doi:10.1246/cl.2012.516

Synthesis of π-Conjugated Two Generation Dendrimer Composed of *p*-Phenylenevinylene Dendron and Triphenylamine Surface Group

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π-Conjugated two generation dendrimer composed of *p*-phenylenevinylene dendron and triphenylamine surface group was synthesized via a convergent route. The dendrimer shows high solubility in organic solvents and fluorescence emission resulting from the *p*-phenylenevinylene site.

π-Conjugated dendrimer is a strong candidate for organic semiconductor materials because of its high solubility in organic solvents and charge-carrier transport and emission properities.[1–3] Most of the π-conjugated dendrimers reported previously have introduced aliphatic moieties such as a dibutylamino group, which do not show the π-conjugation, as a surface group. Hence the charge-carrier transportation would be restricted by the surface group even though the solubility is high. On the contrary, we have focused on the π-conjugated dendrimer composed of *p*-phenylenevinylene dendron and triphenylamine surface group G2D3-PV(TPA) dendrimer **1** shown in Figure 1, which both the dendron and surface group show hole-carrier transport.[4] In this article, we will report a synthesis of the dendrimer **1**. The dendrimer **1** was prepared via a convergent route described below.

4-(Diphenylamino)styrene (**2**) was synthesized as follows. A dry THF solution containing methyltriphenylphosphonium bromide and potassium *tert*-butoxide was stirred for 2 h under N_2 atmosphere at rt. Then, a dry THF solution containing 4-(diphenylamino)benzaldehyde was added dropwise, and stirred for an additional 2 h at rt. After quenching of the reaction by adding acetone, a crude product was obtained by removing the precipitate and evaporating the filtrate under reduced pressure. The purification which was performed by column chromatography on silica gel (eluent: CH_2Cl_2/n-hexane) gave a yellow solid of **2** in 92% yield. The compound **2** was confirmed by ^{1}H NMR analysis.[5] Aldehyde compound of first generation dendron **3** (Scheme 1) was prepared by the following. A *N*,*N*-dimethylacetamide solution containing compound **2**, 3,5-dibromobenzaldehyde, palladium acetate, triphenylphosphine, and sodium carbonate was stirred for 24 h under N_2 atmosphere at 110 °C. After cooling to rt, CH_2Cl_2 and water were added to the reaction mixture, and the organic layer was extracted. The organic layer was washed with water, and dried with $MgSO_4$. Evaporation of the solvent yielded an oily crude product. The crude product was purified by column chromatography on silica gel (eluent: CH_2Cl_2/n-hexane) to give a yellow solid of **3** in 63% yield. The compound **3** was confirmed by ^{1}H NMR analysis.[5] Vinyl compound of first generation dendron **4** (Scheme 1) was then synthesized. A dry THF solution containing methyltriphenylphosphonium bromide and potassium *tert*-butoxide was stirred for 2 h under N_2 atmosphere at rt. Then, a dry THF solution containing compound **3** was added dropwise, and stirred for an additional 2 h at rt. After quenching the reaction by adding acetone, the reaction mixture was filtered. The filtrate was evaporated under reduced pressure to give crude

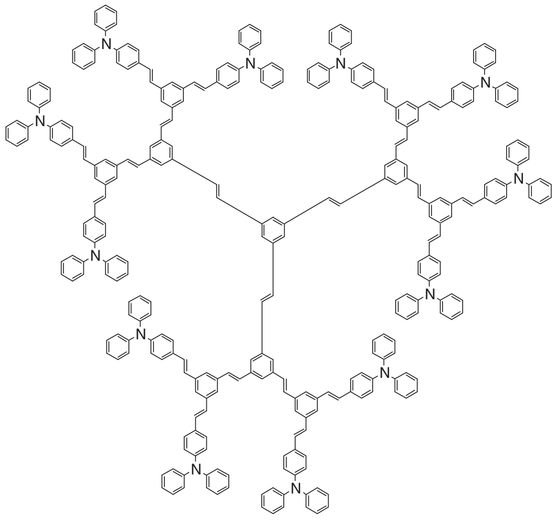
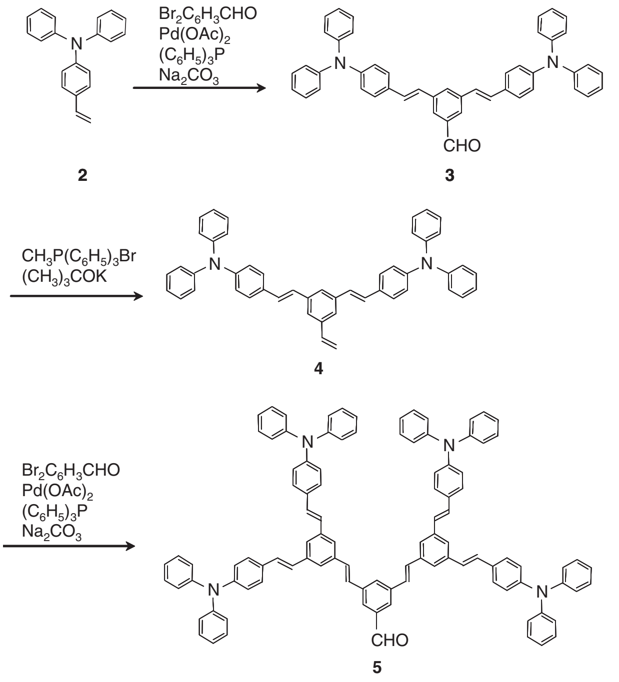
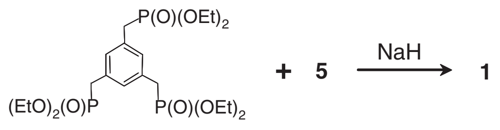


Figure 1. Chemical structure of the dendrimer **1** (G2D3-PV(TPA)).



Scheme 1. Synthesis of the two generation dendron **5**.



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Scheme 2. Synthesis of dendrimer **1**.

product. The crude product was purified by column chromatography on silica gel (eluent: CH_2Cl_2/n-hexane) to give a yellow solid of **4** in 99% yield. The compound **4** was confirmed by ^{1}H NMR analysis.[5] Aldehyde compound of second generation dendron **5** (Scheme 1) was prepared. A *N*,*N*-dimethylacetamide solution containing compound **4**, 3,5-dibromobenzaldehyde, palladium acetate, triphenylphosphine, and sodium carbonate was stirred for 24 h under N_2 atmosphere at 110 °C. After cooling to rt, CH_2Cl_2 and water were added, and the organic layer extracted. The organic layer was washed with water, and dried with $MgSO_4$. Evaporation of the solvent yielded an oily crude product. The crude product was recrystallized from CH_2Cl_2/n-hexane to give a yellow solid of **5** in 60% yield. The compound **5** was confirmed by ^{1}H NMR analysis.[5] G2D3-PV(TPA) dendrimer **1** (Scheme 2) was synthesized as follows. Benzotriphosphonate **6** was prepared following a method reported by Deb et al.[6] A dry THF solution containing **6**, **5**, and sodium hydride was stirred for 3 h under N_2 atmosphere at rt. During the reaction, sodium hydride was added a few times. After the reaction, a small amount of water was added and the solvent evaporated. The residue was dissolved in CH_2Cl_2, and dried with $MgSO_4$. Evaporation of the solvent yielded a crude product. The crude product was purified by column chromatography on silica gel (eluent: CH_2Cl_2/n-hexane) to give a yellow solid of the G2D3-PV(TPA) dendrimer **1** in 72% yield. The dendrimer **1** was confirmed by ^{1}H NMR, ^{13}C NMR, and IR analyses.[7]

The weight-average molecular weight and number-average molecular weight estimated by gel permeation chromatography (GPC) were 4500 and 4300, respectively, and the molecular weight distribution was 1.05. The standard polymer and eluent for GPC were polystyrene and THF, respectively. Since the calculated molecular weight is 4229, the obtained molecular weights by GPC correspond with the calculated value. The dendrimer **1** dissolves in $CHCl_3$, CH_2Cl_2, toluene, *N*-methylpyrrolidone, γ-butyrolactone, and THF up to a concentration of 10 mg mL^{-1}.

Figure 2 represents a UV–visible absorption spectrum. A 50 nm thick dendrimer **1** film prepared by spin-coating from a $CHCl_3$ solution on a quartz substrate was used. Two typical absorption peaks centered at 300 and 400 nm are observed, the former due to the triphenylamine and the latter to the *p*-phenylenevinylene.[4] Steady-state fluorescence spectra were measured with the same sample used for the measurement of absorption spectrum. Figure 3 indicates fluorescence spectra with excitation at 305 and 401 nm. Fluorescence emission with excitation at 401 nm is clearly observed, indicating that the *p*-phenylenevinylene site shows emission. On the contrary, the fluorescence intensity with excitation at 305 nm is comparably weak. There is a possibility that energy transfer occurs from the excited state of the triphenylamine group to the *p*-phenylenevinylene moiety.

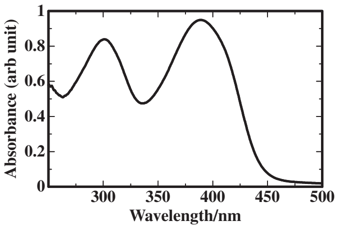

Figure 2. UV–vis absorption spectrum for a thin film of the dendrimer **1**.

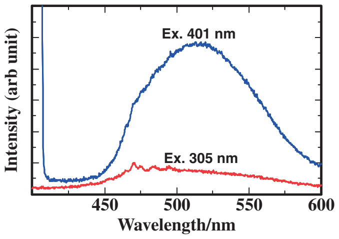

Figure 3. Fluorescence spectra for the thin film of the dendrimer with excitation at 305 and 401 nm.

In conclusion, the π-conjugated dendrimer **1** was synthesized via a convergent route. The dendrimer shows narrow molecular weight distribution, and the molecular weights by GPC correspond with the calculated value. It shows high solubility and emission. Further study related to device performance such as organic light-emitting diodes is now being attempted.

References and Notes

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5 Spectral data for **2**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.22 (m, 6H), 7.08 (d, $J = 8.4$ Hz, 4H), 7.03–6.98 (m, 4H), 6.65 (dd, $J = 18$ Hz, 11 Hz, 1H), 5.63 (d, $J = 18$ Hz, 1H), 5.14 (d, $J = 11$ Hz, 1H). Spectral data for **3**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.85 (d, $J = 1.6$ Hz, 2H), 7.79 (t, $J = 1.6$ Hz, 1H), 7.41 (d, $J = 8.4$ Hz, 4H), 7.27 (t, $J = 7.8$ Hz, 8H), 7.18 (d, $J = 16$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 8H), 7.07–7.02 (m, 8H and 2H). Spectral data for **4**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1H), 7.48 (t, $J = 7.2$ Hz, 8H), 7.39–7.37 (m, 6H), 7.11–6.96 (m, 20H), 6.73 (dd, $J = 18$ Hz, 11 Hz, 1H), 5.81 (d, $J = 18$ Hz, 1H), 5.28 (d, $J = 11$ Hz, 1H). Spectral data for **5**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 7.94 (d, $J = 1.6$ Hz, 2H), 7.91 (t, $J = 1.6$ Hz, 1H), 7.54 (s, 6H), 7.42 (d, $J = 8.8$ Hz, 8H), 7.31–7.17 (m, 4H and 16H), 7.14–7.11 (m, 4H and 16H), 7.08–7.01 (m, 16H and 4H). Spectral data for **1**; mp: 201–222 °C. TLC: $R_f = 0.395$ (One spot was observed with developing solvent of toluene/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 3H), 7.52 (s, 6H), 7.43 (s, 3H), 7.35 (s, 12H), 7.26 (s, 6H), 7.23 (d, $J = 8.4$ Hz, 24H), 7.16–7.12 (m, 12H and 48H), 7.05–6.89 (m, 18H and 96H), 6.80 (d, $J = 16$ Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 147.4, 147.1, 138.0, 137.7, 137.3, 131.2, 129.2, 128.3, 127.4, 126.6, 124.4, 123.4, 122.9.

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7 The ^{1}H NMR and IR spectra, and GPC data of dendrimer **1** are in Supporting Information. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.