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COMMUNICATION

Meta-B-entacenes: new polycyclic aromatics incorporating two fused borepin rings[†]‡

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The synthesis of new boron-containing acenes (*meta-B*-entacenes) is reported. These compounds exhibit slightly non-planar core geometries with blue-shifted spectral properties and more negative electrochemical reduction potentials relative to known *para* isomers. Polarizable π -extended architectures were realized *via* cross-coupling procedures with chloro-functionalized precursors.

The incorporation of tricoordinate boron into organic compounds has led to the realization of a structurally diverse array of π -conjugated scaffolds.¹ Molecules from this continually expanding library have demonstrated promise for n-type charge transport,² non-linear optical materials,³ and selective anion-sensing.⁴ Boron has also served as a useful structural motif to study fundamental properties of non-benzenoid aromatic^{5–11} and antiaromatic¹² systems. Recently we introduced synthetic routes to pentacyclic acenes containing two formally aromatic borepin rings, so-called *B*-entacenes^{13,14} (Fig. 1). We now report the synthesis and characterization of a new *B*-entacene isomer that features a *meta*-orientation of the boron centers (*meta-B*-entacene; Fig. 1, **1a**) as a complement to previously reported structures which feature a *para*-boronboron relationship (*para-B*-entacene; Fig. 1, **2**).

Meta-B-entacene **1a**, in addition to chlorinated derivatives **1b** and **1c**, were synthesized according to Scheme 1. Thus, Wittig olefination of bis(phosphonium) salt **3** (prepared in two steps from 1,5-dibromo-2,4-dimethylbenzene; Electronic Supplementary Information, ESI†) with aldehydes **4a–4c** afforded tetrabrominated *Z*,*Z*-dienes **5a–5c**. TMEDA-assisted lithiumbromine exchange with excess *sec*-butyllithium followed by addition of two equivalents of dimethyltin dichloride provided fused stannocycles **6a–6c**. Tin–boron exchange with boron trichloride, followed by treatment with excess Mes*Li (Mes* = 2,4,6-tri-*tert*-butylphenyl), gave *meta-B*-entacenes **1a–1c** (20–53% yield) in which the benzo-annelated borepin moieties place the two boron centers in a *meta*-arrangement



Fig. 1 Isomeric *meta-B*-entacene (1a) and *para-B*-entacene (2).



Scheme 1 Synthesis of *meta-B*-entacenes. TMEDA = N, N, N', N'-tetramethylethylenediamine.

about the central phenyl ring. Like previously reported B-Mes*-functionalized compounds,^{13–15} the robust kinetic protection afforded to boron by the bulky Mes* groups provided stability in the presence of moisture and oxygen, allowing facile purification and manipulation under ambient laboratory conditions.

Recrystallization of 1a from THF/H₂O yielded colorless block-like single crystals suitable for X-ray structure determination. In addition to confirming the molecular connectivity of 1a, the X-ray data highlights key structural features of the new isomer (Fig. 2a and b). In contrast to *para-B*-entacene 2, the Mes* groups in 1a are positioned along the same edge of the curved acene core. This close proximity leads to a substantial degree of steric occlusion, orienting the Mes* groups away from one another in space and causing a slight twist of the conjugated backbone. DFT calculated structures for *meta-B*-entacenes

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Fig. 2 Displacement ellipsoid plots for **1a** at 110(2) K (50% probability level), showing (a) face-on and (b) edge-on views (H atoms omitted for clarity). Selected bond lengths (Å): B1A–C3A: 1.575(3), C3A–C8A: 1.418(3), C8A–C9A: 1.447(3), C9A–C10A: 1.339(3), C10A–C11A: 1.453(3), C2A–C11A: 1.423(2), B1A–C2A: 1.569(3). (c) Energy optimized structure (DFT; B3LYP/6-31G*) of **1a** with *B*-Ph substituents in place of *B*–Mes* (edge-on view).

incorporating sterically less-demanding pendant phenyl groups (B3LYP/6-31G*, Fig. 2c) possess fully planar geometries, confirming that the twist motif is due to steric interaction between the Mes* groups and is not an inherent structural aspect of the B-entacene core. Intraring bond lengths within the formal borepin subunits of 1a are generally consistent with those found previously for 2,¹³ with C-C bond distances in 1a ranging from 1.339(3) to 1.453(3) Å. The extent of this C-C bond length alternation (± 0.114 Å) is approximately twice as large as the range reported for the unfused 1-chloroborepin⁷ $(\pm 0.058$ A). Such an increase reflects a reduction in the aromatic character of the fused borepin subunits in 1a due to benzo-annelation, and is in agreement with a calculated NICS(1) value¹⁶ of -0.51 indicating little to no aromatic character for the borepin rings.¹⁷ The steric bulk imparted by the Mes* groups of 1a precluded the formation of extended tight π -stacking motifs in the solid-state, however close C–H edge-to-face (2.883(3) Å) and C-C face-to-face (3.369(3) Å) contacts were apparent at unencumbered regions of the molecular periphery (ESI[†]).

We characterized the photophysical properties of *meta-B*entacene **1a** and compared them to the isomeric *para-B*entacene **2**¹³ (Table 1). The UV-Vis spectrum of **1a** in CHCl₃ (Fig. 3a) displayed an absorption onset at 421 nm, with a low energy, low oscillator strength band at 407 nm, which we attribute to optically-induced intramolecular charge transfer (ICT).^{11,13} In addition, higher energy π - π * absorptions with strong vibronic coupling were observed near 340 nm. The spectral features of **1a** are in accord with those found for **2**, albeit significantly blue-shifted (~30-40 nm), suggesting diminished electron delocalization. This can be rationalized

Table 1Photophysical data for 1a, 1b, 2^a, 7a, and 7b

Compound	Abs $\lambda_{\max}^{b,c}$	Abs $\lambda_{onset}^{\ b}$	PL λ_{\max}^{b}	\varPhi^d	$\tau(ns)^e$
1a	407	421	413	0.80	13.2
1b	407	421	411	0.38	8.9
2^a	439	458	456	0.71	9.3
7a	411	425	441	0.39	8.8
7b	400	461	477	0.48	2.8

^{*a*} Ref. 13. ^{*b*} In nm. ^{*c*} Lowest energy absorption maximum. ^{*d*} Relative to quinine sulfate (0.55). ^{*e*} Fitted to a single exponential decay.



Fig. 3 (a) UV-Vis, photoluminescence (PL) and (b) cyclic voltammetry (CV) data for **1a**. UV-Vis and PL spectra were obtained at room temperature in CHCl₃ with excitation at 340 nm. CV was obtained at 2.5 mM in 0.1 M "Bu₄NPF₆ electrolyte solution (THF) and referenced to Ag/Ag⁺. DFT (B3LYP/6-31G*) calculations illustrating frontier molecular orbital surfaces of **1a**: (c) HOMO, (d) LUMO.

in terms of a longer para-like all-carbon conjugation pathway in 2 relative to 1a, the length of which has been shown in related systems to influence optical bandgaps more effectively than the conjugation pathways incorporating boron.¹⁸ Excitation at 340 nm vielded a solution quantum vield (Φ) of 80% and an excited state lifetime (τ) of 13.2 ns for 1a. The PL spectrum of 1a demonstrated a significant degree of fine structure, with maxima at 413 and 437 nm and a high-energy shoulder at 462 nm. This contrasts with the PL spectrum of 2, which shows only a single distinct PL λ_{max} at 456 nm with a small high-energy shoulder. We attribute the accentuated PL spectral fine structure, longer excited-state lifetime, and higher quantum yields in 1a relative to 2 to the greater steric demands imposed by the close proximity of Mes* groups in 1a, leading to a high level of chromophore conformational rigidity and reduced non-radiative decay.

Well-behaved cathodic electrochemistry was observed for **1a** with a single reduction wave $(E_{1/2})$ at -2.12 V vs. Ag/Ag⁺ in THF solution (Fig. 3b). This contrasts with *para-B*-entacene **2**, which demonstrated two distinct one-electron reductions $(E_{1/2} = -1.89 \text{ V}, -2.46 \text{ V})$,¹³ with a less negative first reduction potential than **1a**. The trend of a more facile first reduction for the isomer with the two boron centers in a *para*-orientation relative to the *meta*-orientation mirrors that for the related unfused 1,4-¹⁹ and 1,3-bis(dimesitylboryl)phenylene²⁰ systems, however the *B*-entacene systems are more difficult to reduce than the corresponding unfused triarylboranes. This may reflect a higher energetic barrier to molecular reorganization²¹ of **1a** and **2** upon electrochemical reduction relative to unfused analogues.

The preparation of extended π -conjugated structures based on the *meta-B*-entacene core was achieved by utilizing active palladium-catalyzed cross-coupling procedures for chloroarenes (Scheme 2). Stille cross-coupling of chlorinated *meta-B*-entacene **1b** with 2-tributylstannylthiophene under Fu's conditions²² provided **7a** in 41% yield, while Sonogashira



Scheme 2 Pd-catalyzed cross-couplings of 1b. Conditions: (a) $Pd(P'Bu_3)_2$ (10 mol%), CsF, 1,4-dioxane, 95 °C; (b) $PdCl_2(CH_3CN)_2$ (10 mol%), XPhos (30 mol%), Cs₂CO₃, THF, CH₃CN, 80 °C.

cross-coupling with 4-ethynyl-*N*,*N*-dimethylaniline under Buchwald's conditions²³ provided **7b** in 33% yield. It is noteworthy that the reaction conditions for the preparation of **7a** (excess CsF, 95 °C) did not lead to appreciable decomposition of **1b**, reaffirming the effective kinetic protection of boron by the *B*-Mes* group. Unfortunately, similar to analogous chloro-derivatives of **2**,¹⁴ we could not achieve cross-couplings when the functionalizable chloride handle was situated *meta* to the boron center (as in **1c**).

Photophysical data for 1b, 7a, and 7b are presented in Table 1. Though the major UV-Vis/PL spectral features of 1b and 7a (ESI[†]) are not significantly shifted from 1a by chloro and thienyl groups at the positions *para* to the boron centers, attachment of strongly electron-donating N,N-dimethylaminophenylacetylene substituents in 7b leads to significant red shifts in absorption onset and PL maxima due to the pronounced "push-pull" nature of the chromophore. Large positive solvatochromic effects were observed for solutions of **7b** in solvents with increasing E_T 30 values, with a PL λ_{max} shift of over 100 nm between cyclohexane and THF (Fig. 4a). Calculated frontier molecular orbital surfaces for a simplified analogue of 7b (using B-2,6-dimethylphenyl groups in place of B-Mes*; Fig. 4b and c) demonstrated a significant shift in the location of orbital density between HOMO and LUMO, accounting for the marked solvatochromic behavior. These properties are in accord with those of the corresponding para-B-entacene derivative, which demonstrated similar solvatochromic effects, albeit at relatively longer wavelengths in each case.14 These results suggest that functionalized para- and

Fig. 4 (a) PL spectra for **7b** in cyclohexane, CHCl₃, and THF at room temperature. Calculated frontier molecular orbitals surfaces (DFT; B3LYP/6-31G*) for *B*-(2,6-dimethylphenyl)-**7b**: (b) HOMO; (c) LUMO.

meta-B-entacene isomers might provide complementary platforms for predictably tunable optical materials.

In conclusion, the synthesis of *meta-B*-entacene suggests a general, reliable method for the construction of phenylenefused borepin-containing acenes. The *meta*-arrangement of the boron centers with respect to one another in **1a** leads to hypsochromically shifted UV-Vis/PL signatures and more negative reduction potentials than in *para*-isomer **2**, demonstrating the influence of the unique structure of **1a** on its observed optoelectronic properties. The accessibility of extended π -conjugated derivatives **7a** and **7b** via Pd-catalyzed cross-couplings demonstrates the possibility for incorporation of the *meta-B*-entacene subunit into polarizable π -electron materials. Further investigations into the properties of *B*-entacene systems and related π -electron scaffolds are currently underway.

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