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Synthesis of a BC₆ polymer *via* cyclotrimerization of alkynylborane and its application as a heterogeneous Lewis acid catalyst

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Lewis acidic boron-containing π -conjugated polymer materials have been demonstrated to be promising for sensing and catalysis; however, the synthetic approaches and the number of installed boron atoms have been limited. Herein, we report the synthesis of a BC₆ polymer structure *via* cyclotrimerization of alkynes. The resulting polymer exhibited superior catalytic activity to small-molecule analogues such as BPh₃ and previously reported boron-containing polymers. This enhanced performance is attributed to the high boron content and increased Lewis acidity of BC₆, as supported by theoretical and experimental analyses. Owing to its polymeric nature, the catalyst was readily recovered and reused in the catalytic system. These findings demonstrate that building rigid polymer frameworks with a high density of Lewis acidic boron sites is a promising approach to developing recyclable heterogeneous Lewis acid catalysts, and offers a broadly applicable design principle for functional boron-containing polymeric materials.

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Introduction

Boron-containing π -conjugated polymer materials have attracted significant attention due to their potential application in optoelectronic devices,¹ gas storage,² sensors,^{3–5} and catalysis.^{6–9} The controlled incorporation of boron atoms into the conjugated backbone enables precise modulation of the electronic structure, influencing the physical properties and chemical reactivities of the resulting polymers. Triarylborane (BAR₃) units have attracted considerable interest, as the electron-deficient vacant p-orbital on boron endows them with Lewis acidic character. However, BAR₃ units generally require bulky substituents on the aryl group for kinetic stabilization *via* steric protection. While such substituents improve chemical stability, they also reduce reactivity toward sterically hindered substrates. Recently, conjugated polymers incorporating non-sterically hindered BAR₃ units have emerged, demonstrating that less bulky structures can broaden the chemical utility of boron-containing materials, particularly for sensing and catalysis.^{10–13} Based on these studies, we anticipated that increasing the density of Lewis acidic boron sites would benefit performance across a range of applications. In our previous work, a boron-doped π -conjugated polymer, BC₉, was synthesized *via* B–C coupling between organolithium reagents

and boron halides (Fig. 1a).¹³ This strategy provides an efficient way to synthesize high boron content polymers compared with conventional metal-catalyzed C–C coupling reactions.^{10,13} Pushing the boron content beyond BC₉ is synthetically demanding. BC₆ represents the maximum boron-loading composition while retaining intact BAR₃ units, yet it has not been synthesized to date. This may stem from a limitation of established B–C coupling routes: the key precursor, tri-

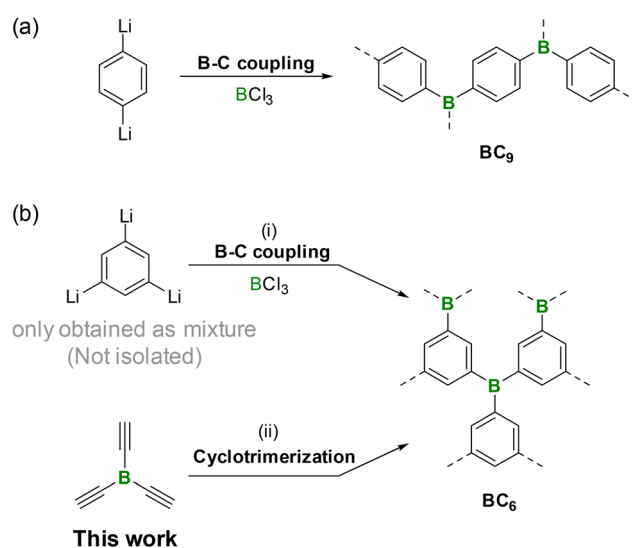


Fig. 1 Synthesis of (a) BC₉ and (b) BC₆ *via* (i) B–C coupling and (ii) cyclotrimerization.

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lithiobenzene, is highly reactive, making its controlled generation and selective isolation challenging, which in turn hampers a selective synthesis of **BC**₆ (Fig. 1bi).¹⁴ To overcome this limitation, we focused on the cyclotrimerization of alkynes.¹⁵ In this approach, boron-containing monomers bearing multiple alkyne units undergo cyclotrimerization to construct aromatic rings within the polymer network.^{16,17} We envisioned that cyclotrimerization of triethynylborane would enable the construction of a **BC**₆ structure (Fig. 1bii).

In this study, we report the synthesis of a Lewis acidic **BC**₆ polymer structure, enabled by alkyne cyclotrimerization. To assess the Lewis acidity of the resulting polymer, we investigated its interaction with pyridine, which was confirmed by Fourier-transform infrared (FT-IR) spectroscopy and thermogravimetry mass spectrometry (TG-MS). The Lewis acidity of **BC**₆ was further evaluated through the transesterification of methyl benzoate. Given the potential of the boron-containing π -conjugated polymer material as a heterogeneous catalyst that enables facile separation, we also examined the recyclability of **BC**₆.

Results and discussion

To evaluate the effect of BAR_3 units in the polymer structure, theoretical calculations of the Lewis acidity of boron-containing compounds were performed. The Global Electrophilicity Index (GEI),¹⁸ a widely used quantitative and base-independent measure of Lewis acidity, was calculated and compared for triphenylborane (BPh_3) and 1,3,5-tris(diphenylboranyl)benzene (TDBB) at the B3LYP/6-31+G(d) level (Fig. 2). To examine the π -conjugation effect between boron and aryl groups, these model compounds were constrained to a planar geometry, which minimizes conformational variations and

enables a direct comparison of electronic properties. As a result, TDBB shows a slightly lower LUMO energy (-2.39 eV) than BPh_3 (-2.26 eV), which can be attributed to the increased number of boron content. This is reflected in a higher GEI value for TDBB (2.40 eV) compared to BPh_3 (2.26 eV). This finding motivated us to synthesize **BC**₆, which is expected to exhibit stronger Lewis acidity than conventional organoborane compounds such as BPh_3 and typical π -conjugated main-chain polymers with sterically hindered BAR_3 units. The same trend was also observed for the optimized structures (Table S1), where TDBB showed a slightly higher GEI value than BPh_3 . The planar-constrained models gave a more pronounced difference, indicating that coplanar π -conjugation between the aryl framework and the boron centers enhances the electron-deficient character. These results support our design concept that increasing the density of boron centers in the **BC**₆ framework can enhance Lewis acidity.

Triethynylborane is unstable and is estimated to have a low boiling point. To improve its handling and chemical stability, triethynylborane-pyridine (TEB-Py) has been reported as a stable and isolable complex.^{19,20} In this work, TEB-Py was used as the starting material for the synthesis of **BC**₆.

Transition metal catalysts have proven effective in facilitating the formation of boron-containing polymers.²¹ On the other hand, many organoboron species, including phenylboronic acid as well as arylboranes and arylborate salts, are known to participate in metal-catalyzed cross-coupling reactions,^{22,23} suggesting that their B-C bonds are easily activated and cleaved under typical catalytic conditions. This poses a challenge for constructing boron-containing frameworks that retain intact B-C bonds. Therefore, we first optimized the cyclotrimerization conditions using a model compound, ethynyl-diphenylborane-pyridine complex (Table 1). The model compound was reacted with acetylene in the presence of a metal catalyst, and the generation of triphenylborane-pyridine ($\text{BPh}_3\cdot\text{Py}$) was analysed by ¹¹B NMR spectroscopy. Metal

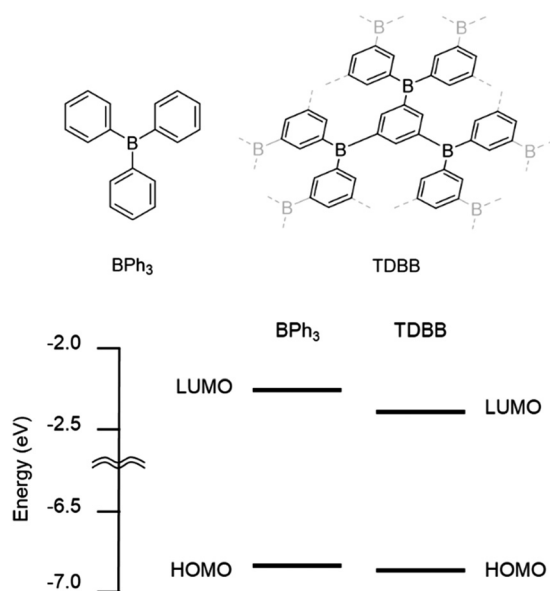


Fig. 2 Theoretical Lewis acidity of BPh_3 and TDBB based on GEI theory at level of B3LYP/6-31+G(d).

Table 1 Screening of metal catalysts^a

Entry	Catalyst	Solvent	Temp. (°C)	Product ratio [%]
1 ^b	PdCl_2	Benzene	40	0
2 ^c	$\text{NiCl}_2\cdot\text{DME}$	CH_3CN	100	0
3 ^d	$\text{Co}_2(\text{CO})_8$	Toluene	120	100

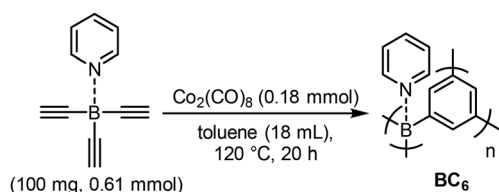
^a Ethynyl-diphenylborane-pyridine complex (0.1 mmol), acetylene (1 atm), 20 h, product ratio of $\text{BPh}_3\cdot\text{Py}$ was determined by integration of the ¹¹B NMR spectrum of the crude reaction mixture. ^b Catalyst: PdCl_2 (0.067 mmol), reagent: CuCl_2 (2.4 mmol), solvent: 1-BuOH (720 μL) and benzene (12 mL), temp: 40 °C. ^c Catalyst: $\text{NiCl}_2\cdot\text{DME}$ (0.12 mmol), solvent: CH_3CN (10 mL), temp: 100 °C. ^d Catalyst: $\text{Co}_2(\text{CO})_8$ (0.12 mmol), solvent: toluene (12 mL), temp: 120 °C.



catalysts commonly used in alkyne cyclotrimerization were selected, regardless of whether they had been previously applied to polymer synthesis.^{16,24,25} When PdCl₂ was used, no formation of BPh₃·Py was observed. ¹¹B NMR spectroscopy revealed that the consumption of the starting material and the formation of diphenylborinic acid (Table 1, entry 1). In the case of NiCl₂, similarly, BPh₃·Py was not formed, and diphenylborinic acid and phenylboronic acid were observed (Table 1, entry 2), suggesting that C–B bond activation occurred in both cases. In contrast, when Co₂(CO)₈ was used, the formation of the BPh₃·Py was confirmed, and neither diphenylborinic acid nor phenylboronic acid was observed (Table 1, entry 3). These results indicate that the alkynylborane underwent successful cyclotrimerization with acetylene in the presence of Co₂(CO)₈, which was selected as the catalyst for the subsequent polymer synthesis.

BC₆ was synthesized from TEB·Py at 120 °C for 20 h using Co₂(CO)₈ as a catalyst (Scheme 1). The resulting product was washed with hexane, water, and methanol, and the insoluble residue was collected. No signals corresponding to the starting material were observed in the ¹H and ¹¹B NMR spectrum of the filtrate (Fig. S14 and S15), suggesting the reaction proceeded quantitatively.

The polymer was initially analysed by solid-state ¹¹B magic-angle spinning (ss MAS) NMR. A single but broad peak at 4.30 ppm was observed, consistent with a polymeric structure with BA₃-pyridine units (Fig. 3a). As demonstrated in the model reaction using ethynyldiphenylborane-pyridine complex, the polymerization *via* cyclotrimerization is expected to proceed selectively, without the formation of other boron species. To further investigate the composition of the polymer, FT-IR spectroscopy analysis was carried out (Fig. 3b). The C≡C–H stretching band at 3260 cm⁻¹ and C≡C stretching band at 2058 cm⁻¹ disappeared in the product, indicating the complete consumption of the starting material (Fig. S10). The absorption at 1600 cm⁻¹ is ascribed to the stretching vibrations of C(sp²) framework,⁴ supporting the formation of benzene rings through alkyne cyclotrimerization. Moreover, the band at 1458 cm⁻¹ and the weak band at 1622 cm⁻¹ are assigned to pyridine coordinated to Lewis acidic boron centers. The ν_{8a} band is indicative of the strength of Lewis acidity.^{26,27} Based on the position of the ν_{8a} band, Lewis acidity of BC₆ (1622 cm⁻¹) is the same as that of TEB·Py (1622 cm⁻¹) and slightly stronger than BPh₃·Py (1618 cm⁻¹). XPS measurement for elemental analysis revealed that the boron and nitrogen contents were 4.4 and 1.4 at%, respectively



Scheme 1 Synthesis of BC₆ from TEB·Py.

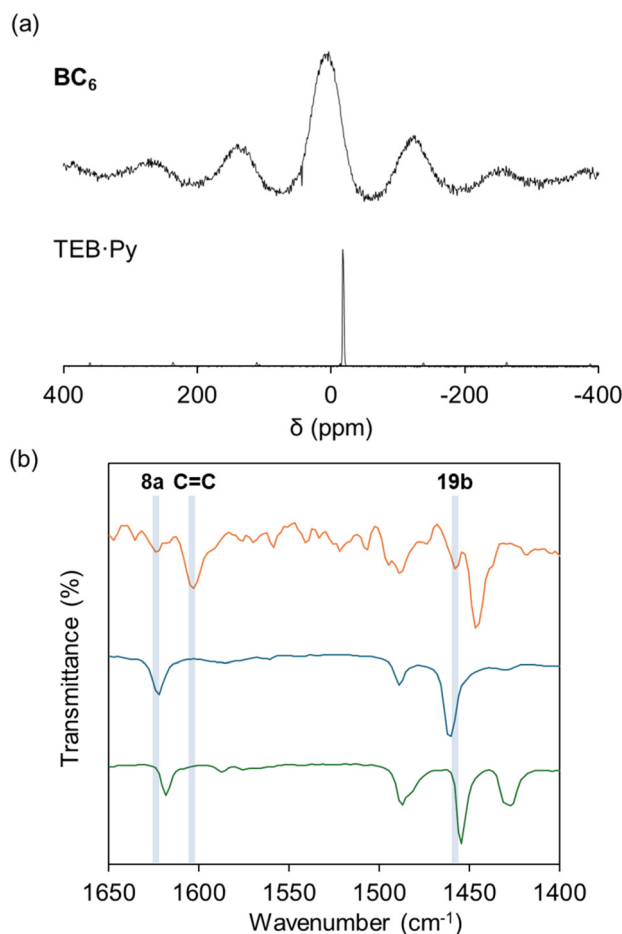
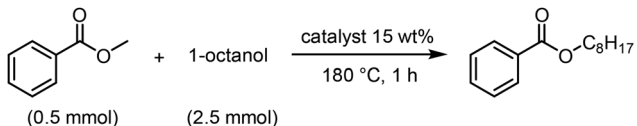


Fig. 3 (a) ¹¹B ss MAS NMR spectrum of BC₆. (b) IR spectra of BC₆ (orange), TEB·Py (blue) and BPh₃·Py (green).

(Table S2), supporting the successful incorporation of boron atoms into the polymer structure while partial removal of pyridine. Additional characterization data further supported the formation of the BC₆ polymer structure. The ¹³C ss MAS NMR spectrum showed a broad signal mainly in the aromatic carbon region, consistent with the formation of an extended aryl framework through alkyne cyclotrimerization (Fig. S11).

Triarylboranes such as BPh₃ are well-known Lewis acid catalysts in metal-free systems, and have been widely employed in various organic transformations.^{28–30} The Lewis acidity of BC₆ was evaluated using a transesterification reaction of methyl benzoate.³¹ As a result, BC₆ catalyzed the formation of octyl benzoate with a yield of 93% in 1 hour (Table 2, entry 1). For comparison, BPh₃·Py was used as a catalyst, but it did not catalyze the reaction, likely due to its stable complexation with pyridine (Table 2, entry 2). BPh₃, a model Lewis acidic BA₃-type organoboron compound, afforded a low yield of the product (Table 2, entry 3). Notably, the polymeric BC₆ exhibited significantly higher catalytic activity than the corresponding small-molecule analogues. This is because small-molecule organoboranes are more susceptible to decomposition under such conditions,¹³ whereas the rigid BC₆ structure is likely more tolerant.



Table 2 Transesterification of methyl benzoate^a


Entry	Catalyst	Yield ^b (%)
1	BC ₆	93
2	BPh ₃ ·Py	0
3	BPh ₃	13
4	BC ₉	83 ^c
5	Pyridine	0 ^d
6	Co ₂ (CO) ₈	7

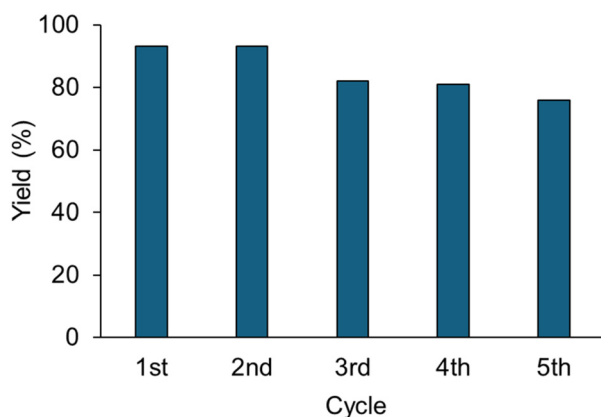
^a Reaction conditions: methyl benzoate (0.5 mmol), 1-octanol (2.5 mmol), catalyst (15 wt% of methyl benzoate), 180 °C for 1 h.

^b Determined by GC using dodecane as an internal standard. ^c Ref. 13.

^d Reaction time: 12 h.

Moreover, BC₆ showed a higher yield than BC₉ (Table 2, entry 4). The enhanced catalytic activity likely arises from the distinct chemical environments surrounding the boron centers. Additionally, pyridine alone was tested as a Lewis base catalyst. Although a small amount of product was obtained after 12 hours, the catalytic activity was negligible (Table 2, entry 5). Finally, Co₂(CO)₈ was examined, but it afforded only a small yield of the product, indicating that the catalytic activity of the residual cobalt was also negligible (Table 2, entry 6). N₂ adsorption–desorption analysis gave a modest BET surface area of 15.9 m² g⁻¹ (Fig. S12), indicating that the high catalytic activity of BC₆ is not simply attributable to a large surface area, but rather to the dense incorporation of Lewis acidic boron sites.

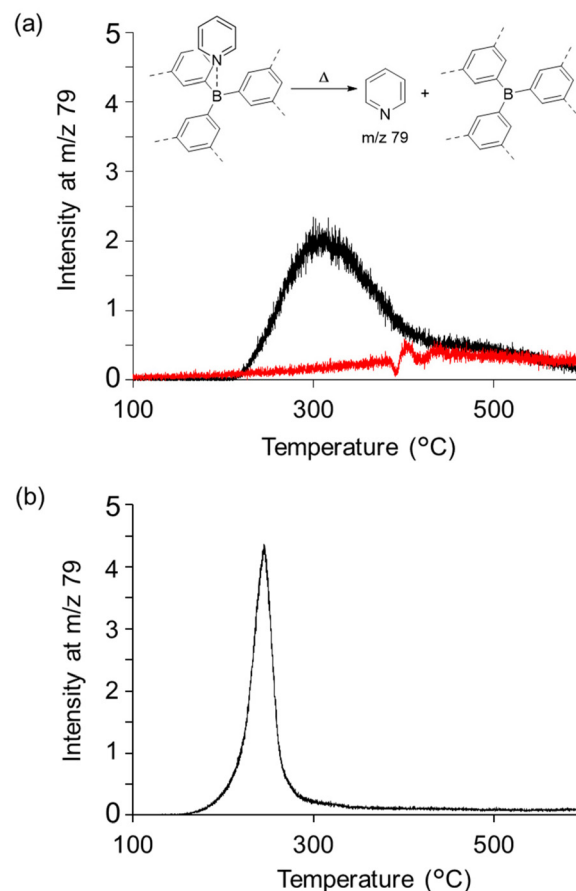
A key advantage of solid catalysts is their recyclability in heterogeneous systems, owing to facile separation from reaction mixtures by filtration or precipitation.^{32–34} To date, recyclable boron-containing polymeric Lewis acid catalysts remain limited.^{6,7} To assess the recyclability of BC₆, the catalyst was recovered after each run by removing the supernatant by decantation and then reused over multiple cycles. Even after the 5th cycle, the catalyst retained activity (Fig. 4). Inductively

**Fig. 4** Reusability of BC₆ in the transesterification of methyl benzoate.

coupled plasma optical emission spectrometry (ICP-OES) analysis revealed that boron leaching after the catalyst recycling test was 1.8% (25.2 ppm in the reaction mixture), indicating minimal catalyst degradation. Together with the low activity observed for Co₂(CO)₈ (Table 2, entry 6), the low boron leaching supports that the observed catalytic activity mainly originates from the BC₆ solid rather than from leached boron species or residual cobalt.

To further clarify the origin of the catalytic activity, control experiments were performed (Fig. S22 and S23). BC₆ preheated at 300 °C under Ar did not promote the reaction at 125 °C, suggesting that simple *ex situ* thermal treatment is insufficient to generate a durable active catalyst. In contrast, when the reaction mixture was first heated at 180 °C for 10 min and then kept at 125 °C, the yield increased to 65%, whereas the reaction conducted only at 125 °C gave 12% yield. The apparent rate constant at 125 °C after the initial high-temperature step was 6.72 × 10⁻³ s⁻¹, approximately three times larger than that without the activation step, 2.13 × 10⁻³ s⁻¹. These results indicate that BC₆ is activated under the catalytic conditions, consistent with pyridine dissociation from the boron centers.

Typically, BAr₃ units without bulky substituents are chemically unstable but have high catalytic activity. Therefore, it is

**Fig. 5** MS traces of *m/z* 79 detected during programmed heating of (a) BC₆ before (black) and after (red) the catalytic reaction, and (b) BPh₃·Py.

important to clarify why **BC**₆ exhibits both high stability and high catalytic activity. One possible explanation is that pyridine coordinates to the boron centers during and after **BC**₆ formation, yet dissociates under catalytic conditions. To verify this hypothesis, we examined the pyridine dissociation behavior of **BC**₆. TG-MS analysis was performed to monitor the release of pyridine during heating.^{35,36} Pristine **BC**₆ exhibited a distinct pyridine release in the range of 200–400 °C (Fig. 5a). In contrast, no pyridine release was detected for **BC**₆ after the catalytic reaction, indicating that pyridine coordinated to the boron centers was removed under the catalytic conditions. As a result, **BC**₆ was activated to perform as a Lewis acid. The pyridine release temperature of **BC**₆ (300 °C) was higher than that of BPh₃·Py (250 °C) (Fig. 5b), indicating stronger coordination of pyridine to the boron centers in **BC**₆. This observation is consistent with the calculated lower LUMO level resulting from the increased boron content (Fig. 2) and the high catalytic activity (Table 2, entry 1).

Conclusions

In conclusion, we have synthesized a boron-rich π -conjugated polymer *via* alkyne cyclotrimerization of TEB-Py. Through the screening of several metal catalysts in a model reaction, Co₂(CO)₈ successfully promoted the cyclotrimerization without the formation of byproduct. Owing to the dense incorporation of boron centers into the polymer backbone, **BC**₆ exhibited enhanced Lewis acidity and superior catalytic performance compared with small-molecule analogues such as BPh₃ and the previously reported polymer **BC**₉. In addition, the heterogeneous nature of **BC**₆ enabled facile recovery and reuse over multiple catalytic cycles. These results demonstrate that constructing rigid polymer structure with high densities of Lewis acidic boron centers is an effective strategy for developing recyclable heterogeneous Lewis acid catalysts, providing a general design concept for functional boron-containing polymeric materials.

Author contributions

N. T.: investigation, formal analysis, writing – original draft. K. O.: formal analysis. Y. N.: conceptualization, supervision, project administration, funding acquisition, writing – review & editing. All authors discussed the results and approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data associated with this study are available in the article and supplementary information (SI). Supplementary infor-

mation: experimental details, spectroscopic data (NMR, IR, and XPS). See DOI: <https://doi.org/10.1039/d6py00177g>.

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