## **Supporting Information**

A Reversible E <sub>m</sub> -FRET Rhodamine-Based Chemosensor for
Carboxylate Anions Using a Ditopic Receptor Strategy
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Scheme S1. Synthetic pathways of L1 and 2



Fig. S1 UV-vis spectra of L1 upon addition of various anions. Conditions: L1 (10  $\mu$ M) in MeCN, TBAX (30 equiv) in MeCN.



Fig. S2 Fluorescence emission spectra of L1 upon addition of various anions. Conditions: L1 (10  $\mu$ M) in MeCN, excitation at 300 nm, TBAX (30 equiv) in MeCN.



a)



b)



c)





**Fig. S3** Proposed binding modes of (a) L1, (b) L1+PhCOO<sup>-</sup> (1:1), (c) L1+PhCOO<sup>-</sup> (2:2), (d) L1+Cu<sup>2+</sup>, (e) L1·Cu<sup>2+</sup>+CH<sub>3</sub>COO<sup>-</sup> (1:1), (f) L1·Cu<sup>2+</sup>+CH<sub>3</sub>COO<sup>-</sup> (2:2) were generated with the MOLEKEL 4.3 program.<sup>S1</sup>







b)

**Fig. S4** Job plot<sup>S2</sup> between receptor L1 and various  $Cu^{2+}$  concentrations. The total concentration of L1 +  $Cu^{2+}$  was kept constant at 10  $\mu$ M. The complex concentration, [HG] was calculated by the equation; [HG] =  $\Delta A/A_0*$ [H]. (a) UV-vis spectra at 275 nm, (b) fluorescent spectra at 490 nm ( $\lambda_{ex}$  300 nm).



**Fig. S5** Mole ratio plots<sup>S3</sup> between receptor L1 and various  $Cu^{2+}$  concentrations (equiv). (a) UV-vis spectra at 558 nm, (b) fluorescent spectra at 584 nm ( $\lambda_{ex}$  300 nm).



b)

**Fig. S6** Time evolution of sensor L1 (10  $\mu$ M) in MeCN in the presence of 5.0 equiv. of Cu<sup>2+</sup> ion. Spectra changes of UV-vis intensity at 275, 560 nm (a) and fluorescence intensity at 490 and 584 nm,  $\lambda_{ex}$  = 300 nm (b) as a function of time (0.0 to 3.0 h).



**Fig. S7** UV-vis spectra excess of  $L1 \bullet Cu^{2+}$  upon addition of various anions. Conditions:  $L1 \bullet Cu^{2+}$  (10  $\mu$ M) in MeCN, TBAX (30 equiv.) in MeCN.



Fig. S8 <sup>1</sup>H NMR spectrum of *N*-(rhodamine B)lactam-ethylenediamine (1).



**Fig. S9** <sup>1</sup>H NMR spectrum of 1-butyl-3-(naphthalen-1-yl)thiourea (2).



**Fig. S10** <sup>1</sup>H NMR spectrum of *N*-(Rhodamine B)lactam-*N*'-naphthylthioureaethylenediamine (L1).



**Fig. S11** <sup>13</sup>C NMR spectrum of N-(Rhodamine B)lactam-N'-naphthylthioureaethylenediamine (L1).



**Fig. S12** ESI-Mass spectrum of *N*-(Rhodamine B)lactam-*N*'-naphthylthioureaethylenediamine (L1).

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