Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Dual chromophore sensor for detection of amines, diols, hydroxy acids, and amino alcohols

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1 General

Materials and Methods. All chemicals were analytical grade and they were used without purification.

Mass spectrometry measurement. Mass spectrometry was performed using Shimadzu AXIMA Performance MALDI TOF mass spectrometer. The positive mode MALDI TOF MS confirmed the formation of the iminoboronate ester with 1:1:1 stoichiometry.

Fluorescence. Fluorescence measurements were performed on a single photon counting spectrofluorimeter from Edinburg Analytical Instrument (FL/FS 920). Using square quartz cuvettes with 10mm path length. Optically dilute solutions used for all photophysical experiments were prepared using acetonitrile. Solution of L-tryptophanol-FPBA-alizarin complexes were excited at 280 nm and 468 nm, L-tryptophanol-FPBA-coumarin complexes at 280 nm and 370 nm. The emission was scanned in 2 nm steps with a dwell time of 0.200 sec under ambient conditions.
Titration isotherms were constructed from the change in the fluorescence maximum at 332 nm for L-tryptophanol, 566 nm for alizarin, and 420 nm for coumarin, respectively. Data analysis and curve fitting were performed according to previously published methods[1].

2 MALDI-TOF Mass Spectra

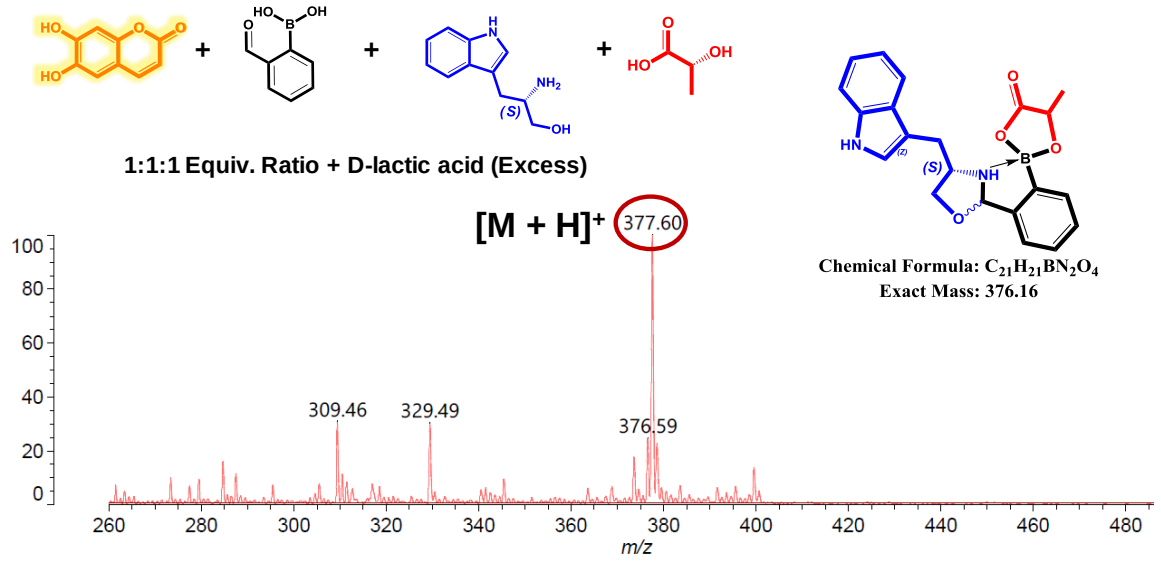


Figure S1. MALDI-TOF mass spectrum of the iminoboronate ester self-assembled from L-tryptophanol, FPBA, 6,7-dihydroxycoumarin, and D-lactic acid.

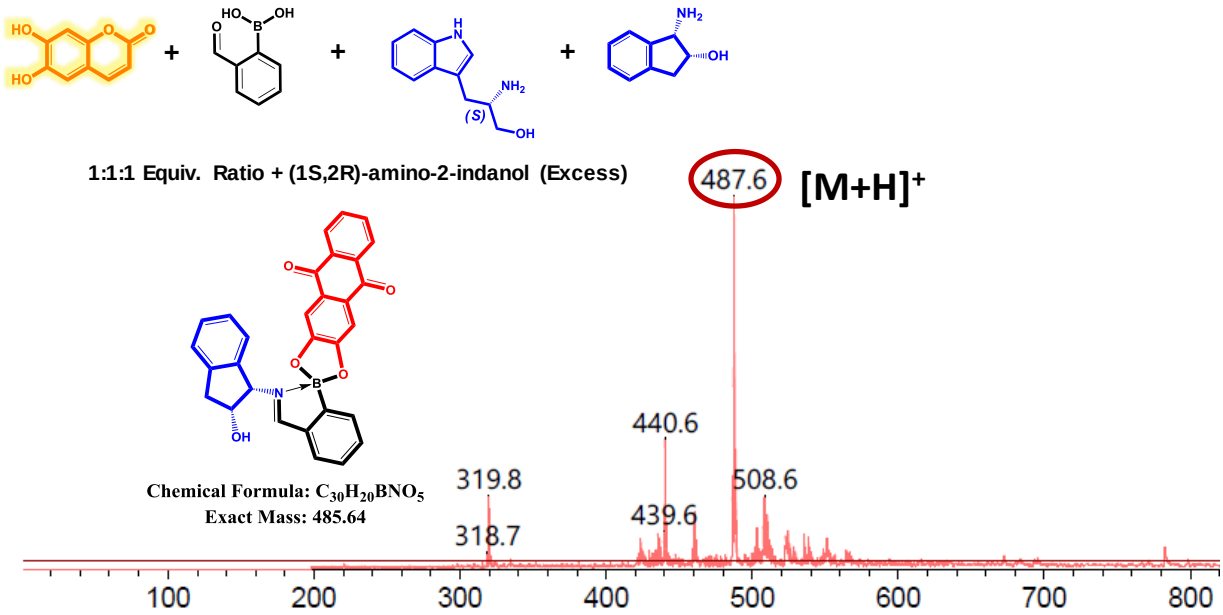
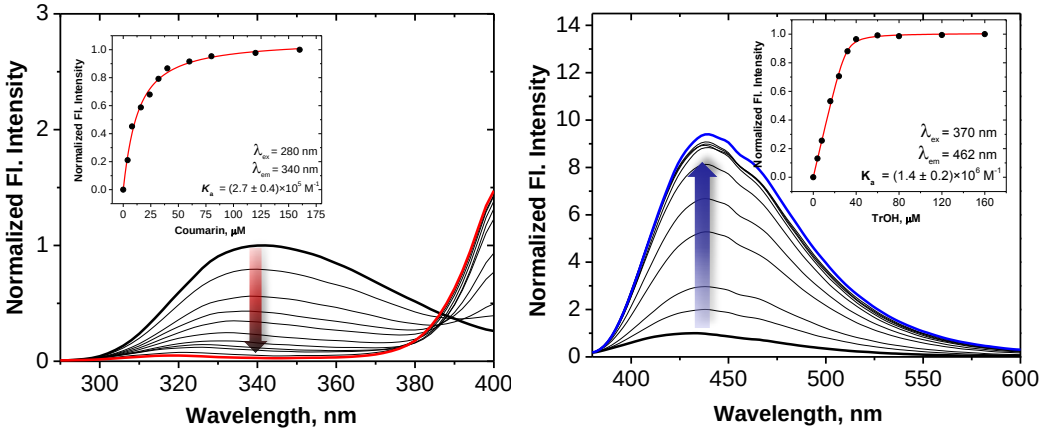


Figure S2. MALDI-TOF mass spectrum of the iminoboronate ester self-assembled from L-tryptophanol, FPBA, 6,7-dihydroxycoumarin, and (1S,2R)-1-amino-2-indanol.

3 Determination of Association Constants (Ka, M^{-1}) by Fluorescence Titrations

Procedure:
Each point of the titrations was pre-mixed from 12 mM stock solutions of alizarin or coumarin, with 12.0 mM stock solutions of 2-formylphenylboronic acid (FPBA) and 12 mM stock solution of L-tryptophanol at 1.1:1 equiv. ratio in order to achieve final concentration 2 mM in acetonitrile.
To prepare 20 mL of 12 mM stock solution of alizarin:
Weigh out 57.67 mg (0.24 mmol) of alizarin (MW=240.21) and transfer to the suitable vial and add 20 mL of DMSO:acetonitrile mix (30:70 v/v).
To prepare 20 mL of 12 mM stock solution of coumarin:
Weigh out 42.75 mg (0.24 mmol) of coumarin (MW=178.14) and transfer to the suitable vial and add 20 mL of of DMSO:acetonitrile mix (30:70 v/v).
To prepare 20 mL of 12 mM stock solution of (*S*)-VAPOL:
Weigh out 129.27 mg (0.24 mmol) of alizarin (MW=538.63) and transfer to the suitable vial and add 20 mL of acetonitrile.
To prepare 20 mL of 12 mM stock solution of 2-FPBA:
Weigh out 35.99 mg (0.24 mmol) of 2-FPBA (MW=149.94) and transfer to the suitable vial and add 20 mL of acetonitrile (MeCN).
To prepare 20 mL of 12 mM stock solution of L-tryptophanol:
Weigh out 45.66 mg (0.24 mmol) of L-tryptophanol (MW=190.24) and transfer to the suitable vial and add 20 mL of acetonitrile (MeCN).
Further transfer the same amount of fluorescent diol, amine and FPBA stocks in the suitable vial, and stir until a homogeneous 2mM pre-mix solution is obtained. Commercially available enantiopure L-tryptophanol, diols and 2-formylphenylboronic acid are air- and moisturestable, and so can be pre-mixed and stored in 2 mM solution. To prepare each point of the titration transfer 0.2 mL of premixed 2 mM acetonitrile solution of iminoboronate complex into the 0.5 mL Eppendorf tubes. Subsequently, different amounts of analyte solution have to be added, to reach a total volume of 0.2 mL with the desired concentration for the analyte. The final mixtures have to be incubated for 90 min in Eppendorf Thermomixer R to allow the displacement of the indicator and the formation of new iminoboronate and oxazolidine-boronate esters. Then each reaction mixture must be diluted by 200 times with acetonitrile to a final concentration of 40 µM and a final volume of 2 mL directly in a square quartz cuvette with 10mm path length. The changes in the fluorescence intensity during the titration of the complexes with different analytes are demonstrated below.



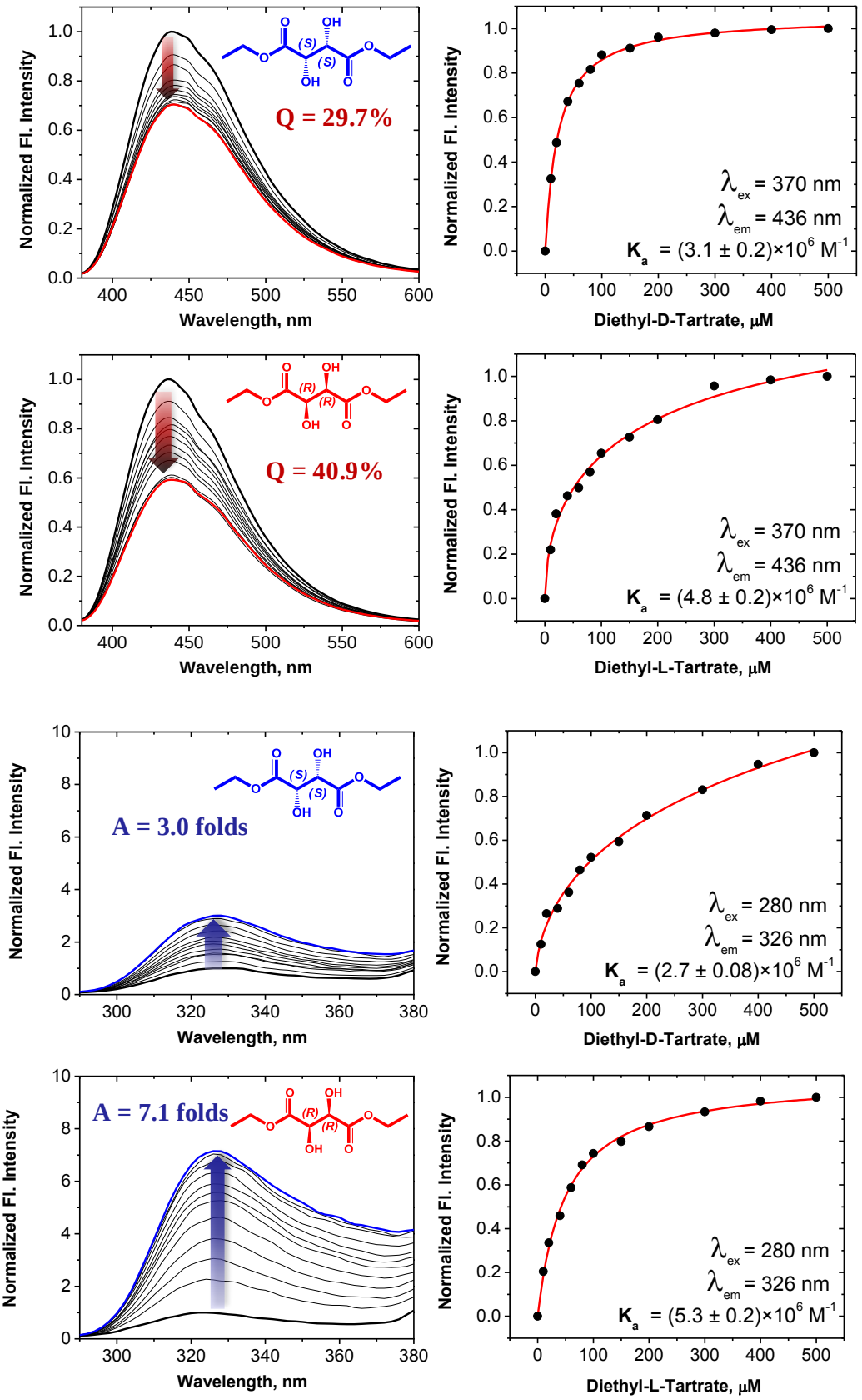
Left: Fluorescence titration spectra (λ_{ex}=280 nm) and isotherm of 2-FPBA, L-tryptophanol (0.2 µM) upon addition of coumarin in MeCN. **Right:** Fluorescence titration spectra (λ_{ex}=370 nm) and isotherm of 2-FPBA, coumarin upon addition of L-tryptophanol in MeCN. The titrations represent the formation of the initial

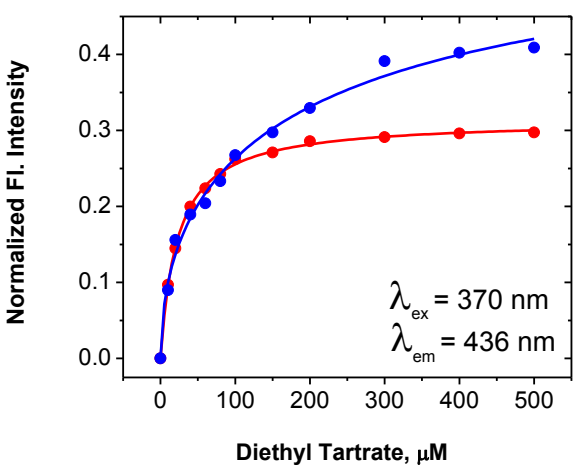
iminoboronate complex between L-tryptophanol. 2-FPBA and coumarin, which was later used as a sensor for the displacement assays for the ee determination in various analytes.

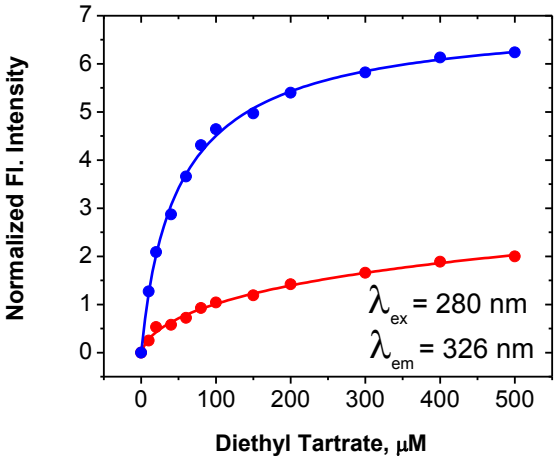
The change in fluorescence profiles of both dyes (tryptophanol and coumarin) upon addition of analytes can be utilized for the calculation of binding affinities of the analytes.[1]

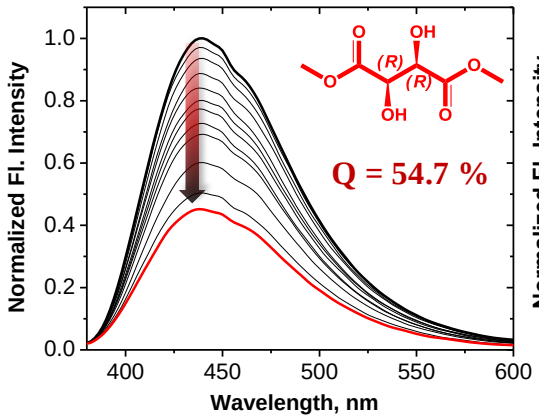
Table S1. The calculated Ka values on the change in fluorescence intensities of the iminoboronate complex formed by FPBA, L-tryptophanol and coumarin upon addition of selected chiral diols in acetonitrile.

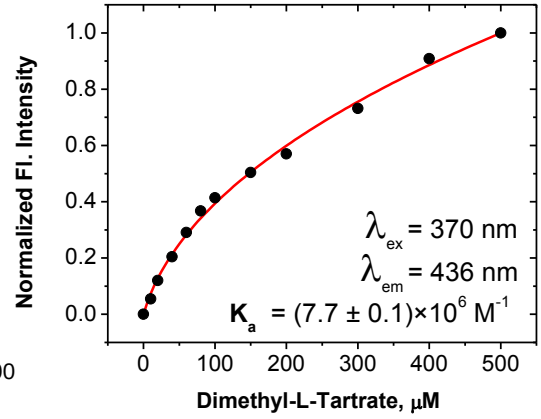
Analytes	K_a ($M^{-1} \times 10^6$) derived from 6,7-dihydroxycoumarin	K_a ($M^{-1} \times 10^6$) derived from L-tryptophanol
(*R*)-(-)-3-Chloro-1,2-propanediol	2.5 ± 0.1	1.1 ± 0.06
(*S*)-(+)-3-Chloro-1,2-propanediol	0.11 ± 0.01	0.33 ± 0.02
(+)-Dimethyl L-tartrate (*R,R*)	7.7 ± 0.1	16 ± 0.8
(–)-Dimethyl D-tartrate (*S,S*)	7.0 ± 0.2	8.5 ± 0.5
(+)-Diethyl L-tartrate (*R,R*)	4.8 ± 0.2	5.3 ± 0.2
(-)-Diethyl D-tartrate(*S,S*)	3.1 ± 0.2	2.7 ± 0.08
(1*R*,2*R*,3*S*,5*R*)-(-)-Pinanediol	4.3 ± 0.7	4.2 ± 0.6
(1*S*,2*S*,3*R*,5*S*)-(+)-Pinanediol	2.8 ± 0.2	2.1 ± 0.2
(*R*)-(-)-Phenyl-1,2-ethanediol	1.1 ± 0.1	2.0 ± 0.2
(*S*)-(+)-Phenyl-1,2-ethanediol	2.0 ± 0.4	1.4 ± 0.06
***meso*-Hydrobenzoin**	2.0 ± 0.2	1.4 ± 0.08
(*R,R*)-(+)-Hydrobenzoin	1.1 ± 0.08	1.5 ± 0.1
(*S,S*)-(-)-Hydrobenzoin	4.2 ± 0.2	2.9 ± 0.3

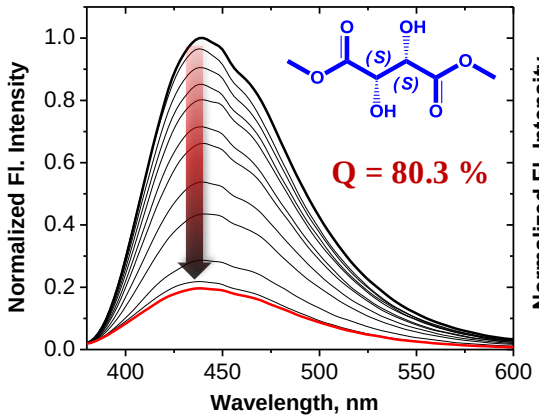

Normalized Fl. Intensity
Wavelength, nm
Q = 29.7%
Diethyl-D-Tartrate, μM
λex = 370 nm
λem = 436 nm
Ka = (3.1 ± 0.2)×10^6 M^-1
Q = 40.9%
Diethyl-L-Tartrate, μM
Ka = (4.8 ± 0.2)×10^6 M^-1
A = 3.0 folds
λex = 280 nm
λem = 326 nm
Ka = (2.7 ± 0.08)×10^6 M^-1
A = 7.1 folds
Ka = (5.3 ± 0.2)×10^6 M^-1

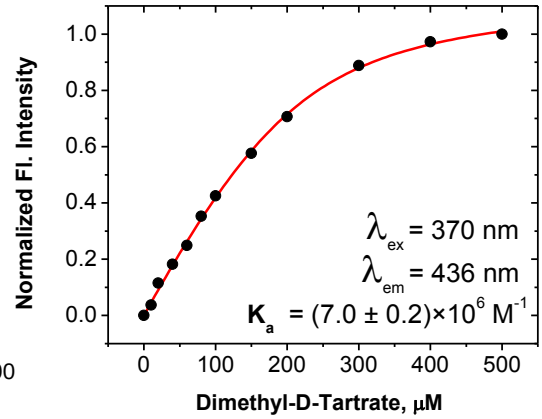

Normalized FI. Intensity
0.0
0.1
0.2
0.3
0.4
0
100
200
300
400
500
Diethyl Tartrate, μM
λex = 370 nm
λem = 436 nm

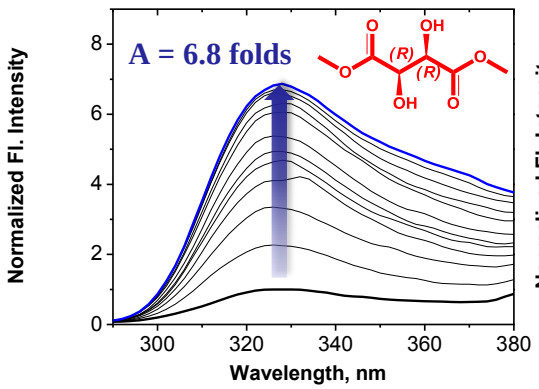

Normalized FI. Intensity
0
1
2
3
4
5
6
7
0
100
200
300
400
500
Diethyl Tartrate, μM
λex = 280 nm
λem = 326 nm


Normalized FI. Intensity
0.0
0.2
0.4
0.6
0.8
1.0
400
450
500
550
600
Wavelength, nm
O
OH
(R)
(R)
O
O
OH
O
Q = 54.7 %


Normalized FI. Intensity
0.0
0.2
0.4
0.6
0.8
1.0
0
100
200
300
400
500
Dimethyl-L-Tartrate, μM
λex = 370 nm
λem = 436 nm
Ka = (7.7 ± 0.1)×10^6 M^-1


Normalized FI. Intensity
0.0
0.2
0.4
0.6
0.8
1.0
400
450
500
550
600
Wavelength, nm
O
OH
(S)
(S)
O
O
OH
O
Q = 80.3 %


Normalized FI. Intensity
0.0
0.2
0.4
0.6
0.8
1.0
0
100
200
300
400
500
Dimethyl-D-Tartrate, μM
λex = 370 nm
λem = 436 nm
Ka = (7.0 ± 0.2)×10^6 M^-1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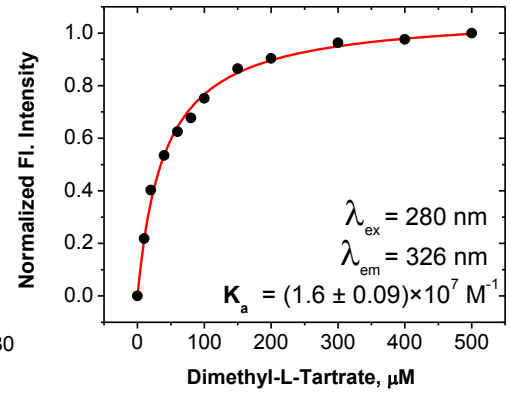
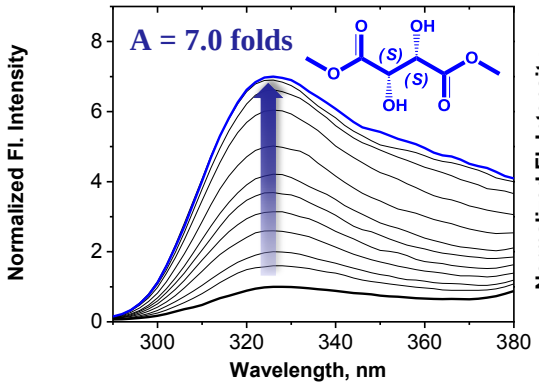
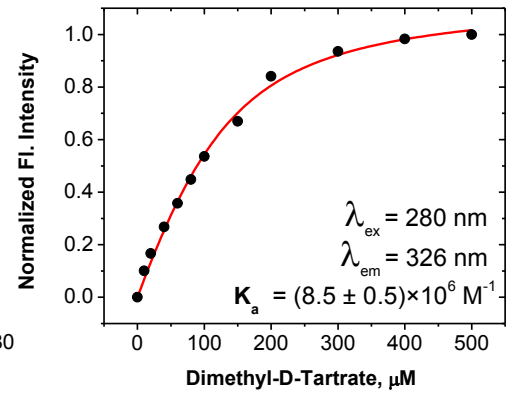
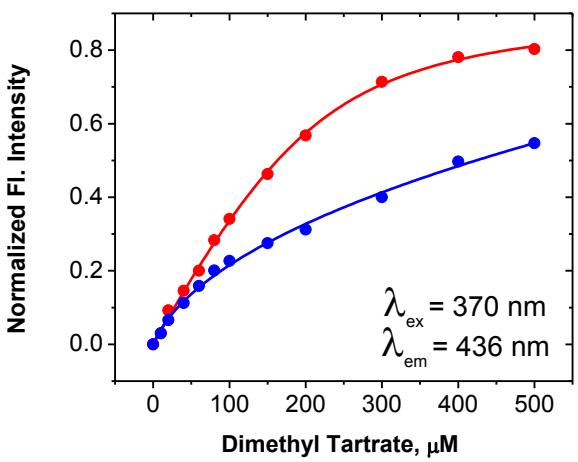
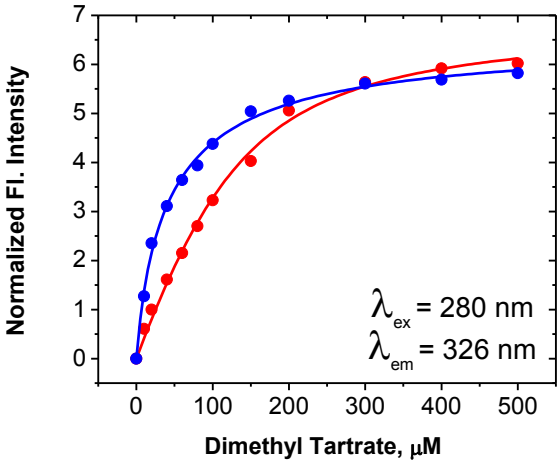
(R)
(R)
OH
OH
O
O
O
O
Normalized Fl. Intensity
Wavelength, nm

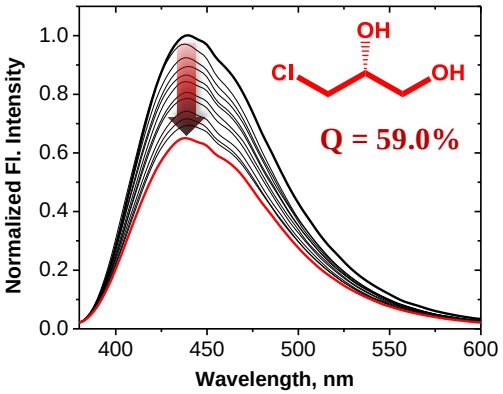

λ_{ex} = 280 nm
λ_{em} = 326 nm
K_a = (1.6 ± 0.09)×10^7 M^{-1}
Normalized Fl. Intensity
Dimethyl-L-Tartrate, μM

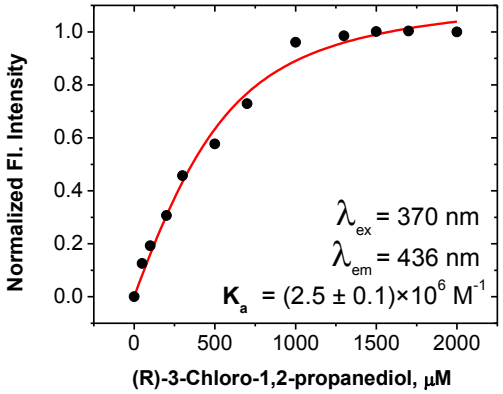

A = 7.0 folds
(S)
(S)
OH
OH
O
O
O
O
Normalized Fl. Intensity
Wavelength, nm

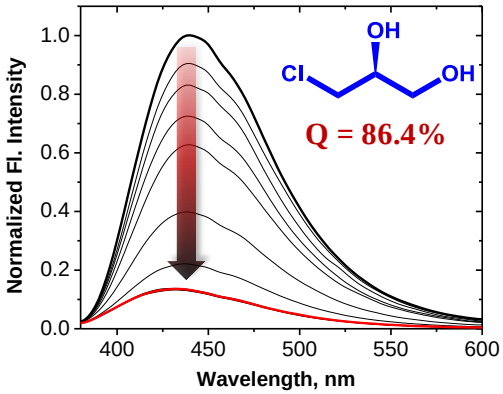

λ_{ex} = 280 nm
λ_{em} = 326 nm
K_a = (8.5 ± 0.5)×10^6 M^{-1}
Normalized Fl. Intensity
Dimethyl-D-Tartrate, μM

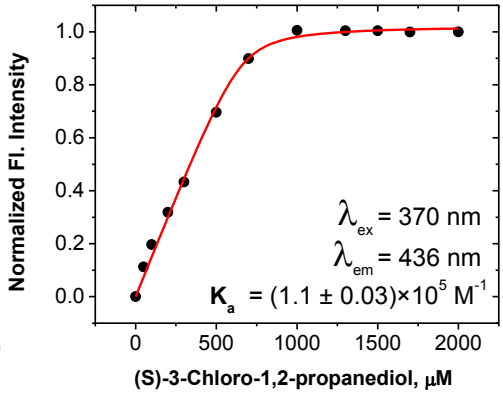

λ_{ex} = 370 nm
λ_{em} = 436 nm
Normalized Fl. Intensity
Dimethyl Tartrate, μM

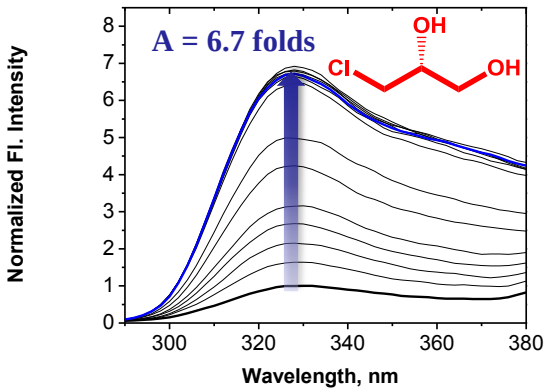

λ_{ex} = 280 nm
λ_{em} = 326 nm
Normalized Fl. Intensity
Dimethyl Tartrate, μM

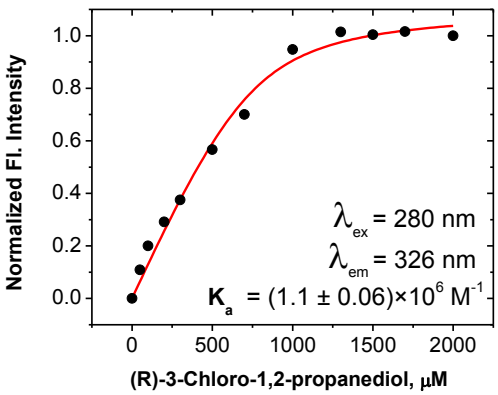

Normalized FI. Intensity
Wavelength, nm
Q = 59.0%
OH
Cl
OH

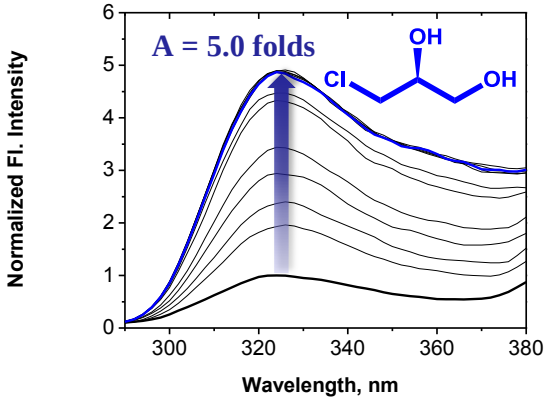

Normalized FI. Intensity
(R)-3-Chloro-1,2-propanediol, μM
λex = 370 nm
λem = 436 nm
Ka = (2.5 ± 0.1)×10^6 M^-1

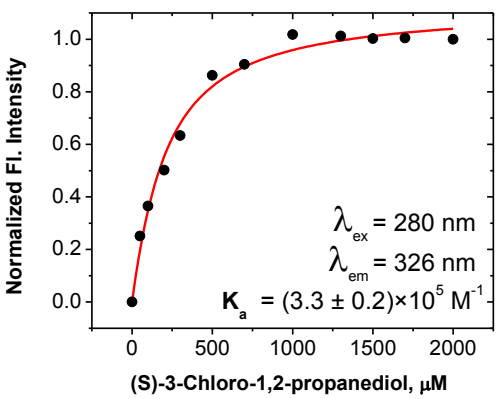

Normalized FI. Intensity
Wavelength, nm
Q = 86.4%
OH
Cl
OH

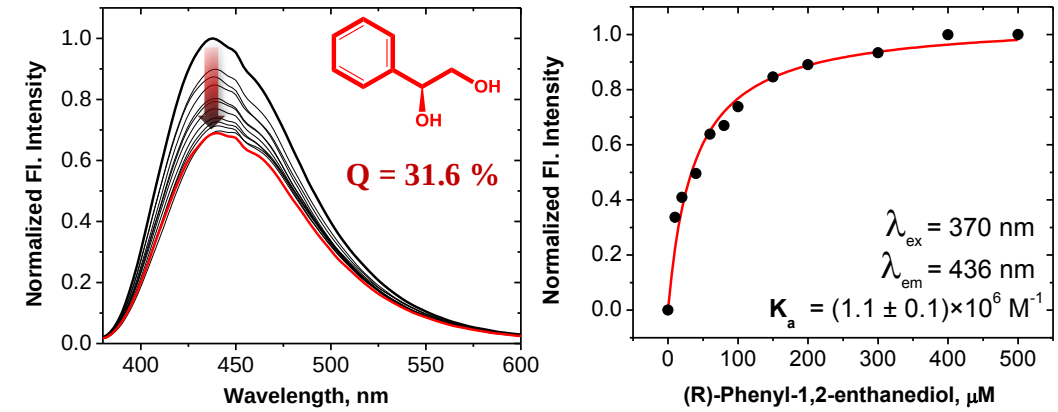

Normalized FI. Intensity
(S)-3-Chloro-1,2-propanediol, μM
λex = 370 nm
λem = 436 nm
Ka = (1.1 ± 0.03)×10^5 M^-1

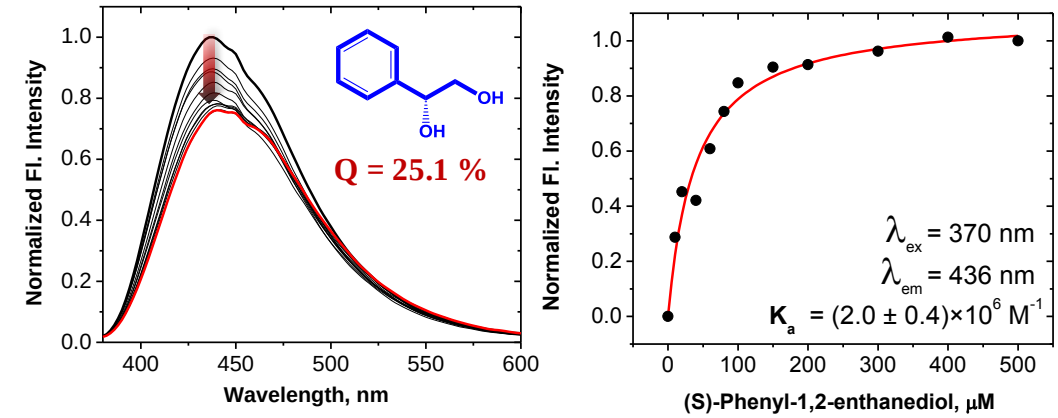

Normalized FI. Intensity
Wavelength, nm
A = 6.7 folds
OH
Cl
OH

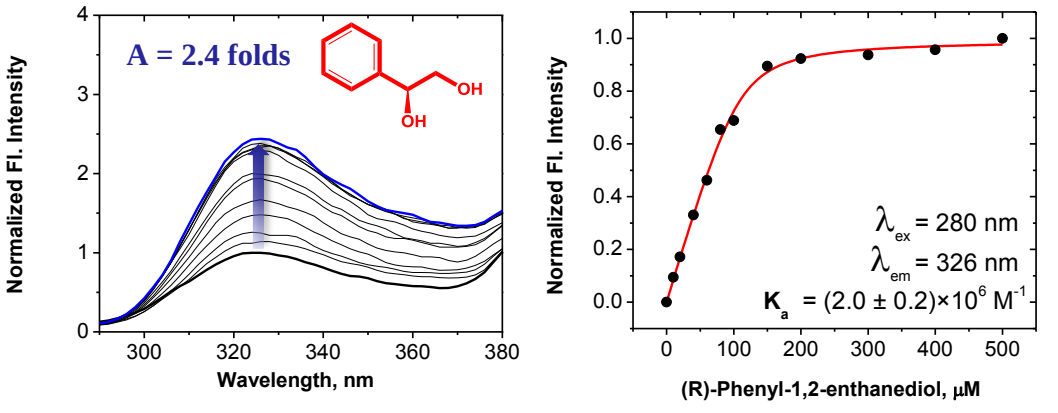

Normalized FI. Intensity
(R)-3-Chloro-1,2-propanediol, μM
λex = 280 nm
λem = 326 nm
Ka = (1.1 ± 0.06)×10^6 M^-1

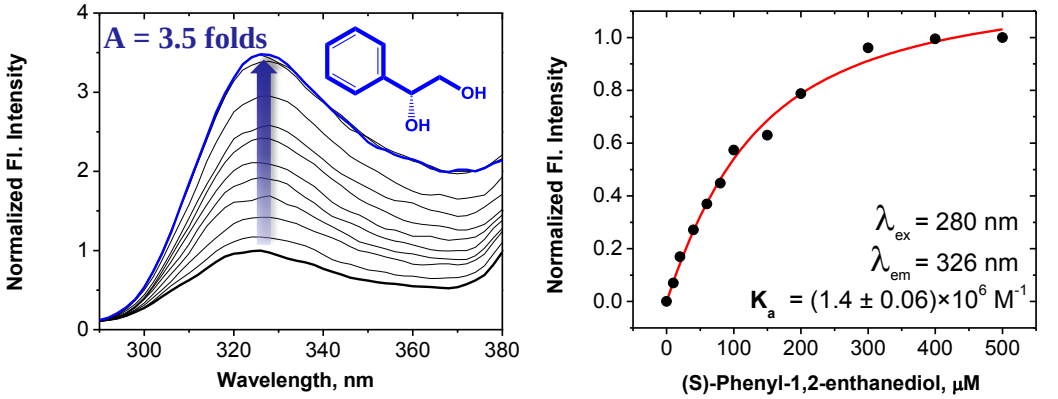

Normalized FI. Intensity
Wavelength, nm
A = 5.0 folds
OH
Cl
OH

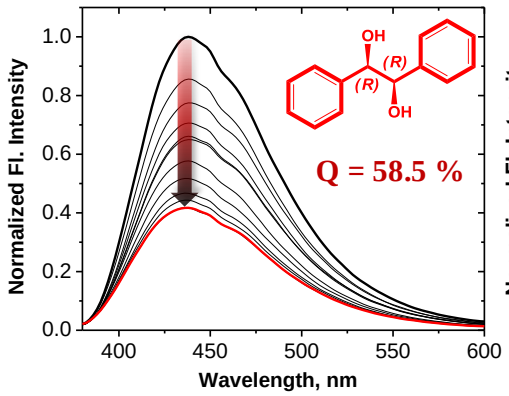

Normalized FI. Intensity
(S)-3-Chloro-1,2-propanediol, μM
λex = 280 nm
λem = 326 nm
Ka = (3.3 ± 0.2)×10^5 M^-1

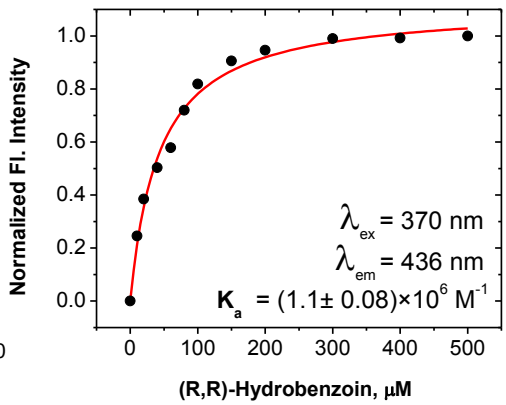

Normalized FI. Intensity
Wavelength, nm
Q = 31.6 %
OH
OH
λex = 370 nm
λem = 436 nm
Ka = (1.1 ± 0.1)×10^6 M^-1
(R)-Phenyl-1,2-enthanediol, μM

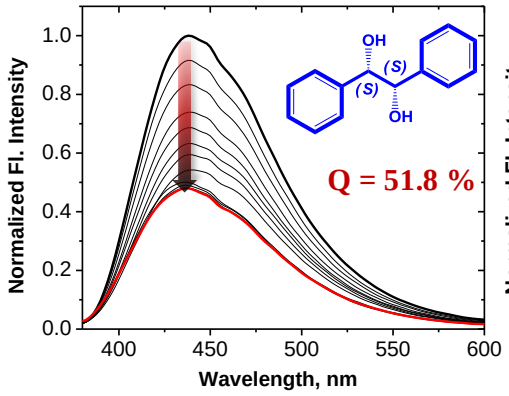

Normalized FI. Intensity
Wavelength, nm
Q = 25.1 %
OH
OH
λex = 370 nm
λem = 436 nm
Ka = (2.0 ± 0.4)×10^6 M^-1
(S)-Phenyl-1,2-enthanediol, μM

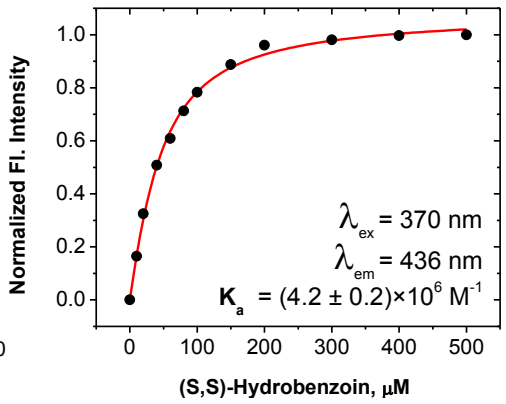

Normalized FI. Intensity
Wavelength, nm
A = 2.4 folds
OH
OH
λex = 280 nm
λem = 326 nm
Ka = (2.0 ± 0.2)×10^6 M^-1
(R)-Phenyl-1,2-enthanediol, μM

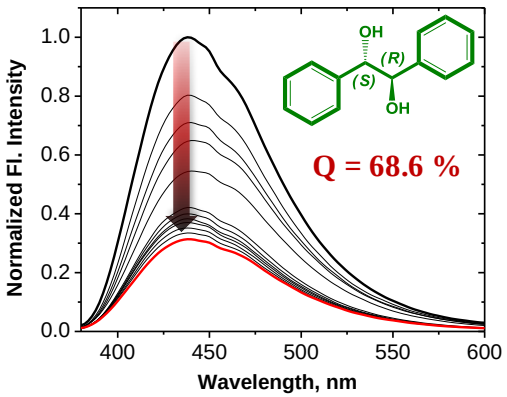

Normalized FI. Intensity
Wavelength, nm
A = 3.5 folds
OH
OH
λex = 280 nm
λem = 326 nm
Ka = (1.4 ± 0.06)×10^6 M^-1
(S)-Phenyl-1,2-enthanediol, μM

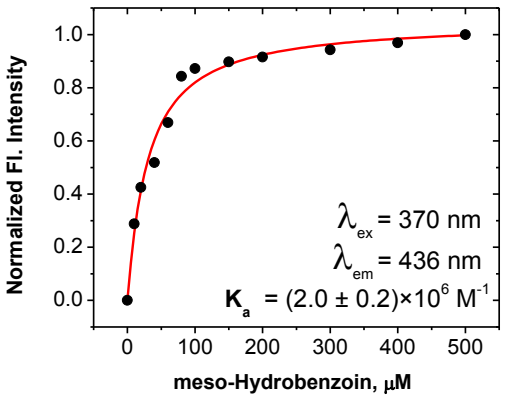

Normalized FI. Intensity
Wavelength, nm
Q = 58.5 %

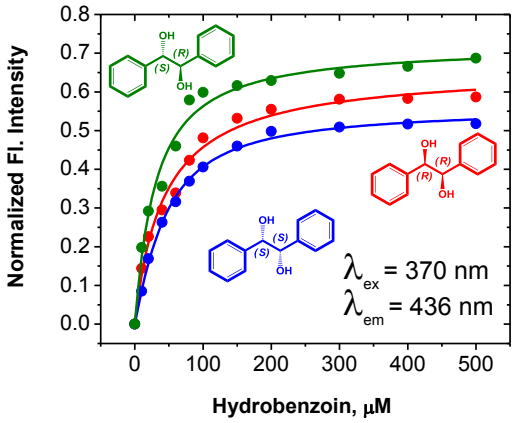

Normalized FI. Intensity
(R,R)-Hydrobenzoin, μM
λex = 370 nm
λem = 436 nm
Ka = (1.1± 0.08)×10^6 M^-1

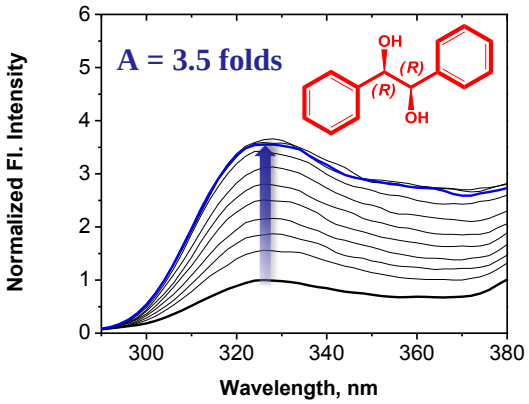

Normalized FI. Intensity
Wavelength, nm
Q = 51.8 %

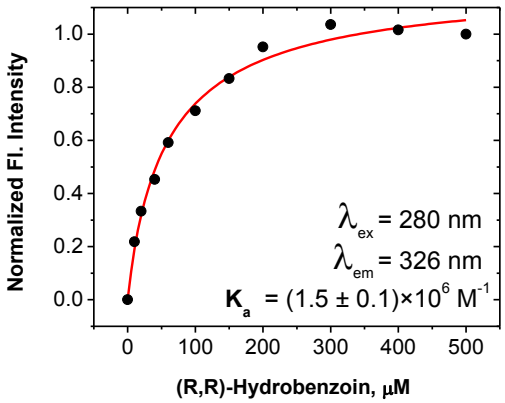

Normalized FI. Intensity
(S,S)-Hydrobenzoin, μM
λex = 370 nm
λem = 436 nm
Ka = (4.2 ± 0.2)×10^6 M^-1

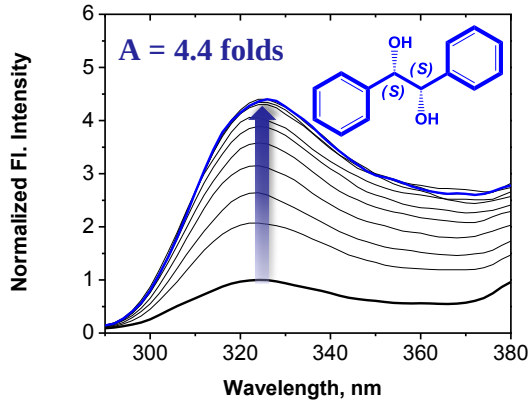

Normalized FI. Intensity
Wavelength, nm
Q = 68.6 %

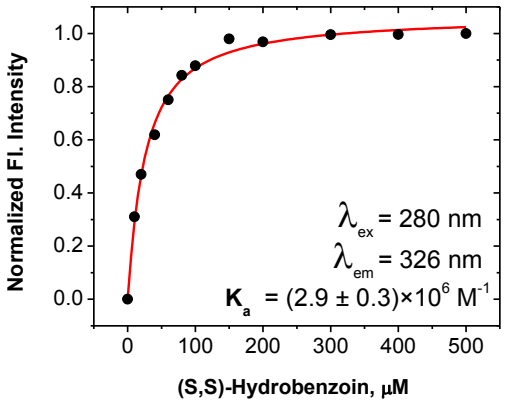

Normalized FI. Intensity
meso-Hydrobenzoin, μM
λex = 370 nm
λem = 436 nm
Ka = (2.0 ± 0.2)×10^6 M^-1

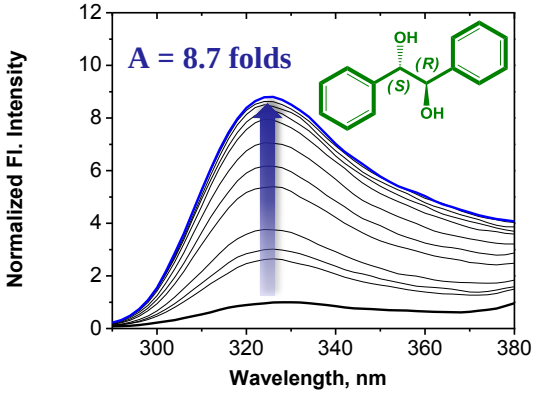

Normalized FI. Intensity
Hydrobenzoin, μM
λex = 370 nm
λem = 436 nm

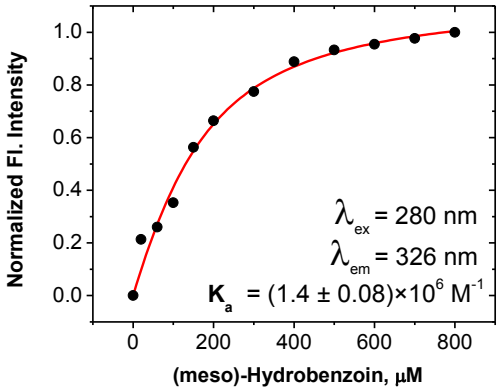

A = 3.5 folds
OH
(R)
(R)
OH
Normalized FI. Intensity
Wavelength, nm

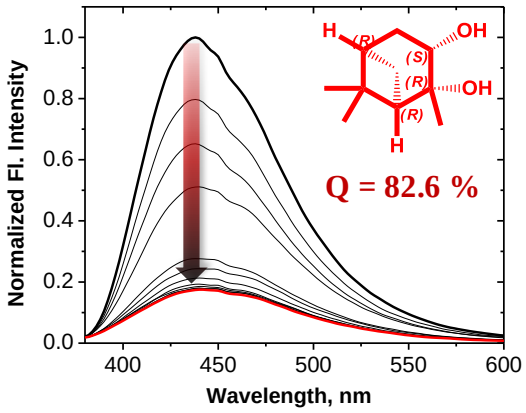

Normalized FI. Intensity
λex = 280 nm
λem = 326 nm
Ka = (1.5 ± 0.1)×10^6 M^-1
(R,R)-Hydrobenzoin, μM

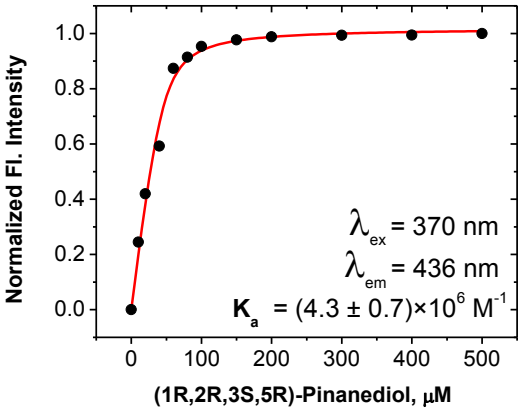

A = 4.4 folds
OH
(S)
(S)
OH
Normalized FI. Intensity
Wavelength, nm

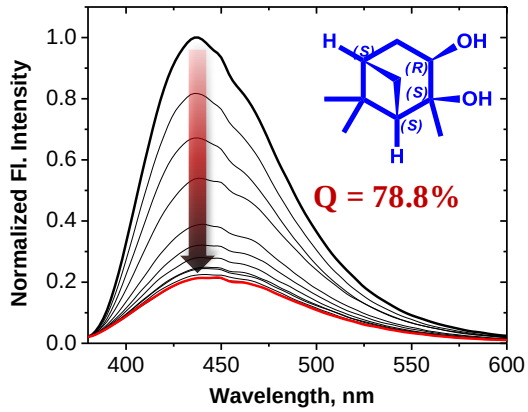

Normalized FI. Intensity
λex = 280 nm
λem = 326 nm
Ka = (2.9 ± 0.3)×10^6 M^-1
(S,S)-Hydrobenzoin, μM

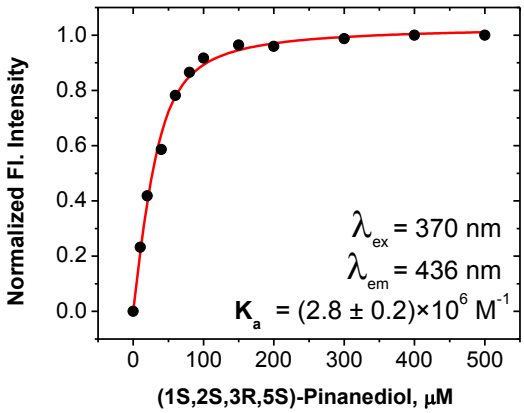

A = 8.7 folds
OH
(R)
(S)
OH
Normalized FI. Intensity
Wavelength, nm

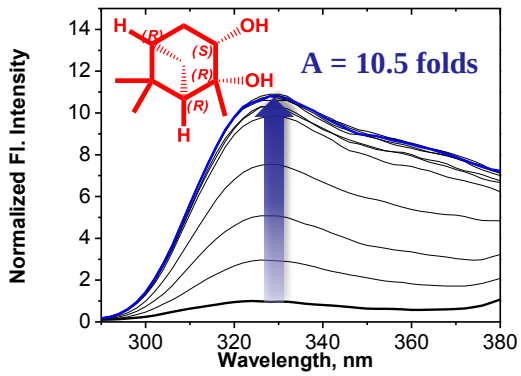

Normalized FI. Intensity
λex = 280 nm
λem = 326 nm
Ka = (1.4 ± 0.08)×10^6 M^-1
(meso)-Hydrobenzoin, μM

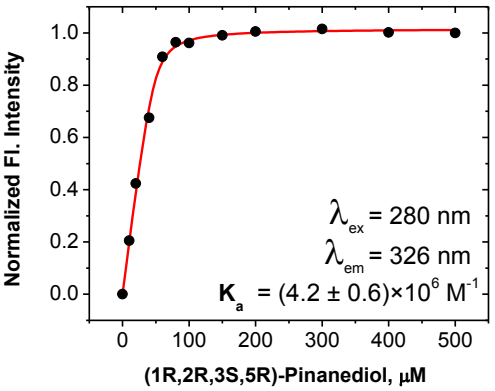

Normalized Fl. Intensity
Wavelength, nm
Q = 82.6 %

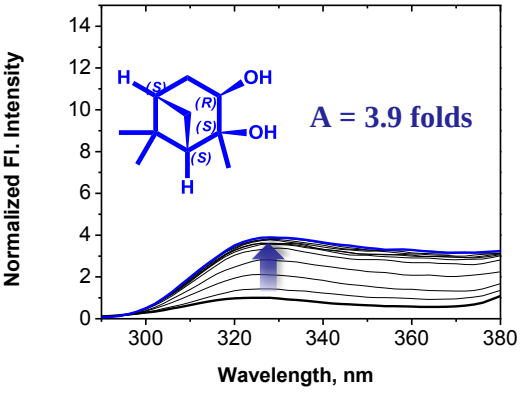

Normalized Fl. Intensity
(1R,2R,3S,5R)-Pinanediol, μM
λex = 370 nm
λem = 436 nm
Ka = (4.3 ± 0.7)×10^6 M^-1


Normalized Fl. Intensity
Wavelength, nm
Q = 78.8%


Normalized Fl. Intensity
(1S,2S,3R,5S)-Pinanediol, μM
λex = 370 nm
λem = 436 nm
Ka = (2.8 ± 0.2)×10^6 M^-1


Normalized Fl. Intensity
Wavelength, nm
A = 10.5 folds


Normalized Fl. Intensity
(1R,2R,3S,5R)-Pinanediol, μM
λex = 280 nm
λem = 326 nm
Ka = (4.2 ± 0.6)×10^6 M^-1


Normalized Fl. Intensity
Wavelength, nm
A = 3.9 folds

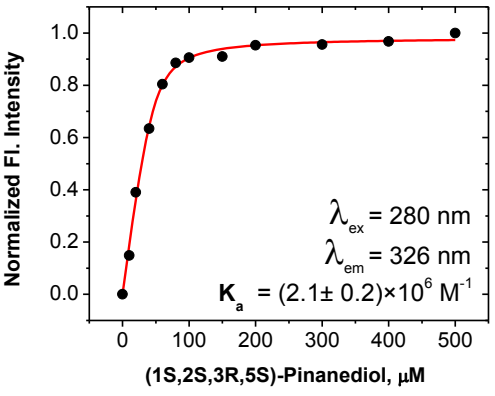
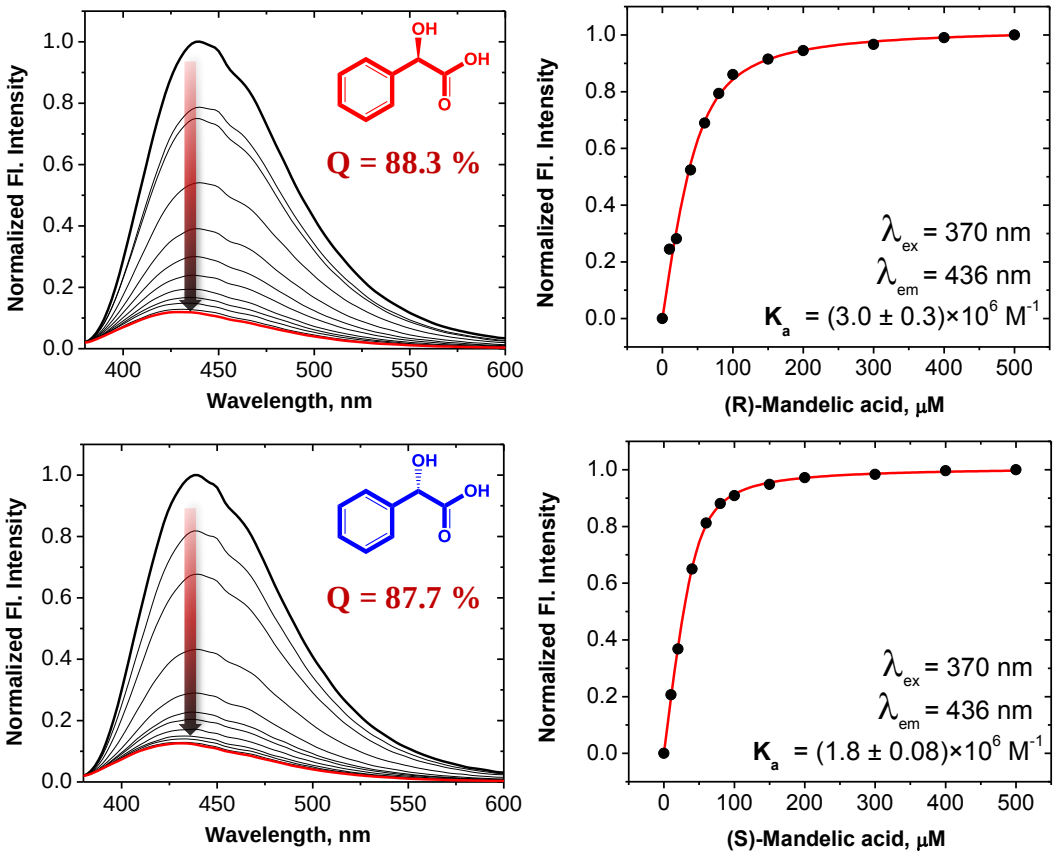
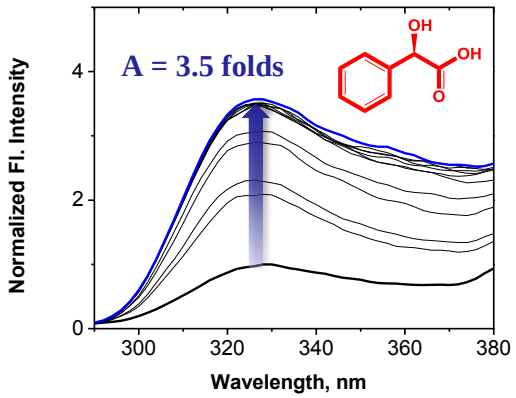
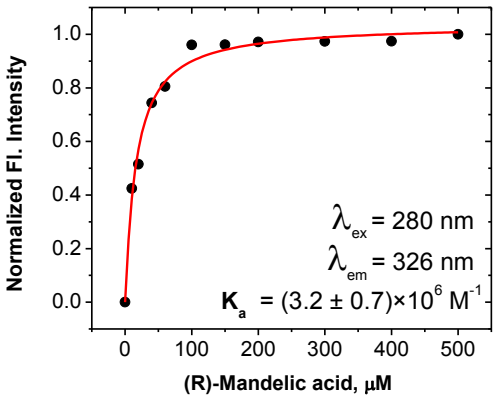

Normalized Fl. Intensity
(1S,2S,3R,5S)-Pinanediol, μM
λex = 280 nm
λem = 326 nm
Ka = (2.1± 0.2)×10^6 M^-1

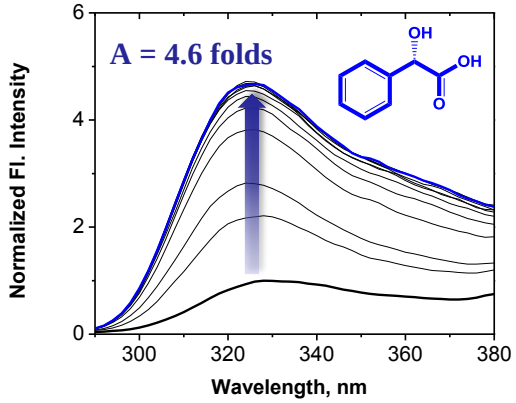
Table S2. The calculated Ka values on the change in fluorescence intensities of the iminoboronate complex formed by FPBA, L-tryptophanol and alizarin upon addition of selected chiral hydroxy acids in acetonitrile.

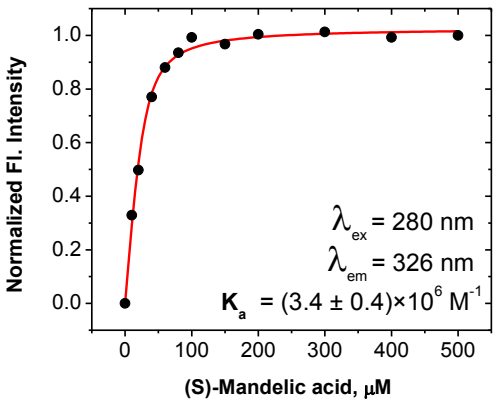
Analytes	K_a ($M^{-1} \times 10^6$) derived from 6,7-dihydroxycoumarin	K_a ($M^{-1} \times 10^6$) derived from L-tryptophanol
(*S*)-Mandelic acid	1.8 ± 0.08	3.4 ± 0.4
(*R*)-Mandelic acid	3.0 ± 0.3	3.2 ± 0.7
L-(-)-3-Phenyllactic acid	3.9 ± 0.3	4.8 ± 0.3
D-(+)-3-Phenyllactic acid	12 ± 1.0	9.3 ± 1.6
L-(+)-Lactic acid	6.9 ± 0.7	8.3 ± 0.8
D-(−)-Lactic acid	1.3 ± 0.07	1.4 ± 0.2
(2*R*)-2-Hydroxy-3-methylbutanoic acid	2.2 ± 0.1	1.3 ± 0.1
(2*S*)-2-Hydroxy-3-methylbutanoic acid	2.1 ± 0.3	3.0 ± 0.7

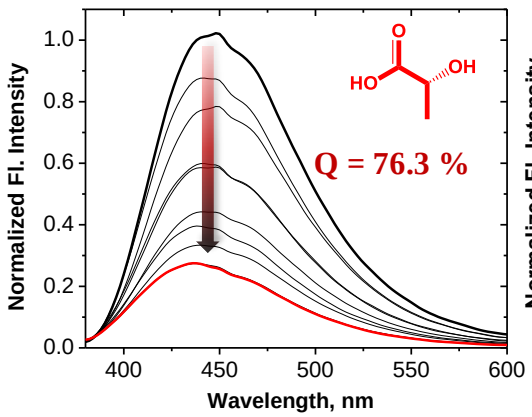


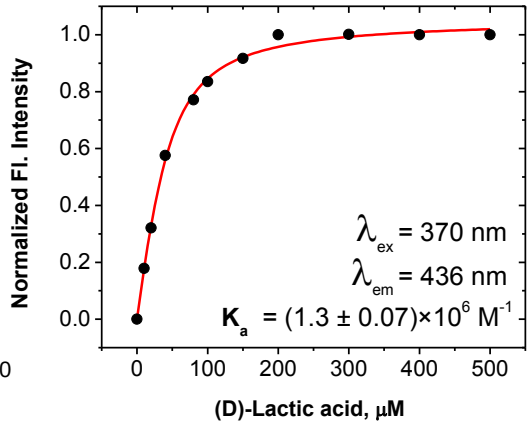

A = 3.5 folds
OH
OH
O
Normalized Fl. Intensity
Wavelength, nm

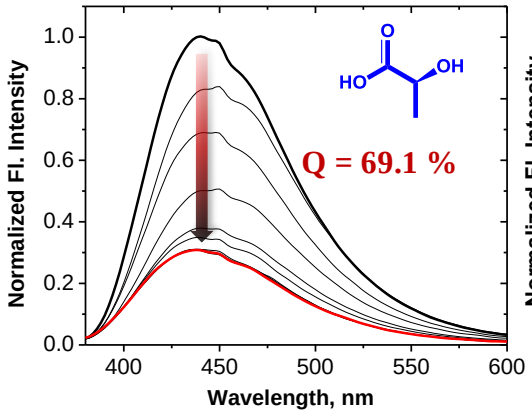

λex = 280 nm
λem = 326 nm
Ka = (3.2 ± 0.7)×10^6 M^-1
Normalized Fl. Intensity
(R)-Mandelic acid, μM

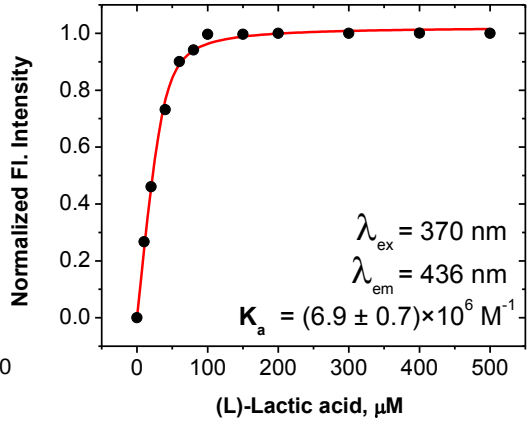

A = 4.6 folds
OH
OH
O
Normalized Fl. Intensity
Wavelength, nm

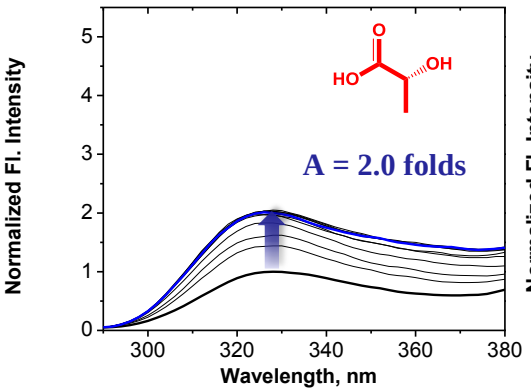

λex = 280 nm
λem = 326 nm
Ka = (3.4 ± 0.4)×10^6 M^-1
Normalized Fl. Intensity
(S)-Mandelic acid, μM

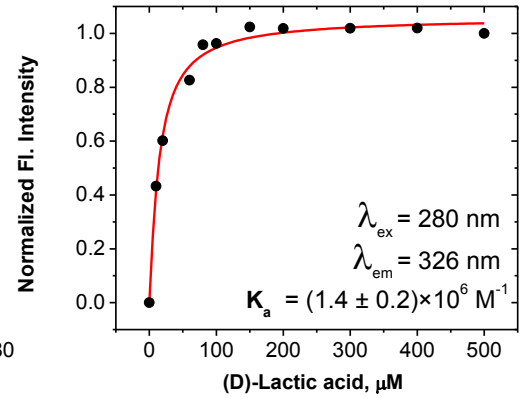

Q = 76.3 %
O
HO
OH
Normalized Fl. Intensity
Wavelength, nm

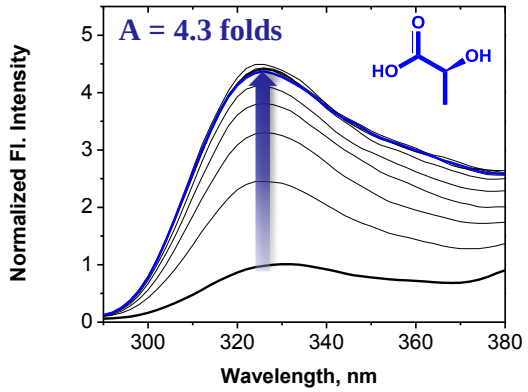

λex = 370 nm
λem = 436 nm
Ka = (1.3 ± 0.07)×10^6 M^-1
Normalized Fl. Intensity
(D)-Lactic acid, μM

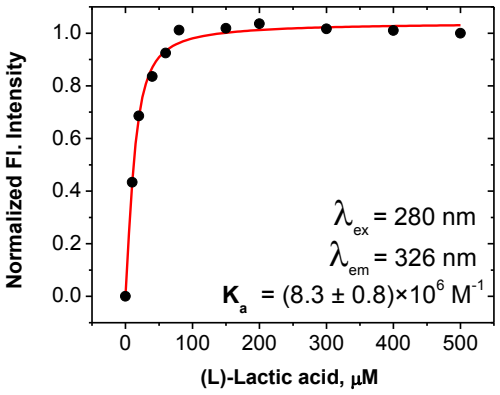

Q = 69.1 %
O
HO
OH
Normalized Fl. Intensity
Wavelength, nm

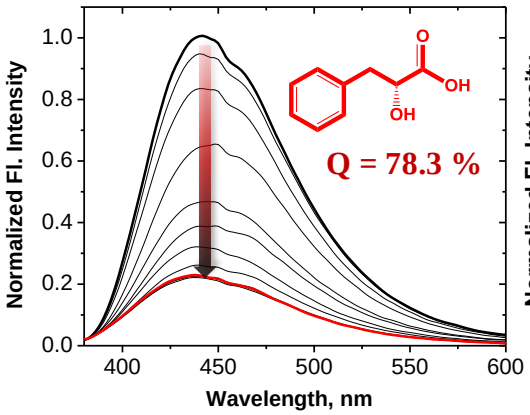

λex = 370 nm
λem = 436 nm
Ka = (6.9 ± 0.7)×10^6 M^-1
Normalized Fl. Intensity
(L)-Lactic acid, μM

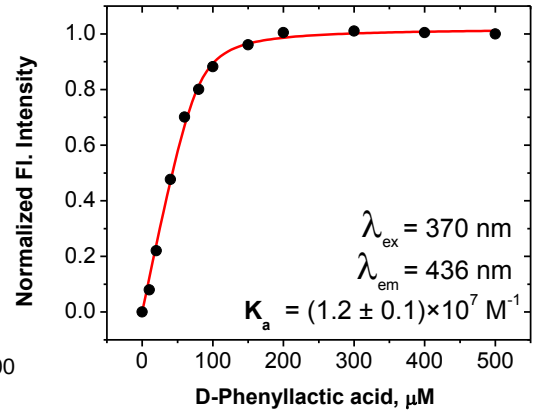

Normalized FI. Intensity
Wavelength, nm
A = 2.0 folds
HO
OH
O

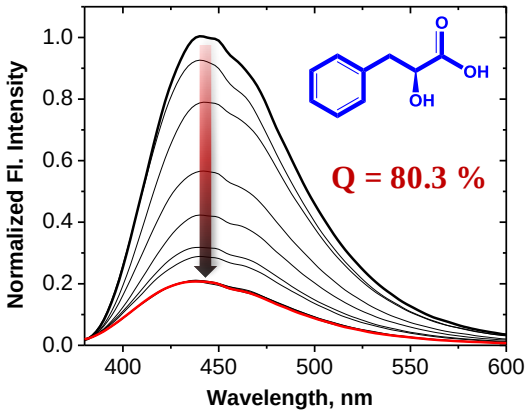

Normalized FI. Intensity
(D)-Lactic acid, μM
λex = 280 nm
λem = 326 nm
Ka = (1.4 ± 0.2)×10^6 M^-1

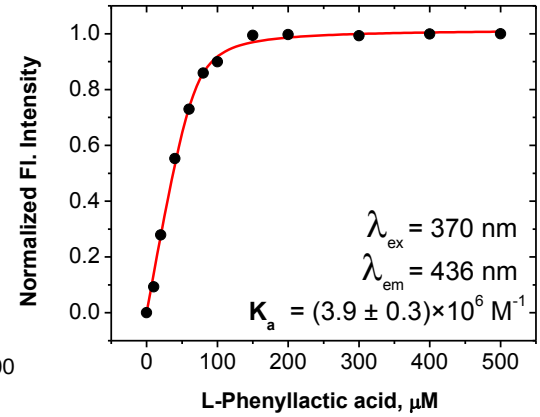

Normalized FI. Intensity
Wavelength, nm
A = 4.3 folds
HO
OH
O

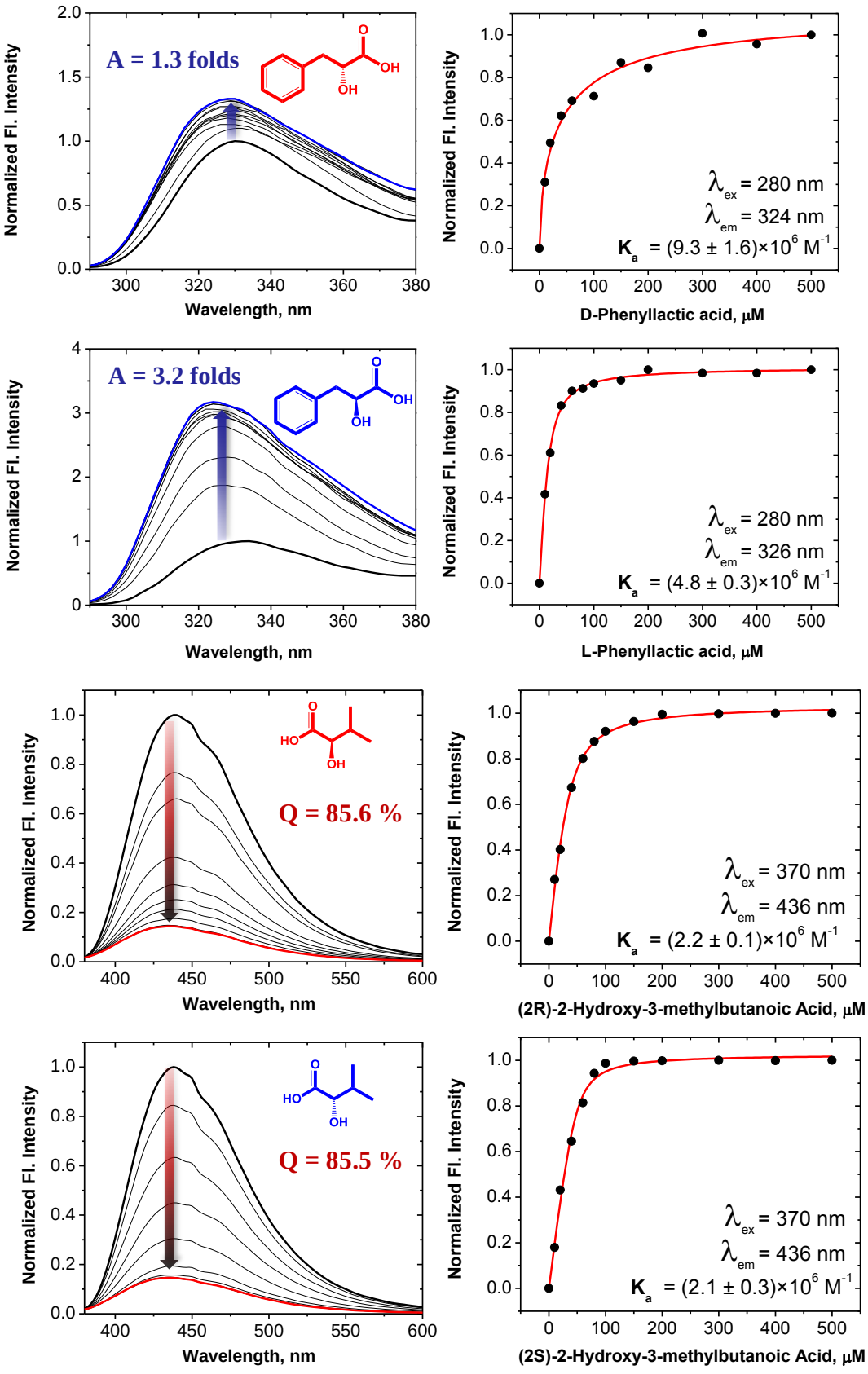

Normalized FI. Intensity
(L)-Lactic acid, μM
λex = 280 nm
λem = 326 nm
Ka = (8.3 ± 0.8)×10^6 M^-1

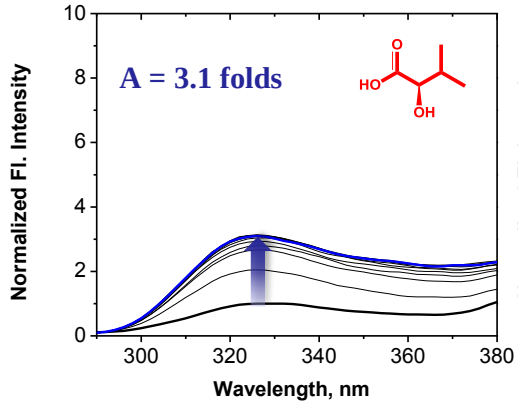

Normalized FI. Intensity
Wavelength, nm
Q = 78.3 %
OH
OH
O

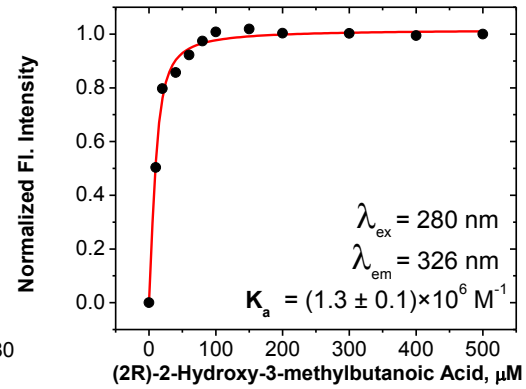

Normalized FI. Intensity
D-Phenyllactic acid, μM
λex = 370 nm
λem = 436 nm
Ka = (1.2 ± 0.1)×10^7 M^-1

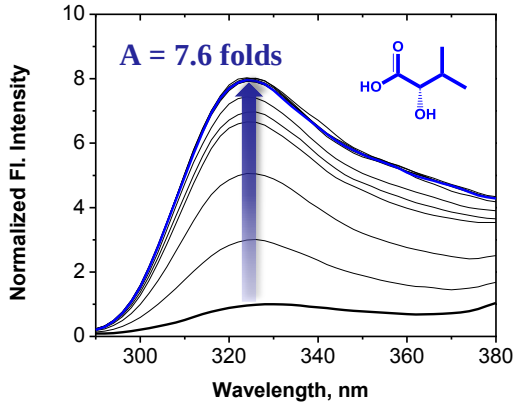

Normalized FI. Intensity
Wavelength, nm
Q = 80.3 %
OH
OH
O

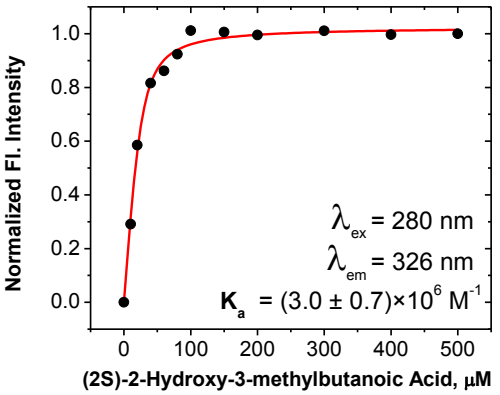

Normalized FI. Intensity
L-Phenyllactic acid, μM
λex = 370 nm
λem = 436 nm
Ka = (3.9 ± 0.3)×10^6 M^-1

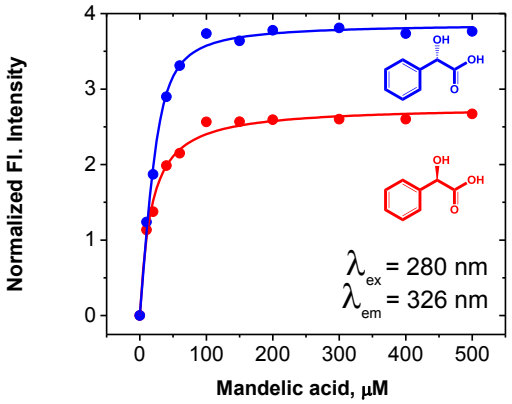

A = 1.3 folds
Normalized Fl. Intensity
Wavelength, nm
λex = 280 nm
λem = 324 nm
Ka = (9.3 ± 1.6)×10^6 M^-1
D-Phenyllactic acid, μM
A = 3.2 folds
Normalized Fl. Intensity
Wavelength, nm
λex = 280 nm
λem = 326 nm
Ka = (4.8 ± 0.3)×10^6 M^-1
L-Phenyllactic acid, μM
Q = 85.6 %
Normalized Fl. Intensity
Wavelength, nm
λex = 370 nm
λem = 436 nm
Ka = (2.2 ± 0.1)×10^6 M^-1
(2R)-2-Hydroxy-3-methylbutanoic Acid, μM
Q = 85.5 %
Normalized Fl. Intensity
Wavelength, nm
λex = 370 nm
λem = 436 nm
Ka = (2.1 ± 0.3)×10^6 M^-1
(2S)-2-Hydroxy-3-methylbutanoic Acid, μM

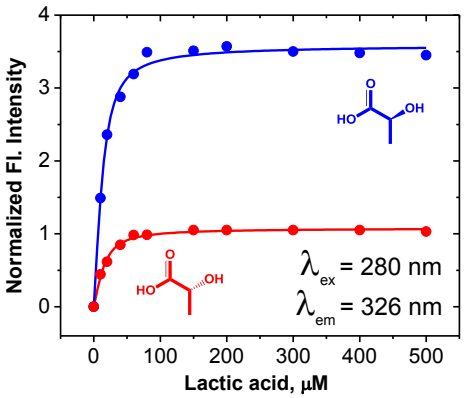

A = 3.1 folds
Normalized FI. Intensity
Wavelength, nm

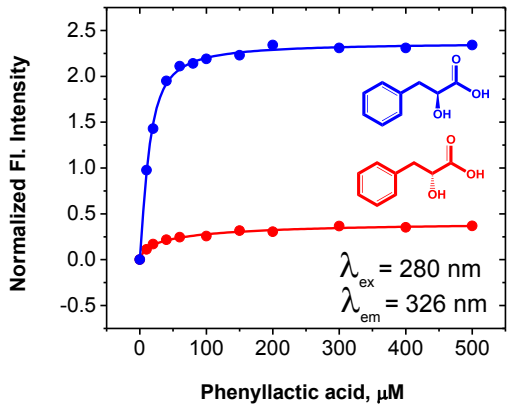

λex = 280 nm
λem = 326 nm
Ka = (1.3 ± 0.1)×10^6 M^-1
Normalized FI. Intensity
(2R)-2-Hydroxy-3-methylbutanoic Acid, μM

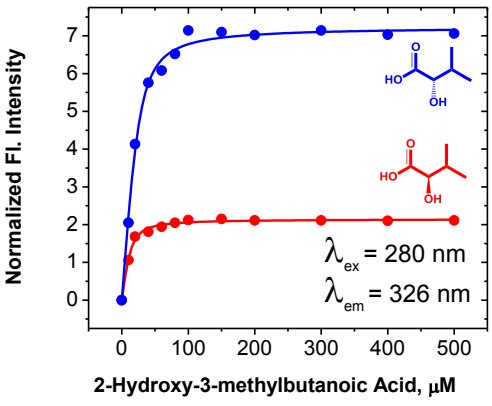

A = 7.6 folds
Normalized FI. Intensity
Wavelength, nm

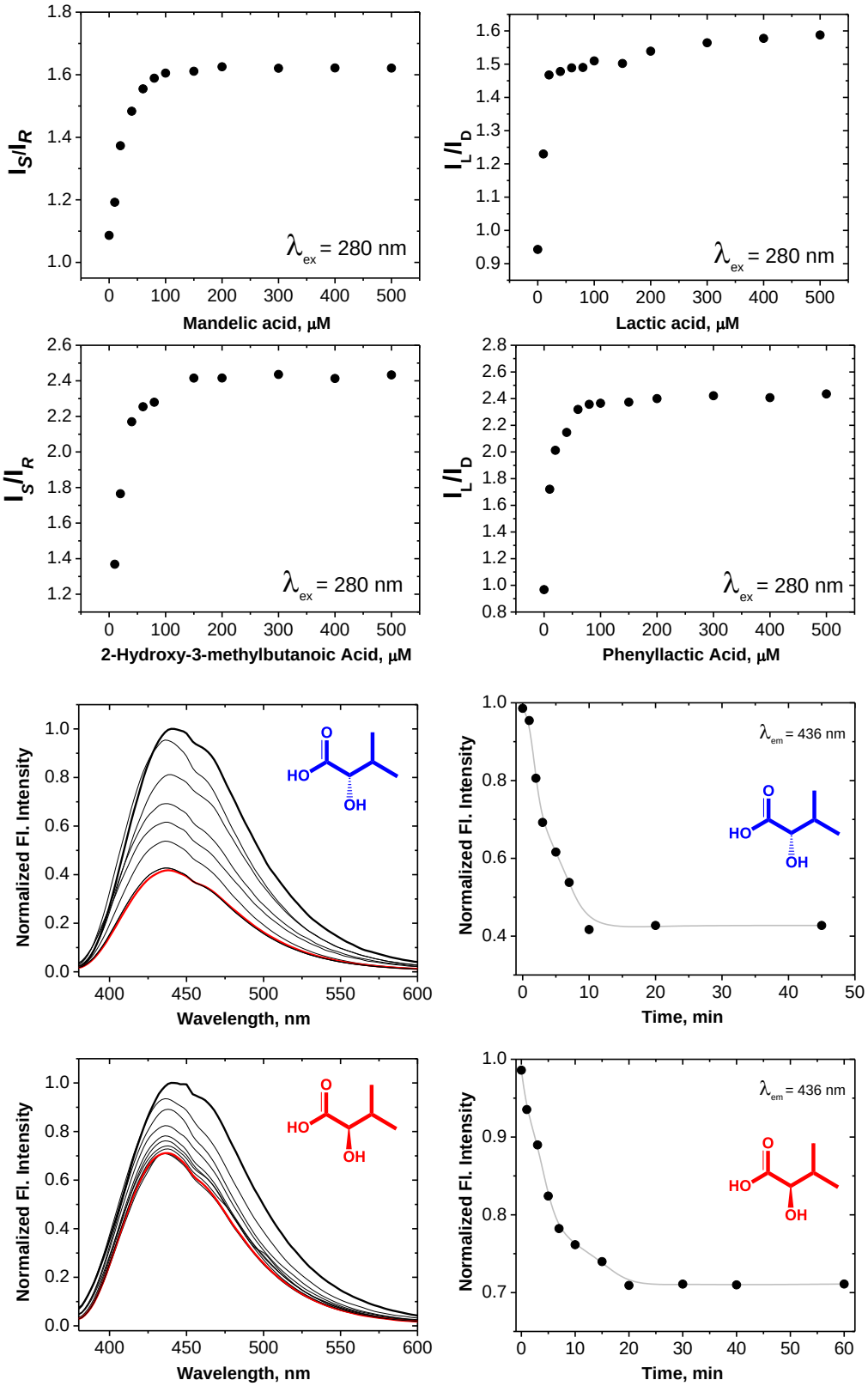

λex = 280 nm
λem = 326 nm
Ka = (3.0 ± 0.7)×10^6 M^-1
Normalized FI. Intensity
(2S)-2-Hydroxy-3-methylbutanoic Acid, μM


λex = 280 nm
λem = 326 nm
Normalized FI. Intensity
Mandelic acid, μM

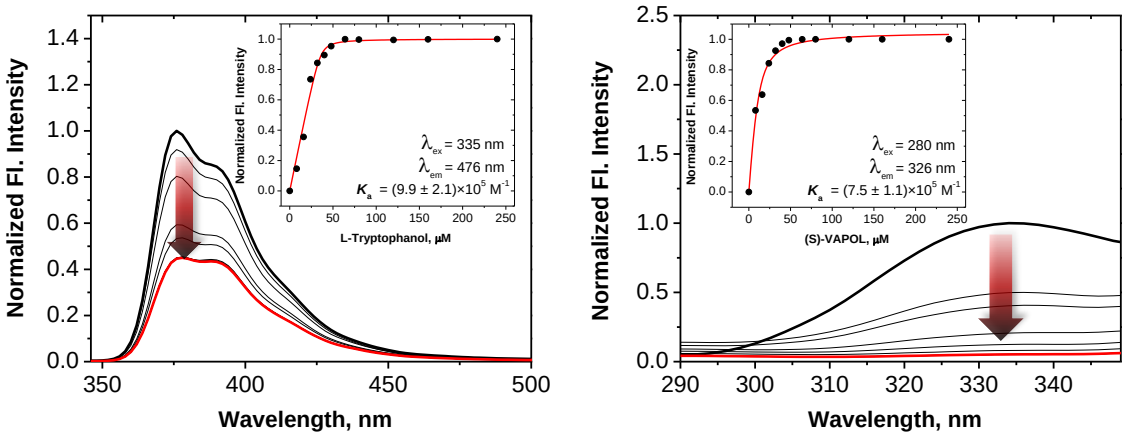

λex = 280 nm
λem = 326 nm
Normalized FI. Intensity
Lactic acid, μM


λex = 280 nm
λem = 326 nm
Normalized FI. Intensity
Phenyllactic acid, μM


λex = 280 nm
λem = 326 nm
Normalized FI. Intensity
2-Hydroxy-3-methylbutanoic Acid, μM



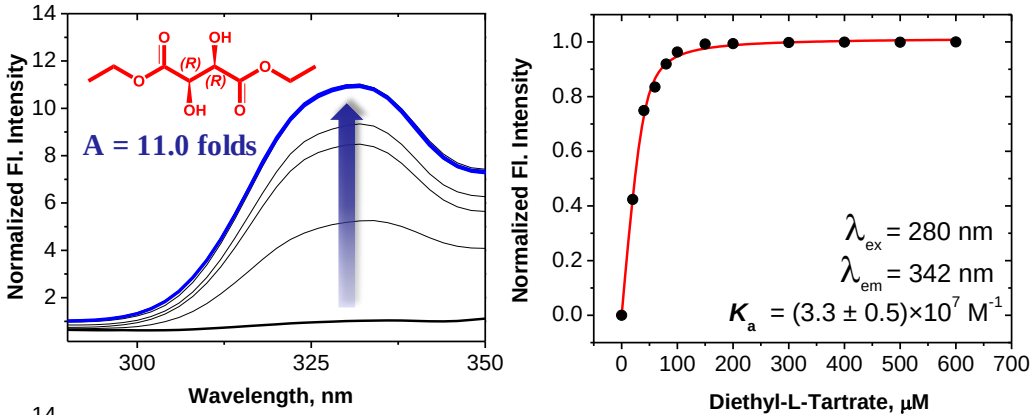
Time-dependent fluorescent titration of the ensemble with enantiomeric lactic acid in acetonitrile

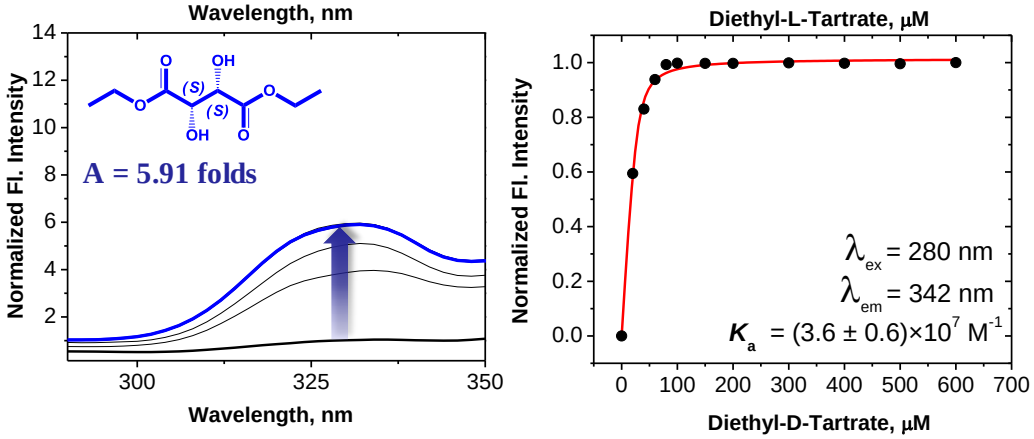


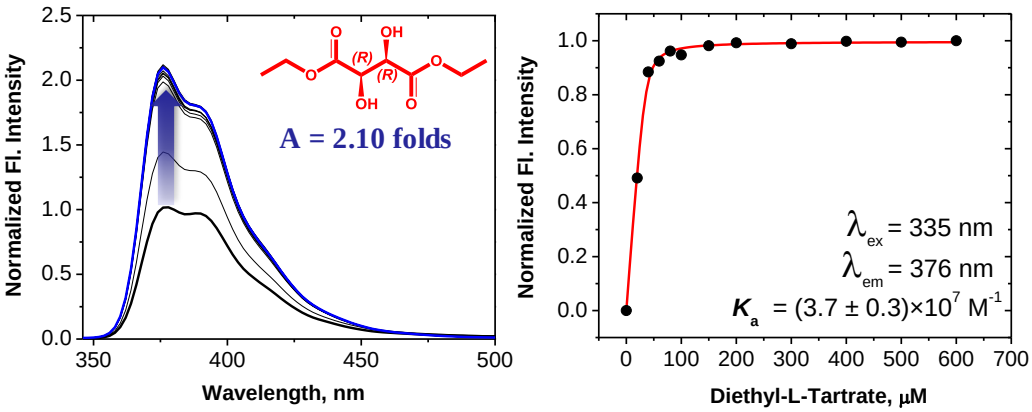
Left: Fluorescence titration spectra (λ_{ex}=335 nm) and isotherm of 2-FPBA, (*S*)-VAPOL (40 μM) upon addition of L-tryptophanol. **Right:** Fluorescence titration spectra (λ_{ex}=280 nm) and isotherm of 2-FPBA, L-tryptophanol (0.2 μM) upon addition of (*S*)-VAPOL in MeCN. The titrations represent the formation of the initial iminoboronate complex between L-tryptophanol. 2-FPBA and (*S*)-VAPOL, which was later used as a sensor for the displacement assays for determination of various analytes.

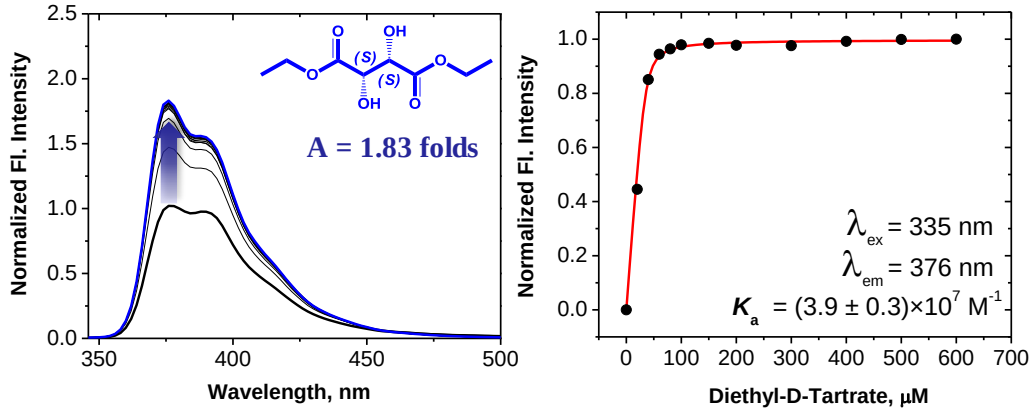
Table S3. The calculated Ka values on the change in fluorescence intensities of the iminoboronate complex formed by FPBA, L-tryptophanol and (*S*)-VAPOL upon addition of selected chiral diols in acetonitrile.

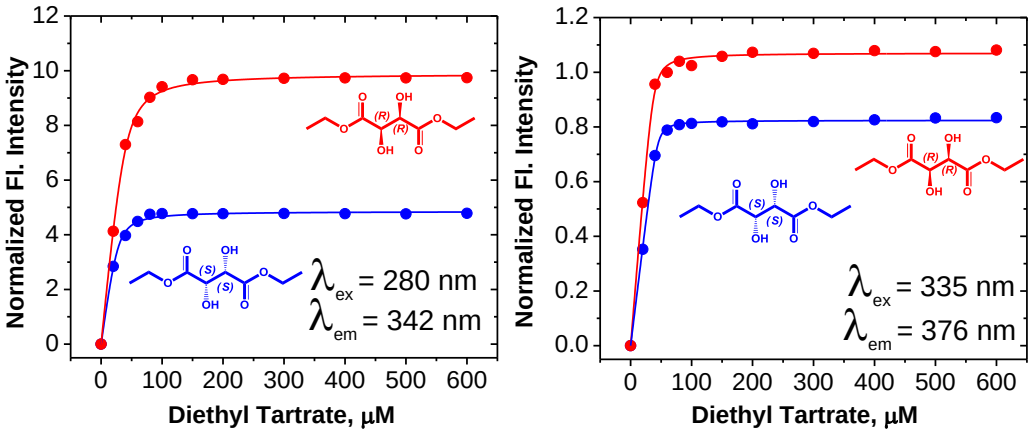
Analytes	**K_a (M^{-1} × 10^6) derived from (*S*)-VAPOL**	**K_a (M^{-1} × 10^6) derived from L-tryptophanol**
(+)-Dimethyl L-tartrate (*R,R*)	39 ± 3.0	30 ± 3.0
(–)-Dimethyl D-tartrate (*S,S*)	8.7 ± 1.0	8.4 ± 0.6
(+)-Diethyl L-tartrate (*R,R*)	37 ± 3.0	33 ± 5.0
(-)-Diethyl D-tartrate(*S,S*)	39 ± 3.0	36 ± 6.0
(1*R*,2*R*,3*S*,5*R*)-(-)-Pinanediol	5.9 ± 1.0	5.6 ± 1.0
(1*S*,2*S*,3*R*,5*S*)-(+)-Pinanediol	16 ± 2.0	16 ± 2.0

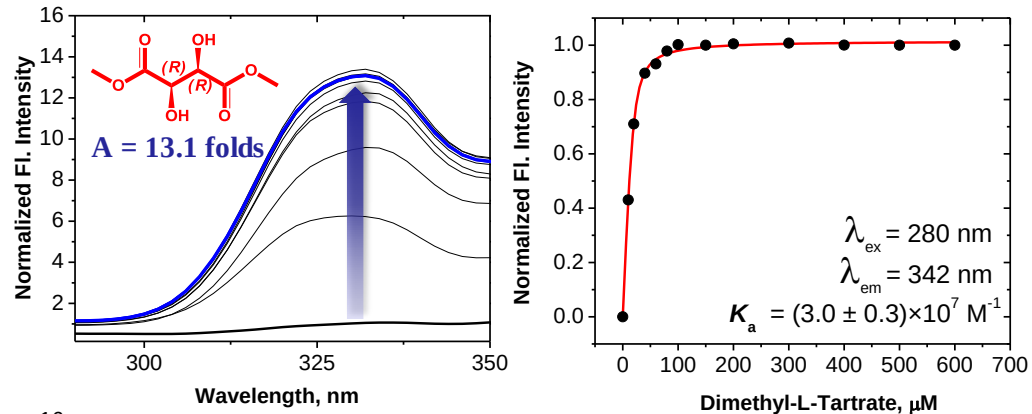

Normalized Fl. Intensity
Wavelength, nm
A = 11.0 folds
Normalized Fl. Intensity
Diethyl-L-Tartrate, μM
λex = 280 nm
λem = 342 nm
Ka = (3.3 ± 0.5)×10^7 M^-1

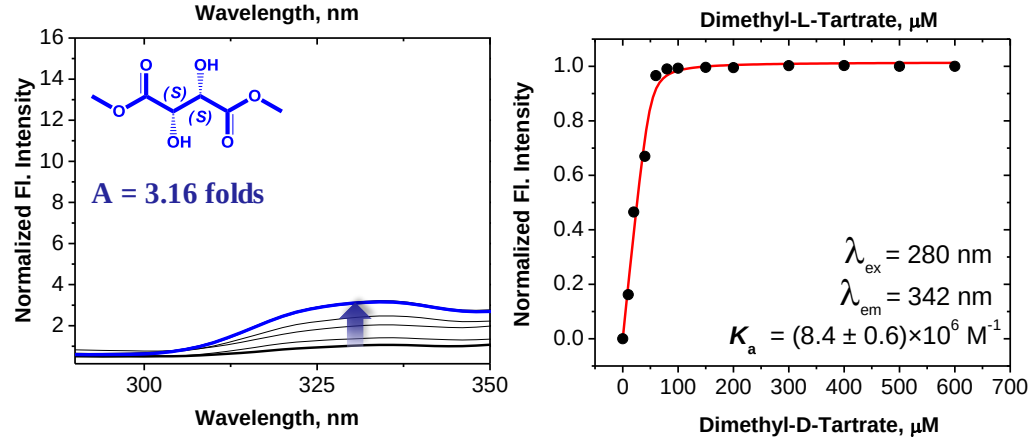

Normalized Fl. Intensity
Wavelength, nm
A = 5.91 folds
Normalized Fl. Intensity
Diethyl-D-Tartrate, μM
λex = 280 nm
λem = 342 nm
Ka = (3.6 ± 0.6)×10^7 M^-1

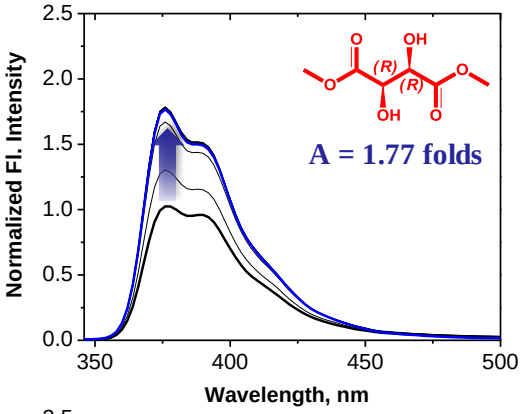

Normalized Fl. Intensity
Wavelength, nm
A = 2.10 folds
Normalized Fl. Intensity
Diethyl-L-Tartrate, μM
λex = 335 nm
λem = 376 nm
Ka = (3.7 ± 0.3)×10^7 M^-1

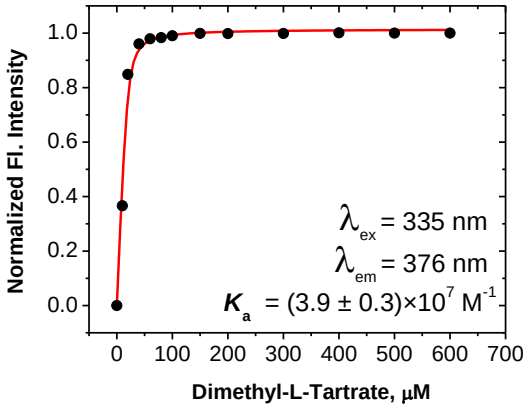

Normalized Fl. Intensity
Wavelength, nm
A = 1.83 folds
Normalized Fl. Intensity
Diethyl-D-Tartrate, μM
λex = 335 nm
λem = 376 nm
Ka = (3.9 ± 0.3)×10^7 M^-1

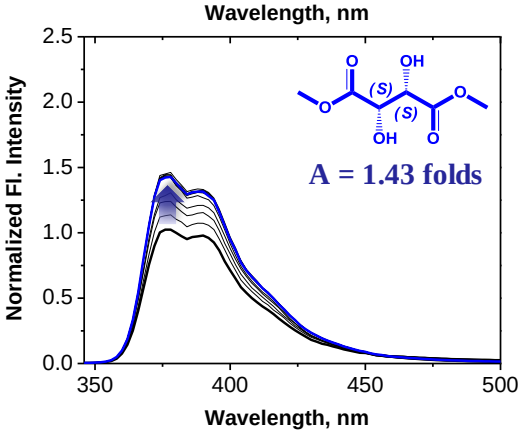

Normalized Fl. Intensity
Diethyl Tartrate, μM
λex = 280 nm
λem = 342 nm
λex = 335 nm
λem = 376 nm

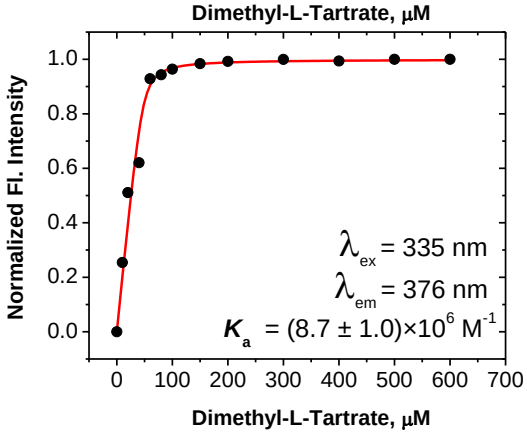

A = 13.1 folds
Wavelength, nm
Dimethyl-L-Tartrate, μM
λex = 280 nm
λem = 342 nm
Ka = (3.0 ± 0.3)×10^7 M^-1

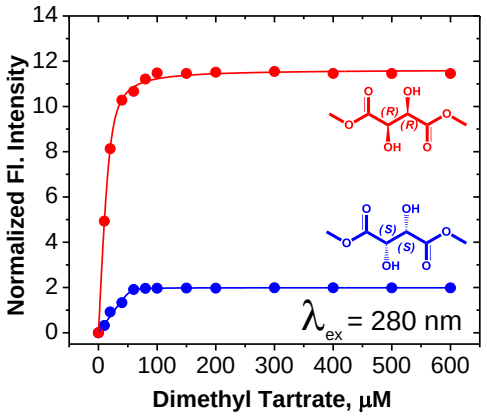

A = 3.16 folds
Wavelength, nm
Dimethyl-D-Tartrate, μM
λex = 280 nm
λem = 342 nm
Ka = (8.4 ± 0.6)×10^6 M^-1

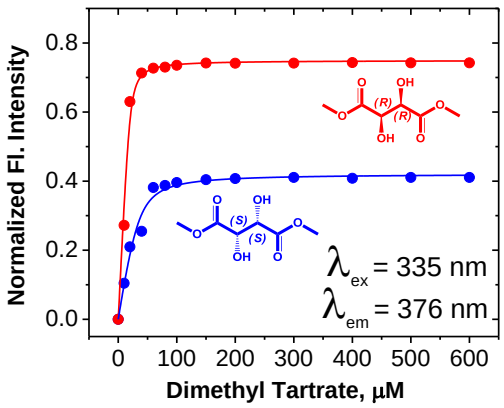

Normalized Fl. Intensity
Wavelength, nm
A = 1.77 folds

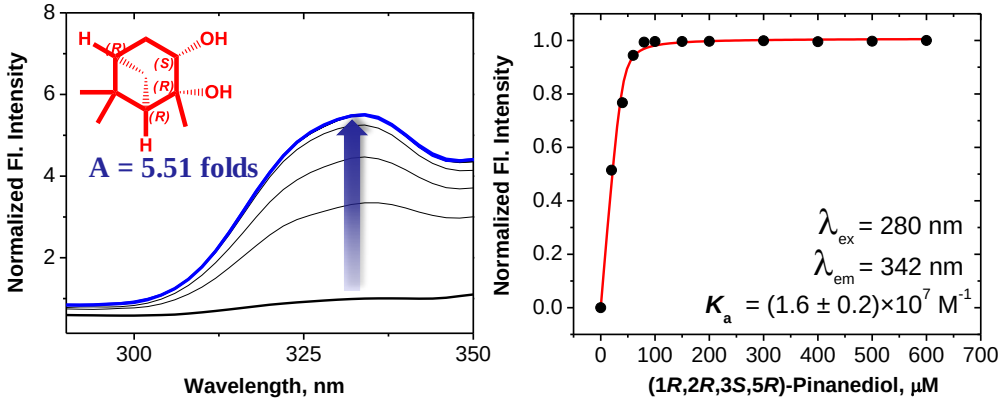

Normalized Fl. Intensity
Dimethyl-L-Tartrate, μM
λex = 335 nm
λem = 376 nm
Ka = (3.9 ± 0.3)×10^7 M^-1

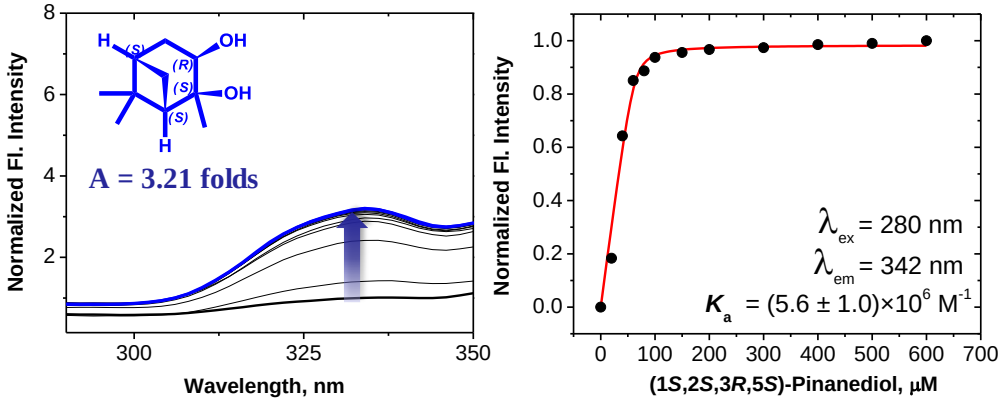

Normalized Fl. Intensity
Wavelength, nm
A = 1.43 folds

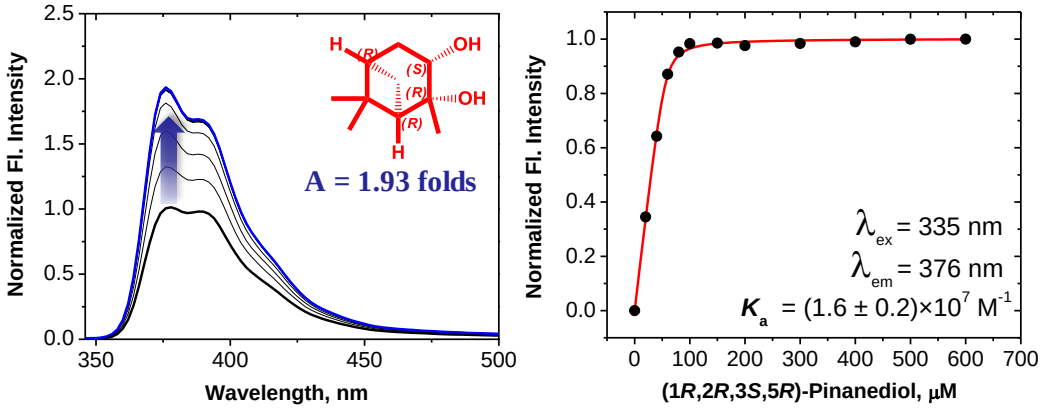

Normalized Fl. Intensity
Dimethyl-L-Tartrate, μM
λex = 335 nm
λem = 376 nm
Ka = (8.7 ± 1.0)×10^6 M^-1

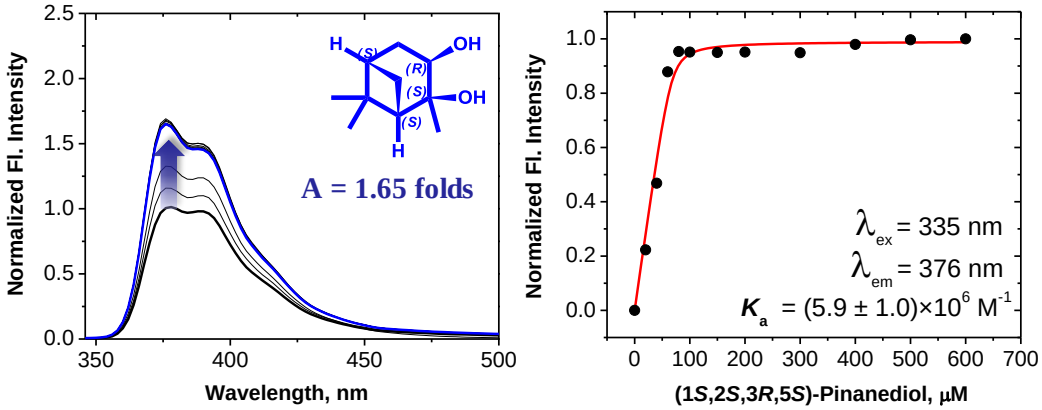

Normalized Fl. Intensity
Dimethyl Tartrate, μM
λex = 280 nm


Normalized Fl. Intensity
Dimethyl Tartrate, μM
λex = 335 nm
λem = 376 nm


Normalized Fl. Intensity
Wavelength, nm
A = 5.51 folds
Normalized Fl. Intensity
(1R,2R,3S,5R)-Pinanediol, μM
λex = 280 nm
λem = 342 nm
Ka = (1.6 ± 0.2)×10^7 M^-1


Normalized Fl. Intensity
Wavelength, nm
A = 3.21 folds
Normalized Fl. Intensity
(1S,2S,3R,5S)-Pinanediol, μM
λex = 280 nm
λem = 342 nm
Ka = (5.6 ± 1.0)×10^6 M^-1


Normalized Fl. Intensity
Wavelength, nm
A = 1.93 folds
Normalized Fl. Intensity
(1R,2R,3S,5R)-Pinanediol, μM
λex = 335 nm
λem = 376 nm
Ka = (1.6 ± 0.2)×10^7 M^-1


Normalized Fl. Intensity
Wavelength, nm
A = 1.65 folds
Normalized Fl. Intensity
(1S,2S,3R,5S)-Pinanediol, μM
λex = 335 nm
λem = 376 nm
Ka = (5.9 ± 1.0)×10^6 M^-1

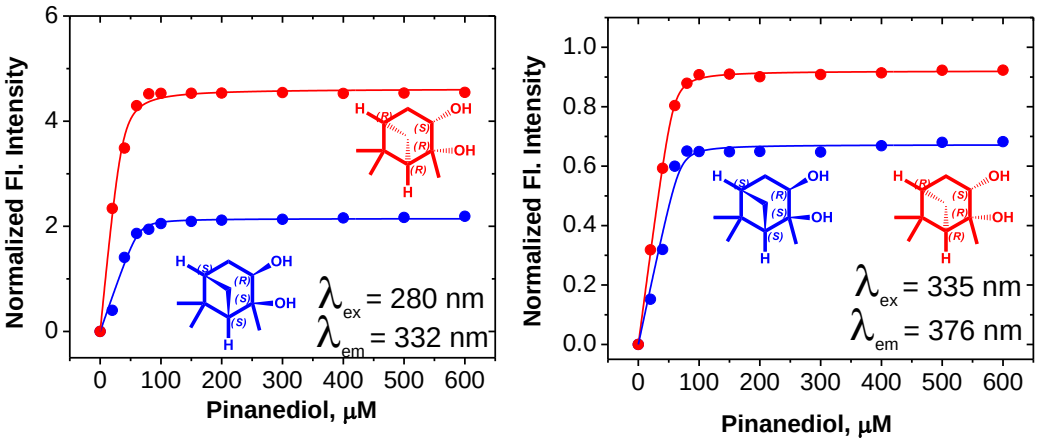
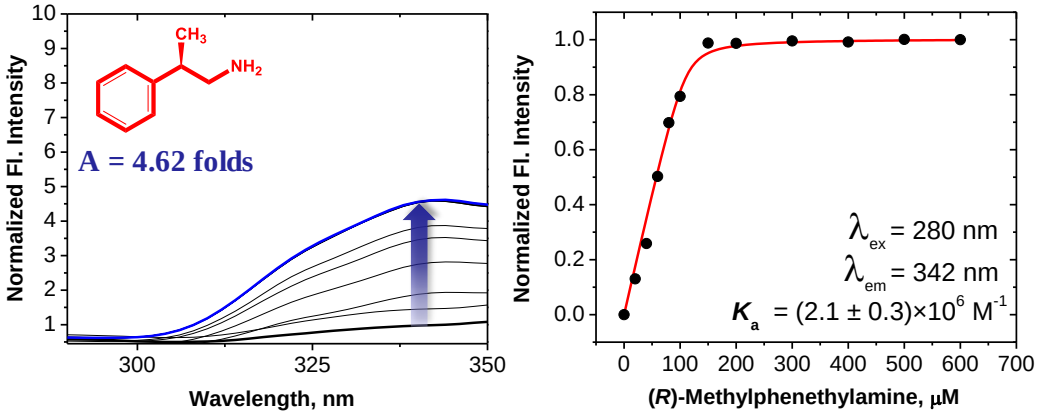
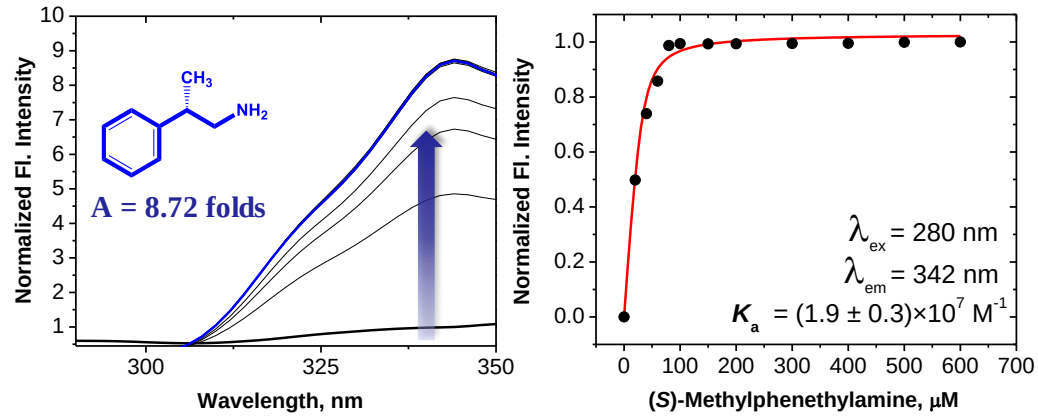
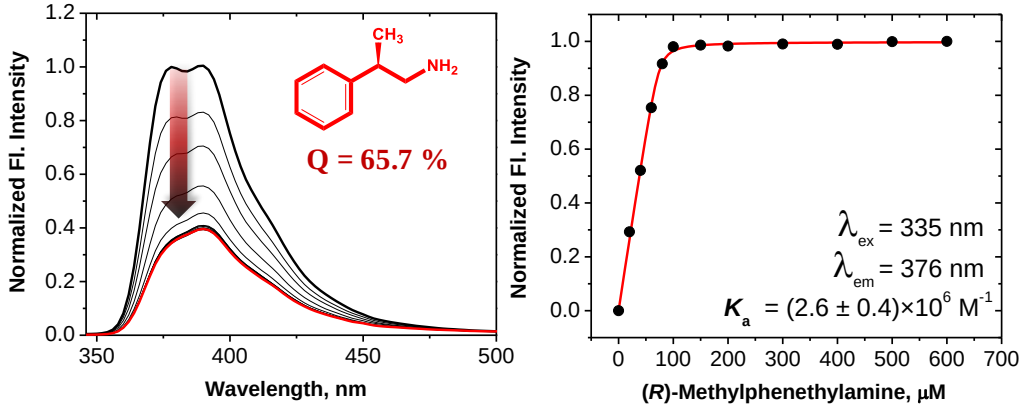


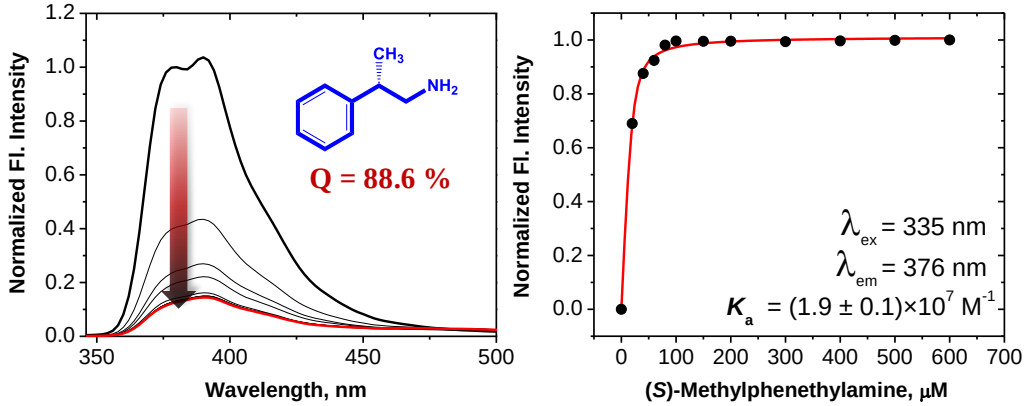
Table S4. The calculated Ka values on the change in fluorescence intensities of the iminoboronate complex formed by FPBA, L-tryptophanol and (*S*)-VAPOL upon addition of selected chiral amines and amino alcohols in acetonitrile.

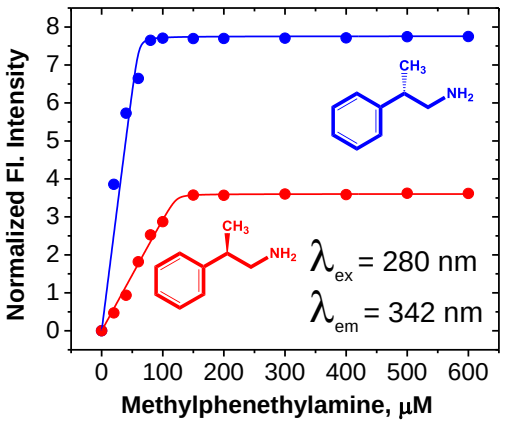
Analytes	K_a ($M^{-1} \times 10^6$) derived from (*S*)-VAPOL	K_a ($M^{-1} \times 10^6$) derived from L-tryptophanol
(*R*)-Methylbenzylamine	15 ± 1.0	4.5 ± 0.5
(*S*)-Methylbenzylamine	20 ± 2.0	3.4 ± 0.5
(*R*)-Methylphenethylamine	2.6 ± 0.4	2.1 ± 0.3
(*S*)-Methylphenethylamine	19 ± 1.0	19 ± 3.0
(*R*)-2-Amino-3-phenyl-1-propanol	7.1 ± 0.7	8.3 ± 1.3
(*S*)-2-Amino-3-phenyl-1-propanol	4.1 ± 0.3	4.3 ± 0.5
(1*R*,2*S*)-1-Amino-2-indanol	1.0 ± 0.1	2.8 ± 0.3
(1*S*,2*R*)-1-Amino-2-indanol	41 ± 3.0	3.3 ± 0.3
(1*R*,2*R*)-2-Amino-1,2-diphenylethanol	8.7 ± 0.6	7.4 ± 0.7
(1*S*,2*S*)-2-Amino-1,2-diphenylethanol	27 ± 2.0	30 ± 5.0
(1*R*,2*S*)-2-Amino-1,2-diphenylethanol	5.7 ± 0.5	3.2 ± 0.4
(1*S*,2*R*)-2-Amino-1,2-diphenylethanol	2.7 ± 0.1	2.9 ± 0.5

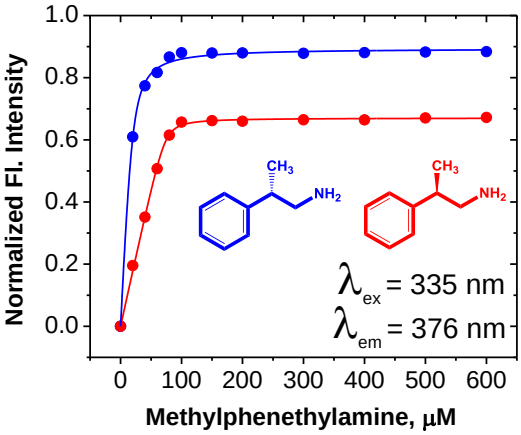

A = 4.62 folds
Normalized Fl. Intensity
Wavelength, nm
λex = 280 nm
λem = 342 nm
Ka = (2.1 ± 0.3)×10^6 M^-1
(R)-Methylphenethylamine, μM

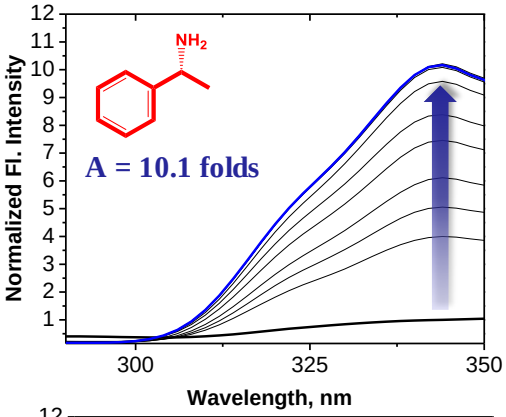

A = 8.72 folds
Normalized Fl. Intensity
Wavelength, nm
λex = 280 nm
λem = 342 nm
Ka = (1.9 ± 0.3)×10^7 M^-1
(S)-Methylphenethylamine, μM

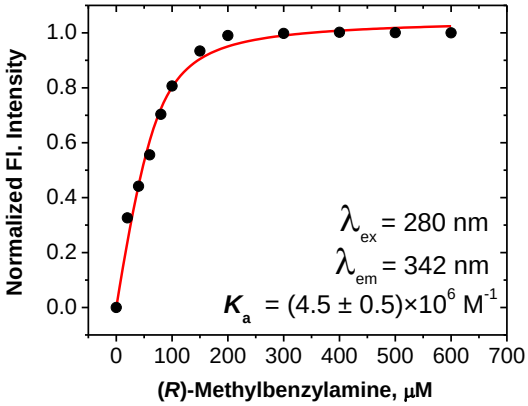

Q = 65.7 %
Normalized Fl. Intensity
Wavelength, nm
λex = 335 nm
λem = 376 nm
Ka = (2.6 ± 0.4)×10^6 M^-1
(R)-Methylphenethylamine, μM

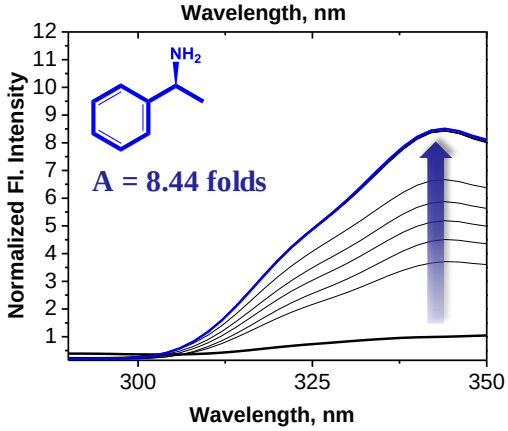

Q = 88.6 %
Normalized Fl. Intensity
Wavelength, nm
λex = 335 nm
λem = 376 nm
Ka = (1.9 ± 0.1)×10^7 M^-1
(S)-Methylphenethylamine, μM

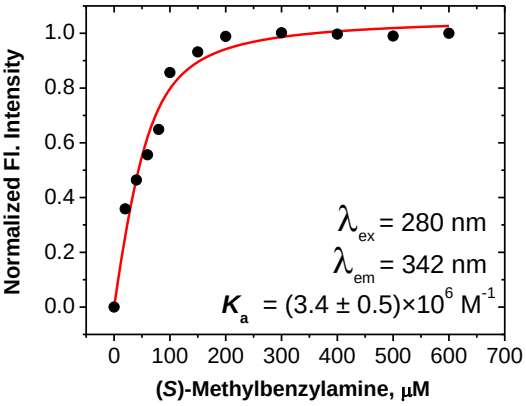

Normalized Fl. Intensity
Methylphenethylamine, μM
λex = 280 nm
λem = 342 nm

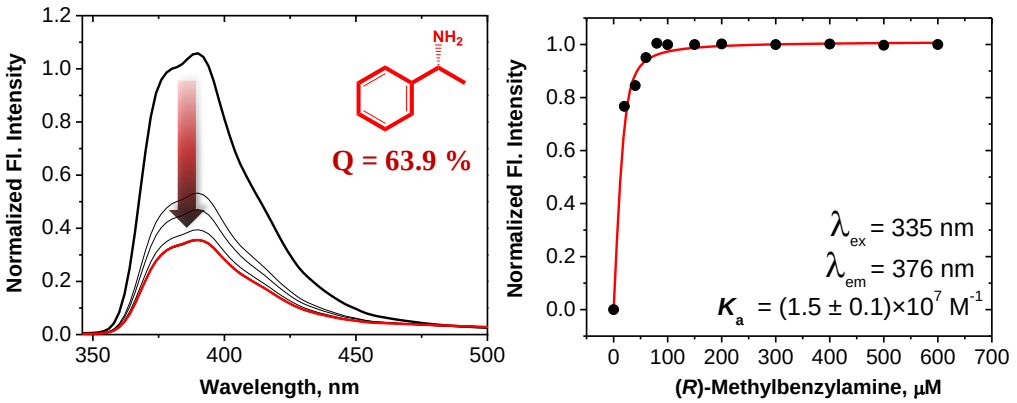

Normalized Fl. Intensity
Methylphenethylamine, μM
λex = 335 nm
λem = 376 nm

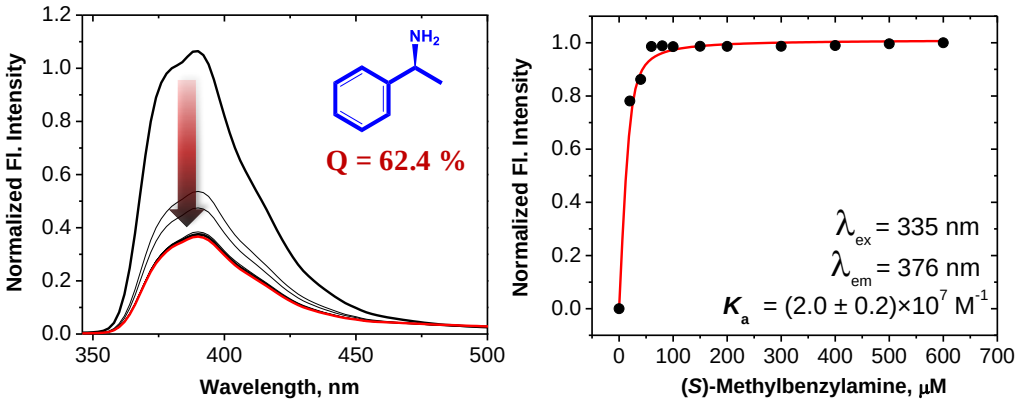

Normalized Fl. Intensity
Wavelength, nm
A = 10.1 folds

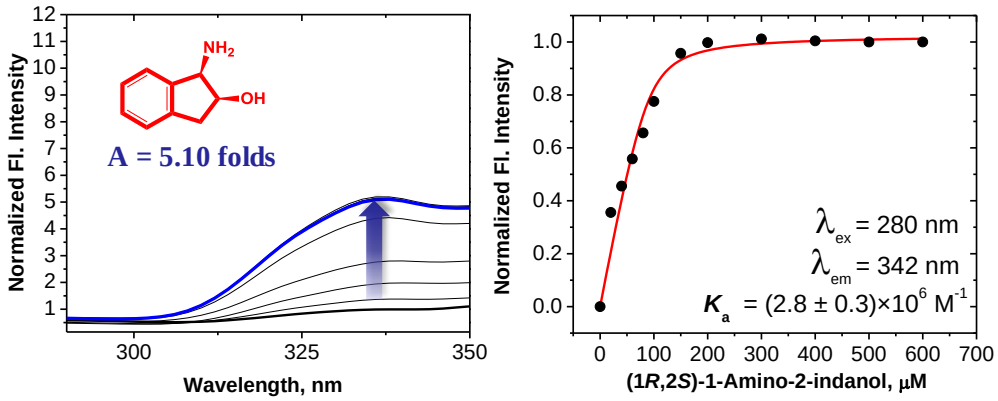

Normalized Fl. Intensity
(R)-Methylbenzylamine, μM
λex = 280 nm
λem = 342 nm
Ka = (4.5 ± 0.5)×10^6 M^-1

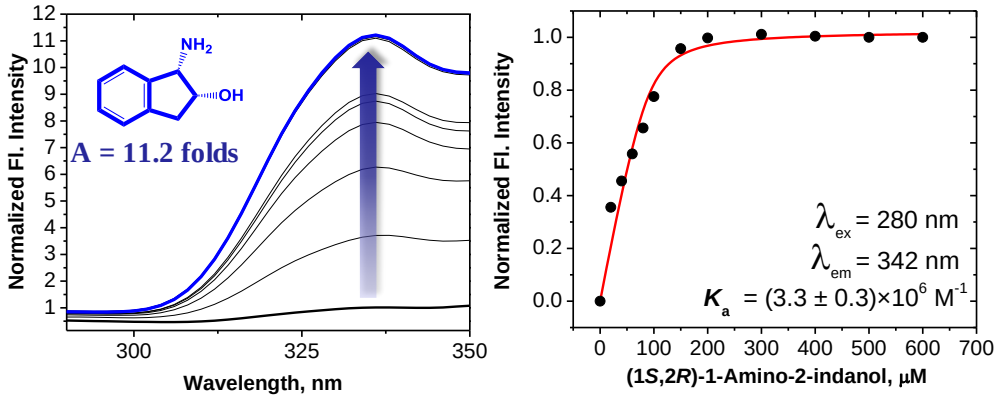

Normalized Fl. Intensity
Wavelength, nm
A = 8.44 folds

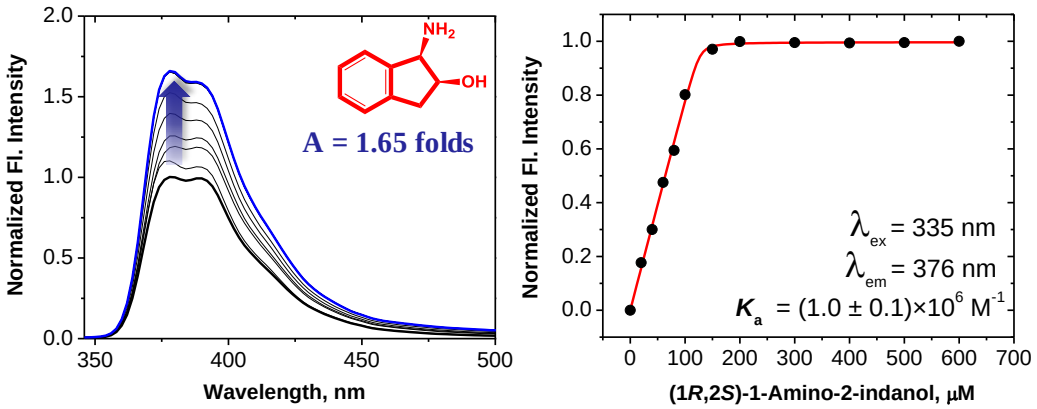

Normalized Fl. Intensity
(S)-Methylbenzylamine, μM
λex = 280 nm
λem = 342 nm
Ka = (3.4 ± 0.5)×10^6 M^-1

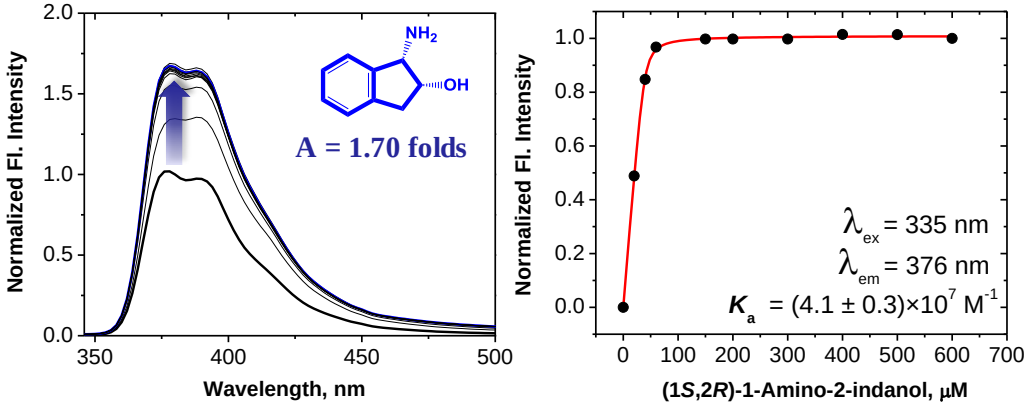

Normalized Fl. Intensity
Wavelength, nm
NH2
Q = 63.9 %
Normalized Fl. Intensity
(R)-Methylbenzylamine, μM
λex = 335 nm
λem = 376 nm
Ka = (1.5 ± 0.1)×10^7 M^-1

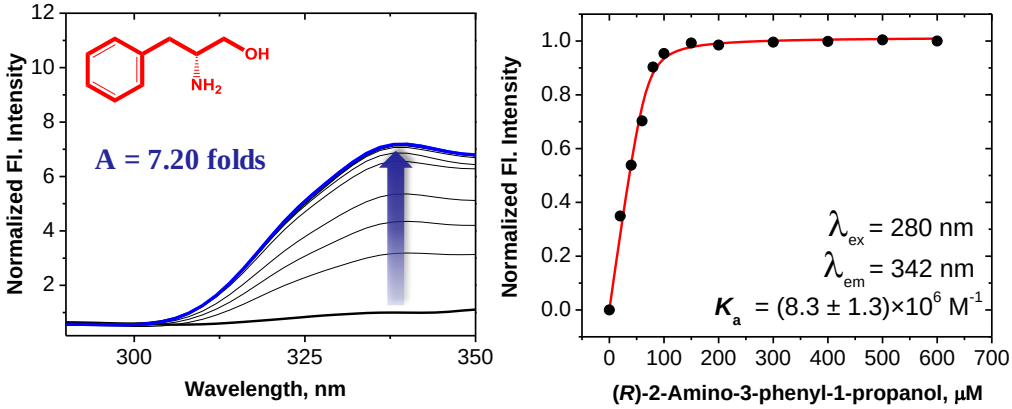

Normalized Fl. Intensity
Wavelength, nm
NH2
Q = 62.4 %
Normalized Fl. Intensity
(S)-Methylbenzylamine, μM
λex = 335 nm
λem = 376 nm
Ka = (2.0 ± 0.2)×10^7 M^-1

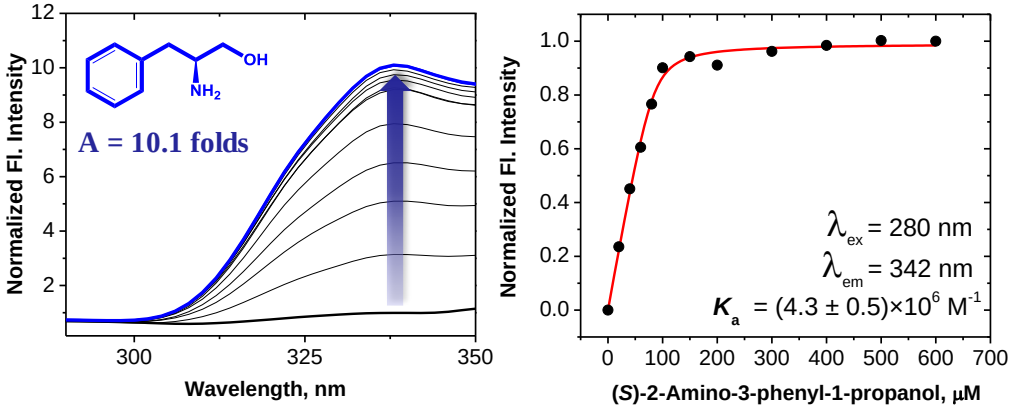

Normalized Fl. Intensity
Wavelength, nm
NH2
OH
A = 5.10 folds
Normalized Fl. Intensity
(1R,2S)-1-Amino-2-indanol, μM
λex = 280 nm
λem = 342 nm
Ka = (2.8 ± 0.3)×10^6 M^-1

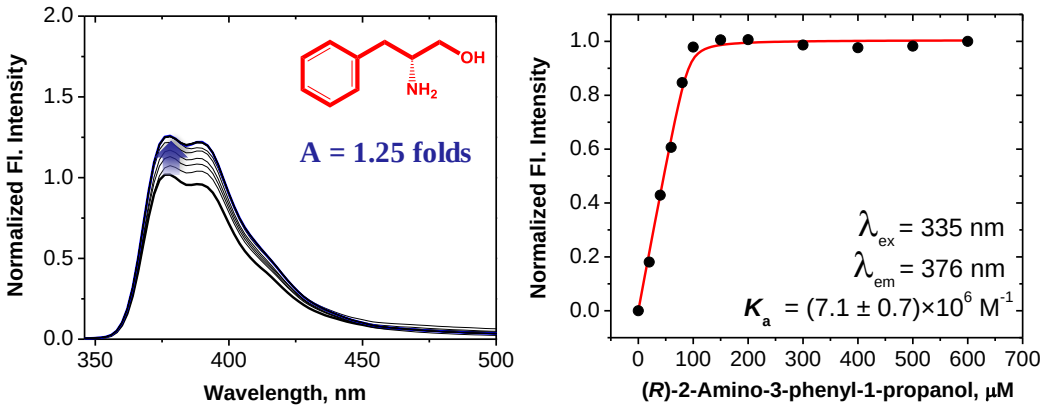

Normalized Fl. Intensity
Wavelength, nm
NH2
OH
A = 11.2 folds
Normalized Fl. Intensity
(1S,2R)-1-Amino-2-indanol, μM
λex = 280 nm
λem = 342 nm
Ka = (3.3 ± 0.3)×10^6 M^-1

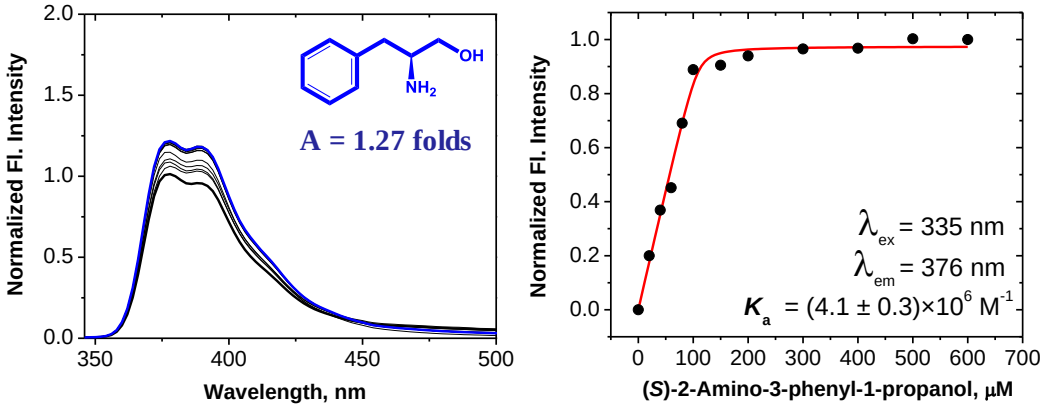

NH2
OH
A = 1.65 folds
Normalized Fl. Intensity
Wavelength, nm
λex = 335 nm
λem = 376 nm
Ka = (1.0 ± 0.1)×10^6 M^-1
(1R,2S)-1-Amino-2-indanol, μM

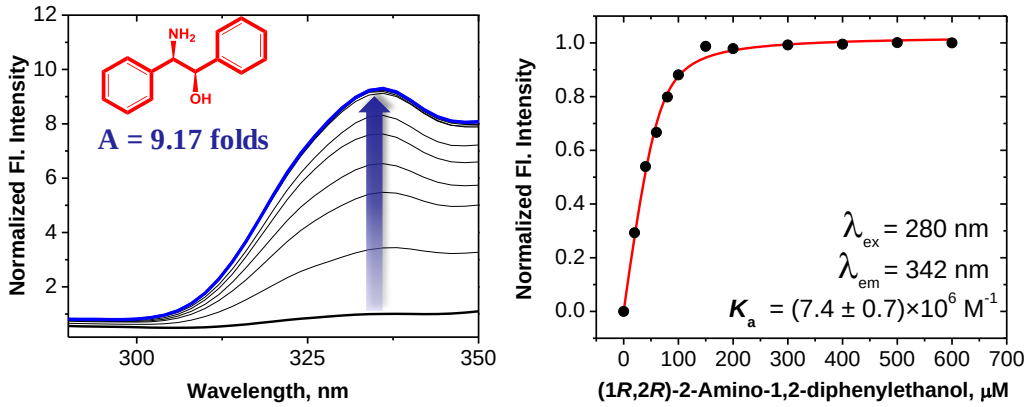

NH2
OH
A = 1.70 folds
Normalized Fl. Intensity
Wavelength, nm
λex = 335 nm
λem = 376 nm
Ka = (4.1 ± 0.3)×10^7 M^-1
(1S,2R)-1-Amino-2-indanol, μM

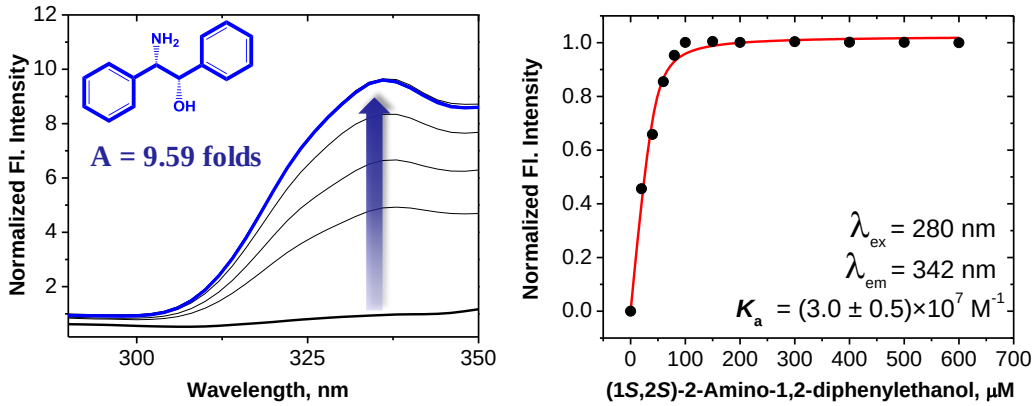

OH
NH2
A = 7.20 folds
Normalized Fl. Intensity
Wavelength, nm
λex = 280 nm
λem = 342 nm
Ka = (8.3 ± 1.3)×10^6 M^-1
(R)-2-Amino-3-phenyl-1-propanol, μM

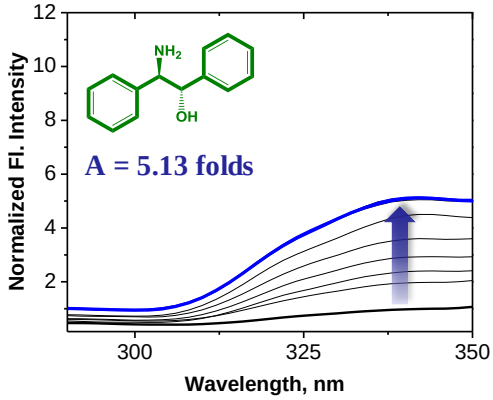

OH
NH2
A = 10.1 folds
Normalized Fl. Intensity
Wavelength, nm
λex = 280 nm
λem = 342 nm
Ka = (4.3 ± 0.5)×10^6 M^-1
(S)-2-Amino-3-phenyl-1-propanol, μM

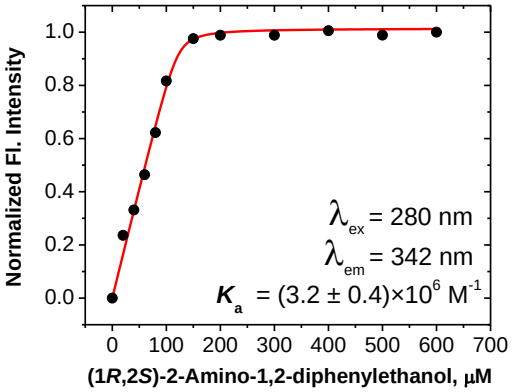

Normalized Fl. Intensity
Wavelength, nm
A = 1.25 folds
OH
NH2
λex = 335 nm
λem = 376 nm
Ka = (7.1 ± 0.7)×10^6 M^-1
(R)-2-Amino-3-phenyl-1-propanol, μM

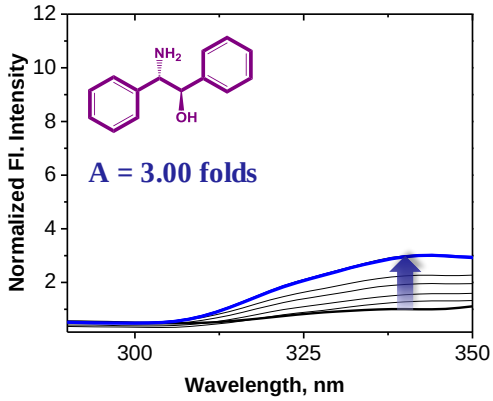

Normalized Fl. Intensity
Wavelength, nm
A = 1.27 folds
OH
NH2
λex = 335 nm
λem = 376 nm
Ka = (4.1 ± 0.3)×10^6 M^-1
(S)-2-Amino-3-phenyl-1-propanol, μM

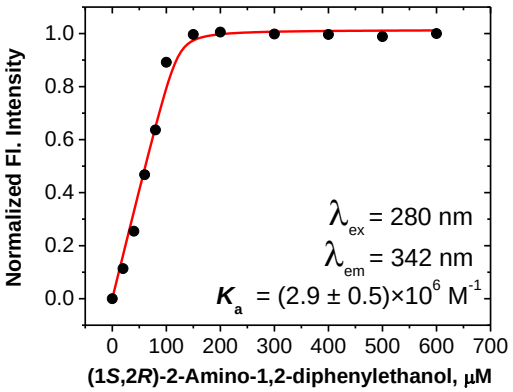

Normalized Fl. Intensity
Wavelength, nm
A = 9.17 folds
NH2
OH
λex = 280 nm
λem = 342 nm
Ka = (7.4 ± 0.7)×10^6 M^-1
(1R,2R)-2-Amino-1,2-diphenylethanol, μM

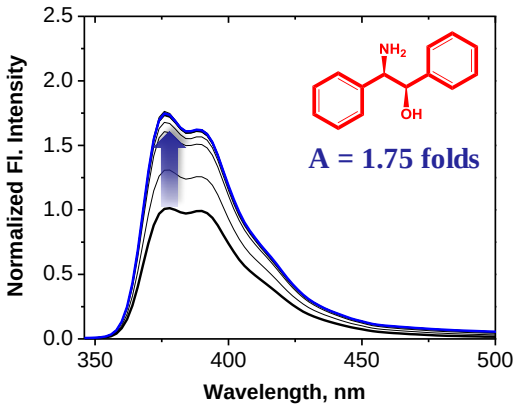

Normalized Fl. Intensity
Wavelength, nm
A = 9.59 folds
NH2
OH
λex = 280 nm
λem = 342 nm
Ka = (3.0 ± 0.5)×10^7 M^-1
(1S,2S)-2-Amino-1,2-diphenylethanol, μM

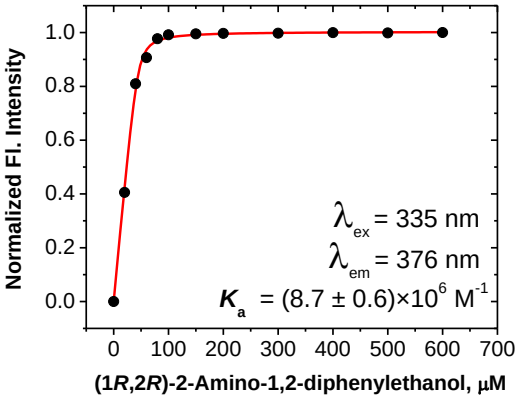

Normalized Fl. Intensity
Wavelength, nm
A = 5.13 folds

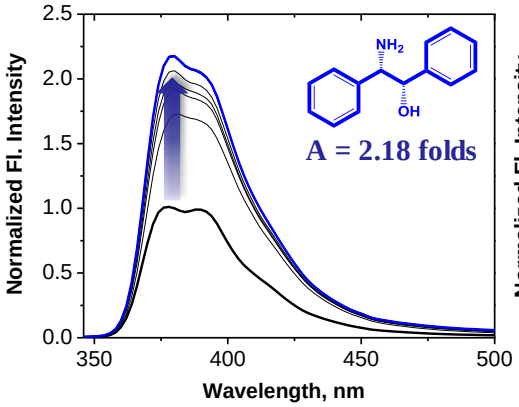

Normalized Fl. Intensity
(1R,2S)-2-Amino-1,2-diphenylethanol, μM
λex = 280 nm
λem = 342 nm
Ka = (3.2 ± 0.4)×10^6 M^-1

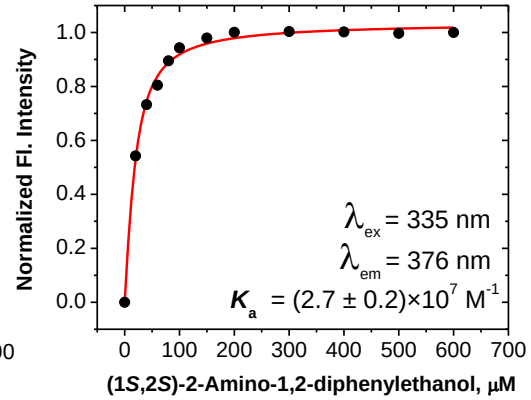

Normalized Fl. Intensity
Wavelength, nm
A = 3.00 folds

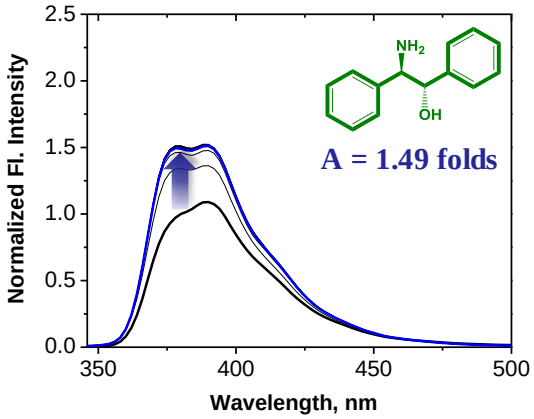

Normalized Fl. Intensity
(1S,2R)-2-Amino-1,2-diphenylethanol, μM
λex = 280 nm
λem = 342 nm
Ka = (2.9 ± 0.5)×10^6 M^-1

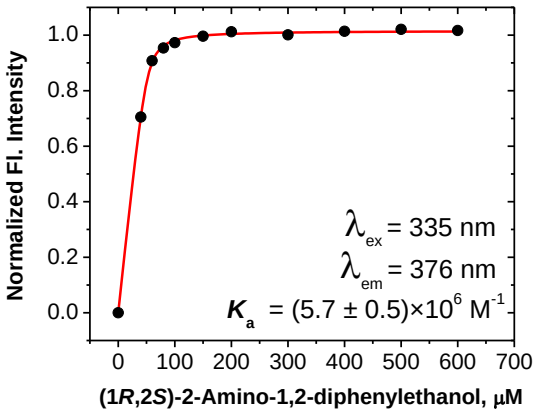

Normalized Fl. Intensity
Wavelength, nm
A = 1.75 folds

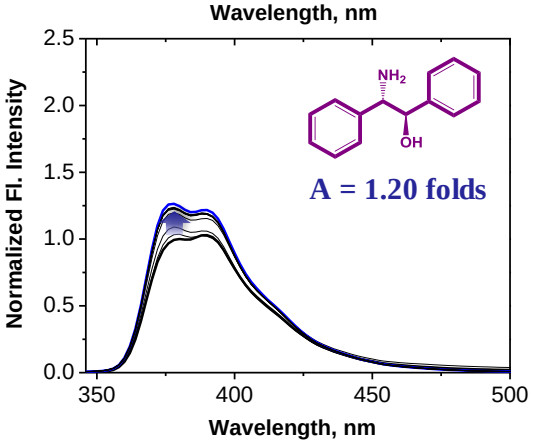

Normalized Fl. Intensity
(1R,2R)-2-Amino-1,2-diphenylethanol, μM
λex = 335 nm
λem = 376 nm
Ka = (8.7 ± 0.6)×10^6 M^-1

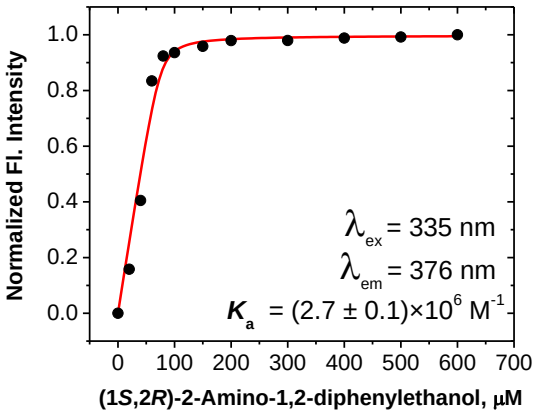

Normalized Fl. Intensity
Wavelength, nm
A = 2.18 folds

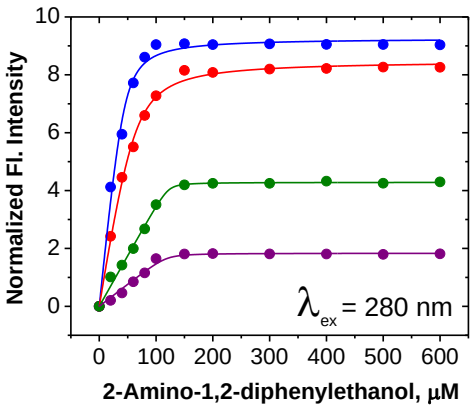

Normalized Fl. Intensity
(1S,2S)-2-Amino-1,2-diphenylethanol, μM
λex = 335 nm
λem = 376 nm
Ka = (2.7 ± 0.2)×10^7 M^-1


Normalized Fl. Intensity
Wavelength, nm
A = 1.49 folds
NH2
OH


Normalized Fl. Intensity
(1R,2S)-2-Amino-1,2-diphenylethanol, μM
λex = 335 nm
λem = 376 nm
Ka = (5.7 ± 0.5)×10^6 M^-1


Normalized Fl. Intensity
Wavelength, nm
A = 1.20 folds
NH2
OH


Normalized Fl. Intensity
(1S,2R)-2-Amino-1,2-diphenylethanol, μM
λex = 335 nm
λem = 376 nm
Ka = (2.7 ± 0.1)×10^6 M^-1


Normalized Fl. Intensity
2-Amino-1,2-diphenylethanol, μM
λex = 280 nm

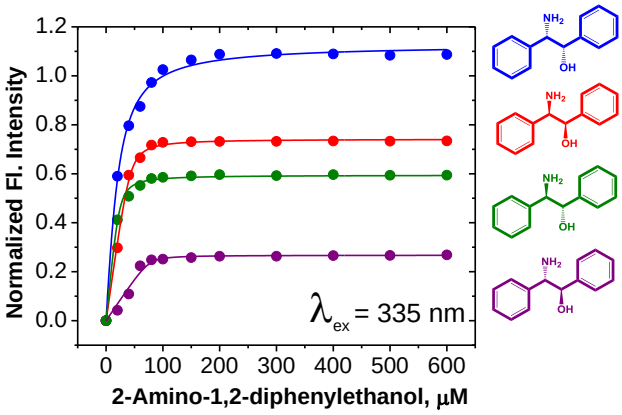
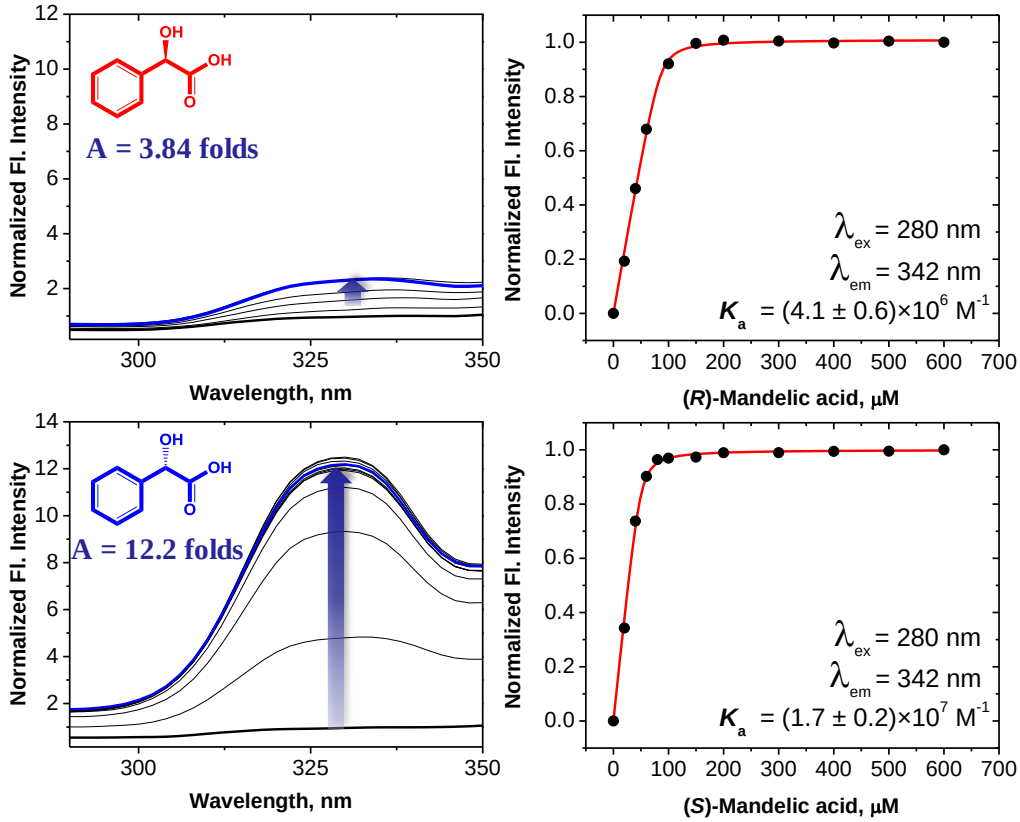
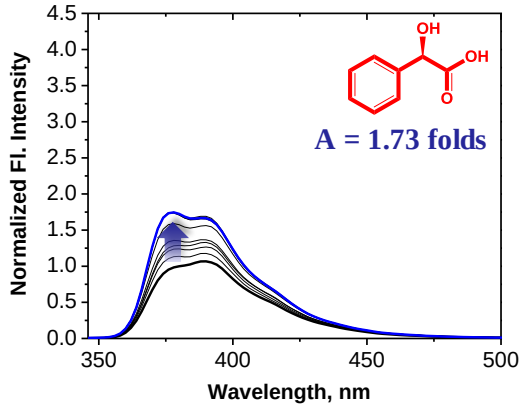
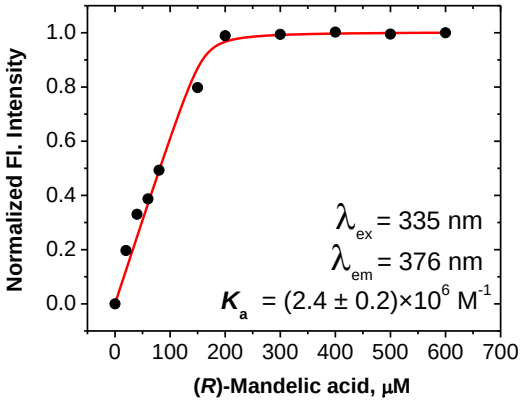

Normalized Fl. Intensity
2-Amino-1,2-diphenylethanol, μM
λex = 335 nm
NH2
OH

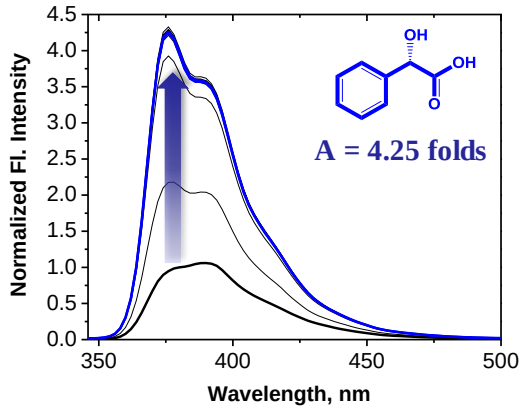
Table S5. The calculated Ka values on the change in fluorescence intensities of the iminoboronate complex formed by FPBA, L-tryptophanol and (*S*)-VAPOL upon addition of selected chiral hydroxy acids in acetonitrile.

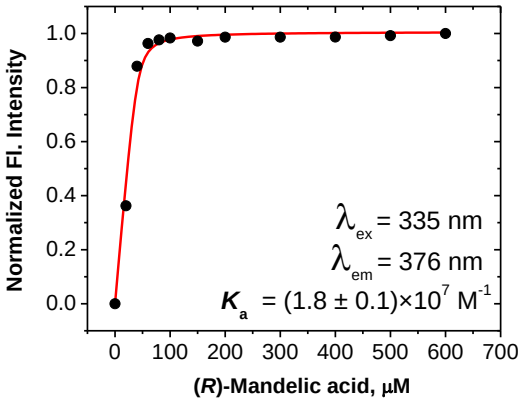
Analytes	K_a ($M^{-1} \times 10^6$) derived from (*S*)-VAPOL	K_a ($M^{-1} \times 10^6$) derived from L-tryptophanol
(*S*)-Mandelic acid	18 ± 1.0	17 ± 2.0
(*R*)-Mandelic acid	2.4 ± 0.2	4.1 ± 0.6
L-(-)-3-Phenyllactic acid	19 ± 2.0	19 ± 2.0
D-(+)-3-Phenyllactic acid	14 ± 1.0	11 ± 1.0
L-(+)-Lactic acid	8.7 ± 0.6	7.9 ± 0.3
D-(−)-Lactic acid	16 ± 1.0	17 ± 2.0
(2*R*)-2-Hydroxy-3-methylbutanoic acid	9.6 ± 1.1	9.5 ± 1.2
(2*S*)-2-Hydroxy-3-methylbutanoic acid	7.0 ± 1.0	7.2 ± 0.9

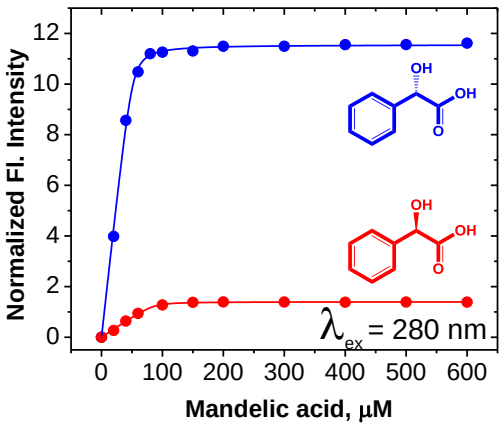


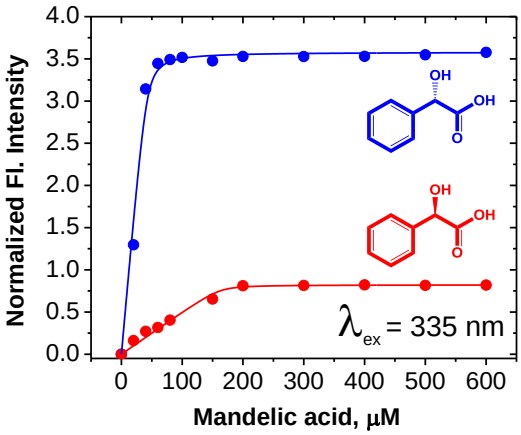

Normalized Fl. Intensity
Wavelength, nm
A = 1.73 folds
OH
OH
O

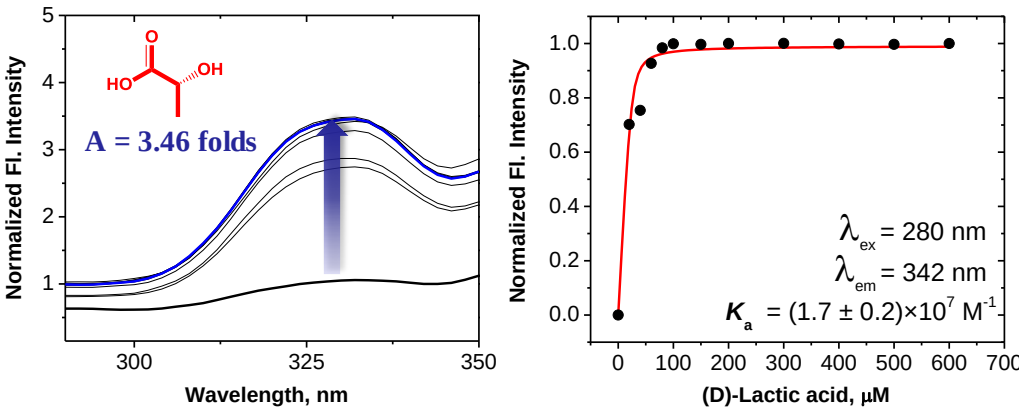

Normalized Fl. Intensity
(R)-Mandelic acid, μM
λex = 335 nm
λem = 376 nm
Ka = (2.4 ± 0.2)×10^6 M^-1

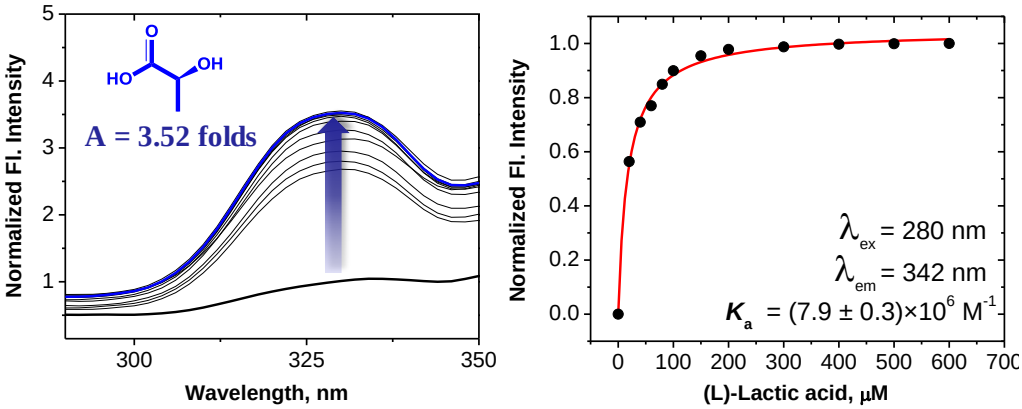

Normalized Fl. Intensity
Wavelength, nm
A = 4.25 folds
OH
OH
O

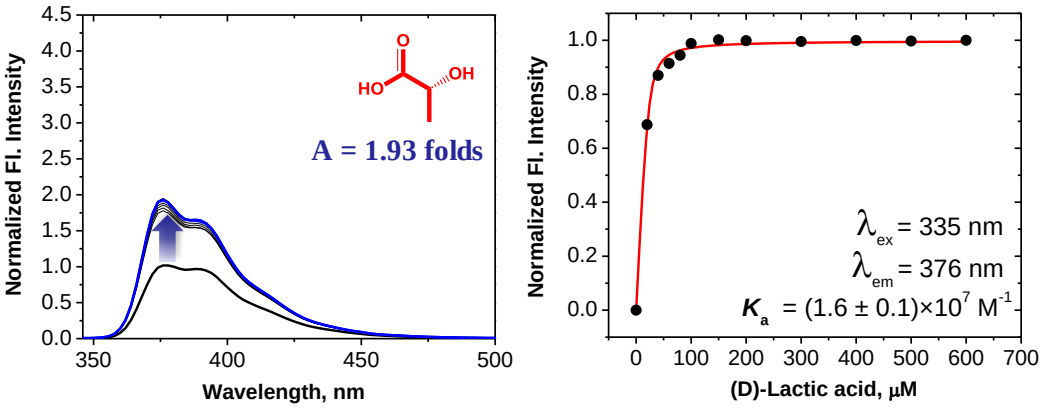

Normalized Fl. Intensity
(R)-Mandelic acid, μM
λex = 335 nm
λem = 376 nm
Ka = (1.8 ± 0.1)×10^7 M^-1

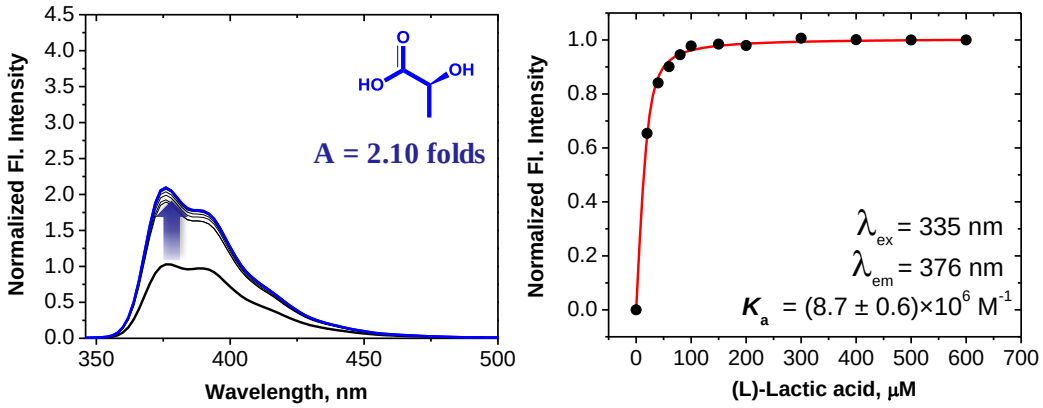

Normalized Fl. Intensity
Mandelic acid, μM
λex = 280 nm
OH
OH
O

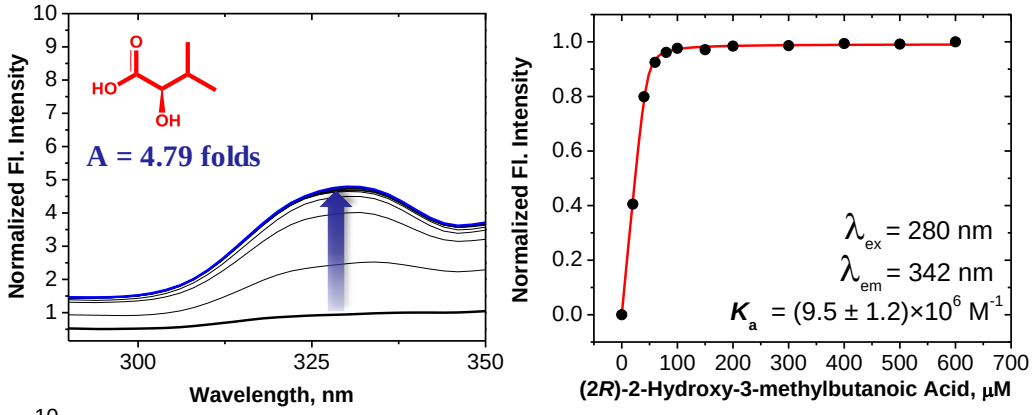

Normalized Fl. Intensity
Mandelic acid, μM
λex = 335 nm
OH
OH
O

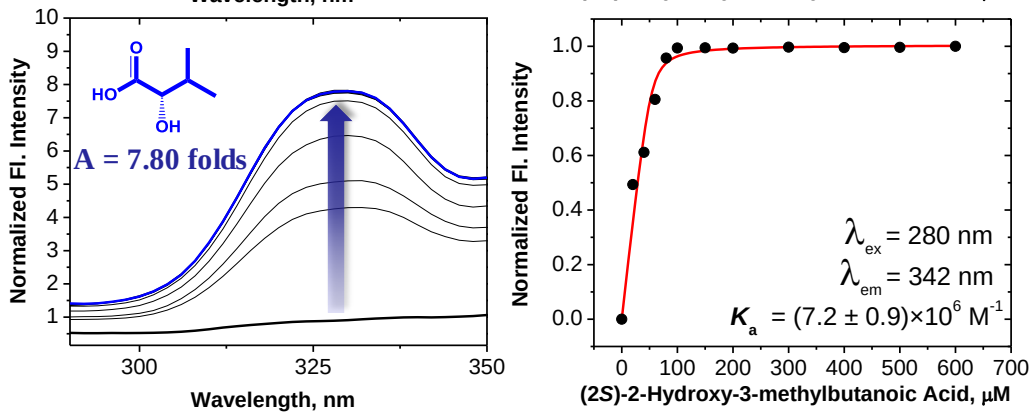

A = 3.46 folds
Normalized FI. Intensity
Wavelength, nm
λex = 280 nm
λem = 342 nm
Ka = (1.7 ± 0.2)×10^7 M^-1
(D)-Lactic acid, μM

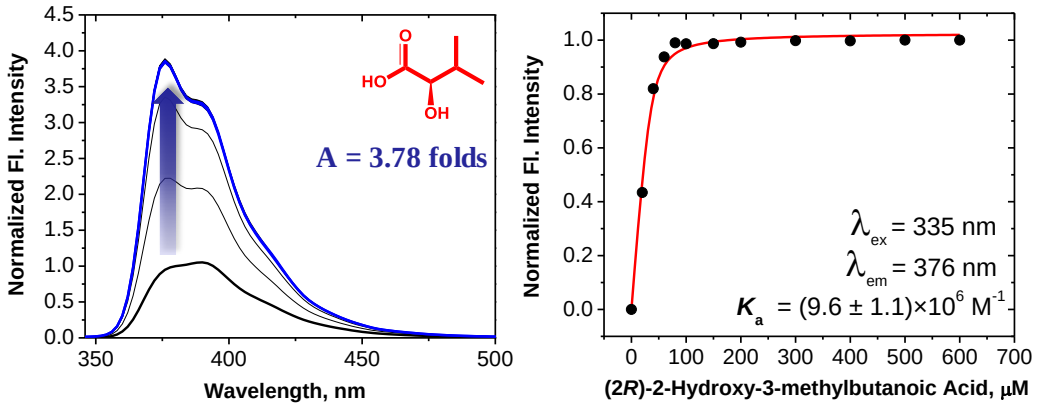

A = 3.52 folds
Normalized FI. Intensity
Wavelength, nm
λex = 280 nm
λem = 342 nm
Ka = (7.9 ± 0.3)×10^6 M^-1
(L)-Lactic acid, μM

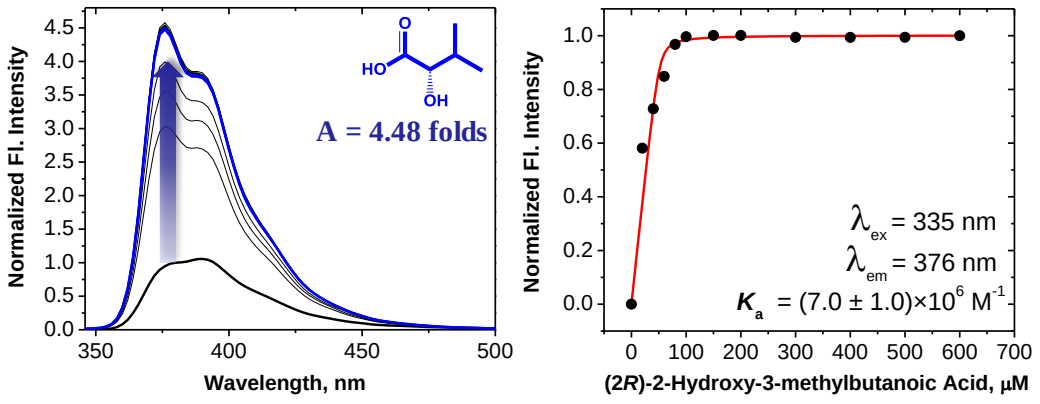

A = 1.93 folds
Normalized FI. Intensity
Wavelength, nm
λex = 335 nm
λem = 376 nm
Ka = (1.6 ± 0.1)×10^7 M^-1
(D)-Lactic acid, μM

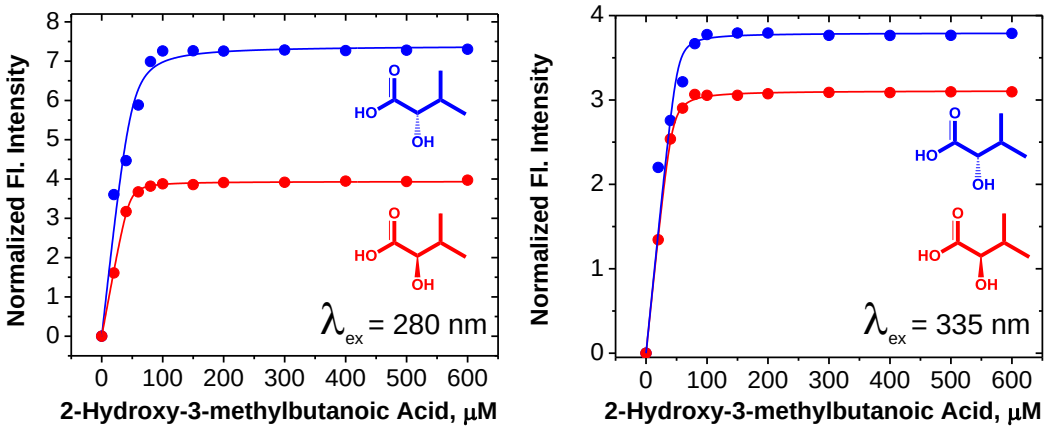

A = 2.10 folds
Normalized FI. Intensity
Wavelength, nm
λex = 335 nm
λem = 376 nm
Ka = (8.7 ± 0.6)×10^6 M^-1
(L)-Lactic acid, μM

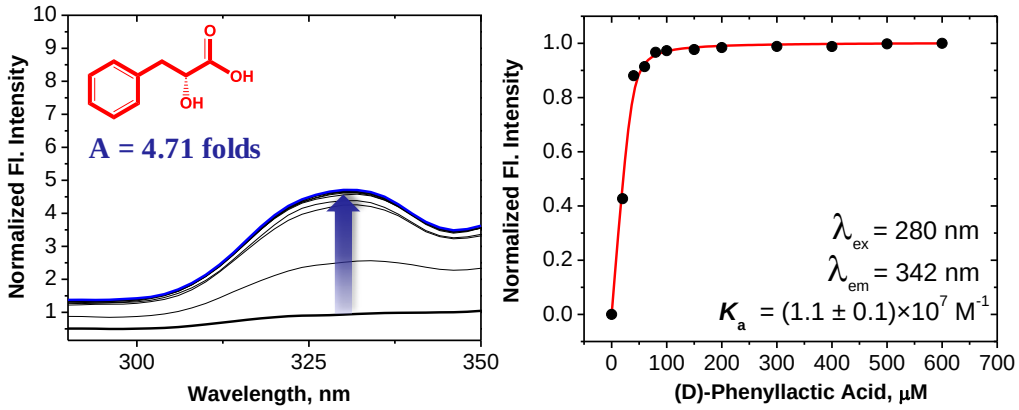

Normalized Fl. Intensity
Wavelength, nm
A = 4.79 folds
Normalized Fl. Intensity
(2R)-2-Hydroxy-3-methylbutanoic Acid, μM
λex = 280 nm
λem = 342 nm
Ka = (9.5 ± 1.2)×10^6 M^-1

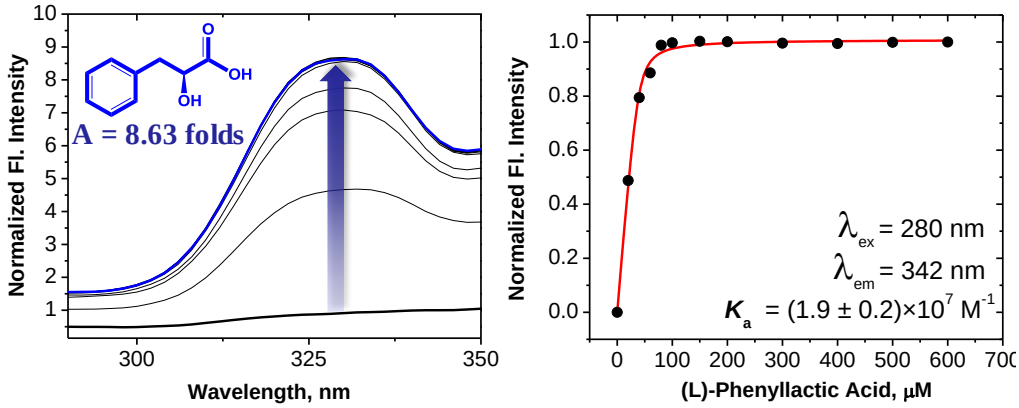

Normalized Fl. Intensity
Wavelength, nm
A = 7.80 folds
Normalized Fl. Intensity
(2S)-2-Hydroxy-3-methylbutanoic Acid, μM
λex = 280 nm
λem = 342 nm
Ka = (7.2 ± 0.9)×10^6 M^-1

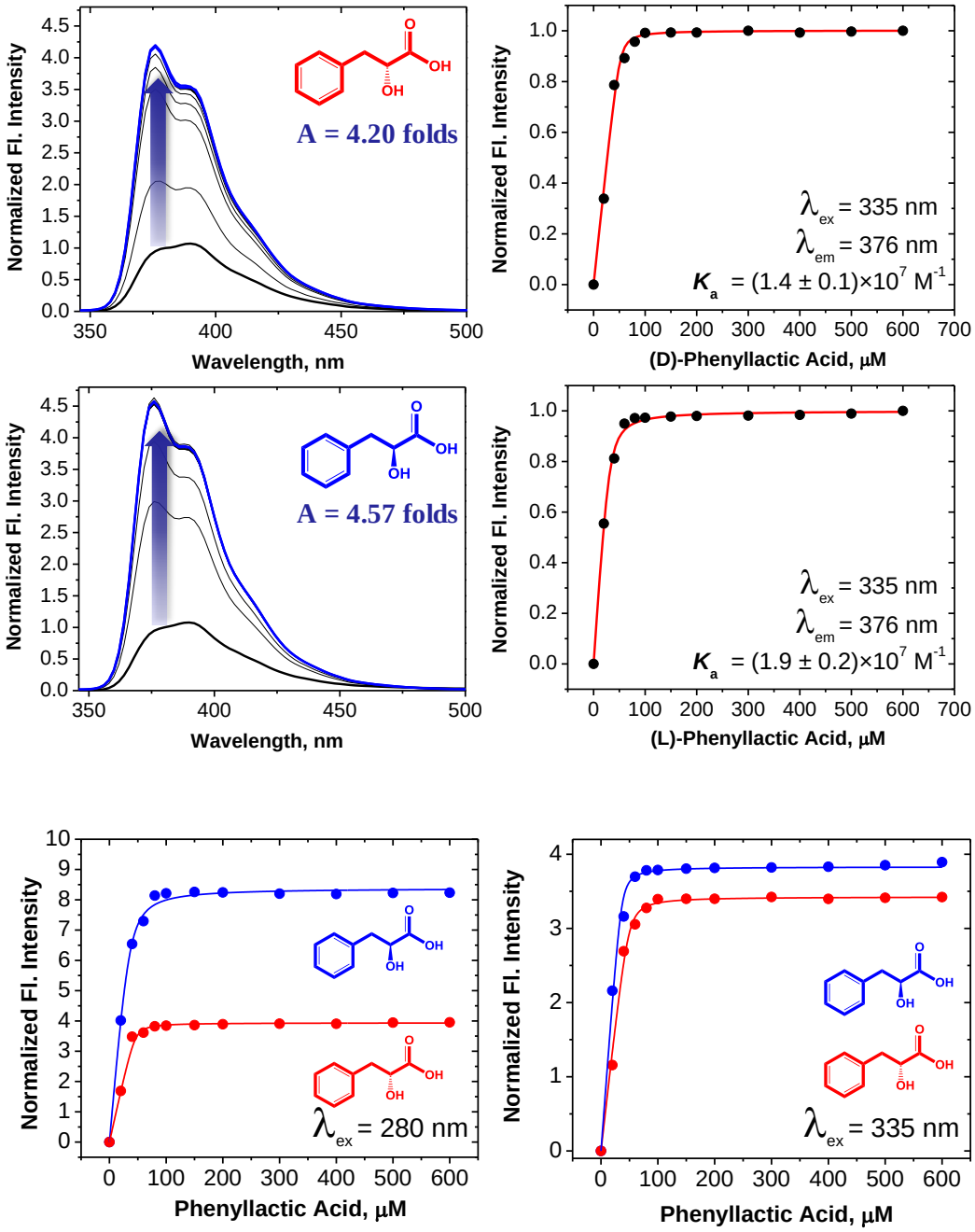

Normalized Fl. Intensity
Wavelength, nm
A = 3.78 folds
Normalized Fl. Intensity
(2R)-2-Hydroxy-3-methylbutanoic Acid, μM
λex = 335 nm
λem = 376 nm
Ka = (9.6 ± 1.1)×10^6 M^-1

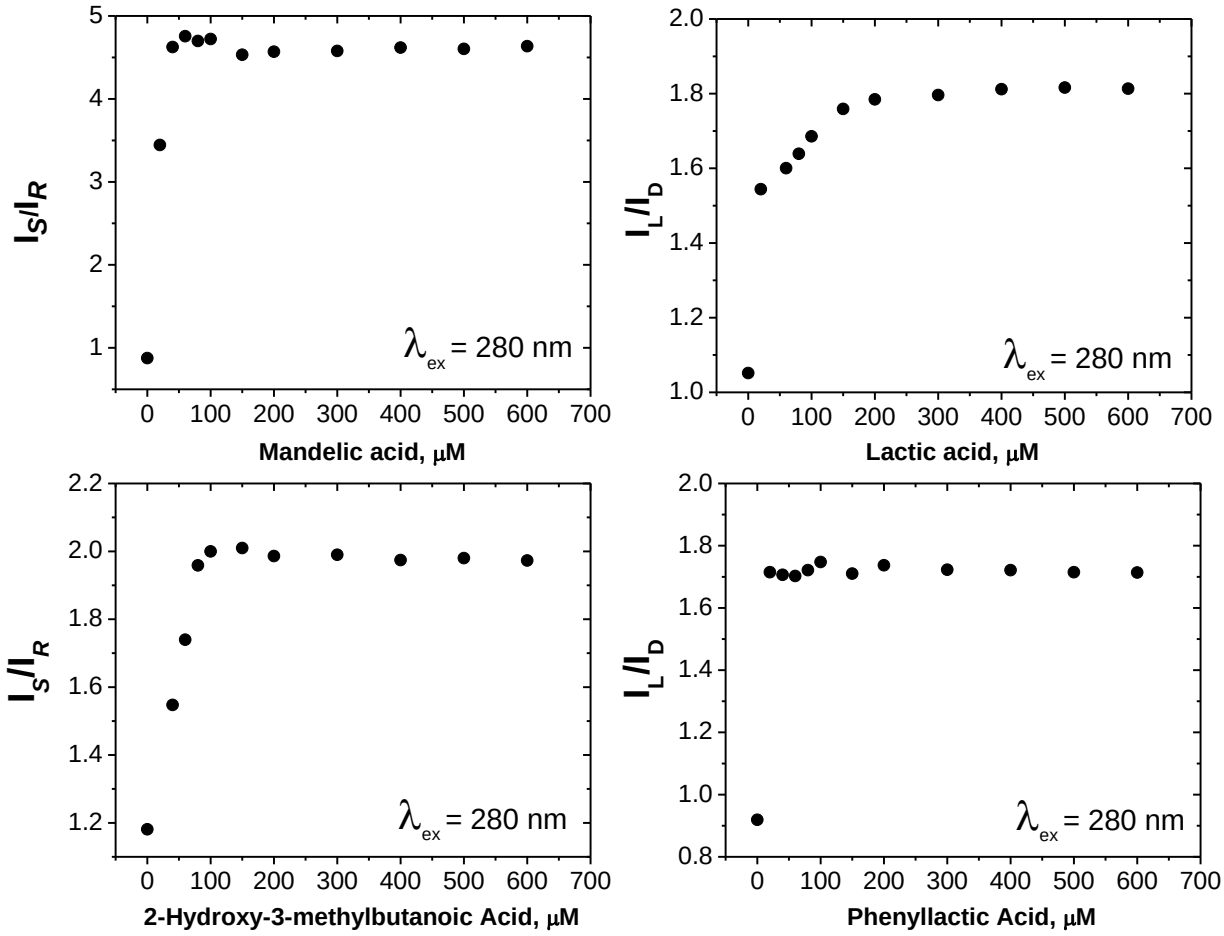

Normalized Fl. Intensity
Wavelength, nm
A = 4.48 folds
Normalized Fl. Intensity
(2R)-2-Hydroxy-3-methylbutanoic Acid, μM
λex = 335 nm
λem = 376 nm
Ka = (7.0 ± 1.0)×10^6 M^-1


Normalized Fl. Intensity
2-Hydroxy-3-methylbutanoic Acid, μM
λex = 280 nm
λex = 335 nm


A = 4.71 folds
Normalized Fl. Intensity
Wavelength, nm
λex = 280 nm
λem = 342 nm
Ka = (1.1 ± 0.1)×10^7 M^-1
(D)-Phenyllactic Acid, μM


A = 8.63 folds
Normalized Fl. Intensity
Wavelength, nm
λex = 280 nm
λem = 342 nm
Ka = (1.9 ± 0.2)×10^7 M^-1
(L)-Phenyllactic Acid, μM


Normalized Fl. Intensity
Wavelength, nm
A = 4.20 folds
Normalized Fl. Intensity
(D)-Phenyllactic Acid, μM
λex = 335 nm
λem = 376 nm
Ka = (1.4 ± 0.1)×10^7 M^-1
Normalized Fl. Intensity
Wavelength, nm
A = 4.57 folds
Normalized Fl. Intensity
(L)-Phenyllactic Acid, μM
λex = 335 nm
λem = 376 nm
Ka = (1.9 ± 0.2)×10^7 M^-1
Normalized Fl. Intensity
Phenyllactic Acid, μM
λex = 280 nm
Normalized Fl. Intensity
Phenyllactic Acid, μM
λex = 335 nm


I_S/I_R
λ_{ex} = 280 nm
Mandelic acid, μM
I_L/I_D
λ_{ex} = 280 nm
Lactic acid, μM
I_S/I_R
λ_{ex} = 280 nm
2-Hydroxy-3-methylbutanoic Acid, μM
I_L/I_D
λ_{ex} = 280 nm
Phenyllactic Acid, μM

4 Array Experiments

Procedure:

1. 1 Equivalent of enantiopure fluorescent amine, 1 equivalent of fluorescent diol and 1 equivalent of 2-formylphenylboronic acid are dissolved in acetonitrile to form **1.25 mM** stock solution of the sensor. 0-5 equivalent of a chiral analyte (diol, hydroxy acid, amine or amino alcohol) is added and the reaction mixture is incubated for 30 min-1 hr to ensure a complete displacement of a dye from the sensor and formation of new diasteriomeric iminoboronate esters.
2. Each reaction mixture (**1.25 mM**) is then diluted by 100 times with pure acetonitrile to a final concentration of **12.5 µM** and dispensed into the microplates using BNX Nanodrop Express.
3. Fluorescence intensities were measured with a microplate reader. The array experiments were performed in 384 well density MATRICAL microplates (working volume 50 µL). Each experiment was performed in 24 repetitions. For the control experiments an equal amount of acetonitrile was added instead of the analyte solutions.
4. The obtained data were subjected to the Student's T-test to exclude 4 data points and then were analyzed using Linear Discriminant analysis (LDA) and Support vector machine (SVM) regression analysis. The coefficient of variability within the class of same repetitions was lower than 2%.

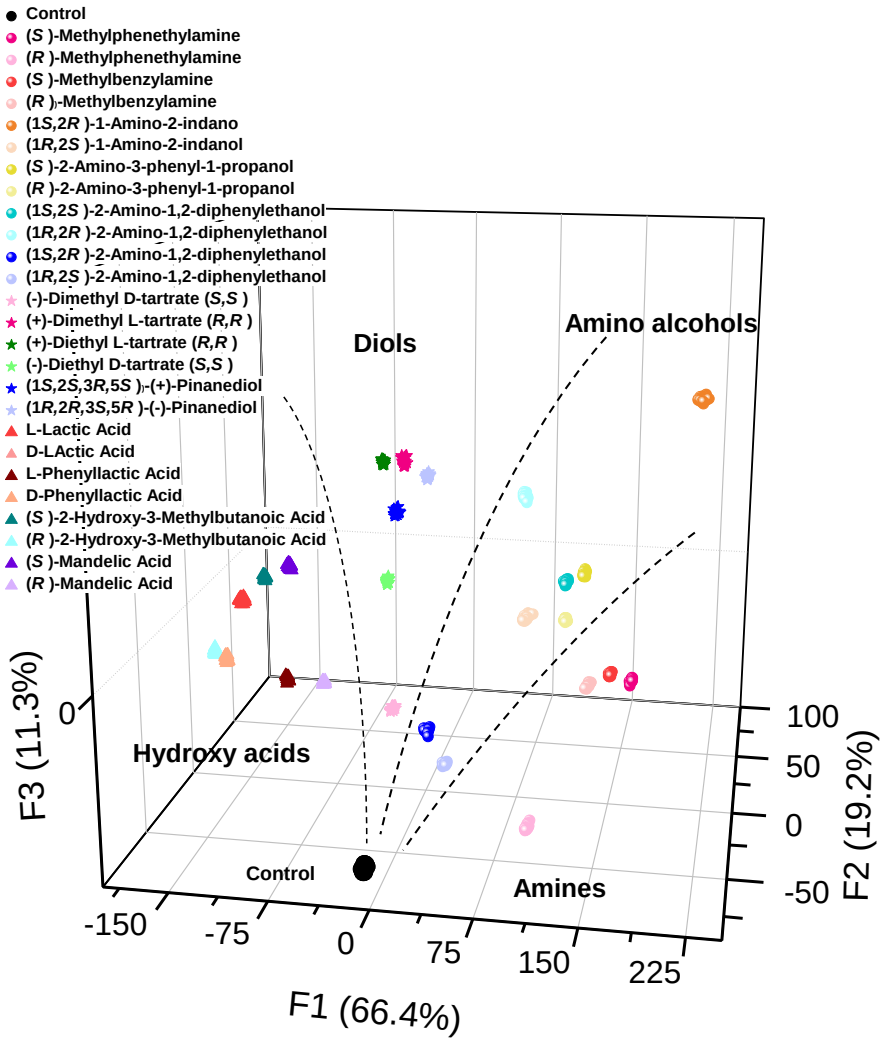


Figure S3. Results of qualitative analysis of various analytes in MeCN using a sensor array based on indicator displacement mechanism.

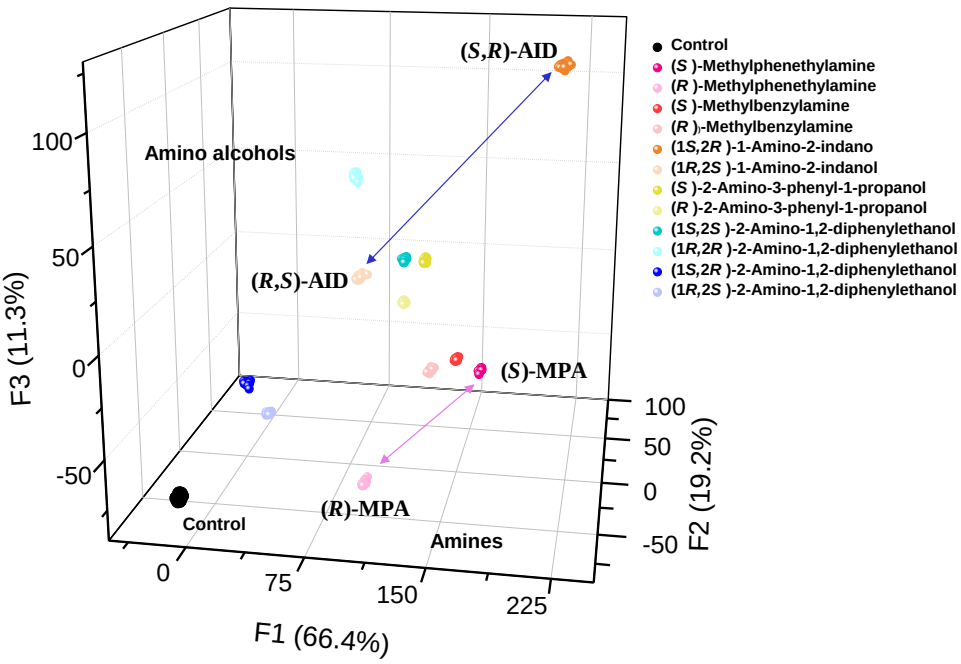


Figure S4. Results of qualitative analysis of amines and amino alcohols in MeCN using a sensor array based on indicator displacement mechanism.

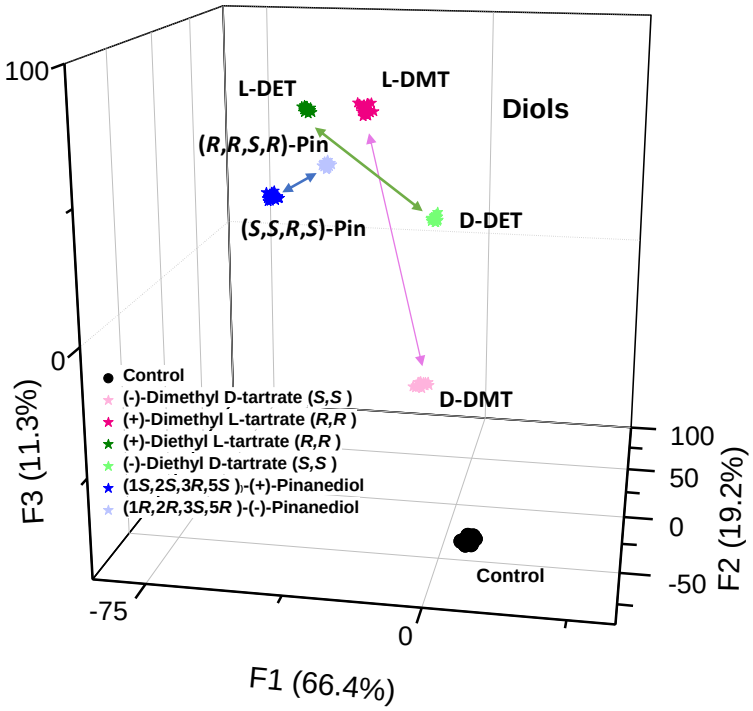


Figure S5. Results of qualitative analysis of diols in MeCN using a sensor array based on indicator displacement mechanism.

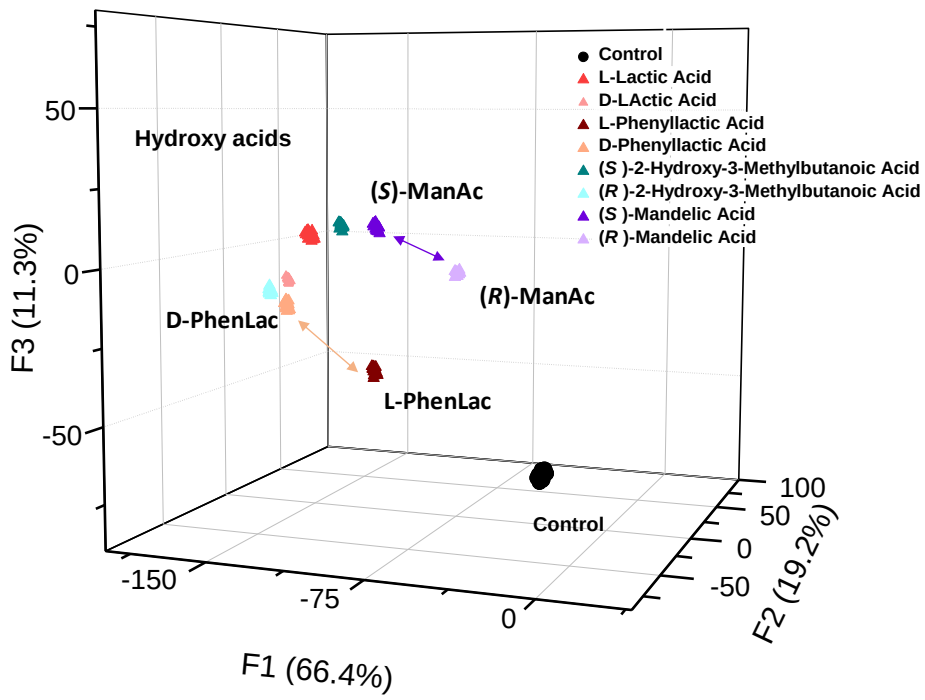


Figure S6. Results of qualitative analysis of hydroxyl acids in MeCN using a sensor array based on indicator displacement mechanism.

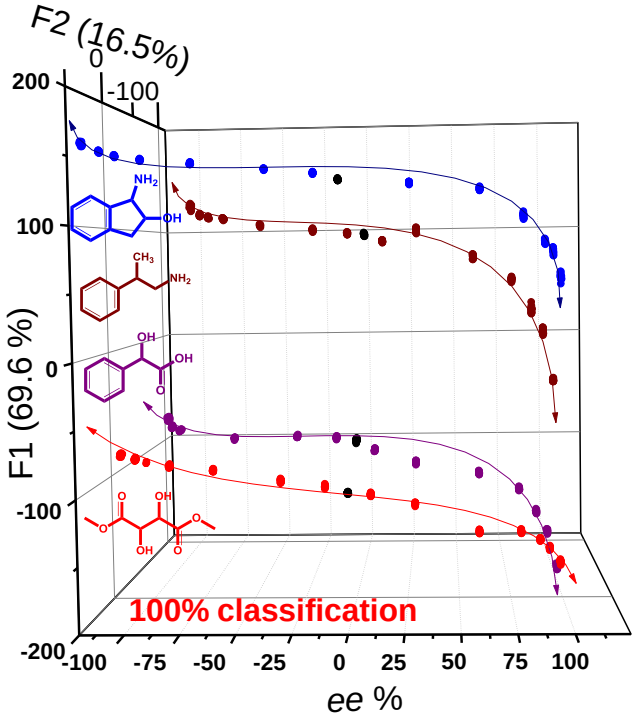


Figure S7. Results of quantitative analysis of enantiomeric excess determination (%*ee*) in MeCN using a sensor array based on indicator displacement mechanism. Array response represented by factors F1, F2 (LDA) and *ee*% in 3D plot for the range from -100 to 100 %*ee*.

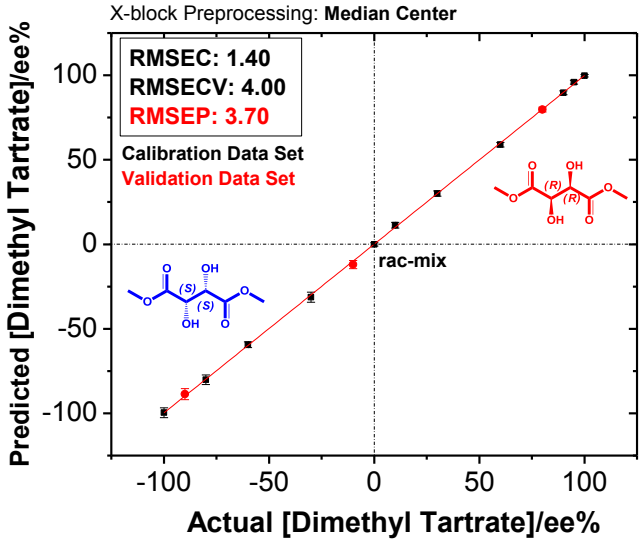


Figure S8. The result of the support vector machine (SVM) regression for enantiomeric excess determination analysis of dimethyl tartrate. The plot of actual vs predicted *ee* shows high accuracy of *ee* prediction. The values of the root-mean-square errors (RMSEs) of calibration (C), cross-validation (CV), and prediction (P) attest to the high quality of the model and prediction.

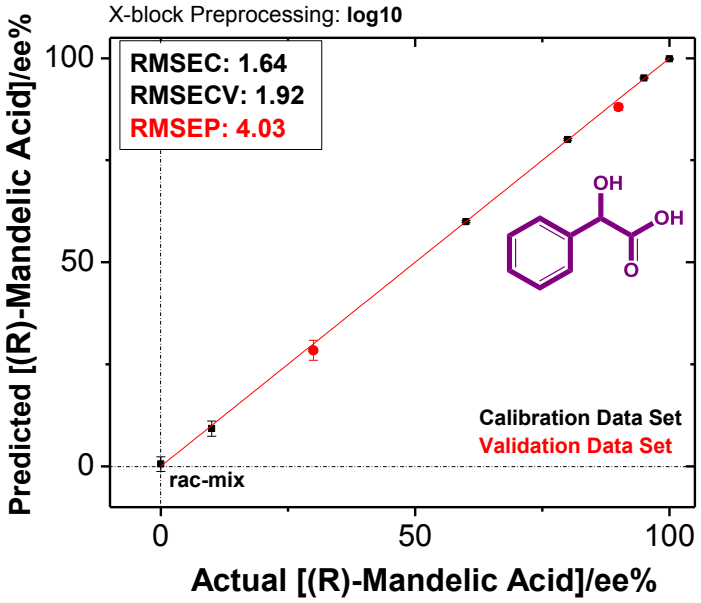


Figure S9. The result of the support vector machine (SVM) regression for enantiomeric excess determination analysis of mandelic acid for the range from 0 % (*rac*-mandelic acid)-100 % (pure *(R)*-mandelic acid) %*ee*. The plot of actual vs predicted *ee* shows high accuracy of *ee* prediction. The values of the root-mean-square errors (RMSEs) of calibration (C), cross-validation (CV), and prediction (P) attest to the high quality of the model and prediction.

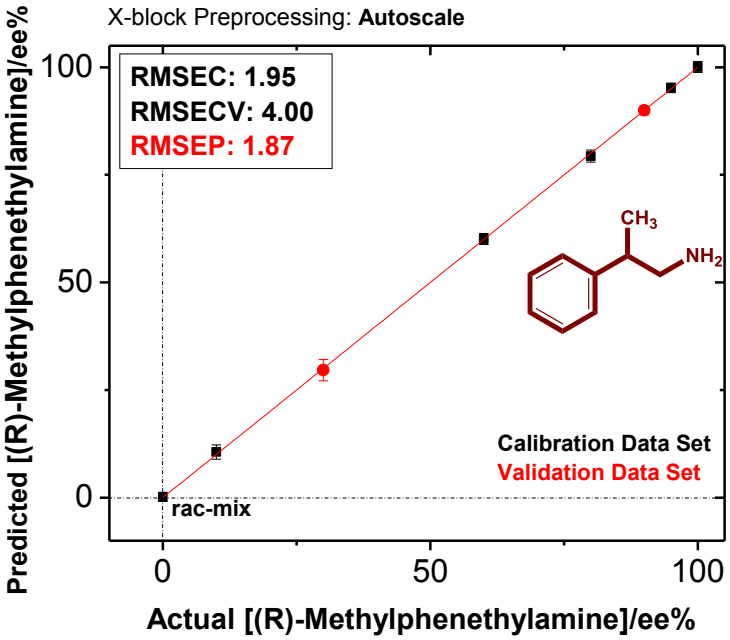


Figure S10. The result of the support vector machine (SVM) regression for enantiomeric excess determination analysis of MPA for the range from 0 % (*rac*-MPA)-100 % (pure *(R)*-MPA) %*ee*.

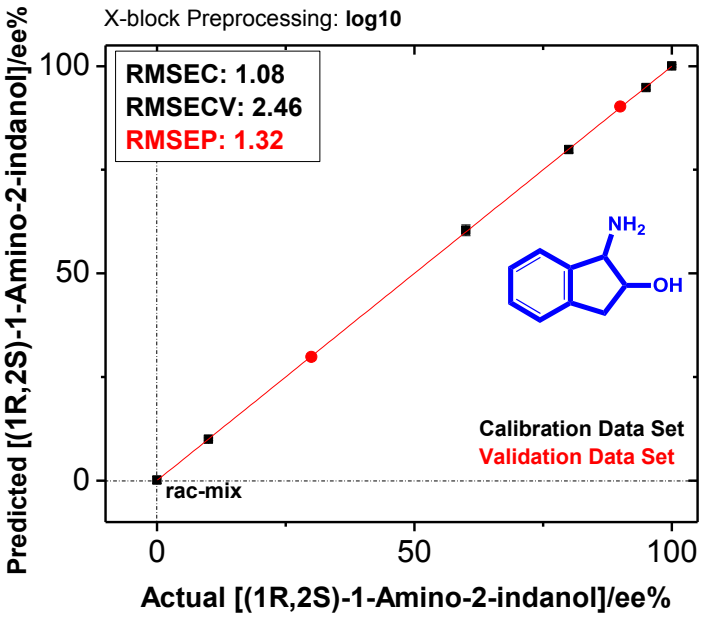


Figure S11. The result of the support vector machine (SVM) regression for enantiomeric excess determination analysis of AID for the range from 0 % (*rac*-AID)-100 % (pure *(1R,2S)*-AID) %*ee*.

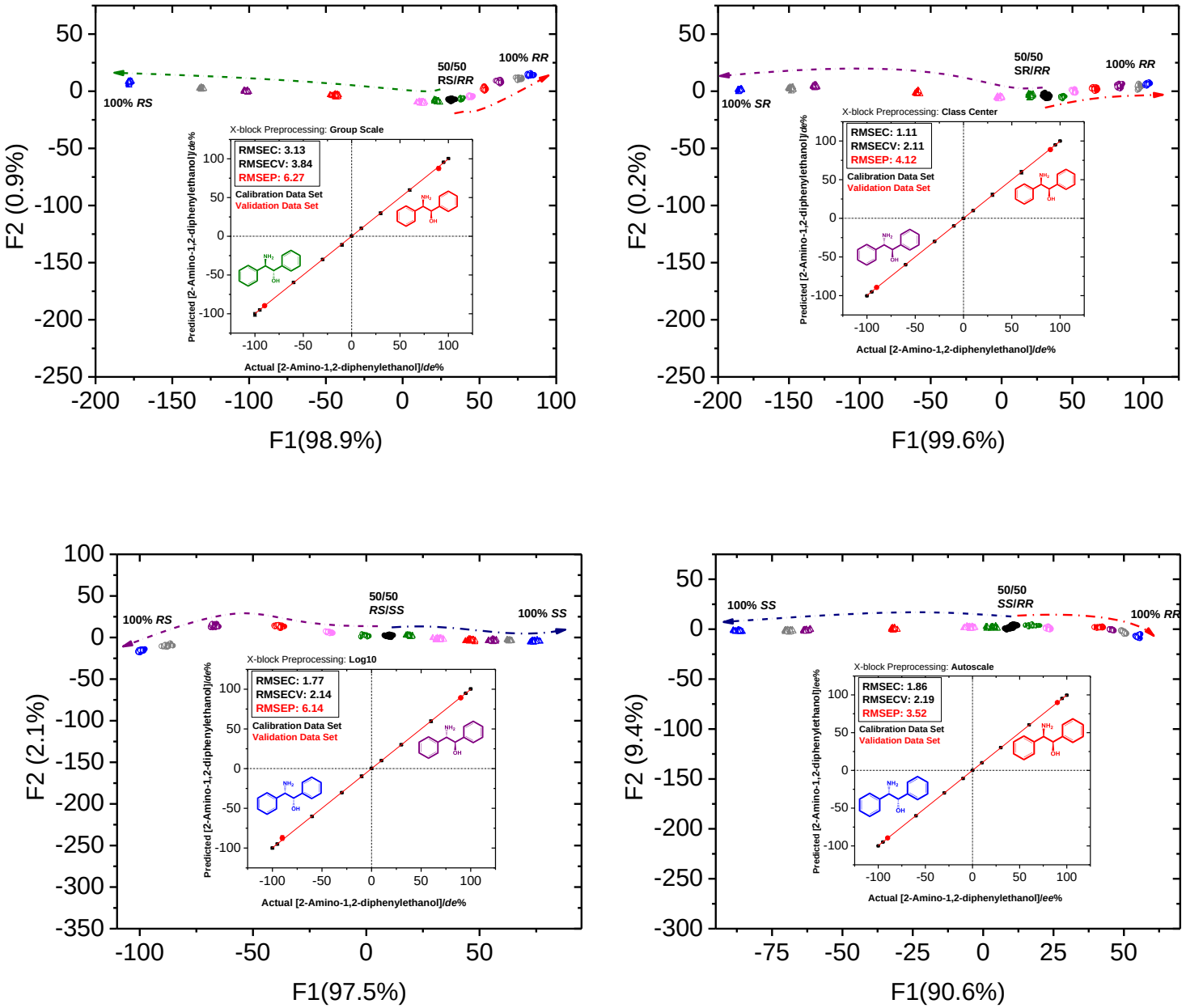


Figure S12. Results of semi-quantitative and quantitative analysis of diastereomeric/enantiomeric excess determination (%de/%*ee*) of 2-amino-1,2-diphenylethanol. Array response represented by factors F1 and F2 (LDA) in 2D plot.

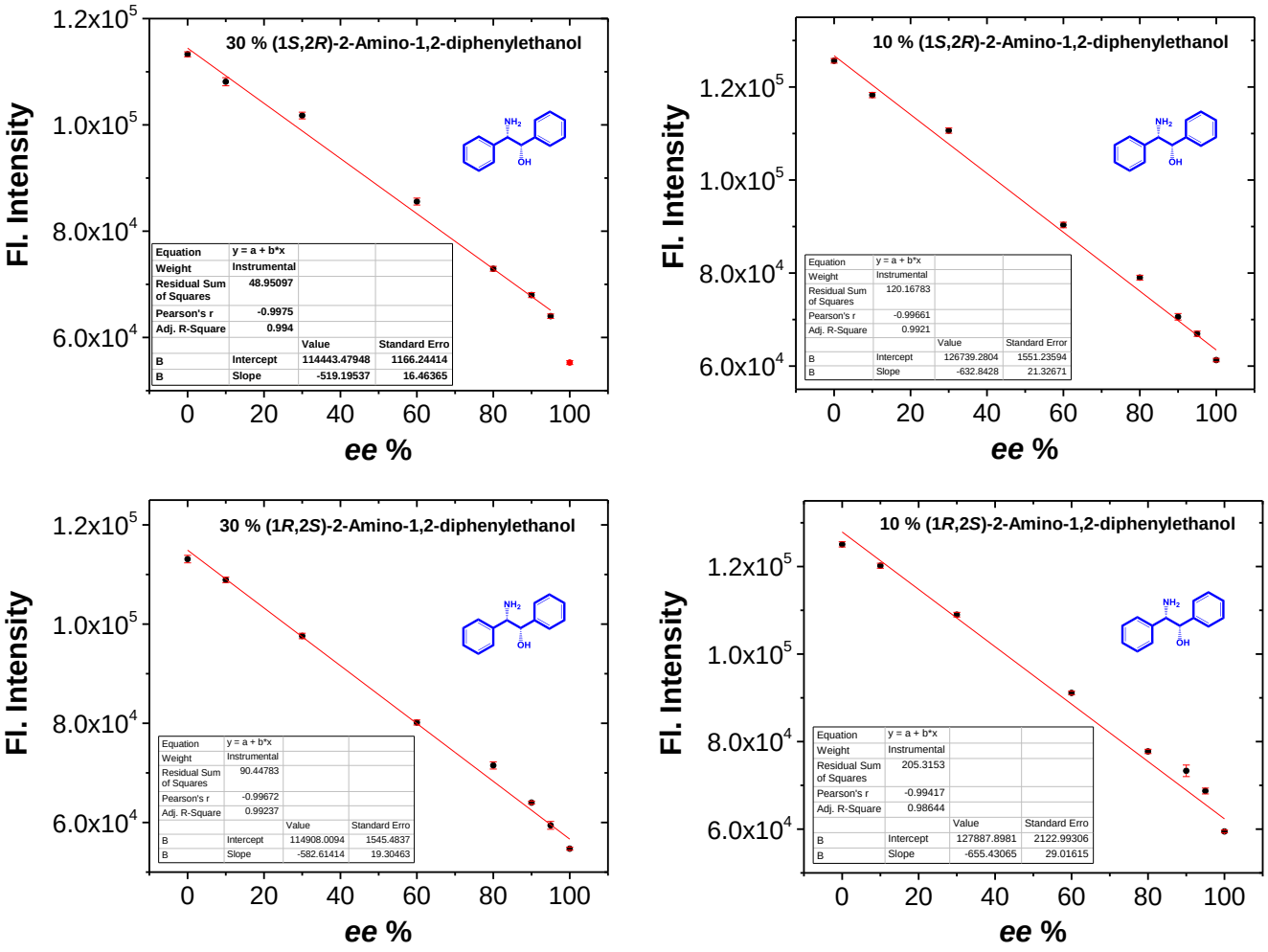


Figure S13. Standard curves for FI readings from a number of ternary mixtures of 2-amino-1,2-diphenylethanol with known *ee*. The resulting graphs of FI *vs. ee* are linear and therefore absolute configuration and *ee* of unknown samples can be determined by interpolation of their fluorescence reading on the graph.

	ee%	%SS	%RR	% RS (or SR)
mix_#1	**0**	45	45	10
mix_#2	**10**	49.5	40.5	10
mix_#3	**30**	58.5	31.5	10
mix_#4	**60**	72	18	10
mix_#5	**80**	86	4	10
mix_#6	**90**	85.5	4.5	10
mix_#7	**95**	87.75	2.25	10
mix_#8	**100**	90	0	10
mix_#9	**0**	35	35	30
mix_#10	**10**	38.5	31.5	30
mix_#11	**30**	45.5	24.5	30
mix_#12	**60**	56	14	30
mix_#13	**80**	63	7	30
mix_#14	**90**	76.5	3.5	30
mix_#15	**95**	68.25	1.75	30
mix_#16	**100**	70	0	30

Supplemental References

[1] A. K. Connors. *Binding Constants: the Measurement of Molecular Complex Stability*; Wiley: New York, **1987**.