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Assemblies of brilliant cresyl violet to DNA in the presence of γ-cyclodextrin

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ABSTRACT

The interactions of brilliant cresyl violet (BCV) with herring sperm DNA in γ-cyclodextrin (γ-CD) supramolecular system were studied by UV-vis absorption spectroscopy and cyclic voltammetry (CV). Both UV-vis absorption and CV data show that the interaction of BCV with DNA depends on the concentration ratio of BCV to DNA (*R*), the initial concentration of BCV and γ-CD. The binding constants of BCV monomer, $(BCV)_2$ dimer and $(BCV)_2$-γ-CD inclusion complex with DNA are 1.64×10^5, 2.56×10^4 and $2.32 \times 10^3\ M^{-1}$, respectively. It was observed that γ-CD can affect the interactive mode of BCV with DNA. If *R* is larger than 0.5, the $(BCV)_2$-γ-CD inclusion complex will retain intact and bind to DNA via the electrostatic attraction forces. By contrast, when *R* is smaller than 0.5, the inclusion complex will be partially dissociated and the free BCV monomer is intercalated into the double-helix structure of DNA attributing to the more favorable microenvironment of DNA for the BCV monomer. Our work postulates the importance of the initial concentration of dye and host molecule on the interaction of dye with DNA in living bodies.

1. Introduction

Investigation on the interaction of organic dyes with DNA have attracted much attention over the past years due to increasing researches in new efficient drugs targeted to DNA, in the structure of DNA and in many intracellular processes [1,2]. Many organic dye molecules have been employed as biological probes because of their good DNA binding affinity [3–5]. Currently there are three primary binding modes of dye molecules with nucleic acids, *i.e.*, intercalative binding, grooving binding, and electrostatic interactions [6,7]. For example, the planar dye molecules, such as acridine dyes, interact with DNA by "intercalation" [8]. Some studies have also shown that the dye molecules are intercalated into DNA when the concentration ratio of dye to DNA is low, on the contrary, the interaction of the dye molecules with DNA turns to a non-intercalative binding mode when the concentration ratio of dye to DNA is high [9,10].

Cyclodextrins (CDs) and their derivatives are a series of polysaccharides comprising six (α), seven (β) or eight (γ) D-glucose units which can provide a hydrophobic cavity in aqueous solution for the hydrophobic molecules or groups to form inclusion complexes [11]. This "micro heterogeneous environment" can be used to control the equilibria among dye monomer, dimer and higher aggregation forms by including them into the cavity of CDs, resulting in the changes of their electronic absorption, fluorescence and electrochemical properties. It has been reported that some phenothiazine dyes easily enter the cavity of β-CD, whereas the dye dimers are preferentially included in the larger cavity of γ-CD [12]. This unique amphiphilic characteristics and the ability to shift dye monomer/dimer equilibrium make CDs particularly important and they have been employed as a host medium to study the interaction between organic dyes and DNA. Electrostatic and intercalative binding with DNA have also been reported for planar dye molecules [13–16]. These reports show that β-CD does not significantly affect the interaction mode of dyes with DNA. However, to some extent, the binding affinity can still be affected. For example, the binding of methylene blue with DNA is inhibited by anionic CD derivative, whereas neutral CD has little influence [16]. Through the binding studies of small molecules with DNA in CD supramolecular system, it is possible to elucidate their exact interactive modes. It is well known that brilliant cresyl violet (BCV), a planar dye molecule, is able to bind directly to DNA. However, their binding mode at various concentration ratios of BCV to DNA is still not clear. As such, this motivates our interest in studying their binding interaction in a CD medium since this can provide solid information to evaluate the interaction of this dye molecule with DNA in living bodies. In this paper, the interaction of BCV with DNA in γ-CD medium is reported. Unlike β-CD medium, γ-CD can affect the interactive mode of BCV

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with DNA. The effect of the concentration ratio of BCV and DNA (R) on their interactive model is discussed in detail.

2. Experimental

2.1. Chemicals

Brilliant cresyl violet (BCV) was obtained from Chroma-Gesellschaft Schmid Gmbh & Co. (Münster, Germany). A stock solution of 0.10 mM BCV was prepared by directly dissolving its crystal in doubly distilled water (DDW). γ-CD was purchased from Aldrich (Milwaukee, WI, USA). A stock solution of 10 mM γ-CD was prepared in DDW. A 68-mM Na_2HPO_4-KH_2PO_4 buffer (pH 6.98) was used to prepare all the solutions. Herring sperm DNA from Beijing Xiasi Biotechnology Co., Ltd. (Beijing, China) was used without further purification. Stock solutions of DNA were prepared by dissolving the solid DNA in 0.10 M NaCl solution and stored at 4 °C for no more than a week. The quality of DNA, determined in terms of the absorbance ratio at 260 and 280 nm, was 1.80–1.90, indicating that the DNA was free of protein. The molar extinction coefficient was taken as 6600 $M^{-1}\cdot cm^{-1}$. All other reagents were analytical reagent grade and DDW was used in all experiments.

2.2. Apparatus

Absorption spectra were recorded on a Puxi TU-1901 double-beam spectrophotometer (Beijing, China). Cyclic voltammetry (CV) was conducted on a CHI 660C electrochemical workstation (Shanghai, China) with a three-electrode system comprising a glassy carbon electrode (GCE, 4-mm diameter) as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode.

2.3. Procedures

Samples for absorption and electrochemical measurements were prepared by mixing known amounts of stock solutions of BCV, DNA and γ-CD in phosphate buffer (pH 6.98) and diluted to the required concentrations. The absorption titrations were performed by keeping the concentration of BCV constant while varying the concentration of γ-CD or DNA, or keeping the concentration of BCV dimer-γ-CD inclusion complex ($(BCV)_2$-γ-CD) constant while varying the concentration of DNA. All the absorption measurements were made against the blank solution treated in the same way. 1.0-cm path-length quartz cuvettes were used for absorption measurements.

For the electrochemical measurements, the surface of the GCE was polished with 0.3 μm and 0.05 μm alumina slurries successively, washed with DDW, and finally ultrasonicated for 5 min before use. The clean GCE electrode was then transferred into an electrolytic cell containing 5.0 mL phosphate buffer (pH 6.98) for activation by applying CV scans between -1.00 and 1.00 V at 0.10 V/s until a stable CV profile was obtained. The GCE was ready for use. 5.0 mL solutions of BCV in phosphate buffer (pH 6.98) were transferred into the electrolytic cell. The solutions were deaerated by purging with a stream of nitrogen gas for 15 min before CV scans. The scan potential ranged from -0.80 to 0.20 V at a scan rate of 0.10 V/s. All measurements were performed at room temperature of 19.0 ± 1.0 °C. After the initial CV scan of BCV, an appropriate amount of γ-CD or DNA was added into the BCV solution and scanned again after 10 min. In this work, all CV measurements were performed in triplicates. In general, the CV peak potentials were reproducible to better than ± 5 mV at a scan rate of 0.10 V/s.

3. Results and discussion

3.1. Spectral properties of BCV

The absorption spectra of the pure BCV solutions from 10.0 to 100 μM are shown in Fig. S1A (Supplementary Material). Similar with methylene blue [12,17], the absorption spectrum of BCV is highly dependent on its concentration. When the concentration of BCV is low, a broad absorption band at 636 nm is observed. However, another absorption band at 599 nm starts to emerge with the increase in BCV concentration. The absorbance ratio (A_{636}/A_{599}) of BCV at 636 and 599 nm was plotted and depicted in Fig. S1B (Supplementary Material). It is obvious that A_{636}/A_{599} decreases with the increase in the concentration of BCV, indicating the conversion of monomer to dimer upon the increase in concentration of BCV [18]. It has been reported that BCV mostly exists as monomeric form when its concentration is in the range 0.00–10.0 μM. However, when its concentration is above 10.0 μM, the monomeric BCV will convert to its dimer $(BCV)_2$. As such, it was concluded that the absorption peak maxima of 636 and 599 nm should correspond to the monomer and dimeric forms of BCV, respectively, and is consistent with the literature results. The dimerization constant of BCV between monomer and dimer was 5000 M^{-1} according to the literature [19].

It is well known that the spectral changes at higher BCV concentrations arise from the formation of $(BCV)_2$ dimer, attributing to the electronic interactions between two BCV molecules [20]. The nature of the molecular association determines the allowed and forbidden electronic transitions. In H-aggregates, the higher energy transition is allowed and the lower energy is forbidden. The hypsochromic band (called 'H-band') appears in the dimer spectrum. In other words, the lower energy transition is permitted and the J-band appears in the spectrum [19,20]. In our case, the emergence of H-band (599 nm) verified the formation of H-aggregates, *i.e.*, a 'sandwich' dimer of BCV.

3.2. Inclusion complex of $(BCV)_2$ dimer with γ-CD

It has been reported that many dyes readily form sandwich dimer in water at higher concentrations [21] and our experimental results (*vide supra*) are consistent with this point. In fact, in the process of dye aggregation, the polarizability and hydrophobicity of the dye can drive dimerization at the expense of coulombic repulsion between two dye monomers. The dimerization reaction occurs at even lower dye concentrations if γ-CD is present, where the hydrophobic interior of the γ-CD toroidal cavity provides stabilizing van der Waals' interactions with the dye dimer and excludes water. In order to better understand the shift of monomer/dimer equilibrium and aggregation behavior of BCV in the γ-CD medium, the UV–vis absorption spectra of BCV in the absence and presence of γ-CD were studied. Fig. 1 depicts the UV-vis absorption spectra of 50.0 μM BCV at various concentrations of γ-CD. The absorbance at 636 nm decreases and the absorbance at 599 nm increases with the increase in the concentration of γ-CD, clearly suggesting the formation of inclusion complex between $(BCV)_2$ dimer and γ-CD as $(BCV)_2$-γ-CD. The inset of Fig. 1 shows that the absorbance ratio of BCV at 636 and 599 nm (A_{636}/A_{599}) decreases with the increase in the concentration of γ-CD. These experimental results reveal that the formation of dimer can be promoted by inclusion of $(BCV)_2$ dimer into the cavity of γ-CD [19]. In general, the proper matching of sizes between the host and guest molecules plays a crucial role for the formation of host-guest inclusion complex. In here, the cavity of γ-CD can enclose $(BCV)_2$ dimer snugly with good protection from the aqueous environment.

The inclusion constant (K) is an important parameter to represent the inclusion capacity, which can be determined by the

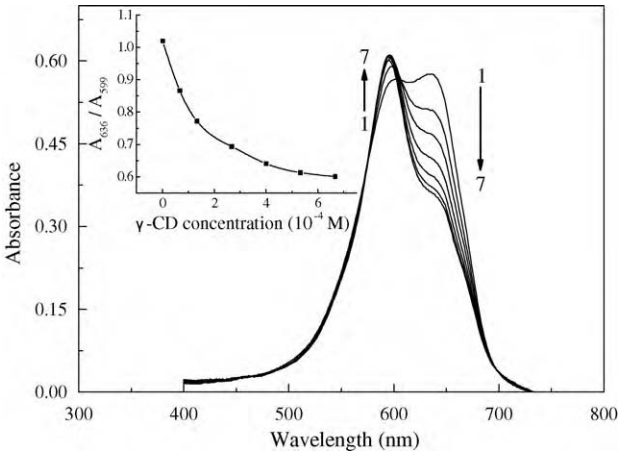

Fig. 1. UV-vis absorption spectra of 50.0 μM BCV at different concentrations of γ-CD: (1) 0.00, (2) 66.7, (3) 133, (4) 267, (5) 400, (6) 533, (7) 667 μM. The inset displays the absorbance ratio of BCV at 636 and 599 nm (A_{636}/A_{599}) in the presence of different concentrations of γ-CD.

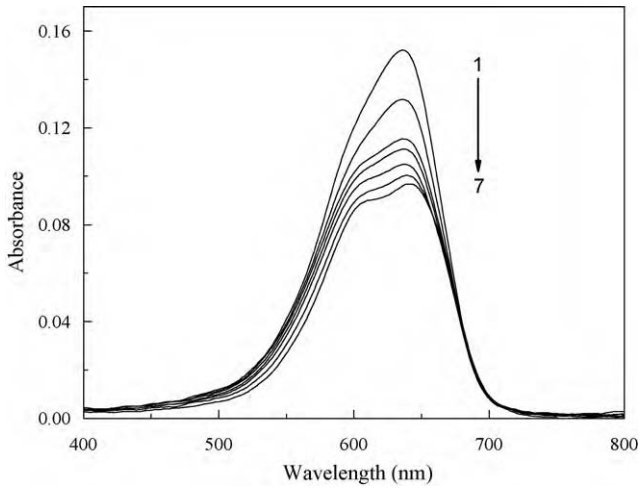

Fig. 2. UV-vis absorption spectra of 10.0 μM BCV at various concentrations of DNA: (1) 0.00, (2) 6.7, (3) 13.3, (4) 20.0, (5) 26.6, (6) 53.1, and (7) 79.7 μM.

double-reciprocal method using the following equation [22]:

$$\frac{1}{\Delta A} = \frac{1}{\alpha} + \frac{1}{\alpha K[CD]_0^n} \quad (1)$$

where $[CD]_0$ is the concentration of γ-CD, α is a constant, ΔA denotes the difference in absorption intensity of guest in the presence and absence of CDs. If the formation of an inclusion complex involves a stoichiometry of 1:1 between $(BCV)_2$ dimer and γ-CD, a linear straight line will be obtained by plotting $1/\Delta A$ against $1/[CD]_0$, where $n = 1$. K is determined from the ratio of the y-intercept to the slope of the line. A linear curve was indeed obtained from our experimental results (not shown here), inferring the formation of 1:1 inclusion complex between $(BCV)_2$ dimer and γ-CD. The K value was calculated to be 6.5×10^3 M^{-1}. In essence, our work demonstrates that the cavity of γ-CD can provide good protective microenvironment for the $(BCV)_2$ dimer, inducing the aggregation of BCV monomer molecules.

3.3. Interaction of BCV with DNA

It is commonly observed that hypochromism and bathochromic shift of the absorption peak of dyes in the presence of DNA are good indication of the binding of these small molecules to DNA. To investigate the interaction of BCV with DNA, the UV-vis absorption spectra of BCV in the absence and presence of DNA were recorded. Fig. 2 displays the UV-vis absorption spectra of 10.0 μM BCV at various concentrations of DNA. The absorption at 636 nm apparently decreases with increasing concentration of DNA until the mole ratio of BCV to DNA (R) reaches approximately 0.75. The hypochromism of the absorption peak at 636 nm indicates that the BCV molecules bind to the DNA. This interaction of BCV with DNA was based on the attenuated absorption at 636 nm, without any sign of dimer formation at 599 nm, indicating that the BCV molecules attach to DNA in its monomeric form. However, on further addition of DNA ($R < 0.75$), the shoulder peak at 599 nm becomes more noticeable although accompanied by almost equal absorption reduction at 636 nm. It is obvious that there are at least two interaction modes of BCV with DNA when the concentration of DNA is higher: (1) BCV monomer with DNA and (2) self-stacking of BCV in the exterior of DNA double helix [23].

The interaction of BCV with DNA was studied at higher concentration of BCV. Fig. 3 shows the UV-vis absorption spectra of 40.0 μM BCV at various concentrations of DNA. At this BCV concentration, some BCV monomer molecules are converted to $(BCV)_2$ dimers, *i.e.*, BCV monomer and dimer can coexist in the solution. When the concentration of DNA increases ($R > 1.0$), the absorptions at 636 nm and 599 nm exhibit the same reduction in intensity. The hypochromism of the absorption peaks at 636 and 599 nm implies that both BCV monomer and dimer bind to the DNA. But the decrease in absorption intensity at 636 nm is more significant than that at 599 nm when $R < 1.0$. This phenomenon suggests that DNA exhibits stronger binding affinity towards BCV monomer than $(BCV)_2$ dimer. It is plausible that $(BCV)_2$ dimer is converted to BCV monomer first and then binds to the DNA since the binding constant of BCV monomer with DNA (1.64×10^5 M^{-1}) is larger than of $(BCV)_2$ dimer (2.56×10^4 M^{-1}) [22,24]. Our work illustrates that the interaction of BCV with DNA largely depends on the concentration of BCV and the mole ratio of BCV to DNA.

3.4. UV-vis absorption studies of the interaction of BCV with DNA in the presence of γ-CD

Fig. 4 depicts the UV-vis absorption spectra of 40.0 μM BCV and 40.0 μM γ-CD at various concentrations of DNA. Initially BCV monomer is converted to $(BCV)_2$ dimer and *in situ* forms inclusion complex with γ-CD as $(BCV)_2$-γ-CD. With the addition of DNA, the absorption of $(BCV)_2$-γ-CD at 599 nm decreases with the increase

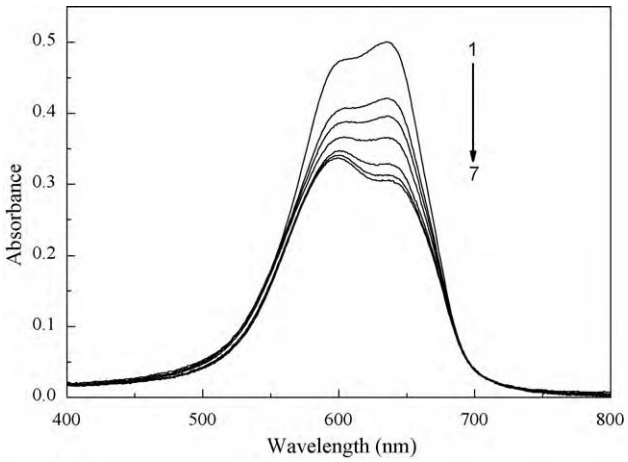

Fig. 3. UV-vis absorption spectra of 40.0 μM BCV in the presence of various concentrations of DNA: (1): 0.00, (2) 13.3, (3) 26.6, (4) 39.9, (5) 53.1, (6) 66.4, and (7) 79.7 μM.

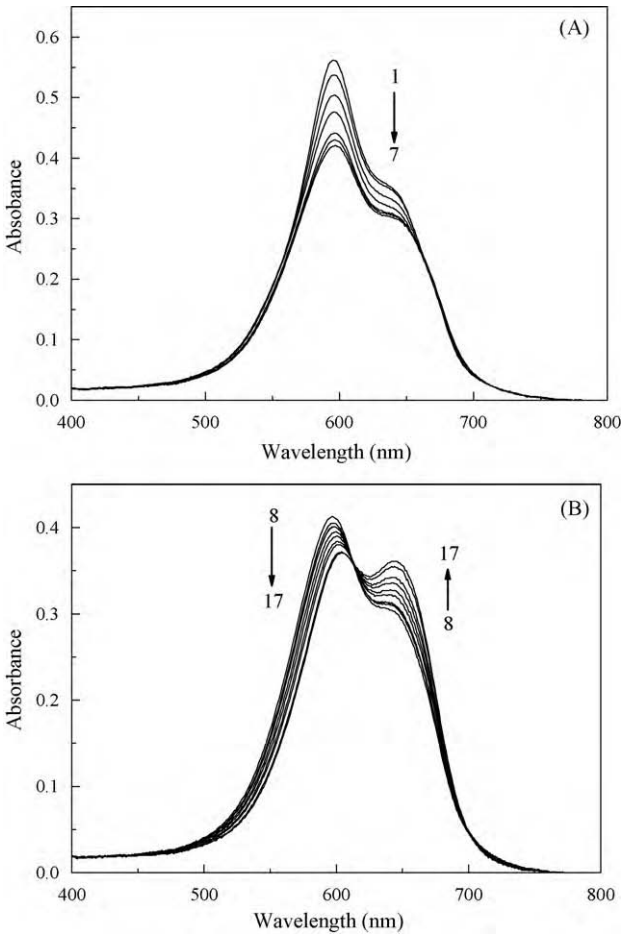

Fig. 4. UV-vis absorption spectra of 40.0 μM BCV and 40.0 μM γ-CD in the presence of various concentrations of DNA: (A) 1: 0.00; 2: 13.3; 3: 26.6; 4: 39.9; 5: 53.1; 6: 66.4; and 7: 79.7 μM, and (B) 8: 93.0; 9: 106; 10: 120; 11: 133; 12: 166; 13: 200; 14: 232; 15: 266; 16: 332; and 17: 399 μM.

in DNA until the ratio of BCV to DNA reaches $R = 0.5$ as displayed in Fig. 4A. On further addition of DNA (*i.e.*, $R < 0.5$), the absorption of $(BCV)_2$-γ-CD at 599 nm changes slowly and the spectrum is ca. 5-nm bathochromically shifted. The shoulder peak at 642 nm is clearer with further increase in the concentration of DNA as shown in Fig. 4B. The spectral changes of BCV in the presence of DNA are different with and without γ-CD, suggesting that γ-CD could affect the interaction of BCV with DNA. It is observed that there are significant differences in the spectral characteristics between $(BCV)_2$-γ-CD and BCV with DNA, showing that $(BCV)_2$ dimer remains in the cavity of γ-CD when it binds to DNA. In fact, the new isosbestic point at 663 nm also confirms that a new adduct of $(BCV)_2$–γ-CD-DNA is formed. As such, it is reasonable to deduce that DNA prefers to interact with $(BCV)_2$-γ-CD inclusion complex when $R > 0.5$. The absorption of $(BCV)_2$-γ-CD at 599 nm decreases linearly with the concentration of DNA when $R > 0.5$. Applying Eq. (1), the corresponding n and K for the interaction of $(BCV)_2$-γ-CD with DNA were determined to be 1 and $2.32 \times 10^3\ M^{-1}$, respectively. On the contrary, the interaction of $(BCV)_2$-γ-CD with DNA is changed when more DNA molecules are present (*i.e.*, $R < 0.5$). The absorption intensity at 599 nm decreases but increases at 642 nm on further increase in the concentration of DNA, inferring that $(BCV)_2$-γ-CD dissociates to BCV monomer and the monomer preferably binds to DNA. In other words, DNA can compete with γ-CD to interact with BCV if its concentration is high enough.

Furthermore, the effect of γ-CD on the interaction between DNA and BCV was investigated at $R = 0.5$ and shown in Fig. 5. The

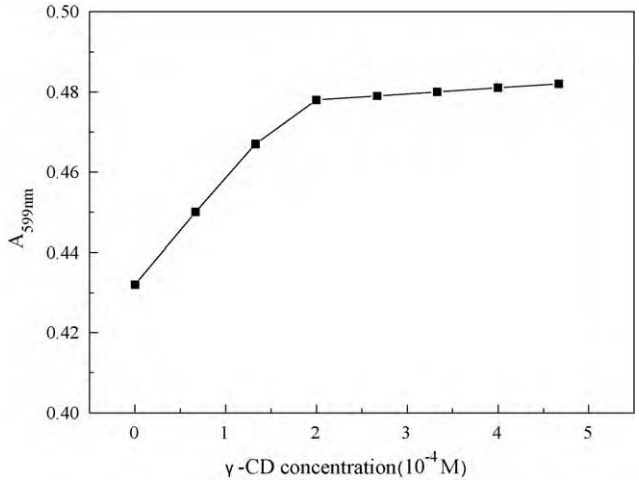

Fig. 5. Effect of the concentration of γ-CD on the binding of 40.0 μM BCV with DNA with $R = 0.5$.

absorption intensity at 599 nm increases with the increase in γ-CD concentration, reaches the highest at 200 μM γ-CD and the spectral feature remains unchanged. This suggests that more BCV molecules are converted to $(BCV)_2$ dimers and form inclusion complexes with γ-CD if γ-CD is in large excess. In summary, our results demonstrate that the binding reaction of BCV to DNA depends on the concentrations of BCV, DNA and γ-CD. When DNA is in large excess, BCV will bind to DNA in its monomeric form. However, if γ-CD is in large excess, BCV turns to its dimeric form and binds with DNA in $(BCV)_2$-γ-CD form.

3.5. Binding modes

It is worthy to discuss the specific binding modes between small dye molecules and DNA in view of the hypochromism and spectral shift of absorption band. In this study, the hypochromism of the absorption peak at 636 nm can be described as the electrostatic attraction of BCV monomer with DNA under low concentration of BCV ($R > 0.75$). When $R < 0.75$, the peak at 599 nm becomes more obvious, clearly indicating that DNA could prompt the self-stacking of BCV in the exterior of DNA double helix to form dimeric $(BCV)_2$. It is plausible that DNA plays the role of supplying negative charges to neutralize the positive charges of BCV molecules, resulting in BCV aggregation. However, the hypochromism of the absorption peaks at 636 nm and 599 nm at higher concentrations of BCV show that both BCV monomer and dimer are capable of binding to DNA via electrostatic attraction forces.

As explained in our previous sections, it has been demonstrated that γ-CD can affect the binding between BCV and DNA. The strong hypochromism at 599 nm and a new isosbestic point at 663 nm suggest that the interaction of $(BCV)_2$–γ-CD with DNA is "electrostatic binding" when $R > 0.5$. On the contrary, if $R < 0.5$, the hypochromism at 599 nm, the bathochromic shift of spectrum, the appearance of an isosbestic point at 611 nm and the absorbance increase at 642 nm are observed (Fig. 4B). All these indicate gradual transition from the electrostatic to intercalative bindings. The absorption peak is shifted from 636 to 642 nm, inferring that the inclusion complex of $(BCV)_2$-γ-CD is preferably converted back to BCV monomer and intercalate with DNA when DNA is in large excess. Thus, a turning point at $R = 0.5$ can be established. When $R < 0.5$ or > 0.5, the binding modes are different; in other words, the interaction process is largely relied on the R value, *i.e.*, the ratio of BCV to DNA in the solution.

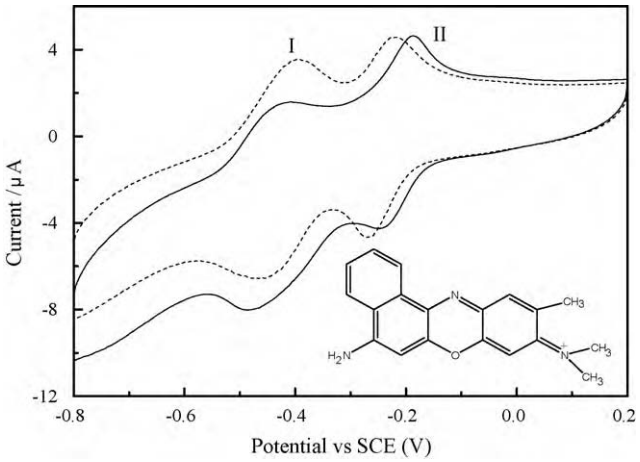

Fig. 6. Cyclic voltammograms of 80.0 μM BCV in the absence (solid curve) and the presence (dashed curve) of 77.0 μM DNA. The scan rate is 0.10 V/s. The inset is the molecule structure of BCV.

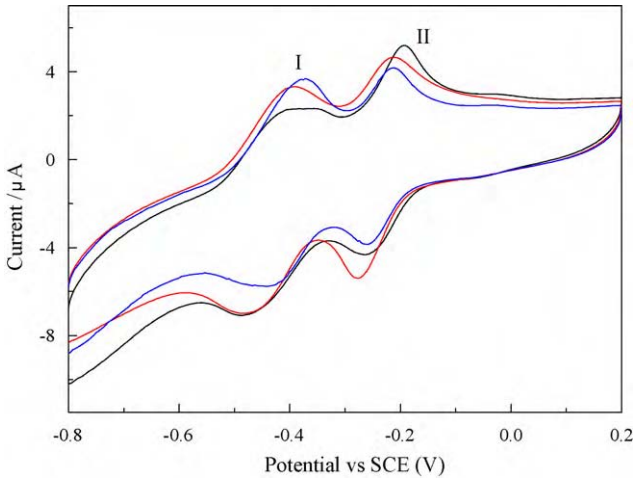

Fig. 7. Cyclic voltammograms of 80.0 μM BCV and 400 μM γ-CD in the absence (black curve) and presence of DNA with $R = 1.0$ (red curve) and $R = 0.35$ (blue curve). The scan rate is 0.10 V/s.

3.6. Electrochemical studies

The electrochemical behavior of BCV binding to DNA in the absence and presence of γ-CD was investigated. Fig. 6 displays the CVs of 80.0 μM BCV without and with DNA (77.0 μM). In the absence of DNA (the solid curve in Fig. 6), BCV features with two redox couples at the cathodic (E_{pc} = -0.486 V) and anodic peaks (E_{pa} = -0.408 V) of couple I, and E_{pc} = -0.248 V and E_{pa} = -0.187 V of couple II, corresponding to the redox reactions of the amino moiety and the π-π conjugated system of BCV molecule, respectively. The peak separation potentials (ΔE_p) of redox couples I and II are 78 and 61 mV respectively, indicating that two quasi-reversible redox processes have taken place. The formal potential E^0 (or voltammetric $E_{1/2}$) of redox couples I and II, taken as the average of E_{pc} and E_{pa}, are -0.447 and -0.218 V respectively. In the presence of DNA (the dashed curve in Fig. 6), both E_{pc} and E_{pa} of redox couple II are more negatively shifted (E_{pc} = -0.270 V and E_{pa} = -0.217 V); however, the redox couple I is only slightly shifted. These results infer that the positively charged π-π conjugation indeed binds to DNA. It has been reported that the shift of redox potentials to more negative values indicates the binding of small molecule to DNA via the electrostatic interaction. Conversely, if the potentials shift to more positive values, significant intercalative interaction is dominant in the binding process [25]. The CV results further support our idea that BCV binds to DNA by electrostatic attraction in the absence of γ-CD.

Fig. 7 depicts the CVs of 80.0 μM BCV and 400 μM γ-CD in the absence and presence of DNA. Comparing to CV of BCV without γ-CD, the redox couples of BCV with γ-CD are negatively shifted: $E_{1/2}$ = -0.448 V for redox couple I and $E_{1/2}$ = -0.229 V for redox couple II. This shift is attributing to the formation of inclusion complex of $(BCV)_2$ dimer with γ-CD as mentioned above. On addition of DNA to the BCV solution containing γ-CD with $R = 1.0$, $E_{1/2}$ of redox couple I basically remains unchanged but $E_{1/2}$ of redox couple II is shifted from -0.229 to -0.245 V (the red curve in Fig. 7), indicating possible interaction of $(BCV)_2$-γ-CD with DNA via electrostatic attraction. However, an interesting phenomenon was observed at higher concentration of DNA ($R = 0.35$). $E_{1/2}$ of redox couple I is positively shifted by 44 mV and redox couple II is slightly positively shifted. This phenomenon further confirms the change in the interactive mode of BCV with DNA at higher concentration of DNA. This can be explained by the fact that the inclusion complex $(BCV)_2$-γ-CD is partially converted back to the BCV monomer and then the amino moiety of the BCV monomer is intercalated into the double-helix of DNA, resulting in the larger positive potential shift of redox couple I. In summary, the electrochemical data concurs with the spectroscopic results that γ-CD may be considered as a local "solvent" environment [25] which can affect the binding mode of BCV with DNA.

4. Conclusion

UV-vis absorption and CV have been used to investigate the binding nature of BCV to DNA in the presence of γ-CD. The results show that the interaction of BCV with DNA depends on the ratio of BCV to DNA (R), the initial concentrations of BCV and γ-CD. In the absence of γ-CD, BCV monomer or dimer would bind to DNA by electrostatic attraction. Furthermore, a high concentration of DNA could prompt the self-stacking of BCV in the exterior of DNA double helix when $R < 0.75$. In the presence of γ-CD, both spectroscopic and electrochemical data support that the inclusion complex $(BCV)_2$-γ-CD binds to DNA via electrostatic binding when $R > 0.5$. However, when R is switched to < 0.5, $(BCV)_2$-γ-CD is partially dissociated to BCV monomer and the amino moiety of the free BCV monomer intercalates into the double-helix structure of DNA. In conclusion, γ-CD can affect the interaction mode between BCV and DNA. These investigations are of potential importance in understanding the interaction and recognition mechanisms of compounds in living bodies.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.05.032.

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