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Interaction of a hemicyanine dye and its derivative with DNA and cucurbit[7]uril†

Shiguo Sun,* Ye Yuan, Zhiyong Li, Si Zhang, Hongyan Zhang and Xiaojun Peng

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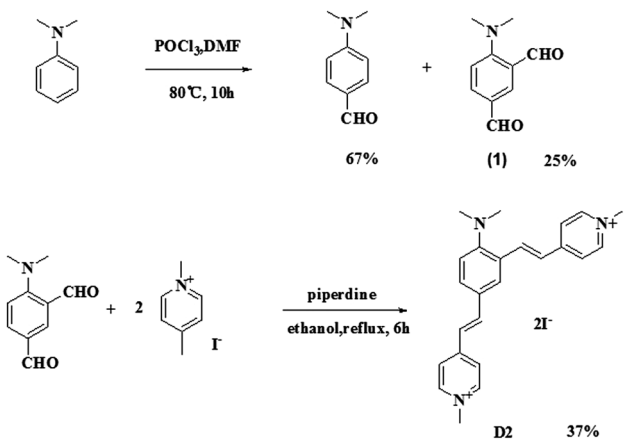
The host–guest interaction of *trans*-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (**DSMI**) with cucurbit[7]uril (CB[7]) was investigated through fluorescence, absorption, ^{1}H NMR and mass spectrometry. **DSMI** can be included by CB[7] with 1 : 2 stoichiometry to form the **DSMI**/CB[7] complex, exhibiting a larger binding affinity than that of DNA. To make a comparison with **DSMI**, another pyridium vinyl group was introduced into the aniline ring of **DSMI** to get a hemicyanine derivative **D2**, and a ternary complex among **D2**, CB[7] and DNA was formed. All these provide new insights to investigate the interaction of organic dyes, CB[7] and DNA.

Introduction

Recently, cucurbit[*n*]urils (CB[*n*]),[1,2] pumpkin-shaped macrocylic compounds comprised of *n* glycoluril units linked by pairs of methylene bridges with rigid cavities, have shown numerous applications ranging from molecular recognition,[3–5] dye encapsulation,[6,7] and drug delivery[8,9] to self-assembly molecular devices.[10,11] The negative charge density on the carbonyl groups and the inner surface of the hydrophobic cavity promote CB[*n*]s to include small guest molecules[12] and binding with metal cations[13] and cationic organic molecules *via* ion–dipole interaction.[14] The effects, such as fluorescence enhancement, fluorescent lifetime extension and photostability improving, caused by the interaction of CB[*n*]s and fluorescent dyes have been extensively studied.[6] However, the cooperation or competitive interaction between CB[*n*] and DNA has been rarely reported.[15–18] These investigations will be helpful for improving the sensitivity of the fluorescent sensor,[15–17] demonstrating the role of CB[*n*] in the fluorescent sensing process. Therefore, it is meaningful to pay attention to the interaction of organic dyes, CB[*n*]s and DNA.

Hemicyanine was often used as a fluorescent probe for DNA analysis,[19] cell microviscosity[20] and metal ion detection.[21] The interactions between some hemicyanine dye derivatives or styryl dyes with similar structure and CB[7] have been investigated,[22–26] and the results demonstrated that CB[7] could bind to the dyes through ion–dipole interaction. In our previous work,[11] the chemically tunable interaction between CB[6] and *trans*-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (**DSMI**, Scheme 1), a common cationic hemicyanine dye always used as a fluorescent probe for DNA analysis, has been investigated. As a homologue of CB[6], the bigger cavity of CB[7] can make it easy to self-assemble with DSMI, providing a further approach to study the interaction of the dye with CB[*n*]s and DNA, and its good solubility in water is more suitable for biological applications. In continuation of our related research,[11] the interaction between **DSMI** and CB[7] was investigated through fluorescence, absorption, ^{1}H NMR and mass spectrometry, then the competitive binding interaction of **DSMI** with CB[7] and DNA was studied and the results demonstrated that CB[7] had a larger binding affinity with **DSMI** than DNA. To make a comparison with DSMI, another pyridium vinyl group was introduced into the aniline ring of **DSMI** to get a hemicyanine derivative **D2** (Fig. 1), in the case of **D2**, one pyridium vinyl of **D2** can be included into the cavity of CB[7] and the other can be intercalated into DNA to form a ternary complex.



Scheme 1 Synthetic route for the **D2**.

State Key Laboratory of Fine Chemicals, Dalian University of Technology, E 224, West Campus, Dalian, 116024, P. R. China. E-mail: shiguo@dlut.edu.cn; Fax: +86 411 84986304

† Electronic supplementary information (ESI) available: NMR and mass spectra of **D2**, MS and the fitting plot for **DSMI**/CB[7] and **D2**/CB[7] complexes. See DOI: 10.1039/c4nj00068d

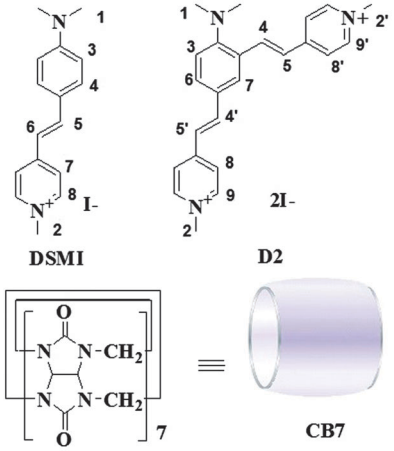


Fig. 1 The structures of **DSMI**, **D2** and CB[7].

Experimental section

Materials and methods

The water used in the test was distilled water. Other solvents and reagents were of analytical grade and used without further purification. **DSMI** was synthesized as described in our previous study[11] and CB[7] was synthesized according to the literature.[27] Calf thymus DNA (ct-DNA) was obtained from Sigma Chemical Co. (USA).

NMR data were recorded in D_2O on a VARIAN INOVA-400 spectrometer. Mass spectrometric data were obtained on a Q-Tof mass spectrometer (Micromass, Manchester, England). Absorption spectra were measured on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. Fluorescence measurements were performed on a VARIAN CARY Eclipse Fluorescence Spectrophotometer. The pH titration measurements were made using a Model PHS-3C meter.

The absorption and fluorescence spectra of **DSMI** with CB[7] were measured in distilled water. The fluorescence titration experiments were performed as follows: 25 μL of 1.0×10^{-3} mol L^{-1} stock solution of **DSMI** and a different amount of 1.0×10^{-3} mol L^{-1} CB[7] aqueous solution were transferred into a 5 mL volumetric flask, then the volumetric flask was filled to the final volume with distilled water. Fluorescence and absorption spectra were measured after 3 minutes of ultrasonic agitation. The NMR spectra were obtained in D_2O with DSS (3-(trimethyl-silyl)-1-propanesulfonic acid sodium salt) as the internal standard; the ratio of dye *versus* CB[7] was calculated by the ratio of their integral areas for special peaks; the protonated form of **DSMI** and **D2** was determined firstly by addition of deuterium chloride to observe the color of the solution changing from yellow to colorless, and then checking the pH of the solution using a pH test paper.

Synthesis

The synthetic route for preparation of **D2** is illustrated in Scheme 1:

Compound 1 (4-dimethylamino-benzol-1,3-dicarbaldehyde). Compound **1** was synthesized according to the literature with little modification.[28] Phosphoryl chloride (50.0 g) was added to DMF (81.2 g) in drops. Then Me_2NPh (12.1 g) was added in drops into the solution, and the reaction lasted for 10 h at 80 °C. The reactant was poured into the mixture of 600 g of ice and 150 mL of 38% NaOH solution, and kept at 0 °C to give a large amount of precipitate. The precipitate was filtered and purified by column chromatography on silica gel (eluting with petroleum ether: ethyl acetate 5 : 1) to give 4.5 g (25% of yield) of (**1**). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 10.04 (s, 1H), 9.86 (s, 1H), 7.92 (d, J = 8.8, 1H), 7.03 (d, J = 8.8, 1H).

Compound D2 (2,4-bis[(*E*)-*N*-methyl-4-pyridinyl ethenyl]1-dimethylamino benzene diiodide). The mixture of 4-dimethylamino-benzol-1,3-dicarbaldehyde (1.77 g, 10.0 mmol), 1,4-dimethylpyridinium iodide (4.7 g, 20.0 mmol) and piperdine (1 mL) in 50 mL ethanol was refluxed for 4 h, the reactant was cooled, and the precipitate was collected. Recrystallization was carried out twice to give the dark purple product, 2.2 g of **D2** with yield of 37%. Anal. Calcd (found): C, 47.15 (47.03); H, 4.45 (4.40); N, 6.87 (6.81). ^{1}H NMR (400 MHz, D_2O, δ in ppm) 8.55 (d, J = 6.6, 2H), 8.50 (d, J = 6.6, 2H), 8.03 (d, J = 6.6, 2H), 7.98 (d, J = 6.6, 2H), 7.93 (s, 1H), 7.84 (d, J = 16.2, 1H), 7.72 (d, J = 16.2, 1H), 7.68 (d, J = 8.4, 1H), 7.31 (d, J = 16.2, 1H), 7.25 (d, J = 18.0, 1H), 7.21 (d, J = 8.8, 1H), 4.26 (s, 3H), 4.22 (s, 3H), 2.82 (s, 6H). ^{13}C NMR (100 MHz, D_2O, δ in ppm) 155.5, 154.0, 153.9, 144.8, 144.6, 140.5, 138.3, 131.1, 128.9, 128.0, 124.4, 124.0, 123.6, 121.6, 119.1, 47.5, 47.4, 44.6. HRMS m/z found: 357.2205 $C_{24}H_{27}N_3$ (M^+): requires M, 357.2204. The corresponding spectra can be found in Fig. S1–S3 (ESI†).

Results and discussion

The host–guest interaction between DSMI and CB[7]

DSMI has an absorption maximum at 450 nm and a fluorescence peak at 605 nm in aqueous solution. As shown in Fig. 2, the absorption maximum changed from 450 nm to 469 nm and the A value decreased from 0.30 to 0.12 with the addition of 10 equiv. of CB[7] in a phosphate buffer solution (pH = 7.4). Another absorption peak aroused by the protonated form of **DSMI** appeared at ~330 nm, suggesting that part of **DSMI** was protonated even at pH = 7.4 after the dye included CB[7]. The fluorescence intensity at the maximum emission wavelength was increased by ~10 times, and the fluorescence peak had a

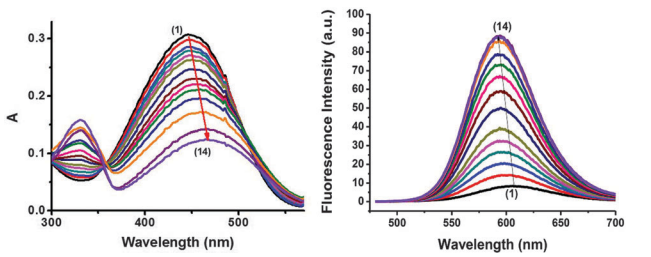


Fig. 2 The absorption and fluorescence (λ_{ex} = 450 nm) spectra of **DSMI** along with the addition of CB[7], from (1) to (14), 0, 0.2, 0.6, 1.0, 1.4, 1.8, 2.2, 2.6, 3.0, 4.0, 5.0, 6.0, 8.0, 10.0 × 10^{-5} M of CB[7] was added, the concentration of the dye was 1 × 10^{-5} M, pH = 7.4.

blue shift from 605 nm to 592 nm, demonstrating the interaction of the dye with CB[7]. The dye was confined in the nonpolar cavity of CB[7], decreased the nonradiative decay of the excited state and hindered the formation of the twisted intramolecular charge transfer (TICT) state, leading to a fluorescence enhancement. The fluorescence enhancement mechanism by CB[7] was similar to that of CB[6] demonstrated in our previous work.[11] However, the fluorescence intensity was less enhanced by CB[7] because of its relative large cavity size compared with that of CB[6].

The fluorescence pH titration of the complexed dye (**DSMI**/CB[7]) was performed under conditions of virtually quantitative complexation[29] (5 μM **DSMI**, 100 μM CB[7], corresponding to >99% dye complexation, Fig. S4, ESI†), permitting a direct estimation of the pK_a' value 5.6 for the complexation, while the pK_a of **DSMI** was 3.1. The pK_a shift of 2.5 units may be caused by the more stable complex of **DSMIH**$^+$/CB[7] compared with **DSMI**/CB[7].

The interaction between **DSMI** and CB[7] was investigated by ^{1}H NMR spectroscopy (Fig. S5, ESI†). Because of the pK_a shift from 3.1 to 5.6, the protonated form of **DSMI** could be formed when the pH was below 8, so the ^{1}H NMR titration experiment was performed in D_2O with a pH value of ~10. When less than 1 equiv. CB[7] was added into the alkaline solution of **DSMI** in D_2O, all the protons shifted to the upfield, and all the signals became broader. This indicated that **DSMI** and CB[7] formed a loosely bonded complex and the bonded CB[7] shifted back and forth on the **DSMI** molecule to undergo a fast exchange process.[12,30,31] All the protons were in the shielding/deshielding microenvironment, and formed a dynamic balance between the free and complexed states, leading to broader signals. When more than 1 equiv. of CB[7] was added, the signals of **DSMI** were difficult to observe due to the precipitation of the complex formed between **DSMI** and CB[7].

The interaction between the protonated form of **DSMI** (**DSMIH**$^+$) and CB[7] was also investigated by ^{1}H NMR titration (Fig. S6, ESI†). A trace amount of acid was added together with CB[7] to ensure the formation of the **DSMIH**$^+$/CB[7] complex (pH = 3). When less than 1 equiv. of CB[7] was added, a stable **DSMIH**$^+$/CB[7] complex was formed, and separated signals of the free **DSMI** and **DSMIH**$^+$/CB[7] complex were observed. H8 was kept fixed at 3.32 ppm and H1, H2 and H7 moved downfield, while H3, H4, H5 and H6 moved upfield, indicating that CB[7] included **DSMIH**$^+$ in the aniline ring and the double bond part. When 1 equiv. of CB[7] was added, the free **DSMI** signal disappeared. When more than 1 equiv. of CB[7] was added into the solution, the unchanged H8 and downfield shifted H7 shifted to the upfield, and H3, H4, H5, and H6 continued to shift to the upfield, while H1 and H2 shifted to the more downfield. This result suggested that the second CB[7] included **DSMI** from the pyridium ring part and the two CB[7] included **DSMI** around H1 and H2. ESI-MS confirmed the formation of the (CB[7]/**DSMI** + H$^+$)$^{2+}$ (1 : 1) complex (Fig. S7, ESI†): *m*/*z* calcd 701.2531, and found 701.2911, but the signal of the 2CB[7]/**DSMI** complex was not found.

From the NMR titration experiments, the stoichiometry of **DSMIH**$^+$ and CB[7] can be determined to be 1 : 2 under acidic conditions. However, the stoichiometry of **DSMI** and CB[7] was not certain in alkaline solution. Therefore, for the complexation of **DSMI** and CB[7], the stoichiometry was determined by a continuous variation technique (Job's plot)[32] based on the fluorescence intensity of **DSMI** in the presence of CB[7]. Different concentration of **DSMI** and CB[7] solutions were prepared and mixed and the sum of the concentrations was kept constant. The typical plot for the **DSMI**/CB[7] complex is shown in Fig. 3. The maximum fluorescence intensity was observed at x = 0.35, indicating that the dye/CB[7] inclusion complex in aqueous solution was mainly formed with 1 : 2 stoichiometry.

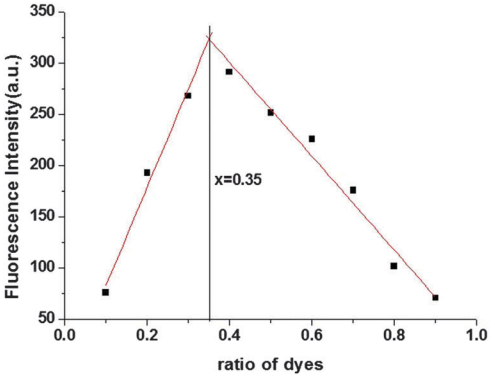


Fig. 3 Job's plot of **DSMI**/CB[7] complexes in an alkaline environment, Asymmetric plot with maximum at ~0.35 mol fraction indicating a 1 : 2 inclusion.

The binding constant values for 1 : 1 and 1 : 2 were evaluated by considering the following complexation equilibrium according to the literature,[33] where K_1 and K_2 are the binding constants for the formation of the corresponding 1 : 1 and 1 : 2 complexes.

$$\begin{aligned} \mathrm{CB[7]} + \mathrm{Dye} &\overset{K_1}{\rightleftharpoons} \mathrm{CB[7]\cdot Dye} \\ \mathrm{CB[7]\cdot Dye} + \mathrm{CB[7]} &\overset{K_2}{\rightleftharpoons} (\mathrm{CB[7]})_2\cdot \mathrm{Dye} \end{aligned} \tag{1}$$

At any stage, the observed fluorescence intensity I_f corresponds to the sum of the fluorescence intensities from dyes, CB[7]·dye and (CB[7])$_2$·dye, and is directly proportional to their corresponding concentrations in the solution. Therefore, one can write the following eqn (2):

$$\begin{aligned} I_f = {} & I_f^0\frac{[\mathrm{Dye}]_{eq}}{[\mathrm{Dye}]_0} + I_{\mathrm{CB7\cdot Dye}}\frac{[\mathrm{CB7\cdot Dye}]_{eq}}{[\mathrm{Dye}]_0} \\ & + I_{(\mathrm{CB7})_2\cdot\mathrm{Dye}}\frac{[(\mathrm{CB7})_2\cdot\mathrm{Dye}]_{eq}}{[\mathrm{Dye}]_0} \end{aligned} \tag{2}$$

Eqn (2) can be rearranged to a modified Benesi–Hildebrand eqn (3).[33]

$$I_f = \frac{I_f^0 + I_{\mathrm{CB7\cdot Dye}}K_1[\mathrm{CB7}]_0 + I_{(\mathrm{CB7})_2\cdot\mathrm{Dye}}K_1K_2[\mathrm{CB7}]_0^2}{1 + K_1[\mathrm{CB7}]_0 + K_1K_2[\mathrm{CB7}]_0^2} \tag{3}$$

where I_f^0 is the fluorescence intensity in the absence of CB[7], $I_{\mathrm{CB7\cdot Dye}}$ is the fluorescence intensity when all the dye molecules interact with CB[7] as a 1 : 1 complex, and $I_{(\mathrm{CB7})2\cdot\mathrm{Dye}}$ is the fluorescence intensity when all the dye molecules are complexed

with CB[7] forming a 2 : 1 complex. And finally $[Dye]_0$ and $[CB7]_0$ are the total concentrations of the dye and the CB[7] used.

Applying eqn (3) to fit the experimental data presented in Fig. S8 (ESI†), the K_1 and K_2 values were estimated to be $(1.35 \pm 0.05) \times 10^5$ M^{-1} and $(3.2 \pm 0.4) \times 10^3$ M^{-1}. The higher value of the first order binding constant and the lower value of the second order binding constant indicated that the first complexation was caused by the strong ion–dipole interaction between the carbonyl laced portals of CB[7] and the positive charge centered on **DSMI**. The second interaction was caused by the hydrophobic nature of the dye.[33] The smaller value of K_2 could be one of the main reasons why the MS signal for the 1 : 2 complex was not found.

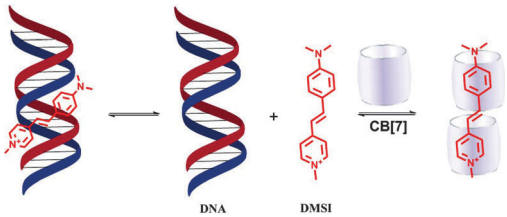
Competitive interaction of DSMI with DNA and CB[7]

DSMI could bind to the double helical DNA with high affinity through a groove binding mode.[19] The groove binding inhibits the non-radiative deactivation of the excited state of **DSMI**, and results in enhanced fluorescence intensity, owing to the geometric restriction imposed by the narrow minor groove of the DNA helix. About 43-fold of fluorescence enhancement and no shift in emission maximum were observed with the addition of 300 equiv. of ct-DNA (Fig. 4a).

As shown in Fig. 4b, when CB[7] was gradually added into the solution of 1000 equiv. of ct-DNA and **DSMI**, the fluorescence intensity decreased dramatically to 21% of the initial fluorescence with a ~8 nm blue shift of the emission peak. Both the fluorescence intensity and the emission peak became similar to the state of **DSMI** in the presence of CB[7]. These results show that CB[7] could bind with **DSMI** competitively although **DSMI** bonded with ct-DNA at first. Therefore, it is easy to deduce that CB[7] has a larger binding affinity with **DSMI** than that of ct-DNA. The competitive process is suggested in Scheme 2.

Host–guest interaction between D2 and CB[7]

To make a comparison with **DSMI**, we introduced another pyridium vinyl group into the aniline ring of **DSMI** to generate a novel fluorescent dye **D2**. Two absorption peaks at 345 and 393 nm were observed in aqueous solution and the absorption



Scheme 2 The competitive binding of **DSMI** with DNA and CB[7].

peak at 393 nm exhibited a hypochromic shift of 57 nm compared with that of **DSMI**. It is reasonable to attribute the hypochromic shift to the reduced electron density on the aniline ring when the electron-withdrawing substituent (pyridium vinyl group) anchored.[34] The decreased electron-donating ability of the aniline ring weakened the TICT process of the parent dye. **D2** exhibited an enlarged Stokes shift up to 230 nm with very low background fluorescence ($\Phi_f < 0.001$), and the emission maximum was located at 623 nm with a red shift of 18 nm compared with that of **DSMI**.

Incremental addition of CB[7] to the **D2** solution resulted in a gradual decrease in the absorbance with ~6 nm and ~16 nm bathochromic shifts for the absorption peaks at 345 nm and 393 nm, respectively (Fig. 5). Meanwhile, the emission peak shifted to 615 nm with ~8 nm red shift and the fluorescence monitored at 623 nm was enhanced about 5-fold with the gradual addition of 10 equiv. of CB[7]. All these can be ascribed to CB[7] can include **D2** around the two pyridium rings, and inhibit the torsional motion of the pyridium groups.

The ^{1}H NMR titration experiments were carried out in pH 10 (Fig. S9, ESI†) solution to ensure that the dye was not to be protonated. H9 and H9′ remained almost unchanged with the addition of CB[7], while H8, H8′, H1 and H2 moved to the downfield, and the proton of the vinyl group moved upfield. The signal changes indicated that the double bond was included in the CB[7] cavity and H1 and H2 were located outside the portal of CB[7].

The interaction between the protonated form of **D2** and CB[7] was also investigated by ^{1}H NMR titration (Fig. S10, ESI†). A trace amount of acid was added together with CB[7] to ensure the formation of the **D2**H^+/CB[7] complex (pH = 3). The signals at down field became broader and difficult observe with the

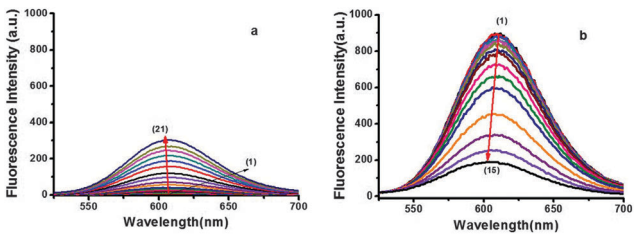


Fig. 4 The fluorescence spectra of **DSMI** with the addition of DNA (a), from (1) to (21), 0, 0.4, 0.8, 1.2, 1.6, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, 15.0, 20.0, 30.0, 40.0, 60.0, 80.0, 100.0, 150.0, 200.0, 300.0 equiv. of DNA was added; and the fluorescence spectra of **DSMI** in the presence of 1000 equiv. DNA with the addition of CB[7] (b), from (1) to (15), 0, 0.4, 0.8, 1.2, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, 12.0, 15.0, 20.0, 25.0 equiv. of CB[7] was added, the concentration of **DSMI** was 1.0×10^{-5} M, pH = 7.4.

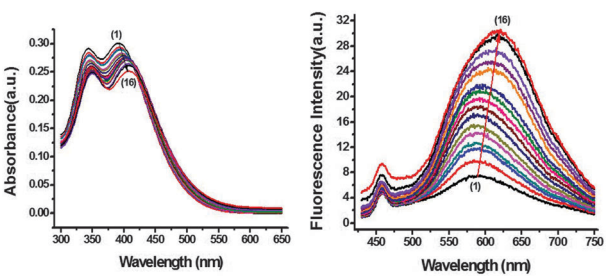


Fig. 5 The absorption and fluorescence spectra of **D2** with the addition of CB[7], from (1) to (16), 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.8, 2.2, 2.6, 3.0, 4.0, 5.0, 6.0, 8.0, 10.0 $\times 10^{-5}$ M of CB[7] was added, the concentration of **D2** was 1×10^{-5} M, pH = 7.4.

addition of CB[7]. However, it was clear H1 shifted downfield until 2 equiv. of CB[7] was added, and H2 and H2′ shifted upfield. These changes indicated that CB[7] interacted with **D2** around each pyridium ring. The MS spectrum further confirmed this result (Fig. S11, ESI†), *m*/*z* found: 506.7834 (calculated for $(\mathbf{D2H}^{+} + \mathrm{CB[7]})^{3+}$: 506.8543), 759.6782 (calculated for $(\mathbf{D2} + \mathrm{CB[7]})^{2+}$: 759.7814), 894.5886 (calculated for $(\mathbf{D2H}^{+} + 2\mathrm{CB[7]})/3$: 894.3021).

The stoichiometry of 1 : 2 for the **D2**/CB[7] complex allowed the binding constant to be calculated according to the above mentioned method for **DSMI**. Applying eqn (3) to fit the experimental data presented in the fluorescent titration spectra (Fig. S12, ESI†), the K_1 and K_2 values were estimated to be $(8.4 \pm 0.4) \times 10^4\ \mathrm{M}^{-1}$ and $(2.3 \pm 0.3) \times 10^4\ \mathrm{M}^{-1}$ for the **D2**/CB[7] complex. The difference between K_1 and K_2 of **D2** is not much, which is different from that of **DSMI**, suggesting that the first and second complexations are caused by a similar ion–dipole interaction. The pK_a shift of 1 unit (Fig. S4, ESI†) with and without the presence of CB[7] can provide some further information.

Competitive interaction of D2 with DNA and CB[7]

The fluorescence response of **D2** to DNA was investigated through optical measurements. When 30 equiv. of DNA was added into the dye solution, the absorption maxima of **D2** at 345 nm and 393 nm exhibited a first hypochromism (with the concentration ratio [DNA]/[**D2**] < 2) and then hyperchromism (with [DNA]/[**D2**] > 2) with bathochromic shifts of 7 nm and 35 nm, respectively (Fig. S13, ESI†). The absorption spectra changes related to the concentration ratio ([DNA]/[**D2**]) demonstrate that the binding mode of **D2** with DNA was different. As suggested in the literature, **D2** may be aggregated on the surface of the DNA helix at a low ratio and intercalated into DNA base pairs at a high ratio.[35] Moreover, **D2** exhibited a significant fluorescence increase with the addition of DNA. The fluorescence intensity at 623 nm was enhanced by *ca.* 35-fold with a red shift of 8 nm in the presence of 100 equiv. of DNA (Fig. S13, ESI†). This may be caused by the restriction on the torsional motion of vinyl groups derived from the interactions between the cationic pyridium unit and the anionic phosphate backbone of DNA;[36] together with the water prohibiting effect in the hydrophobic environment offered by the higher-order structure of DNA.

In the presence of **D2**, the denaturation temperature of ct-DNA was increased, 17.5 °C, while, only 6.8 °C was increased in the case of **DSMI** (Fig. S14, ESI†), suggesting that **D2** interacted with DNA through an intercalation mode, while **DSMI** interacted with DNA through a grove binding mode.[19]

Competitive interaction among **D2**, CB[7] and DNA was performed and the results are shown in Fig. 6. After titration of 25 equiv. CB[7] into **D2** and 100 equiv. DNA solution (Fig. 6a), a 20% decrease was observed in the fluorescence intensity. In comparison, about a 7.5-fold fluorescence increase was observed along with the addition of 60 equiv. of DNA into the solution of **D2** and 10.0 equiv. of CB[7] (Fig. 6b). It should be noted that a quite similar result was reached for the two different procedures. Taking account of the symmetric structure of **D2**, it can be

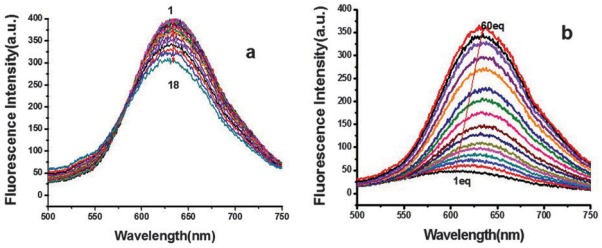
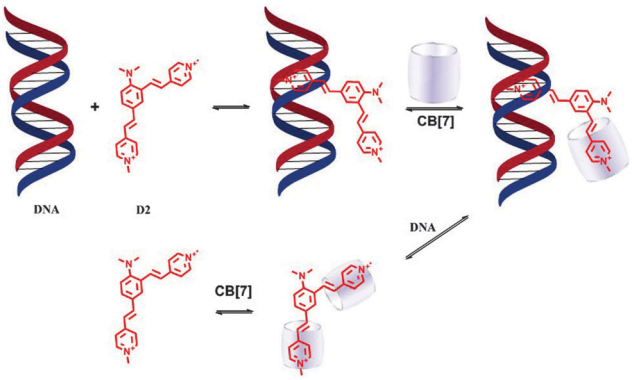


Fig. 6 (a) The fluorescence spectra of **D2**/DNA with the addition of CB[7], from (1) to (18), 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.6, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, 12.0, 15.0, 20.0, 25.0 equiv. of CB[7] was added, the concentration of **D2** was 1×10^{-5} M and DNA was 100 equiv. (b) The fluorescence spectra of **D2**/CB[7] with the addition of 60 equiv. of DNA, CB[7] was 10.0 equiv. of **D2**, the concentration of **D2** was 1.0×10^{-5} M, pH = 7.4.



Scheme 3 The schematic diagram for the formation of the ternary complex among **D2**, CB[7] and DNA.

proposed that one pyridium vinyl of **D2** was included into the cavity of CB[7] and the other intercalated into DNA to form a ternary complex as shown in Scheme 3.

Conclusion

In summary, the interaction between **DSMI** and CB[7] was investigated through UV-Vis, fluorescence, ^{1}H NMR and MS spectrometry. It was found that **DSMI** can be included by CB[7] with a 1 : 2 stoichiometry. When another pyridium vinyl group was introduced into the aniline ring of **DSMI** to get a hemicyanine derivative **D2**, a ternary complex among **D2**, CB[7] and DNA was formed. **D2** interacted with DNA through a intercalation mode, while **DSMI** interacted with DNA through a grove binding mode. All these provide new insights to investigate the interaction of organic dyes, CB[7] and DNA.

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