



Synthesis of chloroboron(III) 3,4,12,13,21,22-hexabromosubnaphthalocyanine under high dilution conditions and comparative studies of effects of halogenation on physicochemical properties of subnaphthalocyanines

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ARTICLE INFO

Article history:

Received 7 April 2018

Received in revised form

13 June 2018

Accepted 16 June 2018

Available online 19 June 2018

Keywords:

Subnaphthalocyanine

Bromine

Optical property

Thermal stability

ABSTRACT

Chloroboron(III) hexabromosubnaphthalocyanine was prepared by cyclotrimerization of 6,7-dibromo-2,3-naphthalenedicarbonitrile in the presence of BCl₃ under high dilution conditions, that is 7.4 mM of dicarbonitrile in *o*-dichlorobenzene-*xylene* (1:1). It was converted to fluoroboron(III) hexabromosubnaphthalocyanine by the reaction with AgBF₄. Fluorescence quantum yields of chloroboron(III) hexafluoro-, hexachloro-, hexabromo-, and hexaiodosubnaphthalocyanine were 0.22, 0.20, 0.11, 0.05, respectively, indicating that heavy atom effects of Br and I effectively deactivated the singlet excited states. Thermal decomposition temperature (5% weight loss in the TG curve) of fluoroboron(III) hexabromosubnaphthalocyanine was the highest (359 °C) and that of chloroboron(III) hexafluorosubnaphthalocyanine was the lowest (221 °C) among hexahalosubnaphthalocyanines. The hexabromosubnaphthalocyanine served as a substrate of Sonogashira coupling, and proved to be a useful intermediate for further functionalization of subnaphthalocyanines.

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1. Introduction

Subphthalocyanines and subnaphthalocyanines have a unique cone-shaped ring structure, and its optical and chemical properties have been the focus of investigations [1]. These molecules have an electric dipole along the B-Cl or B-F bond, and such dipolar properties would be enhanced if the stacked columnar structure forms in the solid state. Halogenation of aromatic core of organic semiconductors has been studied actively for several reasons [2]. Introduction of halogen atoms can alter the HOMO/LUMO energy levels, the dipole moments, and molecular packing, which are important properties to be used as semiconductive electronic materials [3]. Halogenated aromatics can be important intermediates for further functionalization of organic semiconductors via cross-coupling reactions. Halogens attached directly to the aromatic

core can accept electrons via a σ -bond, while they can either donate or accept electrons through a π -bond [4]. The latter effects are dependent on the electronic structure of the aromatic core and the substitution patterns by halogen atoms. Bender and coworkers reported molecular packing of axially and peripherally halogenated subphthalocyanines, where halogen bonds can direct the solid state arrangement of the molecules [5]. Risko, Brédas and coworkers reported that molecular packing of semiconductive molecules impacts their electronic properties [6].

Control of HOMO/LUMO energy levels was proved to be important for fabrication of efficient organic solar cells [7]. Open circuit voltage can be controlled by the frontier orbital energy levels of donor and acceptor molecules. Molecular orbital calculations of halogenated subnaphthalocyanines predicted that stabilization of HOMO/LUMO energy levels are most effective by substitution with Cl, followed by Br and F [8]. The dipole moments of the molecules decreases in the order, F > Br > Cl, showing that the magnitude of electron withdrawing effects increases in this order. Gade and

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coworkers studied effects of halogenation of tetraazaperopyrene, and revealed that the HOMO energy levels were scarcely influenced by halogenation, while the LUMO levels were stabilized [4]. Halogen atoms can act as σ -acceptors and π -donors, so that both of stabilization and destabilization of the frontier orbital can occur.

Since the naphthalene ring is more reactive toward electrophilic reagent than the benzene ring, chlorination of naphthalene during the cyclotrimerization of 2,3-naphthalenedicarbonitrile in the presence of BCl_3 is often a serious side reaction. The pursuit of efficient and clean synthesis of subphthalocyanines and subnaphthalocyanines has been the focus of current research [9]. The halogenated subnaphthalocyanines also served as substrates of cross-coupling reactions, and thus are also important intermediates for further functionalization of subnaphthalocyanines [10,11]. So far, subnaphthalocyanines peripherally substituted with F, Cl and I have been successfully prepared [8], while that with Br was not reported in the literature. In the previous paper, we reported that cyclotrimerization of 6,7-dibromo-2,3-naphthalenedicarbonitrile in the presence of BCl_3 failed to give the desired hexabromosubnaphthalocyanine [8b]. We show herein that cyclotrimerization of commercially available 6,7-dibromo-2,3-naphthalenedicarbonitrile under high dilution conditions afforded hexabromosubnaphthalocyanine in reasonable yields. We also compared optical properties, chemical properties, and thermal stability of hexabromosubnaphthalocyanines with other hexahalo derivatives.

2. Results and discussion

2.1. Synthesis

As reported in the previous paper [8b], cyclotrimerization of 6,7-dibromo-2,3-naphthalenedicarbonitrile in the presence of BCl_3 under standard conditions employed for cyclotrimerization of 6,7-dichloro-2,3-naphthalenedicarbonitrile and 6,7-diiodo-2,3-naphthalenedicarbonitrile gave only a trace amount of the desired hexabromosubnaphthalocyanine. We found that cyclotrimerization under high-dilution conditions gave better results. Typically, cyclotrimerization of 6,7-dichloro and 6,7-diiodo-2,3-naphthalenedicarbonitrile was performed using 0.03 M of 6,7-dihalo-2,3-naphthalenedicarbonitrile. Cyclotrimerization of 0.0074 M 6,7-dibromo-2,3-naphthalenedicarbonitrile at 155 °C afforded hexabromosubnaphthalocyanine **1** in 39% yield (Scheme 1). Cyclotrimerization with higher concentrations of naphthalenedicarbonitrile gave a dark brown tar-like material. Consequently, the yield was poor and isolation of the desired product was time consuming. Under high-dilution conditions, purification was

straightforward: washing with hexane and methanol afforded the blue crystals of **1**. Since a large amount of solvent was used, the progress of the reaction was sensitive to the impurities in the solvent. We used deaerated dry xylene and *o*-dichlorobenzene. The original paper of Meller and Ossko employed 8 M of 1,2-benzenedicarbonitrile in 1-chloronaphthalene to prepare chloroboron(III) subphthalocyanine [12]. Torres [13] and Kennedy [14] used 2 M or 0.14 M of 2,3-naphthalenedicarbonitrile, respectively, for the preparation of subnaphthalocyanines. Therefore, the concentration of dicarbonitrile employed here is much lower. Table 1 shows the yields of **1** under various reaction conditions. A low concentration of 6,7-dibromo-2,3-naphthalenedicarbonitrile (0.0074 M) gave higher yields. Longer reaction time lowered the yield as pointed out by Hanack and coworkers [15] for the preparation of similar subnaphthalocyanines. The heating rate also affected the yields, and the optimum conditions were the reaction at 155 °C for 1.5 h, and with a heating rate of 2 °C/min.

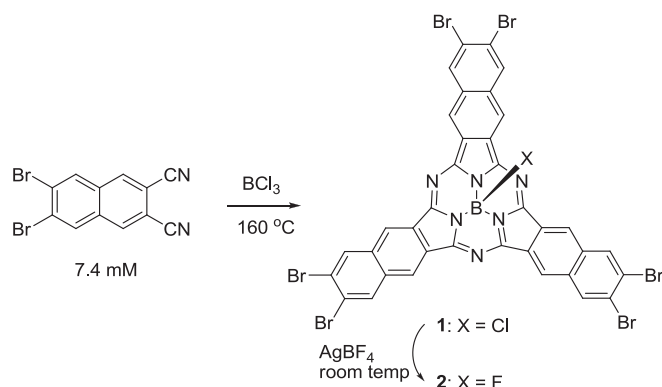
^1H NMR of **1** exhibited two singlets at 8.65 and 9.31 ppm. ^{13}C NMR of **1** showed six signals in sp^2 carbon region at 121.48, 124.37, 129.33, 132.74, 133.71, and 148.89 ppm. DEPT experiments showed that the signals at 121.48 and 133.71 ppm are methine CH carbons. We assigned these signals with the aid of Gaussian *ab initio* calculations as follows: a signal at 121.48 ppm to naphthalene CH closer to subnaphthalocyanine core, that at 124.37 ppm to pyrrole beta carbon, that at 129.33 ppm to naphthalene quaternary carbon bridging two CH carbons, that at 132.74 ppm to ipso carbon carrying bromine, that at 133.71 ppm to naphthalene CH carbon closer to bromine, and that at 148.89 ppm to pyrrole alpha carbon.

Quantum chemical studies on the mechanism of cyclotrimerization of 2,3-naphthalenedicarbonitrile indicated that the reaction proceeds via stepwise addition of (1Z)-3-chloro-*N*-(dichloroboryl)-1*H*-isoindole-1-imine to form a dimer, a trimer, followed by C=N bond isomerization, before the final cyclization step [16]. Although the key intermediate leading to formation of polymeric species is not identified, we speculate that the high dilution conditions can avoid such polymerization process. In the multi-step reactions, it is expected that the heating rate can alter the reaction pathways, to affect the yield of the final product.

Chloroboron(III) subnaphthalocyanine **1** was converted to fluoroboron(III) subnaphthalocyanine **2** by the reaction with AgBF_4 [8]. The fluoroboron derivative is inert to hydrolysis and the smaller van der Waals radius of F would not hinder formation of stacked structures [10]. Axial Cl substitution of subphthalocyanine with F caused a reduced dipole moment and influenced the performance parameters of solar cells prepared from subphthalocyanine and fullerene [17].

2.2. Optical properties

Fig. 1 shows UV–visible spectra of fluoro, chloro, bromo, and iodo subnaphthalocyanines with a B–Cl bond. Structures and



Scheme 1. Synthesis of hexabromosubnaphthalocyanines **1** and **2**.

Table 1

Yields of chloroboron(III) hexabromosubnaphthalocyanine **1** by cyclotrimerization of 6,7-dibromo-2,3-naphthalenedicarbonitrile at 155 °C.

Run	Concentration of dicarbonitrile/M	Reaction time/h	Heating rate/°C min ⁻¹	Yield/%
1	0.03	1.5	2	trace
2	0.012	1.5	2	10
3	0.0074	1.0	2	33
4	0.0074	1.5	2	39
5	0.0074	2.0	2	24
6	0.0074	3.0	2	12
7	0.0074	1.5	5	trace
8	0.0074	1.5	10	trace

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