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Covalently stabilized self-assembled chlorophyll nanorods by olefin metathesis[†]

Sanchita Sengupta and Frank Würthner*

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A new chlorophyll derivative with peripheral olefinic chains has been synthesised and its self-assembly properties have been studied, revealing formation of well-defined nanorods. These nanorods were stabilized and rigidified by olefin metathesis reaction as confirmed by spectroscopic and microscopic methods.

One-dimensional self-assembled architectures such as nanorods of functional molecules have attracted considerable interest as materials for (opto)electronic devices.^{1,2} Since such devices have to operate under changing and demanding environmental conditions, it would be advantageous for durable application to fix the morphology of electronically active self-assembled materials.^{2,3} Post-polymerisation of self-assembled molecular building blocks is often utilized for the enhancement of their structural robustness.^{2–6} This has been achieved by a broad range of reaction strategies such as ring closing metathesis,^{3–5} acyclic diene metathesis (ADMET),² ring opening metathesis polymerization (ROMP),² [3+2] cycloaddition of azides and alkynes,² and radical or photopolymerisation.⁶

The light harvesting (LH) systems of green bacteria, namely, the chlorosomes,⁷ often provide the inspiration for the rational design of one-dimensional supramolecular architectures with desirable optical and electronic properties to function as artificial LH systems and (opto)electronic materials. Chlorosomal LH systems are protein-free tubular ensembles of bacteriochlorophyll (BChl) c, d, or e held together by noncovalent interactions such as hydrogen bonding, metaloxygen coordination and $\pi - \pi$ stacking.⁷ This self-assembly mode of BChls has been mimicked by using semisynthetic zinc chlorin (ZnChl) molecules⁸ that are pre-programmed for an analogous tubular mode of self-assembly in nonpolar and aqueous media.⁹⁻¹² Although post polymerisation of nanotubular assemblies based on π -conjugated systems²⁻⁶ such as hexabenzocoronenes (HBCs) and triphenylenes is well-established, to the best of our knowledge, covalently stabilized nanorods based on chlorophyll derivatives, particularly zinc chlorins, have been to date unprecedented.



Scheme 1 Synthesis of zinc chlorin 1. DCC = dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine, DPTS = 4-(dimethylamino)pyridinium p-toluenesulfonate.

For this purpose, we have synthesised a new zinc chlorin (ZnChl) derivative 1 (Scheme 1) functionalized with peripheral olefinic groups and first studied its self-assembly by spectroscopic and microscopic methods to ensure formation of nanorod assemblies. Subsequently, these assemblies were subjected to olefin metathesis reaction to obtain stabilized nanorods of this chlorophyll derivative.

The target compound ZnChl 1 was synthesised from chlorin derivative 2 in three steps according to the route depicted in Scheme 1. The chlorin carboxylic acid compound 2 was prepared from natural chlorophyll (Chl) a according to the literature procedure¹³ and was esterified with 3.4.5-triundec-10-ene-oxybenzylalcohol in the presence of coupling reagents dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) and *N*-ethyldiisopropylamine in dry dichloromethane as solvent in 56% yield. The 3¹-aldehyde functionality in ester 3 was subsequently reduced to the corresponding 31-alcohol with 10 equivalents of borane-tert-butylamine complex $(BH_3(t-Bu)NH_2)$ in CH_2Cl_2 in 82% yield. The metalation of the free base chlorin 4 with saturated solution of Zn(OAc)₂ in methanol and in tetrahydrofuran (THF) as solvent afforded the target chlorophyll derivative ZnChl 1 in 61% yield. The intermediates 3 and 4 and the final product ZnChl 1 were purified by silica gel column chromatography, followed by HPLC and characterized by ¹H NMR spectroscopy and high-resolution mass spectrometry (HRMS) (see ESI⁺ for details).

Universität Würzburg, Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Am Hubland, 97074 Würzburg, Germany.

E-mail: wuerthner@chemie.uni-wuerzburg.de

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a) 120000

100000

්පි 80000

60000

40000

20000

0+-300

400

ε/M

We have first studied the self-assembly properties of this new zinc chlorin 1 by UV/Vis and CD (circular dichroism) spectroscopy. Molecularly dissolved ZnChl 1 in polar solvent such as THF exhibits characteristic Soret and Q_v absorption bands at 428 nm and 647 nm, respectively (see ESI⁺). For aggregation studies, monomer stock solution of 1 was prepared in THF and subsequently added to nonpolar solvents like n-hexane. The UV/Vis spectrum of a solution of 1 in n-hexane/THF (100 : 1, v/v) indeed revealed the formation of aggregates as typical strongly red-shifted (up to 100 nm) absorption maxima, compared to that of monomers, which was observed due to J-type excitonic coupling¹⁴ between the S_0 - S_1 transition dipole moments of the chlorin Q_v bands (see ESI[†]).¹⁰ For further characterization of the selfassembly of zinc chlorin 1, the aggregation process was investigated by temperature-dependent UV/Vis spectroscopy in the range between 15 and 95 °C in a solution of di- n-butyl ether (20%) and *n*-heptane (80%). With increasing temperature, the aggregate band at 741 nm decreases and the monomer band at 647 nm increases (Fig. 1a). Upon cooling, the Q_v band was completely recovered, which is indicative of the reversibility of the aggregation process. The CD spectra of ZnChl 1 aggregates show a strong bisignate signal in the region of the Q_y band. With increasing temperature, the intensity of the CD signals decreases which suggests dissociation of aggregates, and the observed exciton couplet reversibly arises and disappears upon temperature change, validating again the reversibility of the self-assembly process (see ESI⁺).

Moreover, temperature-dependent UV/Vis studies suggest an isodesmic self-assembly pathway of 1 (Fig. 1b) according to the model published recently¹⁵ (for details and the equations applied for Fig. 1b-d see ESI[†]). The number-averaged degree of polymerisation, DP_N, determined by applying eqn S2[†], decreases with increasing temperature (Fig. 1c).

The average binding constant K at 288 K at two different wavelengths of the aggregate bands (741 and 448 nm) was determined to be $4.5 \times 10^6 \text{ M}^{-1}$ (see ESI⁺). By plotting the logarithm of K versus the reciprocal temperature (van't Hoff plot, Fig. 1d),

0.8

\$ 0.6

0.4

0.2

0.0

800

20

λ = 448 nn

= 3 x 10⁻⁶ N

100

60 T/°C



700 600

n-heptane/di-*n*-butyl ether (80 : 20; $c = 3.1 \times 10^{-6}$ M). (b) Degree of aggregation, α , calculated from the UV/Vis absorption at 448 nm vs. temperature (T) fitted to isodesmic model (black line). (c) Numberaveraged degree of polymerisation, DP_N , as a function of temperature. (d) van't Hoff plot (ln K vs. 1/T) for ZnChl 1.

the ΔH^0 value of -54.4 kJ mol⁻¹ and the ΔS^0 value of $-57.8 \text{ J mol}^{-1} \text{ K}^{-1}$ are obtained from the linear relationship. Gibbs free energy, ΔG^0 of -37.7 kJ mol⁻¹, was obtained at 288 K using the ΔH^0 and ΔS^0 values. Comparison of the enthalpy and entropy contributions to the Gibbs free energy changes for aggregation leads to the conclusion that the selfassembly process of ZnChl 1 is enthalpically driven, whereas it is entropically disfavored. Previously, dimerization constants for Chl a (1.0 \times 10⁴ M⁻¹), Chl b (0.8 \times 10⁴ M⁻¹), and BChl a (2.2 \times 10⁴ M⁻¹) were derived from absorption spectra according to a monomer-dimer model.¹⁶ However, binding constants for extended aggregates of chlorophylls have not been assessed so far and thermodynamic data for self-assembly of zinc chlorins have not been reported before.

Angle-dependent dynamic light scattering (DLS) studies of 1 revealed a broad intensity distribution, which is indicative of anisotropic one-dimensional extended aggregates in solution (for details see ESI[†]). Atomic force microscopy (AFM) confirmed formation of nanorod aggregates with heights of ~ 6 nm (vide infra), in very good accordance with those of previously studied 31-hydroxy zinc chlorin nanorod assemblies.10

Once the self-assembly of ZnChl 1 into nanorod structures was confirmed, olefin metathesis reaction was carried out in situ using Grubbs catalysts.⁵ To a highly diluted aggregate solution of ZnChl 1 (1.1 \times 10⁻⁶ M) in *n*-hexane/THF (100 : 1, v/v), a catalytic amount of Grubbs catalyst benzylidenebis(tricyclohexylphosphine)dichlororuthenium complex ($\sim 1 \text{ mol}\%$) was added at room temperature. The reaction mixture was stirred in the dark for 3-4 hours and subsequently quenched with few drops of ethyl vinyl ether.⁴ The reaction mixture was then filtered to remove the residual catalyst and the filtrate was subjected to UV/Vis, CD, Fourier transform infrared (FTIR) spectroscopy and AFM measurements without further purification. Since dissociation of ZnChl aggregates takes place at increased temperature,¹⁰ and in the presence of polar solvents such as THF or methanol, temperature- and solventdependent UV/Vis studies were performed on the aggregate solution of 1 after metathesis reaction. Addition of THF to aggregate solution of ZnChl 1 in n-hexane/THF (100:1 vol%) before cross-linking leads to a gradual decrease in the Q_{ν} aggregate band at 741 nm and a concomitant increase in the monomer band at 647 nm with increasing amount of THF. Above 10% THF a complete disruption of the nanorod aggregate structures was observed (Fig. 2a) owing to the strong coordination of THF to the Zn(II) metal ion. In contrast, the cross-linked nanorods of 1 after metathesis exhibit strong resistance towards aggregate disrupting solvents like THF as no significant spectral changes were observed upon addition of up to 10% of THF (Fig. 2b), thus providing evidence for the presence of covalently stabilized nanorods. Moreover, upon increasing the temperature up to 50 °C, virtually no changes in UV/Vis and CD spectra of crosslinked aggregates were observed, revealing their thermal stability (see ESI[†]). Cross-linking of the peripheral olefinic groups of rod aggregates of 1 could also be evidenced by FTIR spectroscopy as a strong decrease in the intensity of the C=C vibrational band at 1646 cm^{-1} was observed (see ESI^{\dagger}).

AFM measurements were performed on highly oriented pyrolytic graphite (HOPG) surfaces with aggregate solution $(c = 1.1 \times 10^{-6} \text{ M})$ before and after metathesis reaction. As shown in Fig. 3a and b, well-defined, flexible nanorods of



Fig. 2 (a) Solvent-dependent UV/Vis spectra of ZnChl 1 in *n*-hexane/ THF ($c = 1.1 \times 10^{-6}$ M) with variation of THF content from 1–10%; the arrows indicate spectral changes with increasing content of THF (10% THF: dotted line). (b) Spectrum of cross-linked aggregates containing 10% THF.



Fig. 3 (a) AFM height image of a sample prepared from an aggregate solution ($c = 1.1 \times 10^{-6}$ M) of ZnChl 1 in *n*-hexane/THF (100 : 1, v/v) by spin coating at 4000 rpm onto HOPG before olefin metathesis and (b) corresponding phase image. Inset in (a) shows a cross section analysis with a height of ~6 nm. (c) AFM height image of the aggregate solution of 1 after olefin metathesis reaction ($c = 1.1 \times 10^{-6}$ M) and (d) corresponding phase image.

1 with large contour lengths were observed for aggregates before metathesis reaction, while the aggregates appear much stiffer after cross-linking (Fig. 3c and d). Furthermore, AFM images indicate intra-aggregate cross-linking since isolated nanorods were observed and no bundles or network structures were visible. These observations also suggest that the nanorods are cross-linked and stabilized by the olefin metathesis reaction.

In conclusion, a novel chlorophyll derivative ZnChl **1** functionalized with peripheral olefinic groups was synthesised, which self-assembles into well-defined nanorods. For the first time, binding constants and thermodynamic data for the self-assembly of a ZnChl building block have been determined. Cross-linking within the nanorods of ZnChl **1** provided highly stable and stiff nanorods. Upon considering well-established exciton transport¹⁷ and promising photovoltaic properties¹⁸ of zinc chlorin aggregates, the present covalently stabilized one-dimensional nanorods appear to be highly promising for device application.

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