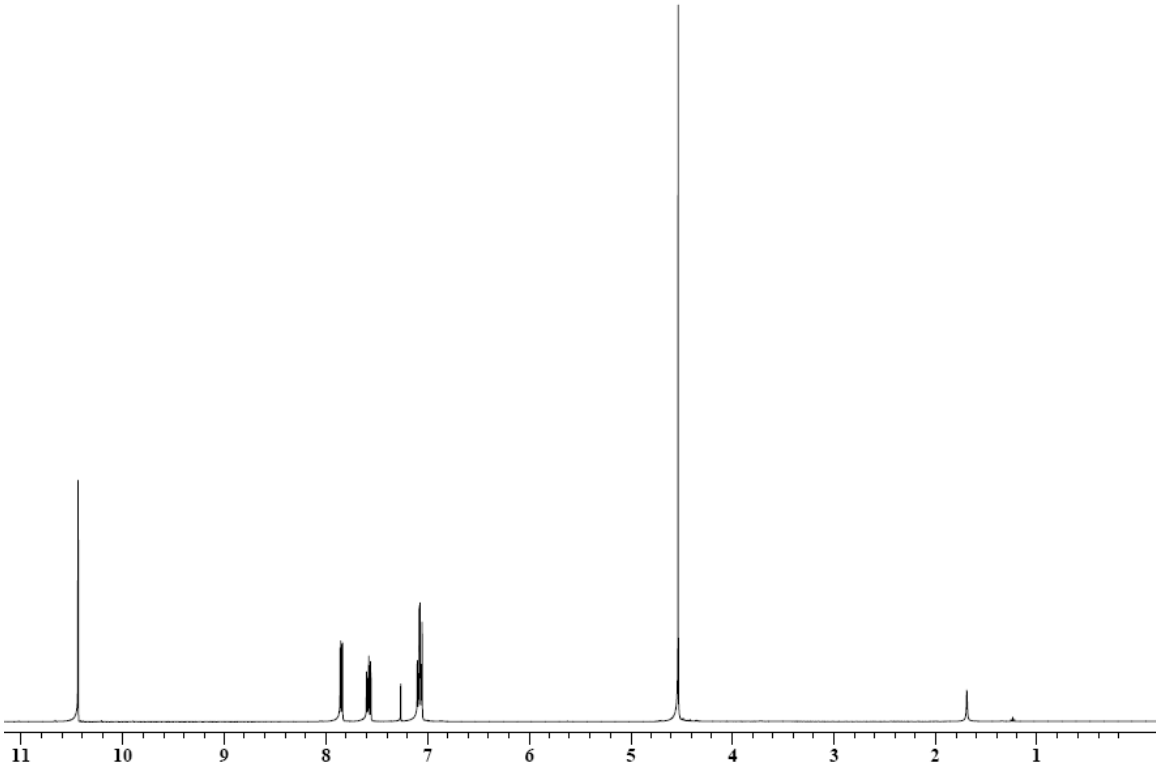
(e). FTIR spectrum of L:



(f). Synthesis and Characterization of 2,2'-(ethane-1,2-diylbis(oxy))dibenzaldehyde(4):

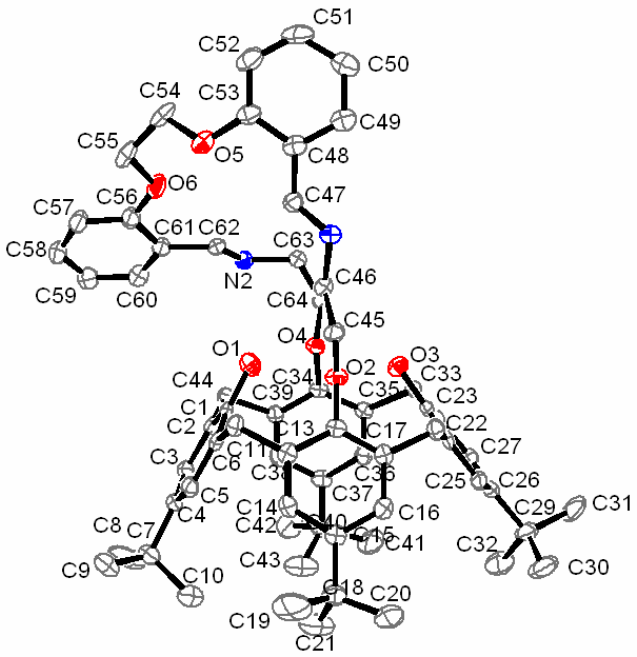
To a mixture of salicylaldehyde (1.2 g, 9.82mmol) in ethanol-water mixture(3:30 v/v), NaOH (0.39g, 9.82mmol) followed by 1,2 dibromoethane (0.92g, 4.91mmol) was added followed by 60 mL ethanol and heated at reflux for 3 hrs. The product settled after cooling the reaction mixture, was filtered and dried. Yield (0.91 g, 33 %). ^{1}H NMR ($CDCl_3$, δ ppm) 4.5 (s, 4H, Ar-OC**H**$_2$), 7-7.2 (m, 4H, Ar-**H**), 7.6 (t, 2H each, Ar-H), 7.8(d, 2H, Ar-H), 10.4(s, 2H, Ar-C**H**O).

(g) ^{1}H-NMR spectrum of 4 in $CDCl_3$



S02: Crystal data of L

(a) ORTEP diagram of single crystal XRD structure of L at 50% ellipsoid probability (hydrogen atoms and solvent molecules are removed for clarity)



(b). Crystallographic parameters for the structure determination and refinement:

	L
Empirical formula	$C_{70}\ H_{85}\ Cl_{15}\ N_2\ O_7$
Formula weight	1598.15
Temperature (K)	150(2)
Crystal System	Monoclinic
Space group	P 21/n
a/Å	16.8707(5)
b/Å	27.9775(7)
c/Å	17.3438(4)
α/°	90
β/°	104.859(3)
γ/°	90
Volume/Å^3	7912.5(4)
Z	4
Absorption Coefficient (mm^{-1})	0.571 mm^{-1}
Density	1.342 Mg/m^3
Reflections collected	57605
Independent reflections	13903
R_{int}	0.0567
Final R (I>2σ(I))	0.0776
$wR2_{obs}$	0.200
Parameters	905

(c) Bond distances (Å)

O(1)-C(1)	1.372(5)	C(14)-C(15)	1.387(6)
O(1)-H(101)	0.8400	C(14)-H(14)	0.9500
O(2)-C(12)	1.392(5)	C(16)-C(17)	1.392(6)
O(2)-C(45)	1.444(5)	C(16)-C(15)	1.397(6)
O(3)-C(23)	1.369(5)	C(16)-H(16)	0.9500
O(3)-H(103)	0.8400	C(15)-C(18)	1.526(6)
O(4)-C(34)	1.399(5)	C(17)-C(22)	1.520(6)
O(4)-C(64)	1.433(5)	C(18)-C(21)	1.524(7)
O(5)-C(53)	1.373(6)	C(18)-C(19)	1.524(7)
O(5)-C(54)	1.433(6)	C(18)-C(20)	1.528(7)
O(6)-C(56)	1.360(6)	C(19)-H(19A)	0.9800
O(6)-C(55)	1.439(5)	C(19)-H(19B)	0.9800
N(1)-C(47)	1.268(5)	C(19)-H(19C)	0.9800
N(1)-C(46)	1.457(6)	C(20)-H(20A)	0.9800
N(2)-C(62)	1.257(5)	C(20)-H(20B)	0.9800
N(2)-C(63)	1.464(5)	C(20)-H(20C)	0.9800
C(1)-C(2)	1.387(6)	C(21)-H(21A)	0.9800
C(1)-C(6)	1.403(6)	C(21)-H(21B)	0.9800
C(2)-C(3)	1.393(6)	C(21)-H(21C)	0.9800
C(2)-C(44)	1.519(6)	C(22)-C(24)	1.524(6)
C(3)-C(4)	1.396(6)	C(22)-H(22A)	0.9900
C(3)-H(3)	0.9500	C(22)-H(22B)	0.9900
C(4)-C(5)	1.399(7)	C(23)-C(28)	1.385(6)
C(4)-C(7)	1.535(6)	C(23)-C(24)	1.406(6)
C(5)-C(6)	1.386(6)	C(24)-C(25)	1.390(6)
C(5)-H(5)	0.9500	C(25)-C(26)	1.386(6)
C(6)-C(11)	1.516(6)	C(25)-H(25)	0.9500
C(7)-C(9)	1.532(7)	C(26)-C(27)	1.393(6)
C(7)-C(8)	1.534(8)	C(26)-C(29)	1.537(6)
C(7)-C(10)	1.535(7)	C(27)-C(28)	1.394(6)
C(8)-H(8A)	0.9800	C(27)-H(27)	0.9500
C(8)-H(8B)	0.9800	C(28)-C(33)	1.513(6)
C(8)-H(8C)	0.9800	C(29)-C(30)	1.534(8)
C(9)-H(9A)	0.9800	C(29)-C(31)	1.535(7)
C(9)-H(9B)	0.9800	C(29)-C(32)	1.537(8)
C(9)-H(9C)	0.9800	C(30)-H(30A)	0.9800
C(10)-H(10A)	0.9800	C(30)-H(30B)	0.9800
C(10)-H(10B)	0.9800	C(30)-H(30C)	0.9800
C(10)-H(10C)	0.9800	C(31)-H(31A)	0.9800
C(11)-C(13)	1.529(6)	C(31)-H(31B)	0.9800
C(11)-H(11A)	0.9900	C(31)-H(31C)	0.9800
C(11)-H(11B)	0.9900	C(32)-H(32A)	0.9800
C(12)-C(17)	1.381(6)	C(32)-H(32B)	0.9800

C(12)-C(13)	1.399(6)	C(32)-H(32C)	0.9800
C(13)-C(14)	1.392(6)	C(33)-C(35)	1.527(5)
C(33)-H(33A)	0.9900	C(54)-H(54B)	0.9900
C(33)-H(33B)	0.9900	C(55)-H(55A)	0.9900
C(34)-C(39)	1.393(6)	C(55)-H(55B)	0.9900
C(34)-C(35)	1.397(6)	C(56)-C(57)	1.399(6)
C(35)-C(36)	1.396(6)	C(56)-C(61)	1.403(6)
C(36)-C(37)	1.387(6)	C(57)-C(58)	1.381(8)
C(36)-H(36)	0.9500	C(57)-H(57)	0.9500
C(37)-C(38)	1.391(6)	C(58)-C(59)	1.379(8)
C(37)-C(40)	1.534(6)	C(58)-H(58)	0.9500
C(38)-C(39)	1.385(6)	C(59)-C(60)	1.375(7)
C(38)-H(38)	0.9500	C(59)-H(59)	0.9500
C(39)-C(44)	1.524(5)	C(60)-C(61)	1.381(7)
C(40)-C(41)	1.507(7)	C(60)-H(60)	0.9500
C(40)-C(42)	1.516(7)	C(61)-C(62)	1.481(6)
C(40)-C(43)	1.555(7)	C(62)-H(62)	0.9500
C(41)-H(41A)	0.9800	C(63)-C(64)	1.512(6)
C(41)-H(41B)	0.9800	C(63)-H(63A)	0.9900
C(41)-H(41C)	0.9800	C(63)-H(63B)	0.9900
C(42)-H(42A)	0.9800	C(64)-H(64A)	0.9900
C(42)-H(42B)	0.9800	C(64)-H(64B)	0.9900
C(42)-H(42C)	0.9800	C(54)-C(55)	1.490(7)
C(43)-H(43A)	0.9800	C(54)-H(54A)	0.9900
C(43)-H(43B)	0.9800		
C(43)-H(43C)	0.9800		
C(44)-H(44A)	0.9900		
C(44)-H(44B)	0.9900		
C(45)-C(46)	1.517(6)		
C(45)-H(45A)	0.9900		
C(45)-H(45B)	0.9900		
C(47)-C(48)	1.465(6)		
C(47)-H(47)	0.9500		
C(46)-H(46A)	0.9900		
C(46)-H(46B)	0.9900		
C(48)-C(49)	1.393(6)		
C(48)-C(53)	1.402(6)		
C(49)-C(50)	1.384(7)		
C(49)-H(49)	0.9500		
C(50)-C(51)	1.378(7)		
C(50)-H(50)	0.9500		
C(51)-C(52)	1.367(8)		
C(51)-H(51)	0.9500		
C(52)-C(53)	1.380(7)		
C(52)-H(52)	0.9500		

(d) Bond angles (º)

C(1)-O(1)-H(101)	109.5	C(7)-C(10)-H(10B)	109.5
C(12)-O(2)-C(45)	118.0(3)	H(10A)-C(10)-H(10B)	109.5
C(23)-O(3)-H(103)	109.5	C(7)-C(10)-H(10C)	109.5
C(34)-O(4)-C(64)	115.0(3)	H(10A)-C(10)-H(10C)	109.5
C(53)-O(5)-C(54)	117.4(4)	H(10B)-C(10)-H(10C)	109.5
C(56)-O(6)-C(55)	118.1(3)	C(6)-C(11)-C(13)	111.6(3)
C(47)-N(1)-C(46)	115.4(4)	C(6)-C(11)-H(11A)	109.3
C(62)-N(2)-C(63)	118.3(4)	C(13)-C(11)-H(11A)	109.3
O(1)-C(1)-C(2)	122.2(4)	C(6)-C(11)-H(11B)	109.3
O(1)-C(1)-C(6)	117.1(4)	C(13)-C(11)-H(11B)	109.3
C(2)-C(1)-C(6)	120.7(4)	H(11A)-C(11)-H(11B)	108.0
C(1)-C(2)-C(3)	119.0(4)	C(17)-C(12)-O(2)	118.5(4)
C(1)-C(2)-C(44)	121.5(4)	C(17)-C(12)-C(13)	122.1(4)
C(3)-C(2)-C(44)	119.3(4)	O(2)-C(12)-C(13)	119.0(4)
C(2)-C(3)-C(4)	122.5(4)	C(14)-C(13)-C(12)	117.2(4)
C(2)-C(3)-H(3)	118.7	C(14)-C(13)-C(11)	120.9(4)
C(4)-C(3)-H(3)	118.7	C(12)-C(13)-C(11)	121.8(4)
C(3)-C(4)-C(5)	116.4(4)	C(15)-C(14)-C(13)	123.0(4)
C(3)-C(4)-C(7)	122.3(4)	C(15)-C(14)-H(14)	118.5
C(5)-C(4)-C(7)	121.2(4)	C(13)-C(14)-H(14)	118.5
C(6)-C(5)-C(4)	123.2(4)	C(17)-C(16)-C(15)	122.3(4)
C(6)-C(5)-H(5)	118.4	C(17)-C(16)-H(16)	118.9
C(4)-C(5)-H(5)	118.4	C(15)-C(16)-H(16)	118.9
C(5)-C(6)-C(1)	118.2(4)	C(14)-C(15)-C(16)	117.1(4)
C(5)-C(6)-C(11)	120.3(4)	C(14)-C(15)-C(18)	120.4(4)
C(1)-C(6)-C(11)	121.5(4)	C(16)-C(15)-C(18)	122.4(4)
C(9)-C(7)-C(8)	108.5(5)	C(12)-C(17)-C(16)	118.1(4)
C(9)-C(7)-C(4)	110.1(4)	C(12)-C(17)-C(22)	121.8(4)
C(8)-C(7)-C(4)	111.8(4)	C(16)-C(17)-C(22)	120.0(4)
C(9)-C(7)-C(10)	109.7(4)	C(21)-C(18)-C(19)	108.9(5)
C(8)-C(7)-C(10)	108.7(5)	C(21)-C(18)-C(15)	108.0(4)
C(4)-C(7)-C(10)	108.1(4)	C(19)-C(18)-C(15)	110.1(4)
C(7)-C(8)-H(8A)	109.5	C(21)-C(18)-C(20)	110.0(5)
C(7)-C(8)-H(8B)	109.5	C(19)-C(18)-C(20)	107.9(5)
H(8A)-C(8)-H(8B)	109.5	C(15)-C(18)-C(20)	112.0(4)
C(7)-C(8)-H(8C)	109.5	C(18)-C(19)-H(19A)	109.5
H(8A)-C(8)-H(8C)	109.5	C(18)-C(19)-H(19B)	109.5
H(8B)-C(8)-H(8C)	109.5	H(19A)-C(19)-H(19B)	109.5
C(7)-C(9)-H(9A)	109.5	C(18)-C(19)-H(19C)	109.5
C(7)-C(9)-H(9B)	109.5	H(19A)-C(19)-H(19C)	109.5
H(9A)-C(9)-H(9B)	109.5	H(19B)-C(19)-H(19C)	109.5
C(7)-C(9)-H(9C)	109.5	C(18)-C(20)-H(20A)	109.5

H(9A)-C(9)-H(9C)	109.5	C(18)-C(20)-H(20B)	109.5
H(9B)-C(9)-H(9C)	109.5	H(20A)-C(20)-H(20B)	109.5
C(7)-C(10)-H(10A)	109.5	C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5	C(29)-C(31)-H(31B)	109.5
H(20B)-C(20)-H(20C)	109.5	H(31A)-C(31)-H(31B)	109.5
C(18)-C(21)-H(21A)	109.5	C(29)-C(31)-H(31C)	109.5
C(18)-C(21)-H(21B)	109.5	H(31A)-C(31)-H(31C)	109.5
H(21A)-C(21)-H(21B)	109.5	H(31B)-C(31)-H(31C)	109.5
C(18)-C(21)-H(21C)	109.5	C(29)-C(32)-H(32A)	109.5
H(21A)-C(21)-H(21C)	109.5	C(29)-C(32)-H(32B)	109.5
H(21B)-C(21)-H(21C)	109.5	H(32A)-C(32)-H(32B)	109.5
C(17)-C(22)-C(24)	112.9(3)	C(29)-C(32)-H(32C)	109.5
C(17)-C(22)-H(22A)	109.0	H(32A)-C(32)-H(32C)	109.5
C(24)-C(22)-H(22A)	109.0	H(32B)-C(32)-H(32C)	109.5
C(17)-C(22)-H(22B)	109.0	C(28)-C(33)-C(35)	110.4(3)
C(24)-C(22)-H(22B)	109.0	C(28)-C(33)-H(33A)	109.6
H(22A)-C(22)-H(22B)	107.8	C(35)-C(33)-H(33A)	109.6
O(3)-C(23)-C(28)	116.9(4)	C(28)-C(33)-H(33B)	109.6
O(3)-C(23)-C(24)	122.4(4)	C(35)-C(33)-H(33B)	109.6
C(28)-C(23)-C(24)	120.7(4)	H(33A)-C(33)-H(33B)	108.1
C(25)-C(24)-C(23)	118.2(4)	C(39)-C(34)-C(35)	120.9(4)
C(25)-C(24)-C(22)	119.9(4)	C(39)-C(34)-O(4)	117.5(3)
C(23)-C(24)-C(22)	121.8(4)	C(35)-C(34)-O(4)	121.5(3)
C(26)-C(25)-C(24)	122.5(4)	C(36)-C(35)-C(34)	117.8(4)
C(26)-C(25)-H(25)	118.7	C(36)-C(35)-C(33)	118.0(4)
C(24)-C(25)-H(25)	118.7	C(34)-C(35)-C(33)	124.1(4)
C(25)-C(26)-C(27)	117.6(4)	C(37)-C(36)-C(35)	123.1(4)
C(25)-C(26)-C(29)	122.7(4)	C(37)-C(36)-H(36)	118.5
C(27)-C(26)-C(29)	119.7(4)	C(35)-C(36)-H(36)	118.5
C(26)-C(27)-C(28)	121.8(4)	C(36)-C(37)-C(38)	116.9(4)
C(26)-C(27)-H(27)	119.1	C(36)-C(37)-C(40)	123.0(4)
C(28)-C(27)-H(27)	119.1	C(38)-C(37)-C(40)	120.1(4)
C(23)-C(28)-C(27)	119.1(4)	C(39)-C(38)-C(37)	122.5(4)
C(23)-C(28)-C(33)	119.2(4)	C(39)-C(38)-H(38)	118.7
C(27)-C(28)-C(33)	121.6(4)	C(37)-C(38)-H(38)	118.7
C(30)-C(29)-C(31)	108.1(4)	C(38)-C(39)-C(34)	118.8(4)
C(30)-C(29)-C(26)	111.8(4)	C(38)-C(39)-C(44)	119.2(4)
C(31)-C(29)-C(26)	109.1(4)	C(34)-C(39)-C(44)	121.6(4)
C(30)-C(29)-C(32)	109.1(5)	C(41)-C(40)-C(42)	109.9(4)
C(31)-C(29)-C(32)	109.9(5)	C(41)-C(40)-C(37)	112.4(4)
C(26)-C(29)-C(32)	108.9(4)	C(42)-C(40)-C(37)	110.4(4)
C(29)-C(30)-H(30A)	109.5	C(41)-C(40)-C(43)	108.5(5)
C(29)-C(30)-H(30B)	109.5	C(42)-C(40)-C(43)	107.0(4)
H(30A)-C(30)-H(30B)	109.5	C(37)-C(40)-C(43)	108.4(4)
C(29)-C(30)-H(30C)	109.5	C(40)-C(41)-H(41A)	109.5

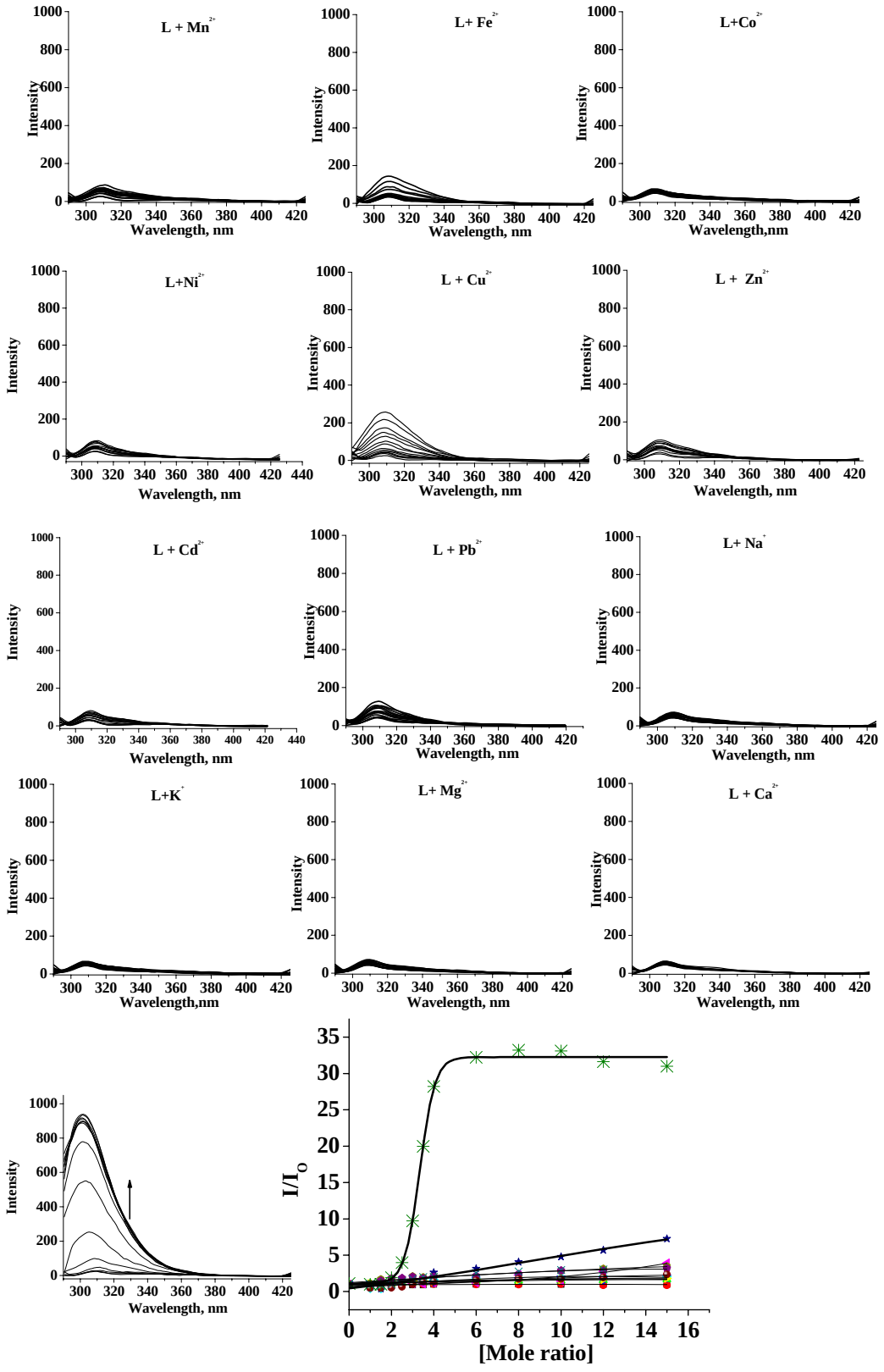
H(30A)-C(30)-H(30C)	109.5	C(40)-C(41)-H(41B)	109.5
H(30B)-C(30)-H(30C)	109.5	H(41A)-C(41)-H(41B)	109.5
C(29)-C(31)-H(31A)	109.5		
C(40)-C(41)-H(41C)	109.5	C(52)-C(51)-C(50)	121.1(5)
H(41A)-C(41)-H(41C)	109.5	C(52)-C(51)-H(51)	119.5
H(41B)-C(41)-H(41C)	109.5	C(50)-C(51)-H(51)	119.5
C(40)-C(42)-H(42A)	109.5	C(51)-C(52)-C(53)	120.0(5)
C(40)-C(42)-H(42B)	109.5	C(51)-C(52)-H(52)	120.0
H(42A)-C(42)-H(42B)	109.5	C(53)-C(52)-H(52)	120.0
C(40)-C(42)-H(42C)	109.5	O(5)-C(53)-C(52)	124.5(4)
H(42A)-C(42)-H(42C)	109.5	O(5)-C(53)-C(48)	115.1(4)
H(42B)-C(42)-H(42C)	109.5	C(52)-C(53)-C(48)	120.4(5)
C(40)-C(43)-H(43A)	109.5	O(5)-C(54)-C(55)	108.4(4)
C(40)-C(43)-H(43B)	109.5	O(5)-C(54)-H(54A)	110.0
H(43A)-C(43)-H(43B)	109.5	C(55)-C(54)-H(54A)	110.0
C(40)-C(43)-H(43C)	109.5	O(5)-C(54)-H(54B)	110.0
H(43A)-C(43)-H(43C)	109.5	C(55)-C(54)-H(54B)	110.0
H(43B)-C(43)-H(43C)	109.5	H(54A)-C(54)-H(54B)	108.4
C(2)-C(44)-C(39)	108.3(3)	O(6)-C(55)-C(54)	107.2(4)
C(2)-C(44)-H(44A)	110.0	O(6)-C(55)-H(55A)	110.3
C(39)-C(44)-H(44A)	110.0	C(54)-C(55)-H(55A)	110.3
C(2)-C(44)-H(44B)	110.0	O(6)-C(55)-H(55B)	110.3
C(39)-C(44)-H(44B)	110.0	C(54)-C(55)-H(55B)	110.3
H(44A)-C(44)-H(44B)	108.4	H(55A)-C(55)-H(55B)	108.5
O(2)-C(45)-C(46)	103.5(3)	O(6)-C(56)-C(57)	124.5(4)
O(2)-C(45)-H(45A)	111.1	O(6)-C(56)-C(61)	115.9(4)
C(46)-C(45)-H(45A)	111.1	C(57)-C(56)-C(61)	119.7(5)
O(2)-C(45)-H(45B)	111.1	C(58)-C(57)-C(56)	119.0(5)
C(46)-C(45)-H(45B)	111.1	C(58)-C(57)-H(57)	120.5
H(45A)-C(45)-H(45B)	109.0	C(56)-C(57)-H(57)	120.5
N(1)-C(47)-C(48)	123.5(4)	C(59)-C(58)-C(57)	121.7(5)
N(1)-C(47)-H(47)	118.2	C(59)-C(58)-H(58)	119.2
C(48)-C(47)-H(47)	118.2	C(57)-C(58)-H(58)	119.2
N(1)-C(46)-C(45)	112.2(4)	C(60)-C(59)-C(58)	118.8(5)
N(1)-C(46)-H(46A)	109.2	C(60)-C(59)-H(59)	120.6
C(45)-C(46)-H(46A)	109.2	C(58)-C(59)-H(59)	120.6
N(1)-C(46)-H(46B)	109.2	C(59)-C(60)-C(61)	121.6(5)
C(45)-C(46)-H(46B)	109.2	C(59)-C(60)-H(60)	119.2
H(46A)-C(46)-H(46B)	107.9	C(61)-C(60)-H(60)	119.2
C(49)-C(48)-C(53)	118.4(4)	C(60)-C(61)-C(56)	119.1(4)
C(49)-C(48)-C(47)	121.8(4)	C(60)-C(61)-C(62)	121.0(4)
C(53)-C(48)-C(47)	119.6(4)	C(56)-C(61)-C(62)	119.9(4)
C(50)-C(49)-C(48)	120.7(5)	N(2)-C(62)-C(61)	122.0(4)
C(50)-C(49)-H(49)	119.6	N(2)-C(62)-H(62)	119.0
C(48)-C(49)-H(49)	119.6	C(61)-C(62)-H(62)	119.0

C(51)-C(50)-C(49)	119.4(5)	N(2)-C(63)-C(64)	110.9(3)
C(51)-C(50)-H(50)	120.3	N(2)-C(63)-H(63A)	109.5
C(49)-C(50)-H(50)	120.3	C(64)-C(63)-H(63A)	109.5
N(2)-C(63)-H(63B)	109.5		
C(64)-C(63)-H(63B)	109.5		
H(63A)-C(63)-H(63B)	108.0		
O(4)-C(64)-C(63)	108.6(3)		
O(4)-C(64)-H(64A)	110.0		
C(63)-C(64)-H(64A)	110.0		
O(4)-C(64)-H(64B)	110.0		
C(63)-C(64)-H(64B)	110.0		
H(64A)-C(64)-H(64B)	108.3		

S03. Fluorescence details:

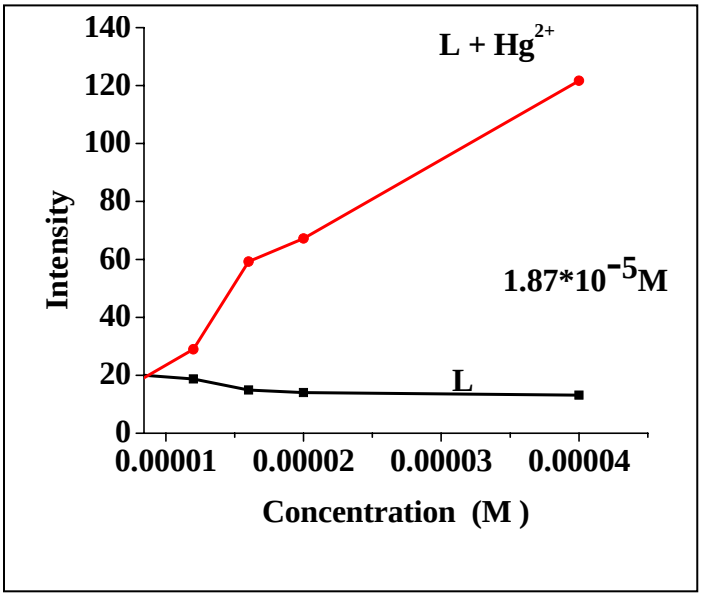
Fluorescence emission spectra were measured on Perkin-Elmer LS55. The bulk solutions of **L** and metal ions were prepared in ethanol in which, 50 μL of $CHCl_3$ was used for dissolving **L**. Bulk solution concentration of **L** & metal ions were maintained at 6×10^{-4} M. All the measurements were made in 1 cm quartz cell and maintained the effective cuvette concentration of **L** as 10 μM in all the titrations. During the titration, the concentration of the metal ions was varied accordingly in order to result in requisite mole ratios of these to **L** by taking a fixed volume of **L** and adding and varying volumes of the solution of the guest metal ions. The total volume of the solution used for the fluorescence measurements was maintained constant at 3 ml in all the cases by simply making up the solution using requisite volume of ethanol. Absorption studies were carried out similarly on JASCO V-570. The bulk solutions of **L** and metal ions were maintained at 1×10^{-3} M. All the measurements were made in 1 cm quartz cell and maintained the effective cuvette concentration of **L** as 33 μM in all the titrations while increasing the concentration of metal ions to obtain requisite mole ratios with respect to **L**.

S04. Fluorescence spectral traces for the titration of L with M^{n+}

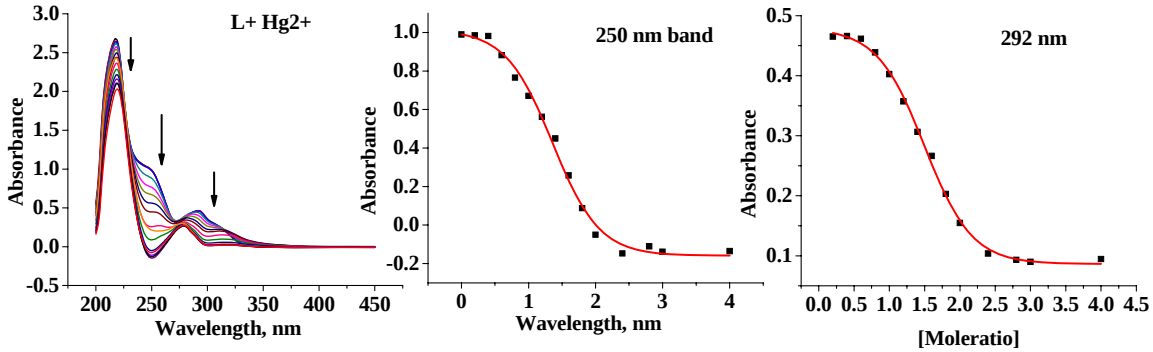


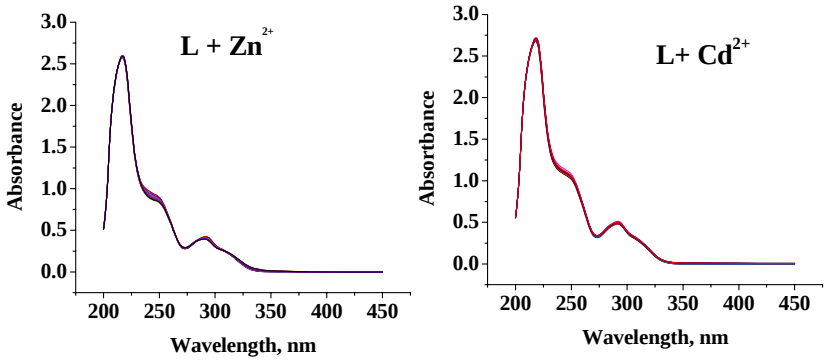
S05. Fluorescence spectral data for minimum detection limit

Minimum detection limit experiment was carried out by recording fluorescence for various incremental concentrations of L as well as L : Hg^{2+}(1:1) separately with initial concentration of 6×10^{-4} and plotted the same as shown below. Point on x-axis at which the intensity difference between two lines is ~50 was considered as minimum detection limit.

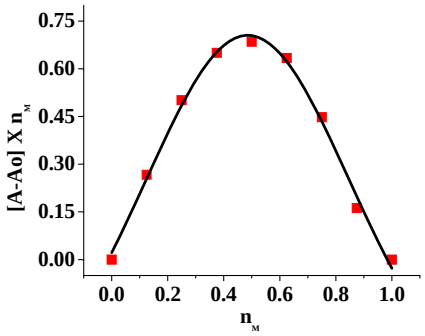


S06. Absorption spectral traces for the titration of L with M^{n+}

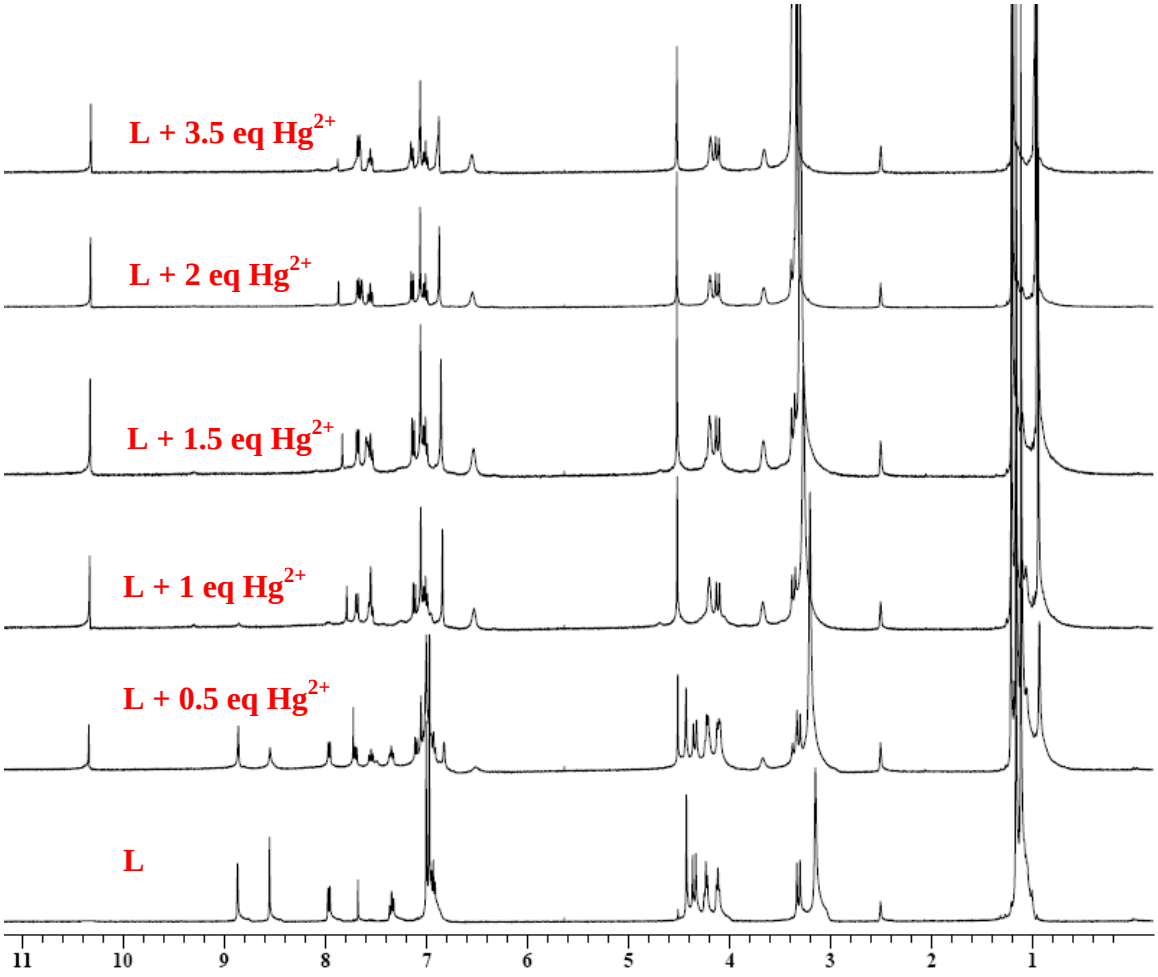




Job's plot for the 1:1 complex formation between L and Hg^{2+} plotted at 218 nm

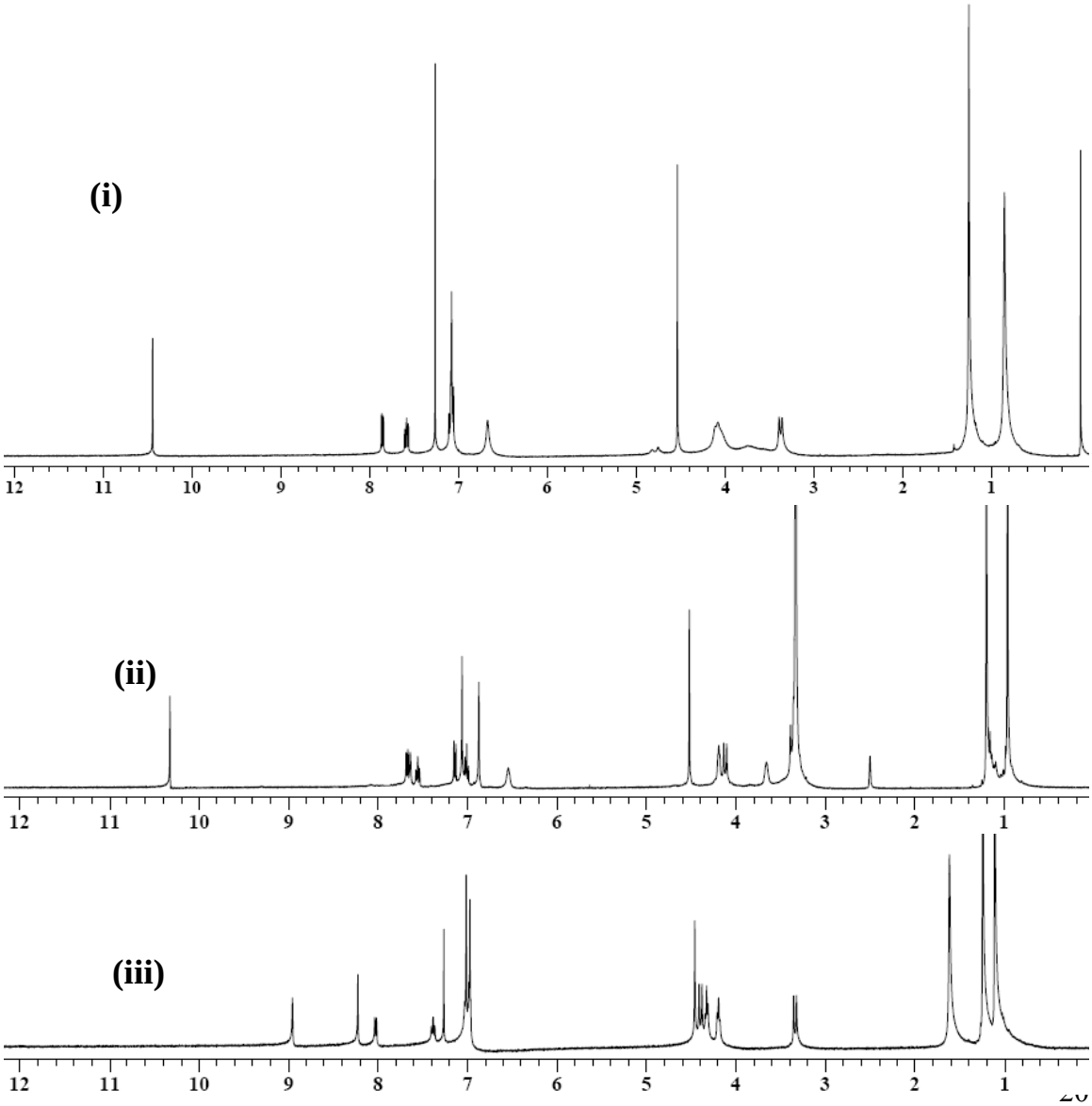


S07. ^{1}H NMR titration of L with mercuric perchlorate in DMSO



S08. Synthesis and characterization of mercury complex of L (HgL): To a solution of **L** (0.10 g, 0.103 mmol) in $CHCl_3$ (5mL), mercuric perchlorate (0.041 g, 0.103 mmol) in 25mL methanol was added drop-wise and stirried for 4 h. Then the reaction mixture was filtered and solvent was evaporated. The product was obtained by trituration with petroleum ether followed by recrystallization from $CHCl_3$ and MeOH. Yield (0.076 g, 63%). ^{1}H NMR ($CDCl_3$, δ ppm): 0.85 (s, 18H, C(C**H**$_3$)$_3$), 1.25(s, 18H, C(C**H**$_3$)$_3$), 3.37 (d, 4H, Ar-C**H**$_2$-Ar, J = 13.33 Hz), 3.74 (br, 4H, CH_2-C**H**$_2$), 4.07 (br, 8H, C**H**$_2$-CH_3 & Ar-C**H**$_2$-Ar), 4.53 (s, 4H, O-C**H**$_2$-C**H**$_2$-O), 7.07(m, 8H, Ar-**H** & 4H, Ar-**H**), 7.58 (t, 2H, Ar-**H**)7.85 (d, 2H, Ar-**H**), 10.44 (s, 2H, Ar-C**H**-N),. HRMS = 1169.5291(-3.4ppm)

^{1}H NMR Spectrum of (i)Isolated mercury complex, (ii) L with Hg^{2+} in DMSO(titration), (iii) L



S09. Mass spectral data for isolated and insitu prepared mercury complex:

(a). HRMS of isolated mercury complex:

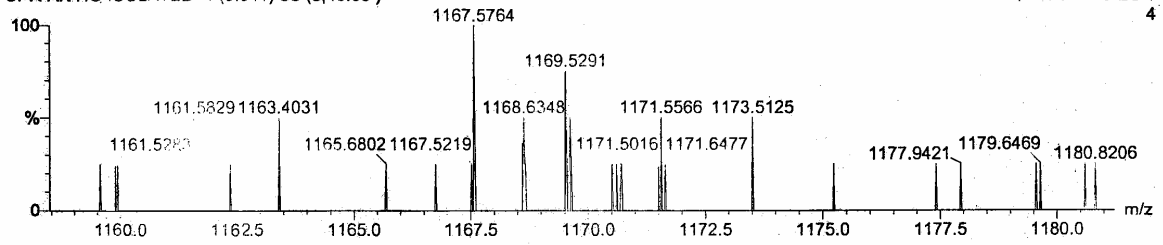
Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Isotope matching not enabled

Monoisotopic Mass, Odd and Even Electron Ions
31 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

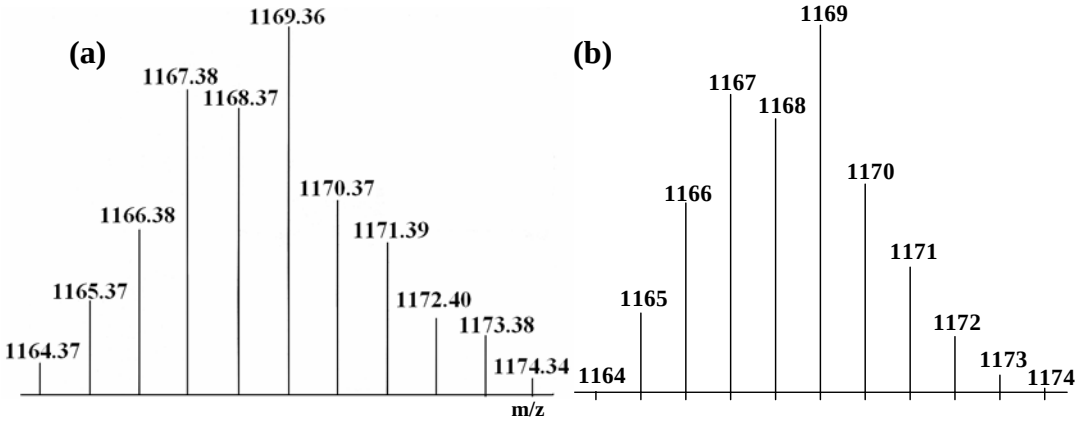
Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 10-Jun-201117:48:03

C64H74HgN2O6
CPR-AK-HG-ISOLATED 4 (0.041) Sb (5,40.00) TOF MS ES+ 4

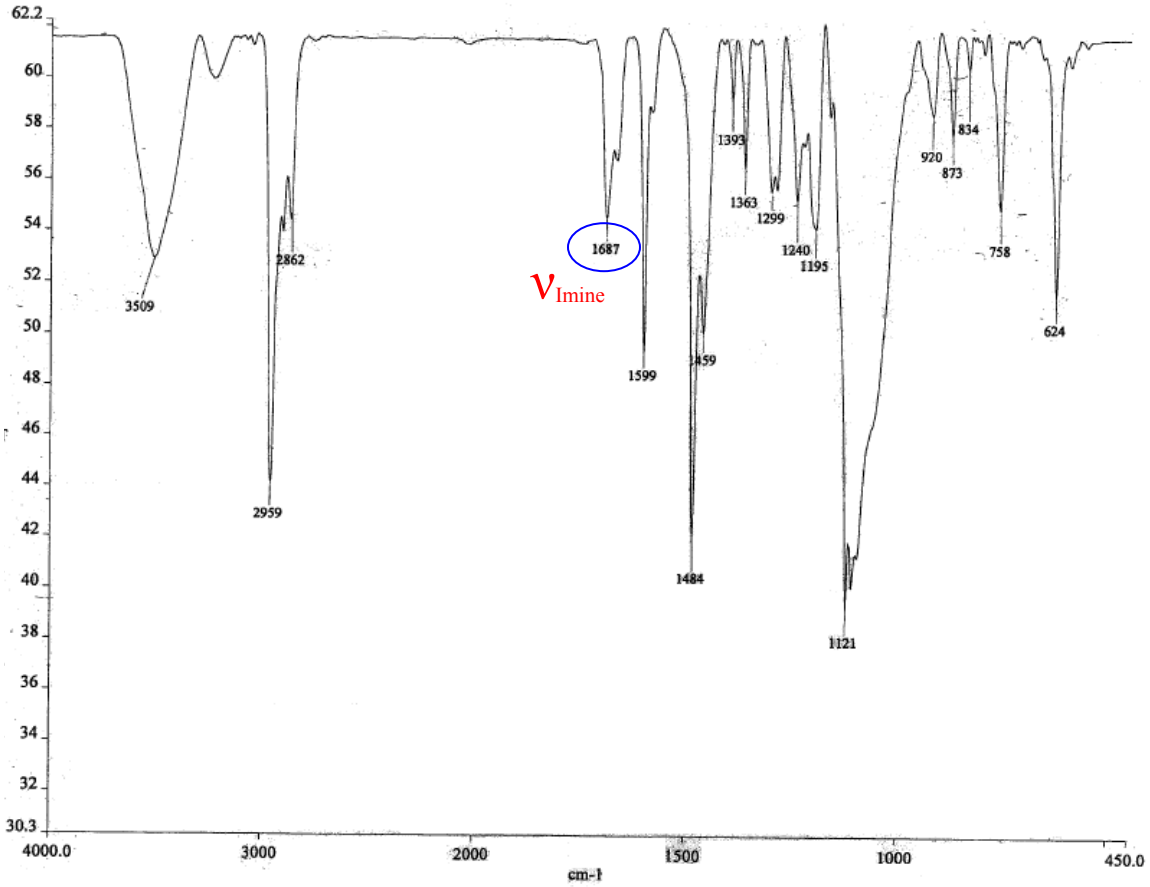


Minimum:				-1.5	
Maximum:		200.0	20.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
1169.5291	1169.5331	-4.1	-3.5	28.5	C64 H75 N2 O6 Hg

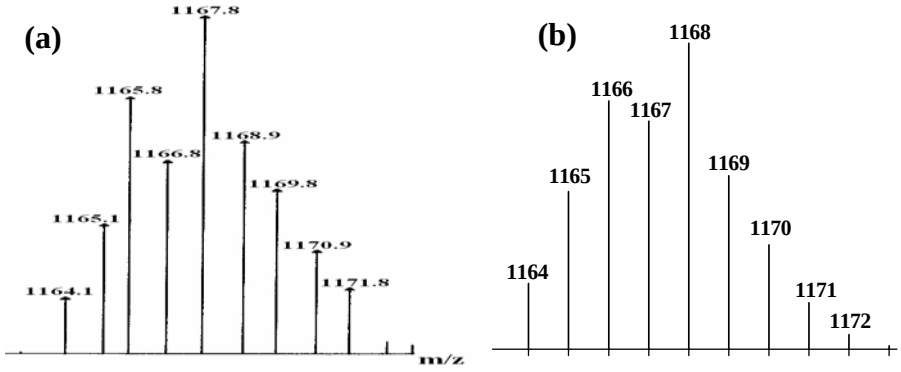
(b). Isotopic peak pattern of (M+1) ion peak for the isolated complex (a) Experimental (b) Calculated.



(c). FTIR spectrum of isolated mercury complx:



(d) **Isotopic peak pattern of (M+1) ion peak for the insitu prepared complex (a) Experimental (b) Calculated.**



S10: Computational data:

(a) Cartesian coordinates of B3LYP/6-31G optimized structure of L'

Z	Coordinates			Z	Coordinates		
	x	y	z		x	y	z
8	0.817116	0.399740	-0.044139	6	-4.953974	3.067913	-2.376254
6	0.454021	1.536867	0.650331	6	1.364588	-3.036555	1.516055
6	0.135717	2.765701	0.029869	6	-3.051033	-2.105522	2.910909
6	0.444293	1.431019	2.054985	6	-2.342131	-3.681724	1.041388
6	-0.143349	3.871927	0.842924	6	-3.966357	-0.579945	4.741830
6	0.052008	2.901391	-1.488735	6	2.285624	0.024780	-3.698171
6	0.174220	2.570151	2.825510	1	0.651654	1.212050	-4.448013
6	0.690397	0.083083	2.722425	1	0.372056	-0.554744	-4.523543
1	-0.377143	4.811859	0.349789	6	-3.066304	-2.074572	-2.397156
6	-0.118851	3.814320	2.247032	1	-2.849389	-1.289964	-4.384557
6	-1.198409	2.244185	-2.067932	1	-1.321082	-1.567194	-3.527327
1	0.032351	3.969316	-1.733183	1	-4.434696	0.454270	-3.235952
1	0.946694	2.483434	-1.961802	6	-6.143085	2.251647	-2.932883
1	0.199996	2.465930	3.904439	6	-4.842920	4.380597	-3.199515
1	1.084970	0.258420	3.731341	6	-5.257909	3.417104	-0.892991
1	1.449924	-0.453171	2.154973	1	1.155512	-4.097548	1.693458
6	-0.580497	-0.762427	2.833415	1	1.748763	-2.589695	2.437648
6	-0.410016	5.082826	3.077510	6	2.328440	-2.844315	0.348393
6	-1.159036	0.939313	-2.594752	1	-4.010303	-2.614009	2.904111
6	-2.432510	2.899151	-2.011992	1	-2.981273	-4.425476	1.529671
6	-0.817536	-1.895056	2.042708	1	-1.403623	-4.187054	0.788610
6	-1.603574	-0.361997	3.711112	6	-3.044310	-3.225972	-0.238571
6	0.623783	6.187163	2.723418	6	-3.558005	0.631186	5.611714
6	-0.326851	4.818115	4.598562	6	-4.323247	-1.757302	5.690407
6	-1.839259	5.600731	2.756409	6	-5.223991	-0.182732	3.920298
8	0.112711	0.305784	-2.629903	7	2.935346	1.237926	-3.182830
6	-2.323194	0.268056	-2.993347	1	2.432802	-0.850130	-3.046100
6	-3.621022	2.292487	-2.456421	1	2.729963	-0.215303	-4.676030
1	-2.458346	3.902255	-1.597241	6	-2.370443	-2.506453	-1.251191
8	0.135001	-2.349869	1.105022	6	-4.416946	-2.411313	-2.549025
6	-2.059925	-2.555507	2.033611	1	-7.059961	2.848664	-2.867053
1	-1.420608	0.508684	4.328347	1	-6.303838	1.329888	-2.362306
6	-2.840486	-1.018742	3.779859	1	-5.992544	1.985024	-3.985490
1	1.642336	5.849711	2.947192	1	-4.639964	4.161788	-4.254322
1	0.425998	7.097031	3.304476	1	-4.038688	5.024155	-2.827641
1	0.582878	6.449750	1.660869	1	-5.781588	4.945351	-3.140034
1	-1.061564	4.070078	4.918501	1	-6.199539	3.975811	-0.820101
1	-0.534206	5.744903	5.146060	1	-4.465086	4.030615	-0.452272
1	0.670000	4.470816	4.893819	1	-5.350193	2.505410	-0.292037
1	-1.950876	5.837991	1.692926	7	3.569556	-3.590749	0.572627
1	-2.055198	6.511082	3.330245	1	1.845387	-3.244903	-0.552925

1	-2.591093	4.845498	3.013135	1	2.487210	-1.766836	0.188810
6	0.802443	0.259077	-3.930088	6	-4.401609	-3.522259	-0.426506
6	-2.342467	-1.202573	-3.415047	1	-4.385212	0.897939	6.279487
6	-3.536734	0.976145	-2.929385	1	-3.327197	1.510176	4.998975
1	-2.685435	0.405227	6.235628	6	5.932517	4.617106	-0.870199
1	-4.658350	-2.637674	5.131820	1	4.297167	5.726607	-1.742594
1	-5.130044	-1.463414	6.373380	1	7.386894	-6.728865	0.885968
1	-3.454142	-2.049308	6.291276	6	8.493127	-4.903475	0.553204
1	-5.591130	-1.016982	3.313350	6	8.045804	-0.697178	-0.367215
1	-4.997680	0.650019	3.244931	1	9.335567	-2.950240	0.231384
1	-6.033298	0.127959	4.592770	1	7.385072	1.014149	0.757703
6	3.992983	1.138740	-2.453131	1	8.438047	1.383689	-0.638959
8	-1.026914	-2.208672	-1.228831	1	6.415758	5.492059	-0.447119
6	-5.116917	-3.142765	-1.575410	1	9.462725	-5.391373	0.552769
1	-4.921197	-2.088425	-3.453103	1	8.182212	-1.006506	-1.410132
6	4.683801	-2.959943	0.427075	1	8.999239	-0.804328	0.166364
1	-4.906235	-4.084355	0.354842	1	0.637587	0.390577	-1.021566
6	4.679897	2.331016	-1.935191	6	7.616258	0.749328	-0.280663
1	4.425579	0.172430	-2.174818	1	7.434020	3.278303	-0.121352
1	-0.559672	-2.283280	-0.352460	8	7.012690	-1.502351	0.257669
6	-6.605210	-3.528556	-1.719654	6	8.423197	-3.518280	0.366993
1	4.716448	-1.893120	0.183564				
6	5.985463	-3.630573	0.529657				
6	5.897234	2.220383	-1.222957				
6	4.129432	3.611652	-2.118917				
6	-7.421387	-2.903554	-0.554666				
6	-6.751935	-5.074536	-1.674460				
6	-7.212393	-3.029618	-3.051147				
6	6.085036	-5.019062	0.721659				
6	7.175374	-2.884343	0.373027				
8	6.439983	0.938383	-1.113268				
6	6.512168	3.357909	-0.682946				
6	4.743372	4.749127	-1.595593				
1	3.202351	3.680465	-2.675512				
1	-7.062144	-3.251173	0.419925				
1	-8.481300	-3.175071	-0.640491				
1	-7.343145	-1.810287	-0.571229				
1	-6.195783	-5.539859	-2.496404				
1	-7.807226	-5.361829	-1.766180				
1	-6.370854	-5.488104	-0.734578				
1	-7.171521	-1.936941	-3.129778				
1	-8.265296	-3.328799	-3.111155				
1	-6.693366	-3.457662	-3.916536				
1	5.161924	-5.575673	0.837259				
6	7.326446	-5.655755	0.740008				

(b) Cartesian coordinates of B3LYP/CEP-121G optimized structure of [HgL']

8	1.065374	-2.024810	-0.869578	1	-1.570109	-2.331013	1.825906
6	2.376990	-2.463673	-0.788249	6	-2.133856	-0.760938	3.238550
6	3.279600	-2.249086	-1.885686	1	3.218196	1.045331	4.631377
6	2.803424	-3.216276	0.358860	1	0.706753	1.899939	4.251386
6	4.546197	-2.882125	-1.857771	1	-0.104589	1.272294	2.800124
6	2.893804	-1.330448	-3.064420	6	1.612317	2.522446	2.389396
6	4.078603	-3.829410	0.339993	7	-1.499128	0.006680	-2.014743
6	1.905484	-3.313539	1.608415	1	-1.229272	2.086712	-2.102695
1	5.221266	-2.755615	-2.704055	1	-1.999199	1.416344	-3.572009
6	4.946436	-3.682646	-0.765165	6	1.365211	2.615394	0.977326
6	3.387398	0.123237	-2.878802	6	3.138487	4.303025	0.780852
1	3.338400	-1.735909	-3.984897	7	-2.438633	0.313290	2.275554
1	1.807348	-1.342616	-3.177610	1	-3.030338	-1.334389	3.551864
1	4.392152	-4.431681	1.192827	1	-1.697516	-0.292599	4.132026
1	2.104884	-4.268955	2.114932	6	2.580654	3.378466	2.966884
1	0.859333	-3.303041	1.294521	6	-2.671875	-0.556035	-2.064077
6	2.176218	-2.157125	2.597879	8	0.285474	1.949641	0.413932
6	2.512771	1.180063	-2.503133	6	3.333050	4.278440	2.179353
6	4.766324	0.438578	-2.978653	1	3.732721	4.980183	0.167100
6	1.304978	-1.037788	2.723896	6	-3.655113	0.520210	1.870175
6	3.387916	-2.119137	3.331359	1	2.741187	3.348254	4.044484
8	1.119702	0.897291	-2.387898	6	-2.971334	-1.853369	-1.404361
6	2.968121	2.455148	-2.065741	6	-3.967390	1.632492	0.931092
6	5.242962	1.729485	-2.663402	6	-4.308317	-2.167131	-1.010903
1	5.468113	-0.336050	-3.279574	6	-1.956485	-2.826484	-1.203915
8	0.047019	-1.075629	2.040470	6	-2.960286	2.570324	0.566312
6	1.678939	0.166636	3.384469	6	-5.272137	1.795770	0.387144
1	4.072235	-2.962666	3.270710	8	-5.257585	-1.140112	-1.181012
6	3.733504	-0.990423	4.104623	6	-4.625768	-3.433828	-0.468266
6	0.162848	1.158049	-3.471754	6	-2.265981	-4.085981	-0.645313
6	2.029662	3.472245	-1.378252	1	-0.928991	-2.598089	-1.477377
6	4.355820	2.717308	-2.182687	1	-1.950285	2.421834	0.939938
6	-1.112688	-1.763813	2.643638	6	-3.256194	3.648610	-0.290760
6	2.904331	0.150947	4.098780	8	-6.280361	0.865357	0.761997
6	0.869311	1.478630	3.248147	6	-5.579134	2.886256	-0.459506
6	-1.229525	1.240693	-2.801334	6	-6.556825	-1.228351	-0.499074
1	0.212326	0.340393	-4.204908	1	-5.645652	-3.683240	-0.192877
1	0.404640	2.109558	-3.966668	6	-3.598707	-4.390824	-0.290333
6	2.176396	3.472105	0.157609	1	-1.476002	-4.819027	-0.506389
1	2.267772	4.477488	-1.754528	1	-2.474113	4.358036	-0.549893

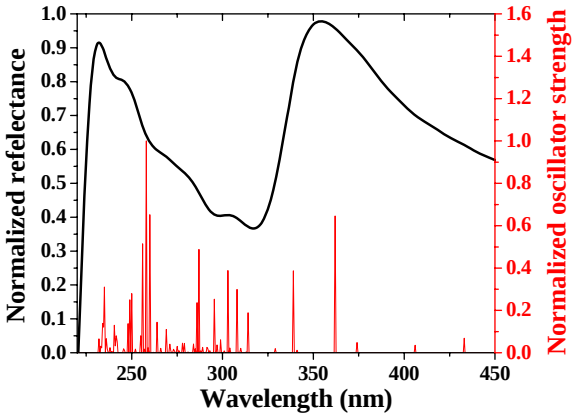
1	0.990347	3.249524	-1.629526	6	-4.569166	3.813674	-0.796795
1	4.742405	3.685786	-1.871946	6	-7.061232	0.204120	-0.299950
1	-0.762089	-2.456257	3.421223	1	-6.593476	3.018037	-0.828175
1	-6.440705	-1.710493	0.479810				
1	-7.260891	-1.807849	-1.116504				
1	-3.847917	-5.366644	0.121813				
1	-4.809103	4.658363	-1.439866				
1	-6.996672	0.765243	-1.239581				
1	-8.101502	0.182626	0.046058				
1	4.060478	4.940372	2.644874				
1	4.662784	-0.983370	4.670794				
1	5.916044	-4.176362	-0.771979				
1	6.304185	1.952173	-2.754562				
80	0.385320	-0.087738	-0.238791				
1	-4.503519	-0.092191	2.209874				
1	-3.494362	-0.098623	-2.630392				

(c). Dihedral angles(°) of the arms obtained upon optimization for L' and its Hg^{2+} complex.

	L (Crystal structure)	**L'**	[**HgL'**]
O2-C29-C31-N1	168.3	174.8	55.1
C29-C31-N1-C30	130.9	129.8	137.4
C31-N1-C30-C32	173.2	175.4	-174.3
N1-C30-C32-C37	169.0	179.4	-154.4
C30-C32-C37-O5	-6.4	-6.1	5.4
C32-C37-O5-C38	150.8	157.9	164.2
C37-O5-C38-C39	-164.8	177.2	-153.4
O5-C38-C39-O6	62.5	66.8	73.1
C38-C39-O6-C40	169.2	177.7	-102.7
C39-O6-C40-C45	179.1	173.9	128.6
O6-C40-C45-C46	-5.9	-3.7	0.04
C40-C45-C46-N2	160.9	175.0	-174.3
C45-C46-N2-C47	179.1	-179.1	-178.1
C46-N2-C47-C48	-141.4	-152.9	-121.4
N2-C47-C48-O4	78.2	73.8	-48.3

S11: TDDFT data

Normalized reflectance spectrum and TDDFT singlet mono electronic transitions calculated for isolated mercury complex [**HgL'**].



(b). Calculated energy levels of the main singlet transitions of L

State	Assignment	coefficient	Energy (eV)	Wavelength	Oscillator strength
S9	HOMO-13 -> LUMO HOMO-12 -> LUMO	31% 10%	4.259	291.5	0.0148
S10	HOMO-6 -> LUMO HOMO-13 -> LUMO HOMO-11 -> LUMO HOMO-11 -> LUMO+5	46% 3% 9% 3%	4.279	290.0	0.0634
S12	HOMO-3 -> LUMO HOMO-3 -> LUMO+1 HOMO-13 -> LUMO+1	16% 47% 3%	4.304	288.4	0.0111
S13	HOMO-7 -> LUMO+1 HOMO-6 -> LUMO+1 HOMO-12 -> LUMO+1 HOMO-4 -> LUMO+1 HOMO-3 -> LUMO+1	15% 37% 4% 8% 2%	4.362	284.5	0.1511
S14	HOMO-13 -> LUMO HOMO-5 -> LUMO	14% 49%	4.368	284.2	0.0237
S15	HOMO -> LUMO+2	83%	4.381	283.2	0.0603
S16	HOMO-4 -> LUMO+1 HOMO-3 -> LUMO+1	70% 9%	4.388	282.8	0.0286
S19	HOMO-6 -> LUMO+1 HOMO-7 -> LUMO HOMO-5 -> LUMO+1	44% 3% 9%	4.470	277.7	0.0217
S26	HOMO-1 -> LUMO+4	84%	4.664	266.1	0.016

S28	HOMO -> LUMO+7	64%	4.737	262.1	0.0122
S30	HOMO-1 -> LUMO+6 HOMO -> LUMO+7 HOMO-1 -> LUMO+4	52% 25% 2%	4.764	260.5	0.0175
S34	HOMO-11 -> LUMO HOMO-1 -> LUMO+5	21% 36%	4.939	251.3	0.0675
S35	HOMO-11 -> LUMO HOMO -> LUMO+5	39% 12%	4.945	251.0	0.112
S36	HOMO-10 -> LUMO	89%	4.959	250.3	0.0147

(c) Calculated energy levels of the main singlet transitions of [HgL']

State	Assignment	coefficient	Energy (eV)	Wavelength	Oscillator strength
S5	HOMO -> LUMO+2	89%	3.429	362.0	0.0892
S7	HOMO-1 -> LUMO+2	90%	3.666	338.6	0.0534
S10	HOMO-5 -> LUMO	69%	3.951	314.1	0.0262
S14	HOMO -> LUMO+4 HOMO-6 -> LUMO	88% 3%	4.035	307.6	0.0411
S16	HOMO-10 -> LUMO HOMO -9 -> LUMO HOMO-4 -> LUMO+1	56% 5% 3%	4.102	302.6	0.0535
S21	HOMO-11 -> LUMO HOMO-14 -> LUMO HOMO-9 -> LUMO HOMO-8 -> LUMO	70% 2% 2% 8%	4.199	295.6	0.0347
S30	HOMO-13 -> LUMO HOMO-5 -> LUMO+1 HOMO-12 -> LUMO+1	45% 29% 3%	4.347	285.5	0.0326

S12: Gaussian 03 reference

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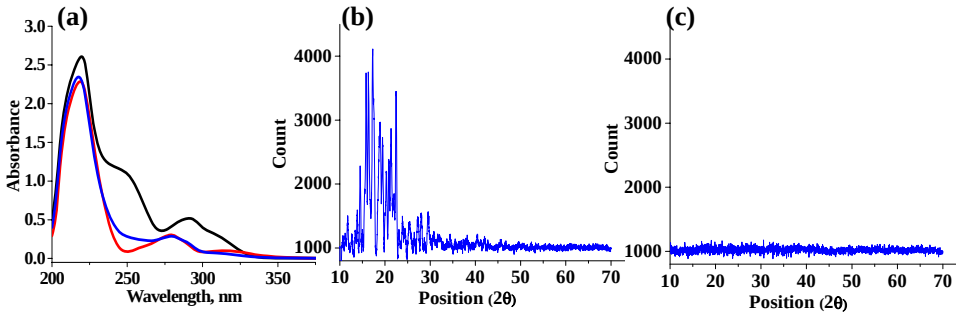
S13: Absorption spectral traces and powder X-ray diffractrograms of **L** and [**HgL**]



(a) Absorption spectral trace for L (—), the *in situ* prepared mercury complex (—) and Isolated mercury complex (—). Powder X-ray diffractograms for: (b) **L** and (c) Isolated mercury complex.