Supporting information

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

Mariia Pushina, Sepideh Farshbaf, Elena G. Shcherbakova, and Pavel Anzenbacher, Jr.

Department of Chemistry, Bowling Green State University Bowling Green, OH 43403, USA E-mail: pavel@bgsu.edu

Table of Contents

1 General 2
2 MALDI-TOF Mass Spectra 3
3 Determination of Association Constants (Ka, M⁻¹) by Fluorescence Titrations 4
4 Array Experiments 40

Supplemental References 49
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 methods¹.
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 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 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 iminoboronic esters 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 iminoboronic and oxazolidineboronate 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\text{ex}=280 nm) and isotherm of 2-FPBA, L-tryptophanol (0.2 μM) upon addition of coumarin in MeCN. **Right:** Fluorescence titration spectra (λ\text{ex}=370 nm) and isotherm of 2-FPBA, coumarin upon addition of L-tryptophanol in MeCN. The titrations represent the formation of the initial
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.

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.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>$K_a$ (M$^{-1} \times 10^6$) derived from 6,7-dihydroxycoumarin</th>
<th>$K_a$ (M$^{-1} \times 10^6$) derived from L-tryptophanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R)-(−)-3-Chloro-1,2-propanediol</td>
<td>2.5 ± 0.1</td>
<td>1.1 ± 0.06</td>
</tr>
<tr>
<td>(S)-(+)3-Chloro-1,2-propanediol</td>
<td>0.11 ± 0.01</td>
<td>0.33 ± 0.02</td>
</tr>
<tr>
<td>(+)-Dimethyl L-tartrate (R,R)</td>
<td>7.7 ± 0.1</td>
<td>16 ± 0.8</td>
</tr>
<tr>
<td>(−)-Dimethyl D-tartrate (S,S)</td>
<td>7.0 ± 0.2</td>
<td>8.5 ± 0.5</td>
</tr>
<tr>
<td>(+)-Diethyl L-tartrate (R,R)</td>
<td>4.8 ± 0.2</td>
<td>5.3 ± 0.2</td>
</tr>
<tr>
<td>(−)-Diethyl D-tartrate(S,S)</td>
<td>3.1 ± 0.2</td>
<td>2.7 ± 0.08</td>
</tr>
<tr>
<td>(1R,2R,3S,5R)-(−)-Pinanediol</td>
<td>4.3 ± 0.7</td>
<td>4.2 ± 0.6</td>
</tr>
<tr>
<td>(1S,2S,3R,5S)-(+)Pinanediol</td>
<td>2.8 ± 0.2</td>
<td>2.1 ± 0.2</td>
</tr>
<tr>
<td>(R)-(−)-Phenyl-1,2-ethanediol</td>
<td>1.1 ± 0.1</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>(S)-(+)Phenyl-1,2-ethanediol</td>
<td>2.0 ± 0.4</td>
<td>1.4 ± 0.06</td>
</tr>
<tr>
<td>meso-Hydrobenzoin</td>
<td>2.0 ± 0.2</td>
<td>1.4 ± 0.08</td>
</tr>
<tr>
<td>(R,R)-(−)-Hydrobenzoin</td>
<td>1.1 ± 0.08</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>(S,S)-(−)-Hydrobenzoin</td>
<td>4.2 ± 0.2</td>
<td>2.9 ± 0.3</td>
</tr>
</tbody>
</table>
Q = 29.7%

$Q = 40.9\%$

$A = 3.0$ folds

$A = 7.1$ folds

$K_a = (3.1 \pm 0.2) \times 10^6$ M$^{-1}$

$K_a = (4.8 \pm 0.2) \times 10^6$ M$^{-1}$

$K_a = (2.7 \pm 0.08) \times 10^6$ M$^{-1}$

$K_a = (5.3 \pm 0.2) \times 10^6$ M$^{-1}$

$\lambda_{ex} = 370$ nm

$\lambda_{ex} = 280$ nm

$\lambda_{em} = 436$ nm

$\lambda_{em} = 326$ nm
Diethyl Tartrate, \( \mu M \)

Normalized Fl. Intensity

\( \lambda_{\text{em}} = 436 \text{ nm} \)

\( \lambda_{\text{ex}} = 370 \text{ nm} \)

Diethyl Tartrate, \( \mu M \)

Normalized Fl. Intensity

\( \lambda_{\text{em}} = 326 \text{ nm} \)

\( \lambda_{\text{ex}} = 280 \text{ nm} \)

Dimethyl-L-Tartrate, \( \mu M \)

Normalized Fl. Intensity

\( K_a = (7.7 \pm 0.1) \times 10^6 \text{ M}^{-1} \)

\( \lambda_{\text{ex}} = 370 \text{ nm} \)

\( \lambda_{\text{em}} = 436 \text{ nm} \)

Dimethyl-D-Tartrate, \( \mu M \)

Normalized Fl. Intensity

\( K_a = (7.0 \pm 0.2) \times 10^6 \text{ M}^{-1} \)

\( \lambda_{\text{ex}} = 370 \text{ nm} \)

\( \lambda_{\text{em}} = 436 \text{ nm} \)
A = 7.0 folds

$A = 7.0$ folds

$\lambda_{ex} = 280 \text{ nm}$

$\lambda_{em} = 326 \text{ nm}$

$K_a = (8.5 \pm 0.5) \times 10^6 \text{ M}^{-1}$

$\lambda_{ex} = 280 \text{ nm}$

$\lambda_{em} = 326 \text{ nm}$

$K_a = (8.5 \pm 0.5) \times 10^6 \text{ M}^{-1}$

$\lambda_{ex} = 280 \text{ nm}$

$\lambda_{em} = 326 \text{ nm}$

$K_a = (8.5 \pm 0.5) \times 10^6 \text{ M}^{-1}$

$\lambda_{ex} = 370 \text{ nm}$

$\lambda_{em} = 436 \text{ nm}$

$\lambda_{ex} = 280 \text{ nm}$

$\lambda_{em} = 326 \text{ nm}$
**Supporting information**

---

**R-3-Chloro-1,2-propanediol, **$\mu$**M**

\[
Q = 59.0\%
\]

\[
\lambda_{\text{ex}} = 370 \text{ nm} \\
\lambda_{\text{em}} = 436 \text{ nm} \\
K_a = (2.5 \pm 0.1) \times 10^6 \text{ M}^{-1}
\]

---

**S-3-Chloro-1,2-propanediol, **$\mu$**M**

\[
Q = 86.4\%
\]

\[
\lambda_{\text{ex}} = 370 \text{ nm} \\
\lambda_{\text{em}} = 326 \text{ nm} \\
K_a = (1.1 \pm 0.03) \times 10^5 \text{ M}^{-1}
\]

---

**R-3-Chloro-1,2-propanediol, **$\mu$**M**

\[
A = 6.7 \text{ folds}
\]

\[
\lambda_{\text{ex}} = 280 \text{ nm} \\
\lambda_{\text{em}} = 326 \text{ nm} \\
K_a = (1.1 \pm 0.06) \times 10^6 \text{ M}^{-1}
\]

---

**S-3-Chloro-1,2-propanediol, **$\mu$**M**

\[
A = 5.0 \text{ folds}
\]

\[
\lambda_{\text{ex}} = 280 \text{ nm} \\
\lambda_{\text{em}} = 326 \text{ nm} \\
K_a = (3.3 \pm 0.2) \times 10^5 \text{ M}^{-1}
\]
$Q = 31.6\%$

$\lambda_{ex} = 370\text{ nm}$

$\lambda_{em} = 436\text{ nm}$

$K_a = (1.1 \pm 0.1) \times 10^6\text{ M}^{-1}$

$\lambda_{ex} = 370\text{ nm}$

$\lambda_{em} = 436\text{ nm}$

$K_a = (2.0 \pm 0.4) \times 10^6\text{ M}^{-1}$

$\lambda_{ex} = 280\text{ nm}$

$\lambda_{em} = 326\text{ nm}$

$K_a = (1.4 \pm 0.06) \times 10^6\text{ M}^{-1}$

$\lambda_{ex} = 280\text{ nm}$

$\lambda_{em} = 326\text{ nm}$

$K_a = (2.0 \pm 0.2) \times 10^6\text{ M}^{-1}$

$\lambda_{ex} = 370\text{ nm}$

$\lambda_{em} = 436\text{ nm}$

$K_a = (1.4 \pm 0.06) \times 10^6\text{ M}^{-1}$
$K_a = (1.1 \pm 0.08) \times 10^6 \text{ M}^{-1}$

$\lambda_{ex} = 370 \text{ nm}$

$\lambda_{em} = 436 \text{ nm}$

Q = 58.5%

$K_a = (4.2 \pm 0.2) \times 10^6 \text{ M}^{-1}$

$\lambda_{ex} = 370 \text{ nm}$

$\lambda_{em} = 436 \text{ nm}$

Q = 51.8%

$K_a = (2.0 \pm 0.2) \times 10^6 \text{ M}^{-1}$

$\lambda_{ex} = 370 \text{ nm}$

$\lambda_{em} = 436 \text{ nm}$

Q = 68.6%
\[ \Lambda = 3.5 \text{ folds} \]

\[ \Lambda = 4.4 \text{ folds} \]

\[ \Lambda = 8.7 \text{ folds} \]

\[ \Lambda = 4.4 \text{ folds} \]

\[ \Lambda = 8.7 \text{ folds} \]

\[ K_a = (1.5 \pm 0.1) \times 10^6 \text{ M}^{-1} \]

\[ K_a = (2.9 \pm 0.3) \times 10^6 \text{ M}^{-1} \]

\[ K_a = (1.4 \pm 0.08) \times 10^6 \text{ M}^{-1} \]

\[ \lambda_{ex} = 280 \text{ nm} \]

\[ \lambda_{em} = 326 \text{ nm} \]
$Q = 82.6\%$

$Q = 78.8\%$

$A = 10.5\text{ folds}$

$A = 3.9\text{ folds}$

$K_a = (4.3 \pm 0.7) \times 10^6 \text{ M}^{-1}$

$K_a = (2.8 \pm 0.2) \times 10^6 \text{ M}^{-1}$

$K_a = (2.1 \pm 0.2) \times 10^6 \text{ M}^{-1}$

$K_a = (4.2 \pm 0.6) \times 10^6 \text{ M}^{-1}$

$\lambda_{ex} = 370 \text{ nm}$

$\lambda_{em} = 436 \text{ nm}$

$\lambda_{ex} = 326 \text{ nm}$

$\lambda_{em} = 280 \text{ nm}$
**Table S2.** The calculated $K_a$ 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.

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

A = 3.5 folds

A = 4.6 folds

Q = 76.3 %

Q = 69.1 %

\[ \lambda_{ex} = 280 \text{ nm} \]

\[ \lambda_{em} = 326 \text{ nm} \]

\[ K_a = (3.2 \pm 0.7) \times 10^6 \text{ M}^{-1} \]

\[ \lambda_{ex} = 280 \text{ nm} \]

\[ \lambda_{em} = 326 \text{ nm} \]

\[ K_a = (3.4 \pm 0.4) \times 10^6 \text{ M}^{-1} \]

\[ \lambda_{ex} = 370 \text{ nm} \]

\[ \lambda_{em} = 436 \text{ nm} \]

\[ K_a = (1.3 \pm 0.07) \times 10^6 \text{ M}^{-1} \]

\[ \lambda_{ex} = 370 \text{ nm} \]

\[ \lambda_{em} = 436 \text{ nm} \]

\[ K_a = (6.9 \pm 0.7) \times 10^6 \text{ M}^{-1} \]
Supporting information

**Lactic acid, µM**

- **K_a = (1.4 ± 0.2)×10^6 M^-1**
  - λ_ex = 280 nm
  - λ_em = 326 nm

**L-Phenyllactic acid, µM**

- **K_a = (3.9 ± 0.3)×10^6 M^-1**
  - λ_ex = 370 nm
  - λ_em = 436 nm

**D-Phenyllactic acid, µM**

- **K_a = (1.2 ± 0.1)×10^7 M^-1**
  - λ_ex = 370 nm
  - λ_em = 436 nm
\[ \text{Normalized Fl. Intensity} \]

**Supporting information**

![Graph showing A = 1.3 folds](image)

**D-Phenyllactic acid, \( \mu M \)**

- \( K_a = (9.3 \pm 1.6) \times 10^6 \) M\(^{-1} \)
- \( \lambda_{em} = 324 \) nm
- \( \lambda_{ex} = 280 \) nm

![Graph showing A = 3.2 folds](image)

**L-Phenyllactic acid, \( \mu M \)**

- \( K_a = (4.8 \pm 0.3) \times 10^6 \) M\(^{-1} \)
- \( \lambda_{em} = 326 \) nm
- \( \lambda_{ex} = 280 \) nm

![Graph showing Q = 85.6%](image)

**Q = 85.6%**

- \( \lambda_{ex} = 370 \) nm
- \( \lambda_{em} = 436 \) nm
- \( K_a = (2.2 \pm 0.1) \times 10^6 \) M\(^{-1} \)

![Graph showing Q = 85.5%](image)

**Q = 85.5%**

- \( \lambda_{ex} = 370 \) nm
- \( \lambda_{em} = 436 \) nm
- \( K_a = (2.1 \pm 0.3) \times 10^6 \) M\(^{-1} \)
### Supporting Information

**A = 3.1 folds**

![Normalized FI vs Wavelength](image1)

**A = 7.6 folds**

![Normalized FI vs Wavelength](image2)

### (2R)-2-Hydroxy-3-methylbutanoic Acid, µM

- **λ<sub>ex</sub>** = 280 nm
- **λ<sub>em</sub>** = 326 nm
- **K<sub>a</sub>** = (3.0 ± 0.7) × 10<sup>6</sup> M<sup>-1</sup>

### (2S)-2-Hydroxy-3-methylbutanoic Acid, µM

- **λ<sub>ex</sub>** = 280 nm
- **λ<sub>em</sub>** = 326 nm
- **K<sub>a</sub>** = (1.3 ± 0.1) × 10<sup>6</sup> M<sup>-1</sup>

### Mandelic acid, µM

- **λ<sub>ex</sub>** = 280 nm
- **λ<sub>em</sub>** = 326 nm

### Phenyllactic acid, µM

- **λ<sub>ex</sub>** = 280 nm
- **λ<sub>em</sub>** = 326 nm

### Lactic acid, µM

- **λ<sub>ex</sub>** = 280 nm
- **λ<sub>em</sub>** = 326 nm

### 2-Hydroxy-3-methylbutanoic Acid, µM

- **λ<sub>ex</sub>** = 280 nm
- **λ<sub>em</sub>** = 326 nm
Time-dependent fluorescent titration of the ensemble with enantiomeric lactic acid in acetonitrile
**Supporting information**

**Left:** Fluorescence titration spectra ($\lambda_{ex}$=335 nm) and isotherm of 2-FPBA, (S)-VAPOL (40 µM) upon addition of L-tryptophanol. **Right:** Fluorescence titration spectra ($\lambda_{ex}$=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 iminoborane 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 $K_a$ values on the change in fluorescence intensities of the iminoborane complex formed by FPBA, L-tryptophanol and (S)-VAPOL upon addition of selected chiral diols in acetonitrile.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>$K_a$ (M$^{-1} \times 10^6$) derived from (S)-VAPOL</th>
<th>$K_a$ (M$^{-1} \times 10^6$) derived from L-tryptophanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-Dimethyl L-tartrate $(R,R)$</td>
<td>39 ± 3.0</td>
<td>30 ± 3.0</td>
</tr>
<tr>
<td>(−)-Dimethyl D-tartrate $(S,S)$</td>
<td>8.7 ± 1.0</td>
<td>8.4 ± 0.6</td>
</tr>
<tr>
<td>(+)-Diethyl L-tartrate $(R,R)$</td>
<td>37 ± 3.0</td>
<td>33 ± 5.0</td>
</tr>
<tr>
<td>(−)-Diethyl D-tartrate $(S,S)$</td>
<td>39 ± 3.0</td>
<td>36 ± 6.0</td>
</tr>
<tr>
<td>(1R,2R,3S,5R)-(−)-Pinanediol</td>
<td>5.9 ± 1.0</td>
<td>5.6 ± 1.0</td>
</tr>
<tr>
<td>(1S,2S,3R,5S)-(−)-Pinanediol</td>
<td>16 ± 2.0</td>
<td>16 ± 2.0</td>
</tr>
</tbody>
</table>
Wavelength, nm
Normalized Fl. Intensity

A = 11.0 folds

λ_{ex} = 280 nm
λ_{em} = 342 nm
K_s = (3.3 ± 0.5) \times 10^7 M^{-1}

A = 5.91 folds

λ_{ex} = 280 nm
λ_{em} = 342 nm
K_s = (3.6 ± 0.6) \times 10^7 M^{-1}

A = 2.10 folds

λ_{ex} = 335 nm
λ_{em} = 376 nm
K_s = (3.7 ± 0.3) \times 10^7 M^{-1}

A = 1.83 folds

λ_{ex} = 335 nm
λ_{em} = 376 nm
K_s = (3.9 ± 0.3) \times 10^7 M^{-1}
Supporting information

Diethyl Tartrate, $\mu$M

$\lambda_{\text{ex}} = 335$ nm

$\lambda_{\text{em}} = 376$ nm

Normalized Fluorescence Intensity

$\lambda_{\text{ex}} = 280$ nm

$\lambda_{\text{em}} = 342$ nm

$K_a = (3.0 \pm 0.3) \times 10^7$ M$^{-1}$

$K_a = (8.4 \pm 0.6) \times 10^6$ M$^{-1}$
$A = 1.77$ folds

$K_a = (3.9 \pm 0.3) \times 10^7 \text{ M}^{-1}$

$\lambda_{\text{ex}} = 335 \text{ nm}$

$\lambda_{\text{em}} = 376 \text{ nm}$

$A = 1.43$ folds

$K_a = (8.7 \pm 1.0) \times 10^6 \text{ M}^{-1}$

$\lambda_{\text{ex}} = 335 \text{ nm}$

$\lambda_{\text{em}} = 376 \text{ nm}$

$\lambda_{\text{ex}} = 280 \text{ nm}$

$\lambda_{\text{em}} = 376 \text{ nm}$
A = \text{5.51 folds}

\begin{align*}
\lambda_{\text{ex}} &= 280 \text{ nm} \\
\lambda_{\text{em}} &= 342 \text{ nm} \\
K &= (1.6 \pm 0.2) \times 10^7 \text{ M}^{-1}
\end{align*}

A = \text{3.21 folds}

\begin{align*}
\lambda_{\text{ex}} &= 280 \text{ nm} \\
\lambda_{\text{em}} &= 342 \text{ nm} \\
K &= (5.6 \pm 1.0) \times 10^6 \text{ M}^{-1}
\end{align*}

A = \text{1.93 folds}

\begin{align*}
\lambda_{\text{ex}} &= 335 \text{ nm} \\
\lambda_{\text{em}} &= 376 \text{ nm} \\
K &= (1.6 \pm 0.2) \times 10^7 \text{ M}^{-1}
\end{align*}

A = \text{1.65 folds}

\begin{align*}
\lambda_{\text{ex}} &= 335 \text{ nm} \\
\lambda_{\text{em}} &= 376 \text{ nm} \\
K &= (5.9 \pm 1.0) \times 10^6 \text{ M}^{-1}
\end{align*}
Table S4. The calculated $K_a$ values on the change in fluorescence intensities of the iminoborurate complex formed by FPBA, L-tryptophanol and (S)-VAPOL upon addition of selected chiral amines and amino alcohols in acetonitrile.

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

**Wavelength, nm**

- **Normalized Fl. Intensity**

<table>
<thead>
<tr>
<th><strong>A = 4.62 folds</strong></th>
<th><strong>A = 8.72 folds</strong></th>
</tr>
</thead>
</table>

**Q = 65.7 %**

- **Wavelength, nm**

**Q = 88.6 %**

- **Normalized Fl. Intensity**

**Ka = (2.1 ± 0.3) \times 10^6 M^{-1}**

- **λ_{ex} = 280 nm**
- **λ_{em} = 342 nm**

**Ka = (1.9 ± 0.1) \times 10^7 M^{-1}**

- **λ_{ex} = 335 nm**
- **λ_{em} = 376 nm**

**Ka = (2.6 ± 0.4) \times 10^6 M^{-1}**

- **λ_{ex} = 335 nm**
- **λ_{em} = 376 nm**

**Ka = (1.9 ± 0.1) \times 10^7 M^{-1}**

- **λ_{ex} = 335 nm**
- **λ_{em} = 376 nm**
Methylphenethylamine, \( \mu \text{M} \)

Normalized Fl. Intensity

\( \lambda_{\text{em}} = 376 \text{ nm} \)

\( \lambda_{\text{ex}} = 335 \text{ nm} \)

\[ K_a = (4.5 \pm 0.5) \times 10^6 \text{ M}^{-1} \]

Methylphenethylamine, \( \mu \text{M} \)

Normalized Fl. Intensity

\( \lambda_{\text{em}} = 342 \text{ nm} \)

\( \lambda_{\text{ex}} = 280 \text{ nm} \)

\[ K_a = (3.4 \pm 0.5) \times 10^6 \text{ M}^{-1} \]
Supporting information

Normalized Fl. Intensity

\[ K_a = \left(2.8 \pm 0.3\right) \times 10^6 \text{ M}^{-1} \]

\[ \lambda_{\text{em}} = 342 \text{ nm} \]

\[ \lambda_{\text{ex}} = 280 \text{ nm} \]

Normalized Fl. Intensity

\[ K_a = \left(2.0 \pm 0.2\right) \times 10^7 \text{ M}^{-1} \]

\[ \lambda_{\text{em}} = 376 \text{ nm} \]

\[ \lambda_{\text{ex}} = 335 \text{ nm} \]

Normalized Fl. Intensity

\[ K_a = \left(3.3 \pm 0.3\right) \times 10^6 \text{ M}^{-1} \]

\[ \lambda_{\text{em}} = 342 \text{ nm} \]

\[ \lambda_{\text{ex}} = 280 \text{ nm} \]

Normalized Fl. Intensity

\[ K_a = \left(1.5 \pm 0.1\right) \times 10^7 \text{ M}^{-1} \]

\[ \lambda_{\text{em}} = 376 \text{ nm} \]

\[ \lambda_{\text{ex}} = 335 \text{ nm} \]
Supporting information

\[ \lambda_{\text{ex}} = 335 \text{ nm} \]
\[ \lambda_{\text{em}} = 376 \text{ nm} \]

\[ K_a = (1.0 \pm 0.1) \times 10^6 \text{ M}^{-1} \]

\[ \lambda_{\text{ex}} = 335 \text{ nm} \]
\[ \lambda_{\text{em}} = 376 \text{ nm} \]

\[ K_a = (4.1 \pm 0.3) \times 10^7 \text{ M}^{-1} \]

\[ \lambda_{\text{ex}} = 280 \text{ nm} \]
\[ \lambda_{\text{em}} = 342 \text{ nm} \]

\[ K_a = (8.3 \pm 1.3) \times 10^6 \text{ M}^{-1} \]

\[ \lambda_{\text{ex}} = 280 \text{ nm} \]
\[ \lambda_{\text{em}} = 342 \text{ nm} \]

\[ K_a = (4.3 \pm 0.5) \times 10^6 \text{ M}^{-1} \]
$A = 1.25$ folds

$\lambda_{\text{ex}} = 335 \text{ nm} \quad \lambda_{\text{em}} = 376 \text{ nm} \quad K_a = (7.1 \pm 0.7) \times 10^6 \text{ M}^{-1}$

$A = 1.27$ folds

$\lambda_{\text{ex}} = 335 \text{ nm} \quad \lambda_{\text{em}} = 376 \text{ nm} \quad K_a = (4.1 \pm 0.3) \times 10^6 \text{ M}^{-1}$

$A = 9.17$ folds

$\lambda_{\text{ex}} = 280 \text{ nm} \quad \lambda_{\text{em}} = 342 \text{ nm} \quad K_a = (7.4 \pm 0.7) \times 10^6 \text{ M}^{-1}$

$A = 9.59$ folds

$\lambda_{\text{ex}} = 280 \text{ nm} \quad \lambda_{\text{em}} = 342 \text{ nm} \quad K_a = (3.0 \pm 0.5) \times 10^6 \text{ M}^{-1}$
A = 5.13 folds

$\lambda_{ex} = 280 \text{ nm}$
$\lambda_{em} = 342 \text{ nm}$
$K_a = (3.2 \pm 0.5) \times 10^6 \text{ M}^{-1}$

A = 3.00 folds

$\lambda_{ex} = 280 \text{ nm}$
$\lambda_{em} = 342 \text{ nm}$
$K_a = (2.9 \pm 0.5) \times 10^6 \text{ M}^{-1}$

A = 1.75 folds

$\lambda_{ex} = 335 \text{ nm}$
$\lambda_{em} = 376 \text{ nm}$
$K_a = (8.7 \pm 0.6) \times 10^6 \text{ M}^{-1}$

A = 2.18 folds

$\lambda_{ex} = 335 \text{ nm}$
$\lambda_{em} = 376 \text{ nm}$
$K_a = (2.7 \pm 0.2) \times 10^7 \text{ M}^{-1}$
$$A = 1.20 \text{ folds}$$

$$A = 1.49 \text{ folds}$$

$$\lambda_{ex} = 335 \text{ nm}$$

$$\lambda_{em} = 376 \text{ nm}$$

$$K_a = (5.7 \pm 0.5) \times 10^6 \text{ M}^{-1}$$

$$\lambda_{ex} = 335 \text{ nm}$$

$$\lambda_{em} = 376 \text{ nm}$$

$$K_a = (2.7 \pm 0.1) \times 10^6 \text{ M}^{-1}$$

$$\lambda_{ex} = 280 \text{ nm}$$

$$\lambda_{ex} = 335 \text{ nm}$$
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.

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

![Graph showing fluorescence intensity changes](image1)

![Graph showing fluorescence intensity changes](image2)
Supporting information

\[ \Lambda = 1.73 \text{ folds} \]

\[ \Lambda = 4.25 \text{ folds} \]

\[ K_a = (2.4 \pm 0.2) \times 10^6 \text{ M}^{-1} \]

\[ K_a = (1.8 \pm 0.1) \times 10^7 \text{ M}^{-1} \]

\[ \lambda_{ex} = 335 \text{ nm} \]

\[ \lambda_{em} = 376 \text{ nm} \]

\[ \lambda_{ex} = 280 \text{ nm} \]

\[ \lambda_{ex} = 335 \text{ nm} \]

\[ (R)-\text{Mandelic acid, } \mu\text{M} \]

\[ \text{Normalized Fl. Intensity} \]

\[ \text{Normalized Fl. Intensity} \]
$K_a = (1.7 \pm 0.2) \times 10^7 \text{ M}^{-1}$

$K_a = (7.9 \pm 0.3) \times 10^6 \text{ M}^{-1}$

$K_a = (1.6 \pm 0.1) \times 10^7 \text{ M}^{-1}$

$K_a = (8.7 \pm 0.6) \times 10^6 \text{ M}^{-1}$
Supporting information

$K_a = (9.6 \pm 1.1) \times 10^6 \text{ M}^{-1}$

$\lambda_{ex} = 376 \text{ nm}$

$\lambda_{em} = 342 \text{ nm}$

$K_a = (7.0 \pm 1.0) \times 10^6 \text{ M}^{-1}$

$\lambda_{ex} = 376 \text{ nm}$

$\lambda_{em} = 342 \text{ nm}$

$K_a = (9.5 \pm 1.2) \times 10^6 \text{ M}^{-1}$

$\lambda_{ex} = 335 \text{ nm}$

$\lambda_{em} = 376 \text{ nm}$

$K_a = (7.2 \pm 0.9) \times 10^6 \text{ M}^{-1}$

$\lambda_{ex} = 280 \text{ nm}$

$\lambda_{em} = 342 \text{ nm}$

$K_a = (7.80 \pm 4.79) \times 10^6 \text{ M}^{-1}$
2-Hydroxy-3-methylbutanoic Acid, $\mu$M
$\lambda_{ex} = 280$ nm
Normalized Fl. Intensity

$A = 4.71$ folds

$\lambda_{ex} = 335$ nm

$A = 8.63$ folds

$K_a = (1.1 \pm 0.1) \times 10^7$ M$^{-1}$

$\lambda_{em} = 342$ nm

$K_a = (1.9 \pm 0.2) \times 10^7$ M$^{-1}$

(D)-Phenyllactic Acid, $\mu$M

(L)-Phenyllactic Acid, $\mu$M
\[ K_a = (1.4 \pm 0.1) \times 10^7 \text{ M}^{-1} \]

\[ \lambda_{\text{ex}} = 335 \text{ nm} \]

\[ \lambda_{\text{em}} = 376 \text{ nm} \]

\[ \Delta = 4.20 \text{ folds} \]

\[ \Delta = 4.57 \text{ folds} \]

\[ \lambda_{\text{ex}} = 280 \text{ nm} \]

\[ \lambda_{\text{ex}} = 335 \text{ nm} \]
Supporting information

![Graph of 2-Hydroxy-3-methylbutanoic Acid](image)

![Graph of Mandelic acid](image)

![Graph of Lactic acid](image)

![Graph of Phenyllactic Acid](image)
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%.
Supporting information

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

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.
**Supporting information**

**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.
Supplemental References