Hole mobilities of thermally polymerized triaryldiamine derivatives and their application as hole-transport materials in organic light-emitting diodes (OLEDs)

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ABSTRACT

This paper describes the synthesis of three triaryldiamine derivatives presenting two thermally polymerizable trifluorovinyl ether groups that can be polymerized through thermal curing to form perfluorocyclobutyl (PFCB) polymers. These PFCB polymers, studied using time-of-flight techniques for the first time, exhibited remarkable non-dispersive hole-transport properties, with values of μ_h of ca. 10^{-4} cm^2 V^{-1} s^{-1}. When we employed these thermally polymerized polymers as hole-transport layers (HTLs) in electroluminescence devices containing tris(8-hydroxyquinolate) aluminum (Alq$_3$) as the emission layer, we obtained high current densities (ca. 3400 mA cm^{-2}), impressive brightnesses (5×10^4 cd m^{-2}), and high external quantum efficiencies (EQEs = 1.43%). These devices exhibited the same turn-on voltage, but higher EQEs, relative to those incorporating the vacuum-processed model compound N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (α-NPD) (EQE = 1.37%) as the HTL under the same device structure.

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1. Introduction

Organic and polymer light-emitting diodes are promising devices for use in future lighting and display applications because of their low power consumption, light weight, fast response, and wide viewing angle [1,2]. To increase their efficiency, most organic light-emitting diodes (OLEDs) are configured with a variety of functional materials into a multilayer structure—fabricated through successive vacuum deposition of small molecules—and then covered by a metal cathode. It is generally inherently difficult to form polymer-based OLEDs in multilayer structures through solution-processing techniques, such as spin-coating, because of solvent erosion of the previously deposited layers during spin-coating [3]. One of the most promising approaches toward achieving purely solution-processed multiple-layer polymer-based OLEDs is utilizing soluble precursor materials to produce insoluble polymer networks through polymerization and/or cross-linking reactions. This strategy allows the sequential deposition of various functional layers [4,5]. The flexibility of using the chemical modifications of a wide variety of materials

possessing various functional moieties—such as siloxan [6–9], norbornene [10,11], oxetane [4,5], vinyl [12,13], and trifluorovinyl ether [14–18] units—as polymerizable groups under UV irradiation or thermal curing allows the construction of copolymers in nearly any designated composition. For example, trifluorovinyl ether (TFVE)-containing compounds are useful as reactive monomers that undergo thermal cyclopolymerization to afford a new class of thermally stable perfluorocyclobutane (PFCB) polymers [19–21]. Taking advantage of this strategy, PFCB-based hole-transport materials have been developed to increase the efficiency of OLED devices [22–28]. This superior performance is ascribed mainly to the homogeneous surface morphology of the thermally treated thin films, as probed using atomic force microscopy (AFM). Nevertheless, to the best of our knowledge, the intrinsic charge transporting characteristic, one of the most critical factors in optoelectronic devices, of PFCB-based hole-transport materials has not been reported previously. In this paper, we report the synthesis, characterization, and application of three triaryldiamine derivatives attached to two thermally polymerizable trifluorovinyl ether (TFVE) groups that can be polymerized through thermal curing to form PFCB polymers. More importantly, we have used time-of-flight (TOF) techniques to study the hole-transport properties of these polymers. We have found that PFCB-based polymers possess remarkable hole-transport properties, with values of μ_h of ca. 10^{-4} cm^2 V^{-1} s^{-1}. These thermally polymerized polymers are useful as hole-transport layers (HTLs) in electroluminescence (EL) applications, as evidenced by the high external quantum efficiency of 1.43% achieved when employing one such system with tris(8-hydroxyquinolate) aluminum (Alq$_3$) as the emission layer.

2. Experimental

2.1. Synthesis

Compound 5: Compound **4** (5.08 g, 10 mmol), *N*-phenyl-1-naphthylamine (4.39 g, 20 mmol), Pd(OAc)$_2$ (67 mg, 0.3 mmol), and sodium *tert*-butoxide (7.68 g, 80 mmol) were dissolved in toluene (100 mL) and then tri-*tert*-butylphospine (6 mL, 0.05 M in toluene, 0.3 mmol) was added. The mixture was heated under reflux under argon for 72 h and then quenched with water. The solution was partitioned between ethyl acetate and brine. The combined organic extracts were dried (MgSO$_4$) and concentrated. The resulting solid was washed with hexane to afford a yellow product (6.41 g, 82%). M.p. 254–255 °C. IR (KBr) ν 3544 (w), 3055 (w), 1609 (m), 1592 (s), 1573 (m), 1507 (s), 1489 (s), 1464 (s), 1434 (m), 1392 (m), 1302 (m), 1269 (s), 1172 (m), 1015 (m) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.29 (s, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.56–7.48 (m, 6H), 7.37 (t, J = 7.4 Hz, 2H), 7.28 (d, J = 7.2 Hz, 2H), 7.16 (t, J = 7.6 Hz, 4H), 6.92–6.84 (m, 8H), 6.78 (s, 2H), 6.51 (d, J = 8.8 Hz, 4H), 6.41 (d, J = 8.4 Hz, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 155.5, 152.2, 147.5, 146.5, 142.6, 135.3, 134.7, 132.9, 130.1, 129.1, 128.4, 128.2, 126.6, 126.4, 126.3, 126.1, 123.4, 121.6, 121.1, 120.4, 120.2, 118.8,

114.6, 63.0. MS (FAB$^+$, m/z) 785 (100), 784 (65), 154 (70), 136 (65), 57 (65). HRMS (FAB$^+$, [M+H]$^+$) Calcd. C$_{57}$H$_{41}$N$_2$O$_2$ 785.3170, found 785.3165.

Compound 6: A mixture of **5** (2.93 g, 3.73 mmol) and triethylamine (3 mL, 21.6 mmol) in dry dichloromethane (260 mL) was cooled to −10 °C. Trifluoromethanesulfonic anhydride (1.9 mL, 11.2 mmol) in dry dichloromethane (90 mL) was added dropwise and then the reaction mixture was warmed to room temperature and stirred for 16 h. The reaction was quenched by pouring the mixture into ice water. The organic layer was separated and the aqueous phase was extracted twice with dichloromethane. The combined organic extracts were washed with saturated NaHCO$_3$ solution and brine and then dried (MgSO$_4$). The solvents were evaporated and the resulting residue was purified through re-precipitation from dichloromethane and methanol to afford a yellow product (3.18 g, 81%). M.p. 136–138 °C. IR (KBr) ν 3059 (w), 1609 (m), 1592 (m), 1573 (m), 1494 (s), 1468 (s), 1455 (m), 1426 (s), 1392 (m), 1271 (m), 1249 (m), 1212 (s), 1140 (s), 884 (m), 774 (m) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.96 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.53–7.46 (m, 4H), 7.37–7.27(m, 8H), 7.15 (t, J = 7.6 Hz, 4H), 7.00 (d, J = 8.4 Hz, 4H), 6.92–6.89 (m, 4H), 6.84 (d, J = 8.4 Hz, 6H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 149.9, 147.7, 147.2, 146.9, 145.0, 142.3, 134.7, 132.8, 129.9, 129.3, 129.0, 128.4, 126.7, 126.5, 126.4, 126.3, 126.0, 123.2, 121.8, 121.3, 121.1, 120.8, 119.6, 118.3,116.4, 63.6. MS (FAB$^+$, m/z) 1048 (100), 916 (15), 690 (20), 218 (40), 217 (35). HRMS (FAB$^+$, M$^+$) Calcd. C$_{59}$H$_{38}$F$_6$N$_2$O$_6$S$_2$ 1048.2075, found 1048.2076.

TFVE1: **1** (380 mg, 0.87 mmol), **2** (515 mg, 2.18 mmol), Pd(OAc)$_2$ (10 mg, 0.04 mmol), and sodium *tert*-butoxide (210 mg, 2.18 mmol) were dissolved in toluene (10 mL) and then tri-*tert*-butyl phosphine (1.6 mL, 0.05 M in toluene, 0.08 mmol) was added. The mixture was heated under reflux under argon for 24 h and then quenched with water. The solvent was evaporated and then the reaction mixture was extracted with dichloromethane and dried (MgSO$_4$). The crude product was purified through column chromatography (SiO$_2$; EtOAc/hexane, 1:15) to afford **TFVE1** (485 mg, 72%) as a white solid. IR (KBr) ν 3046 (w), 1600 (w), 1497 (s), 1460 (w), 1397 (m), 1311 (m), 1274 (s), 1192 (m), 1159 (m), 1136 (m) cm^{-1}. ^{1}H NMR (acetone-d_6, 400 MHz): δ 7.98 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 8.0 Hz, 2H), 7.52–7.45 (m, 6H), 7.43–7.36 (m, 4H), 7.14–7.07 (m, 8H), 7.00 (d, J = 8.0 Hz, 4H). ^{13}C NMR (acetone-d_6, 100 MHz): δ 148.0, 146.3, 143.8, 136.2, 134.5, 131.8, 129.3, 127.9, 127.8, 127.6, 127.3, 127.2, 127.0, 124.5, 124.2, 122.3, 117.6. ^{19}F NMR (acetone-d_6, 376 MHz): δ −117.1 (dd, J = 99.6, 55.6 Hz, 2 F), −124.3 (dd, J = 108.3, 99.3 Hz, 2F), 130.6 (dd, J = 108.3, 56.4 Hz, 2F). MS (FAB$^+$, m/z) 780 (100), 467 (25), 217 (35). HRMS (FAB$^+$, M$^+$) Calcd. C$_{47}$H$_{28}$N$_4$ 780.2211, found 780.2208.

TFVE2: A flask containing **3** (2.46 g, 4.88 mmol), 1-aminonaphthalene (2.09 g, 14.6 mmol), Pd$_2$(dba)$_3$ (224 mg, 0.25 mmol), and sodium *tert*-butoxide (1.41 g, 14.7 mmol) was evacuated and recharged with argon, then dry toluene (30 mL) and tri-*tert*-butylphosphine (9.8 mL,