



Boraacridines: Synthesis and electrooptical properties

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Introduction

One of the main research topics of our group has been the synthesis and characterization of novel boron-containing chromophore systems. Among these, chromophores containing only boron as a heteroatom as well as *B,N*-push-pull-systems have been successfully synthesized. Of the chromophores found, molecules with boron and nitrogen as substituents adjacent to the π -electron system showed the highest stability when exposed to air or moisture^[1,2,3,4].

An alternative to these structures are chromophores with a fully planar π -electron system and integrated boron and nitrogen atoms. Following this general idea, one of the simplest chromophores imaginable would be a tricyclic analogue to anthracene with boron and nitrogen replacing the central carbon atoms. The resulting molecule is basically acridine with a boron atom in the 9-position, thus it can be named 9-boraacridine. This class of compound in general was not unknown before, the *N*-methyl derivative has been synthesized in 1992 already, but the spectroscopic properties had not been examined yet^[5].

Synthesis

Keeping the symmetry of the molecule in mind, one way of synthesizing boraacridines is a dilithiation of a *N*-substituted 2,2'-dibromodiphenylamine followed by the reaction with a boronic ester. To protect the boron atom from nucleophilic attacks, a bulky substituent like a mesityl group should be used. Unsubstituted 2,2'-dibromodiphenylamine is easily available via a 5-step synthesis^[6]. Alkylation of the nitrogen is achieved by deprotonation with sodium hydride or methyl lithium followed by reaction with the respective alkyl iodide. The direct introduction of a phenyl substituent is possible via a copper-catalyzed coupling with iodobenzene.

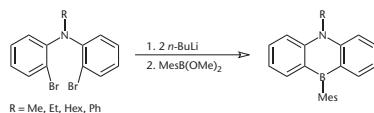


Fig. 1: General synthesis for *N*-substituted boraacridines

The *N*-alkyl boraacridines are light yellow crystalline solids, while the *N*-phenyl derivative has a greenish-yellow color. All chromophores showed very slow decomposition under air but were stable under water.

Fluorescence

All boraacridines showed a strong fluorescence in solution. The spectra recorded were almost similar for all derivatives. The observed Stokes shifts were small. Fluorescence lifetimes were above 9.5 ns in all cases, all quantum yields were high.

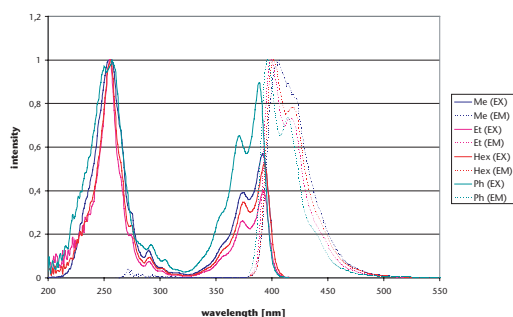


Fig. 2: Fluorescence in solution (cyclohexane)

Table 1: Results of fluorescence spectroscopy

<i>N</i> -substituent	Stokes-shift [nm]	lifetime [ns]	quantum yield
methyl	14	9.97	0.76
ethyl	7	9.52	0.80
hexyl	8	9.50	0.78
phenyl	7	9.50	0.77

The boraacridines also showed fluorescence as solids. Thin films of these compounds showed spectra quite similar to those observed in solution. An interesting exception was the *N*-phenyl boraacridine, which showed green fluorescence under UV light as crystalline solid.

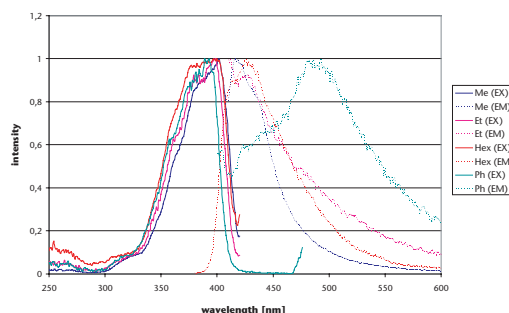


Fig. 3: Fluorescence as thin film

Stimulated emission

The *N*-methyl and *N*-phenyl boraacridines were also tested for stimulated emission. The chromophores were embedded in a Spiro-PBD matrix and pumped at 337 nm. Both compounds showed laser activity with an emission maximum at 425 nm and 419 nm respectively.

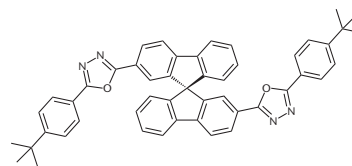


Fig. 4: Structural formula of Spiro-PBD

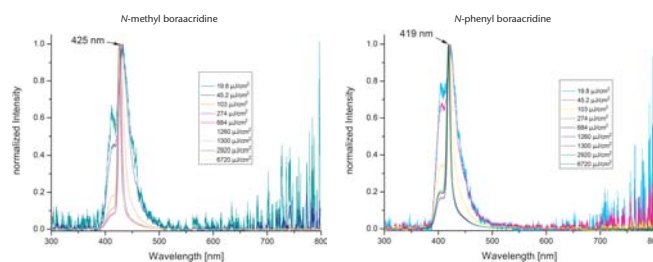


Fig. 5: Stimulated emission spectra

Summary

Boraacridines are easily synthesized and show blue fluorescence with high quantum yields and lifetimes as well as laser activity. Unfortunately, cyclic voltammetric measurements showed decomposition of the chromophore after oxidation, so these chromophores cannot be used as organic emitters in organic light-emitting diodes. Thus, finding a way to stabilize the radical cation is one of our next goals within our research.

Literature

- [1] K. Albrecht, D. E. Kaufmann, *J. Chem. Res.* **1999**, 264-265.
- [2] K. Albrecht, V. Kaiser, R. Boese, J. Adams, D. E. Kaufmann, *J. Chem. Soc. Perkin Trans. 2* **2000**, 2153-2157.
- [3] M. Köster. *Neues und Verbindendes von Bor und Aluminium: 1,3-B,N-chromophore Systeme und durch polymere Aluminiumorganyle vermittelte Reaktionen*. Ph.d. thesis, Institute of Organic Chemistry, Clausthal University of Technology, December 2001.
- [4] C. Burmester. *Untersuchungen im Umfeld B,N-substituierter Oligophenylene - Anwendung chemoselektiver Suzuki-Kupplungen*. Ph.d. thesis, Institute of Organic Chemistry, Clausthal University of Technology, August 2004.
- [5] M. Kranz, F. Hampel, T. Clark, *J. Chem. Soc., Chem. Commun.* **1992**, 1247-1248.
- [6] D. Wiese, R. Tacke, U. Wannagat, *Liebigs Ann. Chem.* **1981**, 1285-1293.
- [7] T. Siemers. *Synthese und elektrooptische Eigenschaften von 9-Boraacridinen*. Diploma thesis, Institute of Organic Chemistry, Clausthal University of Technology, March 2006.