Electronic Supplementary Material (ESI) for Dalton Transactions
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Supplementary Information

for

Photophysical, electrochemical and anion sensing properties of Ru(II) bipyridine complexes with 2, 2'-biimidazole-like ligands

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Measurement Methods

Elemental (C, H, and N) analyses were performed on an Elementar Vario EL analyzer. Electrospray ionization mass spectra (ESI-MS) were obtained on a Thermo LCQ DECA XP mass spectrometer. ^{1}H NMR spectra were obtained on a Varian Mercury-Plus 300 spectrometer. Electronic absorption spectra were obtained with a Shimadzu UV-3150 spectrophotometer. Emission spectra were recorded on a Hitachi F-4500 fluorescence spectrometer. Electrochemical measure-ments were carried out with a CHI-630C electrochemistry system. pH measurements were performed with a Mettler Toledo S20P pH meter equipped with an InLab Science Pro electrode. NMR, UV, luminescence spectra and electrochemical properties were recorded at 298 K.

p*K*a Determination: A 50 cm^3 solution consisted of 40 % acetonitrile, 60 % water, 0.1 $mol \cdot dm^{-3}$ phosphoric acid, and 6×10^{-5} $mol \cdot dm^{-3}$ **3** was prepared in a 25 ^oC titration vessel, magnetic stirring was employed during the whole experiment. 1 $mol \cdot dm^{-3}$ NaOH aqueous solution was added dropwise into the vessel, after each addition, pH value and absorption spectra of the mixed solution were recorded. The p*K*a value was fitted from the equation below:[1]

$$pKa = pH - \log\frac{A - A_{HA}}{A_{A^-} - A}$$

where A_{HA}, A_{A^-}, and A refer to the absorbances at the initial, final, and intermediate pH values at a given wavelength.

UV and Luminescence Titration: Quartz cuvettes with a 1 cm path length and a 3 cm^3 volume were used for all measurements. For a typical titration experiment, 3 μL aliquots of tetrabutylammonium (TBA)

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salts of F^-, OAc^-, Cl^-, Br^-, I^-, NO_3^-, and HSO_4^- (0.005 mol·dm^{-3} in acetonitrile) were added to a 2.5 cm^3 solution of **3** (6×10^{-5} mol·dm^{-3} in acetonitrile). For luminescence titration, the excitation wavelength was 470 nm, the exitation slit width was maintained at 5 nm, and the emission slit width at 10 nm.

Quantum yields were determined in freeze-thaw-pump degassed solutions of the complexes by a relative method using $[Ru(bpy)_3]^{2+}$ in the same solvent as the standard.[2] The quantum yields were calculated by the equation below:[3]

$$\Phi_r = \Phi_{std} \frac{A_{std}}{A_r} \frac{I_r}{I_{std}} \frac{\eta_r^2}{\eta_{std}^2}$$

where Φ_r and Φ_{std} are the quantum yields of unknown and standard samples (Φ_{std} = 0.062,[4] 298 K, in acetonitrile at λ_{ex} = 450 nm), A_r and A_{std} are the solution absorbance at the excitation wavelength (λ_{ex}), I_r and I_{std} are the integrated emission intensities, and η_r and η_{std} are the reflective indices of the solvent. Experimental errors in the reported luminescence quantum yields were about 20 %.

^{1}H NMR Titration: 1.25 μL aliquots of TBA salts of F^-, OAc^-, Cl^-, Br^-, I^-, NO_3^-, and HSO_4^- (0.12 mol·dm^{-3} in acetonitrile-*d*3) were added to a 400 μL solution of **1**, **2** and **3** (0.003 mol·dm^{-3} in acetonitrile-*d*3). Titration of **3** with F^-, OAc^- and OH^- was also performed in DMSO-*d*6 solutions. Spectra were recorded after each addition, and the sample shaken thoroughly before each measurement.

Electrochemical measurements in acetonitrile: A three-electrode assembly comprising of a glassy carbon working electrode, a Pt auxiliary electrode, and a non-aqueous Ag/-$AgNO_3$ reference electrode were used. The cyclic voltammetric (CV) and square wave voltammetric (SWV) measurements were carried out in acetonitrile solution of the complex (0.001 mol·dm^{-3}) and the concentration of the supporting electrolyte ($TBAPF_6$) was maintained at 0.1 mol·dm^{-3}. Nitrogen was bubbled into the solution for 10 min and the glassy carbon electrode was polished with an alumina / water slurry before each measurement. A scan rate of 100 mV·s^{-1} was employed for all measurements. The potentials obtained in acetonitrile were referenced against the $Ag/AgNO_3$ electrode, which under the given experimental conditions gave a value of 0.07 V for the Fc/Fc^+ couple. The $E_{1/2}$ values were determined from CV using the relation $E_{1/2} = 0.5(E_{pc} + E_{pa})$, where E_{pc} and E_{pa} were cathodic and anodic potentials, respectively, and also directly obtained from the peak values of SWV curves.

The diagram of $Ru^{2+/3+}$ potential *vs* pH: A three-electrode assembly comprising of a glassy carbon working electrode, a Pt auxiliary electrode, and an aqueous Ag/AgCl reference electrode were used. The

$Ru^{2+/3+}$ potentials were obtained from SWV measurements, which were carried out in acetonitrile / water (2:3 / V:V) solution of **3** (0.001 mol·dm^{-3}). Different buffer systems (0.1 mol dm^{-3}) were employed over different pH ranges: 0 – 2, perchlorate; 2 – 4, phthalate; 4 – 8, phosphate; 8 – 12, borate.[5] The potentials obtained in acetonitrile / water were referenced against the Ag/AgCl electrode, which under the given experimental conditions gave a value of 0.26 V for the Fc/Fc^+ couple (remained constant over the pH range 0 – 12).

Table S1 Photophysical and Redox Properties of **1**, **2**, **3** and $[Ru(bpy)_3]^{2+}$ in acetonitrile at 298 K

	Abs, λ_{max} / nm ($10^{-4}\varepsilon$ / M^{-1} cm^{-1})	Lum. λ_{max} / nm	Φ_r [a]	Oxid. [b] / V	Red. [b] / V
1	290 (4.98), 341 (0.84), 475 (0.80)	638 [c]	4.5×10^{-3}	0.71	-1.86, -2.14, -2.24
2	290 (4.94), 330 (3.10), 348 (3.53), 465 (0.96)	624 [c]	2.8×10^{-3}	0.73	-1.82, -2.08, -2.19
3	290 (5.01), 332 (3.35), 349 (3.54), 462 (1.08)	617 [c]	2.8×10^{-3}	0.74	-1.80, -2.06, -2.18
$[Ru(bpy)_3]^{2+}$	287 (5.03), 450 (1.00)	597 [d]	6.2×10^{-2} [e]	0.97	-1.65, -1.84, -2.10

[a] Estimated errors were about 20%. [b] *vs.* $Ag/AgNO_3$, which gives $E_{1/2}$ = 0.07 V for Fc/Fc^+. [c] λ_{ex} = 470 nm. [d] λ_{ex} = 450 nm. [e] Ref. 4

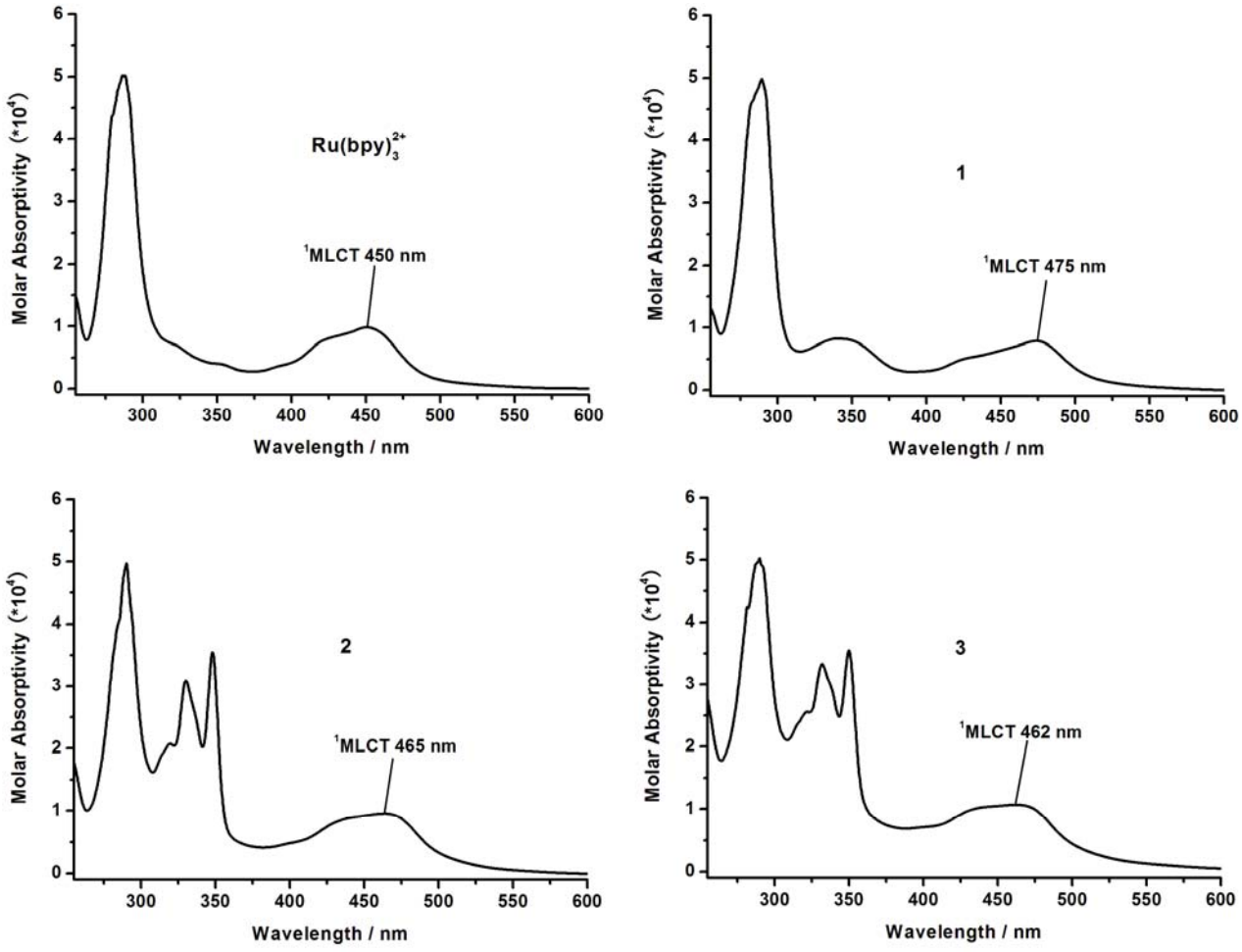

Fig. S1 Absorption spectra of $[Ru(bpy)_3]^{2+}$, **1**, **2** and **3** in acetonitrile at 298 K

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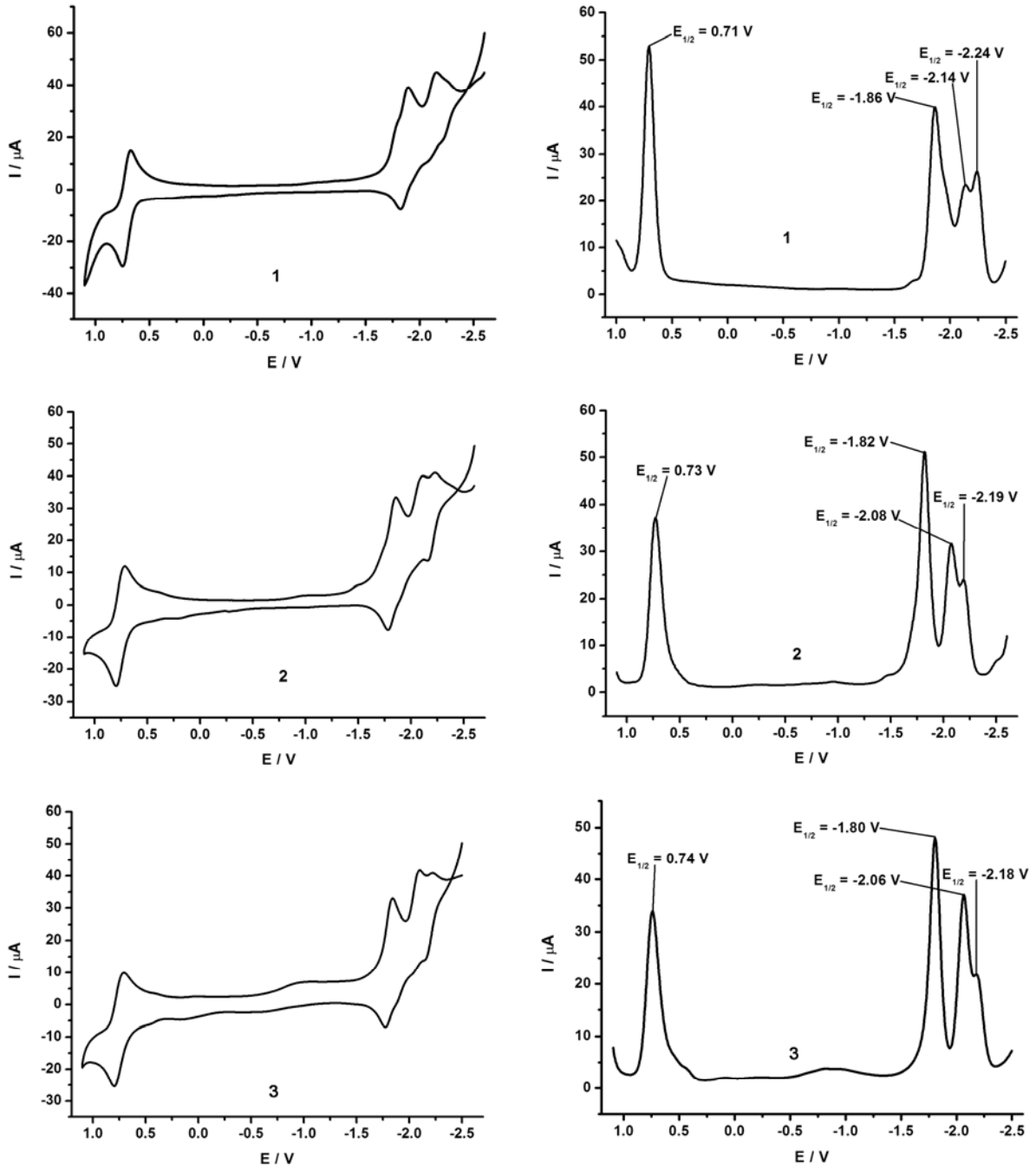

Fig. S2 CV (left) and SWV (right) curves of **1**, **2** and **3** in acetonitrile with a scan rate of 100 $mV \cdot s^{-1}$ at 298 K (vs. $Ag/AgNO_3$)

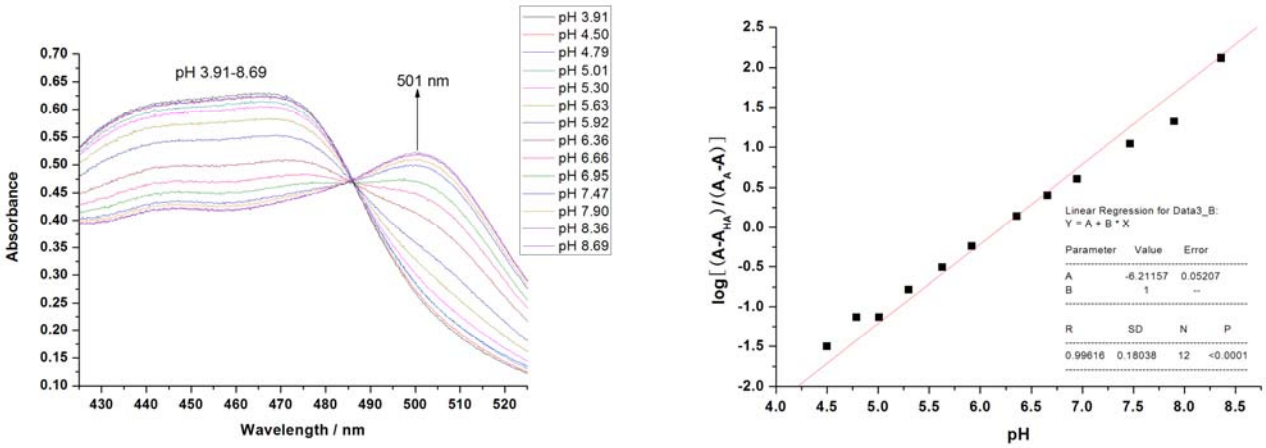

Fig. S3 Determination of pKa_1 of **3** by UV method. Left: Absorption spectral change as pH value increases. Right: Linear fitting of p*K*a value.

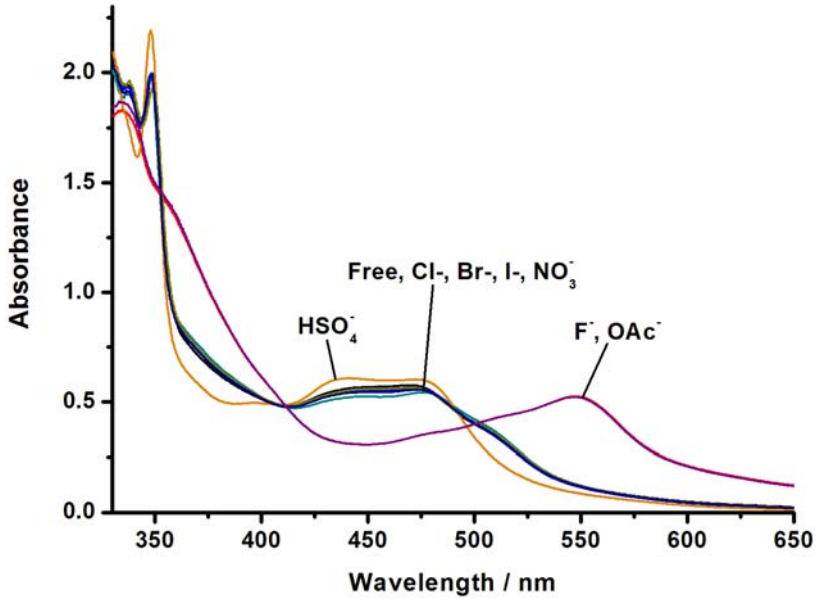

Fig. S4 Absorption spectral changes of **3** (6×10^{-5} mol·dm^{-3}) in acetonitrile upon addition of 10 equiv of different anions.

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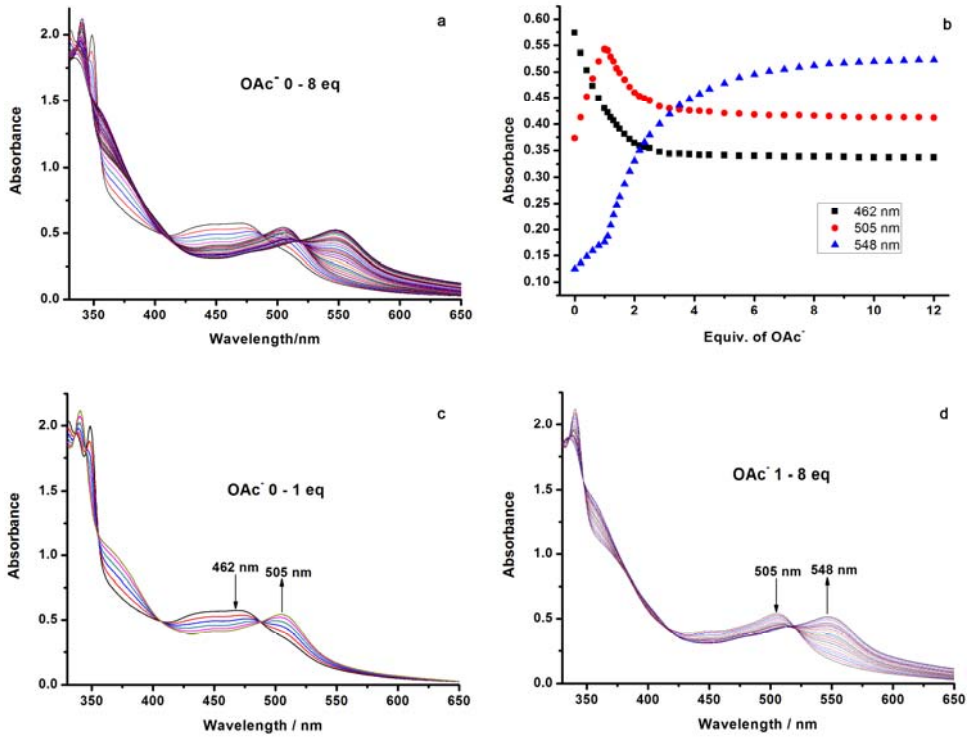

Fig. S5 UV-vis tiration of **3** (6×10^{-5} mol·dm^{-3}) in acetonitrile upon addition of OAc^- (a) 0 – 8 equiv, (c) 0 – 1 equiv, and (d) 1 – 8 equiv. (b) Absorbance at 462, 505 and 548 nm versus equivalents of OAc^-.

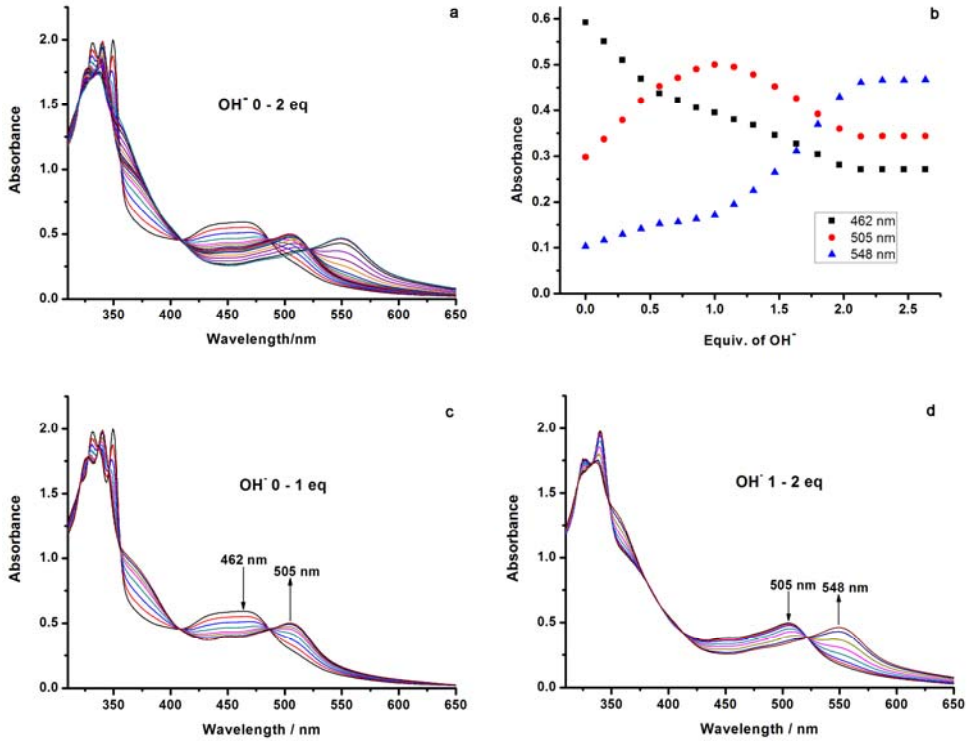

Fig. S6 UV-vis tiration of **3** (6×10^{-5} mol·dm^{-3}) in acetonitrile upon addition of OH^- (a) 0 – 2 equiv, (c) 0 – 1 equiv, and (d) 1 – 2 equiv. (b) Absorbance at 462, 505 and 548 nm versus equivalents of OH^-.

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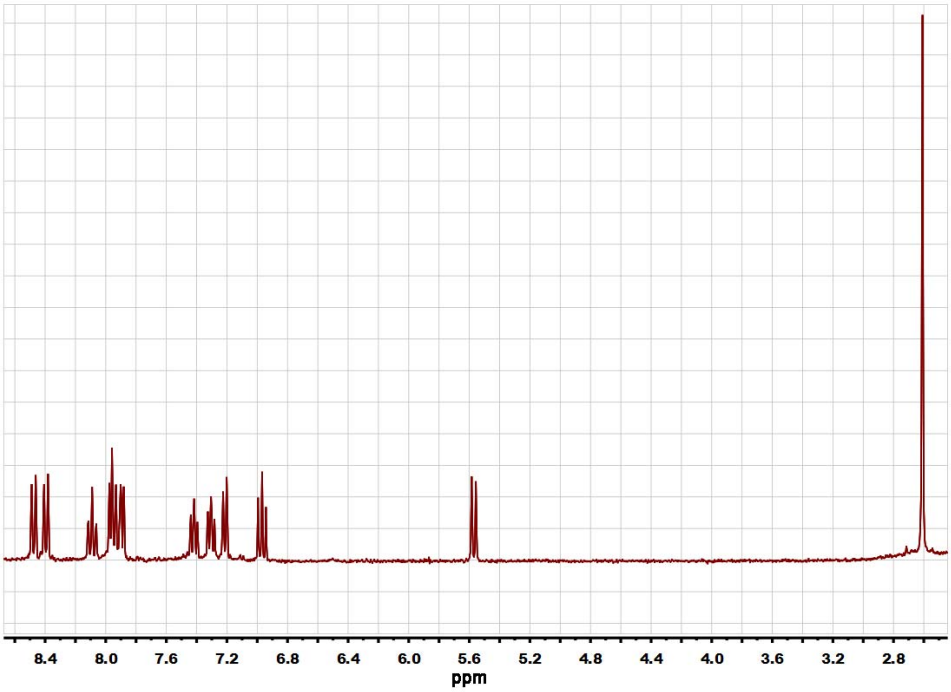

Fig. S7 ^{1}H NMR spectra of **3** in acetonitrile-*d*3 (298K, 300 MHz).

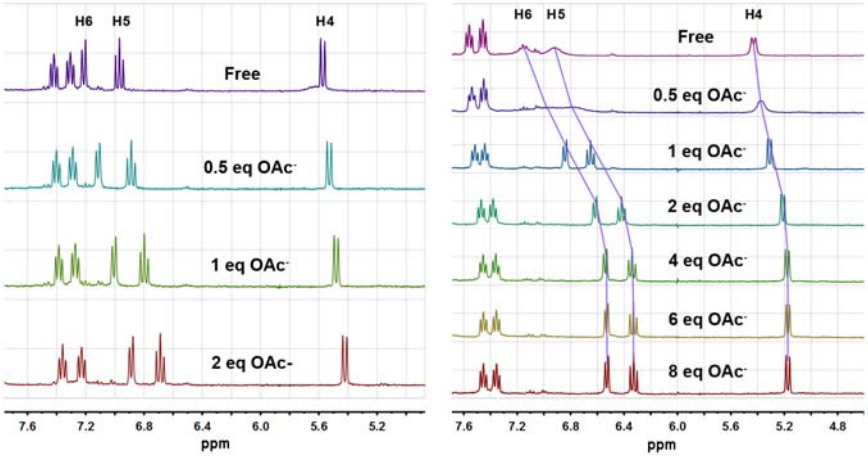

Fig. S8 ^{1}H NMR titration of **3** (0.003 mol·dm^{-3}) in acetonitrile-*d*3 (left) and DMSO-*d*6 (right) with OAc^{-} (298K, 300MHz).

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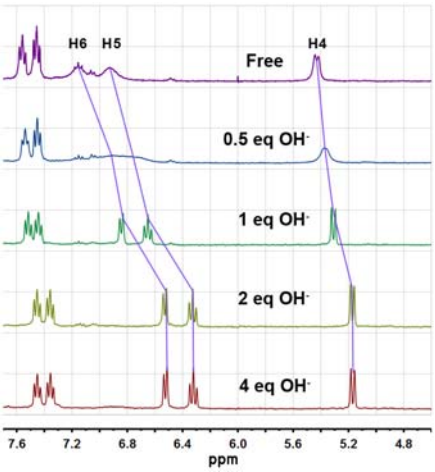

Fig. S9 ^{1}H NMR titration of **3** in DMSO-*d*6 (0.003 mol·dm^{-3}) with OH^- (298K, 300MHz).

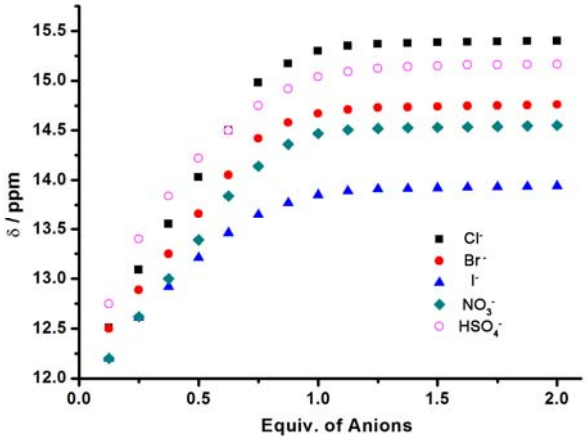

Fig. S10 Chemical shift changes of the N-H signal of **3** (0.003 mol·dm^{-3} in acetonitrile-*d*3) upon addition of Cl^-, Br^-, I^-, NO_3^- and HSO_4^- anions.

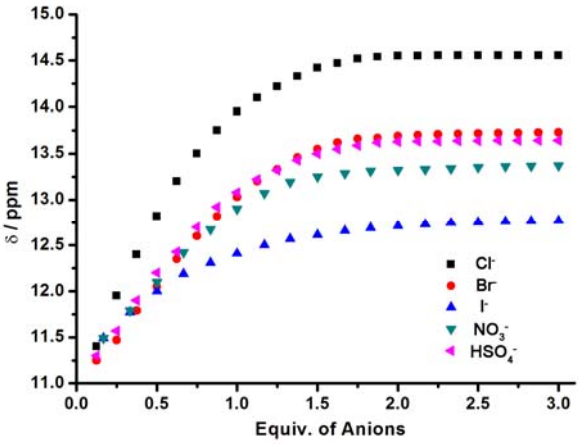

Fig. S11 Chemical shift changes of the N-H signal of **1** (0.003 mol·dm^{-3} in acetonitrile-*d*3) upon addition of Cl^-, Br^-, I^-, NO_3^- and HSO_4^- anions.

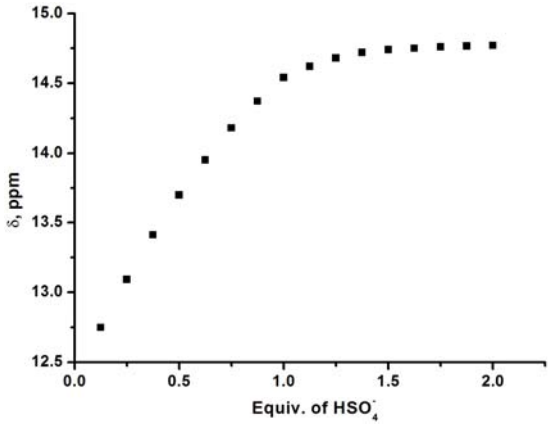

Fig. S12 Chemical shift change of the N-H signal of **2** (0.003 mol·dm^{-3} in acetonitrile-*d*3) upon addition of HSO_4^-.

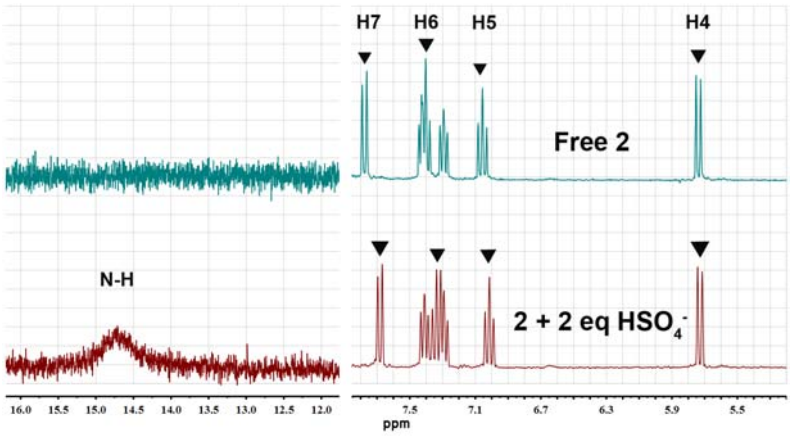

Fig. S13 ^{1}H NMR spectra of **2** (0.003 mol·dm^{-3} in acetonitrile-*d*3) in the absence and presence of 2 equiv of HSO_4^- (298 K, 300 MHz)

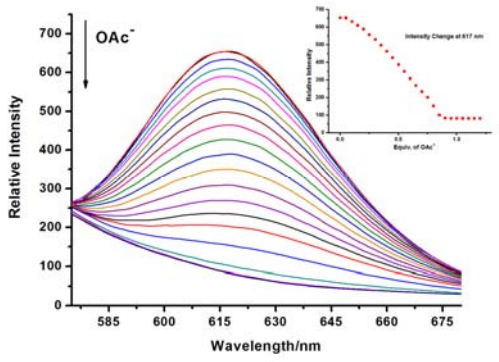

Fig. S14 Emission spectral response of **3** (6×10^{-5} mol·dm^{-3} in acetonitrile, 298K, λ_{ex} = 470 nm) upon addition of OAc^- anion. Inset: Intensity at 617 nm versus equiv of OAc^-.

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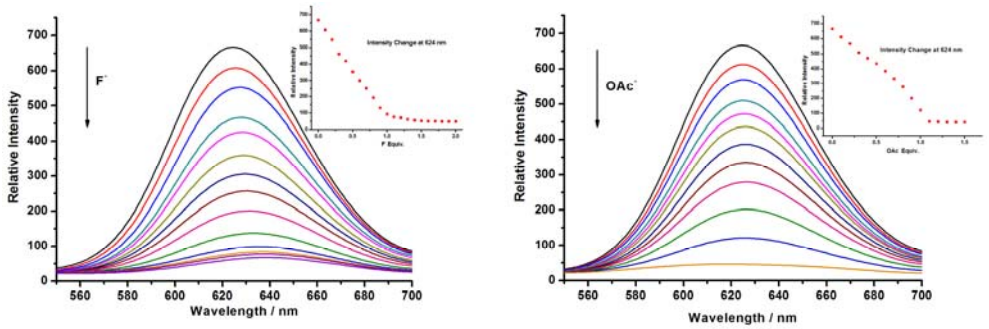

Fig. S15 Emission spectral responses of **2** (6×10^{-5} mol·dm^{-3} in acetonitrile, 298K, λ_{ex} = 470 nm) upon addition of F^- (left) and OAc^- (right). Insets: Intensity at 624 nm versus equiv of anions.

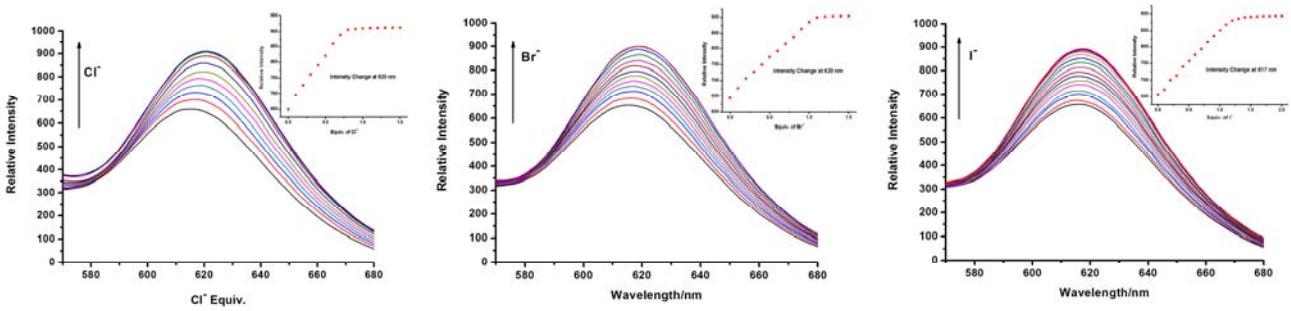

Fig. S16 Emission spectral responses of **3** (6×10^{-5} mol·dm^{-3} in acetonitrile, 298K, λ_{ex} = 470 nm) upon addition of Cl^-, Br^- and I^- anions. Insets: Intensity at 620, 620 and 617 nm versus equiv of anions.

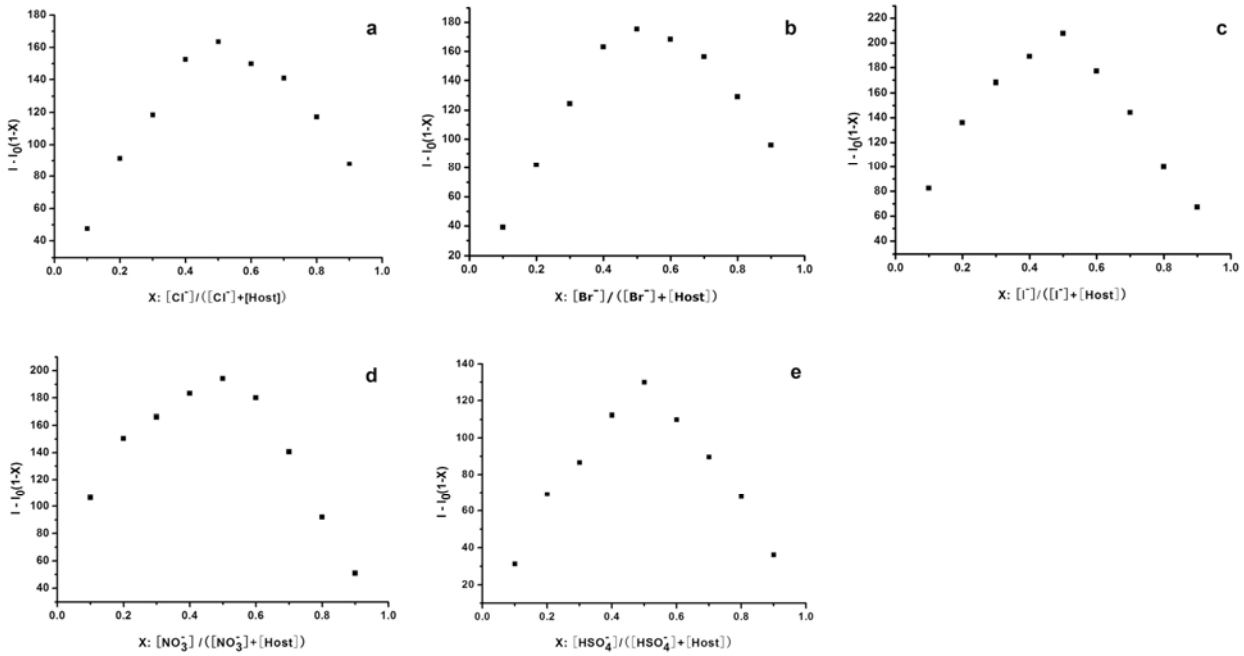

Fig. S17 Job plot analyses for **3** and (a) Cl^-, (b) Br^-, (c) I^-, (d) NO_3^- and (e) HSO_4^-.

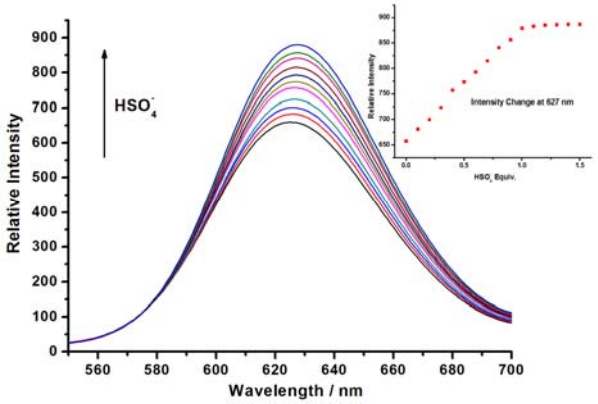

Fig. S18 Emission spectral response of **2** (6×10^{-5} mol·dm^{-3} in acetonitrile, 298K, λ_{ex} = 470 nm) upon addition of HSO_4^-. Inset: Intensity at 627 nm versus equiv of HSO_4^-.

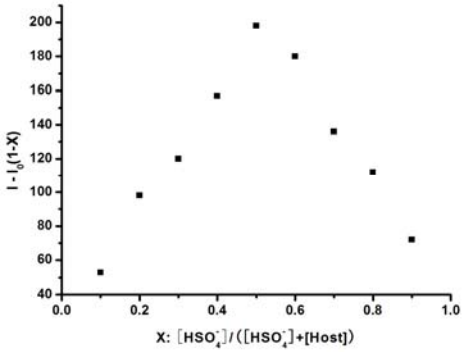

Fig. S19 Job plot analysis for **2** and HSO_4^-.

Table S2 Binding constants of **2** and **3** with 5 different anions in CH_3CN calculated from emission spectra (errors are given in parentheses) [a]

Anion	Log *K*	
	2	**3**
Cl^-	-	5.31 (0.05)
Br^-	-	5.24 (0.07)
I^-	-	5.21 (0.04)
NO_3^-	-	5.18 (0.04)
HSO_4^-	5.16 (0.06)	5.20 (0.05)

[a] Fitted to the equation[6] $\Delta F = \frac{\Delta\varepsilon([H]+[G]+\frac{1}{K}) \pm \sqrt{\Delta\varepsilon^2([H]+[G]+\frac{1}{K})^2 - 4\Delta\varepsilon^2[H][G]}}{2}$

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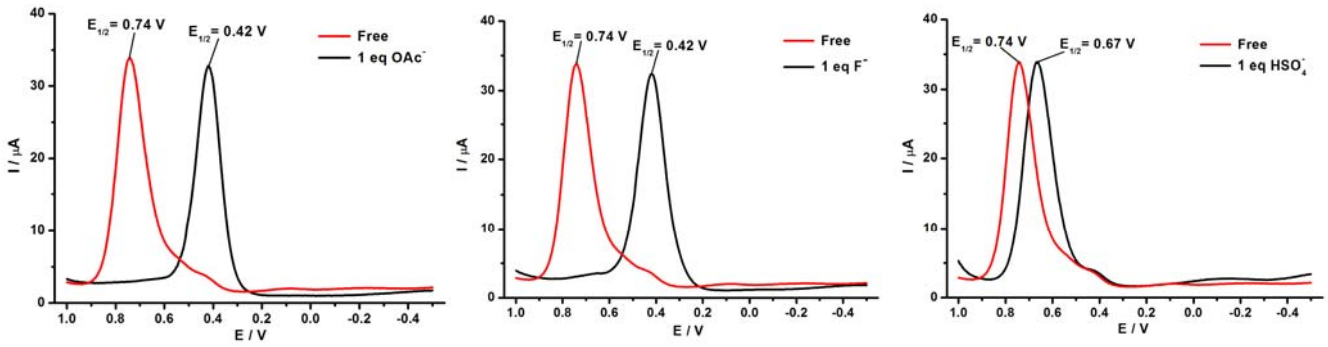

Fig. S20 SWV measurements of **3** in acetonitrile (0.001 mol·dm^{-3}) in the absence and presence of 1 equiv of OAc^- , F^- or HSO_4^- (*vs.* $Ag/AgNO_3$).

References

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2. B. Sullivan, D. Salmon, T. Meyer and J. Peedin, *Inorg. Chem.*, 1979, **18**, 3369-3374.
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