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4-Boratastyrylstilbene and 1,4-Bis(boratastyryl)benzene: Synthesis, Structural Characterization, and Photophysics

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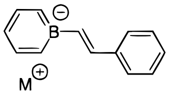
Recent reports highlight the potential use of boron-containing conjugated polymers in emerging optoelectronic applications.[1] To understand the effect of conjugation in these materials, a proper description of the electronic structure in the monomeric or oligomeric constituents is required. This “building up” approach for extrapolating the properties of molecules to those of polymeric materials has proven successful in several families of conjugated polymers and forms the basis of an ever growing area of materials chemistry.[2]

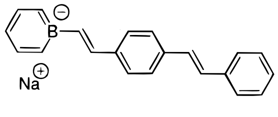
In connection to boron-containing polymers, we recently reported the synthesis, structure, and photophysics of boratastilbene (M-**1**, where M = Li or Na).[3] When compared to stilbene, the isoelectronic B^- for C substitution allows one to examine the effect of a negative charge and an asymmetric charge distribution on excited-state properties.



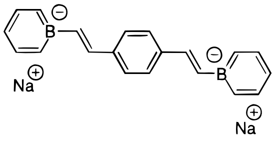
M-**1**
M = Li, Na

Compounds of the type M-**1** show aggregation-dependent photophysics. In nonpolar solvents the solution structure is a tight ion pair, and low photoluminescence quantum yields are observed. In polar solvents, or when crown ethers that encapsulate the countercations are added, the solvent-separated species is highly emissive as a result of an intramolecular charge-transfer process.

A natural progression for extending the conjugation length of these “boratachromophores” is the synthesis and study of the anionic 4-boratastyrylstilbene (Na-**2**) and the dianionic 1,4-bis(boratastyryl)benzene (Na_2-**3**). These molecules are isoelectronic to distyrylbenzene chromophores, which find use in optoelectronic devices and supramolecular engineering.[4]

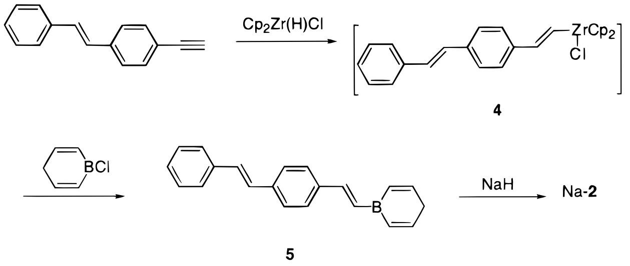


Na-**2**

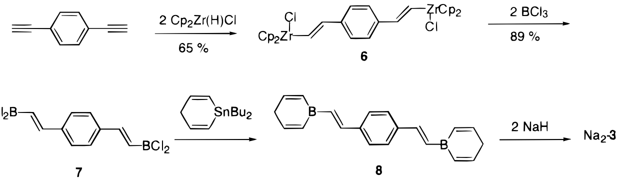


Na_2-**3**

Scheme 1



Scheme 2



Scheme 1 shows the synthesis of Na-**2**. Reaction of 4-ethynylstilbene with $Cp_2Zr(H)Cl$ in toluene provides the zirconium compound **4**, which is subsequently treated in situ with 1-chloro-1-boracyclohexa-2,5-diene.[5] Crystallization from a CH_2Cl_2 solution affords 1-[2-(4-styrylphenyl)ethenyl]-1-boracyclohexa-2,5-diene (**5**) in 57% overall yield. Deprotonation of **5** in THF using excess NaH, followed by crystallization from a THF/ether solution provides Na-**2** in 75% yield.

The synthesis of Na_2-**3** (Scheme 2) requires two transmetalation steps. Addition of 1,4-diethynylbenzene to 2 equiv of $Cp_2Zr(H)Cl$ provides the binuclear species **6**. Reaction of **6** and BCl_3 in toluene gives (1,4-phenylenedi-1,2-ethenediyl)bis(dichloroborane) (**7**), which can be separated from Cp_2ZrCl_2 by extraction with pentane. Transmetalation with 1,1-dibutyl-1-stannacyclohexa-2,5-diene[6] gives 1,1′-(1,4-phenylenedi-1,2-ethenediyl)bis(1-boracyclohexa-2,5-diene) (**8**) in 46% overall yield from 1,4-diethynylbenzene. It should be noted that the direct reaction of **6** with 1-chloro-1-boracyclohexa-2,5-diene gives **8**. However, **8** and Cp_2ZrCl_2 have similar solubility properties and cannot be separated easily. The desired Na_2-**3** is obtained by addition of **8** to a NaH/THF slurry and is an exceptionally air- and moisture-sensitive orange solid.

Figure 1a shows that the absorption maximum of Na-**2** in THF appears at 404 nm ($\epsilon_{404} = 2.7 \times 10^4$ L mol^{-1} cm^{-1}). Compared against Na-**1**, this band is 47 nm red-shifted, a consequence of the extended conjugation length. Addition of 10 equiv of dibenzo-18-crown-6 to Na-**2** in THF causes a bathochromic shift to 447 nm ($\epsilon_{447} = 2.1 \times 10^4$ L mol^{-1} cm^{-1}, Figure 1b). The photoluminescence (PL) spectrum of Na-**2** in THF upon excitation at 404 nm is shown in Figure 1c, and the calculated overall PL quantum efficiency (Φ_{PL}) is approximately 2%. Addition of dibenzo-18-crown-6 causes no change in the fluorescence spectra or Φ_{PL}.

It is likely that, as in the case of Na-**1**, the crown coordinates to sodium and generates the solvent-separated ion pair. Removing the interactions between the boratabenzene ring and sodium allows for a transition that ultimately transfers electron density from boratabenzene to the rest of the molecule. The lower Φ_{PL} of Na-**2** vis-á-vis Na-**1** (16% in THF and 66% in THF with dibenzo-18-

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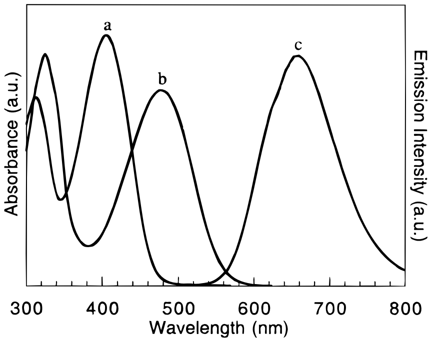

Figure 1. Spectra of Na-**2** in THF. (a) Absorption of Na-**2**, (b) absorption of Na-**2** with 10 equiv of dibenzo-18-crown-6, (c) emission of Na-**2**.

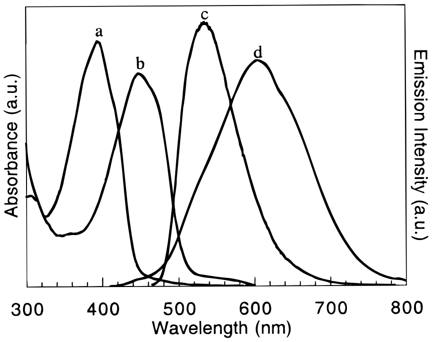

Figure 2. Spectra of Na$_2$-**3** in THF. (a) absorption of Na$_2$-**3**, (b) absorption of Na$_2$-**3** with 50 equivalents dibenzo-18-crown-6, (c) emission of Na-**2** with 50 equiv of dibenzo-18-crown-6, (d) emission of Na$_2$-**3**.

crown-6) is attributed to the smaller HOMO/LUMO gap of **2** (the energy gap law).[7] That the crown ether does not change the emission suggests that sodium does not stabilize the excited state of Na-**2**. Perhaps the charge in the vinylstilbene fragment is too diffuse for a strong Coulombic interaction.

In THF, the absorption of Na$_2$-**3** is centered at 396 nm (ϵ_{396} = 3.1 × 10^4 L mol^{-1} cm^{-1}, Figure 2). The emission band is centered at 604 nm (Φ_{PL} = 16%), but its broad shape suggests more than one emitting species. Upon addition of excess (50 equiv) dibenzo-18-crown-6 the absorption *red* shifts to 447 nm (ϵ_{447} = 1.9 × 10^4 L mol^{-1} cm^{-1}), but the emission *blue* shifts to 534 nm (Φ_{PL} = 44%). The change in absorption corresponds to enhanced charge transfer from the outer charged rings into the inner ring. The relative energies of emission are likely related to the ability of the sodium ions to compensate and stabilize changes in the electron distribution in **3** upon photoexcitation.[8,9] The structure of Na$_2$-**3** in a crystal grown from THF solution shows a sodium ion adjacent to each boratabenzene ring (Figure 3). In solution, these ions can optimize their location relative to **3** with changes in electrostatic distribution and stabilize the excited-state species.[10]

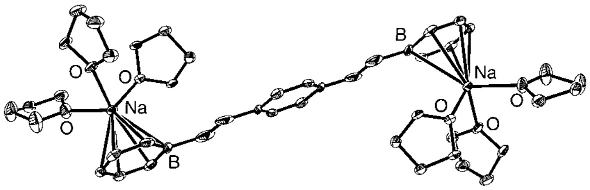

Figure 3. ORTEP drawing of [Na(THF)$_3$]$_2$[**3**].

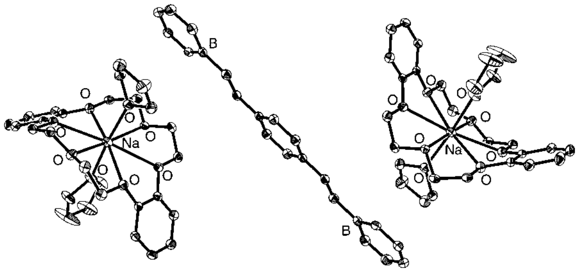

Figure 4. ORTEP drawing of [Na(dibenzo-18-crown-6)THF$_2$]$_2$[**3**].

Figure 4 shows the structure of a single crystal obtained from a solution containing Na$_2$-**3** and dibenzo-18-crown-6. The molecular composition corresponds to [Na(dibenzo-18-crown-6)-THF$_2$]$_2$[**3**]. In this arrangement, the sodium ions are insulated from **3** by the crown and two "axial" THF molecules. It is surprising to us that **3** is present in the lattice without external Coulombic stabilization of the dianionic charge. That the sodium ions are insulated from **3** is consistent with the blue shift in fluorescence when dibenzo-18-crown-6 is added. Under these conditions, the ions cannot stabilize charge redistribution upon photoexcitation, and a normal Stokes shift is observed.

In summary, the synthesis of Na-**2** and Na$_2$-**3** are described. The strategy includes hydrozirconation with Shwartz reagent[11] followed by transmetalation from zirconium to boron.[12] Differences in the optical properties of Na-**2** relative to those of Na-**1**, namely the red-shifted spectra and lower Φ_{PL} values, can be rationalized in terms of the extended conjugation length. For Na$_2$-**3**, the motion of countercations adjacent to the chromophore allows for stabilization of the excited-state energy. Removing these cations from **3** by addition of dibenzo-18-crown-6 results in enhanced charge transfer and less efficient stabilization of the excited state.

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Supporting Information Available: Complete details for the synthesis of all compounds and the crystallographic studies of [Na(THF)$_3$]$_2$-[**3**] and [Na(dibenzo-18-crown-6)THF$_2$]$_2$[**3**] (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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