Vinyl-Type Polynorbornenes with Triarylamine Side Groups: A New Class of Soluble Hole-Transporting Materials for OLEDs

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1. Experimental

General Considerations. All operations were performed under an inert nitrogen atmosphere using standard Schlenk and glove box techniques. Anhydrous grade solvents (Aldrich) were dried by passing through an activated alumina column and stored over activated molecular sieves (5Å). Spectrophotometric-grade dichloromethane was used as received from Aldrich. Commercial reagents were used without any further purification after purchasing from Aldrich (1,4-dibromobenzene, 4,4’-dibromobiphenyl, 1-naphthylamine, (1-naphthyl)phenylamine, NaO\textsubscript{t}Bu, triethylamine, \(n\)-butyllithium (2.5 M solution in hexanes), \(t\)-butyllithium (1.7 M solution in pentanes), and Strem (AgSbF\(_6\), tris(dibenzylideneacetone)dipalladium(0) (Pd\(_2\text{dba}_3\), 1,1′-bis(diphenylphosphino)ferrocene (DPPF)). \(N\)-(4-bromophenyl)-1-naphthylphenylamine (1),\(^1\) \(N\)-phenyl-\(N, N'\)-dinaphthylbenzidine,\(^2\) 5-norbornene-2-pentyl bromide\(^3\) \((\text{endo/exo} = 2:1)\), and allylchloro[\(N, N'\)-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene]palladium(II) \((\text{[(NHC)}\text{Pd(}\eta^3\text{-allyl)Cl]}\)\(^4\) were analogously synthesized according to the published procedures. 1-Octene (Aldrich) was purified by passing through an activated alumina column and stored over activated molecular sieves (5Å). CDCl\(_3\) from Cambridge Isotope Laboratories was used after drying over activated molecular sieves (5Å). NMR spectra of compounds were recorded on a Bruker Avance 400 spectrometer (400.13 MHz for \(^1\)H, 100.62 MHz for \(^{13}\)C) at ambient temperature. Chemical shifts are given in ppm, and are referenced against external Me\(_4\)Si (\(^1\)H, \(^{13}\)C). HR El–MS measurement (JEOL JMS700) was carried out at Korea Basic Science Institute (Daegu). UV–Vis and emission spectra were recorded on a Jasco V-530 and a Spex Fluorog-3 Luminescence spectrophotometer, respectively, in CH\(_2\)Cl\(_2\) solvent with a 1-cm quartz cuvette at ambient temperature. Quinine sulfate was used as the standard for determination of the quantum yields \((1 \times 10^{-5} \text{ M in } 0.5 \text{ M H}_2\text{SO}_4, \Phi_F = 0.55)\). Cyclic voltammetry experiment was performed using an AUTOLAB/PGSTAT12 system. Atomic force microscopy (AFM) measurements were carried out on a NanoMan (Veeco).

Synthesis of 2. To the toluene \((50 \text{ mL})\) slurry containing Pd\(_2\text{dba}_3\) \((0.11 \text{ g}, 0.12 \text{ mmol})\), DPPF \((0.13 \text{ g}, 0.24 \text{ mmol})\), and NaO\textsubscript{t}Bu \((1.15 \text{ g}, 12.0 \text{ mmol})\) was added a toluene solution of \(N\)-phenyl-\(N, N'\)-dinaphthylbenzidine \((3.08 \text{ g}, 6.0 \text{ mmol})\) and 1,4-dibromobenzene \((4.25 \text{ g}, 18.0 \text{ mmol})\) at room temperature. The reaction mixture was heated to reflux and stirred overnight. After cooling to room temperature, the reaction mixture was filtered over a silica bed and the filtrate was evaporated to dryness. The crude product was purified by column chromatography on silica (eluent: toluene/\(n\)-hexane = 2/1), which afforded the product as yellow powder. Yield = 3.36 g (84%).

\(^1\)H NMR (CDCl\(_3\)): \(\delta \) 6.85–6.96 (m, 3H), 7.00–7.08 (m, 6H), 7.15–7.22 (m, 2H), 7.23–7.28 (m, 2H), 7.29–7.39 (m, 8H), 7.43–7.48 (m, 4H), 7.74–7.79 (dd, \(J = 8.5/3.9 \text{ Hz, 2H})\), 7.85–7.90 (dd, \(J = 9.0/4.5 \text{ Hz, 2H})\), 7.91–7.96 (d, \(J = 9.0 \text{ Hz, 2H})\). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta \) 121.79, 122.02, 122.42, 124.02, 124.24, 126.13, 126.25, 126.33, 126.50, 126.57, 127.12, 127.22, 128.38, 128.46, 129.10, 130.97, 131.22, 131.99, 133.54, 134.60, 135.28, 142.92, 143.40, 146.62, 147.39, 147.48, 148.25. HR El–MS: \(m/z\) calcd for \(\text{C}_{44}\text{H}_{31}\text{BrN}_{2}\), 666.1671; found, 666.1671.

Synthesis of M1. To the THF solution \((50 \text{ mL})\) containing 1 \((3.09 \text{ g}, 8.3 \text{ mmol})\) was added slowly 2 equiv of \(t\)-BuLi \((9.7 \text{ mL})\) at \(-78 \text{ °C}\). The reaction mixture was stirred at this temperature for 2 h and then allowed to warm to room temperature. A THF solution \((10 \text{ mL})\) of 5-norbornene-2-pentyl bromide
(2.43 g, 10.0 mmol) was slowly added via cannula at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. After the addition of a saturated aqueous solution of NH₄Cl (30 mL), the organic portion was separated, and the aqueous layer was further extracted with ether (2 × 30 mL). The combined organic portions were dried over MgSO₄, filtered, and evaporated to dryness, affording an oily residue. The crude product was purified by column chromatography on silica (eluent: CH₂Cl₂/n-hexane = 1/4), which afforded M1 as sticky oil. Yield = 3.11 g (82%, mixture of endo and exo isomers (2/1)).

1H NMR (CDCl₃): δ 0.44–0.52 (m), 1.00–1.45 (m) (10H), 1.50–2.03 (m, 3H), 2.44–2.56 (m, 2H), 2.79 (s, 2H), 5.90 (dd, J = 5.8/3.0 Hz, Hendo), 6.00 (dd, J = 5.8/3.0 Hz, Hexo), 6.06–6.08 (m, Hexo), 6.09 (dd, J = 5.8/3.2 Hz, Hendo) (2H), 6.82–6.92 (m, 1H), 6.94–7.04 (m, 6H), 7.09–7.18 (m, 2H), 7.26–7.44 (m, 4H), 7.71 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H). 13C NMR (CDCl₃): δ 28.48, 29.57, 31.47, 32.42, 33.08, 34.70, 35.26, 36.50, 38.72, 41.84, 42.49, 45.20, 45.38, 46.32, 49.54, 120.93, 120.99, 121.60, 121.80, 122.48, 124.24, 124.34, 125.99, 126.15, 126.21, 126.29, 127.02, 127.16, 128.93, 128.97, 129.03, 131.25, 132.37, 135.22, 136.10, 136.58, 136.61, 136.82, 136.86, 143.76, 146.01, 148.42, 148.77. HR EI-MS: m/z Calcd for C₃₄H₃₅N, 457.2770; Found, 457.2766.

Synthesis of M2. A procedure analogous to that for M1 was employed with 2 (3.34 g, 5.0 mmol) to afford M2 as yellow solid. Yield = 2.72 g (72%, mixture of endo and exo isomers (2/1)).

1H NMR (CDCl₃): δ 0.45–0.52 (m), 1.00–1.43 (m) (10H), 1.52–2.03 (m, 3H), 2.46–2.58 (m, 2H), 2.78 (s, 2H), 5.91 (dd, J = 5.8/2.8 Hz, Hendo), 6.01 (dd, J = 5.7/2.8 Hz, Hexo), 6.07–6.09 (m, Hexo), 6.10 (dd, J = 5.8/3.0 Hz, Hendo) (2H), 6.90–7.10 (m, 10H), 7.15–7.22 (m, 3H), 7.30–7.39 (m, 8H), 7.42–7.49 (m, 4H), 7.76 (t, J = 8.3 Hz, 2H), 7.88 (d, J = 8.3 Hz, 2H), 7.96 (d, J = 8.3 Hz, 2H). 13C NMR (CDCl₃): δ 28.48, 28.70, 31.47, 32.41, 33.08, 34.70, 35.28, 36.50, 38.72, 41.84, 42.50, 45.19, 45.39, 46.32, 49.54, 121.07, 121.64, 121.70, 121.87, 121.94, 122.56, 124.27, 124.36, 126.05, 126.10, 126.26, 126.32, 126.36, 126.41, 126.96, 126.99, 127.05, 127.18, 128.35, 129.06, 131.22, 132.40, 133.10, 133.79, 133.93, 135.26, 136.13, 136.79, 136.84, 136.93, 143.46, 143.62, 145.87, 147.11, 147.22, 147.61, 148.34. HR EI-MS: m/z Calcd for C₅₆H₅₆N₂, 750.3974; Found, 750.3970.

Polymerization Procedure. An activated catalyst solution (2.0 μM) was prepared in situ by the addition of chlorobenzene (6.0 mL) to the mixture of [(NHC)Pd(η3-allyl)Cl] (typically ca. 7.0 mg, 12 μmol) and 1.5 equiv AgSbF₆ (ca. 6.2 mg) followed by stirring for 2 h at room temperature. The filtered solution of the activated catalyst (1.1 mL) was introduced into the chlorobenzene solution containing prescribed amounts of monomer (2.2 mmol, [Mon.]/[Pd] = 1,000) and chain transfer agent (1-octene) to initiate polymerization. All the polymerizations were carried out at 25 °C for 20 h. The mixture was poured into the large volume of acidified methanol (5% v/v, 300 mL) to precipitate the polymer. After stirring for 1 h, the precipitated polymer was collected by filtration and washed with methanol (3 × 50 mL). The polymers were purified by dissolving in CHCl₃ and reprecipitating into methanol/acetone (v/v = 4/1), which was repeated three times. The obtained polymers were finally dried in a vacuum oven at 70 °C to constant weight.

P5: 1H NMR (CDCl₃): δ 0.5–1.9 (br, 15H), 2.0–2.8 (br, 4H), 6.89 (bs, 7H), 7.08 (bs, 2H), 7.30 (bs, 4H), 7.66 (bs, 1H), 7.79 (bs, 1H), 7.91 (bs, 1H). 13C NMR (CDCl₃): δ 26.4–49.6 (br), 120.9, 122.5, 124.3,

P6: 1H NMR (CDCl3): δ 0.5–1.9 (br, 15H), 2.0–2.8 (br, 4H), 6.81 (bs, 10H), 6.92 (bs, 3H), 7.07 (bs, 8H), 7.28 (bs, 4H), 7.63 (bs, 2H), 7.76 (bs, 2H), 7.84 (bs, 2H). 13C NMR (CDCl3): δ 26.4–49.6 (br), 119.5, 121.1, 121.6, 122.5, 124.3, 126.1, 126.3, 126.9, 127.1, 128.3, 129.0, 131.2, 132.9, 133.9, 135.2, 136.5, 143.5, 145.9, 147.0, 147.5, 148.3, 150.5. Anal. Calcd for C, 89.56; H, 6.71; N, 3.73. Found: C, 89.51; H, 6.89; N, 3.85.

**Polymer Analysis.** 1H and 13C NMR spectra of the polymers were recorded on a Bruker Avance 400 spectrometer at ambient temperature in CDCl3. The molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$) of the polymers were analyzed by gel-permeation chromatography (GPC) on a Viscotek T60A equipped with UV and RI detectors using THF as an eluent at 35 °C and calibrated with narrow polystyrene standards as a reference. Thermogravimetric analyses (TGA) were performed under N2 atmosphere using a TA Instrument Q500 at a heating rate of 20 °C/min from 50 °C to 800 °C. Differential scanning calorimetry (DSC) measurement was performed on a TA Instrument Q100. Any thermal history in the polymers was eliminated by the first heating the samples at 20 °C/min, and then recording the second DSC scan at 10 °C/min to the decomposition temperature.

**Cyclic Voltammetry.** Cyclic voltammetry measurements were carried out with a three-electrode cell configuration consisting of platinum working and counter electrodes and a Ag/AgNO3 (0.1 M in CH3CN) reference electrode at room temperature. The solvent was CH2Cl2 and 0.1 M tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte. The oxidation potentials were recorded at a scan rate of 50 mV/s and reported with reference to the ferrocene/ferrocenium (Fc/Fc+) redox couple.

**Fabrication of Electroluminescence Devices.** EL devices (I–II) having the following configurations were fabricated: ITO/P5–P6/Alq3/LiF/Al. For a reference device (III), the device incorporating NPB as a hole-transporting layer (HTL) was fabricated by vacuum deposition method: ITO/NPB/Alq3/LiF/Al. The polymer was spin-coated onto a plasma treated (Plasma Cleaner PDC-32G, Harrick Plasma) ITO/glass substrate as a hole-transporting layer (HTL) from a chlorobenzene solution (1 wt%) at 3,000 rpm and then dried at 80 °C on a hot plate for 30 min in the glove box. The film thickness of HTL layer was determined with AFM and was measured to be ca. 50 nm. After the drying process, a sample coated with P5 or P6 and a blank sample were brought into a deposition chamber. Using a selective shadow mask, 50-nm-thick NPB layer was deposited onto the blank samples, and then, the mask was changed with the one having an opening for all the samples. In such way, Alq3 (40 nm), LiF (1 nm), and Al (100 nm) were successively deposited on top of each HTLs (P5–P6 and NPB) at the same time. The vacuum deposition was done under high vacuum (~7 × 10−7 torr) with the following deposition rates: 0.5~1.0 Å/s for NPB and Alq3, 0.5 Å/s for LiF, and 3 Å/s for Al electrode. EL spectra were obtained with a fiber optic spectrometer (EPP2000, StellarNet) in nitrogen environment. Current–voltage ($J$–$V$) and luminance–voltage ($L$–$V$) characteristics were recorded on a source-measure unit (Keithley 2400) and a calibrated photodiode (FDS100, Thorlab).
References

Figure S1. $^1$H (top) and $^{13}$C (bottom) NMR spectra of M1 († from endo isomer and ‡ from exo isomer; endo/exo = 2/1).

Figure S2. $^1$H (top) and $^{13}$C (bottom) NMR spectra of M2 († from endo isomer and ‡ from exo isomer; endo/exo = 2/1).
Figure S3. $^1$H spectra of P5 and P6 (* and § from residual CHCl$_3$ and H$_2$O, respectively, in deuterated chloroform).
Figure S4. TGA curves of P5 and P6.

Figure S5. DSC curves of P5 and P6.
Figure S6. GPC traces of P5 and P6.

Figure S7. UV–vis absorption and PL spectra of M1–M2, P5–P6, and molecular NPB.
Figure S8. Cyclic voltammograms of (a) P5, (b) P6, (c) molecular NPB showing reversible oxidation.
Figure S9. Plots for (a) External quantum efficiency vs. current density and (b) Luminous efficiency vs. current density for the devices (I–III).