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Novel Oligomers of 9,9-Dialkylated Fluorenes for Thermally Stable Hole-Transport Materials in OLEDs

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Using 9,9-dialkyl-functionalized fluorenes as monomers, novel fluorene-based oligomers were prepared in order to improve the thermal stability of a typical hole-transport material (HTM), *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine (TPD), in organic light emitting diodes (OLEDs). 2,7-Bis(diphenylamino)fluorene was utilized as a TPD unit throughout the present synthetic work. 9,9-Bis(2-methylallyl)fluorene and its TPD congener underwent a new cyclopolymerization reaction affording six-membered oligomers under acid catalysis with *p*-toluenesulfonic acid. Intermolecular Suzuki coupling of a 9,9-bis(*p*-bromobenzyl)fluorene analogue with the corresponding bis-boronate afforded a new oligomer containing the TPD substructure. These oligomers (**3** and **6**) for use as HTMs have high glass-transition temperatures (T_g's) (147 and 167 °C, respectively); the values are much higher than the T_g for TPD (63 °C). These materials are soluble in organic solvents to allow easy processing for preparing layered devices, though their electroluminescent performances were lower than that of the single molecule TPD.

Organic light emitting diodes (OLEDs) are being actively developed for full-color flat-panel displays and flexible displays.[1] The materials for these devices need to be thermally stable for long-life driving. For multi-layered devices, numerous triphenylamine derivatives have been developed as the hole-transport material (HTM).[2–5] *N*,*N*′-Bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine (TPD) is a typical HTM, which shows excellent EL characteristics, but its thermal stability is insufficient as indicated by the low glass-transition temperature (T_g) of 63 °C.[6] To overcome the drawback of TPD, two approaches for thermally stable HTMs have been reported. One is based on single-molecule materials, and another is on polymer materials.[2–4] The former is favorable in material purification because of sublimation, but the latter is advantageous in preparation of thin films because of easy coating procedure. The advantage of the polymer-type approach has been illustrated with polystyrene having triphenylamine groups as pendant groups,[7] cross-linkable alkoxylated polymethacrylates,[8] a polymer of 1,1-cyclohexane-bridged triphenylamines,[9] and some condensation polymers.[10–12]

Our polymeric approach utilizes 9*H*-fluorene as the key substance. Introduction of functional groups into fluorene is available not only at the 2 and 7 positions via aromatic electrophilic substitutions, but also at the 9 position via facile alkylation due to the high acidity of the methylene carbon (pK_a 23) giving a stable carbanion.[13] Thus, 2,7-bis(diphenylamino)fluorene (**1**, see Scheme 1) contains the *N*,*N*,*N*′,*N*′-tetraphenylbenzidine substructure of TPD. Our interest was focused on 9,9-diallyl-substituted derivative of **1** because the cyclopolymerization[14] of several diallyl monomers which afforded the famous electroconducting polymer, poly(diallyldimethylammonium chloride), has been reported.[15] However, no attempt to polymerize 9,9-diallylfluorene has been reported to the best of our knowledge, although the analogous 9,9-di-2-propynylfluorene is known to undergo oxidative coupling polymerization.[16] A relevant compound alkylated with *p*-bromobenzyl group is also valuable because aromatic bromides for polymeric HTM are available through intermolecular Suzuki coupling.[17] Here, we report the preparation of polymer-type HTMs of several 9,9-dialkylated 2,7-bis(diphenylamino)fluorenes. Some of the resulting oligomers unexpectedly have high thermal stability indicated by their T_g's. Their electroluminescent (EL) characteristics remain good enough for practical use.

Results and Discussion

Monomers and Oligomers. At the beginning of this study, 9,9-diallylfluorene[18] was chosen as a promising monomer for the cyclopolymerization because it should polymerize similarly to diallyldimethylammonium chloride.[15] Attempts to polymerize 9,9-diallylfluorene in refluxing benzene using AIBN as radical initiator were unsuccessful, i.e., only the starting material was recovered. Use of 9,9-bis(2-methylallyl)fluorene,[19] (9,9-bis(2-methyl-2-propenyl)fluorene), as a substrate in the presence of an acid catalyst *p*-toluenesulfonic acid through cationic polymerization afforded oligomers with 6-membered rings albeit in low yield. When 2,7-bis(diphenylamino)-9,9-bis(2-methylallyl)fluorene (**2**), which is a TPD congener, was used as a substrate, oligomeric material **3** was obtained in 97% yield probably due to its low solubility in solvents (Scheme 1).

As for the degree of polymerization, up to 5-mers were detected with APCI-MS analysis. In the ^{1}H NMR spectrum of **3**,

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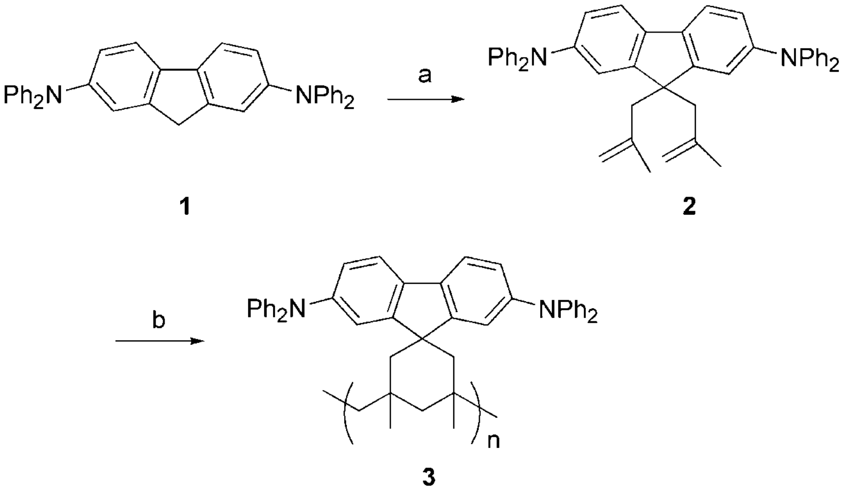


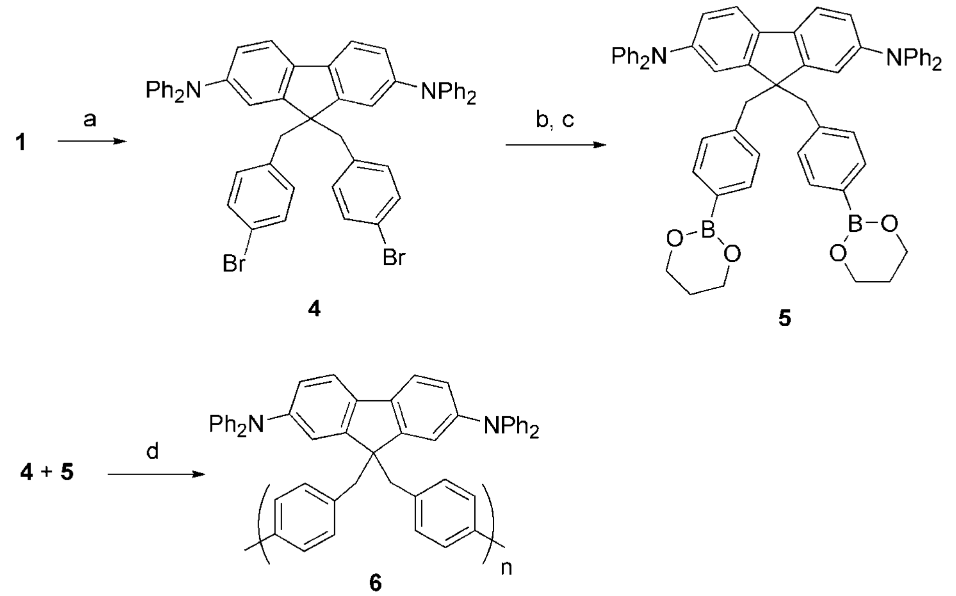
Scheme 1. a) 2-Methylallyl chloride (2.5 equiv), NaH in DMF, rt, 6 h, 72%. b) TsOH (10 mol %), *o*-dichlorobenzene, 130 °C, 1 day, then reprecipitation with MeOH, 97%.

olefinic protons that had appeared at 4.2 and 4.4 ppm in **2** became saturated protons at 2.1 and 2.3 ppm. The broadened methyl signal from 1.1–1.3 ppm contained 4–6 peaks. The structure of 6-membered rings is formed via a cationic polymerization mechanism: (1) initial protonation of a methylallyl group generating a stable tertiary carbocation, (2) which undergoes sequentially both intramolecular cyclization leading to a 6-membered ring and intermolecular C–C bond formation as the propagation step, followed by (3) a termination step such as alkylation of aminophenyl rings (presumably at the para positions) with the resulting carbocations and their deprotonation to an inner olefin. An analogous di-2-propynyl TPD congener was subjected to oxidative polymerization, similar to 9,9-di-2-propynylfluorene,[16] in the presence of oxygen and the copper complex; however, the yield of the polymeric material was low (at best 35% yield). The degree of polymerization was about 5, whereas 50 is reported in the case of simple 9,9-di-2-propynylfluorene.[16] In the ^{1}H NMR spectra of this TPD congener, the peaks for the terminal acetylenic protons completely disappeared; however, new olefinic proton peak did not appear. In other words, no cyclopolymerization leading to any cyclic polyene derivative took place. Accordingly, this oligomer was considered to contain only intermolecular linkages.

Another polymer of TPD congeners was obtained by Suzuki cross-coupling polymerization.[17] Starting dibromide **4** was prepared via dialkylation of **1** with *p*-bromobenzyl bromide, and **4** was then converted into diboronate **5** using a conventional procedure (Scheme 2). Bifunctional Suzuki coupling reaction between **4** and **5** in the presence of a palladium catalyst with tri-*t*-butyl phosphine ligands[20] in refluxing toluene gave polymeric material **6** that was mainly comprised of a 4-mer based on the gel permeation chromatography (GPC) analysis using polystyrene standards (M_n 2800, M_w/M_n 1.67).

Properties of Oligomers and Devices. For practical use in EL devices, it is crucial that the T_g of HTM be high. For example, α-NPD having a high T_g of 95 °C was first commercially used in place of TPD with T_g 63 °C.[21] The T_g's of oligomers **3** and **6** were obtained by DSC analyses, and they are listed in Table 1 together with the results from electrochemical measurements and device performances. Interestingly, oligomers **3** and **6** have T_g's much higher than 100 °C, namely 147 and 167 °C, respectively. These unexpectedly high T_g values are comparable to those of the TPD-pendant polymers (132–151 °C)[7] and of the TPD-PPV copolymer with $M_w = 35810$ (130 °C).[11] Regarding the T_g, **3** and **6** having TPD moiety are superior to the polymers of 1,1-cyclohexane-bridged triphenylamines ($T_g = 107$–134 °C).[9] Formaldehyde or benzaldehyde-condensed polymers TPD-FA and TPD-BzA with high molecular weights ($M_w > 10^4$) have higher T_g's 183 and 239 °C, respectively.[10] In the single-molecule materials, triphenylamine derivatives, like TPD, have been reported to show T_g's up to 145 °C with an increase in number of the triphenylamine unit from 2 to 5.[22] From our recent research, a trispirocycle-incorporated trimeric TPD analogue has a T_g of 170 °C.[23] The simple TPD congener **1** has a T_g of 88 °C. Therefore, the present oligomer-based method can be used to prepare HTM's with a high T_g. The high molecular weight is the dominant factor for raising T_g in accord with requirements reported elsewhere.[24] In order to design an HTM with high T_g, structural aspects may also be important for increasing T_g based on the high T_g for **3**, which has an incorporated spirocycle, and **6**, which has a large number of the aromatic moieties.

Cyclic voltammetric (CV) measurements of **3** and **6** in dichloromethane were carried out for the design of devices. Figure 1 shows a cyclic voltammogram of bis(2-methylallyl) oligomer **3**. Both oligomer **3** and **6** have two reversible waves, which correspond to the successive formation of the corresponding cation radical and dication. The ratios of cathodic current to anodic current[25] for **3** and **6** with the first peak were 0.90 and 1.00, respectively (Table 1); this means that cation radicals formed are highly stable and unreactive. In other words, one may expect efficient hole-transport ability in the solid state. The difference in the oxidation potentials is small among TPD, **3** and **6** (see Table 1). TPD congener **1** is oxidized at 0.60 V vs Ag/AgCl reference electrode (being only by 0.03 V lower than TPD), whereas **3** and **6** at 0.64 and 0.66 V, respectively. In relation to the energy diagram for a device, the HOMO levels of **3** and **6** are shifted to the level lower by 0.01–0.03 eV, or the nearly the same as that of TPD. UV and



Scheme 2. a) *p*-Bromobenzyl bromide, NaH in DMF, rt 6 h, 45%. b) BuLi, THF −70 °C 1 h; $B(OMe)_3$, then H_3O^+. c) 1,3-Propanediol, PhMe reflux overnight, 86% (2 steps). d) $[Pd(PPh_3)_4]$ (3 mol %), K_2CO_3/H_2O, PhMe reflux 2 days, then reprecipitation with MeOH, 76%.

Table 1. Properties and Device Characteristics of Oligomeric HTMs **3** and **6**

Oligomer	Thermal[a]	Electrochemical[b]		Device[c]			
	T_g/°C	E_{ox}/V	i_{pc}/i_{pa}	L_{300}/V	L_{max}/cd m^{-2}	η_e/lm w^{-1}	η_c/cd A^{-1}
3	147	0.64	0.90	13	2600	0.18	0.75
6	167	0.66	1.00	9.5	6300	0.78	2.3

a) DSC analysis, 10 °C min^{-1}. b) CV conditions, 1 mM (M = mol dm^{-3}), in dichloromethane, Bu_4NClO_4 0.1 M, scan rate 0.2 V s^{-1}, vs Ag/AgCl electrode. E_{ox} means the half oxidation potential, i_{pc}/i_{pa} being the ratio of cathodic to anodic peak current. c) The device structure, ITO/HTM 50 nm/Alq3 50 nm/Mg–Ag. L_{300}, L_{max}, η_e, and η_c are already defined in the text.

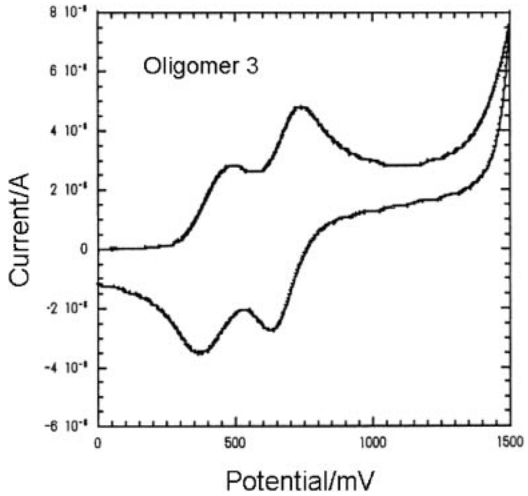


Fig. 1. CV of oligomer **3** measured in dichloromethane containing tetrabutylammonium perchlorate. Values are plotted for calibration vs ferrocene reference electrode.

visible absorption spectra of **3** and **6** were recorded in chloroform in order to estimate the band gap of the HTM. Simple TPD congener **1**, oligomers **3** and **6** have absorption maxima at 362, 367, and 369 nm, respectively. The differences in the HOMO–LUMO gap can be safely estimated to be smaller than 0.1 eV. Therefore, the band diagram involving HOMO and LUMO levels for **1**, **3**, and **6** is almost the same as that for typical TPD (−5.5 and −2.1 eV vs vacuum level, respectively).

Multilayered EL devices for **3** and **6** were fabricated on transparent indium–tin oxide (ITO) glass (anode) via spin-coating, followed by successive vapor deposition of aluminum tris(8-quinolinolate) (Alq3, electron-transport material) and metal cathode. The device configuration was ITO/HTM (**3** or **6**) 50 nm/Alq3 50 nm/Mg–Ag. Upon application of a direct current, emission of green light due to Alq3 was observed at $\lambda_{max} \approx 530$ nm. Figure 2 illustrates the luminance—applied voltage characteristics of oligomers **3** and **6**. The devices using **3** and **6** had a practical level of luminance 200–300 cd m^{-2} at 9–14 V of applied voltage (Table 1). However, these oligomeric materials are significantly inferior in EL characteristics to the single molecules studied by the authors;[22] for example, TPD congeners like **1** can acquire practical luminance L_{300}, which is the voltage required for the luminance of 300 cd m^{-2}, at only about 5 V and has a maximum luminance (L_{max}) of 20000 cd m^{-2}. The L_{max} for oligomers **3** and **6** is generally several thousands cd m^{-2}, similar to those of 9,9-fluorene-bridged triphenylamines.[26] On the basis of easy processability to afford thin films as well as high thermal stability as described before, HTMs **3** and **6** are useful enough. Benzylic-type oligomer **6**

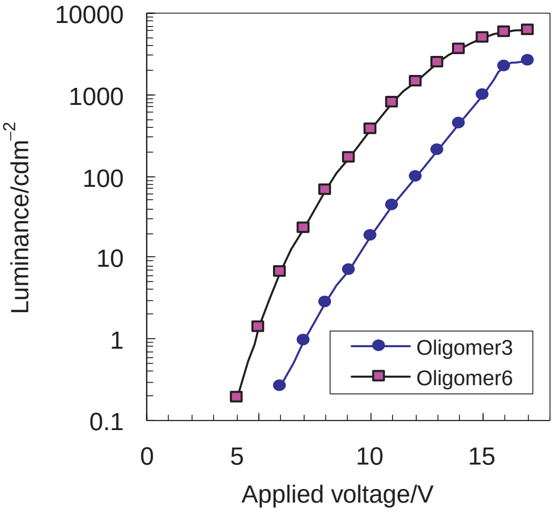


Fig. 2. Luminance–applied voltage characteristics for oligomer **3** (●) and **6** (■). The device structure is shown in the footnote c) in Table 1.

was better than **3** because of its lower L_{300} of 9.5 V and its higher $L_{\max}$ of 6300 cd m^{-2} (see Table 1). This statement is further supported by efficiencies; oligomer **6** had a luminous power efficiency η_e of 0.78 lm W^{-1} and a current efficiency η_c of 2.3 cd A^{-1}. Both values for **6** are larger than those for **3**. Based on the large differences, it should be possible to improve these values by fine tuning the structure via substituents, molecular weights, terminal groups, and device structures. The difference between **3** and **6** in EL performance may be understood in terms of the higher content of electroconductive aromatic rings in **6**; it seems necessary to elucidate not only chemical aspects, such as π-electron interaction,[27] in the solid state but also physical aspects of the surface phenomena, including band bending.[28]

To summarize the present approach to polymers, it is concluded that oligomers like **6** are advantageous due to their high T_g (167 °C) for the purpose of long-life driving in devices as well as facile processing of thin-film devices, though the device performance must be improved. For the molecular design of thermally stable HTMs, it is noted that oligomers with a low number[22] of the degree of polymerization can bring about T_g's > 100 °C for practical use.

Experimental

General. Commercially available reagents including dry solvents were used as received. NMR spectra were recorded on a 200 or 500 MHz spectrometer in $CDCl_3$ using TMS as an internal standard. GPC analysis using polystyrene standards was carried out with a dilute solution of the oligomers in THF solvent. DSC analyses were carried out on a Perkin-Elmer DSC 7000 model under nitrogen; samples were heated to over 300 °C, cooled rapidly to room temperature and heated again with heating rate of 10 °C min^{-1} for record. CV measurements were carried out on a BAS-50W electrochemical analyzer with dichloromethane solutions (10 mL, 0.01 M) containing tetrabutylammonium perchlorate (0.1 M) under nitrogen atmosphere, and were recorded at a scan rate of 0.2 V s^{-1}. The voltammogram in Fig. 1 was plotted after calibration using ferrocene and recording the oxidation potential, an average of peak oxidation and reduction potentials vs Ag/AgCl electrode.

Attempts to Polymerize 9,9-Diallylfluorene. A solution of 9,9-diallylfluorene[18] (1.23 g, 5.0 mmol), AIBN (86 mg, 0.5 mmol) in benzene (10 mL) was heated at reflux for 3 h. The insoluble solid, which was also insoluble in chloroform, was filtered and dried (5 mg). Analysis of the filtrate showed that the most (>90%) of the starting material remained unchanged. Similar attempts with 9,9-diallyl-2,7-bis(diphenylamino)fluorene, prepared similarly as described below, in benzene or *o*-dichlorobenzene resulted in recovery of the starting material.

9,9-Bis(2-methylallyl)fluorene was prepared by the alkylation described below in 91%. However, this substance is a colorless solid, mp 64–66 °C, and not a liquid as reported.[19] A solution of bis(2-methylallyl)fluorene (0.683 g, 2.5 mmol) and *p*-toluenesulfonic acid monohydrate (TsOH, 95 mg, 0.5 mmol) in benzene (2 mL) was heated at reflux for 2 h. Precipitation with methanol gave a yellowish solid (0.12 g).

Preparation of 2,7-Bis(diphenylamino)fluorene (1). A solution of 2,7-dibromofluorene (16.2 g, 50 mmol), diphenylamine (18.6 g, 110 mmol), and sodium *t*-butoxide (11.5 g, 120 mmol) in *o*-xylene (100 mL), to which a prepared solution of palladium(II) acetate (0.33 mmol) and tri-*t*-butylphosphine[20] in *o*-xylene was added as the catalyst, was refluxed at about 120 °C under nitrogen atmosphere for 6 h. After cooling, extraction with chloroform and the usual work-up gave a crude material. Recrystallization from benzene–ethanol (4:1) gave brownish powder of **1** (17.9 g, 71% yield): mp 233–235 °C; ^{1}H NMR: δ 3.75 (s, 2H), 7.68–7.49 (m, 26H).

2,7-Bis(diphenylamino)-9,9-bis(2-methylallyl)fluorene (2). Sodium hydride (NaH 60% in oil, 0.96 g, 24 mmol) was washed repeatedly with hexane. A mixture of NaH, **1** (5.01 g, 10 mmol), and 2-methylallyl chloride (2.5 mL, 25 mmol) in DMF (30 mL) was stirred at room temperature (rt) for 6 h. Work-up, including extraction with benzene and purification by recrystallization from benzene–ethanol (4:1), afforded a faint purple colored solid (4.38 g, 72%). Repeated recrystallization gave an analytical sample of **2**: mp 215–217 °C; APCI-MS *m/z* 609 (M + 1); ^{1}H NMR: δ 1.10 (s, 6H), 2.63 (s, 4H), 4.28 (s, 2H), 4.48 (s, 2H), 7.0–7.5 (m, 26H); Anal. Found: C, 88.72; H, 6.85; N, 4.43%. Calcd for $C_{45}H_{40}N_2$: C, 88.78; H, 6.62; N, 4.60%.

Polymerization of 2. A solution of **2** (1.83 g, 3 mmol) and TsOH (57 mg, 0.3 mmol) in *o*-dichlorobenzene (10 mL) was heated at 130 °C for 1 day. The reaction mixture was poured into methanol (50 mL). The resulting solid was filtered and dissolved in THF. Reprecipitation with methanol gave a greenish solid of **3** (1.79 g): ^{1}H NMR: δ 1.15–1.30 (br s, 6H), 1.61 (br s, 4H), 2.13 (br s, 2H), 2.33 (br s, 2H), 7.0–7.4 (m, 26H); Anal. Found: C, 89.51; H, 6.17; N, 4.32%. Calcd for $(C_{45}H_{40}N_2)_n$: C, 88.78; H, 6.62; N, 4.60%.

Preparation of 9,9-Di-*p*-bromobenzyl-2,7-bis(diphenylamino)fluorene (4). The alkylation described in **2** was carried out with *p*-bromobenzyl bromide (6.25 g, 25 mmol) on **1** (5.01 g, 10 mmol). Purification by recrystallization from benzene–ethanol (5:1) gave a pinkish white solid of **4**: mp 210–212 °C; APCI-MS *m/z* 837 (M − 1, 50%), 839 (M + 1, 100), 841 (M + 3, 50); ^{1}H NMR δ 3.15 (s, 4H), 6.50 (d-like, 4H), 7.0–7.55 (m, 30H); Anal. Found: C, 72.88; H, 4.62; N, 3.27%. Calcd for $C_{51}H_{38}Br_2N_2$: C, 73.03; H, 4.57; N, 3.34%.

Conversion of 4 into the Corresponding Borate 5. To a solution of dibromide **4** (2.10 g, 2.5 mmol) in THF cooled at −70 °C, butyllithium (in hexane 1.6 M, 3.8 mL, 6.1 mmol) was added dropwise for 10 min. After the resulting slurry was stirred for 1 h, trimethyl borate (0.84 mL, 7.5 mmol) was added, and the mixture was allowed to warm up to rt over 4 h. The reaction mixture was treated with benzene (100 mL) successive washing with water and brine, drying over $MgSO_4$, and removal of solvents to give a crude boric acid. This was admixed with 1,3-propanediol (0.43 mL, 6 mmol) and toluene (100 mL), and refluxed overnight. Workup and purification by column chromatography on silica gel using benzene as an eluant gave **5** as a white solid (1.84 g, 86%): mp 140–142 °C; ^{1}H NMR δ 2.40 (quintet, $J = 7$ Hz, 4H), 3.25 (s, 4H), 4.12 (t, $J = 7$ Hz, 8H), 6.5–6.7 (m, 4H), 7.0–7.4 (m, 30H); Anal. Found; C, 80.74; H, 6.06; N, 3.32%. Calcd for $C_{57}H_{50}B_2N_2O_4$: C, 80.67; H, 5.94; N, 3.30%.

Polymerization by Suzuki Coupling of 4 and 5. A mixture of bromide **4** (1.00 g, 1.20 mmol) and boronate **5** (1.02 g, 1.20 mmol), $[Pd(PPh_3)_4]$ catalyst (41 mg, 0.036 mmol), K_2CO_3 (0.433 g, 3.6 mmol), and water (6 mL) with toluene (30 mL) was heated at reflux for 3 days. The resulting reaction mixture was poured into methanol (100 mL). The solid that formed was collected by filteration and dried, and redissolved in THF (30 mL). Reprecipitation gave **6** as a white powder (1.45 g): ^{1}H NMR δ 3.22 (br s, 4H), 6.77 (br d, 4H), 6.95–7.30 (m, 30H); Anal. Found: C, 90.09; H, 5.96; N, 3.94%. Calcd for $(C_{51}H_{38}N_2)_n$: C, 90.23; H, 5.64; N 4.13%.

Devices. An ITO-coated glass substrate (sheet resistance is $10\,\Omega\,sq^{-1}$) was cleaned with a UV-ozone chamber. A 50 nm thick hole-transport layer consisting of the oligomer was formed onto the ITO anode substrate by spin coating of a chloroform solution. Then, an Alq3 layer of 50 nm was deposited under a vacuum of 5×10^{-7} Torr. Finally, a magnesium–silver alloy (10:1 ratio by weight, 500 nm) was deposited as a cathode. The emission area of the device was 4 mm^2. The luminance–current–voltage characteristics of the devices were measured with an Advantest R6243 current/voltage measurement unit and a Minolta CS-100 Chromameter under nitrogen atmosphere at room temperature (Fig. 2). The emission was brilliant green, $x = 0.30$ and $y = 0.53$ in the CIE color coordinate (JIS Z8110).

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