Supporting Information

Colorimetric anion chemosensors based on anthraquinone : naked-eye detection of isomeric dicarboxylate and tricarboxylate anions

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Figure SI-1. Effect of anion (as $(C_4H_9)_4\ N^+$ salt) on colour change of **1** in DMSO after the addition of 1.0 equiv. of anion : (a) **1** only; (b) **1**+hydroxide.

Figure SI-2. NOESY plot of compound **1**

Table 2. Receptor distances of $NH^{\cdots}\ L^-$ hydrogen bonds from *ab initio* HF/6-31G(d) calculations

Figure SI-3. UV-vis spectral change of **1** operated in DMSO (5×10^{-5} M) after the addition of 2.0 equiv. of anions: (a) **1** only; (b) **1**+ maleate; (c) **1+** fumararte.

Figure SI-4a. ^{1}H NMR (400 MHz) spectra of sensor **1** (10 mM) in DMSO-d_6 upon addition of various quantities of *cis*-aconitate: (a) 0 equiv; (b) 0.3 equiv; (c) 1.0 equiv.

Figure SI-4b. ^{1}H NMR (400 MHz) spectra of sensor **1** (10 mM) in DMSO-d_6 upon addition of various quantities of *trans*-aconitate: (a) 0 equiv; (b) 1.0 equiv; (c) 2.0 equiv.

Figure SI-5. Dilution experiment of **1** in DMSO-d_6 by ^{1}H NMR: (a) [**1**] = [*trans*-aconitate] = 1×10^{-2} M; (b) 5×10^{-3} M; (c) 2.5×10^{-3} M; (d) 1.25×10^{-3} M.

Figure SI-6a. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO solution in **1** with a standard solution of *cis*-aconitate at 25℃. Titration profile (insert) indicates the formation of a 1:1 complex.

Figure SI-6b. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO solution in **1** with a standard solution of *trans*-aconitate at 25℃. Titration profile (insert) indicates the formation of a 1:1 complex.

Figure SI-7. Dilution experiment of **1**in DMSO-d_6 by ^{1}H NMR: (a) [**1**] = [malate] = 1×10^{-2} M; (b) 5×10^{-3} M; (c) 2.5×10^{-3} M.

Figure SI-8a. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO solution in **1** with a standard solution of malate at 25℃. Titration profile (insert) indicates the formation of a 1:1 complex.

Figure SI-8b. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO solution in **1** with a standard solution of tartrate at 25℃. Titration profile (insert) indicates the formation of a 1:1 complex.

Figure SI-9a. ^{1}H NMR (400 MHz) spectra of sensor **3** (10 mM) in DMSO-d_6 upon addition of various quantities of maleate: (a) 0 equiv; (b) 0.1 equiv; (c) 1.0 equiv.

Figure SI-9b. ^{1}H NMR (400 MHz) spectra of sensor **3** (10 mM) in DMSO-d_6 upon addition of various quantities of malate: (a) 0 equiv; (b) 0.1 equiv; (c) 1.0 equiv.

Figure SI-9c. Dilution experiment of **1** in DMSO-d_6 by ^{1}H NMR: (a) [**1**] = [malate] = 1×10^{-2} M; (b) 5×10^{-3} M; (c) 2.5×10^{-3} M.

Figure SI-10. Effect of anions (as $(C_4H_9)_4N^+$ salt) on colour changes of **3** in DMSO after the addition of 2.0 equiv of anions. Top : (a) **3** only; (b) **3**+ maleate; (c) **3**+ fumarate, bottom : (a) **3** only; (d) **3**+ malate; (e) **3**+ tartrate.

Figure SI-11. Effect of anions (as $(C_4H_9)_4N^+$ salt) on colour changes of **3** in DMSO after the addition of 2.0 equiv of anions: (a) **3** only, (b) **3**+ *cis*-aconitate, (c) **3**+ *trans*-aconitate.

Table 3. Receptor distances of $NH\cdots L^-$ hydrogen bonds from *ab initio* HF/6-31G(d) calculations

Figure SI-12a. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO/H_2O (95:5 v/v) solution in **1** with a standard solution of maleate at 25℃.

Figure SI-12b. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO/H_2O (95:5 v/v) solution in **1** with a standard solution of malate at 25℃.

Figure SI-12c. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO/H_2O (97:3 v/v) solution in **1** with a standard solution of *cis*-aconitate at 25℃.

Figure SI-12d. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO/H_2O (97:3 v/v) solution in **1** with a standard solution of *trans*-aconitate at 25℃.

Figure SI-13a. Effect of anions (as $(C_4H_9)_4N^+$ salt) on colour changes of **1** in DMSO/H_2O (95:5 v/v) (5×10^{-5} M) after the addition of 2.0 equiv. of anion: Top : (a) **1** only; (b) **1** +maleate; (c) **1** +fumarate, bottom : (a) **1** only; (d) **1** +malate; (e) **1** +tartrate.

Figure SI-13b. Effect of anions (as $(C_4H_9)_4N^+$ salt) on colour changes of **1** in DMSO/H_2O (97:3 v/v) (5×10^{-5} M) after the addition of 2.0 equiv. of anion: (a) **1** only; (b) **1** + *cis*-aconitate; (c) **1** + *trans*-aconitate.

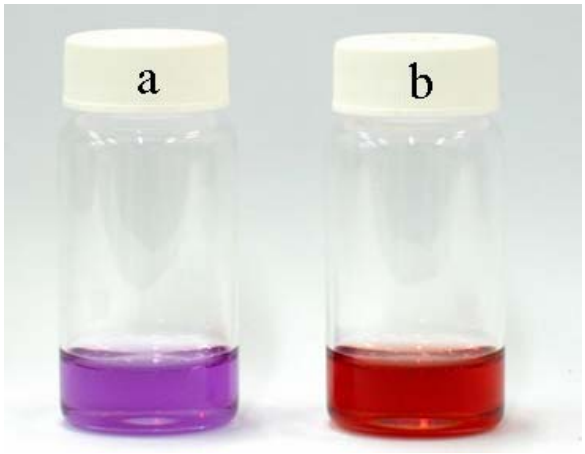


Figure SI-1. Effect of anion (as $(C_4H_9)_4\ N^+$ salt) on colour change of **1** in DMSO after the addition of 1.0 equiv. of anion : (a) **1** only; (b) **1**+ hydroxide.

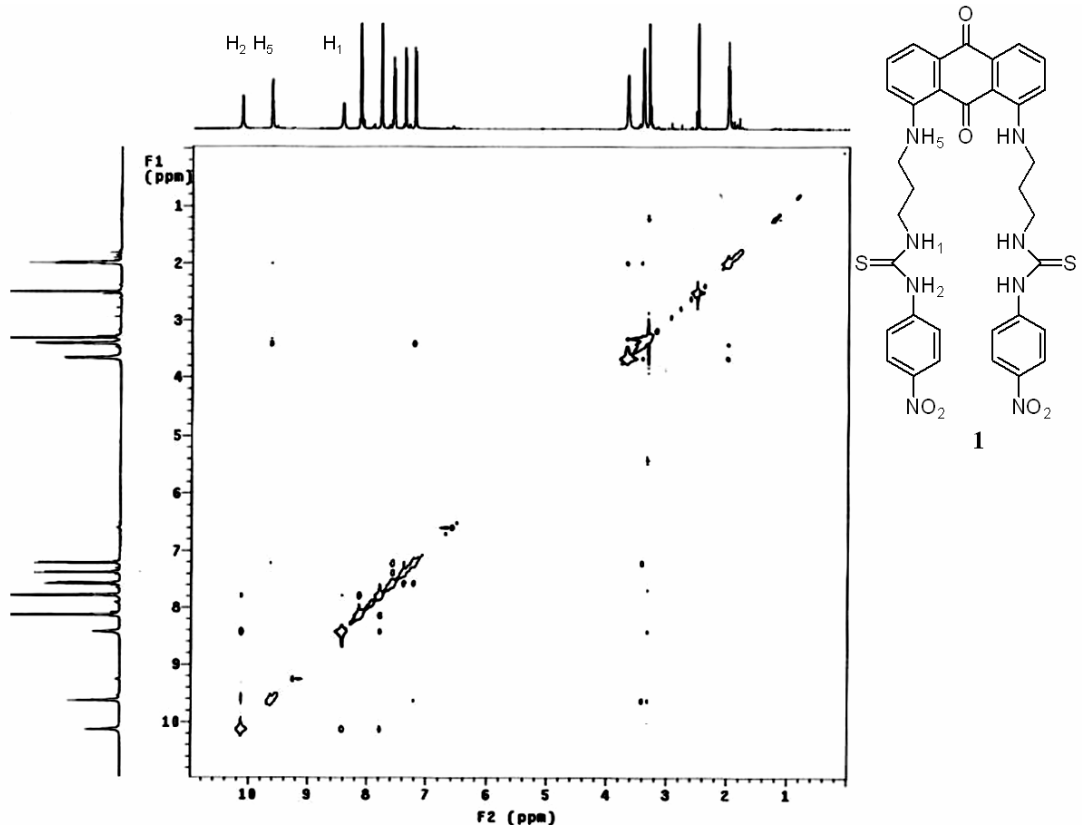
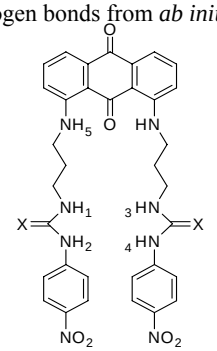


Figure SI-2. NOESY plot of compound **1**

Table 2. Receptor distances[a] of $NH^{\cdots}L^{-}$ hydrogen bonds from *ab initio* HF/6-31G(d) calculations



1. X=S
2. X=O

Receptor	Anion[b]	H(1)$^{\cdots}$L^{-}	H(2)$^{\cdots}$L^{-}	H(3)$^{\cdots}$L^{-}	H(4)$^{\cdots}$L^{-}
1	maleate	2.0865(O6)	0.9755(O7)	1.9105(O8)	1.8085(O9)
	fumarate	1.7565(O6)	1.8005(O7)	1.7535(O8)	1.8175(O9)
	cis-aconitate	2.0545(O6)	0.9675(O7)	1.7535(O8)	1.8085(O9)
	trans-aconitate	1.8585(O6)	1.6925(O7)	1.7455(O8)	1.7215(O9)
	malate	1.7915(O6)	1.7705(O7)	1.8835(O8)	1.7755(O9)
	tartrate	1.8075(O6)	1.8165(O7)	1.9075(O8)	1.8165(O9)
2	maleate	1.8115(O6)	1.7975(O7)	1.8625(O8)	1.7645(O9)
	fumarate	1.7825(O6)	1.8055(O7)	1.7765(O8)	1.8245(O9)
	cis-aconitate	2.0085(O6)	2.6415(O7)	1.8075(O8)	1.7955(O9)
	trans-aconitate	1.8415(O6)	2.8295(O7)	1.7625(O8)	1.7745(O9)
	malate	1.8155(O6)	1.8325(O7)	1.7525(O8)	1.8175(O9)
	tartrate	1.8165(O6)	1.8325(O7)	1.8165(O8)	1.8325(O9)

[a] The unit of computed distances is Å.

[b] Four oxygen atoms (O6, O7, O8 and O9) of guest (L^{-}) form hydrogen bonds with the receptors where O6 is hydrogen-bonded to H1 and O7 to H2 and O8 to H3 and O9 to H4

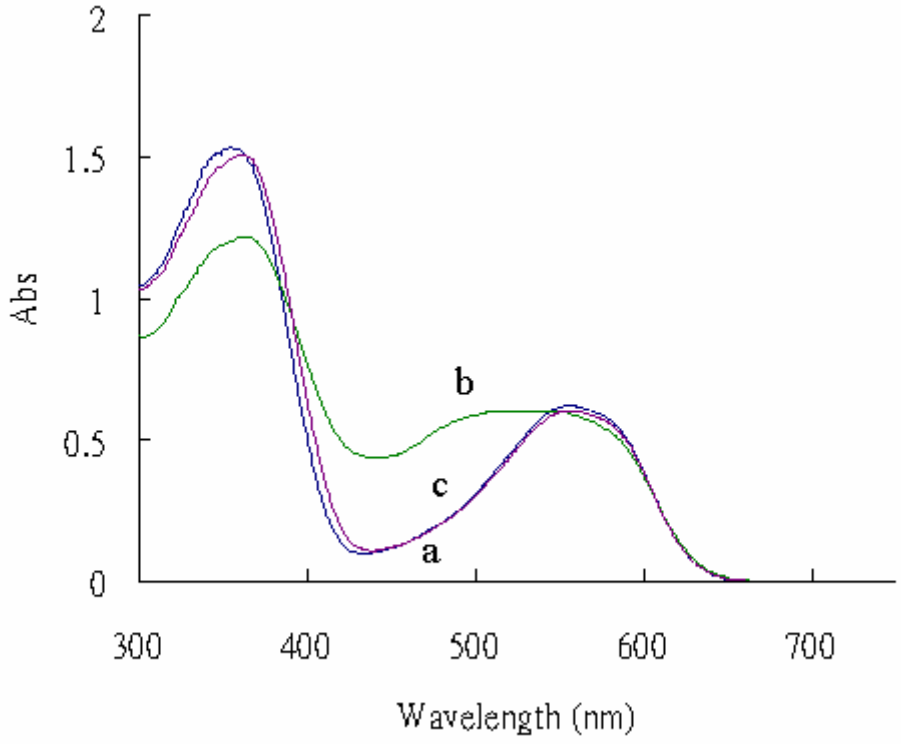


Figure SI-3 UV-vis spectral change of **1** operated in DMSO (5×10^{-5} M) after the addition of 2.0 equiv of anions: (a) **1** only; (b) **1**+ maleate; (c) **1+** fumararte.

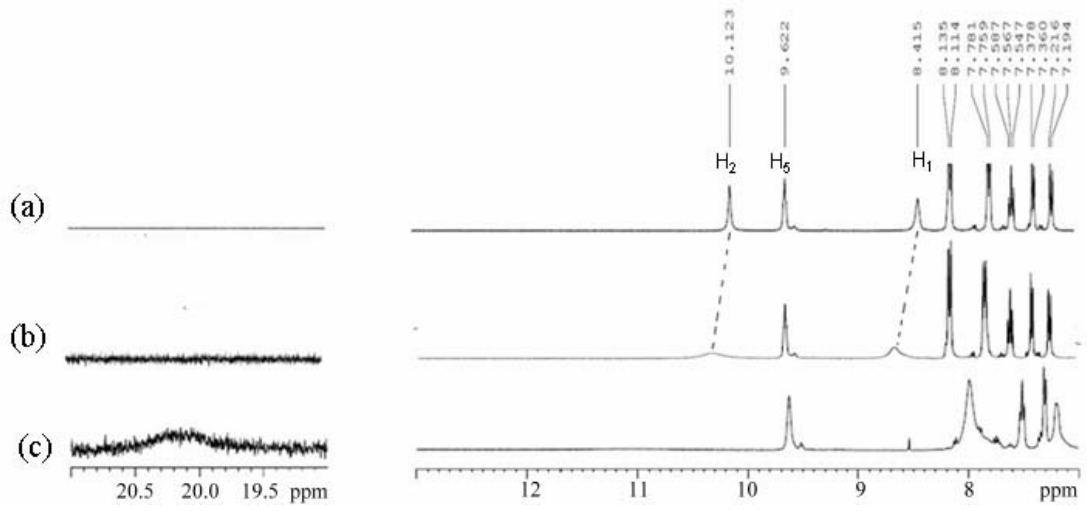


Figure SI-4a. ^{1}H NMR (400 MHz) spectra of sensor **1** (10 mM) in DMSO-d_6 upon addition of various quantities of *cis*-aconitate: (a) 0 equiv; (b) 0.3 equiv; (c) 1.0 equiv.

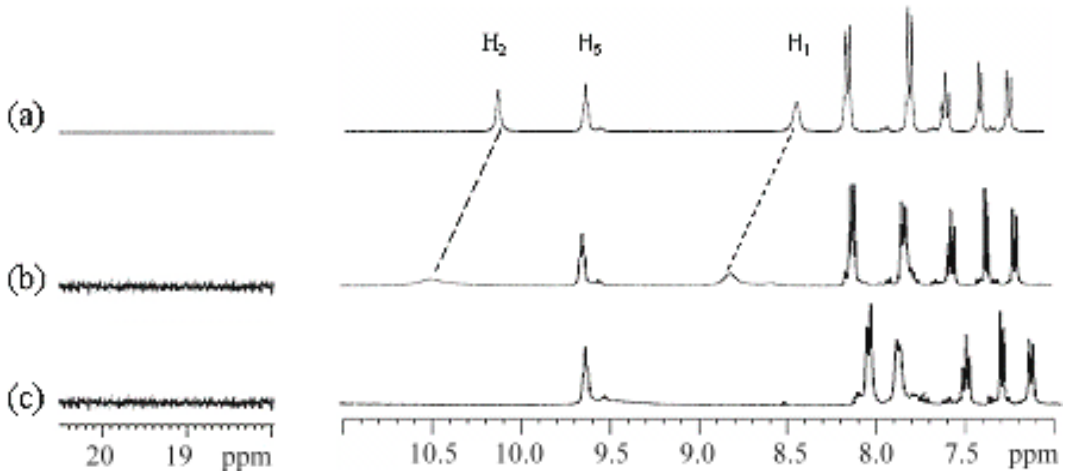


Figure SI-4b. ^{1}H NMR (400 MHz) spectra of sensor **1** (10 mM) in DMSO-d_6 upon addition of various quantities of *trans*-aconitate: (a) 0 equiv; (b) 1.0 equiv; (c) 2.0 equiv.

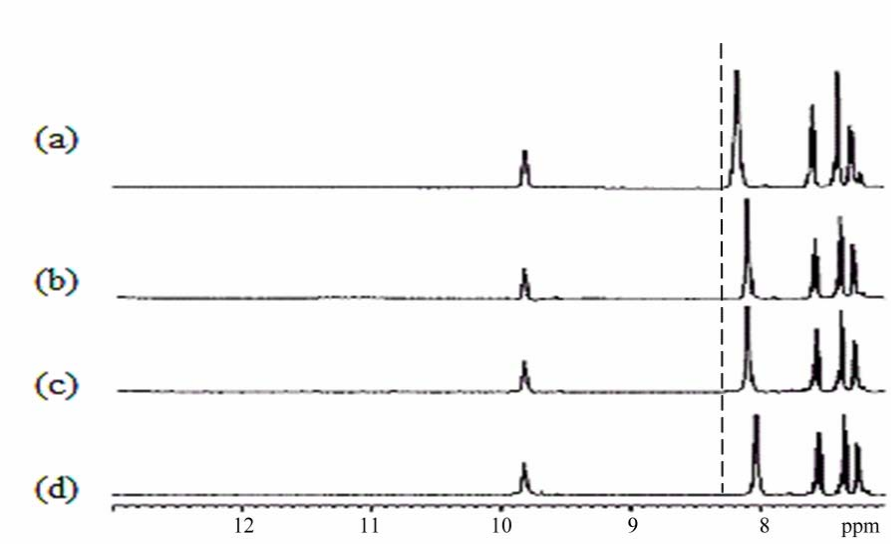


Figure SI-5. Dilution experiment of **1**in DMSO-d_6 by ^{1}H NMR: (a) [**1**] = [*trans*-aconitate] = 1×10^{-2} M; (b) 5×10^{-3} M; (c) 2.5×10^{-3} M; (d) 1.25×10^{-3} M.

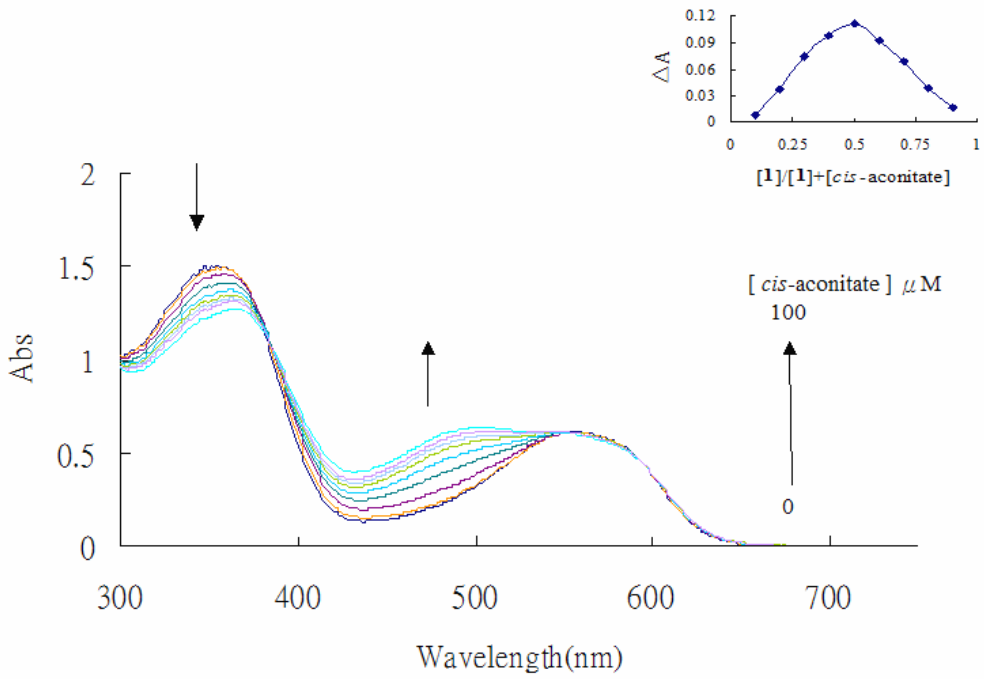


Figure SI-6a. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO solution in **1** with a standard solution of *cis*-aconitate at 25℃. Titration profile (insert) indicates the formation of a 1:1 complex.

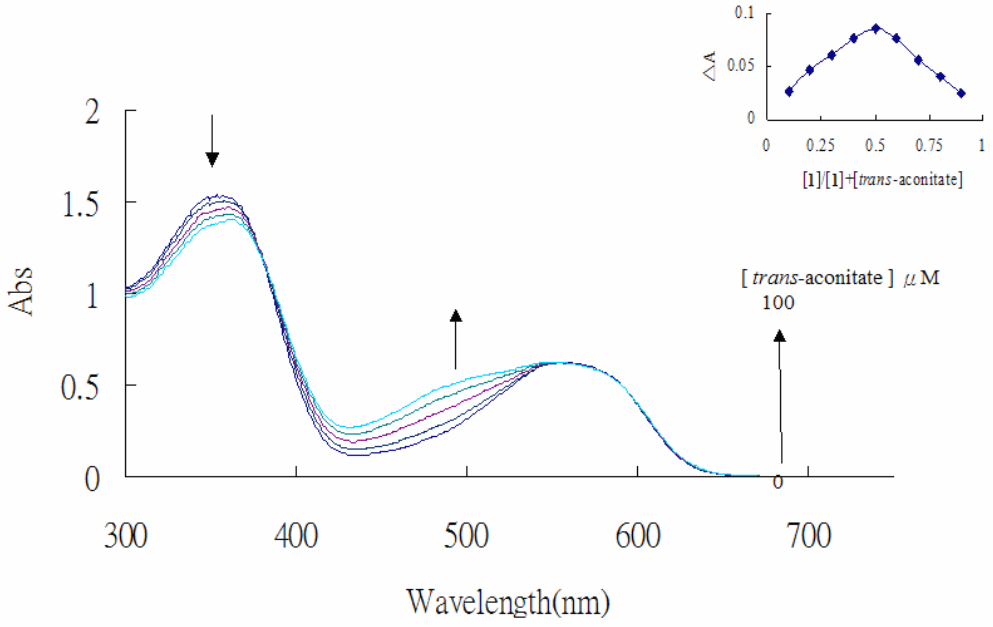


Figure SI-6b. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO solution in **1** with a standard solution of *trans*-aconitate at 25℃. Titration profile (insert) indicates the formation of a 1:1 complex.

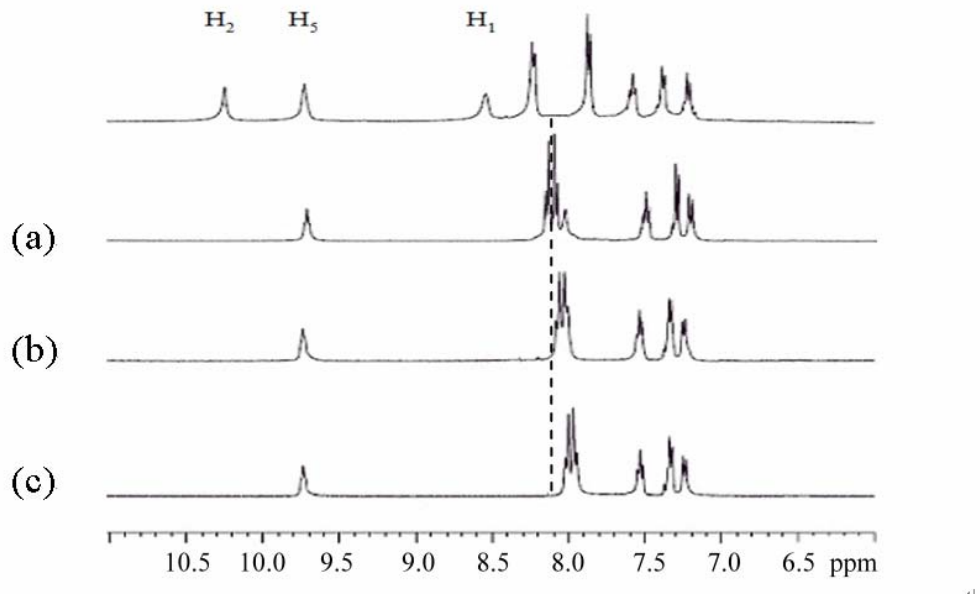


Figure SI-7. Dilution experiment of **1** in DMSO-d_6 by ^{1}H NMR: (a) [**1**] = [malate] = 1×10^{-2} M; (b) 5×10^{-3} M; (c) 2.5×10^{-3} M.

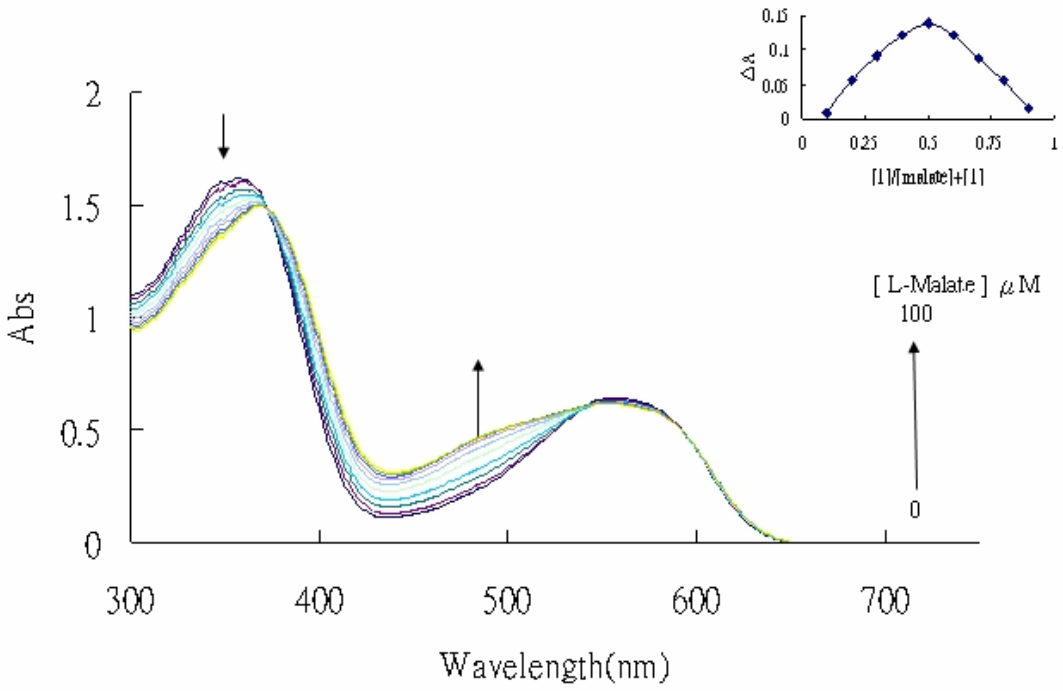


Figure SI-8a. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO solution in **1** with a standard solution of malate at 25℃. Titration profile (insert) indicates the formation of a 1:1 complex.

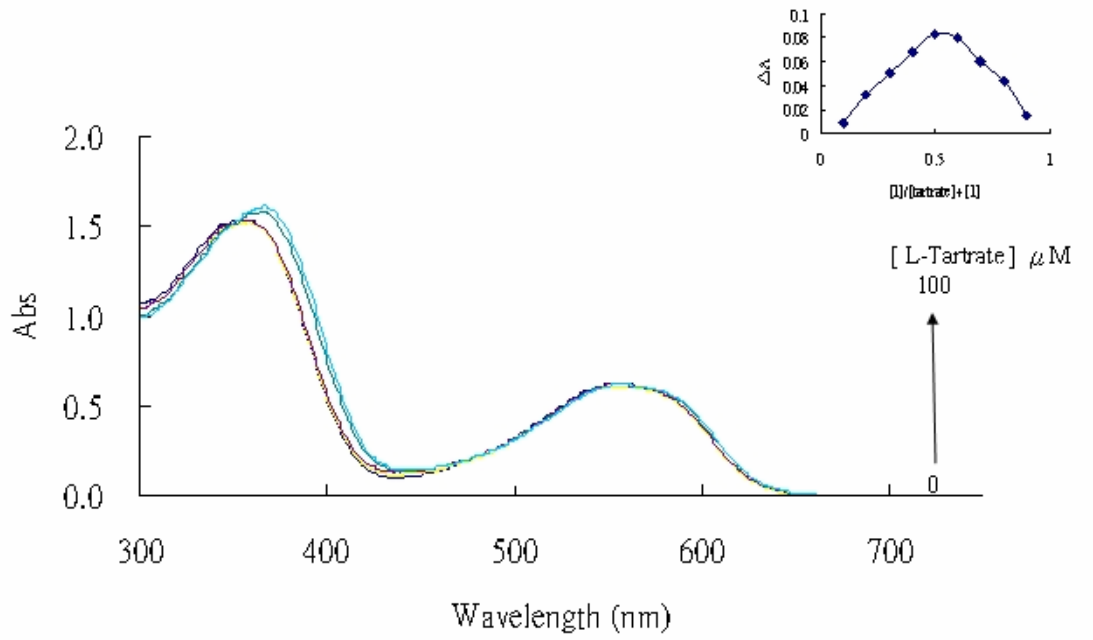


Figure SI-8b. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO solution in **1** with a standard solution of tartrate at 25℃. Titration profile (insert) indicates the formation of a 1:1 complex.

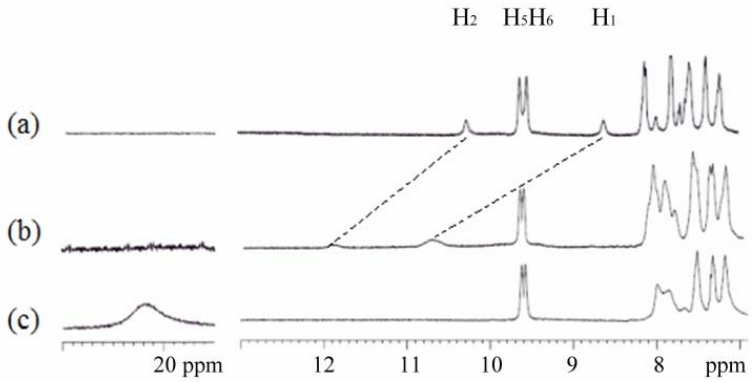


Figure SI-9a. ^{1}H NMR (400 MHz) spectra of sensor **3** (10 mM) in DMSO-d_6 upon addition of various quantities of maleate: (a) 0 equiv; (b) 0.1 equiv; (c) 1.0 equiv.

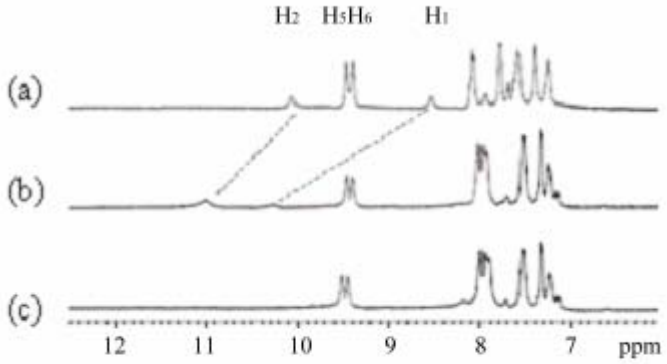


Figure SI-9b. ^{1}H NMR (400 MHz) spectra of sensor **3** (10 mM) in DMSO-d_6 upon addition of various quantities of malate: (a) 0 equiv; (b) 0.1 equiv; (c) 1.0 equiv.

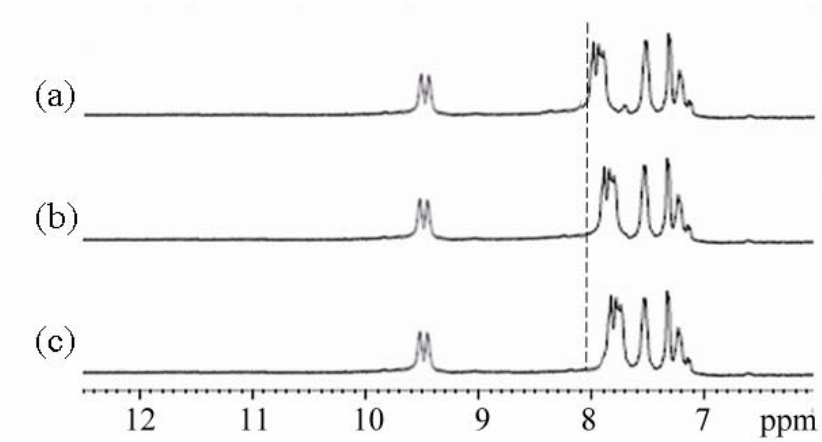


Figure SI-9c. Dilution experiment of **1** in DMSO-d_6 by ^{1}H NMR: (a) [**1**] = [malate] = 1×10^{-2} M; (b) 5×10^{-3} M; (c) 2.5×10^{-3} M.

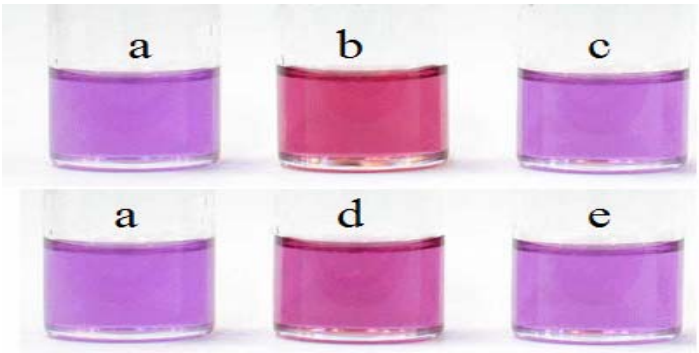


Figure SI-10. Effect of anions (as $(C_4H_9)_4N^+$ salt) on colour changes of **3** in DMSO after the addition of 2.0 equiv of anions. Top : (a) **3** only; (b) **3**+ maleate; (c) **3**+ fumarate, bottom : (a) **3** only; (d) **3**+ malate; (e) **3**+ tartrate.

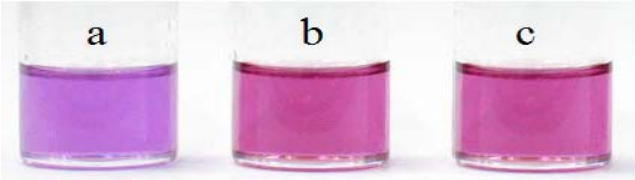
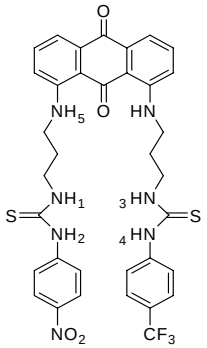


Figure SI-11. Effect of anions (as $(C_4H_9)_4N^+$ salt) on colour changes of **3** in DMSO after the addition of 2.0 equiv of anions: (a) **3** only, (b) **3**+ *cis*-aconitate, (c) **3**+ *trans*-aconitate.

Table 3. Receptor distances[a] of $NH^{\cdots}L^-$ hydrogen bonds from *ab initio* HF/6-31G(d) calculations



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Receptor	Anion[b]	H(1)…L⁻	H(2)…L⁻	H(3)…L⁻	H(4)…L⁻
3	maleate	2.2885(O6)	0.9765(O7)	1.8485(O8)	1.8475(O9)
	fumarate	1.7415(O6)	1.8055(O7)	1.7575(O8)	1.8465(O9)
	malate	1.7485(O6)	1.8395(O7)	1.7875(O8)	1.8105(O9)
	tartrate	1.7955(O6)	1.8265(O7)	1.8095(O8)	1.8515(O9)

[a] The unit of computed distances is Å.

[b] Four oxygen atoms (O6. O7. O8 and O9) of guest (L^-) form hydrogen bonds with the receptors where O6 is hydrogen n-bonded to H1 and O7 to H2 and O8 to H3 and O9 to H4

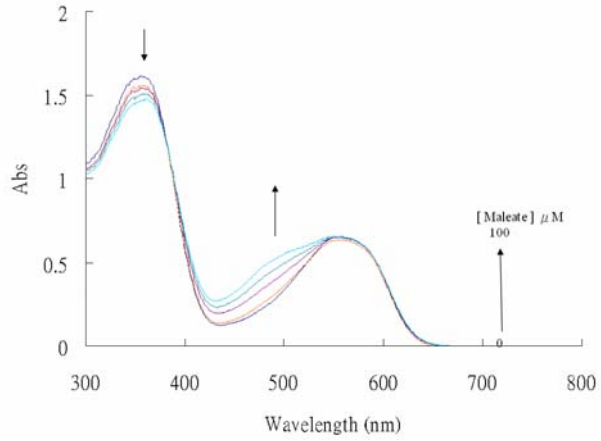

Figure SI-12a. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO/H_2O (95:5 v/v) solution in **1** with a standard solution of maleate at 25℃.

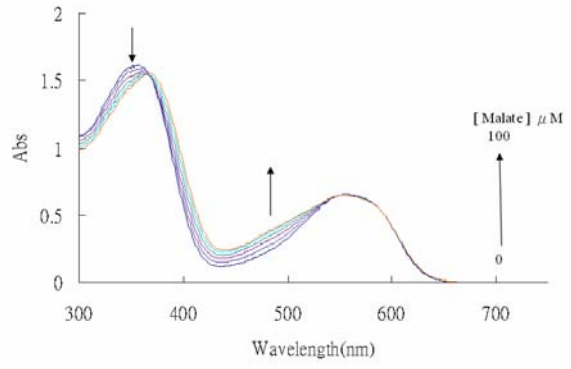

Figure SI-12b. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO/H_2O (95:5 v/v) solution in **1** with a standard solution of malate at 25℃.

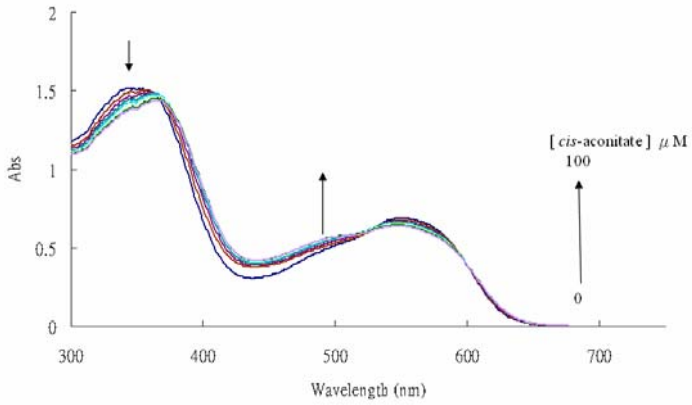

Figure SI-12c. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO/H_2O (97:3 v/v) solution in **1** with a standard solution of *cis*-aconitate at 25℃.

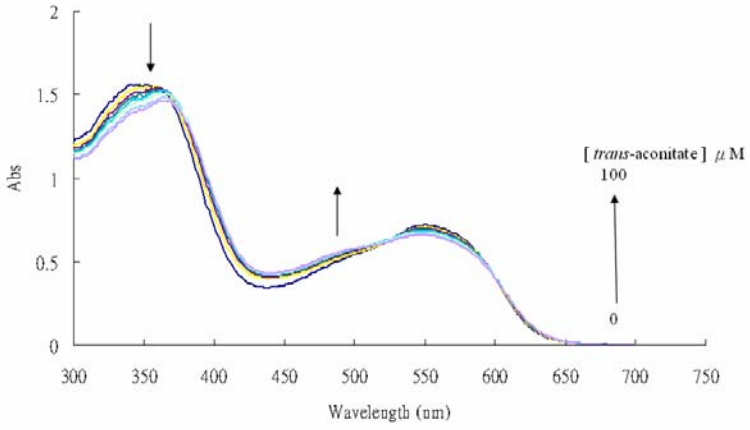

Figure SI-12d. Family of spectra taken in the course of the titration of a 5×10^{-5} M DMSO/H_2O (97:3 v/v) solution in **1** with a standard solution of *trans*-aconitate at 25℃.

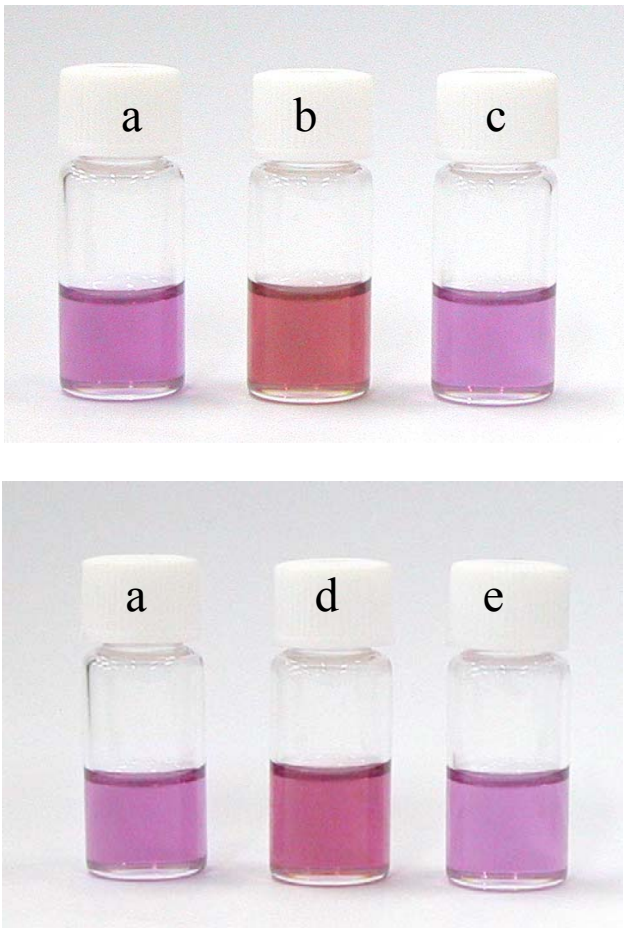

Figure SI-13a. Effect of anions (as $(C_4H_9)_4N^+$ salt) on colour changes of **1** in DMSO/H_2O (95:5 v/v) (5×10^{-5} M) after the addition of 2.0 equiv of anion: Top : (a) **1** only; (b) **1**+ maleate; (c) **1**+ fumarate, bottom : (a) **1** only; (d) **1**+ malate; (e) **1**+ tartrate.

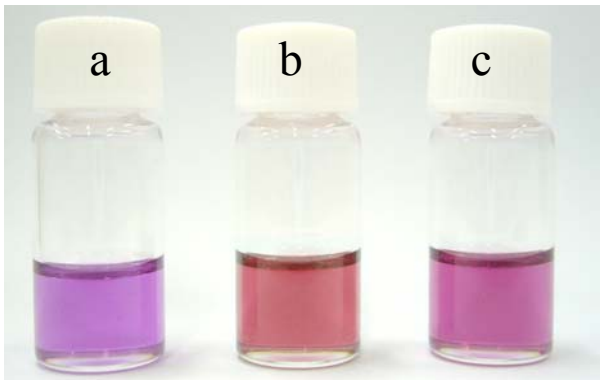

Figure SI-13b. Effect of anions (as $(C_4H_9)_4N^+$ salt) on colour changes of **1** in DMSO/H_2O (97:3 v/v) (5×10^{-5} M) after the addition of 2.0 equiv of anion: (a) **1** only; (b) **1** + *cis*-aconitate; (c) **1** + *trans*-aconitate.