Supporting Information

A new fluorescent probe for Al^{3+} based on rhodamine 6G and its application to bioimaging

Yan Fu,[a] Xiu-Juan Jiang,[a] Yan-Yan Zhu,[a] Bing-Jiang Zhou,[b] Shuang-Quan Zang,[a]* Ming-Sheng Tang,[a] Hong-Yan Zhang,[b]* Thomas C.W. Mak[a,c]

[a] *College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, 450001, P. R. China*

[b] *Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, China*

[c] *Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, People's Republic of China*

Author for correspondence: Dr. S.-Q. Zang, E-mail: zangsqzg@zzu.edu.cn.

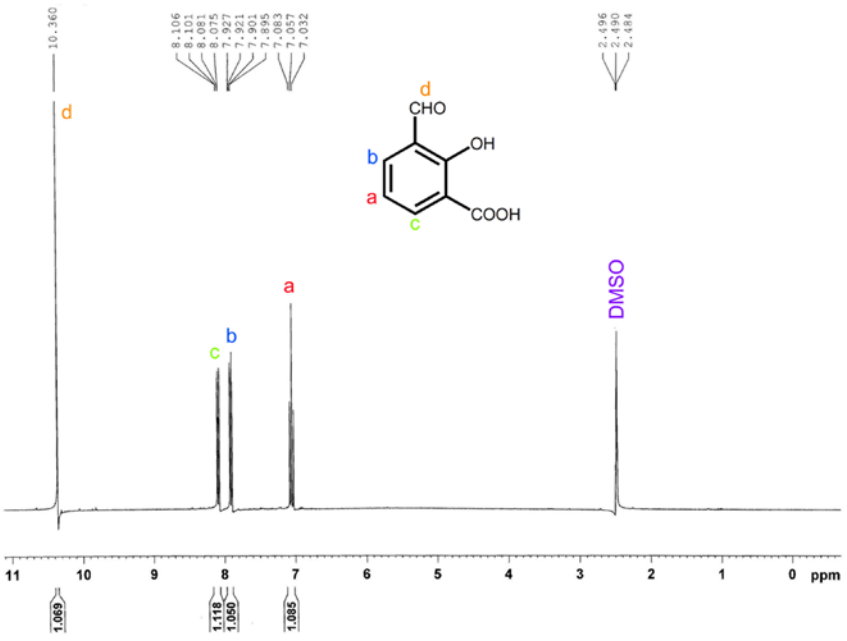

Fig. S1. ^{1}H NMR spectrum of 3-formyl-2-hydroxy benzoic acid in DMSO-d_6.

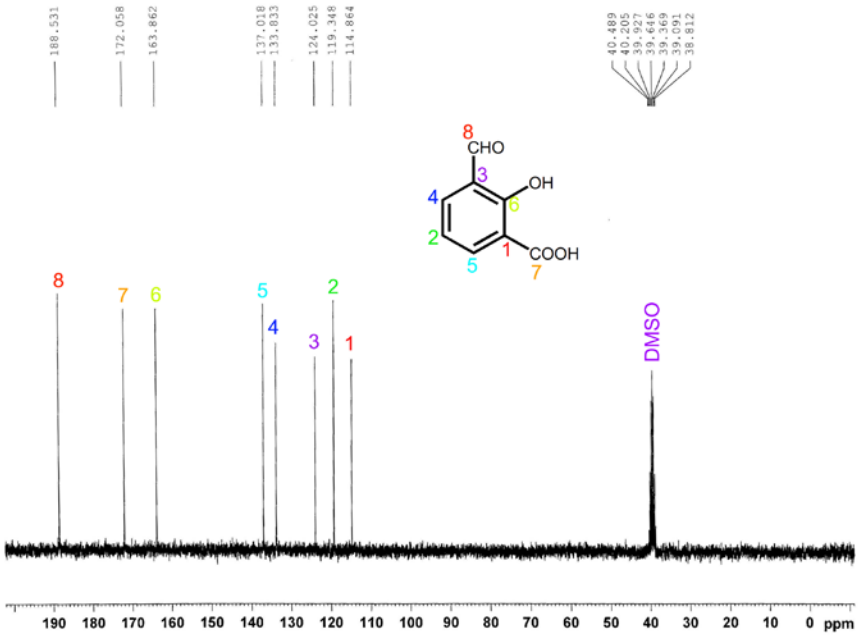

Fig. S2. ^{13}C NMR spectrum of 3-formyl-2-hydroxy benzoic acid in DMSO-d_6.

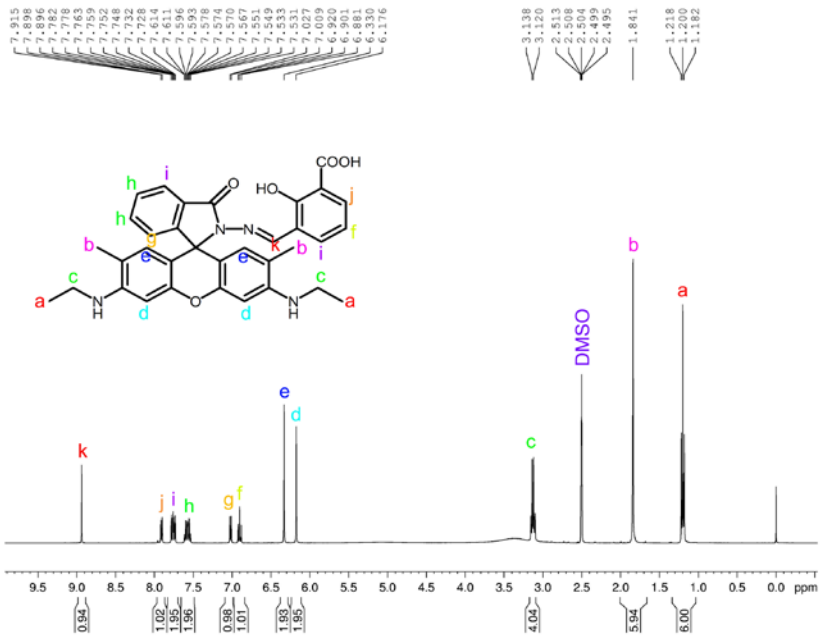

Fig. S3. ^{1}H NMR spectrum of **HL** in DMSO-d_6.

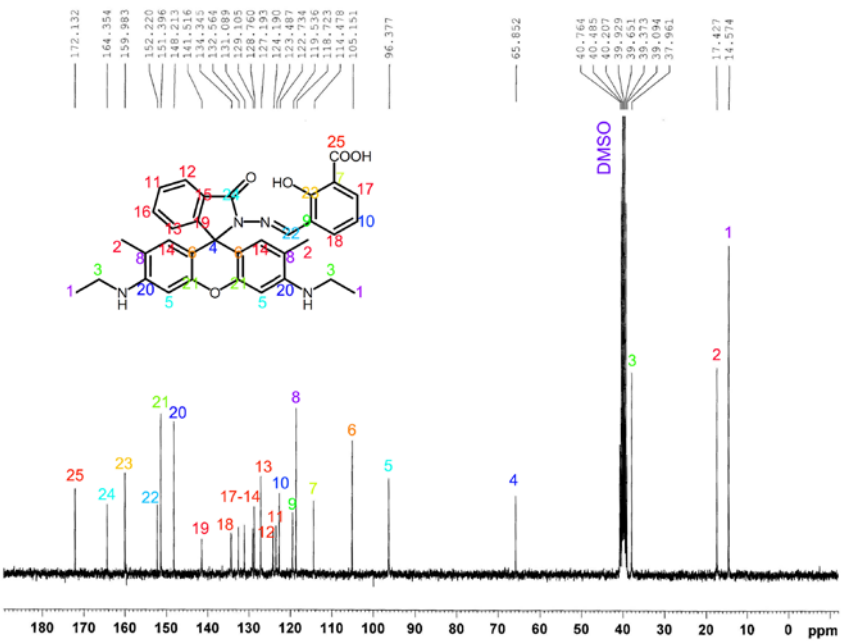

Fig. S4. ^{13}C NMR spectrum of **HL** in DMSO-d_6.

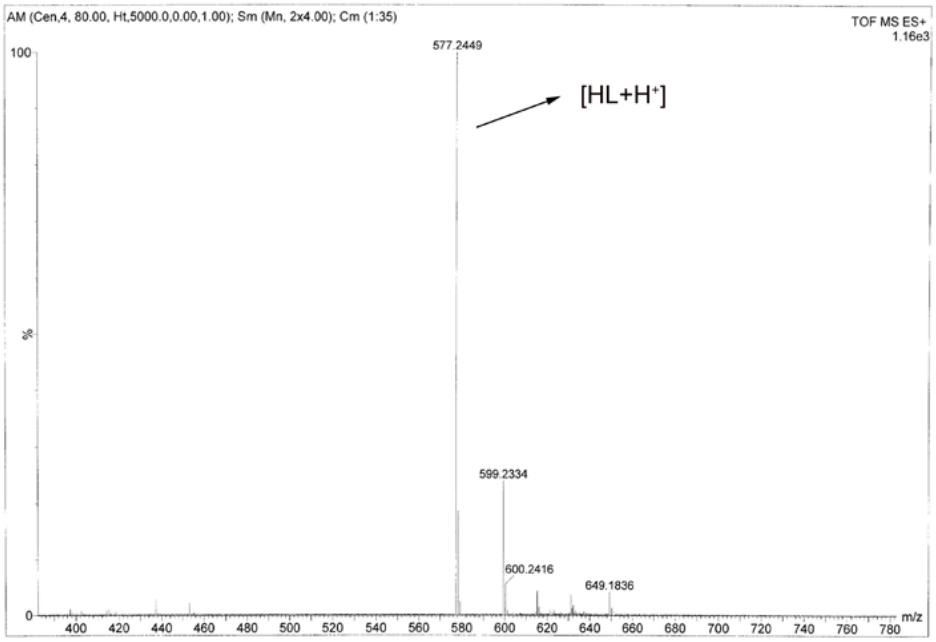

Fig. S5. HR-MS spectrum of **HL** in MeOH

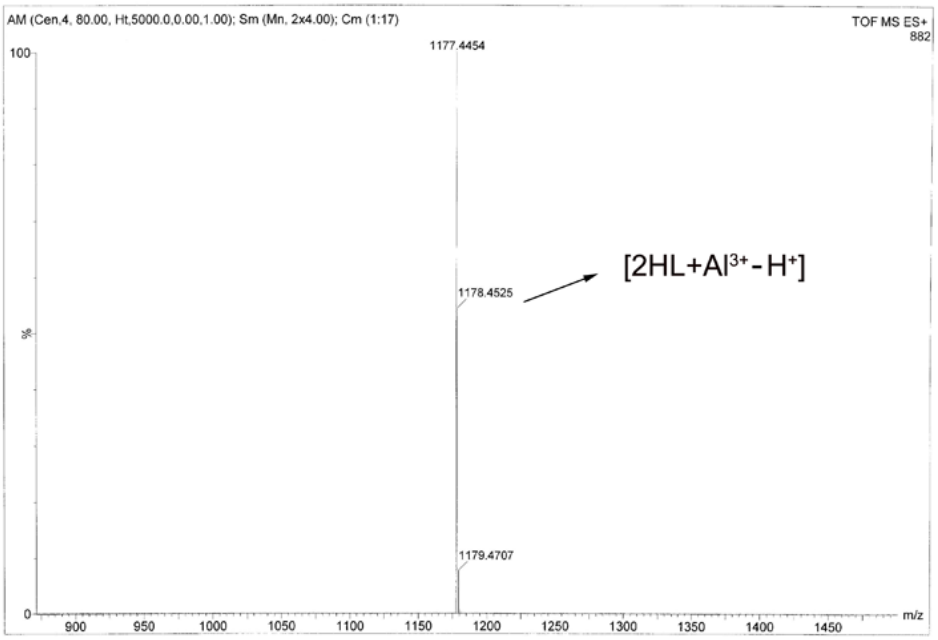

Fig. S6. HR-MS spectrum of **HL** with the addition of $AlCl_3$ (1 equiv) in MeOH.

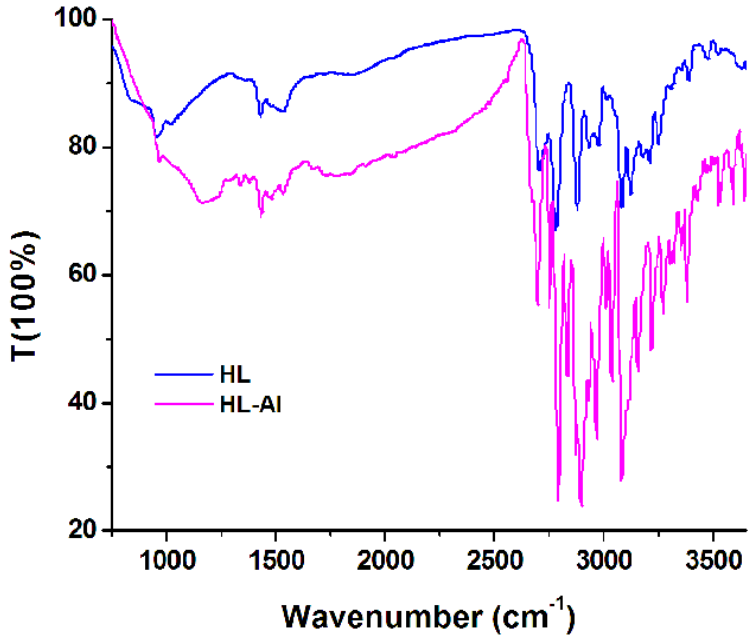

Fig. S7. FT-IR spectra of **HL** and **HL-Al** complex.

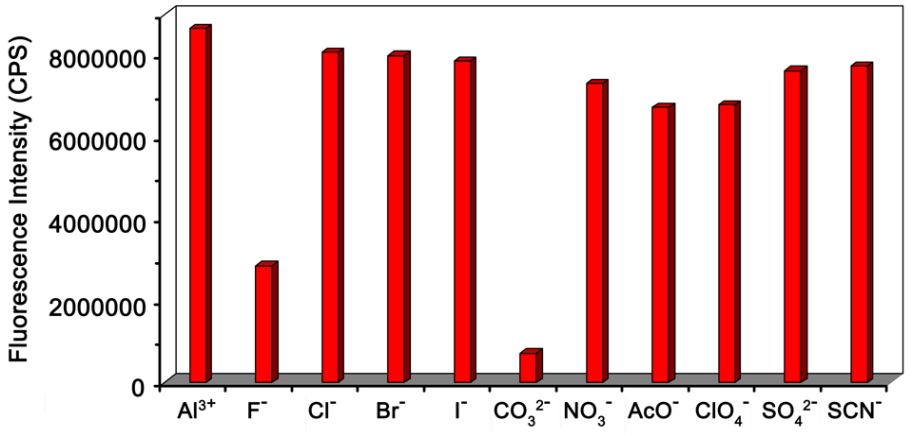

Fig. S8. Anion interference study of **L** for Al^{3+}. Fluorescence intensity of **L** (5 μM) at 556 nm in various mixtures of the sodium salt of anions (50 μM) with Al^{3+} (50 μM) in H_2O-EtOH (4:1, v/v).

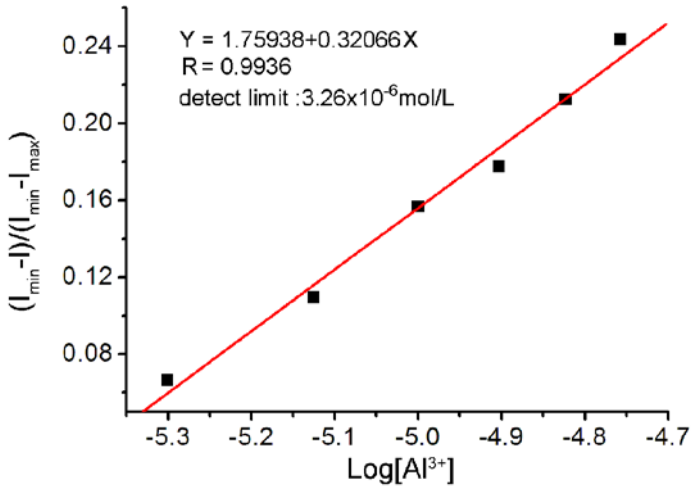

Fig. S9. Emission (556 nm) of **L (**5 μM**)** at different concentrations of Al^{3+} (0.5, 1, 1.5, 2, 2.5, 3 equiv) added, normalized between the minimum emission (0 equiv Al^{3+}) and the maximum emission (3 equiv Al^{3+}). The detection limit for Al^{3+} was determined to be 3.26×10^{-6} M.

Y = A + B * X

Parameter	Value	Error
A	1.75938	0.09117
B	0.32066	0.01828

R	SD	N	P
0.99357	0.00827	6	<0.0001

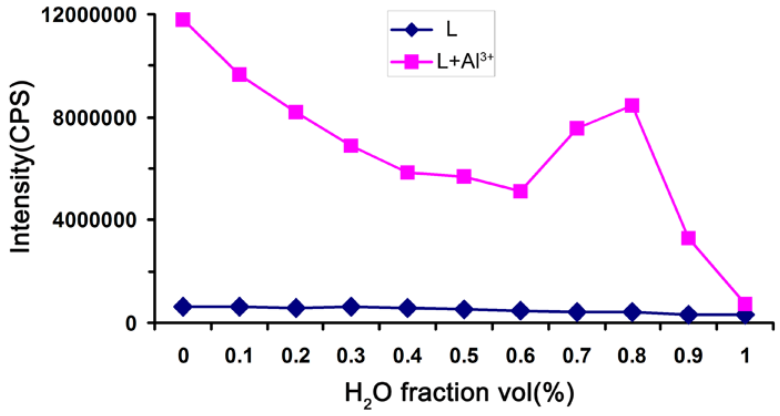

Fig. S10. Plot of fluorescence intensity of **L**, **L-Al** at 556 nm in H_2O/EtOH mixtures. Excitation wavelength: 500 nm.

Table S1. Crystallographic data and structure refinement parameters for **HL**, **HL-Al** and **HL-Cd**.

	HL	**HL-Al**	**HL-Cd**
Empirical formula	$C_{34}H_{32}N_4O_5$	$C_{68}H_{66}AlClN_8O_{12}$	$C_{71}H_{71}CdN_9O_{12}$
Formula weight	576.64	1249.72	1354.77
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	Cc	$P\bar{1}$
a (Å)	14.9309(19)	23.791(3)	9.6254(6)
b (Å)	9.0628(10)	18.3258(18)	17.1742(12)
c (Å)	27.435(6)	15.0315(14)	22.7259(19)
α / deg	90	90	102.047(7)
β / deg	94.605(14)	102.654(11)	98.682(6)
γ / deg	90	90	106.138(6)
V / Å^3	3700.4(10)	6394.4(12)	3440.9(4)
Z	4	4	2
Density (calcd) (Mg m^{-3})	1.035	1.298	1.308
Abs coeff (mm^{-1})	0.070	0.142	0.384

F (000)	1216	2624	1408
Crystal size (mm^3)	0.3 × 0.16× 0.16	0.20 × 0.18 × 0.16	0.28 × 0.18 × 0.18
Reflections	13189	14894	12796
Independent	6850 [R(int) = 0.0805	9645 [R(int) = 0.0836	12796 [R(int) = 0.0000
Data / restraints / parameters	6850 / 3 / 376	9645 / 229 / 844	12796 / 35 / 863
GOF on F^2	1.001	1.016	0.801
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0916, wR2 = 0.2024	R1 = 0.0907, wR2 = 0.1660	R1 = 0.0648, wR2 = 0.0863
R indices (all data)	R1 = 0.2091, wR2 = 0.2346	R1 = 0.2029, wR2 = 0.2250	R1 = 0.1607, wR2 = 0.1102
Largest diff peak and hole (e $Å^{-3}$)	0.400 and -0.229	0.575 and -0.254	0.594 and -0.500

Table S2. Selected bond lengths (Å) and angles [deg] for **HL**.

HL			
C(1)-O(2)	1.232(6)	N(1)-C(8)-C(4)	120.2(4)
C(1)-O(1)	1.304(6)	O(5)-C(9)-N(2)	125.4(5)
C(3)-O(3)	1.349(5)	O(5)-C(9)-C(10)	129.3(5)
C(8)-N(1)	1.289(5)	N(2)-C(9)-C(10)	105.2(4)
C(9)-O(5)	1.221(5)	C(17)-C(18)-N(4)	121.6(6)
C(9)-N(2)	1.394(6)	N(4)-C(18)-C(19)	120.2(6)
C(18)-N(4)	1.371(7)	C(21)-C(20)-O(4)	124.3(4)
C(20)-O(4)	1.397(5)	O(4)-C(20)-C(19)	113.3(5)
C(23)-N(4)	1.461(8)	C(24)-C(23)-N(4)	110.3(9)
C(25)-O(4)	1.387(5)	C(30)-C(25)-O(4)	124.3(4)
C(27)-N(3)	1.409(6)	C(26)-C(27)-N(3)	121.0(5)
C(31)-N(2)	1.496(5)	N(3)-C(27)-C(28)	118.6(5)
C(33)-N(3)	1.432(6)	N(2)-C(31)-C(30)	111.3(4)
N(1)-N(2)	1.387(5)	N(2)-C(31)-C(11)	98.8(4)
O(2)-C(1)-O(1)	120.7(6)	N(3)-C(33)-C(34)	110.2(6)
O(2)-C(1)-C(2)	123.0(6)	C(8)-N(1)-N(2)	118.9(4)
O(1)-C(1)-C(2)	116.3(6)	N(1)-N(2)-C(9)	116.1(4)
O(3)-C(3)-C(4)	116.1(5)	N(1)-N(2)-C(31)	128.0(4)
O(3)-C(3)-C(2)	122.7(5)	C(9)-N(2)-C(31)	115.8(4)
C(27)-N(3)-C(33)	123.4(5)	C(18)-N(4)-C(23)	125.8(6)
C(25)-O(4)-C(20)	116.3(4)		

Table S3. Selected bond lengths (Å) and angles [deg] for **HL-Al**.

HL-Al			
Al(1)-O(5)	1.855(6)	O(8)-Al(1)-O(10)	168.8(3)
Al(1)-O(3)	1.866(6)	O(5)-Al(1)-N(1)	79.4(3)
Al(1)-O(8)	1.874(6)	O(3)-Al(1)-N(1)	89.5(3)
Al(1)-O(10)	1.889(6)	O(8)-Al(1)-N(1)	96.1(3)
Al(1)-N(1)	1.975(7)	O(10)-Al(1)-N(1)	95.1(3)
Al(1)-N(5)	1.986(7)	O(5)-Al(1)-N(5)	94.7(3)
O(5)-Al(1)-O(3)	168.8(3)	O(3)-Al(1)-N(5)	96.2(3)
O(5)-Al(1)-O(8)	91.4(3)	O(8)-Al(1)-N(5)	89.3(3)
O(3)-Al(1)-O(8)	91.6(3)	O(10)-Al(1)-N(5)	79.4(3)
O(5)-Al(1)-O(10)	89.7(3)	N(1)-Al(1)-N(5)	172.0(3)
O(3)-Al(1)-O(10)	89.5(3)		

Table S4. Selected bond lengths (Å) and angles [deg] for **HL-Cd**.

HL-Cd			
Cd(1)-O(8)	2.242(4)	O(8)-Cd(1)-O(10)	146.22(12)
Cd(1)-O(11)	2.282(4)	O(11)-Cd(1)-O(10)	84.01(15)
Cd(1)-O(1)	2.333(4)	O(1)-Cd(1)-O(10)	75.85(15)
Cd(1)-O(1W)	2.339(3)	O(1W)-Cd(1)-O(10)	90.33(14)
Cd(1)-O(10)	2.391(4)	O(8)-Cd(1)-N(5)	77.67(14)
Cd(1)-N(5)	2.415(4)	O(11)-Cd(1)-N(5)	91.18(14)
Cd(1)-O(2)	2.459(4)	O(1)-Cd(1)-N(5)	143.35(16)
Cd(1)-C(1)	2.741(6)	O(1W)-Cd(1)-N(5)	85.23(14)
O(8)-Cd(1)-O(11)	92.60(15)	O(10)-Cd(1)-N(5)	68.83(13)
O(8)-Cd(1)-O(1)	137.90(15)	O(8)-Cd(1)-O(2)	83.74(14)
O(11)-Cd(1)-O(1)	94.66(15)	O(11)-Cd(1)-O(2)	101.70(15)
O(8)-Cd(1)-O(1W)	91.19(14)	O(1)-Cd(1)-O(2)	54.18(15)
O(11)-Cd(1)-O(1W)	174.11(17)	O(1W)-Cd(1)-O(2)	83.19(14)
O(1)-Cd(1)-O(1W)	85.52(14)	O(10)-Cd(1)-O(2)	129.91(13)
N(5)-Cd(1)-O(2)	157.84(14)	O(8)-Cd(1)-C(1)	111.11(18)

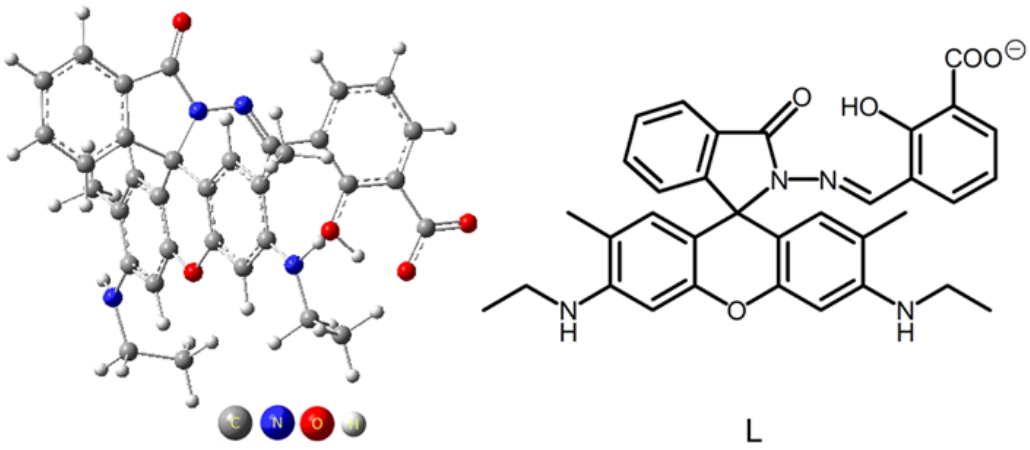

Fig. S11. DFT optimized structure and the schematic representation of **L**, the calculations were carried out with basis set 6-31+G** for C, N, O, and H atoms.

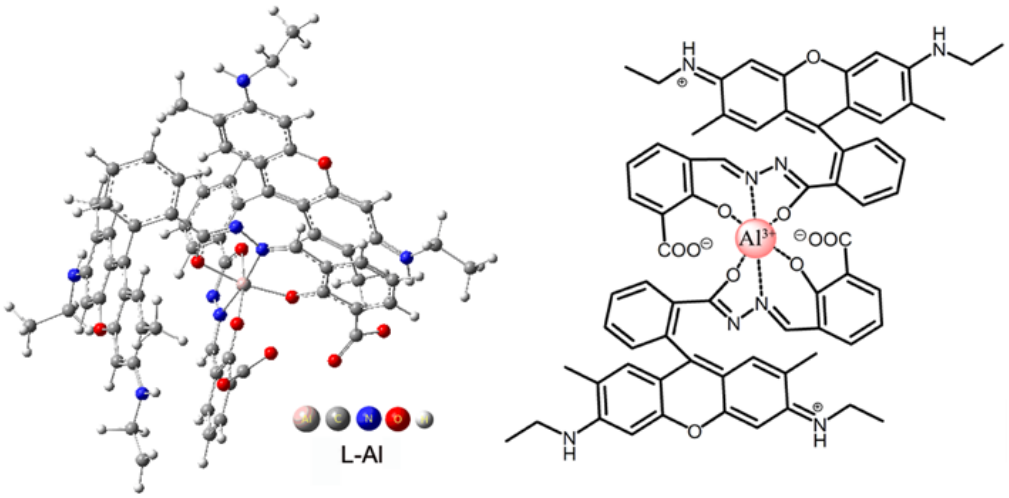

Fig. S12. DFT optimized structure and the schematic representation of **L-Al**, the calculations were carried out with basis set 6-31+G** for C, N, O, H and Al atoms.

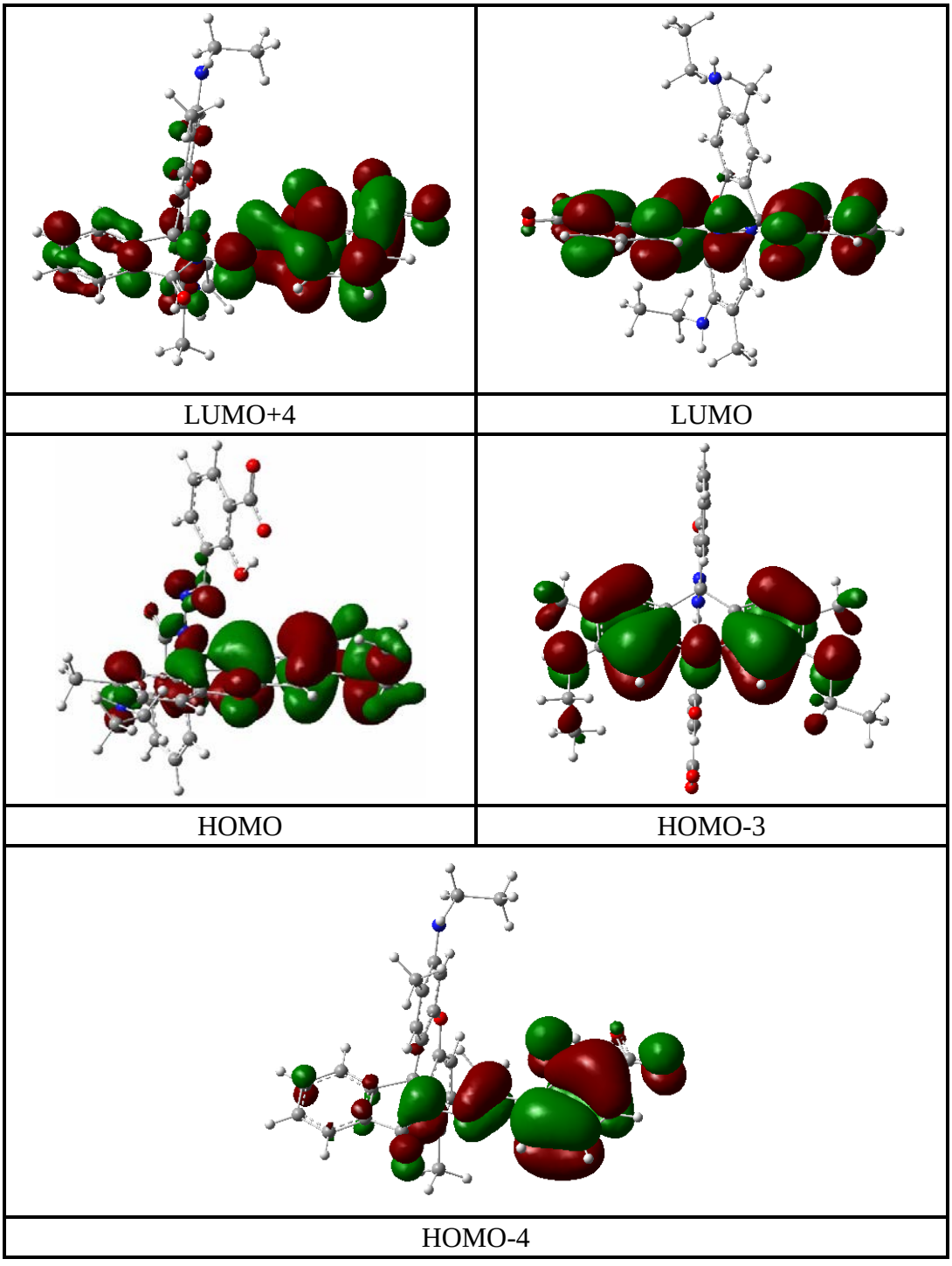

Fig. S13. Frontier molecular orbitals of **L**.

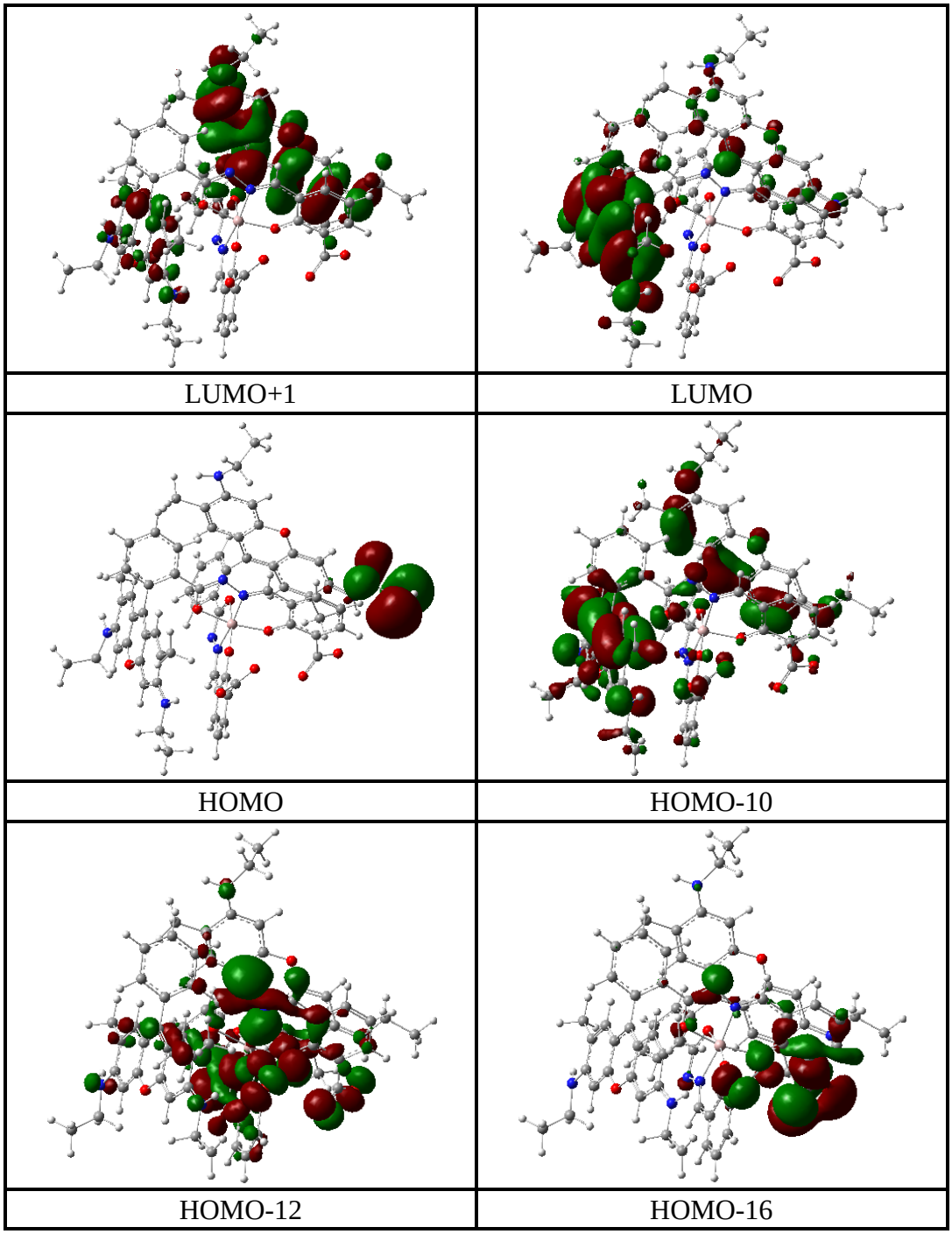

Fig. S14. Frontier molecular orbitals of **L-Al**.

Table S5. The contribution of electronic transitions of **L** and **L-Al**.

electronic transition	**L** oscillator strength (f)	electronic transition	**L-Al** oscillator strength (f)
HOMO→LUMO (98%)	0.4637	HOMO-10→LUMO+1 (54%)	0.2929
HOMO-4→LUMO (92%)	0.2841	HOMO-12→LUMO (27%)	0.2529
HOMO-3→LUMO+4 (75%)	0.6551	HOMO-16→LUMO (45%)	0.1488
HOMO-4→LUMO+4 (55%)	0.3212		