



Synthesis, electrochemistry and optical properties with electroluminescence ability of new multisubstituted naphthalene derivatives with thiophene and carbazole motifs



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ABSTRACT

A series of solution-processable tetrasubstituted naphthalene derivatives bearing thiophene or carbazole units were synthesized using the tandem cycloaddition [2 + 1 + 2 + 1] and Diels–Alder reaction [4 + 2]. Thermal, electrochemical, absorption, and emission properties of synthesized compounds were studied. They can be considered as molecular glasses with glass transition temperature ranging from 37 to 122 °C with high thermal stability up to 300 or 400 °C. The naphthalene derivatives were electrochemically active and showed low energy band gap between 1.64 and 1.85 eV. All derivatives were luminescent and emitted light with maximum emission band located at 379–436 nm with photoluminescence quantum yield in the range of 9.5–19.8% in solution. They photo- and electroluminescence ability in solid state as thin film and blends with poly(9-vinylcarbazole) (PVK) and mixture PVK with (2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole) (PBD) were tested. Together with increase of compound content from 2 to 15 wt% in binary matrix, the increase of electroluminescence intensity was observed. Diodes with guest-host configuration showed electroluminescence with maximum of emission band from 593 to 637 nm. The most intense emission of light under applied voltage characterized devices based on compound bearing carbazole derivatives and one methyl group.

1. Introduction

Current technological progress virtually forces continuous efforts in search for new, better, and more efficient materials. Miniaturization of electronic building blocks, with expectations set by large groups of end-users, puts bigger emphasis on creating new materials for the use in organic electronics. However, before introducing any new material in a device, significant work is required for designing, preparation, and finally testing the desired properties for possible applications. Organic compounds, such as naphthalene and anthracene derivatives with aromatic or heteroaromatic substituents, are still in the focus of ongoing research. Derivatives of these molecules have been tested for possible use in organic light-emitting diodes (OLEDs) [1–9], solar cells [10–14] and organic field-effect transistors (OFETs) [15]. However, with the evolution and constant development of organic electronics, it is necessary to develop novel methods for the synthesis of organic compounds. Very attractive methods for obtaining naphthalene and

anthracene derivatives concern the [4 + 2] Diels-Alder cycloaddition reactions from 2-pyranone with in situ generated benzyne by the Kobayashi method [16–19]. Reactions of this type in the case of naphthalene derivatives can be carried out successfully even at room temperature (20 °C) [16–18]. Benzyne can be easily generated in the reaction from the appropriately chosen precursor (e.g. 2-(trimethylsilyl)phenyl trifluoromethanesulfonate) using addition of tetrabutylammonium fluoride (TBAF) or cesium fluoride (CsF) [16–19]. One of the most important advantages of synthesizing benzyne using the Kobayashi route is the ability to precisely control the rate of benzyne generation [19]. In the case of synthesis of 2-pyranone derivatives, there have been many approaches described in the literature [20–28]. Special care in the synthesis of 2-pyranone derivatives is required for [2 + 1 + 2 + 1] cycloaddition reaction β -keto esters to alkynes, catalyzed by $[\text{ReBr}(\text{CO})_3(\text{THF})_2]_2$ [16–18,29]. Alkynes containing either aromatic or heteroaromatic substituents can be successfully obtained by Sonogashira coupling reaction [30–37]. β -keto esters in many cases are

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commercially available. Moreover [2+1+2+1] cycloaddition reaction can be connected with [4+2] Diels-Alder cycloaddition, generated benzyne in situ in reaction medium, after [2+1+2+1] cycloaddition [16–18]. This significantly reduces both the cost and the time of synthesis. It is worth noting that rhenium coming from the catalytic system can be recycled after completed cycloaddition reactions.

In our previous work [16] we described a series of substituted naphthalene derivatives and one of them with bithiophene units seemed to be the most interesting one, because a device with active layer consisting of this compound in PVK matrix emitted blue light under applied voltage. Encouraged by this result we decided to design and synthesize a next series of naphthalene derivatives in order to explore the properties of such molecular systems. One of them, abbreviated as N1, was described in our previous work [16] and is also included for comparison here with additional experiments aimed at testing this compound as an active layer component OLED in combination with PVK and PBD. Comprehensive studies of the optical, electrochemical and thermal properties of the prepared compounds were conducted, that included preliminary tests of applying the synthesized compounds in devices for optoelectronics

2. Experimental section

2.1. Materials

All chemicals and starting materials were commercially available and were used without further purification. 5-Iodo-2,2'-bithiophene and 1,2-bis(2,2'-bithiophene-5-yl)acetylene were prepared according to the method described in our previous publications [16,30,37]. N-ethylcarbazole was prepared according to the method described in literature [38]. All reactions were carried out under argon atmosphere unless otherwise indicated. Column chromatography was carried out on Merck silica gel. Thin layer chromatography (TLC) was performed on silica gel (Merck TLC Silica Gel 60).

2.2. Preparation of N-ethyl-3-iodo-carbazole

To a stirred solution of N-ethylcarbazole (5.09 g, 26.05 mmol) in CHCl_3 (100 mL) NIS (5.80 g, 26.05 mmol) was added at room temperature under argon atmosphere. Then 30 mL acetic acid was added to the reaction mixture. After 24 h of mixing, the solvent was evaporated from the post-reaction mixture and extracted with CHCl_3 . The organic layer was washed by water (three times), and dried over Na_2SO_4 . Crude product was purified using column chromatography (SiO_2 , hexane: THF 5:1). White solid was obtained. Yield: 56%. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.41 (s, 1H), 8.04 (d, $J = 7.8$ Hz, 1H), 7.71 (dd, $J = 8.5, 1.5$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 1H), 7.40 (d, $J = 8.2$ Hz, 1H), 7.25 (t, $J = 7.4$ Hz, 1H), 7.19 (d, $J = 8.6$ Hz, 1H), 4.33 (q, $J = 7.2$ Hz, 2H), 1.42 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.01, 139.14, 133.88, 129.34, 126.44, 125.57, 121.78, 120.67, 119.41, 110.59, 108.73, 81.29, 37.68, 13.82.

2.3. Preparation of 1,2-Bis(N-ethylcarbazole-3-yl)acetylene

The solution of N-ethyl-3-iodo-carbazole (3.00 g, 9.34 mmol), CuI (0.20 g, 1.07 mmol), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (0.14 g, 0.20 mmol), acetone (91 mL), triethylamine (2.05 mL, 14.75 mmol) was flushed with a steady stream of acetylene (1 mol/6 h) mixed with argon (1:5 v/v) at room temperature for 6 h. After purging was finished, the content of the reactors was left to stir for 24 h at room temperature. Then the volatile fractions from the combined mixtures were evaporated on a rotary evaporator. Crude product was purified using column chromatography (SiO_2 , hexane: toluene 1:1). A yellow solid was obtained with 58% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.37 (s, 1H), 8.14 (d, $J = 7.6$ Hz, 1H), 7.71 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.54–7.48 (m, 1H), 7.45–7.37 (m, 2H), 7.28 (t, $J = 7.4$ Hz, 1H), 4.38 (q, $J = 7.3$ Hz, 2H), 1.47 (t, $J =$

7.2 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.45, 139.51, 129.37, 126.16, 124.03, 123.11, 122.77, 120.75, 119.39, 114.03, 108.79, 108.61, 88.89, 37.83, 14.00.

2.4. Typical procedure for the synthesis of naphthalene derivatives with bithiophene motif (N1-N2)

A mixture of β -keto ester (0.500 mmol) (ethyl 2-methylacetoacetate (N1) or ethyl acetoacetate (N2)) and 1,2-bis(2,2'-bithiophene-5-yl)acetylene (107 mg, 0.600 mmol) in the presence of $[\text{ReBr}(\text{CO})_3(\text{thf})_2]$ (10.6 mg, 0.0125 mmol) and powdered MS4A (21.2 mg, 200 wt%-Re cat.) in toluene (1.0 mL) was heated at 180 °C under argon atmosphere. After 48 h, 2-(trimethylsilyl)phenyl triflate (223.8 mg, 0.750 mmol), cesium fluoride (228 mg, 1.50 mmol), and acetonitrile (1.0 mL) were added. The reaction mixture was stirred at 25 °C for 48 h. Then, the reaction mixture was extracted with ethyl acetate. The organic layer was washed by water (three times), and dried over Na_2SO_4 . Crude product was purified using column chromatography.

2.4.1. 2,3-bis(2,2'-bithiophene-5-yl)-1,4-dimethylnaphthalene (N1)

After purification by silica gel column chromatography (hexane: ethyl acetate 15:1) N1 was obtained as yellow crystals with 63% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.17–8.11 (m, 2H), 7.65–7.60 (m, 2H), 7.16 (dd, $J = 5.1, 1.0$ Hz, 2H), 7.09 (dd, $J = 3.6, 1.0$ Hz, 2H), 6.99 (d, $J = 3.6$ Hz, 2H), 6.97 (dd, $J = 5.1, 3.6$ Hz, 2H), 6.64 (d, $J = 3.6$ Hz, 2H), 2.61 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 141.23, 137.78, 137.65, 132.97, 132.53, 131.95, 129.15, 127.82, 126.71, 125.39, 124.07, 123.43, 123.22, 17.33. **Anal. Calcd** for $\text{C}_{28}\text{H}_{20}\text{S}_4$ (485.72): C, 69.38; H, 4.15; Found: C, 69.16; H, 4.11. DSC: I run: $T_m = 175$ °C; II run: $T_g = 45$ °C, $T_c = 146$ °C, $T_m = 175$ °C.

2.4.2. 2,3-bis(2,2'-bithiophene-5-yl)-1-methylnaphthalene (N2)

After purification by silica gel column chromatography (hexane: ethyl acetate 20:1) N2 was obtained as yellow crystals with 51% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11–8.06 (m, 1H), 7.95 (s, 1H), 7.90–7.86 (m, 1H), 7.61–7.52 (m, 2H), 7.21 (dd, $J = 5.1, 1.0$ Hz, 1H), 7.18–7.15 (m, 3H), 7.11 (dd, $J = 3.6, 1.0$ Hz, 1H), 7.03–6.96 (m, 3H), 6.83 (dd, $J = 3.6, 0.8$ Hz, 1H), 6.79 (dd, $J = 3.8, 0.7$ Hz, 1H), 2.66 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.39, 140.57, 138.52, 137.75, 137.63, 137.57, 136.01, 133.19, 132.96, 132.11, 129.80, 129.66, 128.75, 127.91, 127.88, 127.58, 127.25, 126.89, 126.83, 124.88, 124.33, 124.27, 123.92, 123.75, 123.61, 123.58, 17.18. **Anal. Calcd** for $\text{C}_{27}\text{H}_{18}\text{S}_4$ (470.69): C, 68.89; H, 3.85; Found: C, 68.49; H, 3.18. DSC: I run: $T_m = 122$ °C, $T_c = 128$ °C, $T_m = 151$ °C; II run: $T_g = 37$ °C.

2.5. Typical procedure for the synthesis of naphthalene derivatives with N-ethylcarbazole motif (N3-N4)

A mixture of β -keto ester (0.500 mmol) (ethyl 2-methylacetoacetate (N3) or ethyl acetoacetate (N4)) and 1,2-bis(N-ethylcarbazole-3-yl)acetylene (250 mg, 0.600 mmol) in the presence of $[\text{ReBr}(\text{CO})_3(\text{thf})_2]$ (10.6 mg, 0.0125 mmol) and powdered MS4A (21.2 mg, 200 wt%-Re cat.) in toluene (1.0 mL) was heated at 180 °C under argon atmosphere. After 48 h, 2-(trimethylsilyl)phenyl triflate (223.8 mg, 0.750 mmol), cesium fluoride (228 mg, 1.50 mmol), and acetonitrile (1.0 mL) were added. The reaction mixture was stirred at 25 °C for 48 h. Then, the reaction mixture was extracted with ethyl acetate. The organic layer was washed by water (three times), and dried over Na_2SO_4 . Crude product was purified using column chromatography.

2.6. 2,3-bis(N-ethylcarbazole-3-yl)-1,4-dimethylnaphthalene (N3)

After purification by silica gel column chromatography (hexane: toluene 1:1) N3 was obtained as white solid with 65% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.23–8.17 (m, 2H), 8.02 (d, $J = 7.7$ Hz, 1H), 7.86 (d, $J = 7.7$ Hz, 1H), 7.83 (s, 1H), 7.76 (s, 1H), 7.64–7.59 (m, 2H), 7.42

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