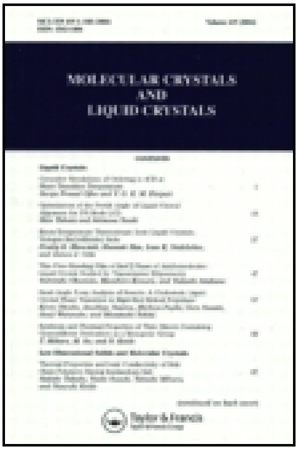


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Electrochemical Properties of N-Substituted Bicarbazyl Derivatives

Yeong Kim [a] , Young Kwon [a] , Kwang Lee [a] , Jong Park [a] , Hyeon Seo [b] & Tae Kim [c]

[a] Department of Chemistry/Center for Nanotechnology Research, The Catholic University, Pucheon, Korea

[b] Display Institute, Vistorm, Seongnam, Korea

[c] Department of Physics, Hong-Ik University, Seoul, Korea

Version of record first published: 18 Oct 2010

To cite this article: Yeong Kim, Young Kwon, Kwang Lee, Jong Park, Hyeon Seo & Tae Kim (2004): Synthesis and Electrochemical Properties of N-Substituted Bicarbazyl Derivatives, Molecular Crystals and Liquid Crystals, 424:1, 153-158

To link to this article: http://dx.doi.org/10.1080/15421400490506090

Mol. Cryst. Liq. Cryst., Vol. 424, pp. 153–158, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490506090

Taylor & Francis
Taylor & Francis Group

SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF N-SUBSTITUTED BICARBAZYL DERIVATIVES

Yeong Eun Kim, Young Soon Kwon, Kwang Soon Lee,
and Jong Wook Park
Department of Chemistry/Center for Nanotechnology Research,
The Catholic University, Pucheon, 420-734, Korea

Hyeon Jin Seo
Display Institute, Vistorm, D503-2 Bundang Techno-Park,
Seongnam, 463-816, Korea

Tae Wan Kim
Department of Physics, Hong-Ik University, Seoul, 121-791, Korea

N,N′-Diethyl-3,3′-bicarbazyl (DEBC) and N,N′-Diphenyl-3,3′-bicarbazyl (DPBC) was synthesized by the oxidative coupling reaction. The electrochemical properties of DEBC and DPBC were characterized by cyclic voltammetric technique. The oxidation of DEBC occurred at 0.56 V and 0.8 V (vs. Ag/Ag$^+$) and the reduction also at 0.47 V and 0.72 V, where the carbazole unit might be oxidized and coupled each other irreversibly to form the paired molecules of DEBC. DPBC also showed the reversible oxidation at 0.74 V and 0.97 V and reduction at 0.53 V and 0.77 V, respectively. The bandgap energy of DEBC and DPBC were estimated to be 3.16 eV and 3.19 eV, respectively, according to each UV-Vis. spectra.

Keywords: band gap; bicarbazyl; cyclic voltammetry; electroluminescence; oxidation potential

1. INTRODUCTION

Since the first report of multilayer high efficiency organic light emitting diodes (OLEDs), there have been intense research activities in organic

Received 1 October 2003; accepted 30 December 2003.

This work was supported by grant No. R01-2002-000-00347-0 from the interdisciplinary research program of the KOSEF.

Address correspondence to Jong Wook Park, Deptartment of Chemistry/Center for Nanotechnology Research, The Catholic University, Pucheon, 420-734, Korea. Tel.: +82-32-340-3821, Fax: +82-32-340-3764, E-mail: hahapark@catholic.ac.kr

electroluminescence (EL) devices [1]. Especially carbazole-containing compounds are widely known as an important class of materials which show intrinsic electronic properties such as luminescence, hole blocking and hole transporting properties [2–4].

We also have been interested in various carbazole based derivatives as well as carbazole bipolar types [5,6]. Recently we synthesized new carbazole dimer molecules, N,N′-diethyl-3,3′-bicarbazyl (DEBC) and N,N′-diphenyl-3,3′-bicarbazyl (DPBC), as good hole transporting materials which show 20% increased EL efficiency relative to NPB in Alq_3 system. In here we firstly report the synthesis and electrochemical properties of DEBC and DPBC since the electrochemical stability is also very important issue for lifetime in OLEDs.

2. EXPERIMENTAL

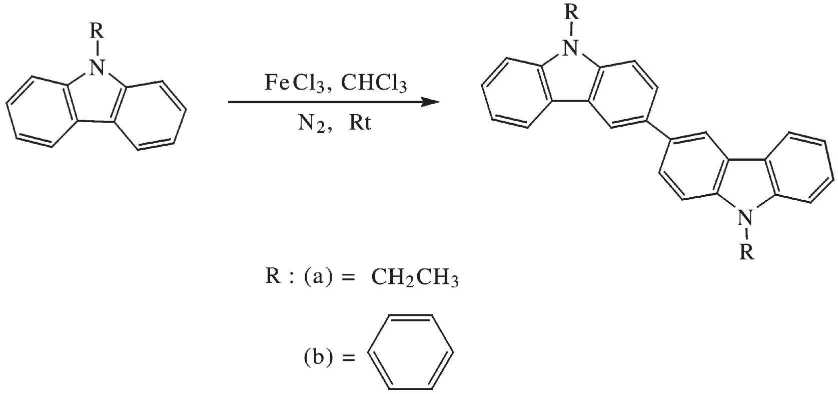
2.1. Materials and Characterization

The cyclic voltammograms were recorded on a computer controlled EG&G 362 electrochemical workstation in 0.1 mol/L tetra(n-butyl)ammonium tetrafluoroborate/acetonitrile. The DEBC and DPBC Film on a ITO electrode with an area of $1\,cm^2$, prepared by drop casting from solution in chloroform, was used as the working electrode. A platinum wire was used as the counter electrode and a silver wire was used as the reference electrode (Ag/Ag^+). The separated anodic and cathodic scans were carried out at various scan rate of at room temperature.

2.2. Synthesis of N,N′-Dsiphenyl-3,3′-bicarbazyl (DPBC)

N,N′-Diphenyl-3,3′-bicarbazyl (DPBC) was synthesized by the oxidative coupling reaction (see Scheme 1). To a 500 ml round flask ware placed Iron (|||) chloride (5.35 g, 32.96 mmol) and $CHCl_3$(200 ml) under N_2. To this mixture was added a solution of 9-phenyl carbazole (2 g, 8.24 mmol) in chloroform (100 ml) very slowly. The mixture was stirred at room temperature for 4 hr. After 10% sodium hydroxide solution was added in the mixture, the aqueous was thoroughly extracted with chloroform. The crude product was dissolved in chloroform (10 ml) and reprecipitated slowly in methanol (200 ml). The product was collected by filtration and dried under vaccum at room temperature. (1.03 g, 52%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.46 (s, 2H), 8.24 (d, 2H), 7.78 (d, 2H), 7.63 (d, 8H), 7.50 (t, 8H), 7.33 (t, 2H); mass (positive ion FAB) 484 (M^+); mp 200°C.



SCHEME 1 Synthesis of (a) N,N′-Diethyl-3,3′-bicarbazyl (DEBC) and (b) N,N′-Diphenyl-3,3′-bicarbazyl (DPBC).

2.2. Synthesis of N,N′-Diethyl-3,3′-bicarbazyl (DEBC)

N,N′-Diethyl-3,3′-bicarbazyl (DEBC) was synthesized by same process with DPBC (see Scheme 1) (2.5 g, 83%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.19 (d, 2H), 7.84 (t, 2H), 7.51 ~ 7.41 (m, 6H), 7.25 (t, 2H), 4.41 (q, 4H) 1.47 (t, 6H); mass (positive ion FAB) 388 (M^+); mp 189°C.

3. RESULT AND DISCUSSION

We have synthesized two carbazole dimer derivatives, N,N′-Diethyl-3,3′-bicarbazyl (DEBC) and N,N′-Diphenyl-3,3′-bicarbazyl (DPBC), which has generally the high hole mobility and is used for hole transportation in organic semiconducting device such as electroluminescence (EL) device and solar cell.

DEBC and DPBC were synthesized by using coupling reaction at room temperature (see Scheme 1). These two products were finally purified with appropriate solvent and reprecipitated to have highly pure beige color powder. The structure was identified by NMR, UV-Vis. spectroscopies and DSC.

The resulting products are soluble in common solvent such as chloroform and THF. The DEBC and DPBC films do not show any particle on the surface and exhibited a smooth surface where observed by microscope. Meanwhile, although N-substituted carbazole (mono unit) before coupling reaction shows low melting temperature at around 74°C, the DEBC and DPBC show high melting temperature at 189°C and 200°C.

In UV spectroscopies, the DEBC and DPBC showed similar absorption spectra with the same UV absorption maximum value at about 353 nm.

The bandgap energy of DEBC and DPBC are estimated to be 3.16 eV and 3.19 eV from the analysis of the absorption edge with a plot of (hv) vs. $(\alpha hv)^2$, where α, h, *and* v are absorbance, Plank's constant, and the frequency of light, respectively.

To investigate electrochemical kinetic behavior, the measured cyclic voltammograms of DEBC and DPBC with the various scan rates (20 mV/s ~200 mV/s) are shown Figures 1 and 2. The peak potentials are gradually shifted to higher potentials as the scan rate is increased. Also we have observed very stable cyclic voltammograms of DEBC and DPBC with the consecutive scan (up to 100 cycles) indicating these two materials have relatively stable redox process.

In Figure 1, the oxidation of DEBC occurred at 0.56 V and 0.8 V (vs. Ag/Ag^+)and the reduction also at 0.47 V and 0.72 V, where the carbazole unit might be oxidized and coupled each other irreversibly to form the paired molecules of DEBC in the first scan [7]. The DPBC also shows the reversible oxidation at 0.74 V and 0.97 V and reduction at 0.53 V and 0.77 V, respectively.

The redox current value gradually increased as the scan rate increased. This result suggests that the electrochemical processes of DEBC and DPBC are reproducible in the potential range of 0 ~2 V vs. Ag/Ag^+.

It has been reported that the relationship between the redox peak current and the scan rate can be expressed as a power law type as follows: [7,8]

$$i_{p,a} = kv^x \tag{1}$$

$$\log i_{p,a} = \log k + x \log v \tag{2}$$

where $i_{p,a}$ = oxidation peak current density, v = scan rate, k = proportional constant, and x = exponent of scan rate.

Assuming that electrode kinetics satisfies Eq. (1), the electrochemical redox reaction on the electrode is controlled by either the electron transfer

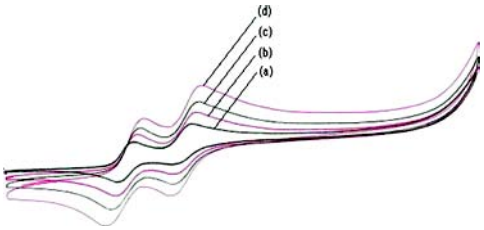


FIGURE 1 Cyclic voltammograms of DEBC with various scan rate (0.1 M $(n\text{-}Bu)_4NBF_4$/Acetonitrile). (a) 20 mV/sec (b) 50 mV/sec (c) 100 mV/sec (d) 200 mV/sec.

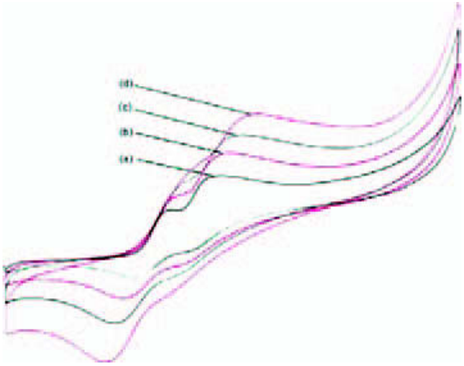
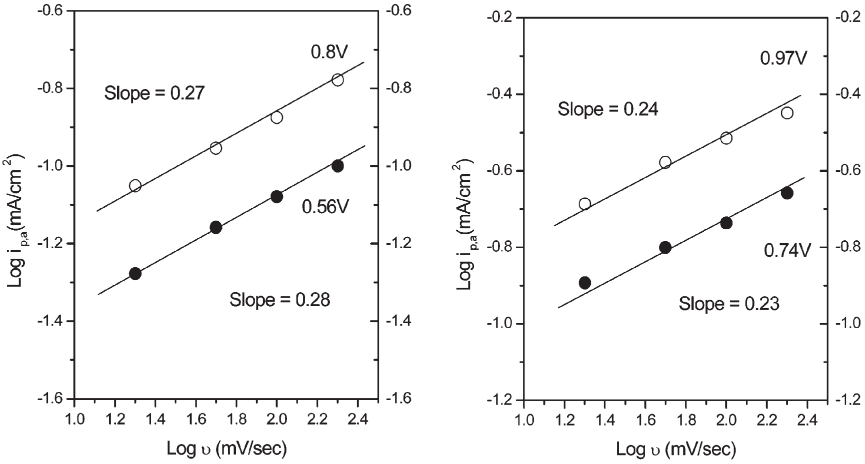


FIGURE 2 Cyclic voltammograms of DPBC with various scan rate (0.1 M $(n\text{-}Bu)_4NBF_4$/Acetonitrile). (a) 20 mV/sec (b) 50 mV/sec (c) 100 mV/sec (d) 200 mV/sec.

process, where $x = 1$, or the reactant diffusion process, where $x = 0.5$ [7,9].

Relations satisfying Eq. (2) between the oxidation current density (log $i_{p,a}$) and the scan rate (log v) are shown in Figure 3.

The oxidation current density of DEBC and DPBC versus the scan rate is approximately linear relationship in the range of $20 \sim 200$ mV/sec. The exponent of scan rate, x, values of DEBC are found to be 0.28 and 0.27



(a) (b)

FIGURE 3 Plot of log $i_{\mathrm{p,a}}$ vs. log v for (a) DEBC and (b) DPBC.

and the x values of DPBC are 0.23 and 0.24, respectively. These values are smaller than the one of electroactive materials.

Further studies on synthesis and electro-optical properties of dimer and trimer are under way.

REFERENCES

[1] Tang, C. W. & Van Slyke, S. A. (1987). *Appl. Phys. Lett.*, *51*, 913.
[2] Kuwabara, Y., Ogawa, H., Inada, H., Noma, N., & Shirota, Y. (1994). *Adv. Mater.*, *6*, 677.
[3] Ikai, M., Tokito, S., Sakamoto, Y., Suzuki, T., & Taga, Y. (2001). *Appl. Phys. Lett.*, *79*, 156.
[4] Baldo, M. A., Thompson, M. E., & Forrest, S. R. (2000). *Nature*, *403*, 750.
[5] Park, J. W., Lee, J. H., Lee, H. S., Kang, D. Y., & Kim, T. W. (2000). *Thin Solid Film*, *363*, 90.
[6] Lee, J. H., Woo, H. S., Kim, T. W., & Park, J. W. (2002). *Optical Materials*, *21*, 225.
[7] Park, J. W., Lee, J. H., Ko, J. M., Cho, H. N., & Choi, S. K. (1994). *J. Polym. Sci.*, *32*, 2789.
[8] Bard, A. J. & Faulker, L. R. (1980). *Electrochemical Methods*, Wiley: New York, chapter 3, 6 and 10.
[9] Ko, J. M., Rhee, H. W., Park, S. M., & Kim, C. Y. (1990). *J. Electrochem. Soc.*, *137*, 905.