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Supplementary Materials

A highly selective and sensitive fluorescent turn-on Al^{3+} chemosensor in aqueous media and living cells: Experimental and theoretical studies

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The method of determination of association constant (*K*). Based on the literatures,[1,2] the association constant (*K*) of sensor **1** (L) with Co^{2+} or Cu^{2+} (M) can be expressed by the following equations, where (L) and (M) are assumed to form a complex with a complexation ratio of m:n.

$$[M]^m = \frac{1}{nK[L]_T^{n-1}} \frac{1-\alpha}{\alpha^n}, \quad \alpha = \frac{[L]}{[L]_T}$$

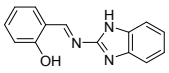
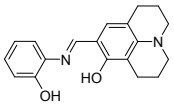
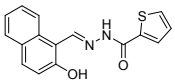
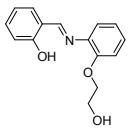
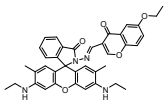
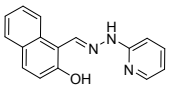
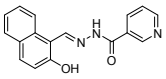
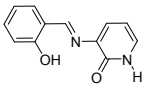
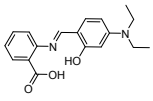
α is defined as the ratio between the free ligand concentration [L] and the initial concentration of ligand $[L]_T$.

References

[1] G. Grynkiewicz, M. Poenie, R. Y. Tsien, *J. Biol. Chem.*, 1985, **260**, 3440.

[2] C.-Y. Li, X.-B. Zhang, Y.-Y. Dong, Q.-J. Ma, Z.-X. Han, Y. Zhao, G.-L. Shen, R.-Q. Yu, *Anal. Chim. Acta*, 2008, **616**, 214.

Table S1. Examples for the detection of Al^{3+} by organic chemosensors.

Sensor	Analyte	Solvent	Method	Detection limit (Zn^{2+})	Reference
	Al^{3+} and Zn^{2+}	MeOH	Fluorescnce	1.2 x 10^8	25
	Al^{3+} and Zn^{2+}	Bis-tris buffer	Fluorescnce	1.0 x 10^7	26
	Al^{3+}	EtOH:H_2O = 1 : 4 (v/v)	Fluorescnce	7.1 x 10^6	27
	Al^{3+}	EtOH:H_2O = 95 : 5 (v/v)	Fluorescnce	3.1 x 10^6	28
	Al^{3+} and Zn^{2+}	CH_3CN:H_2O = 9 : 1 (v/v)	Fluoresence/colorimietry	9.0 x 10^4	30
	Al^{3+}	EtOH:H_2O = 1 : 9 (v/v)	Fluorescnce	4.9 x 10^4	80
	Al^{3+} and Zn^{2+}	Bis-tris buffer	Fluoresence/colorimietry	4.0 x 10^3	81
	Al^{3+}	DMSO	Fluorescnce	5.3 x 10^4	82
	Al^{3+}	Bis-tris buffer:MeOH = 1:1 (v/v)	Fluorescnce	3.1 x 10^8	This work

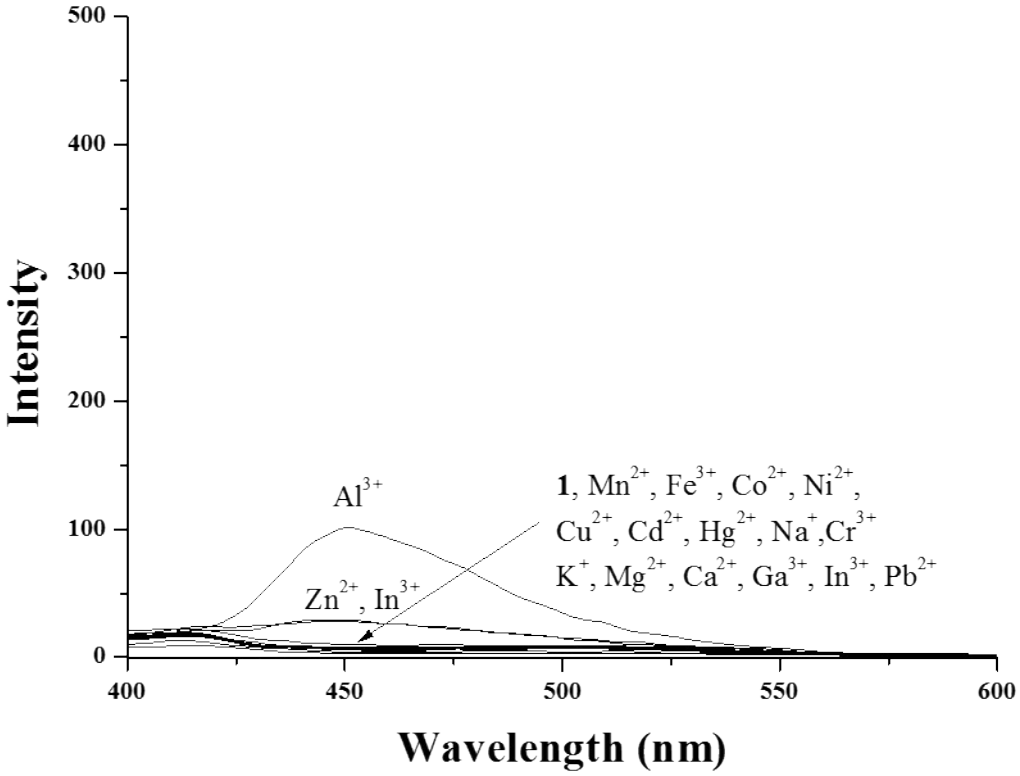


Fig. S1. Fluorescence spectra of sensor **1** (10 μM) upon addition of metal nitrate salts (20 equiv) of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Pb^{2+} and Cr^{3+} with an excitation of 410 nm in bis-tris buffer (10 mM, pH 7.0).

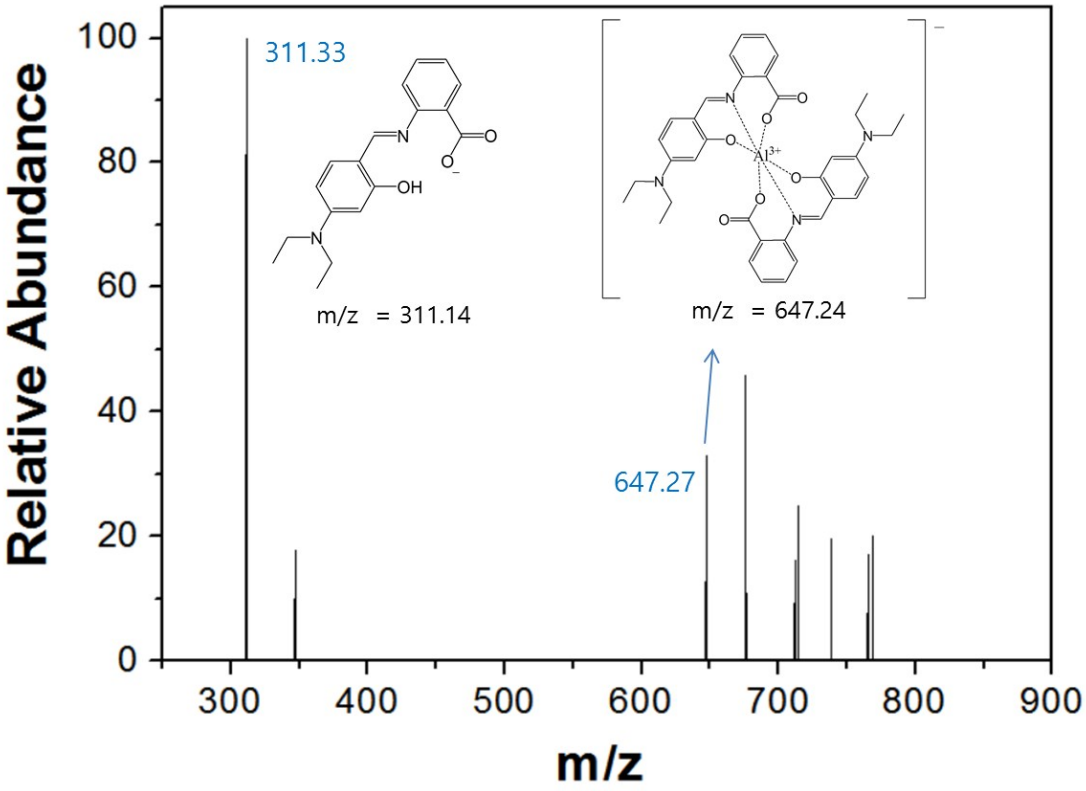


Fig. S2. Negative-ion electrospray ionization mass spectrum of **1** upon addition of 0.5 equiv of Al^{3+}.

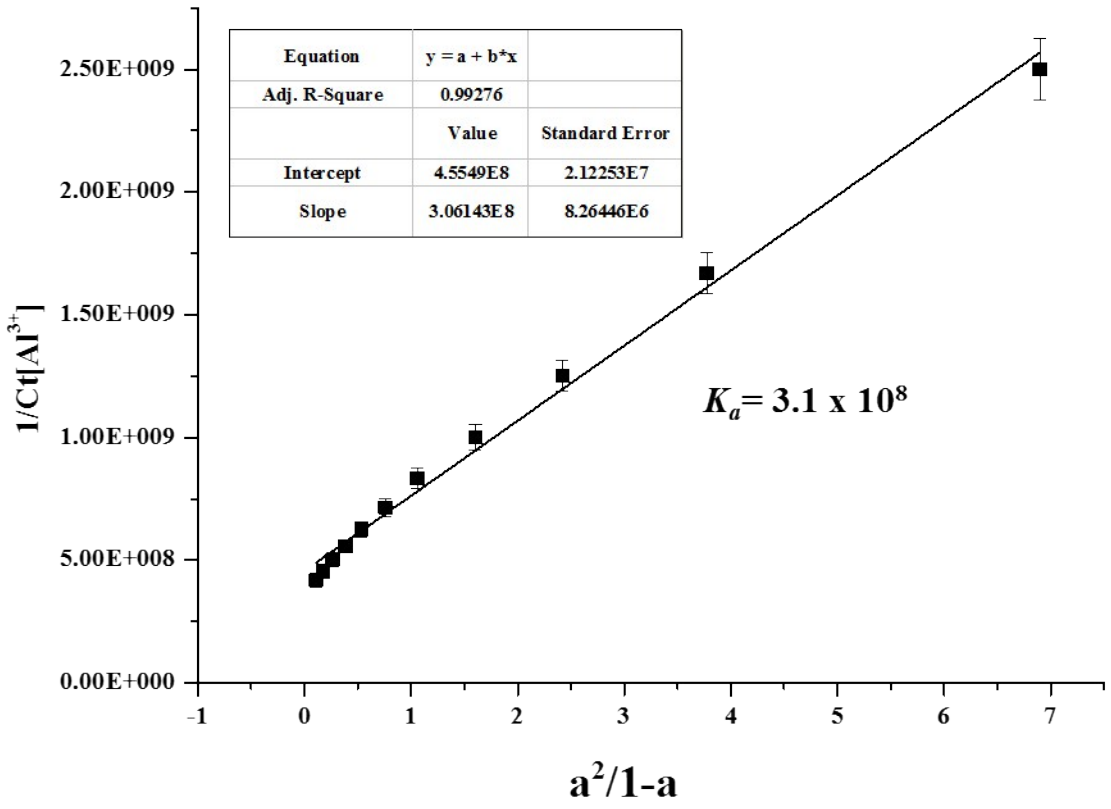


Fig. S3. Association constant (K_a) of **1** (10 μM) for Al^{3+} through fluorescent intensity, assuming 2:1 stoichiometry for association between **1** and Al^{3+} (λ_{ex}=410 nm and λ_{em}=460 nm).

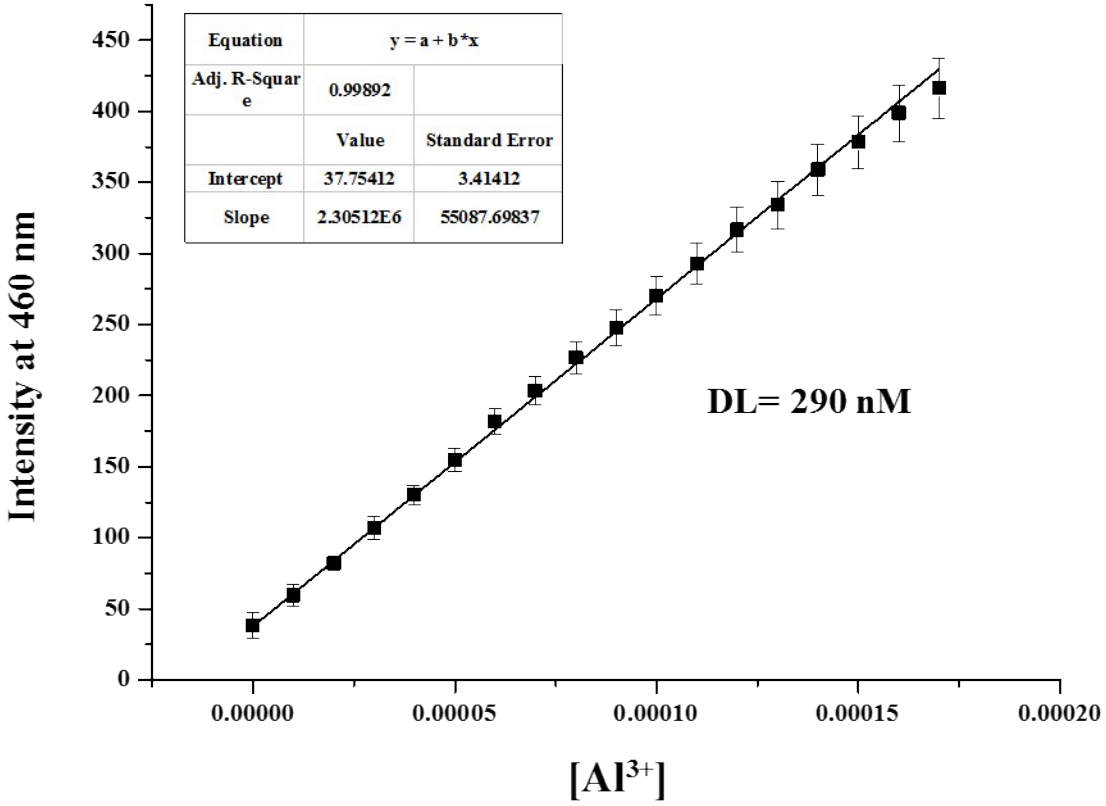
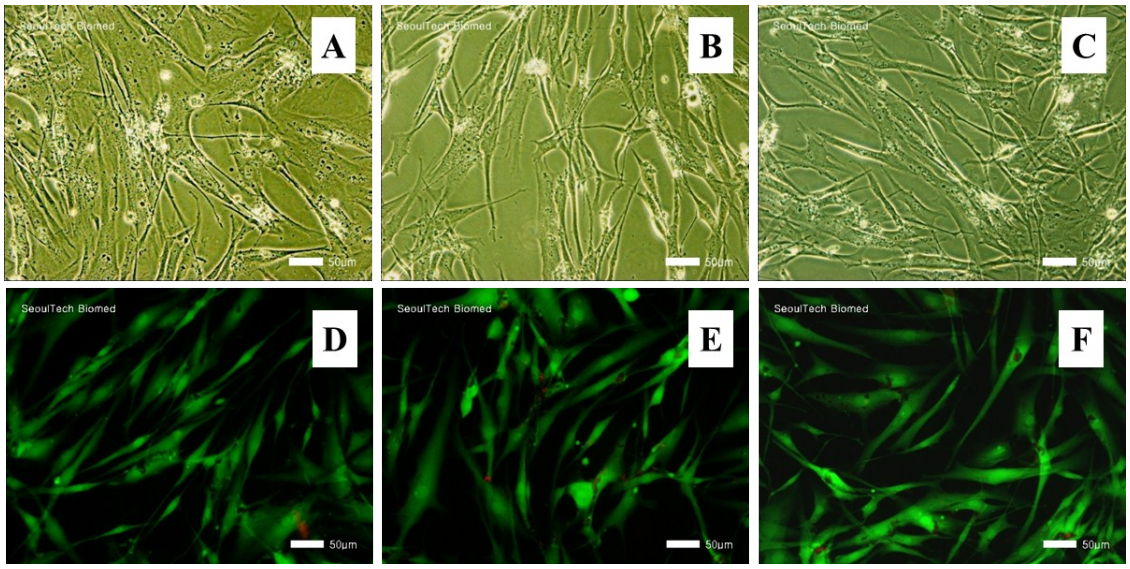


Fig. S4. Detection limit (DL) of **1** (10 μM) for Al^{3+} through fluorescent intensity (λ_{ex}=410 nm and λ_{em}=460 nm).

(a)



(b)

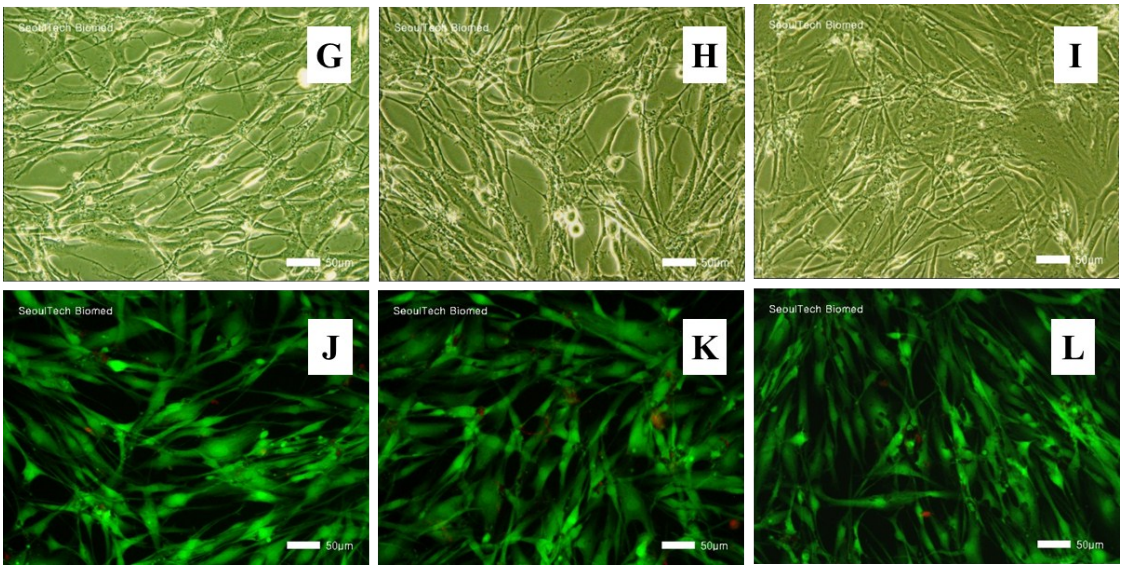
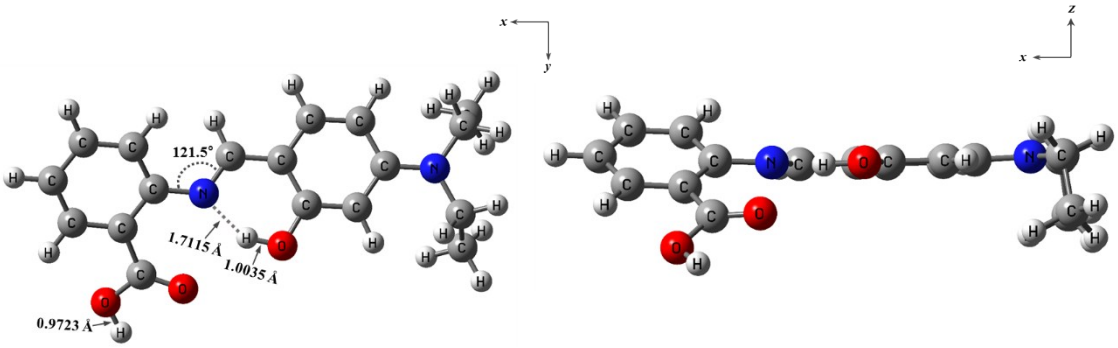


Fig. S5. Images of Live/Dead assays using fibroblasts with (a) **1** and (b) **1**-Al^{3+} complex, respectively. The cells were incubated with **1** (10 μM) or **1**-Al^{3+} complex (**1**: 10 μM, $Al(NO_3)_3$: 150 μM) for 1 h (A, D, G and J), 12 h (B, E, H and K) and 24 h (C, F, I and

L). Green color represents cells alive and red color for dead cells.

(a)



(b)

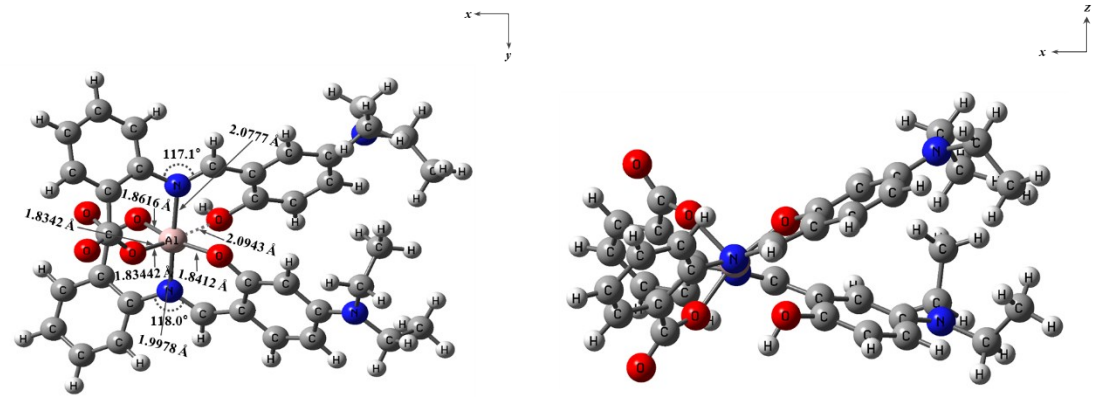
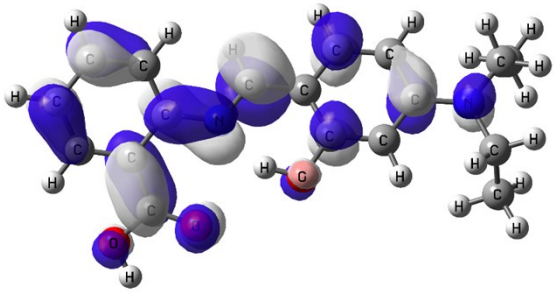
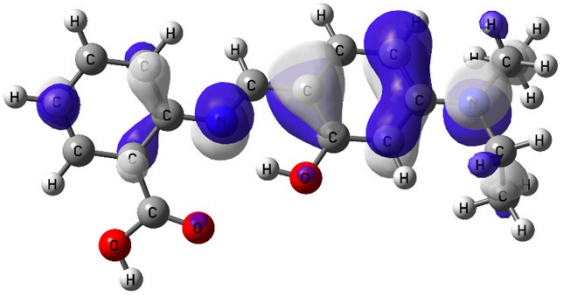


Fig. S6. Energy-minimized structures of (a) **1** and (b) Al^{3+}-2·**1** from B3LYP level.

(a)

Excited State 1	Wavelength	Percent (%)	Oscillator strength
H → L	394.61 nm	97%	0.8349

Molecular orbital (1)	
	
LUMO **(-5.261 eV)**	**HOMO** **(-1.751 eV)**

(b)

Fig. S7. (a) The major electronic transition energies and molecular orbital contributions for **1** (H = HOMO and L = LUMO). (b) Isosurface (0.030 electron bohr^{-3}) of molecular orbitals participating in the major singlet excited states of **1**.

(a)

Excited State 1	Wavelength	Percent (%)	Oscillator strength
H → L	499.43 nm	99%	0.0045
Excited State 5	**Wavelength**	**Percent (%)**	**Oscillator strength**
H → L+1	367.42 nm	83%	0.9022
H-1 → L+1		12%	

(b)

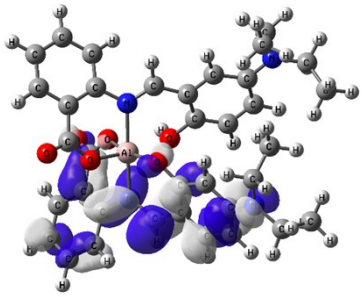
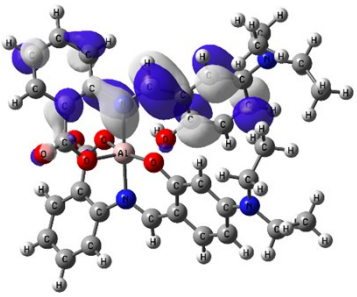
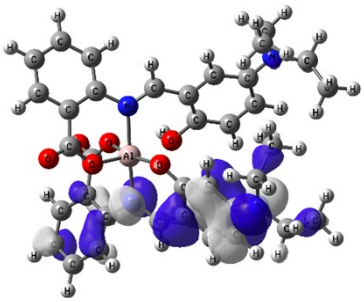
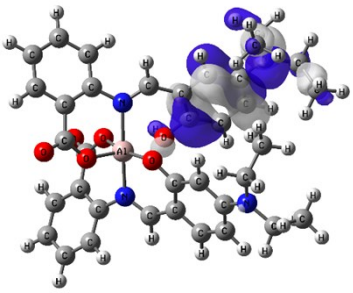
Molecular orbital (Al^{3+}-2•1 complex)		
		
LUMO + 1 (-1.817 eV)	**LUMO (-2.429 eV)**	**HOMO (-5.394 eV)**
		
HOMO - 1 (-5.475 eV)		

Fig. S8. (a) The major electronic transition energies and molecular orbital contributions for Al^{3+}-2·**1** (H = HOMO and L = LUMO). (b) Isosurface (0.030 electron $bohr^{-3}$) of molecular orbitals participating in the major singlet excited states of Al^{3+}-2·**1**.