Synthesis of Cyclic Oligomer Having a Low Ionization Potential

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Synthesis of cyclic oligomer having a low ionization potential (Ip) is described. Ip of this cyclic oligomer was determined as 5.05 eV, which is lowered than that of corresponding poly(3,6-ethynyl-9-tetradecylcarbazole) (5.24 eV). This result indicated that the cyclic oligomer would be new candidate for hole injection and/or transport material in organic light-emitting diodes.

In recent years syntheses of organic electroluminescent (EL) materials have been an active area of research because of their high luminance, low drive voltage, and variety of emission colors.[1-4] 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. In order to increase efficiencies and/or stabilities, a number of methods have been reported. For example, by using low work function metals as cathode,[5] using materials such as poly(*p*-phenylenevinylene) (PPV),[6] copper phthalocyanine (CuPc),[7] star-burst molecules,[8] and polyaniline (PANI)[9] derivatives with low Ip values for hole injection materials (HIM), and by doping.

Recently, carbazole derivatives have been extensively studied for EL applications for hole transport materials (HTM) and/or dopant due to their good hole transport and luminescent properties.[10] In our laboratory, cyclic carbazole oligomers for electron transport and emitter materials have been synthesized and studied for EL properties due to its morphological stability and easy fabrication of organic films by conventional spin-coating method.[11, 12] Here, we report on the synthesis of novel cyclic carbazole oligomer **1a** as shown in Figure 1. This cyclic oligomer exhibited low Ip value, 5.05 eV, which would be new candidate for HIM and/or HTM in organic LEDs.

The molecular design was performed by Corey-Pauling-Koltun (CPK) model. Based on this molecular design, the cyclic oligomer **1a** (shown in Figure 1) was synthesized according to Scheme 1. 3,6-Diethynyl-9-tetradecylcarbazole **2** and 3,6-diiodo-9-tetradecylcarbazole **3** were prepared according to the literature procedures.[12b] A precursor **4** was synthesized by reacting **2** (1.0 eq.) and **3** (4.7 eq.) in the presence of $Pd(PPh_3)_2Cl_2$-CuI as catalysts after purification of column chromatography in 37.1% yield. Finally, the desired molecule **1a** was synthesized by reacting **2** (1.0 eq.) and **4** (1.0 eq.) in the presence of $Pd(PPh_3)_4$-CuI as catalysts after purification of column chromatography following preparative gel permeation chromatography (conditions: columns, Shodex GPC K-2001 and K-2002; eluent, chloroform 3.0 ml/min) to give pure **1a**. In this reaction, we also obtained **1b**. The yields of **1a** and **1b** were 14.3% and 5.4%, respectively. The structures of **1a** and **1b** were assigned by ^1H NMR, FAB-MS or MALDI-TOF-MS, and elemental analyses.[13] From these data, we assigned **1a** and **1b** as cyclic tetramer and cylic octamer, respectively. The corresponding polymer **1c**[14] was synthesized by reacting **2** (1.0 eq.) and **3** (1.0 eq.) in the presence of $Pd(PPh_3)_2Cl_2$-CuI as catalysts and purified by reprecipitation from dichloromethane-methanol three times. The average molecular weight of **1c** was more than 10^6.

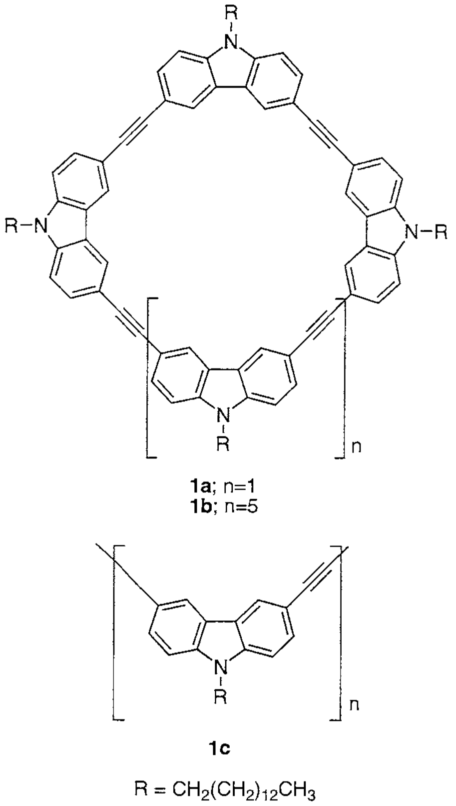
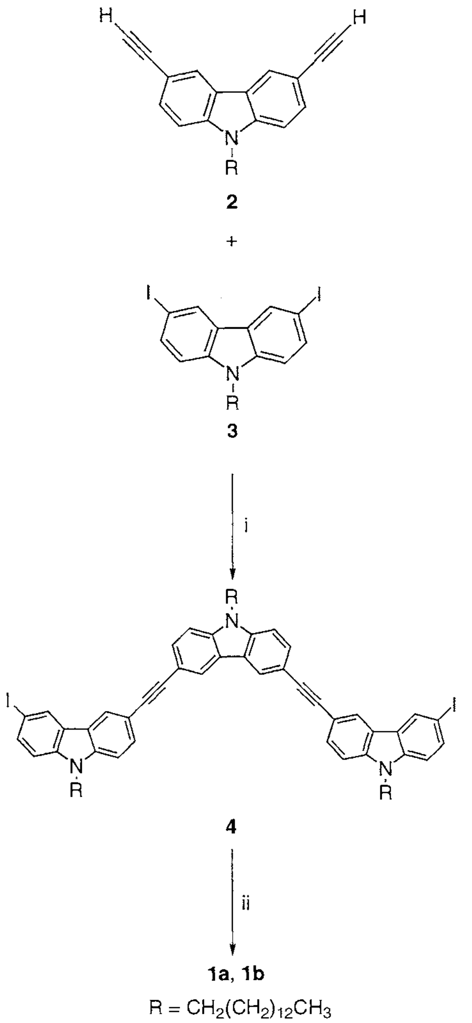


Figure 1. Molecular structures of cyclic oligomer **1a**, **1b**, and polymer **1c**.

We investigated Ip, electron affinity (Ea), and optical energy gap (ΔE) of **1** on spin-coated film in air. The cyclic oligomer **1a**, **1b**, and polymer **1c** were spin-coated using chloroform as a solvent. The emission maxima of **1a**, **1b**, and **1c** were about 490, 470, and 470 nm, respectively (excitation wavelength; 350.0 nm). The results are shown in Figure 2. The Ip values were measured by RIKEN KEIKI AC-1 and obtained Ip value, 5.05 eV for **1a**. The Ea (2.06 eV) of **1a** was estimated from subtraction of ΔE (2.99 eV) determined from absorption edge (415.0 nm, not shown here). The Ip, Ea, and ΔE values of **1b** were 5.32, 2.36, and 2.96 eV, respectively, in the same method. And also the Ip, Ea, and ΔE values of **1c** were 5.24, 2.29, and 2.95 eV,



Scheme 1. *Reagents and conditions:* i) $Pd(PPh_3)_2Cl_2$-CuI, THF-NEt_3, rt, 37.1%; ii) **2**, $Pd(PPh_3)_4$-CuI, THF-NEt_3, rt, high dilution, 14.3% for **1a**, 5.4% for **1b**.

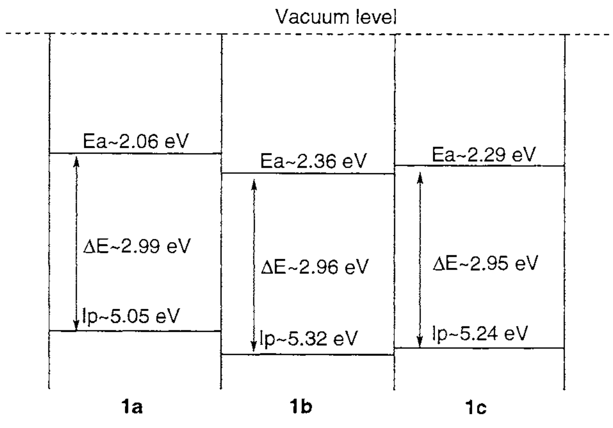


Figure 2. A schematic energy diagram for **1**. The Ip values were measured by RIKEN KEIKI AC-1 using spin-coated film in air. Ea were estimated from subtraction of optical energy gap determined from absorption edge .

respectively. Although the reason why low Ip value for **1a** was obtained compared with that of **1b** and that of corresponding polymer **1c** is unknown, it might be related with conformational rigidity. Further investigation will be needed. However, these results indicated that **1a** would be useful for HTM and/or HIM like PPV,[6] CuPc,[7] star-burst molecules,[8] and PANI[9] in organic LEDs. Systematic researches on the fabrication of EL devices are now underway.

In conclusion, we have synthesized cyclic oligomer **1a** having a low Ip value. This result indicated that **1a** would be expected for new EL material for HTL and/or HIL.

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13 Selected data for **1a**: ^{1}H NMR (300MHz, $CDCl_3$), δ/ppm 0.865 (t, *J* 6.6 Hz, 24H, CH_3), 1.25-1.37 (m, 88H, CH_2), 1.86-1.945 (m, 8H, CH_2), 4.31 (t, *J* 6.9 Hz, 8H, NCH_2), 7.39 (d, *J* 8.4 Hz, 8H, arom. H), 7.71 (dd, *J* 8.4 and 1.5 Hz, 8H, arom. H), 8.42 (d, *J* 1.2 Hz, 8H, arom. H); *m/z* 1542 (M^+) (Found: C, 86.36; H, 9.28; N, 3.50%. $C_{112}H_{140}N_4{\bullet}H_2O$ requires C, 86.21; H, 9.17; N, 3.59%); for **1b**: ^{1}H NMR (300MHz, $CDCl_3$), δ/ppm 0.87 (t, *J* 6.75 Hz, 12H, CH_3), 1.24 (br, 176H, CH_2), 1.74 (br, 16H, CH_2), 3.94 (br, 16H, NCH_2), 7.22 (d, *J* 8.4 Hz, 16H, arom. H), 7.70 (d, *J* 8.4 Hz, 16H, arom. H), 8.36 (s, 16H, arom. H); *m/z* 3085 (M^+) (Found: C, 86.67; H, 9.37; N, 3.56%. $C_{224}H_{280}N_8{\bullet}H_2O$ requires C, 86.71; H, 9.16; N, 3.61%).

14 Selected data for **1c**: ^{1}H NMR (300MHz, $CDCl_3$), δ/ppm 0.85 (m, 3H, CH_3), 1.23 (m, 22H, CH_2), 1.81 (m, 2H, CH_2), 4.205 (m, 2H, NCH_2), 7.31 (m, 2H, arom. H), 7.68 (m, 2H, arom. H), 8.31 (m, 2H, arom. H).