Supporting Information

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1. Synthesis and characterization of F-azo-COOH

Materials. Solvent and starting materials were used as received. α-CD (Energy, 98%), β-CD (Aladdin, 98%), 2,6-difluoroaniline (Energy, 99%), copper (I) cyanide (Aladdin, 99%) were used as received. All other chemicals were of analytical reagent grade and purchased from Sinopharm. Compounds 1a-3 were synthesized according to previous reports. \(^1\)

Scheme 1. Synthetic Procedures of F-azo-COOH.

\[ \begin{align*}
1 & \xrightarrow{\text{Br}_2, \text{acetic acid}} 1b \\
1a & \xrightarrow{\text{CuCN, DMF}} 1b \\
& \xrightarrow{\text{NaOH}} 1c \\
2 & \xrightarrow{\text{C}_2\text{H}_2\text{O}, \text{H}_2\text{SO}_4} \\
& \xrightarrow{\text{FeSO}_4\cdot7\text{H}_2\text{O}, \text{K}_2\text{MnO}_4, \text{CH}_2\text{Cl}_2} 3 \\
& \xrightarrow{1\text{M NaOH, THF, RT}} \text{F-azo-COOH}
\end{align*} \]

**Figure S1.** \(^1\)H NMR spectrum (500 MHz, 298 K, DMSO-d\(_6\)) of F-azo-COOH in 10 mM Na\(_2\)CO\(_3\) aqueous solution.
**Figure S2.** $^{13}$C NMR spectrum (500 MHz, 298 K, D$_2$O) of F-azo-COOH in 10 mM Na$_2$CO$_3$ aqueous solution.

**Figure S3.** $^{19}$F NMR spectrum (400 MHz, 298 K, D$_2$O) of F-azo-COOH in 10 mM Na$_2$CO$_3$ aqueous solution. The $^{19}$F NMR spectrum showed two signals at -121.83 and -119.88 ppm that were assigned to the *trans* and *cis* isomers, respectively.
2. NMR spectra of F-azo-COOH under irradiation with green and blue light

Figure S4. $^1$H NMR spectra (500 MHz, 298 K, D$_2$O) of (a) F-azo-COOH ($trans:cis = 95:5$) in 10 mM Na$_2$CO$_3$ aqueous solution, (b) irradiation with green light for 10 min until the photostationary state ($trans:cis = 16:84$) was reached, (c) then with blue light for 8 min until the photostationary state ($trans:cis = 69:31$) was reached.
3. Partial ROESY spectrum of the mixture of F-azo-COOH and α-CD after irradiation with green light

**Figure S5.** Partial ROESY spectrum (500 MHz, 298 K, D₂O) of the mixture of F-azo-COOH (5 mM) and α-CD (1:1 molar ratio) in 10 mM Na₂CO₃ aqueous solution after irradiation with green light for 10 min. The NOE signals were undetectable between *cis*-F-azo-COOH and α-CD.
4. Partial ROESY spectrum of the mixture of F-azo-COOH and \( \beta \)-CD after irradiation with green light

**Figure S6.** Partial 2D ROESY spectra (500 MHz, 298 K, D\(_2\)O, 5 mM) of the mixture of F-azo-COOH and \( \beta \)-CD (1:1 molar ratio) in 10 mM Na\(_2\)CO\(_3\) aqueous solution after irradiation with green light. This spectra was obtained from magnifying the ROE signals in figure 5B.
5. \(^1\)H NMR spectra in \(\alpha\)-CD part of F-azo-COOH in the presence of various concentrations of \(\alpha\)-CD

\begin{tabular}{cccc}
\hline
\(\alpha\)-CD/F-azo-COOH & H3 & H2 & H1 \\
(\text{mM/mM}) & & & \\
\hline
10:1 & & & \\
8:1 & & & \\
6:1 & & & \\
4:1 & & & \\
2:1 & & & \\
\hline
\end{tabular}

**Figure S7.** \(^1\)H NMR spectra (500 MHz, 298 K, D\(_2\)O) in \(\alpha\)-CD part of 1.0 mM F-azo-COOH in the presence of various concentrations of \(\alpha\)-CD in 10 mM Na\(_2\)CO\(_3\) aqueous solution. The H-5 resonance of \(\alpha\)-CD remains unchanged upon increasing the concentration of \(\alpha\)-CD, indicating that trans-F-azo-COOH molecule was then believed to be inserted shallowly in the cavity of \(\alpha\)-CD.
6. $^1$H NMR spectra in $\alpha$-CD part of F-azo-COOH in the presence of various concentrations of $\alpha$-CD after irradiation with green light

$\alpha$-CD/cis-F-azo-COOH (mM/mM)

- 10:1
- 8:1
- 6:1
- 4:1
- 2:1

Figure S8. $^1$H NMR spectra (500 MHz, 298 K, D$_2$O) in $\alpha$-CD part of 1.0 mM F-azo-COOH in the presence of various concentrations of $\alpha$-CD in 10 mM Na$_2$CO$_3$ aqueous solution after irradiation with green light.
7. $^1$H NMR spectra in $\beta$-CD part of F-azo-COOH in the presence of various concentrations of $\beta$-CD

$\beta$-CD/F-azo-COOH

(mM/mM)

$\begin{array}{cccc}
14:1 \\
12:1 \\
10:1 \\
8:1 \\
6:1 \\
4:1 \\
2:1 \\
\end{array}$

Figure S9. $^1$H NMR spectra (500 MHz, 298 K, D$_2$O) in $\beta$-CD part of 1.0 mM F-azo-COOH in the presence of various concentrations of $\beta$-CD in 10 mM Na$_2$CO$_3$ aqueous solution. The $^1$H NMR signals for the inner C3 protons of $\beta$-CD unchanged at the concentration >10 mM.
8. $^1$H NMR spectra in $\beta$-CD part of F-azo-COOH in the presence of various concentrations of $\beta$-CD after irradiation with green light

$\beta$-CD/cis-F-azo-COOH

(mM/mM)

Figure S10. $^1$H NMR spectra (500 MHz, 298 K, D$_2$O) in $\beta$-CD part of 1.0 mM F-azo-COOH in the presence of various concentrations of $\beta$-CD in 10 mM Na$_2$CO$_3$ aqueous solution after irradiation with green light.
9. $^1$H NMR spectra (500 MHz, D$_2$O) of 1.0 mM F-azo-COOH in the presence of various concentrations of $\alpha$-and $\beta$-CD after irradiation with green light and Benesi-Hildebrand plot$^2$

![Figure S11](image)

$^1$H NMR spectra (500 MHz, 298 K, D$_2$O) of 1.0 mM F-azo-COOH in the presence of various concentrations of $\alpha$- and $\beta$-CD in 10 mM Na$_2$CO$_3$ aqueous solution after irradiation with green light (A and B) and Benesi-Hildebrand plot of $1/\Delta\delta_{obs}$ against $1/[\alpha$-CD] and $1/[\beta$-CD], respectively (C and D). $C_{CD}$: (a) 0, (b) 2, (c) 4, (d) 6, (e) 8 and (f) 10 mM.

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**Figure S11.** $^1$H NMR spectra (500 MHz, 298 K, D$_2$O) of 1.0 mM F-azo-COOH in the presence of various concentrations of $\alpha$- and $\beta$-CD in 10 mM Na$_2$CO$_3$ aqueous solution after irradiation with green light (A and B) and Benesi-Hildebrand plot of $1/\Delta\delta_{obs}$ against $1/[\alpha$-CD] and $1/[\beta$-CD], respectively (C and D). $C_{CD}$: (a) 0, (b) 2, (c) 4, (d) 6, (e) 8 and (f) 10 mM.
10. Benesi-Hildebrand plot\(^2\) of all complexes

![Benesi-Hildebrand plots](image)

**Figure S12.** Benesi-Hildebrand plot (A) of \(1/\Delta\delta_{\text{obs}}\) (trans-F-azo-COOH) against \(1/[^{\alpha}-\text{CD}]\); B) of \(1/\Delta\delta_{\text{obs}}\) (trans-F-azo-COOH) against \(1/[^{\beta}-\text{CD}]\); C) of \(1/\Delta\delta_{\text{obs}}\) (cis-F-azo-COOH) against \(1/[^{\alpha}-\text{CD}]\) and D) of \(1/\Delta\delta_{\text{obs}}\) (cis-F-azo-COOH) against \(1/[^{\beta}-\text{CD}]\).

**Table S1.** The data of detected association constant \((K)\) of trans-F-azo-COOH/\(^{\alpha}-\text{CD}\)

<table>
<thead>
<tr>
<th>(K) (M(^{-1}))</th>
<th>(K)-AVG (M(^{-1}))</th>
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<tbody>
<tr>
<td>1</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>51</td>
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<td>3</td>
<td>42</td>
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<td>50 ± 7</td>
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**Table S2.** The data of detected association constant \((K)\) of cis-F-azo-COOH/\(^{\alpha}-\text{CD}\)

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<th>(K)-AVG (M(^{-1}))</th>
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<tr>
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<td>2</td>
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<td>3</td>
<td>33</td>
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<td>29 ± 7</td>
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**Table S3.** The data of detected association constant \((K)\) of trans-F-azo-COOH/\(^{\beta}-\text{CD}\)
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<th>$K$-AVG (M$^{-1}$)</th>
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<tr>
<td>1</td>
<td>$1.84 \times 10^3$</td>
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<tr>
<td>2</td>
<td>$2.18 \times 10^3$</td>
<td>$2.1 \pm 0.2 \times 10^3$</td>
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<tr>
<td>3</td>
<td>$2.19 \times 10^3$</td>
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**Table S4.** The data of detected association constant ($K$) of $cisis$-F-azo-COOH/$\beta$-CD

<table>
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<th>$K$-AVG (M$^{-1}$)</th>
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<tbody>
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<tr>
<td>2</td>
<td>$2.9 \times 10^3$</td>
<td>$3.0 \pm 0.3 \times 10^3$</td>
</tr>
<tr>
<td>3</td>
<td>$3.4 \times 10^3$</td>
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</tr>
</tbody>
</table>

11. ICD and UV-vis spectra of $5 \times 10^{-5}$ M F-azo-COOH in the presence of 10 mM
$\alpha$-CD before and after irradiation with green light

**Figure S13.** ICD and UV-vis spectra of $5 \times 10^{-5}$ M F-azo-COOH in the presence of 10 mM $\alpha$-CD before (black line) and after irradiation with green light for 10 min (green line) measured in 10 mM Na$_2$CO$_3$ aqueous solution at room temperature.

**Reference:**