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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Host-Guest Interaction between Fluoro-substituted Azobenzene Derivative and Cyclodextrins

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

An azobenzene derivative (F-azo-COOH) was synthesized and could be *E*/*Z* isomerized by visible light. The host-guest interaction between F-azo-COOH and cyclodextrins (CDs) in alkaline aqueous solution was studied by NMR spectroscopy for the first time. The results revealed that F-azo-COOH did not form stable host-guest complex with *α*-CD. However, both *trans*- and *cis*-F-azo-COOH could form stable 1:1 complexes with *β*-CD. Most interestingly, *cis*-F-azo-COOH could fit the cavity of *β*-CD more tightly ($3.0 \pm 0.3 \times 10^3\ M^{-1}$) than its *trans* form ($2.1 \pm 0.2 \times 10^3\ M^{-1}$), which was completely opposite to conventional azobenzene/*β*-CD system.

Introduction

Host-guest chemistry has expanded dramatically in recent years due to its potential applications in a broad range of fields.[1] Materials based on host-guest interactions are prone to external stimuli[2] and can be fabricated as drug delivery capsules,[3] sensors,[4] actuators,[5] protein probes,[6] and functional nanodevices,[7] to name a few. Among all available guest molecules, azobenzene and its derivatives own especial advantages for their responsiveness to various natural stimuli, accompanied by dramatic structural changes[8] and controlled inclusion/exclusion with cyclodextrins (CDs).[9] Owing to this unique property, azobenzene/CD system has secured a prominent role in many high technical applications, such as light-responsive hydrogels,[10] self-healing polymers,[11] and molecular devices and machines.[12] However, high energy ultraviolet (UV) is often required to trigger the isomerization of azobenzene, which brings about several drawbacks, such as low penetration to biological tissues,[13] unwanted side reactions[14] and high background interference.[15] To surmount these obstacles, tremendous efforts have been invested but great challenge still remains in pursuing *E*/*Z* isomerization of azobenzene by visible or even infrared light.

So far several prevalent methods have been reported in literatures. One approach is to use inorganic nanoparticles typically lanthanide-doped upconversion nanoparticles (UCNPs) as light converters. UCNPs can be used as an effective UV source by multiphoton absorption of near-infrared (NIR) light, which shows the deepest tissue penetration and is safe to the biological specimen.[16] Recently, Shi's group modified an azobenzene group into mesoporous silica-coated UCNPs to control the drug release by NIR light.[17] Beyond using UCNPs as the effective UV source, another approach is to alter the absorption of azobenzene by incorporating electron-donating or electron-withdrawing groups in *ortho* and *para* positions of azobenzene.[13,18] For instance, Hecht and co-workers[19] and Woolley and co-workers[20] synthesized *ortho*-fluoro-substituted and *ortho*-methoxy-substituted azobenzene derivatives, respectively. The reversible *trans-cis* photoisomerization of these azobenzene derivatives can be induced by green and blue light. Very recently, Woolley's group substituted all four *ortho* positions next to the azo group with bulky electron-rich substituents, which can be isomerized even by red light.[20b] In addition, the use of bridgehead derivatives[21] and the incorporation of metal complexes[22] have also been used to control the absorption of azobenzene, such as C2-bridged azobenzene species[21a] and BF_2-azo complex.[22b]

Despite these recent progresses, the host-guest chemistry and consequent macroscopic properties of those sterically modified azobenzene derivatives have not been exploited yet. Herein, tetra-*ortho*-fluoro-substituted azobenzene derivative (F-azo-COOH) was synthesized and could be isomerized by visible light. We first investigated the host-guest interaction between F-azo-COOH and CDs in alkaline aqueous solution by ^1H, ^{19}F, 2D ROESY NMR as well as induced circular dichroism (ICD) spectroscopy.

Experimental section

Materials and reagents

2,6-Difluoroaniline (99%) and *α*-cyclodextrin (98%) were purchased from ENERGY. *β*-cyclodextrin (98%) were purchased from Aladdin. Acetic acid (>99.5%), Bromine (Br_2, >99.5%), Copper(I) cyanide (98%) were purchased from *J&K*. All other chemicals and solvent were purchased from Sinopharm Chemical Reagents Co. Ltd, China and used without further purification. The water used in all experiments was deionized water. Compounds **2** and **3** were synthesized according to previous reports.[19]

Characterization

All experiments were performed in 10 mM Na_2CO_3 aqueous solution at ambient temperature. ^1H, ^{13}C and 2D ROESY spectra were recorded on a Bruker 500 MHz spectrometer using residual protonated solvent signals as the internal standard. ^{19}F NMR spectra were recorded on a Bruker 400MHz spectrometer. UV-vis spectra were recorded on a SHIMADZU UV-2550 spectrometer

in H_2O containing 10 mM Na_2CO_3 with 1 cm quartz cell. Irradiation experiments were performed by using a green laser pointer (JD-850, 1W) and a flashlight equipped with a 440 nm filter. ICD spectra were recorded on Jasco J-810 spectrometer in H_2O containing 10 mM Na_2CO_3 with 1 cm quartz cell.

Synthesis of *ortho*-fluoro-substituted 4,4′-azodibenzoic acid (F-azo-COOH)

Compound **3** (337 mg, 0.846 mmol) was dissolved in 15 mL THF and 4 mL 1M NaOH was added, the solution was stirred for 2 h at room temperature. The solution was adjusted to pH = 4 with 1M HCl, extracted with EtOAc and the organic phase was concentrated under reduced pressure to give F-azo-COOH as an orange/red solid (260 mg, 90%).

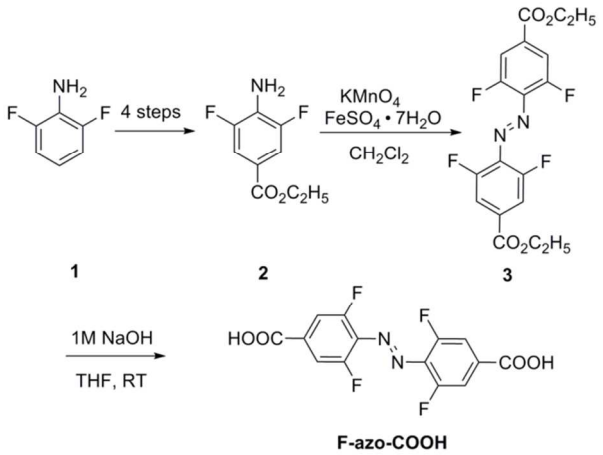
^{1}H NMR (500 MHz, 298 K, DMSO-d_6) (*E*-isomer) δ ppm 13.91 (br s, 2 H), 7.81 (d, *J* = 10.2 Hz, 2 H).

^{13}C NMR (500 MHz, 298 K, DMSO-d6) δ (ppm) 165.00, 155.79, 153.71, 135.67, 133.48.

Results and discussion

Synthesis of F-azo-COOH

The synthesis of F-azo-COOH was proceeded as shown in Scheme 1. F-azo-COOH was generated from the hydrolysis of compound **3**. ^{1}H NMR and ^{19}F NMR spectra confirm the successful synthesis of F-azo-COOH (Figure 1). Most F-azo-COOH molecules initially take the *trans* form (95%) judging from Figure S4.



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

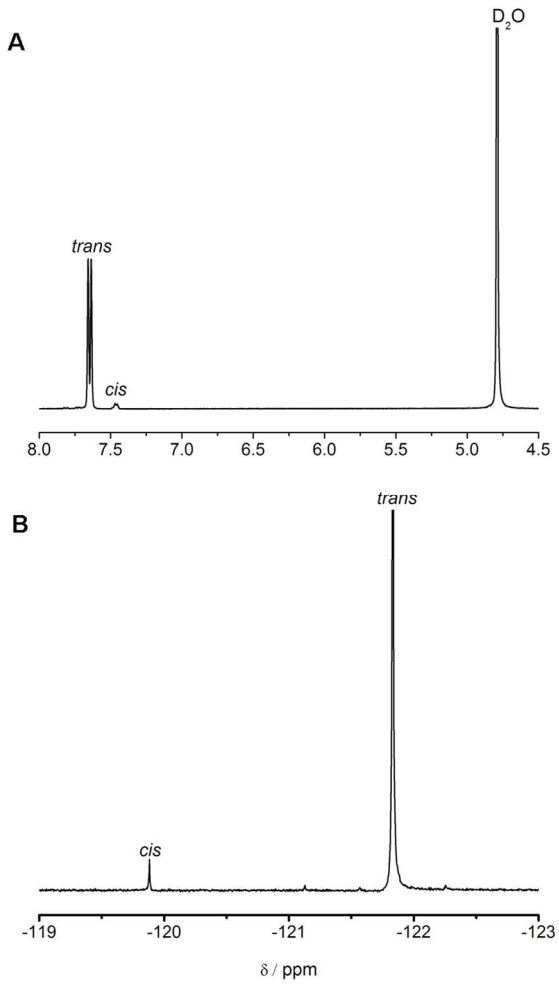


Figure 1. ^{1}H NMR (500 MHz, 298 K, D_2O, A) and ^{19}F NMR (400 MHz, D_2O, 298 K, B) spectra of F-azo-COOH (5 mM) in 10 mM Na_2CO_3 aqueous solution.

Visible-light Photoswitching of F-azo-COOH

UV-vis spectrum (Figure 2) of F-azo-COOH shows a strong π→π* absorption band at 320 nm (P1) and a weak n→π* band at 448 nm (P2).[23] Upon irradiation with green light (540 nm), the intensity of P1 band decreased with a concomitant blue-shift of 20 nm while the P2 band increased slightly with a blue-shift of 27 nm. Macroscopically, the color of the solution altered from red to yellow (see the inlets in Figure 2), an indication of the transition from the *trans* form to the *cis* form. More quantitative results were learned from ^{1}H NMR (Figure S4). The resonances of *trans/cis* isomers were at a ratio of 16:84 after irradiation with green light. When subsequently irradiated by blue light (440 nm), both the P1 and P2 bands red-shifted to their original positions, implying that *cis*-F-azo-COOH was reversibly changed to the *trans* state. Meanwhile, the color of the solution returned to red (see the inlets in Figure 2). However, the intensity of P1 band recovered only partial of its initial value, suggesting a portion of the *cis* form remained unchanged under blue light. Indeed, ^{1}H NMR spectrum gave a ratio of 69:31 (*trans/cis*) after illuminating with blue light. All above results were similar to previous reports.[13, 19]

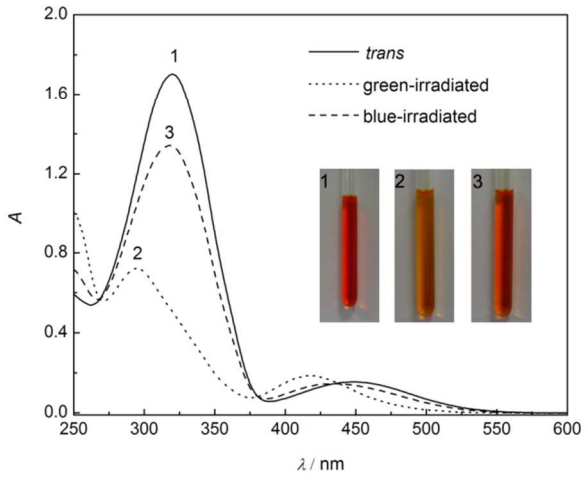


Figure 2. UV-vis spectra of (1) F-azo-COOH (1×10^{-4} M) in 10 mM Na_2CO_3 aqueous solution, (2) after irradiation with green light for 10 min, (3) then with blue light for 8 min in aqueous solution at room temperature. The inlets show the corresponding color of F-azo-COOH solution.

Formation of Host-Guest Complex

After investigating the photochemistry property of F-azo-COOH, we turned to study the host-guest interaction between F-azo-COOH and CDs in aqueous solution.

(a) Host-Guest Interaction Between F-azo-COOH and α-CD

Figure 3Aa and 3Ab show the ^{1}H NMR spectra of α-CD and F-azo-COOH, respectively. After mixing the two compounds with 1:1 molar ratio (Figure 3Ac), the H-3 resonance of α-CD upshifted from 4.02 to 4.00 ppm whereas the H-5 downshifted from 3.89 to 3.91 ppm (see the blue arrows). Meanwhile, the protons of F-azo-COOH downshifted from 7.67 to 7.70 ppm (see the black arrows in Figure 3A). These changes implied the host-guest interaction between α-CD and F-azo-COOH. The magnitude of the chemical shifts of the H-3 and H-5 protons of α-CD can be used as a measure of the complex stability as well as the depth of inclusion.[24] Judging from the small chemical shifts of H-3 ($\Delta\delta_3$ = 0.02 ppm) and H-5 ($\Delta\delta_5$ = 0.02 ppm) protons, we deduced that *trans*-F-azo-COOH was included shallowly in the cavity of α-CD. This conclusion was further confirmed by 2D ROESY spectrum (Figure 3B). Only the H-3 proton of α-CD emerged a weak cross-correlation with the protons of F-azo-COOH.

When the above mixture was irradiated with green light, *cis*-F-azo-COOH was obtained (*trans/cis* = 30/70) and the resonance signals of the H-3 and H-5 of α-CD weaken and broadened (Figure 3Ad). 2D ROESY spectrum was carried out to get more information. The NOE signals were undetectable between *cis*-F-azo-COOH and α-CD in Figure S5. Based on above 2D ROESY spectra, we draw the conclusion that the host-guest interaction between α-CD and *trans*-F-azo-COOH was stronger than its *cis* form. We then isomerized *cis*-F-azo-COOH to the *trans* state by blue light. All signals of the protons of α-CD moved to their previous positions (Figure 3Ae). Collectively, although there exists a weak host-guest interaction between *trans*-F-azo-COOH and α-CD, it's not sure whether they can form stable complex. This result was different from conventional *trans*-azobenzene/α-CD system (~10^4 M^{-1}).[9b,10b,12c,25] *Cis*-F-azo-COOH has no or very weak interaction with α-CD, a result consistent with conventional *cis*-azobenzene/α-CD system.[10b]

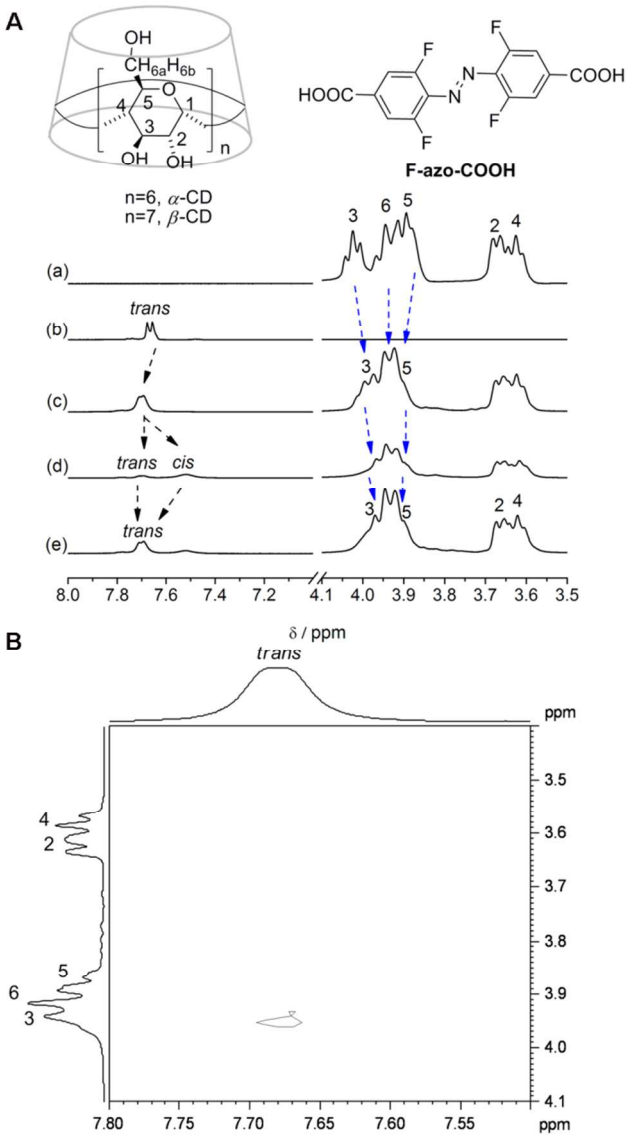


Figure 3. ^{1}H NMR spectra (500 MHz, 298 K, D_2O, 5 mM) of (a) α-CD, (b) F-azo-COOH in 10 mM Na_2CO_3 aqueous solution, (c) F-azo-COOH mixed with α-CD (1:1 molar ratio) in 10 mM Na_2CO_3 aqueous solution, (d) after irradiation with green light, (e) then with blue light, blue arrows show the changes of the resonance of H-3, H-6 and H-5 of α-CD, black arrows show the changes of F-azo-COOH (A); Partial 2D ROESY spectrum (500 MHz, 298 K, D_2O, 5 mM) of the mixture of α-CD and F-azo-COOH (1:1 molar ratio) in 10 mM Na_2CO_3 aqueous solution (B).

(*b*) Host-Guest Interaction Between F-azo-COOH and β-CD

Having understood the host-guest interaction of F-azo-COOH/α-CD system, we enlarged the cavity size of the host molecule by replacing α-CD with β-CD. When F-azo-COOH was mixed with β-CD (Figure 4c), the H-3 and H-5 protons of β-CD shifted upfield remarkably ($\Delta\delta_3$ = 0.12 and $\Delta\delta_5$ = 0.19 ppm), indicating the formation of the inclusion complex between F-azo-COOH

and β-CD.[26] The H-6b protons shifted upfield ($\Delta\delta_{6b}$ = 0.15 ppm) due to the hydrogen bonds formed by the carboxyl group of F-azo-COOH and OH-6 functions of β-CD.[27] Meanwhile, the protons of the guest molecule significantly shifted downfield ($\Delta\delta_{azo}$ = 0.23 ppm). We ascribe this shifting to the reduction of the van der Waals interaction between F-azo-COOH and local environment after complexation. The H-2 and H-4 protons showed relatively small changes upon complexation though situated outside the cavity of β-CD.

When the above mixture was irradiated with green light (Figure 4d), *trans*-F-azo-COOH was isomerized to the *cis* state (*trans/cis* = 36/64). The signal of H-6b shifted downfield ($\Delta\delta_{6b}$ = 0.07 ppm), implying the hydrogen bonds formed before were destroyed. The signal of H-6b shifted to its original position after using blue light (Figure 4e). It's worth noting that the signals of the rest protons of β-CD remained unchanged under irradiation with green light as well as blue light (Figure 4d and 4e). These phenomena suggest that *cis*-F-azo-COOH can also be included in the cavity of β-CD merely with different spatial distribution of two terminal carboxyl groups compared with the *trans* form.

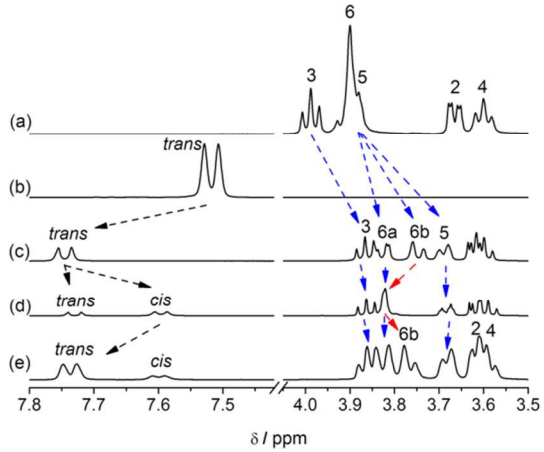


Figure 4. ^{1}H NMR spectra (500 MHz, 298 K, D_2O, 5 mM) of (a) β-CD, (b) F-azo-COOH in 10 mM Na_2CO_3 aqueous solution, (c) F-azo-COOH mixed with β-CD (1:1 molar ratio) in 10 mM Na_2CO_3 aqueous solution, (d) after irradiation with green light, (e) then with blue light, blue arrows show the changes of the resonances of H-3, H-5 and H-6 of β-CD, red arrows show the changes of the resonance of H-6b of β-CD, black arrows show the changes of F-azo-COOH.

2D ROESY spectra were carried out to provide further insight into the interaction of F-azo-COOH and β-CD. The protons of *trans*-F-azo-COOH cross-correlated with H-3, H-5 and H-6b protons of β-CD (Figure 5A). When *trans*-F-azo-COOH was isomerized to the *cis* state by green light (*trans/cis* = 36/64), cross-correlation peaks between H-3, H-5and H-6 protons of β-CD and protons of *cis*-F-azo-COOH were present (Figure 5B).These results further confirmed that both *trans*- and *cis*-F-azo-COOH can be included in the cavity of β-CD.

More evidence came from the ^{19}F NMR spectra of F-azo-COOH titrated with β-CD (Figure 6).[28] The signals of both *trans*- and *cis*-F-azo-COOH gradually shifted downfield when increasing the concentration of β-CD. Most interestingly, the downfield shifts of the *cis* protons (0.42 ppm) were more pronounced than those of the *trans* protons (0.16 ppm). The result reveals that *cis*-F-azo-COOH has a greater binding affinity with β-CD than *trans*-F-azo-COOH under the same conditions. This finding is completely opposite to the conventional azobenzene/β-CD system.[29,10c]

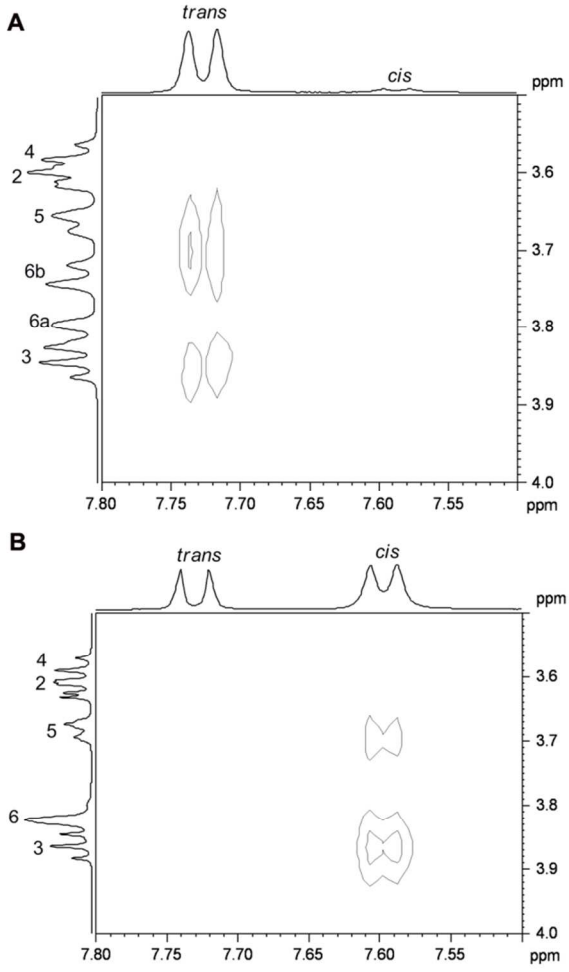


Figure 5. Partial 2DROESYspectra (500 MHz, 298 K,D_2O,5 mM) of the mixture of F-azo-COOH and β-CD (1:1 molar ratio) in 10 mM Na_2CO_3 aqueous solution (A) and after irradiation with green light (B).

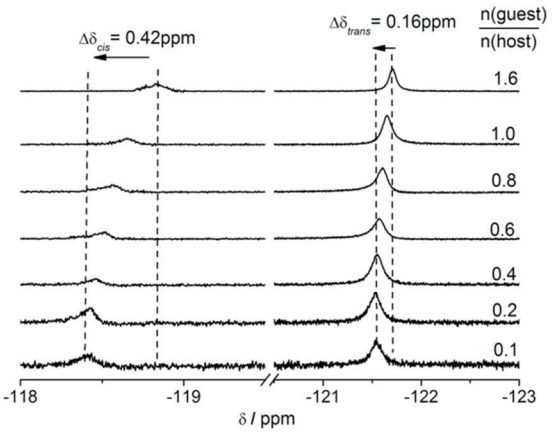


Figure 6. ^{19}F NMR spectra (400 MHz, 298 K, D_2O, 5 mM) of F-azo-COOH (5 mM) titrated with β-CD in 10 mM Na_2CO_3 aqueous solution.

Stoichiometry of Complexes and Association Constants

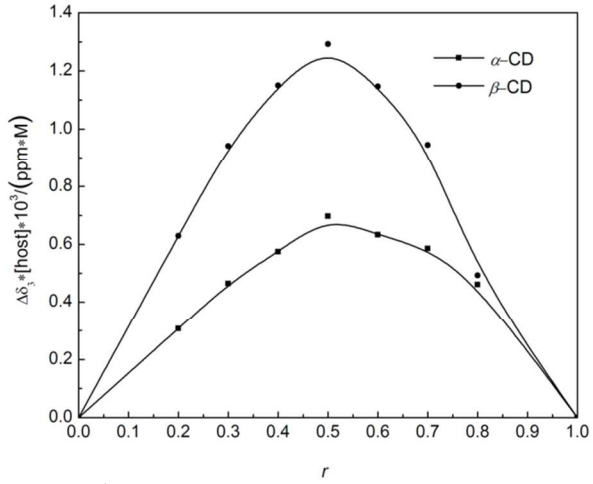


Figure 7. Job's plot to determine the stoichiometry of F-azo-COOH/CDs complexes by ^{1}H NMR spectroscopy (500 MHz, 298 K, D_2O) in 10 mM Na_2CO_3 aqueous solution.

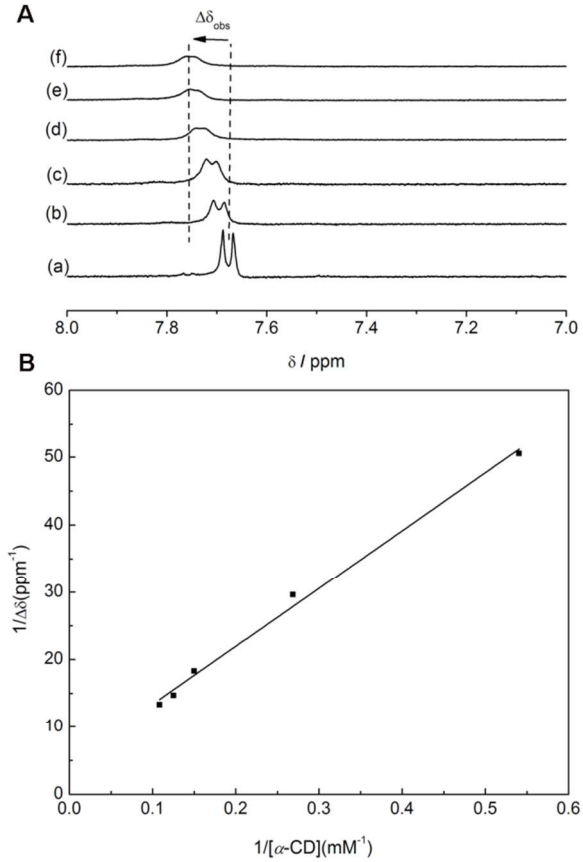


Figure 8. ^{1}H NMR spectra (500 MHz, 298 K, D_2O) of 1.0 mM F-azo-COOH in the presence of various concentrations of α-CD in 10 mM Na_2CO_3 aqueous solution (A) and Benesi-Hildebrand plot (B) of $1/\Delta\delta_{obs}$ against $1/[\alpha\text{-CD}]$. C_{CD}: (a) 0, (b) 2, (c) 4, (d) 6, (e) 8 and (f) 10 mM.

To quantitatively understand the host-guest interactions between F-azo-COOH and CDs, efforts were directed to determine the stoichiometry and corresponding association constants (*K*s) of these complexes. The stoichiometry in aqueous solution was determined by Job's method using ^{1}H NMR spectroscopy.[30] ^{1}H NMR spectra were obtained from a series of solutions in which the total concentration of the host and guest was fixed (20 mM) while the ratio *r* (*r* = [host]/[host]+[guest]) was varied between 0 and 1. The maximum of in the Job's plot appeared at *r* = 0.5 (Figure 7), which confirmed a 1:1 stoichiometry for the F-azo-COOH/CDs complexes.

We followed Benesi-Hildebrand's method to evaluate *K*s of *trans*- and *cis*-F-azo-COOH with α- and β-CD by ^{1}H NMR spectroscopy.[31] *Trans*-F-azo-COOH was very stable in the dark but the *cis*-F-azo-COOH would slowly isomerize to the *trans* state in the solution in the dark. When *cis*-F-azo-COOH changed to the *trans* form, only the intensity of resonance signals of *cis*-F-azo-COOH decreased. The chemical shifts of all characteristic protons of *cis*-F-azo-COOH remained unchanged (Figure S4). It should be noted that only the changes of chemical shift are required in Benesi-Hidebrand plot to calculate the complexation constants. Therefore, the instability of *cis*-F-azo-COOH would not affect the complexation experiments. Figure 8 and Figure 9 show the ^{1}H NMR spectra of *trans*-F-azo-COOH in the presence of varying concentrations of α- and β-CD, respectively. As [α-CD] was increased, the signals due to the protons of *trans*-F-azo-COOH shifted downfield and broadened (Figure 8A), implying the interaction of *trans*-F-azo-COOH and α-CD. As [β-CD] was increased, more significant downfield shift was observed (Figure 9A). The reciprocals of the peak shifts ($1/\Delta\delta_{obs}$) were then used to calculate *K*s by the following equation.

$$\frac{1}{\Delta\delta_{obs}} = \frac{1}{K\Delta\delta[CD]} + \frac{1}{\Delta\delta}$$

Where $\Delta\delta_{obs}$ is the measured change in chemical shift from either *cis*- or *trans*-F-azo-COOH (upon addition of the host) referenced to that of the uncomplexed guest and $\Delta\delta$ is the difference in chemical shift between that observed in the guest molecule and that observed in the complex.[31a] The value of *K* was obtained from the intercept and the slope. Similar procedures were repeated to get *K*s of *cis*-F-azo-COOH with α- and β-CD. *Cis*-F-azo-COOH was obtained by the irradiation with green light. α- and β-CD were added when the photostaionary state was reached (Figure S11). We performed three independent measures for each combination of the host molecule (α-CD or β-CD) and the guest molecule (*trans*- or *cis*-F-azo-COOH). All plots showed good linearity (Figure S12) and the fitting results were summarized in Table 1. The association constant (*K*) is expressed in the form of "average value ± stand error".

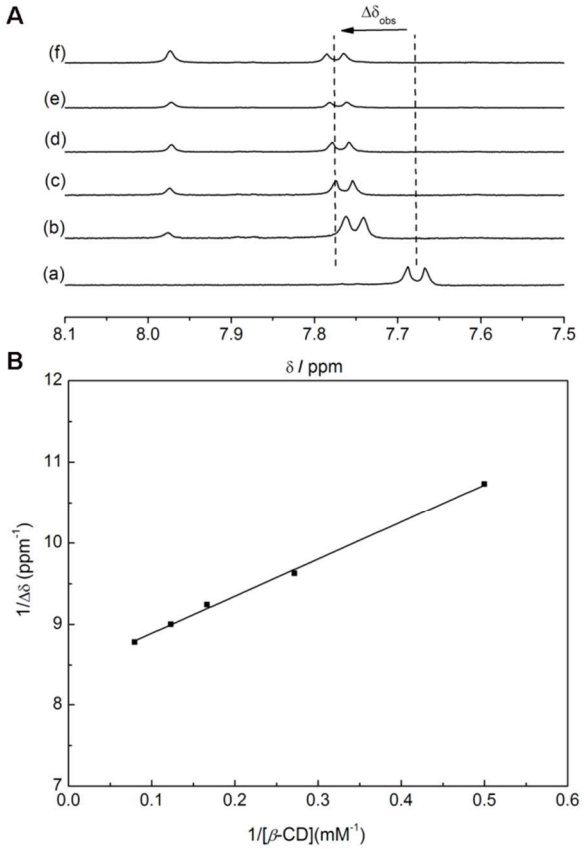


Figure 9. ^{1}H NMR spectra (500 MHz, 298 K, D_2O) of 1.0 mM F-azo-COOH in the presence of various concentrations of *β*-CD in 10 mM Na_2CO_3 aqueous solution (A) and Benesi-Hildebrand plot (B) of $1/\Delta\delta_{obs}$ against $1/[\beta\text{-CD}]$. C_{CD}: (a) 0, (b) 2, (c) 4, (d) 6, (e) 8 and (f) 10 mM.

Table 1. Association Constants (*K*s) for *α*- and *β*-CD with F-azo-COOH and azobenzene

compound	*α*-CD/M^{-1}	*β*-CD/M^{-1}
trans-F-azo-COOH	50 ± 7	2.1 ± 0.2 × 10^3
trans-azobenzene	2.0 × 10^3	8.3 × 10^2
cis-F-azo-COOH	29 ± 7	3.0 ± 0.3 × 10^3
cis-azobenzene	21	5.0 × 10^2

The concentration of the CDs may affect the association constant in the complexation experiments. The good linearity of all plots showed that the concentrations of the CDs were reliable. To our surprise, we found the *K* of *trans*-F-azo-COOH/*α*-CD system was 50 ± 7 M^{-1} whereas the *K* of *trans*-4,4′-azodibenzoic acid (ADA)/*α*-CD[25] system is around 1.0 × 10^4 M^{-1} and the *K* of *trans*-azobenzene/*α*-CD[32] system is around 2.0 × 10^3 M^{-1}. The dramatic drop of host-guest interaction in *trans*-F-azo-COOH/*α*-CD complex further confirmed the previous observation in Figure 2 and could be ascribed to the steric effect of fluoro-substitution.[33] The size of conventional *trans*-azobenzene subtly matches the volume of the inner cavity of *α*-CD (174 Å^3).[9f] When tetra-*ortho*-hydrogen atoms of azobenzene were all fluoro-substituted, the volume increase of F-azo-COOH might hinder deep inclusion into the cavity of *α*-CD, resulting in a decline of *K* by three order of magnitude.[27] The conventional *cis*-azobenzene cannot form host-guest complex with *α*-CD and the detected *K* of *cis*-azobenzene/*α*-CD system was around 21 M^{-1}.[32] Analysis of *K* values of the F-azo-COOH/*α*-CD system (50 ± 7 and 29 ± 7 M^{-1} for the *trans* and *cis* form, respectively) showed that neither *trans*- nor *cis*-F-azo-COOH could form stable host-guest inclusion complexes with *α*-CD.

However, the above scenario may not work in F-azo-COOH/*β*-CD system since the volume of the inner cavity of *β*-CD is sufficiently large (262 Å^3). The obtained *K* of *trans*-F-azo-COOH/*β*-CD complex (2.1 ± 0.2 × 10^3 M^{-1}) was comparable or even slightly better than that of non-fluorinated *trans*-azobenzene/*β*-CD (1.7 × 10^3 M^{-1}).[34] The *K* value of *cis*-F-azo-COOH/*β*-CD complex (3.0 ± 0.3 × 10^3 M^{-1}) is larger than that of its *trans* form (2.1 ± 0.2 × 10^3 M^{-1}). This result confirms the more stable complexation of *cis*-F-azo-COOH/*β*-CD as revealed by 2D ROESY (Figure 5) and ^{19}F NMR (Figure 6) spectra. When the guest molecule is included in the cavity of CDs in aqueous solution, a major factor in the stability of the resulting complex is the fitness of the guest molecule within the cavity of CDs.[35] Our results suggested that *cis*-F-azo-COOH probably fit the cavity of *β*-CD more tightly than *trans*-F-azo-COOH. To the best of our knowledge, this phenomenon was discovered in azobenzene/*β*-CD system for the first time.

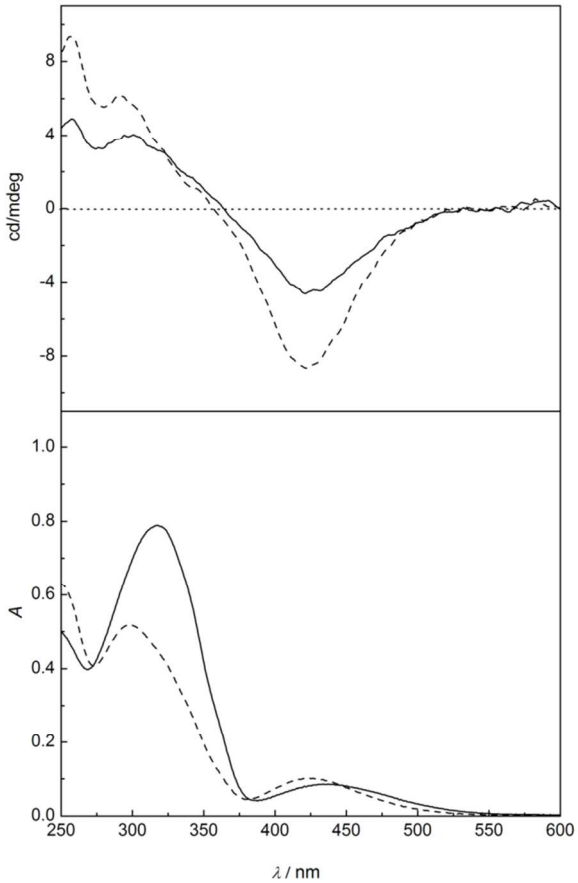


Figure 10. ICD and UV-vis spectra of F-azo-COOH (5×10^{-5} M) in the presence of 8×10^{-3} M *β*-CD (black line), then irradiation with green light for 10 min (dot line) in 10 mM Na_2CO_3 aqueous solution at room temperature.

To gain deep insight into the host-guest geometry of F-azo-COOH/*β*-CD complex, ICD and UV-vis spectra of the mixture of F-azo-COOH and *β*-CD before and after irradiation with green light were performed (Figure 10). The spectra exhibit the positive ICD band in π-π* transition at 320 nm and negative ICD band in n-π* transition at 448 nm, revealing that the transition moments of π-π* and n-π* in the *trans*-F-azo-COOH are parallel and perpendicular to the axis of *β*-CD, respectively (see the black line).[36] After irradiated with green light, the negative ICD band in n-π* transition increased remarkably (see the dot line), suggesting the same geometry of n-π* transition of *cis*-F-azo-COOH in *β*-CD cavity.

Based on the above ICD and NMR spectra, we gained the possible structures of F-azo-COOH/*β*-CD complexes (Figure 11). We believed that *β*-CD could include both *trans*- and *cis*-F-azo-COOH completely inside its cavity with different spatial structures. Two charged carboxyl groups of *trans*-F-azo-COOH preferred to locate outside the cavity of *β*-CD and form hydrogen bonds with OH-6 functions of *β*-CD. The planar *trans*-F-azo-COOH loosely inserted in the cavity of *β*-CD (Figure 11A). When *trans*-F-azo-COOH isomerized to the *cis* form, the hydrogen bonds formed before were destroyed. The bent *cis*-F-azo-COOH snugly fits the cavity of *β*-CD and consequently had a higher binding affinity than its *trans* form (Figure 11B).

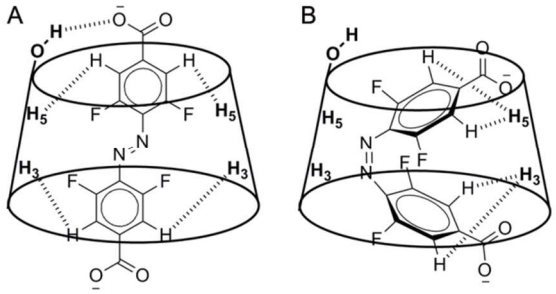


Figure 11. The possible structures of host-guest complexes of *β*-CD and F-azo-COOH in the *trans* (A) and *cis* (B) form.

Conclusions

In summary, we investigated the host-guest interaction between F-azo-COOH and CDs by NMR spectroscopy in aqueous solution for the first time. The results revealed that F-azo-COOH can only form stable 1:1 complex with *β*-CD. According to the *K* values, we found that *cis*-F-azo-COOH fits the cavity of *β*-CD more tightly ($3.0 \pm 0.3 \times 10^3\ M^{-1}$) than its *trans* form ($2.1 \pm 0.2 \times 10^3\ M^{-1}$). The findings were different from conventional azobenzene/CDs systems. Our work emphasizes the consideration of sterical changes of azobenzene derivatives and the necessity to investigate their host-guest chemistry. This study may expand the light controlled host-guest chemistry and have potential applications in fundamental researches.

Acknowledgements

This work was supported by Natural Science Foundation of Fujian Province (No. 2014J01060). National Natural Science Foundation of China (No. 21304076) and China Postdoctoral Science Foundation (No.2013M541857).

Notes and references

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† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

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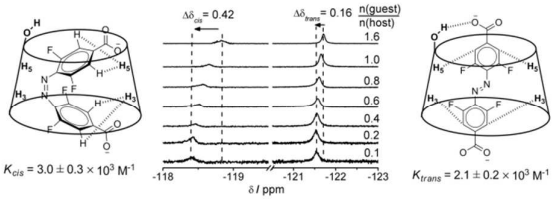

This system is completely opposite to conventional azobenzene/*β*-CD system that *cis*-F-azo-COOH fits *β*-CD more tightly than its *trans* form.