One-Shot Multiple Borylation toward BN-Doped Nanographenes
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Supporting Information

ABSTRACT: One-shot double, triple, and quadruple borylation reactions of triarylamines were developed through a judicious choice of boron source and Brønsted base. With the aid of borylation reactions, a variety of BN-doped nanographenes were synthesized in two steps from commercially available starting materials. An organic light-emitting diode device employing BN-doped nanographene as an emitter exhibited deep pure-blue emission at 460 nm, with CIE coordinates of (0.13, 0.11), and an external quantum efficiency of 18.3%.

Heteroatom doping of graphene is one of the most promising strategies of engendering fascinating properties into this material. In particular, boron-, nitrogen-, phosphorus-, and sulfur-doped graphenes have been intensively studied as efficient materials for supercapacitors, anodes in Li-ion batteries, cathode catalysts in fuel cells, and sensors, among others.1 Syntheses of these heteroatom-doped graphenes has mostly been accomplished by chemical vapor deposition of carbon and heteroatom sources, or by the thermal annealing of graphene oxides with dopants. However, these approaches produce structurally nonuniform materials, which may prevent the detailed elucidation of the effect of the dopant, and the fine-tuning of physical properties. For these reasons, it is desirable to develop a bottom-up synthesis, based on the surface-assisted coupling2 or amplified growth3 of heteroaromatic compounds, which is potentially advantageous for the production of well-defined heteroatom-doped graphenes.

Recently, heteroatom-doped nanographenes4 have attracted significant attention not only as starting units for bottom-up syntheses, but also as well-defined substructures for heteroatom-doped graphenes. A powerful synthetic method is dehydrogenative C–C coupling (Scholl reaction); N-5 and B-doped6 nanographenes have been successfully synthesized by Müllen et al. and Yamaguchi et al., respectively. Another powerful method is the Friedel−Crafts-type carbon−heteroatom bond-forming reaction, which has provided a variety of polycyclic heteroaromatic compounds.7−11 However, this reaction has been mostly limited to intramolecular processes, and requires precursors possessing hydroxyl7 amino,8 imino,9 halogeno,10 or trimethylsilyl groups,11 which can facilitate initial intermolecular reaction.12 As a consequence, conventional approaches to doped nanographenes13 often require multistep syntheses from commercially available sources. Herein, we report the two-step synthesis of a B4N3-doped nanographene B4 (Scheme 1). The key to success is the quadruple borylation of triarylamines via intra- and intermolecular bora-Friedel−Crafts-type reactions, which converts 11 C−H bonds into C−B bonds in one shot. Moreover, we have succeeded in the development of the selective double and triple borylation of triarylamines, demonstrating the potential of the present strategy.

The two-step synthesis of B4 is summarized in Scheme 1. The first step involves the palladium-catalyzed C−N coupling (Scholl reaction) between the commercially available starting materials, 1,3,5-tribromobenzene and di-p-tolylamine, which proceeded smoothly at 60 °C to afford N1,N1,N3,N3,N5,N5-hexakis(4-methylphenyl)-1,3,5-benzenetriamine 1 in 98% yield. The second step is the one-shot quadruple borylation of 1; in the presence of 12 equiv of BI3, the borylation proceeded under reflux conditions (bath temperature, 200 °C) to afford the target compound B4 in 41% yield (35% isolated yield) and triple borylation compound B3 in 3%.14 While mono- and
diborylated compounds were not observed under these conditions, a considerable amount of unidentified side products were formed. Judging by the formation of di-p-tolyamine, we assume that C–N bond cleavage completed with the borylation reaction. Notably, other boron sources, BCl3 and BBr3, did not give any B4 at all.

After screening of the reaction conditions,14 we succeeded in the double and triple borylation of triarylamines 1 as shown in Scheme 2. In the presence of 5.0 equiv of BI3 and 2.0 equiv of Ph3B, the selective double borylation took place under reflux conditions (bath temperature: 190 °C) to give B2 in 80% yield (76% isolated yield). On the other hand, at elevated temperature (bath temperature: 200 °C) in a high boiling point solvent, 1,2,4-trichlorobenzene, the triple borylation took place to give B3 in 48% yield (45% isolated yield) with 6% yield of B2. Notably, other Brønsted bases, EtN+-BF4-, and other bases, such as NaOH or silver, and the C–N bond cleavage was not observed even at 240 °C.

Figure 1. ORTEP drawing (a) of B3 obtained by X-ray crystallographic analysis. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. NICS(0) values for B3 (b) and the carbon analogue (c) calculated at the B3LYP/6-311+G(d,p) level of theory.

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The triple helical structure of triazatriborahexabenzo-[a,d,g,j,m,p]-coronene B3 was determined by X-ray crystallography (Figure 1a). B3 has a C3 axis of symmetry that passes through B1–C3–C6–N2, but exhibits an almost D3 symmetry conformation due to the large difference between the C–B and C–N bond lengths and the methyl substituents, which is in contrast to the isoelectronic carbon analogue, hexabenzo-[a,d,g,j,m,p]-coronene that adopts an almost D4h conformation.15 In particular, the dihedral angles between the planes of the peripheral benzene rings are very different to each other (A–A′, 30.3°; A–B, 46.4°; B–C, 33.1°; C–C′, 48.2°), while those of the carbon analogue are in the range of 43–45°.

After treatment with 1 N HCl or NaOH, or heating at 300 °C under reflush conditions, the triple and quadruple borylation did not take place at all, even at 240 °C.
separated by the multiple resonance effects of the boron and nitrogen atoms, the phosphorescence maxima at 77 K ($\lambda_{\text{em}}$ = 488, 466, and 475 nm for B2–B4, respectively) are very close to the fluorescence maxima. Based on these emission maxima, the energy difference between the excited singlet and triplet states ($\Delta E_{\text{ST}}$) are estimated to be 0.15–0.18 eV. These are promising characteristics for thermally activated delayed-fluorescence (TADF) materials for organic light-emitting diodes (OLEDs).

To demonstrate the potential of BN-embedded nanographenes, an OLED employing B2 as the emitter was fabricated with the following structure: indium tin oxide (ITO, 50 nm); N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB, 40 nm); tris(4-carbazolyl-9-ylphenyl)amine (TCTA, 15 nm); 1,3-bis(N-carbazolyl)benzene (mCP, 15 nm); 1 wt% B2 and 99 wt% of mCBP (20 nm); diphenyl-4-triphenylsilylphenylphosphine oxide (TSPO1, 40 nm); LiF (1 nm); Al (100 nm). The results are summarized in Table 1. The device exhibited excellent performance for blue OLEDs, demonstrated high performances in the field of materials chemistry. This simple and scalable protocol is useful not only for providing new functional materials but also for the further extension of the π-system, which can spur the further development of bottom-up approaches toward BN-doped nanocarbons.

In summary, we developed one-shot multiple borylation reactions for the successful two-step synthesis of BN-doped nanographenes. The key to success is the judicious choice of boron source and Brønsted base. The BN-doped nanographenes show deep pure-blue fluorescence and small $\Delta E_{\text{ST}}$ values. The OLED device employing B2 as a TADF emitter exhibited an excellent performance for blue OLEDs, demonstrating high potential in the field of materials chemistry. This simple and scalable protocol is useful not only for providing new functional materials but also for the further extension of the π-system, which can spur the further development of bottom-up approaches toward BN-doped nanocarbons.

**Table 1. Properties of OLED Employing B2 as an Emitter**

<table>
<thead>
<tr>
<th>$V_{\text{on}}$ (V)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>CIE (x,y) fwhm (nm)</th>
<th>$\eta_c$ (cd A$^{-1}$)</th>
<th>$\eta_p$ (lm W$^{-1}$)</th>
<th>$\eta_{\text{ext}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8$^a$</td>
<td>460</td>
<td>0.13, 0.11</td>
<td>16.7$^a$</td>
<td>11.5$^a$</td>
<td>7.1$^a$</td>
</tr>
<tr>
<td>5.1$^b$</td>
<td>37 (0.21 eV)</td>
<td>(0.15)</td>
<td>(0.14)</td>
<td>(0.09)</td>
<td>(0.09)</td>
</tr>
</tbody>
</table>

$^a$Abbreviations: $V_{\text{on}}$ voltage required for 1 or 100 cd m$^{-2}$; $\lambda_{\text{max}}$ emission maximum; $\eta_c$ current efficiency; $\eta_p$ maximum power efficiency; $\eta_{\text{ext}}$ maximum external quantum efficiency. $^b$Data at 1 cd m$^{-2}$. Data at 100 cd m$^{-2}$.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b10578.

**Notes**

The authors declare no competing financial interest.

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