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ORIGINAL PAPER

Efficient Encapsulation of Chloroform with Cryptophane-M and the Formation of Exciplex Studied by Fluorescence Spectroscopy

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Abstract Efficient encapsulation of small molecules with supermolecules is one of significantly important subjects due to strong application potentials. This article presents the interaction between cryptophane-M and chloroform by fluorescence spectroscopy. The sonicated cryptophane-M solution exhibits light green color in chloroform, and the solid obtained from the evaporation of chloroform also has different color from that of cryptophane-M. In contrast, the sonicated cryptophane-M solutions in other solvents are colorless, and the solid obtained from the evaporation of these solvents has the same color as that of cryptophane-M. Furthermore, the freshly prepared cryptophane-M solution in different solvents is almost colorless, and the solid obtained from the evaporation of these solvents displays the same color as that of cryptophane-M. Although the sonicated cryptophane-M solutions in different solvents have very similar absorption spectra, they exhibit quite different emission spectra in chloroform. In contrast, the freshly-prepared cryptophane-M solutions show similar absorption and emission spectroscopy in various solvents. The variation of the fluorescence spectroscopy in binary solvents with the increasing chloroform ratio suggests that cryptophane-M and chloroform form a 1:1 exciplex, and the binding constant is estimated to be 292.95 M^{-1}. Although all solvents are able to enter into the cavity of cryptophane-M, only chloroform can stay in the cavity of cryptophane-M for a while, which is mostly due to the strong intermolecular interaction between cryptophane-M and chloroform, and this results in the formation of the exciplex between them.

Keywords Supramolecule · Cryptophane-M · Exciplex · Encapsulation · Chloroform

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Introduction

The inclusion complexes of the neutral or charged species in the inner cavity of organic hosts have been received considerable attention [1, 2]. Such complexes are generally characterized by weak but specific non-covalent interaction between the host and the guest [3], which have been found in a wide range of applications, including molecular recognition [4], drug delivery [5], separation and storage [6], biosensing [7] and catalysis (*chemical reaction occurs inside the confined space of a molecular nanoreactor*) [8]. Hence, an excellent selectivity between the host and the guest could guarantee application potentials, which means a long-staying of the guest inside the host. However, it is hard to predict the interaction between the hosts and the guests. Therefore, the development of organic receptors, which can encapsulate the guests with specific selectivity, is a huge challenge for chemists. As supramolecules, the cryptophanes (Fig. 1)

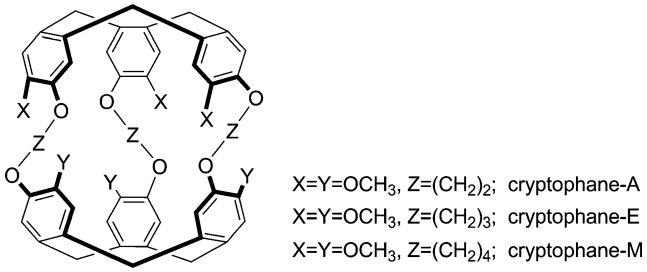


Fig. 1 The structure of cryptophanes

are globularly shaped and contain two cone-shaped cyclotriveratrylene (CTV) units attached to one another via three O-Z-O bridges, and hence they feature a preorganized, there-dimensional enforce cavity suitable for accommodating organic substrates [9–14], representing an important class of supramolecular hosts that can form stable inclusion complexes with neutral and cationic molecules [15–17]. For instance, cryptophanes-A and -E act as encapsulating host with neutral molecules such as chloroform, dichloromethane, or methane [18], and chiral cryptophane-C is able to discriminate the two enantiomers of CHFClBr [19], and water-soluble cryptophane-O encapsulates easily choline and acetylcholine [20]. More recently, the discovery of the binding of xenon in organic or aqueous solution by cryptophanes opens a new and fascinating supramolecular field [21].

Mass spectrometry (MS) and NMR spectroscopy are reliable techniques for the characterization of cryptophane molecules, and for the investigation of their remarkable host-guest properties [22, 23]. X-ray crystal structure determination confirms the usual ball shape for the cryptophanes [24]. Raman microspectrometry provides exceptional spatial resolution and extreme sensitivity that allow researchers to study micrometer scale solid samples such as single crystals of cryptophane complexes [25]. Dong and co-workers surveyed the interactions of cryptophane-A and cryptophane-E with neutral molecules CH_nCl_{4-n} (n=0, 1, 2) with the absorption and emission spectroscopy [26, 27]. Cryptophane-M has larger size than other cryptophanes so thus it could encapsulate various guests easily, and it could have more broaden application potentials. On the other hand, the guest could leave easily if the interaction between the cryptophane-M and the guest is not strong enough since the inner exit of cryptophane-M is large. To our limited knowledge, there are few reports on the interaction of cryptophane-M with various solvents. This inspires us to investigate the interaction between cryptophane-M and the solvents because the results could provide useful suggestions on the development of new hosts. In this article, we report our recent endeavors to clarify if cryptophane-M could encapsulate various guests with high selectivity with fluorescence spectroscopy.

Experimental

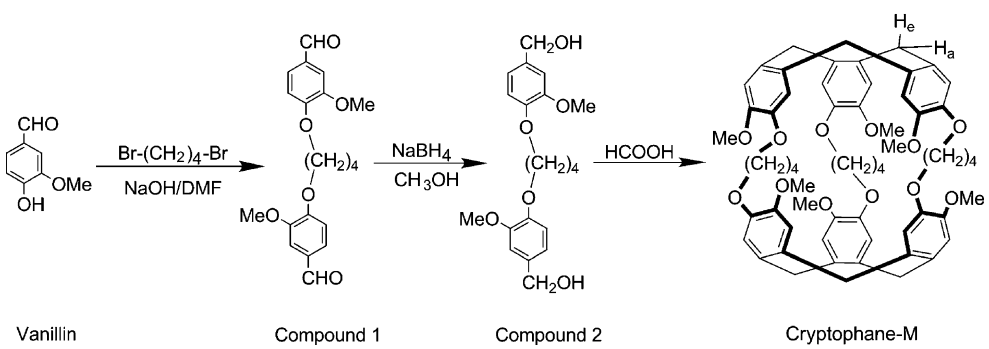
Materials

Organic solvents were obtained from Chongqing Medical and Chemical Corporation. Other chemicals and reagents were purchased from Aldrich unless otherwise specified. The organic solvents were dried using standard laboratory techniques [28]. The starting materials were purified further with redistillation or recrystallization before use. Cryptophane-M was synthesized according to a well-known method with modified procedures [29], and the route was presented in Scheme 1.

Experimental Details and Apparatus

All experiments on the preparation and the spectroscopic determination of the sample solutions were carried out in dark. We performed contrast experiments for the detection of encapsulation of the solvents by cryptophane-M. To guarantee efficient and full encapsulation, the solution was sonicated for 2 h, and was kept for a week. The sonicated solution was employed for the spectral detection. For comparison, the

Scheme 1 Synthesis of cryptophane-M



absorption and emission spectroscopy of the freshly-prepared cryptophane-M solution was determined.

The UV/visible absorption spectra were recorded with a Cintra spectrophotometer. The emission spectra were checked with Shimadzu RF-531PC spectrofluorophotonmeter. Quinine sulfate in 0.5 M H_2SO_4 (Φ=0.546, 1×10^{-6}–$\times10^{-5}$ mol/L [30]) was used as a reference to determine the fluorescence quantum yields of the samples in this study. The melting point was detected using a Beijing Fukai melting point apparatus. Nuclear Magnetic Resonance (NMR) was carried out at room temperature with a Bruker 500 MHz apparatus with tetramethylsilane (TMS) as internal standard. Element analysis was detected by CE440 elemental analysis meter from Exeter Analytical Inc.. FT-IR spectra were recorded on a Nicolet Magna-IR 550-II in the region of 4000–400 cm^{-1} using KBr pellets spectrophotometer. All the measurements of the absorption and fluorescence were made against the blank solution treated in the same way by using 1.0 cm quartz cell and carried out at room temperature.

The fluorescence quantum yields of the samples in various solvents were determined based on the following equation [31, 32]:

$$\Phi_f = \Phi_f^0 \frac{n_0^2 A^0 \int I_f(\lambda_f)\mathrm{d}\lambda_f}{n^2 A \int I_f^0(\lambda_f)\mathrm{d}\lambda_f} \quad (1)$$

Wherein n_0 and n are the refractive indices of the solvents, A^0 and A are the absorption at the excited wavelength, Φ_f and Φ_f^0 are the quantum yields, and the integrals denote the area of the fluorescence bands for the reference and sample, respectively.

Synthesis of Cryptophane-M

1, 4-Bis(4-formyl-2-methoxyphenoxy)butane (Compound **1***)*

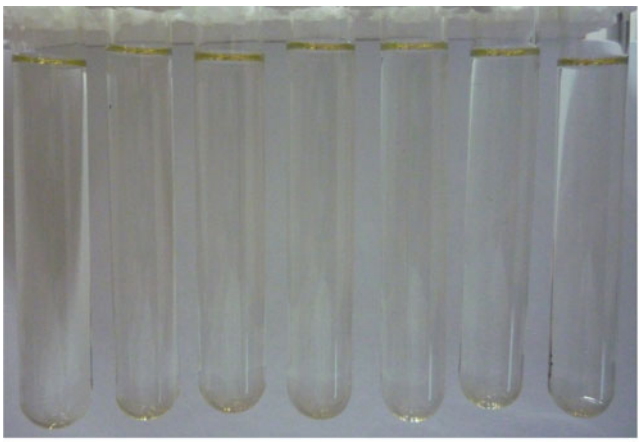
A solid of NaOH (8 g) and 1,4-dibromobutane (11.8 ml) was added in the solution of vanillin (30 g) dissolved in DMF (100 ml), respectively. The mixture was stirred for 8 h under reflux. After cooling to room temperature, the solid compound was obtained by the filtration to give 28.64 g of **1** as a beige powder (yield, 80%). ^{1}H-NMR (DMSO-d_6, δ, ppm), 9.84 (s, 2H, CHO), 7.55 (d, 2H, Ar), 7.39 (s, 2H, Ar), 7.18 (d, 2H, Ar), 4.18 (s, 4H, OCH_2), 3.83 (s, 6H, OCH_3), 1.93 (q, 4H, CH_2).

1,4-Bis(4-Hydroxymethyl-2-Methoxyphenoxy)Butane (Compound **2***)*

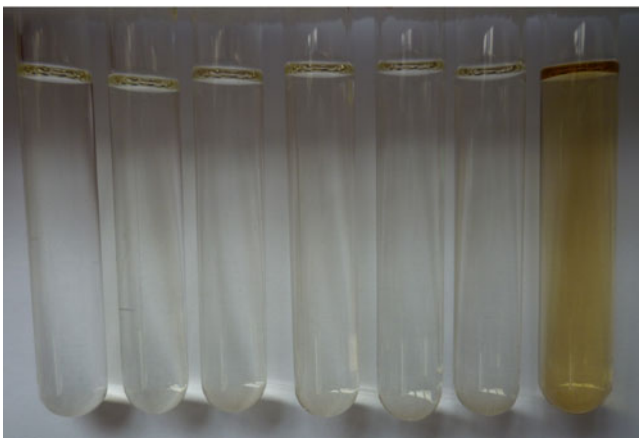
To a mixture of **1** (17.9 g) in methanol (200 ml) was slowly added $NaBH_4$ (5 g, 131.6 mmol) at 0°C. The mixture was stirred for 15 h. After the filtration, the solid was washed with a methanol/water mixture (100 ml) and methanol (50 ml) to give 17.01 g of compound **2** as a white powder (yield, 94%). ^{1}H-NMR (DMSO-d_6, δ, ppm), 6.90 (m, 6H, Ar), 5.06 (t, 2H, OH), 4.41 (d, 4H, CH_2OH), 3.99 (s, 4H, OCH_2), 3.74 (s, 6H, OCH_3), 1.85 (m, 2H, CH_2).

Cryptophane-M

A solution of **2** (9.05 g) in formic acid (1.72 L) was stirred at 55°C for 4 h, and then a residue was obtained after the evaporation under vacuum, in which the desired cryptophane-M was isolated by column chromatography on silica gel (CH_2Cl_2/acetone 9:1) to give 1.956 g of cryptophane-M as a solid (yield, 8%). ^{1}H-NMR ($CDCl_3$, δ, ppm), 6.77 (s, 6H, Ar), 6.67 (s, 6H, Ar), 4.54 (d, 6H, CHa), 3.72–3.98 (m, 12H, OCH_2), 3.80 (s, 18H, OCH_3),



(a)



(b)

Fig. 2 Colors of the solutions (**a** freshly-prepared solution, **b** sonicated solution). From left to right: acetone, ethyl acetate, 1,2-dichloroethane, 1,4-dioxane, dichloromethane, acetonitrile, chloroform

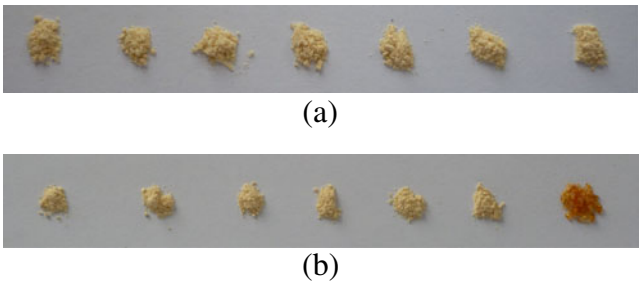


Fig. 3 Colors of solids after the evaporation of the solvents in **a** freshly-prepared solution, **b** sonicated solution). From left to right: acetone, ethyl acetate, 1,2-dichloroethane, 1,4-dioxane, dichloromethane, acetonitrile, chloroform

3.41 (d, 6H, CHe), 2.18 (m, 12H, CH_2). IR (KBr) ν:3408, 2932, 1608, 1510, 1466, 1400, 1265, 1142, 1087, 854, 741, 621 cm^{-1}. Anal. Calcd for $C_{60}H_{66}O_{12}$: C, 73.60; H, 6.79; O, 19.61. Found: C, 73.71; H, 6.84; O, 19.52.

Table 1 Absorption and fluorescence spectral data of cryptophane-M in various solvents (A: freshly-prepared solution, B: sonicated solution)

Solvent		λ_{abs}(nm)	log ε	λ_{em}(nm)	Φ_f
1,4-dioxane	*A*	283	4.65	435	0.286
	B	283	4.66	430	0.248
ethyl acetate	*A*	284	4.64	435	0.262
	B	283	4.65	432	0.208
1,2-dichloroethane	*A*	283	4.64	435	0.270
	B	282	4.65	434	0.229
dichloromethane	*A*	283	4.65	435	0.230
	B	284	4.64	435	0.206
acetone	*A*	284	4.66	433	0.293
	B	284	4.65	434	0.233
acetonitrile	*A*	284	4.65	434	0.296
	B	283	4.64	434	0.171
chloroform	*A*	283	4.65	433	0.276
	B	283	4.64	443	0.050

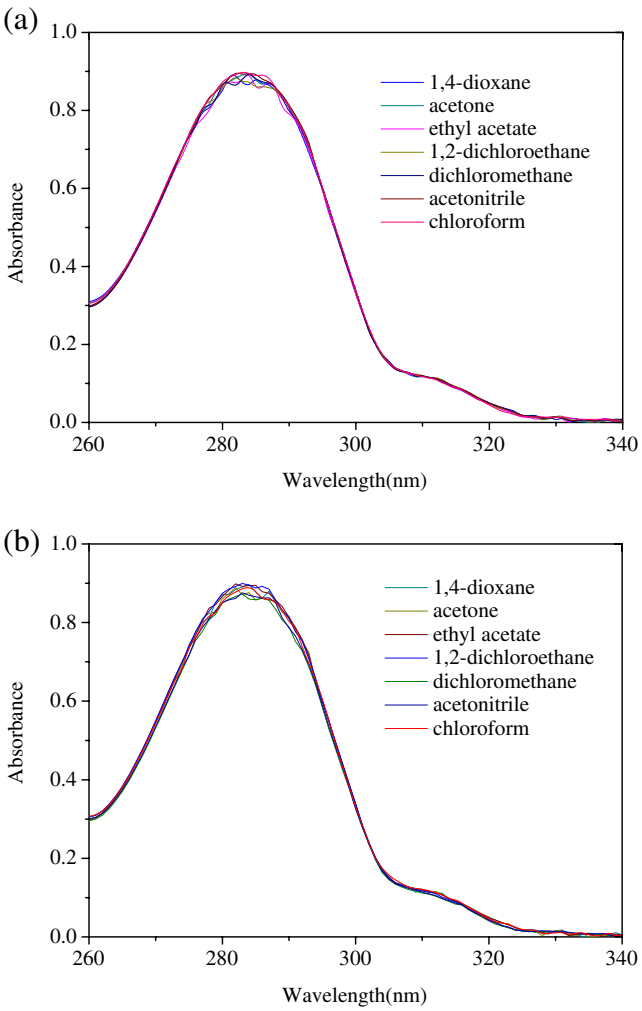


Fig. 4 UV-visible absorption spectra of cryptophane-M (2.0×10^{-5} mol·L^{-1}) in various solvents (**a** freshly-prepared solution, **b** sonicated solution)

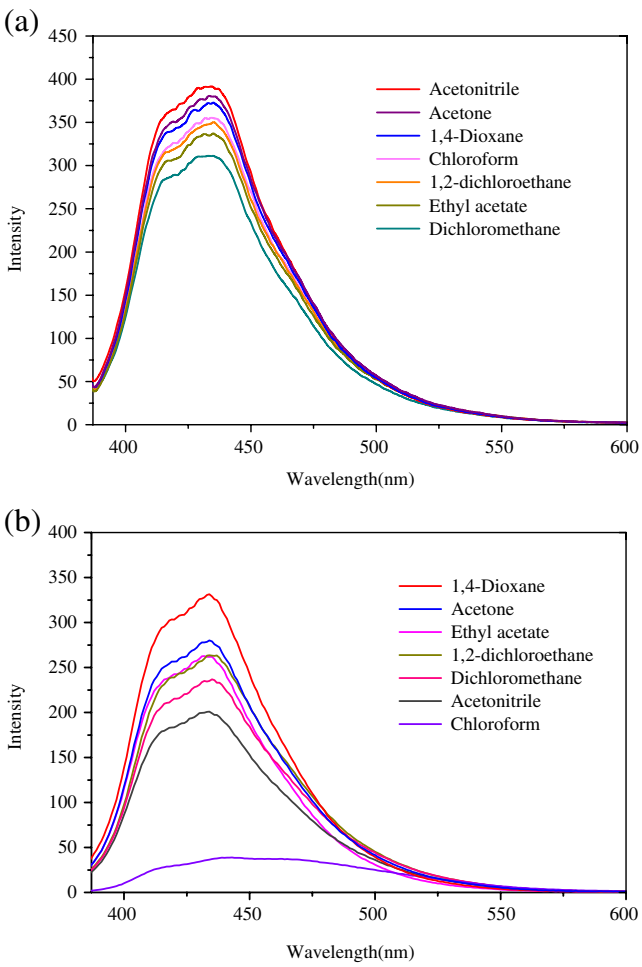


Fig. 5 Fluorescence emission spectra of cryptophane-M(2.0×10^{-5} mol·L^{-1}) in solvents when excited at 376 nm (**a** freshly-prepared solution, **b** sonicated solution)

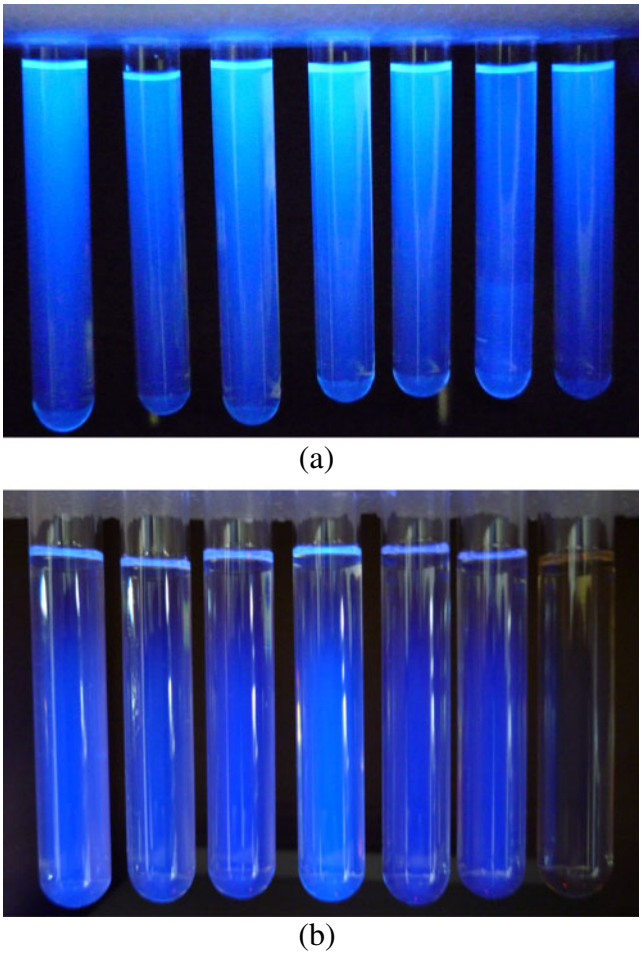


Fig. 6 Emission photographs of solutions (**a** freshly-prepared solution, **b** sonicated solution). From left to right: acetone, ethyl acetate, 1,2-dichloroethane, 1,4-dioxane, dichloromethane, acetonitrile, chloroform

Results and Discussions

Solvents as Guests

We chose various solvents as guests because they could be encapsulated by cryptophane-M since they have small molecular sizes. While, the solvents could leave easily if intermolceular interaction between cryptophane-M and the solvents is not strong enough. It is interesting to observe that the color of the sonicated cryptophane-M solution in chloroform changes from colorless to light green, while it does not exhibit any color in other solvents such as 1,4-dioxane, ethyl acetate, 1,2-dichloroethane, dichloromethane, acetonitrile and acetone, as shown in Fig. 2 (b). In contrast, the freshly-prepared cryptophane-M solution is colorless in various solvents, as shown in Fig. 2 (a). Furthermore, the red-brown solid is obtained after the evaporation of chloroform from sonicated cryptophane-M solution. The color is much different from that of cryptophane-M. In contrast, the solids obtained from the evaporation of other solvents of the sonicated cryptophane-M solutions display the same color as that of cryptophane-M, as shown in Fig. 3 (b). While, the solids obtained from the evaporation of the solvents of various fresh-prepared cryptophane-M solutions have the same color as that of cryptophane-M, as shown Fig. 3 (a). The results indicate that cryptophane-M is able to encapsulate chloroform, and the strong interaction between them makes chloroform remained inside the cavity. In other words, an inclusion complex-like of cryptophane-M and chloroform could be formed. Although the other solvents could enter into the cavity, they could run out of the cavity quickly as well if the interaction between cryptophane-M and the solvents are weak.

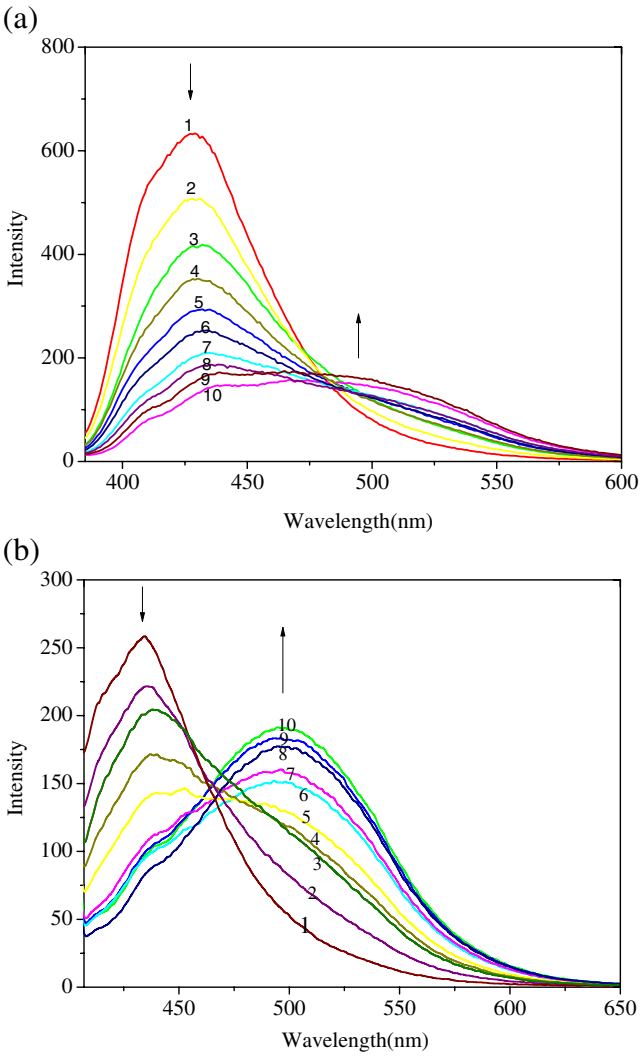


Fig. 7 Fluorescence spectra of cryptophane-M (4×10^{-6} mol·L^{-1}) in ethyl acetate/chloroform binary solvents (v/v). 1.100:0; 2.90:10; 3.80:20; 4.70:30; 5.60:40; 6.50:50; 7.40:60; 8.30:70; 9.20:80; 10.10:90. **a** excited at 376 nm and **b** excited at 397 nm

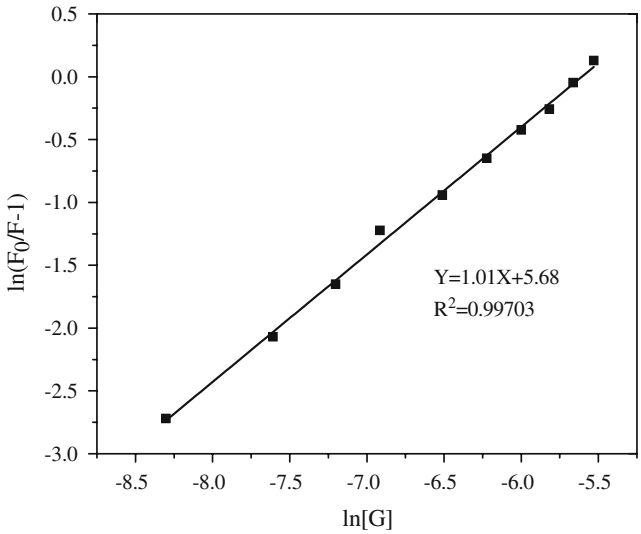


Fig. 8 Benesi–Hildebrand plot for inclusion complexes

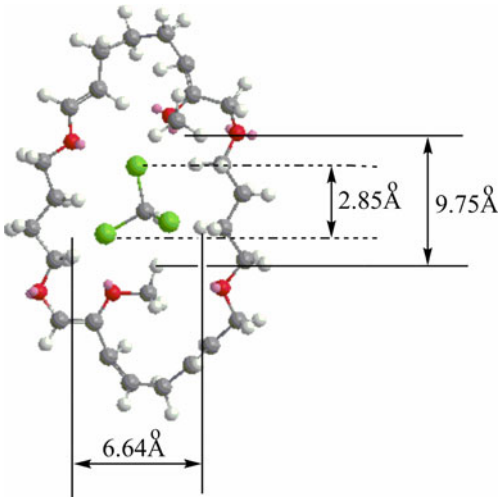


Fig. 9 Simulation of host and guest sizes

Fig. 4 (a) shows that no obvious difference is observed for the absorption spectra of cryptophane-M in various solvents, such as 1,4-dioxane, ethyl acetate, 1,2-dichloroethane, dichloromethane, chloroform, acetonitrile and acetone. Table 1 presents the spectral data of cryptophane-M in various solvents. The data suggest that the maximal absorption wavelength and the molar extinction coefficients of cryptophane-M are almost the same in various solvents. The results seem some strange because the color of cryptophane-M solution in chloroform is different from that in other solvents (see Fig. 2 (a)). The absorption spectra indicate that the complex-like of cryptophane-M and chloroform is not a real molecule at the ground state, and thus the electron transition nature of cryptophane-M is not affected by the chloroform. Although the strong non-covalent interaction between cryptophane-M and chloroform could keep chloroform stayed inside the cavity, it is still not an actual complex. As a consequence, the absorption spectra of the freshly-prepared cryptophane-M solutions are almost the same in various solvents, and they are almost identical to that of the sonicated cryptophane-M solution (Fig. 4 (b)).

Table 2 The molecular sizes of solvents (Å)

Solvent	Molecular size (length)
1,4-dioxane	4.78
acetone	4.35
ethyl acetate	6.61
1,2-dichloroethane	4.28
dichloromethane	2.85
acetonitrile	3.16
chloroform	2.85

On the other hand, a large difference is observed for the emission spectra of the sonicated cryptophane-M solution in chloroform from that in other solvents, for instance 1,4-dioxane, ethyl acetate, 1,2-dichloroethane, dichloromethane, acetonitrile and acetone. As shown in Fig. 5 (b), in chloroform, the maximal emission wavelength of the sonicated cryptophane-M solution is red-shifted, and its emission intensity is much reduced. Table 1 shows that the maximal emission wavelength of the sonicated cryptophane-M solution exhibits about 10 nm red-shift in chloroform with respect to that in other solvents, and the fluorescence quantum yield of the sonicated cryptophane-M solution in chloroform is much lower than that in other solvents. In contrast, the emission spectra of the freshly-prepared cryptophane-M solution display only a little difference in various solvents (Fig. 5 (a)). We shall point out the emission intensity of the sonicated cryptophane-M solution are lower than that of the freshly-prepared cryptophane-M solution in various solvents at the same excitation conditions, and as a result, the fluorescence quantum yields of the freshly-prepared cryptophane-M solutions are higher than those of the sonicated cryptophane-M solution in various solvents. However, the emission of cryptophane-M is much lower and it displays a larger change in chloroform after sonication (Fig. 6). The above results demonstrate that chloroform can not only be encapsulated by cryptophane-M, but stay inside the cavity for a while. In contrast, although the other solvent molecules could enter cavity, they can not remain inside the cavity for a long time.

Exciplex of Cryptophane-M with Chloroform

In order to reveal the deep reason on the large changes of the emission spectra of the sonicated cryptophane-M

solution in chloroform, we detected further the emission spectra of the sonicated cryptophane-M solution in various chloroform/other solvent binary solvents. Fig. 7 shows the typical variation of emission spectra of sonicated cryptophane-M solution in chloroform/ethyl acetate binary solvents. Seen from Fig. 7 (a), with increasing chloroform ratio, the fluorescence intensity decreases gradually, and the emission wavelength is red-shifted gradually. This demonstrates that chloroform has a stronger interaction with cryptophane-M than other solvents. It is interesting to observe that a new emission band with a maximal emission wavelength of 497 nm is formed with increasing ratio of chloroform in the mixed solvents (Fig. 7), and an equal emission point (482 nm) appears. This indicates that an inclusion complex between cryptophane-M and chloroform could be formed at the excited state. This explains well why the emission intensity of the sonicated cryptophane-M solution is much reduced in chloroform. While in contrast, such variation is not observed for the freshly-prepared cryptophane-M solution in various chloroform/other solvent binary solvents, which demonstrates that the encapsulation is prerequisite for the formation of cryptophane-M and chloroform exciplex. It is reasonable to assume that the intermolecular interaction time between cryptophane-M and chloroform in the excited state could be very short, thus no guests could not enter into or leave out of the cavity in such small period. This in turn indicates that there are so enough chloroform molecules in the cavity of cryptophane-M as the sample is excited that the exciplex could be formed. However, due to weak interaction between cryptophane-M and other solvents, the amount of the guest molecules in the cavity of cryptophane-M could be too few to interact with the host.

We further determined the formation constant (K) of the exciplex of cryptophane-M and chloroform. The complex formation between a host (H) and a guest (G) can be described by a chemical reaction as:

$$\mathrm{H} + \mathrm{G} \overset{K}{\longleftrightarrow} \mathrm{H} \cdot \mathrm{G}$$

The formation constant (K) and the ratio of the complex were calculated from the data [33] using the modified Benesi–Hildebrand equation [34]:

$$\ln \frac{F_0 - F}{F} = \ln K + n \ln[\mathrm{G}] \qquad (2)$$

wherein F and F_0 represent the fluorescence intensity of cryptophane-M in the presence and absence of chloroform, respectively; K and n are the binding constant and the number of binding sites; K and n are constants. Fig. 8 shows the plot of $\ln(F_0/F\text{-}1)$ versus $\ln[\mathrm{G}]$ exhibits excellent linearity, which implies that the inclusion exciplex has a stoichiometry of 1:1. The value of K is 292.95 M^{-1}. The sizes of the host and guest are calculated by HyperChem 8.0 [35], and the data are shown in Table 2 and Fig. 9. It is obvious that all solvents could enter into cryptophane-M based on the molecular size. While, the strong non-covalent interaction (*could be dipole-dipole interaction*) could stabilize the association between cryptophane-M and chloroform. On the other hand, the red-brown color of the solid obtained from the sonicated cryptophane-M after the evaporation of chloroform changes to cryptophane-M's color if the solid is kept in dark for a very long time, which confirms that the interaction between cryptophane-M and chloroform is non-covalent. It demonstrates that there exists a non-covalent interaction between cryptophane-M and chloroform.

Conclusions

The present study demonstrates that chloroform could be encapsulated efficiently by cryptophane-M, and it could stay inside of the cavity for a while. We show powerful evidences that a real exciplex is formed between cryptophane-M and chloroform as it is excited. The binding constant of exciplex reaches 292.95 M^{-1}. The results suggest that the other solvents could enter into the cavity of cryptophane-M, while the weak interaction between the host and the guest could not keep these solvents remained inside of the cavity. The interaction between chloroform and cryptophane-M would be an ideal model for the molecular recognition of cryptophane-M in terms of the size and shape-fit as well as the recognition model between the host and the guest molecules.

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