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Electroluminescent applications of a cyclic carbazole oligomer

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A cyclic carbazole oligomer for organic light-emitting diodes is described. This cyclic oligomer has a high glass transition temperature (105 °C), and high quality amorphous film can be prepared by the conventional spin-coating technique. We examined the characteristics of this cyclic oligomer for electron transport layer applications. The device structure of indium tin oxide/hole transport layer/electron transport layer/Al was used. The EL device exhibited green light with a luminance of 60 cd m^{-2} at 15 V and the external quantum efficiency was 0.44%.

Introduction

In recent years, organic electroluminescent (EL) devices have been an active area of research for display applications.[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 low mass molecules,[2,3] linear oligomers,[4] polymers,[5] dye doped polymers,[6] starburst molecules,[7] dendrimers,[8] and metal complex molecules[9] and polymers[10] for organic LEDs have been synthesized and investigated. Bright white emissions have also been obtained by doping with different organic luminescent dyes of various colors.[6]

The EL materials which are used in LED devices are mainly two species. One is low mass molecules; the LED devices are generally fabricated by vacuum-deposition. However, undesirable recrystallization effects are generally observed in vacuum-deposited layers of low mass molecules.[11] The other is polymers; the LED devices are generally fabricated by the spin-coating method. The spin-coating method is easier and the products can be fabricated with large areas and with patterns, in contrast with vacuum-deposition. However, polymers generally have a wide range of molecular weights, which might affect the EL properties. It is reported that several alternating silylene–divinylarene copolymers which have the same monomer unit but different average molecular weights showed different emissive properties.[12] Structures which have the good characteristics of both low mass molecules and polymers are oligomers.[13] The advantages of oligomers are exact control of molecular weight and no terminal groups, unlike polymers. Moreover, the solubility in solvents such as chloroform can be increased to perform spin-coating if alkyl chains are introduced. However, it is difficult to synthesize oligomers because a stepwise reaction must be used.

Recently, polycarbazoles have also been extensively studied for EL applications due to their good hole transport and luminescent properties. A device using poly(N-vinylcarbazole) (PVK) doped with other luminescent organic dyes has shown a remarkable enhancement of luminescence efficiency.[14] In our laboratory, several carbazole derivatives have been synthesized and their nonlinear optical and photorefractive properties studied.[15,16] Among them, we found that cyano-vinyl substituted carbazole main-chain[17] and hyperbranched polymers[18] have been useful as electron transport layers (ETLs) in organic LEDs. Here, we report a cyclic carbazole oligomer for electroluminescent applications.[19] This cyclic oligomer contains the cyano-vinyl substituted carbazole in the main-chain ring. The advantages of cyclic oligomers are exact control of molecular weight and no end effect like polymers. Moreover, the LED device of this cyclic oligomer can be easily prepared by a conventional spin-coating method and we expect the reliable evaluation of EL characteristic of pure material. That is, this cyclic oligomer has the good characteristics of both polymers and low mass molecules. It is reported that heat-resistive and stable nonpolymeric dye glasses can be formed from large, symmetric, and rigid molecules.[20] It is thought that the structure of the cyclic oligomer is fitted to the conditions. And also, 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 a high dilution method and their yields are low.[21] However, this cyclic oligomer can be easily synthesized by a one-pot Knoevenagel reaction in a high yield without using a high dilution method and purification by column chromatography.

Results and discussions

Synthesis of cyclic carbazole oligomer 1

The cyclic carbazole oligomer **1** for ETL (shown in Fig. 1) was synthesized according to a route similar to those in refs. 22 and 23 (Scheme 1). A carbazole **3** was reacted with 1-bromotetradecane in the presence of sodium hydride to give 9-tetradecylcarbazole **4**. 3,6-Diformyl-9-tetradecylcarbazole **5** was synthesized by Vilsmeier formylation from **4** using excess DMF and phosphorus oxychloride. Reduction of **5** with sodium borohydride gave 3,6-bis(hydroxymethyl)-9-tetradecylcarbazole **6**. 3,6-Bis(cyanoacetoxymethyl)-9-tetradecylcarbazole **7** was obtained by the treatment of **6** with cyanoacetic acid in dichloromethane by using DCC as a water acceptor. From the Knoevenagel condensation of 3,6-diformyl-9-tetradecylcarbazole **5** and 3,6-bis(cyanoacetoxymethyl)-9-tetradecylcarbazole **7** in THF in the presence of DMAP as a base at 40 °C, we could obtain cyclic oligomer **1** as a precipitate. The product **1** was purified by reprecipitation from chloroform–methanol following recrystallization from chloroform–THF. The yield of this final step was 45.1%. The chemical

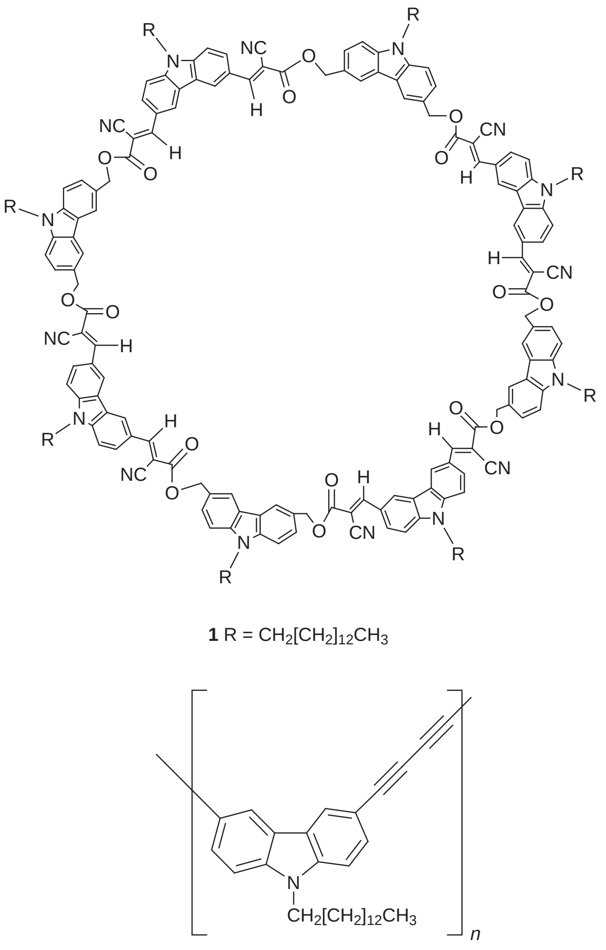
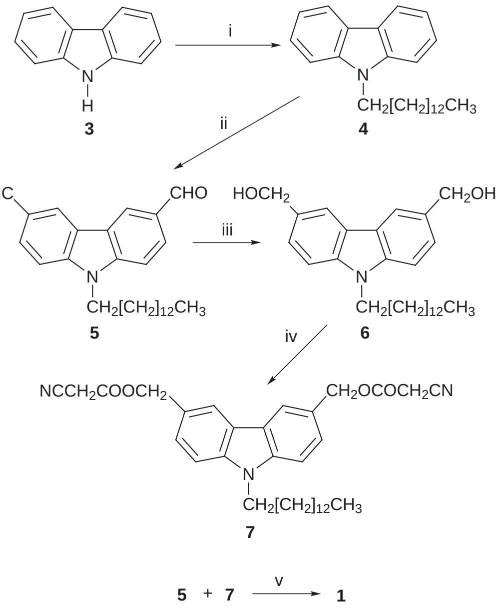


Fig. 1 Molecular structures of cyclic carbazole oligomer **1** (ETL) and HTL polymer **2**.

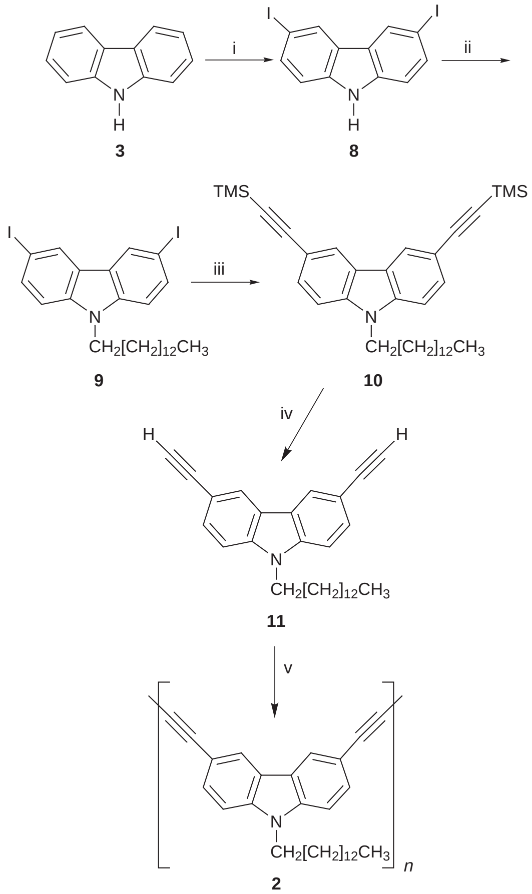


Scheme 1 *Reagents and conditions:* i) $Me[CH_2]_{12}CH_2Br$, NaH, THF–DMF (3 : 1 v/v), rt, quant.; ii) DMF–$POCl_3$, 1,2-dichloroethane, 90 °C, 40.0%; iii) $NaBH_4$, THF–EtOH (1 : 1 v/v), rt, 99.4%; iv) $NCCH_2COOH$–DCC, dichloromethane, <5 °C, quant.; v) DMAP, THF, 40 °C, 45.1%.

structure of **1** was assigned by ^1H NMR, IR, fast atom bombardment mass spectrometry (FAB-MS), and elemental analysis. As the gel permeation chromatography (GPC) spectrum of **1** (not shown here) showed monodispersity of molecular weight, it indicated that only one species was present. The proton resonance signals of the terminal groups, such as the proton of the formyl group (C*H*O) and cyanoacetate ($NCCH_2COO$), were not observed in the ^1H NMR spectrum and a symmetrical spectrum was obtained. This result indicated that **1** has a cyclic structure. Based on the FAB-MS (requires *m*/*z* 3765; found *m*/*z* 3766), the structure of **1** was assigned as a cyclic tetramer. The IR spectrum of **1** showed the signals of CN, C=O, the carbazole ring and the flexible long chain. In the IR spectrum of **1**, a small OH signal was observed. It seemed that water was included during recrystallization from chloroform–methanol.

Synthesis of hole transport layer (HTL) polymer 2

Poly(3,6-dibutadyynyl-9-tetradecylcarbazole) **2** for HTL (shown in Fig. 1) was synthesized as shown in Scheme 2.[18] A carbazole **3** was iodinated with potassium iodide and potassium iodate to give 3,6-diiodocarbazole **8**. 3,6-Diiodo-9-tetradecylcarbazole **9** was obtained by the reaction of **8** with 1-bromotetradecane. Trimethylsilylacetylene and **9** were cross-coupled following deprotection of trimethylsilyl groups to give 3,6-diethynyl-9-tetradecylcarbazole **11**. The HTL material **2** was synthesized by the copper chloride catalyzed polymerization of **11**. The weight average (M_w) and number average (M_n) molecular weight determined by GPC are 21200 and 5100, respectively, calibrated to a polystyrene standard.



Scheme 2 *Reagents and conditions*: i) KI, KIO_3, AcOH, reflux, 84.0%; ii) $Me[CH_2]_{12}CH_2Br$, K_2CO_3, DMF, rt, 96.2%; iii) TMSCCH, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, rt, 99.1%; iv) NaOH, H_2O–EtOH, rt, 95.2%; v) CuCl, TMEDA, toluene, 60 °C.

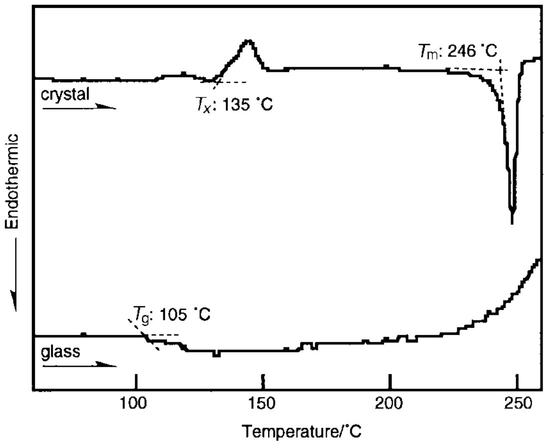


Fig. 2 The DSC analyses of cyclic carbazole oligomer **1**.

The glass transition temperature (T_g) and powder X-ray diffraction of cyclic oligomer 1

We obtained DSC measurements for cyclic oligomer **1** to find out whether **1** exhibited T_g or not. Firstly, the temperature was raised; powder **1** exhibited a melting point (T_m) about 250 °C (heat, $q = -10.565$ cal g^{-1}) and T_x (135 °C). T_x is unknown, but might be a latent heat. In a second scan, T_g was observed at 105 °C (heat capacity change, $\Delta C_p = -1.40$ kcal K^{-1} mol^{-1}) and no melting point was observed (Fig. 2). It indicated that **1** is an amorphous material. In order to obtain further evidence, we obtained powder X-ray diffraction measurements for **1**. When powder **1** was measured, several sharp signals were observed, indicating that powder **1** is a crystal. After **1** was melted, no sharp signal was observed, indicating that melt sample **1** is amorphous (Fig. 3). The T_g of **2** was 90 °C.

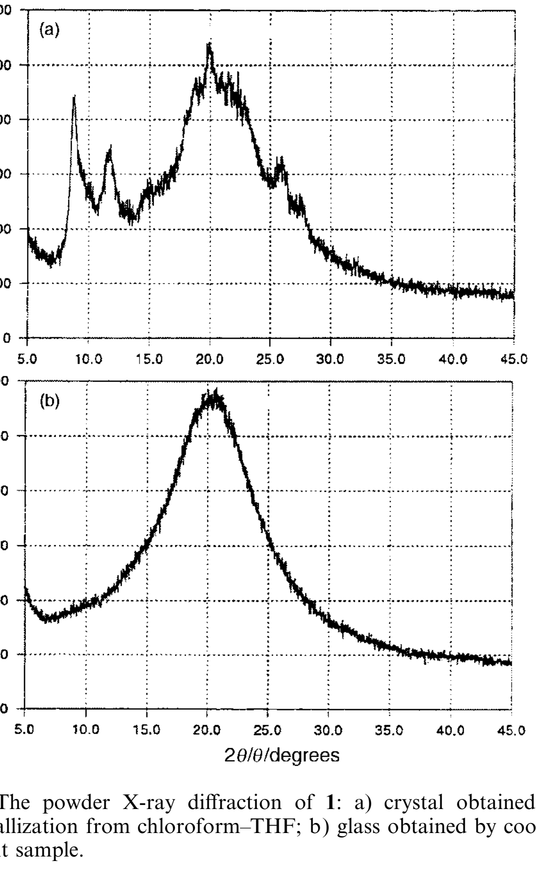


Fig. 3 The powder X-ray diffraction of **1**: a) crystal obtained by recrystallization from chloroform–THF; b) glass obtained by cooling the melt sample.

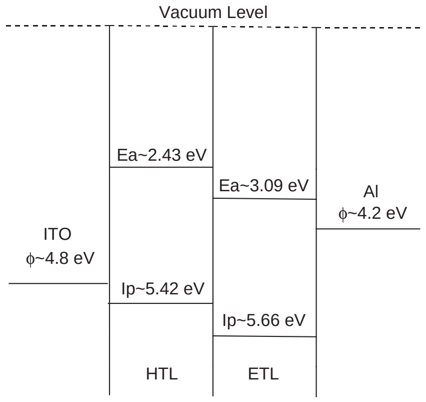


Fig. 4 A schematic energy diagram for the double-layer device [ITO/**2** (HTL)/**1** (ETL)/Al]. The work functions for ITO and Al were taken from ref. 18.

Ionization potentials (Ip) and electron affinities (Ea) of 1 and 2

The Ip and Ea for used device materials were measured using spin-coated films in air by a photoemission apparatus (RIKEN KEIKI AC-1). The results are shown in Fig. 4. The cyclic oligomer **1** and polymer **2** have 5.66 and 5.42 eV as Ip, respectively. The Ea of **1** (3.09 eV) and **2** (2.43 eV) were estimated from subtraction of optical energy gaps determined from absorption edges in Fig. 5 (484 nm) and 6 (415 nm), respectively. The energy levels of a double-layer device using indium tin oxide (ITO) as an anode and Al as a cathode are also shown in Fig. 4.[18] From these results, cyclic oligomer **1** and polymer **2** can be used for ETL and HTL, respectively, in the double-layer device. The injection barriers of electrons and

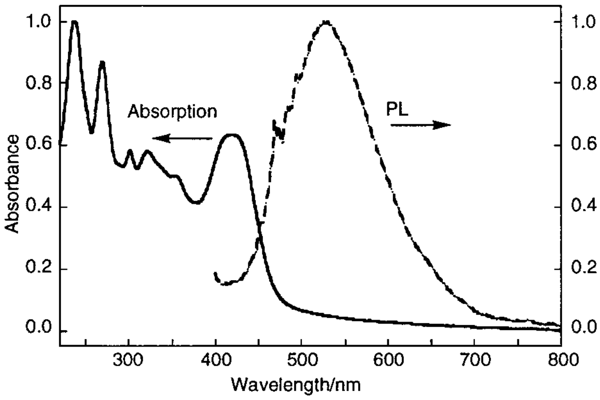


Fig. 5 The absorption and PL spectra of **1** (ETL) in spin-coated film in air.

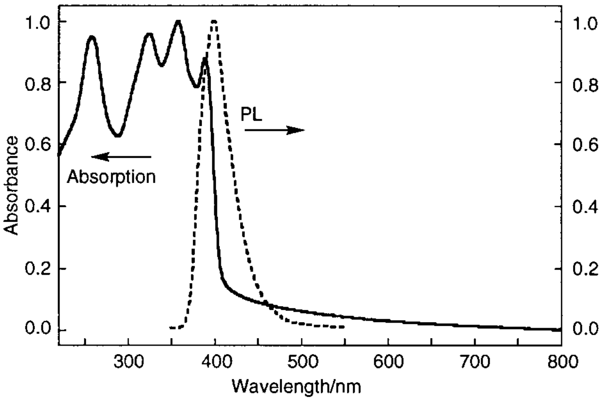


Fig. 6 The absorption and PL spectra of **2** (HTL) in spin-coated film in air.

holes from electrodes into **1** (ETL) and **2** (HTL) are about 0.9 and 0.6 eV, respectively. These results indicated that holes can be injected more easily into **2** (HTL) than electrons into **1** (ETL). Moreover, a barrier to holes of 0.2 eV exists at the **2** (HTL)/**1** (ETL) interface, but electrons face a significantly higher barrier (0.7 eV) at this interface. Therefore, the injected carriers should recombine in the **1** (ETL) layer, and luminescence mainly comes from the relative decay of **1** (ETL) singlet excited states formed by the recombination of electrons and holes.

Fabrication of the organic light-emitting diodes

The LED fabricated from cyclic oligomer **1** was a double-layer device, 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 thicknesses of ETL and HTL were in the range 80–100 nm, respectively. As the solvent for spin-coating is the same, there might be partial dissolution of the first polymer layer. The Al cathode was vacuum-evaporated on the ETL.

The EL properties of the double-layer device

Absorption and photoluminescence (PL) spectra of **1** (ETL) and **2** (HTL) in spin-coated film in air are shown in Fig. 5 and 6. The onset of the absorption of **1** and **2** occurred around 484 and 415 nm, respectively. The PL spectra of **1** and **2** showed emission maxima around 520 and 400 nm, respectively, under an excitation wavelength of 350 nm. Firstly, we measured a single-layer device of ITO/**1**/Al. However, no emission was observed although an apparent current could be observed. These results indicated that an improvement to the EL efficiency can be produced using a double-layer device so that the heterojunction between two layers can confine charges and thus bring about efficient electron-hole capture to generate excitons. The PL and EL spectra of the double-layer LEDs in air are shown in Fig. 7. The EL spectrum was measured by scanning the emission from a forward-biased cell under a bias voltage of 17 V. The PL spectrum was measured under an excitation wavelength of 350 nm. The PL spectrum shows an emission maximum around 520 nm which corresponds to the green region. As the ETL and HTL show emission maxima around 520 and 400 nm, respectively, 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 suggests that an exciplex might be formed between ETL and HTL. Exciplex formation in organic LEDs has been reported in several systems.[5g,24]

A typical luminance–voltage curve of the double layer device ITO/HTL(~100 nm)/ETL(~100 nm)/Al is shown in Fig. 8. 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%, which is higher than that of carbazole main-chain polymer (0.12%)[17] and/or carbazole hyperbranched polymer (0.08%).[18] These results indicate that the cyclic oligomer is effective for the EL materials.

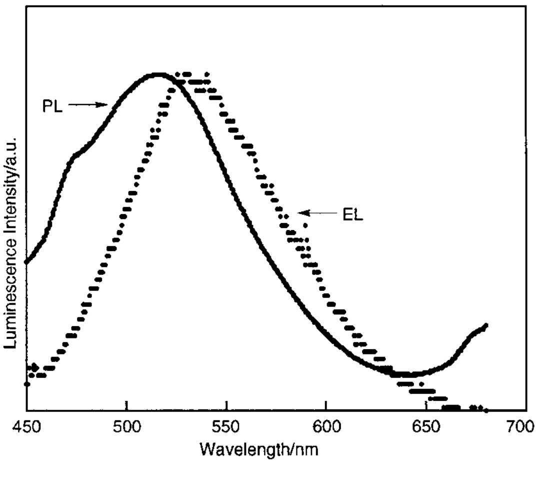


Fig. 7 The PL and EL spectra of the double-layer LEDs device in air.

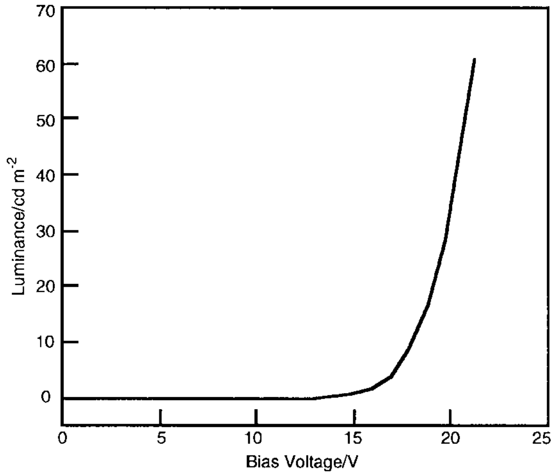


Fig. 8 The luminance–voltage characteristics of the double-layer LEDs device.

Conclusion

We have shown EL properties of the cyclic carbazole oligomer in organic LEDs. We used the cyclic carbazole oligomer **1** as an ETL and a carbazole conjugated polymer **2** as an HTL. This cyclic oligomer **1** can be easily synthesized by a one-pot Knoevenagel reaction in high yield. Besides, the glass transition temperature is high (105 °C), so that the thermal stability is good due to the morphology of the material being maintained in the amorphous glassy state. High quality amorphous film can be prepared by the conventional spin-coating technique. The external quantum efficiency is improved in this compound compared to our former systems of main-chain polymer and/or hyperbranched polymer. From these results we believe that cyclic carbazole oligomers are new candidates for emitting materials in organic LEDs.

Experimental

Materials

All chemical reagents and dehydrated solvents were commercially available and used without further purification. Analytical thin layer chromatography was performed on commercial Merck plates coated with silica gel 60F$_{254}$. Silica gel used for chromatography was Merck silica gel 60. 3,6-Diiodocarbazole **8** was prepared according to the procedure of Tucker.[25]

Instrumentation

^{1}H NMR spectra were recorded in CDCl$_3$ solution with a JEOL EX-270 spectrometer (270 MHz). Chemical shifts are reported in ppm downfield from tetramethylsilane, and coupling constants are in Hz. FAB-MS was recorded on a JEOL JMS-HX110 mass spectrometer using 3-nitrobenzyl alcohol as a matrix. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu FTIR-4100 infrared spectrometer using potassium bromide (KBr) as a pellet. Elemental analyses were performed at the Division of Chemical Analysis of RIKEN. The number and weight average molecular weight of polymer **2**, calibrated to a polystyrene standard, were estimated by GPC (columns: Waters Ultrastyragel HR2, HR3, and HR4; detector: Shimadzu SPD-10A; eluent: chloroform). Glass transition temperatures (T_g) were obtained on a RIGAKU TG-DSC8111BS with a heating rate of 5 °C min^{-1} in argon. Powder X-ray diffraction measurements were taken on a RIGAKU RAD-IIIB (conditions: 45 kV, 40 mA). Ionization potentials were measured on a RIKEN KEIKI AC-1 (condition: 50 nW). The thicknesses of the film were measured by a Sloan Dektak IIA stylus profilometer. Absorption spectra were recorded on a Shimadzu UV-3100PC UV–vis/NIR scanning spectrophotometer. Photoluminescence (PL) spectra were recorded on a Jasco FP-777 spectrofluorometer. The electroluminescence spectrum was recorded on the same instrument used for the PL measurements by blocking the xenon excitation lamp and scanning the emission from forward-biased cells. The bias voltage was 17 V. The cell was biased by an Iwatsu SP 6005P DC power supply and an Advantest R5451A auto ranging multimeter was used for current measurements. The cell luminance was determined under dark conditions through the front end of the ITO glass with a Minolta LS-100 luminescence meter.

Synthesis of ETL material 1

9-Tetradecylcarbazole 4. Carbazole **3** (20.000 g, 0.120 mol) was stirred in THF–DMF (90 ml: 30 ml) at rt, and 1-bromotetradecane (33.187 g, 0.120 mol) was added to the solution. NaH (60% in oil, 7.209 g, 0.180 mol) was gradually added to the solution and stirred for 1 h. To the solution methanol was added to quench the remaining NaH and the solvent was evaporated *in vacuo*. The residue was extracted with dichloromethane (200 ml)–3 M HCl aq. (200 ml) twice. The organic layer was washed with water (250 ml), dried with anhydrous $\mathrm{Na_2SO_4}$, and filtered. The solvent was evaporated *in vacuo* and the residue was reprecipitated using methanol to give the product. This material was used for the following step without further purification; δ_H (270 MHz; $\mathrm{CDCl_3}$; TMS) 0.88 (3H, t, *J* 6.6 Hz, $\mathrm{C}H_3$), 1.23–1.34 (22H, m, $\mathrm{C}H_2$), 1.84–1.89 (2H, m, $\mathrm{NCH_2C}H_2$), 4.29 (2H, t, *J* 7.2 Hz, $\mathrm{NC}H_2$), 7.19–7.25 (2H, m, arom. H), 7.38–7.49 (4H, m, arom. H), 8.10 (2H, d, *J* 7.9 Hz, arom. H).

3,6-Diformyl-9-tetradecylcarbazole 5. To DMF (40.614 g, 0.556 mol) at 0 °C, phosphorus oxychloride (84.718 g, 0.553 mol) was added dropwise under nitrogen atmosphere. The solution was allowed to warm to rt, and **4** (10.800 g, 29.704 mmol) and 1,2-dichloroethane (40 ml) were added. The reaction mixture was heated to 90 °C and kept at this temperature for 2 days. It was poured into water and extracted with chloroform. The chloroform extract was washed with water, and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography using chloroform–ethyl acetate (99: 1 v/v) as an eluent to give **5** (4.982 g, 40.0%); δ_H (270 MHz, $\mathrm{CDCl_3}$; TMS) 0.87 (3H, t, *J* 6.6 Hz, $\mathrm{C}H_3$), 1.23–1.40 (22H, m, $\mathrm{C}H_2$), 1.89–1.94 (2H, m, $\mathrm{NCH_2C}H_2$), 4.39 (2H, t, *J* 7.3 Hz, $\mathrm{NC}H_2$), 7.56 (2H, d, *J* 8.6 Hz, arom. H), 8.09 (2H, dd, *J* 8.6 and 1.6 Hz, arom. H), 8.68 (2H, d, *J* 1.3 Hz, arom. H), 10.14 (2H, s, $\mathrm{C}H\mathrm{O}$).

3,6-Bis(hydroxymethyl)-9-tetradecylcarbazole 6. A mixture of **5** (1.502 g, 3.580 mmol) and $\mathrm{NaBH_4}$ (0.678 g, 17.921 mmol) was stirred in THF–ethanol (20 ml : 20 ml) at rt for 5 h. The solution was poured into water (300 ml) and the resulting precipitate was collected and dried (1.508 g, 99.4%); δ_H (270 MHz; $\mathrm{CDCl_3}$; TMS) 0.87 (3H, t, *J* 6.9 Hz, $\mathrm{C}H_3$), 1.22–1.30 (22H, m, $\mathrm{C}H_2$), 1.835 (4H, br, $\mathrm{NCCH_2C}H_2$ and $\mathrm{O}H$), 4.26 (2H, t, *J* 7.1 Hz, $\mathrm{NC}H_2$), 4.82 (4H, s, $\mathrm{C}H_2\mathrm{OH}$), 7.36 (2H, d, *J* 8.55 Hz, arom. H), 7.46 (2H, d, *J* 6.9 Hz, arom. H), 8.05 (2H, s, arom. H).

3,6-Bis(cyanoacetoxymethyl)-9-tetradecylcarbazole 7. A mixture of **6** (2.000 g, 4.721 mmol) and DCC (2.136 g, 10.352 mmol) was stirred in dichloromethane (60 ml) below 5 °C. To the solution, cyanoacetic acid (1.022 g, 12.015 mmol) was added and the resulting solution was stirred for 1 day. The solution was filtered to remove the resulting dicyclohexylurea and washed with water (200 ml) three times. The organic layer was dried with anhydrous $\mathrm{Na_2SO_4}$, filtered, and the solvent was evaporated *in vacuo*. The residue was dissolved in dichloromethane and the resulting solution was filtered and passed through silica gel using dichloromethane as an eluent. The solvent was evaporated *in vacuo* and the residue was recrystallized from acetone–water to give **7**. This material was used for the following step without further purification; δ_H (270 MHz; $\mathrm{CDCl_3}$; TMS) 0.87 (3H, t, *J* 6.6 Hz, $\mathrm{C}H_3$), 1.235–1.33 (22H, m, $\mathrm{C}H_2$), 1.85 (2H, br, $\mathrm{NCH_2C}H_2$), 3.49 (4H, s, $\mathrm{NCC}H_2\mathrm{CO}$), 4.30 (2H, t, *J* 7.3 Hz, $\mathrm{C}H_2$), 5.415 (4H, s, $\mathrm{C}H_2\mathrm{O}$), 7.41 (2H, d, *J* 8.2 Hz, arom. H), 7.51 (2H, dd, *J* 8.3 and 1.6 Hz, arom. H), 8.12 (2H, d, *J* 1.6 Hz, arom. H).

Synthesis of cyclic oligomer 1. A mixture of **5** (0.451 g, 1.076 mmol) and **7** (0.600 g, 1.076 mmol) was stirred in THF (7 ml) in the presence of DMAP (0.296 g, 2.423 mmol) at 40 °C for 2 days. The solution was poured into methanol and the resulting precipitate was collected. The precipitate was reprecipitated from chloroform–methanol twice following recrystallization from chloroform–THF to give **1** (0.457 g, 45.1%) as a yellow powder (Found: C, 78.21; H, 8.21; N, 5.68. Calcd. for $\mathrm{C_{248}H_{304}N_{16}O_{16}\cdot 2H_2O}$: C, 78.36; H, 8.17; N, 5.895%); δ_H (270 MHz; $\mathrm{CDCl_3}$; TMS) 0.83–0.88 (24H, m, $\mathrm{C}H_3$), 1.22–1.23 (176H, m, $\mathrm{C}H_2$), 1.85 (16H, br, $\mathrm{C}H_2$), 4.29–4.31 (16H, m, $\mathrm{NC}H_2$), 5.57 (16H, s, $\mathrm{C}H_2\mathrm{O}$), 7.42 (8H, d, *J* 8.2 Hz, arom. H), 7.43 (8H, d, *J* 8.6 Hz, arom. H), 7.595 (8H, d, *J* 8.5 Hz, arom. H), 8.26 (8H, s, arom. H or vinyl H), 8.29 (8H, d, *J* 8.6 Hz, arom. H), 8.38 (8H, s, arom. H or vinyl H), 8.56 (8H, s, arom. H); *ν*(KBr)/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 ($\mathrm{M^+}+1$).

Synthesis of HTL material 2

3,6-Diiodo-9-tetradecylcarbazole 9. A mixture of 3,6-diiodocarbazole **8** (12.57 g, 30 mmol), 1-bromotetradecane (12.48 g, 45 mmol) and $\mathrm{K_2CO_3}$ (30 g, 217 mmol) in DMF (80 mL) was stirred at rt for 27 h. The reaction mixture was poured into water and the precipitate was collected. The precipitate was washed with water, dried, and purified by column chromatography on silica gel using hexane–dichloromethane (20 : 1 v/v) as an eluent to give **9** (17.76 g, 96.2%) as a white solid; δ_H (270 MHz; $\mathrm{CDCl_3}$; TMS) 0.84 (3H, t, *J* 6.6 Hz, $\mathrm{C}H_3$), 1.17–1.26 (22 H, m, $\mathrm{C}H_2$), 1.76 (2 H, m, $\mathrm{NCH_2C}H_2$), 4.17 (2 H, t, *J* 7.1 Hz, $\mathrm{NC}H_2$), 7.12 (2 H, d, *J* 8.6 Hz, arom. H), 7.66 (2 H, dd, *J* 8.6 and 1.7 Hz, arom. H), 8.28 (2 H, d, *J* 1.7 Hz, arom. H).

3,6-Bis[(trimethylsilyl)ethynyl]-9-tetradecylcarbazole 10. 3,6-Diiodo-9-tetradecylcarbazole **9** (6.4 g, 10.4 mmol) was dissolved in THF (25 mL) and triethylamine (15 mL) in a Schlenk flask. After vigorous stirring of this solution for 20 min under nitrogen atomosphere, (trimethylsilyl)acetylene (14 mL, 0.1 mol), bis(triphenylphosphine)palladium(II) chloride (0.14 g, 0.2 mmol), and copper(I) iodide (0.032 g, 0.17 mmol) were added and the flask was sealed. The reaction mixture was stirred at rt for 2 days, filtered to remove insoluble salt and then the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel using hexane–dichloromethane (10 : 1 v/v) as an eluent to give **10** (5.73 g, 99.1%) as a yellow viscous oil; δ_H (270 MHz; $\mathrm{CDCl_3}$; TMS) 0.29 (18 H, s, $\mathrm{SiC}H_3$), 0.88 (3 H, t, *J* 6.6 Hz, $\mathrm{C}H_3$), 1.22–1.30 (22 H, m, $\mathrm{C}H_2$), 1.83 (2 H, m, $\mathrm{NCH_2C}H_2$), 4.24 (2 H, t, J 7.1 Hz, NCH_2), 7.29 (2 H, d, J 8.6 Hz, arom. H), 7.57 (2 H, dd, J 8.6 and 1.3 Hz, arom. H), 8.19 (2 H, d, J 1.3 Hz, arom. H).

3,6-Diethynyl-9-tetradecylcarbazole 11. To a solution of 3,6-bis[(trimethylsilyl)ethynyl]-9-tetradecylcarbazole **10** (5.56 g, 10 mmol) in 400 mL of ethanol was added a solution of sodium hydroxide (0.8 g, 20 mmol) in 10 mL of water. After stirring at rt for 1 h, the solvent was evaporated and the residue was extracted with chloroform. The organic layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated *in vacuo* and the crude product was purified by column chromatography on silica gel using hexane–ethyl acetate (20:1 v/v) as an eluent to give **11** (3.92 g, 95.2%) as a yellow oil which solidified on standing in air (Found: C, 87.14; H, 9.24; N, 3.28. Calcd. for $C_{30}H_{37}N$: C, 87.54; H, 9.06; N, 3.40%); δ_H (270 MHz; $CDCl_3$; TMS) 0.88 (3H, t, J 6.6 Hz, CH_3), 1.22–1.31 (22H, m, CH_2), 1.84 (2H, m, NCH$_2$CH_2), 3.08 (2H, s, alkyne-H), 4.26 (2H, t, J 7.3 Hz, NCH_2), 7.33 (2H, d, J 8.6 Hz, arom. H), 7.56 (2H, dd, J 8.6 and 1.4 Hz, arom. H), 8.21 (2H, d, J 1.4 Hz, arom. H); ν(KBr)/cm^{-1} 3288.04, 2919.70, 2848.35, 2103.96, 1626.66, 1600.63, 1482.99, 1464.67, 1290.14, 1236.15, 1151.29, 891.92, 814.78.

Synthesis of polymer 2. A mixture of 3,6-diethynyl-9-tetradecylcarbazole **11** (0.801 g, 1.946 mmol), copper(I) chloride (0.089 g, 0.899 mmol), and TMEDA (0.621 g, 5.344 mmol) was stirred, bubbling air, at 60 °C for 7 h. The solvent was removed and the resulting residue was extracted with chloroform, washed with 3 M HCl aq. twice, and dried with anhydrous Na_2SO_4. The solvent was evaporated and the residue was reprecipitated from chloroform–methanol twice to give 2 (0.697 g). The weight average (M_w) and number average (M_n) molecular weight determined by GPC are 21200 and 5100, respectively, calibrated to a polystyrene standard; δ_H (270 MHz; $CDCl_3$; TMS) 0.85 (3H, m, CH_3), 1.22 (22H, m, CH_2), 1.755 (2H, m, NCH$_2$CH_2), 4.08–4.26 (2H, m, NCH_2), 7.18–7.35 (2H, m, arom. H), 7.57–7.99 (2H, m, arom. H), 8.085–8.43 (2H, m, arom. H); ν(KBr)/cm^{-1} 2923.56, 2851.24, 2139.63, 1626.66, 1594.84, 1482.03, 1382.71, 1350.89, 1285.32, 1236.15, 1132.01, 881.31, 805.13.

Preparation of the double-layer device

The ITO glass was cleaned by ultrasonic treatment in acetone and methanol. The ETL (15 mg ml^{-1} concentration) and HTL (12 mg ml^{-1} concentration) chloroform solutions were filtered through a 0.45 μm Teflon filter before spin-coating. Firstly the HTL was spin-coated on the ITO substrate at 4000 rpm for 30 s, then ETL was spin-coated on the HTL at 4000 rpm for 30 s. The film thicknesses of ETL and HTL were in the range 80–100 nm, respectively. The Al cathode was evaporated *in vacuo* (below 4×10^{-6} Torr), using a mask capable of patterning contacts for nine EL cells. The active area for each cell was about 12 mm^2.

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