Calixphyrin Complexes

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Boron Difluoride Complexes of Expanded N-Confused Calix[*n*]phyrins That Demonstrate Unique Luminescent and Lasing Properties

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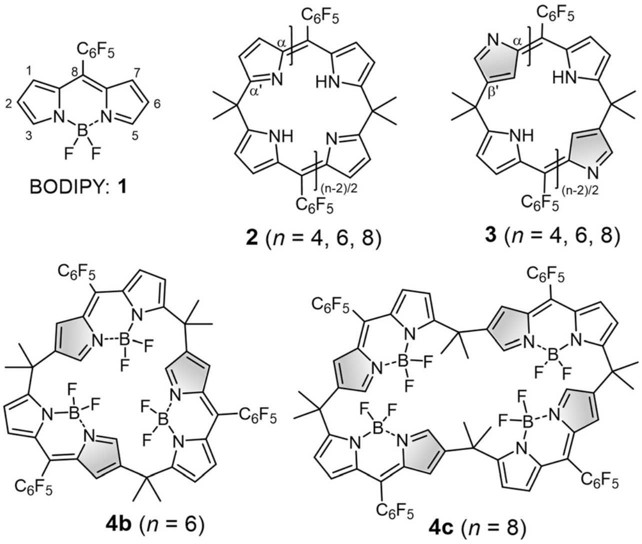
Dedicated to Professor Jonathan L. Sessler on the occasion of his 60th birthday

Abstract: *Complexation of novel multiply N-confused expanded calix[n]phyrins with boron difluoride afforded a new class of cyclic BODIPY (boron-dipyrromethene) arrays. The structures of circularly arranged BODIPY subunits linked in an N-confused fashion give rise to such photophysical properties unique to the macrocycles as red-shifted emission wavelengths along with apparent large Stokes shifts, long emission lifetimes, and solid-state lasing. The DFT calculations support the size-dependent excited-state dynamics of the macrocycles.*

Molecular engineering of multi-chromophoric architectures with well-defined shape has attracted tremendous attention, with a special focus of interest being on their photophysical properties, in the context of mimicking the light-harvesting antenna complex (LHC) naturally present in photosynthetic systems.[1] It is widely known that porphyrin-related macrocycles play vital roles in the photon capture and subsequent energy transfer to the acceptor units.[2] The BODIPY dye (namely, 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene; **1**), often referred to as porphyrin's little sister, can be an alternative chromophore unit in which a half porphyrin skeleton is coordinated with a difluoroboron moiety.[3] It has proven useful as an imaging dye or a photosensitizer for several reasons: high emissivity, insensitivity of fluorescence to the environment pH or the polarity of media, and reasonable stability.

From the viewpoint of synthetic chemistry of BODIPYs, circularly arranged BODIPYmers offer a unique multichromophoric platform to investigate the shape-dependent photophysical properties. The spatially enforced cyclic structures (such as cycloparaphenylene, cyclothiophene, cycloperylenediimide) enables the tuning of their excited-state dynamics, including light harvesting and subsequent energy transfer.[4] However, to date, such cyclic systems with BODIPYs have been little-studied, and their photophysical properties are unexplored.[5]

In creating the relevant architectures, we were inspired by the structure of an expanded calix[*n*]phyrin scaffold (for example, **2**; Scheme 1).[6] The calixphyrin is a hybrid compound of porphyrin and calixpyrrole composed of dipyrromethene units connected at the 3,5-positions through the sp^3 carbon atoms. The desired cyclic BODIPYmers are available



BODIPY: **1**

2 (*n* = 4, 6, 8)

3 (*n* = 4, 6, 8)

4b (*n* = 6)

4c (*n* = 8)

Scheme 1. Chemical structures of *meso*-C_6F_5-BODIPY (**1**), calix[*n*]phyrin (**2**: *n* = 4, 6, 8), N-confused calix[*n*]phyrin (**3**: *n* = 4, 6, 8), and their boron difluoride complexes (**4b**: *n* = 6; **4c**: *n* = 8).

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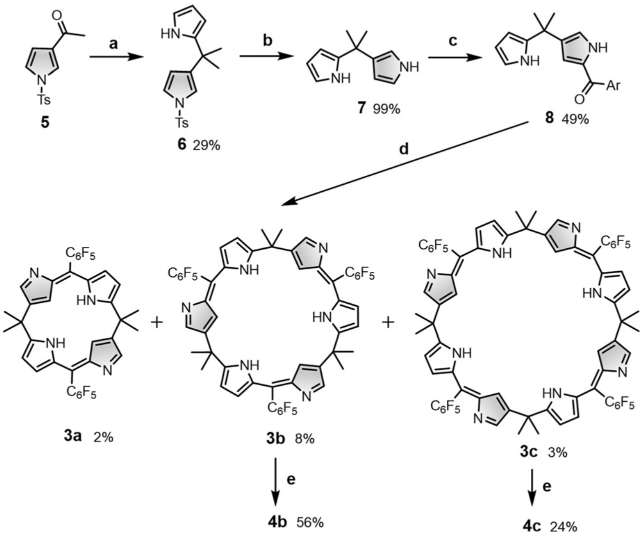
through the binding of boron atoms at the dipyrrin subunits present in the calixphyrin scaffold. Our initial experiment shows, however, that the complexation reaction with the corresponding calix[*n*]phyrin derivatives **2** ($n=6$ or 8) is unlikely (Supporting Information). Instead, complicated reaction mixtures occurred under typical conditions. This is presumably due to the steric hindrance of two *meso*-methyl groups that are resistant to modification of the macrocyclic cores.

In this study, we have designed new cyclic BODIPY arrays with a simple structural mutation of the parent ligand platform, that is, calixphyrins, following an N-confusion synthetic approach.[7] The resulting complexes can be considered as the first BODIPY macrocycles with N-confused motifs (thus, we use a trivial name, confused BOIDPY nanoring). Implementing N-confused pyrrole units into the calixphyrin skeleton enables the relocation of pyrrolic nitrogen atoms, which is critical for facile boron complexation (see below). The macrocycles are created by using novel triply and quadruply N-confused calix[*n*]phyrin boron difluoride complexes (**4b**; $n=6$ and **4c**; $n=8$), in which the BODIPY cores are connected through sp^3-methane bridges from the pyrrolic α(C3) and β'(C6) positions. Both complexes revealed the structure-dependent photophysical properties: far-red emission ($\Phi_{FL}\approx 48\,\%$) and long lived fluorescence lifetimes ($\tau_{FL}\approx 38$ ns). Lasing action was observed for **4c** in the solid state.

The multiply N-confused calixpyrrole analogues were prepared from the corresponding 2-acylated N-confused dipyrromethane **8** as a key precursor through an acid-catalyzed self-cyclization (Scheme 2). Reduction of **8** with NaBH$_4$ in THF gave the corresponding dipyrromethane monocarbinol in situ. Subsequent self-condensation using Yb(OTf)$_3$ catalyst, followed by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation, gave a mixture of multiple N-confused calix[*n*]phyrin derivatives (**3a–c**). Silica gel gravity column chromatography in combination with gel permeable chromatography (GPC-HPLC) was successful in isolating pure **3a–c** in 2%, 8%, and 3% yields, respectively (Supporting Information, Figure S1). It should be noted that the product ratio in this cyclization reaction varied with the concentration of the solution of **8**: the higher the concentration, the higher the portion of large macrocyclic products ($n>8$).[8] The open bidentate nitrogen sites of **3b** and **3c** are available for subsequent boron complexation (Figure 1a,b). As a result, the desired boron difluoride complexes (**4b** and **4c**) were obtained in 59% and 24% yields, respectively, via complexation with BF$_3$·Et$_2$O in the presence of diisopropylethylamine (DIPEA).



Scheme 2. Synthetic routes for multiply N-confused calix[*n*]phyrin boron difluoride complexes (**4b** and **4c**). Reaction conditions: a) 1) CH$_3$MgBr in THF, 2) BF$_3$·Et$_2$O in pyrrole, b) KOH(aq) in MeOH, c) 1) EtMgBr in THF, 2) *S*-2-pyridyl-pentafluorobenzothioate, d) 1) NaBH$_4$ in THF/MeOH, 2) Yb(OTf)$_3$ in CH$_2$Cl$_2$, 3) DDQ, e) 1) DIPEA in toluene, 2) BF$_3$·Et$_2$O.

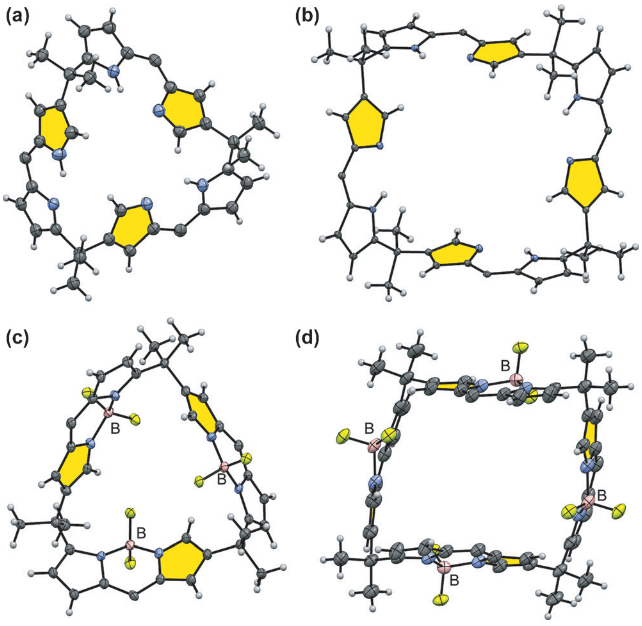


Figure 1. Crystal structures of a), b) N-confused calix[*n*]phyrins (**3b**: $n=6$; **3c**: $n=8$) and c), d) their boron difluoride complexes (**4b**: $n=6$; **4c**: $n=8$). The *meso*-pentafluorophenyl groups and solvent molecules are omitted for clarity. Ellipsoids are set at 50% probability. The confused pyrrole subunits are highlighted in yellow.

The structures of **4b** and **4c** were identified by NMR, mass spectroscopy, and X-ray crystallographic analysis (Supporting Information). The ^{1}H NMR spectrum of **4b** in CD$_2$Cl$_2$ simply exhibited four sets of pyrrolic proton resonance in the region of 6–8 ppm. This suggests a pseudo C_3-symmetric structure for **4b** in solution, which occurs because of the flexible *meso*-sp^3-carbon linkage between the BODIPY units. Likewise, the structure of **4c** was inferred on the basis of the four symmetric sets of pyrrolic CH signals in the ^{1}H NMR spectrum. The symmetric features of **4b** and **4c** were also confirmed from the ^{19}F NMR spectra.

The X-ray crystallographic analysis of **4b** and **4c** demonstrated the multiply N-confused BODIPY units (Figures 1c,d; Supporting Information, Table S1).[9] Their unique orientations, namely triangle (**4b**) and square (**4c**) box-like shapes, along with the alternate orientations of the BODIPY planes, were identified. Owing to the asymmetric conformation, the dihedral angles between the BODIPY planes are 60 and 85° for **4b**, while the corresponding angles for **4c** are almost identical (ca. 76°). Their symmetry considerations could be relevant to the individual molecular dipoles of the BODIPY units to cancel it out. Interestingly, a nano-tubular assembly was observed along the *b*-axis of the packing structure of **4c** (Supporting Information, Figure S15): Each core unit in the individual column is separated by approximately 14 Å and unidirectional stacking occurs owing to the nonbonding interaction between the fluorine and β-pyrrolic hydrogen atoms.

Enforced arrangement of the BODIPY chromophores in **4b** and **4c** in solution gives rise to intriguing photophysical properties. The UV/Vis absorption of **4b** in toluene showed an intense band that goes through a maximum at $\lambda_{abs} = 515$ nm ($\varepsilon = 149000$ L mol^{-1} cm^{-1}) with a weak shoulder on the lower energy side (> 550 nm; Figure 2a). Considering the photophysical properties of the monomeric BODIPY **1** ($\lambda_{abs} = 520$ nm; $S_0 \rightarrow S_1$ transition), the split in the lowest band of **4b** could be explained by the presence of complicated inter-chromophore exciton coupling between the moderately angular-aligned BODIPY units.[10] For **4c**, the redshifted absorption peak at $\lambda_{abs} = 534$ nm ($\varepsilon = 189000$ L mol^{-1} cm^{-1}) and a shoulder band tailing up to ca. 650 nm (Figure 2b) are seen. The DFT (B3LYP/6-31 G(d,p)) calculation indicates the through-bond interactions between the molecular orbitals of the BODIPY units for both **4b** and **4c** (Supporting Information, Figures S16–S18 and Tables S4 and S5).

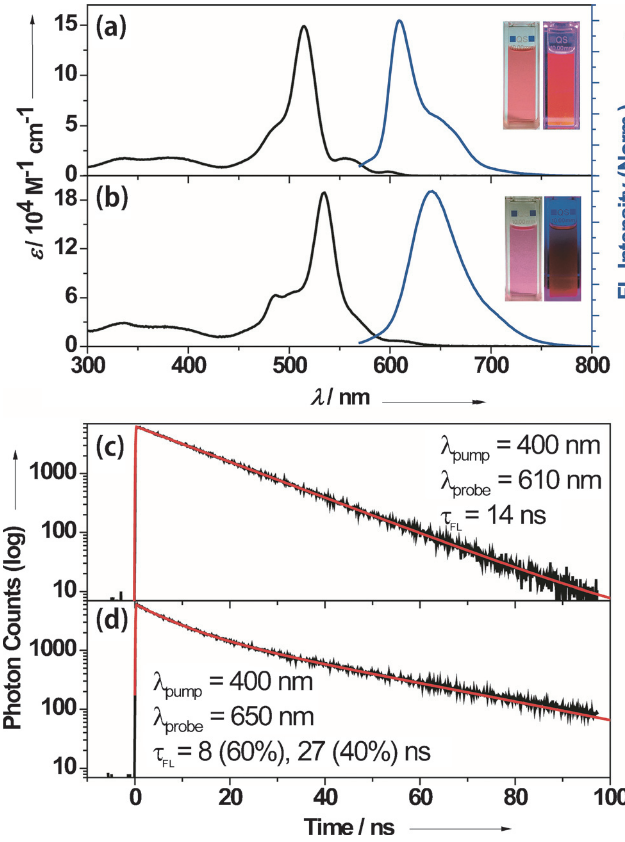


Figure 2. Spectra of UV/Vis absorption (black line) and fluorescence (blue line) taken from a) **4b** and b) **4c** in toluene. The excitation wavelength was set at the absorption maxima. Inset: comparison of images of the solution under ambient light (left) and a UV lamp (right). c), d) Fluorescence decay profiles of c) **4b** and d) **4c**. Also shown are theoretical fits (red lines).

Accordingly, the emission wavelengths were ranged in the far-red ($\lambda_{em} = 609$ and 641 nm for **4b** and **4c** in toluene, respectively), so that the apparent Stokes shift ($\Delta\nu_{max}$) amounted to 2997 and 3126 cm^{-1}, respectively (Supporting Information, Table S2). The absolute fluorescence quantum yield (Φ_{FL}) was determined to be 0.19 and 0.42 for **4b** and **4c**, respectively. The fluorescence lifetime (τ_{FL}) was investigated by means of time-correlated single photon counting (TCSPC). Assuming a single exponential decay, the fluorescence lifetime of **4b** was measured as 14 ns, which is remarkably longer than that of the monomer **1** ($\tau_{FL} = 4$ ns) and the noncyclic BODIPY oligomers (Figure 2c).[11] In the case of **4c**, the fluorescence decay profile could be fitted with a double exponential function, giving rise two decay constants with 8 ns (60 %) and 27 ns (40 %). This suggests the presence of two excited-state components (Figure 2d), which may arise from the interconversion between the potential open–close box conformers owing to the pronounced, inherent molecular flexibility.[12] According to the Strickler–Berg law, the fluorescence lifetime must be inversely proportional to the integrated molar absorption coefficient.[13] This is consistent with the fact that the cyclization of BODIPY fluorophores present in **4b** and **4c** allows long-lived emission.[14]

Interestingly, remarkable solvent effects were found in the photophysical properties of **4b** and **4c**. First, the spectral shape of absorption remained unchanged irrespective of the solvent media, such as acetonitrile, THF, CH_2Cl_2, and cyclohexane (Supporting Information, Figure S19 and Table S2). In contrast, an increased solvent polarity was found to bring a decrease in both the quantum yield and the singlet state lifetimes (for example, $\Phi_{FL} \approx 0.001$ and $\tau_S = 35$ ps estimated by femtosecond transient absorption (TA) spectroscopy in acetonitrile), and the vibrational features in fluorescence were even lost (Supporting Information, Figures S20 and S21). The kinetic parameters of the radiative and nonradiative decay rates (k_r and k_{nr}) are summarized in the Supporting Information, Table S2. In view of these, it is inferred that the excited-state structures of **4b** and **4c** are altered by the intramolecular charge transfer (ICT) in the excited states. The electronic redistribution in the chromophores that follows possibly accompanies geometric relaxation involving S_0 and S_1 states.

In fact, the structural relaxation of **4b** in the singlet excited-state (S_1) was found to be significant in comparison with that of **4c** as inferred from the excited-state energies (Supporting Information, Figures S22 and S23). Since the $S_0 \rightarrow S_1$ (HOMO–LUMO) transitions in **4b** and **4c** evidently involve ICT character, the $S_1 \rightarrow S_0$ transition becomes virtually forbidden ($f = 0.0003 \approx 0.0005$; Supporting Information, Figure S17, Tables S4 and S5). The smaller energy gap ($\Delta E_{S0\text{-}S1} = 1.76$ eV) for **4b** than that for **4c** (2.10 eV) may cause more significant structural relaxation in the excited states. These energy level considerations may explain the lower fluorescence quantum yield and shorter lifetimes for **4b** (Supporting Information, Table S2).

Finally, the emission characteristics were studied under high pump conditions.[15] In a preliminary experiment, a glass capillary tube of 1 mm diameter was loaded with diluted toluene solution of **4b** and **4c**. As such, the Fresnel reflection at the solution/glass interface (1.1 %) allows easy closure of the round trip of light in the radial direction, while the whispering-gallery modes along the inner wall of the capillary can support multimode lasing. The stimulated emission peaked at 660 nm was observed only for **4c** (Supporting Information, Figure S25), which was stable enough to attempt lasing in the solid-state. The plastic samples doped with **4c** were used (Supporting Information, Figure S26 and Table S3). Figure 3 a shows the surface emission spectra with increasing pumping intensity. The stimulated-emission wavelength, 660 nm, remained the same (Figures 3 a; Supporting Information, Figure S27). Above the threshold (ca. 80 μJ), spectral narrowing was observed and the peak intensity grew linearly with increasing pump intensity (Figure 3 b). The slope efficiency of the stimulated emission was five times as large as that of the spontaneous emission. With these in mind, it is fair to conclude that solid-state lasing was achieved although longitudinal modes were not clearly resolved. As opposed to capillary tubes, ad-hoc cavities might have been formed owing to the inhomogeneity of refractive index across the planar sample. It should be further noted that the lasing capability in the solid state lasted more than several years after preparation.

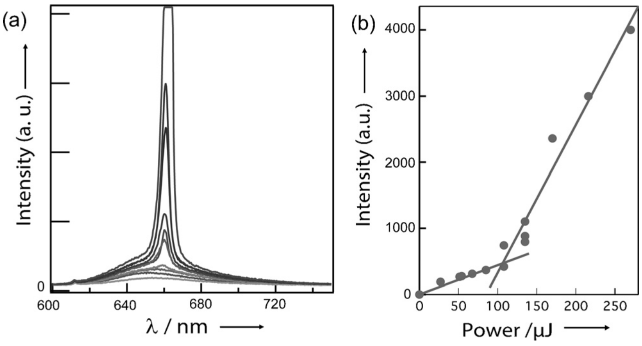


Figure 3. a) Fluorescence spectra of the **4c**-doped PMMA film pumped by a pulsed 532 nm light source. Spectral narrowing is observed above the lasing threshold (ca. 80 μJ). b) Light output from **4c** as a function of the pump intensity.

In summary, we have synthesized new macrocyclic families of multiply N-confused calix[n]phyrins and their boron difluoride complexes. Upon strapping each BODIPY in a confused fashion, the resulting complexes **4b** and **4c** demonstrated unique shape-dependent photophysical properties, in particular retaining their brightness ($\Phi_{FL} \times \varepsilon \approx 7.94\,\mathrm{L\,mol^{-1}\,cm^{-1}}$), despite long emission lifetimes ($\tau_{FL} \approx 27$ ns probed at 610 nm) and apparent large Stokes shifts. The lasing capability of **4b** was also demonstrated. The present BODIPY-based N-confused nanorings have potential in their use for organic photonic materials, such as laser dyes, time-gated bio-imaging probes, and solar-cell dyes.

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Keywords: BODIPY · calixphyrins · fluorescence · laser dye · macrocycles

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