

Electronic Supporting Information

Selective recognition of fluoride and acetate by the newly designed ruthenium framework. Experimental and theoretical investigations

Tanaya Kundu,^a Abhishek Dutta Chowdhury,^a Dipanwita De,^a Shaikh M Mobin,^a
Vedavati G. Puranik,^b Anindya Datta*^a and Goutam Kumar Lahiri*^a

^a*Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India. E-mail: lahiri@chem.iitb.ac.in*

^b*Center for Materials Characterization, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune – 411008, India*

Table S1 Selected bond lengths (Å) for H₃L

	Bond lengths	
	X-ray	DFT
O(1)-C(1)	1.270(2)	1.326
O(2)-C(1)	1.247(2)	1.220
N(1)-C(3)	1.341(2)	1.357
N(1)-C(2)	1.363(2)	1.374
N(2)-C(3)	1.319(2)	1.320
N(2)-C(4)	1.384(2)	1.376
N(3)-C(5)	1.333(2)	1.322
N(3)-C(11)	1.395(2)	1.386
N(4)-C(5)	1.335(2)	1.367
N(4)-C(6)	1.392(2)	1.384
C(1)-C(2)	1.491(2)	1.487
C(2)-C(4)	1.387(2)	1.391
C(4)-C(5)	1.443(2)	1.445
C(6)-C(11)	1.385(2)	1.418

Table S2 Distances (Å) and angles (°) of hydrogen bonds in H₃L

Intramolecular					
D-H...A		d(D-H)	d(H...A)	d(D...A)	∠D-H...A
N3-H3...O1	(0)	0.88	1.89	2.663(2)	144
Intermolecular					
D-H...A		d(D-H)	d(H...A)	d(D...A)	∠D-H...A
O111-H111...O333(1)		0.84(3)	2.15(3)	2.956(3)	164(3)
O111-H222...O333(1)		0.89(3)	1.93(1)	2.805(2)	168(2)
O222-H555...O333(0)		0.88(2)	2.00(2)	2.871(2)	177(2)
O222-H666...N2	(3)	0.96(2)	1.92(2)	2.861(2)	164(2)
O333-H333...O2	(4)	0.93(2)	1.78(2)	2.697(2)	171(2)
O333-H444...O1	(1)	0.92(2)	1.85(2)	2.716(2)	158(2)
N4-H4...O111	(2)	0.88	1.88	2.725(2)	163

- (0) x,y,z
 (1) -x+1,-y,-z+1
 (2) x,+y,+z+1
 (3) x,+y,+z-1
 (4) x+1,+y,+z

Table S3 Distances (Å) and angles (°) of hydrogen bonds in [1](ClO₄)

Intramolecular				
D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
N2-H2...O11	0.88	1.87	2.739(11)	172
N3-H3...O2	0.88	1.88	2.675(6)	149
C3-H(3A)...O4	0.95	2.38	3.291(15)	160
Intermolecular				
D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
C(10)-H(10)...O(12) ⁱ	0.95	2.35	3.109(9)	137
C(15)-H(15)...O(8) ⁱⁱ	0.95	2.59	3.534(9)	173
C(18)-H(18)...O(8) ⁱⁱⁱ	0.95	2.55	3.472(8)	162

$i = 3/2-x, 1/2-y, 2-z$

$ii = 1/2+x, -1/2+y, 1+z$

$iii = 1/2+x, 1/2-y, 1/2+z$

Table S4 Selected bond lengths (Å) and angles (°) for **1** (DFT: molecule 1 only)

Bond lengths			Bond angles		
	X-ray	DFT		X-ray	DFT
Ru(1)-N(5)	2.052(4)	2.088	N(6)-Ru(1)-N(8)	86.94(16)	96.23
Ru(1)-N(6)	2.054(4)	2.110	N(6)-Ru(1)-N(7)	101.32(18)	100.09
Ru(1)-N(7)	2.037(4)	2.069	N(8)-Ru(1)-N(7)	78.78(16)	78.07
Ru(1)-N(8)	2.023(4)	2.094	N(8)-Ru(1)-N(1)	98.49(16)	95.92
Ru(1)-N(1)	2.054(4)	2.064	N(7)-Ru(1)-N(1)	85.23(15)	88.94
Ru(1)-O(1)	2.103(3)	2.085	N(6)-Ru(1)-N(5)	78.71(15)	77.85
Ru(2)-N(13)	2.049(4)		N(1)-Ru(1)-N(5)	94.74(18)	93.14
Ru(2)-N(14)	2.047(4)		N(6)-Ru(1)-O(1)	97.00(14)	89.95
Ru(2)-N(15)	2.018(4)		N(7)-Ru(1)-O(1)	93.26(15)	92.90
Ru(2)-N(16)	2.032(4)		N(1)-Ru(1)-O(1)	78.34(14)	79.01
Ru(2)-N(9)	2.061(4)		N(5)-Ru(1)-O(1)	86.76(14)	87.45
Ru(2)-O(3)	2.111(3)		N(8)-Ru(1)-N(5)	101.20(16)	101.74
O(1)-C(1)	1.307(5)	1.319	N(6)-Ru(1)-N(1)	172.25(18)	166.13
O(2)-C(1)	1.214(6)	1.242	N(7)-Ru(1)-N(5)	180.0(2)	177.91
O(3)-C(32)	1.282(5)		N(8)-Ru(1)-O(1)	171.71(15)	169.81
O(4)-C(32)	1.267(6)		O(1)-C(1)-O(2)	124.4(4)	121.62
N(1)-C(3)	1.343(7)	1.351	N(15)-Ru(2)-N(16)	79.73(16)	
N(1)-C(2)	1.350(6)	1.379	N(15)-Ru(2)-N(14)	88.14(15)	
N(2)-C(4)	1.362(6)	1.369	N(16)-Ru(2)-N(14)	101.03(18)	
N(2)-C(3)	1.340(7)	1.333	N(15)-Ru(2)-N(13)	100.70(15)	
N(3)-C(5)	1.370(6)	1.324	N(14)-Ru(2)-N(13)	78.60(15)	
N(3)-C(11)	1.369(6)	1.380	N(15)-Ru(2)-N(9)	97.71(15)	
N(4)-C(5)	1.315(6)	1.380	N(16)-Ru(2)-N(9)	85.75(15)	
N(4)-C(6)	1.384(7)	1.374	N(13)-Ru(2)-N(9)	94.59(18)	
N(9)-C(34)	1.334(7)		N(16)-Ru(2)-O(3)	93.37(14)	
N(9)-C(33)	1.361(6)		N(14)-Ru(2)-O(3)	97.14(14)	
N(10)-C(34)	1.363(7)		N(13)-Ru(2)-O(3)	86.23(14)	
N(10)-C(35)	1.371(6)		N(9)-Ru(2)-O(3)	77.67(14)	
N(11)-C(36)	1.379(6)		N(15)-Ru(2)-O(3)	172.04(14)	
N(11)-C(42)	1.394(6)		N(14)-Ru(2)-N(9)	171.79(18)	
N(12)-C(36)	1.335(6)		N(16)-Ru(2)-N(13)	179.41(18)	
N(12)-C(37)	1.381(6)		O(3)-C(32)-O(4)	120.9(4)	
C(1)-C(2)	1.511(6)	1.478			
C(4)-C(5)	1.465(7)	1.457			
C(2)-C(4)	1.379(7)	1.408			
C(6)-C(11)	1.415(7)	1.423			
C(32)-C(33)	1.457(7)				
C(33)-C(35)	1.405(7)				
C(35)-C(36)	1.435(7)				
C(37)-C(42)	1.399(7)				

Table S5 TD-DFT for **1⁺**

State	Energy (eV)	λ (nm)	f^a	Transition	Character
5	2.75	450.22	0.1265	HOMO-2→LUMO(0.52) HOMO-2→LUMO+1 (0.20)	Ru(d π)→bpy(π^*)
6	2.92	424.02	0.0725	HOMO-2→LUMO+2(0.45)	Ru(d π)→bpy(π^*)
21	3.73	332.36	0.1056	HOMO→LUMO+6(0.31) HOMO-2→LUMO+3(0.30)	Ru(d π)/ H ₂ L(π^*)→bpy (π^*)/ H ₂ L(π^*)
28	3.97	312.32	0.7294	HOMO-3→LUMO+2(0.56) HOMO-2→LUMO+6(0.21)	Ru(d π)/ H ₂ L(π^*)→bpy (π^*)/ H ₂ L(π^*)
40	4.49	275.88	0.5706	HOMO-5→LUMO+1(0.35) HOMO-6→LUMO(0.33)	H ₂ L (π^*)→bpy (π^*)

^a Oscillator strength.

Table S6 Selected molecular orbitals along with their energies and compositions of **A** (**1**⁺ with F⁻ in Scheme 1)

M.O.	Energy (eV)	Composition (%)			
		Ru	bpy	H ₂ L	F
LUMO+5	-1.388	2	97	1	0
LUMO+4	-1.429	3	97	0	0
LUMO+3	-1.514	7	92	1	0
LUMO+2	-1.754	2	97	1	0
LUMO+1	-2.475	9	90	1	0
LUMO	-2.541	6	93	1	0
HOMO	-4.524	5	2	93	0
HOMO-1	-5.048	1	0	99	0
HOMO-2	-5.399	68	12	20	0
HOMO-3	-5.450	67	14	19	0
HOMO-4	-5.556	63	15	22	0
HOMO-5	-5.860	6	2	92	0

Table S7 TD-DFT for **A** (**1**⁺ with F⁻ in Scheme 1)

State	Energy (eV)	λ (nm)	f^a	Transition	Character
5	2.5665	485.08	0.1628	HOMO-2→LUMO(0.58)	Ru(d π)→bpy(π^*)
6	2.7183	456.11	0.0636	HOMO-2→LUMO+1(0.56)	Ru(d π)→bpy(π^*)
15	3.5080	353.44	0.1310	HOMO-1→LUMO+4(0.35)	Ru(d π)/ H ₂ L(π^*)
				HOMO→LUMO+3(0.26)	→bpy(π^*)
21	3.6257	341.96	0.2670	HOMO→LUMO+4(0.56)	Ru(d π)/ H ₂ L(π^*)
				HOMO-2→LUMO+5(0.21)	→bpy(π^*)

^a Oscillator strength.

Table S8 Selected molecular orbitals along with their energies and compositions for **B**
(**1**⁺ with OAc⁻ in Scheme 1)

M.O.	Energy (eV)	Composition (%)			
		Ru	bpy	H ₂ L	OAc
LUMO+6	-0.159	3	96	1	0
LUMO+5	-1.374	3	97	0	0
LUMO+4	-1.411	4	96	0	0
LUMO+3	-1.486	6	92	2	0
LUMO+2	-1.725	2	97	1	0
LUMO+1	-2.452	9	90	1	0
LUMO	-2.522	6	93	1	0
HOMO	-4.406	4	2	94	0
HOMO-1	-4.935	0	0	100	0
HOMO-2	-5.357	68	12	20	0
HOMO-3	-5.400	67	14	19	0

Table S9 TD-DFT for **B** (**1**⁺ with OAc⁻ in Scheme 1)

State	Energy (eV)	λ (nm)	f^a	Transition	Character
5	2.5544	485.38	1633	HOMO-2→LUMO(0.58)	Ru(d π)→bpy(π^*)
6	2.7066	458.08	0.0630	HOMO-2→LUMO+1(0.56)	Ru(d π)→bpy(π^*)
16	3.5019	354.05	0.1004	HOMO-1→LUMO+4(0.36) HOMO→LUMO+4(0.24)	Ru(d π)/ H ₂ L(π^*) →bpy(π^*)
21	3.6186	342.63	0.3417	HOMO→LUMO+6(0.43)	Ru(d π)/ H ₂ L(π^*) →bpy(π^*)

^a Oscillator strength.

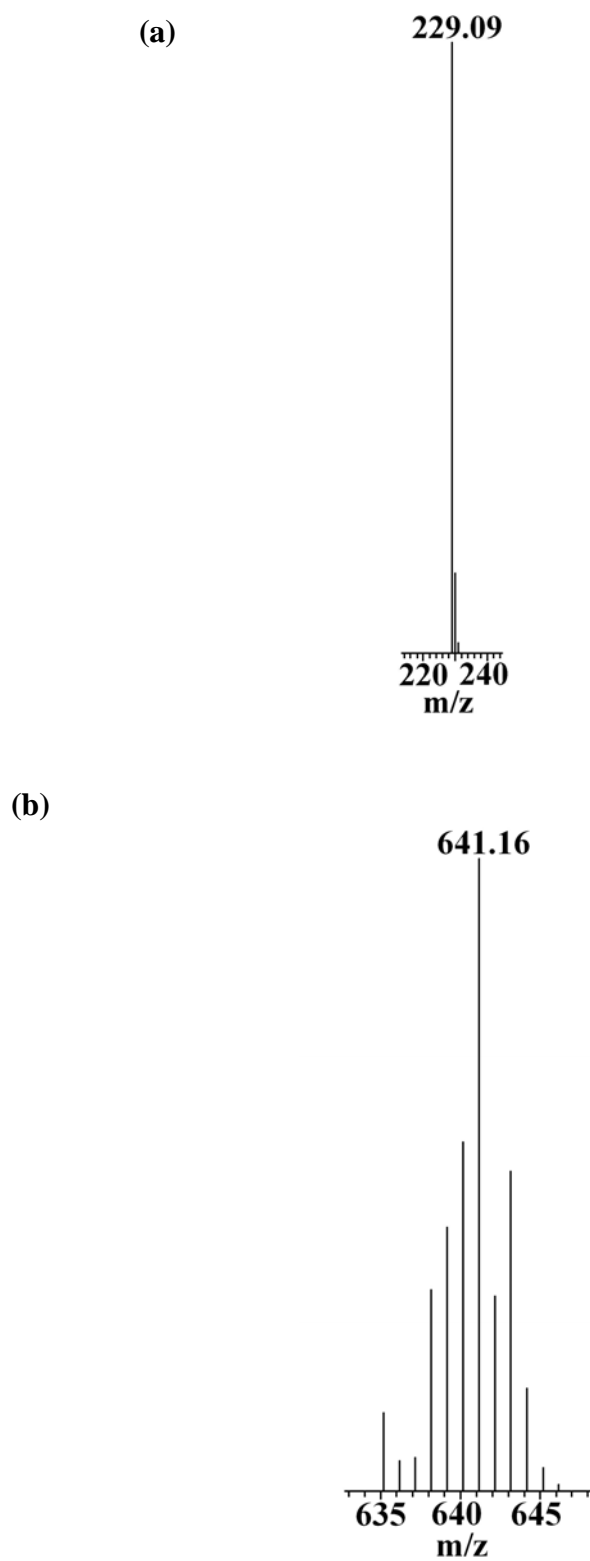


Fig. S1 Mass spectra of (a) H₃L in CH₃OH and (b) [1](ClO₄) in CH₃CN.

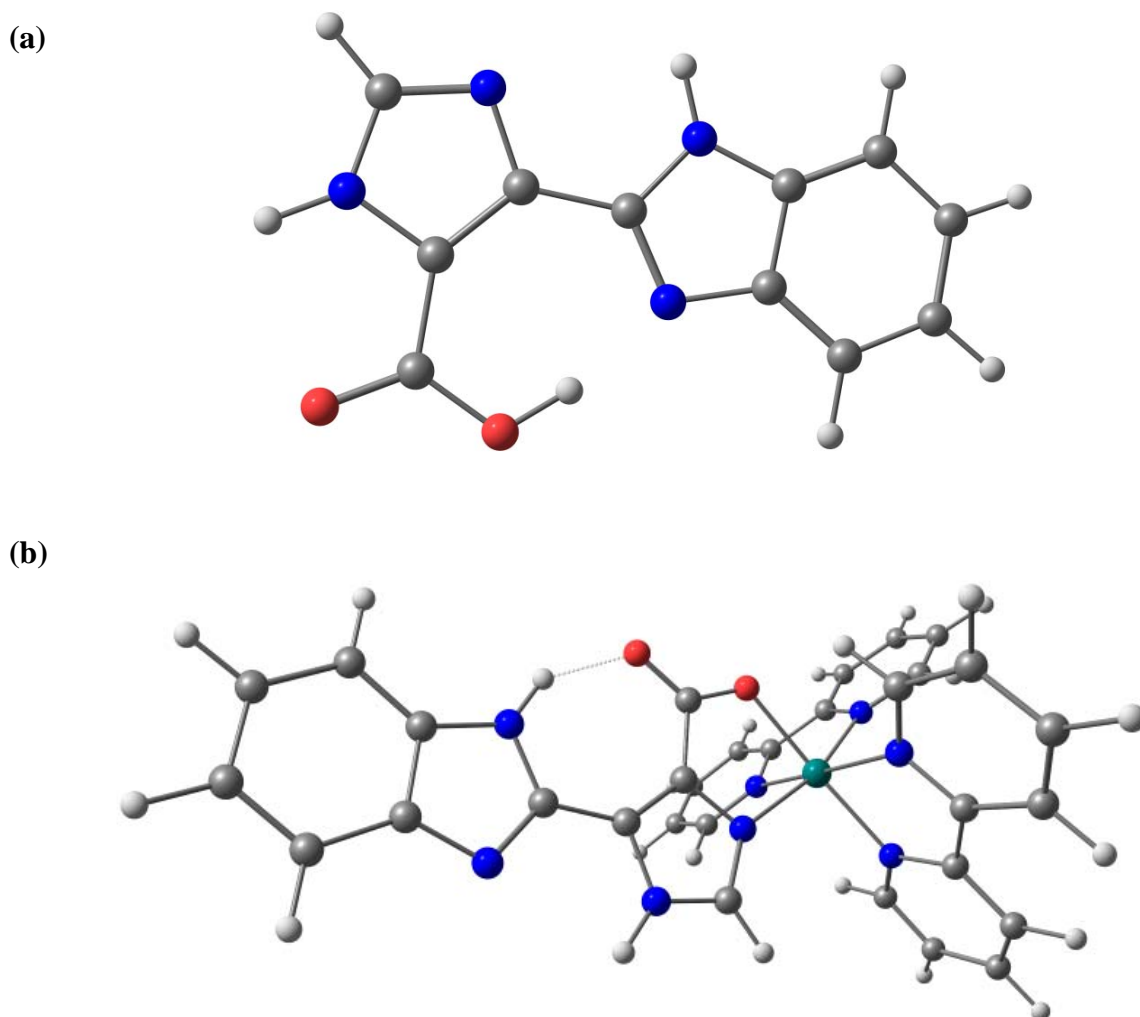
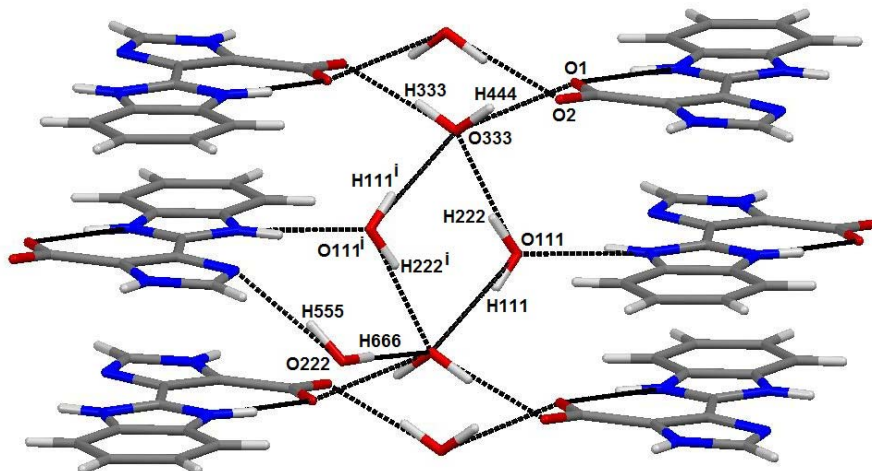


Fig. S2 DFT optimised structures of (a) H_3L and (b) 1^+

(a)



(b)

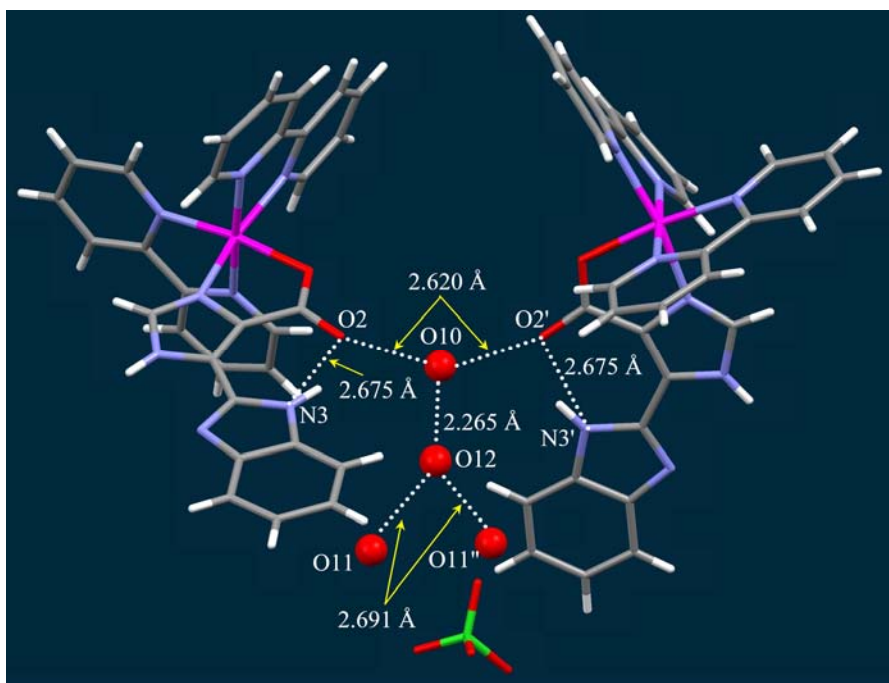


Fig. S3 (a) Packing diagram of H₃L along the *b*-axis with symmetry equivalent position, (i): $-x+1, -y, -z+1$. (b) Packing diagram of [1](ClO₄) along the *c*-axis. Symmetry related atoms O2', N3' and O11'' are O2': $2-x, y, 2.5-z$; N3': $2-x, y, 2.5-z$; O11'': $1-x, y, 1.5-z$.

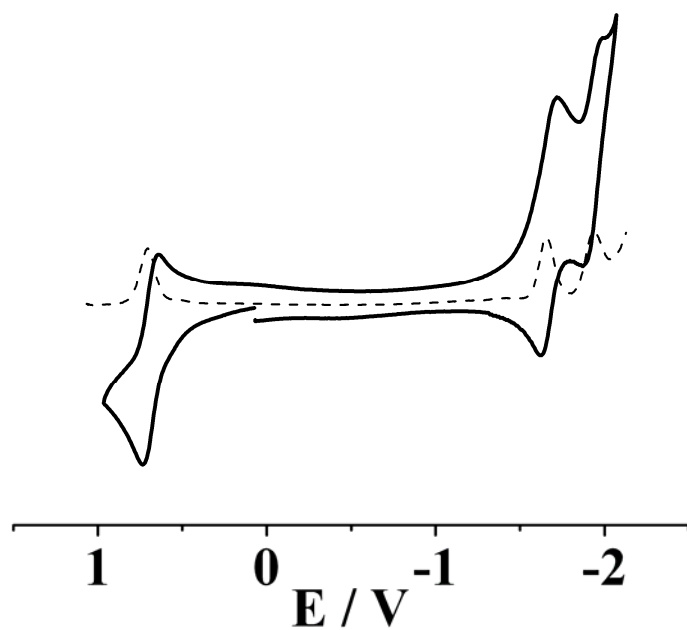


Fig. S4 Cyclic (—) and differential pulse (-----) voltammograms of [1](ClO₄) (10⁻³ mol dm⁻³) versus SCE in CH₃CN. Scan rate 100 mV s⁻¹.

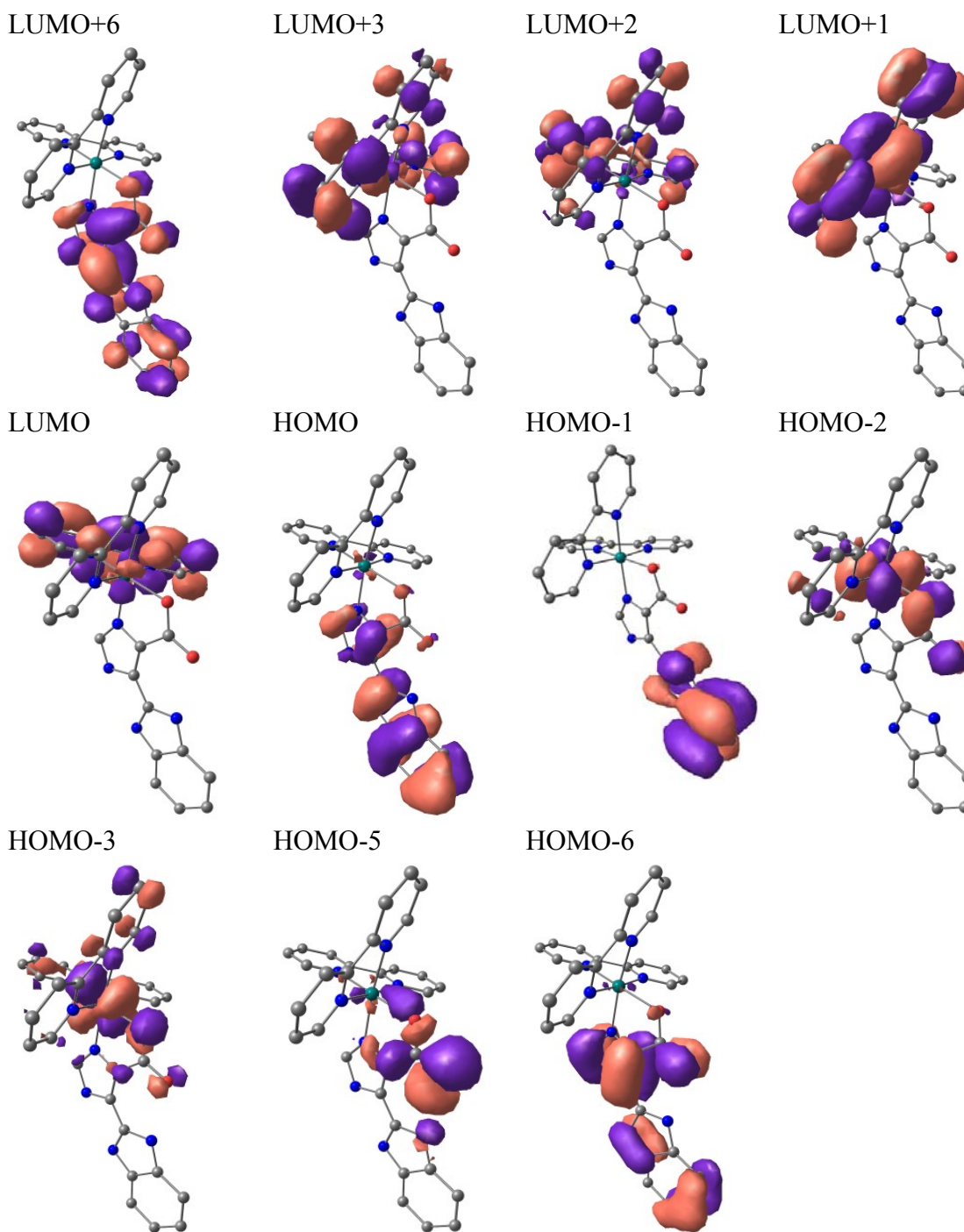
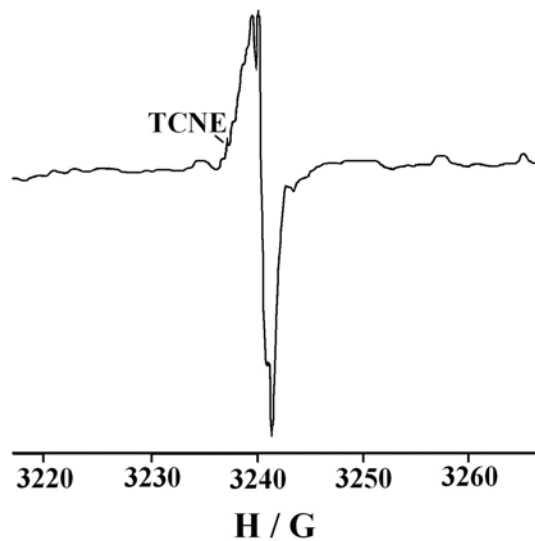


Fig. S5 Selected molecular orbitals of 1^+ .

(a)



(b)

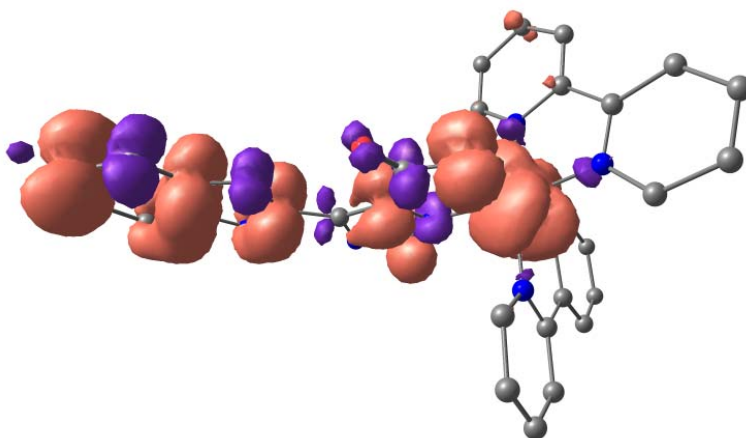


Fig. S6 (a) EPR spectrum of the coulometrically generated oxidised species (1^{2+}) at 110 K and (b) spin-density plot of 1^{2+} .

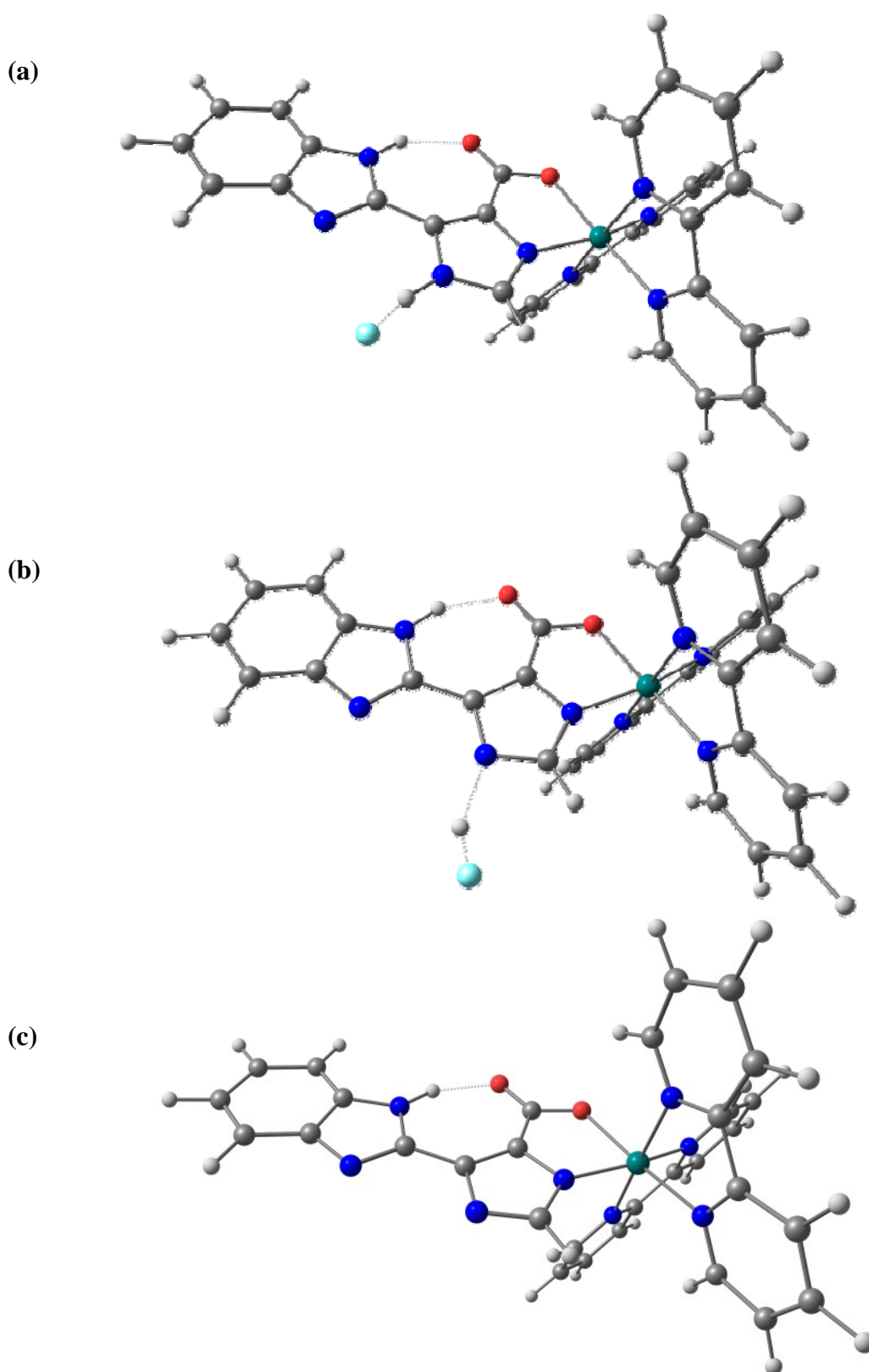


Fig. S7 Molecular structures of (a) initial A, (b) DFT optimised A and (c) DFT optimised 1.

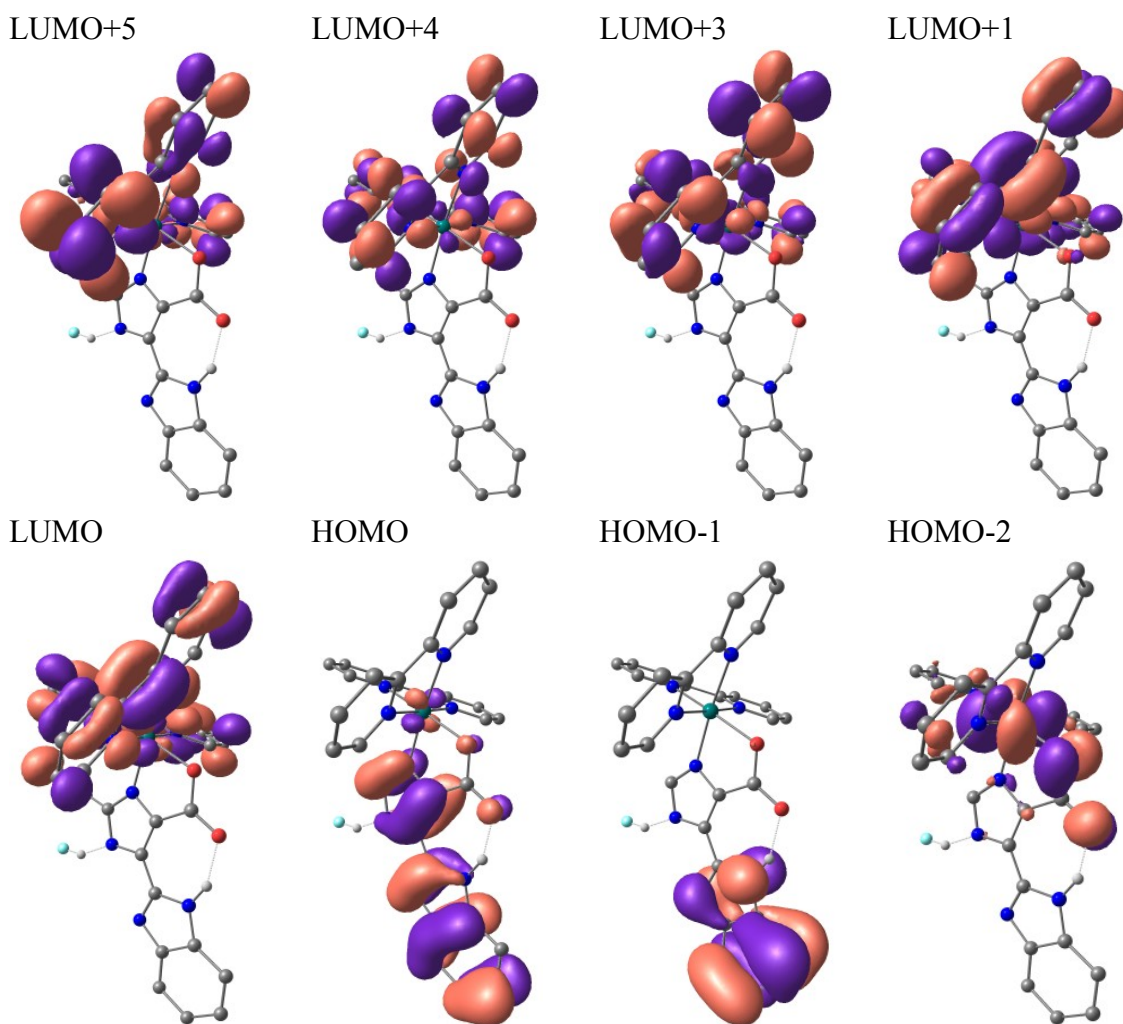


Fig. S8 Selected molecular orbitals for 1^+ with F^- (A).

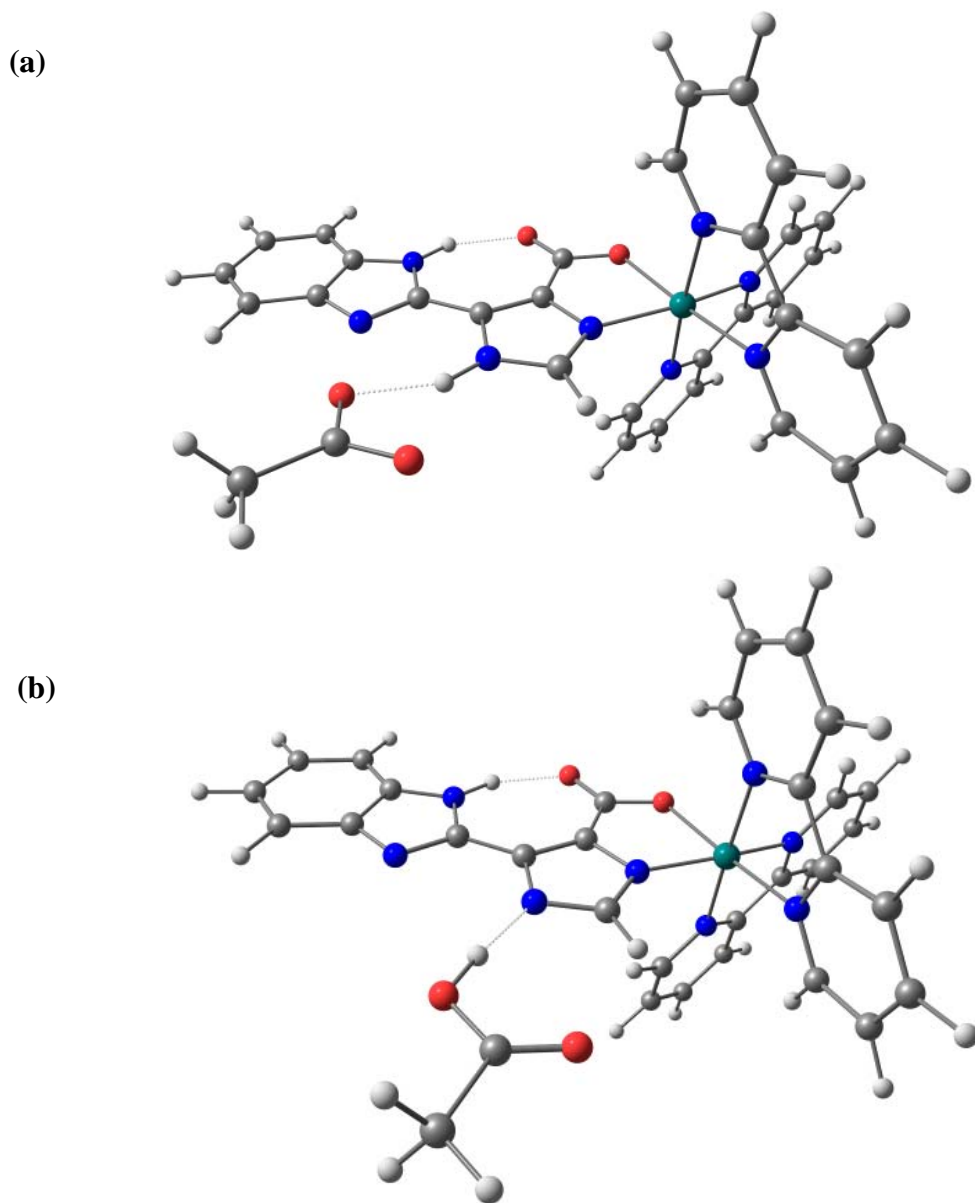


Fig. S9 Molecular structures of (a) initial **B** and (b) DFT optimised **B**.

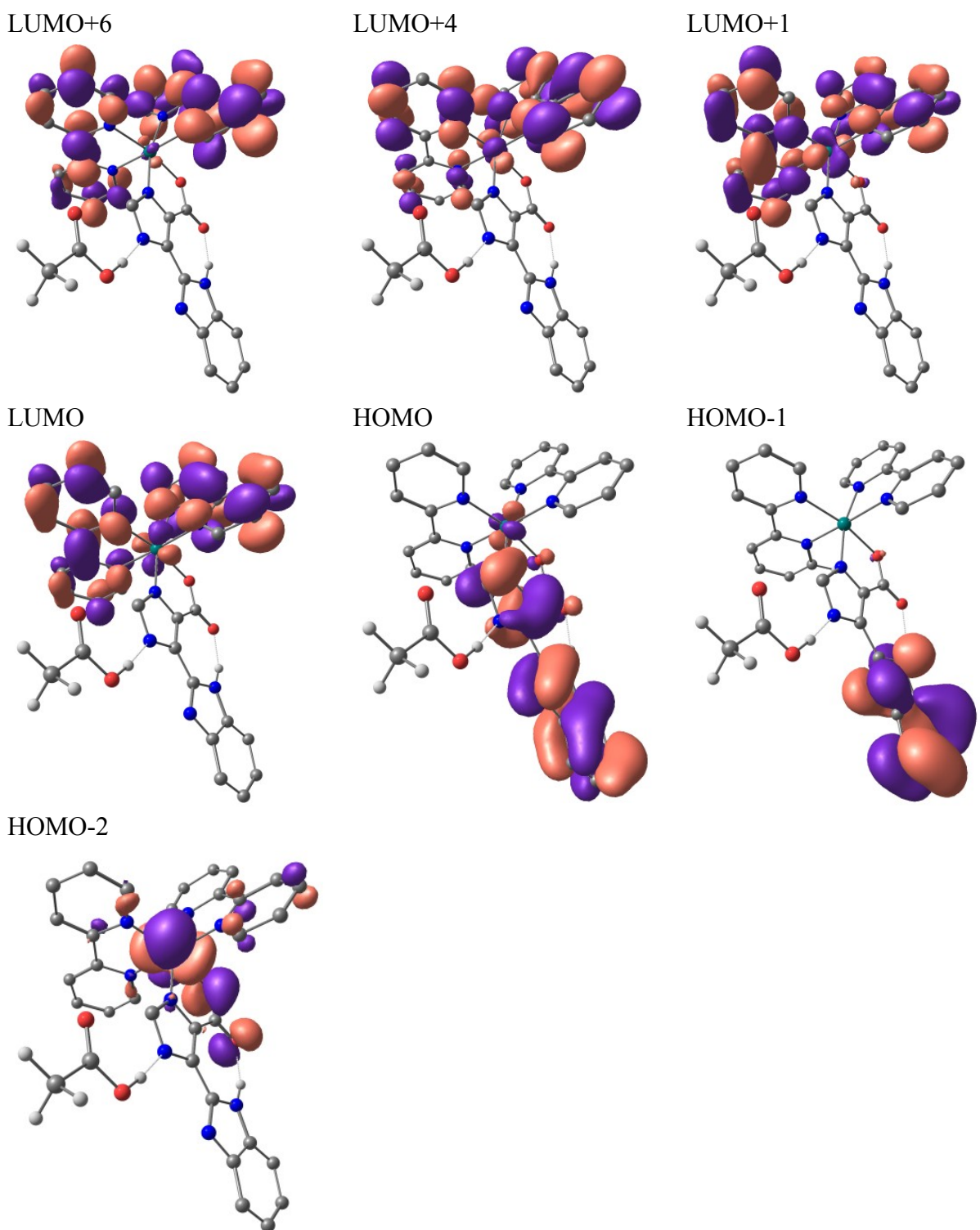
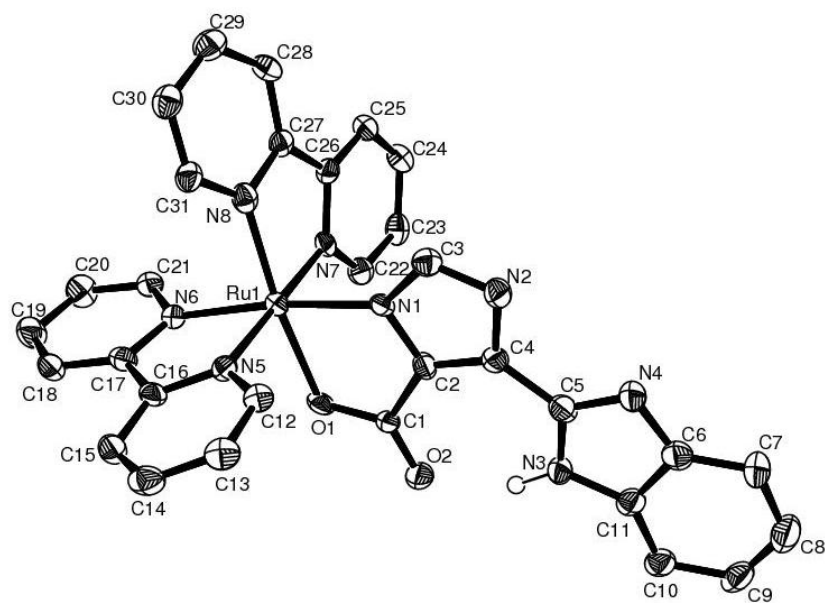
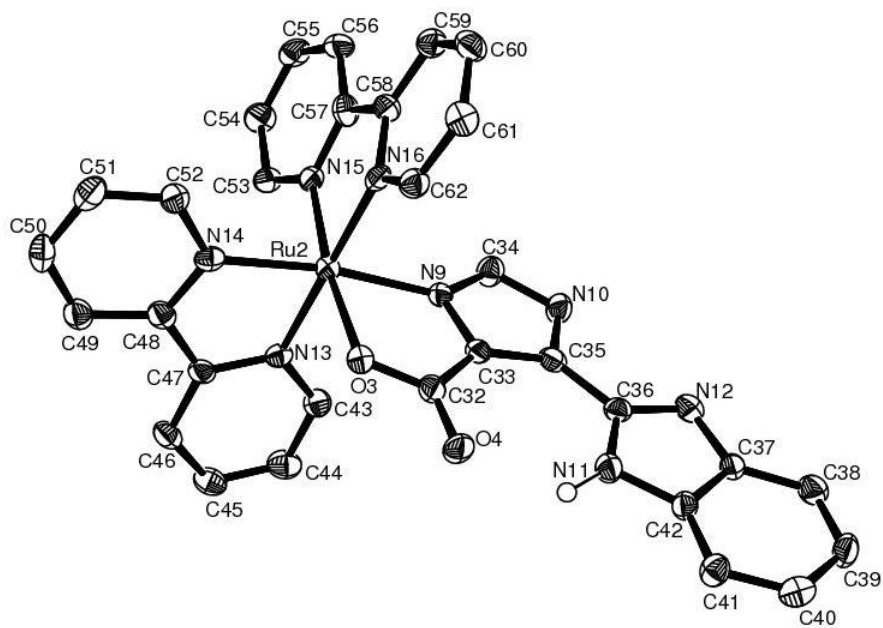


Fig. S10 Selected molecular orbitals of 1^+ with OAc^- (**B**).

(a)



(b)



Intramolecular				
D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
N3-H3N ...O2 (1)	0.954	1.821	2.707	153.11
N11-H11N...O4(1)	1.030	1.924	2.680	127.62

(1) x,y,z

Fig. S11 ORTEP diagram of **1** (two molecules in the asymmetric unit) from the crystal of 2[**1**]. 5CH₃CN. Ellipsoids are drawn at 50% probability level. Table shows the intramolecular hydrogen bonding parameters.

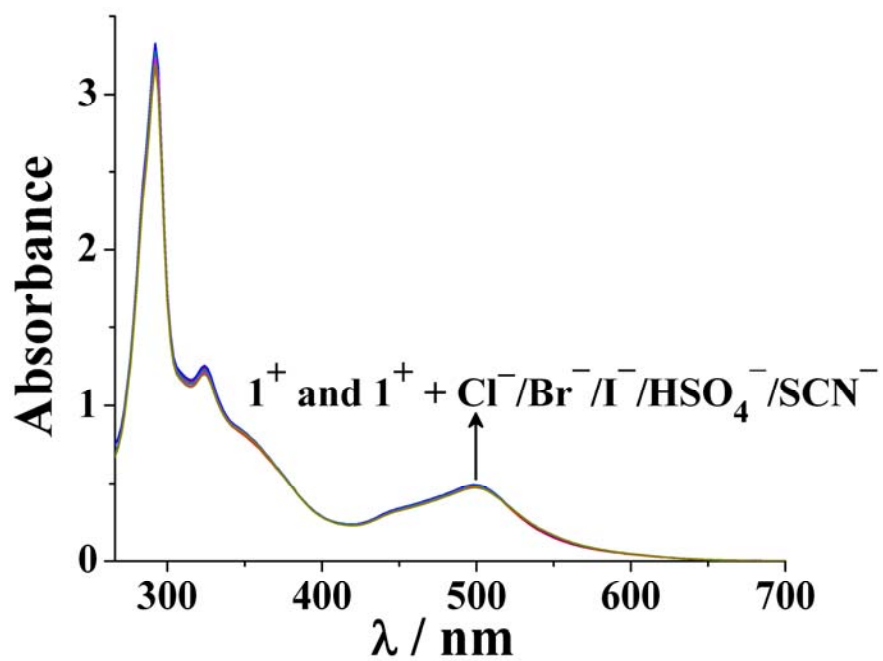


Fig. S12 Absorption spectra of 1^+ ($5 \times 10^{-5} \text{ mol dm}^{-3}$) in CH_3CN and 1^+ in presence of one equivalent TBA salts of Cl^- , Br^- , I^- , HSO_4^- , SCN^- .

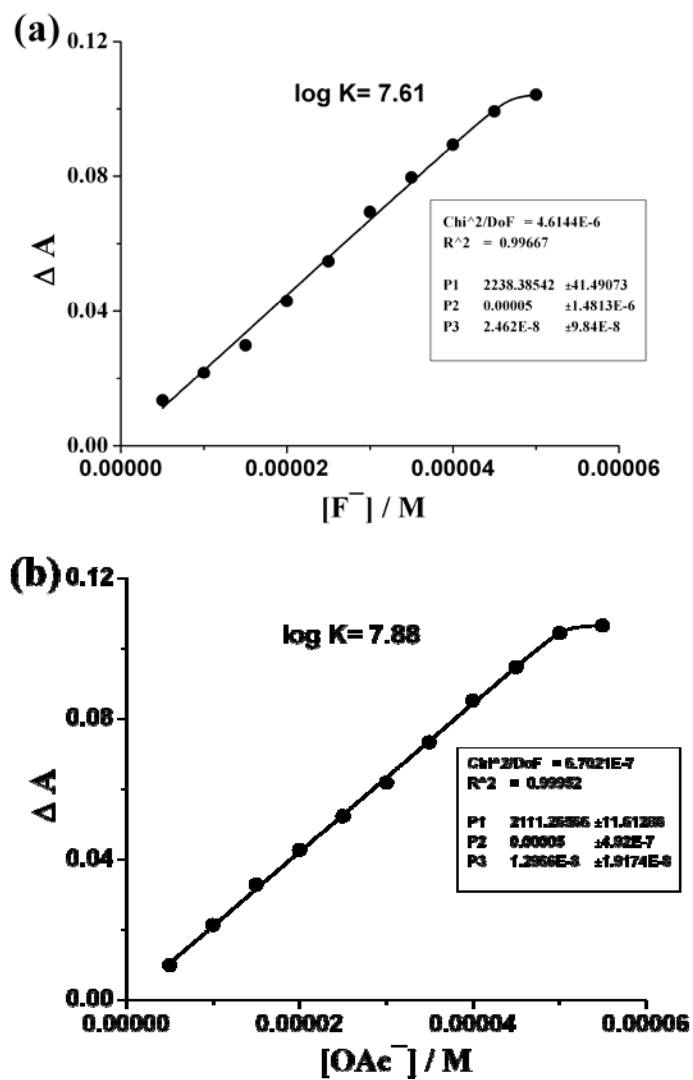


Fig. S13 Plots represent the change in absorbance (ΔA) of CH_3CN solution of 1^+ at 498 nm in presence of (a) F^- and (b) OAc^- versus the concentration of F^- and OAc^- , respectively.

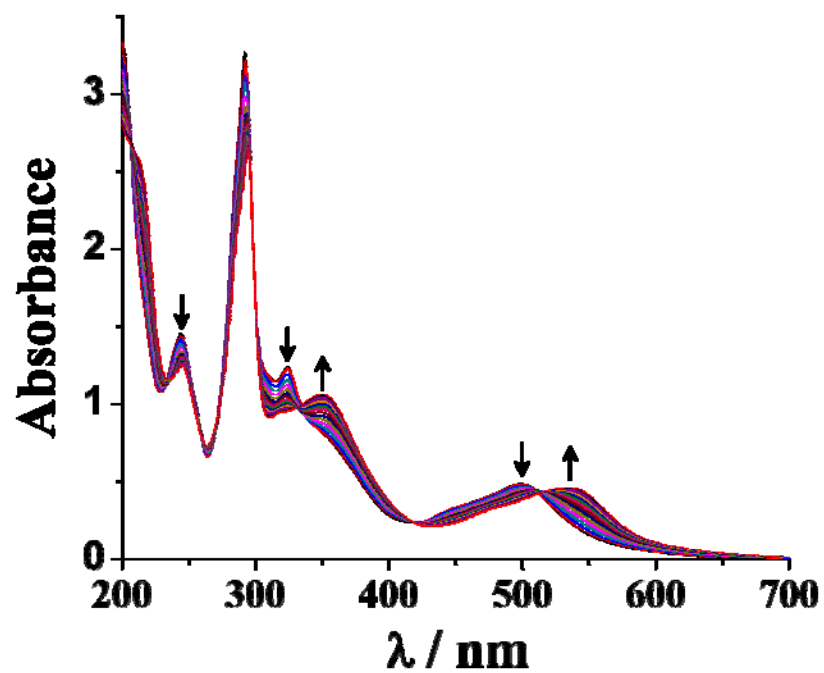


Fig. S14 Absorption spectral changes of 1^+ ($5 \times 10^{-5} \text{ mol dm}^{-3}$) in CH_3CN on gradual additions of 0-3 equivalents of $[\text{TBA}][\text{H}_2\text{PO}_4]$.

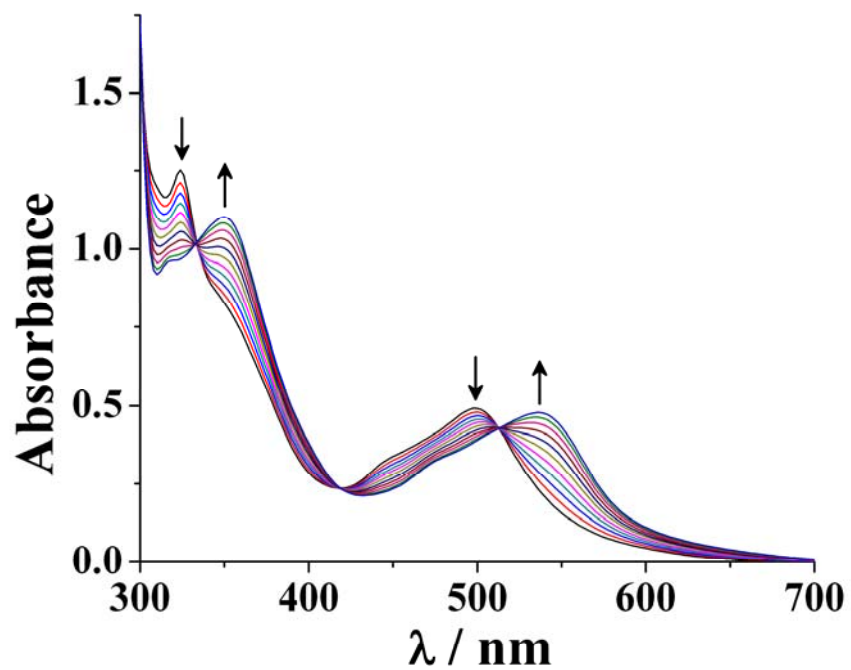


Fig. S15 Absorption spectral changes of 1^+ ($5 \times 10^{-5} \text{ mol dm}^{-3}$) in CH_3CN on gradual additions of 0-1 equivalent of $[\text{TBA}][\text{OH}]$.

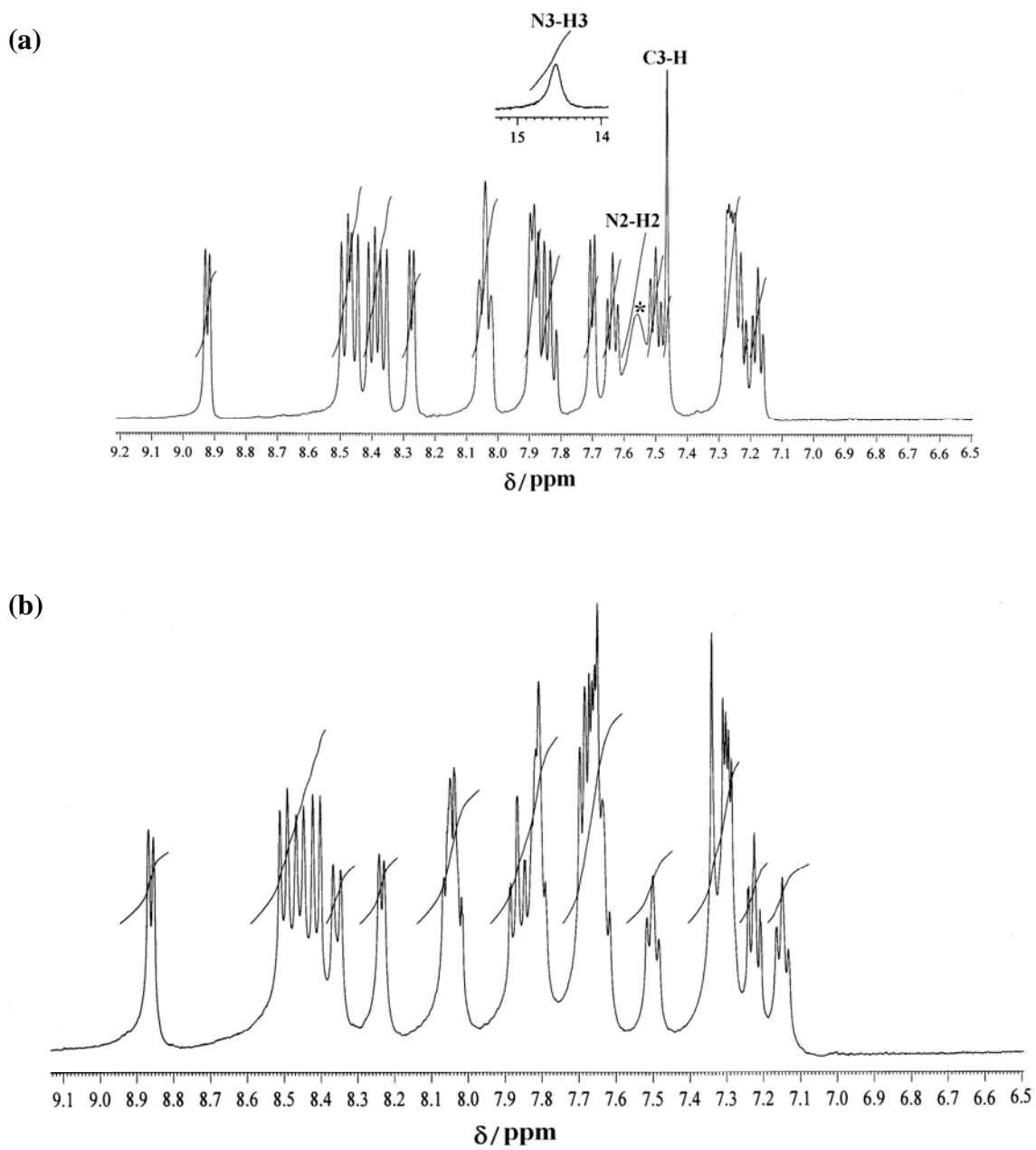


Fig. S16 ^1H NMR spectra of (a) 1^+ in CD_3CN and (b) in presence of D_2O .

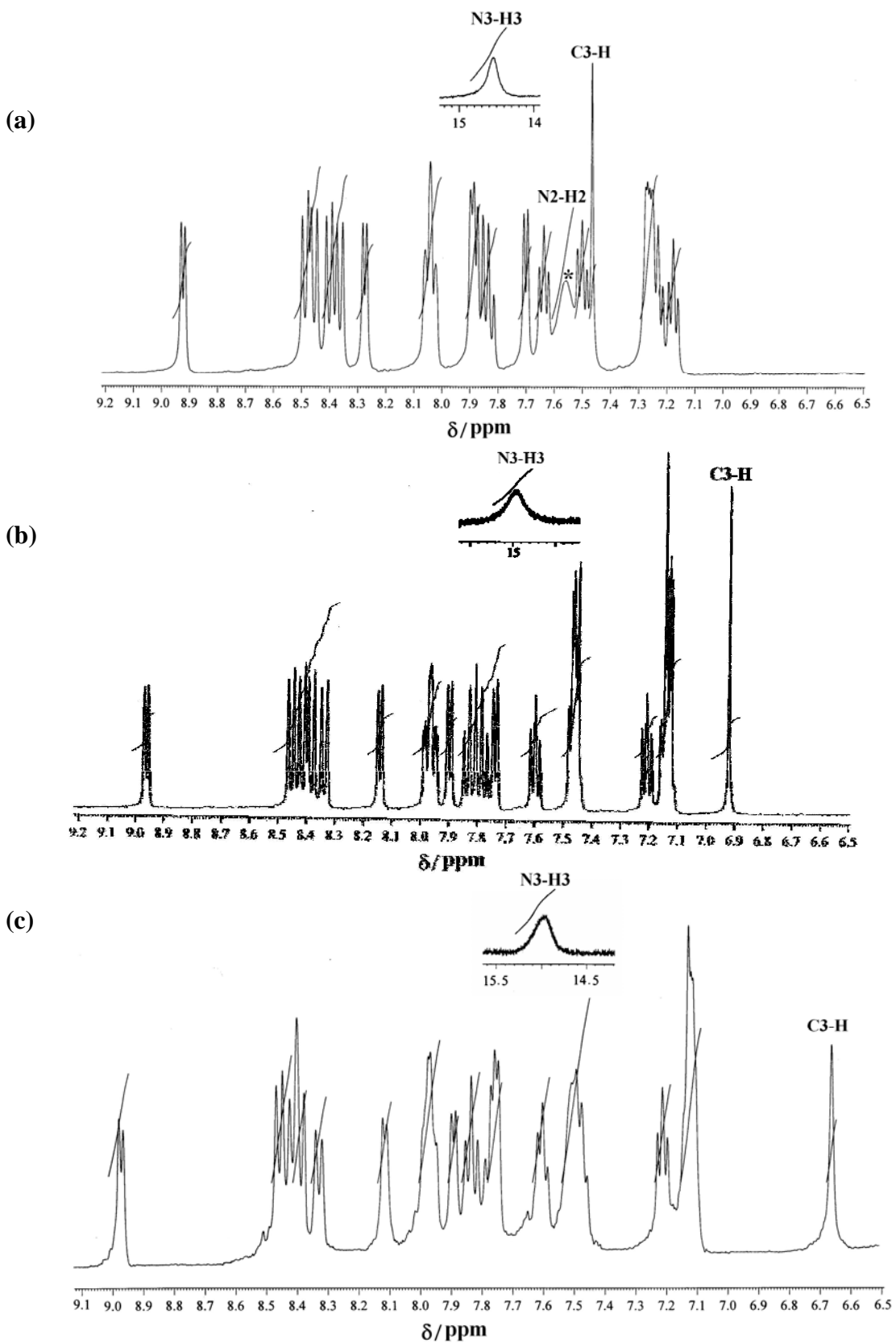


Fig. S17 ^1H NMR spectra in CD_3CN of (a) 1^+ , (b) 1^+ in presence of one equivalent of [TBA][F] and (c) 1^+ in presence of one equivalent of [TBA][OAc].

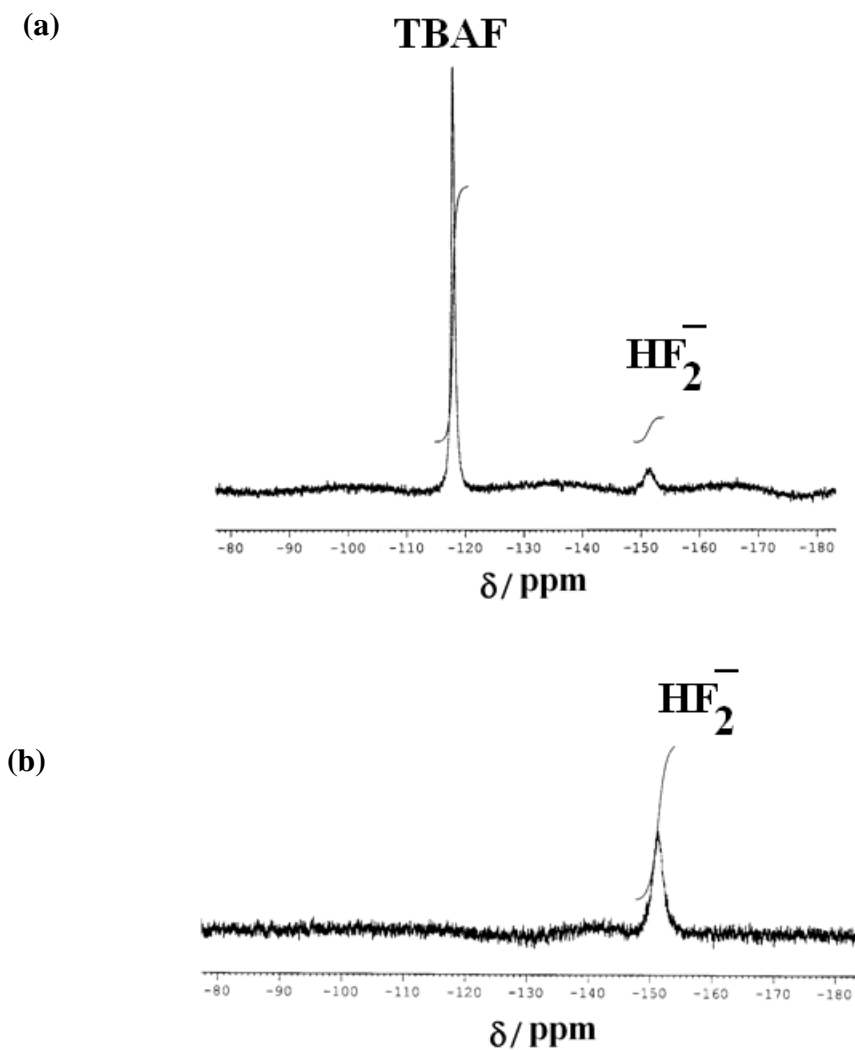


Fig. S18 ^{19}F NMR spectra in CD_3CN of (a) TBAF and (b) TBAF in presence of 0.6 equivalent of $\mathbf{1}^+$. Trifluoro-toluene is used as an internal standard ($\delta = -62.23$) at 298K.

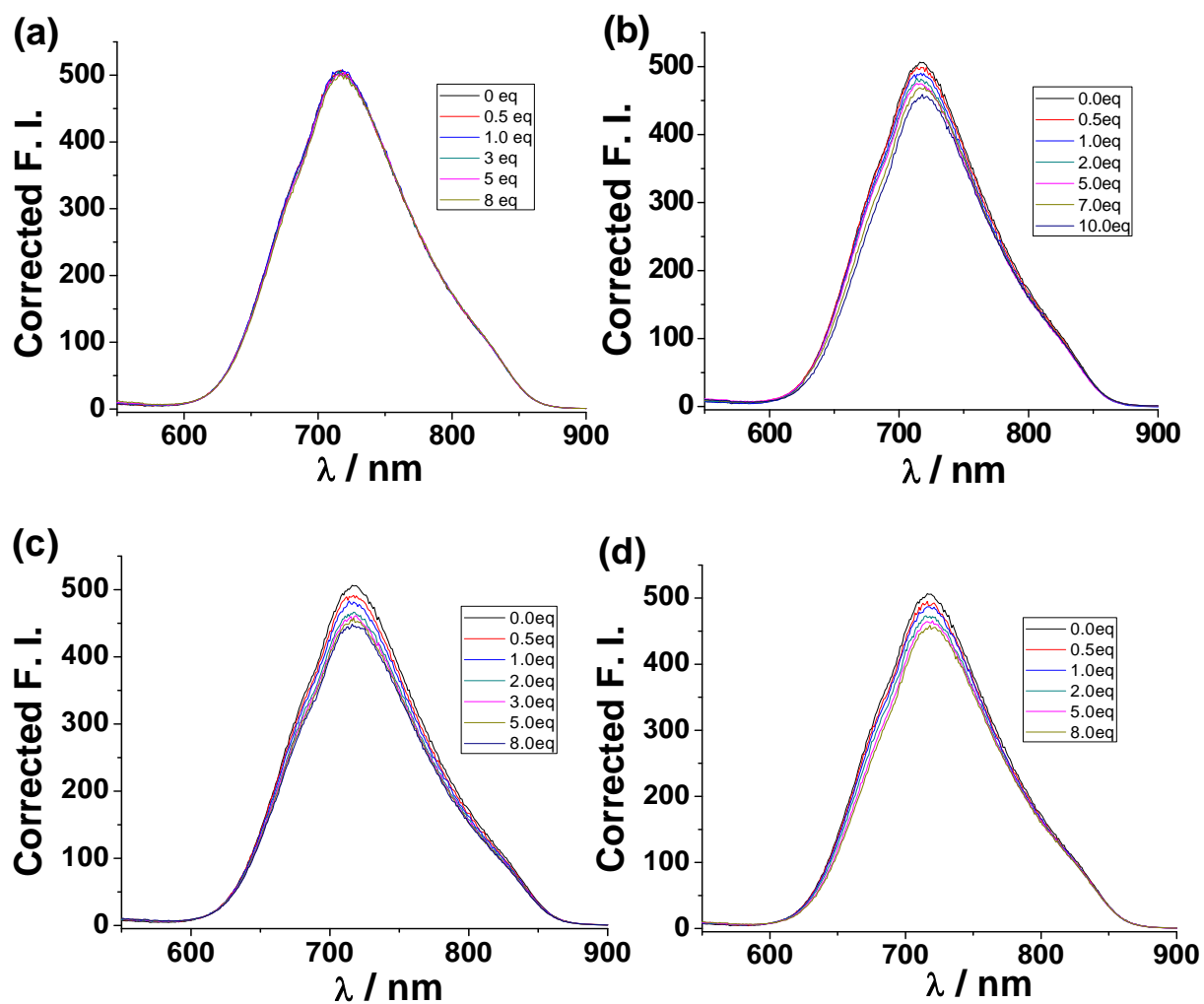


Fig. S19 Quenching of emission intensity of 1^+ during the additions of 0 to 8 equivalents of (a) TBACl, (b) TBABr, (c) TBAI and (d) TBAHSO₄ in CH₃CN at 298K.

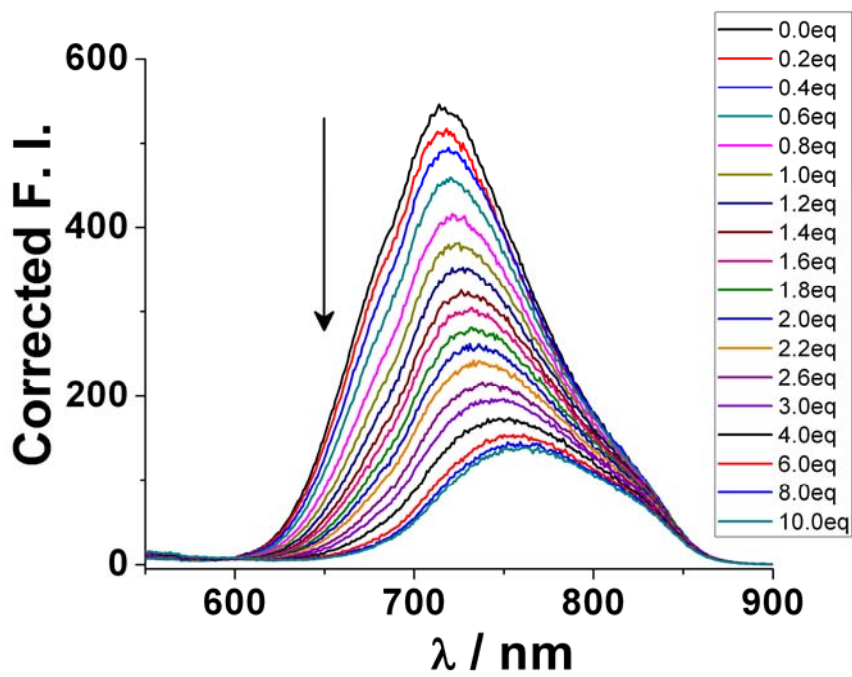


Fig. S20 Quenching of emission intensity of 1^+ during the addition of 0 to 10 equivalents of TBAH₂PO₄ in CH₃CN at 298K.

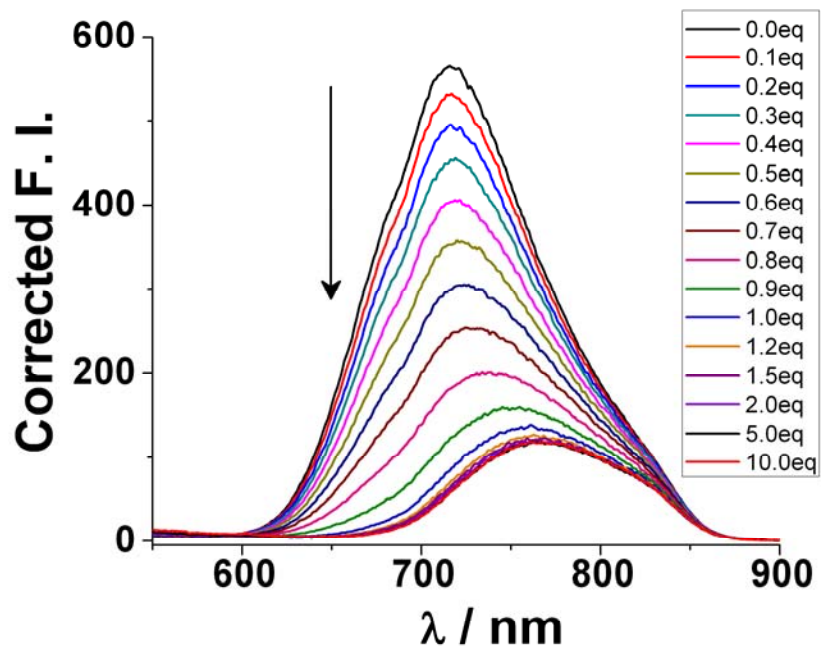


Fig. 21 Quenching of emission intensity of 1^+ during the additions of 0 to 10 equivalents of TBAOH in CH_3CN at 298K.

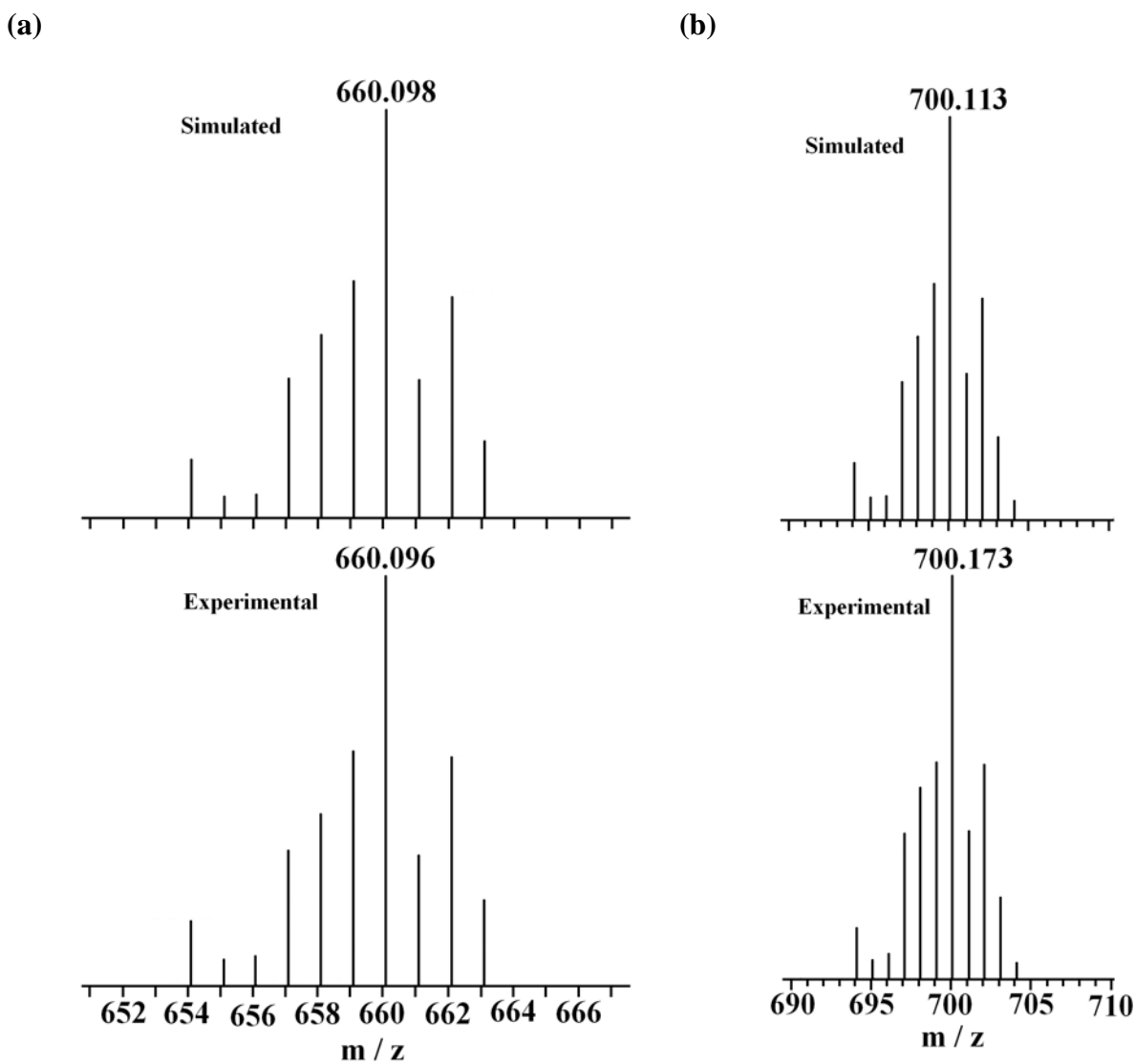


Fig. S22 The simulated and experimental ESI-MS peaks in CH_3CN of (a) $[1^+ \cdot F^-]$ (A) and (b) $[1^+ \cdot OAc^-]$ (B), in situ generated by the additions of one equivalent of $[TBA][F]$ and $[TBA][OAc]$, respectively, in the solution of 1^+ .