191 THIEME



#### Short Review

# **Progress of Polycyclic Boron-Doped Molecular Carbons**

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Abstract Molecular carbons, namely molecular cutout of carbon materials, are of importance for understanding accurate structures of carbon allotropes and developing functional  $\pi$ -electron materials. Doping the boron atoms into π-conjugated skeletons of molecular carbons enables the construction of boron-doped molecular carbons (BMCs), further leading to new chemistry and attractive material systems, which are distinct from carbon-based and other heteroatom-doped molecular carbons. Herein, the bottom-up organic synthesis methodologies have been employed to synthesize BMCs that feature the boron atoms at the edge or in the center of  $\pi$ -skeletons. They have not only amazing topological structures and good stability but also intriguing photophysical and electronic properties. Moreover, they have sufficient Lewis acidity and can coordinate with Lewis bases to form Lewis acid-base complexes, which exhibit stimuli-responsive functions. Notably, some of these BMCs can be utilized in the fields of organic reactions, optical and electronic devices, as well as supramolecular chemistry and photothermal materials. In this short review, we aim to highlight the design and synthetic strategies of polycyclic BMCs, and their unique physical properties and practical applications.

Key words: molecular carbons, boron, electron deficiency, Lewis acidity, topological structures

## Introduction

Molecular carbons (MCs), namely molecular cutout of carbon materials, have attracted great attention because they are not only excellent candidates for understanding accurate structures of carbon allotropes but also promising organic optical, electronic and magnetic materials.<sup>1,2</sup> Till now, various MC systems that feature fascinating topological structures with planar, curved, helical or cyclic conformation and interesting physical properties have been developed.<sup>3,4</sup> The replacement of the sp<sup>2</sup>-hybrized carbon atoms in MCs with heteroatoms is an effective approach to alter their



structural, electronic and physical properties by virtue of the characteristics of the new atoms.<sup>5–7</sup> For example, nitrogen-doped polycyclic MCs are a family of high-performance electron-transporting materials for organic electronic devices.<sup>8</sup> Phosphorus-doped MCs are attractive functional molecules for the fields of supramolecular chemistry and biology.<sup>9</sup> Therefore, the development of heteroatom-doped MCs is of great importance for synthetic chemistry and materials science.

Boron has an intrinsic empty p orbital, making it readily interact with an adjacent  $\pi$ -electron. Thus, the introduction of boron into  $\pi$ -frameworks of MCs may endow the resulting boron-doped MCs (BMCs) with Lewis acidity and electron deficiency, which are completely different from carbonbased or other heteroatom-doped MCs.<sup>10</sup> However, BMCs are more challenging to design and synthesize, due to the instability of boron toward air and moisture. There are two widely used strategies for stabilizing the boron atom, i.e. the first one is to use a large protective group, such as 2.4.6trimethylphenyl (Mes) and 2,4,6-triisopropylphenyl (Tip), to sterically stabilize the boron atom and the second one is to embed the boron atom directly into the annulated core of  $\pi$ -framework to implement structural constraint on the boron atom.<sup>11</sup> As a result, a variety of BMCs with the boron atoms at the edge or in the center of  $\pi$ -skeletons have been reported. The intensive research on BMCs is mainly focused on the development of synthetic methods, construction of topological structures, and exploration of new properties and useful functions.<sup>12,13</sup>

In this context, the bottom-up organic syntheses, such as the Si–B exchange reaction, intramolecular Ni-mediated Yamamoto reaction, tandem intramolecular electrophilic arene borylation, Scholl reaction, and photocyclization reaction, have been employed to synthesize BMCs that feature one, two and even three boron atoms. They have not only amazing topological structures and good stability but also intriguing photophysical and electronic properties. Moreover, they have sufficient Lewis acidity and can coordinate with Lewis bases to form Lewis acid-base complexes, which exhibit stimuli-responsive functions. Notably, some of these BMCs have already been utilized in the fields of organic reacOrganic Materials

L. Yuan et al.



192

**Short Review** 

Biosketches



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tion, optical and electronic devices, as well as supramolecular chemistry and photothermal materials. A number of reviews dedicating to boron-containing  $\pi$ -systems have been published. Herein, this review aims to highlight the design and synthetic strategies of polycyclic BMCs reported in the last decade, and their unique physical properties and practical applications.

# Polycyclic Boron-Doped Molecular Carbons

Yamaguchi's group first proposed a design concept of structural constraint on the B atom for stabilization of the tricoordinate B-containing  $\pi$ -skeleton. They successfully synthesized the completely planarized B-centered BMC **1**, starting from 9,10-dibromo-9,10-diboraanthracene as a key precursor (Figure 1).<sup>14a</sup> Despite the absence of steric protection in the vertical direction with respect to the B atoms, this compound is quite stable against air and water, and has a high thermal stability with the decomposition temperature



**Figure 1** Examples of boron-doped molecular carbons from Yamaguchi's group, and schematic illustration of the formation and dissociation of a Lewis acid–base adduct based on **4**.

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#### **Short Review**

THIEME

Organic Materials L. Yuan et al.

above 350 °C. The single-crystal structure of 1 proves its planar configuration. 1 maintains sufficient Lewis acidity and can react with fluoride ion to form the fluoroborate complex **1**•2 F<sup>-</sup>, leading to a plane-to-bowl conversion of configuration. Subsequently,  $1 \cdot 2F^{-}$  can revert to the neutral 1 upon addition of Lewis acid BF<sub>3</sub>·OEt<sub>2</sub>, achieving reversibility of the plane-to-bowl conversion. Recently, another neutral  $\pi$ radical BMC 2 that contains a B atom in a planarized triphenylmethyl radical framework was reported.<sup>14b</sup> The incorporation of the B atom enhances the spin delocalization, leading to its remarkable stability. This compound exhibits ambipolar transport characteristic with well-balanced electron and hole mobilities. Thus, it can be regarded as a representative example for an organic Mott-insulator transistor that works at room temperature. Notably, the BMC 2 exhibits a relatively large on-site Coulomb repulsion (~1 eV), which cannot be achieved for conventional organic charge-transfer complexes.

The BMCs **3a-3c** were prepared by the bottom-up organic synthesis via intramolecular oxidative cyclodehydrogenation (Scholl reaction).<sup>14c,d</sup> The single-crystal structures depict their nonplanar configurations because of steric overcrowding in the cove regions. The broad absorption that covers the entire visible region is attributed to the significant contribution of the B atoms, whose p orbital contributes to the molecular orbitals that are involved in the electronic transitions for the absorption spectra. They can react with some Lewis bases, leading to the obviously changed absorption and fluorescence spectra, as well as molecular conformations. For instance, the THF solution of **3a** shows a weak near-infrared (NIR) fluorescence ( $\Phi_{PI} = 0.03$ ). Upon exposure to gaseous NH<sub>3</sub>, the complex exhibits bright yellowish green fluorescence with the emission peak at 526 nm  $(\Phi_{PI} = 0.42)$ . In addition, they exhibit reversible multiredox properties, and thus **3a** and **3b** can be applied as active materials for Li battery electrodes. Notably, **3b** possesses a high capacity and stable charge/discharge performance in the voltage range of 1.5 – 4.0 V.

The partially fused BMC 4 was synthesized via treatment of tris(8-bromonaphthyl)borane with (Me<sub>3</sub>Si)<sub>3</sub>SiH and 1,1'azobis(cyclohexanecarbonitrile) as a radical initiator.<sup>15a</sup> This compound shows high chemical and thermal stability, and its sufficient Lewis acidity enables it to generate Lewis adducts with pyridine derivatives. The solution of **4** shows an orange emission with a fluorescence peak at 573 nm and  $\Phi_{\rm PL}$  of 0.15. Incremental addition of pyridine leads to a new emission band at 500 nm that originates from 4-pyridine, but along with only a slight decrease in intensity for the fluorescence of 4. This observation is in virtue of the photodissociation of partial 4-pyridine molecules in the excited state, and thus the dual fluorescence arising from both of 4 and 4-pyridine is observed. This coordination/dissociation dynamics of the B-N Lewis adduct is used for the fabrication of organic field-effect transistors (OFETs).<sup>15b</sup> The solubility of **4** is drastically enhanced by the addition of 1 wt% of Lewis basic pyridines. Spin coating of these soluble Lewis complexes affords amorphous thin films, which can be converted into polycrystalline films of **4** by simple thermal annealing. Therefore, an OFET device with **4** as the semiconductor is prepared, which exhibits a typical p-type characteristic with a hole mobility of  $2.5 \times 10^{-4}$  cm<sup>2</sup>·V<sup>-1</sup>·s<sup>-1</sup> that is higher than that of the corresponding vapor-deposited OFET device. This coordination/dissociation strategy may inspire new device fabrication methods for organic semiconductors with low solubility.

Another partially fused BMC **5**, in which an antiaromatic borole moiety is embedded within the polycyclic  $\pi$ -system, exhibits a planar structure with a distorted geometry around the B center and forms the columnar structures with slipped face-to-face  $\pi$ -stacking.<sup>13e</sup> It exhibits remarkably high Lewis acidity, which is contributed by the antiaromatic character and strained structure of the borole substructure. Notably, its Lewis acidity allows an unprecedented interaction with P-containing polycyclic  $\pi$ -systems to form a Lewis acid-base complex. The single-crystal structure of the thusobtained complex reveals the coordination between the Band P-embedded  $\pi$ -systems via the formation of a B–P dative bond. Furthermore, this complex exhibits an interesting stimuli-responsive fluorescence behavior upon photoirradiation.

The BMC 6 bearing hydrophilic side chains was synthesized. This compound shows relatively low Lewis acidity compared to the partially fused counterparts, such as 4 and 5.<sup>15c</sup> The B–N Lewis acid–base adduct based on 6 and strong, charge-neutral Lewis base N.N-dimethylaminopyridine (DMAP) can provide the photo-dissociation behavior. In particular, **6** is an amphiphilic derivative owing to its hydrophilic side chains, and thus shows intriguing supramolecular assembly properties. Increasing water content in DMSO/H<sub>2</sub>O mixed media of 6 leads to significant spectral changes and the formation of sheet-like aggregates. Hence, making use of the labile complexation ability of the B center, the assembly and disassembly processes from the aggregates are facilely manipulated via the successive addition of DMAP and trifluoroacetic acid in an aqueous system. The approach for stabilization of the B atom by structural constraint proposed by Yamaguchi et al. dramatically promotes the development of BMCs and their related functional materials.

Wagner's group developed a rational synthetic strategy based on Peterson olefination, stilbene-type photocyclization, and Si–B exchange reaction to obtain a series of BMCs, such as **7** and **8** (Figure 2).<sup>16a</sup> The single-crystal structure of **8** shows a fully planar  $C_i$ -symmetric configuration. It emits the bright blue fluorescence with a high  $\Phi_{PL}$  of 78%, compared to the planarized double silicon-bridged congener and the parent molecule dibenzo-[*g*,*p*]chrysene. This is mainly attributed to the specific electronic effect of the B atoms with their  $\pi$ -conjugated p orbitals. Therefore, replacing two C

#### **Organic Materials**

L. Yuan et al.



Figure 2 Examples of boron-doped molecular carbons from Wagner's group, and two different cyclization modes of 10.

atoms in bisanthene by the B atoms affords an efficient blue luminophore. Then, they disclose the Ru-catalyzed cyclization of aryl energies as a useful approach to annulate benzene rings onto pre-existing aryl scaffolds. The two BMCs 9a and 9b were steadily synthesized.<sup>16b</sup> As the dangling phenyl ring in **9b** is a part of a stilbene-type substructure, **9b** can undergo a photocyclization reaction to obtain a fully fused BMC. All of them are inert toward air and moisture and highly luminescent in the short-wavelength region. By combining a Peterson olefination with Ru-catalyzed and/or photoinduced cyclization reactions, several related B/Nand B/S-containing MCs were further developed.<sup>16c</sup>

This group adopted a two-step synthesis and furnished quadruply annulated borepins in high yields.<sup>16d</sup> A nucleophilic substitution reaction affords 10, and then an intramolecular Ni-mediated Yamamoto reaction on 10 produces the borepin **11** via the formation of the seven-membered ring. The formation of **11** is accompanied by a C–H activation reaction, simultaneously affording compound **12** that contains a six-membered boracycle. The product ratio 11/12 is dominated by the local Ni(0) concentration. The long-wavelength absorption peaks of 11 and 12 are observed at 444 and 415 nm, respectively, whereas their emission maxima are similar ( $\lambda_{em}$  = 462 nm for **11** and  $\lambda_{em}$  = 468 nm for **12**). Thus, a larger Stokes shift of 53 nm is observed for 12. In addition, while 11 undergoes a reversible one-electron reduction, the electrochemical reduction of 12 is fully irreversible. Notably, this mesityl-substituted borepin **11** is stable enough toward air and moisture, which is different from most of the reported borepins that are sterically protected by more demanding supermesityl groups, such as 2,4,6-tri-tert-butylphenyl.

The intramolecular Ni-mediated Yamamoto reaction was further employed for the synthesis of the BMC 13 from the tetrabrominated 9,10-di(naphth-1-yl)-9,10-dihydro-9,10diboraanthracene.<sup>16e</sup> It is notable that this intramolecular C-C heterocoupling reaction exhibits an obvious solvent dependence: 13 was synthesized only in pyridine with a yield of 79%, whereas an oxadiborepin was formed in THF with a vield of 81%. The single-crystal structure of 13 has a  $C_2$  symmetry and two different kinds of axial chiral units, thus leading to its good solubility even in *c*-hexane. Compared to its parent compound tetrabenzo[de,hi,op,st]pentacene, the emission color of 13 shifts from red to blue. The titration experiment proves that **13** behaves as a Lewis acid, but only monoadduct is possibly formed, even with the strong Lewis base DMAP. Additionally, 13 is an electron acceptor and undergoes reversible reduction at half-wave potential of  $E_{1/2} = -1.73 \text{ V}$  (vs. Fc/Fc<sup>+</sup>) in the cyclic voltammogram curve. Thus, the synthetic strategies developed by Wagner et al. are very desirable for the construction of BMCs with fascinating structures and properties.

Ingleson's group developed a facile yet versatile strategy to synthesize BMCs in a controlled manner.<sup>17a</sup> They adopted one-pot borylative cyclization/intramolecular electrophilic C-H borylation of naphthyl-alkynes, oxidation using [Ph<sub>3</sub>C] [BF<sub>4</sub>]/2,4,6-tri-tert-butyl pyridine and final reaction with MesMgBr to generate the polycyclic BMC 14 (Figure 3). For the doubly B-doped MC 15, the corresponding diyne precursor was employed and the similar reactions were per-



Figure 3 Examples of boron-doped molecular carbons from Ingleson's group, and two different cyclization modes of 17.

194

THIEME

#### **Organic Materials**

L. Yuan et al.

195

THIEME

formed. In addition, the B-Cl-containing intermediates could also react with (2,6-di(prop-1-en-2-yl)phenyl)lithium, and then treatment of the resulting compounds with Sc(OTf)<sub>3</sub> may afford the fully planarized BMCs via intramolecular Friedel-Crafts cyclization. On the other hand, the electrophilic bromination on 14, Sonogashira coupling, and then the similar electrophilic borvlation and oxidation as described above may produce the triply B-doped MC 16.17b From **14** to **15** to **16**, the  $\pi$ -electron delocalization is extended and the LUMO energy level gradually decreases, leading to the decreased optical band gap and red-shifted lowest energy adsorption/emission maxima.

This group reported using the borylative cyclization to achieve pristine B-doped phenalene (1-boraphenalene), which can be regarded as the smallest-size polycyclic BMCs.<sup>17c</sup> Phenalenyl is an open-shell MC molecule that contains 13 C atoms and 13  $\pi$  electrons, whereas the phenalenyl cation is isoelectronic to 1-boraphenalene (C<sub>12</sub>B). 18 and 19 containing no additional annulation were steadily synthesized starting from 17 (1-ethynylnaphthalene for 18 and 1-(*p*-tolylethynyl)naphthalene for **19**) in the presence of BBr<sub>3</sub>. Both of them have planar structures and good bench stability. The density functional theory calculation results indicate that the nature of the LUMOs in 18 and 19 is closely comparable to that in carbon-based phenalenyl cation analogues, but 18 and 19 have obviously lower aromatic stabilization of the C<sub>5</sub>B ring than observed in each ring in the D<sub>3</sub>h phenalenyl cations, owing to the less delocalized nature of the occupied orbitals of  $\pi$  symmetry in the 1-boraphenalenes. Based on this facile synthesis strategy, the BMC 20 was synthesized starting from 1,6-bis((4-(tert-butyl)phenyl)ethynyl)pyrene.<sup>17d</sup> Cyclic voltammetry study reveals that it has a low LUMO energy level of -4.12 eV, indicative of its potential application as an electron acceptor unit in organic electronic devices. Subsequently, the C-Br units in 20 enable the construction of an electron donor-acceptor-donor (D-A-D) molecule using Negishi cross-coupling reaction. The thus-synthesized compound bearing two triphenylamine moieties displays a broad absorption band stretching up to 750 nm and a narrow optical gap of 1.65 eV. Thus, the electron-accepting character of 20 along with the electrondonating effect of the triphenylamine group contributes to the small energy gap. The simplicities of these synthetic approaches make them be a powerful tool for rapidly generating stable BMCs, which are of importance for facilitating structure-property relationship studies and optoelectronic applications.

Würthner's group reported an alternative one-pot synthetic strategy to develop novel BMCs. The alkene hydroboration and C-H borylation with a N-heterocyclic carbene (NHC)-borenium ion 21 followed by dehydrogenation and hydrolysis enabled the successful synthesis of the BMC 22 (Figure 4).<sup>18a</sup> The single-crystal structure of 22 exhibits infinite 1D π-stacking along with significant structural over-



Figure 4 Examples of boron-doped molecular carbons from Würthner's group, and one representative synthetic route for 23.

lap. It exhibits the absorption maximum at 561 nm and a fluorescence peak at 603 nm with a  $\Phi_{PI}$  of 0.63. It can undergo two-step reversible one-electron reductions at -1.30 and -1.64 eV vs. Fc/Fc<sup>+</sup> in DMSO. Despite the absence of steric protection or planar constraint on the B center, it also achieves good stability and relatively facile electrochemical reductions. Furthermore, the reaction of 22 with BBr<sub>3</sub> and subsequent MesMgBr in toluene generates the BMC 23.18b Compared to 22, the absorption and emission spectra of 23 are significantly red-shifted, and notably, the fluorescence band of 23 appears in the NIR region with the main peak at 668 nm. Two-step reversible one-electron reductions of 23 occur at -1.07 V and -1.47 V, along with the first reduction at a more positive potential, suggesting a lower LUMO energy level of 23. Furthermore, the application of 23 as an active material in organic electronic devices is demonstrated. Notably, the OTFT device using it as n-type semiconductor exhibits the electron mobility of  $3 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ , and organic solar cells using it as electron acceptor achieve the power conversion efficiency up to 3%. This latter application represents the first use of BMC as an acceptor material in organic photovoltaics.

This group further devised and executed a new synthesis for BMCs based on the above strategy.<sup>18c</sup> The consecutive hydroboration/electrophilic borylation/dehydrogenation and BBr<sub>3</sub>/AlCl<sub>3</sub>/2,6-dichloropyridine-mediated C-H borylation steps afforded the BMC 24. The single-crystal structure of **24** shows a moderately planar  $\pi$ -surface and thus exhibits 1D columnar  $\pi$ -stacking with an intermolecular packing distance of 3.4 Å. This strong intermolecular interaction decreases the solubility of 24 in most organic solvents. This compound absorbs strongly in the visible region and emits in the NIR region up to 1150 nm with the fluorescence peak at 757 nm. In addition, 24 exhibits two reversible reductions at -1.00 V and -1.17 V vs. Fc/Fc<sup>+</sup>, indicating its facile reduction ability and low-lying LUMO level. Following this synthetic strategy, they further developed two BMCs 25 and 26 using the corresponding alkenes.<sup>18d,e</sup> Interestingly, Pd-catalyzed [5+2] annulation with suitable aryl dihalides toward 25 or 26 generates carbon-based MCs that feature sevenmembered rings. This method is very useful to expand the scope of available nonplanar MCs with both positive and negative curvatures.

Hatakevama's group developed the tandem intramolecular electrophilic arene borylation to facilitate access of BMCs.<sup>19</sup> Precursor 27 is subjected to lithium-halogen exchange, followed by trapping of the resulting aryllithium with BBr<sub>3</sub> to afford the key intermediate (Figure 5). Then, 2 equiv of EtNiPr<sub>2</sub> promotes the cyclization to afford **28** with the yield of 55%. Notably, Wagner et al. also reported the synthesis of 28 but using a different method, namely through a Ni-mediated Yamamoto C-C-coupling reaction. The single-crystal structure of 28 adopts a helical configuration due to the steric repulsion of the cove region. Although 28 owns a nonplanar structure, it is stable enough toward oxygen, 1 N HCl, and 1 N NaOH. Its toluene solution exhibits strong visible absorption and fluorescence with a  $\Phi_{PL}$  of 0.90. It undergoes one reversible reduction with a peak potential at -1.76 V vs. Fc/Fc<sup>+</sup> in CH<sub>3</sub>CN. Thus, the use of 28 as an active material in organic light-emitting diode (OLED) and OFET devices is reported.

Feng's group disclosed a novel one-pot synthetic strategy for the synthesis of BMCs, from the easily accessed alkyne precursors.<sup>20</sup> The reaction mechanism involves a sequence of borylative cyclization, 1,4-boron migration, and electro-



**Figure 5** Examples of boron-doped molecular carbons from Hatakeyama's group, Feng's group, Wagner's group and Wang's group, and their representative synthetic routes.

philic C–H borylation, determined by experimental and theoretical investigations. For instance, BBr<sub>3</sub> is added into a solution of **29** and 2,4,6-tri-*tert*-butylpyridine (TBP) in 1,2,4trichlorobenzene, and the mixture is heated at 200 °C, leading to the successive formation of **29a**, **29b** and **29c** (Figure 5). Subsequently, treatment of the solution with MesMgBr directly affords the BMC **30**. Using the corresponding dialkyne precursor, doubly B-doped MC **31** was also obtained. From **30** to **31**, the longest-wavelength absorption peak and emission maximum are red-shifted owing to the increase of the conjugation length. **31** displays a high photoluminescence quantum yield ( $\Phi$  = 0.91) and thus can be used to fabricate the OLED device, further demonstrating the promising application of BMCs in organic optoelectronics.

Two examples of B-doped acenes as linearly fused BMCs are also shown and discussed. Wagner's group reported using a vicinal electrophilic diborylation reaction to synthesize a variety of BMCs.<sup>21</sup> For example, 4,5-dichloro-1,2-bis(trimethylsilyl)benzene (**32**), BBr<sub>3</sub> and anthracene (**33**) in hexane were heated at 120 °C for 2.5 days. After removing the residual BBr<sub>3</sub>, MesMgBr was added to afford **34**. Its cyclohexane solution shows a bright fluorescence ( $\lambda_{em}$  = 470 nm) with a small Stokes shift (5 nm) and a quantum efficiency of 90%. The dechlorinated derivative was thus employed as the emissive material in the OLED device.

Wang's group synthesized the longest doubly B-doped acenes.<sup>22</sup> The Si/B exchange reaction on **35** with BBr<sub>3</sub> affords the linear dihydrodiboraheptacene backbone, and subsequently treatment of this intermediate with TipMgBr leads to **36**. Single crystals prove that **36** adopts a nearly coplanar  $\pi$ -conjugated framework. In particular, **36** can undergo chemical reductions in THF to generate radical anion and dianion derivatives by adding 1 or 2 equiv potassium, respectively. Furthermore, the THF solution of **36** exhibits an ultrahigh photoluminescence quantum yield ( $\Phi_{PL}$ =98±2%), indicating its promising application as luminescent materials in organic optoelectronics.

Dou's group proposed controlled cyclization of conjugated organoboranes as an efficient methodology to construct BMCs. This approach includes two key advantages: (1) rapid  $\pi$ -extension of the framework can be achieved, which is very desirable to design large-size and even nanoscale BMCs, and (2) the edge structures and B-doping modes of BMCs can be precisely controlled, which are of importance for manipulating electronic structures and properties and further exploring new functions.

They designed and synthesized a new B-containing building block, namely doubly B-doped heptazethrene **37**, via double Si–B exchange reaction (Figure 6).<sup>23</sup> Treatment of **37** with MesMgBr generates the BMC **38**, which is stable enough for purification and characterization. Compared with the P=O- and Si-containing analogues, **38** has a smaller energy gap and thus remarkably red-shifted absorption and fluorescence bands by over 80 nm, which are attributed to

196

THIEME

### Organic Materials L. Yuan et al. THIEME OPEN ACCESS Short Review

197

the presence of unique  $p-\pi$  conjugation of the B atoms. Treatment of **37** with 9-lithium-bis(mesityloxy)anthracene followed by Scholl reaction on **39** affords the fully fused BMC **40**. As determined by the single-crystal structure, **40** 



Figure 6 Examples of boron-doped molecular carbons from Dou's group, and the synthetic routes for 38 and 40.

has 19 hexagonal rings that are fused together to construct its planar graphene nanoflake with a C<sub>54</sub>B<sub>2</sub> skeleton. Despite the presence of the large steric hindrance at the periphery of **40**. one molecule is rotated by about 60° to stack on the other molecule with the formation of a  $\pi$ - $\pi$  stacking dimer. Thus, this unprecedented bilayer offset-assembled dimer may be regarded as a molecular cutout of layered B-doped graphene, which is useful for understanding the structure and properties of B-doped graphene at the molecular level. **40** possesses the very broad light absorption that covers the entire visible range of 350 - 750 nm with absorption peaks at 725, 603 and 556 nm, and sharp NIR fluorescence with a peak at 729 nm and an FWHM of only 26 nm. Such unique photophysical properties contributed by the B atom are very rarely achieved for other reported BMC systems. On the other hand, 40 displays five-step reversible redox ability, and in situ vis-NIR spectroelectrochemistry measurements prove the formation of three reduced species of 40. The theoretical calculations show that 40 has obvious aromatic character, whereas the dicationic species of its all-carbon analogue has dominant global aromaticity. This result reveals that Bdoping of polycyclic  $\pi$ -systems may alter their electronic structures, which cannot be easily obtained by oxidative manipulation of their all-carbon analogues.

This group then reported two organoborane cyclophanes including **41**, which are composed of B-doped  $\pi$ -skeletons and flexible alkyl chain linkers, thus representing a new kind of non-conjugated organoborane macrocycles.<sup>24a</sup> They selected the BMC **28** as the key building block and employed the ruthenium-catalyzed olefin metathesis reaction for the synthesis. The photophysical properties and Lewis acidity of these two molecules are fully investigated, and notably, their Lewis acid–base adducts with DMAP may dissociate in the excited state and thus display intriguing photo-responsive fluorescence properties, which can be further modulated by temperature.

Molecular ribbons (MRs), namely graphene nanoribbons with accurate and monodisperse structures, have wonderful topologies and properties. Herein, they disclosed that the modular synthetic method that involves mild photochemical cyclization methodology is desirable for the synthesis of B-doped MRs.<sup>24b</sup> The BMCs 42-44 with multiple cove edges were prepared through Mallory photochemical cyclization on conjugated organoboranes in solution. The single-crystal structures of **43** and **44** feature the isomeric  $C_{68}B_2 \pi$ -skeletons with 2.2 nm in length, thus representing a new kind of B-doped MRs. From 42 to 43 and 44, the absorption and emission wavelengths are comparable, but the molar absorption coefficients are enhanced by more than two times. The B atoms endow them with sufficient Lewis acidity, and notably, the formed Lewis acid-base adducts based on 43 and 44 containing two B atoms display the unprecedented photo-induced dual-dissociation progress, further inducing stimuli-responsive fluorescence properties. In addition, deTHIEME

Organic Materials L. Yuan et al.

spite the highly contorted topological conformations, their potential utility as organic semiconductors is demonstrated by fabrication of the single-crystal OFET devices. Both **42** and **43** exhibit unipolar p-type charge carrier transport in air, along with a higher hole mobility of  $0.06 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  for **42**. Although this value is modest, it remains among the best for pristine tricoordinate B-doped MCs. Different from the use of on-surface synthesis to produce B-doped graphene nanoribbons, this study reports the first example for in-solution synthesis of B-doped MRs.<sup>25</sup>

Through in-depth combination of cyclization methodologies, BMCs with more sophisticated polycyclic structures were constructed.<sup>26</sup> A class of BMCs (45-47) that feature the  $C_{56}B_2$  or  $C_{84}B_2$  polycyclic  $\pi$ -skeletons with selective cove/fjord or cove/bay edges, respectively, were achieved by sequential cyclization via rational combination of Mallory photoreaction and Scholl reaction. Among them, 47 has a molecular length of 2.2 nm, thus representing not only the largest B-doped  $\pi$ -system but also a new kind of B-doped MRs that feature the angular (Z-shaped) one-dimensional topology. From 45 to 46 and 47, the energy gaps determined by the onset absorptions are significantly decreased from 2.47 eV to 2.01 eV and 1.69 eV, and the main fluorescence peaks are red-shifted from 504 nm to 612 nm and 721 nm, respectively. These obvious spectral changes are ascribed to the different delocalization extents of  $\pi$  electrons in BMCs, which are closely related to the variation of fusion mode and  $\pi$ -extension of the frameworks. On the other hand, in the femtosecond transient absorption (fs-TA) spectra, 46 displays the characteristic excited-state absorption and ground-state bleach bands, as well as an unexpected negative bump centered at 667 nm. This latter signal is assigned to the stimulated emission (SE) of 46, suggesting that it may display the optical-gain property. The detailed amplified spontaneous emission (ASE) measurements were performed on the **46**/polystyrene blend film. The ASE function is undoubtedly realized for 46, along with the narrow emission at 669 nm and the final FWHM of 6.4 nm. The threshold value, a pump laser energy that can trigger ASE, is estimated to be  $120 \text{ kW} \cdot \text{cm}^{-2}$ . For **45** and **47**, the doped films do not show any ASE behaviors under various conditions. Thus, precise edge control leads to the first example of ASE-active BMC, which may promote the creation of new ASE and even lasing materials and will open new avenue for polycyclic MCs for organic photonics.

Organic diradicaloids, possessing open-shell electronic structures and properties, have drawn great attention in organic electronics and spintronics. Recently, Dou's group reported the borylation of antiaromatic  $\pi$ -skeletons to design B-containing organic diradicaloids.<sup>27</sup> Based on this strategy, they developed B/O-type and B/N-type diradicaloid compounds. These molecules have excellent ambient stability and open-shell singlet diradical structures, as well as intriguing magnetic and optoelectronic properties, such as ther-

mally accessible triplet species, reversible multiredox ability, narrow energy gaps and NIR absorptions. Moreover, these diradicaloids possess Lewis acidity and thus can coordinate with Lewis bases to form supramolecular diradicaloids, achieving dynamic modulation of diradical character and properties.

Very recently, this group proposed a new strategy to design open-shell BMCs, namely pentagon-fusion of the organoborane  $\pi$ -system (Figure 7).<sup>28</sup> Starting from the B-doped precursors 48 and 51, they successfully synthesized **53** and **54** that feature the  $C_{24}B$  and  $C_{38}B$   $\pi$ -skeletons containing a pentagonal ring, respectively, in four steps based on the Suzuki-Miyaura cross-coupling, nucleophilic addition, intramolecular Friedel-Crafts alkylation and oxidative dehydrogenation reactions. Such pentagon fusion not only gives rise to their local antiaromaticity, but also incorporates an internal quinoidal substructure and thereby induces open-shell singlet diradical states, as determined by variable-temperature <sup>1</sup>H NMR and ESR measurements and theoretical calculations. It is notable that their solutions display very broad absorption bands that cover the visible and NIR regions with the range of 300-920 nm for 53 and 300 – 1030 nm for 54. Furthermore, the solid powders of 53 and 54 display further red-shifted absorptions with the range of 300 - 1050 nm and 300 - 1200 nm, respectively. As a result, they can be used as organic photothermal materials, and 54 exhibits a photo-thermal power conversion efficiency of 21.2% and a solar-driven water evaporation effi-



**Figure 7** Example of diradicaloid boron-doped molecular carbons from Dou's group, and the synthetic routes for **53** and **54**.

Organic Materials L. Yuan et al.

199

ciency of 93.5%. The solar-driven water evaporation performance of **54** is among the highest for organic photothermal materials and comparable to inorganic solar-thermal materials.

# Conclusions

Doping the boron atoms into  $\pi$ -conjugated skeletons of MCs enables the construction of BMCs, further leading to new chemistry and attractive material systems, which are completely different from carbon-based and other heteroatomdoped MCs. Great developments have been made in chemistry and materials of BMCs in the last decade. In this short review, we aim to highlight the design and synthetic strategies of polycyclic BMCs, and their unique physical properties and practical applications. (1) The inherently reactive boron atom surrounded by sterically bulky aryl groups or protected via structural constraint is rationally designed, producing highly stable BMCs with the boron atoms at the edge or in the center of  $\pi$ -skeletons, respectively. (2) The bottomup organic syntheses are widely utilized to synthesize BMCs. For instance, the Si-B exchange reaction, intramolecular Nimediated Yamamoto reaction and tandem intramolecular electrophilic arene borylation are quite useful for small-size BMCs and boron-doped building blocks, whereas the Scholl reaction and photocyclization reaction are more desirable for large-size BMCs with sophisticated topologies. (3) The electronic structures and properties of BMCs can be effectively modulated by controlling the  $\pi$ -extended and edge structures, as well as boron-doping modes. For instance, the energy gaps are significantly decreased by varying fusion mode and increasing  $\pi$ -extension, and incorporation of a five-membered ring imparts BMCs with local antiaromaticity and diradical structures. (4) The new properties and unexpected functions of BMCs are continuously being explored and discovered. For instance, BMCs exhibit diverse potentials in organic optoelectronics, e.g. as an electron acceptor in organic photovoltaics, a hole-transporting semiconductor in OFETs, and an ambipolar semiconductor in organic Mott-insulator transistors. The unique Lewis acidity of BMCs makes them coordinate with Lewis bases to form Lewis acid-base adducts, which may dissociate upon photo-, thermal- or acid-stimulus, and thus display stimuli-responsive fluorescence, assembly and diradical properties. The SE behavior, ASE and photothermal conversion functions are observed, opening an avenue of BMCs for organic photonics and energy field.

Despite these significant advances, it is still needed to make more efforts on BMCs to achieve deep understanding and quantitative prediction of the fundamental properties of more sophisticated polycyclic  $\pi$ -systems, such as boron-doped nanographenes and MRs, as well as negatively curved BMCs and even open-shell BMCs. Precise introduction of the

boron atoms into the  $\pi$ -framework, control over topological structures and expansion of the  $\pi$ -system as well as induction of open-shell electronic states remain a great challenge, and improvement in synthetic methodologies is an important factor for achieving these goals and thereby developing new functional materials with tunable characteristics. We believe that this review gives insight into understanding and opportunity of BMCs, which may help promote the rapid development of chemistry and materials of MCs.

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# **Conflict of Interest**

The authors declare no conflict of interest.

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200

THIEME

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201

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