# A Cyclic Carbazole Oligomer for Electroluminescence Applications

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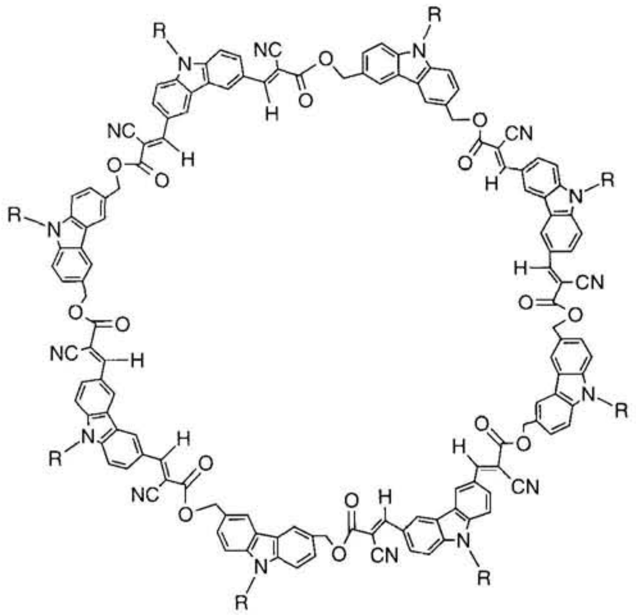
A novel cyclic carbazole oligomer, which contains the EL chromophore in the main-chain, for organic light-emitting diodes is described. The device structure of glass substrate/indium tin oxide/hole transport layer/cyclic oligomer (electron transport layer)/Al was employed. The EL device exhibited green light with a luminance of 60 cd/m$^2$ at 15 V.

In recent years, organic electroluminescenct (EL) devices have been an active area of research because of their high luminance, low drive voltage, and a variety of emission colors.[1,2] The operation of organic light-emitting diodes (LEDs) is based on the injection of electrons and holes within the region of the organic layer from cathode and anode, followed by formation of singlet excitons whose radiative decay results in light emission at a wavelength depending on the characteristics of the materials. Until now, a variety of molecules,[2,3] linear oligomer,[4] polymer,[5] dye doped polymer,[6] starburst molecule,[7] dendrimer,[8] and metal complex molecule[9] and polymer[10] for organic LEDs have been synthesized and investigated.

Recently, polycarbazoles have extensively studied for EL applications due to their good hole transport and luminescent properties.[11] In our laboratory, several carbazole derivatives have been synthesized and studied for the nonlinear optical properties.[12] Among them, we found that cyano-vinyl substituted carbazole main-chain[13] and hyperbranched polymer[14] have been useful as an electron transport layer (ETL). In this study, our objective is to design and synthesize a new structure having a cyano-vinyl substituted carbazole derivative for organic LEDs. Here, we report a novel cyclic carbazole oligomer to construct new materials for organic LEDs. To the best of our knowledge, cyclic oligomers for organic LEDs have not been reported so far, probably due to difficulties in synthesis. In general, cyclic compounds are synthesized by high dilution method and their yields are low. Previously we found that cyclic carbazole oligomer can be easily synthesized by one-pot Knoevenagel reaction in high yield.[15] However, this material (R = heptyl in Figure 1) can be hardly dissolved in common organic solvent such as chloroform, so that tetradecyl group was introduced to increase solubility instead of heptyl group. We used the cyclic carbazole oligomer as an ETL and a carbazole conjugated polymer as a hole transport layer (HTL). Naito et al. reported that heat-resistive and stable nonpolymeric dye glasses can be formed from large, symmetric, and rigid molecules.[16] It is thought that the structure of cyclic oligomer for this study is fitted to the conditions. The glass transition temperature of this cyclic oligomer is 105 ℃, so that the thermal stability is good to maintain the morphology of the material in the amorphous glassy state. The high quality amorphous film can be prepared by the conventional spin-coating technique. In the case of polymers, they have generally wide molecular weight distribution, which might affect the EL properties.[17] On the other hand, the advantages of cyclic oligomer are the exact control of molecular weight and no end effects. Therefore we expect the reliable evaluation of EL characteristic of pure material.




1; R = $CH_2(CH_2)_{12}CH_3$

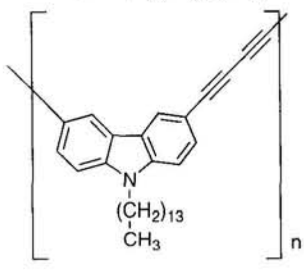



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**Figure 1.** Molecular structures of cyclic oligomer **1** (ETL) and HTL polymer **2**.

The cyclic carbazole oligomer **1**[18] for ETL (shown in Figure 1) was synthesized according to the similar route to Ref. 15. That is, reacting 3,6-diformyl-9-tetradecylcarbazole and 3,6-bis(cyanoacetoxymethyl)-9-tetradecylcarbazole in tetrahydrofuran (THF) in the presence of 4-dimethylaminopyridine as a base at 40 ℃, we could obtain the mixture of cyclic oligomer **1** and polymer. The product **1** was purified by reprecipitation from chloroform-methanol twice following recrystallized from chloroform-THF. The yield was 45%. Poly(3,6-dibutadinyl-9-tetradecylcarbazole)

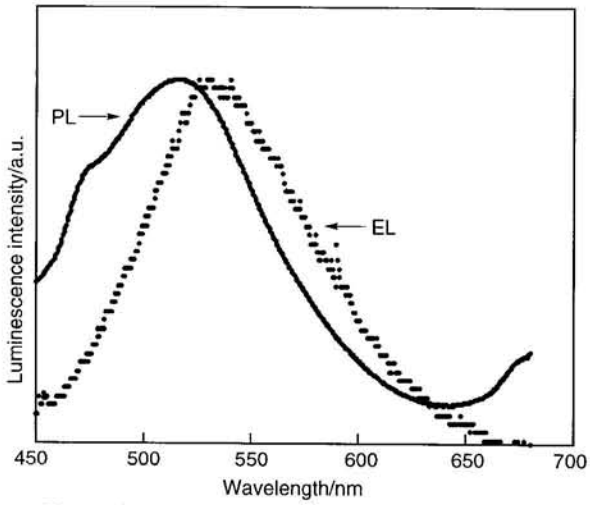


**Figure 2.** The PL and EL spectra of the double-layer LED device.

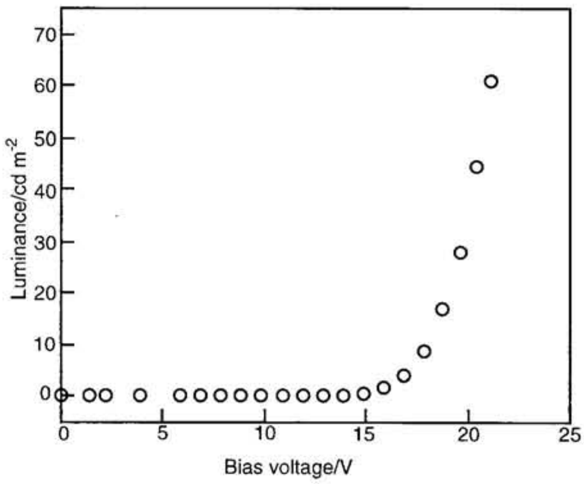


**Figure 3.** The luminance-voltage characteristic of the double-layer LED device.

**2** for HTL (shown in Figure 1) was synthesized by the CuCl catalyzed polymerization of 3,6-diethynyl-9-tetradecylcarbazole according to Ref. 13. The molecular weight determined by GPC was Mw = 21200, Mn = 5100, calibrated to a polystyrene standard.

The LED fabricated from compound **1** was a double-layer device, indium tin oxide (ITO)/HTL/ETL/Al. The HTL was spin-coated on the ITO substrate, then the ETL was spin-coated on the HTL from a solution in chloroform. The film thickness of ETL and HTL were in the range of 80-100 nm. The Al cathode was vacuum-evaporated on the ETL.

Photoluminescence (PL) and EL spectra of the double-layer LED in air are shown in Figure 2. The EL spectrum was measured by scanning the emission from a forward-biased cell under the bias voltage of 17 V. The PL spectrum was measured under the excitation wavelength of 350 nm. The PL spectrum shows an emission maximum around 515 nm which corresponds to the green region. As the HTL and ETL show emission maximum around 450 and 515 nm, respectively (not shown here), it is thought that emission occurs from ETL. The EL spectrum is similar to the PL spectrum. However, a red shift (~20 nm) is observed in the EL spectrum as compared to the PL spectrum. This phenomenon is that the exciplex might be formed between ETL and HTL. Exciplex formation in organic LEDs has been reported.[19]

A typical luminance-voltage curve of the double layer device ITO/HTL(~100 nm)/ETL(~100 nm)/Al is shown in Figure 3. The turn-on voltage of luminance is about 15 V and the luminescence of 60 cd/m$^2$ and current density of 22 mA/cm$^2$ were reached at 21 V. The external quantum efficiency (photons/electron) of the device is 0.44%. Further improvement of luminance might be achieved using low work function metals as a cathode. Systematic research on the fabrication of EL devices with increased EL efficiency and extended operating lifetime are now underway.

In conclusion, we have demonstrated that the cyclic carbazole oligomer is useful for ETL in organic LEDs.

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18 The cyclic oligomer **1** was identified by $^1$H NMR, FT-IR, FAB-MS, and elemental analysis. $^1$H NMR (270MHz, $CDCl_3$), δ/ppm 0.83-0.88 (m, 24H), 1.22-1.23 (m, 176H), 1.85 (br, 16H), 4.29-4.31 (m, 16H), 5.57 (s, 16H), 7.42 (d, *J* 8.2 Hz, 8H), 7.43 (d, *J* 8.6 Hz, 8H), 7.595 (d, *J* 8.5 Hz, 8H), 8.26 (s, 8H), 8.29 (d, *J* 8.6 Hz, 8H), 8.38 (s, 8H), 8.56 (s, 8H); FT-IR (KBr), ν/cm$^{-1}$ 2923.56, 2852.20, 2218.70, 1719.23, 1580.38, 1492.63, 1230.36, 1196.61, 1160.94, 1088.62, 953.63, 885.17, 806.10, 759.82; *m/z* 3766 ($M^+$+1) (Found: C, 78.21; H, 8.21; N, 5.68. $C_{248}H_{304}N_{16}O_{162}$•$2H_2O$ requires C, 78.36; H, 8.17; N, 5.895).
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