Fluorescent and cooperative ion pair receptor based on tolan for Na\(^+\) (or Li\(^+\)) and HSO\(_4^-\): logic AND gate

June-Ho Shin, Jung-Ho Hong, Min-Sung Ko, and Dong-Gyu Cho*

Department of Chemistry, Inha University, Functional Molecule Synthesis Laboratory, Incheon 402-751, Republic of Korea

dgcho@inha.ac.kr

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1. General experimental and synthetic details

General experimental

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields of synthesized compounds were measured after chromatographic purification. UV-vis spectra were recorded on a UV 1800 (Shimadzu) spectrophotometer. Proton and $^{13}$C-NMR spectra were measured at 25 ºC using Jeol 400 instruments.

Synthetic Details

2,2'-(phenylazanediyl)bis(ethan-1-ol) (1)

In a round-bottom flask fitted with a reflux condenser, 2-iodoaniline (1 g, 2.56 mmol), CaCO$_3$ (0.9 g, 5.12 mmol), KI (90 mg, 0.26 mmol), and water (6 mL) were charged. The resulting solution was then stirred at reflux for 12 h. After cooling to room temperature, the mixture was filtered and then the solution was extracted with water and EtOAc. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and then filtered; the filtrate was concentrated under reduced pressure to obtain the residue. The residue was purified over silica gel to afford 1 (250 mg, 54%).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.86 (d, $J = 9.4$ Hz, 1H), 7.39 – 7.32 (m, 1H), 7.28 (dd, $J = 8.0$, 1.7 Hz, 1H), 6.92 (ddd, $J = 8.0$, 7.2, 1.7 Hz, 1H), 3.59 (m, 4H), 3.19 (m, $J = 9.5$ Hz, 4H), 2.47 (s, 2H), $^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 151.71, 139.69, 129.87, 127.92, 126.23, 102.86, 60.02, 57.94, HRMS–EI: m/z [M]$^+$ calcd for C$_{10}$H$_{14}$NO$_2$I: 307.0069; found:307.0070.

13-(2-iodophenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (2)

In a round-bottom flask fitted with a reflux condenser, compound 1 (0.5 g, 1.63 mmol) and di-tosylate (0.60 g, 1.30 mmol) were dissolved in THF (40 mL). NaH (0.31 g, 13.04 mmol) was slowly added to the mixture, which was then stirred at reflux for 3 days. After cooling to room temperature, the solution was concentrated under reduced pressure to afford a residue. The residue was extracted with water and EtOAc. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and then filtered; the filtrate was concentrated under reduced pressure to obtain the residue. The residue was purified over silica gel to afford 2 (137 mg, 20%).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.82 (dd, $J = 7.9$, 1.4 Hz, 1H), 7.33 – 7.25 (m, 2H), 6.77 (ddd, $J = 7.9$, 6.7, 2.1 Hz, 1H), 3.69 (s, 4H), 3.68 – 3.58 (m, 12H), 3.38 (t, $J = 6.2$ Hz, 4H), $^{13}$C NMR (101 MHz, CHLOROFORM-D) δ 152.92, 139.99, 128.91, 125.85, 125.40, 100.83, 70.95, 70.73, 70.57, 70.45, 54.47, HRMS–EI: m/z [M]$^+$ calcd for C$_{16}$H$_{24}$NO$_4$I: 421.0750; found:421.0751.

1-(2-((2-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)phenyl)ethynyl)phenyl)-3-hexylurea (4)

3a (160 mg, 0.712 mmol) and tributyltin methoxide (0.056 mL, 0.024 mmol) were charged in a pressure bottle. The solution was stirred at 120 ºC for 4 h. The resulting solution of 3b was used without purification. To a well stirred solution of 2 (200 mg, 0.475 mmol) in DMF (4 mL), Pd(PPh$_3$)$_4$ (37 mg, 0.0475 mmol) and the solution of 3b was added and then flushed with argon for 5-10 min. The solution was stirred at 70 ºC for 5h. After cooling to room temperature, the solution was concentrated under reduced pressure to afford a residue. The residue was extracted with water and EtOAc. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and then filtered; the filtrate was concentrated under reduced pressure to obtain the residue. The residue was purified over silica gel to afford 4 (66 mg, 26%).

$^1$H NMR (400 MHz, Acetone-d$_6$) δ 8.24 (dd, $J = 8.5$, 1.2 Hz, 1H), 7.69 (s, 1H), 7.44 (ddd, $J = 7.7$, 1.6, 0.5 Hz, 1H), 7.41 (dd, $J = 7.7$, 1.7 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.08 (dd, $J = 8.5$, 1.1 Hz, 1H), 6.93 (td, $J = 7.6$, 1.2 Hz, 1H), 6.83 (td, $J = 7.4$, 1.1 Hz, 1H), 6.41 (s, 1H), 3.78 – 3.63 (m, 8H), 3.60 – 3.49 (m, 12H), 3.19 (td, $J = 7.0$, 5.7 Hz, 2H), 1.57 – 1.42 (m, 2H), 1.38 – 1.21 (m, 6H), 0.85 (t, $J = 7.0$ Hz, 3H), $^{13}$C NMR (101 MHz, ACETONE-D$_6$) δ 155.73, 153.11, 142.23, 136.10, 142.23, 136.10, 132.76, 130.45, 129.89, 122.08, 120.62, 119.97, 119.67, 114.67, 112.73, 96.15, 90.26, 71.76, 71.11, 70.75, 54.07, 40.62, 40.50, 32.44, 31.03, 27.46, 23.39, 14.42, HRMS–EI: m/z [M]$^+$ calcd for C$_{31}$H$_{43}$N$_3$O$_5$: 537.3203; found: 537.3201.
2. Spectroscopic titrations

Stock solutions of all of the compounds studied were made up in CH$_3$CN with the final concentrations being between $2.0 \times 10^{-5}$ M. ACS grade solvents were purchased and used without purification. The stock solutions were appropriately diluted with the solvents for the ensuing studies.

Binding Constants by UV-vis titrations

Upon addition of incremental amounts of anions to the solution of receptor 4, absorbance change of 4 ($2.0 \times 10^{-5}$ M of 4 was used, unless otherwise stated) were recorded in CH$_3$CN. Equilibrium constants of complexes were calculated using the equation, $y = (b \times x)/(1 + x \times K)$, where $x = [G]$, $y = A - A_o$ ($A$ is the absorbance of the solution of 4 at a certain concentration of anions and $A_o$ is the absorbance of the solution of 4 without anions).

Binding constants by fluorescent titrations

Upon addition of incremental amounts of anion to the solution of receptor 4, fluorescence change of each chemosensor ($2.0 \times 10^{-5}$ M) were recorded in CH$_3$CN by irradiating the solution at $\lambda_{ex} = 340$ nm. Equilibrium constants of complexes were calculated using the equation below.

$$y = \frac{1 + b \times x \times K}{1 + x \times K},$$

where $x = [G]$, $y = F/F_o$ ($F$ intensity at a certain concentration of anions/$F_o$ intensity without anions).

The observed fluorescent intensities were shown below at a various concentrations of 4 in CH$_3$CN at 420nm.

![Fluorescent titration graph](image)

Binding Constants by $^1$H NMR titrations

Upon addition of incremental amounts of anions to the solution of receptor 4, chemical shift change of 4 ($4$ mM of 4 was used, unless otherwise stated) were recorded in CD$_2$CN. Equilibrium constants of complexes were calculated using the equation, $y = (b \times x)/(1 + x \times K)$, where $x = [G]$, $y = \delta - \delta_o$ ($\delta$ is a chemical shift of 4 at a certain concentration of anions and $\delta_o$ is a chemical shift of 4 without anions).
$\text{Cl}^-$

Graph 1: Absorbance vs. Wavelength (nm)

Graph 2: Fluorescence Intensity vs. Wavelength (nm)

Graph 3: $\Delta S$ (ppm) vs. [Q]

Equation: $y = \beta_0 + \beta_1 x$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_0$</td>
<td>58.05</td>
<td>7.73979</td>
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<tr>
<td>$\beta_1$</td>
<td>91.23</td>
<td>2.52955</td>
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</table>
**BzO⁻**

![Fluorescence intensity vs. Wavelength (nm)](image1)

![Absorbance vs. Wavelength (nm)](image2)
**H$_2$PO$_4^-$**
HSO₄⁻
\[ \Delta S (\text{ppm}) \]

Equation: \[ y = (b_2x^2 + b_1x + b_0) \]

<table>
<thead>
<tr>
<th>( b )</th>
<th>Value</th>
<th>Standard Err</th>
</tr>
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<tr>
<td>( k )</td>
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<td>( 2.778 )</td>
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<tr>
<td>( b )</td>
<td>( 2.953 )</td>
<td>( 0.170 )</td>
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</table>

**Li\(^+\)ClO\(_4\)^-**

**Absorbance**

Equation: \[ y = (b_2x^2 + b_1x + b_0) \]

<table>
<thead>
<tr>
<th>( b )</th>
<th>Value</th>
<th>Standard Err</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k )</td>
<td>( 524 )</td>
<td>( 15.9 )</td>
</tr>
<tr>
<td>( b )</td>
<td>( 0.562 )</td>
<td>( 0.007 )</td>
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</table>

**Fluorescence Intensity**

Equation: \[ y = (b_2x^2 + b_1x + b_0) \]

<table>
<thead>
<tr>
<th>( b )</th>
<th>Value</th>
<th>Standard Err</th>
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</thead>
<tbody>
<tr>
<td>( k )</td>
<td>( 982.54 )</td>
<td>( 136 )</td>
</tr>
<tr>
<td>( b )</td>
<td>( 0.3055 )</td>
<td>( 0.007 )</td>
</tr>
</tbody>
</table>
NaHSO₄
KHSO₄
Job Plot for $4\cdot\text{M}^+\text{HSO}_4^-$

Figure S1. Job plots for LiHSO$_4$ obtained by UV-vis titrations

Figure S2. Job plots for NaHSO$_4$ obtained by a) UV-vis titrations b) fluorescent titrations
**Figure S3.** Job plots for KHSO$_4$ obtained by UV-vis titrations

**Figure S4.** UV-vis spectra changes of 4 (20 μM in CH$_3$CN) were recorded upon the addition of various anions (10 equiv.) in the presence of Na$^+$ (4 equiv.) at 25 °C.
Figure S5. Fluorescent changes of 4 (20 μM in CH$_3$CN) Upon the addition of various amount of HSO$_4^-$ at 25 °C.
Figure S6. Fluorescent changes of 4 (20 μM in CH₂Cl₂) after the extraction of various inorganic salts (excess amount of solid salts) with the solution at 25 °C.
Figure S7. Partial $^1$H-NMR spectra recorded during the titration of 4 ([H] = 4.0 × 10^{-3} M in CD$_3$CN) with LiBPh$_4$ in the presence of 1 equiv. of TBA·HSO$_4$.
Figure S8. (a) $^1$H-NMR spectra of 4 and 4 containing NaHSO$_4$ after the extraction of solid NaHSO$_4$ with 4 (4 mM in CD$_3$CN) (b) left (4 + NaHSO$_4$) and right (only 4) under a laboratory hand-held UV light.
Figure S9. Evolution of the fluorescent spectrum of 4 (2.0 × 10^{-5} M in CH_{3}CN containing 4 equiv. of Na^+ and HSO_4^- during the titration with water (from 0 – 6%)
Figure S10. (a) Evolution of the fluorescent spectrum of 4 (2.0 × 10⁻⁵ M in CH₃CN containing 1% water and 32 equiv. of Na⁺) during the titration with tetrabutylammonium HSO₄⁻ (TBA·HSO₄; 0 – 6.4 equiv.) (b) The fluorescent intensities of 4 at 422 nm vs equiv. of HSO₄⁻ obtained from Figure S10a.
3. DFT calculation

**Figure S11.** Optimized structures of $\mathbf{4} \cdot \text{KHSO}_4$ based on DFT methods at the EDF2/6–31G* level of theory. Bond distances were denoted and all of hydrogen atoms are omitted for clarity.

**Figure S12.** Optimized structures of $\mathbf{4} \cdot \text{NaHSO}_4$ based on DFT methods at the EDF2/6–31G* level of theory. Bond distances were denoted and all of hydrogen atoms are omitted for clarity.

**Figure S13.** Optimized structures of $\mathbf{4} \cdot \text{LiHSO}_4$ based on DFT methods at the EDF2/6–31G* level of theory. Bond distances were denoted and all of hydrogen atoms are omitted for clarity.
Figure S14. Optimized structures of 4·NaCl based on DFT methods at the EDF2/6–31G* level of theory. Bond distances were denoted and all of hydrogen atoms are omitted for clarity.

Figure S15. Optimized structures of 4·H$_2$PO$_4$ based on DFT methods at the EDF2/6–31G* level of theory. Bond distances were denoted and all of hydrogen atoms are omitted for clarity.
4. Quantum Yields

Table S1. Summarized slopes and the relative quantum yields of 4 from those of coumarin 120.

<table>
<thead>
<tr>
<th></th>
<th>Slop in CH(_2)Cl(_2)</th>
<th>Slop in CH(_3)CN</th>
<th>Q* in CH(_2)Cl(_2)</th>
<th>Q* in CH(_3)CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2.96133E+6</td>
<td>3.00872E+6</td>
<td>0.558 (56%)</td>
<td>0.392 (39%)</td>
</tr>
<tr>
<td>Coumarin 120</td>
<td>4.35014E+6</td>
<td>4.68023E+6</td>
<td>0.82 (82%)</td>
<td>0.61 (61%)</td>
</tr>
</tbody>
</table>

Q* denotes quantum yields.

Figure S16. Plots of absorbance against the area under the fluorescence curve of 4. a) In CH\(_2\)Cl\(_2\). b) In CH\(_3\)CN.
5. NMR Spectra

$^1$H NMR spectrum of 1 recorded in CDCl$_3$
$^{13}$C NMR spectrum of 1 recorded in CDCl$_3$
$^1$H NMR spectrum of 2 recorded in CDCl$_3$
$^{13}$C NMR spectrum of 2 recorded in CDCl$_3$
$^1$H NMR spectrum of 4 recorded in Acetone-$d_6$. 

[Image of the NMR spectrum and chemical structure of 4]
$^1$H NMR spectrum of 4 recorded in Acetone-$d_6$. 

[Chemical structure image]

Acetone-$d_6$