Supplementary Material

Table S1 Hydrogen bonds (Å and deg) in **1**

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
N2-H2N...N4#1	0.81(5)	2.022(5)	2.836(5)	177.47
N6-H6N...N8#3	0.76(7)	2.127(3)	2.870(4)	165.59

#1: -x,+y,-z+1/2

#3: x+1/2,+y-1/2,+z

Table S2 Hydrogen bonds (Å and deg) in **2**

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
N2-H2N...O111(#1)	0.818(5)	2.498(9)	3.062(10)	127.19(8)
N2-H2N...O333(#2)	0.818(4)	2.351(5)	2.988(16)	135.21(8)
N4-H4N ...O111(#1)	0.880(9)	2.340(8)	3.049(12)	137.75(6)
N4-H4N ...O111(#3)	0.880(9)	2.330(10)	3.016(14)	134.77(6)

#1: x,y,z
#2: -x+1/2+1,+y+1/2,-z-1/2
#3: -x+1/2+1,+y-1/2,-z-1/2

Table S3 List of Fourier peaks showing coordinates and distances in the asymmetric unit of **1**.

	x	y	z	sof	U	Peak	Distances to nearest atoms (including symmetry equivalents)
Q1	1	0.4737	0.1513	0.7023	1.00000	0.05	0.79	1.01 N5 1.06 RU2 2.08 C24 2.17 C22
Q2	1	0.2582	0.0790	0.2945	1.00000	0.05	0.75	1.03 RU1 1.13 O4 1.89 O2 1.96 C9
Q3	1	0.0244	0.2004	0.7953	1.00000	0.05	0.68	0.98 RU3 1.42 O7 1.54 O8 2.06 O7
Q4	1	0.4727	0.2164	0.7034	1.00000	0.05	0.65	0.94 O6 1.08 RU2 1.95 C20 2.23 O5
Q5	1	0.0291	0.2595	0.7992	1.00000	0.05	0.62	1.07 RU3 1.44 N7 1.48 O8 2.08 N7
Q6	1	0.2056	0.0772	0.2076	1.00000	0.05	0.60	1.02 RU1 1.26 N3 1.86 O3 2.05 O4
Q7	1	0.2527	0.0149	0.3017	1.00000	0.05	0.59	1.02 RU1 1.22 O2 2.01 N1 2.02 O1
Q8	1	0.2622	0.0578	0.2242	1.00000	0.05	0.51	1.00 RU1 1.07 O3 1.99 C7 2.05 O2
Q9	1	0.2026	0.0148	0.2141	1.00000	0.05	0.51	1.01 RU1 1.14 O1 1.90 N3 2.16 N1
Q10	1	0.0689	0.2378	0.7793	1.00000	0.05	0.46	0.76 O8 1.46 RU3 1.77 C28 2.24 N7
Q11	1	0.5000	0.0510	0.7500	0.50000	0.05	0.42	0.74 C24 1.81 N6 1.89 N5 2.82 H5B
Q12	1	0.4618	0.1856	0.7865	1.00000	0.05	0.41	0.87 O5 1.13 RU2 1.86 C18 2.27 O6
Q13	1	0.1910	0.0465	0.3022	1.00000	0.05	0.41	0.89 N1 1.25 RU1 1.74 C13 2.01 N3
Q14	1	0.2792	0.2083	0.4120	1.00000	0.05	0.39	0.77 H10C 0.83 C10 0.98 H10A 1.72 H10B
Q15	1	0.3218	-0.0492	0.2780	1.00000	0.05	0.38	0.69 C3 0.74 C4 1.47 H3 1.72 O2
Q16	1	0.0302	0.2243	0.7204	1.00000	0.05	0.37	0.91 RU3 1.56 O7 1.76 O8 1.85 N7
Q17	1	0.3368	0.0025	0.3927	1.00000	0.05	0.37	0.85 O2 1.36 C4 1.83 C5 1.91 H5C
Q18	1	0.3218	0.1583	0.0619	1.00000	0.05	0.37	0.83 H6C 0.94 C6 0.99 H6B 1.82 H6A
Q19	1	-0.0111	0.3729	0.6001	1.00000	0.05	0.35	0.77 C31 0.90 N8 1.54 C30 1.57 C32

Q20 1 0.1835 -0.1124 0.0764 1.00000 0.05 0.35 0.86 H1A 1.04 H1C 1.04 C1 1.90 H1B

Q21 1 -0.0188 0.4299 0.6471 1.00000 0.05 0.35 0.84 N8 1.90 C32 2.00 C31 2.03 N6

Q22 1 0.3736 -0.0387 0.3373 1.00000 0.05 0.35 0.73 C4 0.85 C5 1.38 H5B 1.42 H5A

Q23 1 0.1601 0.0499 0.2295 1.00000 0.05 0.34 1.03 N3 1.45 C14 1.46 RU1 1.64 N1

Q24 1 0.0553 0.2772 0.7332 1.00000 0.05 0.34 1.24 N7 1.69 RU3 1.76 O8 2.02 C32

Q25 1 0.1157 0.2138 0.8134 1.00000 0.05 0.34 0.70 O8 0.74 C28 1.88 C29 1.89 C27

Q26 1 0.2114 0.1861 0.8769 1.00000 0.05 0.34 0.64 C29 0.77 H29A 0.90 H29B 1.55 H29C

Q27 1 0.4746 0.1207 0.6594 1.00000 0.05 0.34 0.59 N5 1.56 C24 1.59 C22 1.92 RU2

Q28 1 0.3004 0.0376 0.2996 1.00000 0.05 0.34 0.84 O2 1.51 RU1 1.79 C4 2.08 O3

Q29 1 0.0842 0.0491 0.2437 1.00000 0.05 0.33 0.82 C14 0.88 C13 1.70 N4 1.81 N2

Q30 1 0.2050 0.0718 0.2827 1.00000 0.05 0.32 0.96 RU1 1.53 O4 1.61 N1 1.75 N3

Q31 1 0.3309 0.1156 0.1363 1.00000 0.05 0.32 0.72 C6 0.81 C7 1.29 H6A 1.43 H6C

Q32 1 0.3353 0.0937 0.0486 1.00000 0.05 0.31 0.89 H6C 0.96 H6A 1.02 C6 1.83 H6B

Q33 1 0.4670 -0.0264 0.6543 1.00000 0.05 0.31 1.00 N6 1.86 N8 2.04 C24 2.16 C23

Q34 1 0.4785 0.1617 0.7828 1.00000 0.05 0.31 0.91 RU2 1.32 O5 1.81 N5 1.93 N5

Q35 1 0.0899 0.1398 0.7339 1.00000 0.05 0.31 0.65 C27 0.80 C26 1.47 H27 1.72 C28

Q36 1 -0.0090 0.3364 0.5501 1.00000 0.05 0.31 0.83 C30 0.90 C31 1.40 H30 1.48 H31

Q37 1 0.4488 0.2733 0.6777 1.00000 0.05 0.30 0.68 O6 0.96 C20 2.00 C21 2.10 C19

Q38 1 0.2809 0.1055 0.1401 1.00000 0.05 0.30 0.75 C7 0.88 O3 1.70 C6 1.88 H6C

Q39 1 0.2550 -0.0397 0.3808 1.00000 0.05 0.30 1.89 O2 1.90 H11 2.25 C11 2.28 C4

Q40 1 0.4656 0.2618 0.6191 1.00000 0.05 0.30 0.88 O6 1.79 C20 2.20 H21A 2.31 C21

Q41 1 0.2310 -0.0380 0.1618 1.00000 0.05 0.29 0.67 O1 0.88 C2 1.94 C1 2.03 C3

Q42 1 0.0184 0.0804 0.5930 1.00000 0.05 0.28 0.66 H25A 0.90 C25 1.18 H25C 1.80 H25B

Q43 1 0.1285 0.0874 0.1251 1.00000 0.05 0.28 0.65 C16 0.77 N3 1.44 H16 1.65 C15
Q44 1 0.2721 0.1395 0.3184 1.00000 0.05 0.28 0.64 O4 0.66 C9 1.81 C8 1.91 C10
Q45 1 0.1612 0.1823 0.8672 1.00000 0.05 0.28 0.72 C29 0.79 C28 1.35 H29B 1.39 H29C
Q46 1 0.3666 0.2272 0.8416 1.00000 0.05 0.28 0.75 C17 0.84 C18 1.25 H17B 1.39 H17A
Q47 1 0.0291 0.1608 0.6436 1.00000 0.05 0.28 0.54 O7 1.13 C26 2.06 C25 2.22 H25C
Q48 1 0.4600 0.0873 0.7133 1.00000 0.05 0.27 0.75 C24 0.81 N5 1.71 C24 1.88 N6
Q49 1 0.2394 0.1360 0.3727 1.00000 0.05 0.27 0.86 O4 1.73 C9 1.94 H21B 2.11 H10C
Q50 1 0.2616 0.1482 0.2978 1.00000 0.05 0.27 0.70 C9 0.79 O4 1.73 C8 1.96 C10

Fig. S1 EPR spectrum of $[(acac)_2Ru^{III}(HL^-)]$ (**1**) in 1:1 CH_2Cl_2-tolene at 77 K.

Fig. S2 ^1H NMR spectra in $CDCl_3$ of (a) $[(acac)_2Ru^{III}(HL^-)]$ (**1**) and (b) $[(acac)_2Ru^{III}(HL_2)](ClO_4)$ (**2**).

Fig. S3 Showing Q-peaks over N6 as Q33 (Green, Molecule $\mathbf{2}^+$) and N8 as Q21 (Green, Molecule $\mathbf{3}^-$) in the crystal of **1**.

Fig. S4 Single crystal X-ray structure of the cation of $[(acac)_2Ru^{III}(H_2L)](ClO_4)$ (**2**).

Fig. S5 UV-vis. spectra of **2** (5×10^{-5} mole dm^{-3}) in CH_3CN and on addition of one equivalent TBA salts of Cl^-, Br^-, I^-, HSO_4^-, OAc^- and $H_2PO_4^-$ and six equivalents of F^- (TBA = Tetrabutylammonium).

Fig. S6 UV-vis. spectral changes of **2** (5×10^{-5} mole dm^{-3}) in CH_3CN on gradual additions of 0-5 equivalents TBA salts of (a) Cl^-, (b) Br^-, (c) I^- and (d) HSO_4^- (TBA = Tetrabutylammonium).

Fig. S67 (a) The plot of the change in absorbance (ΔA) with respect to the initial absorbance of **2** at 516 nm in CH_3CN on each addition of OAc^- versus the concentration of OAc^-.

(b) The plot of the change in absorbance (ΔA) with respect to the initial absorbance of **2** at 516 nm in CH_3CN on each addition of F^- versus the concentration of OAc^-.

Fig S8 UV-vis. spectral changes of **2** (5×10^{-5} mole dm^{-3}) in CH_3CN on gradual additions of 0-7 equivalents of [TBA][OAc].

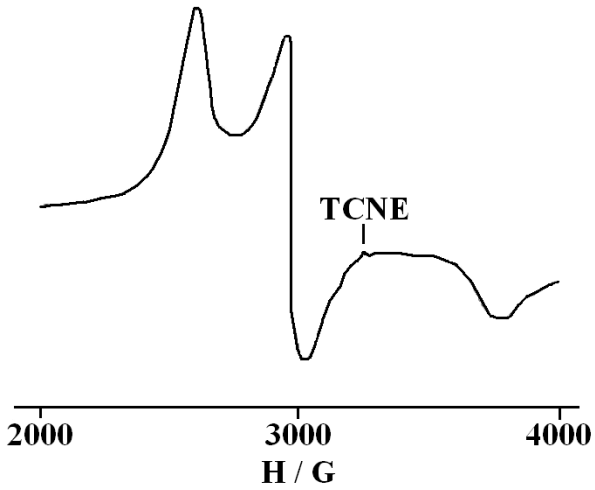

Fig. S1

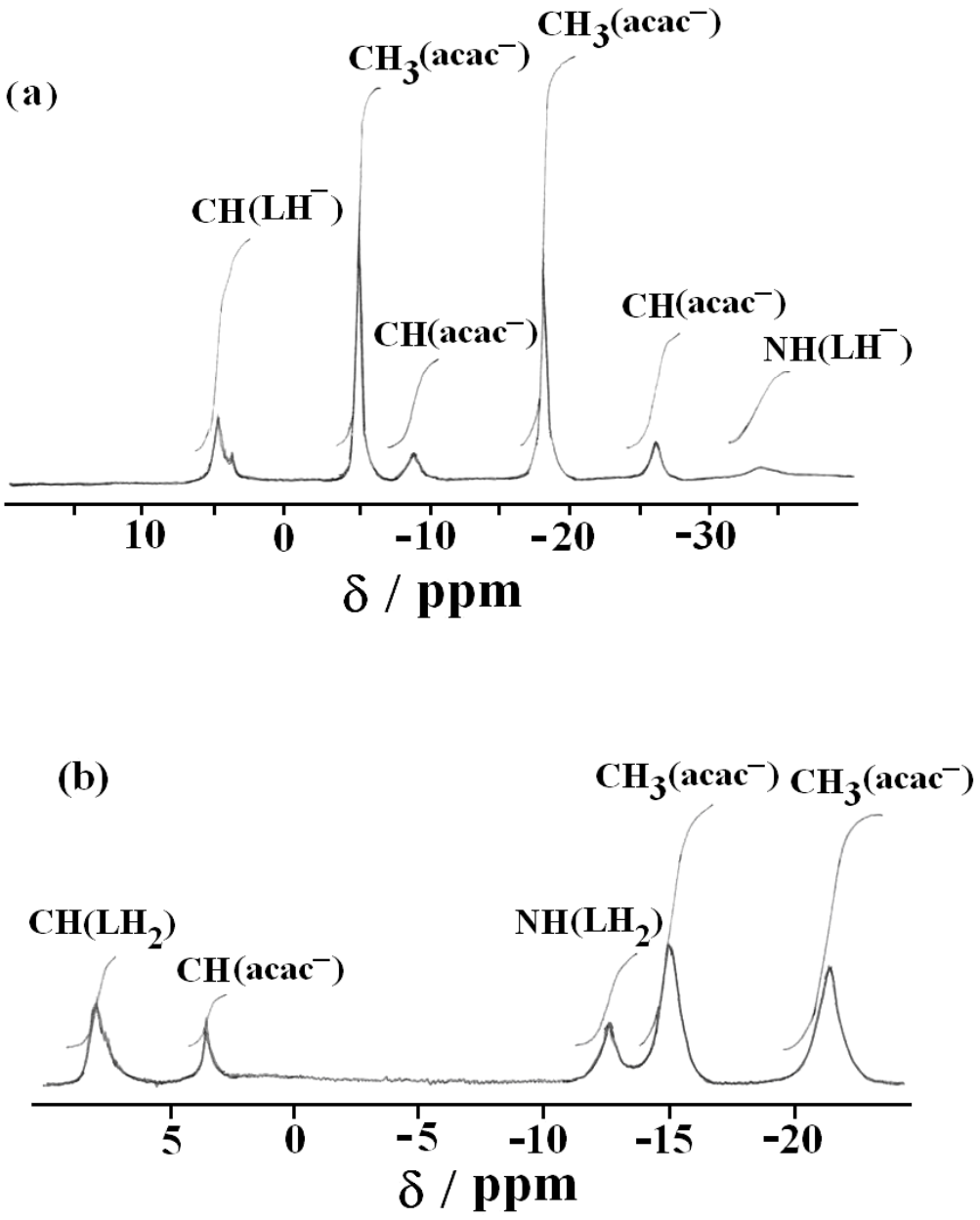

Fig. S2

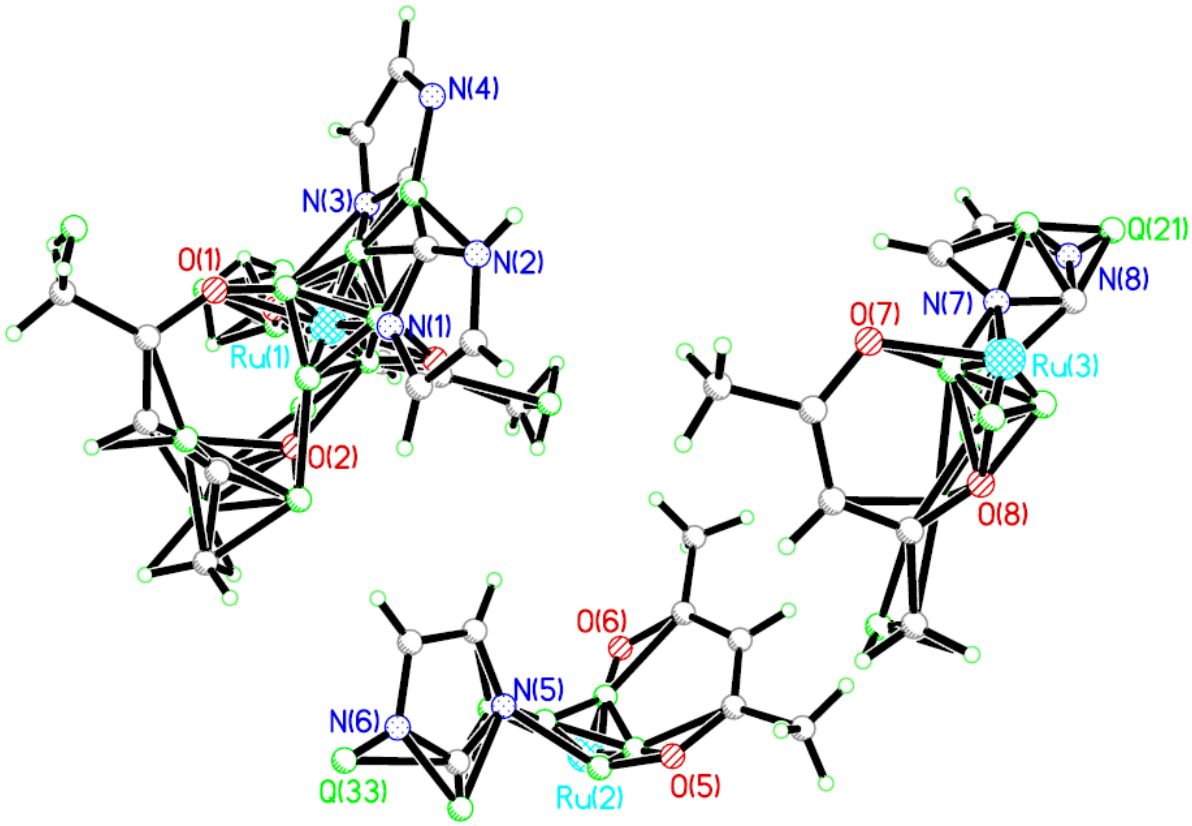

Fig. S3

The proton over nitrogen atom, N6 in $\mathbf{2}^{+}$ could be generated via Fourier map (Fig S3 and Table S3) with low intense peak of Q33= 0.31 e/Å^3 at a distance of N6-Q33 = 1.002 Å. This proton retains the realistic geometry on refinement.

We have also seen one low-intense peak at N8 of molecule $\mathbf{3}^{-}$ with Q21 = 0.35 e/Å^3 but at a shorter distance of N8-Q21 = 0.84 Å. However, it fails to retain the realistic geometry after refinement, therefore the said peak was neglected.

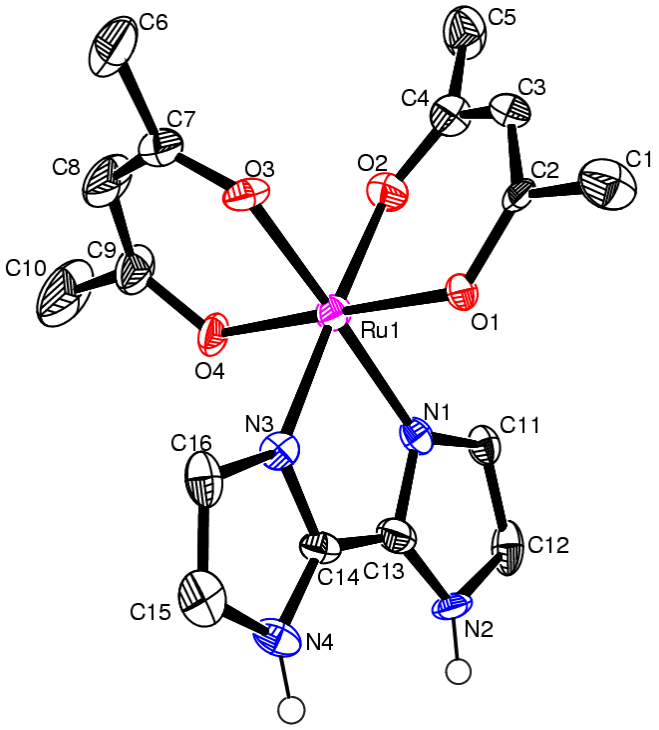
C6
C5
C4
C3
C7
C8
O3
O2
C2
C1
C9
C10
Ru1
O1
O4
N3
N1
C11
C16
C12
C14
C13
C15
N4
N2

Fig. S4

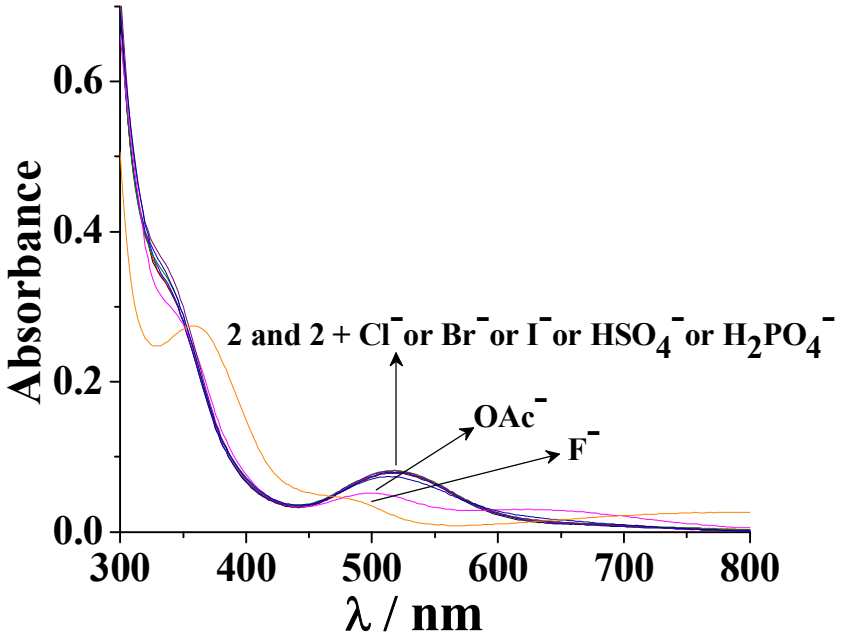

Fig. S5

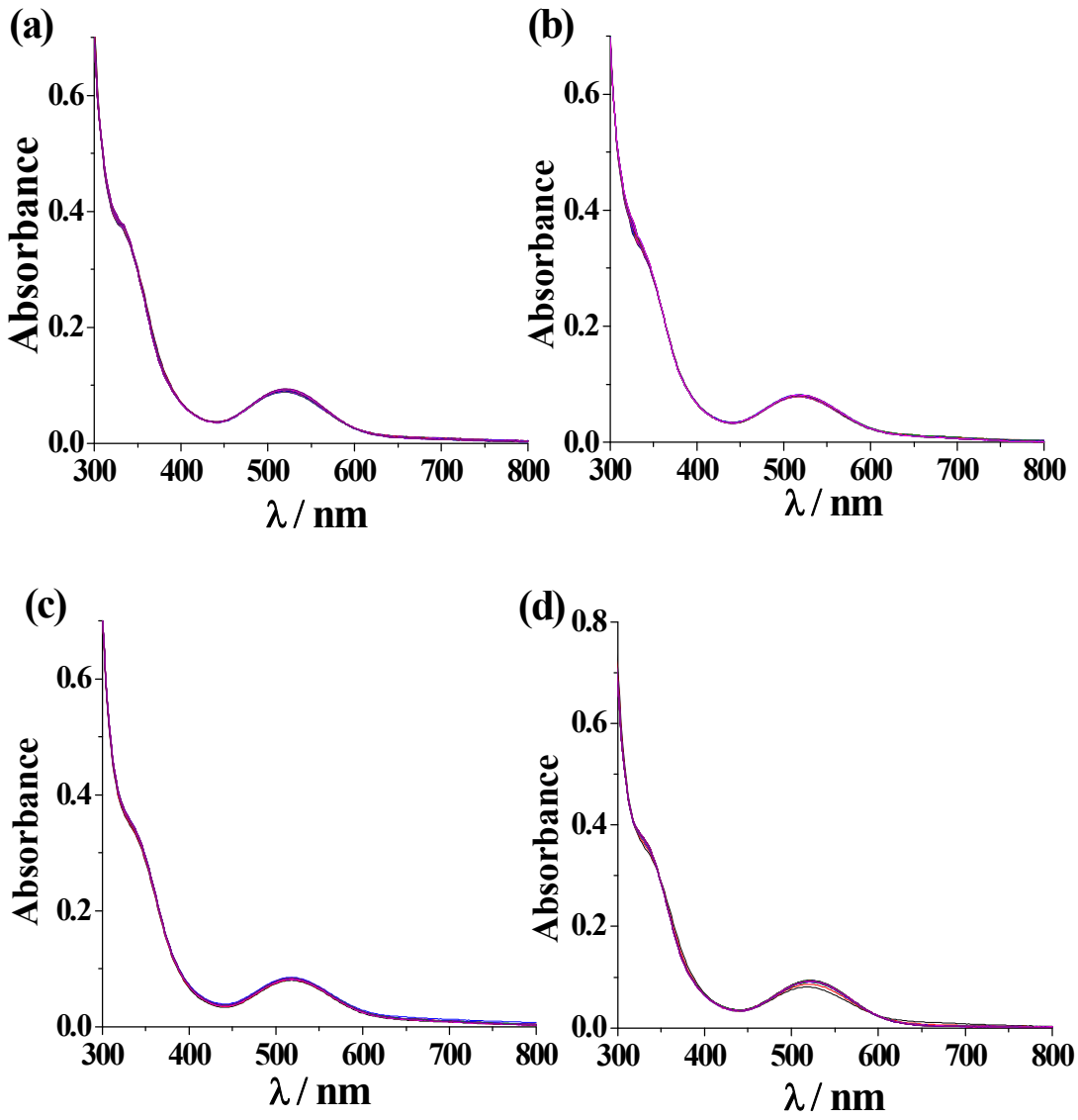

Fig. S6

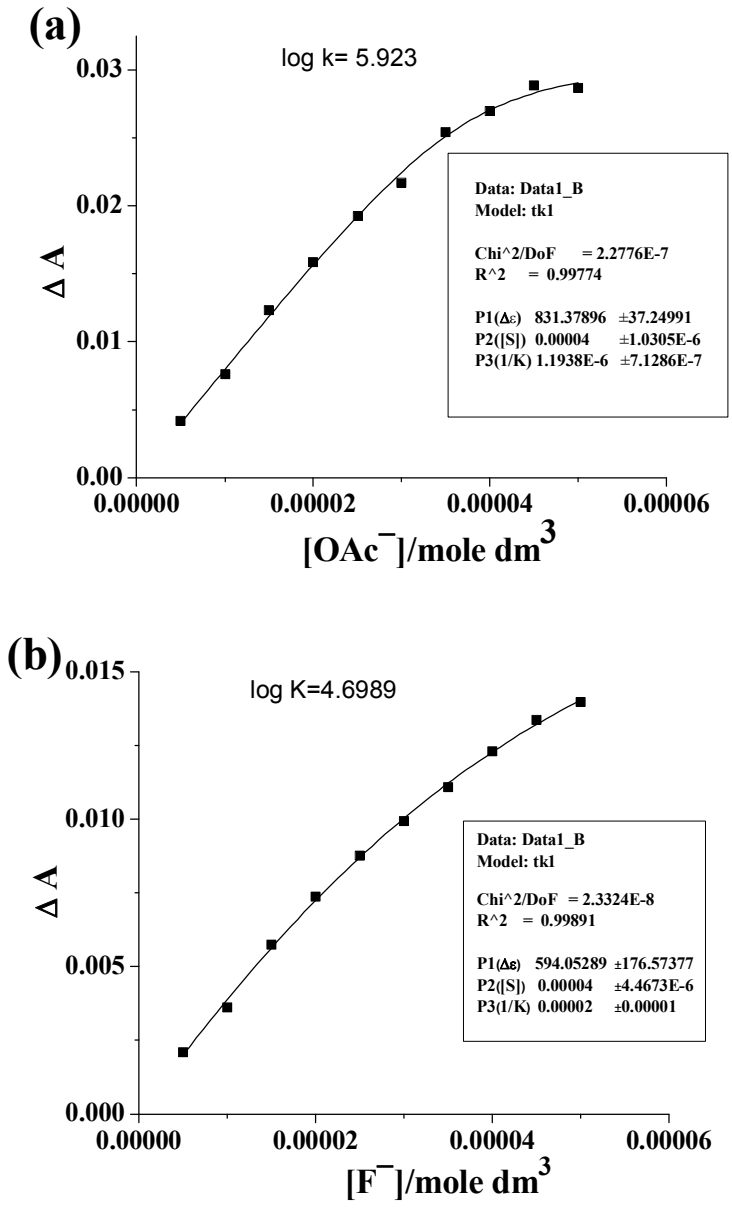
(a)
log k= 5.923
Data: Data1_B
Model: tk1
Chi^2/DoF = 2.2776E-7
R^2 = 0.99774
P1(Δε) 831.37896 ±37.24991
P2([S]) 0.00004 ±1.0305E-6
P3(1/K) 1.1938E-6 ±7.1286E-7
Δ A
0.03
0.02
0.01
0.00
0.00000
0.00002
0.00004
0.00006
[OAc⁻]/mole dm3
(b)
log K=4.6989
Data: Data1_B
Model: tk1
Chi^2/DoF = 2.3324E-8
R^2 = 0.99891
P1(Δε) 594.05289 ±176.57377
P2([S]) 0.00004 ±4.4673E-6
P3(1/K) 0.00002 ±0.00001
Δ A
0.015
0.010
0.005
0.000
0.00000
0.00002
0.00004
0.00006
[F⁻]/mole dm3

Fig. S7

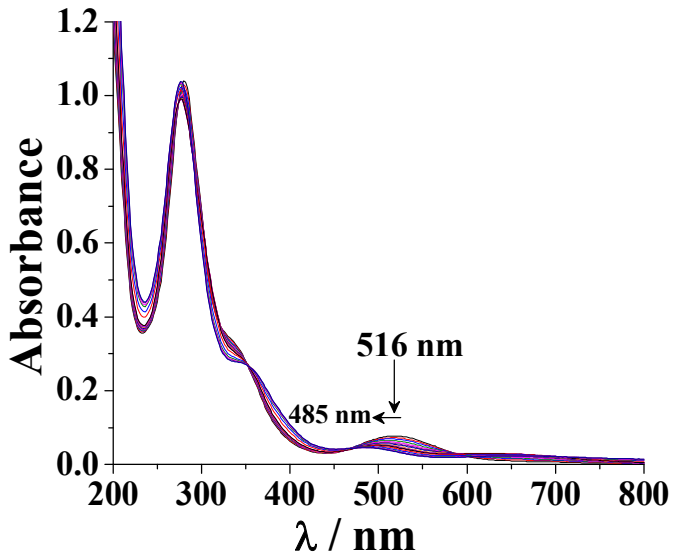

Fig. S8