Supporting Information for

Precise control over supramolecular nanostructures via manipulation of H-bonding in π-amphiphiles

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Materials and Methods: All chemicals and reagents were purchased from either Sigma Aldrich, Fisher Chemicals, Acros Chemicals or Alfa Aesar and used as received. Solvents were purchased from Fisher Scientific and used as received. Dry solvents were used directly from a drying and degassing solvent tower delivery system. NMR spectra were recorded on a Bruker Avance 300, a Bruker Avance III HD 400 or a Bruker Avance III HD 500 spectrometer at 298 k and 300, 400 and 500 MHz, respectively. Shifts are quoted in δ in parts per million and quoted relative to the internal standard trimethylsilane (TMS). High Resolution Mass Spectra (ESI-MS) were conducted on a Bruker UHR-Q-ToF MaXis spectrometer with electrospray ionization. Infrared spectra were recorded in transmittance mode on an Agilent 660-IR instrument using liquid cell holder. UV/Vis spectroscopy was carried out on an Agilent Cary 60 UV-Vis Spectrometer at room temperature unless specified. Fluorescence spectra were recorded using an Agilent Cary Eclipse Fluorescence spectrophotometer. Confocal microscopy images were taken using a Zeiss LSM 880 confocal fluorescent microscope. The solution of the assembly being studied (5 μL of aqueous solution) was dropped onto a plasma-cleaned microscope slide and left to dry overnight. Atomic force microscopy (AFM) imaging and analysis were performed on an Asylum Research MFP3D-SA atomic force microscope in tapping mode. Samples for AFM analysis were prepared by drop casting 5 μL of solution onto a silicon wafer that had been freshly cleaned with water and ethanol, then activated using plasma treatment to generate a hydrophilic surface. Transmission electron microscopy (TEM) observations were performed on a JEOL 2000FX electron microscope at an acceleration voltage of 200 kV. All TEM samples were prepared on

carbon-coated carbon grids without staining. Generally, a drop of sample (10 μL) was pipetted on a grid, blotted immediately and left to air dry. Cryo-TEM imaging was performed on a JEOL JEM-2100 plus microscope operating at an acceleration voltage of 200 kV. Samples for cryo-TEM were prepared on lacey carbon grids (EM Resolutions). After 200-fold dilution with deionized water, 8 μL of sample were deposited onto the grid followed by blotting for approximately 5 s and plunging into a pool of liquid ethane, cooled using liquid nitrogen in order to vitrify the samples. Then, transfer into a pre-cooled cryo-TEM holder using liquid nitrogen, was performed prior to the microscopic analysis. TEM images were analyzed using the ImageJ software, and over 100 particles were counted for each sample to obtain either number-average diameter of the cylindrical micelle, the wall-thickness of the nanotubes or the width of the nanoribbons. Small-angle X-ray scattering (SAXS) data were collected using a laboratory SAXS instrument (Xeuss 2.0, Xenocs, France) equipped with a GeniX3D microfocus Cu Kα source, two sets of motorized scatterless slits for beam collimation, a Dectris Pilatus 300k pixel SAXS detector (sample-to-detector distance 2.481 m and 1.185 m). SAXS patterns were each recorded for a total of 5 h (five 1 h periods) over a q range of 0.006 $Å^{-1} < q < 0.3$ $Å^{-1}$, where $q = (4\pi\sin\theta)/\lambda$ is the length of the scattering vector and θ is one-half of the scattering angle. Borosilicate glass capillaries of 1 mm diameter were used as a sample holder. Data were integrated using the Foxtrot software package supplied with the instrument and corrected (normalization and background subtraction) using Excel. Finally, the data were rescaled to absolute intensities using a glassy carbon standard[1] and modelled using Irena SAS macros[2] for Igor Pro. In general, the intensity of X-rays scattered by a dispersion of nano-objects [as represented by the scattering cross-section per unit sample volume, $\frac{d\Sigma}{d\Omega}(q)$] can be expressed as:

$$\frac{d\Sigma}{d\Omega}(q) = NS(q) \int_0^\infty \dots \int_0^\infty F(q, r_1, \dots, r_k)^2 \Psi(r_1, \dots, r_k)\, dr_1, \dots, dr_k \qquad \text{(S1)}$$

where () is the form factor, is a set of k parameters describing the structural morphology, () is the distribution function, $S(q)$ is the structure factor and N is the number density of nano-objects per unit volume expressed as:

$$N = \frac{\varphi}{\int_0^\infty \dots \int_0^\infty V(r_1, \dots, r_k)\Psi(r_1, \dots, r_k)dr_1, \dots, dr_k} \quad \text{(S2)}$$

where () is the volume of the nano-object and is its volume fraction within the dispersion. It is assumed that $S(q)$ = 1 at the sufficiently low copolymer concentrations used in this study (1.0% w/w).

The worm-like micelle form factor for Equation S1 is given by:[3]

()()()() (S3)

where is the radius of gyration of the hydrophilic segment in each amphiphile (in all cases, was found to be 8 Å). The X-ray scattering length contrasts for the hydrophobic and hydrophilic segments are given by and respectively. Here, , and are the X-ray scattering length densities of the hydrophobic segment, hydrophilic segment and water, respectively. and are the volumes of the hydrophobic segment and the hydrophilic segment in each amphiphile, respectively. The self-correlation term for the worm core cross-sectional volume-average radius R_{sw} is:

() (S4)

Where,

$$A_{CS_{worm}}{}^2(q, R_{sw}) = \left[2\frac{J_1(qR_{sw})}{qR_{sw}}\right]^2 \quad \text{(S5)}$$

and is the first-order Bessel function of the first kind, and a form factor for self-avoiding semi-flexible chains represents the worm-like micelles, where is the Kuhn length and is the mean contour length. A complete expression for the chain form factor can be found elsewhere.[4]

The mean aggregation number of the worm-like micelle, , is given by:

$$N_w = (1 - x_{sol}) \frac{\pi {R_{sw}}^2 L_w}{V_s} \quad \text{(S6)}$$

where is the volume fraction of solvent within the worm-like micelle cores, which was found to be zero in all cases. The possible presence of semi-spherical caps at both ends of each worm is neglected in this form factor.

A polydispersity for one parameter ( ) is assumed for the micelle model, which is described by a Gaussian distribution. Thus, the polydispersity function in Equation S1 can be represented as:

$$\Psi(r_1) = \frac{1}{\sqrt{2\pi {\sigma_{R_{\mathrm{sw}}}}^2}} exp\left[-\frac{(r_1 - R_{\mathrm{sw}})^2}{2{\sigma_{R_{\mathrm{sw}}}}^2}\right] \quad \text{(S7)}$$

where $\sigma_{R_{\mathrm{sw}}}$ is the standard deviation for . In accordance with Equation S2, the number density per unit volume for the worm-like micelle model is expressed as:

$$N = \frac{\varphi}{\int_0^\infty V(r_1)\Psi(r_1)dr_1} \quad \text{(S8)}$$

where is the total volume fraction of copolymer in the worm-like micelles and () is the total volume of copolymer in a worm-like micelle [()].

SAXS data collected for NDI-1 exhibited a subtle peak centred around q~0.076 Å^{-1}, which was accounted for in the model using an additional population represented by a Gaussian peak ($A\exp\left[-\left(\frac{q - q_{\mathrm{peak}}}{width}\right)^2\right]$). For NDI-1, A = 0.00358, q_{peak} = 0.076 Å^{-1}, and $width$ = 0.012 Å^{-1}.

For NDI-3, an additional population represented by a power law dependence of scattering intensity (, where B is a constant and p is an exponent) was incorporated to enable the increased scattering intensity observed at low q to be approximated. It is reasonable to assume that this corresponds to nanoparticle aggregation, where the overall structural morphology can be

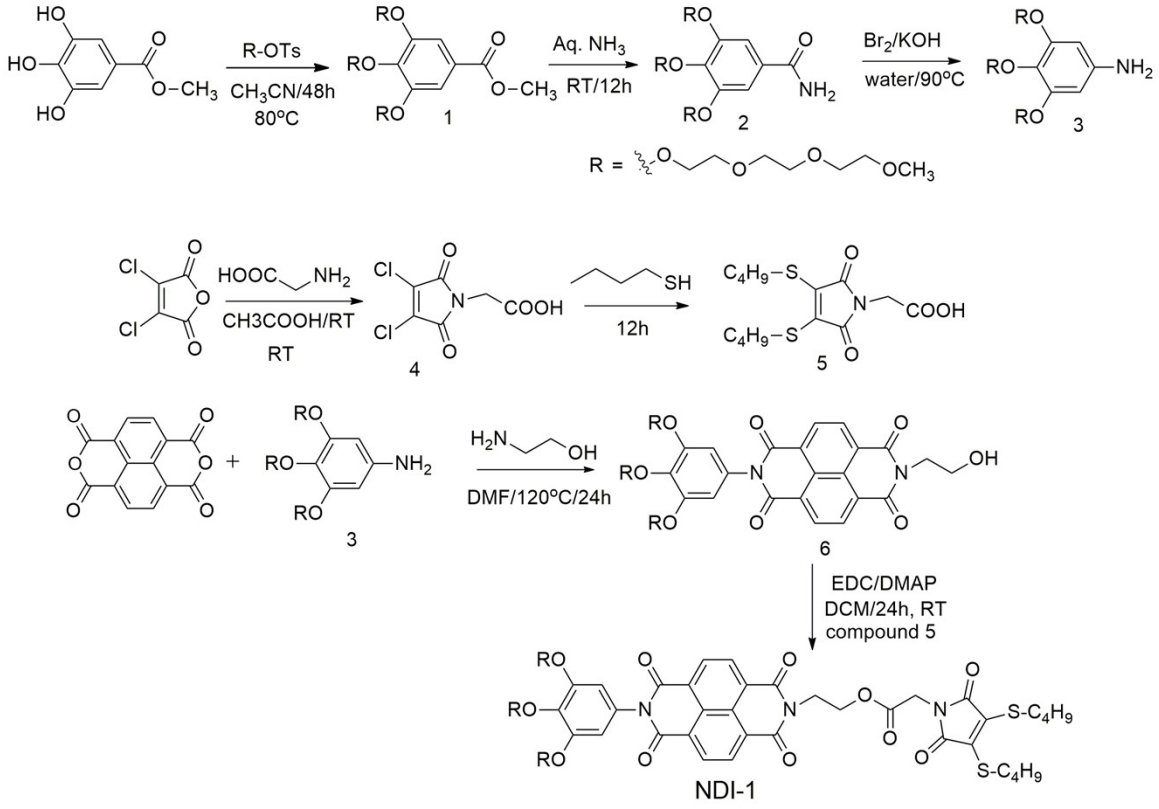
described by mass fractals where p corresponds to the fractal dimension (for NDI-3, p = 1.36, B = 0.0015).

Thus, the entire scattering pattern would be described as:

$$()–()\left[\left(–\right)\right] \quad \text{(S9)}$$

Additionally, a constant low-intensity background was required to satisfactorily fit data at high q in each case, which was attributed to the poor scattering contrast of the NDI nano-objects and the aqueous phase.

Synthesis and Characterization: Syntheses of the compounds NDI-1, NDI-2 and NDI-3 were achieved in multiple steps using the synthetic protocol as outlined in Scheme S1-S3. DTM-1 was synthesized in a single step synthesis (Scheme S4). All the final compounds have been characterized by ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, ESI-MS mass spectroscopy and extinction coefficient.



Scheme S1. Synthesis of **NDI-1**.

Compound 1: Compound 1 was prepared by following the method from the previous literature.[5]

Compound 2: Compound **1** (1.0 g, 1.6 mmol) was dissolved in 10 mL of methanol. To it 10 mL of 35% aqueous ammonia solution was added. The reaction mixture was stirred for 12 hours at room temperature. After reaction methanol was evaporated under reduced pressure the product was extracted with CH_2Cl_2 and washed with brine solution. CH_2Cl_2 solution was evaporated and dried over anhydrous Na_2SO_4 and solvent was evaporated to obtain the product as light brown viscous liquid (product obtained-0.88 g, yield-91%). ^{1}H NMR (300 MHz, $CDCl_3$,): δ (ppm) = 7.20 (2H, s), 4.21 (8H, m), 3.82(8H, m), 3.66-32.47 (14H, m), 3.34 (9H, t, J = 3Hz), 1.7 (2H, bs).

Compound 3: Compound **2** (0.66 g, 1.086 mmol) was dissolved in 5 mL of aqueous KOH (5 M) solution and cooled to 0 °C. To it bromine (86.3 µL, 1.6 mmol) dissolved in 5 M KOH solution was added dropwise. The reaction mixture was stirred at 90 °C for 12 hours. After reaction the reaction mixture was cooled to room temperature and the product was extracted with ethyl acetate (30 mL) and washed with brine solution (20 mL). The ethyl acetate solution was dried over anhydrous Na_2SO_4 and evaporated to obtain the product as light brown liquid (product obtained-0.6 g, quantitative yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 5.83 (2H, s), 4.03 (2H, t, J= 6Hz), 3.95 (4H, t, J = 6Hz), 3.88 (2H, t, J = 6Hz), 3.68-3.39 (22H, m), 3.24 (9H, t, J = 3Hz).

Compound 4: 2,3-dichloromaleic anhydride (3.0 g, 17.96 mmol) and aminoacetic acid (1.48 g, 19.76 mmol) in acetic acid (20 ml) was heated at 70 °C for 4 hours. Acetic acid was evaporated under reduced pressure. The product was purified by column chromatography (R_f = 0.40) using silica gel as a stationary phase and hexane / ethylacetate (1:1) as eluent to get the desired product as white solid (product obtained-3.5 gm, yield-87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 8.2 (1H, bs), 4.41 (2H, s).

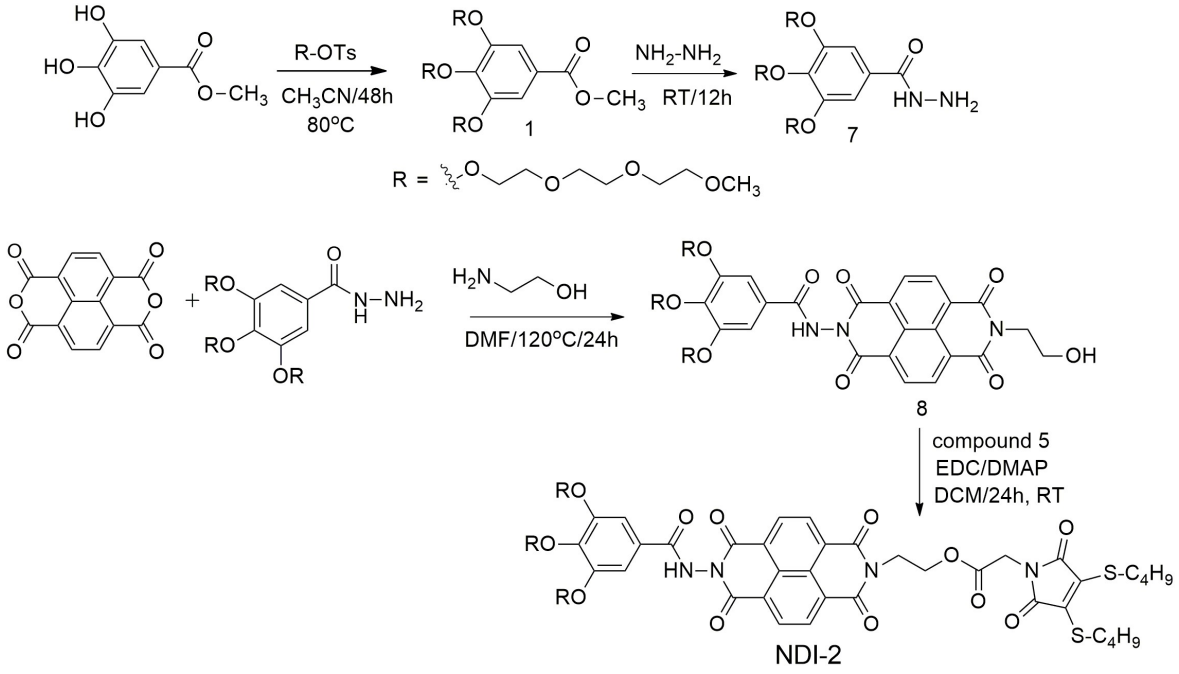
Compound 5: Compound 4 (1.0 g, 4.48 mmol) was dissolved in 10 mL of dry CH_2Cl_2 and cooled to 0 °C in an ice bath. To it 1-butanethiol (0.89 g, 9.86 mmol) was added and the solution mixture was stirred for 5 minutes. Finally, triethylamine (0.99 g, 9.86 mmol) was added dropwise and the solution was allowed to stir at room temperature for 12 hours. CH_2Cl_2 was evaporated under reduced pressure. The product was purified by column chromatography (R_f =

0.55) using silica gel as a stationary phase and hexane / ethylacetate (3:1) as eluent to get the desired product as yellow solid (product obtained-0.86 g, yield- 61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 8.5 (1H, bs) 3.21 (4H, t, J = 6 Hz), 3.58-3.51 (4H, m), 3.39-3.32 (2H, m), 0.85 (6H, t, J = 6Hz).

Compound 6: Compound **3** (0.25 g, 0.43 mmol), 1,4,5,8- naphthalenetetracarboxylic bisanhydride (0.116 g, 0.43 mmol) and commercially available 2-aminoethanol (0.026 g, 0.43 mmol) were taken together in a round bottom flask containing 10 mL of dry dimethylformamide and the reaction mixture was stirred for 12 hours at 120 ^{o}C. Then reaction was stopped and cooled to room temperature and dimethylformamide was evaporated under reduced pressure and resulted in a pasty mass. The reaction mixture was redissolved in CH_2Cl_2 and washed with water (40 mL) and then with brine (40 mL) and dried over anhydrous Na_2SO_4. Solvent was evaporated to get the crude product as a sticky brown solid. The product was purified by column chromatography (R_f = 0.45) using silica gel as a stationary phase and CH_2Cl_2/ CH_3OH (98:2) as eluent to get the desired product as orange solid (product obtained-0.11 g, yield-29%). ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 8.88-8.80 (4H, dd, J = 6 Hz and 9 Hz), 6.60 (2H, s), 4.50 (2H, t, J = 6 Hz), 4.26 (2H, t, J = 6Hz), 4.18 (6H, m), 4.04 (2H, t, J = 6Hz), 3.79-3.37 (28H, m), 3.23 (9H, t, J = 6 Hz).

NDI-1: Compound **6** (0.1 g, 0.11 mmol), compound **5** (0.034 g, 0.11 mmol) and 4-dimethylaminopyridine (0.021 g, 0.16 mmol) were dissolved in 5 mL of dry CH_2Cl_2 taken in a round bottom flask. The reaction mixture was stirred for 15 minutes at 0 ^{o}C, then to it 1.5 equivalent of N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (0.026 g, 0.16 mmol) was added and it was stirred for 24 hours at room temperature. After the reaction was over, the compound was extracted with CH_2Cl_2 (15 mL) and washed with 4N HCL (15 mL), then with $NaHCO_3$ (15 mL) solution and finally with brine solution (15 mL). CH_2Cl_2 solution was passed through anhydrous Na_2SO_4 and evaporated the solvent to get crude product. It was purified by column chromatography using CH_2Cl_2/ CH_3OH (98:2) (R_f = 0.65) solvent mixture as an eluent to get the pure compound as orange solid (product obtained-0.088 g, yield-68%). ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm) = 8.69-8.60 (4H, dd, J = 6 Hz and 9 Hz), 6.75 (2H, s), 4.39 (2H, t, J = 6 Hz), 4.25 (2H, t, J = 6 Hz), 4.14 (2H, s), 4.08-3.9 (8H, m), 3.69-3.53(28H, m), 3.19 (9H, t, J = 6 Hz), 3.12 (4H, t), 1.45 (4H, m), 1.27 (4H, m), 0.78(6H, t, J = 6 Hz). ^{13}C NMR

(DMSO-d6): 168.0, 165.6, 163.3, 163.2, 152.7, 138.0, 136.1, 131.3, 131.2, 130.9, 127.3, 126.9, 126.7, 108.7, 72.4, 71.8, 71.7, 70.5-70.1, 69.3, 69.0, 62.8, 58.5, 32.5, 31.2, 21.4, 13.8. HRMS (ESI): m/z calculated for $C_{57}H_{75}N_3O_{20}S_2$ [Na]+: 1208.42; found: 1208.43, UV-Visible (THF): λ_{max}= 378 nm (19280 M^{-1} cm^{-1}), 357 nm (16660 M^{-1} cm^{-1}), 340 nm (10680 M^{-1} cm^{-1}). C.H.N analysis: % calculated: Carbon-57.7, Hydrogen-6.37, Nitrogen-3.54, Sulphur-5.4; obtained: Cabon-57.1, Hydrogen-6.51, Nitrogen-3.73, Sulphur-5.9; Melting point-125-127°C.



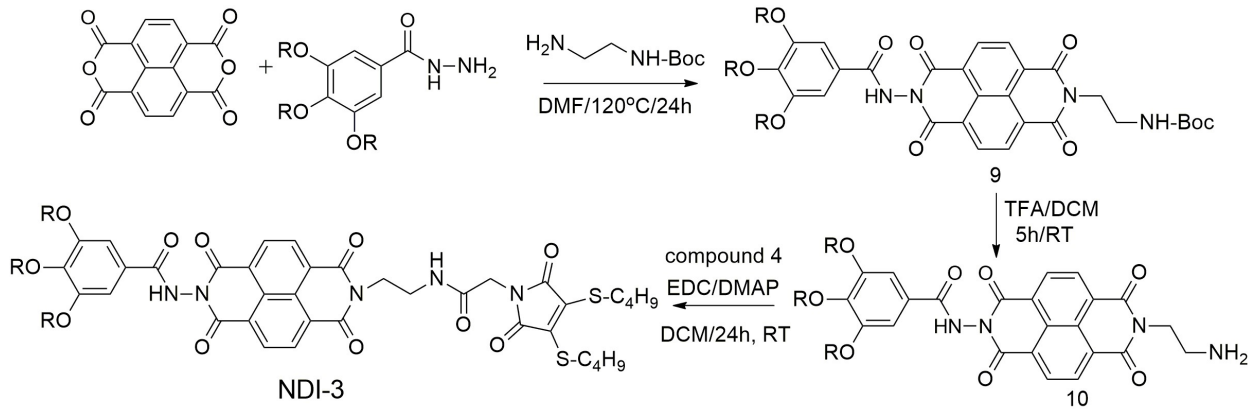
Scheme S2. Synthesis of **NDI-2**.

Compound 7: Compound **7** was prepared by following the method from the previous literature.[4]

Compound 8: Compound **7** (0.53 g, 0.85 mmol) and 1,4,5,8- naphthalenetetracarboxylic bisanhydride (0.228 g, 0.85 mmol) and commercially available 2-aminoethanol (0.051 mg, 0.85 mmol) were taken together in a round bottom flask containing 15 mL of dry dimethylformamide and the reaction mixture was stirred for 24 hours at 120 °C under inert atmosphere. Then the reaction was stopped and cooled to room temperature and dimethylformamide was evaporated under reduced pressure and the pasty mass was dissolved in 30 mL of CH_2Cl_2 and filtered through Whatman filter paper. The filtrate was washed with water (40 mL) and then with brine

(40 mL) and dried over anhydrous Na_2SO_4. Solvent was evaporated to get the crude product as a sticky brown solid. The product was purified by column chromatography (R_f =0.4) using silica gel as a stationary phase and CH_2Cl_2/ MeOH (98:2) as eluent to get the desired product as orange sticky solid (product obtained- 233 mg, yield-30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 9.69 (1H, s), 8.81 (4H, s), 7.45 (2H, s), 4.51 (2H, t, J= 6 Hz), 4.30 (6H, m), 4.28 (2H, t), 4.06-4.35 (30H, m). 3.23 (9H, t, J=6 Hz).

NDI-2: Compound 7 (0.14 g, 0.15 mmol), compound 4 (0.046 g, 0.15 mmol) and 4-dimethylaminopyridine (0.028 g, 0.23 mmol) were dissolved in 5 mL of dry CH_2Cl_2 taken in a round bottom flask. The reaction mixture was stirred for 15 minutes at 0 ^{o}C, then to it 1.5 equivalent of N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (0.036 g, 0.23 mmol) was added and it was stirred for 24 hours at room temperature. After the reaction was over, the compound was extracted with CH_2Cl_2 (15 mL) and washed with 4 N HCL (15 mL), then with $NaHCO_3$ (15 mL) solution and finally with brine solution (15 mL). CH_2Cl_2 solution was passed through anhydrous Na_2SO_4 and evaporated the solvent to get crude product. It was purified by column chromatography (R_f =0.63) using silica gel as a stationary phase and CH_2Cl_2/ MeOH (98:2) as eluent to get the pure compound as orange solid (product obtained-0.11 g, yield-62%). ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm) = 11.45 (1H, s), 8.87-8.81 (4H, dd, J = 6 Hz and 9 Hz), 7.43 (2H, s), 4.52 (2H, t, J = 6 Hz), 4.44 (2H, t, J = 6 Hz), 4.28-4.20 (8H, m), 3.87-3.31 (30H, m), 3.18 (9H, t, J = 6 Hz), 3.14 (4H, t, J = 6 Hz), 1.51 (4H, m), 1.35 (4H, m), 0.87(6H, t, J = 6 Hz). ^{13}C NMR (DMSO-d6):168.0, 165.5, 164.9, 163.1, 161.4, 152.6, 141.6, 136.1, 131.9, 131.3, 127.4, 127.1126.6, 126.4, 126.3, 107.4, 72.4, 71.7, 70.5-70.1, 69.4, 69.0, 62.7, 58.5, 32.5, 31.1, 21.3, 13.8. HRMS (ESI): m/z calculated for $C_{58}H_{76}N_4O_{21}S_2$[Na]+: 1151.42; found: 1151.44, UV-Visible (THF): λ_{max}= 378 nm (20800 $M^{-1}cm^{-1}$), 357 nm (17120 $M^{-1}cm^{-1}$), 340 nm (10340 $M^{-1}cm^{-1}$). C.H.N analysis: % calculated: Carbon-56.7, Hydrogen-6.23, Nitrogen-4.55, Sulphur-5.21; obtained: Cabon-56.89, Hydrogen-6.20, Nitrogen-4.69, Sulphur-5.17; Melting point-113-116^{o}C.



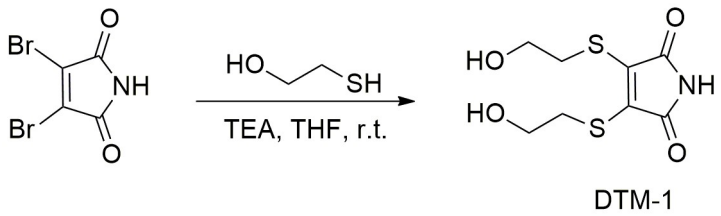
Scheme S3. Synthesis of **NDI-3**.

Compound 9: Compound **7** (0.53 g, 0.85 mmol) and 1,4,5,8- naphthalenetetracarboxylic bisanhydride (0.228 g, 0.85 mmol) and commercially available N-Boc-1,2-diaminoethane (0.136 g, 0.85 mmol) were taken together in a round bottom flask containing 15 mL of dry dimethylformamide and the reaction mixture was stirred for 24 hours at 120 °C under inert atmosphere. Then reaction was stopped and cooled to room temperature and dimethylformamide was evaporated under reduced pressure and the pasty mass was dissolved in 30 mL of CH_2Cl_2. The CH_2Cl_2 solution was washed with water (40 mL) and then with brine (40 mL) and dried over anhydrous Na_2SO_4. Solvent was evaporated to get the crude product as a sticky brown solid. The product was purified by column chromatography (R_f =0.6) using silica gel as a stationary phase and CH_2Cl_2/ CH_3OH (98:2) as eluent to get the desired product as orange sticky solid (product obtained- 0.25 g, yield=29%). ^{1}H NMR (300 MHz, DMSO-d6): δ(ppm) = 11.39 (1H, s), 8.81-8.73 (4H, dd), 7.37 (2H, s), 6.95 (1H, t), 4.23-4.14 (8H, m), 3.81 (4H, t), 3.62 (2H, t), 3.57-3.23 (35H, m), 1.32 (9H, s).

Compound 10: Compound **9** (0.2 g, 0.20 mmol) was taken in a 50 mL round bottom flask containing 4 mL of dry CH_2Cl_2. The solution was cooled to 0 °C. To it 0.3 mL of trifluoroacetic acid dissolved in 1 mL of dry CH_2Cl_2 was added dropwise. The reaction mixture was stirred for 5 hours, after that to it 10 equivalents of Na_2CO_3 was added and stirred for another 30 minutes to

neutralize the solution. The product was extracted in CH_2Cl_2 and washed with water (10 mL) and then with brine (10 mL) and dried over Na_2SO_4. The product was obtained as orange sticky solid (product obtained-0.18 g, quantitative yield). ^{1}H NMR (300 MHz, DMSO-d6): δ(ppm) = 11.41 (1H, s), 8.84-8.76 (4H, dd), 7.85 (2H, broad peak), 7.37 (2H, s), 4.37(2H, t, J = 6 Hz), 4.22-4.14 (8H, m), 3.85- 3.23 (39H, m).

NDI-3: Compound 10 (0.14 g, 0.15 mmol), compound 4 (0.046 g, 0.15 mmol) and 4-dimethylaminopyridine (0.028 g, 0.23 mmol) were dissolved in 4 mL of dry CH_2Cl_2 taken in a round bottom flask. The reaction mixture was stirred for 15 minutes at 0 ^{o}C, then to it 1.5 equivalent of N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (0.036 g, 0.23 mmol) was added and it was stirred for 24 hours at room temperature. After the reaction was over, the compound was extracted with CH_2Cl_2 (15 mL) and washed with 4 N HCL (15 mL), then with $NaHCO_3$ (15 mL) solution and finally with brine solution (15 mL). CH_2Cl_2 solution was passed through anhydrous Na_2SO_4 and evaporated the solvent to get crude product. It was purified by column chromatography (R_f=0.58) using silica gel as a stationary phase and CH_2Cl_2/ CH_3OH (98:2) as eluent to get the pure compound as orange solid (product obtained-0.12 g, yield-71%). ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm) = 11.38 (1H, s), 8.83-8.75 (4H, dd, J=6 Hz and 9 Hz), 8.31 (1H, t, J = 6 Hz), 7.37 (2H, s), 4.21-4.14 (8H, m), 3.90-3.45 (44H, m), 3.23 (9H, t, J= 6 Hz), 3.14 (4H, t, J = 6Hz), 1.46 (4H, m), 1.34 (4H, m), 0.83(6H, t, J = 6 Hz). ^{13}C NMR (DMSO-d6):166.8, 166.0, 164.9, 163.2, 161.5, 152.5, 141.6, 136.0, 131.9, 131.1, 127.7, 127.1, 126.5, 126.4, 126.0, 107.4, 72.4, 71.7, 70.05-70.1, 69.4, 69.0, 58.5, 32.4, 31.1, 21.3, 13.8. HRMS (ESI): m/z calculated for $C_{58}H_{77}N_5O_{20}S_2$ $[Na]^+$: 1250.15; found: 1250.45, UV-Visible (THF): λ_{max}= 378 nm (19840 $M^{-1}cm^{-1}$), 358 nm (16850 $M^{-1}cm^{-1}$), 340 nm (10280 $M^{-1}cm^{-1}$). C.H.N analysis: % calculated: Carbon-56.7, Hydrogen-6.31, Nitrogen-6.23, Sulphur-5.22; obtained: Cabon-56.79, Hydrogen-6.34, Nitrogen-6.34, Sulphur-5.41; Melting point-105-108^{o}C.



DTM-1

Scheme 4. Synthesis of **DTM-1**.

DTM-1: DTM-1 was synthesized according to our previous report with minor revision. 3,4-dibromo-1H-pyrrole-2,5-dione (0.8 g, 3.2 mmol) and 2-mercaptoethanol (0.25 g, 6.4 mmol) was dissolved in THF (50 mL) and cooled in an ice bath for 10 minutes. Then, triethylamine was added dropwise to the cooled solution and the reaction was stirred for 16 hours at room temperature. CH_2Cl_2 (150 mL) was added and the mixture was washed with water (200 mL×3) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by flash chromatography (Rf= 0.4, 1:2, n-hexane: EtOAc) as an orange solid (product obtained-0.5 g, yield-63%.).^{1}H NMR (400 MHz, Methanol-d4): δ (ppm)= 3.86-3.68 (2H, t, J= 6 Hz), 3.58- 3.40 (2H, t, J= 6Hz). ^{13}C NMR (Methanol-d4): δ 167.53, 136.17, 61.35, 33.42. HRMS (ESI): m/z calculated for $C_8H_{11}NO_4S_2$: 250.0208, found 250.0207.

Experimental Procedures:

Solution preparation: A stock solution of NDI-1/NDI-2/NDI-3 was made in THF (2.0 mM). measured volume of the aliquot was taken in a vial and the solvent was evaporated completely. A thin yellow film obtained was dissolved in miliQ water to make the desired concentration. The solutions were allowed to equilibrate for 1 hour at room temperature before any physical studies and considered as freshly prepared solutions. Further, the solutions were aged for three weeks at ~20 ^{o}C to perform experiments with aged solutions unless specified. For Cryo-TEM and dry state TEM sample preparation: 0.5 mM aqueous solution (fresh solution and aged solution both) of NDI-1/NDI-2/NDI-3 was prepared without any staining agent**.** For AFM 0.5 mM solution was diluted to 0.25 mM prior to deposition on the mica surface.

Molar extinction coefficients for the final molecules were determined from the Lambert Beer equation. For self-assembly study, solvent dependent UV/Vis spectra were taken using 0.1 cm quartz cuvettes. 0.5 mM solution was used for recording UV/Vis and fluorescence spectra 0.5 mM.

Temperature dependent studies were done with 0.5 mM aqueous solution of NDI-1/NDI-2/NDI-3 (aged solution) from 20 ^{o}C to 95 ^{o}C (1 ^{o}C time interval, heating rate 2 ^{o}C/min) taken in quartz cuvette of 1 cm pathlength with constant stirring at 600 nm.

Reaction kinetics study with thiophenol: To a 2 mL aqueous solution (0.5 mM, aged for three weeks at 20 °C) of NDI-1/NDI-2/NDI-3 1 M of thiophenol dissolved in 10 µL of DMF was added. Change in fluorescence emission was monitored over time. Excitation wavelength 420 nm.

Table-S1: Sizes of the nanostructures obtained by different measurements. X-analyses could not be performed.

Amphiphile	Morphology	Size of nanostructures measured by different techniques			
		Cryo-TEM	AFM	Confocal	SAXS
NDI-1	cylindrical micelle	Length: >10 µm Width: 6.5±0.5 nm	Length: >10 µm Width: 7±1 nm	Length: >10 µm Width: X	Length: 292 nm Width: 8.5 nm
NDI-2	nanoribbon	Length: >10 µm Width: 300±50 nm Height: NA	Length: >10 µm Width: 450±50 nm Height: 5±0.5 nm	Length: >10 µm Width: X Height: X	Length: X Width: X Height: X
NDI-3	nanotube	Length: >10 µm Width: 15±1nm Membrane thickness: 5.3±0.3 nm	Length: >10 µm Width: 23±3 nm Membrane thickness: X	Length: >10 µm Width: X Membrane thickness: X	Length: >1.5 µm Width: X Membrane thickness: 8.8 nm

Additional Figures:

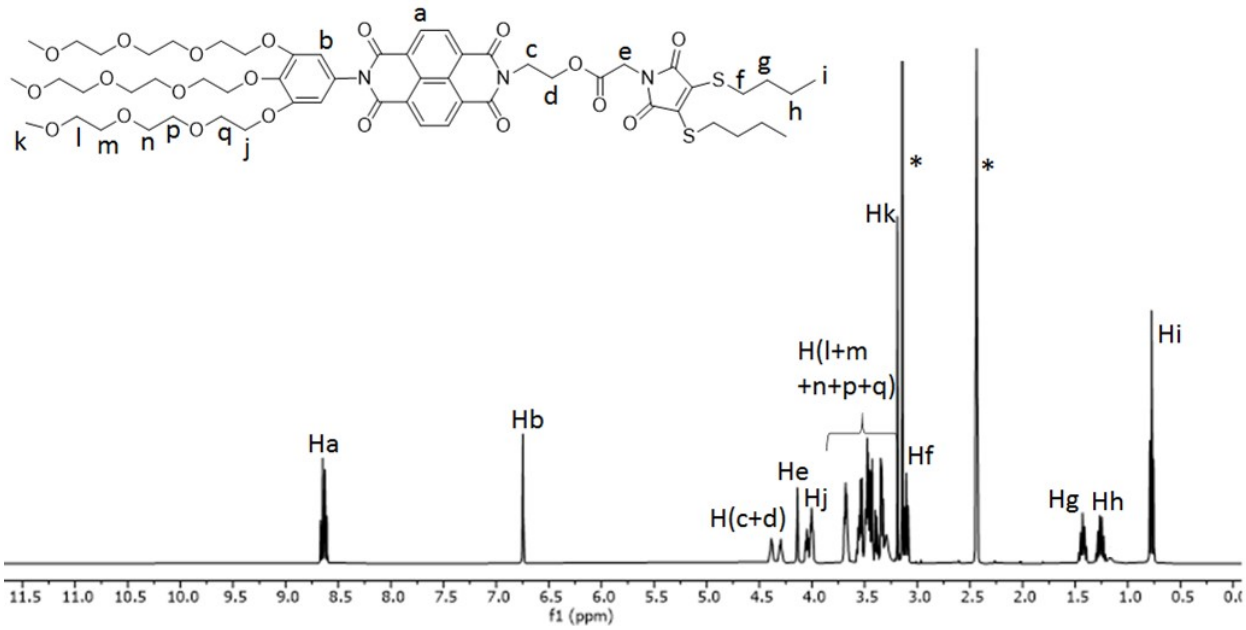


Figure S1. ^{1}H NMR spectrum of NDI-1. Solvent DMSO-d6. * Denotes solvent peak.

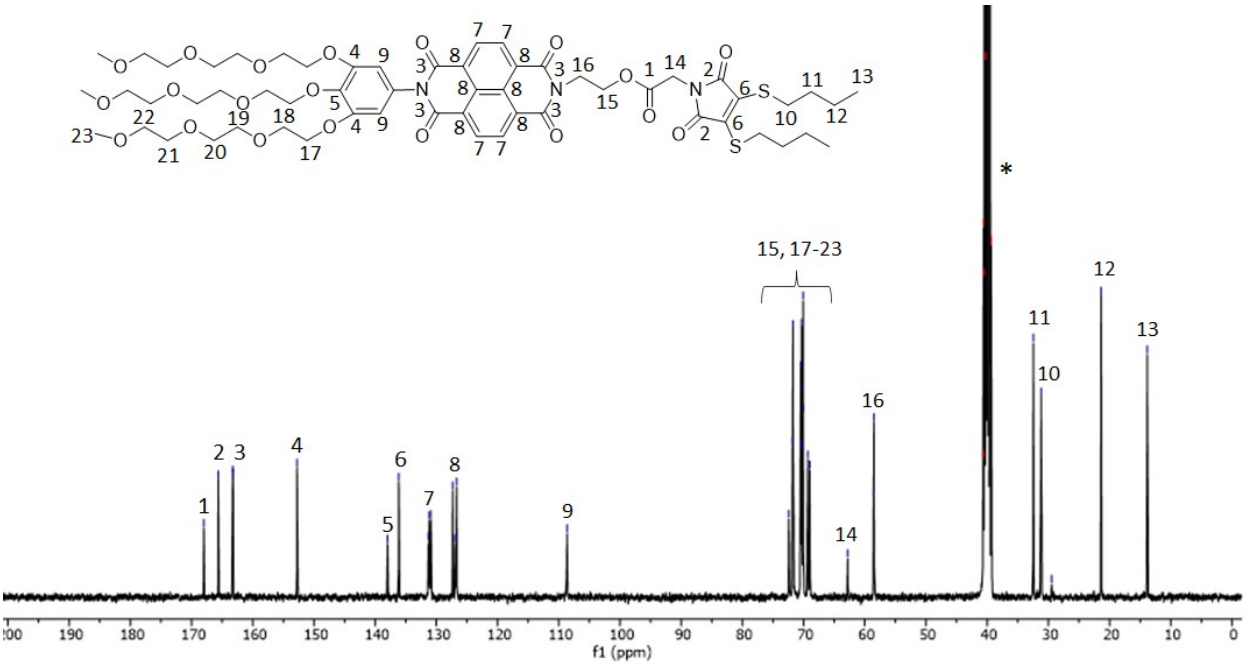


Figure S2. ^{13}C NMR spectrum of NDI-1. Solvent DMSO-d6. * Denotes solvent peak.

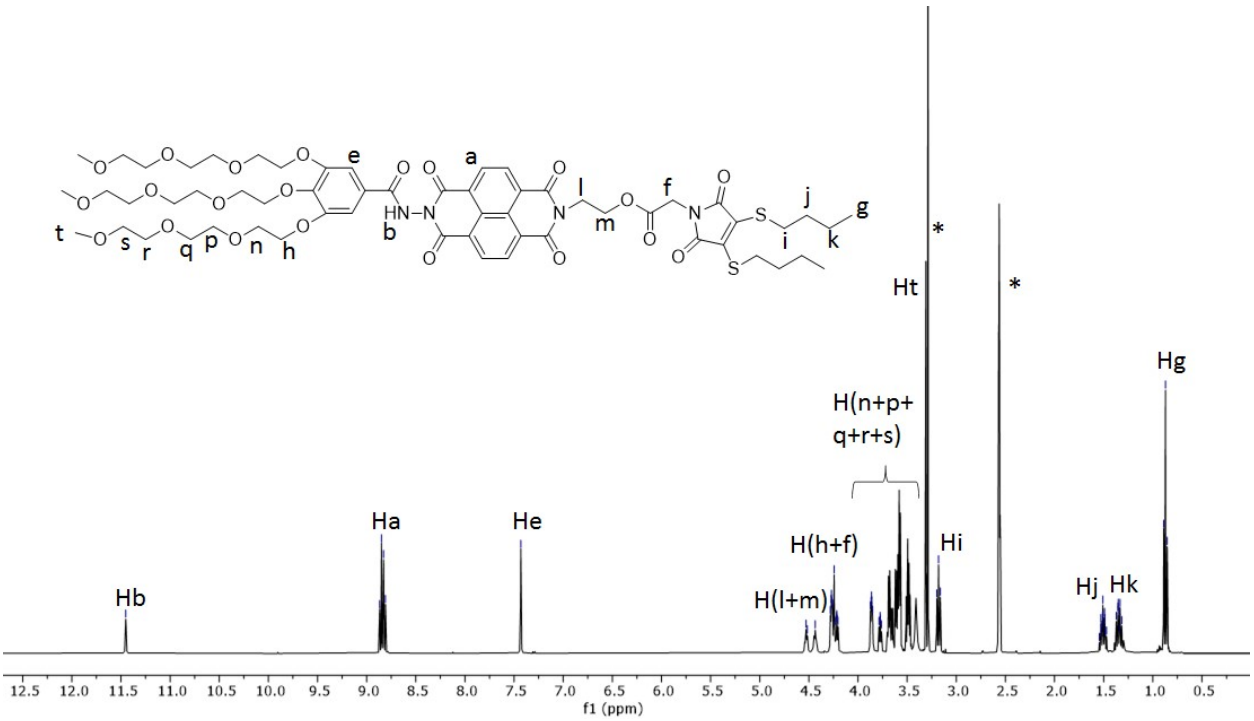
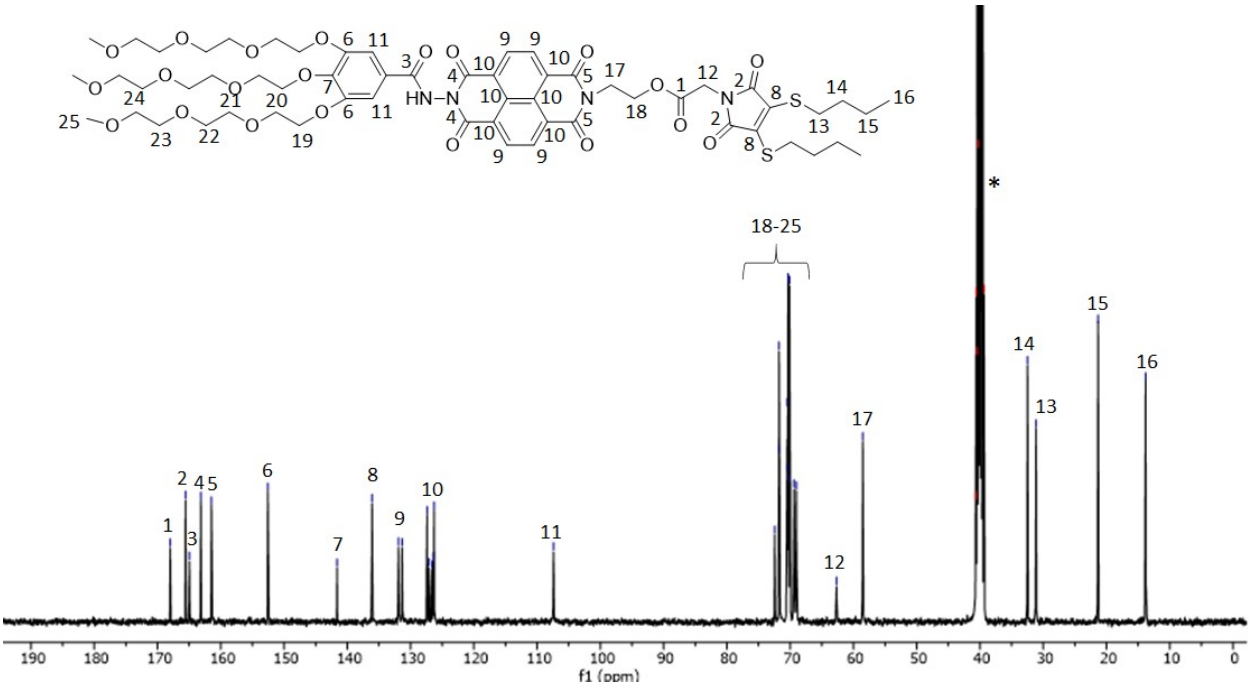


Figure S3. ^{1}H NMR spectrum of NDI-2. Solvent DMSO-d6. * Denotes solvent peak.

Figure S4. ^{13}C NMR spectrum of NDI-2. Solvent DMSO-d6. * Denotes solvent peak.



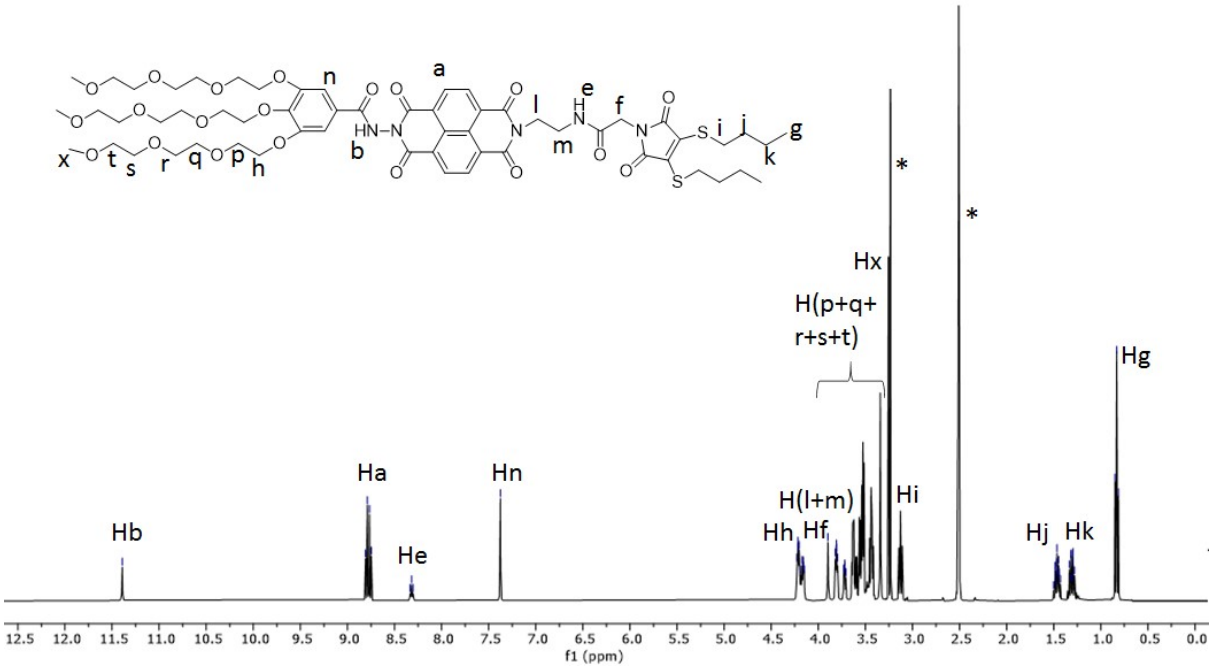


Figure S5. ^{1}H NMR spectroscopy of NDI-3. Solvent DMSO-d6. * Denotes solvent peak.

Figure S6. ^{13}C NMR spectrum of NDI-3. Solvent DMSO-d6. * Denotes solvent peak.

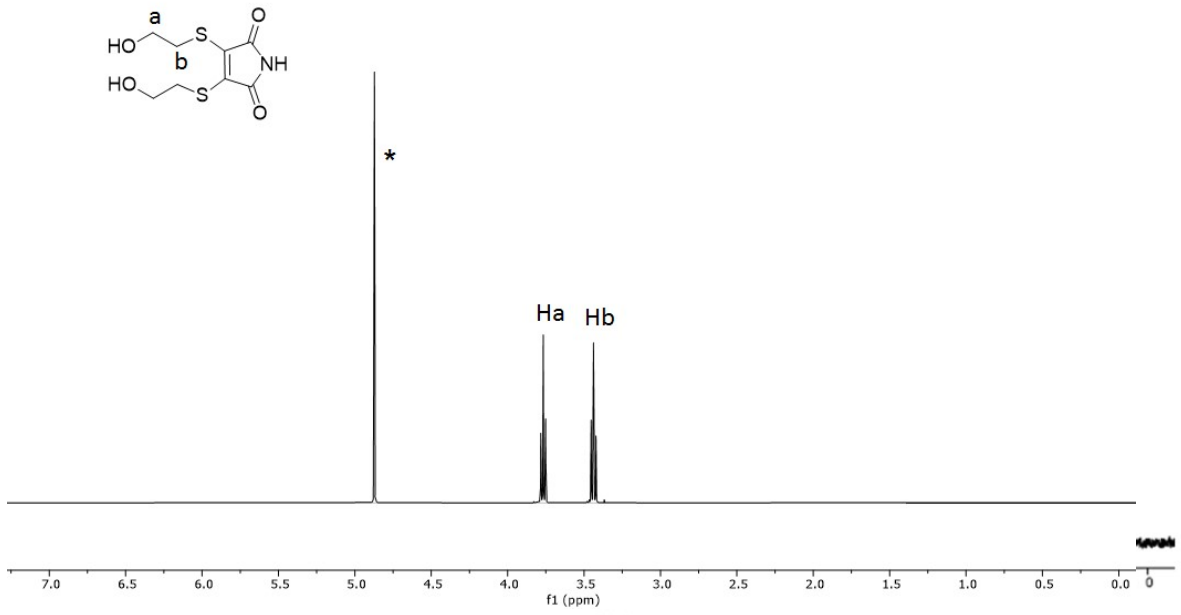


Figure S7. ^{1}H NMR spectrum of DTM-1. Solvent Methanol-d4. * Denotes solvent peak.

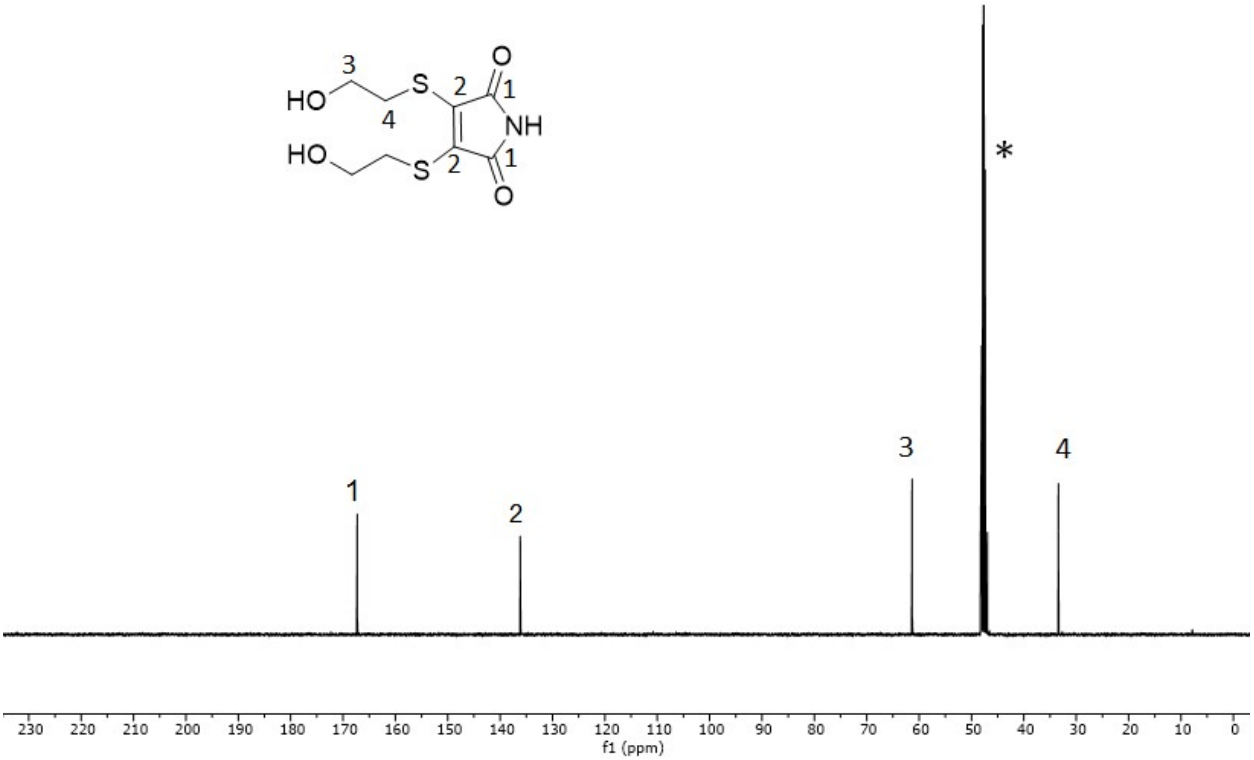


Figure S8. ^{13}C NMR spectrum of DTM-1. Solvent Methanol-d4. * Denotes solvent peak.

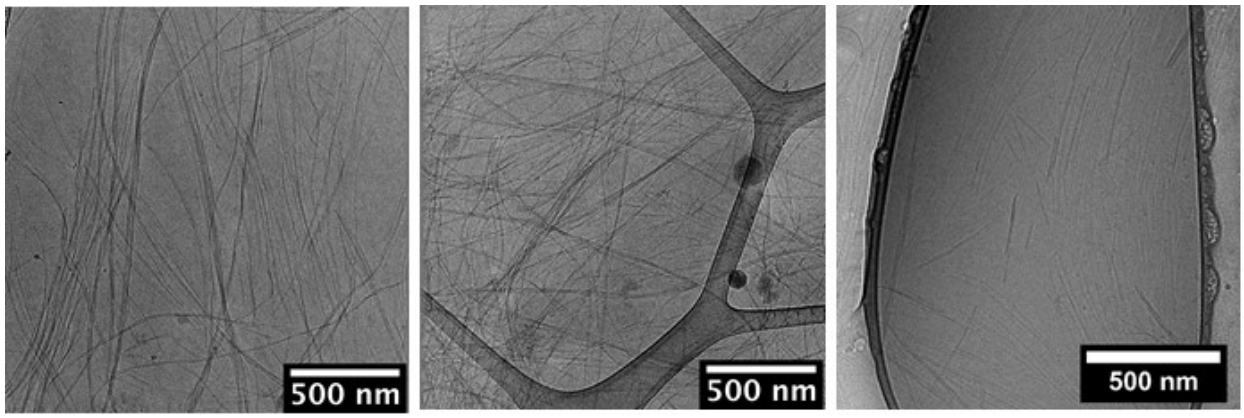


Figure S9. Cryo-TEM images of NDI-1 collected from different positions on the grid. (Conc.=0.5 mM).

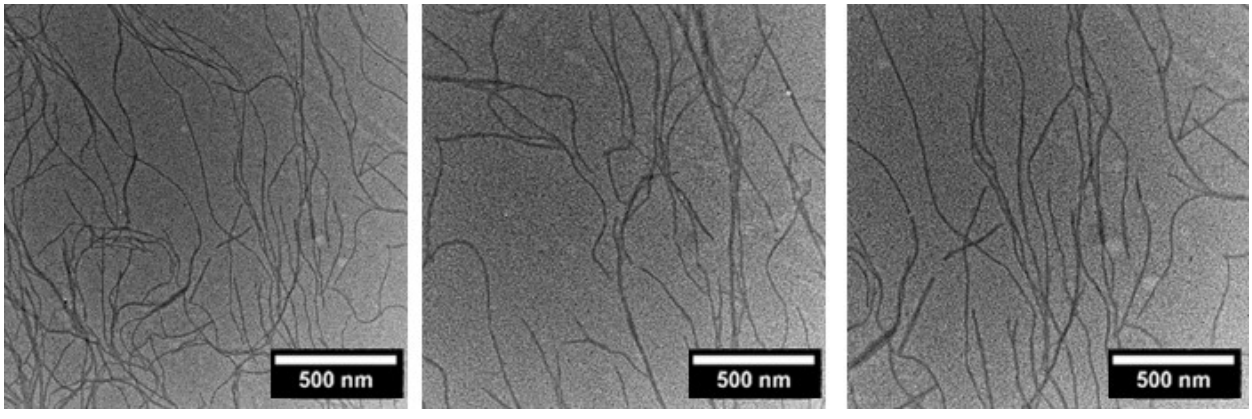
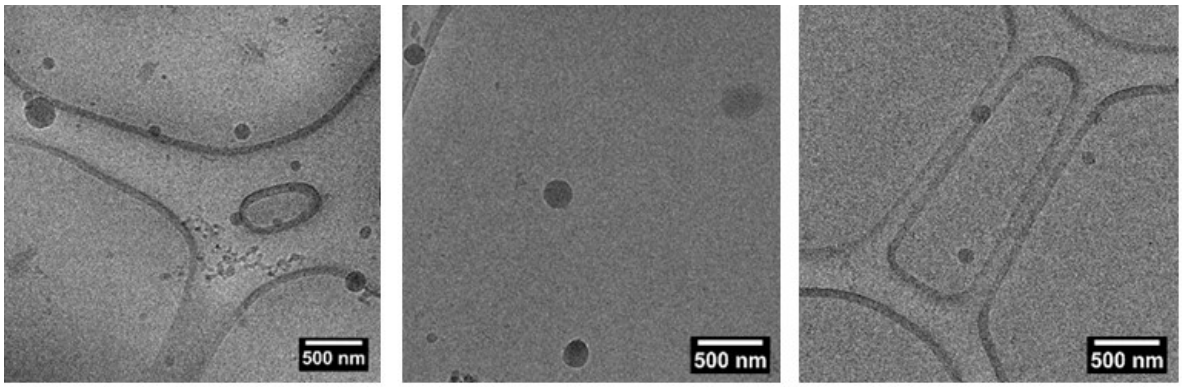


Figure S10. Dry state TEM images of NDI-1 collected from different positions on the grid. (Conc.=0.5 mM).

Figure S11. AFM image of NDI-1 (a) and corresponding height-width profile (b).



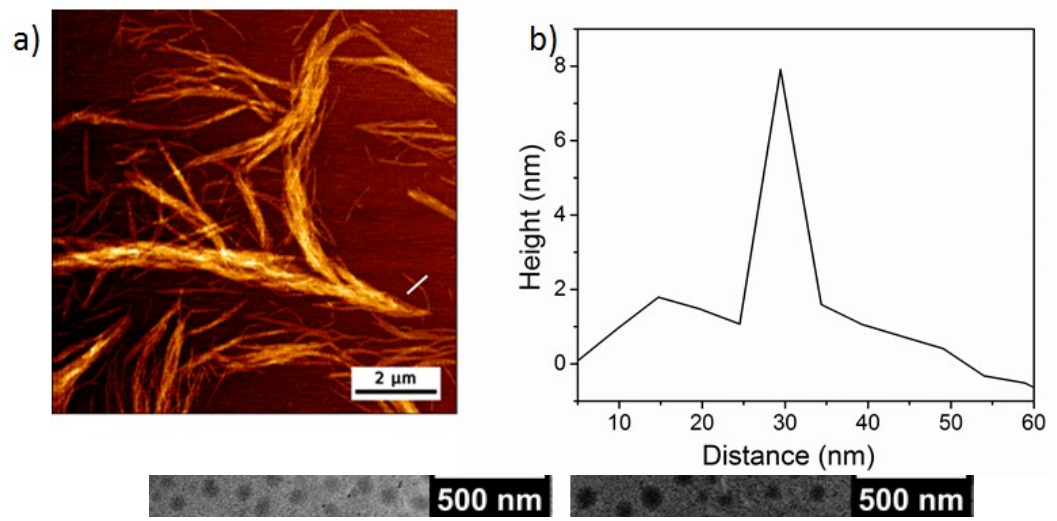


Figure S12. Cryo-TEM images of NDI-2 fresh solution, collected from different positions on the grid. (Conc.= 0.5 mM).

Figure S13. Dry state TEM images of NDI-2 fresh solution, collected from different positions on the grid. (Conc.= 0.5 mM).

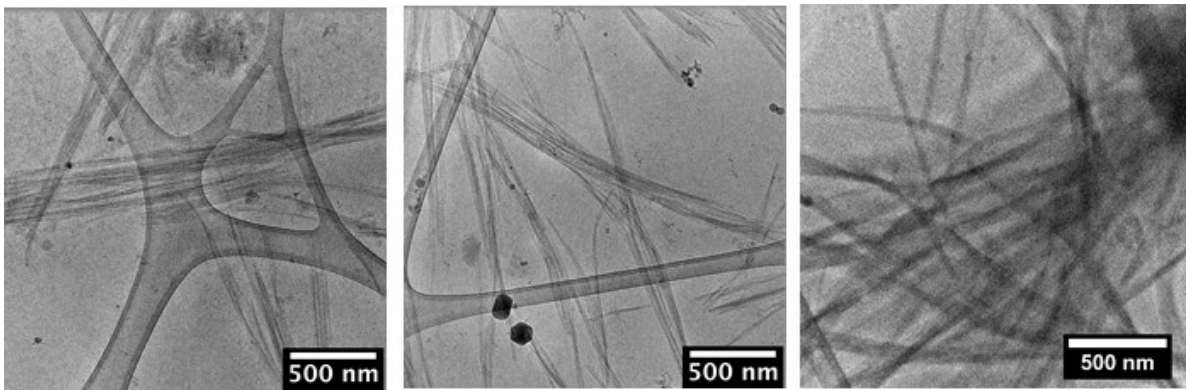


Figure S14. Cryo-TEM images of NDI-2 aged solution, collected from different positions on the grid. (Conc.= 0.5 mM).

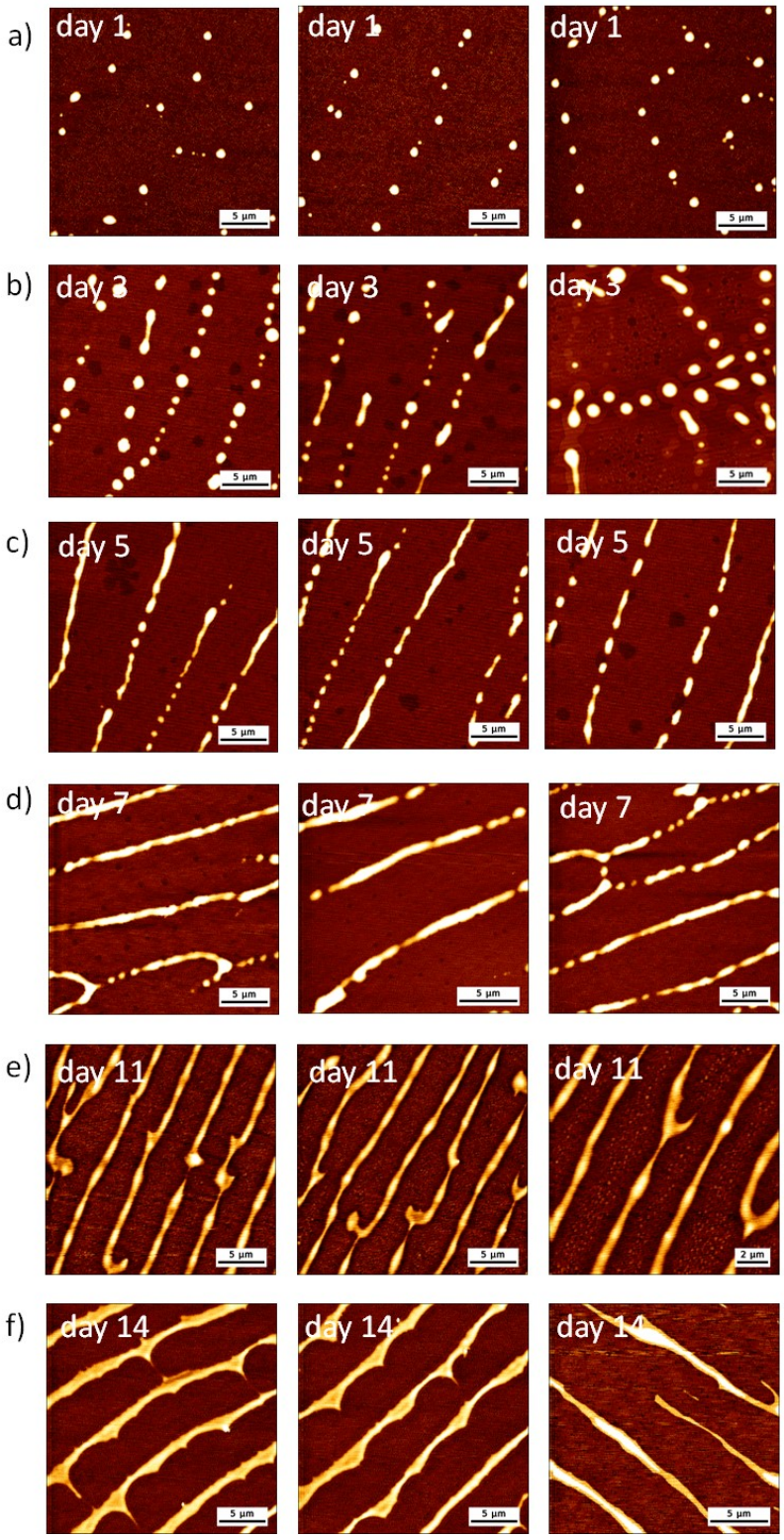


Figure S15. Time dependent AFM image of NDI-2 taken at different area of the mica surface. (a) day1; (b) day 3; (c)day-5; (d) day-7; (e) day-11; (f) day-14 (Conc.=0.5 mM)

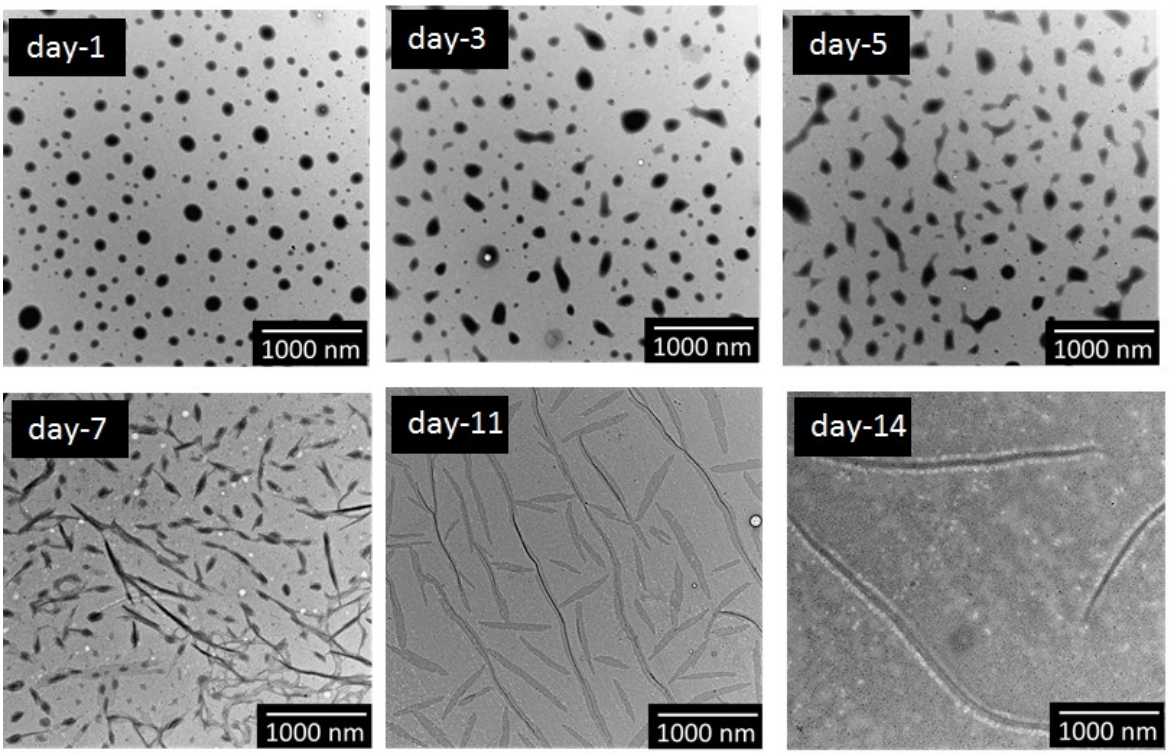
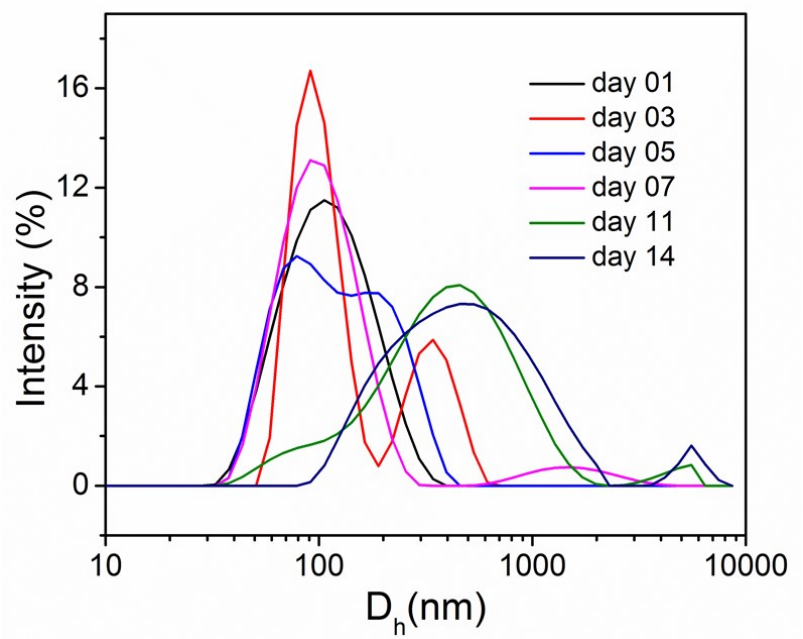


Figure S16. Time dependent HRTEM image of NDI-2 taken. (Conc.=0.5 mM).

Figure S17. Time dependent DLS measurement of NDI-2 (Conc.=0.5 mM).



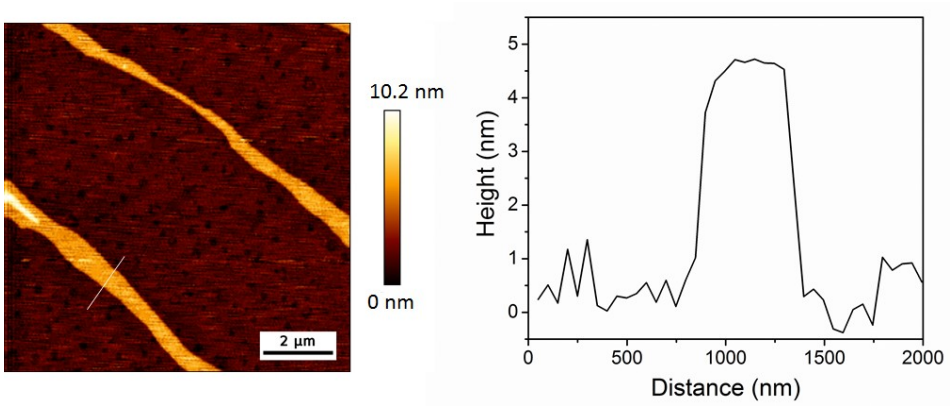


Figure S18. AFM image of NDI-2 (aged solution) and corresponding height-width profile.

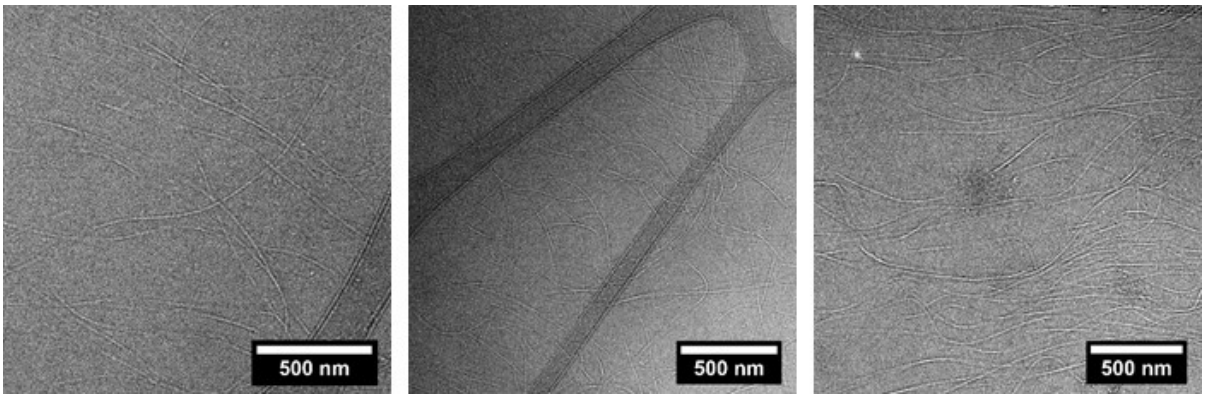


Figure S19. Cryo-TEM images of NDI-3 solution, collected from different positions on the grid. (Conc.= 0.5 mM).

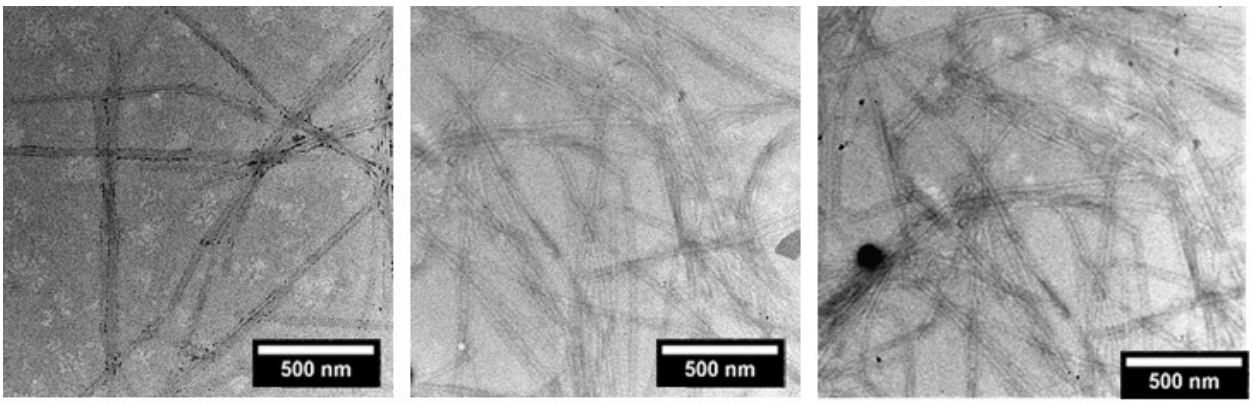


Figure S20. Dry state TEM images of NDI-3 collected from different positions on the grid. (Conc.= 0.5 mM).

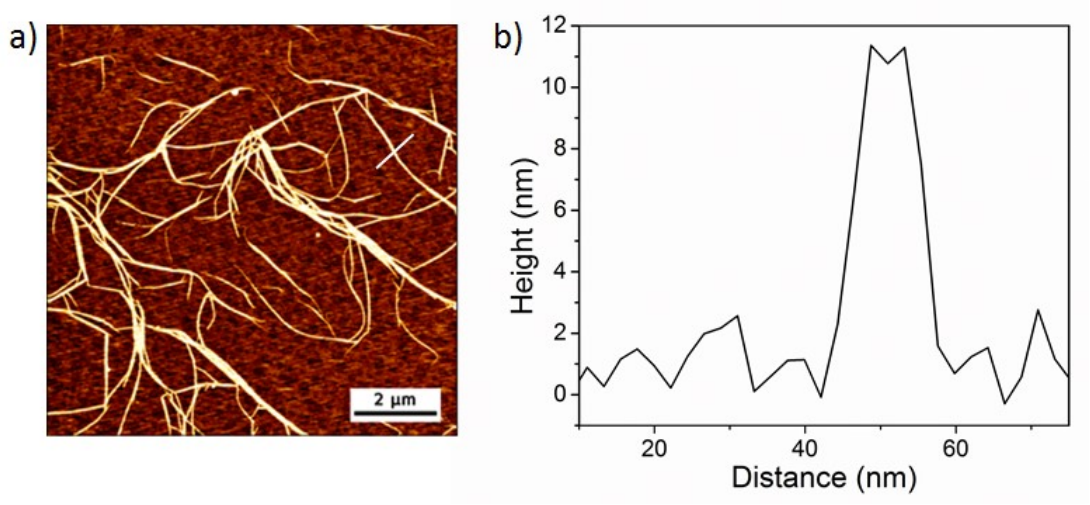


Figure S21. AFM image of NDI-3 (a) and corresponding height-width profile (b).

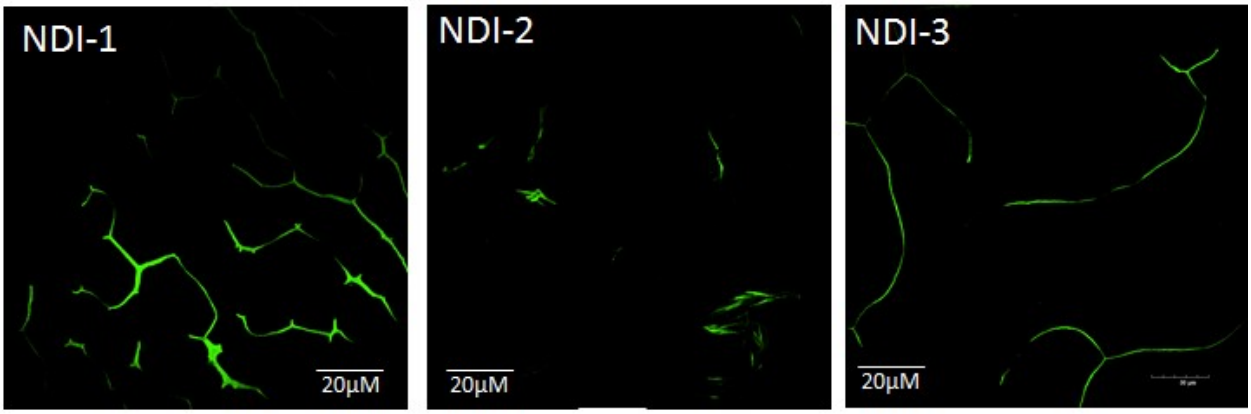


Figure S22. Confocal microscopy of NDI-1, NDI-2 and NDI-3. Conc.=0.25 mM, green laser channel, λex-405nm.

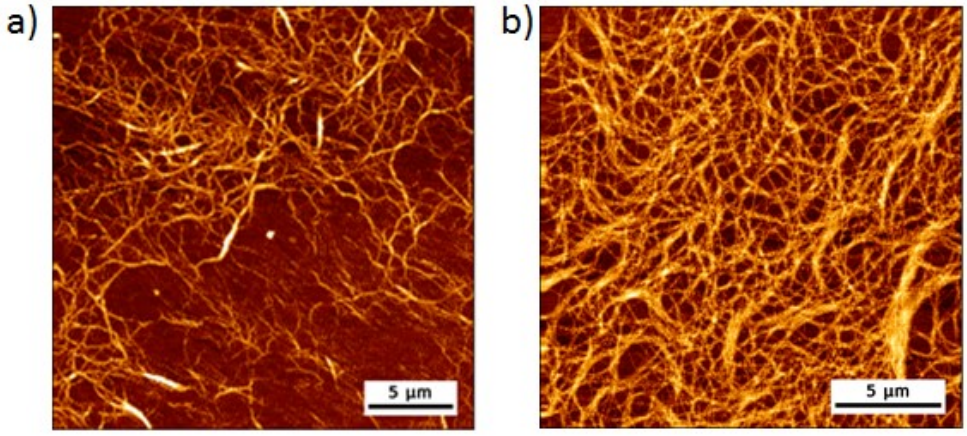


Figure S23. AFM images NDI-1(a) fresh solution, (b) 90 days aged solution. (Conc.=0.25 mM)

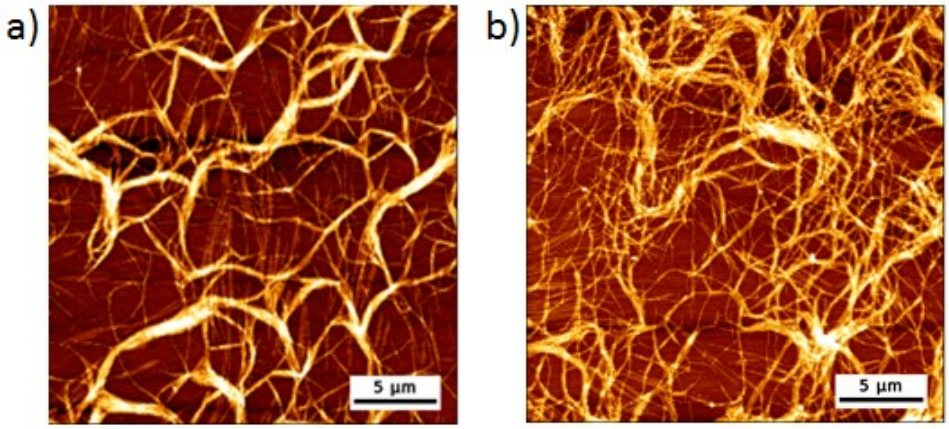
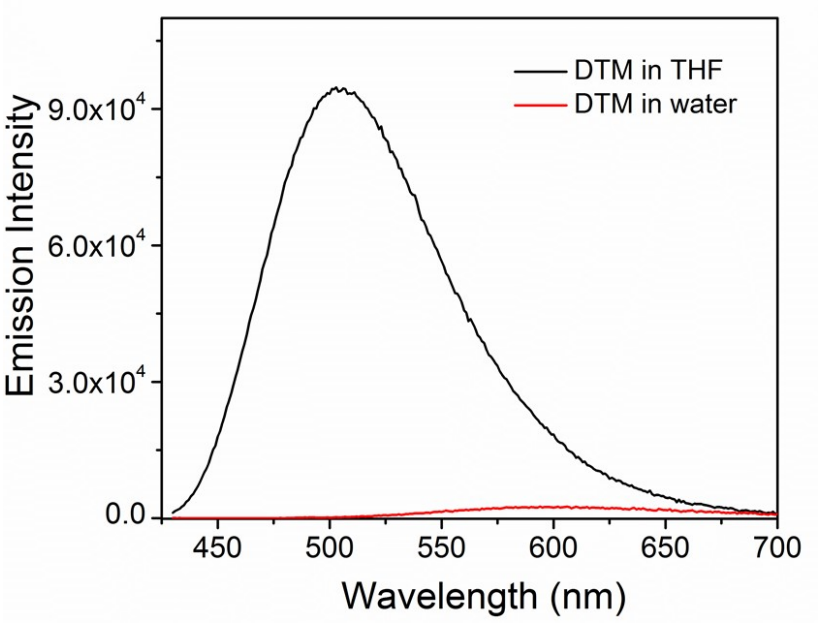


Figure S24. AFM images NDI-3 (a) fresh solution, (b) 90 days aged solution. (Conc.=0.25 mM)

Figure S25. Solvent dependent fluorescence spectra of DTM-1, Conc.=0.5 mM, λex=420 nm, slit-2.



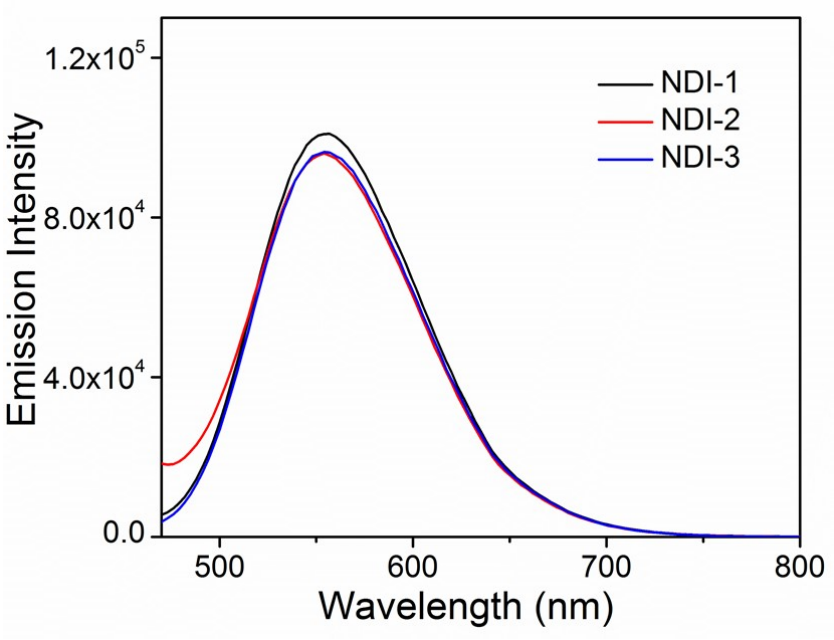
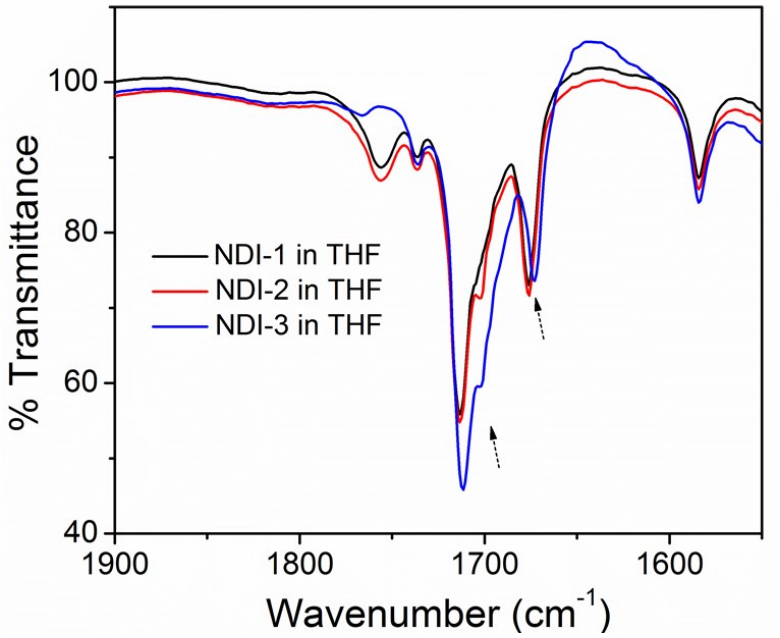


Figure S26. Emission spectra of NDI-1/2/3 in THF; Conc.=0.5 mM.

Figure S27. FTIR spectra of NDI-1/2/3 in THF; Conc.=0.5 mM.



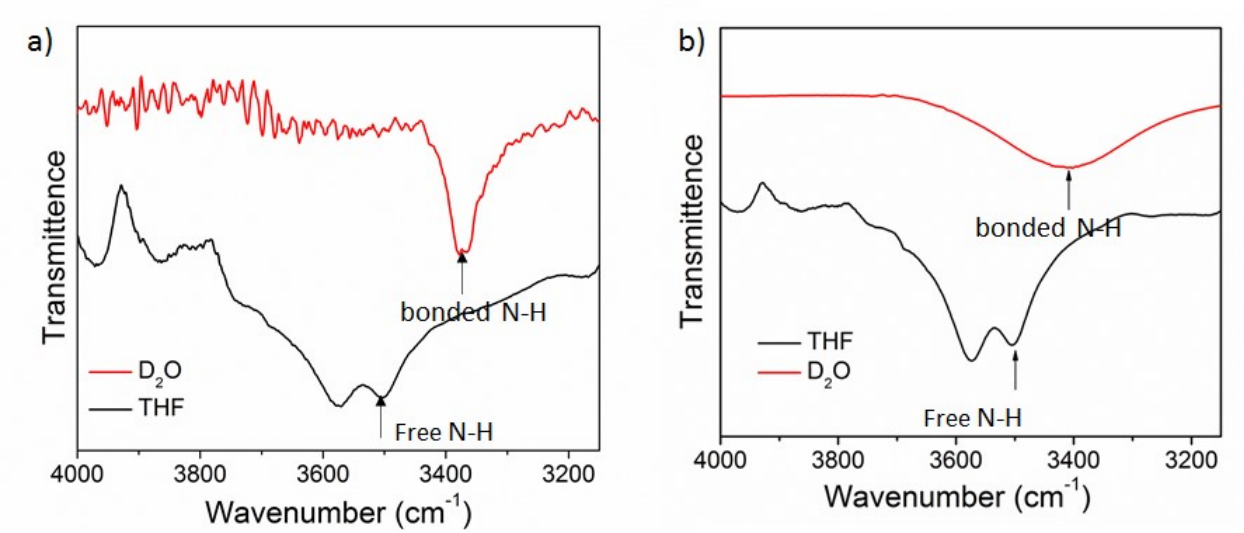
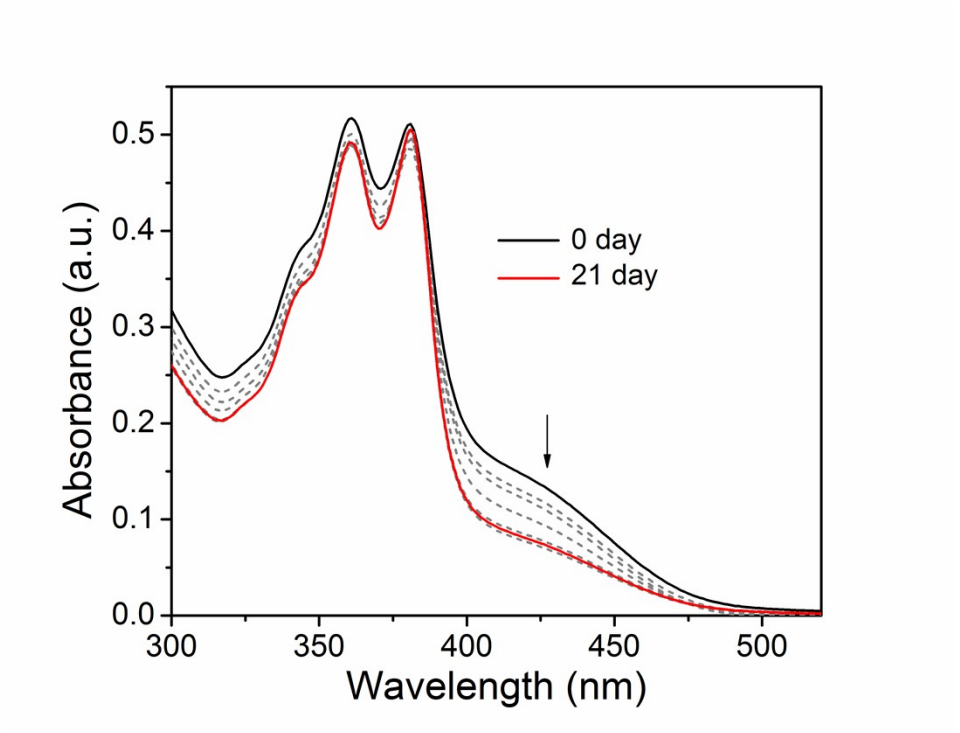


Fig 28. Solvent dependent FTIR spectra of (a) NDI-2 and ()NDI-3. Conc=0.5 mM

Figure S29. Time dependent UV/Vis spectroscopy of NDI-2; Conc.=0.5 mM, l=0.1 cm, T=20



°C.

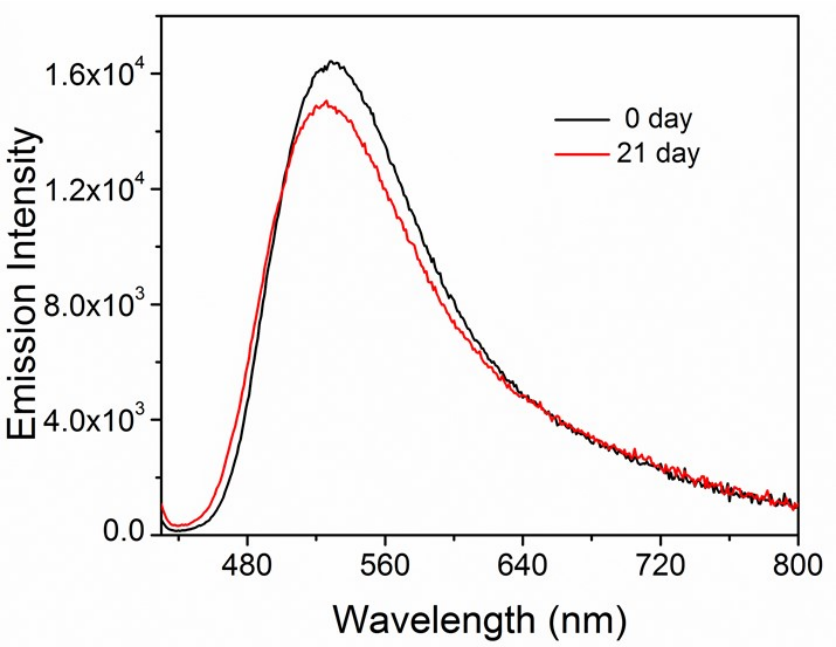


Figure S30. Fluorescence spectroscopy of fresh and aged solution of NDI-2; Conc.=0.5 mM, λ_{ex}=420 nm, slit-2.

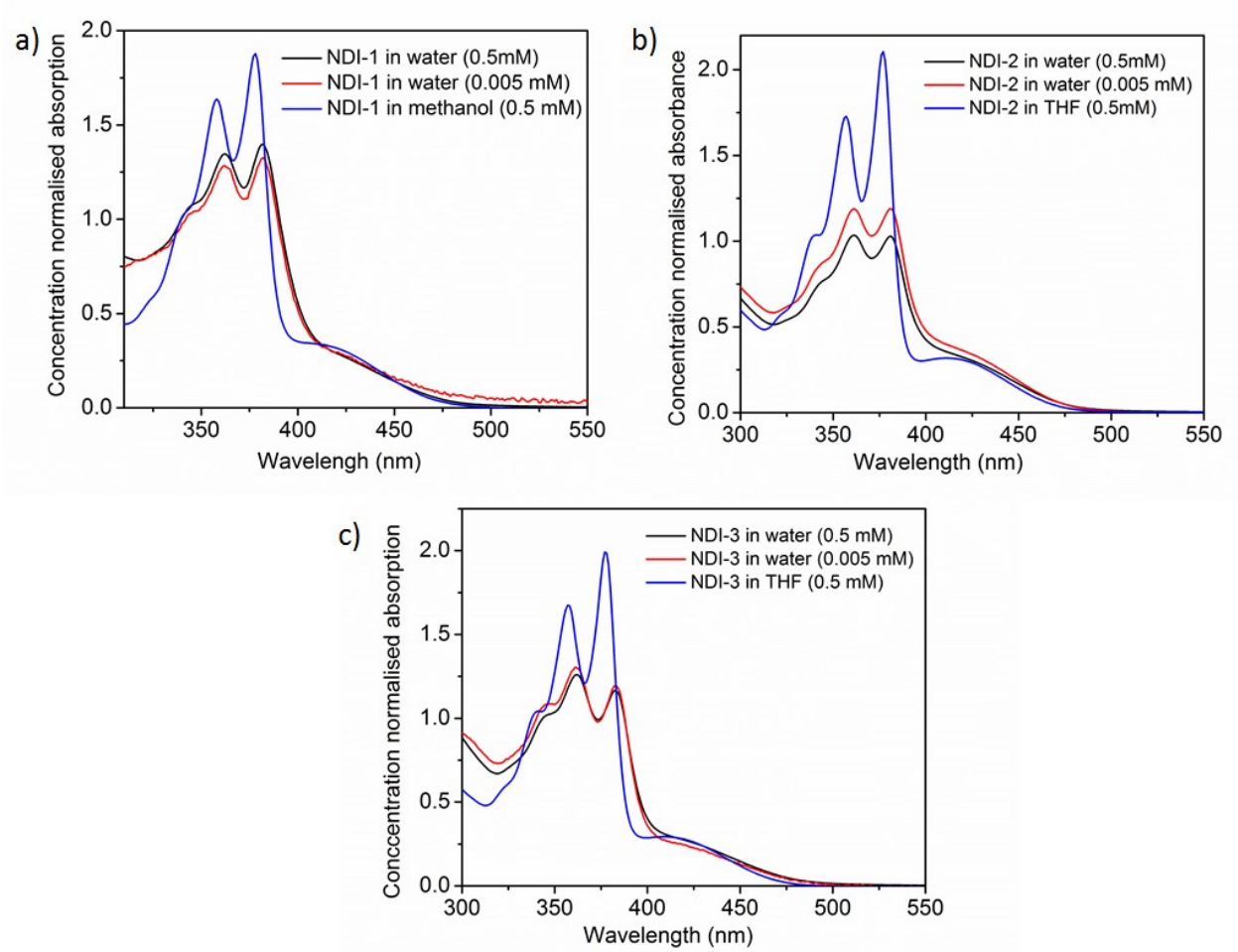


Figure S31. Concentration normalised UV/Vis spectra of NDI-1, NDI-2 and NDI-3. No signature of disassembly up to 0.005 mM concentration.

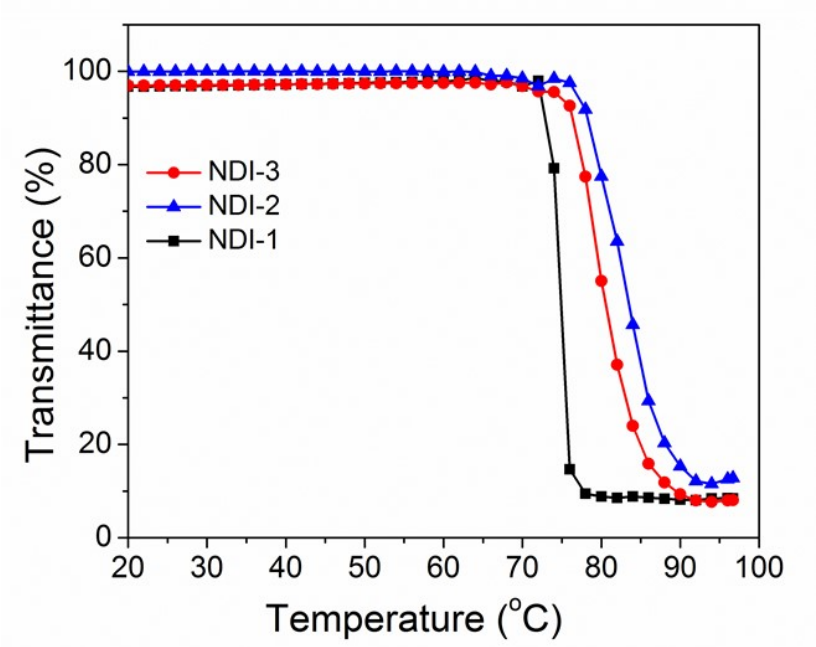


Figure S32. Temperature-dependent transmittance (monitored at 600 nm) of aqueous solution of NDI-1, NDI-2, and NDI-3. Conc.=0.5 mM, *l*=1cm.

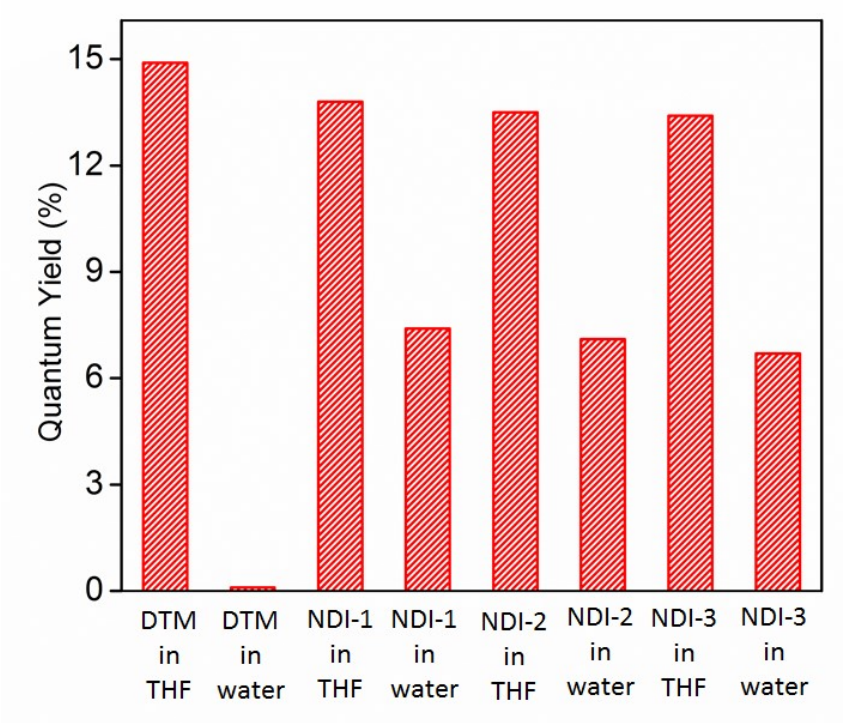


Figure S33. Comparison of relative quantum yield of NDI-1, NDI-2, NDI-3 and control molecule DTM-1 in THF/water.

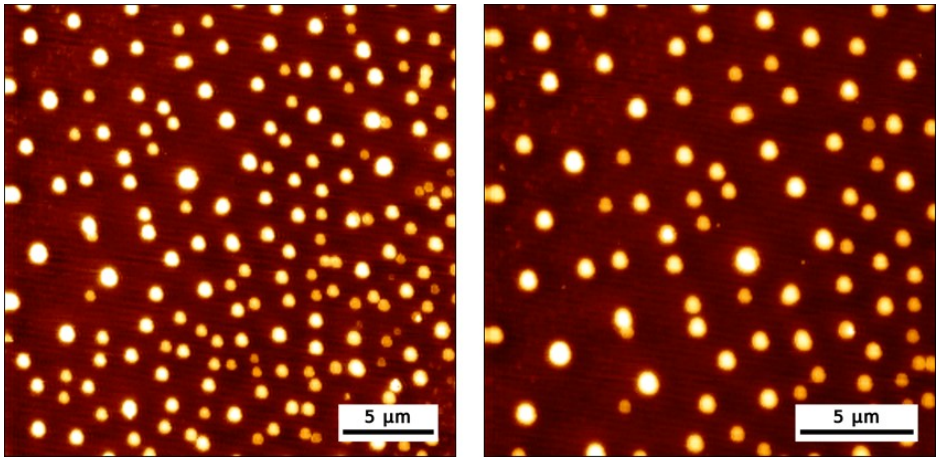


Figure S34. AFM image of NDI-1 in 95:5 cyclohexane/CH_2Cl_2. Conc.=0.25 mM.

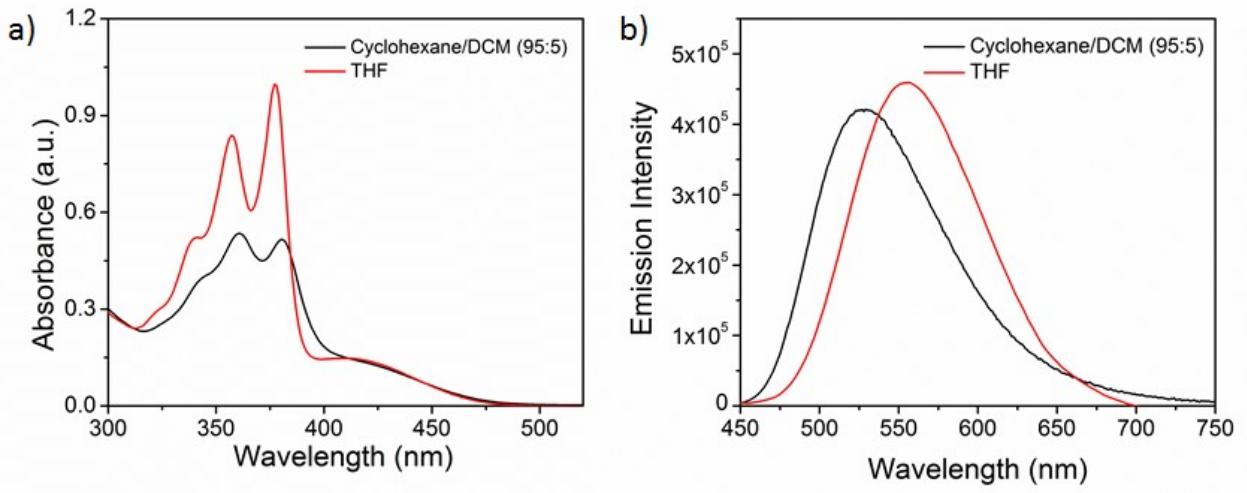


Figure S35. Comparison of solvent dependent (a) UV/Vis spectra and (b) fluorescence spectra of NDI-1 in 95:5 cyclohexane/CH_2Cl_2 and water. Conc.=0.5 mM, *l*=0.1 cm, λ_{ex}=420 nm, slit=2.

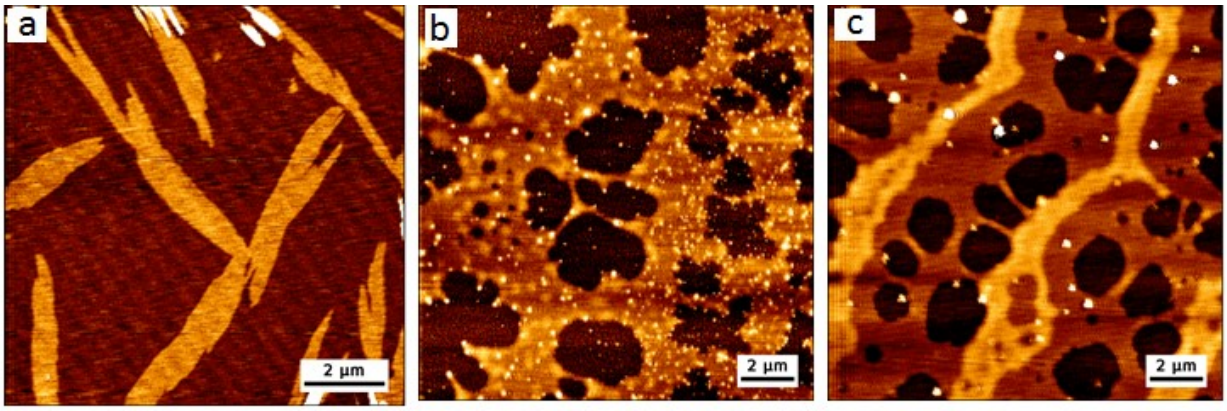


Figure S36. Representative AFM images of thiol modified (a) NDI-1; (b) NDI-2 and (c) NDI-3. Samples were prepared by drop casting the final solution after thiophenol exchange reaction. (Concentration of NDI= 0.25 mM).

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2. J. Ilavsky and P. R. Jemian, *J. Appl. Cryst.* 2009, **42**, 347-353.

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