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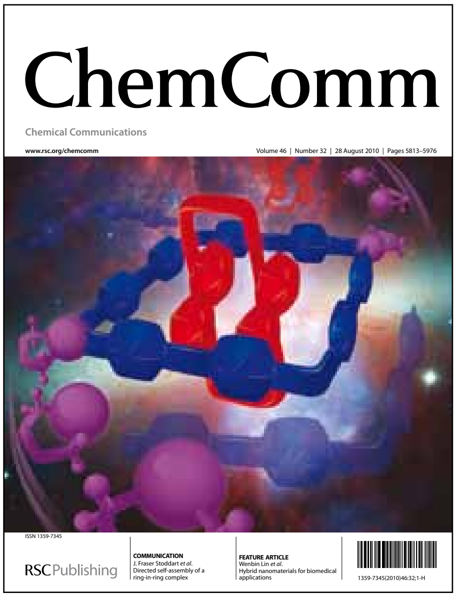

ChemComm
Chemical Communications
www.rsc.org/chemcomm
Volume 46 | Number 32 | 28 August 2010 | Pages 5813–5976
ISSN 1359-7345
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ARTICLE TYPE

Synthesis and Properties of B,N-Bridged *p*-Terphenyls

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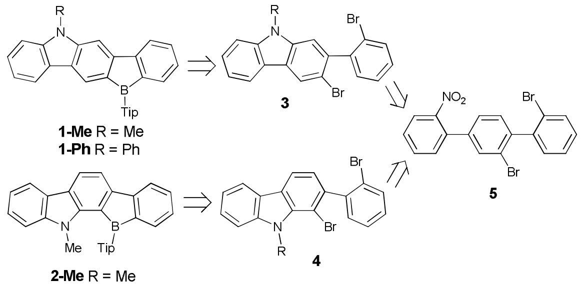
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The efficient synthesis has been described to achieve a new class of ladder π-conjugated molecules, B,N-bridged *p*-terphenyls. The bridging B atom exhibits more significant effect than the bridging N atom on photophysical properties.

Organic π-conjugated materials have received considerable attention owing to their great potential uses in optical and electronic devices.[1] In particular, ladder-type π-systems with fully fused polycyclic conjugated skeletons are attractive because of their rigid planar structure, which would lead to more efficient electron delocalization and strong intermolecular π-π interactions and thus give rise to highly desirable electronic and photophysical properties like intense fluorescence and high carrier mobility.[2] As a representative example, ladder-type oligo(*p*-phenylene)s (LOPPs) with carbon as bridging atoms have been extensively investigated and applied in electronic devices.[3] To fine tune the electronic structures, replacement of bridging carbon atoms with heteroatoms such as Si,[4] N,[5] P,[6] S[7] has emerged as an effective strategy. Incorporation of heteroatoms can endow the conjugated hydrocarbon framework with interesting features such as special orbital interactions, change in the dipole moments and diversity in coordination numbers. For instance, the N atom in N-bridged biphenyl (carbazole), is isoelectronic to carbanion and makes carbazole exhibit reversible oxidation processes. As a result, carbazole has been proved to be a versatile electron-donating unit to construct new functional optoelectronic materials.

In addition to the above mentioned heteroatoms, B is another particularly interesting element for the creation of new organic optoelectronic materials.[8] The most important feature of a trivalent boron center in a π-conjugated framework is its vacant p-orbital and thus isoelectronic to a carbocation, allowing the effective electron delocalization throughout the whole system. The research on the B-bridged biphenyl (dibenzoborole) has demonstrated that it can act as an efficient electron-accepting unit.[9] Encouraged by the great utility of carbazole and dibenzoborole and significant effect of N and B on their photophysical properties, we were interested in the ladder-type LOPP, in which both the electron-donating nitrogen atom and the electron-accepting boron atom are introduced as bridging atoms. Although a number of B-bridged ladder-type π-systems have been reported in the past few years,[10] those with bridging nitrogen atoms still remain unexplored so far due to the absence of efficient synthetic method. Herein we now disclose a new class of ladder π-conjugated molecules, B,N-bridged *p*-terphenyls **1**–**2**, including their synthesis and basic photophysical properties.

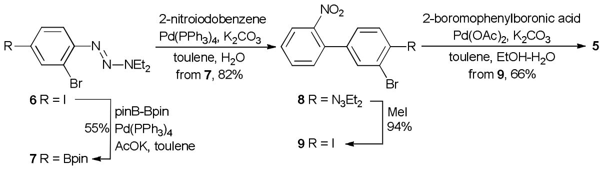


Scheme 1 Retrosynthesis of B,N-bridged *p*-terphenyls **1**–**2**.

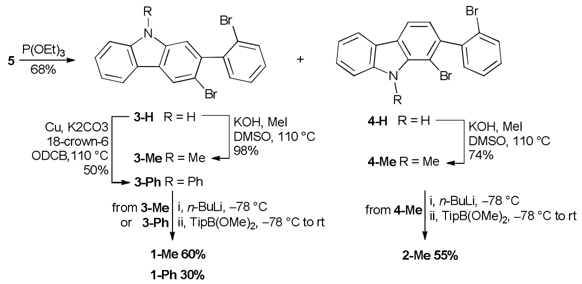
The strategy for the synthesis of B,N-bridged *p*-terphenyls is described in Scheme 1. The reaction of dimetalated biphenyl with $ArBX_2$ has been the most the straightforward synthetic route to dibenzoborole.[9] Hence we designed two regioisomers, 3-bromo-2-(2-bromophenyl)carbazole **3** and 1-bromo-2-(2-bromophenyl)carbazole **4** as key precursors, which were envisioned to be available via Cadogan cyclization from a common intermediate 2,2'-dibromo-2''-nitro-*p*-terphenyl **5**.[11] And thus the main point for this synthetic route is the preparation of the key synthetic intermediate **5**.

As illustrated in Scheme 2, compound **5** was prepared in four steps starting from a triazene derivative **6**[12]. The initial attempt to synthesize compound **8** directly through Suzuki-Miyaura coupling reaction of **6** with 2-nitrophenylboronic acid was unsuccessful, which might be ascribed to the particularly strong electron-withdrawing effect of nitro substituent.[13] And thus compound **6** was first transformed to its pinacol ester derivative **7**, the following Suzuki-Miyaura coupling of which with 2-nitroiodobenzene proceeded smoothly to provide **8** in an excellent yield. The subsequent iodization of triazeno group with iodomethane led to compound **9**, which was further coupled successfully with 2-bromophenylboronic acid to produce **5**.

With **5** in hand, we next conducted Cadogan cyclization in presence of triethyl phosphite, which afforded two regioisomers of carbazole derivatives **3-H** and **4-H** in 68% total yield. **3-H** and **4-H** were readily converted to the N-methylated products **3-Me** and **4-Me**, respectively. The N-phenylated derivative **3-Ph** was also obtained utilizing Ullman coupling reaction. The final dilithiation of **3**–**4** followed by quenching with $TipB(OMe)_2$ produced the B,N-bridged terphenyls with moderate yields (30–60%). The B,N-bridged *p*-terphenyls **1** are tolerant of air and moisture and can be purified by flash chromatography. **2-Me** is less stable than its regioisomer **1-Me** and decomposes slowly in



Scheme 2. Synthesis of 2,2'-dibromo-2''-nitro-*p*-terphenyl **5**.



Scheme 3 Synthesis of B,N-bridged *p*-terphenyls **1**–**2**.

dilute solution and during flash column. A blue fluorescent point was observed on TLC under irradiation of 365 nm for its eluted solution from column and dilute solution that was kept for several hours in air. The lower stability of **2-Me** is probably ascribed to the steric congestion between Tip group and Me group on N since the chemical shift of Me on N in **2-Me** (3.29 ppm) is greatly up-fielded compared with that in **1-Me** (3.88 ppm) due to the ring-current effect of phenyl on Tip group, suggesting possible C-H···π interactions. The crystal structure of the decomposed product of **2-Me** (ESI), which was obtained unexpectedly during preparation of single crystals of **2-Me**, indicates the bond between B and terminal benzene ring was broken.

Numerous efforts to prepare crystals of **1** and **2** suitable for X-ray analysis failed. To get an insight into their molecular structures, the geometries were optimized using density functional theory (DFT) at B3LYP/6-31G(d) level of theory (ESI). A highly coplanar conjugated framework was observed for all the B,N-bridged *p*-terphenyls. Both the boron and nitrogen centers adopt a trigonal planar structure. The Tip groups are essentially perpendicular to the borole rings. As for the borole geometry, the extent of the bond alternation is rather small with C-C bond lengths varying within the range of 1.414–1.486 Å. The B-C1 bond lengths (1.572–1.574 Å) and C-B-C bond angles (103.6°–104.0°) are comparable to those of other reported arene-fused boroles.[10] It is notable that B-C4 bond length (1.559 Å) is relatively shorter than B-C1 (1.574 Å) in **1**, indicating stronger bonding between B and the central benzene ring. And B-C4 bond length is elongated to 1.582 Å in **2-Me**, which might arise from the steric congestion between Me group on N and Tip group, as demonstrated by a short distance between the hydrogen atoms of Me on N and the phenyl ring centroid of Tip (2.795–4.340 Å). The significant steric congestion in **2-Me** and thus the elongated B-C4 bond would presumably result in lower stability of borole, which is in good agreement with the experimental results. In addition, the NICS values of borole rings calculated by DFT calculations (B3LYP/6-31++G(d,p))[14] are very close (NICS$(1)_{zz}$ = +24.8 for **1-Me**; +25.4 for **2-Me**; +24.2 for **1-Ph**), precluding the antiaromaticity effect on the stability of borole.

Regarding the optoelectronic properties, we were most interested in the effect of the bridging atoms on the electronic structures and thus the photophysical properties. In cyclohexane, the B,N-bridged *p*-terphenyl **1-Me** shows a weak shoulder band at 430 nm (log ε = 3.28) in the absorption spectrum and exhibits a yellowish green fluorescence at 529 nm with a moderate quantum yield of 0.21 (Fig. 1). According to DFT calculations (B3LYP/6-31G(d)) (ESI), the HOMO of **1-Me** is delocalized over the entire *p*-terphenyl framework, including the bridging N atom and the LUMO is mainly located on the dibenzoborole moiety with a large contribution from the vacant p orbital on B atom. Notably, the LUMO still consists of some contribution from N atom and the terminal benzene ring fused to pyrrole. The TD-DFT calculations (B3LYP/6-31G(d)) indicate that the longest shoulder absorption band is assignable to the HOMO→LUMO transition. To elucidate the effect of bridging atoms, we compared the photophysical properties of **1-Me** with those of the related compounds **10** and **11**, which lack one bridging N and B atoms, respectively. The longest absorption at 442 nm (log ε = 2.76) and the emission at 503 nm of **10** are very close to those of **1-Me**. In contrast, the absorption and emission of **1-Me** are significantly red shifted compared with the longest absorption of a shoulder band at 340 nm (log ε = 3.89) and the emission at 366 nm of **11** (Fig. 1). These results suggest the much more significant contribution of the bridging B atom to the frontier orbitals than the bridging N atom, which was further confirmed by the theoretical calculations (ESI). Compared with compound **10**, the introduction of bridging N only leads to the slight elevation in the HOMO and LUMO with almost the same extent (0.28 eV for HOMO and 0.29 eV for LUMO). In contrast, the LUMO of **1-Me** is decreased remarkably by 0.91 eV while the HOMO remains almost unchanged relative to **11**. In view of the fluorescence efficiency, the quantum yield of **1-Me** is much lower than that of **11** (Φ_F = 0.96 for **11** in cyclohexane), which mainly due to the deceleration of radiative decay (ESI). Another noteworthy thing for the photophysical properties of **1-Me** is that it exhibits no obvious solvent dependence not only on absorption but also even on fluorescence (ESI), which is quite different from the large bathchromism of fluorescence with increasing solvent polarity for other organoboron compounds containing electron-donating amino groups.[15] The trivial solvatochromism on both absorption and emission denotes the little polarity change from the ground state to the excited state. This is probably due to the greatly efficient electron delocalization in the ground state as a result of the rigid ladder framework, which would lead to the location of the positive center close to the center of the molecular structure and thus no obvious charge separation in the exited state.

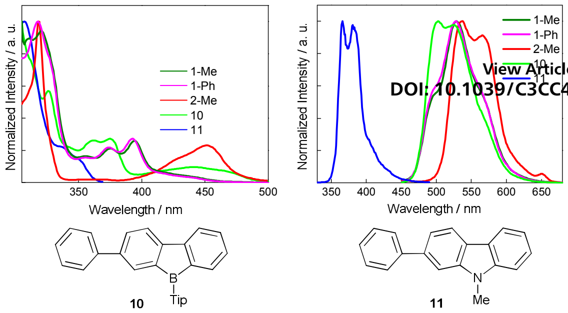


Fig. 1 UV/vis absorption and fluorescence spectra of B,N-bridged terphenys **1**–**2** and related compounds.

In addition, we also examined the effect of substituent on N

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and the relative position of the bridging B and N atoms on the photophysical properties. As shown in Fig. 1, no difference was observed in the absorption and emission with the change of the substituent on N from methyl (**1-Me**) to phenyl in (**1-Ph**), contrary to our assumption that aryl substituent on nitrogen generally gives rise to the lower electron-donating ability of amino groups and thus blue shift in the absorption and fluorescence spectra. This is possibly ascribed to the large torsion angle between the phenyl group and pyrrole, which would make the phenyl group contribute greatly to neither the HOMO nor the LUMO (ESI). It is interesting to find that both the absorption and emission of **2-Me** display obvious bathochromism compared with those of **1-Me** (Fig. 1), which is mainly due to decreased LUMO, as evidenced by the calculation results (ESI).

In order to obtain insights into the electrochemical properties of the B,N-bridged terphenyls, the cyclic voltammograms of **1**–**2** and **10**–**11** were measured (ESI). An irreversible oxidation and an irreversible reduction waves were observed for compound **11** and **10** only showed an irreversible reduction wave. It is notable that all the B,N-bridged terphenyls exhibited both oxidation and reduction waves and the reduction waves were shifted to a less negative potential compared with **10**–**11**. More importantly, the reduction wave of **1-Ph** is reversible and the oxidation wave is quasireversible, indicating its potential application as an ambipolar carrier transporting material.

In summary, we have built up an efficient synthetic route to a new class of ladder-type π-conjugated system, B,N-bridged *p*-terphenyl. The bridging B atom exhibits more significant effect than the bridging N atom on the photophysical properties. And the absorption and emission are not influenced by the substituent on the N atom, but influenced by the relative position of B and N atoms. The elucidation on the structure-property relationships would provide some important basis for the further ration design of functional ladder-type π-conjugated molecules. In addition, this new class of ladder-type π-conjugated system exhibits great potential uses as bipolar transporting materials. Further study along this line is now in progress in our laboratory.

This work was supported by the National Nature Science Foundation of China (Grant Nos. 21072117, 21272141) and Promotive Research Fund for Excellent Young and Middle-aged Scientists of Shandong Province (No BS 2012CL021).

Notes and references

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† Electronic Supplementary Information (ESI) available: experimental dtails, spectrostropic data, computational details and copies of NMR spectra. CCDC 960740 (decomposed compound of **2-Me**) See DOI: 10.1039/b000000x/

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