

New ferrocenyl derivative with controllable aggregation-induced emission (AIE) characteristics

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A novel molecular switch, 7-(N,N-diethylamino)-2-oxo-2H-chromen-4-yl ferrocene carboxylate (FCC), was synthesized and fully characterized by ^1H NMR, ^{13}C NMR, and HRMS. Taking advantage of the properties of ferrocene as an electron donor active unit and the coumarin as a fluorescent unit, the dyad FCC shows a fast and reversible redox-switchable fluorescence emission. In sharp contrast to most photoluminescent chromophores, FCC has a unique enhanced emission through aggregation. The change of electrochemical signals (CV and DPV) indicated that the ferrocene (Fc) unit of FCC could form inclusion complex with Me- β -cyclodextrin (CD). This inclusion complex could further weaken the aggregation-induced emission (AIE) effect remarkably. This advance paves the way to introduce AIE property into molecular devices applications.

Keywords ferrocene, cyclodextrin, molecular switch, fluorescence, aggregation-induced emission (AIE)

1 Introduction

Molecular devices have developed at a good pace in the past decades with ever-increasing interest for molecular computation and molecular electronics [1–8]. As a fundamental and important class of molecular devices, fluorescence molecular switches [9,10] can realize fluorescent “on-off” function by controlling the chemical changes, such as coordination, redox, energy transfer, protonation, and isomerism.

One general mechanism in fluorescence molecular switches is photo-induced electron transfer (PET). In the off state of the

switch, PET could quench the fluorescence. Ferrocene has a sandwich-type molecular structure and a high degree of electron-rich aromatic system, and hence can be used as a donor in the PET system [11]. Its emergence is a milestone in the development of modern chemistry since it can be experienced reversible one-electron oxidation in most common solvents. In addition, coumarins are interesting fluorophores with regard to their photochemical and photophysical properties. Herein, we designed a new fluorescence molecular switch, FCC, based on electroactive ferrocene linking with a coumarin as a fluorescent unit (Figure 1).

The fluorescence of many chromophoric organics becomes weak when forming aggregation. Through aggregating, the molecules would form less emissive species, for example, excimers, and would lead to a reduction in the luminescence efficiency. This is a thorny problem in the development of photoluminescent materials [12]. Meanwhile, the “concentration quenching” in the fluorescence signal is the important challenge that restricts the application of multifunctional photochromic molecules to high-density optical memory systems [13]. The best approach is to develop new luminophoric materials that have an “aggregation-induced emission (AIE)” property [14]. This technology can be applied in areas of biologic probes [15], chemical sensors [16], photochromic materials [17], and organic light-emitting diodes (OLED) [18]. In addition, some positive attempts of AIE materials have been made in the area of fluorescence molecular switches [19]. In the same way, the target molecule (FCC) we reported here presents AIE property in mixed acetonitrile-water media. Furthermore, because β -cyclodextrin (β -CD) can form stable 1:1 complex with ferrocene or ferrocenyl derivatives [20], we use randomly methylated β -CD (Me- β -CD) to form inclusion complex with the ferrocene (Fc) unit of FCC, which can influence the aggregation of FCC and can further bring great impact to the AIE property.

2 Experimental

2.1 Chemicals and instruments

Oxalyl chloride and DMF were dried by 4A molecular sieve and distilled before use. Anhydrous CH_2Cl_2 was distilled from calcium hydride. Anhydrous THF was distilled from sodium wire. Commercially available reagents were used without further purification unless otherwise stated. Compounds were visualized with UV light at 254 and 365 nm. Melting points were determined on a hot-plate melting point apparatus and are corrected. ^1H NMR and ^{13}C NMR spectra were obtained by using a Bruker AV 400 spectrometer. High-resolution mass spectra were performed with an HP5989 mass

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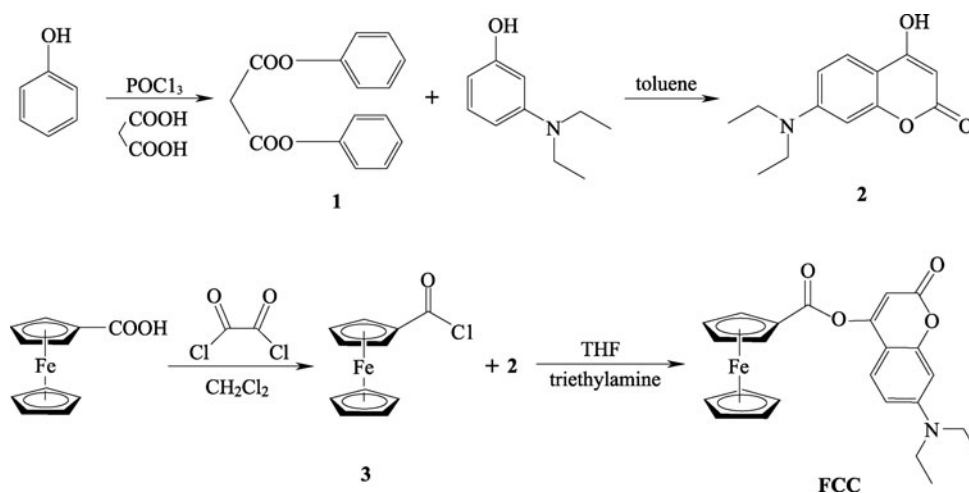


Figure 1 The synthetic route of FCC.

spectrometer and UV-Vis spectra on a Varian Cary 500 spectrophotometer (1-cm quartz cell used). Fluorescent spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed with a CHI 660C electrochemical workstation using a normal three-electrode cell with a Pt working electrode, a Pt wire auxiliary electrode, and Ag/AgCl reference electrode in saturated KCl solution. All potentials are quoted with respect to F_c^+/F_c under a nitrogen atmosphere at 25°C. The experiments were carried out in solutions containing $0.1 \text{ mol} \cdot \text{L}^{-1}$ of $[(n\text{Bu})_4\text{N}]\text{PF}_6$ as supporting electrolyte. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min, and the working electrode was cleaned after each run. CV curves were recorded at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$, and DPV curves were recorded at a scan rate of $20 \text{ mV} \cdot \text{s}^{-1}$.

2.2 Diphenyl malonate (1) [21]

A mixture of malonate (22.0 g, 212 mmol) and phenol (39.9 g, 424 mmol) was protected by argon. Through the addition funnel, phosphorus oxychloride (23 mL, 246 mmol) was slowly added dropwise at 0°C – 5°C over a period of 50 min. The reaction was immediate as evidenced by the evolution of hydrogen chloride. The reaction mixture was stirred 1.5 h at 115°C , and then, hydrogen chloride evolution ceased. When the mixture was cooled to 80°C , the upper clear liquid was poured into water (100 mL) and extracted with ethyl ether ($75 \text{ mL} \times 3$). The combined organic phase was washed with brine and dried over anhydrous MgSO_4 . The filtrate was evaporated under reduced pressure to afford **1** (41.7 g, 77%). $^1\text{H NMR}$ (400MHz, CDCl_3 , 25°C , TMS): δ (ppm) 3.87 (s,

2H, CH_2), 7.17 (d, 4H, $J = 8.4 \text{ Hz}$, Ph–H), 7.28 (t, 2H, $J = 8.8 \text{ Hz}$, Ph–H), 7.42 (t, 4H, $J = 7.2 \text{ Hz}$, Ph–H).

2.3 7-N,N-diethylamino-4-hydroxycoumarin (2) [22]

A mixture of diphenyl malonate (**1**) (41.7 g, 163 mmol), 3-(diethylamino)phenol (26.88 g, 163 mmol) and toluene (250 mL) was protected by argon. The mixture was refluxed for 9 h. Upon cooling to room temperature, compound **2** was precipitated and filtered off and washed with toluene, giving yellow powder. Yield: 13.4 g; 35%. $^1\text{H NMR}$ (400MHz, $\text{DMSO}-d_6$, 25°C , TMS): δ (ppm) 1.09 (t, 6H, $J = 7.2 \text{ Hz}$, CH_3), 3.39 (d-d, 4H, $J = 7.2 \text{ Hz}$, CH_3), 3.43 (s, 2H, CH_2), 6.42 (s, 1H, Ar–H), 6.64 (d, 1H, $J = 8.8 \text{ Hz}$, Ar–H), 7.53 (d, 1H, $J = 8.8 \text{ Hz}$, Ar–H).

2.4 Ferrocene carbonyl chloride (3)

A mixture of ferrocene carboxylic acid (2.32 g, 10 mmol), dry methylene chloride (50 mL), freshly distilled oxalyl chloride (6.4 g, 50 mmol), and DMF (7 drops) was stirred in the dark for 12 h at room temperature. Then, the contents evaporated to dryness under reduced pressure. The residue was dissolved in anhydrous THF (30 mL) for the next step reaction without further purification.

2.5 7-(N,N-Diethylamino)-2-oxo-2H-chromen-4-yl ferrocenecarboxylate (FCC)

A mixture of 7-N,N-diethylamino-4-hydroxycoumarin (**2**) (2.56 g, 11 mmol), anhydrous THF (50 mL), and triethylamine (2.1 mL) was protected by argon. A solution of ferrocene carbonyl chloride (10 mmol) in anhydrous THF (30 mL) was

added dropwise at 0°C–5°C over a period of 50 min. The reaction mixture was stirred for 10 h at room temperature. Then, the solution was filtered free of triethylamine hydrochloride, and the solvent evaporated under reduced pressure. The crude product was further purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/3) to afford orange solid. The product was recrystallized from methanol to give pure **FCC** as orange needle-like crystals. Yield: 3.80 g, 85%; m.p. 112°C–114°C. ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ (ppm) 1.23 (t, 6H, *J* = 7.2 Hz, CH₃), 3.44 (d-d, 4H, *J* = 7.2 Hz, N-CH₂), 4.33 (s, 5H, Cp-H), 4.60 (t, 2H, *J* = 2 Hz, Cp-H), 5.01 (t, 2H, *J* = 2 Hz, Cp-H), 6.22 (s, 1H, Ar-H), 6.55 (d, 2H, *J* = 2.4 Hz, Ar-H), 6.62 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.50 (d, 2H, *J* = 8.8 Hz, Ar-H). ¹³C NMR (400 MHz, CDCl₃, 25°C, TMS): δ (ppm) 12.44 (2C, CH₃), 44.86 (2C, N-CH₂), 68.70 (1C), 70.20 (5C, CpC), 70.79 (2C, CpC), 72.66 (2C, CpC), 97.58 (1C), 98.42 (1C), 104.17 (1C), 108.66 (1C), 123.67 (1C), 151.31 (1C), 156.42 (1C), 159.76 (1C), 163.15 (1C), 168.10 (1C). HRMS (EI): *m/z* [**FCC**] calc. 445.2909, found 445.0972.

3 Results and discussion

3.1 Synthesis

Figure 1 outlines the synthesis of the target molecule, 7-(*N,N*-Diethylamino)-2-oxo-2H-chromen-4-yl ferrocene carboxylate (**FCC**). Esterification of phenol followed by reaction with phosphorus oxychloride led to diphenyl malonate (**1**) in good yield of 77%. 7-*N,N*-Diethylamino-4-hydroxycoumarin (**2**) was synthesized easily in toluene, which was precipitated during the reaction and separated by simple filtration. The treatment of ferrocene carboxylic acid with an excessive amount of freshly distilled oxalyl chloride and a catalytic amount of DMF afforded ferrocene carbonyl chloride (**3**), which was dissolved in anhydrous THF for the final reaction without further purification. The final esterification in anhydrous THF at temperature around 0°C–5°C for 50 min and then at room temperature for 10 h afforded **FCC** in high yield of 85%. Compounds **1**, **2**, and **FCC** have been characterized by ¹H NMR spectroscopy, ¹³C NMR spectroscopy, and HRMS (EI) spectrometry.

3.2 Fluorescence molecular switch

The optical properties of **FCC** were measured by UV-Vis and fluorescence spectroscopy in THF solution, as shown in Figure 2. **FCC** shows an intense absorption at 350 nm (λ_{\max} , black line), and the molar extinction coefficient at λ_{\max} is determined to be $2.26 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. The fluorescence spectrum of **FCC** was excited at 340 nm (blue line), which

resulted in little fluorescence. However, the emission intensity of **FCC** was enhanced dramatically upon the addition of Fe(ClO₄)₃ to the solution (red line). The emission spectrum of oxidized **FCC** in THF displays typical emission band at 390 nm ($\lambda_{\text{ex}} = 340 \text{ nm}$), which is indeed the mirror images of the UV-Vis absorption spectrum, implying that the fluorescence of **FCC** is due to the coumarin unit. Because in the initial state, the photo-induced electron transfer (PET) from the F_c unit to the excited electron acceptor coumarin unit would result in fluorescence quenching, with **FCC** showing no fluorescence basically. However, after oxidation by Fe(ClO₄)₃, the electron-donating abilities of the F_c unit are reduced, and the PET function would be restrained, leading to fluorescence enhancement. Importantly, the electron donating abilities of the F_c unit can be reversibly modulated by the chemical or electrochemical redox reaction [11]. This result demonstrates the possibility of establishing a new redox-fluorescence switch based on **FCC**.

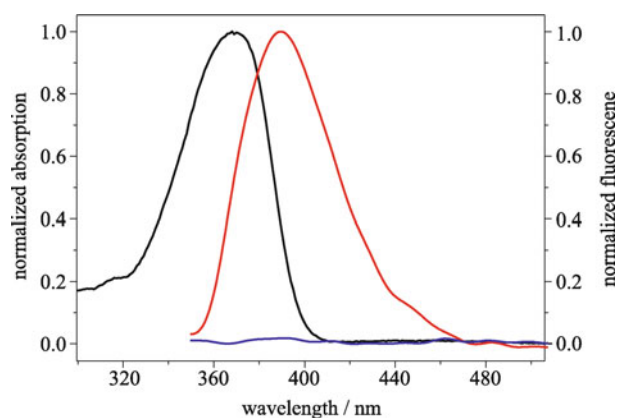


Figure 2 Normalized absorption (black) and fluorescence (blue, $\lambda_{\text{ex}} = 340 \text{ nm}$) spectra of the THF solution ($1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) of **FCC**, at 298 K, and change in fluorescence spectra (red, $\lambda_{\text{ex}} = 340 \text{ nm}$) toward oxidation (in the presence of Fe(ClO₄)₃).

3.3 AIE property

FCC shows a clear AIE property in mixed acetonitrile-water media (Figure 3) with different water/acetonitrile ratios. The emission from the acetonitrile solution of **FCC** is quite weak. However, with the increase in the proportion of water, the fluorescence gradually increased. When the volume fraction of water was increased to 60%, the fluorescence intensity increased to the strongest. However, the fluorescence started to decrease swiftly upon further increase in the proportion of water. Under UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$), this AIE phenomenon could be clearly observed by photograph (Figure 4). Since water is an antisolvent for **FCC**, the molecules must have aggregated in the acetonitrile-water and exhibited strong

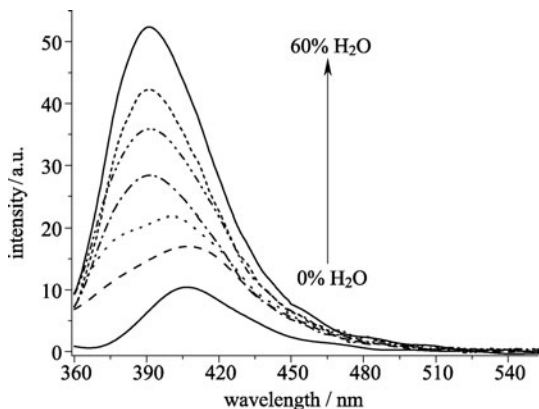


Figure 3 Fluorescence spectra ($\lambda_{\text{ex}} = 340 \text{ nm}$) of FCC ($4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, at 298 K) in acetonitrile with different amount of H_2O .

fluorescence. This phenomenon indicates that FCC molecules aggregated markedly when the volume fraction of water reached 60%. The aggregation should be nanodimensional [23,24]. Scanning electron microscopy (SEM) shows the nanoparticle size distributions of the sample, which was prepared by a reprecipitation method from acetonitrile solution with distilled water (Figure 5).

The restriction of intramolecular rotation (RIR) in the aggregates is the main cause of the AIE effect [25]. The intramolecular rotation is active in the solutions, which is restricted in the aggregates due to the physical constraint. As any molecular motions consume energy, the aggregation changes the nonradiative path to the radiative decay, resulting in the enhancement of fluorescence. In addition, the aggregation could weaken the energy loss from the ruleless circumcolumnar movement of ferrocene unit [26]. However, it will form aggregates with larger dimensions when the water content is very high ($> 70\%$). Moreover, these amorphous aggregates are only weakly fluorescent (Figure 4), which is similar to the fluorescence of solid of FCC. Therefore, AIE is a unique phenomenon only in the particular size range. Unfortunately, we could not evaluate whether oxidized FCC has AIE property. Using anthracene as the standard ($\Phi_{\text{F}} = 0.27$) [27], we observed that the fluorescence quantum yield of

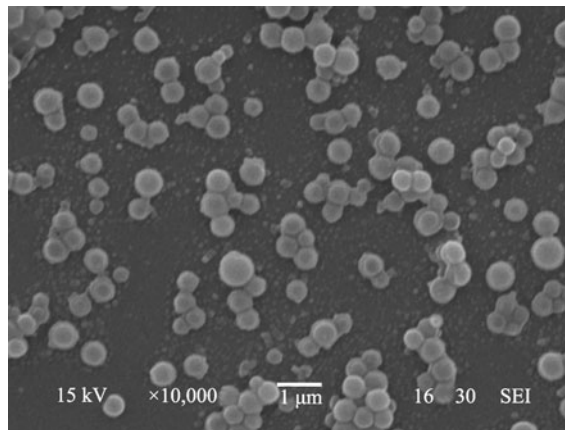


Figure 5 SEM image of FCC nanoparticles obtained from its suspension containing 60% volume fractions of water in acetonitrile.

oxidized FCC ($\Phi_{\text{F}} = 0.523$) is much higher than FCC in the solutions (free, $\Phi_{\text{F}} = 0.002$) as well as aggregates (AIE, $\Phi_{\text{F}} = 0.014$). Therefore, whether oxidized FCC has AIE property, it is hard to detect.

3.4 Adduct formed with cyclodextrins

Cyclodextrins (CDs) has internal cavities, which can accommodate a wide range of guest molecules, ranging from polar compounds to apolar compounds. The slightly apolar cyclodextrin cavity tends to be occupied by appropriate “guest molecules”, which are less polar than solvent molecules [28]. The ability of CDs to include a part of an organometallic compound has been demonstrated by numerous researchers [29]. This kind of inclusion generally modifies the chemical, electrochemical, and photochemical properties of organometallics. Ferrocenyl derivatives have been most studied in these organometallics.

Moreover, it has been demonstrated that the orientation of ferrocene in β -CD is nearly parallel to the molecular axis of β -CD. The electrochemical parameters of redox active ferrocene unit are often strongly affected by the presence of the host, β -CD, affording a valuable tool to investigate the complexation

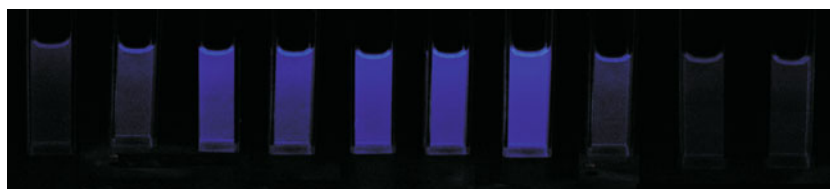


Figure 4 Photograph of the emission of FCC ($4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, $\lambda_{\text{ex}} = 365 \text{ nm}$, at 298 K) in acetonitrile with different amount of H_2O (from left to right: 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90%).

processes [30]. The apolar FCC is hard to dissolve in water; also the solubility of β -CD in nonaqueous solvents have similar difficulty. However, Me- β -CD has a good solubility in a variety of organic solvents, which were introduced to determine the inclusion complex. Figure 6 shows the CV and DPV data in CH₃CN solution containing 0.1 mol·L⁻¹ [(*n*-Bu)₄N]PF₆ as supporting electrolyte, contrasting the effect of Me- β -CD on the electrochemical behavior of FCC. The comparison of CV (Figure 6 (a)) demonstrates that the complexation of F_c unit of FCC with Me- β -CD is detected experimentally by a shift in the half-wave potential ($E_{1/2}$) to more positive values ($\Delta E_{1/2} = +48$ mV) and by a decrease in the peak currents (I_{pa}). The anodic potential shift reveals that the reduced form (F_c) of the guest is more stabilized by complexation than the oxidized form (F_c⁺). The comparison of the DPV (Figure 6 (b)) about the inclusion complex exhibits similar electrochemical signal change.

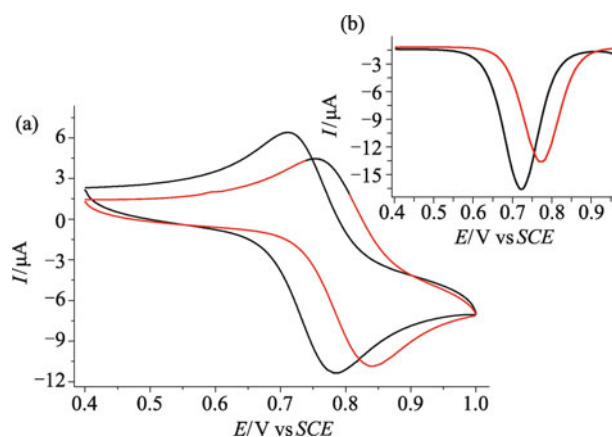


Figure 6 Evolution of the (a) CV and (b) DPV of FCC (1×10^{-3} mol·L⁻¹) in CH₃CN with [(*n*-Bu)₄N]PF₆ (0.1 mol·L⁻¹) as supporting electrolyte, scanned at 20 mV·s⁻¹, from 0.4 V to 1.0 V when Me- β -CD is added: from 0 (black line) to 5 equiv. (red line).

While these voltammetric data are qualitative observations of inclusion complex, the best and more general methodology to obtain the corresponding equilibrium constants relies on the experimental voltammograms. However, this approach may show limitations as the mechanism of the complexation reactions becomes more complicated [20]. The association constants (K_{ass}) between β -CD and F_c unit [29] is greater than K_{ass} between β -CD and coumarin unit [31]. Moreover, from such large changes of electrochemical signals (Figure 6), we can determine that the Me- β -CD formed an inclusion complex with the Fc unit of FCC, rather than the coumarin unit.

3.5 Influence of AIE with cyclodextrins

FCC possesses the AIE property and can form an adduct with Me- β -CD besides. Could Me- β -CD affect its AIE property? We examined the dependence of fluorescence quantum yield (Φ_F) on the solvent composition of the acetonitrile-water mixture using anthracene as the standard ($\Phi_F = 0.27$) [27]. As seen in Figure 7, in the presence of Me- β -CD, the Φ_F of FCC has a similar change with AIE property as mentioned above. However, the magnitude of this Φ_F change is so weak that it is hard to be detected.

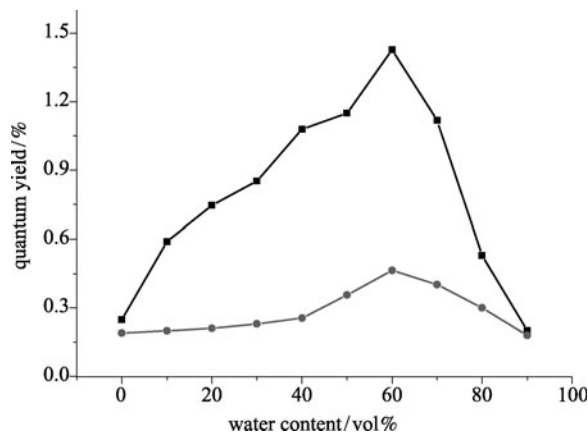


Figure 7 Relative quantum yields of FCC (4.0×10^{-5} mol·L⁻¹, at 298 K) versus solvent composition of the water/acetone mixture, in the absence (black) of and presence of Me- β -CD (10 equiv.).

The adduct formed with Me- β -CD has better solubility than free FCC in the mixed solvent with high proportion of water. Thus, the aggregation is difficult to form, and SEM shows no nanoparticle. Therefore, Me- β -CD could indirectly affect the AIE property though inclusion complexation.

4 Conclusion

In summary, we have designed and synthesized a novel ferrocenyl derivative containing a coumarin fluorophore—FCC. The synthetic strategy is straightforward with high yield. FCC is a redox-controlled fluorescence molecular switch due to PET mechanism, which is the first example with AIE property based on ferrocene at the same time. Though forming adducts with Me- β -CDs, the AIE property could be affected greatly. We introduced this unique AIE performance into the field of molecular devices for the first time.

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References

- Zhang, H.; Wang, Q.; Liu, M.; Ma, X.; Tian, H., *Org. Lett.* **2009**, *11*, 3234–3237
- Ma, X.; Tian, H., *Chem. Soc. Rev.* **2009**, *39*, 70–80
- Balzani, V., *Molecular Devices and Machines: A Journey into the Nano World*; Wiley-VCH: Weinheim, Germany, 2003
- Badjic, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F., *Science* **2004**, *303*, 1845–1849
- Zhou, Y. C.; Wu, H.; Qu, L.; Zhang, D. Q.; Zhu, D. B., *J. Phys. Chem. B* **2006**, *110*, 15676–15679
- de Silva, A. P.; Uchiyama, S., *Nat. Nanotechnol.* **2007**, *2*, 399–410
- Kou, S.; Lee, H. N.; van Noort, D.; Swamy, K. M. K.; Kim, S. H.; Soh, J. H.; Lee, K. M.; Nam, S. W.; et al, *Angew. Chem. Int. Ed.* **2008**, *47*, 872–876
- Amendola, V.; Dallacosta, C.; Fabbrizzi, L.; Monzani, E., *Tetrahedron* **2008**, *64*, 8318–8323
- Feringa, B. L., *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001
- Martínez, R.; Ratera, I.; Tárraga, A.; Molina, P.; Veciana, J., *Chem. Commun.* **2006**, *36*, 3809–3811
- Zhang, R.; Wang, Z.; Wu, Y.; Fu, H.; Yao, J., *Org. Lett.* **2008**, *10*, 3065–3068
- Zhao, Q.; Li, L.; Li, F.; Yu, M.; Liu, Z.; Yi, T.; Huang, C., *Chem. Commun.* **2008**, *6*, 685–687
- Lim, S. J.; An, B. K.; Jung, S. D.; Chung, M. A.; Park, S. Y., *Angew. Chem. Int. Ed.* **2004**, *43*, 6346–6350
- Zeng, Q.; Li, Z.; Dong, Y.; Di, C.; Qin, A.; Hong, Y.; Ji, L.; Zhu, Z.; et al, *Chem. Commun.* **2006**, *1*, 70–72
- Huang, J.; Wang, M.; Zhou, Y.; Weng, X.; Shuai, L.; Zhou, X.; Zhang, D., *Bioorg. Med. Chem.* **2009**, *17*, 7743–7748
- Zheng, Y. S.; Hu, Y. J., *J. Org. Chem.* **2009**, *74*, 5660–5663
- Lim, S. J.; An, B. K.; Jung, S. D.; Chung, M. A.; Park, S. Y., *Angew. Chem. Int. Ed.* **2004**, *43*, 6346–6350
- Liu, Y.; Tao, X.; Wang, F.; Dang, X.; Zou, D.; Ren, Y.; Jiang, M., *J. Phys. Chem. C* **2008**, *112*, 3975–3981
- Yang, Z.; Chi, Z.; Yu, T.; Zhang, X.; Chen, M.; Xu, B.; Liu, S.; Zhang, Y.; Xu, J., *J. Mater. Chem.* **2009**, *19*, 5541
- Kaifer, A. E., *Acc. Chem. Res.* **1999**, *32*, 62–71
- Jabin, I.; Revial, G.; Monnier-Benoit, N.; Netchitaïlo, P., *J. Org. Chem.* **2001**, *66*, 256–261
- Chen, Y. S.; Kuo, P. Y.; Shie, T. L.; Yang, D. Y., *Tetrahedron* **2006**, *62*, 9410–9416
- Kang, L.; Wang, Z.; Cao, Z.; Ma, Y.; Fu, H.; Yao, J., *J. Am. Chem. Soc.* **2007**, *129*, 7305–7312
- Ning, Z.; Chen, Z.; Zhang, Q.; Yan, Y.; Qian, S. X.; Cao, Y.; Tian, H., *Adv. Funct. Mater.* **2007**, *17*, 3799–3807
- Hong, Y.; Lam, J. W. Y.; Tang, B. Z., *Chem. Commun.* **2009**, *29*, 4332–4353
- Zhang, D.; Zhang, Q.; Su, J.; Tian, H., *Chem. Commun.* **2009**, *13*, 1700–1702
- Dawson, W. R.; Windsor, M. W., *J. Phys. Chem.* **1968**, *72*, 3251–3260
- Szejtli, J., *Chem. Rev.* **1998**, *98*, 1743–1754
- Hapiot, F.; Tilloy, S.; Monflier, E., *Chem. Rev.* **2006**, *106*, 767–781
- Buriez, O.; Heldt, J. M.; Labbé, E.; Vessières, A.; Jaouen, G.; Amatore, C., *Chemistry* **2008**, *14*, 8195–8203
- These literatures describe the association constants (*K_{ass}*) between β -CD and coumarin: a) Scypinski S. and Drake J. M., *J. Phys. Chem.* **1985**, *89*, 2432–2435; b) Takakusa H., Kikuchi K., Urano Y., Higuchi T., and Nagano T., *Anal. Chem.* **2001**, *73*, 939–942