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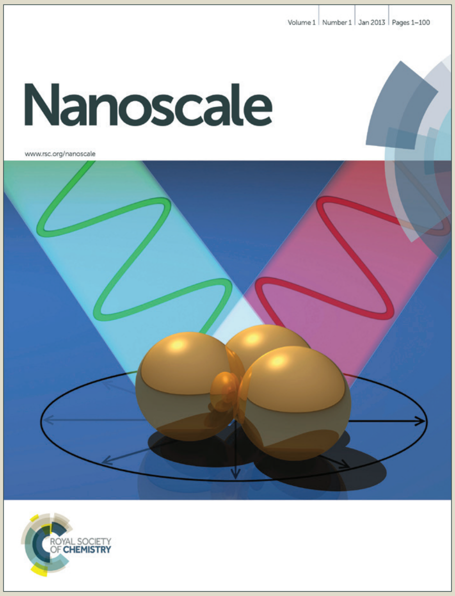

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Nanoscale bio-inspired light-harvesting system develop from self-assembled alkyl-functionalized metallochlorins nano-aggregates

Kasim Ocakoglu[a]*, Khurram S. Joya[b,c,d]*, Ersan Harputlu[a], Anna Tarnowska[e] and Daniel T. Gryko[e,f]*

Self-assembled supramolecular organization of nano-structured biomimetic light harvesting modules inside solid-state nano-templates can be exploited to develop excellent light harvesting materials for artificial photosynthetic devices. We present here a hybrid light-harvesting system mimicking the chlorosomal structures of natural photosynthetic system using synthetic zinc chlorin units (ZnChl-C_6, ZnChl-C_{12} and ZnChl-C_{18}) that are self-aggregated inside the anodic aluminum oxide (AAO) nano-channels membranes. AAO nano-templates were modified with a TiO_2 matrix and functionalized with long hydrophobic chains to facilitate the formation of supramolecular Zn-chlorin aggregates. The transparent Zn-chlorin nano-aggregates inside the alkyl-TiO_2 modified AAO nano-channels have a diameter of ~120 nm in a 60 µm length channels. UV-Vis studies and fluorescence emission spectra further confirm the formation of the supramolecular ZnChls aggregates from monomers molecules inside the alkyl-functionalized nano-channels. Our results show a novel and unique method to produce efficient and stable light harvesting assemblies for effective solar energy capture through transparent and stable nano-channels ceramic materials modified with bio-mimetic molecular self-assembled nano-aggregates.

1. Introduction

The ability of natural leaves to generate chemical energy from water and CO_2 using sunlight serves as a model guide to solve the world's current and/or future energy problem.[1-3] One strategy based on the examples provided by nature is the development of an Artificial Leaf, which employs similar chemistry and architecture utilized by natural leaves. The main components of current artificial photosynthetic solar fuel systems include robust water oxidation catalyst and efficient light harvesting modules.[4] The majority of research to date has tended to focus on the area of molecular water oxidation catalysts rather than on the development of suitable light-harvesting (LH) systems capable of trapping solar energy, which is a crucial step for an artificial photosynthetic device.[5,6] Chlorophylls and bacteriochlorophylls (BChl) in photosynthetic systems are organized to form photoactive, highly ordered self-assembled supramolecular nanostructures. These structures have been of great interest in the field of supramolecular electronics and photochemistry as well as artificial photosynthesis.[7] Nature has devised an excellent light-harvesting antenna, which is called a chlorosome and consists of self-assembled aggregates of bacteriochlorophyll molecules (BChls-c, d, and e derivatives) surrounded by galactolipid monolayer.[7,8]

These self-aggregates of chlorosomal chlorins show excellent light harvesting ability even under low light conditions as a result of non-covalent supramolecular interactions.[9-13] This supramolecular organization can be reproduced or mimicked by completely synthetic molecules and nano-structures programmed for self-assembly to make bio-mimetic chlorosomal nano-structures.[14-18] The pioneering work of Balaban and co-workers proved that simplified porphyrin-based models also undergo self-organization.[19] To demonstrate an artificial light-harvesting system based on highly-ordered chlorin units for artificial solar conversion nanodevices, it is important to develop micro/nano scale templated fabrication for aggregation on molecular level.[8,20] The macroscopic organization using an ordered porous solid therefore represents a promising approach for attaining the desired architecture and properties.[20] This provides increased stability to the antenna unit and greatly simplifies its integration into the modular architecture of an artificial solar-fuels conversion device.[20,21]

We demonstrate here, for the first time, the development of a biomimetic light harvesting module based on supramolecular metallochlorins nano-architecture inside solid-state anodic aluminum oxide (AAO) nano-channels templates. The inner walls of the AAO are coated with a sol-gel matrix of titanium (IV) propoxide. After annealing (to make TiO_2 matrices), they are treated with myristic acid to functionalizes with long hydrophobic chains as the carboxylic-groups on alkyl chains serve as surface anchoring-units. This treatment supports the formation of the supramolecular zinc chlorin (ZnChl) aggregates in AAO membranes (Figure 1a). In this study, three zinc chlorin derivatives (ZnChl-C_6, ZnChl-C_{12} and ZnChl-C_{18}) containing a hydroxyl group on 31-position and different

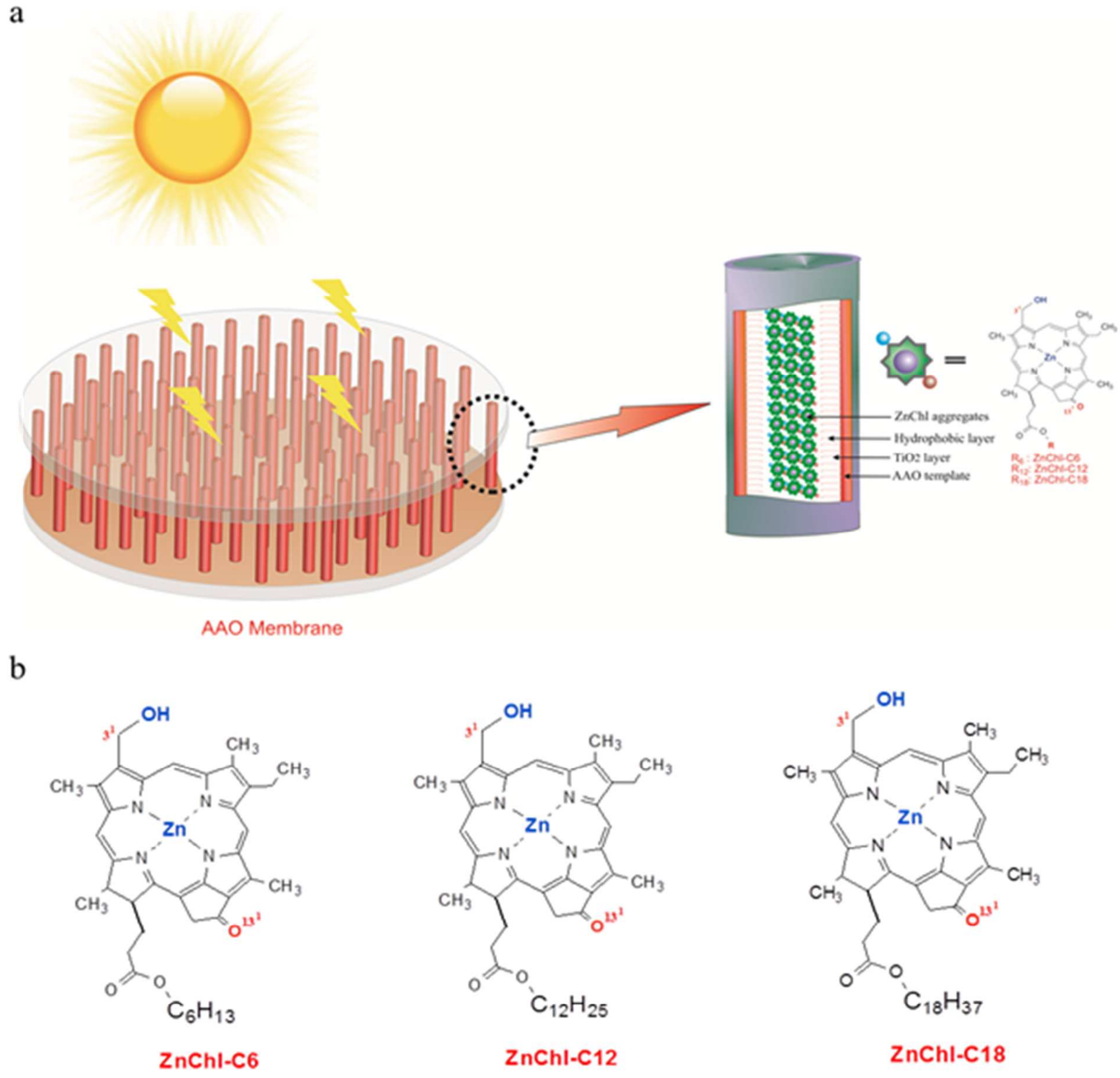

Figure 1. (a) Schematic view of AAO nanotemplates impregnated with Zn chlorin aggregates and chemical structures of zinc chlorin derivatives; (**b)** Chemical structures of zinc chlorin derivatives ZnChl-C_6, ZnChl-C_{12} and ZnChl-C_{18}.

chain lengths in the ester group were chosen as the model light-harvesting chromophores (Figure 1b) because of the self-aggregation properties exhibited in hydrophobic environments.[20] To investigate the aggregation properties of the ZnChls in the AAO system, UV-Vis absorption and steady-state fluorescence emission measurements were carried out. Herein, we report the design and synthesis of a new artificial chlorosome based light-harvesting device using an alkyl-TiO_2-AAO envelope (Figure 1a). In order to mimic a chlorosomal antenna complex, self-aggregates of semi-synthetic zinc chlorin derivatives in the presence of long hydrophobic chains displayed on the inner walls of the pores in a solid membrane have been prepared and studied.

2. Experimental

Anhydrous solvents were either distilled from appropriate drying agents or purchased from Merck and degassed prior to use by purging with dry argon and kept in air-tight bottles with molecular sieves. Synthesis details for the preparation of Zn chlorin derivatives are described in the supporting information. The self-assembled ZnChl supramolecular aggregates inside alkyl-TiO_2 modified AAO nano-channels templates (AAO-Ti-C_{13} ZnChl-C_6, AAO-Ti-C_{13} ZnChl-C_{12} and AAO-Ti-C_{13} ZnChl-C_{18}) are prepared inside the glove box under green light conditions.

2.1 Preparation of TiO_2 sol-gel

TiO_2 sol-gel was prepared by adding 14.21 g (0.05 mol) of titanium (IV) propoxide (Ti(OPr^i)$_4$) and 53.4 mL (42 g) of isopropyl alcohol were mixed and stirred for 10 min under inert atmosphere. After mixing, 1.9 g (0.1 mol) of deionized water containing two drops of HNO_3 was slowly added to this mixture. The resulting solution was stirred for an additional 30 min and then the sol was ready for coating.

2.2 Preparation of anodic aluminum oxide (AAO) templates

The AAO membranes were formed by four-step anodization in 0.3 M oxalic acid solution before TiO_2 coating step to obtain highly ordered nano channels. Subsequent treatment with a 0.1 M phosphoric acid solution (60 min at RT) widened the pores and thinned the barrier layer, simultaneously. Afterward, AAO membranes were rinsed with distilled water, ethanol, and acetone, and annealed at 90 ^{o}C for one hour under vacuum to expose Al-O bonds on the pore wall surface.

2.3 Preparation of alkyl-TiO_2-coating inside AAO nano-channels templates (AAO-Ti-C_{13})

Alumina membranes were derivatized with alkyl-TiO_2 using a two-step method. In order to introduce TiO_2 sol into the nanopores of the anodic alumina, the specimens were first treated with ethanol and then 10% of TiO_2 sol (prepared in isopropyl alcohol from the stock solution described above) at room temperature by the assistance of filter holder. The excess of the sol was removed by gas flow. To obtain porous TiO_2 coated AAO membrane, the specimen was dried at room temperature, and then annealed at 450 ^{o}C for 1 h in air. In the second step, TiO_2 coated membranes were placed in a solution of 0.05 M Myristic acid in ethanol for overnight, and washed with copious amounts of ethanol upon removal. The membranes were finally dried under vacuum.

2.4 Preparation of self-assembled ZnChl aggregates in alkyl-TiO_2 modified AAO nano-channels templates (AAO-Ti-C_{13} ZnChl)

For the preparation of self-assembled metallochlorins in TiO_2 coated nano-channels templates, an ultra-high vacuum was initially applied to the templates to remove trapped air in the nano-channels. After this important step, the templates were treated $1.25x10^{-2}$ M THF solution of metallochlorin. An excess of dry hydrocarbons such as n-hexane (THF: n-Hex, 1:99%) was added slowly and carefully into the solution, and it was left for at least 3 days (depending on the type of ZnChl derivative) without shaking. In the final step, the ZnChl imprinted inside the AAO nano-channels templates were rinsed with copious amounts *n*-hexane to clean the surface materials, and then dried under inert atmosphere.

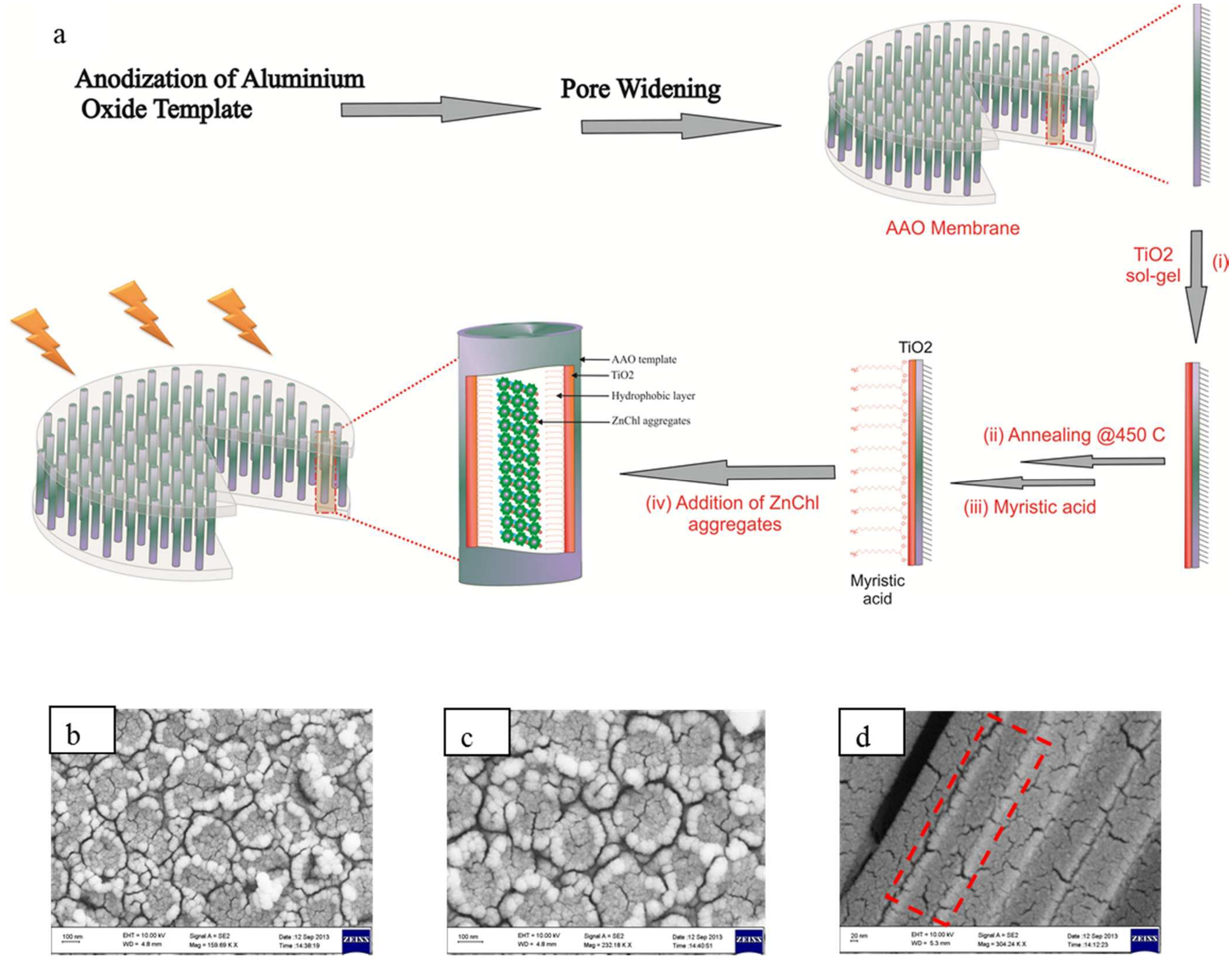

Figure 2. (**a**) Schematic view of preparation of alkyl-TiO_2 modified AAO nano-channels templates (AAO-Ti-C_{13}) and imprinting of self-assembled zinc chlorin aggregates (AAO-Ti-C_{13} ZnChl); (**b, c**) top and (**d**) cross-sectional FE-SEM images of AAO-Ti-C_{13} nano-channels template with self-assembled molecular zinc chlorin aggregates.

3. Results and discussion

3.1. Design and preparation of anodic aluminum oxide nano-channels membranes modified with alkyl-TiO_2 matrix

Despite the tremendous effort directed towards preparing chlorins[22] and bacteriochlorins[23] based entirely on synthetic procedures only a recent publication by Lindsey and co-workers has been produced. Because of the challenges associated with purely synthetic chemistry methods the semi-synthetic approach is still the preferable way to obtain chlorins able to self-organize.[24] In principle, it is possible to isolate bacteriochlorophyll c from bacteria, difficulties associated from their cell culturing prompted us to follow another approach described by Holzwarth and Tamiaki.[25] This approach consists of isolation of chlorophyll a from Spirulina maxima followed by its transformation into Zn-chlorins bearing crucial substituents, i.e. 31-hydroxy-131-oxo (Figure S1).[7,14-19] Esters containing chains varying in length were used to determine the effects of length on self-organization. Analogous compounds were previously studied in the solution (see synthetic details in SI).[14] The bio-mimetic Zn-chlorins (ZnChl-C_6, ZnChl-C_{12} and ZnChl-C_{18}) comprised within the artificial antenna unit self-assembled inside the AAO nano-template to form a solid-state unit (Figures 1-2) which displays enhanced stability compared to previous liquid phase self-assembled nanostructures.[26] This design also permits the large scale fabrication of bio-inspired light harvesting system.

The AAO membrane containing the self-assembled BChl antenna in the nano-channels combines excellent optical transparency with high chemical and mechanical stability. AAO nano-templates are prepared by a four-step anodization process followed by a pore widening treatment (see Supporting Information). In order to provide a favourable environment for the formation of supramolecular ZnChl aggregates in the nano-channels of the AAO membranes, the inner walls were coated with a sol-gel matrix of titanium dioxide. TiO_2 sol-gel was prepared from titanium (IV) propoxide and isopropyl alcohol under inert atmosphere and is detailed in the experimental section (see Supporting Information). The sol-gel process is one of the most promising methods which allow the construction of artificial light-harvesting systems similar to a lipid monolayer in a chlorosome. Condensation of alkoxide of titanium(IV) under appropriate conditions, and annealing steps give rise to the formation of a TiO_2 network. The XRD pattern of TiO_2 modified AAO nano-channels templates is shown in Figure S2 (see Supporting Information for XRD details). The substrate peaks are indicated by stars. The synthesized titanium oxide resembles the anatase phase of titanium oxide (JCPDS file no. 00-021-1272). The calculated lattice parameters of TiO_2 were found to be a= 0.3786 nm, and c= 0.9515 nm. Thus the XRD patterns of the synthesized TiO_2 confirmed the anatase phase of TiO_2 present in the AAO nano-templates. Next, the inner walls of the TiO_2 coated AAO nano-channels were functionalized with a layer of long alkyl myristic acid. These long hydrophobic chains displayed on the inner surface promote the formation of self-aggregate chlorins molecules inside the nano-channels (Figure 2a). Alkyl-TiO_2-coating AAO nano- channels templates (AAO-Ti-C_{13}) were highly uniform and produced optimal optical transparency (Figure S3).

The presence of organic species (alkyl chains) on TiO_2 network inside the AAO nano-channels was verified by Fourier transform infrared attenuated total reflection (FTIR-ATR) spectroscopy. Solid-state FTIR-ATR spectrum of alkyl-TiO_2 modified AAO templates is shown in Figure S4 (see Supporting Information for further details). The C-H stretch vibrations of the alkyl chain of myristic acid are observed in both spectra between 2847 and 2954 cm^{-1}. The spectrum of pure myristic acid shows the C=O stretch vibration at 1697 cm^{-1}. The new bands were observed in the spectrum of the myristic acid treated TiO_2 surface at 1640, 1697, 1588, 1463 and 1426 cm^{-1} originate from carboxylate binding to the TiO_2 surface.[27,28] The interaction between myristic acid and TiO_2 give rise to two different complex formations; a bridging complex and a bidentate complex. The absorption bands observed at ν_a(1588 cm^{-1}) and ν_s(1463 cm^{-1}) can be ascribed to the a bridging complex, and the bands observed at ν_a(1554 cm^{-1}) and ν_s(1426 cm^{-1}) can be attributed to a bidentate complex as previously reported for stearic acid.[27,28] The FTIR spectrum shows that complexation of the myristic acid to the TiO_2 surface occurs via a strong ionic/covalent bond.[27] This ensures that the inner walls of the nano-channels are compatible for different organic solvents.

3.2. Self-assembly of ZnChl aggregates inside alkyl-TiO_2 modified AAO nano-channels templates

Next, self-assembled ZnChl aggregates were prepared in alkyl TiO_2 modified AAO nano-channels templates (AAO-Ti-C_{13} ZnChl). The controlled filling of the AAO-Ti-C_{13} nano-channels with the self-assembled Zn chlorin molecular units (ZnChl-C_6, ZnChl-C_{12} and ZnChl-C_{18}) is the most crucial step in the preparation process. The supramolecular organization of ZnChl's and formation of their nano-aggregates inside the AAO-Ti-C_{13} nanotemplates is the first stage of organization. Monomeric ZnChl units, in the presence of a polar organic solvent such as THF, diffuse into the AAO-Ti-C_{13} nano-channels and the supramolecular aggregation is carefully controlled through the slow exchange of the non-aggregating solvent with n-hexane. A time-wise gradient of increasing nonpolar solvent was used until complete transformation of the Zn chlorin units into supramolecular nano-aggregates was achieved. The solvent was evaporated slowly in vacuum to obtain a solid-state unit of AAO-Ti-C_{13} ZnChl assembly (Figure 2a). All AAO nano-channels templates, AAO-Ti-C_{13} and self-assembled AAO-Ti-C_{13} ZnChl were highly uniform and exhibited optical transparency (Figure S3).

Structural properties of the ZnChl aggregates inside the nanochannels were further elucidated by Field emission-scanning electron microscopy (FE-SEM) studies. The organization of nano-channels in a hexagonal arrangement can be clearly observed by FE-SEM images (Figures 2b-d). The obtained TiO_2 coated nanotemplates were transparent and highly uniform, with a wormhole-like disordered structure (Figure S5). The metallochlorin aggregates were also successfully located inside the pores of the AAO nano-channels using this applied method. Metallochlorin bearing TiO_2 coated nanotemplate films examined herein have a pore diameter of ~120 nm (Figures 2, S6). The cross-sectional FE-SEM analyses show vertically oriented self-assembled tubular aggregate of ZnChl packed within the AAO-Ti- C_{13} with approximately ~120 nm diameters in a 60 µm length AAO channels (Figure 2c, S6).

3.3. Optical properties of ZnChl's monomers and solid-state ZnChl's aggregates inside AAO-Ti-C_{13}

The optical properties of ZnChls monomers and their J-aggregates formation, both in solution and inside the AAO-Ti-C_{13} nano-channels, were characterized by UV-Vis absorption and fluorescence emission spectroscopies. The formation of aggregates can be easily observed by a colour change from turquoise in monomer solutions to a pale green colour in the aggregate for both solutions and solid-state AAO modified alkyl-TiO_2 membrane. The typical UV absorbance of monomeric zinc chlorin units is around 644-647 nm and approximately 740-743 nm for supramolecular aggregates.[20,26] Figure 3 depicts UV-Vis absorption spectra of solution phase monomeric zinc chlorin derivatives (ZnChl-C_6, ZnChl-C_{12} and ZnChl-C_{18}) in a THF solution (blue-line), solution phase free-standing aggregates in THF/n-Hexane (1:99%) (red-line). The UV absorption of the solid-state ZnChl aggregates in alkyl-TiO_2 modified AAO nano-channels templates is represented by the black-line (Figure 3). The absorption spectra of ZnChls in THF/n-hexane (1:99) reveals red-shifted Soret (ca. 450 nm) and Q_y (ca. 742 nm) bands relative to the monomeric form (423, 646 nm). The decrease of the Q_y band intensity of the monomer at 646-647 nm and the increase of the aggregates band at 742 nm over time is a characteristic feature for a *J*-type excitonic coupling.[29] The solution phase nano-aggregates of the zinc chlorin are tubular with approximately 10 nm diameter and length in the range of 3-6 µm.[7,26]

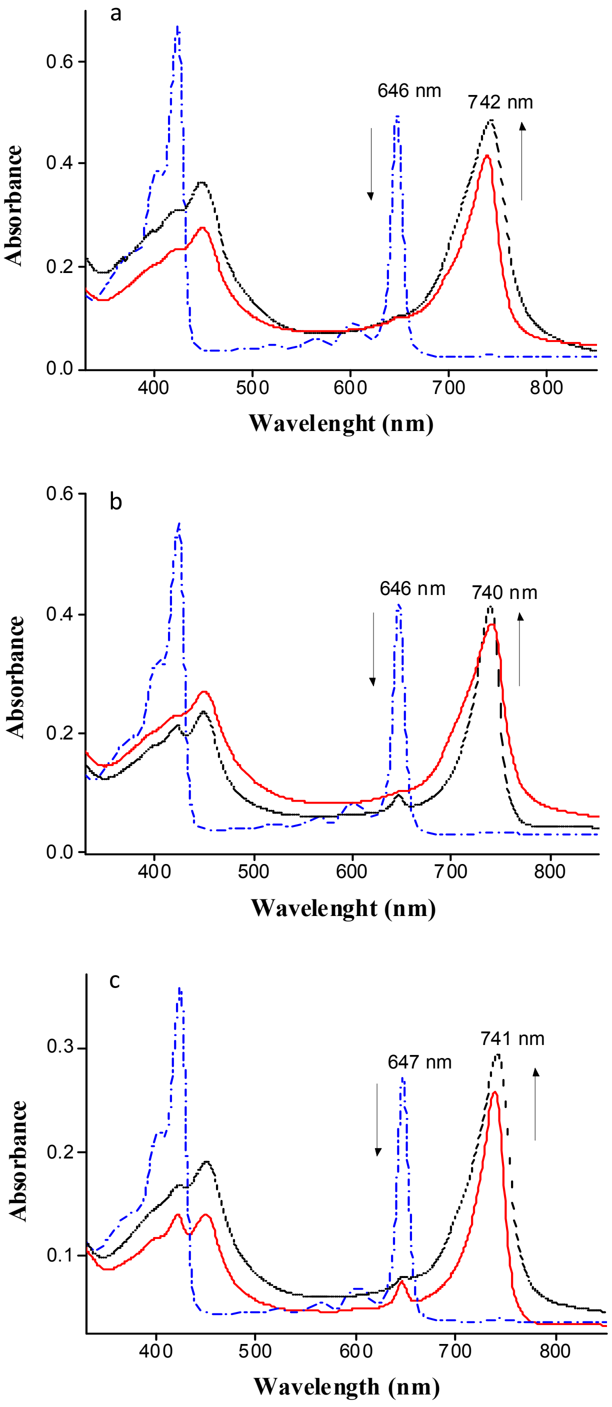

Figure 3. UV-Vis spectra of the ZnChl derivatives (**a**) ZnChl-C_6 (**b**) ZnChl-C_{12} and (**c**) ZnChl-C_{18} in (blue-line) monomeric form in THF; (red-line) solution phase free-standing aggregates in THF/n-Hexane (1:99%) and (black-line) solid-state nano-aggregates developed inside AAO-Ti-C_{13} nano-channels templates.

Compared with the absorption bands of the monomeric ZnChls, the aggregates show red-shifted absorption maxima. Such a large bathochromic shift (~100 nm) for the aggregate Q_y band compared to that of the corresponding monomers is due to spatial interactions of the transition dipole moments of the aggregated chromophores.[29] The absorption spectra of solid-state ZnChl aggregates in alkyl-TiO_2 modified AAO nano-channels templates (AAO-Ti-C_{13} ZnChl) were similar to those of solution phase free-standing aggregates in THF/n-Hexane (1:99%). These results indicated that alkyl-TiO_2 modified AAO nano-channels provided an appropriate environment for self-assembly of ZnChl by surrounding the aggregates similar to natural chlorosomes. The small baseline increase in absorbance of the AAO-Ti-C_{13} ZnChl system at shorter wavelength is ascribed to the scattering of light by the large aggregates in solid state.

Figure 4 shows a comparison of Steady-State Fluorescence Spectra of zinc chlorin derivatives, ZnChl-C_6, ZnChl-C_{12} and ZnChl-C_{18}, both monomer forms in THF and solid-state aggregates in AAO-Ti-C_{13} nano-channels. Monomer forms of the ZnChls in THF at 298 K exhibit a luminescence consisting of a single band and one small shoulder with a maximum at 650 nm and 703 nm (λ_{ex}: 450

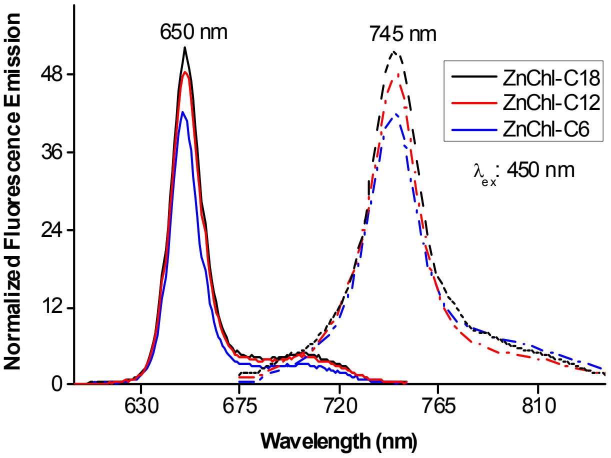

Figure 4. Steady-State Fluorescence Spectra of zinc chlorin derivatives, ZnChl-C_6 (blue-line), ZnChl-C_{12} (red-line) and ZnChl-C_{18} (black-line). Solid-lines show monomer forms in THF, and dashed-lines show solid-state aggregates in *AAO-Ti-C_{13}* nano-channels. λ_{ex}: 450 nm.

nm), respectively for all compounds. A small shoulder observed in polar solvents such as THF for monomer forms might be ascribed to small aggregate formations, most likely trimers and tetramers. The ZnChl solid-state aggregate forms in AAO-Ti-C_{13} nano-channels exhibit an emission spectra consisting of a single band with a maximum at 745nm (λ_{ex}: 450 nm). A pronounced bathochromic shift of the emission maxima upon self-assembly from 650 nm (monomers in solution) to 745 nm (aggregates in AAO-Ti-C_{13} nano-channels) is an indication of tightly packed ZnChls aggregates.

4. Conclusions

In conclusion, we developed a novel bio-mimetic supramolecular nanostructured light harvesting module using synthetically modified zinc chlorin units self-assembled inside a solid-state AAO nano-template. Additionally, we demonstrated the ability to form self-assembled *J*-aggregates of non-natural chlorins in inorganic nanochannels. Our hybrid light-harvesting system mimics the chlorosomal structures of the green photosynthetic bacteria, and is prepared from bio-mimetic Zn-chlorins derivatives (ZnChl-C_6, ZnChl-C_{12} and ZnChl-C_{18}) self-assembled inside an AAO nano-template. As predicted, the designed solid-state platform provided an enhanced stability than previous self-assembled nanostructures. Commercially available AAO nano-templates were modified by a four-step anodization process followed by a pore widening treatment. The inner walls of the AAO nano-channels were coated with alkyl-TiO_2 to provide a favorable environment for the formation of supramolecular ZnChl aggregates inside the nano-channels of the AAO membranes. This design permits the large scale fabrication of these bio-mimetic light harvesting materials and exhibits excellent optical transparency with high chemical and mechanical stability. The formation of nano-aggregates inside the alkyl-TiO_2 modified AAO nano-channels templates were examined by FE-SEM studies revealing has a pore diameter of ~120 nm in a 60 μm length AAO channels. Optical studies further confirmed the development of the supramolecular ZnChls *J*-aggregates from monomers molecules inside the alkyl-TiO_2 modified AAO nano-channels templates (AAO-Ti-C_{13} ZnChl). Our results show a unique strategy for efficient and stable light harvesting modules for solar energy capture through transparent ceramic light-harvesting materials modified with bio-mimetic molecular self-assembled nano-aggregates. Although the study was focused on metallochlorins, this method can be extended to other light harvesting dye systems for solar cell applications or artificial photosynthesis. Moreover, this method paves the way for easy implementation of alternatives (e.g. carbon nanotube structures) for a wide range of electronic applications. In combination with solar energy capture and appropriate water splitting catalyst[30] along with H_2 generating complex,[31] this system can be employed to develop the stand-alone photocatalytic device, the artificial leaf, for making solar fuels.

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Notes and references

[a] Advanced Technology Research & Application Center, Mersin University, Ciftlikkoy Campus, TR-33343 Mersin, Turkey. E-mail: kasim.ocakoglu@mersin.edu.tr; Fax: (+90) 324-361-0153
[b] Leiden Institute of Chemistry, Leiden University
Einsteinweg 55, P.O. Box 9502, 2300 RA, Leiden, The Netherlands. E-mail: khurramsj@chem.leidenuniv.nl; Fax: (+31) 71-527-4603
[c] Division of Physical Sciences and Engineering, KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST), 4700 KAUST, Thuwal 23955-6900, Saudi Arabia
[d] Department of Chemistry, University of Engineering and Technology, GT Road, 54890, Lahore, Punjab, Pakistan
[e] Faculty of Chemistry, Warsaw University of Technology
Noakowskiego 3, 00-664 Warsaw, Poland. E-mail: dtgryko@icho.edu.pl; Fax: (+48) 22-632-6681
[f] Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44-52, 01-224 Warsaw, Poland

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