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# Synthesis and photophysical processes of 9-bromo-10-naphthalen-2-yl-anthracene

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#### Abstract

A novel luminescent compound, 9-bromo-10-naphthalen-2-yl-anthracene (BNA) is synthesized by Suzuki Cross-coupling reaction of 9-bromoanthracene and naphthalene-2-boronic acid. The structure is characterized by <sup>1</sup>H NMR, IR and UV–vis spectroscopy. The photophysical processes of 9-bromo-10-naphthalen-2-yl-anthracene have been carefully investigated by UV–vis absorption and fluorescence spectra. The results show that the compound emits blue and blue-violet light. The emission spectra exhibit obvious solvent effect. With the difference in polarity of solvents, The emission spectra is not only slightly blue shift with the increase of the solvent polarity but also change on the intensity of fluorescence at room temperature .The light emitting can be quenched by electron donor, *N*,*N*-dimethylaniline (DMA). On adding gradually DMA into the solution of BNA, the emission intensities of fluorescence are gradually decreased. The quenching effect follows the Stern–Volmer equation. © 2006 Elsevier B.V. All rights reserved.

Keywords: 9-Bromo-10-naphthalen-2-yl-anthracene; Interaction; N,N-dimethylaniline

# 1. Introduction

Organic electroluminescent (organic EL) devices [1] have emerged as a propitious novel technology for the next generation of flat and thin panel displays, overcoming the drawbacks of contemporary electronic displays, such as low powerefficiency, narrow view angle, and a lack of brightness and flexibility. Recent interest in developing practical EL devices for long-term use with high power-efficiency is focused on those with a multilayered structure which comprises hole-injecting, hole-transporting, light-emitting, hole-blocking, and electroninjecting layers between the indium-tin-oxide (ITO) electrode and the cathode. A hole-injecting layer (HIL) has been used to intermediate between the ITO electrode and a hole-transporting layer (HTL) to demonstrate higher operational half-life compared with that without HIL, several materials such as copper phthalocyanine (CuPc) [2] and aryl-substituted tetraamine [3], were reported for HIL materials. Among these, CuPc was introduced by Kodak researchers and was a widely used material. However, CuPc itself has strong absorption in a visible light range so that the device containing it shows color fade, particularly at a range of 550–700 nm, depending on the thickness.

1386-1425/\$ – see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2006.04.015 In this paper, we have synthesized a novel compound, 9-bromo-10-naphthalen-2-yl-anthracene from 9-bromo-anthracene and naphthalene-2-boronic acid by Suzuki cross-coupling reaction [4,5]. The photophysical properties are investigated, the photoluminescence of BNA are examined in different solvent. Moreover, the molecular interaction of BNA with N,N-dimethylaniline (DMA) is investigated. It displays not only a potential candidate as HIL materials for organic electroluminescent devices, but also an intermediate for luminescent materials.

# 2. Experimental

## 2.1. Materials and measurements

The reagents and chemicals for preparation of 9-bromo-10-naphthalen-2-yl-anthracene were used as received unless noted otherwise. Ethanol, acetonitrile, acetone, THF, dichloromethane, ethyl acetate, petroleum ether were purchased from Beijing Chemical Plant and treated according to standard methods used before, which were all applied to measurement of the lightemitting properties. The synthetic routes used are shown in Scheme 1.

Melting points are determined on a Sanyo Gallenkamp MPD350 melting point apparatus and uncorrected. The IR spec-

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Scheme 1. The chemical structures of BNA in the study.

tra were determined on a PE-1700 IR spectrophotometer by dispersing samples in KBr disks. <sup>1</sup>H NMR spectra are measured on a Bruker ARX300 spectrometer with DCCl<sub>3</sub> as solvent. UV–vis and fluorescence spectra are obtained on a Shimadzu UV-265 spectrophotometer and Perkin-Elmer LS-50B spectrophotometer, respectively. Both excitation and emission bands are set at 5 nm. All the experiments are carried out at  $20 \pm 1$  °C.

## 2.2. Synthesis

#### 2.2.1. Synthesis of 2-bromonaphalene

Synthesis of 2-bromonaphthalene is prepared according to Ref. [6]. The yield is 75%, m.p. 50-52 °C.

#### 2.2.2. Synthesis of naphthalene-2-boronic acid

To a stirred solution of 2-bromonaphthalene (4.14 g, 0.02 mol) in dry THF (50 ml) was added dropwise a 2.5 M *n*-pentane solution of t-butyllithium (9.6 ml, 0.024 mol) at  $-78 \degree C$  under an argon atmosphere. After stirring for 1 h, the B(OMe)<sub>3</sub> was added dropwise to the mixture at  $-78 \degree C$ , the mixture was

allowed to warm to room temperature, and was stirred for 8 h, and adding HCl (1 N) at 0 °C. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the organic layer was washed with hexane, Give a white product. The yield is 70%, m.p. 267–268 °C.

## 2.2.3. Synthesis of 9-naphthalen-2-yl-anthracene

9-Bromo-anthracene (0.5 g) under a N<sub>2</sub> atmosphere was added to a stirred solution of the naphthalene-2-boronic acid in DME/H<sub>2</sub>O and K<sub>2</sub>CO<sub>3</sub> solution, the mixture was refluxed for 8 h, the reaction mixture was concentrated and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The crude product was purified by column chromatography (*n*-hexane), The yield is 92%. m.p. 213 °C. <sup>1</sup>H NMR (DCCl<sub>3</sub>, ppm)  $\delta$ : 8.56 (1H), 8.02–8.11 (4H), 7.91–7.96 (2H), 7.70–7.73 (2H), 7.57–7.62 (3H), 7.46–7.51 (2H), 7.32–7.37 (2H).

#### 2.2.4. Synthesis of 9-bromo-10-naphthalen-2-yl-anthracene

Br<sub>2</sub> (0.01 mol) was added to a stirred solution of 9naphthalen-2-yl-anthracene in CCl<sub>4</sub> (40 ml) at 0 °C. The solution was stirred at room temperature overnight. The reaction mixture was washed with 20% aqueous potassium hydroxide, saturated aqueous sodium thiosulfate, and water, and the organic layer was dried over anhydrous sodium sulfate and concentrates under reduced pressure to leave a reside, which was reprecipitated with hexane to give 9-bromo-10-naphthalen-2-yl-anthracene as a yellow solid. The yield is 65%, m.p. 171–173 °C. <sup>1</sup>H NMR (DCCl<sub>3</sub>, ppm)  $\delta$ : 8.64–8.67 (2H), 8.02–8.08 (2H), 7.92 (2H), 7.52–7.69 (7H), 7.34 (2H). IR (KBr, cm<sup>-1</sup>): 1628, 1597, 1327, 1258, 1140, 1030, 927, 895, 856, 822, 758, 745, 669, 642, 621, 606, and 478.

## 3. Results and discussion

#### 3.1. Synthesis and characterization

Although this is a well-estabilished method for C–C bond formation, but the contents of catalyst and reaction solvent have a significant influence on the Suzuki cross-coupling reaction. It has been found by experiment that the appropriate ratio of Pd (OAc)<sub>2</sub> to PPh<sub>3</sub> is 1:4 (mol), which can successfully form the reactive catalyst. And the ratio of DME to H<sub>2</sub>O is 9:1 (ml).

## 3.2. UV-vis absorption and fluorescence emission spectrum

The UV–vis absorption and fluorescence emission spectra of BNA in ethyl acetate are shown in Fig. 1. It can be seen from Fig. 1 that the BNA has two maximum absorption, 265 and 376 nm, respectively. But the emission peak is only at 418 nm. These phenomena can be attributed to its nuclear geometry arrangement is different between in excitated state and in ground state. Because the life of S<sub>1</sub> electron state is longer than the higher electron state, there is a possible remove before emission.

# 3.3. Solvent effects on photoluminescence

600

500

400

200

100

C

200

LL 300

The BNA has good solubility in common organic solvents, such as dichloromethane, THF, ethyl acetate, etc. the emis-

а



400

/nm

500

600

300



Fig. 2. Emission spectra of BNA solution in different solvents.

sion spectra of BNA are investigated in different solvents and all results are showed in Figs. 2 and 3. It can be seen from Figs. 2 and 3 that the emission spectra of BNA is not only slightly blue shift with the increase of the solvent polarity but also change on the intensity of fluorescence, and the emission intensity of fluorescence are initially increased and then decreased with the increase of the solvent polarity. Based on the experimental facts and references, the following explanations can be given: It is well known that BNA has greater  $\pi$ -system conjugation and rigid configuration, so charge transfer between the conjugates system may be dramatically modified. Further research toward a better understanding of this effect is currently in progress.

## 3.4. Interactions of BNA with N,N-dimethylaniline

In order to go further into the fluorescence property of BNA, the quenching process of BNA with *N*,*N*-dimethylaniline (DMA) is also examined and shown in Fig. 4. DMA is a typical electron donor [7,8]. The studies of interactions between BNA



Fig. 3. Emission spectra of BNA solution in different solvents.



Fig. 4. Fluorescence spectra of BNA at different concentration of DMA. Concentration of BNA,  $1.36 \times 10^{-5}$  M. Concentration of DMA (mol/L, M): (1) 0.00; (2)  $7.89 \times 10^{-6}$ ; (3)  $2.10 \times 10^{-5}$ ; (4)  $3.42 \times 10^{-5}$ ; (5)  $4.73 \times 10^{-5}$ ; (6)  $6.05 \times 10^{-5}$ ; (7)  $8.68 \times 10^{-5}$ .



Fig. 5. Dependence of  $F_{\rm M}^0/F_{\rm M}$  on concentration of DMA. Concentration of BNA,  $1.36 \times 10^{-5}$  M.

and DMA are helpful to understanding the photo-electronic properties of BNA. When DMA is added to a solution of BNA in ethyl acetate, the fluorescence of BNA is efficiently quenched and the quenching process follows the Stern–Volmer equation,  $F_{\rm M}^0/F_{\rm M} = 1 + K_{\rm sv}[Q]$ . And shown in Fig. 5. The apparent quenching coefficient,  $K_{\rm sv}$ , is  $1.94 \times 10^4 \,{\rm M}^{-1}$  and no exciplex emission spectra are observed.

# 4. Conclusions

In summary, 9-bromo-10-naphthalen-2-yl-anthracene was synthesized from 9-bromo-anthracene by a straightforward way of Pd-catalyzed Suzuki coupling with naphthalene-2-boronic acid and subsequent halogenating reaction. The resulting compounds have excellent solubility in common organic solvents. The emission peak of BNA in ethyl acetate is at 418 nm. It displays high photoluminescence quantum yields and is potential candidate as HIL materials for organic electroluminescent devices.

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