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Synthesis and optical properties of a new class of pyrromethene–BF_2 complexes fused with rigid bicyclo rings and benzo derivatives

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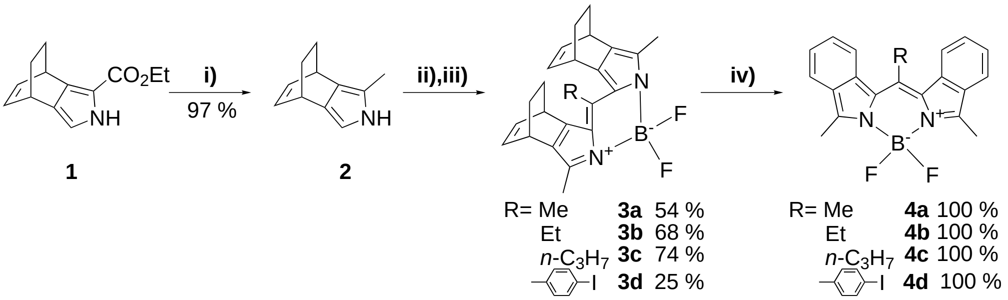
Abstract—A new class of boron dipyrromethene (BDP) dyes fused with rigid bicyclo[2.2.2]octadiene units are prepared, which are converted into benzo BDP dyes via a retro Diels–Alder reaction; the absorption and fluorescence spectra of the new dyes are discussed. © 2001 Elsevier Science Ltd. All rights reserved.

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) dyes are highly fluorescent material and have been extensively used in various fields of science. They are important for laser dyes,[1] molecular probes for biochemical experiments,[2] fluorescent sensors[3] or various optoelectronic devices.[4] For the design of more advanced molecular devices based on boron dipyrromethene (BDP) dyes, it is crucial to control the electronic properties of BDP. Recently, Burgess and co-workers have reported chemical modification of BDP by introduction of 3,5-diaryl groups[5] or restricted bond rotation using fused ring systems.[6] In this paper we present a new method for chemical modification of BDP. Our method is based on our recent synthesis of benzoporphyrins via a retro Diels–Alder reaction of porphyrins fused with bicyclo[2.2.2]octadiene (BCOD) units.[7]

Synthesis of BDP **3** fused with BCOD units and its conversion into **4** fused with a benzene ring is presented in Scheme 1.

The starting material, ethyl 4,7-dihydro-4,7-ethano-2*H*-isoindole carboxylate **1**, was converted into 2-methyl



Scheme 1. *Reagents and conditions*: (i) $LiAlH_4$ (5 equiv.), dry THF, reflux, 2 h; (ii) RCOCl, CH_2Cl_2, reflux, 3 h; (iii) Et_3N, $BF_3{\cdot}Et_2O$, $PhCH_3$, 80°C, 30 min; (iv) 220°C, 2 h.

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pyrrole **2** by reduction with excess $LiAlH_4$ under reflux in THF for 2 h. It should be noted that **1** was converted into the corresponding porphyrin via reduction with $LiAlH_4$ at 0°C, where the ester group was reduced to a hydroxymethyl group.[7] Pyrrole **2** was converted into BDP **3**[8] having fused BCOD units by the reaction with acid chlorides followed by treatment of Et_3N and $BF_3{\cdot}Et_2O$. BDP **3** was purified by column chromatography, and was converted into BDP **4** by heating at 220°C at reduced pressure (10 mmHg) for 2 h. The reaction proceeds very cleanly to give pure **4**[8] in quantitative yield without any purification process.

A dramatic change in the UV–vis absorption spectra of **3a** and **4a** is shown in Fig. 1.

The absorption of **4a** is red-shifted by ca. 70 nm compared to that of precursor **3a**. Intensity of absorption is also increased by extended conjugation. Some important optical properties of **3** and **4** are presented in the Table 1.

The optical properties of BDP **3** are similar to those of the usual alkyl-substituted BDP.[1] On the other hand, BDP **4** is colored solid with a metallic (gold) luster, and the color of **4** is deep-blue in solution with a strong and beautiful red fluorescence when irradiated. The fluorescence spectra of all compounds **3** and **4** show mirror symmetry with their absorption spectra. The Stokes shifts of dyes **3** and **4** are smaller than those of other reported BDPs.[1] This is due to the rigid-fused systems of **3** and **4**, which prevent a non-radiative deactivation of the excited states. The quantum yields for fluorescence of **3** and **4** were measured in EtOH relative to fluorescein ($\Phi=0.97$). The absorption and emission spectra of **3** and **4** are independent of solvent polarity. The quantum yields of **3** were about 0.7 and those of **4** were decreased, but still high ($\Phi=0.28$–0.36). For biological applications, BDP dyes with large Stokes shifts and high quantum yields are highly desirable.[9] BDP dyes **4** have two absorption maxima at 557–561 nm and 601–606 nm. Excitation of **4** at 554–560 nm and 600–605 nm provides identical emission spectra. When excited at 600–605 nm, Stokes shifts of **4** are regarded to be 6–8 nm. On the other hand, the peak wavelength was separated about 50–60 nm from the excitation wavelength (554–560 nm); therefore, dyes **4** may be useful for biological applications.[9]

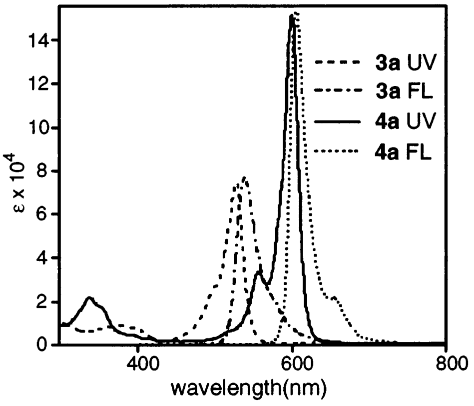

Figure 1. UV–vis and fluorescence spectra of **3a** and **4a**.

Table 1. Optical properties of pyrromethene–BF_2 complexes **3a**–**d** and **4a**–**d**

Entry	λ_{max}/nm (log ε)[a]	Stokes shifts (nm)[b]	Φ[c]
3a	530 (4.89)	11	0.77
3b	529 (4.87)	10	0.78
3c	530 (4.78)	12	0.80
3d	534 (4.85)	16	0.62
4a	558 (4.52), 603 (5.19)	6	0.28
4b	557 (4.50), 601 (5.16)	7	0.33
4c	557 (4.40), 602 (5.12)	6	0.36
4d	561 (4.42), 606 (5.13)	8	0.26

[a] Measured in $CHCl_3$.

[b] Measured in $CHCl_2$.

[c] Measured in EtOH using fluorescein in EtOH as reference ($\Phi=0.97$).

Cyclic voltammetry (200 mV s^{-1}, Pt disk electrode, tetrabutylammonium perchlorate in MeCN) showed that **4c** was reversibly oxidized at $E_{1/2}=0.35$ V (versus $Ag/AgNO_3$), whereas **3c** was irreversibly oxidized at a peak potential $E_{pa}=0.72$ V. Both compounds are reduced at similar peak potentials $E_{pc}=-0.85$ V. Unfortunately, we could not obtain good CV spectra of the other compounds **4** due to the poor solubility of **4**. The HOMO energy levels of BDP dyes were more affected than the LUMO energy levels by the introduction of fused benzene rings at the pyrrole rings. This result is in good agreement with that reported in BDP dyes with extended conjugation.[6]

The conversion of **3** into **4** by heating provides an important strategy for controlling the properties of dyes. Namely, dyes **3** consisted of rigid three-dimensional frameworks, which prevent π stacking to increase their solubility or fluorescence quantum yields in various circumstances. When bicyclo BDP **3** was converted to benzo BDP **4** by heating, the properties were completely changed. Both dyes may find utility in the field of material science. In fact, dyes **3** are more effective than **4** or other BDP dyes with alkyl substituents as sensitizers to initiate photo-induced polymerization of acrylate monomers for laser printing.[10]

We have presented new BDP dyes fused with rigid bicyclo units, which are converted into BDP dyes fused with a benzene ring. Further transformation of BDP dyes **3** and **4** through reactive double bonds, methyl or aromatic halogen groups leads to more sophisticated dyes, which can be used as sensors or molecular switches.[4]

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