Supplementary Information

Understanding the Selective-sensing Mechanism of Al^{3+} cation by a Chemical Sensor Based on Schiff-base. New Theoretical Methodology

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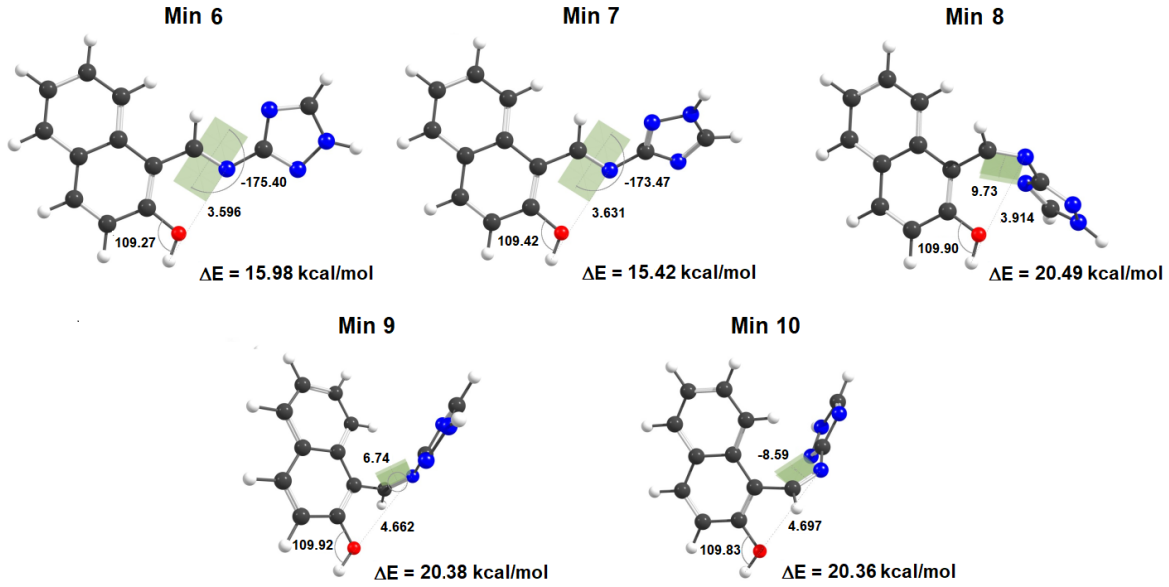

Figure S1. Conformational analyze of the L1. ΔE is the relative energy of conformers that change in distance of Hydrogen bond in L1.

Table S1. Singlet→Singlet absorption data in L1 and M/L1.

Systems	B3LYP				CAMB3LYP			
	λ_a	*f*	Active MOs	A	λ_a	*f*	Active MOs	A
L1	349	0.447	H-L	π–π*	321	0.508	H-L	π–π*
	314	0.109	H-1-L	π–π*	281	0.201	H-1-L	π–π*
	252	0.206	H-L+1	π–π*	226	0.421	H-L+1	π–π*
Al^{3+}/L1	452	0.230	H-L	π–π*	381	0.409	H-L	π–π*
	428	0.106	H-1-L	π–π*	344	0.148	H-1-L	π–π*
	285	0.501	H-2-L	π–π*	270	0.380	H-L+1	π–π*
Ni^{2+}/L1	442	0.014	H-L	dNi–π*	383	0.030	H-L	dNi–π*
	397	0.214	H-1-L+1	π–π*	355	0.281	H-1-L+1	π–π*
	372	0.134	H-2-L+1	π–π*	322	0.255	H-2-L+1	π–π*
Zn^{2+}/L1	403	0.277	H-L	π–π*	356	0.380	H-L	π–π*
	385	0.101	H-1-L	π–π*	334	0.181	H-1-L	π–π*
	282	0.403	H-2-L	π–π*	257	0.158	H-2-L	π–π*

Where λ_a is the theoretical absorption wavelength in nm, A is assignment of transitions, *f* is the oscillator strength, H (HOMO) and L (LUMO).

Table S2. Singlet→Singlet emission data in L1 and M/L1.

	B3LYP					CAMB3LYP				
Systems	λ_e	*f*	$k_{rd}*10^8$	$\tau*10^{-9}$	**A**	λ_e	*f*	$k_{rd}*10^8$	$\tau*10^{-9}$	**A**
L1	381	0.414	4.8	2.1	$\pi-\pi^*$	350	0.496	6.9	1.5	$\pi-\pi^*$
Al^{3+}/L1	453	0.138	0.7	13	$\pi-\pi^*$	450	0.213	1.8	56	$\pi-\pi^*$
Ni^{2+}/L1	425	0.004	1.4	7.3	$dNi-\pi^*$	380	0.022	1.6	6.4	$dNi-\pi^*$
Zn^{2+}L1	464	0.054	1.5	6.7	$\pi-\pi^*$	396	0.125	3.2	3.1	$\pi-\pi^*$

Where λ_e is the theoretical emission wavelength in nm, A is assignment of transitions, *f* is the oscillator strength, H (HOMO), L (LUMO), k_{rd} is the emission radiative rate (s^{-1}) and τ is the emission-radiative lifetime (s).

Table S3. Data from the study of intramolecular charge transfer.

Systems	k_{et}	τ_{et}	λ_{et}	**ΔG**
$L1_{314}$	$1.4*10^{14}$	$7.1*10^{-15}$	3.55	0.13
$Al^{3+}/L1_{428}$	$6.2*10^{5}$	$1.6*10^{-6}$	0.71	0.28
$Ni^{2+}/L1_{397}$	$1.9*10^{8}$	$5.2*10^{-9}$	2.78	0.53
$Zn^{2+}/L1_{385}$	$2.3*10^{13}$	$4.3*10^{-14}$	2.47	0.30

Where k_{et}: rate of electron transfer (s^{-1}), τ_{et}: electron transfer lifetime (s), λ_{et}: reorganization energy (eV) and ΔG (eV): total change in free energy (ΔG) between the two charge-transfer state, $L1_{335}$: Free sensor with the band at 335 nm.