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Tetrahedron Letters 44 (2003) 5747–5750

TETRAHEDRON
LETTERS

Synthesis of *t*-butylated diphenylanthracene derivatives as blue host materials for OLED applications

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Received 21 November 2002; revised 14 May 2003; accepted 22 May 2003

Abstract—This paper describes the cost-effective synthesis and the photoluminescence of diphenylanthracene derivatives, which are found to be potential blue host materials for organic light emitting diode (OLED) technology.
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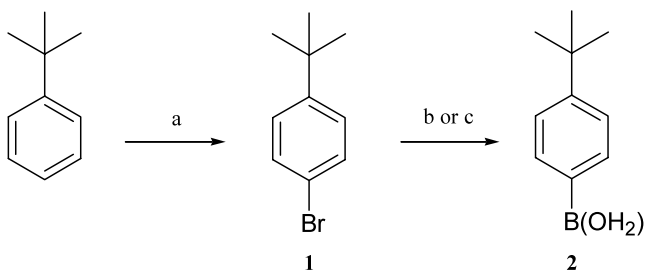
Since the ground-breaking discovery of the work of Tang et al., intense research and development have brought organic light emitting devices to the brink of penetrating the market of flat panel displays.¹ For full color organic electroluminescent displays, highly efficient and stable blue host emitters are vital. 9,10-Di(2-naphthyl)anthracene (ADN) is one of the best blue host materials with an efficiency as high as 5.1 cd/A.^{2,3} However, the synthesis of ADN involves 2-bromonaphthalene which in turn is synthesized from 2-aminonaphthalene, which is a suspected carcinogen. We have continued our research towards the cost-effective and eco-friendly synthesis of alternative blue emitting materials which retain a fluorescence quantum efficiency comparable to that of ADN. Among the blue fluorescent materials, 9,10-diphenylanthracene (DPA) has near unity fluorescence quantum efficiency in dilute solution and is also highly fluorescent in the solid state, but has an inherent problem of crystallization as a thin film in the device.⁴ To avoid the formation of polycrystalline films and to improve thermal properties, we decided to introduce *t*-butyl groups in DPA without altering its photophysical characteristics, as a similar strategy has been used in improving other emitters in OLED with considerable success.^{5,6} In this paper, we describe the facile and large scale synthesis of novel *t*-butyl substituted diphenylanthracene derivatives designed for OLED applications as bipolar blue host materials.

Keywords: synthesis; diphenylanthracene; blue; photoluminescence; OLED; electroluminescence.

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A perusal of the literature disclosed that the preparation of diarylanthracenes either involve Grignard type reagents⁷ or Suzuki–Miyaura cross couplings⁸ as the key step, but only the latter leads to good yields. So, we adapted the Suzuki–Miyaura cross coupling to synthesize the hitherto unknown 2-(*t*-butyl)-9,10-diphenylanthracene **4b**, 9,10-di-(4-*t*-butylphenyl)anthracene **4c** and 2-(*t*-butyl)-9,10-di-(4-*t*-butylphenyl)anthracene **4d** on an industrial scale. However, this still required the use of expensive 4-*t*-butylbenzeneboronic acid **2**, and the literature reveals low yields (~50%) of **2** from 1-bromo-4-*t*-butylbenzene.⁹ So, we decided to develop a better procedure for the synthesis of the key intermediate 4-*t*-butylbenzeneboronic acid **2**, for the synthesis of compounds **4c–d**.

The commercially available and cheap raw material, *t*-butylbenzene was brominated at 0°C catalyzed by iodine (1–2% w/w) to form 1-bromo-4-*t*-butylbenzene **1** in quantitative yield. Lithiation of **1** at –78°C followed by the addition of tributyl borate, led to the corresponding boronic acid **2** in very good yield (90%). Tributyl borate can be prepared on the kilo-scale from *n*-butanol and boric acid using a Dean–Stark apparatus at reflux followed by fractional distillation, and can be stored even at room temperature under anhydrous conditions for months.¹⁰ Compound **2** can also be obtained in about 70% yield by quenching the corresponding Grignard reagent, generated using magnesium turnings in THF, with tributyl borate at –78°C. 4-*t*-Butylbenzeneboronic acid **2** is an off-white solid and also highly polar in nature, and hence can be easily purified by washing with *n*-hexane to remove the unreacted starting material (Scheme 1).¹¹



Scheme 1. Synthesis of 4-*t*-butylbenzeneboronic acid **2**.
Reagents and conditions: (a) Br₂, I₂ (cat.)/neat, 0°C, 100%; (b) i. *n*-BuLi/THF, -78°C, ii. (*n*-BuO)₃B, -78°C (iii) H⁺, 90%; (c) i. Mg/THF, reflux, ii. (*n*-BuO)₃B, -78°C, iii. H⁺, 70%.

Suzuki–Miyaura cross coupling of boronic acids with 9,10-dibromoanthracenes **3a–b** in the presence of Pd(PPh₃)₄ as a catalyst in refluxing toluene–aqueous sodium carbonate solution formed the *t*-butyl substituted diphenylanthracenes **4a–d** in about 90% yield (Scheme 2).¹¹ A cold ethanolic wash of the crude reaction product furnished **4a–d** of high purity (~98% by HPLC). To study the photophysical properties, these compounds were further sublimed to ensure very high purity (>99.9% by HPLC). The compounds in the study were well characterized by means of NMR and mass spectroscopy.¹²

Preliminary experiments such as analysis of thermal properties, feasibility of oxidation and photoluminescence in solution were undertaken to ensure their performance before the fabrication of OLED devices. Thermogravimetric and differential scanning calorimetric analyses of **4a–d** revealed that the *t*-butylated diphenylanthracenes **4b–d** are stable up to 330°C and possess high melting points, suggesting them to be suitable for coating by evaporation under vacuum.

Table 1. Energy values of HOMO and LUMO of **4a–d**

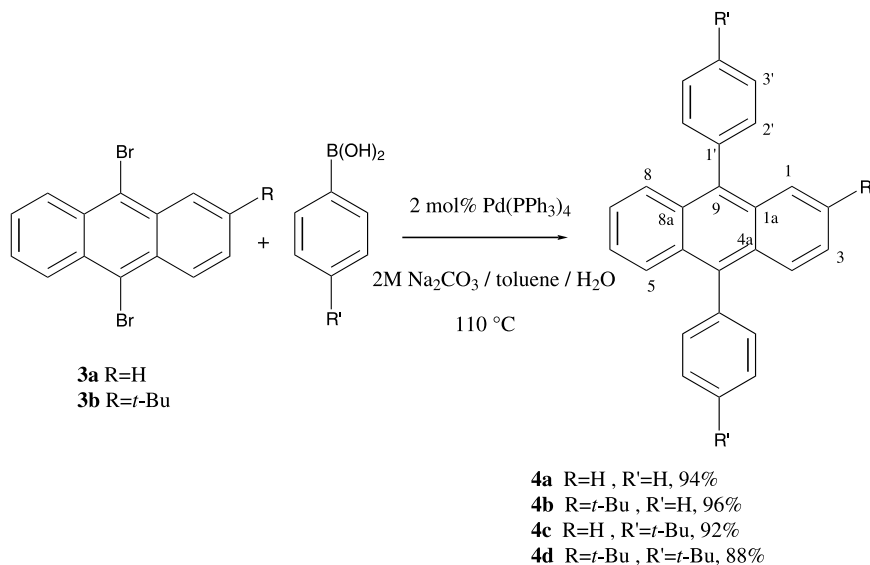
Compound	Eox (eV) ^a	HOMO (eV) ^b	LUMO (eV) ^b	Eg (eV)
ADN	1.48	5.88	2.87	3.01
4a	1.44	5.84	2.89	2.95
4b	1.38	5.78	2.82	2.96
4c	1.56	5.96	2.99	2.97
4d	1.27	5.67	2.70	2.97

^a Oxidation potential relative to Ag/AgCl electrode.

^b HOMO=(Eox+4.4) eV; LUMO=(HOMO–Eg) eV.¹³

Further, from cyclic voltammetric measurements with reference to ferrocene (in 1,2-dichloroethane) and the bandgap energies (Eg), which were estimated from the onset of absorption, the energy of the highest occupied molecular orbital (HOMO) and that of the lowest unoccupied molecular orbital (LUMO) of the diphenylanthracenes **4a–d** were determined and are compared with those of ADN in Table 1. The UV absorption of all compounds overlapped with each other resulting in similar bandgap energies. A slight variation in the HOMO values were observed upon incorporation of a *t*-butyl group onto the anthracene molecular skeleton. These results showed their facile reversible redox behavior and hence they can be applied as bipolar transport materials for electroluminescence.

The photoluminescent spectra of compounds **4a–d** were measured in 1,2-dichloroethane and are presented in Table 2. We observed a slight bathochromic shift upon introduction of a *t*-butyl group into the anthracene as well as on the phenyl pendants. This in fact would facilitate a better sensitization of the dopants such as the 2,5,8,11-tetra(*t*-butyl)perylene (TBP) employed for multi-layer OLED.¹⁴ Figure 1 illustrates that the new blue materials **4b–d** exhibit a relatively higher quantum efficiency than ADN, indicating their potential for OLED applications.



Scheme 2. Synthesis of diphenylanthracenes **4a–d**.

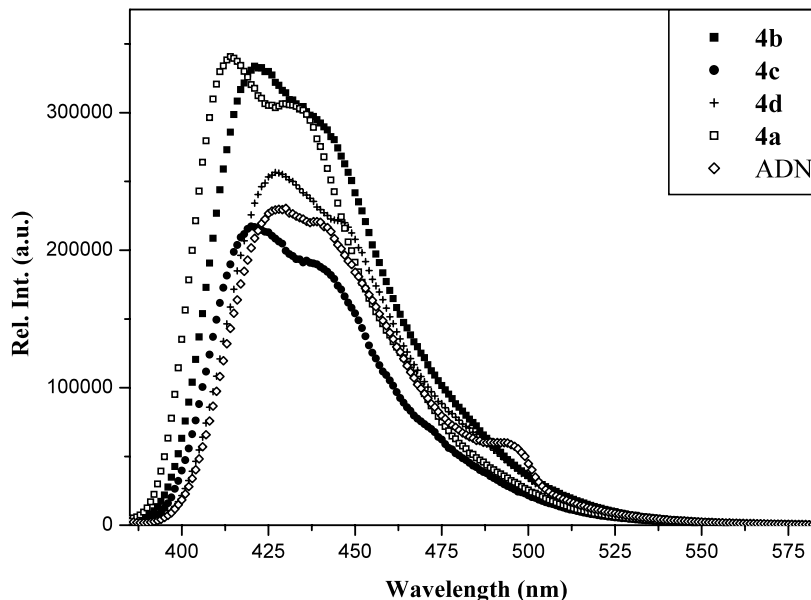


Figure 1. Photoluminescence spectra of 4a–d.

Table 2. Emission wavelength and bandwidth of 4a–d in comparison with ADN

Compound	λ emission (nm)	Bandwidth (nm)
ADN	430	54
4a	414	52
4b	421	54
4c	420	52
4d	427	53

To summarize, we have developed a cost-effective synthesis of the key intermediate 4-*t*-butylbenzene boronic acid **2** for the preparation of the novel *t*-butyl substituted diphenylanthracenes **4b–d**. Initial experiments showed them to have potential as blue bipolar host materials for OLED. Further studies on the electroluminescent properties of **4b–d** are currently under investigation and will be presented elsewhere.

Acknowledgements

We like to thank the National Science Council, Taiwan, Republic of China for providing a post-doctoral fellowship for B.B. We wish to thank Ms. Yun Ming Li, NCTU, Taiwan for providing us with elemental analyses data. Financial support for this project is provided by PPUAE 91-E-FA04-2-4B.

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- Preparation of tributyl borate: Boric acid (309 g, 5 mol) was refluxed with *n*-butanol (1.5 L, 16.2 mol) in a three necked round-bottomed flask fitted with a Dean–Stark apparatus. After removal of 270 mL of water, excess *n*-butanol was distilled off at atmospheric pressure. The distillate at 230°C was collected as tributyl borate (1.3 L, 96%), purged with nitrogen and stored at room temperature for months.
- Typical experimental procedure:**
Synthesis of 4-*t*-butylbenzeneboronic acid **2**:
Method A: 1-bromo-4-*t*-butylbenzene (**1**, 42.6 g, 200 mmol) was dissolved in dry THF (300 mL) and *n*-butyllithium (240 mmol) was added via cannula at –78°C. The reaction mixture was stirred for 3 h maintaining the temperature well above –45°C. Tributyl borate (80 mL, 300 mmol) was added at –78°C and the reaction mixture was equilibrated to room temperature. The reaction was quenched with conc. HCl at –10°C until pH ~ 2 to 3. The mixture was then extracted with ether (3×200 mL) and the organic layer was washed with saturated NaHCO₃ solution, water, dried over anhydrous MgSO₄ and the

solvent evaporated to dryness to yield 4-*t*-butylbenzeneboronic acid as an off-white solid (32 g, 90%). Method B: (*t*-butyl)phenylmagnesium bromide was prepared from 10.4 g of magnesium and 42.6 g of 1-bromo-4-*t*-butylbenzene (**1**, 200 mmol) in THF. Tri-*n*-butylborate (80 mL, 300 mmol) was added at -78°C and the reaction mixture was equilibrated to room temperature. Following the above work-up, 4-*t*-butylbenzeneboronic acid was obtained in 70% yield.

In either case, compound **2** was further purified by washing off the unreacted starting material with *n*-hexane. The authenticity of this sample was in excellent agreement with the literature.⁹

General Suzuki–Miyaura coupling towards the synthesis of **4a–d**:

Synthesis of 9,10-di-(4-*t*-butylphenyl)anthracene (**4c**): 9,10-dibromoanthracene (13.4 g, 40 mmol), 4-*t*-butylbenzeneboronic acid (**2**, 17.8 g, 100 mmol), 2 M aq. Na_2CO_3 solution (40 mL) and toluene (50 mL) were mixed and degassed with nitrogen. Tetrakis(triphenylphosphine)palladium(0) (0.92 g, 2 mol%) was added and the mixture refluxed for about 8 h under an inert atmosphere until complete disappearance of the starting material (monitored by TLC). The reaction mixture was extracted with ethyl acetate (2×30 mL), the organic layer was washed with water, dried over anhydrous MgSO_4 and evaporated to dryness to yield 16 g of 9,10-di-(4-*t*-butylphenyl)anthracene (**4c**, 90%). Further washing with cold ethanol furnished **4c** with 98% purity.

12. Spectral characteristics:

2-(*t*-Butyl)-9,10-diphenylanthracene (**4b**): pale yellow solid (mp 232°C). ^1H NMR (CDCl_3 , 300 MHz) δ 1.24 (s, 9H); 7.28 (m, 2H); 7.46 (m, 6H); 7.56 (m, 5H); 7.58 (s, 1H); 7.66 (m, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 30.72

(Me); 34.90 (>C<); 121.13 (C-1); 124.51 (C-7); 124.57 (C-6); 124.75 (C-3); 126.59 (C-8); 126.87 (C-5); 127.35 (C-4'); 128.30 (C-4); 128.33 (C-2'); 128.44 (C-1a); 129.54 (C-5a); 129.81 (C-8a); 129.98 (C-4a); 131.30 (C-3'); 136.58 (C-10); 136.85 (C-9); 139.18 (C-1'); 147.17(C-2). Anal. calcd for $\text{C}_{30}\text{H}_{26}$ (386.53): C, 93.22; H, 6.78. Found: C, 93.05; H, 6.99.

9,10-Di-(4-*t*-butylphenyl)anthracene (**4c**): pale yellow solid (mp 284°C). ^1H NMR (CDCl_3 , 300 MHz) δ 1.23 (s, 18H); 7.09 (m, 4H); 7.25 (d, $J=8.4$ Hz, 4H); 7.49 (d, $J=8.4$ Hz, 4H); 7.63 (dd, $J=8.2, 1.4$ Hz, H-1, H-4, H-5, H-8). ^{13}C NMR (CDCl_3 , 75 MHz) δ 31.36 (Me); 31.61 (>C<); 125.16 (C-3'); 125.30 (C-2); 127.17 (C-1); 128.33 (C-1a); 130.60 (C-9); 134.22 (C-2'); 139.60 (C-1'); 146.10 (C-4'). Anal. calcd for $\text{C}_{34}\text{H}_{34}$ (442.64): C, 92.26; H, 7.74. Found: C, 92.45; H, 7.81.

2-(*t*-Butyl)-9,10-di-(4-*t*-butylphenyl)anthracene (**4d**): pale yellow solid (mp 267°C). ^1H NMR (CDCl_3 , 300 MHz) δ 1.27 (s, 9H); 1.48 (s, 18H); 7.32 (m, 2H); 7.41 (d, $J=8.4$ Hz, 2H); 7.43 (dd, $J=7.8, 2.1$ Hz, 3H); 7.59 (d, $J=8.4$ Hz, 2H); 7.62 (d, $J=7.8$ Hz, 2H); 7.63 (s, 1H); 7.73 (m, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 30.77, 31.59 (Me); 34.79, 34.96 (>C<); 121.30 (C-1); 124.41 (C-6); 124.48 (C-7); 124.66 (C-3'); 125.14 (C-8); 125.14 (C-5); 126.79 (C-1a, C-5a); 127.11 (C-3); 128.69 (C-4a, C-8a); 129.76 (C-10); 130.07 (C-9); 130.98(C-4); 131.03 (C-2'); 136.10 (C-1'); 147.00 (C-2); 150.15 (C-4'). Anal. calcd for $\text{C}_{38}\text{H}_{42}$ (498.75): C, 91.51; H, 8.49. Found: C, 91.29; H, 8.48.

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