Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information for

Highly Selective and Sensitive Fluorescent Sensing of Oxalate in Water

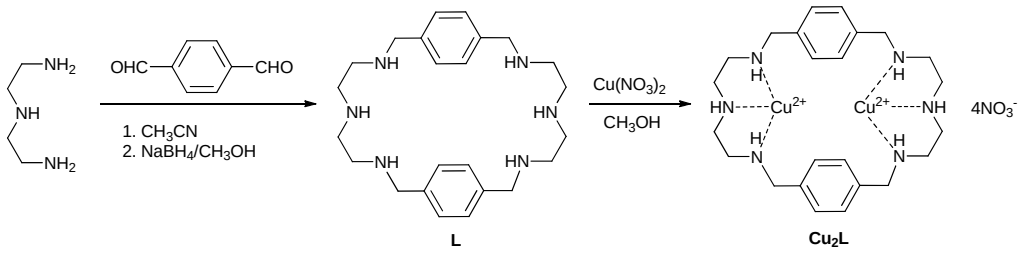
Min Hu, Guoqiang Feng*

Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P.R. China,
gf256@mail.ccnu.edu.cn

1. General Experimental Details.

Starting materials were purchased from commercial suppliers and were used without further purification. All solvents were purified by the most used methods before use. N-(2-hydroxyethyl)piperazine-N'-(2-ethane-sulfonic acid) (HEPES) was used to prepare buffer solution and all solutions were prepared with using distilled water that had been passed through a Millipore-Q ultrapurification system. UV-vis spectra and fluorescent spectra were recorded on an Agilent Cary 100 UV-vis spectrophotometer and an Agilent Cary Eclipse fluorescence spectrophotometer, respectively.

2. Synthesis of Cu_2L



The macrocycle ligand L can be prepared very easily by [2+2] condensation of terephthaldehyde with diethylenetriamine followed by reduction using $NaBH_4$ (above scheme).[1] The copper complex **Cu_2L** was prepared according to the procedure published by Fabbrizzi *et al*[2] and was recrystallized from MeOH/H_2O (v/v, 9:1) to afford the pure compound. Yield: 76%. Elemental analysis calcd for $C_{24}H_{38}N_6Cu_2{\cdot}(NO_3)_4{\cdot}H_2O$: C 35.87, H 5.02, N 17.43; found: C 35.93, H 5.32, N 17.11.

References:

1. Chen, D.; Martell, A. E. *Tetrahedron* **1991**, *47*, 6895.
2. Fabbrizzi, L.; Marcotte, N.; Stomeo, F.; Taglietti, A. *Angew. Chem. Int. Ed.* **2002**, *41*, 3811-3824.

3. Job's plot examined for Cu_2L with fluorescein and Eosin Y

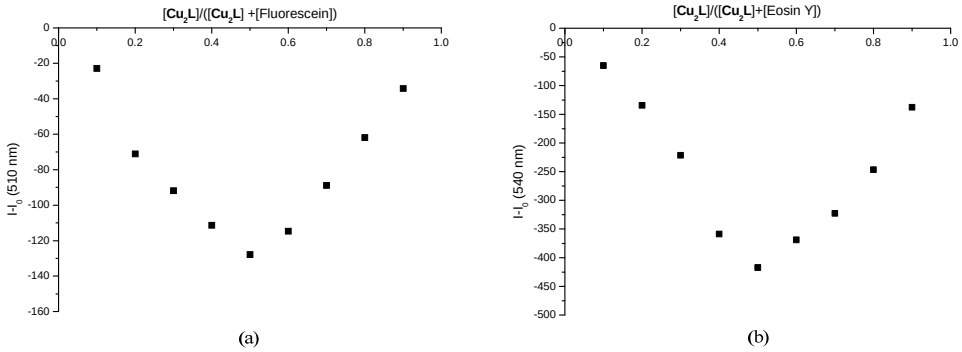
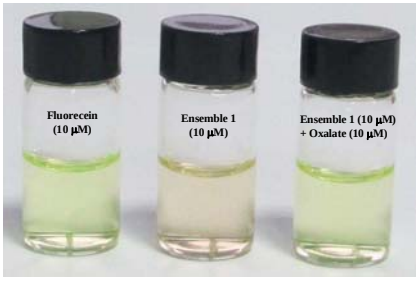
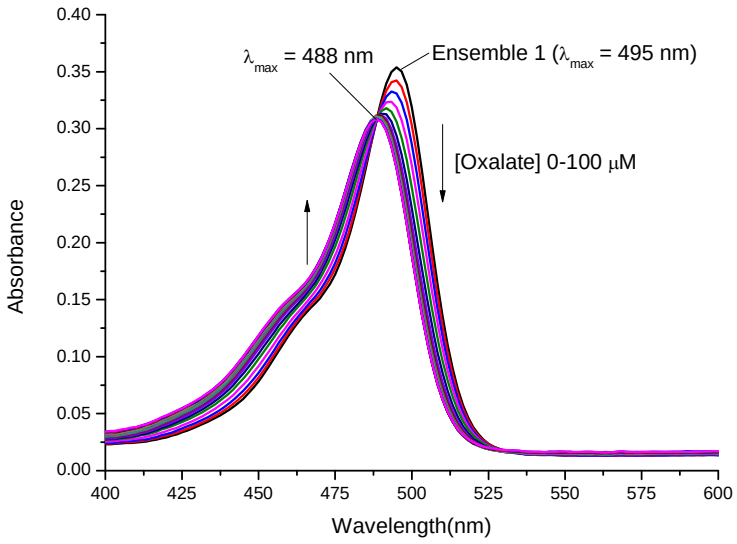


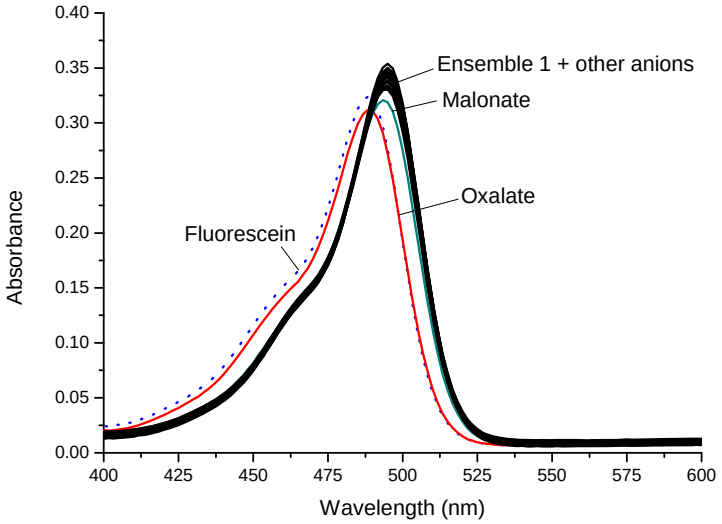
Figure S1. Job's plot examined between **Cu_2L** with indicator fluorescein (a) and Eosin Y (b). [**Cu2L**] + [indicator] = 10 μM. All the spectra were measured in pure aqueous solution of 10 mM HEPES buffer (pH 7.0) at 25℃.

4. UV studies of ensemble 1 on sensing oxalate over other anions





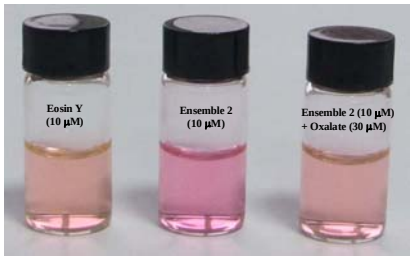
(a)

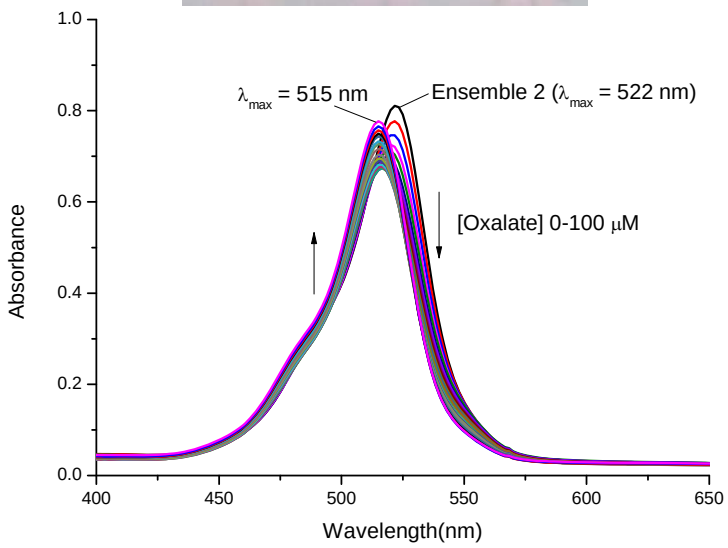


(b)

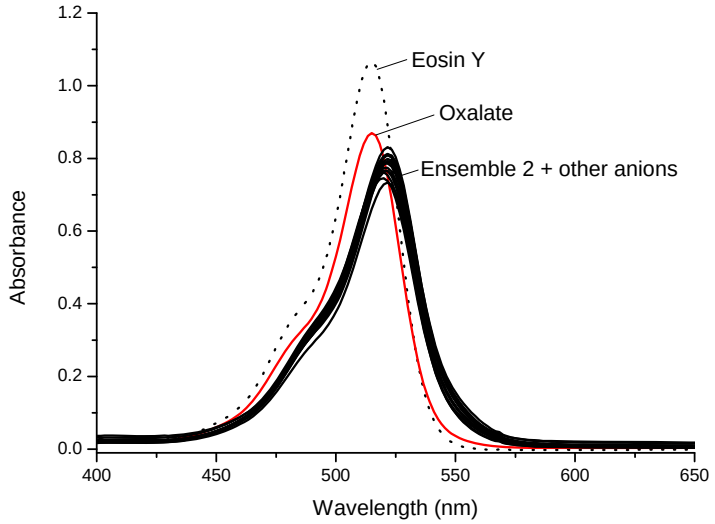
Figure S2. (a) UV-vis spectra changes of ensemble **1** (10 μM) upon addition 0-10 equiv of oxalate (Sodium salt) in pure aqueous solution of 10 mM HEPES buffer (pH 7.0) at 25℃. (b) UV-vis spectra changes of ensemble **1** (10 μM) in the presence of various anions (10 μM) (Sodium salt). Dashed line is the UV-vis spectra of fluorescein (10 μM). All spectra are measured in pure aqueous solution of 10 mM HEPES buffer (pH 7.0) at 25℃.

5. UV studies of ensemble 2 on sensing oxalate over other anions





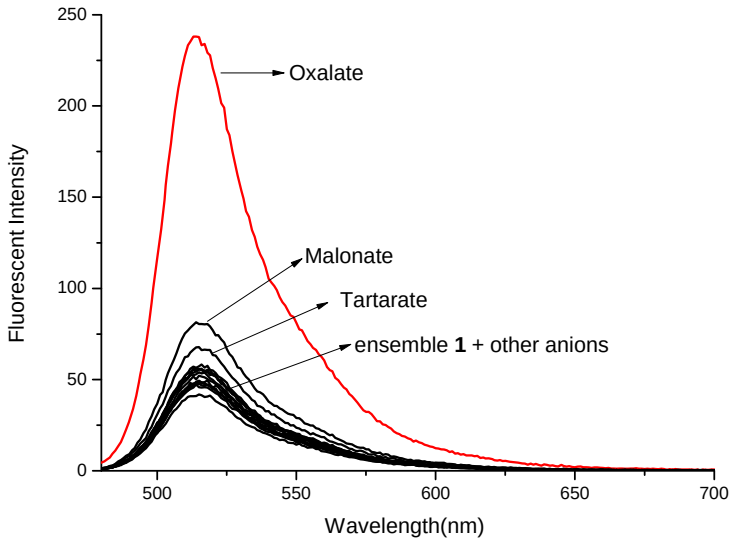
(a)



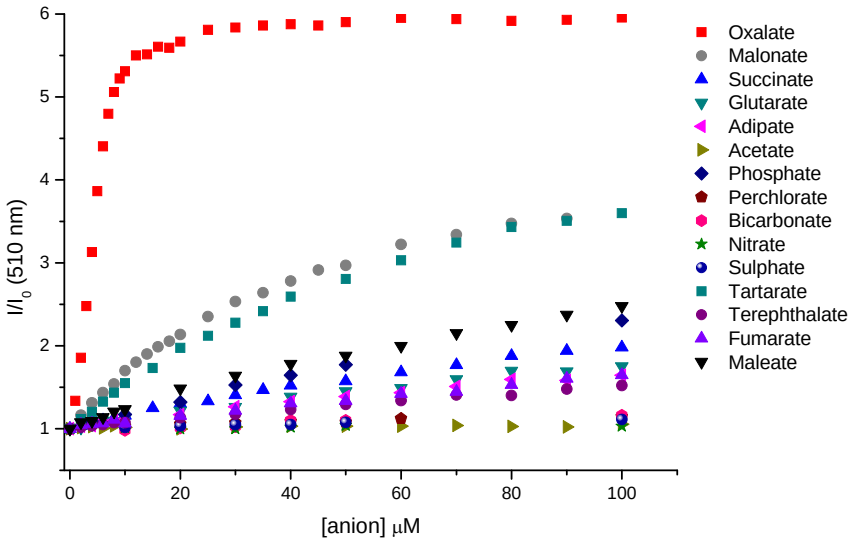
(b)

Figure S3. (a) UV-vis spectra changes of ensemble **2** (10 μM) upon addition 0-10 equiv of oxalate (Sodium salt). (b) UV-vis spectra changes of ensemble **2** (10 μM) in the presence of various anions (30 μM) (Sodium salt). Dashed line is the UV-vis spectra of Eosin Y (10 μM). All spectra are measured in pure aqueous solution of 10 mM HEPES buffer (pH 7.0) at 25℃.

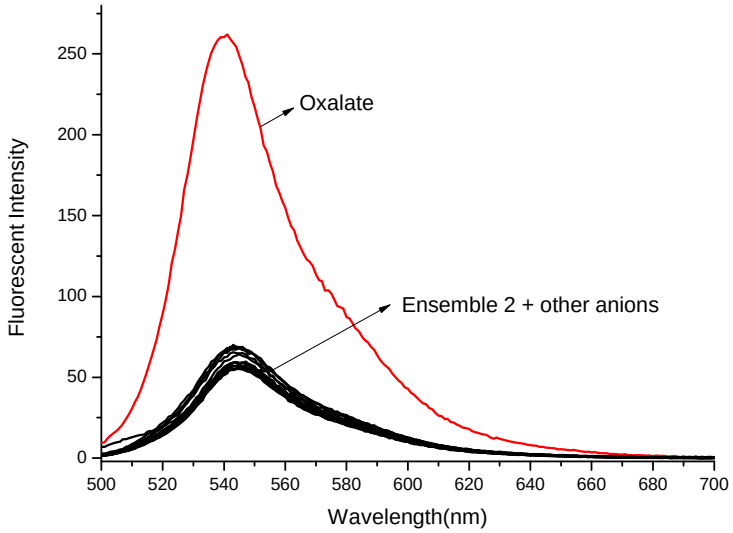
6. Comparison of fluorescent sensing oxalate with other anions using ensemble 1 and 2



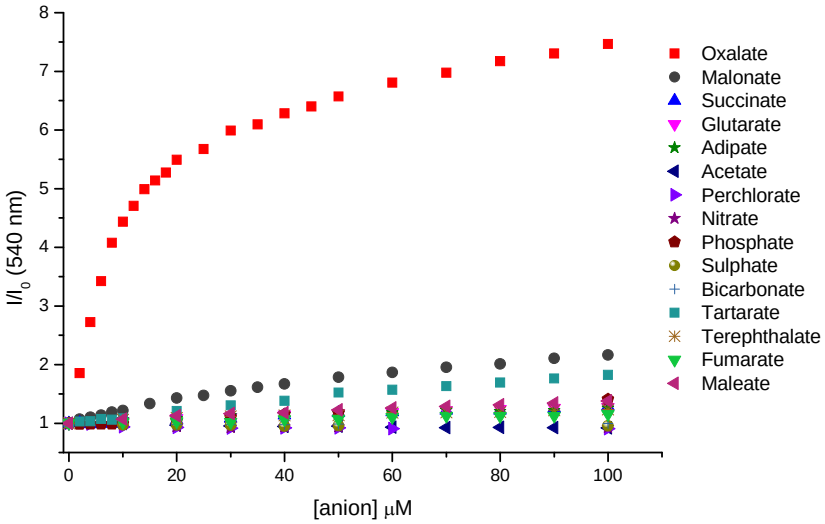
(a)



(b)



(c)



(d)

Figure S4. (a) Fluorescence spectra changes of ensemble 1 (10 μM) upon addition of different anions (1 equiv). (b) A plot of relative fluorescence intensity of ensemble **1** at 510 nm (I/I_0) vs concentrations for different anions. (c) Fluorescence spectra changes of ensemble 2 (10 μM) upon addition of different anions (1 equiv). (d) A plot of relative fluorescence intensity of ensemble **2** at 540 nm (I/I_0) vs concentrations for different anions. I_0 is the fluorescence intensity of ensemble, I is the fluorescence intensity of ensemble after addition of anions. λ_{ex} for ensemble **1** is 470 nm. λ_{ex} for ensemble **2** is 490 nm. All spectra are measured in pure aqueous solution of 10 mM HEPES buffer (pH 7.0) at 25℃.

7. Determination of the apparent association constants (K_a) for oxalate anion with Cu_2L

H is the host (metal complex here), I is the indicator, G is the guest (anions).
H with I (and G) forms 1:1 binding complex:

$$H + I \overset{K_{a1}}{\rightleftharpoons} HI \qquad K_{a1} = \frac{[HI]}{[H][I]} \qquad (1)$$

$$H + G \overset{K_{a2}}{\rightleftharpoons} HG \qquad K_{a2} = \frac{[HG]}{[H][G]} \qquad (2)$$

For indicator displacement approach:

$$HI + G \underset{k}{\rightleftharpoons} HG + I \qquad k = \frac{[HI][G]}{[HG][I]} = \frac{K_{a1}}{K_{a2}} \qquad (3)$$

	HI	+ G	HG	+ I
Initial concentration	$[HI]_0$	$[G]_0$		
At equilibrium	$[HI]_0 - [I]$	$[G]_0 - [I]$	$[I]$	$[I]$

From $k[I]^2 = ([HI]_0 - [I])([G]_0 - [I]) = [I]^2 - ([HI]_0 + [G]_0)[I] + [HI]_0[G]_0$

We can get the concentration of I:

$$[I] = \frac{[HI]_0 + [G]_0 - \sqrt{([HI]_0 + [G]_0)^2 - 4(1-k)[HI]_0[G]_0}}{2(1-k)} \qquad (4)$$

The concentration of HI: $[HI] = [HI]_0 - [I]$ (5)

The observed fluorescent intensity is the sum of the fluorescent intensity of free HI and I:

$$F_{obs} = F_{HI} + F_I \qquad (6)$$

Equations (4), (5) and (6) are used for a nonlinear fitting the titration data, then k is obtained.
K_{a1} is obtained from the titration experiments of the indicator with metal complex.
Now we have K_{a1} and k, then we can get the value of K_{a2} from equation (3).

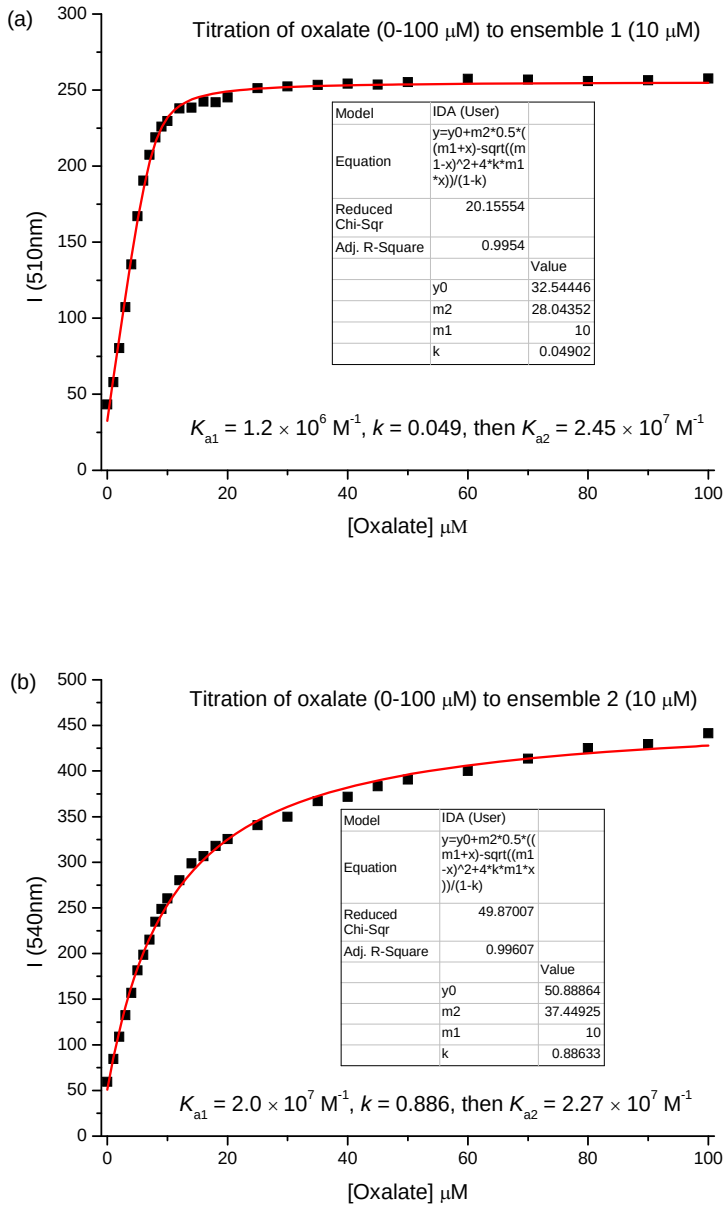


Figure S5. Curve fitting of the titration date. (a) Titration of oxalate (0-100 μM) to ensemble 1 (10 μM). (b) Titration of oxalate (0-100 μM) to ensemble 2 (10 μM).

8. Determination of the detection limit:

The detection limit DL of ensemble 2 for oxalate was determined from the following equation:

$$DL = K*S_b/S$$

Where:

K = 3,

S_b is the standard deviation of the blank solution, which was found to be 0.64 from ten repeat measurements of the blank solution,

S is the slope of the calibration curve.

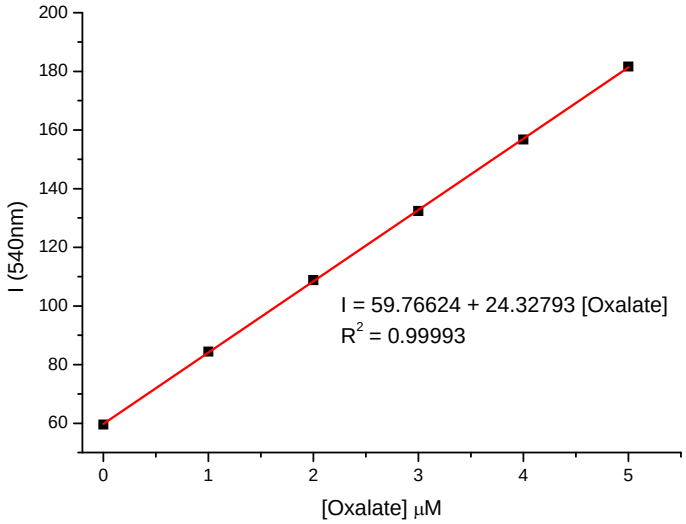
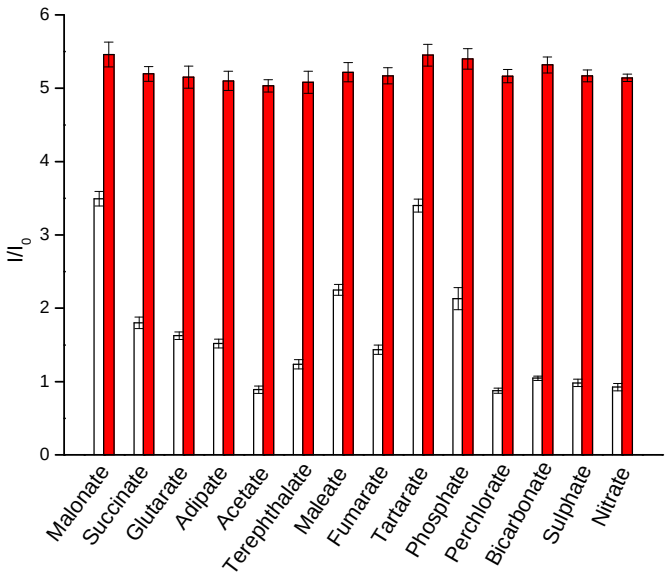
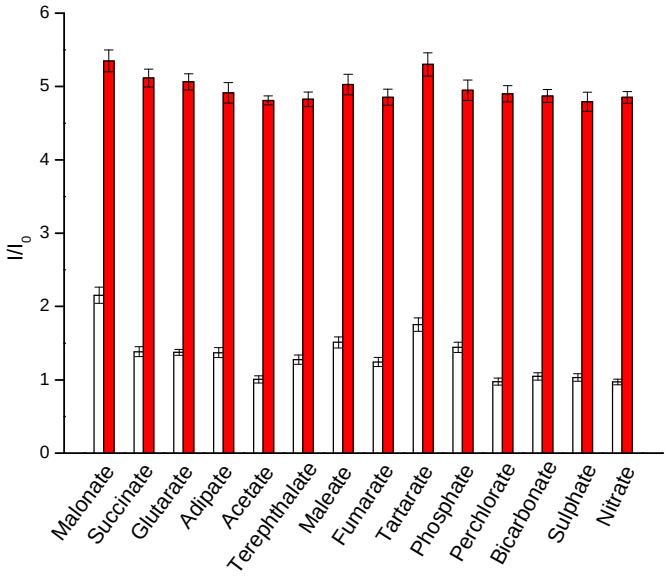


Figure S6. Calibration curve of the fluorescence changes of ensemble 2 (10 μM) upon addition of oxalate (1-5 μM).

9. Sensing oxalate in the presence of other anions



(a) Using ensemble 1.



(b) Using ensemble 2.

Figure S7. The sensing selectivity of ensemble (10 μM) for oxalate in the presence of the appropriate anion (100 μM) of interest in 10 mM HEPES buffer (pH = 7.0). I_0 is the fluorescence intensity of ensemble, I is the fluorescence intensity of ensemble after addition of anions. The white bars represent the fluorescence response of ensemble in the presence of the appropriate anion (100 μM) of interest. The red bars represent the fluorescence response upon addition of 10 μM oxalate to a solution of ensemble in the presence of the appropriate anion (100 μM) of interest. (a) ensemble 1 (λ_{ex} = 470 nm, λ_{em} = 510 nm); (b) ensemble 2 (λ_{ex} = 490 nm, λ_{em} = 540 nm). Each experiment was repeated 3-5 times.