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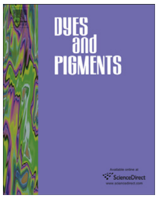

New derivatives of triphenylamine and naphthalimide as ambipolar organic semiconductors: Experimental and theoretical approach

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ABSTRACT

Four new derivatives of triphenylamine containing different number of naphthalimide moieties were designed and synthesized by Suzuki condensation and their properties were studied by the experimental and theoretical tools. The compounds obtained are capable to form molecular glasses with glass transition temperatures ranging from 45 °C to 84 °C. They exhibit very high thermal stabilities with 5% weight loss temperatures ranging from 429 °C to 483 °C. Fluorescence quantum yields of the dilute solutions in nonpolar solvents of the synthesized materials range from 0.63 to 0.78. Due to the pronounced electron donor–acceptor character, the compounds show dramatic solvatochromic red shifts of fluorescence (up to 250 nm) in polar solvents. The ionization potentials of the solid samples of the compounds established by electron photoemission spectrometry in air ranged from 5.57 to 6.01 eV. 4-(4′-(Di-(4″-methoxyphenyl)amino)phenyl)-*N*-(2-ethylhexyl)-1,8-naphthalimide (**5**) was found to show ambipolar charge transport in air with the mobilities of charges exceeding 10^{-4} $cm^2 V^{-1} s^{-1}$ at high electric fields. The electron mobility of the compounds containing no methoxy groups were found to exceed the hole mobility by 2–3 orders of magnitude. The special role of methoxy groups in the ambipolar charge transport character of compound **5** is discussed in the frame of hopping Marcus theory, by applying a static theoretical analysis followed by a qualitative discussion of the positional disorder in some of these materials.

1. Introduction

In the last decades many kinds of organic hole-transporting amorphous molecular materials were reported [1]. Lesser assortment is available of glass-forming electron-transporting organic molecular materials especially those capable of working in air [2,3]. Even smaller amount of amorphous organic molecular materials capable of effectively transporting both holes and electrons were reported, however such materials recently attract much attention [4,5]. Ambipolar charge-transporting materials are of interest for applications in organic light emitting diodes (OLED) [6] and in particular in electrophosphorescent devices [7a]. In the continual effort to search for ideal materials for OLEDs, small molecules with ambipolar charge transporting character are extremely attractive as they offer the possibility to achieve efficient and stable OLEDs even in a simple single-layer configuration. Organic ambipolar semiconductors are divided into two categories [4]. One category is represented by materials the molecules of which consist both of donor and acceptor moieties. Such materials are widely studied as dyes for dye sensitized solar cells [7b]. The materials composed of the molecules having no donor–acceptor structure are assigned to another category. The molecules of the latter category usually have extended systems of conjugated π-electrons. Most of the ambipolar organic semiconductors are capable of transporting both holes and electrons when protected from air. Much less information is reported on the materials capable of transporting both negative and positive charges at ambient conditions [8,9].

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In this article we report on the synthesis and properties of organic semiconductors consisting of 1,8-naphthalimide and triphenylamine (TPA) moieties capable of effectively transporting both holes and electrons in air. 1,8-Naphthalimide derivatives represent an interesting group of electron-deficient organic materials with promising electron-transporting properties [10]. Electron-rich TPA derivatives have been typically used as hole-transporting materials and/or blue light emitting materials [11] due to the easy oxidizability of the nitrogen centre and the ability to transport positive charges via the radical-cation species. These properties are related to the presence of nitrogen atom linked to three electron rich phenyl groups in a three-dimensional propeller-like shape [12]. The photoinduced electron transfer was recently observed in the solutions of the derivatives of 1,8-naphthalimide and TPA [13]. Hydrazones containing 1,8-naphthalimide and triphenylamino moieties were found to be capable of transporting only positive charges in air [14]. To our knowledge no studies demonstrating ambipolar charge transport in the derivatives of 1,8-naphthalimide and TPA were yet reported.

The role of different substituents on the ionization potentials and other parameters of TPA-based compounds has been already considered [15–18]. It is well established that methoxy groups decrease the ionization potentials of the TPA-based compounds [15,16], influencing consequently the hole-injection barrier in the devices. However, lower charge mobility was recorded for instance in the case of *p*-methoxy and *p*-buthoxy substituted *N*,*N*′-bis(*m*-tolyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (TPD) as compared to the non-substituted TPD, which was in part explained by the role of the disorder on the dipole moments of these molecules [17]. Interestingly, the hole transporting properties of TPA-based compounds were recently found to be enhanced by the presence of methoxy groups in para-positions of the phenyl moieties [19], which was partly explained by the hydrogen-bonding capacity of the methoxy groups. As it will be shown in the following, among the newly synthesized compounds, the ambipolar charge transport properties of one of them containing methoxy groups are superior, as compared to the compounds containing no methoxy groups. It is consequently very intriguing to understand the reasons for the higher electron-versus hole mobilities on the one hand, and for the higher hole mobility of the methoxy-substituted compound (by three orders of magnitude) as compared to the non-substituted ones.

By applying a joint experimental and theoretical approaches, the aim of this study is twofold: (i) report on the synthesis of four new derivatives of TPA containing direct linkages with a different number of naphthalimide moieties (ii) characterization of the four new compounds for better understanding of the structure–property relationships. The hole-transport properties of these amorphous compounds are discussed in the frame of Marcus theory [20–23].

2. Experimental

2.1. Synthesis

Materials. 4-Bromo-1,8-naphtalic anhydride, 4-bromoaniline and 2-ethylhexylamine purchased from TCI, TPA, 1-iodo-4-methoxybenzene, tris(4-bromophenyl)amine, 4-(diphenylamino)phenylboronic acid, *n*-BuLi (2.5 mol L^{-1} in hexane), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, bis(-triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$), *N*-bromosuccinimide (NBS) and 1,10-phenanthroline purchased from Aldrich were used as received. Dimethylformamide (DMF, Lachema) was dried by distillation over CaH_2. THF was dried and distilled over sodium and benzophenone. Dichloromethane (POCH), ethyl acetate and *n*-hexane (Penta) were purified and dried using the standard procedures [24]. 4-Bromo-*N*-(2-ethylhexyl)-1,8-naphthalimide (**1**) [14], (4-bromo-phenyl)-di-(4-methoxyphenyl)-amine (**2b**) [25], bis(4-bromophenyl)phenylamine (**2c**) [26], bis(4-(4,4,5,5-tetramethyl-(1,3,2)dioxaborolan-2-yl)-phenyl)phenylamine (**3c**) [27], 4-(4,4,5,5-tetramethyl-(1,3,2)dioxaborolan-2-yl)-phenyl)-di-(4-methoxyphenyl)-amine (**3b**) [28], tris(4-(4,4,5,5-tetramethyl-(1,3,2)dioxaborolan-2-yl)-phenyl)phenylamine (**3d**) [29] were prepared according to the published procedures.

2.1.1. 4-(4′-Diphenylaminophenyl)-N-ethylhexyl-1,8-naphthalimide (4)

The solution of 4-bromo-1,8-naphthalimide (**1**) (0.5 g, 1.29 mmol) and $Pd(PPh_3)_2Cl_2$ (0.03 g, 0.04 mmol) in THF (15 mL) was purged with nitrogen, and the solution of 4-(diphenylamino)phenylboronic acid (0.37 g, 1.28 mmol) in THF (3 mL) and aqueous K_2CO_3 solution (1.70 g, 12.32 mmol) in H_2O (2 mL) were added with a syringe. The reaction mixture was stirred at 80 °C for 24 h. After cooling down, the product was extracted with CH_2Cl_2, washed with water and dried over $MgSO_4$. The solvent was evaporated to afford a crude product. After column chromatography on silica gel with the eluent mixture of ethyl acetate and hexane (1:8, V:V), compound **4** was obtained as yellow powder with the yield of 0.55 g (78%). M.p. 127–128 °C; $R_f = 0.54$; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.67 (d, 1H, $J = 7.32$ Hz, $H_{Naphthalene}$), 8.66 (d, 1H, $J = 8.52$ Hz, $H_{Naphthalene}$), 8.46 (d, 1H, $J = 1.16$ Hz, $H_{Naphthalene}$), 8.43 (d, 1H, $J = 1.15$ Hz, $H_{Naphthalene}$), 7.75 (t, 1H, $J = 7.56$ Hz, $H_{Naphthalene}$), 7.44–7.31 (m, 6H, –Ar), 7.27–7.09 (m, 8H, –Ar), 4.26–4.11 (m, 2H, $-CH_2$, $-H_{aliphatic}$), 2.06–1.95 (m, 1H, –CH, $-H_{aliphatic}$), 1.48–1.31 (m, 8H, 4 × CH_2, $-H_{aliphatic}$), 1.01–0.89 (m, 6H, 2 × CH_3, $-H_{aliphatic}$). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 167.43, 147.76, 146.75, 146.14, 132.85, 131.90, 131.48, 131.29, 130.31, 130.05, 129.31, 128.42, 127.93, 126.73, 125.78, 124.77, 123.83, 121.64, 43.87, 38.14, 31.73, 28.88, 24.59, 23.47, 14.44, 10.82. IR (KBr, υ cm^{-1}): 3060 (CH_{ar}), 2954, 2925, 2858 ($CH_{aliphatic}$), 1697 ($C{=}O_{anhydride}$), 1656, 1584, 1505, 1486 ($C{=}C_{ar}$), 1350, 1279 (C–N), 784, 759, 695 (CH_{ar}); Anal. Calcd. for $C_{38}H_{36}N_2O_2$: C, 82.58; H, 6.57; N, 5.07; O, 5.79. Found: C, 82.63; H, 6.60; N, 5.08. MS (APCI$^+$, 20 V), *m*/*z*: 553 ($[M + H]^+$)

2.1.2. 4-(4′-(Di-(4″-methoxyphenyl)amino)phenyl)-N-(2-ethylhexyl)-1,8-naphthalimide (5)

4-(4′-(Di-(4″-methoxyphenyl)amino)phenyl)-*N*-(2-ethylhexyl)-1,8-naphthalimide (**5**) was prepared by the similar procedure as **4** using **3b** (0.58 g, 1.42 mmol), **1** (0.5 g, 1.29 mmol), $Pd(PPh_3)_2Cl_2$ (0.03 g, 0.039 mmol), K_2CO_3 (1.78 g, 12.89 mmol). The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (1:8, V:V) as an eluent to obtain **5** as amorphous material with the yield of 0.59 g (75%); $R_f = 0.51$; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (d, 1H, $J = 7.37$ Hz, $H_{Naphthalene}$), 8.64 (d, 1H, $J = 7.44$ Hz, $H_{Naphthalene}$), 8.45 (d, 1H, $J = 1.14$ Hz, $H_{Naphthalene}$), 7.73 (t, 2H, $J = 8.19$ Hz, $H_{Naphthalene}$), 7.35 (d, 2H, $J = 8.81$ Hz, –Ar), 7.20 (d, 4H, $J = 9.05$ Hz, –Ar), 7.08 (d, 2H, $J = 8.78$ Hz, –Ar), 6.92 (d, 4H, $J = 9.05$ Hz, –Ar), 4.24–4.12 (m, 2H, $-CH_2$, $-H_{aliphatic}$), 3.85 (s, 6H, 2 × OCH_3), 2.04–1.94 (m, 1H, –CH, $-H_{aliphatic}$), 1.48–1.30 (m, 8H, 4 × CH_2, $-H_{aliphatic}$), 1.01–0.90 (m, 6H, 2 × CH_3, $-H_{aliphatic}$). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 164.95, 156.78, 149.49, 147.29, 140.44, 133.20, 131.33, 130.87, 130.09, 127.87, 127.71, 127.32, 126.84, 123.12, 121.28, 119.63, 115.12, 55.72, 44.33, 38.15, 30.97, 28.96, 24.38, 23.33, 14.36, 10.89. IR (KBr, υ cm^{-1}): 3037 (CH_{ar}), 2955, 2927, 2856 ($CH_{aliphatic}$), 1698 ($C{=}O_{anhydride}$), 1657, 1586, 1504, 1463 ($C{=}C_{ar}$), 1440, 1425 (OCH_3), 1354, 1282 (C–N), 784, 758, 656 (CH_{ar}). Anal. Calcd. for $C_{40}H_{40}N_2O_4$: C, 78.40; H, 6.58; N, 4.57; O, 10.44. Found: C, 78.45; H, 6.65; N, 4.52. MS (APCI$^+$, 20 V), *m*/*z*: 613 ($[M + H]^+$)