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Building Blocks for Self-Assembled Porphyrinic Photonic Wires

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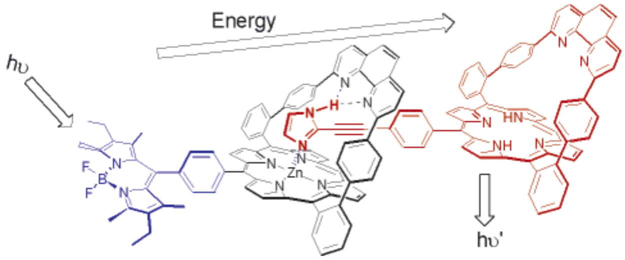
ABSTRACT



Based on the high affinity of phenanthroline-strapped porphyrins for imidazoles, building blocks for self-assembled, linear porphyrin architectures have been designed. Their synthesis is reported, and the assembly principle is illustrated by the formation of the shortest possible scaffold. Only one type of assembly is observed, and the stepwise energy transfer from the boron dipyrrylmethane (BODIPY) input to the free base output is highly efficient.

Initially inspired by naturally occurring light harvesting systems,[1] linear arrays of porphyrins for photonic conduction have been produced by either covalent[2] or noncovalent assembling.[3] Far from its original goal, this field is now definitely oriented toward the design of new multiporphyrinic materials such as photonic wires,[4] optoelectronic gates,[5] nonlinear optic devices,[6] or photovoltaic cells.[7] As illustrated by Lindsey's pioneering work on covalent photonic wires, energy input can be performed by boron dipyrrylmethane (BODIPY) primary energy donors, and free base porphyrins may be used as terminal energy acceptors.[8] Covalent assembly has multiple advantages. It provides complete control over the location of primary energy donors and acceptors, thus allowing the energetic gradient to be tuned. It is also a means of controlling the orientation of the chromophores involved in the stepwise or cascade energy transfer.[9] On the other hand, using noncovalent approaches, rather simple building blocks can be assembled into more complex yet well-defined circular[10] or linear arrays.[11] The drawback of such a noncovalent approach is that it remains

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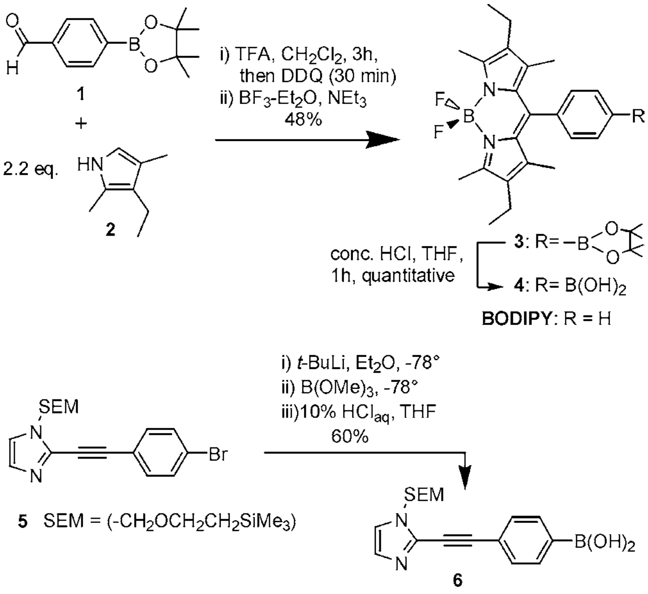
difficult to introduce an energetic gradient in self-assembled species.

We report hereafter the design, synthesis, and preliminary photophysical properties of building blocks that can self-assemble to perform a stepwise energy transfer along a gradient. The design of the assembling process is based on the exceptional affinity of phenanthroline-strapped zinc porphyrins for N-unsubstituted imidazoles,[12] which has already led to the successful preparation of self-assembled energy dyads.[13] The synthetic availability of the basic strapped porphyrin structure,[14] which can be prepared on a multigram scale, has prompted us to investigate the possible synthesis of simple building blocks for self-assembled, oriented linear photonic wires.

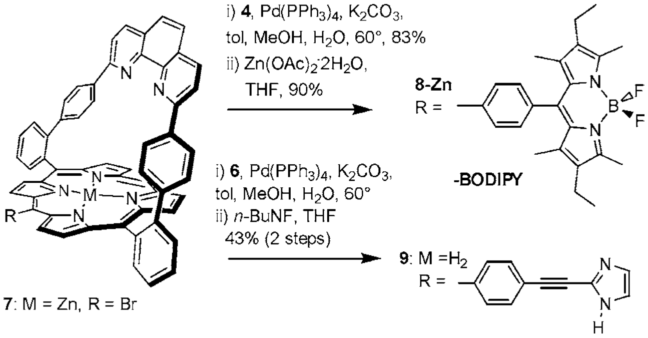
A simple synthetic approach has been designed on the basis of the Suzuki coupling of boronic acids with 5-bromodiarylporphyrins.[12] The benzaldehyde boronic ester **1**[15] (Scheme 1) was condensed with 2,4-dimethyl-3-ethyl pyrrole **2** and then oxidized with 2,3-dichloro-5,6-dicyanoquinone (DDQ). Further cyclization with BF_3 etherate afforded the functionalized BODIPY intermediate **3** in an overall 48% yield. Conversion to the corresponding boronic acid **4** was carried out with 10% HCl (aq) in THF. In parallel, the SEM-protected-2-[2-(4-bromophenyl)ethynyl]imidazole[13b] **5** was transformed to its boronic acid by treatment with *t*-BuLi at −78 °C, quenching with $B(OMe)_3$, and a subsequent acidic workup.

Scheme 1. Synthesis of Intermediates **4** and **6**



Precursor **4** was then coupled with **7** under biphasic Suzuki conditions (Scheme 2) to afford **8** in 83% yield. Metalation with zinc(II) gave **8-Zn** in 90% yield. Imidazole derivative **6** was coupled with **7** under identical conditions, and then the SEM protecting group was removed with *n*-Bu_4NF to afford **9** in 43% overall yield (two steps).

Scheme 2. Synthesis of Building Blocks **8-Zn** and **9**



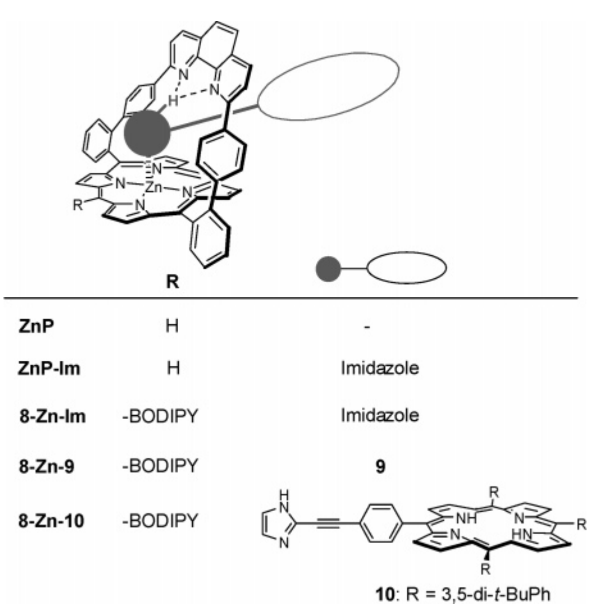


Figure 1. Triad **8-Zn-9**, reference triad **8-Zn-10**, and model compounds **8-Zn-Im**, **ZnP**, and **ZnP−Im**.

The association of the photodyad **8-Zn** (Figure 1), composed of the BODIPY energy donor (input element) and the zinc porphyrin primary energy acceptor (transmission element), with the free base secondary energy acceptor **9** (output element) was monitored by UV−visible absorption in the 400−800 nm spectral window. This window corresponds to the low-lying energies of BODIPY (λ^{max}= 525 nm) and the porphyrinic Q transitions (for **8-Zn**, λ^{max} = 553

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and 595 nm; for **9**, $\lambda^{max} = 514, 543, 586$, and 643 nm; for **10**, $\lambda^{max} = 518, 553, 591$, and 648 nm). From these spectrophotometric titrations (see Supporting Information) the stability constant, log $K_{\mathbf{8-Zn-9}} = 6.0(3)$, was determined. This value is comparable to that of triad **8-Zn-10** with a log $K_{\mathbf{8-Zn-10}} = 6.1(5)$. Fluorescence titrations confirmed all stability constants. These stability constants are similar to that determined for the model complex **8-Zn-Im** (log $K_{\mathbf{8-Zn-Im}} = 6.2(1)$; see Supporting Information), which demonstrates the absence of steric hindrance between the two porphyrinic units in the triads. Moreover, the electronic spectra of the triads **8-Zn-9** and **8-Zn-10** correspond to the sum of the spectral properties of the individual constituents and suggest weak interactions in the ground state between **8-Zn** and **9** (or **10**) (see Supporting Information).

^{1}H NMR monitoring of the self-assembly shows spectral changes similar to those previously observed for the binding of imidazole derivatives in the phenanthroline pocket.[12,13] Furthermore, NMR indicates that a unique type of linear threading of the imidazolyl-porphyrin **9** is observed (see Supporting Information). Since no changes are observed in the BODIPY signals, it is reasonable to assume that, for steric reasons, the free base moiety is located opposite the BODIPY moiety as depicted in Figure 1 or in the abstract figure.

Efficient energy transfer via a Förster mechanism[16] requires significant overlap of the donor's emission spectrum and the acceptor's absorption spectrum. Figure 2 shows the electronic overlaps between the emission spectrum of the isolated BODIPY moiety and the absorption spectrum of the **ZnP-Im** complex (Figure 2a), as well as between the emission spectrum of the latter complex and the absorption of the free base moiety **9** (or **10**) (see Supporting Information). These electronic spectra of the components, as well as the absolute quantum yield of the donors[17] in the sequential energy migration (BODIPY → **ZnP-Im** → **9** (or **10**)), allowed an estimation of the Förster critical distance R_0[18] at which the energy transfer is as efficient as the other deactivation pathways of the donors. Values of ca. 62, 27, and 32 Å for **BODIPY** → **ZnP-Im**, **ZnP-Im** → **9**, and **ZnP-Im** → **10**, respectively, were obtained.

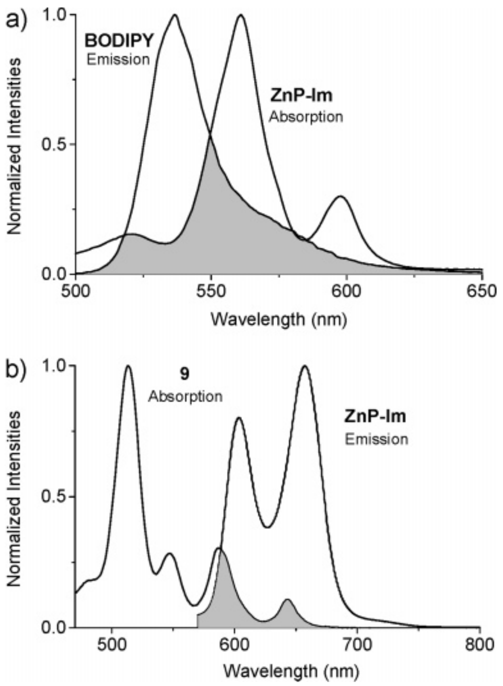

Figure 2. Overlaps of donor emission and acceptor absorption spectra in the stepwise energy transfer migration: (a) **BODIPY** → **ZnP-Im**; (b) **ZnP-Im** → **9**.

In triads **8-Zn-9** and **8-Zn-10**, the center-to-center distances between BODIPY and zinc(II) porphyrin and between the latter and **9** (or **10**) were estimated from molecular mechanics to be ~11.6 and 13 Å, respectively. For Förster-type energy transfer, the efficiency can be calculated from $\Phi_{ET} = 1/[1 + (r/R_0)^6]$, where r is the center-to-center distance between chromophores Therefore, quantitative stepwise energy-transfer efficiencies could be theoretically expected for the photochemical triads considered in this work. The energy transfer efficiency from the BODIPY unit to the central transmission component (**BODIPY*-Zn-Im** → **BODIPY-(Zn-Im)***, Figure 1) was calculated by first determining the quantum yields of the energy donor in the dyad **8-Zn-Im** ($\Phi^{abs} = 0.01$) and of **BODIPY** (Scheme 1) ($\Phi^{abs} = 0.30$). The intramolecular energy-transfer yield was calculated as follows: $\Phi_{ET1} = 1 - \Phi_{Donor-Dyad}/\Phi_{Donor}$ and is equal to 0.96 ± 0.05 ($\lambda_{exc} = 495$ nm).[19] Intermolecular processes were excluded since no quenching or energy transfer mechanism was observed between isolated **BODIPY** and **ZnP** or **ZnP-Im** moieties under our experimental conditions. The yields of energy transfer between the two porphyrins units in the photochemical triads were evaluated by spectrofluorimetric titrations of **8-Zn** with **9** (or **10**), and with 1*H*-Imidazole (Figure 3 and Supporting Information). When the BODIPY residue is preferentially (but not exclusively) excited at 495 nm, the emission arising from the optical input

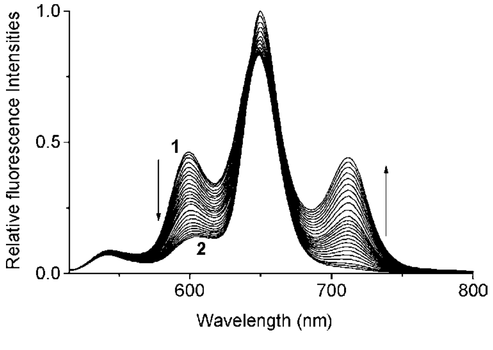

Figure 3. Spectrofluorimetric titration of **8-Zn** with **9**. Solvent: 1,2-dichloroethane (+0.02 wt % of 2,6-lutidine); $T = 25.0(2)$ °C; $\lambda_{exc} = 495$ nm (↓BODIPY); $[\mathbf{8\text{-}Zn}]_{tot} = 5.02 \times 10^{-6}$ M. (1) $[\mathbf{9}]_{tot}/[\mathbf{8\text{-}Zn}]_{tot} = 0$; (2) $[\mathbf{9}]_{tot}/[\mathbf{8\text{-}Zn}]_{tot} = 1.69$. ($[\mathbf{9}]_{free}/[\mathbf{9}]_{tot} = 0.518$). At the end of the titration, 83% of the light is absorbed by the BODIPY unit.

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remains constant, while the emission centered on the central zinc porphyrin decreases with a concomitant increase of the emission arising from the optical output (free base porphyrin). These observations strongly suggest an efficient energy transfer along the noncovalent assembly.

To evaluate the yields of energy transfer from **8-Zn*-9** to **8-Zn-9*** excited states, the zinc-containing subunit was excited at $\lambda_{exc} = 560$ nm and a spectrofluorimetric titration was carried out by monitoring the fluorescence (S1 → S0) of porphyrin moieties. Relative emission spectra were recalculated and compared to that determined for **8-Zn-Im** (Figure 4). These results show that the excited **ZnP-Im** complex transfers energy efficiently to the free base porphyrins **9** and **10** with Φ_{ET2} equal to 0.85 ± 0.09 and 0.83 ± 0.08, respectively (see Supporting Information).

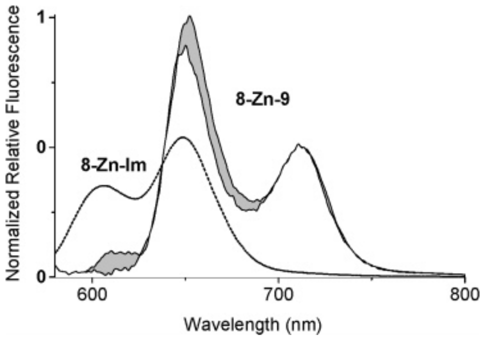

Figure 4. Normalized relative fluorescence spectra of **8-Zn-Im** (dotted line) and **8-Zn-9** (solid line). Solvent: 1,2-dichloroethane (0.02 wt % 2,6-lutidine); $T = 25.0(2)$ °C; $\lambda_{exc} = 560$ nm (↓Zn unit). The area filled in gray corresponds to the nontransmitted emission arising from the central zinc porphyrin in the triads.

It is noteworthy that intermolecular deactivation between excited states of the BODIPY subunit in **8-Zn** and the free base porphyrin in **9** (or **10**) could occur since intermolecular quenching or energy transfer between **BODIPY** and **9** or **10** was measured with K_{SV} values being equal to $2.5(2) \times 10^4$ and $3.0(2) \times 10^4$ M^{-1}, respectively (see Supporting Information). This feature could contribute to a lowering of energy transfer in the photochemical triads. The global energy transfer efficiencies of $\sim$0.80 ± 0.08% for **8-Zn-9** and **8-Zn-10** demonstrate that the noncovalent approach is of interest and should be considered in the preparation of new photonic wires with high energy migration yields. Due to intrinsic topographic constraints of **8-Zn** and **9**, these synthetically accessible porphyrin building blocks are programmed to form linear coordination polymers suitable for photonic conduction based on zinc metalation of **9**. Research in this direction is currently in progress.

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Supporting Information Available: Experimental details for synthetic procedures, spectroscopic (absorption and emission) data, NMR spectra of **8-Zn-10** and its components. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Absolute quantum yields of the donors given in Figure 2: Φ_D (**BODIPY**) = 0.30; Φ_D (**ZnP** in **8-Zn**) = 0.01. Absolute quantum yields of the acceptors: Φ_A (**9**) = 0.02, Φ_A (**10**) = 0.04. Errors = 10%.

(18) R_0 is calculated by using $R_0 = 9.78 \times 10^3 [k^2 n^{-4} \Phi_D J(\lambda)]^{1/6}$, where k is the orientation factor that describes the relative orientation of the donor and acceptor dipoles ($k^2 = 2/3$), n is the refractive index of the solvent (for dichloroethane $n = 1.4448$), Φ_D is the absolute quantum yield of the donor, $J(\lambda)$ is the overlap integral, which is calculated from the normalized acceptor absorption spectrum $\epsilon(\lambda)$ and the normalized donor emission spectrum $F(\lambda)$ according to the following equation $J(\lambda) = \int F(\lambda)\epsilon(\lambda)\lambda^4 d\lambda$ (for **BODIPY** → **ZnP-Im** $J(\lambda) = 1.45 \times 10^{-12}$ M^{-1} cm^3, for **ZnP-Im** → **9** $J(\lambda) = 2.83 \times 10^{-13}$ M^{-1} cm^3**,** and for **ZnP-Im** → **10** $J(\lambda) = 7.44 \times 10^{-13}$ M^{-1} cm^3. (a) Förster, T. *Naturwissenchaften* **1946**, *33*, 166−175. (b) Förster, T. *Ann. Phys*. **1948**, *2*, 55−73. (c) *Biological Physics*; Mielczarek, E., Knox, R. S., Greenbaum, E., Eds.; American Institute of Physics: New York, 1993; pp 148−160. (d) Knox, R. S. *J. Phys. Chem. B* **2002**, *106*, 5289−5293.

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