Light Harvesting

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Guest-Induced Photophysical Property Switching of Artificial Light-Harvesting Dendrimers**

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Abstract: *An artificial light-harvesting multiporphyrin dendrimer (**$8P_{Zn}P_{FB}$**) composed of a focal freebase porphyrin (**P_{FB}**) with eight zinc(II) porphyrin (**P_{Zn}**) wings exhibited unique photophysical property switching in response to specific guest molecule binding. UV/Vis titration studies indicated stable 1:2 host–guest complex formation between **$8P_{Zn}P_{FB}$** and meso-tetrakis(4-pyridyl)-porphyrin (**TPyP**) for which the first and second association constants were estimated to be $>10^8\,\mathrm{M}^{-1}$ and $3.0\times10^7\,\mathrm{M}^{-1}$, respectively. **$8P_{Zn}P_{FB}$** originally shows 94 % energy transfer efficiency from **P_{Zn}** to the focal **P_{FB}**. By the formation of the host–guest complex (**$8P_{Zn}P_{FB}$·2TPyP**) the emission intensity of **$8P_{Zn}P_{FB}$** is significantly decreased, and an ultrafast charge separation state is generated. The energy transfer process from **P_{Zn}** wings to the **P_{FB}** core in **$8P_{Zn}P_{FB}$** is almost entirely switched to an electron transfer process by the formation of **$8P_{Zn}P_{FB}$·2TPyP**.*

Mimicking the photosynthetic system is one of the most attractive subjects in terms of understanding of biological mechanisms as well as one potential solution for the current and upcoming energy crisis.[1] Natural light–energy conversion is initiated by photon absorption of complex molecular assemblies called light-harvesting antenna complexes (LHC).[2] Well-ordered three-dimensional multiporphyrin arrays in LHC2 facilitate effective photon capture and energy migration to the reaction center of LHC1, which is composed of a non-covalently associated pair of chromophore units capable of forming a charge separation state on an ultrafast timescale.[3] In this context, we have recently synthesized porphyrin-based dendrimers to mimic LHC2, in which light energy collection occurs through vectorial energy transfer from a number of energy-donating zinc porphyrins (**P_{Zn}**) to the focal freebase porphyrin (**P_{FB}**).[1e] The large number of **P_{Zn}** in the dendrimers allows efficient photon capture and results in a highly efficient photoinduced energy transfer to the focal **P_{FB}**. Since the dendrimer exhibited efficient photon capturing and excitation energy transfer to the focal point, the next step for the LHC mimic would be charge separation (CS).[4] A number of different electron-accepting units such as fullerenes, carbon nanotubes, and ferrocene have been covalently conjugated to multi-chromophore donor systems to achieve an efficient donor–acceptor pair mimicking LHC.[5] However, what renders natural LHC systems unique is that the formation of the CS state is induced by the excitation energy transfer from a multi-chromophore array to a non-covalently associated pair of chromophore units.[6] Herein we report a supramolecular host–guest complex between multiporphyrin dendrimers and monomeric porphyrins that exhibits efficient light absorption and ultrafast conversion into a CS state.

A series of porphyrin dendrimers made up of focal **P_{FB}** and **P_{Zn}** wings were synthesized to mimic the light-harvesting antenna complex (Figure 1), and their host–guest complex

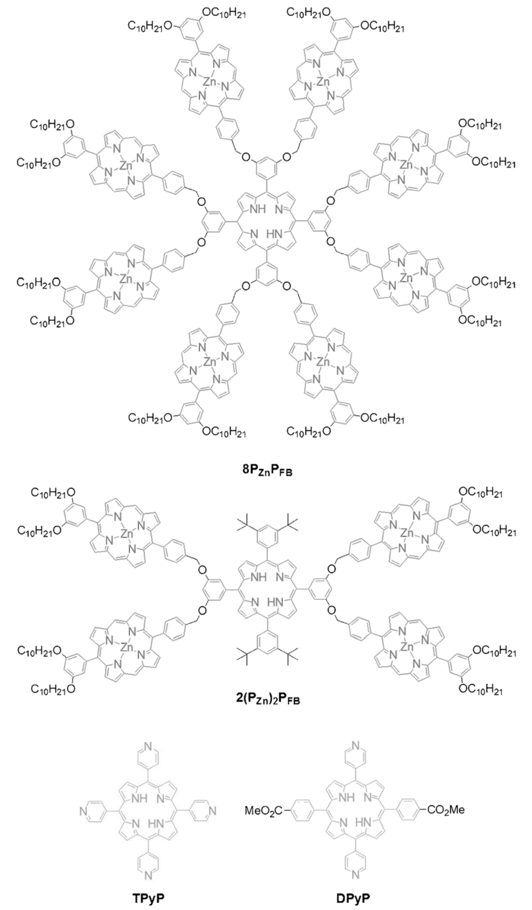

Figure 1. Structures of dendrimers and guests studied in this work.

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formation with pyridyl-bearing guest molecules was investigated by UV/Vis titration in CH$_2$Cl$_2$ at 20 °C (Figure 2). Pyridyl-bearing porphyrins are capable of forming host–guest complexes with the porphyrin dendrimers because pyridyl groups can coordinate to the zinc atoms in $\mathbf{P_{Zn}}$ as axial ligand. Due to the overlapping of the absorption bands between the host and guest compounds their differential spectra had to be recorded through titration of guests to host dendrimers, which were obtained by subtracting the absorption spectra of dendrimers and guests alone from the spectra of the dendrimer–guest mixtures of equal concentrations. When **TPyP** was titrated to $\mathbf{8P_{Zn}P_{FB}}$ the differential UV/Vis absorption spectra exhibited isosbestic points at 380, 429, and 544 nm, being saturated at 2 equivalents of **TPyP** addition (Figure 2 a). Continuous variation analysis (Job's plot) indicated the formation of a 1:2 host–guest complex between **TPyP** and $\mathbf{8P_{Zn}P_{FB}}$ ($\mathbf{8P_{Zn}P_{FB}{\cdot}2TPyP}$).[7] From nonlinear curve fitting analysis, the first and second association constants for **TPyP** to $\mathbf{8P_{Zn}P_{FB}}$ were estimated to be $> 10^8\,\text{M}^{-1}$ and $(3.0 \pm 0.3) \times 10^7\,\text{M}^{-1}$, respectively. Similarly, when **DPyP** was titrated to $\mathbf{2(P_{Zn})_2P_{FB}}$, isosbestic points were found at 419, 430, and 575 nm (Figure 2 b). Continuous variation analysis also indicated the formation of a 1:2 host–guest complex between $\mathbf{2(P_{Zn})_2P_{FB}}$ and **DPyP** ($\mathbf{2(P_{Zn})_2P_{FB}{\cdot}2DPyP}$); the first and second association constants for **DPyP** to $\mathbf{2(P_{Zn})_2P_{FB}}$ were estimated to be $(3.5 \pm 0.3) \times 10^5\,\text{M}^{-1}$ and $(8.8 \pm 0.4) \times 10^4\,\text{M}^{-1}$, respectively.

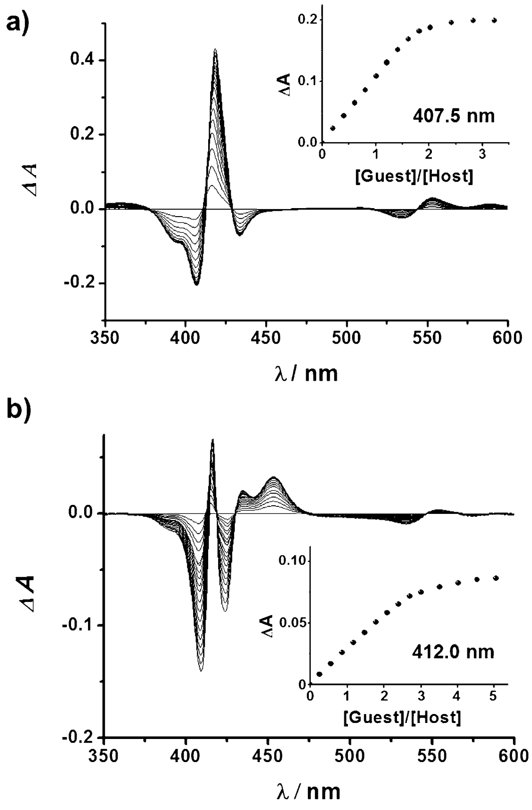

Figure 2. UV/Vis spectroscopic titration of a) **TPyP** to $\mathbf{8P_{Zn}P_{FB}}$ and b) **DPyP** to $\mathbf{2(P_{Zn})_2P_{FB}}$. Inset: binding isotherms of each titration.

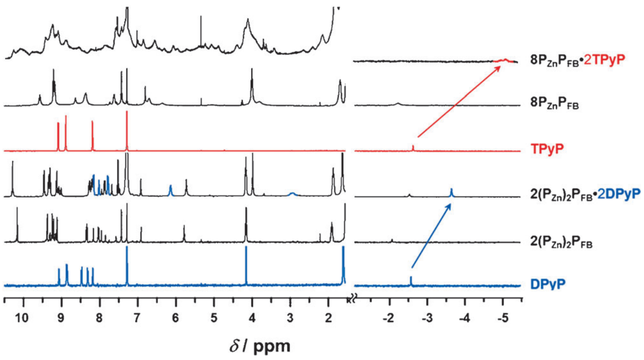

Figure 3. ^{1}H NMR spectra of dendrimers and host–guest complexes.

^{1}H NMR studies were conducted to collect further information on the structures of each host–guest complex (Figure 3). Unfortunately, the ^{1}H NMR spectrum of $\mathbf{8P_{Zn}P_{FB}}$ was significantly broadened upon addition of **TPyP**, indicating that the conformational fluctuations are slow on the NMR timescale due to the tight binding of **TPyP** to $\mathbf{8P_{Zn}P_{FB}}$ and their high molecular weight. Although all $\mathbf{8P_{Zn}P_{FB}}$ peaks were broadened by the addition of **TPyP**, the pyrrolic proton signals in **TPyP** were still assignable: upon formation of the host–guest complex, the pyrrolic proton signals were shifted strongly upfield from −2.9 to −5.2 ppm. This is because the pyrrolic protons in the axial ligand **TPyP** are allocated onto the $\mathbf{P_{Zn}}$ wings where they experience a strong shielding effect due to the influence of the ring current of the π electrons in $\mathbf{P_{Zn}}$. Similar changes were observed in the ^{1}H NMR spectra of the complex formation of $\mathbf{2(P_{Zn})_2P_{FB}}$ and **DPyP**, but the change in the chemical shifts was relatively small because only two $\mathbf{P_{Zn}}$ are able to bind simultaneously to a **DPyP** guest molecule. Unlike $\mathbf{8P_{Zn}P_{FB}}$, $\mathbf{2(P_{Zn})_2P_{FB}}$ exhibited sharp ^{1}H NMR peak patterns and clear changes upon complex formation with **DPyP**, implying a fast conformational fluctuation of the host–guest complex due to weak binding as well as structural flexibility. Upon guest binding, all **DPyP** peaks exhibited strong upfield shifts, whereas the peaks originating from $\mathbf{2(P_{Zn})_2P_{FB}}$ were slightly downfield-shifted. Such spectral changes are good evidence for the formation of the proposed host–guest complex structures as expected from the energy-minimized molecular models calculated using MM2 force field (Figure 4).

Considering our previous findings that $\mathbf{8P_{Zn}P_{FB}}$ formed a stable host–guest complex with **TPyP**, we have investigated the photophysical behaviors of $\mathbf{8P_{Zn}P_{FB}}$ and $\mathbf{8P_{Zn}P_{FB}{\cdot}2TPyP}$. We have reported previously[1e] that the existence of a large number of $\mathbf{P_{Zn}}$ wings in $\mathbf{8P_{Zn}P_{FB}}$ facilitates excellent energy transfer from $\mathbf{P_{Zn}}$ to the focal $\mathbf{P_{FB}}$ through cooperative interactions, the efficiency of which was estimated to be 94 %. Evidence of this efficient energy migration process is found in the fluorescence emission spectrum of $\mathbf{8P_{Zn}P_{FB}}$, which reveals a striking resemblance to that of a $\mathbf{P_{FB}}$ (Figure S1 in the Supporting Information). The fluorescence decay profiles (Figure 5 a and Table S1) upon photoexcitation of the Soret bands (417 nm) reveal the picoscond timescale of this process, in which a fast decay component with a time constant of approximately 50 ps was observed when moni-

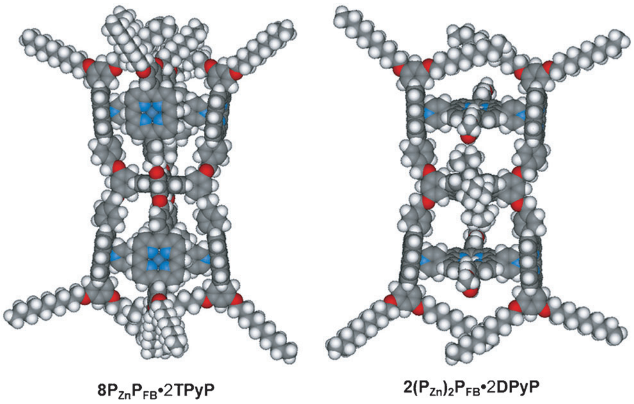

Figure 4. Energy-minimized molecular models for the host–guest complexes $\mathbf{8P_{Zn}P_{FB}{\cdot}2TPyP}$ (left) and $\mathbf{2(P_{Zn})_2P_{FB}{\cdot}2\,DPyP}$ (right) calculated by using MM2 force field. blue, N; red, O; black, C; white, H.

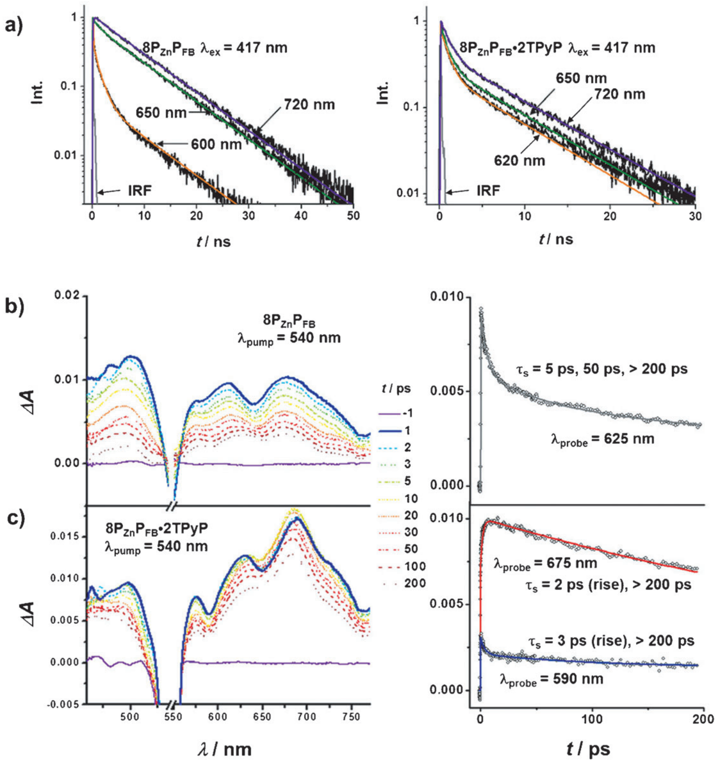

Figure 5. a) Fluorescence decay profiles of $\mathbf{8P_{Zn}P_{FB}}$ (left) and $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$ (right) at the indicated wavelengths. Transient absorption spectra and the kinetic traces of b) $\mathbf{8P_{Zn}P_{FB}}$ and c) $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$ with the pump wavelength of 540 nm.

tored at 600 nm (the fluorescence region of a $\mathbf{P_{Zn}}$ wing) and a corresponding rise was seen at 720 nm (the fluorescence region of a $\mathbf{P_{FB}}$). The long-lived residuals with small amplitudes (1.3 and 7.8 ns) can be assigned to the fluorescence lifetimes from the $\mathbf{P_{Zn}}$ and $\mathbf{P_{FB}}$ units, respectively.

The fluorescence emission of $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$ was also investigated to gain insight into the efficient energy transfer process. Interestingly, the emission intensity of $\mathbf{8P_{Zn}P_{FB}}$ was significantly reduced by the formation of $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$, which is likely due to a photoinduced electron transfer (PET) process.[8] Time-resolved fluorescence observations also showed an appreciable decrease in the fluorescence lifetimes of $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$ along with a much faster (≈20 ps) decay component than in the case of $\mathbf{8P_{Zn}P_{FB}}$. In order to shed light on the ultrafast dynamics responsible for the rigorous fluorescence quenching of $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$ we also measured the femtosecond transient absorption (TA) of $\mathbf{8P_{Zn}P_{FB}}$ and $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$. As shown in Figure 5b, the TA spectra of $\mathbf{8P_{Zn}P_{FB}}$ exhibited three different lifetime components (5 ps, 50 ps, and long residual) at the probe wavelength of 625 nm. Of these three, we assign the major 50 ps component to the energy transfer dynamics from $\mathbf{P_{Zn}}$ to the focal $\mathbf{P_{FB}}$, and the 5 ps component to the singlet–singlet annihilation process of multiple $\mathbf{P_{Zn}}$ excitons formed by excitation with high-density photons. Analysis of the TA spectra also provides evidence for the energy transfer process from the peripheral $\mathbf{P_{Zn}}$ wings to the $\mathbf{P_{FB}}$ core, in which a negative peak at 640 nm, assignable to the 0–1 stimulated emission (SE) signal of $\mathbf{P_{Zn}}$, gradually shifted to 655 nm, ascribable to the 0–0 SE band of the focal $\mathbf{P_{FB}}$. In contrast, the TA spectra of $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$ exhibited completely different shapes. As shown in Figure 5c, $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$ exhibits a broad excited-state absorption (ESA) from 600 to 750 nm, which clearly matches the cationic radical bands of diphenyl-substituted $\mathbf{P_{Zn}}$ found in literature.[8a,e] Under careful observation, an ultrafast component (2 ps) followed by a long residual of 650 ps was observed when this region was directly probed. Moreover, the initial TA spectra exhibit the SE signal of $\mathbf{P_{Zn}}$ at 645 nm, which disappeared within 2 ps, indicating that the singlet excitation state of $\mathbf{P_{Zn}}$ immediately transforms into cation radicals through an ultrafast PET process. Therefore, we can assign the former 2 ps lifetime component to the formation time of the CS state and the latter 650 ps lifetime to the corresponding charge recombination time.

The PET process from $\mathbf{P_{Zn}}$ to $\mathbf{TPyP}$ can be explained by the electronic density changes of both $\mathbf{P_{Zn}}$ and $\mathbf{TPyP}$ due to the axial coordination of pyridyl groups in $\mathbf{TPyP}$ to $\mathbf{P_{Zn}}$.[9] Sauvage et al. demonstrated the PET process from $\mathbf{P_{Zn}}$ to $\mathbf{TPyP}$ in a similar system, which occurs by the formation of a 1:2 complex between $\mathbf{TPyP}$ and oblique $\mathbf{P_{Zn}}$ dimers with a rigid bridge.[9a] The coordination of pyridyl groups in $\mathbf{TPyP}$ to the oblique $\mathbf{P_{Zn}}$ dimers resulted predominantly in photoinduced energy transfer from $\mathbf{P_{Zn}}$ to $\mathbf{TPyP}$, followed by a HOMO–HOMO electron transfer to form the CS state, which is one possible reason for the rather slow formation of the CS state (≈160 ps). In contrast, only 2 ps were needed to form the CS state in $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$, possibly due to the flexible nature of $\mathbf{8P_{Zn}P_{FB}}$ and its ability to induce very tight and close binding of $\mathbf{P_{Zn}}$ to $\mathbf{TPyP}$. The excited electron in $\mathbf{P_{Zn}}$ migrates directly to the closely contacted, electron-deficient $\mathbf{TPyP}$ within an ultrafast timescale.

As reported in our previous paper,[1e] 94 % of the excitation energy in $\mathbf{8P_{Zn}P_{FB}}$ was emitted from the $\mathbf{P_{FB}}$ core, and the remaining 6 % was emitted from $\mathbf{P_{Zn}}$ wings due to the efficient energy transfer. The emission at 600 nm, originating from $\mathbf{P_{Zn}}$, completely vanished after the formation of $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$, which indicates that the total excitation energy of $\mathbf{P_{Zn}}$ should migrate to the $\mathbf{P_{FB}}$ core or **TPyP** through either energy or electron transfer processes. The emissions originating from the $\mathbf{P_{FB}}$ core at 650 and 720 nm were also greatly reduced by the formation of $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$; only 7 % of the emission remained after complete formation of $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$, implying a considerable decrease in the contribution from the energy transfer process from $\mathbf{P_{Zn}}$ to the focal $\mathbf{P_{FB}}$. Assuming that the remaining 7 % of emission from the $\mathbf{P_{FB}}$ originates fully from the energy transfer from $\mathbf{P_{Zn}}$, it is the rest (93 %) of the excitation energy of $\mathbf{P_{Zn}}$ that remains and is able to contribute to the PET process. However, because the weak emission from $\mathbf{8P_{Zn}P_{FB}{\cdot}2\,TPyP}$ at 650 and 720 nm eventually includes the result of the direct excitation of the focal $\mathbf{P_{FB}}$ and **TPyP**, the actual efficiency of PET from $\mathbf{P_{Zn}}$ to **TPyP** would be much greater than 93 %. We can therefore conclude that the efficient energy transfer process from $\mathbf{P_{Zn}}$ wings to the $\mathbf{P_{FB}}$ core in $\mathbf{8P_{Zn}P_{FB}}$ is switched almost exclusively to the PET process by coordination of **TPyP** to $\mathbf{8P_{Zn}P_{FB}}$.

In summary, the efficient energy transfer process in $\mathbf{8P_{Zn}P_{FB}}$ switches to an ultrafast photoinduced electron transfer process to induce a long-lived CS state by the formation of a host–guest complex with **TPyP**. It is noteworthy that the CS state is induced by a non-covalent assembly of the same porphyrin units, which strongly mimics LHC1 in purple photosynthetic bacteria. Therefore, $\mathbf{8P_{Zn}P_{FB}}$ can be considered as a novel biomimetic model which can serve both functions of LHC1 and LHC2 in a switchable manner through the binding of **TPyP**.

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[1] a) M. R. Wasielewski, *Acc. Chem. Res.* **2009**, *42*, 1910 – 1921; b) H. Imahori, *J. Phys. Chem. B* **2004**, *108*, 6130 – 6143; c) M. S. Choi, T. Yamazaki, I. Yamazaki, T. Aida, *Angew. Chem.* **2004**, *116*, 152 – 160; *Angew. Chem. Int. Ed.* **2004**, *43*, 150 – 158; d) N. Aratani, D. Kim, A. Osuka, *Acc. Chem. Res.* **2009**, *42*, 1922 – 1934; e) W.-D. Jang, C.-H. Lee, M.-S. Choi, M. Osada, *J. Porphyrins Phthalocyanines* **2009**, *13*, 787 – 793; f) J. Davila, A. Harriman, L. R. Milgrom, *Chem. Phys. Lett.* **1987**, *136*, 427 – 430.

[2] G. D. Scholes, G. R. Fleming, A. Olaya-Castro, R. van Grondelle, *Nat. Chem.* **2011**, *3*, 763 – 774.

[3] X. Hu, A. Damjanović, T. Ritz, K. Schulten, *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 5935 – 5941.

[4] J. P. Dekker, R. Van Grondelle, *Photosynth. Res.* **2000**, *63*, 195 – 208.

[5] a) D. Kuciauskas, S. Lin, G. R. Seely, A. L. Moore, T. A. Moore, D. Gust, T. Drovetskaya, C. A. Reed, P. D. Boyd, *J. Phys. Chem.* **1996**, *100*, 15926 – 15932; b) M. S. Choi, T. Aida, H. Luo, Y. Araki, O. Ito, *Angew. Chem.* **2003**, *115*, 4194 – 4197; c) D. Baskaran, J. W. Mays, X. P. Zhang, M. S. Bratcher, *J. Am. Chem. Soc.* **2005**, *127*, 6916 – 6917; d) K. Uosaki, T. Kondo, X.-Q. Zhang, M. Yanagida, *J. Am. Chem. Soc.* **1997**, *119*, 8367 – 8368.

[6] a) B. Dohse, P. Mathis, J. Wachtveitl, E. Laussermair, S. Iwata, H. Michel, D. Oesterhelt, *Biochemistry* **1995**, *34*, 11335 – 11343; b) W. Kühlbrandt, *Curr. Opin. Struct. Biol.* **1994**, *4*, 519 – 528.

[7] K. A. Connors, *Binding Constants: The Measurement of Molecular Complex Stability*, Wiley, New York, **1987**.

[8] a) J.-P. Collin, A. Harriman, V. Heitz, F. Odobel, J.-P. Sauvage, *J. Am. Chem. Soc.* **1994**, *116*, 5679 – 5690; b) S. Fukuzumi, H. Imahori, H. Yamada, M. E. El-Khouly, M. Fujitsuka, O. Ito, D. M. Guldi, *J. Am. Chem. Soc.* **2001**, *123*, 2571 – 2575; c) K. Li, D. I. Schuster, D. M. Guldi, M. Á. Herranz, L. Echegoyen, *J. Am. Chem. Soc.* **2004**, *126*, 3388 – 3389; d) K. Kadish, L. Shiue, R. Rhodes, L. Bottomley, *Inorg. Chem.* **1981**, *20*, 1274 – 1277; e) J. C. Chambron, A. Harriman, V. Heitz, J. P. Sauvage, *J. Am. Chem. Soc.* **1993**, *115*, 6109 – 6114.

[9] a) B. Ventura, L. Flamigni, M. Beyler, V. Heitz, J. P. Sauvage, *Chem. Eur. J.* **2010**, *16*, 8748 – 8756; b) S. Ikeda, N. Aratani, A. Osuka, *Chem. Commun.* **2012**, *48*, 4317 – 4319; c) P. Hemant Kumar, S. Prashanthi, P. R. Bangal, *J. Phys. Chem. A* **2011**, *115*, 631 – 642; d) S. Anderson, H. L. Anderson, A. Bashall, M. McPartlin, J. K. Sanders, *Angew. Chem.* **1995**, *107*, 1196 – 1200; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1096 – 1099.