

Electrochemical behavior and DNA-binding properties of binuclear copper(II) complex containing mixed ligands of *N*-hydroxyethylaminoethyl oxamido and 2,2'-bipyridine

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Abstract The electrochemical property of dinuclear copper (II) complex containing mixed ligands of *N*-hydroxyethylaminoethyl oxamido and 2,2'-bipyridine $[\text{Cu}_2(\text{bpy})_2(\text{HAO})_2]^{2+}$ was studied with cyclic voltammetry. $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ had irreversible oxidation peaks in 0.1 mol/L NaCl solution at the stearic acid-modified carbon paste electrode. Cyclic voltammetry and absorption spectra measurements were used to study the interaction between $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ and herring fish sperm DNA. All the experimental results showed that $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ interacted with DNA mainly through electrostatic affinity to make tiny difference between $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ -ssDNA and $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ -dsDNA. The binding ratio and the binding constant of DNA- $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ were calculated as 1:1 and 6.41×10^4 , respectively. The redox peak current of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ decreased markedly after its interaction with DNA. This was used to detect the concentration of DNA quantitatively.

Keywords Dinuclear copper(II) complex · DNA · Cyclic voltammetry · Absorption spectra

Introduction

There is continuing interest in small molecules, especially metal complexes which can interact with DNA [1–4]. A precise understanding of the DNA-binding affinity and the

cleavage mechanism would provide insight into the nature and structure of the reactive intermediate and would be potentially useful in the design of new site-specific scission reagents and chemical probes. Copper is a bioessential element with relevant oxidation states. Copper complexes are involved in a variety of important biochemical processes [5, 6]. Some copper complexes with different types of ligands have been synthesized and studied. Electrochemical techniques are used to characterize their electrochemical behaviors since the biochemical reactions related to the redox processes. Among the copper complexes explored so far, attention has been primarily focused on the copper complexes with rigid bidentate ligands, such as 2,2'-bipyridine [1, 3] or 1,10-phenanthroline and their derivatives [7–10] due to their high nucleolytic efficiency and their potential application in the recognition of the DNA sequence. Herein, we characterized the electrochemical property of a new dinuclear copper(II) complex containing mixed ligands of *N*-hydroxyethylaminoethyl oxamido and 2,2'-bipyridine $[\text{Cu}_2(\text{bpy})_2(\text{HAO})_2]^{2+}$. Its interaction with herring fish sperm DNA was also investigated with cyclic voltammetry and spectroscopy.

Experimental

Materials

Double-strand herring fish sperm DNA from Sigma was used as received. The stock solution of DNA (pH 8.1) was prepared by dissolving appropriate amount of DNA in 10 mM Tris containing 1 mM EDTA and stored at 4 °C. The ratio of the absorbance at 260 and 280 nm (A_{260}/A_{280}) was checked to be 1.89, indicating that the DNA was sufficiently free from protein. Its concentration was determined

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by ultraviolet absorption at 260 nm ($\epsilon=6,600 \text{ L mol}^{-1} \text{ cm}^{-1}$). Denatured single-strand DNA (ssDNA) was obtained by heating double-stranded DNA (dsDNA) in a water bath at 100 °C for 10 min, followed by rapidly cooling in an ice bath. $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ was kindly supplied by Professor Yantuan Li, who works in Marine Drug and Food Institute, Ocean University of China. Stearic acid, carbon powder, and other reagents were all purchased from Shanghai Reagent Company and used as received.

Procedure

A CHI 832 electrochemical analyzer (Shanghai CH Instrument Company, China), which was in connection with a homemade carbon paste-modified working electrode (Φ 4 mm), a saturated calomel reference electrode, and a platinum wire auxiliary electrode, was used for the electrochemical measurement. Absorption spectra were recorded on a Varian 300 spectrophotometer. Spectrometric titrations were performed by adding successive aliquots of DNA to $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ solution, in a 10-mm quartz cell, and recording the spectrum after each addition.

Results and discussion

The electrochemical properties of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$

The structure of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ was illustrated in Fig. 1. The carbon paste electrodes were prepared according to our previous works [11].

As shown in Fig. 2, the peak currents of $2.0 \times 10^{-4} \text{ mol/L}$ $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ at the carbon glassy electrode (GCE, Φ 3 mm) were very small. Modified carbon paste electrodes (CPEs) were made to enhance the electrochemical signals of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$. Different mass ratio of graphite powder, stearic acid, and solid paraffin was heated at 80 °C for 2 h and ground intensively to obtain uniform carbon paste. The hot carbon paste was tightly packed into the cave of a glass tube (Φ 4 mm) and a copper wire was introduced for electrical contact. And

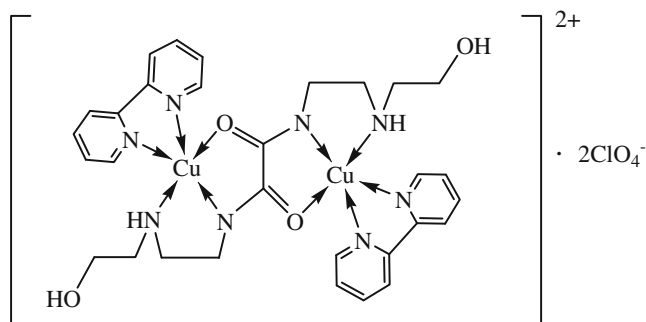


Fig. 1 The structure of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$

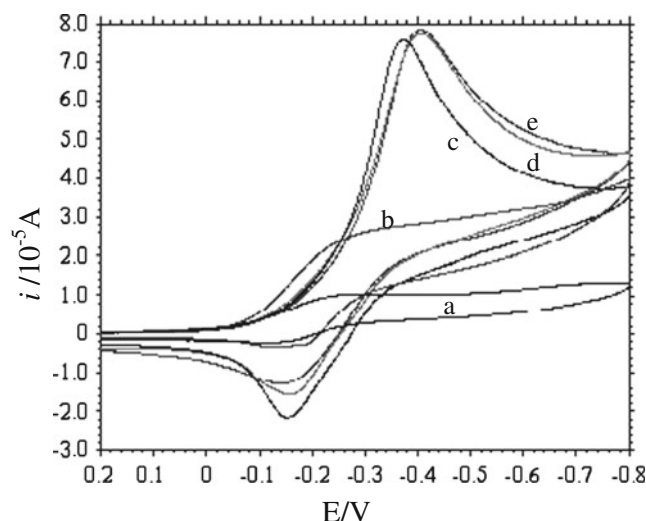


Fig. 2 Cyclic voltammograms of $2.0 \times 10^{-4} \text{ mol/L}$ $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ in 0.1 mol/L NaCl solution at (a) GCE and (b–e) CPE. The mass ratio of solid paraffin, stearic acid, and carbon powder was 1 : 0 : 4; 0 : 1 : 4; 0 : 1 : 3; and 1 : 3 : 12, respectively. The starting potential was 0.2 V and the direction of scan was negative

then, the carbon paste was allowed to cool down to the ambient temperature under certain pressure. The obtained electrode was smoothed on a weighing paper before use.

The electrochemical signals of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ were a little bigger at pure carbon paste electrode (the mass ratio of carbon powder to solid paraffin was 4:1), but still too small to detect exactly. Considering the positively charged $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ and the hydrophilic ligands of *N*-hydroxyethylaminoethyl oxamide, stearic acid was added to the carbon paste to improve the hydrophilicity and the charged property of the electrode surface. The peak currents increased evidently at the stearic acid-modified CPE. The reversibility of the electrochemical reaction became worse when the percentage of stearic acid exceeded 20 %. On the other hand, when the percentage of stearic acid was too small, the obdurability of the electrodes decreased and $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ was easy to penetrate into the carbon paste, which made it difficult to eliminate the remaining signal of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ at the test electrode. Considering both the obdurability of the electrodes and the reversibility of the reaction of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$, the mass ratio of carbon powder to stearic acid employed in all the subsequent work was 4 : 1.

The multi-sweep cyclic voltammograms of $1.5 \times 10^{-4} \text{ mol/L}$ $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ in 0.1 mol/L NaCl solution were recorded after the CPE soaking in the test solution for 5 min (Fig. 3). With the increase of the scan cycle (a→f), the cathodic peak potential experienced a positive shift and the cathodic peak current decreased markedly. By contrast, the anodic peak currents increased slightly and the anodic peak potentials experienced slightly negative shift up to the third

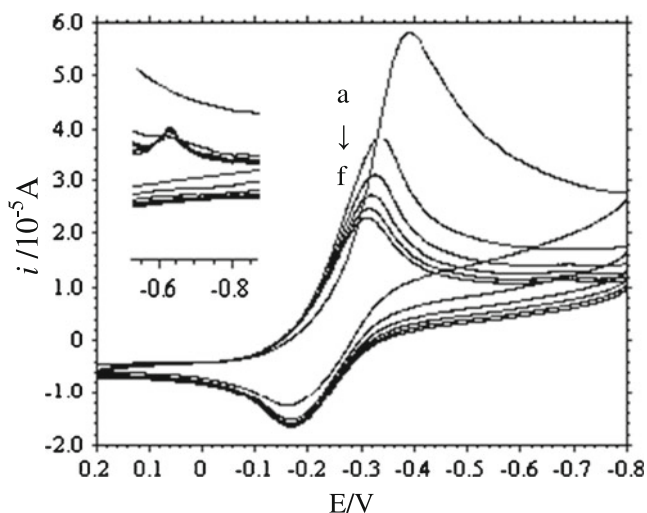


Fig. 3 Successive voltammograms (a→f) of 1.5×10^{-4} mol/L $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ in 0.1 mol/L NaCl. Inset The voltammograms between the potential of -0.6 to approximately -0.8 V when the scan range was from 0.2 to -1.4 V. The starting potential was 0.2 V and the direction of scan was negative

scan cycle and then tended to keep constant. A new cathodic peak appeared at the third scan cycle between the potential of -0.6 to approximately -0.7 V and the peak current increased with the increase of the scan cycle. All the above characteristics indicated that the electroreduction of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ at the CPE is irreversible. The new cathodic peak increased markedly when the terminal scan potential negatively shifted to -1.4 V (the inset of Fig. 3). In other words, the more negative terminal potential favored the new substance.

When the scan rate changed in the range from 20 to 250 mV/s, the i_{pc} and i_{pa} of 2.0×10^{-4} mol/L $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ were directly proportional to the scan rate. The linear regression equations of i_{pc} and i_{pa} were $i_{pa} = 10.695 v + 1.3569$ ($r = 0.9971$) and $i_{pc} = 11.28 v + 4.0179$ ($r = 0.9957$), respectively, where i_{pa} was in 10^{-5} A and v in volts per second. Thus, the electrochemical reaction of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ at CPE was an adsorption-controlled process.

The dissociation process of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ from the CPE was also discussed (Fig. 4). After the CPE was inserted into the $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ solution for 5 min, it was transferred into 0.1 mol/L NaCl solution immediately and subsequently scanned in the potential range of 0.2 to approximately -0.8 V. The peak currents of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ decreased gradually with the prolonging of the dissociation time. A linear relation between the logarithmic value of the i_{pa} of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ and the dissociation time was obtained with the corresponding regression equation $\lg i_{pa} = -0.0028 t - 4.697$ ($r = 0.993$), which suggested that the dissociation of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ from the CPE obeyed the model of first-order kinetic process. The new cathodic peak above also appeared and increased with the

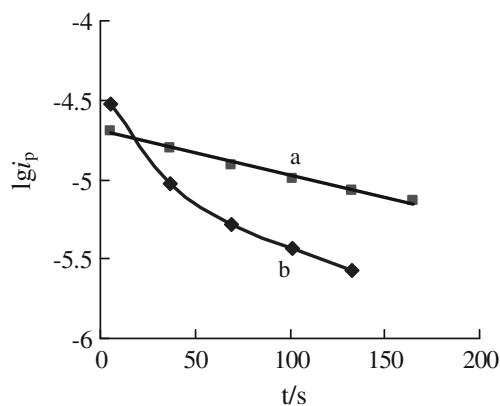


Fig. 4 Relationship between the logarithmic value of the peak current and the dissociation time, (a) i_{pa} , and (b) i_{pc}

scan cycle. Some $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ being translated into the new substance in addition to the dissociation of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ led to its i_{pc} decreasing more quickly than the i_{pa} and the regression curve of i_{pc} was bended down.

Electrochemical study of the interaction between $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ and DNA

Typical CV behaviors of 2.0×10^{-4} mol/L $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ in the absence and presence of DNA were shown in Fig. 5. When 3.2×10^{-5} mol/L ssDNA or dsDNA was added, the i_{ps} of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ decreased along with the widening of the $\Delta E_p (E_{pa} - E_{pc})$, and no other new peak appeared. On the other hand, the formal potential [$E_f = 1/2 (E_{pa} + E_{pc})$] of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ exhibited ~ 8 mV (mean value of five measurements with the standard deviation of 1.91 mV) negative shift after adding ssDNA or dsDNA,

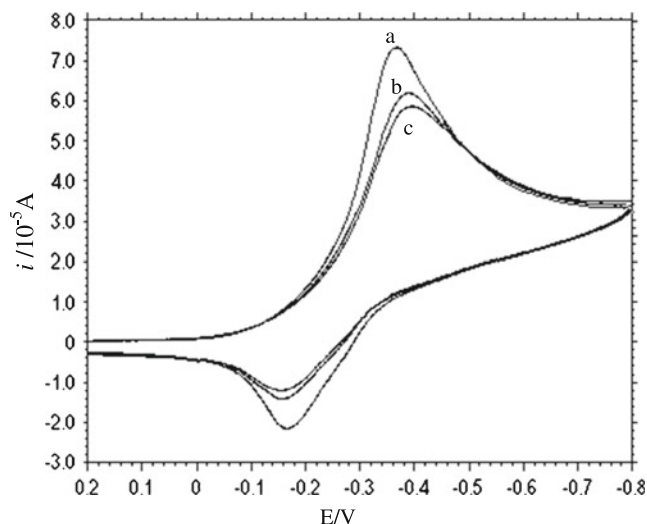


Fig. 5 The effect of DNA on the cyclic voltammograms of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ in (a) 2.0×10^{-4} mol/L $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$; (b) a + 3.2×10^{-5} mol/L dsDNA; (c) a + 3.2×10^{-5} mol/L ssDNA. The starting potential was 0.2 V and the direction of scan was negative

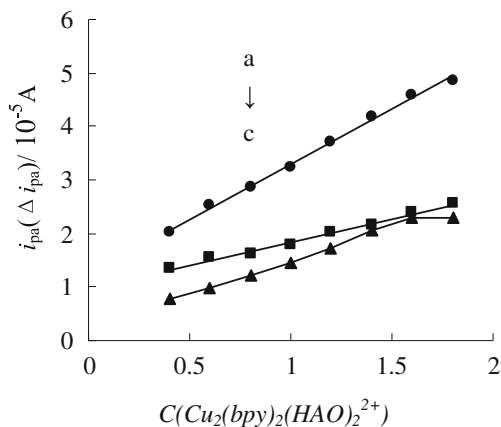


Fig. 6 Relationship between i_p and $C(\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+})$ (a, b), Δi_p and $C(\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+})$ (c): a $C_{(\text{dsDNA})} = 0$; b $C_{(\text{dsDNA})} = 3.2 \times 10^{-5} \text{ mol/L}$; c $i_{p(a)} - i_{p(b)}$

which indicated that $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ was associated with DNA through electrostatic binding [12]. The ratio of the equilibrium constants, K_{2+}/K_+ for the binding of the Cu (II) and Cu(I) forms of complexes to DNA could be estimated from the net shift in $E_{1/2}$, using the equation:

$$E_b^{0'} - E_f^{0'} = 59.15/n \lg(K_{2+}/K_+)$$

where $E_f^{0'}$ and $E_b^{0'}$ are the formal potentials of the Cu(II)/Cu(I) couple in the free and bound species, respectively. For both of ssDNA and dsDNA, K_{2+} was higher than K_+ . DNA tended to stabilize the Cu(II) over the Cu(I) state by electrostatic interaction. The i_{pa}/i_{pc} ratio of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ both increased after adding ssDNA or dsDNA suggesting that the adsorption of the Cu(I) tended to be suppressed in the presence of DNA. $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ cannot be used to distinguish ssDNA from dsDNA because there was no obvious difference between the i_{ps} of dsDNA + $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ and ssDNA + $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$.

According to reference [13], the binding ratio and binding constant of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ -DNA complex can be

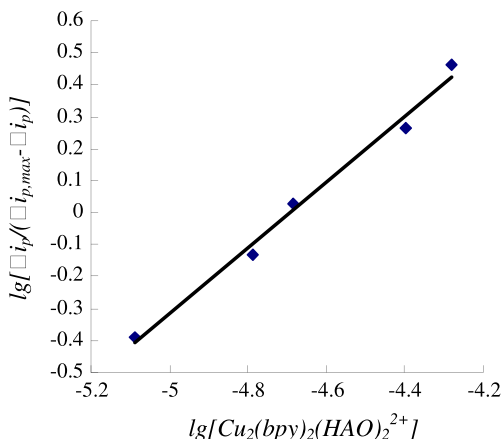
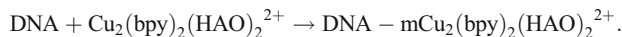


Fig. 7 Relationship between $\lg[\Delta i_p/(\Delta i_{p,\text{max}} - \Delta i_p)]$ and $\lg[\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}]$ $C_{\text{dsDNA}} = 3.2 \times 10^{-5} \text{ mol/L}$

determined. It is assumed that $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ and DNA produce only a single complex $\text{DNA}-m\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$:



The binding constant is

$$\beta = [\text{DNA} - m\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}] / ([\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}]^m [\text{DNA}])$$

Because of: $[\text{DNA}] = C_{(\text{DNA})} - [\text{DNA} - m\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}]$

$$\Delta i_{p,\text{max}} = K C_{(\text{DNA})}$$

$$\Delta i_p = K [\text{DNA} - m \text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}]$$

Therefore, $\Delta i_{p,\text{max}} - \Delta i_p = K [\text{DNA}]$

and the following equations can be deduced:

$$\lg[\Delta i_p/(\Delta i_{p,\text{max}} - \Delta i_p)] = \lg\beta + m \lg[\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}]$$

$$1/\Delta i_p = 1/i_{p,\text{max}} + 1/(\beta \cdot \Delta i_{p,\text{max}}) \times 1/[\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}]^m$$

where $\Delta i_{p,\text{max}}$ represents the maximum difference of the peak currents before and after the addition of DNA. If DNA and $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ form a single complex, the plot of $\lg[\Delta i_p/(\Delta i_{p,\text{max}} - \Delta i_p)]$ versus $\lg[\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}]$ is linear. In Fig. 6, curve a showed the relationship between the current i_p and the concentration of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$. Curve b typically represented i_p change at $C_{(\text{DNA})} 3.2 \times 10^{-5} \text{ mol/L}$ on varying the concentration of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$. Curve c was the relationship between Δi_p , which was $i_{p(a)} - i_{p(b)}$ and the concentration of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$. When the concentration of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ was over $1.6 \times 10^{-4} \text{ mol/L}$, Δi_p tended to be a stable value, which indicated that here was almost no free DNA in the solution. Figure 7 showed the dependence of $\lg[\Delta i_p/(\Delta i_{p,\text{max}} - \Delta i_p)]$ on $\lg[\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}]$, by showing a fine straight line ($y = 1.0243x + 4.8071$, $r = 0.9945$).

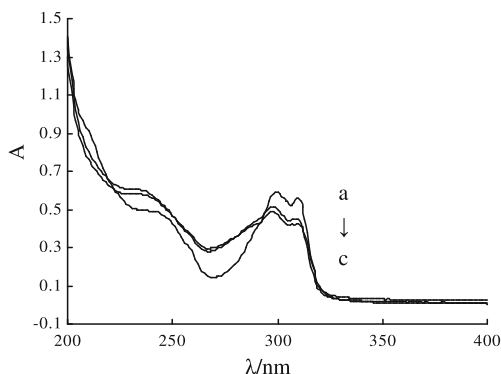


Fig. 8 UV-Vis absorption spectra of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ interaction with DNA (a) $2.0 \times 10^{-5} \text{ mol/L}$ $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$; (b) a + $3.2 \times 10^{-5} \text{ mol/L}$ dsDNA; (c) a + $3.2 \times 10^{-5} \text{ mol/L}$ ssDNA

Table 1 Determination of DNA

Nucleic acid	Coexisting substance	Added (10^{-6} mol/L)	Found (10^{-6} mol/L, mean value of five measurements)	Recovery (%)	RSD (%)
(fs)DNA	L-Lysine, citric acid, glucose, Cu^{2+} , Mg^{2+} , Hg^{2+}	4.00	4.24	105.2	4.1
(fs)DNA	L-Leucine, L-cysteine, glucose, Ca^{2+} , Mg^{2+}	4.00	3.89	97.25	3.3

$\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ (2.0×10^{-4} mol/L); Cu^{2+} , Mg^{2+} , Hg^{2+} , Ca^{2+} (1.0×10^{-5} mol/L); L-lysine, citric acid, glucose, L-leucine, L-cysteine (10.0 mg/L)

From the slope and the intercept of the straight line, the values of m and β were calculated as 1 and 6.41×10^4 , respectively. A tentative idea was that the binding ratio of DNA and $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ is 1:1. In Figs. 6 and 7, $C(\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+})$ and $[\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}]$ represent the concentration added and the equilibrium concentration of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$, respectively. $[\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}]$ in Fig. 7 can be obtained from the data in Fig. 6.

Electronic spectral study of the interaction between $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ and DNA

$\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ absorbed in the ultraviolet range with maxima at 310 and 299 nm, respectively. With the addition of DNA, $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ showed a decrease in molar adsorptivity (hypochromism) as well as a slightly blue shift (1–2 nm). The hypochromism induced by ssDNA was almost the same as dsDNA to indicate that the interaction between $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ and ssDNA made no obvious difference with that between $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ and dsDNA. The intrinsic binding constant K_b of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ for dsDNA had been determined from the spectral titration data using the equation [14]:

$$[\text{DNA}]/(\varepsilon_a - \varepsilon_f) = [\text{DNA}]/(\varepsilon_b - \varepsilon_f) + 1/K_b(\varepsilon_b - \varepsilon_f)$$

where ε_a , ε_f , and ε_b corresponded to $A_{\text{obsd}}/[\text{Cu}]$, the extinction coefficient for the free copper complex, and the extinction coefficient for the copper complex in the fully bound form, respectively. In the plot of $[\text{DNA}]/(\varepsilon_a - \varepsilon_f)$ Vs $[\text{DNA}]$, K_b was given by the ratio of the slope to intercept. The K_b value was calculated to be 5.24×10^4 , which was closed to the result of electrochemical method (6.41×10^4), but lower than those observed for typical classical intercalators. $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ should interact with DNA mainly by electrostatic interaction (Fig. 8).

Analytical application

Keeping the concentration of DNA as 4.0×10^{-6} mol/L, the influence of 20 times of substances such as L-lysine, L-glutamate, L-arginine, L-leucine, L-cysteine, citric acid, glucose, and 1.0×10^{-5} mol/L of cations such as Mg^{2+} , Ni^{2+} , Zn^{2+} , Ca^{2+} ,

Cu^{2+} , and Ba^{2+} , on the Δi_p of DNA– $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ system was tested according to the standard procedure. The relative errors of the results were smaller than $\pm 8.7\%$, which illustrates that these usual coexisting substances have little effects on the determination of DNA. It shows that the interaction of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ with DNA provides a possibility for detecting the content of DNA. The decrease of i_{pc} (Δi_{pc}) was proportional to the added concentration of dsDNA over the range from 1.2×10^{-6} to 1.1×10^{-5} mol/L, with the regression equation $\Delta i_p = 1.5628 C - 0.0487$ (Δi_p , 10^{-5} A; C, 10^{-5} mol/L, $r = 0.9982$). The limit of detection was given by the equation limit of detection (LOD) = 3α , where α is the standard deviation of the blank measurements ($n = 11$); here, the LOD was 4.8×10^{-7} mol/L.

To test this new method, the DNA contents in two synthetic samples, constructed based on the effects of foreign substances, were analyzed under the optimum conditions, namely, 2.0×10^{-4} mol/L $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ in 0.10 mol/L NaCl solution. As shown in Table 1, the results are reproducible and reliable.

Conclusion

$\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ had irreversible oxidation peaks in 0.1 mol/L NaCl buffer solution at the stearic acid-modified carbon paste electrode. A new substance with more negative cathodic potential was produced during the reductive process. All the experimental results from cyclic voltammetry and absorption spectra measurements showed that $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ interacted with DNA mainly through electrostatic affinity. There was only a tiny difference between $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ –ssDNA and $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ –dsDNA. The decreases of the cathodic peak current of $\text{Cu}_2(\text{bpy})_2(\text{HAO})_2^{2+}$ were proportional to the added concentration of dsDNA over the range from 1.2×10^{-6} to 1.1×10^{-5} mol/L.

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