

## Electrochemistry and *In-situ* Spectroelectrochemistry Studies of Carbazole and 9-Ethylcarbazole

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**Abstract:** Mechanisms of electron transfer of carbazole (CZ) and 9-ethylcarbazole (ECZ) were studied by electrochemistry and *in-situ* spectroelectrochemistry. The result indicated that the electrochemical reaction mechanism of ECZ was the same as that of CZ. Both of them undergo ECE process: the initial step is removal of one electron to generate very reactive cation radical, this species then proceeded by deprotonation-coupling reaction to form the corresponding dimer, which was oxidized continuously.

**Keywords:** Carbazole, *in-situ* spectroelectrochemistry, cation radical.

Carbazole and its derivatives has been the subject of numerous investigations over the past 30 years. Carbazoles has been used as a functional building block in the fabrication of organic photoconductors, non-linear optical (NLO) materials and photorefractive materials<sup>1</sup>. Recent investigations focus on biological activity<sup>2</sup>, modified electrodes<sup>3</sup> and functional conduction polymers<sup>4</sup>. The feature of carbazoles, is apt to be oxidized to generate active radical cation, this feature plays an important role in its functions. The redox process of CZ has been investigated earlier<sup>5</sup>, but we found that few data concerning the change of molecular structure was available at present. However, *in-situ* spectroelectrochemistry is a powerful tool in obtaining information on structural and molecular properties during the process of electrochemical reaction. In this paper, *in-situ* UV and FTIR spectroelectrochemistry techniques have been employed to investigate the electrochemical behavior of CZ and ECZ on bare Pt electrode in CH<sub>3</sub>CN solution. The reaction mechanism of ECZ as well as the redox species of CZ was elucidated based on the electrochemical and *in-situ* spectroscopic data.

### Experimental

All experiments were performed in anhydrous CH<sub>3</sub>CN solution using 0.1 mol/L tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The technique details of electrochemistry and *in-situ* FTIR spectroscopy developed in our laboratory were described in ref 6.

*In-situ* UV spectroelectrochemistry was carried out in TU-1901 spectrophotometer

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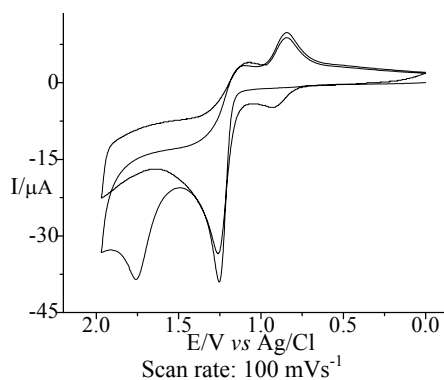
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with a home-made optically transparent layer cell. The resulting spectra were described as:  $\Delta A = A_S - A_R$ . Here,  $A_S$  is absorbency at sample potential and  $A_R$  is absorbency at reference potential. All potential values are referred to Ag/AgCl electrode.

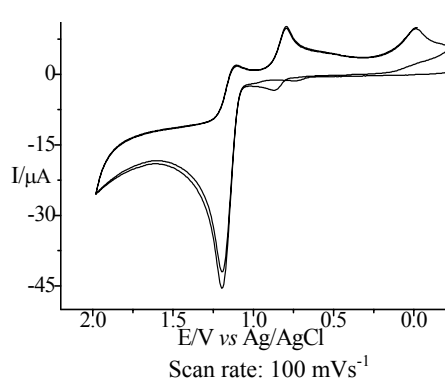
## Results and Discussion

In  $\text{CH}_3\text{CN}$  solution containing 0.1 mol/L TBAP as supporting electrolyte, the cyclic voltammograms (CV) of CZ and ECZ were observed to oxidize at  $E_p = 1.252$  V (**Figure 1**) and  $E_p = 1.215$  V (**Figure 2**) in an irreversible redox process, respectively. The values are close to that reported in ref 5, single electron oxidizing process to generate a very unstable cation radical.

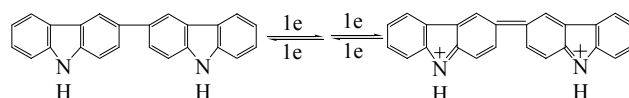
**Figure 1** CV response of 2 mmol/L CZ



**Figure 2** CV response of 2 mmol/L ECZ



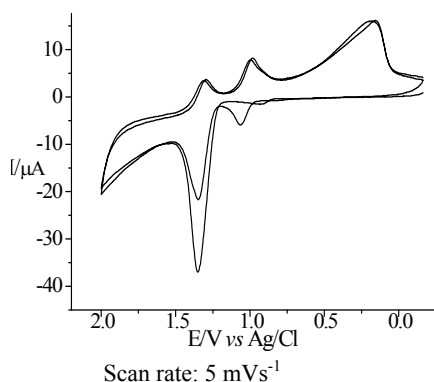
In **Figure 1**, the CV shows another oxidized peak at 0.925 V on the second anodic-going scan, this can be attributed to the oxidation of the 3, 3'-dicarbazole<sup>5</sup>. On the second cycle, the CV shows two *quasi*-reversible redox processes of the dimer, both of which are one electron process. Consequently, the mechanism of the 3, 3'-dicarbazyl may be represented schematically as follows:



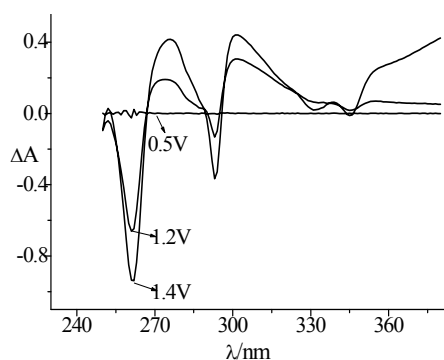
In comparison to ECZ, the CV of CZ shows an additional oxidized peak at 1.760 V due to the oxidation of 9, 9'-dicarbazole<sup>5</sup> which undergoes an irreversible process owing to the twisted nature of ring-N-N-ring probably. This peak missed in ECZ system because of somewhat steric hindrance of ethyl and only corresponding 3, 3'-dicarbazyl formed. On the cycling back of ECZ, cathodic peak at about 0.1V corresponds to the reduction of protons released in the coupling reaction.

Due to the electro-donating effect of ethyl, the electron density of N atom in ECZ is larger than that of CZ. Therefore, the potentials of oxidized peaks of ECZ system are lower than CZ's, while potentials of reductive peaks are higher. The CV of ECZ in home-made thin layer cell with the low scan rate of 5 mVs<sup>-1</sup> (**Figure 3**) is similar to that showed in bulk solution (**Figure 2**), which also implies that the dimer of ECZ is relatively stable.

**Figure 3** Thin layer CV of 2 mmol/L ECZ



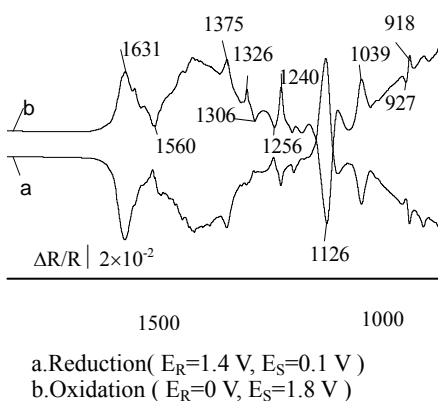
**Figure 4** *In-situ* UV spectrum of 5 mmol/L ECZ



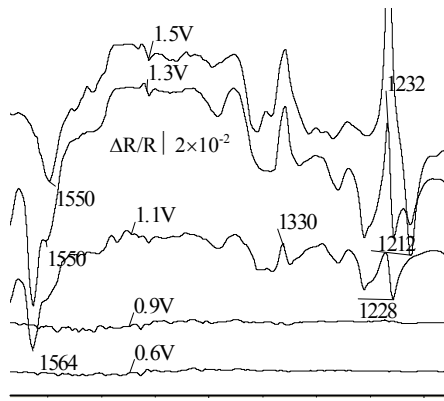
**Figure 4** is the *in-situ* UV spectroelectrochemistry. The reference potential was set at 0V where no oxidation of ECZ had occurred. In **Figure 4**, a beeline was observed when oxidized potential was set at 0.5V because it had no oxidation at this potential. The maximal peaks at 261 (-), 293 (-), 274 (+), 331 (-) and 345 (+) when oxidized potential was set 1.2 V or 1.4 V. (+) presents the decrease of the response species while (-) represents the increase of them. From **Figure 4**, the red shifts from 261 (-) nm ( $\pi \rightarrow \pi^*$ ) to 274 (+) nm and from 293 (-) nm ( $\pi \rightarrow \pi^*$ ) to 300 (+) nm indicated the conjugated system was extended during the redox process, which agrees with the estimation that ECZ underwent the process of single electron oxidation at initial step and then coupled to form the dimer, which has larger conjugated plane.

In order to investigate the mechanism of electrochemical reaction of CZ and ECZ, *in-situ* FTIRS was used to track the whole process of the electrochemical reactions. Difference FTIR spectra of CZ recorded at  $E_S=1.8$  V during the oxidation process and  $E_S=0.1$  V during the reduction process in the spectral range of 2000-800  $\text{cm}^{-1}$  are shown in **Figure 5**. The assignment of bands shown in **Figure 5** is summarized in **Table 1**, which is the direct proof of the mechanism of CZ's electrochemical reaction.

**Figure 5** *In-situ* FTIR spectra of 10 mmol/L CZ



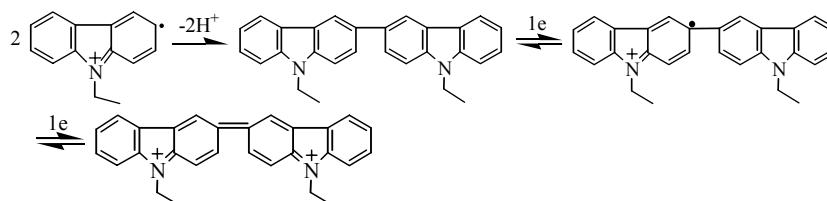
**Figure 6** *In-situ* FTIR spectra of oxidation of 10 mmol/L ECZ



**Table 1** Assignment of the main vibration frequencies in **Figure 5**

Bands( $\text{cm}^{-1}$ )	Assignment	Remarks
1631 (+)	(C=C)ring	1,2,4-substitute benzene ring ,proof of 3,3'-dicarbazyl
1560 (-)	(C=N)	increase or produce of C=N
1326 (+) 1306 (-)	$\sigma_{\text{S}}$ (C-N)	influenced by chemical environments around, leading to red-shift
926 (+) 917 (-)	$\sigma_{\text{as}}$ (C-N)	influenced by chemical environments around, leading to red-shift

Figure 6 showed *in-situ* FTIR difference spectra of ECZ in the wavenumber range 1600 -1200  $\text{cm}^{-1}$  recorded in the process of oxidation.  $E_{\text{R}}$  was set at potential of 0 V because no oxidation had occurred. At 0.9 V, the positive going band at 1330  $\text{cm}^{-1}$  was assigned to asymmetric C-N stretching mode of carbazole ring and the negative going band at 1564  $\text{cm}^{-1}$  was assigned to  $\nu$  (C=N), indicating the beginning of ECZ oxidation at this potential, and the peak intensities were increased as the electrode potential increased. This suggested that the C-N character decreased while the C=N character increased. A pair of dipolar peaks at 1228 and 1232  $\text{cm}^{-1}$ , which were assigned to the C-N asymmetric stretching mode influenced by changes of chemical environment, were observed from the potential of 1.1 V. Oxidation of ECZ C-N band shifted from 1228 to 1212  $\text{cm}^{-1}$  and C=N band from 1564 to 1550  $\text{cm}^{-1}$  from the potential of 1.3 V, which implies that the oxidation process was a two-step electron loss process and also provided the evidence of existence of the possible intermediate. Thus, electron transfer through the conjugated system in ECZ may be represented as follows:



### Acknowledgments

We are grateful to the National Natural Science Foundation of China (No.20475001) for the financial support.

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Received 21 February, 2005