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Efficient Energy Transfer from Peripheral Chromophores to the Self-Assembled Zinc Chlorin Rod Antenna: A Bioinspired Light-Harvesting System to Bridge the "Green Gap"

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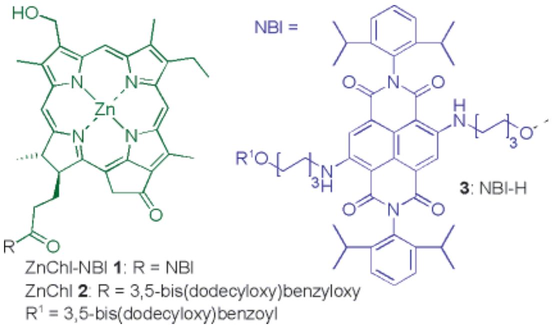
In the course of evolution, nature has developed highly complex light-harvesting (LH) systems.[1] In particular, the protein-free bacteriochlorophyll *c* (BChl *c*), *d*, and *e* aggregates in the chlorosomes of green phototrophic bacteria exhibit the highest chromophore density of all LH systems[2] and show the most extended exciton diffusion length known for dye aggregates.[2c,3] Zinc chlorins (ZnChl), which can be prepared by derivatization of Chl *a*, serve as appropriate model compounds for BChl *c* since they self-assemble into rod-shaped structures in the same way as their natural analogues.[4]

Assemblies of BChl *c* and ZnChl are very efficient in harvesting blue and red light; however, they cannot utilize the significant green region of the solar spectrum. It would be a major advancement toward efficient utilization of solar energy if such assemblies, especially those of zinc chlorins, could be connected functionally with auxiliary LH chromophores to bridge the "green gap". Here we report on such a biomimetic LH system based on the ZnChl−NBI dyad **1** that self-assembles into rod antennae, in which efficient energy transfer occurs from peripheral blue naphthalene bisimide (NBI) dyes to the core ZnChl rod. The synthesis and characterization of dyad **1** and isolated NBI **3** (Chart 1) is described in detail in the Supporting Information. The reference chromophore ZnChl **2** was prepared according to literature.[4c]

Chart 1. Chemical Structures of ZnChl−NBI **1** and Isolated Chromophores **2** and **3**



ZnChl-NBI **1**: R = NBI
ZnChl **2**: R = 3,5-bis(dodecyloxy)benzyloxy
R¹ = 3,5-bis(dodecyloxy)benzoyl

The self-assembly of BChl *c* and its ZnChl model system into tubular dye aggregates with *J*-type electronic coupling is facilitated by the interplay of three noncovalent intermolecular interactions: hydrogen bonding, $\pi-\pi$ stacking, and metal ion coordination.[5] Since the present ZnChl−NBI dyad possesses the required structural features for such interactions, it should also form self-assembled aggregates in nonpolar aprotic solvents. Indeed, UV−vis spectra of **1** (Figure 1A) revealed the characteristic bathochromic shift[4b,c] of the zinc chlorin Q_Y-band from 646 nm in THF (monomer of **1**) to 731 nm in cyclohexane/tetrachloromethane (1%), indicating *J*-type excitonic coupling of ZnChl units in the aggregates of **1**. For comparison, the UV−vis spectrum of the aggregate of the isolated chromophore ZnChl **2** is given in Figure 1B. Notably, the absorption maximum of the NBI unit in the **1** aggregate (λ_{max} = 611 nm) is slightly changed compared to that of the isolated NBI chromophore **3** (λ_{max} = 604 nm, Figure 1B), suggesting insignificant interaction between the NBI units at the periphery of ZnChl rods. This interpretation is supported by the fact that an exciton couplet was observed in the circular dichroism (CD) spectrum for the ZnChl-related optical transition at 731 nm of the self-assembly (Figure S1 in Supporting Information) due to the induced CD effect,[4c] but no CD signal is present for the NBI absorption band at 611 nm. Furthermore, the fluorescence spectrum of the aggregated species (Figure 1A) revealed a small Stokes shift of only 6 nm, which is characteristic for chlorin *J*-aggregates.[4]

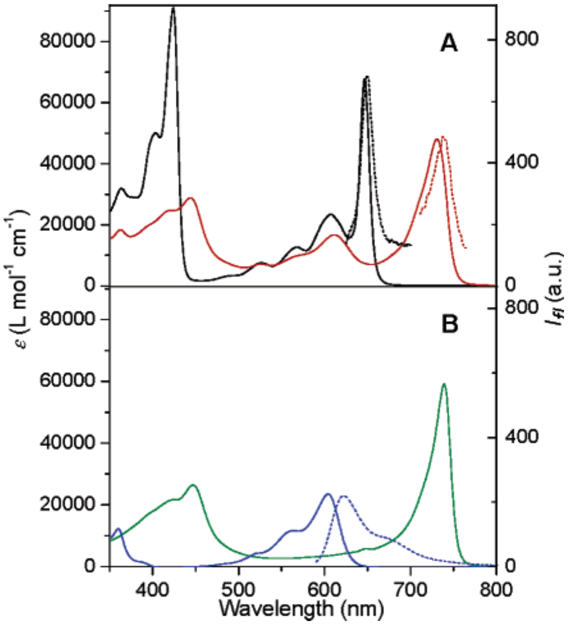


Figure 1. (A) UV−vis (solid lines) and normalized fluorescence (dashed lines, λ_{ex} = 620 nm) spectra of **1**. Monomers in THF (black); aggregates in cyclohexane/tetrachloromethane (1%) (red) at room temperature. (B) UV−vis (blue solid line) and normalized fluorescence spectrum (blue dashed line, λ_{ex} = 575 nm) of NBI **3** in cyclohexane/tetrachloromethane (1%), and UV−vis spectrum of ZnChl **2** (green) in cyclohexane/tetrachloromethane (1%)/THF (0.1%).

Not only the spectroscopic properties (vide supra) but also the structural features of ZnChl−NBI **1** self-assemblies are quite similar

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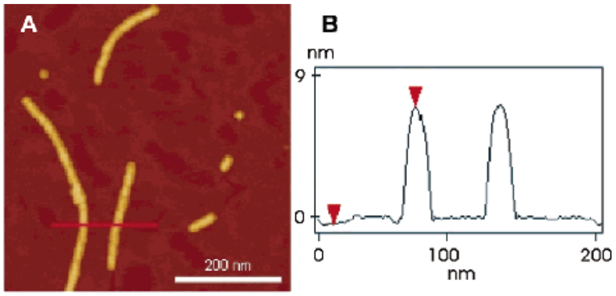

Figure 2. (A) Tapping mode AFM image of a ZnChl−NBI **1** sample, which was prepared by spin-coating from a solution of **1** ($c \sim 1 \times 10^{-5}$ M) in cyclohexane/THF (1%) onto highly ordered pyrolytic graphite (HOPG) and measured under ambient conditions. (B) Profile of the red line in (A); the vertical distance between the red triangles provides the height of the rod aggregate.

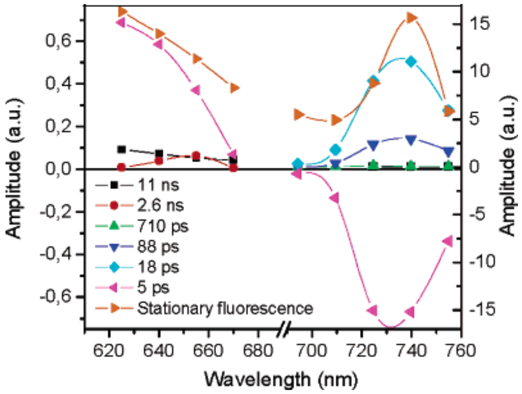

Figure 3. Fluorescence decay-associated spectra of aggregates of **1** (λ_{ex} = 620 nm; $c \sim 0.76 \times 10^{-5}$ M) in cyclohexane/tetrachloromethane (1%).

to those of the natural BChl *c* and its ZnChl model systems.[4,6] Thus, rod aggregates are observed for self-assembled dyad **1** by atomic force microscopy (AFM), as shown in Figure 2A. Direct measurements of the contour lengths of 362 rods revealed a mean value of 93 ± 75 nm. The longest observed aggregates show contour lengths in the range of 300−380 nm, and the longer rods (>100 nm) are slightly curved. The persistence length of curved rods has been estimated to be 200 ± 30 nm, indicating a pronounced stiffness of these assemblies. All rods possess a height of 7.3 ± 0.2 nm (Figure 2B), which is slightly higher than that observed previously for ZnChl rods without additional NBI dyes (5.8 ± 0.4 nm).[4c]

Having established the structural features of ZnChl−NBI self-assemblies to be a ZnChl rod bearing NBI dyes at the periphery, their suitability as artificial LH antennae was addressed. To get a detailed insight into the excited state properties of **1** aggregates, time-resolved fluorescence studies were carried out using the single photon timing technique. Selective excitation of the NBI moiety with 620 nm picosecond laser pulses resulted in three positive amplitude decay-associated (DAS) components in the wavelength region of the NBI emission ($\lambda \leq 670$ nm) (Figure 3). The dominant component shows a lifetime of 5 ps, which reflects energy transfer from NBI to the ZnChl aggregate, as evidenced by its large negative amplitude in the ZnChl emission band. Further, two small amplitude components with $\tau_F = 11$ ns and $\tau = 2.6$ ns occur in the NBI emission region. The former can be attributed to a small amount of unquenched NBI ($\tau \sim 10.5$ ns), while the latter is apparently due to small amounts of residual **1** monomer present in equilibrium with the aggregate.[7] The 5 ps component clearly describes an energy transfer process with a quantum efficiency $\phi_{\text{ET}} = k_{\text{ET}}/(k_{\text{ET}} + k_F) \geq 0.99$ (if the small amount of unquenched NBI is ignored).[8] In the ZnChl emission region, two large positive amplitude components are observed with the lifetimes $\tau = 88$ and 18 ps and a minor one of 710 ps. These components reflect the decay of the ZnChl excited states in the tubular self-assemblies of **1** that are generated by energy transfer from excited NBI dyes. Multiexponential fluorescence decay with similar lifetimes, attributed to emission from several exciton states with high oscillator strength, has been reported earlier for ZnChl aggregates without appended dyes in L-α-lecithin vesicles.[3] In previous work[3], short lifetime (<100 ps) components were assigned to quenching processes caused by small amounts of oxidized chlorin. Such quenching processes cannot be excluded for the present system. We note that such lifetimes are characteristic for intact chlorosomes. It has been shown both for chlorosomes as well as artificial chlorin aggregates that these quenching processes do not adversely affect their LH efficiencies if effective acceptors are present.[3]

It is a remarkable feature of the bichromophoric system **1** that self-assembly leads to a well-defined rod aggregate composed of strongly coupled ZnChl chromophores, while the second NBI dye at the periphery of the rod does not form aggregates. Thus, NBI provides additional LH functionality to the ZnChl antenna and thereby improves its efficiency. From the ratio of the respective cross sections of solar light absorption by aggregates of ZnChl−NBI **1** and ZnChl **2**, an increase of 26% of the total LH efficiency of ZnChl−NBI aggregates lent by appended NBI dyes is calculated.[9] The present antenna system is promising for utilization of a wider part of the solar spectrum in potential LH devices, in which the subsequent processes should be much faster than the observed decay times of the aggregate excitation. Obviously, dyad **1** differs from other known bichromophoric systems which form either amorphous materials,[10] charge transfer complexes,[11] or coaggregated stacks.[12]

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Supporting Information Available: Synthetic procedures, characterization, spectroscopic data of **1** and **3**, and complete ref 12. This material is available free of charge via Internet at http://pubs.acs.org.

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(8) The energy transfer in **1** monomers is also quantitative as time-resolved emission spectroscopy revealed (Figure S3, Supporting Information).
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