Supplementary Supporting Information

Dye Encapsulation and Release by a Zinc-Porphyrin Pincer System through Morphological Transformations

Betsy Marydasan, Akhil. K. Nair and Danaboyina Ramaiah*
Photosciences and Photonics, Chemical Sciences and Technology Division
CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST)
Trivandrum 695 019, INDIA
Tel: (+91) 471 2515362; Fax: (+91) 471 2490186 or 2491712
E-mail: rama@niist.res.in or d_ramaiah@rediffmail.com

1. Experimental Techniques

A. General Methods. Melting points of various compounds were determined on Mel Temp melting point apparatus. The electronic absorption spectra were recorded on a Shimadzu UV-3101 or 2401PC UV-VIS-NIR scanning spectrophotometer. The fluorescence spectra were recorded on a SPEX-Fluorolog F112X spectrofluorimeter. ^{1}H and ^{13}C NMR spectra were recorded on a 300 or 500 MHz Bruker advanced DPX spectrometers with chemical shifts reported relative to TMS. All the solvents used were purified and distilled before use.

B. Microscopic analysis of samples. The picolylamine linked porphyrins **1**-**3** (10^{-4} M) were dissolved in methanol as well as in water and drop casted on the top of Al grid for scanning electron microscope (SEM), Cu grid for transmission electron microscope (TEM) and mica surface for atomic force microscope (AFM) analysis. The AFM images were recorded under ambient conditions using a NTEGRA (NT-MDT) and operated with the use of tapping mode regime. Micro-fabricated TiN cantilever tips (NSG10) with a resonance frequency of 299 kHz and a spring constant of 20-80 Nm^{-1} were used. AFM section analysis was done offline. Samples for the imaging were prepared by drop casting the solution of compounds **1-3** on freshly cleaved mica surfaces at the required concentrations and at ambient conditions. TEM measurements were carried out in JEOL 100 kV high resolution transmission electron microscope and the samples were prepared by drop casting the same solution (10^{-4} M) used for other spectroscopic investigation onto a carbon coated copper grid and solvent was allowed to evaporate. The SEM images were recorded by using ZEISS EVO MA and LS series scanning electron microscope. The operating range was between 100-230V at 50-60Hz single phase with a consumption of 2.5 kVA. The sample solution (10^{-4} M) in methanol and in water was drop casted directly on the top of the aluminium grid and the solvents were allowed to evaporate at ambient conditions.

C. Calculation of association constants (K_{ass}). The compound **3** (7.5 μM) and HPTS dye ($8\ \mu M$) were prepared in methanol. The binding affinities were calculated using Benesi-Hildebrand equation 1,

$$\frac{1}{(I_f - I_{ob})} = \frac{1}{(I_f - I_{fc})} + \frac{1}{K\,(I_f - I_{fc})\,[Ligand]} \quad (1)$$

where, K is the equilibrium constant, I_f is the fluorescence of **3**, I_{ob} is the observed fluorescence and I_{fc} is the fluorescence at saturation.

2. Synthesis and characterization of compounds 1, 2 and 3

A. *Synthesis of (2,2'-dipicolylamino)methyl 5,10,15,20 tetrakis- phenyl- porphyrin (**1**)*: To a mixture of 5,10,15,20-tetrakis(α-bromo-*p*-tolyl)porphyrin (500 mg,0.507 mmol), 2,2`-dipicolylamine (300 mg, 1.52 mmol) and K_2CO_3 (275 mg, 2.02 mmol) in anhydrous DMF (10 mL) was added KI (82 mg, 0.507 mmol, dissolved in 4 mL of anhydrous DMF) drop wise over a period of 1 h at 25 ^{o}C. After stirring for 30 min at 25 ^{o}C, the reaction mixture was diluted with 1N HCl (15 mL) and washed twice with ethyl acetate. The aqueous layer was treated with 4N NaOH (50 mL), and extracted twice with a mixture (1:1) of ethyl acetate and THF. The combined organic layers were washed with water followed by dried over Na_2SO_4. After removal of the solvent under vacuum, the residue was washed with toluene to remove the unreacted starting material. Further the obtained

compound was purified through recrystallization from a mixture (1:1) of dichloromethane and methanol to give purple colored porphyrin derivative **1**.

Yield: 76%. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) (δ) -2.8 (s, 2H), 8.77 (s, 8H), 8.61 (d, 8H, J=4.5Hz), 8.14 (d, 8H, J= 7.5Hz), 7.77 (t, 24H, J=15Hz), 7.22 (t, 8H, J= 11Hz), 4.0 (d, 24H, J=11.5Hz). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 194.1, 159.4, 152.8, 150.7, 149.6, 138.9, 137.8, 135.3, 134.4, 128.7, 127.6, 124.1, 123.8, 122.7, 120.26, 60.24, 58.43, 50.97. Anal; HRMS (FAB): m/z calcd for $C_{96}H_{82}N_{16}$: 1459.69; found (M+1) $^{+}$ 1461.52.

B. *Synthesis of Zn(II) (2,2'-dipicolylamino)methyl-5,10,15,20-tetrakisphenylporphyrin (**2**):* A solution of 5,10,15,20-tetrakis(α-bromo-*p*-tolyl)porphyrin (200 mg, 0.2 mmol) in a mixture (3:1) of methanol and chloroform was added one equivalent of zinc nitrate (0.2mmol) drop wise ovser a period of 1 h and the reaction mixture was stirred for 1 h at 25 ^{o}C. Evaporation of the solvent gave a residue which was washed with chloroform and a mixture (1:1) of hexane and dichloromethane to remove the unreacted starting material. To a mixture of the above obtained product (200 mg, 0.19 mmol), 2,2`-dipicolylamine (95 mg, 0.48 mmol), and K_2CO_3 (105 mg, 0.76 mmol) in anhydrous DMF (10 mL), KI (31 mg, 0.19 mmol); dissolved in 4 mL of DMF was added drop wise over a period of 1 h at 25 ^{o}C. After stirring the reaction mixture for 30 min, it was diluted with 1N HCl (15 mL) and washed twice with ethyl acetate. The aqueous layer was treated with 4N NaOH (50 mL), and extracted twice with a mixture (1:1) of ethyl acetate and THF. The combined organic layers were washed with water followed by dried over Na_2SO_4. After removal of the solvent under vacuum gave the residue which was washed with toluene to remove the unreacted starting material. The compound **2** thus obtained was further purified through recrystallization from a mixture (1:1) of dichloromethane and methanol.

Yield: (80%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) (δ) 8.98 (s, 8H), 8.71 (d, 8H, J=5Hz), 8.51 (d, 8H,J= 7Hz), 7.70 (t, 12H, J= 14.5Hz), 7.57 (t, 12H, J= 14.5Hz) 7.22 (t, 8H, J= 5Hz), 4.20 (d, 24H,J=11.5Hz)^{13}C NMR (125 MHz, DMSO- d^6, TMS) δ 165.9, 161.7,156.2, 152.5, 150.3, 149.8, 148.1, 137.8, 136.7, 128.4, 126.6, 124.5, 123.1, 122.9, 122.7, 99.4, 52.1, 44.1. Anal; MALDI-TOF MS: m/z calcd for [$C_{96}H_{80}N_{16}Zn$]: 1523.12; found 1523.09 (M^{+}).

C. *Synthesis of $(Zn(II))_5$ (2,2'-dipicolylamino)methyl-5,10,15,20-tetrakisphenylporphyrin (**3**):* A solution of **1** (200 mg, 0.13 mmol) in a mixture (3:1) of methanol and chloroform was added 5 equivalents of zinc nitrate (0.65 mmol) drop wise and allowed the reaction mixture to stir for 1 h at 25 ^{o}C. Evaporation of the solvent gave a residue which was washed with chloroform and a mixture (1:1) of hexane and dichloromethane to remove the unreacted starting material. The Zinc complex **3** thus obtained was further purified through recrystallization from a mixture (1:1) of dichloromethane and methanol.

Yield: (85%). ^{1}H NMR [500 MHz, CD_3OD , TMS] δ: 8.94 (s, 8H) 8.84 (d,8H, J= 5Hz), 8.37 (d,8H, J=7.5Hz), 8.30 (t, 8H, J=14.5Hz), 7.96 (d,8H, J=8Hz), 7.85 (t, 8H, J=13Hz), 7.68 (d, 8H, J=7.5Hz), 4.8 (d, 8H, J=8Hz), 4.24 (d, 8H, J=16.5Hz), 3.99 (s, 8H). ^{13}C NMR (125 MHz, DMSO- d^6, TMS) δ 172.9, 162.6, 151.9, 149.6, 149.4, 148.7, 139.1, 137.8, 128.7, 126.9, 124.1, 123.9, 123.4, 122.9, 122.3, 99.9, 50.8, 42.1. Anal; MALDI-TOF MS: m/z calcd for [$C_{96}H_{80}N_{16}Zn_5$]: 1778.32; found 1778.48 (M^{+}).

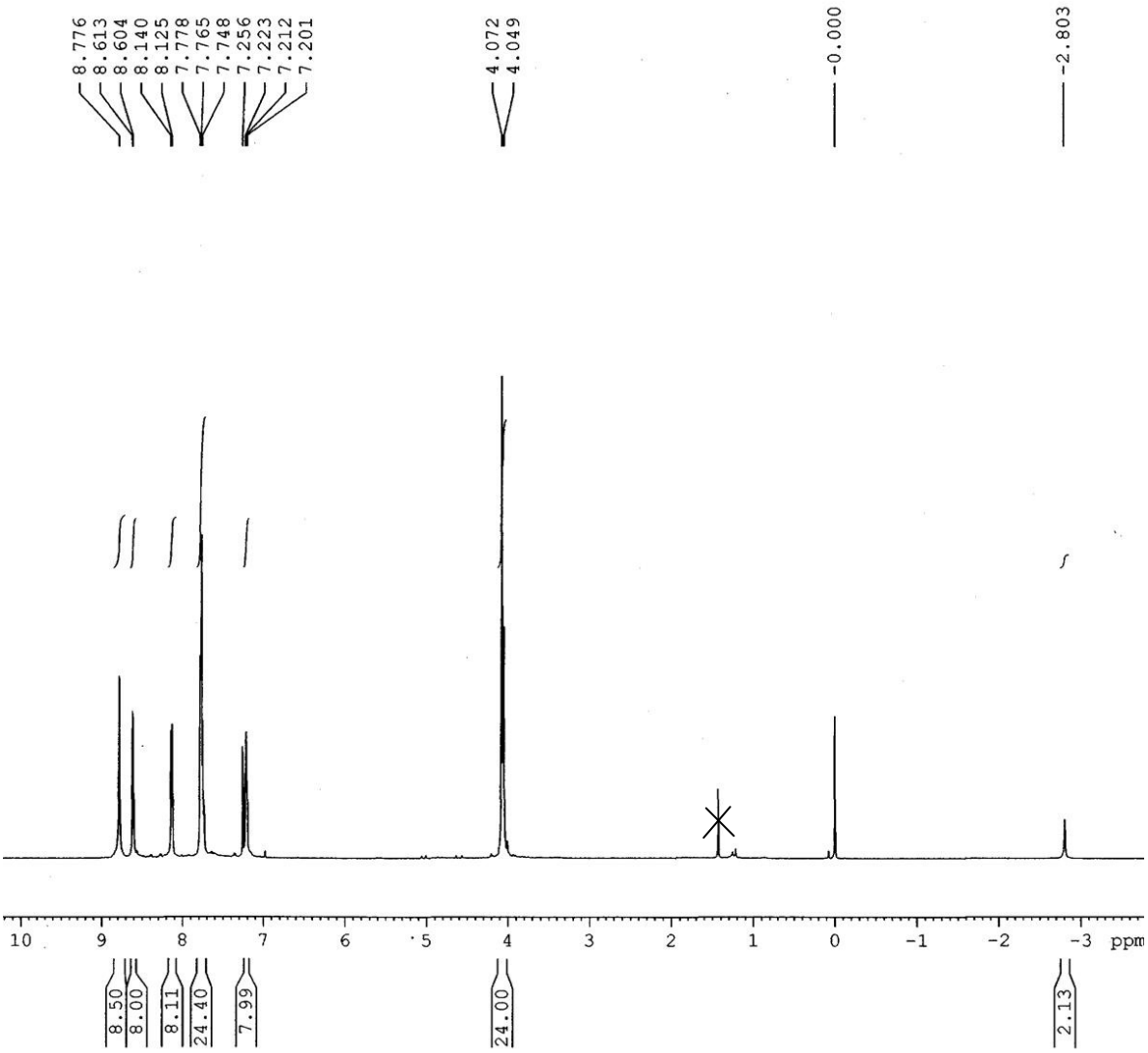

Fig S1. ^{1}H NMR spectrum of the compound **1** in $CDCl_3$

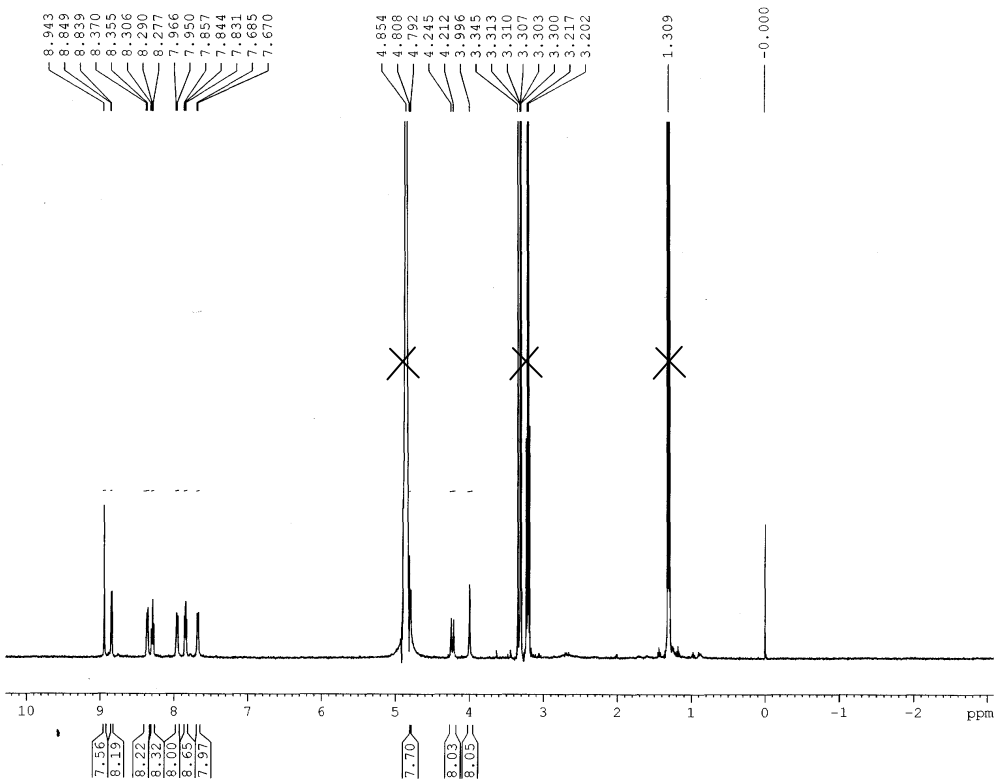

Fig S2. ^{1}H NMR spectrum of the compound **3** in CD_3OD**.**

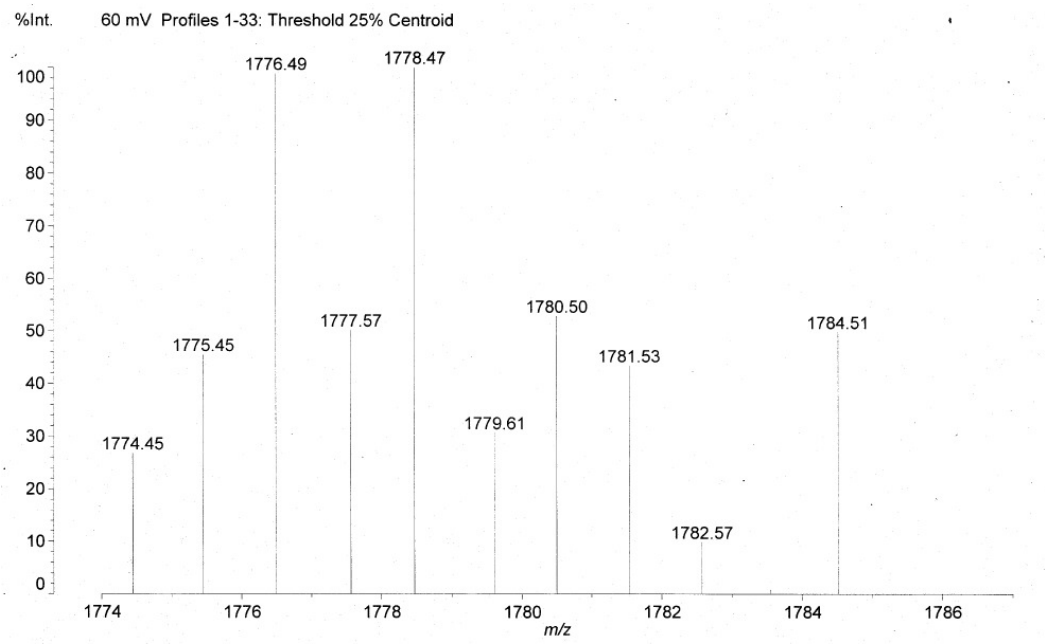

Fig S3. MALDI-TOF spectrum of the compound **3** in CD_3OD**.**

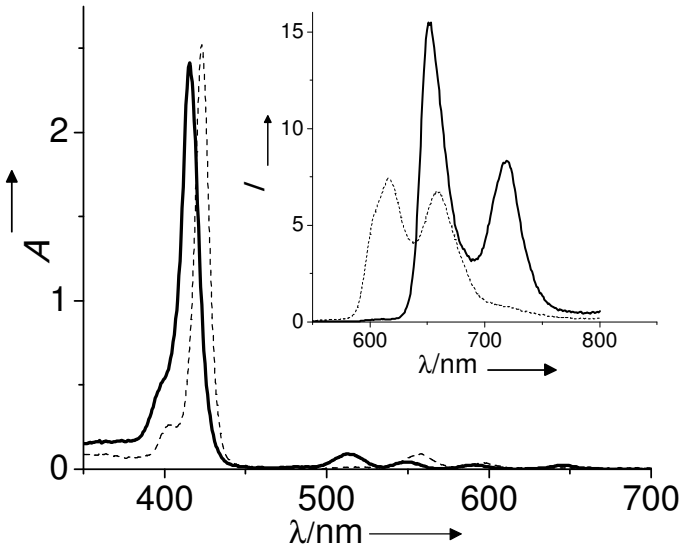

Fig S4. Absorption and emission (inset) spectra of **1** (—) and **2** (---) in methanol.

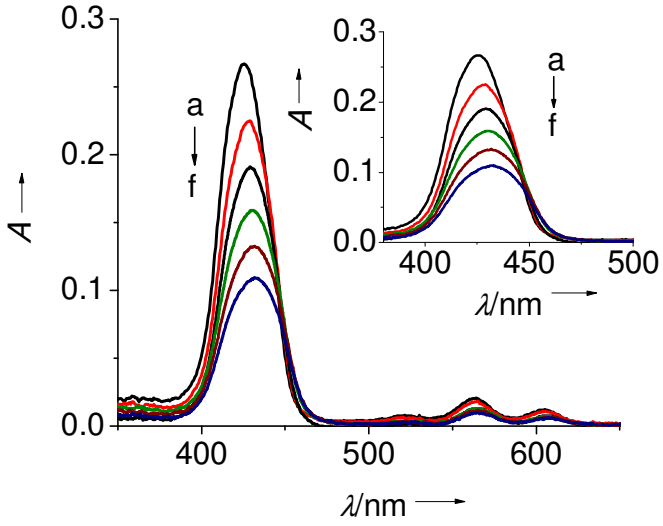

Fig S5. Time-dependent absorption spectra of **3** in water (8 μM) at a) 0, b) 24, c) 48, d) 72, e) 96, and f) 120 h. Inset of figure shows the zoomed version of the absorption changes under similar conditions vs time.

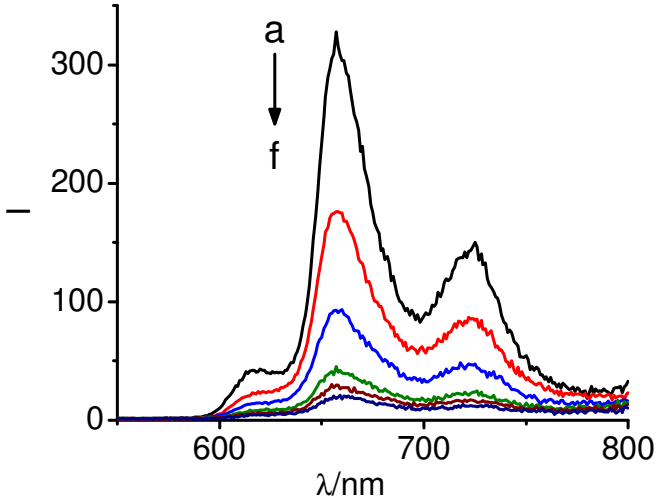

Fig S6. Time-dependent emission spectra of the compound **3** in water (8 µM) at a) 0, b) 24, c) 48, d) 72, e) 96, and f) 120 h.

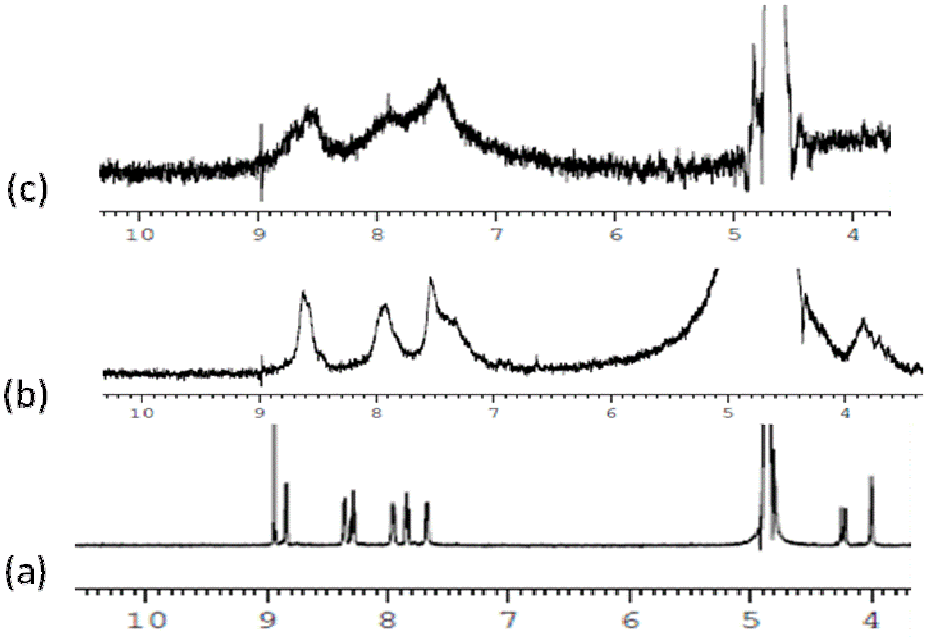

Fig S7. ^{1}H NMR spectra of the compound **3** in (a) CD_3OD, (b) 1:1 D_2O-CD_3OD and (c) in D_2O at 293 K.

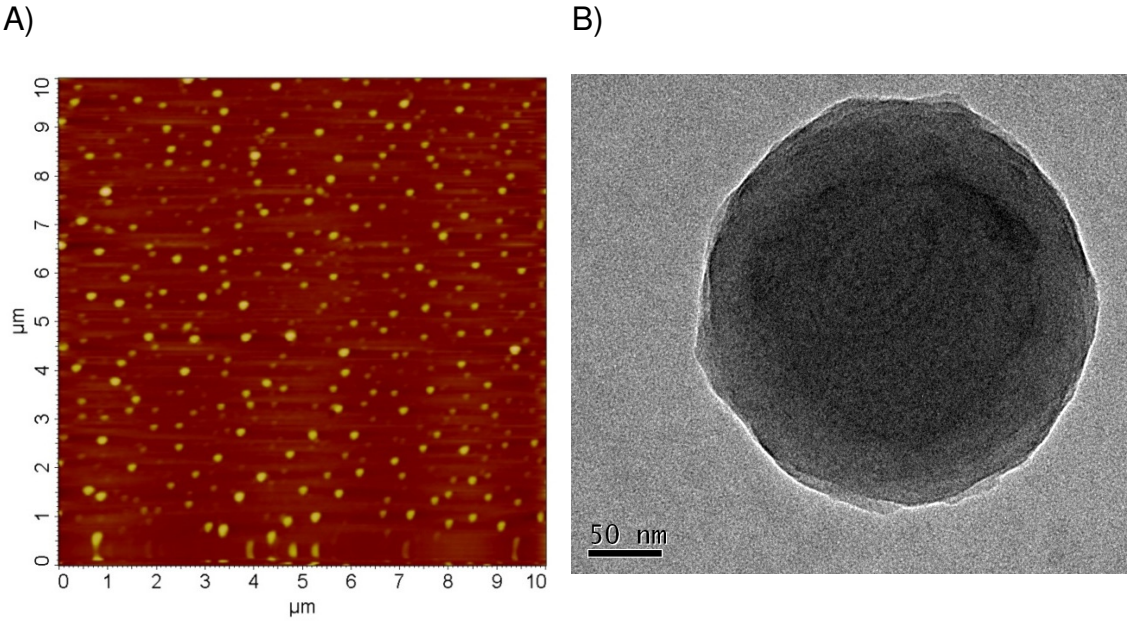

Fig S8. A) AFM image and B) Zoomed TEM image of **3** (10^{-4} M) in methanol.

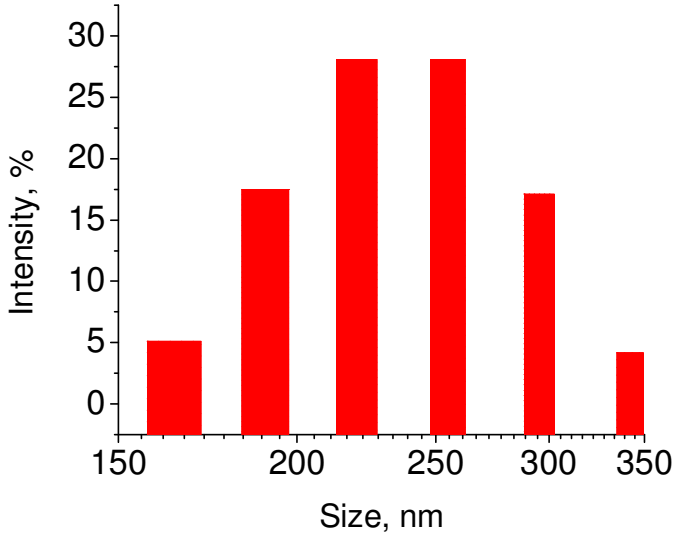

Fig S9. Histogram of DLS experiment of **3** (10^{-4} M) in methanol.

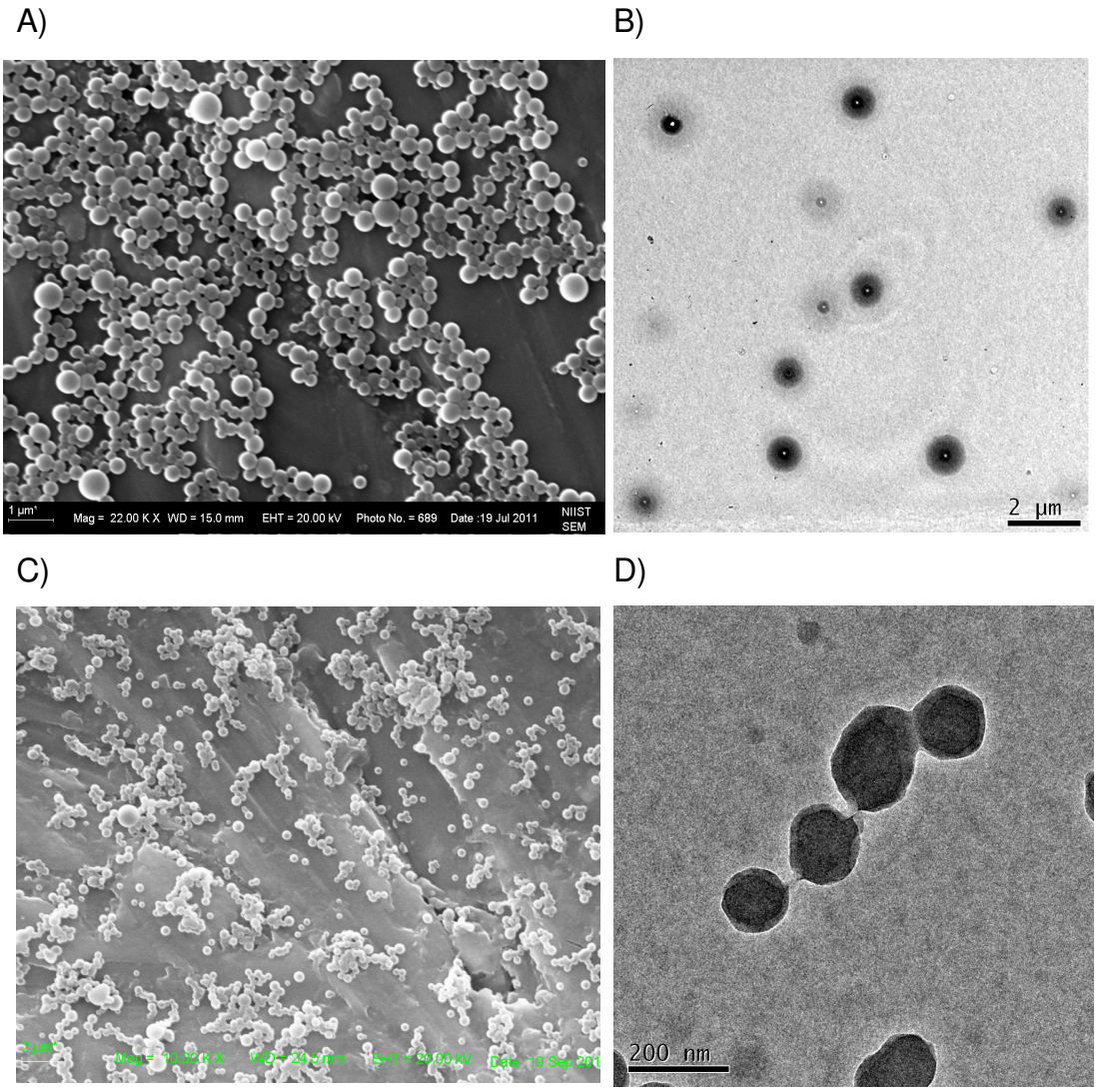

Fig S10. A) SEM and B) TEM images of **1** (10^{-4} M), C) SEM and D) TEM images of **2** (10^{-4} M), in methanol.

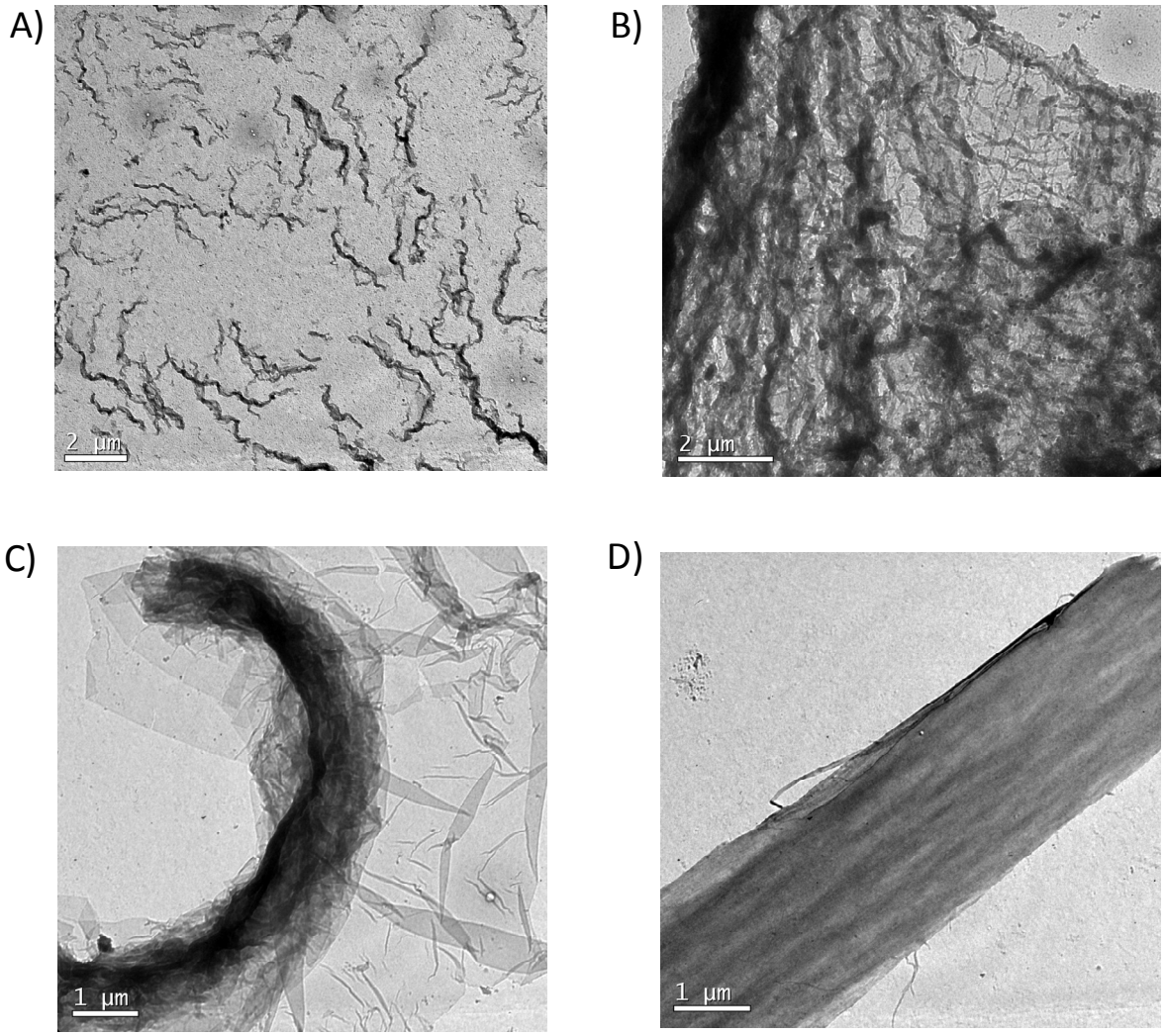

Fig S11. TEM images showing the morphological transformations of **3** (100 µM**)** in water. A) nanofiber obtained after 8 h; B) networks after 24 h; C) initial stage of sheet formation after 96 h; D) sheet like structures observed after 120 h.

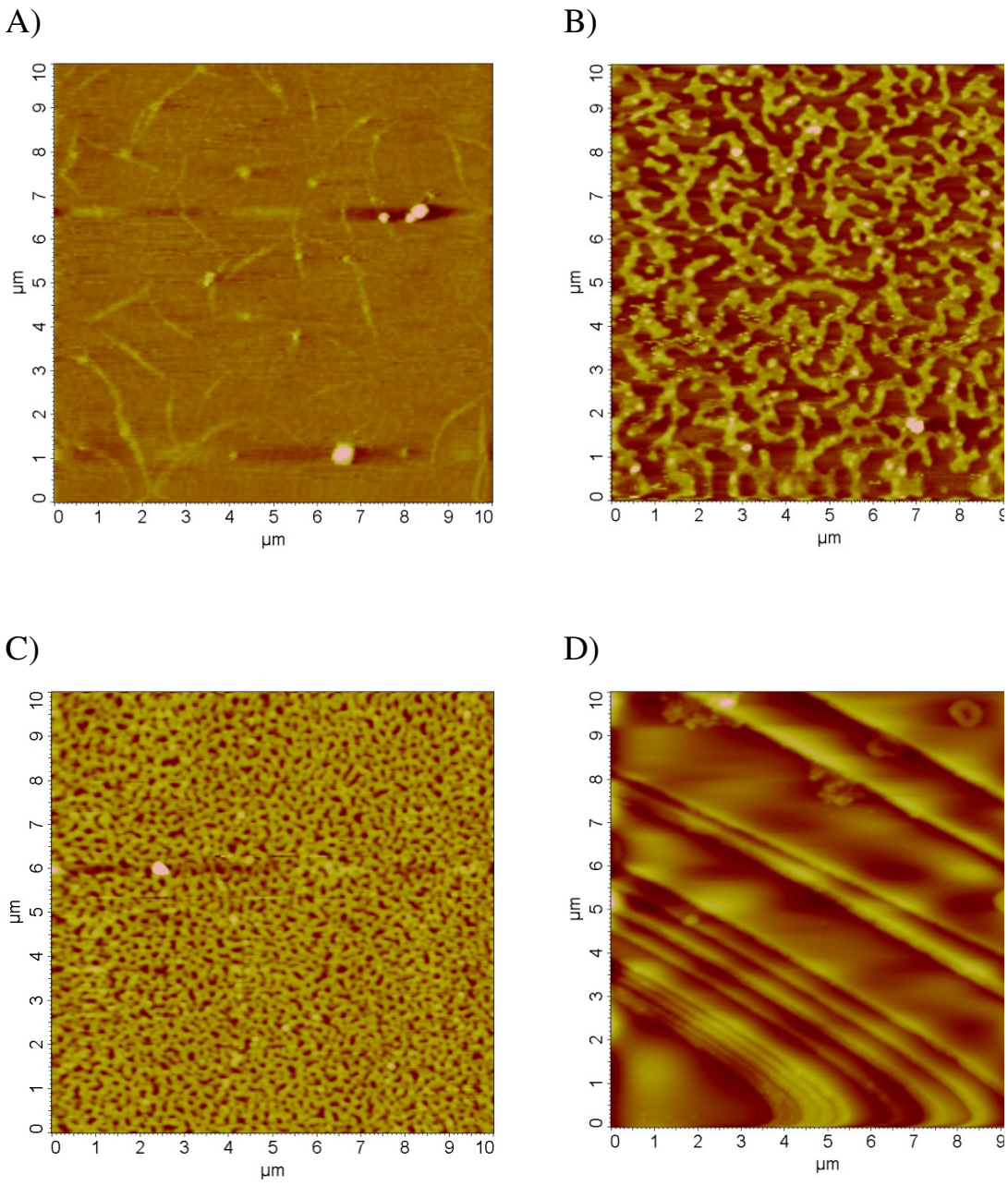

Fig S12. AFM images showing the morphological transformations of **3** (10^{-4} M): A) nanofibers obtained in water after 8 h, B) networks originated from entangled fibers in water after 16 h, C) network structures in water after 24 h and D) sheet like structures observed in water after 96 h.

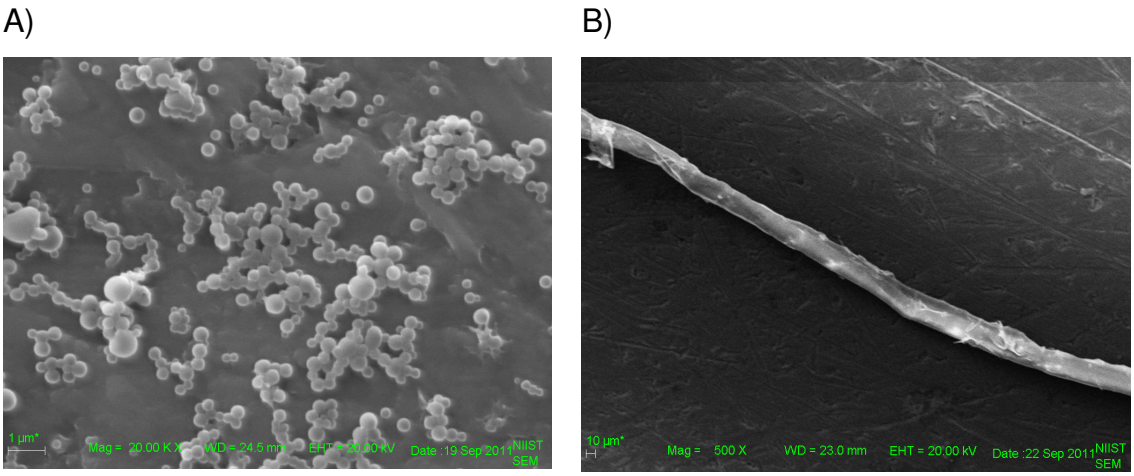

Fig S13. SEM images of the compounds A) **1** and B) **2** in a mixture (1:9) of water and methanol.

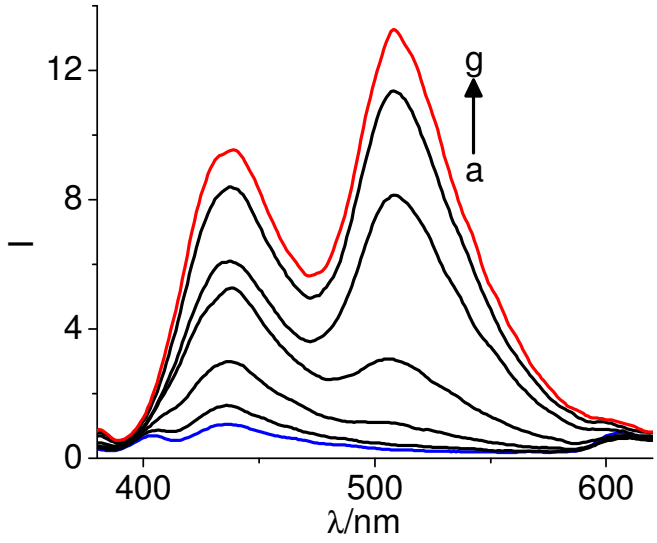

Fig S14. Emission spectra of sodium 8-hydroxy-1,3,6-pyrene trisulfonate (HPTS; 8.2 μM) in presence of **4** (7.5 μM) vs varying time interval of 24 h in a mixture (1:9) of water and methanol. (a) 0, (b) 24, (c) 48, (d) 72, (e) 96, (f) 120 and (g) 144 h.