

**Electronic Supplementary Information (ESI)**

**pH-driven optical changes of platinum(II) complexes having carboxy-appended salophen ligands**

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## EXPERIMENTAL SECTION

**Synthesis.** All reagents were commercially available and used without further purification.

*(COOH)<sub>2</sub>-salophen ligand (L1).* *o*-Phenylenediamine (0.11 g, 1.0 mmol) was dissolved in MeOH (15 mL) after which a solution of 5-carboxysalicylaldehyde (0.34 g, 2.0 mmol) in MeOH (15 mL) was added dropwise to the solution followed by stirring for 2 h at room temperature. The solution was observed to take on a yellow coloration. The resulting precipitate was removed by filtration and washed with a small amount of MeOH to give **L1**. Yield: 35.7%. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): δ = 9.02 (s, 1H), 8.30-8.29 (d, 1H, *J* = 4.0 Hz), 7.93-7.90 (dd, 1H, *J* = 8 Hz), 7.48-7.39 (m, 2H), 7.00-6.98 (d, 1H, *J* = 8 Hz).

*(COOH)<sub>3</sub>-salophen ligand (L2).* A quantity of 3,4-diaminobenzoic acid (0.44 g, 2.9 mmol) was dissolved in MeOH (60 mL) after which a solution of 5-carboxysalicylaldehyde (0.97 g, 5.8 mmol) in MeOH (60 mL) was added dropwise to the solution followed by stirring for 2 h at room temperature. The solution was observed to take on a yellow coloration. The resulting precipitate was removed by filtration and washed with a small amount of MeOH to give **L2**. The crude product of **L2** was then used for a subsequent reaction without purification.

*(COOH)-salophen ligand (L3).* A quantity of 3,4-diaminobenzoic acid (1.0 g, 6.6 mmol) was dissolved in MeOH (40 mL) after which a solution of salicylaldehyde (0.16 g, 13.2 mmol) in MeOH (40 mL) was added dropwise to the 3,4-diaminobenzoic acid solution followed by stirring for 2 h at room temperature. The solution was found to take on a yellow coloration. The precipitate was removed by filtration and washed with a small amount of MeOH to give **L3**. Yield: 57.2%. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): δ = 9.04 (s, 1H), 8.97 (s, 1H), 7.99-7.98 (d, 1H, *J* = 4.0 Hz), 7.96-7.94 (dd, 1H, *J* = 8.0 Hz), 7.75-7.70 (m, 2H), 7.54-7.52 (d, 1H, *J* = 8.0 Hz), 7.47-7.40 (m 2H), 7.01-6.96 (m, 4H).

**Physical measurements.** <sup>1</sup>H-NMR spectra were acquired with a Bruker AVANCE NEO 400 instrument operating at 400 MHz, using the deuterated solvent to provide the lock signal and residual solvent tetramethylsilane as the internal reference. Elemental analyses for C, H and N were carried out at the Instrumental Analysis Centre of Josai University. SC-XRD measurements were recorded on an Oxford Gemini Ultra diffractometer employing graphite monochromated Mo K $\alpha$  radiation generated from a sealed tube ( $\lambda$  = 0.7107 Å). Data integration and reduction were undertaken with APEX4 program. The structures were solved by Olex2 with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. Hydrogen atoms were included in idealized positions and refined using a riding model. UV spectra and luminescence spectra were recorded on a JASCO V-730 and FP-8300, respectively. Absolute luminescence quantum yield values were measured using a Hamamatsu Photonics K.K. C9920-02.

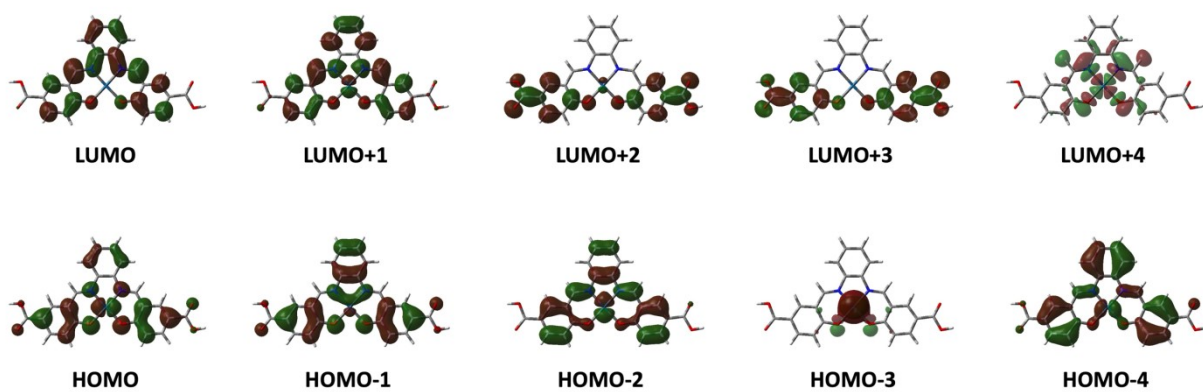
**Table S1** Crystal parameters for **1**·DMF and **3**·2H<sub>2</sub>O.

	<b>1</b> ·DMSO	<b>3</b> ·H <sub>2</sub> O
CCDC number	2251726	2251727
Formula	C <sub>22</sub> H <sub>14</sub> N <sub>2</sub> O <sub>6</sub> Pt·C <sub>2</sub> H <sub>6</sub> OS	C <sub>21</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> Pt·H <sub>2</sub> O
T/K	100	100
Crystal system	Monoclinic	Trigonal
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)	<i>P</i> -3 <i>c</i> 1 (#165)
<i>a</i> / Å	15.900(2)	19.9491(5)
<i>b</i> / Å	7.7115(10)	19.9491(5)
<i>c</i> / Å	18.708(2)	8.8324(3)
<i>α</i> / °	90	90
<i>β</i> / °	94.105(4)	90
<i>γ</i> / °	90	120
<i>V</i> / Å <sup>3</sup>	2288.1(5)	3044.08(18)
<i>Z</i>	4	6
GOF	1.074	1.065
<i>R</i> 1	0.0346	0.0407
<i>wR</i> 2	0.1023	0.1136

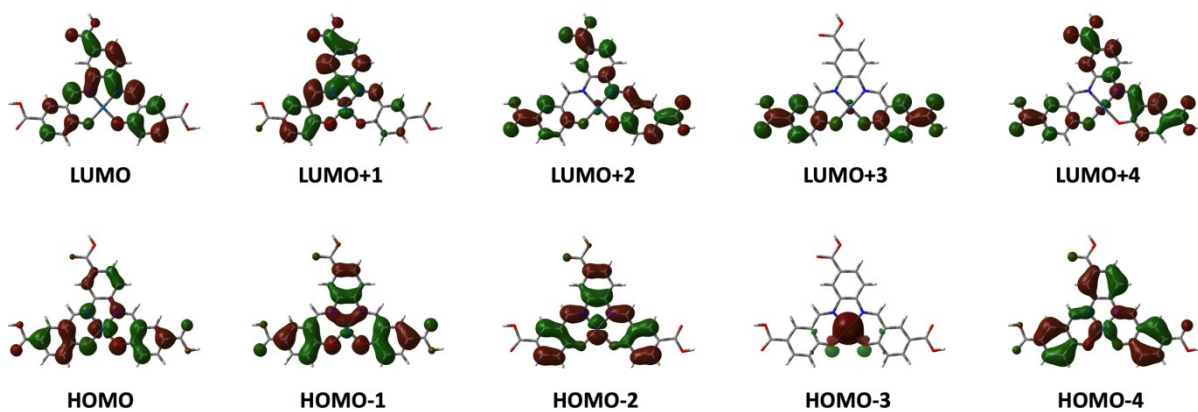
**Table S2** Selected calculated excitation energy values (E), dominant contributing transitions with associated percent contributions and assignments for complexes **1**, **2** and **3**.<sup>a</sup>

	$S_n$	E/eV	E/nm	Dominant transitions (percent contribution <sup>b</sup> )	Assignment	Oscillator strength
Complex <b>1</b>	1	2.53	491	HOMO → LUMO (98.3%)	MLCT	0.0854
	2	2.94	421	HOMO-1 → LUMO (94.2%) HOMO → LUMO+1 (3.5%)	MLCT ILCT	0.1387
	3	3.10	400	HOMO-1 → LUMO (3.8%) HOMO → LUMO+1 (93.2%)	MLCT ILCT	0.0128
Complex <b>2</b>	1	2.45	507	HOMO → LUMO (98.1%)	MLCT	0.1037
	2	2.89	429	HOMO-1 → LUMO (89.0%) HOMO → LUMO+1 (8.9%)	MLCT ILCT	0.1327
	3	2.98	416	HOMO-1 → LUMO (9.2%) HOMO → LUMO+1 (88.2%)	MLCT ILCT	0.0118
Complex <b>3</b>	1	2.36	526	HOMO → LUMO (98.1%)	MLCT	0.1048
	2	2.79	444	HOMO-1 → LUMO (95.9%) HOMO → LUMO+1 (2.3%)	MLCT ILCT	0.0674
	3	2.86	433	HOMO-1 → LUMO (2.4%) HOMO → LUMO+1 (95.2%)	MLCT ILCT	0.0097

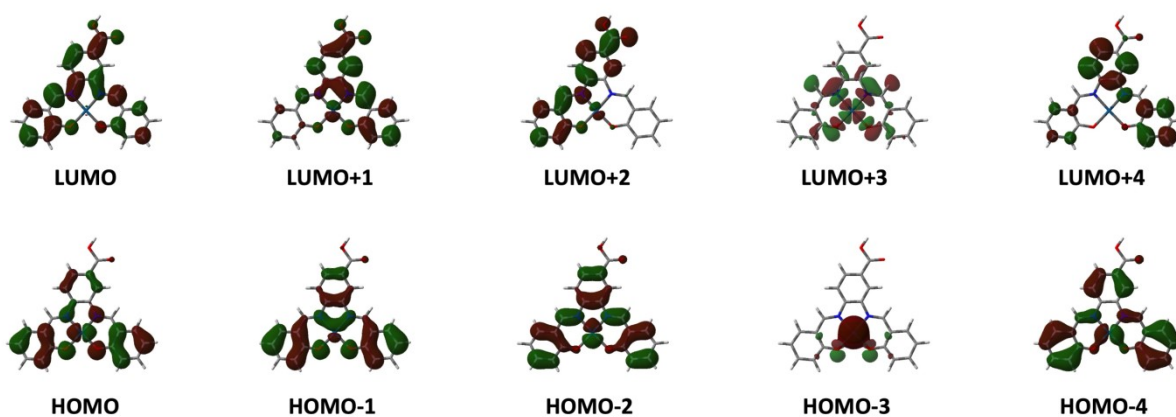
<sup>a</sup>Computed at the B3LYP/LANL2DZ/6-31G\* theoretical level. <sup>b</sup>The actual percent contribution = (configuration coefficient)<sup>2</sup> × 2 × 100%.



**Fig. S1.** Isodensity plots of the frontier orbitals of **1**.



**Fig. S2.** Isodensity plots of the frontier orbitals of **2**.

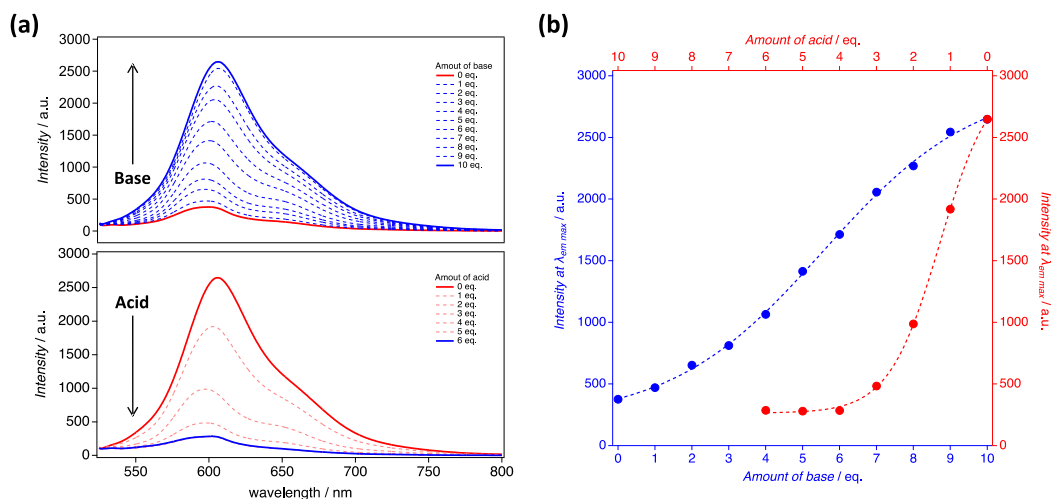


**Fig. S3.** Isodensity plots of the frontier orbitals of **3**.

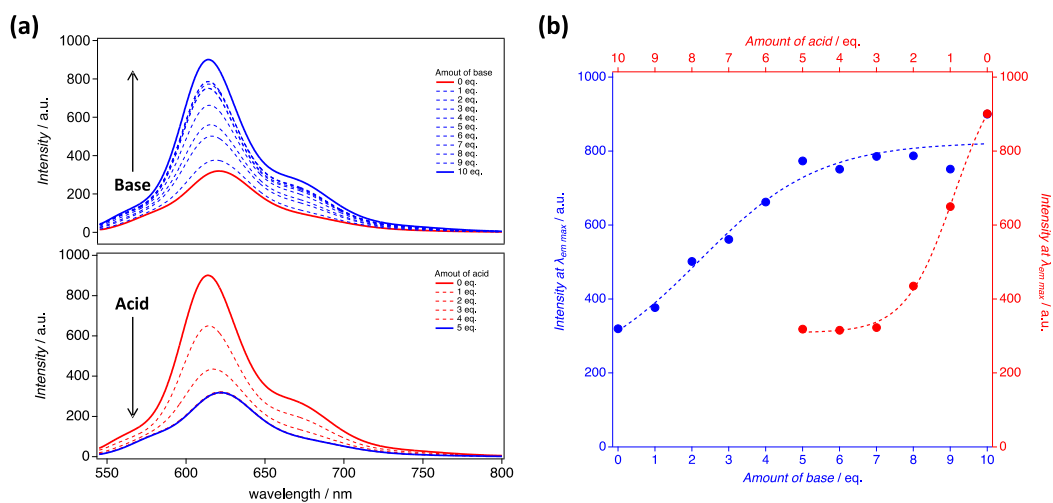
**Table S3** Selected calculated excitation energy values (E) for the deprotonated states of complexes **1**, **2** and **3**.<sup>a</sup>

	$S_n$	E/eV	E/nm	Oscillator strength
Deprotonated <b>1</b>	1	2.41	514	0.0859
	4	2.78	446	0.0485
	7	2.95	420	0.0051
Deprotonated <b>2</b>	1	2.43	510	0.0962
	4	2.78	446	0.0779
	8	2.99	414	0.0059
Deprotonated <b>3</b>	1	2.45	506	0.0984
	3	2.84	436	0.0959
	5	3.03	409	0.0087

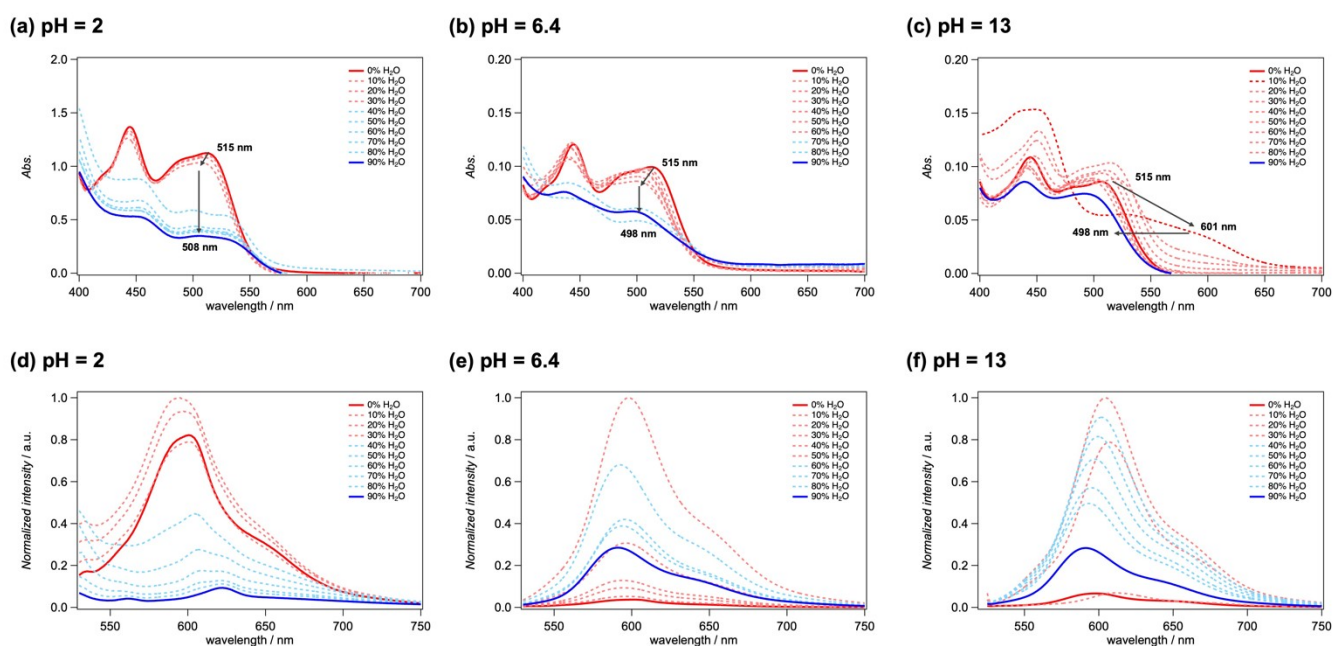
<sup>a</sup>Computed at the B3LYP/LANL2DZ/6-31G\* theoretical level.



**Fig. S4.** (a) Luminescence spectra of **2** (20  $\mu$ M in DMSO at 25  $^{\circ}$ C) while titrating with (top) *t*-BuOK from 0 to 10 eq. and (bottom) TsOH from 0 to 6 eq. (b) Titration plots of intensity changes at  $\lambda_{emmax}$  of **2**. Blue and red plots indicate the titration by base and acid, respectively.



**Fig. S5.** (a) Luminescence spectra of **3** (20  $\mu$ M in DMSO at 25  $^{\circ}$ C) while titrating with (top) *t*-BuOK from 0 to 10 eq. and (bottom) TsOH from 0 to 5 eq. (b) Titration plots of intensity changes at  $\lambda_{emmax}$  of **3**. Blue and red plots indicate the titration by base and acid, respectively.

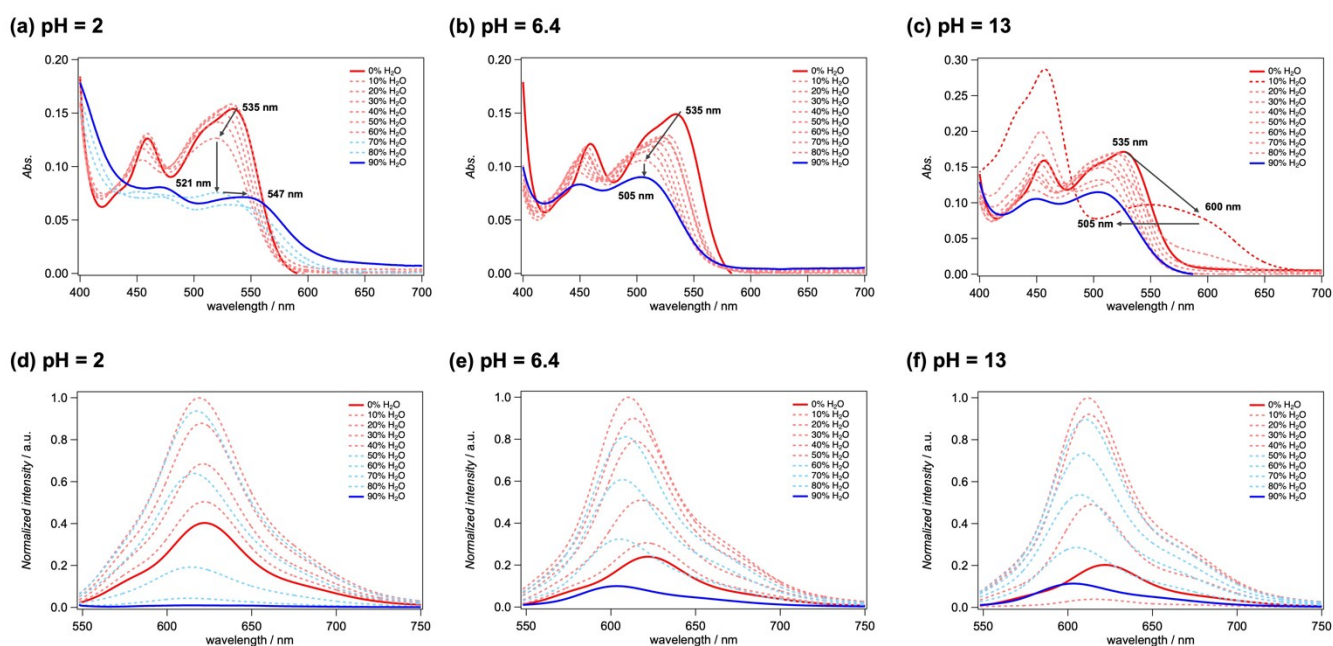


**Fig. S6.** (a) – (c) UV-vis spectra obtained from complex **2** in DMSO/H<sub>2</sub>O mixtures having various proportions of water. (d) – (f) Luminescence spectra obtained from complex **2** in DMSO/H<sub>2</sub>O mixtures having various proportions of water. The pH of the H<sub>2</sub>O was adjusted to 2.0, 6.4 or 13.0. Data were acquired with  $\lambda_{\text{ex}} = 515$  nm and a complex concentration of 20  $\mu\text{M}$ .

**Table S4** Variations in the UV-vis spectra of complex **2** with changes in pH.

	pH = 2.0	pH = 6.4	pH = 13.0
Initial	515 nm	515 nm	515 nm
Red shift	–	–	+ 86 nm
Blue shift	– 7 nm	– 17 nm	– 17 nm
$\Delta\lambda_{\text{max}}$	7 nm	17 nm	103 nm

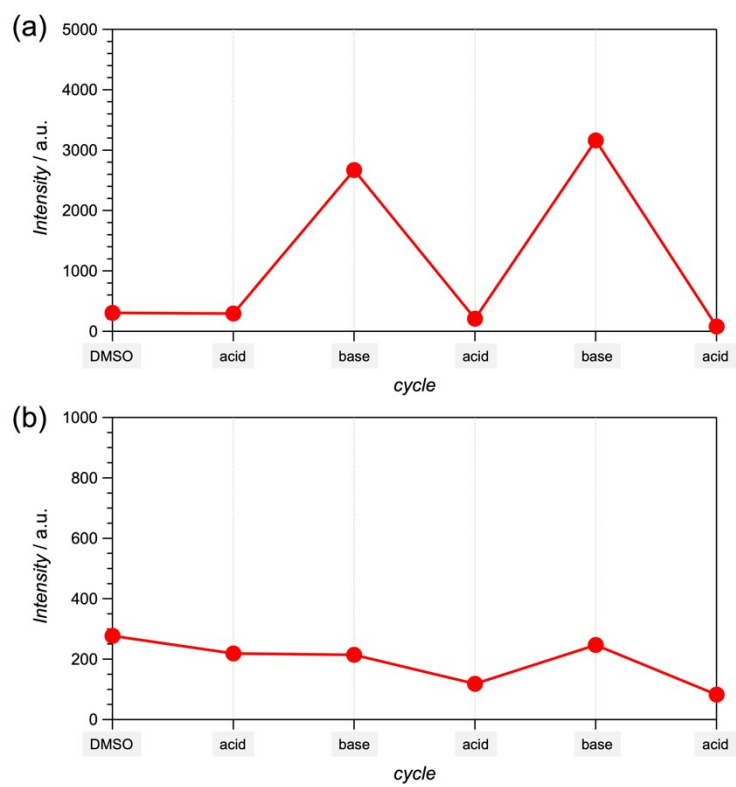




**Fig. S7.** (a) – (c) UV-vis spectra obtained from complex **3** in DMSO/H<sub>2</sub>O mixtures having various proportions of water. (d) – (f) Luminescence spectra obtained from complex **3** in DMSO/H<sub>2</sub>O mixtures having various proportions of water. The pH of the H<sub>2</sub>O was adjusted to 2.0, 6.4 or 13.0. Data were acquired with  $\lambda_{\text{ex}} = 535$  nm and a complex concentration of 20  $\mu\text{M}$ .

**Table S5** Variations in the UV-vis spectra of complex **3** with changes in pH.

	pH = 2.0	pH = 6.4	pH = 13.0
Initial	535 nm	535 nm	535 nm
Red shift	+ 12 nm	–	+ 65 nm
Blue shift	– 14 nm	– 30 nm	– 30 nm
$\Delta\lambda_{\text{max}}$	26 nm	30 nm	95 nm



**Fig. S8.** Luminescence switching behaviour of (a) complex 2 and (b) complex 3 by addition of acid and base.