



Symmetry *versus* asymmetry: Synthesis and studies of benzotriindole-derived carbazoles displaying different electrochemical and optical properties



Renji R. Reghu, Dmytro Volyniuk, Nataliya Kostiv, Karolis Norvaisa, Juozas V. Grazulevicius*

Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu pl. 19, LT-50254, Kaunas, Lithuania

ARTICLE INFO

Article history:

Received 29 July 2015

Received in revised form

4 October 2015

Accepted 6 October 2015

Available online 29 October 2015

Keywords:

Benzotriindole

Carbazole

Hole-transport

Cyclic voltammetry

Ionization potential

Glass-transition

ABSTRACT

Symmetrically and asymmetrically derived benzotriindole (diindolocarbazole) cores and their triply functionalized carbazolyl derivatives were synthesized and characterized. The synthesized compounds showed relatively high glass-transition temperatures. Carbazolyl substitutions at the periphery of benzotriindole cores improved their glass-forming ability as well as the thermal stability. Asymmetric benzotriindoles showed red-shifted absorption and emission spectra. Relatively decreased optical band gaps of the asymmetric derivatives suggested pronounced electronic communication between the indole segments and more effective π -conjugation in these derivatives. Oxidative redox profiles were distinct for differently linked benzotriindoles as characterized by cyclic voltammetry. Asymmetric benzotriindoles oxidized at comparatively lower potential and facilitated electropolymerization. Ionization potentials of thin films of the benzotriindole derivatives measured by photoelectron spectroscopy ranged from 4.95 to 5.43 eV. The method of charge extraction by linearly increasing voltage unlocked the hole-transport in both the symmetric and asymmetric benzotriindoles. Symmetric nature of benzotriindoles promoted the hole-transport in thin films.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Broad academic and industrial interest on new organic electroactive materials for the development of economically viable electronic devices like organic light emitting diodes, organic and hybrid solar cells or organic field-effect transistors has been continuously growing over the years [1–4]. Most of the known organic electronic devices extensively utilize hole-transporting materials not only to transport the charges but also to deliver other inherited properties, for example, light absorption and emission, facile and stable oxidation and reduction under applied potential, competent stability under heat and/or capability of glass-formation [5–7]. Carbazole-based compounds occupy the foremost position of widely studied hole-transporting materials since they offer feasible functionalization at various positions and thus afford the fine-tuning of their decisive properties for electronic applications [8–10]. Tailoring the properties of carbazoles and the related

derivatives *via* the manipulation of their molecular structures constitutes an intense research topic in recent years [11,12].

Benzotriindole can be regarded as a derivative of triply bounded carbazoles that share a benzene ring. Symmetric benzotriindoles, readily available by either cyclocondensation of indolin-2-one or bromine-mediated cyclocondensation followed by reductive dehydrohalogenation of indole, were extensively studied for organic electronics [13–19]. Tuning of key molecular properties of this cyclic trimer was also explored by incorporating either various alkyl chains for enhancing both solution processability and π -stacking capability or bulky chromophores for promoting both morphological stability and electronic coupling through the molecular backbone [16–21]. Despite of the fact that the symmetric benzotriindole derived compounds were thoroughly investigated to survey their electronic properties, limited attempts were made to engineer the triindole core to improve the electronic communication between the indole segments [22]. It is known that the structural modification of benzotriindole by symmetry lowering is an interesting strategy for improving their electronic properties [22]. However, in contrast to the well-studied symmetric

* Corresponding author. Tel.: +370 37 300193; fax: +370 37 300152.

E-mail address: juozas.grazulevicius@ktu.lt (J.V. Grazulevicius).

benzotriindole, its asymmetric analogue remains relatively unexplored for the application in organic electronics.

We have previously reported on the dissimilar characteristics including charge-transporting properties of carbazolyl derivatives with the different linking topologies [23–26]. Synthesis, properties and various potential applications of indolocarbazole derivatives, which can be regarded as dimerised carbazoles sharing a benzene ring, were also well documented [27–30]. Since benzotriindole is an annulated carbazolyl derivative that offers synthetic accessibility and flexibility towards functionalization, we envisaged that comparing the properties of triindole-derivatives with the different linking topology would be of interest to thoroughly elucidate their structure-property relationship. We report herein the synthesis, thermal, electrochemical, photophysical and photoelectrical properties of symmetric and asymmetric benzotriindole-derived carbazoles.

2. Experimental section

2.1. Materials

All commercially available materials were used as received. Solvents were dried and distilled prior to use. The reagents and required materials, i.e., 5-bromoisatin, 5-bromoindole, carbazole, 1-bromohexane, 1-bromoethane, hydrazine hydrate, phosphoryl chloride, tetrakis(triphenylphosphine) palladium(0), potassium carbonate, glacial acetic acid, lithium aluminum hydride, 3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetra-n-butylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$), were purchased from Sigma Aldrich. 5-Bromo-*N*-ethylisatin [20], 5-bromo-*N*-ethylindole [31], 5-bromo-*N*-ethylloxindole [20], 3, 8, 13-tribromo-5, 10, 15-triethyltriindole [20,21] and 9-hexyl-9*H*-carbazol-3-yl boronic acid pinacol ester [32] were synthesized according to the literature procedures. Synthetic procedures and structural characterization data for the new compounds are given below.

2.2. 3, 3-Bis(5-bromo-*N*-ethyl indolyl)- 5-bromo-*N*-ethylloxindole (5)

To a solution of 5-bromo-*N*-ethylindole (2 g, 8.92 mmol) in glacial acetic acid (40 mL), 5-bromo-*N*-ethylisatin (1.14 g, 4.46 mmol) was added and the reaction mixture was thoroughly stirred for 24 h at 35 °C under argon. The resulting slurry was collected by filtration, washed with ethanol and dried under vacuum. Yield = 91%; white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ ppm): 7.48–7.45 (m, 3H), 7.36 (d, $J = 2$ Hz, 1H), 7.25–7.22 (m, 2H), 7.18 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8$ Hz, 1H), 6.79 (s, 2), 4.08 (q, $J = 7.2$ Hz, 4H), 3.88 (q, $J = 7.2$ Hz, 2H), 1.41–1.35 (m, 9H). Found: C, 52.83; H, 3.71; N, 6.30%; molecular formula $\text{C}_{30}\text{H}_{26}\text{Br}_3\text{N}_3\text{O}$ requires C, 52.66; H, 3.83; Br, 35.03; N, 6.14; O, 2.34%. MS (EI) $m/z = 685.2$ ($[\text{M}+1]^+$).

2.3. 5, 5', 5''-Tribromo-1, 1', 1''-triethyl-3,2':3',3''-ter-1*H*-indole (6)

A solution of compound 5 (1.2 g, 1.75 mmol) in dry THF (25 mL) was cooled to 0 °C and lithium aluminium hydride solution (1.75 mL, 1 M in THF) was added dropwise under argon atmosphere. The mixture was stirred for 1 h at 0 °C and then at room temperature for additional 12 h. The reaction mixture was cooled to 0 °C and water was added slowly. The organic layer was extracted using ethyl acetate, dried over sodium sulfate and evaporated. The crude product was purified by silica gel column chromatography using hexane and ethyl acetate in a volume ratio of 5:1 as an eluent. Yield = 80%; white solid. $^1\text{H NMR}$ (700 MHz, CDCl_3 , δ ppm): 7.76 (d, $J = 1.4$ Hz, 1H), 7.46 (d, $J = 2.1$ Hz, 1H), 7.36–7.32 (m, 2H), 7.27–7.24 (m, 2H), 7.20 (d, $J = 9.1$ Hz, 1H), 7.16 (d, $J = 1.4$ Hz, 1H), 7.13–7.05 (m,

3H), 4.22 (q, $J = 7$ Hz, 2H), 4.11 (q, $J = 7$ Hz, 4H), 1.38 (t, $J = 7$ Hz, 3H), 1.33 (t, $J = 7$ Hz, 3H), 1.25 (t, $J = 7$ Hz, 3H). Found: C, 53.65; H, 4.09; N, 6.15%; molecular formula $\text{C}_{30}\text{H}_{26}\text{Br}_3\text{N}_3$ requires C, 53.92; H, 3.92; Br, 35.87; N, 6.29%. MS (EI) $m/z = 669.2$ ($[\text{M}+1]^+$).

2.4. 2,9,14-Tribromo-5,6,11-triethyl-6,11-dihydro-5*H*-diindolo[2,3-*a*:2',3'-*c*]carbazole (4)

DDQ (240 mg, 1.06 mmol) in dry 1,4-dioxane (10 mL) was added dropwise to a solution of compound 6 (600 mg, 0.89 mmol) in dry 1,4-dioxane (5 mL) under argon atmosphere. The resulting reaction mixture was stirred thoroughly for 72 h at room temperature. The solid formed in the reaction mixture was filtered off and washed with 1,4-dioxane. The filtrate was evaporated at reduced pressure, washed with 10% NaOH solution and extracted using ethyl acetate. The organic layer was dried over sodium sulfate and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane: ethyl acetate (5:1) mixture as eluent. Yield = 58%; yellow solid. $^1\text{H NMR}$ (700 MHz, CDCl_3 , δ ppm): 8.91 (s, 1H), 8.85 (s, 1H), 8.54 (s, 1H), 7.64–7.58 (m, 3H), 7.56–7.52 (m, 3H), 4.94–4.60 (m, 6H), 1.75 (t, $J = 7$ Hz, 3H), 0.90 (t, $J = 7$ Hz, 3H), 0.79 (t, $J = 7$ Hz, 3H). IR (KBr, ν cm^{-1}): (aliphatic C–H) 2967, 2927, 2868; (Ar C=C) 1604, 1571; (Ar C–N) 1464, 1445. Found: C, 54.25; H, 3.61; N, 6.47%; molecular formula $\text{C}_{30}\text{H}_{24}\text{Br}_3\text{N}_3$ requires C, 54.08; H, 3.63; Br, 35.98; N, 6.31%. MS (EI) $m/z = 666.2$ (M^+).

2.5. General procedure for Suzuki–Miyaura reactions

Tribromo benzotriindole 3 or 4 (150 mg, 0.22 mmol), 9-hexyl-9*H*-carbazol-3-yl boronic acid pinacol ester (280 mg, 0.74 mmol), potassium carbonate (182 mg, 1.32 mmol) and tetrakis(triphenylphosphine) palladium(0) (12 mg, 0.01 mmol) were charged into a Schlenk flask and degassed. A degassed solvent mixture of THF (12 mL) and water (2 mL) was added to the reaction mixture and purged with argon for 5 min. The reaction mixture was stirred for 16 h at 80 °C under argon atmosphere. After cooling down to the room temperature, the reaction mixture was diluted with water and extracted using ethyl acetate. The organic layer was dried over sodium sulfate and evaporated under reduced pressure. The resulting crude product was purified by column chromatography using silica gel as stationary phase. A solvent mixture of hexane and ethyl acetate in a volume ratio of 10:1 was used as eluent for both the compounds 1 and 2.

2.6. 3,8,13-Tri(9-hexyl-9*H*-carbazol-3-yl)-5,10,15-triethyl-10,15-dihydro-5*H*-diindolo[3,2-*a*:3',2'-*c*]carbazole (1)

Yield = 67%; white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ ppm): 8.72 (s, 3H), 8.51 (s, 3H), 8.25 (d, $J = 4.4$ Hz, 3H), 7.92 (d, $J = 5.2$ Hz, 3H), 7.85 (d, $J = 4.4$ Hz, 3H), 7.77 (d, $J = 4.4$ Hz, 3H), 7.57–7.52 (m, 6H), 7.48 (d, $J = 4.4$ Hz, 3H), 7.31 (t, $J = 4.4$ Hz, 3H), 5.15 (q, $J = 4$ Hz, 6H), 4.37 (t, $J = 4$ Hz, 6H), 1.98–1.93 (m, 6H), 1.81 (t, $J = 4$ Hz, 9H), 1.49–1.23 (m, 24H), 0.92 (t, $J = 4$ Hz, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , δ ppm): 140.9, 140.0, 139.6, 139.2, 134.4, 133.9, 125.8, 125.6, 124.1, 123.5, 123.1, 122.8, 120.5, 120.4, 119.0, 118.8, 110.4, 109.0, 108.9, 103.6, 43.3, 42.1, 31.7, 29.1, 27.1, 22.7, 16.0, 14.1. IR (KBr, ν cm^{-1}): (arene C–H) 3046; (aliphatic C–H) 2951, 2924, 2852; (Ar C=C) 1599, 1562; (Ar C–N) 1463. Found: C, 85.61; H, 7.15; N, 7.08%; molecular formula $\text{C}_{84}\text{H}_{84}\text{N}_6$ requires C, 85.67; H, 7.19; N, 7.14%. MS (EI) $m/z = 1177.6$ (M^+).

Download English Version:

<https://daneshyari.com/en/article/6599830>

Download Persian Version:

<https://daneshyari.com/article/6599830>

[Daneshyari.com](https://daneshyari.com)