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Supporting Information

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Pseudo-Allosteric Recognition of Mandelic Acid With an Enantioselective Coordination Complex

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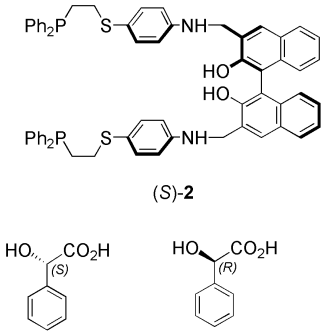
General Methods/Instrument Details All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques or an inert atmosphere glovebox unless otherwise noted. Methylene chloride and pentane were dried and distilled over calcium hydride. All solvents were degassed via N_2 bubbling prior to use. 2,2'-Dihydroxy-[1,1']binaphthalenyl-3,3'-dicarbaldehyde was prepared via a literature procedure.[1] Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received.

All other chemicals were used as received from Aldrich Chemical Company. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer and

referenced relative to TMS resonances in $CDCl_3$ and to residual proton resonances in CD_2Cl_2. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer at 121.4 MHz and referenced relative to an external 85% H_3PO_4 standard. All chemical shifts are reported in ppm. UV-Vis spectra were recorded on a Varian Cary 50 Bio spectrophotometer in HPLC grade CH_3CN. Circular Dichroism (CD) spectra were recorded on a Jasco J-715 spectrometer. Electrospray mass spectra (ESI-MS) were recorded on a Micromas Quatro II triple quadrapole mass spectrometer. Electron ionization mass spectra (EI-MS) were recorded on a Fisions VG 70-250 SE mass spectrometer. Elemental analyses were performed by Quantitative Technologies Inc. Whitehouse, NJ.

Fluorescence Measurements and Data: Both enantiomers of mandelic acid were purchased from Adrich and purified according to literature procedures.[2] Mandelic acid stock solution (0.1 M in CH_2Cl_2 containing 10% DME), fluorophore stock solution (2.0 mM in CH_2Cl_2) and DME were mixed and diluted to the desired concentration in a volumetric flask (see graph below). DME was used to enhance the solubility of mandelic acid and the concentration was adjusted to 2%. All of the samples were prepared under air-free conditions, and air-free cuvettes were used to prevent oxidation of the sensor molecule.



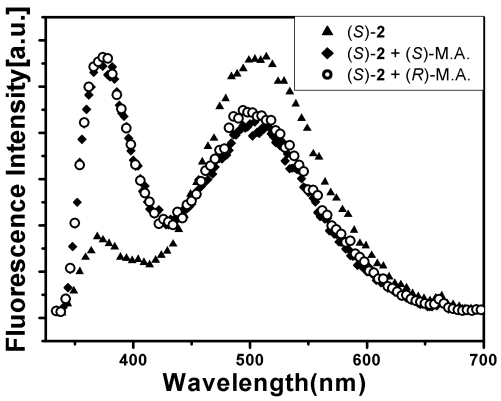
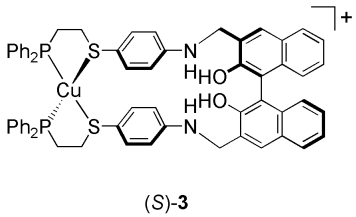


Figure S1. Fluorescence Spectra of (*S*)-**2** in the presence or absence of Mandelic Acid (λ_{ex} = 330 nm).



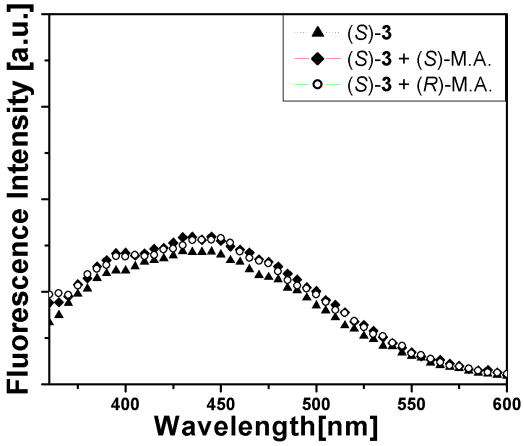
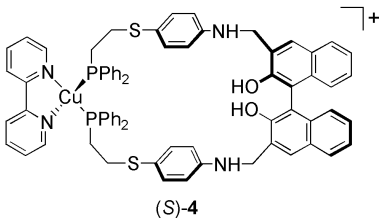


Figure S2. Fluorescence Spectra of (*S*)-**3** in the presence or absence of Mandelic Acid (λ_{ex} = 360 nm).



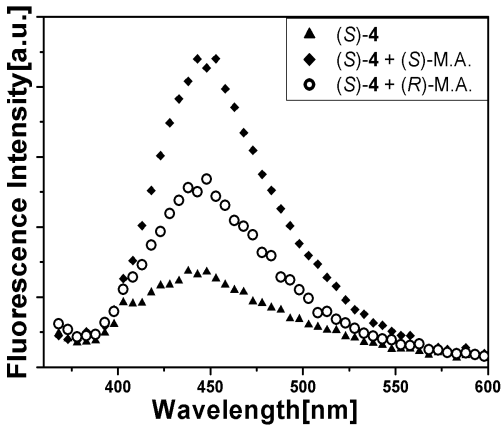


Figure S3. Fluorescence Spectra of (*S*)-**4** in the presence or absence of Mandelic Acid (λ_{ex} = 360 nm).

a)

$$\frac{I_0}{(I-I_0)} = \frac{b}{a-b}\left(\frac{1}{K_a \cdot [M]} + 1\right)$$

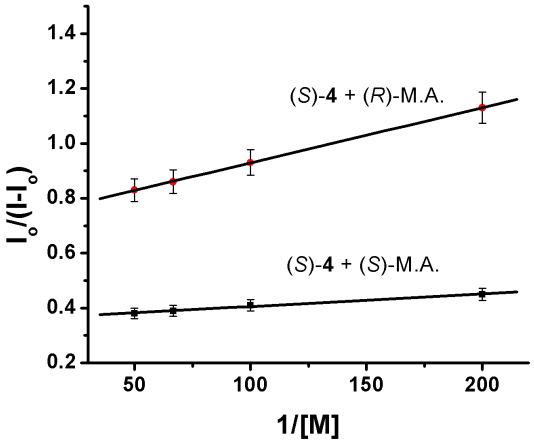
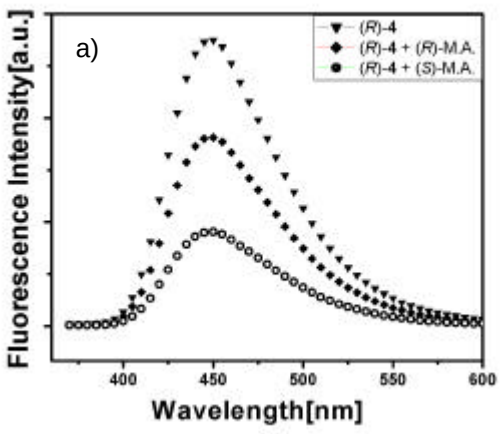


Figure S4. The Benesi-Hildebrand Plot of open-complex (*S*)-**4** (1.0×10^{-4} M in CH_2Cl_2 containing 2% of DME) in the presence of mandelic acid. In the equation, I is fluorescence intensity of (*S*)-**4** with the acid; I_0 is the fluorescence intensity of (*S*)-**4** without the acid; K_a is the association constant; [M] is the concentration of the acid.



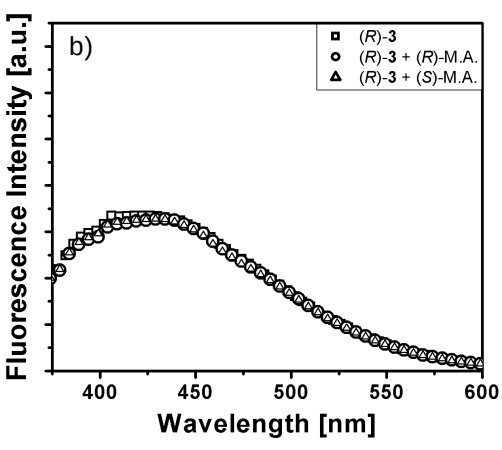


Figure S5. (a) Fluorescence Spectra of (*R*)-**3** in the presence or absence of Mandelic Acid (λ_{ex} = 360 nm). (b) Fluorescence Spectra of (*R*)-**4** in the presence or absence of Mandelic Acid (λ_{ex} = 360 nm).

$$\frac{I_0}{(I - I_0)} = \frac{b}{a - b}\left(\frac{1}{K_a \cdot [M]} + 1\right)$$

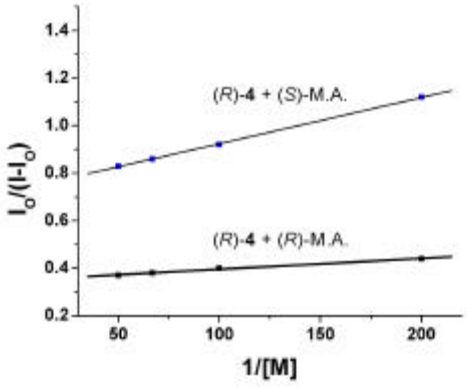


Figure S6. The Benesi-Hildebrand Plot of open-complex (*R*)-**4** (1.0×10^{-4} M in CH_2Cl_2 containing 2% of DME) in the presence of mandelic acid. In the equation, I is fluorescence intensity of (*R*)-**4** with the acid; I_0 is the fluorescence intensity of (*R*)-**4** without the acid; K_a is the association constant; [M] is the concentration of the acid.

Reference

1. Zhang, H.-C.; Huang, W.-S.; Pu, L. *J. Org. Chem.* **2001**, *66*, 481–487.
2. Lin, J.; Hu, Q.-S.; Xu, M.-H.; Pu, L. *J. Am. Chem. Soc*. **2002**, *124*, 2088-2089.