Supporting Information

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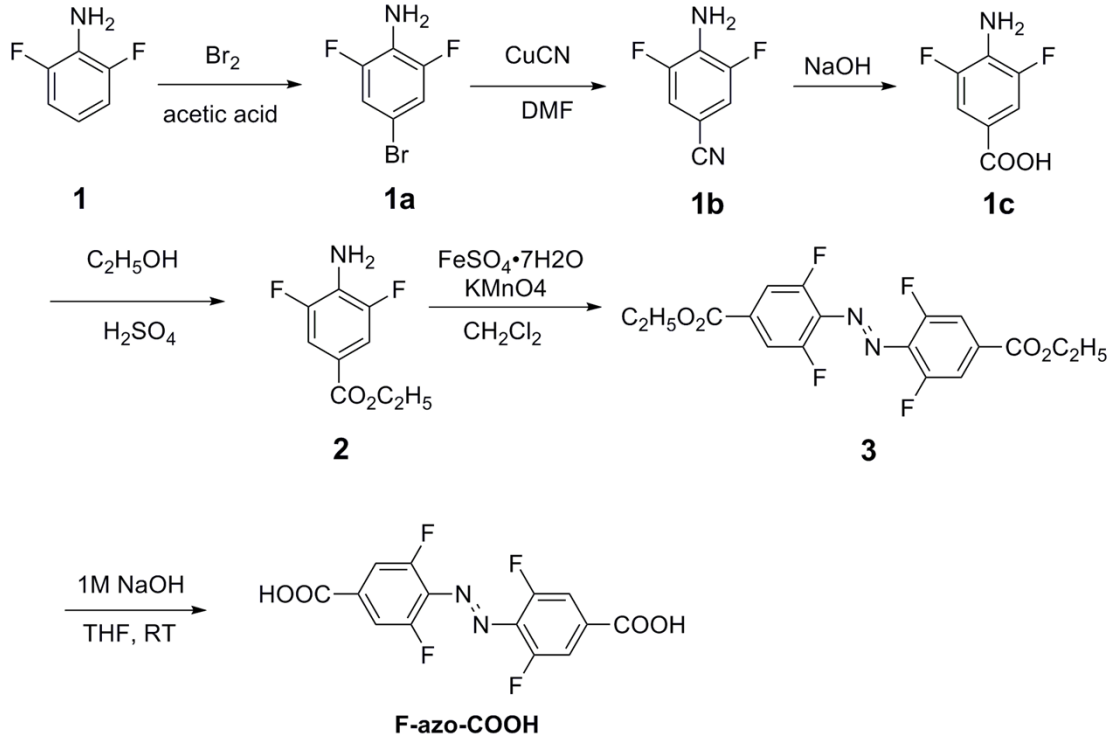
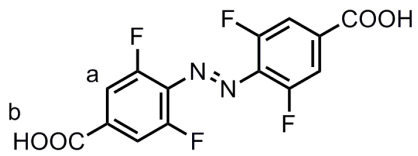
1. Synthesis and characterization of F-azo-COOH[1]

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.





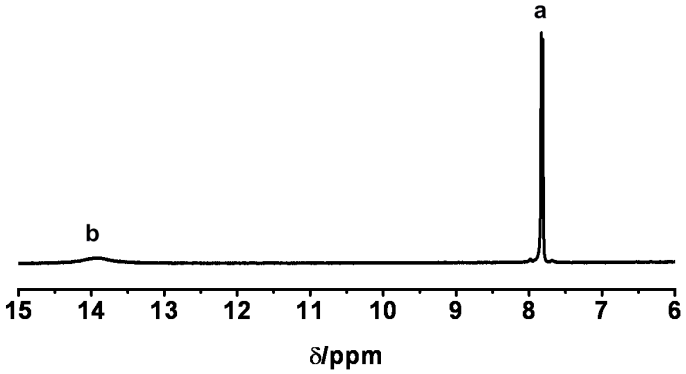


Figure S1. ^{1}H NMR spectrum (500 MHz, 298 K, DMSO-d_6) of F-azo-COOH in 10 mM Na_2CO_3 aqueous solution.

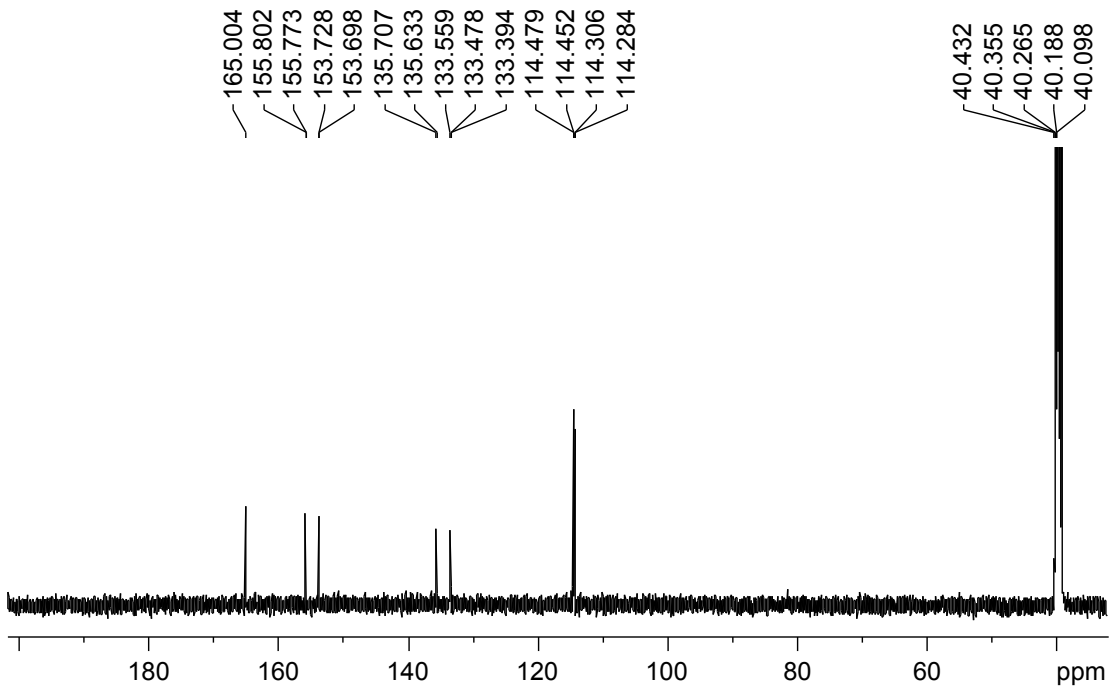


Figure S2. ^{13}C NMR spectrum (500 MHz, 298 K, D_2O) of F-azo-COOH in 10 mM Na_2CO_3 aqueous solution.

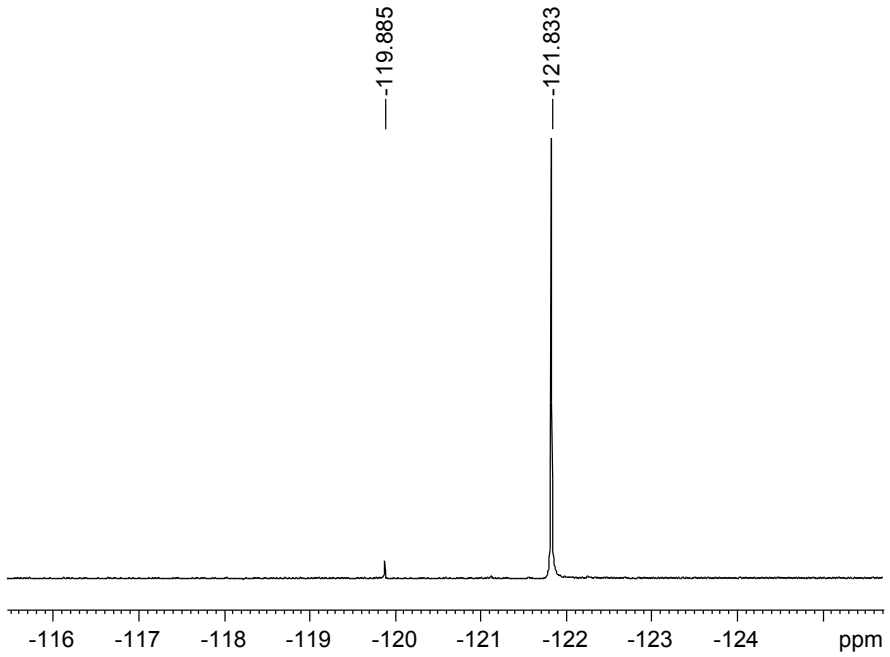


Figure S3. ^{19}F NMR spectrum (400 MHz, 298 K, D_2O) of F-azo-COOH in 10 mM Na_2CO_3 aqueous solution. The ^{19}F NMR spectrum showed two signals at -121.83 and -119.88 ppm that were assigned to the *trans* and *cis* isomers, respectively.

2. NMR spectra of F-azo-COOH under irradiation with green and blue light

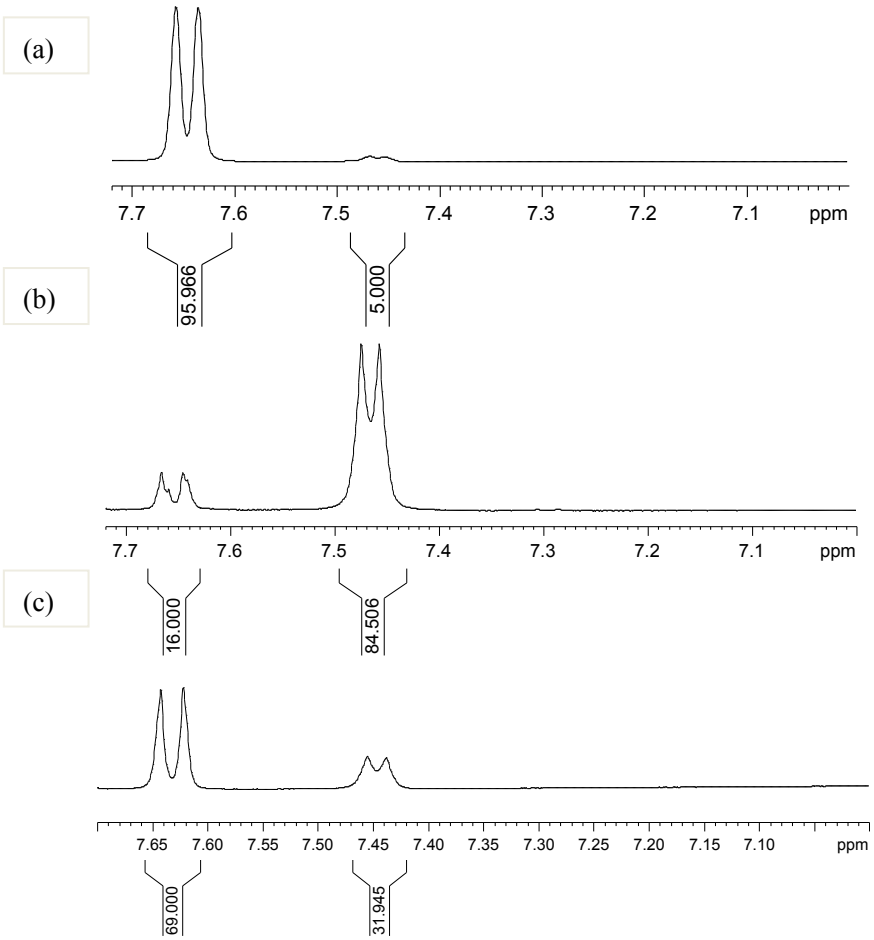


Figure S4. ^{1}H NMR spectra (500 MHz, 298 K, D_2O) of (a) F-azo-COOH (*trans*:*cis* = 95:5) in 10 mM Na_2CO_3 aqueous solution, (b) irradiation with green light for 10 min until the photostationary state (*trans*:*cis* = 16:84) was reached, (c) then with blue light for 8 min until the photostationary 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

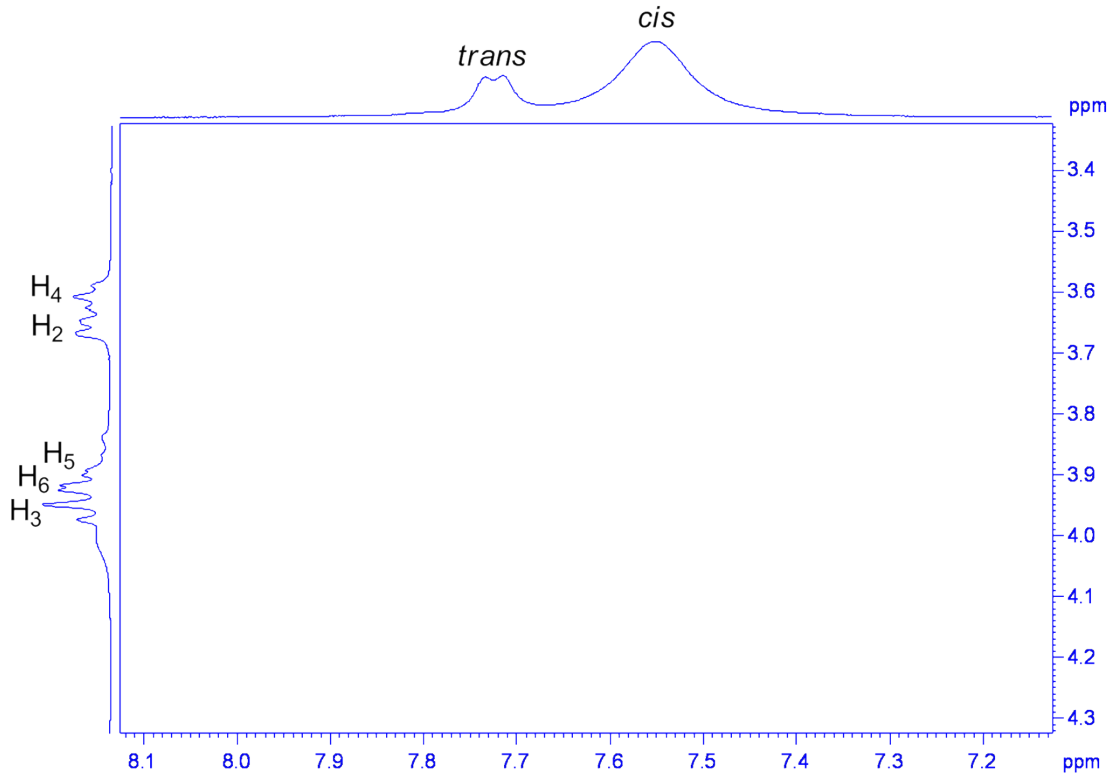


Figure S5. Partial ROESY spectrum (500 MHz, 298 K, D_2O) of the mixture of F-azo-COOH (5 mM) and *α*-CD (1:1 molar ratio) in 10 mM Na_2CO_3 aqueous solution after irradiation with green light for 10 min. The NOE signals were undetectable between *cis*-F-azo-COOH and *α*-CD.

4. Partial ROESY spectrum of the mixture of F-azo-COOH and *β*-CD after irradiation with green light

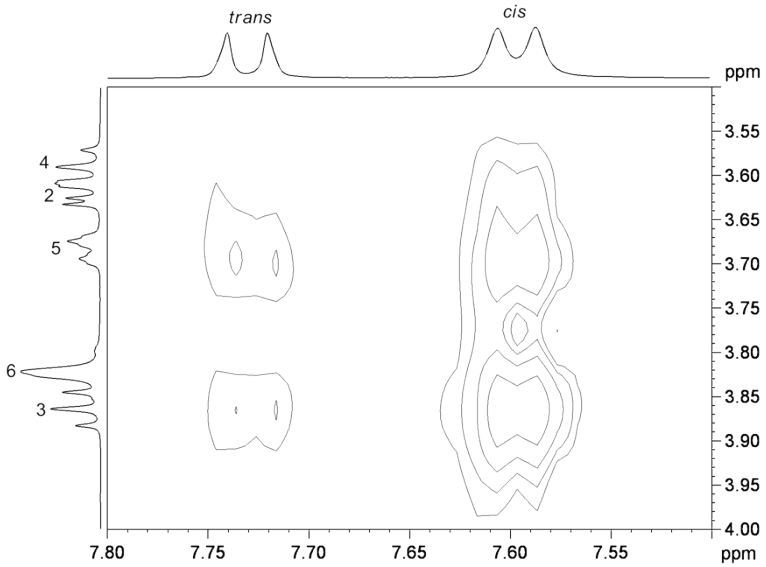


Figure S6. Partial 2D ROESY spectra (500 MHz, 298 K,D_2O,5 mM) of the mixture of F-azo-COOH and *β*-CD (1:1 molar ratio) in 10 mM Na_2CO_3 aqueous solution after irradiation with green light. This spectra was obtained from magnifying the ROE signals in figure 5B.

5. ^{1}H NMR spectra in α-CD part of F-azo-COOH in the presence of various concentrations of α-CD

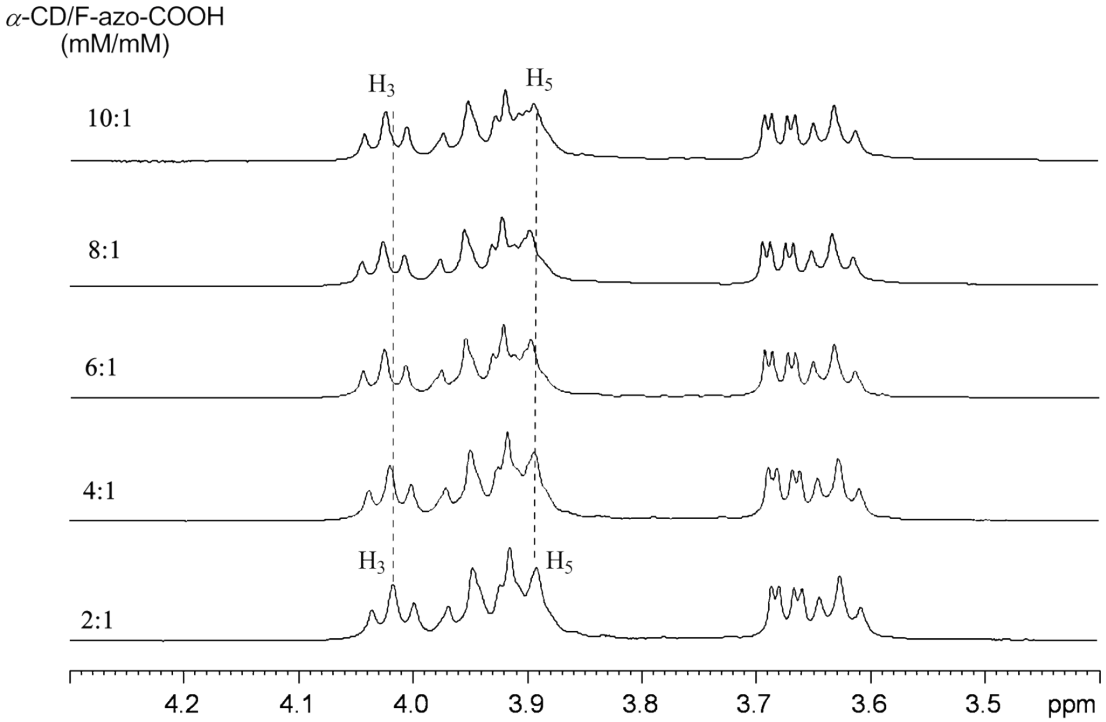


Figure S7. ^{1}H NMR spectra (500 MHz, 298 K, D_2O) in α-CD part of 1.0 mM F-azo-COOH in the presence of various concentrations of α-CD in 10 mM Na_2CO_3 aqueous solution. The H-5 resonance of α-CD remains unchanged upon increasing the concentration of α-CD, indicating that *trans*-F-azo-COOH molecule was then believed to be inserted shallowly in the cavity of α-CD.

6. ^{1}H NMR spectra in α-CD part of F-azo-COOH in the presence of various concentrations of α-CD after irradiation with green light

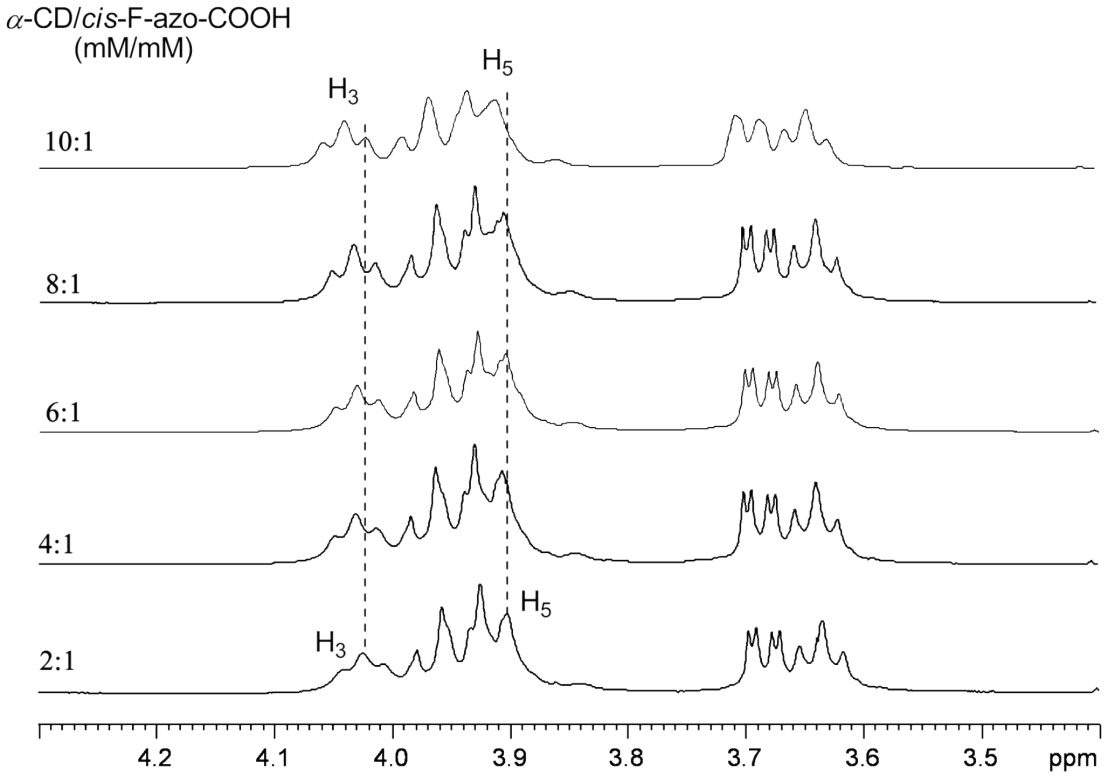


Figure S8. ^{1}H NMR spectra (500 MHz, 298 K, D_2O) in α-CD part of 1.0 mM F-azo-COOH in the presence of various concentrations of α-CD in 10 mM Na_2CO_3 aqueous solution after irradiation with green light.

7. ^{1}H NMR spectra in β-CD part of F-azo-COOH in the presence of various concentrations of β-CD

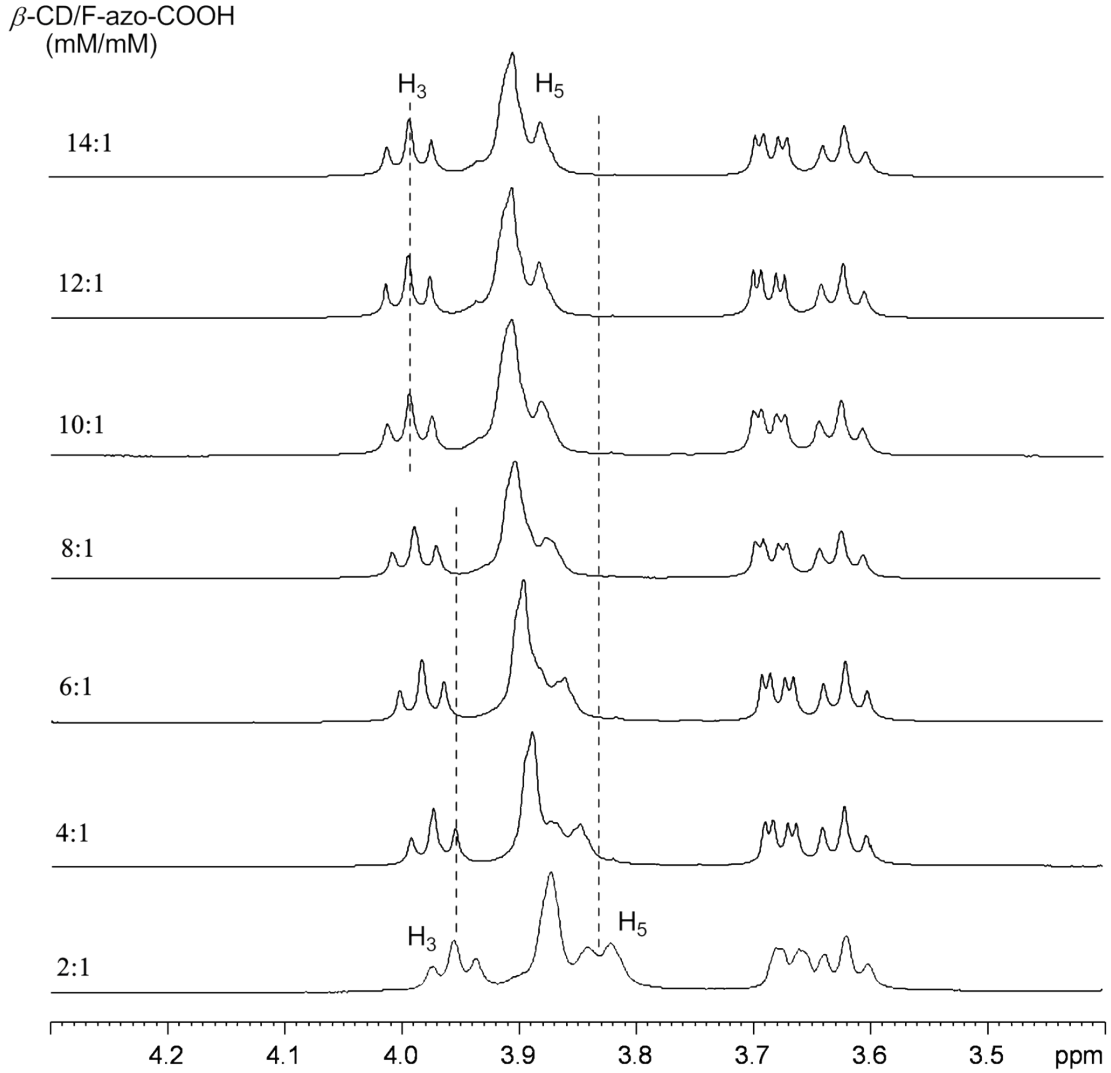


Figure S9. ^{1}H NMR spectra (500 MHz, 298 K, D_2O) in β-CD part of 1.0 mM F-azo-COOH in the presence of various concentrations of β-CD in 10 mM Na_2CO_3 aqueous solution. The ^{1}H NMR signals for the inner C3 protons of β-CD unchanged at the concentration >10 mM.

8. ^{1}H NMR spectra in *β*-CD part of F-azo-COOH in the presence of various concentrations of *β*-CD after irradiation with green light

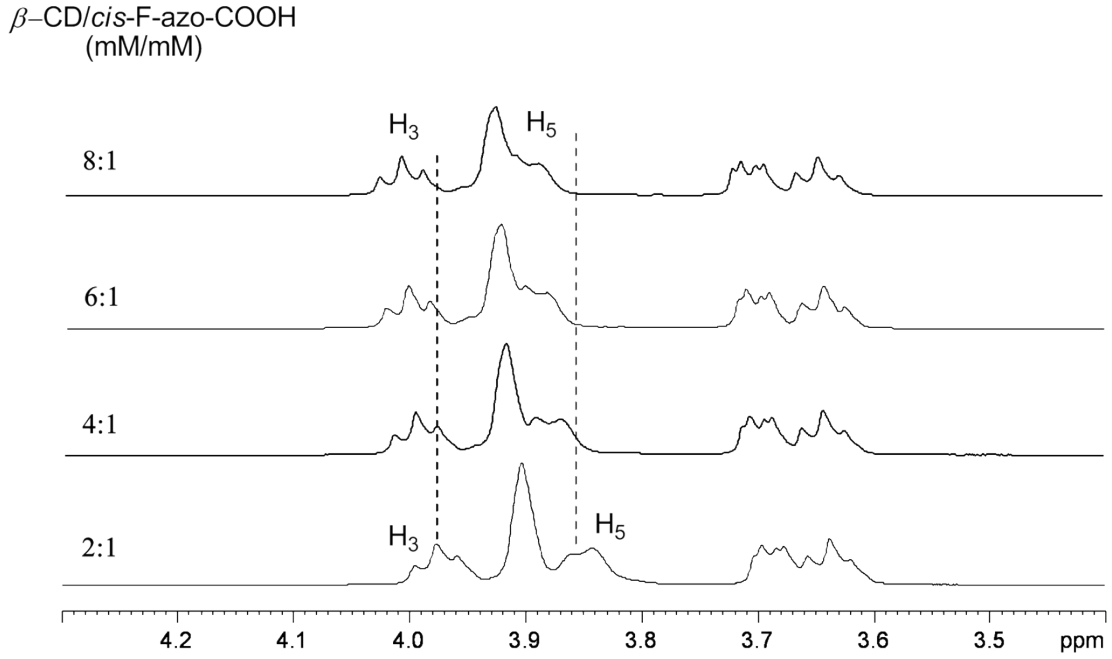


Figure S10. ^{1}H NMR spectra (500 MHz, 298 K, D_2O) in *β*-CD part of 1.0 mM F-azo-COOH in the presence of various concentrations of *β*-CD in 10 mM Na_2CO_3 aqueous solution after irradiation with green light.

9. ^{1}H NMR spectra (500 MHz, D_2O) of 1.0 mM F-azo-COOH in the presence of various concentrations of α-and β-CD after irradiation with green light and Benesi-Hildebrand plot[2]

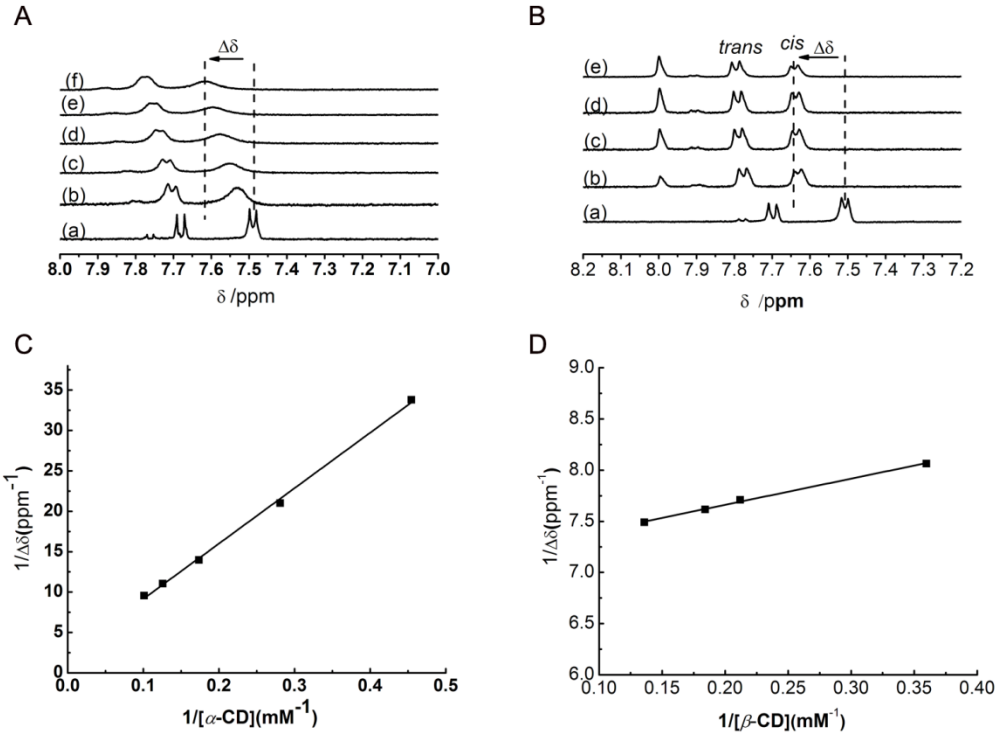


Figure S11. ^{1}H NMR spectra (500 MHz, 298 K, D_2O) of 1.0 mM F-azo-COOH in the presence of various concentrations of α- and β-CD in 10 mM Na_2CO_3 aqueous solution after irradiation with green light (A and B) and Benesi-Hildebrand plot of $1/\Delta\delta_{obs}$ against 1/[α-CD] and 1/[β-CD], respectively (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

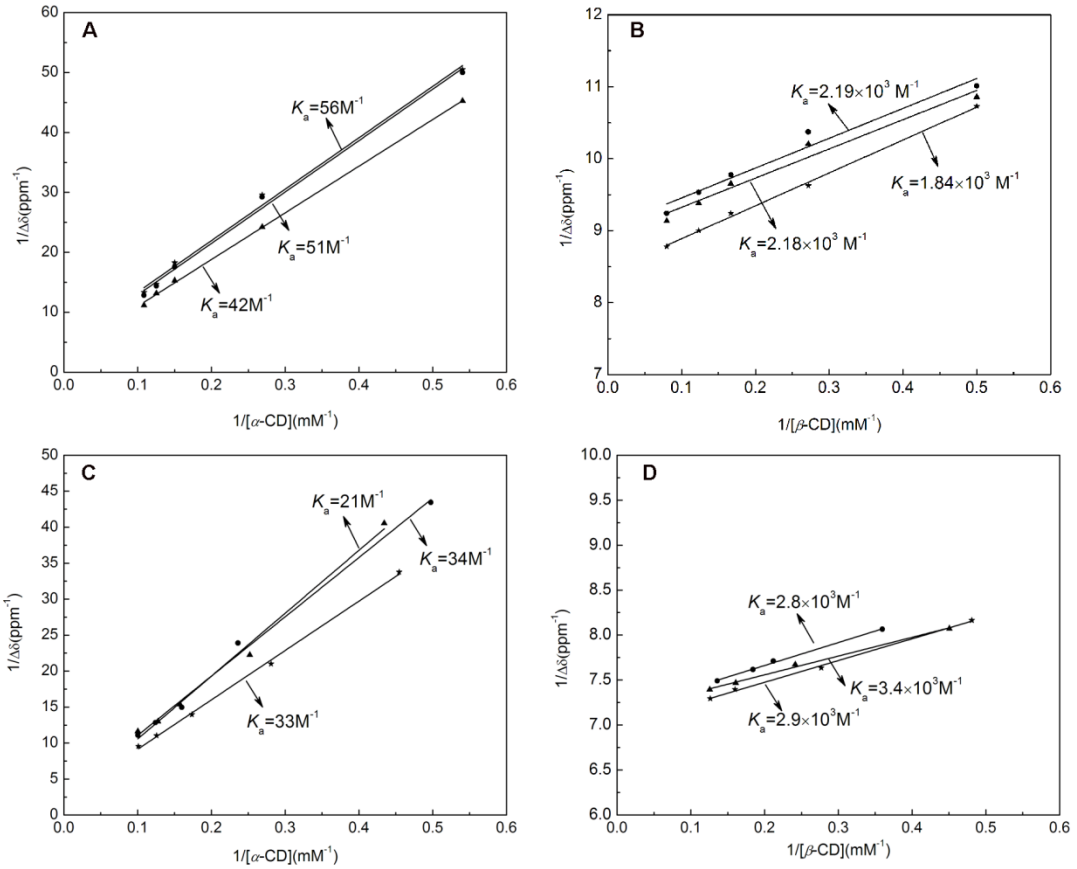


Figure S12. Benesi-Hildebrand plot (A) of $1/\Delta\delta_{obs}$ (*trans*-F-azo-COOH)against 1/[*α*-CD]; B) of $1/\Delta\delta_{obs}$ (*trans*-F-azo-COOH) against 1/[*β*-CD]; C) of $1/\Delta\delta_{obs}$ (*cis*-F-azo-COOH)against 1/[*α*-CD] and D) of $1/\Delta\delta_{obs}$ (*cis*-F-azo-COOH) against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

Table S1. The data of detected association constant (*K*) of *trans*-F-azo-COOH/*α*-CD

	K (M^{-1})	*K*-AVG (M^{-1})
1	56	50 ± 7
2	51	
3	42	

Table S2. The data of detected association constant (*K*) of *cis*-F-azo-COOH/*α*-CD

	K (M^{-1})	*K*-AVG (M^{-1})
1	21	29 ± 7
2	34	
3	33	

Table S3. The data of detected association constant (*K*) of *trans*-F-azo-COOH/*β*-CD

	K (M^{-1})	K-AVG (M^{-1})
1	1.84×10^3	$2.1 \pm 0.2 \times 10^3$
2	2.18×10^3	
3	2.19×10^3	

Table S4. The data of detected association constant (K) of *cis*-F-azo-COOH/β-CD

	K (M^{-1})	K-AVG (M^{-1})
1	2.8×10^3	$3.0 \pm 0.3 \times 10^3$
2	2.9×10^3	
3	3.4×10^3	

11. ICD and UV-vis spectra of 5×10^{-5} M F-azo-COOH in the presence of 10 mM

α-CD before and after irradiation with green light

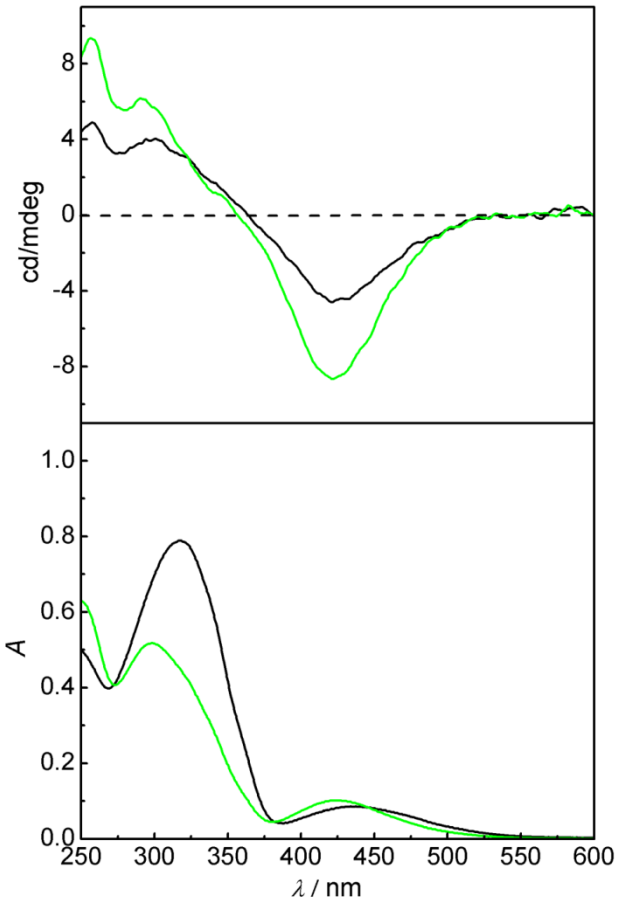


Figure S13. ICD and UV-vis spectra of 5×10^{-5} M F-azo-COOH in the presence of 10 mM α-CD before (black line) and after irradiation with green light for 10 min (green line) measured in 10 mM Na_2CO_3 aqueous solution at room temperature.

Reference:

(1) Bléger, D.; Schwarz, J.; Brouwer, A. M.; Hecht, S. *J. Am. Chem. Soc.* 2012, *134*, 20597-20600.
(2) Fielding, L. *Tetrahedron* 2000, *56*, 6151-6170.