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Tuning the emission of a water-soluble 3-hydroxyflavone derivative by host-guest complexation

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3-Hydroxyflavone derivatives have great potential as fluorescence probes for bio-labeling in aqueous medium. They were extensively studied in various organic solvents on the "excited state intramolecular proton transfer" process, but seldom addressed in aqueous solution due to the poor water solubility. Herein, an amphiphilic molecule bearing 3-hydroxyflavone and oligo(ethylene oxide) (denoted by 3HF-EO) was designed and synthesized. Different from the fluorescence in organic solvents, 3HF-EO in aqueous solution showed a remarkable single fluorescence emission, which is ascribed to the fluorescence of its anionic species. We found that the fluorescence intensity could be efficiently tuned via host-guest complexation. α-CD has little effect on the emission, while β-CD and γ-CD lead to enhanced and reduced emission of 3HF-EO, respectively. The ^{1}H NMR and 2D NOESY NMR spectra indicate that α-CD barely had interaction with 3HF-EO, while β-CD and γ-CD formed complexes with one and two 3HF-EO molecules, respectively. These results make a sound explanation for the modulated fluorescence intensity.

1 Introduction

Flavonoids are a group of polyphenolic compounds, which ubiquitously exist in various plants and foods (e.g. gingko, honeysuckle, apple and soy product).[1, 2] Since the first report on flavonoids by S. Rusznyák and A. Szent-Györgyi in 1936,[3] various bioactive flavonoids have been discovered and applied in clinic because of their antioxidant and free radical scavenging activity.[4-8] 3-Hydroxyflavone (3HF) derivatives normally possess a large stokes shift and exclusion of self-absorption,[9-11] and thus have great potential as ideal candidates for fluorescence probes in bio-labeling. This class of molecules are known for "the excited state intramolecular proton transfer" process, and extensively studied in organic solvents,[12-22] but seldom addressed in aqueous solution due to the poor water solubility.[23]

From the published literatures,[2, 24, 25] 3HF derivatives were often confined by host-guest interactions to promote the emission of the corresponding tautomer. Chattopadhyay et al. reported the disruption of probe-solvent cluster formed by a 3HF derivative because of the confinement of the probe with cyclodextrin (CD) nano-cavity, and the disruption resulted in the increase in fluorescence anisotropy of the probe compared to its value in the aqueous solution.[26] Rodembusch et al. found that the confinement effect caused by octa acid was able to alter the nature of the fluorescence emission of 3HF derivatives.[23] Through complexation with cucurbit[7]uril, Seth et al. modulated the photophysical behavior of 3HF.[27] The above examples demonstrate that the confinement effect generated from host-guest interaction should be feasible method to tune the fluorescence emission of 3HF derivatives. The supramolecular encapsulation can effectively prevent self-aggregation and alter the micro-environment of the guest molecules, and hence can be used to tune the amphiphilicity and the emission of chromophores.[28, 29]

To obtain stable and hydrophilic complexes, the selection of host molecules becomes critically important. On board, we have crown ether, CD, cucurbituril, calixarene, pillararene, octa acid and so on.[30-41] CDs present a truncated cone with the both rims displaying hydroxyl groups, which make the outside of the molecular cavity hydrophilic, whereas the inner surface is hydrophobic lined with ether-like oxygen atoms and hydrogen atoms. The hydrophilic CD molecules are able to bind size-fit organic compounds. Such binding also allows CDs to be used to increase the water solubility and stability of normally hydrophobic compounds.[41, 42] Therefore, CDs will be ideal host molecules to encapsulate the 3HF derivatives. Apart from the complexation, we anticipated that the fluorescence due to the confinement effect can also be tuned by using different CDs to encapsulate the guest molecules.[43]

In this study, 3HF was covalently linked to oligo(ethylene oxide) with click reaction, and the resulting compound is denoted by 3HF-EO. We found that the cavity size of the CDs is critical to the host-guest complexation with 3HF-EO. The cavity of α-CD is too small to encapsulate 3HF-EO, and it has little effect on the fluorescence emission. In contrast, β-CD and γ-CD formed complexes with one and two 3HF-EO molecules, and

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thus resulting in the enhanced and reduced fluorescence emission, respectively. This research conducted a comprehensive study on the emission of 3HF-EO in aqueous solution, and modulated its emission via host-guest complexation. It is anticipated that the strategy developed in this research can be applied to the analogous light-emitting chromophores.

2 Experimental

2.1 Materials

Triethylene glycol mono(2-propynyl) ether, *p*-toluenesulfonyl chloride, cuprous bromide (CuBr) and 1,1,4,7,7-pentamethyl diethylenetriamine (PMDETA) were purchased from Aladdin Reagent Co., Ltd (Shanghai, China). Ethyl acetate, petroleum ether, dichloromethane, methanol, ethanol, *n*-hexane, tetrahydrofuran, N,N'-dimethyl formamide and toluene were purchased from Yonghua Chemical Technology Co., Ltd (Jiangsu, China). 2-N-methylanilinoethannol, α-CD, γ-CD, deuterated chloroform, deuteroxide were purchased from J&K chemical Ltd. β-CD was purchased from TCI Co., Ltd. Triethylamine and phosphoryl chloride were bought from Sinopharm Chemical Reagent Co., Ltd. Sodium azide was acquired from Alfa Aesar (China) chemical Co., Ltd. Milli-Q water with a resistivity of 18.0 MΩ·cm was used in the study.

2.2 Instruments

^{1}H NMR spectra were recorded on an Avance III 400 MHz NMR spectrometer (Bruker Co.). 2D Nuclear Overhauser effect spectroscopy (NOESY) spectra were recorded on a 600 MHz Direct Drive 2 NMR spectrometer manufactured by Agilent Technologies. Electrospray Ionization Mass spectra (ESI-MS) of 3HF-EO was carried out on a micro Q-TOF III Mass spectrometer (Bruker Co.). The MS of complexes of 3HF-EO/β-CD and 3HF-EO/γ-CD were performed on a Q-Exactive mass spectrometer with ESI source. The UV-vis spectra were recorded on a Cary 60 produced by Agilent Technologies (USA). Steady-state emission spectra (excited by 404 nm) were recorded on a Hitachi F-2700 fluorescence spectrophotometer (Japan). Fluorescence quantum yield (QY) was measured at 25 °C using a Flurolog-3 spectrofluorometer with a 450 W Xe lamp as light source.

2.3 Synthesis and characterization

2.3.1. Synthesis of N-(2-azidoethyl)-N-methylaniline (compound 1 in Scheme 1). 2-N-methylanilinoethannol (3.0 g, 20 mmol) and *p*-toluenesulfonyl chloride (7.6 g, 40 mmol) were dissolved in dry dichloromethane (60 mL) in an ice bath. Subsequently, trimethylamine (3.5 mL, 25 mmol) was added dropwise, and the reaction mixture was then warmed to room temperature. After being stirred for 4 h, the resulting mixture was poured into 150 mL of deionized water, extracted with dichloromethane (4 × 20 mL). The organic phase was dried over anhydrous Na_2SO_4, and then the solvent was removed under reduced pressure to obtain the crude product 2-(methyl(phenyl)amino) ethyl 4-methylbenzenesulfonate.

Sodium azide (2.6 g, 40 mmol) was added to the above obtained crude product dissolved in 80 mL of dry N,N'-dimethylformamide. The mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the resulting mixture was poured into 200 mL of deionized water. The product was extracted with dichloromethane (6 × 30 mL), and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether (1:25, v/v)) to afford a faint yellow oil. Yield: 2.5 g, 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.23 (m, 2H), 6.75 (d, J = 8.1 Hz, 3H), 3.55 (t, J = 5.9 Hz, 2H), 3.46 (t, J = 6.1 Hz, 2H), 3.02 (s, 3H).

2.3.2. Synthesis of 4-((2-azidoethyl) (methyl) amino) benzaldehyde (compound 2 in Scheme 1). Under nitrogen atmosphere, phosphoryl chloride (2.8 mL, 30 mmol) was added dropwise to dry N,N'-dimethylformamide (20 mL) in an ice bath. After being stirred for 30 min, the solution of compound 1 (2.6 g, 15 mmol) in dry N,N'-dimethylformamide (20 mL) was added dropwise to the above solution. After warmed to room temperature, the mixture was continuously stirred for 1 h. Subsequently, the reactant was quenched by deionized water (150 mL), and continuously stirred for 12 h. The product was extracted with dichloromethane (6 × 30 mL), and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether (2:7, v/v)) to afford a faint yellow oil. Yield: 2.45 g, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.76 (d, J = 9.0 Hz, 2H), 6.75 (d, J = 8.1 Hz, 2H), 3.64 (t, J = 6.0 Hz, 2H), 3.52 (t, J = 6.0 Hz, 2H), 3.13 (s, 3H).

2.3.3. Synthesis of (E)-3-(4-((2-azidoethyl) (methyl) amino) phenyl)-1-(2-hydroxyphenyl) prop-2-en-1-one (Compound 3 in Scheme 1). Under nitrogen protection, potassium tert-butoxide (673 mg, 6 mmol) was added into the solution of compound 2 (612 mg, 3 mmol) and 2-hydroxyacetophenone (542 μL, 4.5 mmol) in toluene (20 mL). The reaction mixture was stirred for 1 h at room temperature and then poured into 1 mol/L HCl (160 mL). The resulting product was extracted with dichloromethane (6 × 30 mL), and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether (1:4, v/v)). Yield: 0.82 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.14 (s, 1H), 7.95–7.87 (m, 2H), 7.59 (d, J = 8.7 Hz, 2H), 7.51–7.43 (m, 2H), 7.01 (d, J = 8.4 Hz, 1H), 6.93 (t, J = 7.8 Hz, 1H), 6.74 (d, J = 8.8 Hz, 2H), 3.63 (t, J = 6.0 Hz, 2H), 3.51 (t, J = 6.0 Hz, 2H), 3.11 (s, 3H).

2.3.4. Synthesis of 2-(4-((2-azidoethyl) (methyl) amino) phenyl)-3-hydroxy-4H-chromen-4-one (compound 4 in Scheme 1). Under nitrogen atmosphere, 5% sodium hydroxide solution (5 mL) was added into a solution of compound 3 (483 mg, 1.5 mmol) in the mixed solvents of THF (5 mL) and ethanol (15 mL) in an ice bath. After the mixture solution was warmed up to room temperature, and then 30% hydrogen peroxide (600 μL) was dropwise added into the reactant in an ice bath, and the reactant was then warmed to room temperature and continuously stirred for 4 h. The product was extracted with dichloromethane (6 × 30 mL), and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by recrystallization from ethyl acetate to acquire a yellow solid. Yield: 310 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ

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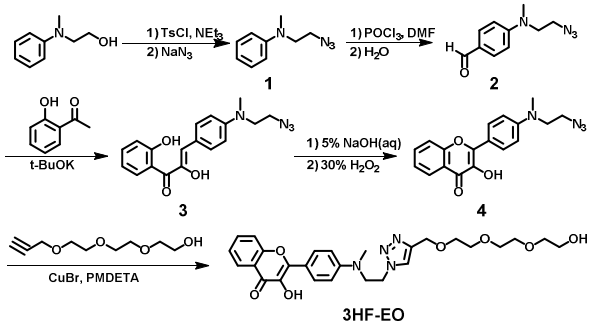
8.22 (dd, J = 10.5, 7.9 Hz, 3H), 7.67 (ddd, J = 8.5, 6.9, 1.7 Hz, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.43–7.36 (m, 1H), 6.91 (s, 1H), 6.84 (d, J = 8.9 Hz, 2H), 3.65 (t, J = 6.0 Hz, 2H), 3.53 (t, J = 6.0 Hz, 2H), 3.13 (s, 3H).

2.3.5. Synthesis of 3-hydroxy-2-(4-((2-(4-((2-(2-(2-hydroxyethoxy) ethoxy) ethoxy) methyl)-1H-1,2,3-triazol-1-yl) ethyl) (methyl) amino) phenyl)-4H-chromen-4-one (denoted by 3HF-EO). Under nitrogen atmosphere, 3HF-EO was synthesized via click reaction between compound 4 and triethylene glycol mono(2-propynyl) ether. Typically, compound 4 (168 mg, 0.5 mmol) and triethylene glycol mono(2-propynyl) ether (94 mg, 0.5 mmol) were dissolved in dry N,N'-dimethylformamide (60 mL). Subsequently, CuBr (72 mg, 0.5 mmol) and PMDETA (173 mg, 1 mmol) were added into the mixture and the reaction was then stirred for 24 h. The product was poured into deionized water (100 mL), extracted with dichloromethane (10 × 20 mL), and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was washed 3 times with *n*-hexane, and purified by recrystallization from ethyl alcohol to afford a yellow solid. Yield: (159 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.7 Hz, 1H), 8.18 (d, J = 8.7 Hz, 2H), 7.68 (t, J = 7.3 Hz, 1H), 7.60–7.49 (m, 2H), 7.40 (t, J = 7.5 Hz, 1H), 6.97 (s, 1H), 6.77 (d, J = 8.7 Hz, 2H), 4.67 (s, 2H), 4.61 (t, J = 6.1 Hz, 2H), 3.98 (t, J = 6.0 Hz, 2H), 3.74–3.67 (m, 2H), 3.68–3.51 (m, 10H), 2.93 (s, 3H), 2.01 (s, 1H). MS (ESI): Calculated for $C_{27}H_{32}N_4O_7$, m/z=524.23; found, 524.22.

3 Results and discussion

The amphiphilic molecule 3HF-EO was designed and synthesized by using the synthetic route illustrated in Scheme 1. Briefly, the synthesis of 2-(4-((2-azidoethyl) (methyl) amino) phenyl)-3-hydroxy-4H-chromen-4-one (i.e. compound 4 in scheme 1) referred to the literature,[19] and the detailed description is shown in the experimental section. The rigid 3HF and the flexible oligo(ethylene oxide) residue linked by a triazole group with click reaction, which happens in mild conditions to avoid the damage of 3HF derivative during synthesis. The 3HF moiety is hydrophobic and acts as the light-emitting chromophore, and the oligo(ethylene oxide) provides hydrophilicity. The target molecule was characterized by ^{1}H NMR and mass spectra, as shown in Figure S1.



Scheme 1 The synthetic route of 3HF-EO.

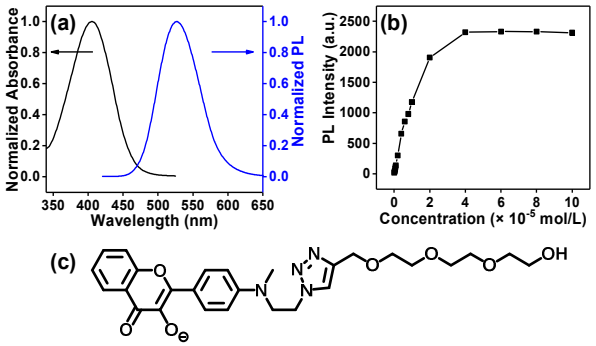


Fig. 1 (a) Normalized UV-vis and PL spectra of 1 × 10^{-4} mol/L 3HF-EO in aqueous solution; (b) Plot of fluorescence intensity at 525 nm versus the concentration of 3HF-EO; (c) The anionic species of 3HF-EO.

As shown in Fig. 1a, the maximum absorption and photoluminescence of 3HF-EO in water located at around 404 and 525 nm, respectively. The large stokes shift (approximately 120 nm) allows 3HF-EO to have a very little self-absorption during emitting process. The remarkable single fluorescence mission should be assigned to the anionic species, as shown in Fig. 1c.[23, 45, 46]

The emission of 3HF-EO showed a concentration dependent feature. As shown in Fig. 1b, the fluorescence intensity increases with the concentration of 3HF-EO until the centration was ~ 4 × 10^{-5} mol/L, and thereafter the fluorescence intensity showed little increase with concentration. This phenomenon should be attributed to the aggregation caused quenching, which is categorized as static quenching due to the formation of ground state complexes.[47]

The confinement effect supplied by host-guest complexation can possibly disrupt the ground state aggregates, so that modulating the emission of the 3HF-EO. Therefore, α-CD, β-CD and γ-CD were applied as hosts to assemble with 3HF-EO. To make a parallel comparison, the concentrations of 3HF-EO were all controlled to 1 × 10^{-4} mol/L, and 8 equivalents of α-CD, β-CD or γ-CD was added into the aqueous solution. During the measurement, the temperature of the solution was kept at 25 °C (our experiment indicated that 3HF-EO is quite sensitive

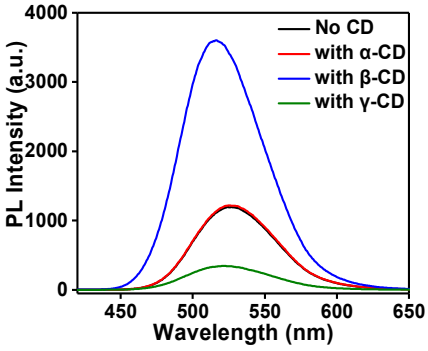


Fig. 2 The PL spectra of 3HF-EO upon addition of 8 equivalents of α-CD, β-CD and γ-CD. The concentration of 3HF-EO was 1 × 10^{-4} mol/L.

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to temperature). As shown in Fig. 2, α-CD had little effect on the PL spectrum of 3HF-EO; whereas β-CD and γ-CD showed opposite effect on the emission intensity: the former enhanced the fluorescent emission, and the latter suppressed the emission. These results suggest that the three CDs should have different interactions with 3HF-EO.

QY was determined to confirm the steady state fluorescence results. The QY of neat 3HF-EO in aqueous solution was 14.8%. The addition of α-CD did not cause significant change of QY, and a value of 14.4% was acquired. Addition of equimolar β-CD and γ-CD led to the enhanced and reduced QY to 22.7% and 10.5%, respectively. The QY changes are consist with the results indicated by the steady fluorescence spectra. It is worth to note that the QY of 3HF-EO also depends on the amount of β-CD. A QY as high as 62.7% was acquired as 8 equivalents of β-CD was added into the solution. In comparison, the QY of 3HF-EO did not show further decrease as adding more than one equivalents of γ-CD in the solution.

We speculated that fluorescence difference upon addition of these three CDs should be caused by the host-guest complexation. The cavity of α-CD is too small to encapsulate 3HF-EO, while the cavity of β-CD and γ-CD are both big enough for host-guest interactions. To verify this assumption, a series of experiments were designed as follows.

Firstly, the association ratio between 3HF-EO and β-CD (or γ-CD) was determined through Job's plot using the change of chemical shift (Δδ) of proton H-f on 3HF-EO as variable.[48] The corresponding NMR spectra are presented in the supporting information (Figure S2 and S3). Thus, the value of Δδ (for β-CD) or -Δδ (for γ-CD) times the concentration of 3HF-EO (denoted as C_1) was plotted against the molar ratio of 3HF-EO in the mixed solution of 3HF-EO and β- (or γ-CD) (denoted by R). As shown in Fig. 3, the intersections of the linear fitting meet at approximately 0.52 and 0.66 for the systems containing β-CD and γ-CD, respectively. These results indicate that the association ratio between 3HF-EO and β-CD is 1:1, and between 3HF-EO and γ-CD is 2:1. The above results was further supported by ESI-MS data. As shown in Fig. 4, the experimental isotopic distributions of the complexes of 3HF-EO/β-CD and 3HF-EO/γ-CD agreed well with corresponding theoretical predictions.

Secondly, ^{1}H NMR spectra were applied to investigate the host-guest complexation formed by 3HF-EO and the CDs. For this purpose, the NMR spectra of the neat 3HF-EO and the CDs,

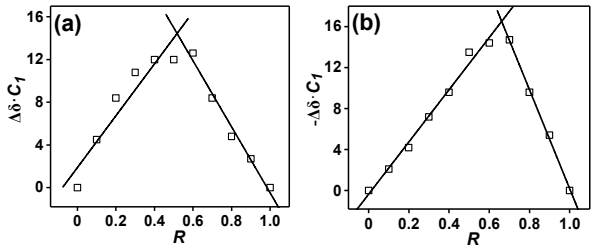

Fig. 3 The Job's plot for determining the association ratio of 3HF-EO to (a) β-CD or (b) γ-CD. The total concentration of 3HF-EO and β-CD (or γ-CD) was kept at 3 × 10^{-4} mol/L.

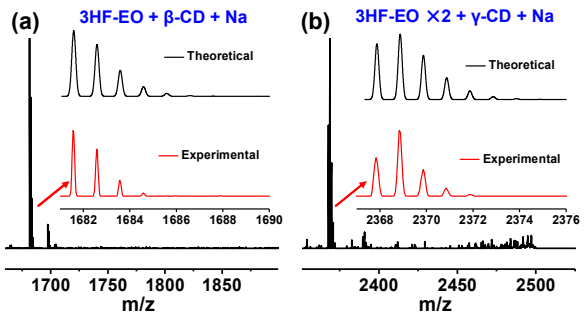

Fig. 4 ESI-MS of the complexes of (a) 3HF-EO/β-CD, (b) 3HF-EO/γ-CD. Inset: magnified theoretical isotopic distributions for the complexes.

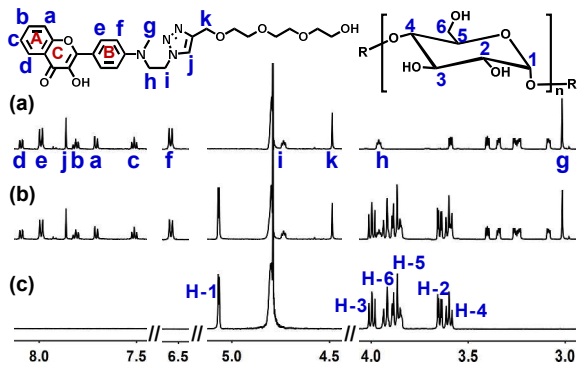

Fig. 5 ^{1}H NMR spectra of (a) 3HF-EO, (b) 3HF-EO in the presence of equimolar α-CD, (c) α-CD. The concentration of 3HF-EO is 1 × 10^{-4} mol/L. The solvent is D_2O.

as well as the mixture of 3HF-EO and the respective CDs were recorded. The H-3 and H-5 protons locate inside of the hydrophobic cavity, and H-2, H-4 and H-6 protons reside on the outer surface of the corresponding CDs. The chemical shifts of H-3 and H-5 protons are readily affected as guest molecule threads into the cavity of CD, which is because that the guest molecule will cause a shielding effect on the interior protons. Therefore, this characteristic is often used as an indicator to judge the formation of host-guest complexation.[49] As shown in Fig. 5, the addition of α-CD did not cause any change of chemical shift of the protons of 3HF-EO or α-CD, which indicates that there is no interaction between 3HF-EO and α-CD. This result is consistent with that being reflected by steady state fluorescence spectra.

The addition of β-CD into the aqueous solution of 3HF-EO induced chemical shift of protons on 3HF-EO and β-CD (shown in Fig. 6). Most of the chemical shifts of protons on β-CD moved to up-field, especially for that of the H-3 and H-5 protons, which indicates that β-CD and 3HF-EO formed host-guest complex. As for 3HF-EO, the chemical shifts of almost all protons on aromatic region moved to down-field, which should be explained by the reduced electron density around the protons owing to the formation of host-guest complex.[50] Herein, the concentration of 3HF-EO was 1 × 10^{-4} mol/L, and the 3HF-EO molecules are apt to aggregate, which should result in a relatively dense electron density around the protons.

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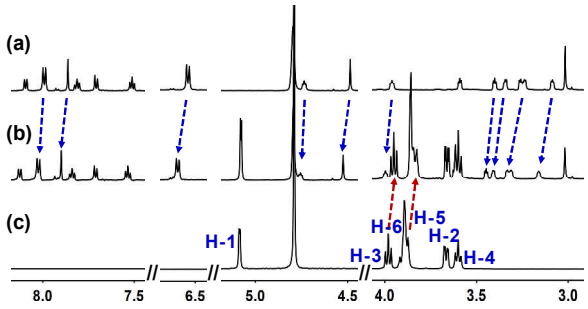

Fig. 6 ^{1}H NMR spectra of (a) 3HF-EO, (b) 3HF-EO in the presence of equimolar β-CD, (c) β-CD. The concentration of 3HF-EO is 1×10^{-4} mol/L. The solvent is D_2O.

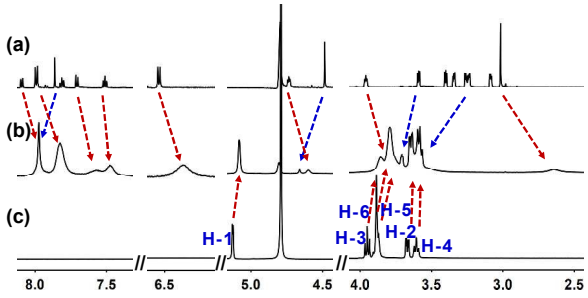

Fig. 7 ^{1}H NMR spectra of (a) 3HF-EO, (b) 3HF-EO in the presence of equimolar γ-CD, (c) γ-CD. The concentration of 3HF-EO is 1×10^{-4} mol/L. The solvent is D_2O

The formation of 3HF-EO/β-CD complex will definitely alleviate this effect, so that leading to the decrease of electron density around the protons. In addition, the up-field shift of the protons on benzene ring B (H-e and H-f, marked in the molecular structure) and the H-h, H-i, H-j and H-k protons in the vicinity are more obvious than that of the rest, suggesting that β-CD should mainly bond to the benzene ring B of 3HF-EO. As shown in Fig. 7, the addition of γ-CD into solution of 3HF-EO also caused the change of NMR spectra of 3HF-EO and γ-CD, but the situation is different with that happened in the 3HF-EO and β-CD system. The chemical shifts of the H-3 and H-5 protons on γ-CD moved to much higher field, which indicates that γ-CD formed inclusion complex with 3HF-EO. Most of the protons in aromatic part of 3HF-EO shifted to high-field upon addition of γ-CD. These results suggest that strong interaction between 3HF segments should exist in the complex, which is consistent with the 1:2 association ratio of γ-CD and 3HF-EO. As 3HF-EO was encapsulated with γ-CD, two molecules of 3HF-EO was confined in one cavity. This effect should be similar with the formation of aggregates of 3HF-EO, and the π–π stacking interaction should be even stronger. This explains the decrease of fluorescence intensity as well as the quantum yield This result also explains the broadened NMR signals of 3HF-EO upon addition of γ-CD due to the retarded mobility of 3HF-EO molecule.[51]

Protons in distance less than 0.4 nm can produce cross correlation named by Nuclear Overhauser Effect (NOE).[52] Therefore, 2D NOESY spectra are often used to investigate the spatial proximity of protons in host-guest complex by monitoring the intermolecular dipolar correlations. As shown

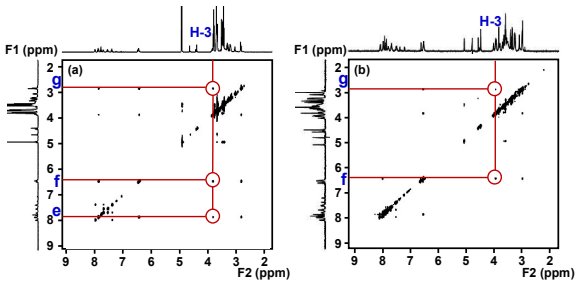

Fig. 8 2D NMR NOESY spectra of 3HF-EO in the presence of (a) β-CD or (b) γ-CD in D_2O

in Fig. 8, the H-3 protons of β-CD and H-e, H-f, H-g protons of 3HF-EO showed strong correlations, and the NOE effect between the H-3 and H-e protons was weaker than that between the H-3 and H-f protons, implying that the H-3 proton should be spatially closer to H-f proton. These results further confirm that β-CD should bind to benzene ring B of 3HF-EO. For the complexation of 3HF-EO and γ-CD, the correlations between the H-3 and H-f, H-g protons were observed. This result also indicates that 3HF-EO are thread in the cavity of γ-CD. Combining the 2D NMR results with that obtained from Job's plot, we can conclude that every γ-CD should encapsulate two 3HF-EO molecules due to the larger cavity of γ-CD. These results are in good accordance with those obtained from the Job's plot and ^{1}H NMR spectra.

4 Conclusions

A novel amphiphilic molecule 3HF-EO containing 3HF and oligo(ethylene oxide) was designed and synthesized. Being dispersed in water, 3HF-EO showed a remarkable single fluorescence emission, which can be assigned to the emission of its anionic species. The complexation with different CDs was employed to modulate the fluorescence intensity. α-CD with relatively small cavity is unable to encapsulate 3HF-EO, and hence it has little effect on the fluorescence emission. β-CD and γ-CD own suitably-sized cavity, and form complexes with one and two 3HF-EO molecules, respectively. The different type of complexation resulted in different effect on the fluorescence emission. β-CD showed enhancement effect, and reached to a QY as high as 62.7% in aqueous solution. On the contrary, γ-CD showed moderate reduction effect on the emission of 3HF-EO, and a relatively low QY of 10.5% was acquired.

Conflicts of interest

There are no conflicts to declare.

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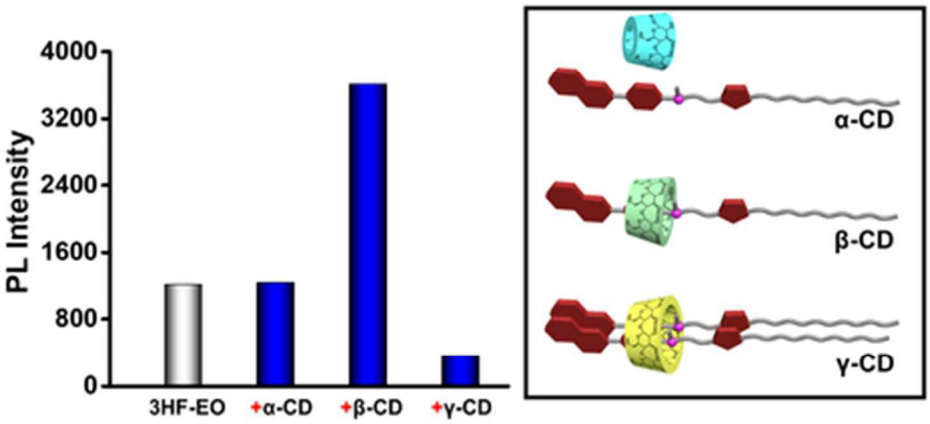

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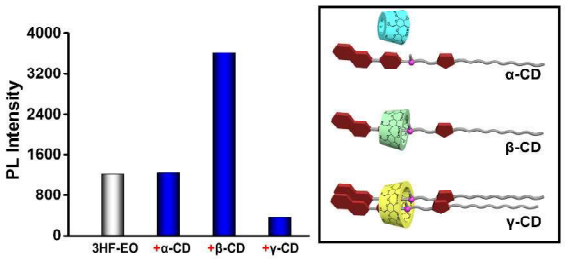

The remarkable single fluorescence emission of a water-soluble 3-hydroxyflavone derivative was modulated by host-guest complexation with different cyclodextrins.