

Synthesis and electroluminescent properties of highly twisted anthracene derivatives

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Abstract

The anthracene derivatives were synthesized by Suzuki coupling reaction. The thermal, optical and electronic properties of MNAn and BIPAn were investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV-vis absorption, photoluminescence spectroscopies, and cyclic voltammetry. The materials exhibit high thermal stability and high performance in EL devices.

1. Introduction

Recently, organic light-emitting devices (OLEDs) have been attracting considerable attention because of their potential application. OLEDs have been widely investigated for their applications in high-efficiency, low-drive-voltage, large-display-area, full-color flat-panel displays.¹⁻³ Anthracene derivatives have interesting photoluminescence (PL) and EL properties and good electrochemical properties. And the highly twisted structures mitigate unfavorable steric interactions that limit intermolecular interactions and lead to pure-blue emission.⁴ We have designed new blue-light-emitting materials, 2-(2-Methyl naphthalene-1-yl)-9,10-di(naphthalene-2-yl)anthracene (MNAn) and 2-(Biphenyl-2-yl)-9,10-di(naphthalene-2-yl)anthracene (BIPAn).

2. Experimental

2.1 Synthesis

2.1.1. 2-methylnaphthalen-1-ylboronic acid (1)

n-BuLi (2.5 M, 19.9 mL, 50 mmol) was added

dropwise to a solution of 1-bromo-2-methylnaphthalene (10 g, 45 mmol), in THF (100 mL) at -78 °C. The reaction mixture was stirred for 30 min at -78 °C, then triethylborate (19.8 g, 140 mmol) was added. The resulting mixture was stirred -78 °C for a further 30 min and then allowed to warm to rt. The reaction mixture was acidified with aq 10% HCl solution and extracted with ethyl acetate. The organic layer was then dried with MgSO₄ and concentrated under vacuum to afford a cream white solid. Yield : 5.76 g (68.5 %), m.p. ¹H-NMR (300 MHz, CDCl₃, ppm): δ = 2.57 (s, 3H), 5.06 (s, 2H), 7.31 (d, J = 8.40 Hz, 1H), 7.50-7.40 (m, 2H), 7.84-7.75 (m, 3H).

2.1.2. phenylboronic acid

Yield : 15.81 g (67.90 %), ¹H-NMR (300 MHz, CDCl₃, ppm): δ = 5.02 (s, 2H), 7.35-7.32 (m, 5H).

2.1.3 2-bromobiphenyl

To a solution of 1,2-dibromobenzene (19.34 g, 82 mmol) and phenylboronic acid (5.00 g, 41 mmol) dissolved in toluene (120 mL) was added a aqueous 2 M K₂CO₃ solution (20 mL) and THF (40 mL). The mixture was bubbled with nitrogen for 10 min. Then, tetrakis(triphenylphosphine) palladium(0) (0.5 g) was added. The mixture was heated to 110 °C for 24 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into a aqueous 2 N HCl (400 mL). The reaction mixture was extracted with dichloromethane. The resulting crude product was purified by chromatography with hexane. Colorless oil compound. Yield: 4 g (41.8 %), ¹H-NMR (300 MHz, CDCl₃, ppm): δ = 7.27-7.21 (m, 1H),

7.41-7.36 (m, 2H), 7.47-7.43 (m, 5H), 7.72 (d, J = 7.96 Hz, 1H).

2.1.4 2-(biphenyl-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2).

n-BuLi (2.5 M, 16.47 mL, 41 mmol) was added drop wise to a solution of 1-bromo-2-methylnaphthalene (8 g, 34 mmol), in THF (100 mL) at -78 °C. The reaction mixture was stirred for 30 min at -78 °C, then 2-(biphenyl-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.66 g, 41 mmol) was added. The resulting mixture was stirred -78 °C for a further 30 min and then allowed to warm to rt. Yield : 6.5 g (60.1 %) ¹H-NMR (300 MHz, CDCl₃, ppm): δ = 7.77 (d, J = 7.34, 1H), 7.52-7.35 (m, 8H), 1.25 (s, 12H)

2.1.5 2-bromoanthracene-9,10-dione

2-aminoanthraquinone (15 g, 67.2 mmol) and cupric bromide (33.77 g, 151.19 mmol) were dissolved in CH₃CN (250 mL). Tert-Butylnitride (15.59 g, 151.19 mmol) was added to the reaction mixture with stirring. The reaction mixture was stirred for 2 hours. It was filtered with water and CH₃CN. The product was purified by column chromatography. Yield : 4.9 g (25.4 %), ¹H-NMR (300 MHz, CDCl₃, ppm): δ = 7.80-7.86 (m, 2H), 7.93 (dd, J = 8.30 2.12 Hz, 1H), 8.18 (d, J = 8.3 Hz), 8.28- 8.33 (m, 2H), 8.43 (d, J = 1.98 Hz, 1H)

2.1.6 2-bromo-9,10-di(naphthalen-2-yl)anthracene

2-bromonaphthalene (16.59 g, 0.035 mol) was dissolved in THF (100 mL). The solution was cooled to -78 °C and 2.5 M of n-BuLi (35.25 mL, 0.088 mol) was slowly added thereto and stirred for one hour. Then, 2-bromo-antraquinone (10 g, 0.035 mol) was added and the reaction solution was stirred for overnight. Aqueous solution of ammonium chloride was added. An organic layer was separated, dried over magnesium sulfate and filtered. The filtered solution was dried under reduced pressure to remove solvents and recrystallized with diethyl ether to obtain the compound. To acetic acid (100 mL), the compound (19 g, 0.035 mol), a potassium iodide (17.4 g, 0.105 mol) and a hypophosphite soda (22.23 g, 0.210 mol) were added and then heated and stirred for 6 hours. The solution was cooled to normal temperature, and then the produced precipitation was filtered and washed with water. The resulting crude product was purified by chromatography with hexane. Yield : 14 g (78.9 %), ¹H-NMR (300 MHz, CDCl₃, ppm): δ = 8.14-8.10 (m, 2H), 8.09-8.05 (m, 2H), 8.01-7.94 (m, 4H), 7.91 (d, J = 3.15, 1H), 7.76-7.71 (m, 2H), 7.69-

7.61 (m, 7H), 7.38-7.34 (m, 3H)

2.1.7 2-(biphenyl-2-yl)-9,10-di(naphthalen-2-yl)anthracene (BIPAn)

To a solution of 2-bromo-9,10-di(naphthalen-2-yl)anthracene (6.00 g, 0.012 mol) and 2-(biphenyl-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.3 g, 0.015 mol)(2) dissolved in toluene (80 mL) was added a aqueous 2 M K₂CO₃ solution (40 mL) and THF (25 mL). The mixture was bubbled with nitrogen for 10 min. Then, tetrakis(triphenylphosphine) palladium(0) (0.35 g, 2 mol %) was added. The mixture was heated to 110 °C for 48 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into a aqueous 2 N HCl (300 mL). The reaction mixture was extracted with dichloromethane. The resulting crude product was purified by chromatography with dichloromethane and hexane. Yield : 5.15 g (75.1 %), ¹H-NMR (300 MHz, CDCl₃, ppm): δ = 7.03-7.01 (m, 2H), 7.15-7.10 (t, 2H), 7.23-7.18 (m, 2H), 7.74 (d, J = 8.26 Hz, 2H), 7.30-7.26 (m, 3H), 7.36-7.34 (m, 3H), 7.42-7.39 (m, 1H), 7.50 (d, J = 1.41 Hz, 1H), 7.69-7.60 (m, 7H), 7.76-7.72 (m, 2H), 7.91-7.88 (m, 1H), 8.06-8.00 (m, 3H), 8.10 (d, J = 8.34 Hz, 1H).

2.1.8 2-(2-methylnaphthalen-1-yl)-9,10-di(naphthalen-2-yl)anthracene (MNAAn)

Yield : 1.96 g (29.17 %), ¹H-NMR (300 MHz, CDCl₃, ppm): δ = 2.25 (d, J = 2.77, 3H), 7.30-7.26 (m, 2H), 7.38-7.31 (m, 4H), 7.57-7.47 (m, 3H), 7.67-7.62 (m, 3H), 7.71-7.70 (m, 1H), 7.84-7.73 (m, 5H), 8.02-7.88 (m, 6H), 8.09-8.05 (m, 1H), 8.17-8.12 (m, 2H)

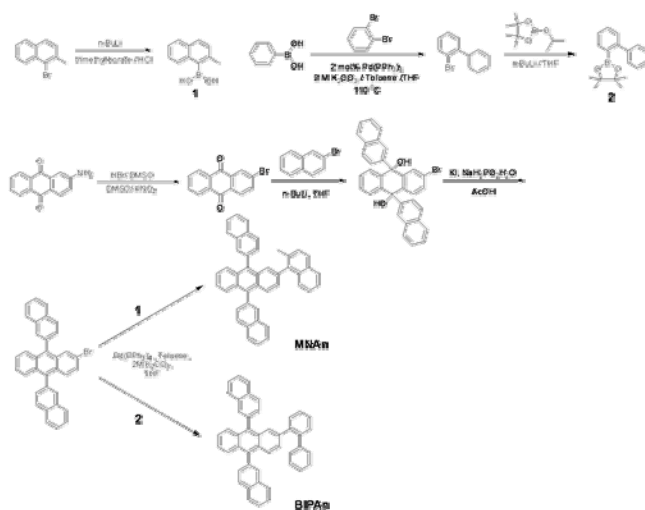


Fig 1. Scheme

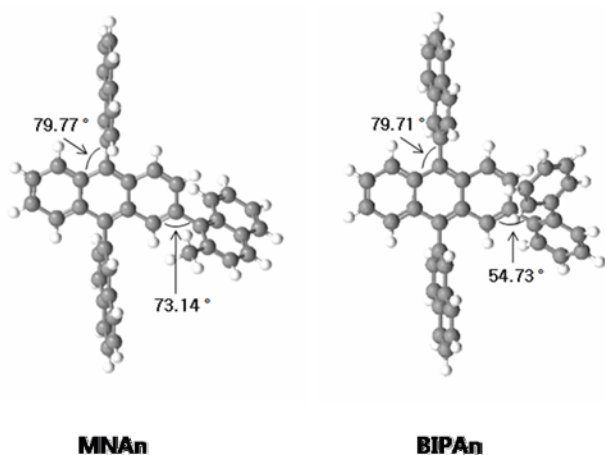


Fig 2. the three-dimensional structures of MNAn and BIPAn

3. Results and discussion

The materials were synthesized by Suzuki coupling reaction. The structures of MNAn and BIPAn were confirmed by $^1\text{H-NMR}$, FT-IR and Mass spectrometers. Theoretical calculation using the PM3 parameterizations in the HyperChem 5.0 program (Hypercube) were carried out to characterize the three-dimensional structures and the energy densities of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states of each material. The thermal properties of MNAn and BIPAn were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The decomposition temperatures of materials, which correspond to a 5 % weight loss upon heating, are around $382\text{ }^\circ\text{C}$ for MNAn and $386\text{ }^\circ\text{C}$ for BIPAn. MNAn and BIPAn show melting transitions (T_m) of $292\text{ }^\circ\text{C}$ and T_g of $132\text{ }^\circ\text{C}$, respectively. The maximum emission of MNAn and BIPAn were reached at 431 nm and 435 nm in the solution state and at 454 nm and 445 nm in the film state, respectively. The oxidation peak potential is $E_{ox} = 1.14$ for MNAn and $E_{ox} = 1.15$ for BIPAn. The energy bandgaps of MNAn and BIPAn are 2.90 and 2.86 eV , respectively: consistent with data calculated from the optical absorption threshold. From the electrochemical data, the HOMO and LUMO were calculated to be -5.58 eV and -2.88 eV for MNAn, and -5.59 eV and -2.73 eV for BIPAn. To study the EL properties of MNAn and BIPAn, multilayer devices with the configuration indium tin oxide(ITO) / $\text{N,N}'$ -di(4-($\text{N,N}'$ -diphenyl-amino)phenyl)- $\text{N,N}'$ -diphenylbenzidine(DNTPD)(700)/ $\text{N,N}'$ -diphenyl- $\text{N,N}'$ -bis(1-naph

thyl)-1,1-biphenyl-4,4'-diamine (NPD) (300 \AA) / 9,10-di(naphthalen-2-yl)anthracene (AND) : MNAn or BIPAn(3%)/tris(8-hydroxyquinoline)aluminum (Alq3) (400 \AA)/LiF(5 \AA)/Al were fabricated. The dopant MNAn and BIPAn exhibited high performance in EL devices : λ_{max} $456, 456\text{ nm}$, current efficiency of $3.55, 3.61\text{ cd/A}$, power efficiency of $2.11, 2.15\text{ lm/W}$ at 10 mA/cm^2 , external quantum efficiency of $3.38, 3.70\%$, and Commission Internationale de l'Éclairage (CIE) coordinates of $(0.15, 0.13), (0.15, 0.12)$, respectively. In view of the fact that the blue-light-emitting layer is host/dopant system, the devices achieved very high color purity and very high efficiency.

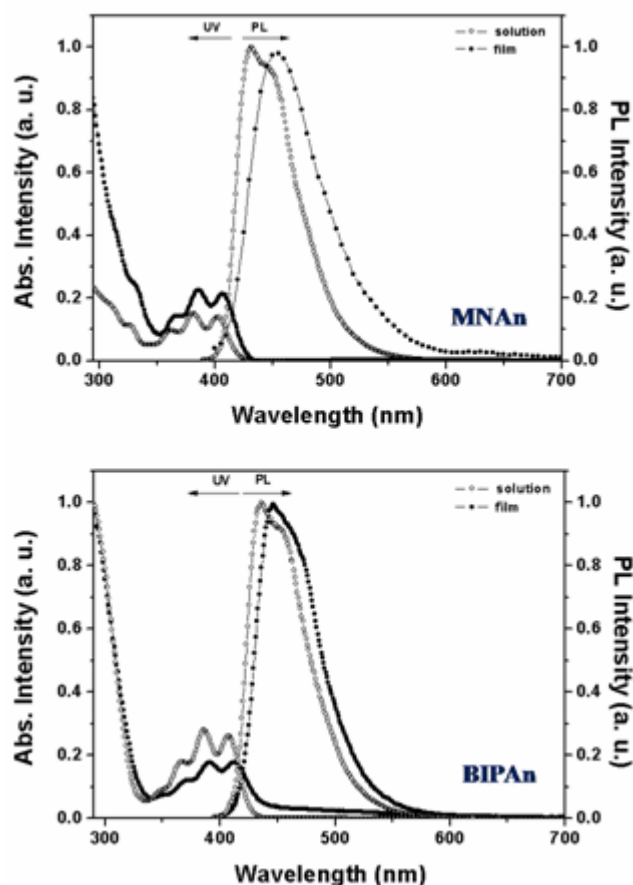


Fig 3. UV-vis and PL spectra of MNAn and BIPAn.

4. Summary

The blue emitting materials of highly twisted structures were synthesized by Suzuki coupling reaction. The materials showed high thermal stability, as

evidenced by a 5 % weight loss of 382 °C and 386 °C, respectively. The materials exhibited high EL properties as current efficiency of 3.55, 3.61 cd/A, external quantum efficiency of 3.38, 3.70 %, and pure-blue emission

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