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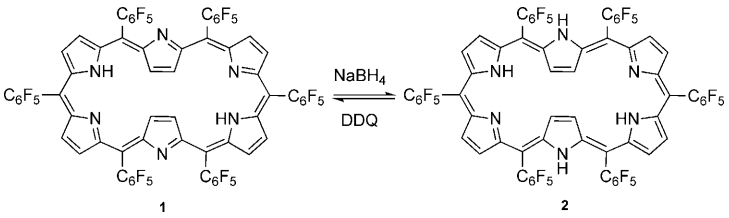
BODIPY–Hexaphyrin Hybrids**

Ji-Young Shin,[a] Takayuki Tanaka,[b] Atsuhiro Osuka,*[b] Qing Miao,[a] and David Dolphin*[a]

Currently, expanded porphyrins have emerged as a promising class of molecules in light of their interesting structural, electronic, and coordination properties.[1] Among these, *meso*-aryl-substituted [26]hexaphyrins have been most extensively studied, since they exhibit intriguing attributes, such as rectangular molecular shapes, strong aromaticity, large two-photon absorption cross sections, and versatile metal-coordinating abilities, which allow for multiple metal complexes with interesting properties.[1g,2,3] As a further step in the use of the hexaphyrin moiety for the creation of functional molecules, hybrid systems are conceivable, in which the hexaphyrin segment is linked with other electronically active groups. However, synthetic efforts along such this path has been rather limited to date.[4] In this paper, we report the synthesis and characterization of boron dipyrromethene (BODIPY)-hexaphyrin hybrids. BODIPY dyes have advantageous properties,[5] such as high molar-extinction coefficients, high fluorescence quantum yields, and reasonably long excited singlet-state lifetimes and thermal/photochemical stability. As a result they have been extensively used as biological labels,[5c] fluorescent sensors,[5d] synthetic light harvesting antenna,[5e] and as a drug delivery reagent.[5f]

In 1999, Cavaleiro's group reported the first synthesis of *meso*-hexakis(pentafluorophenyl) substituted [26] and [28]hexaphyrins, **1** and **2**, in an overall yield of about 1%, under unique reaction conditions,[2] this was followed with our improved synthesis that provided **1** in much better yields along with a set of other *meso*-pentafluorophenyl-substituted expanded porphyrins under modified Rothemund–Lindsey conditions.[3] Hexaphyrins **1** and **2** are both in stable oxidation states, which can be interconverted through a two-electron reduction with $NaBH_4$ and a two-electron oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Scheme 1). Although **1** is a purple-colored aromatic macrocycle showing a strong diatropic ring current along its rectangular molecular shape, the moderate diatropic ring current of [28]hexaphyrin **2** has long been puzzling, since it should be antiaromatic in its planar, rectangular conformation. Recently, we have shown that there is a fast dynamic equilibrium among twisted Möbius aromatic conformers and antiaromatic rectangular conformers for **2** in solution at room temperature, and that these two different types of conformers are energetically close but the formers are slightly more stable.[6] Thus, the ^1H NMR spectrum at room temperature represents a snapshot of the averaged such fast conformational dynamics. In accordance with this interpretation, lowering the temperature to 173 K showed **2** predominantly takes a twisted conformation having a diatropic ring current, which has been assigned as a Möbius aromatic species.[6a,7]



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Scheme 1. Interconversions between *meso*-pentafluorophenyl [26]-hexaphyrin **1** and *meso*-pentafluorophenyl [28]hexaphyrin **2**.

The formation of hexaphyrin hybrids is complicated by the fact that *meso*-aryl [26]- and [28]hexaphyrins are only stable when the *meso*-aryl substituents are 2,6-disubstituted. In fact, *meso*-hexaphenyl-substituted [26]hexaphyrin-

[a] Dr. J.-Y. Shin, Q. Miao, Prof. D. Dolphin
Department of Chemistry
University of British Columbia
2036 Main Mall, Vancouver, BC V6T 1Z1 (Canada)
Fax: (+1) 604-822-9678
E-mail: david.dolphin@ubc.ca

[b] T. Tanaka, Prof. A. Osuka
Department of Chemistry
Kyoto University
Oiwake-cho, Kitashirakawa, Sakyo-Ku, Kyoto, 606-852 (Japan)
Fax: (+81) 075-753-3970
E-mail: osuka@kuchem.kyoto-u.ac.jp

[**] BODIPY = boron dipyrromethene.

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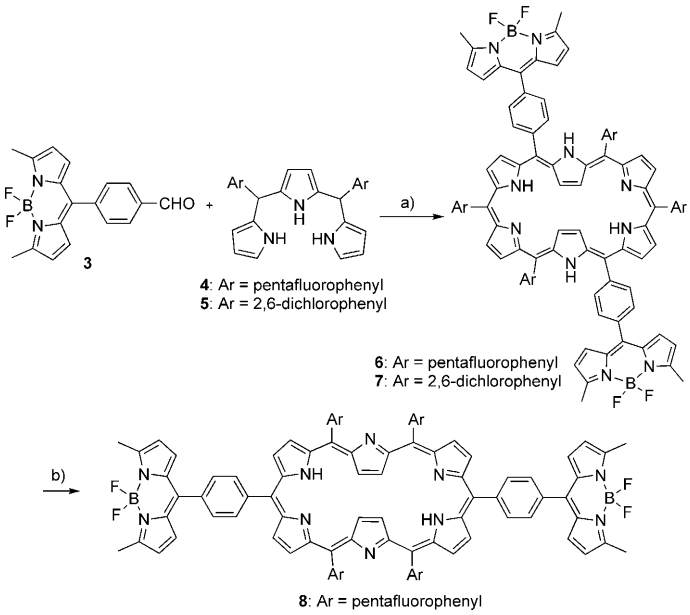
(1.1.1.1.1.1) has been shown to be particularly unstable.[8] We found a rare exception, however, in that 5,20-diphenyl-10,15,25-30-tetrakis(pentafluorophenyl)-substituted [26]hexaphyrin is surprisingly stable, taking a rectangular conformation having two small *meso*-phenyl substituents at the short side.[9]

With these results in hand, a mixture of the formyl-BODIPY compound **3** (Scheme 2) and tripyrrane **4** was treated with $BF_3{\cdot}OEt_2$ at low temperature under anaerobic



Scheme 2. Formation of the Hexaphyrin–BODIPY hybrids **6**–**8**: a) 1. CH_2Cl_2, 2.5 M $BF_3{\cdot}OEt_2$ (CH_2Cl_2), 1.5 h, 0 °C, Ar; 2. DDQ; b) CH_2Cl_2, DDQ.

conditions and the resulting mixture was oxidized with DDQ. After a standard work-up, chromatographic separation on a silica gel column and recrystallization, [28]hexaphyrin **6** was obtained as a dark shiny solid in a 32% yield. Similarly, [28]hexaphyrin **7** was prepared from the reaction of **3** and **5** in a 43% yield. Finally, the further oxidization of **6** with DDQ quantitatively gave [26]hexaphyrin **8**.

High-resolution electrospray ionization time-of-flight (HR ESI-TOF) mass spectroscopy revealed the parent ion peaks of **6** and **8** at *m*/*z* 1717.3539 (calcd for $C_{88}H_{43}B_2F_{24}N_{10}$ $[M-H]^-$: 1717.3505) and *m*/*z* 1715.3372 (calcd for $C_{88}H_{41}B_2F_{24}N_{10}$ $[M-H]^-$: 1715.3348, respectively. The ^{19}F NMR spectra of **6** and **8** show different patterns (Figure 1). The ^{19}F NMR spectrum of **8** displays single sets of signals for the fluorine atoms in the pentafluorophenyl groups and a quartet signal for the fluorine atoms in the BODIPY part, indicating its D_{2h} symmetry. This evidence strongly suggests that **8** takes a rectangular conformation where the two BODIPY units are attached on the short sides. On the other hand, the ^{19}F NMR spectrum of **6** shows two sets of signals in a 1:1 ratio for the fluorine atoms of the pentafluorophenyl groups (Figure 1b). This spectral feature did not change even at

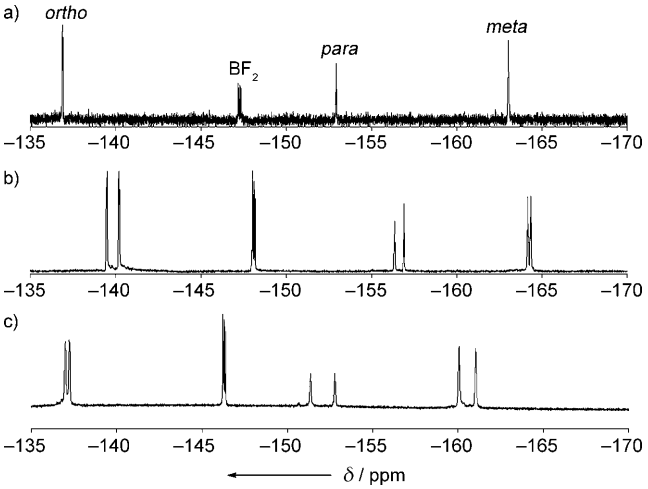


Figure 1. ^{19}F NMR spectral comparison between a) **8** in $CDCl_3$, b) **6** in $[D_8]$THF at 298 K, and c) **6** in $[D_2]$1,1,2,2-tetrachloroethane at 373 K.

373 K at which temperature it is considered that [28]hexaphyrin **6** undergoes rapid conformational interconversion that is faster than ^{19}F NMR time-scale. As a result, the two BODIPY units of **6** are considered to be linked at the longer side of hexaphyrin with an averaged C_{2h} symmetry (Scheme 2).

The ^1H NMR spectra of **6** and **8** are consistent with the above structural assignments. The ^1H NMR spectrum of **8** in $CDCl_3$ exhibits two doublets for the outer pyrrolic β-protons at $\delta = 9.43$ and 9.25 ppm, two doublets for the phenylene protons at $\delta = 8.53$ and 8.08 ppm, two doublets for the BODIPY pyrrolic protons at $\delta = 7.16$ and 6.50 ppm, a singlet for the BODIPY methyl protons at $\delta = 2.79$ ppm and a singlet for the inner pyrrolic β-protons at $\delta = -2.52$ ppm, respectively (Figure 2). These spectral data are fully consistent with the rectangular shape placing two BODIPY groups at the short side. The ^1H NMR spectrum (Figure 3) of [28]hexaphyrin **6** in CD_2Cl_2 presents broad singlets for the outer and inner pyrrolic NH protons at $\delta = 8.36$ and 5.11 ppm, four signals for the outer β-protons at $\delta = 7.74$, 7.72, 7.68, and 7.51 ppm, signals for the phenylene protons at $\delta = 7.58$ ppm, two doublets for the BODIPY pyrrolic protons at $\delta = 6.70$ and 6.32 ppm, and a singlet for the BODIPY methyl protons at $\delta = 2.61$ ppm, respectively. The inner β-protons of hexaphyrin are observed as two highly shielded signals at $\delta = 2.98$ ppm (Figure 3a) and split as two

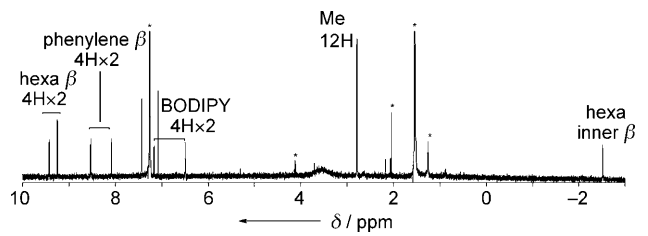


Figure 2. ^1H NMR spectrum of **8** in $CDCl_3$ at 298 K: * indicates solvent or impurity peaks.

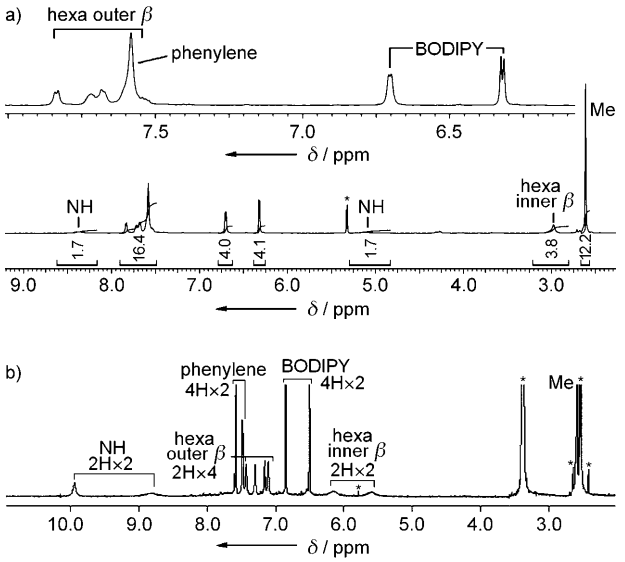


Figure 3. ^{1}H NMR spectra of **6** in a) [D_6]DMSO and b) CD_2Cl_2 at 298 K: * indicates solvent and its side peaks.

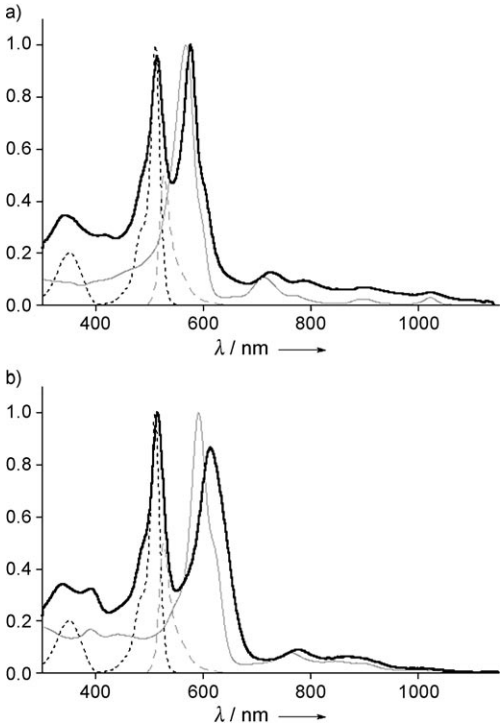


Figure 4. Optical spectra of a) **1** (——) and **8** (——) and b) **2** (——) and **6** (——) with a spectrum of reference BODIPY in CH_2Cl_2 (normalized at absorption maxima); absorption (-----) and emission (– – –).

slightly shielded broad signals in [D_6]DMSO, which support rapid interconversions among the twisted Möbius aromatic and antiaromatic-rectangular conformations. Solvent plays a key in the conformational dynamics. As shown in Figure 3 a, the NH peaks are significantly downfield shifted owing to hydrogen bonding between DMSO and the amino hydrogen′s. As expected, the ^{1}H NMR spectra of **6** in [D_8]THF shows that the conformational interconversions slow down at reduced temperature (Figure S8 in the Supporting Information).

As shown in Figure 4, the optical spectra of [28]hexaphyrin **6** and the [26]hexaphyrin **8** show bands at $\lambda = 515$ and 614 nm and at $\lambda = 514$ and 576 nm, corresponding to the absorption band of BODIPY and the Soret-like band of hexaphyrin, respectively, which are red-shifted from the original bands of BODIPY ($\lambda = 510$ nm), [28]hexaphyrin **2** ($\lambda = 590$ nm), and [26]hexaphyrin **1** ($\lambda = 567$ nm). The observed larger red-shift for the Soret-like band of **6** may not necessarily indicate a larger electronic interaction between the [28]hexaphyrin and BODIPY segments, but rather the non-negligible influence of the attached BODIPY groups upon the conformational dynamics of the [28]hexaphyrin moiety. In line accordance with this conjecture, variable-temperature optical spectra of **6** in the range of 173–298 K showed typical spectral changes for a [28]hexaphyrin (Figure S23 in the Supporting Information). Thus, the Soret-like absorption band of the [28]hexaphyrin segment was sharpened and red-shifted by 14 nm upon lowering the temperature from 298 K to 173 K. Similar temperature-dependent spectral changes were also observed for **7** (Figure S24 in the Supporting Information). On the other hand, the temperature-dependent red shift was only modest for **8**, in line with the conformational rigidity of the [26]hexaphyrin segment.[6b]

The fluorescence spectra of **6** and **8** (Figure 5) were measured at 298 K and 77 K in 2-methyltetrahydrofuran (2-MTHF). Upon photoexcitation at the Soret-like band of the hexaphyrin segment, the fluorescence of **6** was observed to be broad, showing peaks at $\lambda = 1055$ and 1235 nm at 298 K but became sharper, showing peaks $\lambda = 1014$, 1164, and 1198 nm upon lowering the temperature to 77 K. This temperature dependence is analogous to that of **2**, indicating the restricted conformational dynamics that favor the twisted Möbius conformation at low temperature. On the other hand, the fluorescence of **8** is relatively sharp with a peak at $\lambda = 1029$ nm even at 298 K and becomes even sharper with peaks at $\lambda = 1016$, 1165, and 1203 nm at 77 K. Intramolecular singlet excitation energy transfer from the BODIPY segments to the hexaphyrin segment was examined by comparing the fluorescence intensities upon excitation at the peak of the Soret-like band of the hexaphyrin segment versus at the peak of the BODIPY absorption. Figure 5 shows the fluorescence spectra of **6** and **8** taken upon excitation at indicated wavelengths with adjusted absorbance so that the optical densities of the two excitation positions are identical. It is important to note that illumination at $\lambda > 570$ nm only excites the hexaphyrin segment, but that at the peak of the BODIPY absorption excites both the chromophores. By comparing the absorbances of the reference molecules, the ratios of the absorptions were estimated to BODIPY (87%) and [28]hexaphyrin (13%) for **6** at $\lambda = 509$ nm, and BODIPY (76%) and [26]hexaphyrin (24%) for **8** at $\lambda = 512$ nm, respectively (Figure S27 and S28 in the Supporting Information). On the basis of these data, the relative fluorescence intensities for the hexaphyrin unit upon the

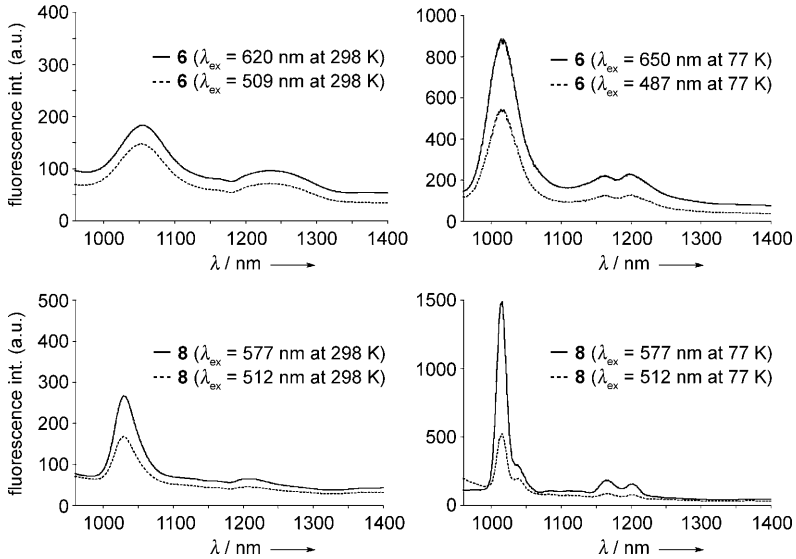


Figure 5. Fluorescence spectra of **6** (top) and **8** (bottom) at room temperature (left) and 77 K (right) in 2-methyltetrahydrofuran measured upon photoexcitation at the Soret region of hexaphyrin (——) and BODIPY (-----).

BODIPY-excitation versus the direct hexaphyrin-excitation have been determined to be about 67% for **6** and 39% for **8** at 298 K, which can be regarded as the extent of the intramolecular energy transfer from the BODIPY to the hexaphyrin part.

In summary, the facile synthesis of BODIPY–hexaphyrin hybrids **6**, **7**, and **8** was achieved from the formyl-substituted BODIPY **3** and tripyrranes **4** and **5** in moderate yields. In the hybrid **8**, the two BODIPY parts are attached at the short side of the rectangular [26]hexaphyrin segment, whereas the [28]hexaphyrin segment in the hybrid **6** exhibits temperature-dependent conformational dynamics similar to the parent [28]hexaphyrin **2**. In the hybrids, efficient singlet excitation-energy transfer occurs from the BODIPY segments to the [28]hexaphyrin or [26]hexaphyrin. It is to be noted that the intramolecular-energy transfer in **6** and **7** is the first example involving a Möbius aromatic molecular part as the energy acceptor. Detailed time-resolved photophysical properties of these compounds and advanced multi-hexaphyrin–BODIPY arrays will be examined in the future.

Experimental Section

BODIPY–hexaphyrin hybrids 6–8: Compound **3** (114.5 mg, 353.3 μmol) was dissolved in CH_2Cl_2 (12 mL) at 0°C under Ar. To this solution, BF_3·OEt in CH_2Cl_2 (70 μL, 2.5 M) was added and the resulting solution was stirred for 5 min. A CH_2Cl_2 (8 mL) solution of **4** (179 mg, 321.3 μmol) was added and the solution was stirred for 2.5 h. DDQ (149 mg) was then added and the resulting solution was stirred for 30 min. The reaction was quenched by the addition of water. The products were extracted with CH_2Cl_2 and separated by silica gel column chromatography using 1% MeOH/CH_2Cl_2 as eluent. A distinct blue fraction was collected to give [28]hexaphyrin **6** in 32% yield. Similarly, **7** was prepared from **5** in 43% yield under the same conditions. [28]Hexaphyrin **6** was oxidized with DDQ (1.5 equiv) at 0°C to give [26]hexaphyrin **8** quantitatively. Purification through a short silica gel column was sufficient to obtain pure **8** with violet color.

Compound 6: ^{1}H NMR (600 MHz, [D$_6$]DMSO, 298 K): $\delta = 9.94$ (bs, outer-NH, 2H), 7.58 (d, $J = 8.0$ Hz, 4H, phenylene), 7.48 (d, 2H, $J = 8.0$ Hz, phenylene), 7.43 (bs, 2H, hexa-βCH), 7.29 (bs, 2H, hexa-βCH), 7.16 (bs, 2H, hexa-βCH), 7.10 (bs, 2H, hexa-βCH), 6.85 (d, $J = 4.2$ Hz, 4H, BODIPY-βCH), 5.10 (d, $J = 4.2$ Hz, 4H, BODIPY-βCH), 6.11 (bs, 2H, inner βCH of hexaphyrin), 5.60 (bs, 2H, inner βCH of hexaphyrin), 2.90 (bs, 4H, inner βCH of hexaphyrin), 2.59 ppm (s, 12H, CH_3); ^{19}F NMR (564.73 MHz, [D$_8$]THF, 298 K): $\delta = -139.53$ (d, $J = 19.0$ Hz, 4F, C_6F_5-*ortho*), −140.24 (d, $J = 19.0$ Hz, 4F, C_6F_5-*ortho*), −148.13 (q, $J = 31.1$ Hz, 4F, BF_2), −156.40 (t, $J = 20.7$ Hz, C_6F_5-*para*), −156.95 (t, $J = 20.7$ Hz, 2F, C_6F_5-*para*), −164.21 (m, 4F, C_6F_5-*meta*), −164.38 ppm (m, 4F, C_6F_5-*meta*); HR-ESI-MS: *m*/*z*: calcd for $C_{88}H_{43}B_2F_{24}N_{10}$:1717.3505 $[M-H]^-$; found: 1717.3539; UV/Vis (MTHF) $\lambda_{max}(\varepsilon) = 513$ (144000), 620 (135000), 772 nm (14000 M^{-1} m^3 cm^{-1}).

Compound 7: ^{1}H NMR (600 MHz, [D$_6$]DMSO, 298 K): $\delta = 9.10$ (bs, 2H, outer NH), 7.78 (d, $J = 8.4$ Hz, 4H, Ar), 7.64 (t, $J = 8.0$ Hz, 2H, Ar), 7.57 (d, $J = 8.4$ Hz, 4H, Ar), 7.50 (d, $J = 7.9$ Hz, 4H, Ar), 7.41 (d, $J = 4.4$ Hz, 2H, hexa-βCH), 7.38 (m, 4H, Ar), 6.91 (d, $J = 4.4$ Hz, 2H, hexa-βCH), 6.84 (d, $J = 4.1$ Hz, 4H, BODIPY-βCH), 6.65 (d, $J = 4.4$ Hz, 2H, hexa-βCH), 6.57 (d, $J = 4.1$ Hz, 4H, BODIPY-βCH), 6.49 (d, $J = 4.4$ Hz, 2H, hexa-βCH), 6.16 (bs, 2H, inner βCH of hexaphyrin), 5.58 (bs, 2H, inner βCH of hexaphyrin), 2.59 ppm (s, 12H, CH_3); HR-ESI-MS: *m*/*z*: calcd for $C_{88}H_{56}B_2Cl_8F_4N_{10}$:1634.2310 $[M]^+$; found: 1634.2352; UV/Vis (MTHF) $\lambda_{max}(\varepsilon) = 341$ (52000), 512 (149000), 618 (84000), 780 (16000), 860 nm (15000 M^{-1} dm^3 cm^{-1}).

Compound 8: ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) $\delta = 9.51$ (d, $J = 4.6$ Hz, 4H, hexa-βCH), 9.25 (d, $J = 4.6$ Hz, 4H, hexa-βCH), 8.53 (d, $J = 8.0$ Hz, 4H, Ar), 8.09 (d, $J = 8.0$ Hz, 4H, Ar), 7.16 (d, $J = 3.9$ Hz, 4H, BODIPY-βCH), 6.50 (d, 4H, $J = 3.9$ Hz, BODIPY-βCH), 2.79 ppm (s, 12H, CH_3); ^{19}F NMR (564.73 MHz; $CDCl_3$) $\delta = -136.93$ (d, $J = 18.1$ Hz, 8F, C_6F_5-*ortho*), −147.31 (q, $J = 31.9$ Hz, 4F, BF_2), −152.97 (t, $J = 20.7$ Hz, 4F, C_6F_5-*para*), −163.07 ppm (t, $J = 18.1$ Hz, 8F, C_6F_5-*meta*); HR-ESI-MS: *m*/*z*: calcd for $C_{88}H_{41}B_2F_{24}N_{10}$:1715.3348 $[M-H]^-$; found: 1715.3372; UV/Vis (MTHF) $\lambda_{max}(\varepsilon) = 512$ (135000), 573 (163000), 721 nm (17000 M^{-1} m^3 cm^{-1}).

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Keywords: aromaticity · BODIPY · expanded porphyrin · electron transfer · hexaphyrin

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