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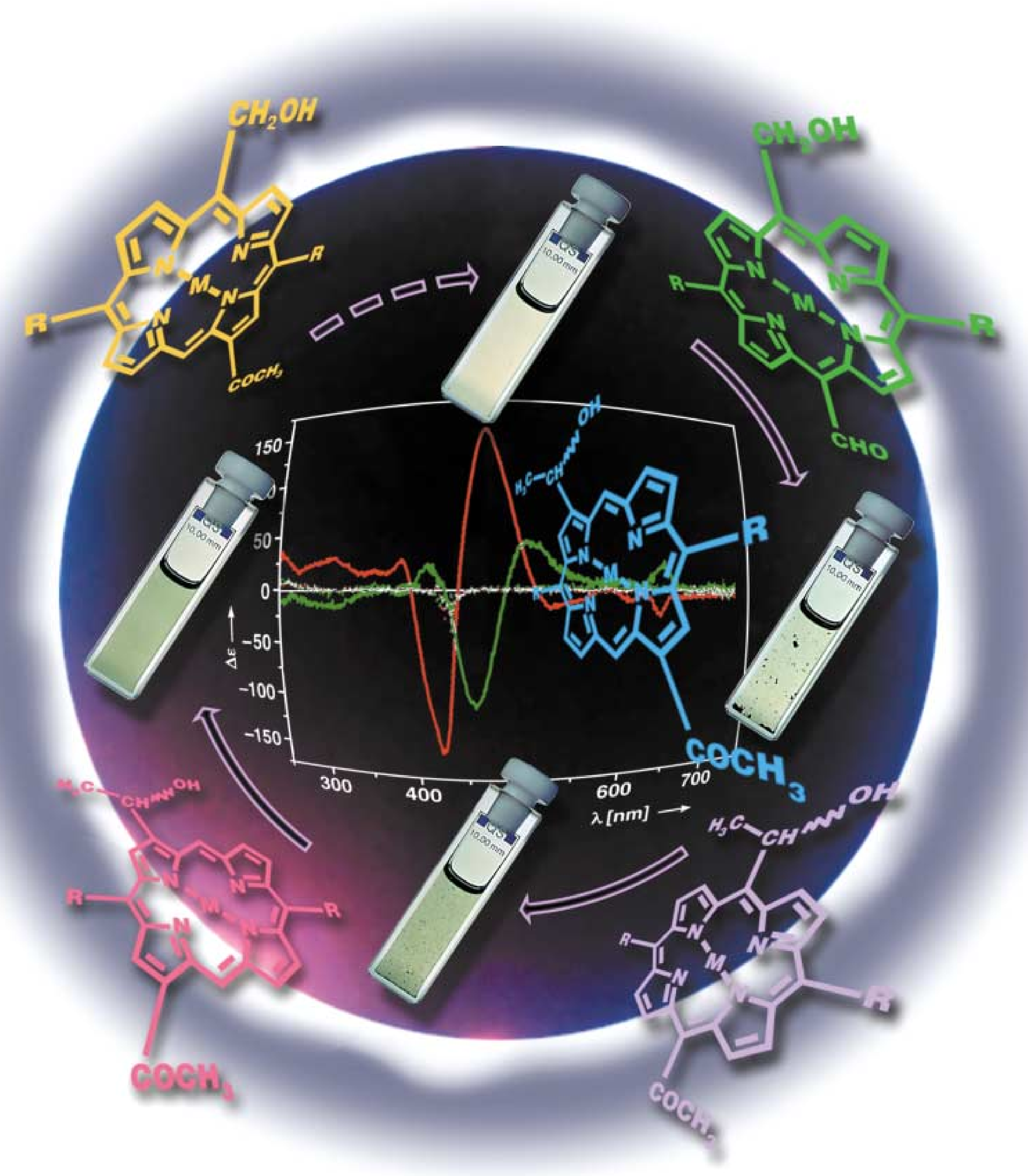

Mit dem Ziel, die Selbstorganisation der natürlichen Bacteriochlorophylle *c*, *d* und *e* nachzuahmen, wurden verschiedene neue Porphyrine synthetisiert. Diese künstlichen Antennensysteme sollten Sonnenlicht sogar bei geringen Strahlungsintensitäten, angedeutet durch die Sonnenfinsternis im Bildhintergrund, absorbieren können. Darüber berichten T. S. Balaban et al. auf den folgenden Seiten.

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Artificial Light-Harvesting Antenna

Controlling Chirality and Optical Properties of Artificial Antenna Systems with Self-Assembling Porphyrins**

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Dedicated to Professors Klaus Hafner and Emanuel Vogel, magisters of chromophore chemistry, on the occasion of their 75th birthday

A fascinating example of self-assembly encountered in nature is provided by green photosynthetic bacteria. These bacteria developed early during evolution, under the pressure of synthetic and genetic economy, an organelle capable of capturing sunlight even at 10 m below the surface of water to trigger photosynthesis. In this organelle the so-called chlorosome, bacteriochlorophyll (BChl) molecules, self-organize without the use of proteinaceous scaffolding.[1,2] Later in evolution, purple bacteria and plants perfected their light-harvesting apparatus by assembling much more complicated (bacterio)chlorophyll-protein complexes.[3–6] These complexes are presently beyond the scope of synthetic chemistry. However, the earlier antennas, which are fully functional, can be mimicked with synthetic molecules by controlling their self-assembly in view of achieving artificial photosynthesis.

Essential for the self-assembly algorithm to be able to operate are 1) the ligation of the central magnesium atom by the 3^1-hydroxy group of another molecule; 2) cooperative hydrogen bonding of the same OH group to the 13^1-carbonyl group of a third BChl *c* molecule; and 3) π–π interactions between the chlorin macrocycles, which are organized into stacks. These supramolecular interactions are detailed in Figure 1.

The elucidation of the molecular mechanism, by which the self-assembly occurs has involved various spectroscopic techniques and studies on both natural chlorosomes and on isolated BChl *c*, which was induced to self-assemble. These studies included solid state NMR on ^{13}C-labelled samples,[2,7,8] FTIR,[9] circular dichroism (CD),[10] as well as visible absorption on semisynthetic mimics, in which the positions of the carbonyl and hydroxy groups have been reversed[11] and zinc is the central metal atom instead of magnesium.[12] However, the sole presence of these groups is not sufficient for engineering the self-assembly; a rather careful tailoring of the whole molecular architecture has to be assured, as shown in a previous study.[13] From single crystal X-ray crystallography one could conclude which interactions have to be favored and which interactions have to be inhibited or suppressed.[13] Remarkably, by sequencing the entire genome of *Chlorobium tepidum*, a photosynthetic green sulfur bacterium, genetic evidence was recently brought forth for the self-assembly process of BChls as a way of obtaining functional antenna systems.[14]

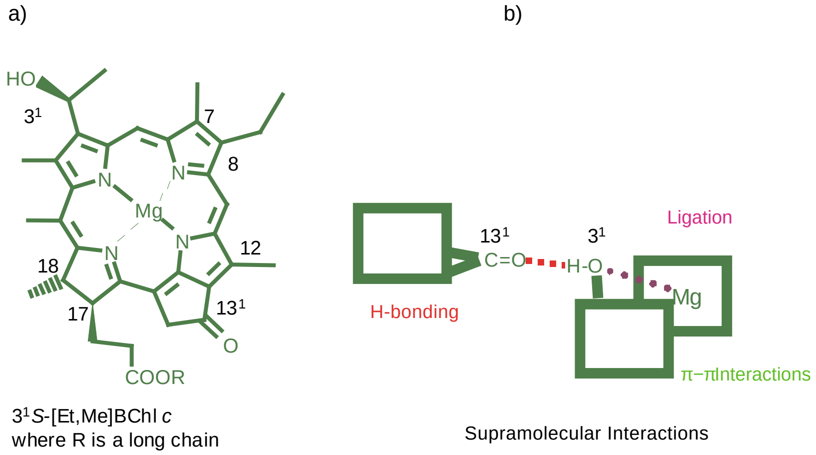

Figure 1. a) Molecular formula and atom numbering for a typical natural bacteriochlorophyll *c*—the 3^1-carbon atom may have either *R* or *S* configuration while the 17- and 18-carbon atoms are both *S*. Different substituents in the 8- and 12-positions (depicted are ethyl and methyl) as well as various long chain alcohols (such as farnesyl, stearyl, cetyl, oleyl, etc.) may esterify the 17-propionic acid side chain. b) The three important supramolecular interactions are presented schematically.

We have now developed very selective synthetic methods which have allowed us to synthesize the new porphyrinic systems **1**–**5** (Scheme 1), where R is a solubility-inducing group, namely the 3,5-di-*tert*-butylphenyl group. Both a hydroxy group, either as the achiral hydroxymethyl or as the chiral hydroxyethyl, and a carbonyl group, either as formyl or acetyl residues have been appended into desired positions onto the porphyrin periphery. In the self-assembled suprastructures, the interchromophoric interactions can now

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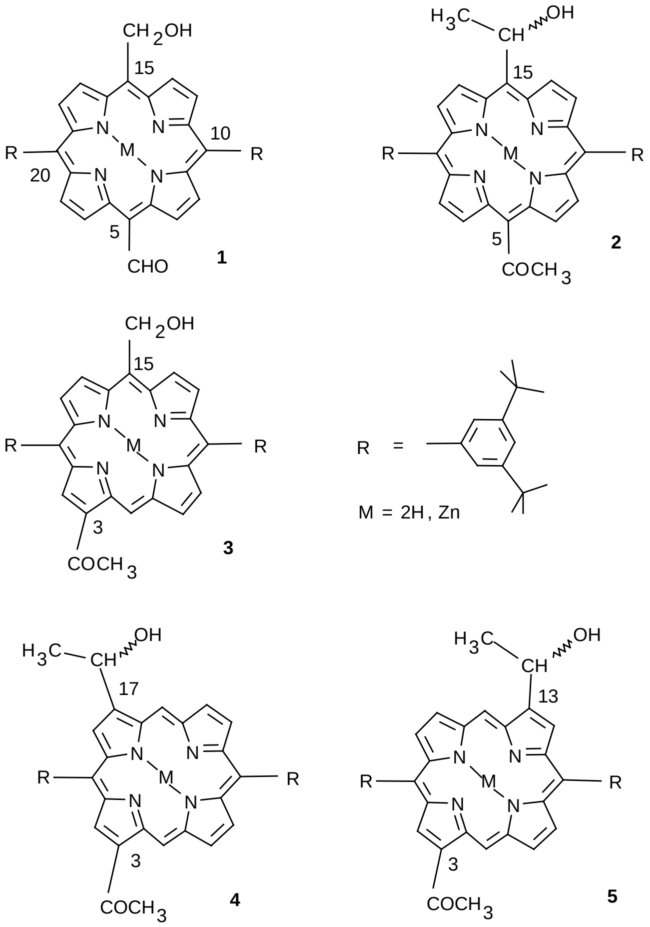

Scheme 1. The new porphyrins.

be fine tuned because of the slight but controlled variations in their geometry.

Different synthetic strategies were employed with full characterization of the intermediates (see Supporting Information). The structures of the new compounds were ascertained on the basis of their ^{1}H, ^{13}C NMR, FTIR and HRFAB mass spectra. NMR signals could be fully assigned on the basis of NOESY and COSY spectra.

The free bases **1**–**5** (M = 2H) could be metallated by using zinc acetate in a chloroform/methanol (4:1) mixture at room temperature with almost quantitative yields. Compounds **1**–**5** (M = Zn) are the first fully synthetic mimics of bacteriochlorophyll *c* that can self-assemble. The three structural elements responsible for the self-assembly, namely a hydroxy group, a central metal atom with affinity for a fifth ligand, and a carbonyl group are allowed to interact so that the algorithm leading to self-assembly is able to become operative. Previous attempts to program such self-assembly with porphyrins were not successful.[13] Semisynthetic products, which were derived from chlorophyll *a*, and which are also capable of self-assembly, were recently described.[15] If practical uses are envisaged, our synthetic strategies, which are high yielding and use cheap starting materials, are superior as the starting material, copper 10,20-bis-(3,5-di-*tert*-butylphenyl) porphyrin[16] is easily available in multigram quantities.

Compounds **1**–**5** self-assemble in nonpolar solvents such as *n*-heptane or *n*-hexane, just as the natural BChls *c*, *d* and *e* do. If the critically micellar concentration is surpassed, self-assembly leads to the separation of "fluffs" which are thermodynamically stable and usually settle at the bottom of the reaction vessel. These macroaggregates are visible to the eye, and upon gentle shaking are disrupted by shearing forces to nanoaggregates of about 100 nm, as indicated by dynamic light scattering and statistical analysis. This size shearing is illustrated in Figure 2 with self-assembled **1** (M = Zn) and is intriguingly similar both in general appearance and in the colors seen as the process that was reported for the natural BChl *c*.[17] After a few hours the macroaggregates reappear and this sequence may be repeated for several months because of their high stability in the absence of oxygen, even in the presence of light.

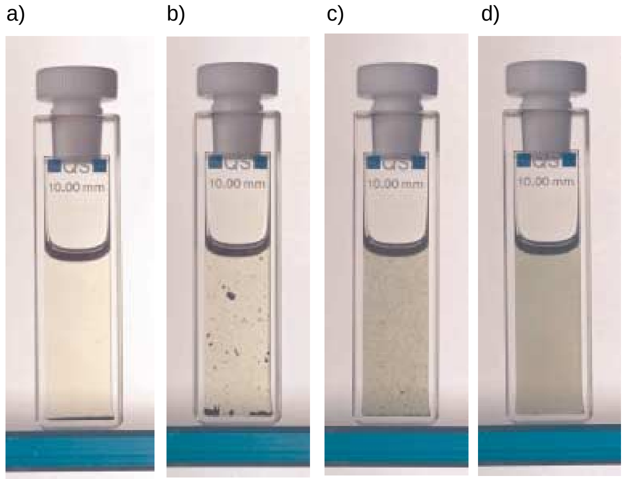

Figure 2. A quartz cuvette with self-assembled **1**. From left to right: a) the macroaggregates have settled to the bottom and the solution is only weakly colored. b) Gentle heating of the bottom of the cuvette leads to convection, the fluffs circulate slowly and are visible to the eye. c) The same cuvette after a longer period of convection. d) The same cuvette after shaking—a homogeneous, strongly colored solution is obtained, which arises from shearing forces.

The self-organization process is accompanied by drastic changes in the absorption spectra arising from electronic interactions between neighboring units within the supramolecular species. As only weak interactions are involved, the addition of small amounts of methanol, for example, leads to complete disassembly. This is illustrated in Figure 3 by means of UV/Vis absorption spectra. Very different behavior is encountered for each compound **1**–**5** because of the different positions at which the hydroxy and carbonyl groups are appended onto the porphyrin macrocycle. The supramolecular assemblies have different optical properties because of the fine tuning of the π–π overlap and the direction of the transition dipole moments.

Importantly, because of the self-assembly, the intense Soret band characteristic for porphyrins is "spread out" for **1**-**Zn**, **5**-**Zn**, and especially **2**-**Zn**; the much smaller Q bands are also affected. The absorption bands characteristic of the self-

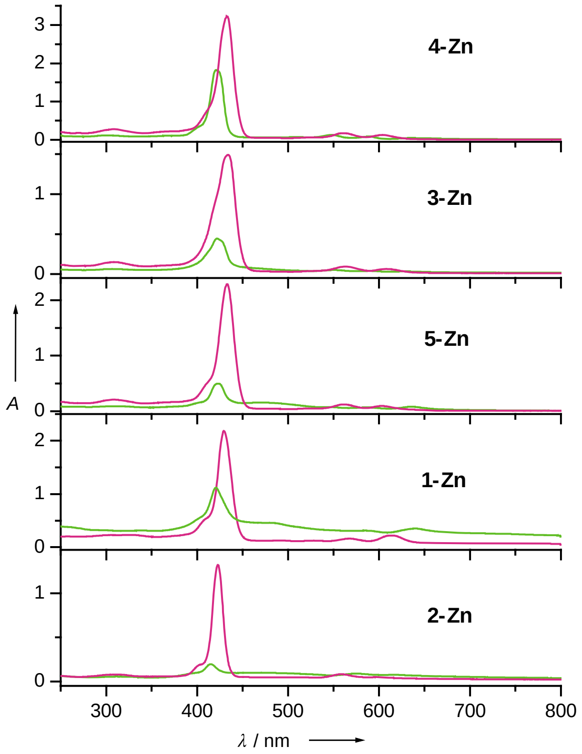

Figure 3. Visible absorption spectra of synthetic porphyrinic BChl *c* mimics. Green curves are samples after self-assembly in dry *n*-heptane (1.5 mL) obtained by dilution of a concentrated dry dichloromethane solution (30–100 μL). Magenta curves are measured in the same sample after the addition of methanol (50 μL) to the quartz cuvette with a path length of 0.5 cm and show complete disassembly of the aggregates to the monomeric zinc–methanol adducts. For the disassembly of **5-Zn**, which forms the most stable supramolecular structures, more methanol (100 μL) was needed. For **1-Zn** and **2-Zn** the solutions were strongly light-scattering. For **1-Zn** the magenta trace was recorded for the same solution as the green trace but with 1 mm path length. A similar experiment with a more concentrated solution of **2-Zn** and **5-Zn** are shown in the Supporting Information.

assembled species are red shifted in comparison to the monomers, as encountered in J aggregates,[18,19,20] or in the natural BChls *c*, *d* and *e*.[21] The Soret bands are shifted by about 50 nm, but because of the severe broadening they now overlap partially with the Q bands in the monomers. Thus these self-assembled species have a nonzero absorption coefficient between 400 and 700 nm, which is beneficial for light harvesting over a broad spectral range. In contrast to this behavior, in the self-assembled **4-Zn,** only a slight broadening and small red shift is encountered because of the limited π–π overlap, which perturbs only marginally the chromophores. In self-assembled **3-Zn** the situation is intermediate between **4-Zn** and the other cases. When methanol is added in very small amounts (but over the stoichiometric amount), the broad absorption bands completely disappear, and the Soret band drastically sharpens and red shifts by about 10 nm because of the formation of the monomeric Zn-methanol adducts. Methanol per se is not a better solvent, but competes for the zinc ligation and totally disrupts the hydrogen bonding network. This is clearly evident from FTIR spectra, in which the broad δ_{OH} vibrations between 3300 and 3200 cm^{-1} disappear upon methanol addition concomitantly with a shifting of the strong $\tilde{\nu}_{CO}$ arising from the acetyl group in compounds **2-Zn**–**5-Zn** from a very low frequency of 1639 cm^{-1} (in **5-Zn**), which we ascribe to a Zn−O−H···O=C< carbonyl group in conjugation with the porphyrin ring, to normal value of 1720 cm^{-1} (in **2-Zn**, where the acetyl group is forced out of the porphrin plane).[22] The self-assembly process is also responsible for the stacking of chromophores, as in J aggregates, which can be seen from the absorption spectra in dichloromethane at different concentrations (see Supporting Information). As the concentration decreases, the red-shifted aggregate peaks become less prominent and they are entirely absent in dilute solutions.

Racemates of **4-Zn** and **5-Zn** could be resolved satisfactorily on a chiral carbamate modified polysaccharide HPLC column (Chiralcel, OD-H), which provided fractions with enrichments varying between 78 and 95 %. Compound **2-Zn** could not be separated into enantiomers under the same conditions. With both enantiomers of **5-Zn**, after the removal of any traces of 2-propanol and water (from the HPLC eluent), self-assembly was induced in *n*-heptane and the CD-spectra of both fractions were recorded at room temperature. Signals with intense ellipticity are encountered, which are mirror imaged in the two fractions (Figure 4). While a single Cotton effect is observed for the Q aggregate band at 635 nm, an excitonic couplet appears for the broadened Soret aggregate band. For the first fraction, which was more dilute and contained less self-assembled species, the couplet is not as symmetric as for the second fraction. In the latter case the longest wavelength Cotton effect of the couplet is positive, and has a maximum at 464 nm. The trough appears at 424 nm, thus indicating that indeed the rotary power stems

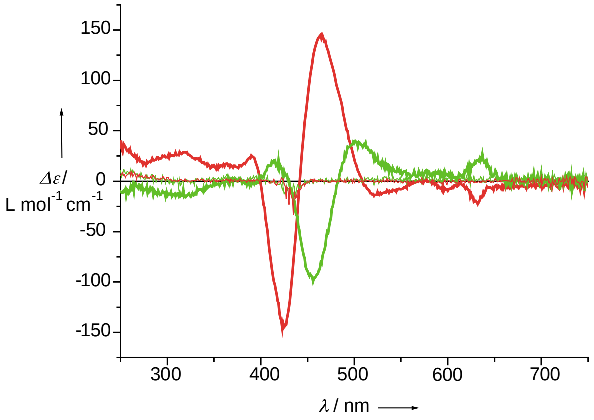

Figure 4. CD spectra of enantiomerically enriched **5-Zn** after self-assembly in *n*-heptane and after addition of methanol which disrupts the assemblies. The concentrations were 2.7 μmolar for the fraction of the firstly eluted enantiomer (green lines) and 4.7 μmolar for the fraction containing the secondly eluted enantiomer (red lines) which contained more self-assembled species as inferred from the absorption spectra. After addition of methanol the intense mirror imaged CD-signals disappear (thin red and green lines overlapping the 0 line). Pathlength was 1 cm and the averaging time was 2 s nm^{-1}. The spectra are corrected by subtracting the baseline which was measured in the same cuvette with *n*-heptane alone.

from the red-shifted broad Soret band. The addition of methanol leads to complete disassembly, and the intense CD signals vanish, which indicates that the observed chirality is not because of the chirality of the monomeric porphyrins. However, the different configurations (*R* or *S*) of the hydroxethyl groups induce the different chirality in the self-assembled species. From the intense CD signals this chirality appears to be helical in origin, and opposite helicities (*M* or *P*) are generated from the two enantiomers. Giant CD, sometimes referred as Polymer and Salt Induced (PSI) CD may appear if the chiral objects (absorbing light at around 500 nm) are greater than 50 nm.[23,24] This also affects the overall shape of the CD curves, which can vary widely because of the different sizes of self-assembled species and the scattering contribution to the CD. However, the application of the exciton chirality method[25] leads the firstly eluted enantiomer to a self-assembled species in which the chirality of the transition dipole moments must be counterclockwise (defined as negative chirality). Whereas, the second eluted enantiomer leads to an aggregate with positive chirality (i.e. a clockwise arrangement of the transition dipole moments).

The very broad absorption of a film cast from self-assembling **5-Zn** is spectacular. If light harvesting is to be harnessed by artificial devices, a broad absorption with high extinction coefficients over the entire spectral range is beneficial. This is certainly the case with the aggregates of **5-Zn** and **2-Zn**. The fluorescence is not quenched and intense signals are observed as well in solution as from cast films (see Supporting Information), which is untypical for aggregated chromophores, and in our case arises from the well defined supramolecular architecture. This should allow photosensitization of a wide band semiconductor, such as nanocrystalline titania. Until now, photosensitization has been realized only with ruthenium polypyridine complexes in the most efficient artificial solar energy conversion devices, which were pioneered by Grätzel and coworkers[26,27] or very recently with phthalocyanine dyes.[28]

Confocal fluorescence microsocopy images of self-assembled **5-Zn** onto TiO_2 nanoparticles with average dimensions of 5 nm show bright spots proving that intense fluorescence is coming out from the porphyrin aggregates that have sizes of several hundred nm. This high fluorescence could be used in a solid device similar to the dry Grätzel solar cell[29] but with appreciably lower production costs and environmentally more friendly materials than the currently used ruthenium complexes. In a fully operational device in which a hole transporter is also present, part of this fluorescence should be quenched because of the competing electron injection into the conduction band of the TiO_2 semiconductor. Efforts employing our self-assembling porphyrins as photosensitizers in such photovoltaic devices are currently under way.

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Keywords: chirality · light harvesting · photosynthesis · porphyrinoids · self-assembly

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[1] R. E. Blankenship, J. M. Olson, M. Miller in *Anoxygenic Photosynthetic Bacteria* (Eds.: R. E. Blankenship, M. T. Madigan, C. E. Bauer), Kluwer Academic Publishers, The Netherlands, **1995**, pp. 399–435.

[2] T. S. Balaban, A. R. Holzwarth, K. Schaffner, G.-J. Boender, H. J. M. de Groot, *Biochemistry* **1995**, *34*, 15259–15266.

[3] G. McDermott, S. M. Price, A. A. Freer, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdell, N. W. Isaacs, *Nature* **1995**, *374*, 517–521.

[4] W. Kühlbrandt, D. N. Wang, Y. Fujiyoshi, *Nature* **1994**, *367*, 614–621.

[5] A. Zouni, H.-T. Witt, J. Kern, P. Fromme, N. Krauss, W. Saenger, P. Orth, *Nature* **2001**, *409*, 739–743.

[6] P. Jordan, P. Fromme, H. T. Witt, O. Klukas, W. Saenger, N. Krauß, *Nature* **2001**, *411*, 909–917.

[7] B.-J. van Rossum, G.-J. Boender, F. M. Mulder, J. Raap, T. S. Balaban, A. R. Holzwarth, K. Schaffner, S. Prytulla, H. Oschkinat, H. J. M. de Groot, *Spectrochim. Acta Part A* **1998**, *54*, 1167–1176.

[8] B.-J. van Rossum, D. B. Steensgaard, F. M. Mulder, G.-J. Boender, A. R. Holzwarth, K. Schaffner, H. J. M. de Groot, *Biochemistry* **2001**, *40*, 1587–1595.

[9] J. Chiefari, K. Griebenow, F. Fages, N. Griebenow, T. S. Balaban, A. R. Holzwarth, K. Schaffner, *J. Phys. Chem.* **1995**, *99*, 1357.

[10] T. S. Balaban, A. R. Holzwarth, K. Schaffner, *J. Mol. Struct.* **1995**, *349*, 183–186.

[11] A. Jesorka, T. S. Balaban, A. R. Holzwarth, K. Schaffner, *Angew. Chem.* **1996**, *108*, 3019–3021; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2861–2863.

[12] T. S. Balaban, H. Tamiaki, A. R. Holzwarth, K. Schaffner, *J. Phys. Chem.* **1997**, *101*, 3424–3431.

[13] T. S. Balaban, A. Eichhöfer, J.-M. Lehn, *Eur. J. Org. Chem.* **2000**, 4047–4057.

[14] J. A. Eisen et al. , *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 9509–9514.

[15] S. Yagai, T. Miyatake, H. Tamiaki, *J. Org. Chem.* **2002**, *67*, 49–58.

[16] a) A. A. Bhuiyan, J. Seth, N. Yoshida, A. Osuka, D. F. Bocian, *J. Phys. Chem. B* **2000**, *104*, 10757–10764; b) K. Susumu, T. Shimidzu, K. Tanaka, H. Segawa, *Tetrahedron Lett.* **1996**, *37*, 8399–8402; c) H. Tamiaki, Y. Nagata, S. Tsuduki, *Eur. J. Org. Chem.* **1999**, 2471–2473; d) A. Tsuda, A. Nakano, H. Furuta, H. Yamochi, A. Osuka, *Angew. Chem.* **2000**, *112,* 572–575; *Angew. Chem. Int. Ed.* **2000**, *39*, 558–561;e) N. Yoshida, N. Aratani, A. Osuka, *Chem. Commun.* **2000**, 197–198; f) T. E. O. Screen, I. M. Blake, L. H. Rees, W. Clegg, S. J. Borwich, H. L. Anderson, *J. Chem. Soc. Perkin Trans. 1* **2002**, 320–329.

[17] T. S. Balaban, J. Leitich, A. R. Holzwarth, K. Schaffner, *J. Phys. Chem.* **2000**, *104*, 1362–1372.

[18] L. Dähne, *J. Am. Chem. Soc.* **1995**, *117*, 12855–12860, and references therein.

[19] M. Wang, G. L. Silva, B. A. Armitage, *J. Am. Chem. Soc.* **2000**, *122*, 9977–9986.

[20] A kind referee indicated the similar behavior between cyanine dyes, which form J aggregates in water and are disassembled by methanol, and our porphyrin assemblies which, however, are formed only in nonpolar solvents. Furthermore, similar effects such as red-shifted and broadened absorption bands, as well as the precipitation of fluffs, which are disrupted upon shaking, were observed with a water insoluble porphyrin, which was slightly soluble in methanol. These latter aggregates could be seen with TEM and had dimensions between 50 and 110 nm. It appears that this same mesoscopic behavior can thus be engineered with different supramolecular interactions. In our case, because the same functional groups are present as those in the natural self-assembling BChls, we are surely mimicking these

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antenna systems only in the absence of solvents which can compete for hydrogen bonding or zinc ligation.

[21] a) M. I. Bystrova, I. N. Mal'gosheva, A. A. Krasnovskii, *Mol. Biol.* **1979**, *13*, 440–451; b) K. M. Smith, L. A. Kehres, J. Fajer, *J. Am. Chem. Soc.* **1983**, *105*, 1387–1389.

[22] a) Two factors are responsible for the shift to lower wavenumbers of the $\tilde{\nu}_{CO}$ frequency: 1) conjugation with the porphyrin macrocycle and 2) the presence of hydrogen bonding >C=O···H–O, which can occur either with or without simultaneous ligation of the central zinc atom. In the latter case a cooperative interaction occurs: because of zinc-atom coordination, the O–H bond becomes more polarized and is thus a better hydrogen bond donor. By comparison with the corresponding diacetyl compounds, either as free bases or as the Zn complexes, one can discern the individual contributions of factors 1) and 2). An acetyl group in a β-pyrrolic position, where it is coplanar with the porphyrin plane and thus strongly conjugated, has $\tilde{\nu}_{CO} \sim 1669\ \mathrm{cm}^{-1}$ in **13** and 1666 cm^{-1} in **14**, the diacetyl precursors of **4** and **5**, respectively (for their formulae see the Supporting Information). In the self-assembled species, obtained either in concentrated dry dichloromethane solutions or in *n*-heptane, this frequency is further shifted up to 1639 cm^{-1} for **Zn-5**. This value corresponds well to that encountered in the epimers of the natural Mg complexed BChl *c* (1643 and 1653 cm^{-1}),[9] or even of the Zn complexed BChl *d* (1651 cm^{-1}).[12] A different behavior is encountered for *meso*-acetyl groups, which are twisted out of the porphyrin plane as indicated also by their longest wavelength absorption. In the 5,15-diacetyl free base porphyrin (**12**), one band is encountered at 1697 cm^{-1}. In **12-Zn** two carbonyl bands appear at 1693 cm^{-1} (with a shoulder). Also in self-assembled (*rac*)-**2-Zn** the carbonyl band is splitted (1696 and 1685 cm^{-1}). This latter case is indicative of diastereomeric assemblies, for example, a dimer, and may be present either as the *meso RS* dimer or as the enantiomorphic *RR* and *SS* dimers. In all cases the (Zn or H_2)-porphyrin breathing mode which appears between 1592 and 1605 cm^{-1} serves as a marker band; b) T. S. Balaban, D. Moss, unpublished results.

[23] D. Keller, C. Bustamante, *J. Chem. Phys.* **1986**, *84*, 2972–2980.

[24] M.-H. Kim, L. Ulibarri, D. Keller, M. F. Maestre, C. Bustamante, *J. Chem. Phys.* **1986**, *84*, 2981–2989.

[25] N. Berova, K. Nakanishi in *Circular Dichroism. Principles and Applications 2nd ed.* (Eds.: N. Berova, K. Nakanishi, R. W. Woody), Wiley-VCH, New York, **2000**, pp. 337–382.

[26] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737–740.

[27] A. Hagfeldt, M. Grätzel, *Chem. Rev.* **1995**, *95*, 49–68.

[28] J. He, G. Benkö, F. Korodi, T. Polivka, R. Lomoth, B. Akermark, L. Sun, A. Hagfeldt, V. Sundström, *J. Am. Chem. Soc.* **2002**, *124*, 4922–4932.

[29] U. Bach, D. Lupo, P. Comte, J.-E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, M. Grätzel, *Nature* **1998**, *395*, 583–585.