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Electrochemical and Spectral Characterizations of 9-Phenylcarbazoles

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A series of 9-phenylcarbazoles have been synthesized and characterized for their electrochemical as well as spectral properties. For 3,6-substituted carbazoles, the oxidation is reversible and the potential is affected by the substituents. For 3,6-unprotected carbazoles, on the other hand, the oxidized forms can undergo dimerization. Their corresponding dimers have been independently synthesized by chemical methods and have exhibited identical spectral properties. The *para* position of the 9-phenyl group is relatively insensitive for redox and chemical reactions. The amino derivatives are unstable in carbazole cation radical form compared with their triphenylamine counterparts.

Keywords: 9-Phenylcarbazoles; Cyclic voltammetry; Spectroelectrochemistry; Fluorescence.

INTRODUCTION

Recently, carbazole derivatives and polymers have been intensively studied for charge carrier transporting materials and their applications in light-emitting diodes (LED).[1] Poly(9-vinylcarbazole)s (PVK) exhibits a low-lying highest occupied molecular orbital (HOMO) energy level of -5.9 eV[2-3] and is widely used as polymeric host for LEDs. Carbazole-based building blocks with extended conjugated systems have been used for optoelectronic applications and electrochromics.[4-7] Calculation were performed using density function theory (DFT) in order understand the ground and excited states carbazole monomer and polymers.[8-9] Thus, the synthesis and characterization of carbazoles are important for material fabrications.

Carbozole (Cz)[10] and triphenylamine (TPA)[11] possess electroactive nitrogen atom as the redox center. The oxidized nitrogen-containing compounds have very strong interaction between the nitrogen atom and the phenyl rings and exhibit characteristic electrochemical and spectral properties. Thus, their derivatives have been used as photo- and electroactive materials.[12-13]

In 1966, Adams[14] found that triphenylamine could form tetraphenylbenzidine (TPB) by way of oxidation and dimerization. A series of work on the oxidation of aniline[15] and diphenylamine[16-17] was furtherly pursued later on. Triphenylamines with different substituents had been exhaustively studied for their effect at the *para*-position of the phenyl rings. It was then found that triphenylamine can undergo carbazole formation when the potential was set at the second oxidation wave.[18]

The electrochemical oxidation of carbazole (Fig. 1) and *N*-substituted derivatives was first reported by Nelson in 1968.[19] Nelson et al.[20] further studied comprehensively 76 carbazole derivatives about their substituent effects. TPA has three equivalent phenyl groups but 9-phenylcarbazole has two phenyl moieties fused with the nitrogen atom. The oxidation potential of each carbazole is more positive than its corresponding triphenylamine (TPA) by about +0.3 V. The 3,6-positions are more reactive than *para* position in the TPA by three orders upon oxidation. The 3,6-unprotected carbazole cation radicals rapidly undergo dimerization reactions.

In this work, we have synthesized a series of 9-phenylcarbazoles (Scheme I). The 3,6-positions of carbazole or *para* position of the 9-phenyl group have been substituted with various groups. This work has been concerned with 9-phenylcarbazoles and has the following purposes: (i) to establish the spectral pattern of carbazole cation radicals,

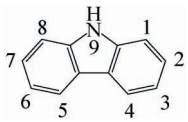

Fig. 1. Structure of carbazole.

Dedicated to the memory of Professor Yung-Son Hon (1955–2011).

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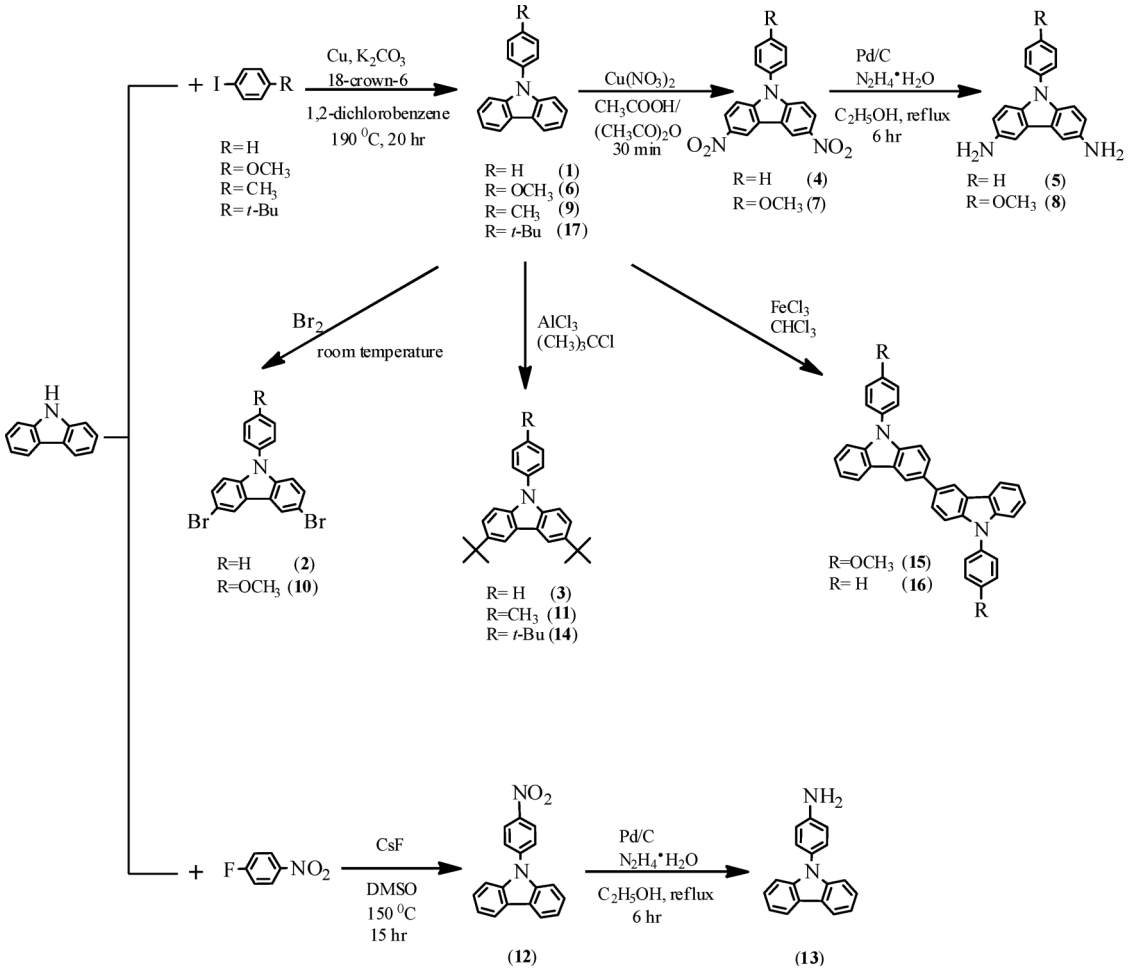
Scheme I



(ii) to study the substituent effect on the redox properties of carbazoles, (iii) to investigate the redox and spectral properties of carbazole dimers, (iv) to probe the reactivity of *para*-position of the 9-phenyl group, and (v) to compare the properties between carbazoles and their corresponding triphenylamines.

EXPERIMENTAL

All the chemicals were purchased from ACROS. Solvents were purified according to standard procedures.[21] TBAP (tetra-*n*-butylammonium perchlorate) was recrystallized from ethyl acetate twice before use.

Synthesis

Compounds **1**,[22] **2**,[23] **3**,[24] **4**,[25] **5**,[26-27] **6**,[22] **7**,[25] **8**,[26-27] **9**,[22] **10**,[23] **11**,[24] **12**,[26-27] **13**,[26-27] **14**,[22,24] **15**[28] were synthesized according to literature methods. Those 9-phenylcarbazoles have substituents at 3,6-positions or at the *para* position of the 9-phenyl group. The reaction procedures can be summarized as Scheme I.

Electrochemistry

Electrochemistry methods were performed according to the procedures in reference.[21]

RESULTS AND DISCUSSION

9-Phenylcarbazole with alkyl substituents at 3,6 positions

Fig. 2 shows the cyclic voltammetry of **14** which exhibits a reversible redox wave at $E_{1/2}$ = +1.26 V. The CV reaches a steady state without new wave formation after continuous cycling. Compound **14** has absorption peaks at 243 and 296 nm in UV region. Those peaks decrease in absorbance upon oxidation while a new broad band in the region of 550 to 900 nm appears. The resulting spectrum has peak wavelength at 280 and 800 nm and the product is assigned as the cation radical $\mathbf{14}^{+\cdot}$. After reset at 0.00 V, the original spectrum was obtained.

Its analogue compound **11** is oxidized at $E_{1/2}$ = +1.28 V and the pattern of absorption spectral change for cation radical is very similar to that of compound **14**. Compound **10**, which has bromo groups at 3 and 6 positions, has an $E_{1/2}$ at +1.49 V. The electron-withdrawing of bromo groups apparently have substantial shift in oxidation potential.

In order to probe the chemical reactivity of the *para*-position of the *N*-phenyl group in 9-phenylcarbazole, several 3,6-disubstituted 9-phenylcarbazoles were synthesized and characterized. Compound **3** exhibits a reversible redox couple at +1.23 V and continuous cycling does not generate any new wave in 0.0 to +1.50 V region (Fig. 3). The spectroelectrochemistry of compound **3** also exhibits a broad band in 550 to 900 nm with peak wavelength at 275 and 800 nm, a pattern very similar to that of compound **14** on the oxidation reaction.

For compound **2**, the oxidation potential is at $E_{1/2}$ = +1.53 V, substantially more positive than that for compound **3**. The shift in potential is conceivably due to the electron-withdrawing effect of the bromine atoms. The absorption spectrum of $\mathbf{2}^{+\cdot}$ exhibits the same pattern as these of $\mathbf{11}^{+\cdot}$ and $\mathbf{14}^{+\cdot}$. The absorption spectrum of cation radical $\mathbf{2}^{+\cdot}$ has a longer peak wavelength (814 nm) than that of compound $\mathbf{3}^{+\cdot}$ (800 nm). Compound **4**, which has nitro groups at 3 and 6 positions, cannot be oxidized in the potential window, conceivably due to strong electron-withdrawing effect of the substituents. However, its reduction waves could be observed in the potential region < -1.0 V.

The redox potential of carbazoles are thus listed in Table 1. Based on above results in electrochemical and spectral observations, the cation radical of 3,6-disubsti-

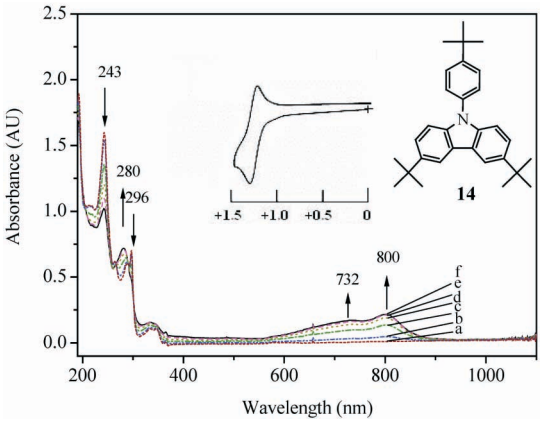


Fig. 2. Spectral changes of compound **14** during the first electron oxidation at +1.20 V in CH_3CN containing 0.2 M TBAP. Time interval = 1.0 min.

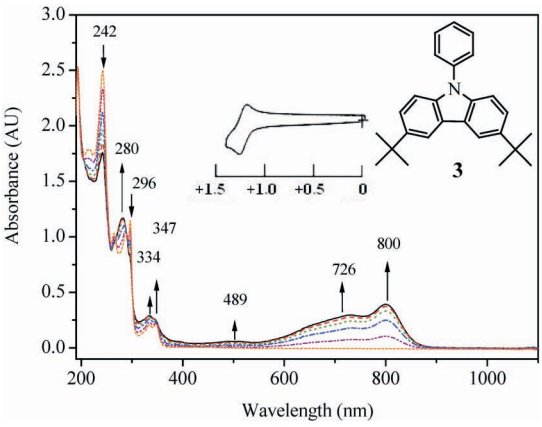


Fig. 3. Spectral changes of compound **3** during the first electron oxidation at +1.15 V in CH_3CN containing 0.2 M TBAP. Time interval = 0.5 min.

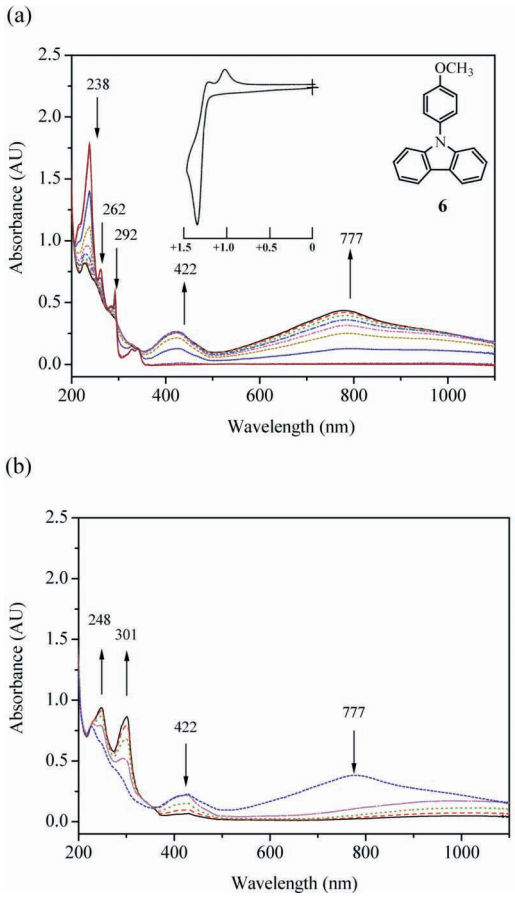


Fig. 4. (a) Spectral changes of compound **6** during the first oxidation in CH_3CN containing 0.2 M TBAP. Time interval = 0.5 min. (b) Spectral changes of compound **6** during the reduction recovery procedure at applied potential back to 0.00 V. Time interval = 1.0 min.

Table 1. Half-wave potentials ($E_{1/2}$, V vs. Ag/AgCl) of carbazole derivatives in CH_3CN containing 0.1 M TBAP. Scan rate = 0.1 V/s

Compounds	Oxidation			Reduction		
	3rd	2nd	1st	1st	2nd	3rd
1			1.38 [a]			
2			1.53			
3			1.23			
4				-1.10	-1.29 [a]	-1.8 [a]
5	1.65 [a]	0.79 [a]	0.50 [a]			
6			1.33 [a]			
7			1.80 [a]	-1.00 [a]	-1.23 [a]	
8	1.88 [a]	0.83 [a]	0.51 [a]			
9			1.38 [a]			
10			1.49			
11			1.26			
12			1.48 [a]	-0.96	-1.63 [a]	
13		1.31 [a]	0.93 [a]			
14			1.23			
15		1.26	1.03			
16		1.29	1.10			

$Fc^{+/0}$ = +0.48 V vs. Ag/AgCl (sat'd)
[a] Irreverible peak potential.

tuented 9-phenylcarbazoles do not undergo dimerization as their corresponding TPA's do.[14] *The para-positions of the N-phenyl group are relatively insensitive to coupling during carbazole cation radical formation.*

9-Phenylcarbazole with an alkyl substituent at 9-phenyl group

The CV of compound **6** is shown in Fig. 4a. In the oxidative scan, a sharp peak at $E_{p,a}$ = +1.33 V is observed. In the reversed scan, two reduction waves at $E_{p,c}$= +1.01 and +1.20 V are observed, respectively. In the continuous scans, an oxidation wave at $E_{p,a}$ = +1.05 V gradually grows, indicative of a new species formation.

In order to characterize the properties of the oxidation product, spectroelectrochemistry was performed for spectral change. In Fig. 4a, the characteristic peak for compound **6** at 238 nm decreases rapidly which a new band at about 422 nm and a broad band ranging from 500 to 2000 nm (λ = 777 nm) grow gradually at $E_{appl.}$ = +1.16 V. After equilibrium is reached, the potential is stepped to 0.00 V to reduce the oxidation product. Two UV peaks at 248 and 301 nm corresponding to the dimer (vide infra) are observed while the broad absorption in the visible and near-IR (NIR) region disappears (Fig. 4b).

In a parallel experiment, compound **16** was studied because it is the expected dimerization product of compound $\mathbf{6}^{+\cdot}$. Fig. 5 shows the CV of compound **16** and two reversible redox couple in the oxidation scan are observed at $E_{1/2}$ = +1.03 and +1.26 V, respectively. Cycling scan in the potential range 0.0 to +1.5 V does not generate any observable new wave.

Compound **16** in its neutral from has two sharp absorption peaks at 248 nm and 301 nm, respectively. Upon first oxidation a new band at about 411 nm and another broad band (600-2150 nm) appear. The latter is assigned as the intervalence charge transfer (IVCT) band of the cation radical $\mathbf{16}^{+\cdot}$.[30] A big shoulder at about 1300 nm (not shown) is comparable with the cation radical of tetraphenylbenzidine (TPB).[30] However, above absorption bands decrease in absorbance significantly while a new broad band at 779 nm appears during the second oxidation. For TPB^{2+}, the dominant absorption is at 780 nm but with much smaller full-width at half-maximum (FWHM). The resulting spec-

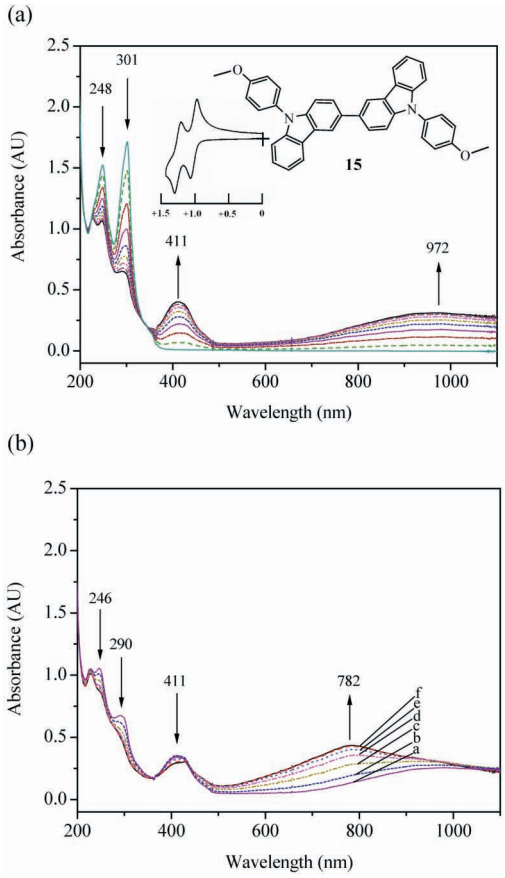


Fig. 5. (a) Spectral changes of compound **15** during the first oxidation in CH_3CN containing 0.2 M TBAP. Time interval = 1.0 min. (b) Spectral changes of compound **15** during the second oxidation. Time interval = 1.0 min.

Table 2. Absorption wavelengths of the carbazole derivatives in CH_3CN

Compounds	UV (nm)		Vis (nm)		NIR (nm)
1	239	292			
2	242	268			
$\mathbf{2}^{+\bullet}$	290	330	729		814
3	242	265			
$\mathbf{3}^{+\bullet}$	280	334	489	726	800
6	238	262			
9	239	260			
10	244	270			
$\mathbf{10}^{+\bullet}$	270	340	720		807
11	245	298			
$\mathbf{11}^{+\bullet}$	287	326	736		804
14	243	296			
$\mathbf{14}^{+\bullet}$	280	332	732		800
15	248	301			
$\mathbf{15}^{+\bullet}$			411		972
$\mathbf{15}^{2+}$			422	779	
16	249	296			
$\mathbf{16}^{+\bullet}$			412		901
$\mathbf{16}^{2+}$			426	729	

trum of $\mathbf{16}^{2+}$ (Fig. 5b) is nearly identical with that in Fig. 4a.

For the prototype compound **1** (9-phenylcarbazole), a sharp and irreversiable wave about $E_{p,a}$ = +1.38 V is observed in the oxidative scan. In the reversed scan, two oxidation waves appear at $E_{p,c}$ = +1.28 and +1.05 V, respectively. In the spectroelectrochemistry for **1** oxidation the characteristic sharp peak at 239 and 292 nm of **1** decreases upon oxidation, and new bands at 420, 728 nm together with a broad band ranging from 500 to 2000 nm arises.

Compound **15**, dimerization product of compound **1**, exhibits two reversible oxidation at $E_{1/2}$ = +1.10 and +1.29 V, respectively. In the spectroelectrochemistry of compound **15**, stepwise oxidations produce spectral changes of the same pattern as the case of compound **16**.

The above experiments have established the electrochemical dimerization of 9-phenylcarbazoles without substituents at 3,6-positions based on electrochemical and spectral results (Table 2).

9-Phenylcarbazole with amino substituents at 3,6 positions

For amino-substituted 9-phenylcarbazole compounds **5**, **8** and **13**, the electrochemical oxidations had been carried out and compared with the corresponding amino triphenylamines. When the 3,6-positions of 9-phenylcarbazole are substituted with amino groups (compound **5**), an irreversible oxidation wave at $E_{p,a}$ = +0.50 V and a small wave at $E_{p,c}$ = +0.32 V (Fig. 6a) were observed. Its counterpart, bis(4-aminophenyl)phenylamine, exhibits two reversible redox couples at +0.38 and +0.74 V, respectively (Fig. 6b).

9-Phenylcarbazole with an amino substituent at 9-phenyl group

9-(4-Aminophenyl)carbazole (**13**) exhibits two irreversible oxidation waves at $E_{p,a}$ = +0.93 and +1.31 V, respectively (Fig. 7a). In the cyclic scan between 0.0 to +1.0 V, a new reduction wave at $E_{p,c}$ = +0.63 V was observed. However, cyclic scan between 0.0 to +1.38 V renders film growth on the electrode. *N*,*N*-diphenyl-*p*-phenylenediamine, however, has two reversible redox couples at +0.54 and +1.03 V, respectively (Fig. 7b).[31]

9-Phenylcarbazole oxidation at a potential more positive by about +0.3 V than its TPA counterparts probably reflects less delocalization of the cation radical of nitrogen onto the 13-member carbazole skeleton. The 9-phenyl group is nearly perpendicular to the carbazole plane and the resonance effect is minimal.[20] In aminocarbazoles, although the amino groups are at the *para* positions of the

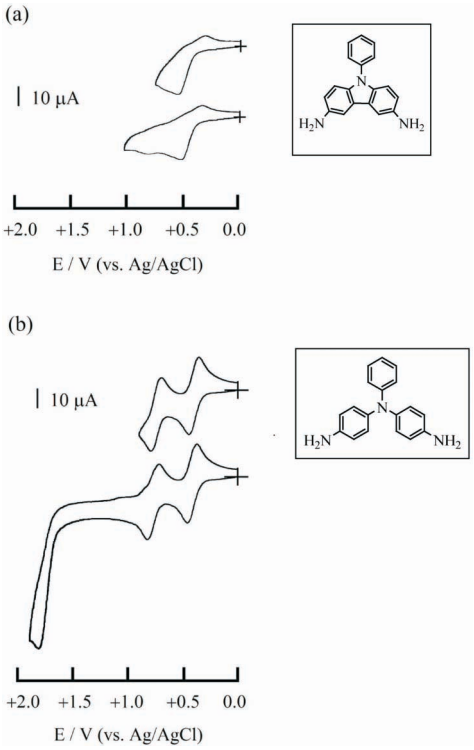


Fig. 6. Cyclic voltammograms of (a) 1.0×10^{-3} M compound **5** (b) 1.0×10^{-3} M bis(4-aminophenyl)-phenylamine in CH_3CN containing 0.1 M TBAP. Scan rate = 0.1 V/s. Working electrode: glassy carbon.

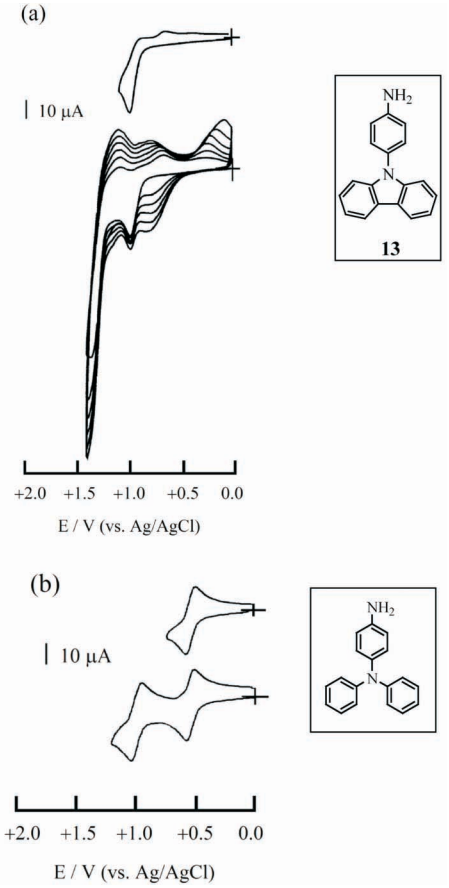


Fig. 7. Cyclic voltammograms of (a)1.0×10^{-3} M compound **13** (b) 1.0×10^{-3} M *N*,*N*-diphenyl-*p*-phenylenediamine in CH_3CN containing 0.1 M TBAP. Scan rate = 0.1 V/s. Working electrode: glassy carbon.

carbazole nitrogen, the oxidized form of compounds **5** and **13** appears not stabilized as their TPA counterparts are. Hence, the oxidized amino groups in compound **13** could not receive as much electron cloud for stabilization from the carbazole nitrogen at the *para* position as those in the TPA's. By the same token, compounds **5** and **8** have less resonance with phenyl group than their TPA counterparts.

CONCLUSIONS

Based on the electrochemical and spectral properties of carbazoles, the following conclusions are thus reached: (i) 9-Phenylcarbazole cation radicals have characteristic broad absorption in 550-900 nm region. (ii) The oxidation potential of 9-phenylcarbazoles is sensitive to the substituents at 3,6-positions but is relatively less sensitive to those at the *para* position of the 9-phenyl group. (iii) Carbazole dimers exhibit strong IVCT absorption in the near IR region (600-2150 nm) in their cation radical forms. (iv) The *para* position of the 9-phenyl group in 9-phenylcarbazoles is not reactive towards dimerization. (v) Carbazole cation radicals are relatively unstable comparing with their triphenylamine counterparts.

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