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A nanoscale bio-inspired light-harvesting system developed from self-assembled alkyl-functionalized metallochlorin nano-aggregates

Kasim Ocakoglu[1], Khurram S.Joya[2*], Ersan Harputlu[1], Anna Tarnowska[3] and Daniel T. Gryko[3,4*]*

[1]Advanced Technology Research & Application Center, Mersin University, Ciftlikkoy Campus, TR-33343 Mersin, Turkey.

[2]Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands.

[3]Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland.

[4]Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44-52, 01-224 Warsaw, Poland.

Experimental details. All chemicals were purchased from commercial sources, and used as received. Titanium (IV) propoxide ($Ti(OPr^i)_4$), were purchased from Sigma-Aldrich. Anodic aluminum oxide (AAO) membranes with an average pore diameter of 0.2 μm (Anodisc 13) and stainless steel syringe type holder (suitable for Anodisc 13) were purchased from Whatman International Ltd. Field emission-scanning electron microscopy (FE-SEM) images were acquired using a Zeiss/Supra 55 FE-SEM, and the samples were platinum coated prior to FE-SEM measurements. The phase purity and structural analysis of the films were determined by X-ray diffraction (XRD) using a Bruker D8 Advanced powder diffractometer with a CuKα (0.15406 nm) radiation source. The infrared (IR) spectra are obtained by using Perkin-Elmer, FT-IR/MIR-FIR (ATR) spectrophotometer. Absorption spectra were recorded with a Shimadzu UV-2102 UV-Vis spectrophotometer either using a 1 cm path length quartz cell for the samples in solution or a specially prepared cell composed of two sealed windows between which the membranes were placed (path length 60 μm). Chemical structures of zinc chlorin derivatives are shown in Figure 1. ^1H NMR spectra were performed on a Varian on a Varian 500 MHz NMR spectrometer using residual solvent peaks as internal standards. The mass spectra were obtained via electrospray ionization (ESI-MS), and matrix-assisted laser desorption/ionization (MALDI). Chlorophyll *a* was extracted from Spirulina Maxima purchased from Bienenschwarmmm (Germany). Zinc chlorin derivatives were synthesized according to previously reported method [1]. Synthetic details and characterization of the compounds are described below.

Synthesis and Chemical Characterization of Zinc chlorophyll-a derivatives

Synthesis of zinc hexyl 3-devinyl-3-hydroxymethyl-pyropheophorbide-a (ZnChl-C_6)

Hexyl 3-devinyl-3-hydroxymethylpyropheophorbide-*a* **4** (248 mg, 398.7 μmol) was dissolved in the mixture of MeOH (25 ml) and CH_2Cl_2 (100 ml). Subsequently, $Zn(OAc)_2$ (anhydrous) (88.5 mg, 398.7 μmol) was added to the resulted solution and mixture was refluxed for 3.5 h. After reaction completion, 4% $NaHCO_3$(aq) was added and stirred for additional 15 min. Then it was washed with water, dried over sodium sulfate and evaporated. The resulting residue was washed with hexane to give the corresponding zinc complex ***ZnChl-C6*** (229.7 mg, 334.8 μmol, 84%) as a dark green solid. UV-VIS (MeOH) λ_{max} 652 (0.835), 605 (0.154), 575 (0.080), 528 (0.028), 426 (0.920), 407 (0.721), 324 (0.320). ^{1}H NMR (DMSO) 9.58, 9.34, 8.46 (each 1H, s, 5, 10, 20-H), 5.61 (2H, d, *J* = 5 Hz, 3-CH$_2$), 5.54 (1H, t, *J* = 5.5 Hz, 3^1-OH), 5.09, 5.01 (each 1H, d, *J* = 19.5 Hz, 13^1-CH$_2$), 4.54-4.48 (1H, m, 18-H), 4.27 (1H, m, 17-H), 3.95-3.90, 3.87-3.83 (each 1H, m, 17^2-COOCH$_2$), 3.76 (2H, q, *J* = 7 Hz, 8-CH$_2$), 3.58 (3H, s, 12-CH$_3$), 3.26 (3H, s, 2-CH$_3$), 3.24 (3H, s, 7-CH$_3$), 2.61–2.52, 2.25–2.17 (each 2H, m, 17-CH$_2$CH$_2$), 1.74 (3H, d, *J* = 7.5 Hz, 18-CH$_3$), 1.66 (3H, t, *J* = 7.5 Hz, 81-CH$_3$), 1.19-1.15 (8H, m, 172-COOC(CH$_2$)$_4$), 0.79 (3H, t, *J* = 7 Hz, 17^2-COOC$_5$CH$_3$). MS (ESI) found: *m*/*z* 684.3. Calcd. for $C_{38}H_{44}N_4O_4Zn$: M$^+$, 684.3.

Synthesis of zinc dodecyl 3-devinyl-3-hydroxymethyl-pyropheophorbide-a (ZnChl-C_{12})

Similar to the synthesis of ***ZnChl-C6***, zinc metalation of **8** (300 mg, 424.9 μmol) gave ***ZnChl-C12*** (281 mg, 364.9 μmol, 86%) as a dark green solid. UV-VIS (MeOH) λ_{max} 649 (0.606), 602 (0.116), 554 (0.061), 513 (0.050), 423 (0.957), 403 (0.611), 313 (0.221). ^{1}H NMR (DMSO) 9.59, 9.36, 8.46 (each 1H, s, 5,15, 20-H), 5.62 (2H, s, 3-CH$_2$), 5.59 (1H, br-s, 3^1-OH) 5.11, 5.02 (each 1H, d, *J* = 19.5 Hz, 13^1-CH$_2$), 4.51 (1H, m, 18-H), 4.25 (1H, m, 17-H), 3.92, 3.84 (each 1H, m, 17^2-COOCH$_2$), 3.77 (2H, q, *J* = 7.5 Hz, 8-CH$_2$), 3.59 (3H, s, 12-CH$_3$), 3.27 (3H, s, 2-CH$_3$), 3.25 (3H, s, 7-CH$_3$), 2.64–2.53, 2.27–2.18, (each 2H, m, 17-CH$_2$CH$_2$), 1.75 (3H, d, *J* = 7.5 Hz, 18-CH$_3$), 1.67 (3H, t, *J* = 7.5 Hz, 8^1-CH$_3$), 1.36 (2H, m, 17^2-COOCCH$_2$), 1.22–1.04 (18H, m, 17^2-COOC$_2$(CH$_2$)$_8$), 0.80 (3H, t, *J* = 7 Hz, 17^2-OOC$_{10}$CH$_3$). MS (MALDI) found: *m*/*z* 768.4. Calcd. for $C_{44}H_{56}N_4O_4Zn$: M$^+$, 768.4.

Synthesis of zinc octadecyl 3-devinyl-3-hydroxymethyl-pyropheophorbide-a (ZnChl-C_{18})

Similar to the synthesis of ***ZnChl-C6***, zinc metalation of **9** (300 mg, 379.3 μmol) gave ***ZnChl-C18*** (271 mg, 317.1 μmol, 84%) as a dark green solid. UV-VIS (MeOH) λ_{max} 652 (0.623), 607 (0.112), 575 (0.057), 528 (0.018), 426 (0.676), 408 (0.524), 324 (0.222). ^{1}H NMR (DMSO) 9.57 , 9.34 , 8.45 (each 1H, s, 5, 10, 20-H), 5.61(2H, s, 3-CH$_2$), 5.54 (1H, br-s, 3^1-OH), 5.09, 5.00 (each 1H, d, *J* = 19.5 Hz, 13^1-CH$_2$), 4.55-4.46 (1H, m, 18-H), 4.27-4.21 (1H, m, 17-H), 3.94-3.3.88, 3.86-3.79 (each 1H, m, 17^2-COOCH$_2$), 3.75 (2H, q, *J* = 7 Hz, 8-CH$_2$), 3.57 (3H, s, 12-CH$_3$), 3.25 (3H, s, 2-CH$_3$), 3.24 (3H, s, 7-CH$_3$), 2.65–2.50, 2.30–

2.15, (2H, 1H, m, 17-CH_2CH_2), 1.74 (3H, d, J = 7 Hz, 18-CH_3), 1.66 (3H, t, J = 7.5 Hz, 8^1-CH_3), 1.30-1.04 (32H, m, 17^2-$COOC_2(CH_2)_{16}$), 0.82 (3H, t, J = 7 Hz, 17^2-$COOC_{17}CH_3$). MS (MALDI) found: *m*/*z* 852. Calcd. for $C_{50}H_{68}N_4O_4Zn$: M^+, 852.

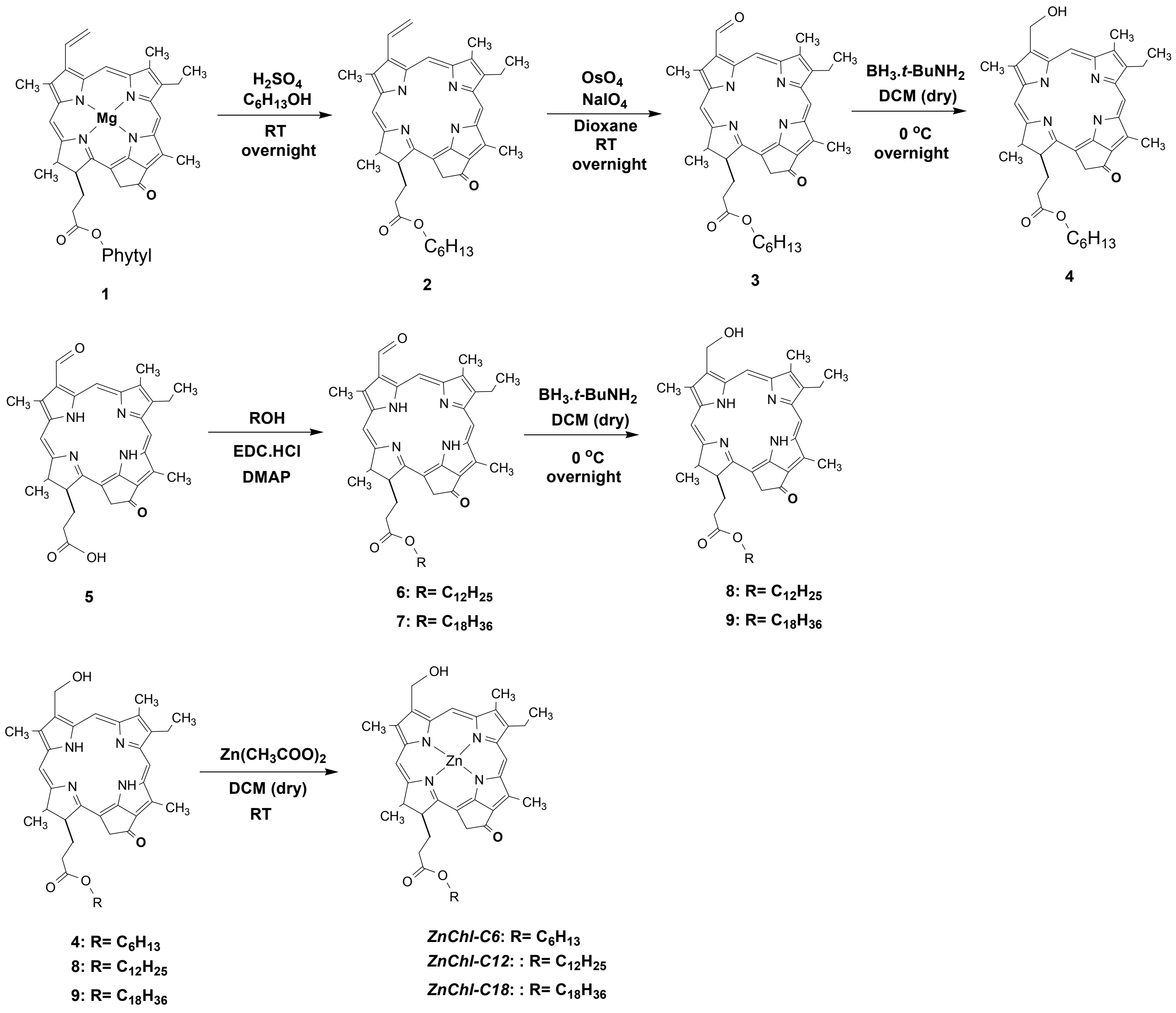

Figure S1. Synthetic Routes for the Zinc Chlorin Complexes, *ZnChl*-C_6, *ZnChl*-C_{12} and *ZnChl*-C_{18}.

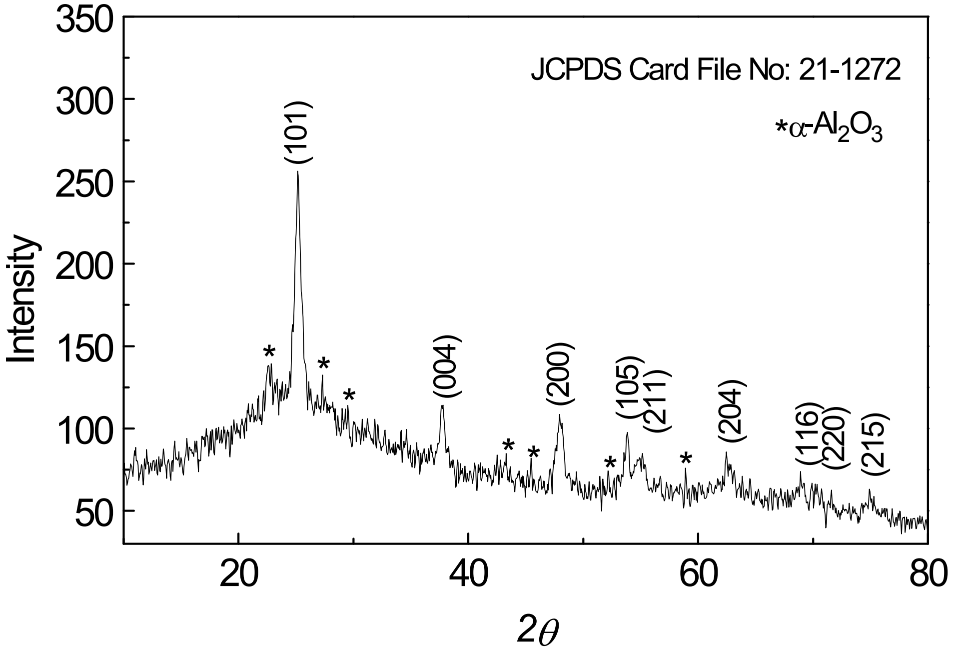

Figure S2. XRD pattern of TiO_2-coated AAO nano-template.

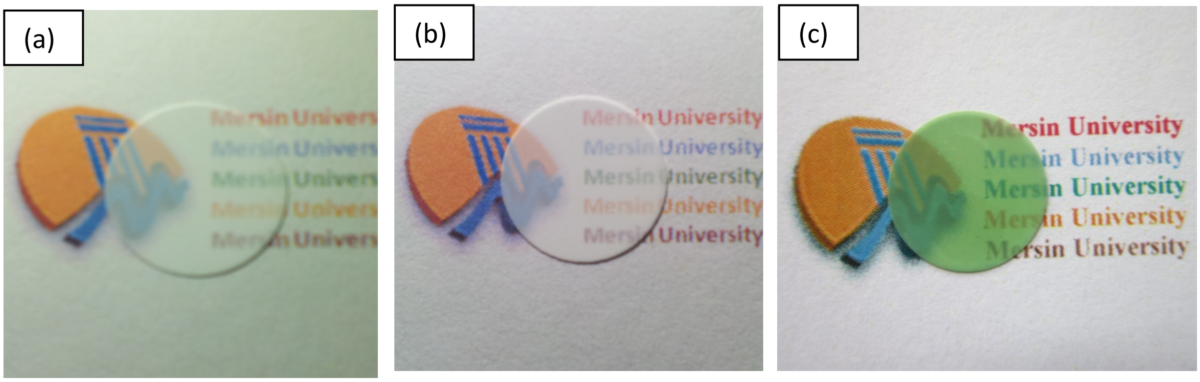

Figure S3. Pictures of AAO nano-channels templates (a), alkyl-TiO_2 modified AAO nano-channels templates (*AAO-Ti-C_{13}*) (b), and ZnChl aggregates in alkyl-TiO_2 modified AAO nano-channels templates (*AAO-Ti-C_{13} ZnChl*) (c).

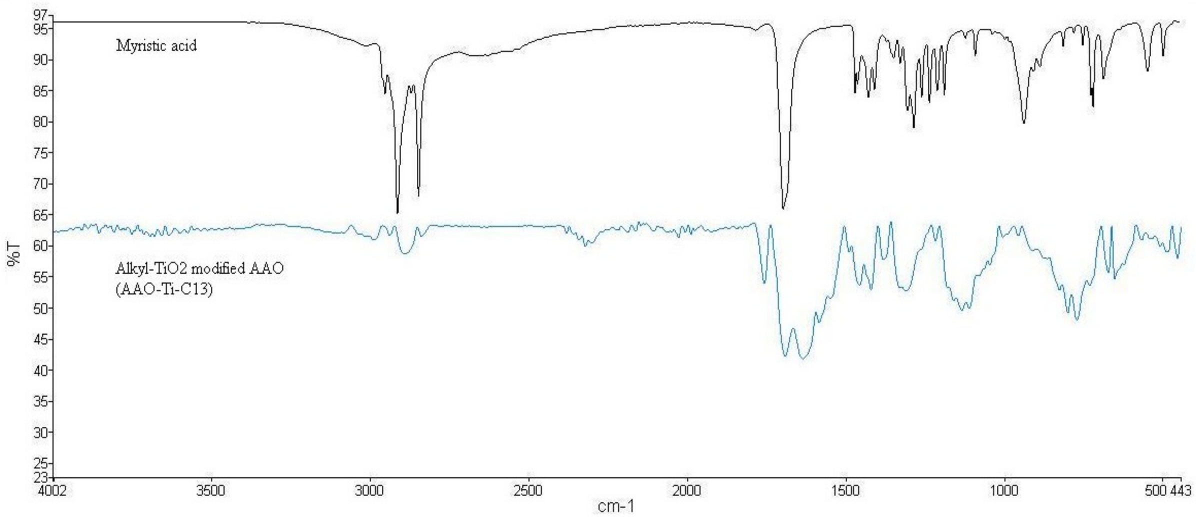

Figure S4. FTIR-ATR spectra of myristic acid (black line) and alkyl-TiO_2 modified AAO nano-channels templates (*AAO-Ti-*C_{13}) (blue line).

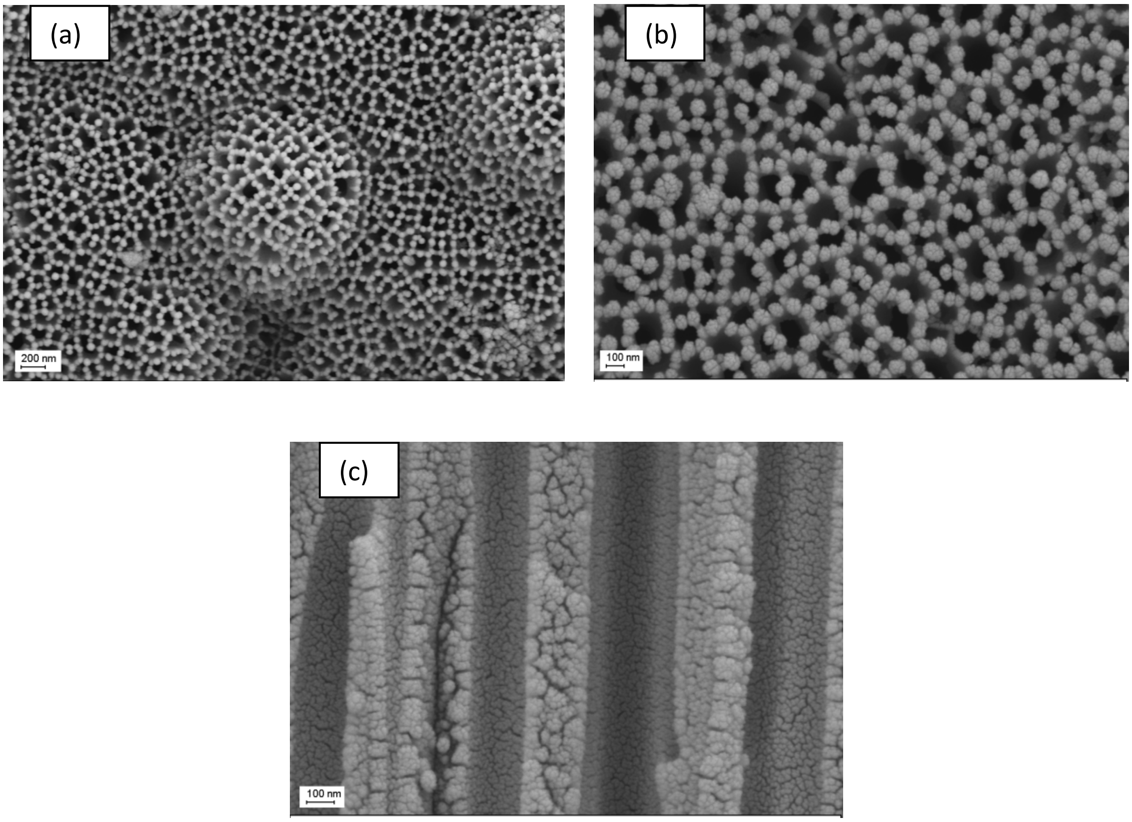

Figure S5. Top (a, b) and cross-sectional (c) view FE-SEM images of alkyl-TiO_2-coated nano-template (*AAO-Ti-*C_{13}).

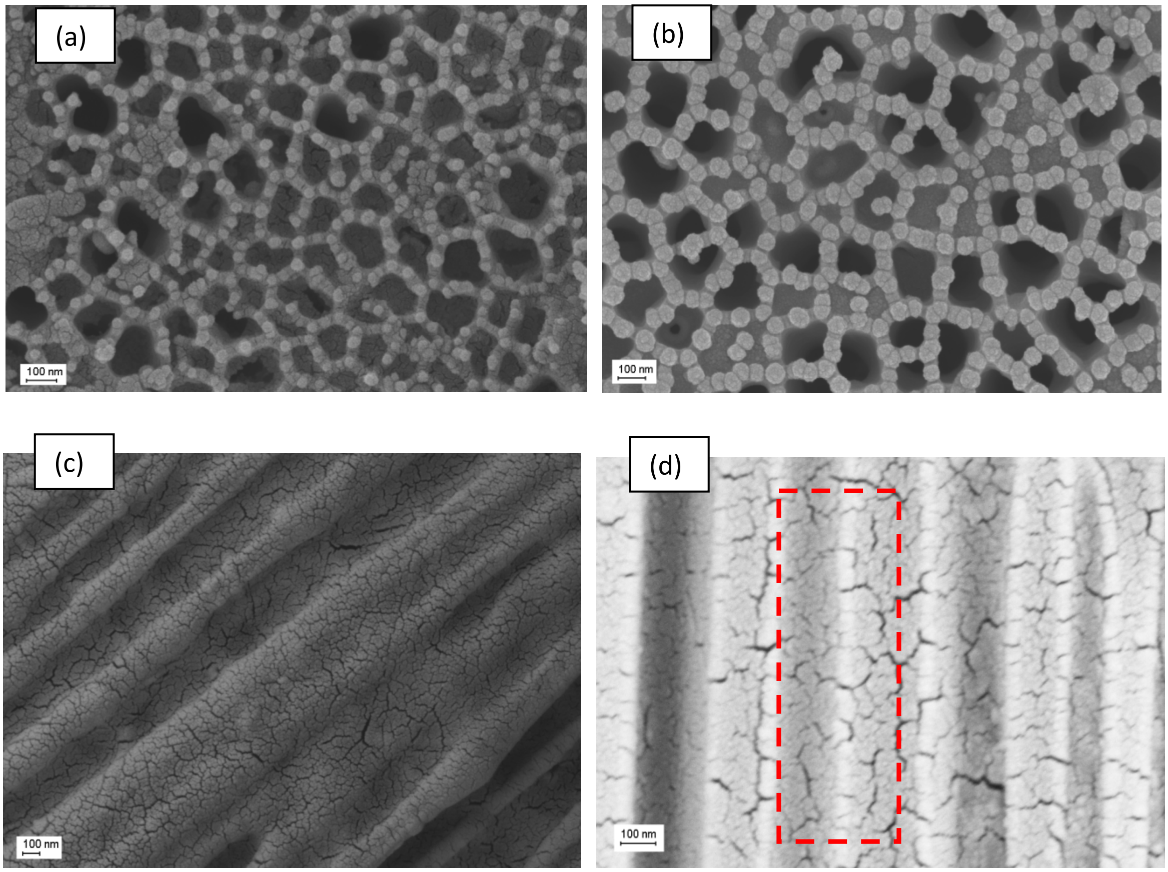

Figure S6. Top (a, b) and cross-sectional (c-d) view FE-SEM images of self-assembled ZnChl-C_{12} aggregates in alkyl-TiO_2 modified AAO nano-channels templates (*AAO-Ti-C_{13} ZnChl*).

References

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