Construction and modulation of dual responsive fluorescent aggregates combined with molecular dynamics simulation

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Abstract
The fluorescent functional material prepared by combining 16-alkyl (ferrocenyl-methyl) ammonium bromide (Fc16AB) and dye molecule Congo red (CR) via ionic self-assembly strategy exhibits double stimuli-responsive behavior triggered by redox and pH value. Both the fabrication and switching mechanism of aggregates are proposed according to the cooperative binding of noncovalent interactions, including π-π stacking, electrostatic interactions, charge transfer interaction, and amphiphilic hydrophobic association. The optimal geometry and energy transfer between monomers and aggregate are studied by means of quantum chemistry calculation and wavefunction analysis, which provides a deep and theoretical understanding for formation mechanism of ionic self-assemblies. Moreover, the fluorescent switching behavior of assemblies upon pH was studied in detail, which opens the new way for the construction of organic light-emitting diode (OLED).

KEYWORDS
ionic self-assembly, pH, quantum chemistry calculation, redox species, stimuli-responsive

1 | INTRODUCTION

The supramolecular self-assembly with multiple stimuli-responsive behaviors has gained much exposure due to its potential applications in biomaterial, photoelectric material, and functional nano-devices.[1–4] Among the techniques, ionic self-assembly (ISA), that is, the coupling of oppositely charged building blocks by electrostatic attraction, has been widely used to construct supramolecular self-assembly due to its advantages, such as simplicity, designability, flexibility, and reliability.[5–7] The microscopic structures and properties of functional materials could be altered by changing the property of building blocks.[8–10] In recent years, the self-assembly of dye molecule and surfactant has received increasing attention because of their multiple stimuli-responsive behaviors, including redox species,[11–13] temperature,[14–17] pH,[18–21] light,[22–25] and so on. As a common dye molecule, congo red (CR) was widely used in the preparation of self-assembly because of the existence of sensitive units amino and azo groups. Rounaghi et al.[26] constructed a pH optode by fixing CR on a triacetyl cellulose film, and the sensor showed good repeatability and stability. Li et al.[27] designed a photo-switchable sulfonic-azobenzene (the analog of CR), and the results showed that trans-cis photoisomerization of azobenzene under UV irradiation...
was responsible for the morphological transition of assemblies from branched to vesicle-like structure. Our group obtained hierarchical materials by complexing surfactant 16-alkyl (ferrocenyl-methyl) ammonium bromide (Fc16AB) and anionic alizarin red (AR), which exhibited multiple stimuli-responsive behaviors, including redox, pH, and β-cyclodextrin inclusion.[28]

As we all know, the structure, size, and morphology of self-assembly can be characterized by a variety of advanced experimental characterization.[29] However, it is still a great challenge to observe the dynamic transformation at the micro level, especially for the self-assembly process. As the theoretical extension and supplement of experimental data, the mesoscopic quantum chemical computation, including geometrical optimization and wave function analysis, enabled a dynamic simulation to provide theoretical support for self-assembly at microsecond scale.[30] However, current simulation studies about the chemical computation mainly focused on describing molecular geometry and microcosmic self-assembly process, and few work has been done to understand the mechanism underlying the self-assembly process. Molla et al.[31] studied the self-assembly of the naphthalene diimide (NDI) ring and carboxylic acid group using DFT calculations method, and the results showed that the aggregation of carboxylic acid-appended NDI chromophores was ascribed to the H-bonding of carboxylic acid groups, which was verified by Gibbs free energy calculation. Jayaraman et al.[32] constructed the assembly by combining dimers/oligomers of allomelanin and 1,8-dihydroxynaphthalene (DHN), and the influence of dimer structure and mixture composition on nanostructure of assemblies was studied by explicit-solvent atomistic molecular dynamics simulations.

Herein, the supramolecular self-assembly constructed by complexing CR and Fc16AB exhibited double stimuli-responsive behaviors upon redox species and pH value. The morphology transformation from spherical particles to rod-like fibers was observed by changing pH value of the system. Meanwhile, the rod-like micelle was obtained by the addition of oxidant Ce(SO₄)₂. Furthermore, the dynamic process of self-assembly was investigated by implementation quantum chemical computation method and the total energy of assembly was calculated. According to the data obtained by molecular simulation in combination with stacking parameter formula, the formation mechanism of micelle was proposed.

2 | EXPERIMENTAL SECTION

2.1 | Materials

(N,N-Dimethylamino)methylferrocene (purity 97wt%) and congo red (CR) were purchased from Adams-beta (Shanghai, China). 1-Bromohexadecane was obtained from Sinopharm Chemical Reagent Ro. Ltd., Shanghai. The surfactant Fc16AB was synthesized according to the procedure described in the literature.[33]

2.2 | Preparation of the CR-Fc16AB assembly

The CR-Fc16AB assembly with ferrocene group in reduced form was prepared by mixing two aqueous solutions of CR and Fc16AB with the equal concentration (2.0 mmol.L⁻¹) and different volume (CR:Fc16AB = 1:2). Then, the samples were placed in an incubator at 25°C for at least 7 days.

2.3 | Preparation of the CR-Fc⁺ 16AB assembly

The Fc16AB was oxidized by adding Ce(SO₄)₂ equal to half the molar amount of Fc16AB to obtain aqueous solution in oxidized form (Fc⁺ 16AB). Then two aqueous solutions of Fc⁺ 16AB and CR were mixed to prepare CR-Fc⁺ 16AB assembly, and the process were similar to that of CR-Fc16AB assembly.

2.4 | Preparation of the CR-Fc16AB at different pH values

The CR-Fc16AB aqueous solutions with different pH values were obtained by adding HCl or NaOH solutions. The resulting products were stored in an incubator for preservation.

2.5 | Computational studies

Preliminary computational studies were conducted using Gaussian 16 software based on density functional theory (DFT), B3LYP/ 6–31G (d, p) (for CR and Fc16AB), and wB97X-D / 6–31G (d,p) (for CR-Fc16AB) basis set, respectively. The calculations were carried out at 298.15 Kelvin and 1 atm using the water as solvent. In addition, liquid-phase Gibbs free energy was obtained according to optimized monomers and aggregate. The π-π stacking interaction between CR molecules was calculated by adjusting the distance between them, and the molecular dimensions were measured by Gaussian View software.

2.6 | Characterization

The transmission electron microscopy (TEM) (Tecnai G2 20) and high-resolution TEM (HRTEM) (Tecnai G2
FIGURE 1 1H NMR spectrum of CR-Fc16AB complex at the molar ratio of 1:2

F20 S-TWIN) characterizations were carried out with the accelerating voltage at 120 and 200 kV, respectively. The scanning electron microscopy (SEM) images were obtained by a Quanta 250 (FEI, USA) with the voltage of 30 kV. The aqueous solution of aggregates was dropped onto a clean silicon wafer and dried overnight before being sprayed by gold. The 1H NMR spectra were conducted on a Bruke AVANCE III HD 400 NMR spectrometer at room temperature. Fourier-transform infrared (FTIR) spectra were recorded on a Bruker-500 spectrometer in the range of 4000–400 cm–1. The UV-vis absorption spectra were carried out on a HP8452A UV-vis absorption spectrophotometer equipped with a 10 mm light path quartz cell. The fluorescence spectra of complexes were obtained by using Britton Robinson (B-R) buffer solution on a fluorescence spectrometer (Hitachi F-7000) with a quartz cell (1×1 cm). Electrochemical measurement was carried out according to the procedures described in the literature.[28]

3 | RESULTS AND DISCUSSION

The binary complex of CR-Fc16AB may aggregate and precipitate out of the mixed dilute aqueous solutions of CR and Fc16AB because of the enhancement of hydrophobicity when they were mixed together. Only a small amount of aggregates could be obtained when the concentration of CR and Fc16AB was 0.5 mmol.L–1, and a large amount of aggregates could be observed when the concentration increased to 2.0 mmol.L–1. Further increase of concentration did not have significant effect on the visual observation and morphology of self-assembly (see Supporting Information, Figure S1). Therefore, the concentration 2 mmol.L–1 was chosen to prepare assemblies in the following experiments. At the same time, the composition of binary complex was determined by 1H NMR spectroscopy as shown in Figure 1. All proton signals for CR and Fc16AB were obtained and a slight shift could be distinctly observed in the downfield position for H-4 (6H, -N-(CH3)2), H-5 (2H, N(CH3)2-CH2), and H-8 (2H, FcCH2N(CH3)2) compared with that of Fc16AB (Figure S2). The stoichiometry between CR and Fc16AB in the binary complex was determined as a 1:2 molar ratio by comparing the peak integral intensities. Moreover, the 1H NMR of complex were almost the same when the molar ratio of CR/ Fc16AB were 1:1 and 2:1 respectively (Figure S3 and Figure S4), indicating that the precipitates were not the simple mixture of CR and Fc16AB from the solution but the ISA complex of them.

At the same time, FTIR spectra of CR, Fc16AB and binary complex were recorded and shown in Figure 2. It can be seen that for CR molecule (curve A), the bands at 1600, 1584, and 1447 cm–1 were attributed to infrared characteristic peak of benzene, which correspond to C-H and C=C stretching vibration, respectively. Meanwhile, the band at 3467 cm–1 corresponds to the N-H stretching vibration of CR molecule. For Fc16AB (curve B), the FTIR bands located at 2918, 2850, and 1387 cm–1 were characteristic peaks of the methyl functional groups, and the band at 3443 cm–1 was attributed to C-H stretching vibration of ferrocene. All the signals could be observed for infrared spectrum of CR-Fc16AB (curve C), and a slight shift for the signal corresponding to C=C stretching vibration of benzene implying the formation of CR-Fc16AB self-assembly.
In addition, the liquid-phase Gibbs free energies for the optimized geometries of CR, Fc16AB and aggregates were calculated by B3LYP and wB97X-D/6-31G (d,p) basis set,[31] and the optimized energy indicated that the aggregates formed by complexing CR and Fc16AB was stable with an overall total energy change $\Delta G = \eta 677.70 \text{ kcal.mol}^{-1}$ according to Equation (1). The corresponding optimized geometries were shown in Figure 3. The interaction of CR and Fc16AB resulted from intramolecular charge transfer (ICT), and the change of electronic push-pull capability led to the redistribution of $\pi$-electron and the decrease of energy. Thus, the stable supramolecular structure was formed.

$$
\Delta rG_m^\theta = \left( \sum_i v_i \Delta f \cdot G_{m,i}^\theta \right)_{\text{products}} - \left( \sum_i v_i \Delta f \cdot G_{m,i}^\theta \right)_{\text{reactants}}
$$

(Figure 2) FTIR spectrums of CR (A), Fc16AB (B), and CR-Fc16AB (C)

To further explore the assembly mechanism of CR-Fc16AB aggregates, UV-vis absorption spectra of CR and binary complex were recorded as shown in Figure 4A. The absorption peaks at 350 nm and 498 nm ($n-\pi^*$ transition) correspond to the characteristic absorption of CR chromophore. After the formation of CR-Fc16AB aggregates, the absorption peak decreased dramatically, and a blue shift was clearly observed, which indicated that they adopted an H-aggregate arrangement (face to face).[35] The $\pi-\pi$ stacking distance could be calculated as 3.47 Å according to B3LYP/6-31G (d, p) basis set (Figure 4B). The SEM and TEM observations shown in Figure 4C and 4D indicated that the morphology of precipitated aggregates was rod-like structure with length of 1.5 µm and width of 30 nm. Moreover, the formation mechanism of rod-like structure could be simulated by quantitative calculation. As shown in Figure 5, CR molecule adopted a two-dimensional plane conformation with width at 0.726 nm and length at 2.60 nm, and Fc16AB molecule contained a hydrophobic chain with length at 2.10 nm. When the solutions containing CR and Fc16AB molecules were mixed together, two sides (sulfonic acid group) of CR molecule could be bound to the head group of Fc16AB molecule with long hydrophobic chains, thus a rod-like structure was formed.

Based on the redox property of ferrocene group, we wonder if the property of CR-Fc16AB assembly can be modulated by redox species.[36] In order to verify this, electrochemical measurement for CR-Fc16AB assemblies was performed by cyclic voltammetry (CV) using CR-Fc16AB/GC as working electrode. Figure 6A depicts the CV curve of CR-Fc16AB complex with the potential ranging from 0 to 1.0 V. As can be seen from Figure 6A, a pair of reversible redox peaks at 0.52 and 0.60 V could be observed, corresponding to the transition of CR- Fc16AB and CR- $\text{Fc}^{+}$16AB. Moreover, the potential difference of 0.08 V proved the fine electrochemical reversibility of complex. After adding oxidant Ce(SO$_4$)$_2$ into Fc16AB solution, the aggregates formed by CR and Fc16AB disappeared, and the solution exhibited only a transparent

(Figure 3) Partial optimized geometries and total Gibbs free energies of CR (A), Fc16AB (B), CR-Fc16AB (C)
FIGURE 4  UV-vis absorption spectra for CR and CR-Fc16AB at pH = 7 (A), π-π stacking between CR molecules (B), SEM (C), and TEM (D) micrographs of CR-Fc16AB assemblies at pH = 7

FIGURE 5  The optimized geometries and molecular size of CR-Fc16AB based on 6–31G (d,p) basis set

appearance, indicating the formation of new aggregates. The transition from Fc16AB to Fc+16AB was supported by the change of UV–vis absorption spectra as shown in Figure 6B. It can be seen that the characteristic absorption peak for oxidized Fc16AB (Fc+16AB) (630 nm) became more obvious, meanwhile the absorption peak for Fc16AB (431 nm) was suppressed. Moreover, when a beam of light passed through the reagent bottle filled with CR-Fc+16AB mixture solution, a bright “path” can be observed from the direction of perpendicul ar distance, which proved the formation of colloidal dispersed system by CR and Fc+16AB (Figure 7B, inset). The detailed information for CR-Fc+16AB assemblies could be characterized by HRTEM as shown in Figure 7A and 7B, which revealed the presence of the rod-like micelle with width of 200 nm and length of 500 nm. The formation mechanism of rod-like micelles could also be explored by the wB97X-D/6-31G (d, p) basis set. The area for hydrophilic group (ferrocene group) with 0.19 nm² were obtained, and the area for hydrophobic group (long alkyl chain) was 0.088 nm². Therefore, the stacking parameter of assembly could be calculated as 0.46 according to the stacking parameter formula (Equation (2)), which make it easy to form rod-like micelles.

\[ p = \frac{a_c}{a_0} \]  

where \( a_c \) and \( a_0 \) was the cross-sectional area of the hydrophobic groups and hydrophilic groups, respectively. Moreover, this transition process could be repeated at least three times by adding oxidant and reductant alternatively (see Supporting information, Figure S5).

In view of the essence of amidogen groups in the CR molecule, pH value could be another stimulus for CR-Fc16AB complex due to the protonation and/or deprotonation of CR molecule (Figure 8A). The aqueous
solution with different pH values were obtained by adding HCl and NaOH (see Supporting information, Figure S6). Further exploration was manifested based on UV-Vis spectra of CR solutions with the initial concentration of 0.1 mmol L⁻¹. As shown in Figure 8B, when the pH value increased from 3.0 to 5.0, a slight blue shift at the maximum absorption peak could be observed, and the absorption intensity also increased slightly, which corresponded to the deprotonation of CR. Further increase of pH value to above 6.0, a dramatic blue shift occurred accompanied by the significant increase of absorption intensity, which was ascribed to the n-π* transition and the deprotonation of CR. At the same time, the influence of protonation and/or deprotonation on CR molecule could be obtained by quantum chemical calculations as shown in Figure 8C. It can be seen that the decrease of pH values could not result in the structural transformation of CR molecule, but only affected the distance of π-π stacking, which increased from 3.8 Å to 3.9 Å. Thus, the increase of pH value led to the change of the morphology and property of self-assembly. As can be seen from Figure 9, when the pH value increased to 9, the essence of highly alkaline aroused the aggregation of rod-like structure (Figure 9C). However, when the pH value decreased to 1, large number of sphere structure with diameter about 300–500 nm was formed because of the transformation of CR molecule from deprotonation to protonation (Figure 9A).

Moreover, the CR-Fc16AB assemblies exhibited different fluorescence intensity by adjusting pH value of the system. The results obtained by fluorescence spectrometer showed that the intensity at 420 nm increased with the increase of pH value (Figure 9D and 9E). Therefore, a pH fluorescent switch was designed successfully, which make it have potential application in the field of organic light-emitting device (OLED). As shown in Scheme 1, the multi-layer OLED device was a sandwiched structure with a luminescent layer and two transmission layers between positive and negative electrodes. The aggregate film obtained by different pH was sprayed by spin coater device to obtain the good luminous layer for OLED. Driven by an electric...
**FIGURE 9** The SEM images (A-C), fluorescence spectra (D), and changing trend of fluorescence intensity (E) for CR-Fc16AB with different pH values. The excitation wavelength was 348 nm.

**SCHEME 1** Schematic diagram of OLED device constructed by CR-Fc16AB assemblies at different pH value.
field, both holes and electrons could move around in the luminescent material to form excitons. Then, the light was released by excitons radiation attenuation and the heat was generated by non-radiation attenuation.[39]

### 4 | CONCLUSION

In summary, the binary complex prepared by complexing CR and Fc16AB via ISA strategy exhibited dual responsive behaviors. The CR-Fc16AB assemblies showed rod-like structure with electrochemical properties, which could be transferred to micelle by the addition of oxidant. And the transformation of morphology from spherical to rod-like fibers was observed by changing pH values. Meanwhile, the CR-Fc16AB assemblies exhibited different fluorescence intensity by adjusting pH value, which provided a novel construction method of the fluorescent switching device for organic light-emitting diode (OLED). In addition, it was worth emphasizing that the stable configuration of CR, Fc16AB, CR-Fc16AB, CR-Fc16A were simulated by quantum chemistry calculation and wavefunction analysis. The assembly process was confirmed successfully by comparing the Gibbs free energy changes of two monomers and binary complex.

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### CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

### DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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