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Highly Luminescent, Electron-Deficient Bora-cyclophanes

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Supporting Information

ABSTRACT: A highly luminescent conjugated organoboron macrocycle containing six Lewis acidic boron centers was synthesized. Comparison of the optical and electronic properties with those of a hexameric linear oligomer revealed important differences due to delocalization within the highly symmetric cyclic conjugated structure. Exposure of this unique electron-deficient bora-cyclophane to fluoride or cyanide results in amplified fluorescence quenching and can be exploited to switch between an electron-deficient macrocycle and a highly charged, electron-rich borate cycle.

Macrocycles continue to attract tremendous interest, in part because of their ability to act as hosts for guest molecules and their pronounced tendency to form well-defined porous supramolecular structures in the solid state.[1] The channels generated during the assembly process can, for example, be used for selective ion transport, as catalytically active sites or for photochemical reactions in a confined environment, leading to unexpected selectivities.[2] Conjugated macrocycles in particular have received much attention in recent years as they also offer desirable optical, electronic, or sensory properties; in addition, they are important from a fundamental standpoint, because they represent polymer chains without the presence of end groups, which tend to influence the photophysical and electronic characteristics of the linear counterparts.[3]

Conjugated organoborane macrocycles would be especially interesting in that they feature an "anti-crown"-like structure, in which more commonly encountered donor atoms (e.g., O, S, N, P) are replaced with Lewis acid sites.[4] Such an arrangement could be beneficial for the selective detection of anions and other electron-rich substrates.[5] In addition, the unusual electronic properties of conjugated organoborane oligomers and polymers that result from p-π overlap of the empty p-orbital on boron with π-conjugated organic groups continue to fascinate researchers as they suggest potential applications in optoelectronic devices.[6] However, although several reports on boron-containing macrocycles have appeared in the literature, in most cases the Lewis acidity of boron is low due to π-overlap with amino or alkoxy substituents or the borons are tetracoordinate, and thus no significant electron delocalization is present.[7] Herein we describe a rational approach to hitherto unprecedented bora-cyclophanes that feature multiple highly electron-deficient organoborane moieties as an integral part of the ring system and thus constitute the first "charge-reverse" analogues of electron-donating macrocycles such as porphyrins, phthalocyanines, calixarenes, oligopyrrols, and recently introduced triarylamine-based aza-cyclophanes.[2,8] We also discuss the effect of cyclization on optical and electronic characteristics and present preliminary results on the complexation of anions, which can act as a stimulus to turn the electron-deficient macrocycle into an electron-rich one.

Treatment of Br_2B-Fl-BBr_2 (Fl = 9,9-dihexyl-2,7-fluorenediyl) with Me_3Sn-Fl-$SnMe_3$ is known to lead to polycondensation, and the resulting polymer $[\text{Fl-B(Br)}]_n$ can be converted with TipCu (Tip = 2,4,6-triisopropylphenyl) to a Lewis acidic organoboron polymer $[\text{Fl-B(Tip)}]_n$ that is highly luminescent and exhibits good stability in air.[9] Very recently we have succeeded in the preparation of a series of well-defined conjugated fluoreneborane oligomers $Me_3Si\text{-}[\text{Fl-B(Tip)}]_n\text{-Fl-}SiMe_3$ (**LFn**, n = 1−6; Fl = 9,9-dimethylfluorene-2,7-diyl) using a novel iterative procedure.[10] We reasoned that some of the longer monodisperse oligomers should be promising as precursors for macrocycles because the formation of so-called "overshooting oligomers"[11] that lead to larger linear structures rather than cyclics can be prevented. Moreover, the number of possible cyclic products is limited since ring closure of, for example, a tetraboryl precursor with a fluorene linker can only lead to a tetramer, octamer, dodecamer, etc., while a hexaboryl species would result in a hexamer, dodecamer, etc., without any of the intermediate ring sizes. This should greatly facilitate isolation of a specific desired cyclic product.

We first converted the oligo(fluoreneborane)s **LFn** (n = 2,4)[10] into species $Br_2B\text{-}[\text{Fl-B(Tip)}]_n\text{-Fl-}BBr_2$ (n = 2, 4) by reaction with 2 equiv of BBr_3 in CH_2Cl_2 at RT (Scheme 1). The resulting BBr_2-terminated species were then treated *in situ* with 2,7-distannyl-9,9-dimethylfluorene under dilute conditions, followed by reaction with TipCu, which serves to replace the reactive Br substituents with bulky groups that sterically stabilize the borane centers. The gel permeation chromatography (GPC) trace of the product obtained from the precursor **LF2** revealed a polymodal profile with distinct peaks at 1300, 2000, 3800, 6500 Da, and MALDI-TOF MS data suggested the presence of multiple linear and cyclic species, including the tetrameric and octameric macrocycles (**MC4**, **MC8**).[12] In contrast, a similar reaction sequence starting from the longer oligomer **LF4** led to highly efficient cyclization with formation of **MC6** as the major product in >80% yield based on NMR and GPC analysis of the crude mixture.[13] Column chromatography on silica gel followed by crystallization from a 10/1 mixture of hexanes/toluene at −35 °C gave monodisperse **MC6** as a white microcrystalline solid.

The identity of macrocycle **MC6** was unequivocally confirmed by GPC analysis, high-resolution mass spectrometry,

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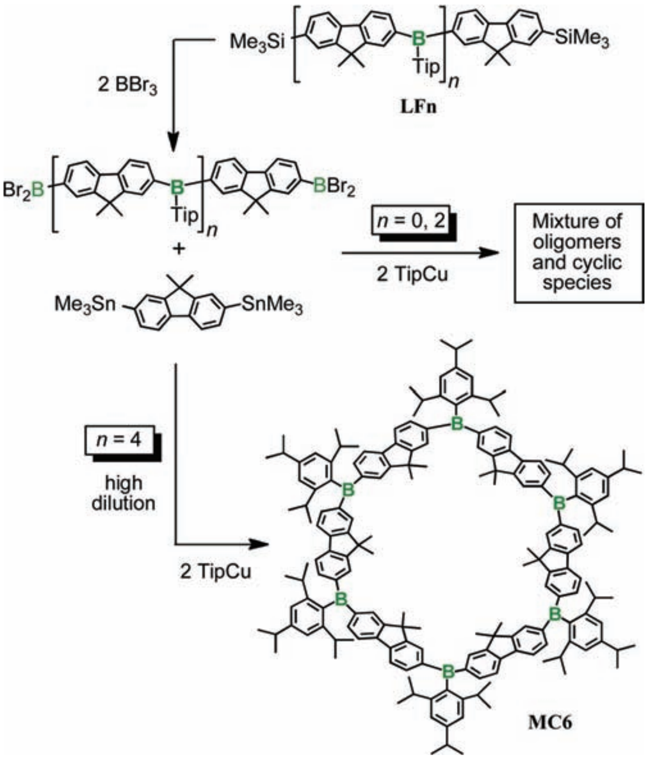
Scheme 1. Synthesis of the Bora-cyclophane MC6



and multinuclear NMR spectroscopy; moreover, the cyclic arrangement of six Lewis acidic boron centers in **MC6** is reflected in the electrochemical and anion-binding behavior.[14] Based on GPC against PS standards (Figure 1a), **MC6** has a molecular weight of M_n = 2470 Da (M_w/M_n = 1.01), which is close to the expected value of 2437 Da but significantly lower than that of the respective linear hexamer **LF6** (M_n = 3360 Da). This observation is consistent with a more compact cyclic structure that gives rise to a relatively smaller hydrodynamic volume. The structure of **MC6** was further confirmed by multinuclear NMR. Most strikingly, the ^{1}H and ^{13}C NMR spectra show only one distinct set of signals for the fluorene and Tip moieties, which is in stark contrast to the linear precursor, for which complex patterns arise from multiple nonequivalent repeating units.[13] In the ^{11}B NMR a single broad resonance is observed at 70 ppm, which is in the expected chemical shift range and consistent with the presence of only one type of triarylborane moieties. Finally, the negative ion mode MALDI-TOF MS shows a major peak with a mass of 2437.667 (calcd for $[M-H]^-$ 2437.701) and an isotope pattern that suggests an overlap of $[M]^-$ and $[M-H]^-$ ions (Figure 1b). A smaller peak to the left corresponds to fragment ions of $[M-CH_3]^-$ overlapping with $[M-CH_3-H]^-$. No other signals were observed.

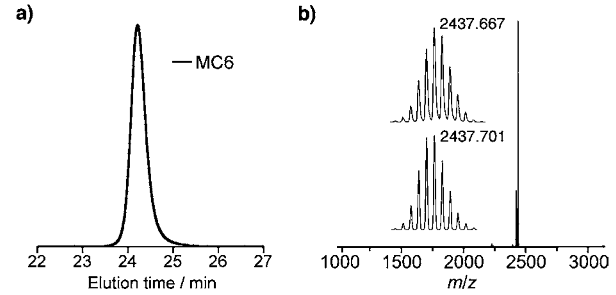


Figure 1. (a) GPC trace of **MC6** in THF. (b) MALDI-TOF MS data of **MC6**. Insets: Comparison of experimental (top) and calculated (bottom: $[M-H]^-$) peak patterns.

Analysis of the electronic structure of the macrocycle revealed characteristic differences in comparison to the respective linear oligomers. Both cyclic[13] and square wave voltammograms show six distinct peaks, where the first two processes to give $[\mathbf{MC6}]^{2-}$ occur almost simultaneously, whereas reduction of the following four boron centers occurs at increasingly cathodic potentials (Figure 2). In comparison to the linear analogue **LF6**, all reductions except for the first one occur at more negative potentials, which is attributed to larger Coulombic repulsion in the cyclic framework (in the fully reduced cyclic species every boron center experiences the effect of two neighboring boron radical anions, while in the linear species the terminal borons only have one neighboring boron radical anion).

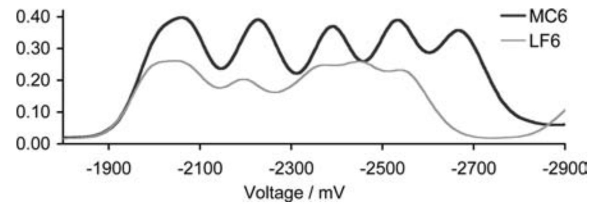


Figure 2. Comparison of square wave voltamograms of **MC6** and the linear hexamer **LF6** (THF, 0.1 M Bu$_4$NPF$_6$, 100 mV/s).

The macrocycle **MC6** absorbs at a slightly shorter wavelength than linear **LF6** (Figure 3). This effect could be due to a more restricted conformation, which may not allow for optimal overlap of the empty *p* orbitals on B with the adjacent fluorene π-systems. However, this is unlikely as the calculated structure (DFT, B3LYP 6-31G(d); alkyl groups were omitted)[15] shows little strain with endocyclic B−C bond lengths of 1.568 Å and angles about B that range from 120.3° to 120.4°.[12,16] Moreover, the HOMO for **MC6-calc** is localized on the six fluorene moieties, while the LUMO shows delocalization of all six empty *p* orbitals on B with the organic π-systems (Figure 4). This stands in contrast to the observations for **LF6-calc**,[10] for which the LUMO is mostly concentrated on just four of the six available boron centers. The difference is attributed to the absence of fluorene end groups and the resulting higher symmetry in the cyclic system.

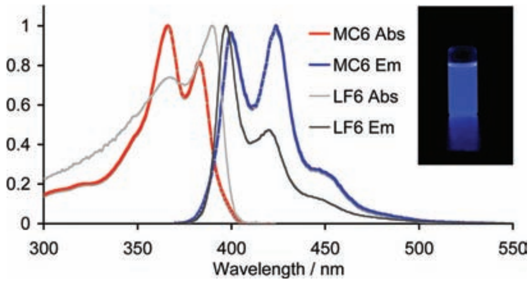


Figure 3. Comparison of the UV−vis and fluorescence spectra of **MC6** with those of linear **LF6** in CH$_2$Cl$_2$ (excited at λ_{max}). Inset: Photograph of **MC6** in CH$_2$Cl$_2$ exposed to a UV lamp (365 nm).

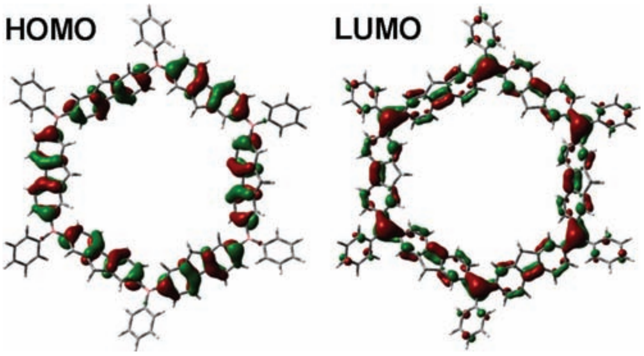


Figure 4. HOMO and LUMO orbital representations for **MC6-calc**.

TD-DFT calculations[13] were also performed, and they suggest another reason for the differences in the absorption profiles, which is that, in contrast to **LF6-calc**, the lowest energy absorption for **MC6-calc** is symmetry-forbidden (HOMO→LUMO, 415 nm, $f = 0.000$), making higher energy transitions that involve contributions primarily from the HOMO−1 and HOMO−2 to the LUMO orbital (389 nm, $f = 2.439$; 388 nm, $f = 2.434$) and the 0−1 vibronic transition dominant.[17−19] Indeed, the experimental absorption onsets (**LF6**, 402 nm vs **MC6**, 404 nm) and the calculated HOMO−LUMO gaps follow the expected trend with a decrease from linear **LF6-calc** (3.51 eV) to the "infinite chain" of **MC6-calc** (3.49 eV). Also consistent is that similar blue emissions are observed in both cases and the maxima are even slightly red-shifted for the cyclic species. A remarkable quantum yield of 0.98 was measured for **MC6**. A relatively modest solvatochromic effect is consistent with some degree of polarization of the excited state, and the emission profiles proved to be slightly concentration-dependent, suggesting possibly the formation of aggregates at high concentrations.[13]

The presence of electron-deficient boron centers allows for binding of electron-rich substrates. For instance, borate cycles are generated in the presence of F^- or CN^-.[5] This process is very effective with large stepwise binding constants that are in the range typical of highly electron-deficient triarylboranes ($\sim 10^5 - 10^8$ M^{-1}) and decrease slightly as the cycle becomes more highly charged.[20] Another interesting aspect is that the presence of only 1 equiv of the anion for each hexameric macrocycle results in ca. 75% quenching of the luminescence, although the absorbance decreases by less than 40% (Figure 5). Based on the fitting of the absorption data (Figure S11, Supporting Information), at a 1:6 ratio of F/B, the relative abundance of species [**MC6**], [**MC6**]F, [**MC6**]F_2, [**MC6**]F_3, [**MC6**]F_4, [**MC6**]F_5, [**MC6**]F_6 is 29:49:20:2:0:0:0, while the amount of free [**MC6**] decreases to 4% after addition of 2 equiv of F^-. This suggests that the emission of all the cycles that are complexed with even just one anion is effectively quenched, consistent with an amplified quenching mechanism.[21] Addition of an excess of $[Bu_4N]F$ or $[Bu_4N]CN$ leads to highly charged species $\{[(\mathbf{MC6})X_6](Bu_4N)_n\}^{(6-n)-}$ (X = F, CN), which were also identified by high resolution ESI-MS analysis (Figure S10, Supporting Information).[13]

In conclusion, we have succeeded in the preparation of the first example of a highly electron-deficient bora-cyclophane. The macrocycle is strongly blue luminescent and can be reversibly reduced in six separate redox steps. Important differences in comparison to the electronic structure of the respective linear species were deduced. Another unique aspect is the presence of multiple electron-deficient organoborane moieties, which leads to high affinity for electron-rich substrates. There has been immense recent interest in the binding of anions to organoborane Lewis acid receptors, and **MC6** binds strongly to F^- and CN^- as evidenced by UV−vis titration and ESI FT-MS, thus suggesting potential use in anion recognition and as stimuli-responsive optoelectronic materials. Anion binding to **MC6** results in amplified fluorescence quenching with formation of a highly charged hexaborate species. This offers a facile means to convert an electron-deficient macrocycle into an electron-rich one using anion addition as an external stimulus.

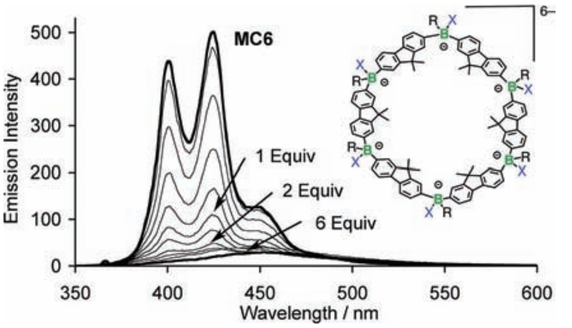


Figure 5. Emission spectra (λ_{ex} = 366 nm) for the titration of **MC6** (4.474×10^{-6} M) with F^- in THF at RT and illustration of the charged macrocycle $[\mathbf{MC6} \bullet X_6]^{6-}$ (X = F^- or CN^-) obtained in the presence of an excess of the anion X^-. The amounts of F^- added per cycle (from top to bottom) are as follows: 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.6, 2.0, 4.0, 6.0 equiv.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and data; complete ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

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(12) In comparison to **MC6**, the formation of **MC4** is considerably less favorable. This is attributed to significant ring strain in **MC4** as confirmed by DFT calculations on **MC4-calc**. The calculated endocyclic B−C bond distances for **MC4-calc** amount to 1.570 Å, while the C−B−C bond angles of 118.1° are smaller than in **MC6-calc** (see the Supporting Information).

(13) See the Supporting Information for further details.

(14) Single crystals suitable for X-ray diffraction analysis could not be obtained. Polyfunctional arylboranes of relatively large size such as the macrocycle described here are known to be difficult to crystallize, and amorphous molecular materials are often obtained instead (see for example the research by Shirota on borylated oligothiophenes as molecular glasses for OLED applications: Noda, T.; Shirota, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9714−9715. The presence of the triisopropylphenyl substituents is also unfavorable and efforts in our labs are under way to explore other related macrocycles with substituents that favor packing in the solid state.

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(16) For **MC6-calc** 10 different conformations that vary with respect to the relative orientation of the fluorene C9 bridges are possible. Optimization of all possible conformers showed that the conformer, in which all the fluorene groups point into the same direction with respect to the plane spanned by the six B centers, is lowest in energy. In this conformer all the B centers are essentially in one plane (maximum deviation of 0.054 Å), while more strongly folded cycles are observed when the orientation of the fluorene moieties is changed.

(17) Similar observations were made also for **MC4-calc**.

(18) The effect of the silyl groups in **LF6-calc** is not significant. No contributions to the frontier orbitals were observed, and a comparison of the calculated absorption spectra of the silylated and desilylated species reveals only very minor differences ($\leq$1nm).

(19) For discussions of symmetry-forbidden transitions in macrocycles, see: (a) Bednarz, M.; Reineker, P.; Mena-Osteritz, E.; Bäuerle, P. *J. Lumin.* **2004**, *110*, 225−231. (b) Hoffmann, M.; Kärnbratt, J.; Chang, M.-H.; Herz, L. M.; Albinsson, B.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 4993−4996.

(20) The decrease in anion affinity is less pronounced for the linear species **LF6** as reflected in comparatively larger binding constants β_{14}, β_{15}, and β_{16} (see Figure S12 in the Supporting Information). We attribute the weaker binding of F^- to **MC6** to stronger Coulombic interactions in the macrocyclic architecture. This interpretation is consistent with the electrochemical data.

(21) Similar effects were observed for the linear species **LF6**. See also ref 9 and citations therein.