

## Photochemistry

# Photodynamics of [26]- and [28]Hexaphyrin-Bodipy Hybrids

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**Abstract:** A set of hybrids having gradual variation in distances between hexaphyrin and bodipy moieties, given by uses of phenylene, biphenylene, and triphenyelene bridges was prepared. Efficient PET processes from bodipy (donor) to [26]- or [28]hexaphyrin (acceptor) were successfully observed, where the PET speed was controlled by intramolecular distances between the donor and the acceptor. UV irradiation at 515 nm raised a band corresponding to the bodipy absorption. As the time delayed, the bodipy bands decreased and new absorption bands at 615 and 580 nm corresponding to respective absorption bands of [28]- and [26]-

### Introduction

Expanded porphyrins having a larger macrocycle and longer  $\pi$ electron conjugation pathway than regular porphyrins exhibit advanced optical, electrochemical, and coordination properties.<sup>[1]</sup> Consequently, these molecules have been utilized in various applications, such as PDT sensitizers,<sup>[2]</sup> MRI contrast agents,<sup>[3]</sup> multimetallic chelates for catalysis,<sup>[4]</sup> chelating ligands for actinide and lanthanide metals,<sup>[5]</sup> receptors for anions,<sup>[6]</sup> models assembled for energy and electron transfer,<sup>[7]</sup> and sequence-specific DNA (or RNA) photomodifying agents.<sup>[8]</sup>

Since *meso*-pentafluorophenyl substituted hexaphyrin was first introduced by Cavaleiro et al.<sup>[9]</sup> and a facile synthesis for the family of corresponding expanded porphyrins was reported by Osuka and collaborators,<sup>[10]</sup> *meso*-aryl hexaphyr-in(1.1.1.1.1)s have been intensively explored. These molecules have exhibited attractive photophysical properties, such as multiredox behavior,<sup>[11]</sup> conformationally rigid and twisted Möbius aromaticity,<sup>[12]</sup> large TPA (two-photon absorption) value,<sup>[13]</sup> temperature-dependent dynamic interconversion between Hückel antiaromaticity and Möbius aromaticity,<sup>[11,14]</sup> and multiple metal complexations.<sup>[15]</sup>

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hybrids gradually appeared. Whereas the femtosecond transient absorption spectra of [28]/[26]-hybrids having terphenylene bridges completely showed energy transfers from bodipy to hexaphyrin, irradiation of the hybrids using 615 and 580 nm pulses did not induce opposite ways of the PET process. On the basis of enlarged center-to-center-distances of [26]-hybrids than those of [28]-hybrids, the set of [26]-hybrids resulted in slow decay/rise processes. PET parameters obtained with the experiments were fairly consistent with the PET parameters calculated.

meso-Aryl hexaphyrin(1.1.1.1.1)s also exhibit multiredox behaviors with two stable oxidation states: [26]hexaphyrins and [28] hexaphyrins, which are interconvertible. Although [26] hexaphyrins show distinct Hückel aromaticity with structural planarity, [28]hexaphyrins exhibit a structurally dynamic mixture of predominantly Möbius aromatic structure. Since multichromophoric species have been considered as being useful for lightharvesting and storage, hybrid systems in which hexaphyrins are connected with other photodynamically responsible groups have been considered as being useful for new functional materials.<sup>[16]</sup> A potential candidate of the groups is the bodipy dye. Over the past decade, bodipys have shown enormously advantageous properties including thermal/photochemical stabilities,<sup>[17]</sup> high fluorescence quantum yields ( $\Phi=$ 0.6–0.9),<sup>[18]</sup> negligible triplet-state formation,<sup>[19]</sup> intense absorption profiles (FWHM = 25–30 nm,  $\varepsilon$  = 40 000–110 000 cm<sup>-1</sup>),<sup>[20]</sup> good solubilities<sup>[21]</sup> and chemical robustness.<sup>[22]</sup>

Novel hybrids covalently connected between meso-aryl hexaphyrin(1.1.1.1.1) and bodipy were thus designed with an expectation that an intramolecular donor (bodipy) tolerantly harvests light energy and efficiently transfers the harvested energy to an acceptor (hexaphyrin). The lowest electronic state of bodipy is located at slightly higher than the Soret-like absorption bands of both [26]- and [28]hexaphyrins. The emission band of bodipy preferably overlaps with the absorption bands of [26]- and [28]hexaphyrins, in which a photoinduced energy transfer (PET) is likely to occur (Figure 1). As a result, Förstertype processes can efficiently funnel the energy to the interiors of the compounds when bodipy and hexaphyrin components are connected by a suitable linker.<sup>[23]</sup> Herein, we synthesized six novel hexaphyrin-bodipy hybrids with various center-tocenter distances between [26]- and [28]hexaphyrin and bodipy moieties, and then examined their photophysical properties. Efficient photoinduced energy transfer from bodipy to both [26]- and [28]hexaphyrins was successfully observed. Also, [28]hexaphyrin-bodipy hybrids ([28]-hybrids) having shorter center-to-center distances than [26]hexaphyrin-bodipy hybrids ([26]-hybrids) performed faster energy transfer. The details are reported herein.

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Figure 1. Spectral overlap between emission of the reference bodipy (donor) and absorption of [26]- and [28]hexaphyrins (acceptors).

### **Results and Discussion**

#### Synthesis

We synthesized three sets of [28]- and [26]-hybrids, 1 and 4, 2 and 5, and 3 and 6, in which hexaphyrins and bodipys were connected by three different bridging groups, phenylene, biphenylene, and terphenylene, respectively.<sup>[24]</sup> The bodipy precursor of hybrids 1 and 4, meso-(4-formylphenyl)bodipy, was prepared according to the synthetic method previously reported.<sup>[25]</sup> Similarly, meso-(4-formylbiphenyl)bodipy, precursor of hybrids 2 and 5, was prepared using 4'-formyl-4-biphenylcarbonitrile. On the other hand, bodipy precursors containing longer linkers, meso-(4-formylterphenyl)bodipy and meso-(4-formylquaterpenyl)bodipy, were prepared by heterolytic Suzuki-Miyaura coupling among meso-(4-bromophenyl)bodipy, 4-bromobenzaldehyde, and benzene diboronic acid and among meso-(4-bromopheyl)bodipy, 4-bromo-4'-biphenylaldehyde, and benzene diboronic acid, respectively (Scheme 1). All bodipy precursor aldehydes were characterized by <sup>1</sup>H NMR analysis. Increased numbers of proton peaks were found at the aromatic region to match with the number of phenylene bridges (Figure 2). Formyl protons were assigned at 10.14, 10.10, 10.11, and 10.11 ppm, for phenylene, biphenylene, terphenylene, and quarterphenylene bodipys, respectively. Sets of arylene protons were found as two doublets (8.01 and 7.68 ppm) for meso-(4-formylphenyl)bodipy, four doublets (8.01, 7.83, 7.76, and 7.62 ppm) for meso-(4-formylbiphenyl)bodipy, four set of doublets (8.00, 7.84, 7.77, and 7.62 ppm) and one singlet with double integration (7.80 ppm) for meso-(4-formylterphenyl)bodipy, and four set of doublets (8.00, 7.84, 7.77, and 7.62 ppm) and one singlet with triple integration (7.80 ppm) for meso-(4-formylquaterphenyl)bodipy.

The hexaphyrin cores were constructed according to the reported procedure.<sup>[25]</sup> BF<sub>3</sub>·OEt<sub>2</sub>-catalyzed condensation of tripyrrane and formyl-bodipys at low temperature under anaerobic conditions and subsequent oxidation with DDQ (2.0 equiv) successfully provided [28]-hybrids **1–3** (Scheme 2). On the other hand, poor solubility of 4-formylquaterphenyl bodipy prevented the formation of quaterphenylene-bridged hybrids.<sup>[24]</sup> Chro-



**Scheme 1.** Preparation of bodipy precursors, CHO-Ph-bodipy, CHO-diPhbodipy, and CHO-terPh-bodipy. Reagents and condition: a) TFA,  $CH_2Cl_{2^r} 2 h$ , 0 °C, 71%; b) i) 1 M DIBAL  $CH_2Cl_2$ , 6 h; ii)  $NH_4Cl$ , 1.5 h, 71%; c) i) DDQ (1 equiv),  $CH_2Cl_2$ , 9 h; ii)  $Et_3N$ ,  $BF_3$ - $OEt_2$ , 1 h, 35%; d) TFA,  $CH_2Cl_2$ , 2 h, 0 °C, 71%; e) i) DDQ (1 equiv),  $CH_2Cl_2$ , 9 h; ii)  $Et_3N$ ,  $BF_3$ - $OEt_2$ , 1 h, 45%; f)  $Pd(PPh_3)_4$ , 2 M  $K_2CO_3$ , toluene, MeOH, 80 °C, 9 h, 36–46%.



**Figure 2.** <sup>1</sup>H NMR spectra of precursor bodipys containing: a) phenylene, b) biphenylene, c) terphenylene, and d) quaterphenylene bridges in CDCl<sub>3</sub>; solvent impurities are highlighted with \*.

matographic separations over silica gel column and recrystallizations from CH<sub>2</sub>Cl<sub>2</sub>/hexane gave dark, lustrous powders of the hybrids. <sup>1</sup>H NMR spectra of the [28]-hybrids **1–3** are shown in Figure 3. Outer- $\beta$ -protons of hexaphyrin moieties in [28]-hybrids **2** and **3** were found at the aromatic region (7.5–7.9 ppm) overlapping with the proton peaks of arylene bridges (total number of protons for **2** is 24: 16 for two biphenylene-protons and eight for outer- $\beta$ -protons of hexaphyrin; total number of protons for **3** is 32: 24 for two terphenylene-protons and eight for outer- $\beta$ -protons of hexaphyrin).  $\beta$ -Protons of bodipy moiet-

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Scheme 2. Preparation of [28]-hybrids 1–3 and [28]-hybrids 4–6. Reagents and condition: a) i)  $BF_3$ ·OEt<sub>2</sub>, 2.5 M CH<sub>2</sub>Cl<sub>2</sub>; ii) DDQ, CH<sub>2</sub>Cl<sub>2</sub>, 30–46 %; b) DDQ, CH<sub>2</sub>Cl<sub>2</sub>, 60–73 %.



Figure 3. <sup>1</sup>H NMR spectra of [28]hexaphyrin-bodipy hybrids: a) 1, b) 2, and c) 3 in  $CDCI_3$ ; solvent impurities are highlighted with \*.

ies and inner- $\beta$ -protons of hexaphyrin were found as two doublets at 6.78 and 6.30 ppm and a broad singlet at 3.08 ppm for **2**. Similarly, those protons of **3** were assigned at 6.81 and 6.30 ppm as two doublets and at 3.09 ppm as a broad singlet, respectively.

Further oxidation of **1–3** with DDQ followed by column purification using toluene gave [26]-hybrids **4–6**. All compounds were characterized by <sup>1</sup>H NMR analysis (Figure 4). The <sup>1</sup>H NMR spectrum of [26]-hybrids **4** in CDCl<sub>3</sub> presents two doublets at 9.43 and 9.25 ppm (for outer- $\beta$ -protons in the hexaphyrin moiety), two doublets at 8.53 and 8.08 ppm (for phenylene-protons), two doublets at 7.16 and 6.50 ppm (for pyrrolic- $\beta$ -protons of the bodipy moiety), a singlet at 2.79 ppm (for methyl protons of the bodipy moiety), and a singlet at –2.52 ppm (for inner- $\beta$ -protons of hexaphyrin). Increased



Figure 4. <sup>1</sup>H NMR spectra of [26]-hybrids: a) 4, b) 5, and c) 6 in  $CDCI_3$ ; solvent impurities are highlighted with \*.

number of proton peaks at 9.0–7.5 ppm were assigned as the peaks of the phenylene bridges in **5** and **6**. These spectral features of [28]-hybrids **1–3** and [26]-hybrids **4–6** clearly elucidated the aromatic nature of the [28]- and [26]hexaphyrin cores in these hybrids, which indicate that [28]-hybrids **1–3** take Möbius aromatic conformation whereas [26]-hybrids **4–6** have Hückel aromatic structure as demonstrated in the literatures.<sup>[14,25]</sup>

#### **DFT calculations**

Hückel rule predicting aromaticity for [4n+2] annulens and antiaromaticity for [4n]annulenes has been the basis of understanding the aromatic character. Simultaneously, Möbius aromaticity has been demonstrated for [4n]annulenes with twisted aromatic strips. Moderate diatropic ring current of [28]hexaphyrins was explained on the basis of the twisted Möbius conformation.[11] However, both single crystal data of [26]- and [28]hexaphyrins revealed planar rectangular structures. Optimized structures of [26]- and [28]hexaphyrins used for the measurement of center-to-center distances between hexaphyrin and bodipy moieties are based on the solid structures. Structures of rectangular 5,20-diaryl-10,15,25,30-tetrakis(pentafluorophenyl)-substituted [26]hexaphyrins have been demonstrated to place two meso-phenyl substituents at their short sides.<sup>[14]</sup> On the other hand, 5,20-diaryl-10,15,25,30-tetrakis(pentafluorophenyl)-substituted [28]hexaphyrin has been demonstrated to predominantly take the longer side of the rectangular hexaphyrin for the position of two bodipys.<sup>[14,25]</sup> Structures of [26]- and [28]-hybrids were geometrically optimized on the basis of the information (Figure 5). Geometry optimizations and time-dependent DFT (TD-DFT) calculations were performed with the Lee-Yang-Parr correlation functional (B3LYP) and 6-31G(d). Center-to-center distances on the geometrically optimized structures of [28]-hybrids are 12.12, 16.26, and 20.52 Å whereas the center-to-center distances on the optimized structures of [26]-hybrids are 14.23, 18.50, and 22.79 Å.  $^{\rm [26]}$  TD-DFT of each hybrid was performed on the basis of the optimized structures to simulate the absorption spectra for ground states of the hybrids (Figure 6).

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Figure 5. Geometrically optimized structures of [28]-hybrid 3 and [26]-hybrid 6 showing different center-to-center distance between hexaphyrin and bodipy moieties.

#### **Optical properties**

Figure 6 shows absorption spectra of [28]-hybrids **1–3** and [26]-hybrids **4–6** in toluene. Compared with absorption bands of nonhybridized [26]- and [28]hexaphyrins, the corresponding bands of [26]- and [28]-hybrids in toluene are slightly red-shifted. This is probably due to the attached bodipy moieties, which induce small electronic structural changes. Overall, the spectra are fairly consistent with the excitation energy calculated using TD-DFT operation to simulate the absorption spectra for ground states of the hybrids. In addition, no spectral red-shift relating to the number of phenylene bridges was observed and the hybrid dyes showed almost identical absorption spectra. Based on these results, we can conclude that the hexaphyrins and bodipy moieties are electronically separated.<sup>[26]</sup> Considering the spectral overlap between fluorescence

emission of bodipy and B-like absorption band of hexaphyrins, the efficient photoinduced energy transfer from bodipy to hexaphyrin moieties was expected. In principle, Förster theory argues that the transfer rate should be inversely proportional to the distance between donor and acceptor. In the energy transfer processes of bodipy (donor)–hexaphyrin (acceptor) hybrid's system, the length of phenylene bridges is a crucial factor. To elucidate the relationship between the length of phenylene bridge and energy transfer process, we utilized femtosecond (fs) transient absorption measurements. The time evolutions of transient species of the hybrids reveal energy transfer from bodipy to hexaphyrin moieties.

#### **PET measurements**

The fs-transient absorption spectra of [28]-hybrid 3 and [26]hybrid 6 are shown in Figure 7 and Figure 8, respectively. The band that initially appeared at 515 nm by UV irradiation, which consists of bodipy absorption, gradually decreased and new absorption bands at 615 and 580 nm corresponding to respective absorption bands of [28]- and [26]-hybrids steadily appeared as the delay time increased. As a comparison, [28]- and [26]hexaphyrin moieties were also irradiated by 615 and 580 nm pulses, respectively. However, the opposite process of the relaxation dynamics was not observed and only transient decay dynamics of individual [28]- and [26]hexaphyrins were elucidated. This result strongly indicates the efficient PET process from bodipy to hexaphyrin moieties. The PET rates were depended on the length of bridges between donor and acceptor. Steady-state absorption spectra of donor (starting point of PET, spectrum with red lines) and acceptor (ending point of PET, spectrum with blue lines), given in the PET processes with corresponding hybrids and the delay and rise times obtained by global analysis, are shown in Figure 9. The PET results are summarized in Table 1. Förster-type PET rates of



Figure 6. Absorption spectra of: a) [28]hexaphyrin-bodipy hybrids 1–3, and b) [26]hexaphyrin-bodipy hybrids 4–6 measured in toluene (each top spectrum) and vertical excitation energy data calculated using TD-DFT. The absorption spectra are normalized to the peak at around 515 nm originated from the bodipy moieties.

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**Figure 7.** fs-Transient absorption spectra of [28]-hybrid **3** in toluene: selective excitations at bodipy ( $\lambda_{pump} = 515 \text{ nm}$  for a) and hexaphyrin ( $\lambda_{pump} = 615 \text{ nm}$  for b). The time profile of bodipy and hexaphyrin moieties in initial time domain of -5-45 ps is presented in the spectra a.



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**Figure 8.** fs-Transient absorption spectra of [26]-hybrid **6** in toluene: selective excitations at bodipy ( $\lambda_{pump} = 515 \text{ nm}$  for a) and hexaphyrin ( $\lambda_{pump} = 580 \text{ nm}$  for b). The time profile of bodipy and hexaphyrin moieties in initial time domain of -5-45 ps is presented in the spectra a.

Table 1. Summary of the Förster-type energy transfer efficiencies of hybrids 1–6 measured and calculated.					
Hybrids <sup>[a]</sup>	Linkage	Center-to-center distance [Å] <sup>[b]</sup> (overlap integral J [cm <sup>6</sup> ] <sup>[c]</sup> )	Transfer rate [s <sup>-1</sup> ] measured (calcd)	D–A decay and rise [ps] measured (calcd)	
1	phenylene	12.12 (5.27×10 <sup>-13</sup> )	$2.50 \times 10^{12} (2.45 \times 10^{12})$	0.6 (0.41)	
4		14.23 (9.22×10 <sup>-13</sup> )	0.83×10 <sup>12</sup> (1.64×10 <sup>12</sup> )	1.2 (0.61)	
2	biphenylene	16.26 (5.27×10 <sup>-13</sup> )	6.67×10 <sup>11</sup> (4.19×10 <sup>11</sup> )	1.5 (2.4)	
5		18.50 (9.22×10 <sup>-13</sup> )	2.63×10 <sup>11</sup> (3.39×10 <sup>11</sup> )	3.8 (2.9)	
3	terphenylene	20.52 (5.27×10 <sup>-13</sup> )	$1.82 \times 10^{11} (1.04 \times 10^{11})$	5.5 (9.6)	
6		22.79 (9.22×10 <sup>-13</sup> )	1.61×10 <sup>11</sup> (9.69×10 <sup>10</sup> )	6.2 (10.3)	
[a] Hybrids 1, 2, and 3 are [28]hexphyrin–bodipy hybrids and 4, 5, and 6 are [26]hexaphyrin–bodipy hybrids. [b] Intermolecular distances were measured on the geometrically optimized structures (DFT calculation: B31YP/ 6-31G(d). [b], [c] Values were estimated with Photocheme CAD software. D–A: donor-acceptor.					

## Conclusion

We have succeeded in the preparation of [28]- and [26]hexphyrin-bodipy hybrids **1–6** from the formyl-substituted bodipys and tripyrrane precursors. We have resolved the decay/rise dynamics of the transient species corresponding to the bodipy and hexaphyrin, respectively. Efficient PET processes from bodipy to [26]- and [28]hexaphyrins were well observed in the [28]- and

the hybrids were calculated with the center-to-center distances on Photochem CAD software (Table 1). In each set of the [28]and [26]-hybrids, hybrids **3** and **6** containing terphenylene bridges gave the slowest conversion (5.5 ps from bodipy to hexaphyrin) absorptions due to the influence of the longest center-to-center distance. Similarly, [28]-hybrids afforded faster energy transfer than [26]-hybrids. The calculated PETs are fairly consistent with the measured PETs in which the speed of Förster-type PET in the hybrids decreases as the intermolecular center-to-center distance increases. [26]-hybrids in which the PET speed was controlled by the intermolecular distances between bodipy and hexaphyrin (center-to-center distances). Interestingly, [28]-hybrids exhibited faster energy transfer than [26]-hybrids, which was attributed to decreased center-to-center distances in their distinct structural orientations. This result indicates the potential use of this class of compounds in applications such as energy harvester antennae, and energy storage.

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Figure 9. PET processes of: a) [28]-hybrids 1-3, and b) [26]-hybrids 4-6 obtained by global analysis.

#### **Experimental Section**

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#### General

All reagents were either prepared following literature synthetic methods or purchased from commercially available suppliers and used without further purification. Column chromatography was performed on silica gel (Silica 60, 0.040-0.064 mm) and biobeads (S-X3 Beads, 200-400 mesh). Optical spectra in UV/Vis or near-IR region were recorded with a HP 8453 spectrophotometer using a 1 cm path-length cuvette. All NMR spectra were obtained on Bruker Avance 500 MHz NMR spectrometer in CDCl<sub>3</sub> using tetramethylsilane (TMS) as an external standard (chemical shifts for CDCl<sub>3</sub>: <sup>1</sup>H at 7.27 ppm and <sup>13</sup>C at 77.0 ppm). Mass spectra were performed on time-of-flight (TOF) spectrometers equipped with MALDI or ESI ion sources. Transient absorption spectra were measured on the femtosecond time-resolved transient absorption spectrometer collaborating with a homemade noncollinear optical parameter amplifier (NOPA) pumped by a Ti-sapphire regenerative amplifier system. Gaussian 03 was used for all calculations. Optimized molecular structures of the hybrids and their molecular orbitals were obtained by DFT (density functional theory) calculation using B3LYP Hamiltonian and 6-31G(d) basis set.

#### Synthesis

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 $\label{eq:cho-ph-bodipy} \textbf{CHO-Ph-bodipy} \text{ was prepared by the synthetic method which we previously reported.} \end{tabular}$ 

**CHO-biPh-bodipy**: To a  $CH_2CI_2$  (50 mL) solution of CN-biPh-DPM (440 mg, 1.25 mmol), 2.6 mL of 1 m DIBAL-H in hexane was added

dropwise. The reaction mixture was stirred for 6 h and then NH<sub>4</sub>Cl aqueous solution was added. After being stirred for 1.5 h, the organic layer was washed with NaOH aqueous solution and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was chromatographed on silica gel using neat CH<sub>2</sub>Cl<sub>2</sub>. Pure CHO-biPh-DPM was obtained as a light yellow powder (250 mg, 71%). DDQ (130 mg, 0.57 mmol) was added to a CH<sub>2</sub>Cl<sub>2</sub> (50 mL) solution of CHO-biPh-DPM (200 mg, 0.57 mmol) and the resulting solution was stirred for 9 h. Et<sub>3</sub>N (0.5 mL) followed by BF<sub>3</sub>·OEt<sub>2</sub> (0.5 m) were added to the solution. After being stirred for 1 h, the solution was poured on silica gel and the first red-fraction was separated by using neat CH<sub>2</sub>Cl<sub>2</sub>. A red powder of CHO-biPh-bodipy was obtained in 35% yield.

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CHO-terPh-bodipy: To a CH<sub>2</sub>Cl<sub>2</sub> (60 mL) solution of 4-bromobenzaldehyde (1.08 mg, 5.87 mmol) and 2-methylpyrrole (952 mg, 11.75 mmol), TFA (100  $\mu$ L) was added under anaerobic condition. The reaction mixture was stirred for 2 h and then quenched with NaOH aqueous solution. The resulting solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent by rotary evaporation, the crude product was purified by column chromatography on silica gel using neat CH<sub>2</sub>Cl<sub>2</sub> and by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane. A pale color powder of 4-bromophenyl substituted dipyrromethane (Br-Ph-DPM) was obtained in 83%. DDQ (1.0 g, 0.57 mmol) was added to a  $\text{CH}_2\text{Cl}_2$ solution of Br-Ph-DPM (1.6 g, 4.88 mmol) and the reaction mixture was stirred for 9 h. Et<sub>3</sub>N (2.5 mL) followed by BF<sub>3</sub>·OEt<sub>2</sub> (2.5 mL) were added to the solution. After being stirred for 1 h, the solution was poured on silica gel and the first red-fraction was separated by using neat CH<sub>2</sub>Cl<sub>2</sub>. A red powder of pure 4-bromophenyl

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bodipy (Br-Ph-bodipy) was obtained in 45% yield (830 mg) after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane. CHO-terPh-bodipy was prepared by heterolytic Suzuki–Miyaura coupling. A mixture of Br-Phbodipy (375 mg, 1 mmol), benzene boronic acid (116 mg, 1 mmol), and bromobenzaldehyde (185 mg, 1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (30 mg, 25.7 µmol), 2N Na<sub>2</sub>CO<sub>3</sub> aqueous solution (1 mL) with MeOH (15 mL), and toluene (50 mL) was refluxed for 9 h under Ar. After being washed with water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed by rotary evaporation, and the residue was purified by column chromatography on silica gel using neat CH<sub>2</sub>Cl<sub>2</sub> followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane. A red power of pure CHO-terPh-bodipy was obtained in 46% yield.

**[28]-Hybrids 1–3 and [26]-hybrids 4–6**: [28]- and [26]Hexaphyrinbodipy hybrids **1–6** were respectively prepared by acid-catalyzed condensation of 5,10-di(pentafluorophenyl)tripyrrane and corresponding bodipys, CHO-Ph-bodipy, CHO-biPh-bodipy, and CHOterPh-bodipy followed by DDQ oxidation as reported.<sup>[25]</sup> [28]-Hybrids **1–3** were successfully produced when 2.0 equiv of DDQ was used and purified by column chromatography on silica gel using neat CH<sub>2</sub>Cl<sub>2</sub> (~30% yield for **3**). Further oxidation of [28]-hybrids using 2.0 equiv of DDQ gave [26]-hybrids **4–6**. Each [26]-hybrid was purified by column chromatography on silica gel using neat toluene (~60% yield for **3**). Compared with [28]-hybrids, [26]-hybrids showed lower stability and was slowly decomposed. Consequently, PET rates of [28]- and [26]-hybrids were measured using fresh hybrids that were purified again by preparative thin layer chromatography (prep-TLC) right before the measurement.

#### Spectral data

[28]-Hybrid 2: Four shielded peaks for outer-β-protons of hexaphyrin were assigned by its HH COSY NMR data. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.81 (brs, 2 H; outer-βH), 7.73 (d, <sup>3</sup>*J*(H, H) = 7.5 Hz, 8 H; Ph-H), 7.62 (shielded, 2 H; outer-βH), 7.61 (d, <sup>3</sup>*J*(H, H) = 8.5 Hz, 8 H; Ph-H), 7.61 (shielded, 2 H; outer-βH), 7.53 (brs, 2 H; outer-βH), 6.78 (d, <sup>3</sup>*J*(H, H) = 3.5 Hz, 4 H; bodipy-βH), 6.30 (d, <sup>3</sup>*J*(H, H) = 4.0 Hz, 4 H, bodipy-βH), 3.08 (brs, 4 H; inner-βH), 2.68 ppm (s, 12 H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 157.8, 149.6, 141.9, 141.59, 140.4, 138.1, 136.8, 136.0, 134.5, 133.9, 133.7, 132.0, 131.1, 130.3, 130.1, 127.2, 126.8, 120.7, 119.5, 117.9, 14.9 ppm; MALDI-TOF (*m/z*) found 1871.36, calcd 1873.44 for C<sub>100</sub>H<sub>52</sub>B<sub>2</sub>F<sub>24</sub>N<sub>10</sub>.

[28]-Hybrid 3: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =7.82 (brs, 2H; outerβH), 7.77 (brs, 12H; Ph-H), 7.70–7.50 (shielded, 3brs, 8H; outerβH), 7.61 (d, <sup>3</sup>*J*(H, H)=8.1 Hz, 12H; Ph-H), 6.81 (d, <sup>3</sup>*J*(H, H)=3.5 Hz, 4H; bodipy-βH), 6.30 (d, <sup>3</sup>*J*(H, H)=3.7 Hz, 4H; bodipy-βH), 3.09 (brs, 4H; inner-βH), 2.68 ppm (s, 12H; CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ =157.6, 142.1, 139.5, 136.9, 134.5, 131.0, 130.3, 127.6, 126.7, 119.4, 14.9 ppm; MALDI-TOF (*m/z*) found 1869.10, calcd 1869.41 for C<sub>100</sub>H<sub>50</sub>B<sub>2</sub>F<sub>24</sub>N<sub>10</sub>.

**[26]-Hybrid 5**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.50–9.20 (4brs, 4H; outer-βH), 8.96 (brs, 4H; outer-βH), 8.89 (brs, 4H; Ph-H), 8.29 (d, <sup>3</sup>J(H, H) = 8.2 Hz, 4H; Ph-H), 8.10 (d, <sup>3</sup>J(H, H) = 8.2 Hz, 4H; Ph-H), 7.82 (d, <sup>3</sup>J(H, H) = 8.2 Hz, 4H; Ph-H), 6.97 (d, <sup>3</sup>J(H, H) = 3.5 Hz, 4H; bodipy-βH), 6.40 (d, <sup>3</sup>J(H, H) = 3.7 Hz, 4H; bodipy-βH), 2.74 (s, 12H; CH<sub>3</sub>), -1.46 (brs, 2H; NH), -2.56 ppm (s, 4H; inner-βH); MALDI-TOF (*m/z*) found 2023.35, calcd 2023.48 for C<sub>112</sub>H<sub>60</sub>B<sub>2</sub>F<sub>24</sub>N<sub>10</sub>.

[26]-Hybrid 6: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ =9.50-9.20 (4brs, 4H; outer-βH), 8.94 (brs, 4H; outer-βH), 8.90 (brs, 4H; Ph-H), 8.29 (d, <sup>3</sup>J(H, H)=8.2 Hz, 4H; Ph-H), 8.13 (d, <sup>3</sup>J(H, H)=8.2 Hz, 4H; Ph-H), 7.99 (d, <sup>3</sup>J(H, H)=8.2 Hz, 4H; Ph-H), 7.91 (d, <sup>3</sup>J(H, H)=8.2 Hz, 4H; Ph-H), 7.70 (d, <sup>3</sup>J(H, H)=8.2 Hz, 4H; Ph-H), 6,88 (d, <sup>3</sup>J(H, H)=3.5 Hz, 4H; bodipy-βH), 6.35 (d, <sup>3</sup>J(H, H)=3.7 Hz, 4H; bodipy-βH), 2.71 (s,

12H; CH<sub>3</sub>), -1.46 (brs, 2H; NH), -2.56 ppm (s, 4H; inner- $\beta$ H); MALDI-TOF (*m/z*) found 2019.10, calcd 2021.47 for C<sub>112</sub>H<sub>58</sub>B<sub>2</sub>F<sub>24</sub>N<sub>10</sub>.

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**Keywords:** bodipy • hexaphyrin • photochemistry • photoinduced energy transfer • porphyrinoid

- [1] a) D. Dougherty, Acc. Chem. Res. 1991, 24, 88-94; b) H. Iwamura, N. Koga, Acc. Chem. Res. 1993, 26, 346-351; c) W. T. Borden, H. Iwamura, J. A. Berson, Acc. Chem. Res. 1994, 27, 109-116; d) J. L. Sessler, S. J. Weghorm, Expanded, Contracted and Isomeric Porphyrins, Elsevier, New York, 1997; e) A. Jasat, D. Dolphin, Chem. Rev. 1997, 97, 2267-2340; f) T. Kubo, M. Sakamoto, M. Akabane, Y. Fujiwara, K. Yamamoto, M. Akita, K. Inoue, T. Takui, K. Nakasuji, Angew. Chem. 2004, 116, 6636-6641; Angew. Chem. Int. Ed. 2004, 43, 6474-6479; g) S. Hiroto, K. Furukawa, H. Shinokubo, A. Osuka, J. Am. Chem. Soc. 2006, 128, 12380-12381; h) H. L. Anderson, S. J. Martin, D. D. C. Bradleu, Angew. Chem. 1994, 106, 711-713; Angew. Chem. Int. Ed. Engl. 1994, 33, 655-657; i) T. E. O. Screen, J. R. G. Throne, R. G. Denning, D. G. Bucknall, H. L. Anderson, J. Am. Chem. Soc. 2002, 124, 9712-9713; j) S. M. LeCours, H.-W. Guan, S. G. DiMagno, C. H. Wang, M. J. Therien, J. Am. Chem. Soc. 1996, 118, 1497-1503; k) K. Ogawa, A. Ohashi, Y. Kobuke, K. Kamada, K. Ohta, J. Am. Chem. Soc. 2003, 125, 13356-13357; I) M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor, H. L. Anderson, J. Am. Chem. Soc. 2004, 126, 15352-15353; m) M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Tavlor, H. L. Anderson, J. Phys. Chem. B 2005, 109, 7223-7236; n) M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikel, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu, C. Xu, Science 1998, 281, 1653-1656.
- [2] a) B. G. Maiya, M. Cyr, A. Harriman, J. L. Sessler, J. Phys. Chem. 1990, 94, 3597–3601; b) J. L. Sessler, G. Hemmi, T. D. Lash, T. Murai, A. K. Burrell, S. W. Young, Acc. Chem. Res. 1994, 27, 43–50; c) B. Franck, A. Nonn, Angew. Chem. 1995, 107, 1941–1957; Angew. Chem. Int. Ed. Engl. 1995, 34, 1795–1811.
- [3] a) J. L. Sessler, A. Gebauer, A. Guba, M. Scherer, V. Lynch, *Inorg. Chem.* 1998, *37*, 2073–2076; b) S. J. Weghorn, J. L. Sessler, V. Lynch, T. F. Baumann, J. W. Sibert, *Inorg. Chem.* 1996, *35*, 1089–1090.
- [4] a) A. K. Burrell, G. Hemmi, V. Lynch, J. L. Sessler, J. Am. Chem. Soc. 1991, 113, 4690-4692; b) J. L. Sessler, T. D. Mody, G. W. Hemmi, V. Lynch, Inorg. Chem. 1993, 32, 3175-3187.
- [5] a) M. Shionoya, H. Furuta, V. Lynch, A. Harriman, J. L. Sessler, J. Am. Chem. Soc. 1992, 114, 5714–5722; b) A. Andrievsky, F. Ahuis, J. L. Sessler, F. Vögtle, D. Gudat, M. Moini, J. Am. Chem. Soc. 1998, 120, 9712–9713; c) B. Sridevi, S. J. Narayanan, R. Rao, T. K. Chandrashekar, Inorg. Chem. 2000, 39, 3669–3677; d) G. L. Iverson, K. Shreder, V. Král, P. Sansom, V. Lynch, J. L. Sessler, J. Am. Chem. Soc. 1996, 118, 1608–1616; e) J. L. Sessler, V. Král, J. W. Genge, R. E. Tomas, B. L. Iverson, Anal. Chem. 1998, 70, 2516–2522.
- [6] S. L. Springs, D. Gosztola, M. R. Wasielewski, V. Král, A. Andrievsky, J. L. Sessler, J. Am. Chem. Soc. 1999, 121, 2281–2289.
- [7] a) J. L. Sessler, P. I. Sansom, V. Král, D. O'Connor, B. L. Iverson, J. Am. Chem. Soc. 1996, 118, 12322-12330; b) D. Magda, S. Crofts, A. Lin, D. Miles, M. Wright, J. L. Sessler, J. Am. Chem. Soc. 1997, 119, 2293-2294; c) D. Magda, M. Wright, S. Crofts, A. Lin, J. L. Sessler, J. Am. Chem. Soc. 1997, 119, 6947-6948.
- [8] a) J. L. Sessler, N. A. Tvermes, D. M. Guldi, T. D. Mody, W. E. Allen, J. Phys. Chem. A 1999, 103, 787–794; b) D. M. Guldi, T. D. Mody, N. N. Gerasim-chuk, D. Magda, J. L. Sessler, J. Am. Chem. Soc. 2000, 122, 8289–8298; c) J.-P. Gisselbrecht, M. Gross, E. Vogel, J. L. Sessler, Inorg. Chem. 2000, 39, 2850–2854; d) J. L. Sessler, N. A. Termoes, D. M. Guldi, G. L. Hug, T. D. Mody, D. Magda, J. Phys. Chem. B 2001, 105, 1452–1457; e) S. J.

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Narayanan, B. Sridevi, T. K. Chandrasheker, A. Vij, R. Roy, *J. Am. Chem. Soc.* **1999**, *121*, 9053–9068; f) J. L. Sessler, A. Andrievsky, V. král, V. Lynch, *J. Am. Chem. Soc.* **1997**, *119*, 9385–9392.

- [9] M. G. P. M. S. Neves, R. M. Martins, A. C. Tomé, A. J. D. Silvestre, A. M. S. Silva, V. Félix, M. G. B. Drew, A. Cavaleiro, *Chem. Commun.* **1999**, 385–386.
- [10] a) J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, J. Am. Chem. Soc. 2001, 123, 7190–7191; b) S. Shimizu, J.-Y. Shin, H. Furuta, R. Ismael, A. Osuka, Angew. Chem. 2003, 115, 82–86; Angew. Chem. Int. Ed. 2003, 42, 78–82; c) Y. Tanaka, J.-Y. Shin, A. Osuka, Eur. J. Org. Chem. 2008, 1341– 1349.
- [11] J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, J. Am. Chem. Soc. 2008, 130, 13568–13579.
- [12] a) J. M. Lim, M. Inoue, Y. M. Sung, M. Suzuki, T. Higashino, A. Osuka, D. Kim, *Chem. Commun.* **2011**, *47*, 3960–3962; b) T. Higashino, J. M. Lim, T. Miura, S. Saito, J.-Y. Shin, D. Kim, A. Ouska, *Angew. Chem.* **2010**, *122*, 5070–5074; *Angew. Chem. Int. Ed.* **2010**, *49*, 4950–4954.
- [13] T. K. Ahn, J. H. Kwon, D. Y. Kim, D. W. Cho, D. H. Jeong, S. K. Kim, M. Suzuki, S. Shimizu, A. Osuka, D. Kim, J. Am. Chem. Soc. 2005, 127, 12856–12861.
- [14] M. C. Yoon, S. Cho, M. Suzuki, A. Osuka, D. Kim, J. Am. Chem. Soc. 2009, 131, 7360-7367; b) M. Suzuki, A. Osuka, Chem. Commun. 2005, 3685-3687.
- [15] a) S. Shimizu, V. G. Anand, R. Taniguchi, K. Furukawa, T. Kato, T. Yokoyama, A. Osuka, J. Am. Chem. Soc. 2004, 126, 12280-12281; b) M. Suzuki, M.-C. Yoon, D. Y. Kim, J. H. Kwon, H. Furuta, D. Kim, A. Osuka, Chem. Eur. J. 2006, 12, 1754-1759; c) S. Mori, S. Shimizu, R. Taniguchi, A. Osuka, Inorg. Chem. 2005, 44, 4127-4129; d) S. Mori, A. Osuka, Inorg. Chem. 2008, 47, 3937-3939; e) S. Mori, A. Osuka, J. Am. Chem. Soc. 2005, 127, 8030-8031; f) S. Mori, K. S. Kim, Z. S. Yoon, S. B. Noh, D. Kim, A. Osuka, J. Am. Chem. Soc. 2007, 129, 11344-11345; g) Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, A. Osuka, Angew. Chem. 2008, 120, 693-696; Angew. Chem. Int. Ed. 2008, 47, 681-684.
- [16] N. Banerji, G. Duvanel, A. Perez-Velasco, S. Maity, N. Sakai, S. Matile, E. Vauthey, J. Phys. Chem. A 2009, 113, 8202-8212.

- [17] S. Luo, E. Zhang, Y. Su, T. Cheng, C. Shi, *Biomaterials* **2011**, *32*, 7127–7138.
- [18] a) D. K. Prusty, A. Herrmann, J. Am. Chem. Soc. 2010, 132, 12197 12199;
  b) J. Karolin, L. B.-A. Jonansson, L. Strandberg, T. Ny, J. Am. Chem. Soc. 1994, 116, 7801 7806.
- [19] J. H. Ryu, Y. K. Eom, J.-C. Bünzli, H. K. Kim, New J. Chem. 2012, 36, 723– 731.
- [20] a) B. Kim, B. Ma, V. R. Donuru, H. Liu, J. M. J. Fréchet, *Chem. Commun.* 2010, 46, 4148–4150; b) W. Qin, V. Leen, W. Dehaen, J. Dui, C. Xu, X. Tang, W. Liu, T. Rohand, D. Beljonn, B. Van Averbeke, J. N. Clifford, K. Driesen, K. Binnemans, M. Van der Auweraer, N. Boens, *J. Phys. Chem. C* 2009, 113, 11731–11740.
- [21] W. Qin, V. Leen, T. Rohand, W. Dehaen, P. Dedecker, M. Van der Auweraer, K. Robeyns, L. Van Meervelt, D. Beljonne, B. Van Averbeke, J. N. Clifford, K. Driesen, K. Binnemans, N. Boens, J. Phys. Chem. A 2009, 113, 439–447.
- [22] a) A. Loudet, K. Burgess, *Chem. Rev.* 2007, 107, 4891–4932; b) G. Ulrich,
  R. Ziessel, A. Harriman, *Angew. Chem.* 2008, 120, 1202–1219; *Angew. Chem. Int. Ed.* 2008, 47, 1184–1201.
- [23] a) A. Harriman, R. Siessel, in *Carbon-Rich Compounds* (Eds.: M. M. Halery, R. R. Tykwinski), Wiley-VCH, Weinheim, **2006**, p. 26; b) A. Roda, M. Guardigli, E. Michelini, M. Mirasoli, *Anal. Biochem.* **2009**, *393*, 109–123.
- [24] One phenylene longer (n=4) bodipy-carboxaldehyde was also prepared to create a hybrid producing a longer center-to-center distance between hexaphyrin and bodipy. However, its poor solubility prevents the formation of target hydrides and we stopped increasing the length of spacer at terphenylene.
- [25] J.-Y. Shin, T. Tanaka, A. Osuka, M. Qing, D. Dolphin, Chem. Eur. J. 2009, 15, 12955–12959.
- [26] MO energy diagrams based on the DFT data are shown in Figure S41 (for [28]-hybrids 1-3) and Figure S42 (for [26]-hybrids 4-6) in the Supporting Information.

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## FULL PAPER

## Photochemistry

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## 

Photodynamics of [26]- and [28]Hexaphyrin–Bodipy Hybrids



**Speed control**: A set of hybrids having gradual variation in distances between hexaphyrin and bodipy moieties was prepared (see figure). Efficient PET processes from bodipy to [26]/[28]hexaphyrin were successfully observed on terphenylene-containing hybrids. [26]-Hybrids performed slower speeds of decay/rise processes than [28]-hybrids on the basis of enlarged center-tocenter distances.

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#### **Photoinduced Energy Transfer**

A set of hybrids having gradual variation in distances between hexaphyrin and bodipy moieties was prepared. Efficient photoinduced energy transfer (PET) processes from bodipy to [26]/[28]hexaphyrin were successfully observed on terphenylene-containing hybrids. [26]-Hybrids performed slower decay/rise processes than [28]-hybrids on the basis of their enlarged center-to-center distances. These PET parameters were fairly consistent with calculated ones. More detail can be found in the Full Paper by J.-Y. Shin, K. Kim, D. Kim, et al. on page ■ ff.

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