Supporting Information

Organobase Triggered Controlled Supramolecular Ring Opening Polymerization and 2D Assembly

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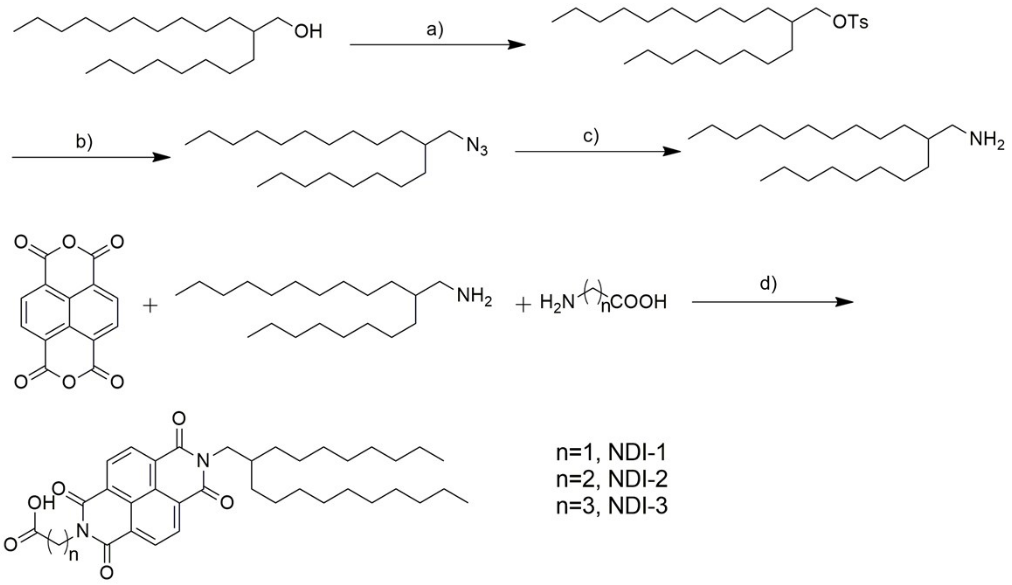
1) Experimental Procedures

Methods and materials:

All the reagents and starting materials were purchased from Sigma Aldrich Chemical Co., Tokyo Chemicals Industries (TCI) or local suppliers and used without further purification. Solvents used for synthesis were purchased from commercial sources and purified by standard procedures.[1] Physical studies were performed using spectroscopy grade solvents. ^{1}H NMR experiments were performed on a Bruker DPX-500 MHz, 400 MHz, 300 MHz spectrometer and TMS was used as an internal standard for calibration. UV/Vis studies were done in a Jasco V-750 spectrometer. The high resolution mass spectrometry analysis was performed using an electron spray ionization (ESI) technique on a Q-tof-micro quadruple mass spectrometer. FT-IR spectra data were recorded in a Perkin Elmer Spectrum 100FT-IR spectrometer. Fluorescence spectra were recorded in FluoroMax3 spectrometer from Horiba. AFM images were captured in an Innova instrument from Bruker.

Synthesis and characterization of NDI-1, NDI-2, NDI-3



Reagents and conditions: a) TsCl, Pyridine, dry DCM, 0 ^{o} C to RT, 3days, 88%; b) NaN_3, DMF, 100 ^{o} C, 88%; c) Pd-charcoal, H_2 gas, ethyl acetate, quantitative yield; d) Dry DMF, 140 ^{o} C.

Scheme 1. Synthetic route for NDI-1, NDI-2 and NDI-3

Compound 1: To a cold solution of pyridine (12 g, 0.0168 mole) in 15mL freshly dried $CH_2Cl_2,$ a solution of *p*-toluene-sulfonyl chloride (TsCl) (3.84 g, 0.020 mole) and 2-octyl dodecanol (5 g, 0.0168 mole) in 10 mL freshly dried CH_2Cl_2 was added drop-wise. After the addition was over, the solution was allowed to stir at room temperature for 72 h. Then stirring was stopped, solvent was evaporated and the pasty mass obtained was dissolved in CH_2Cl_2 (50 mL) and was washed with 2N HCl solution (2 x 30 mL) followed by brine solution (2 x 30 mL). The organic layer was passed through anhydrous Na_2SO_4 and solvent was removed and product was purified by column chromatography using silica gel (100-200 mesh) as a stationary state and 2 % ethyl acetate in petroleum ether as eluent to get the desired product as colorless liquid. Yield= 6.65g (88 %); ^{1}H NMR ($CDCl_3$, 400MHz, TMS): δ (ppm) = 7.79 (2H, d), 7.32 (2H, d), 3.91 (2H, d), 2.44 (3H, s), 1.57-1.33 (33H, m), 0.88 (6H, t).

Compound 2: A mixture of octyl dodecanol tosylate (compound **1**, 1.618 g, 0.0036 mole) and sodium azide (0.697 g, 0.011 mole) in dry N, N-dimethylformamide (DMF) (15 mL) was stirred at 100 °C under inert atmosphere for 12 h. Then heating was stopped. The reaction mixture was allowed to settle at room temperature and diluted with 25 mL water and the product was extracted with ethyl acetate (2 x 25 mL). The organic layer was washed with brine solution and passed through anhydrous Na_2SO_4. The solvent was removed under reduced pressure producing colorless liquid which was used in next step without further purification. Yield= 1.1 g (88 %); ^{1}H NMR ($CDCl_3$, 400MHz, TMS): δ (ppm) = 3.22 (2H, d), 1.54 (1H, s), 1.27 (32H, m), 0.88 (6H, t).

Compound 3: 10% palladium-charcoal (100 g) was added to a solution of compound **2** (1.079 g, 0.004 mole) in 15 mL ethyl acetate and the reaction mixture was stirred at room temperature at 50-55 psi pressure of H_2 gas for 24 h. Then the solution was filtered to remove the catalyst using Whatman filter papers. The filtrate was concentrated to get the branched amine as light yellow liquid which was used in next step without further purification. Quantitative yield; ^{1}H NMR ($CDCl_3$, 300MHz, TMS): δ (ppm) = 4.326 (1H, broad), 2.763 (2H, d), 1.54 (1H, broad), 1.27 (32H, m), 0.88 (6H, t).

NDI-1: Glycine (0.252 g, 0.0034 mole), napthalenetetracarboxylic dianhydride (0.901 g, 0.0034 mole) and compound **3** (1 g, 0.0034 mole) were taken in dry N, N-dimethylformamide (DMF) (10 mL) and the reaction mixture was stirred at 140 °C in inert atmosphere along with triethylamine (0.340 g, 0.0034 mole) for 12 h. The heating was stopped and the reaction mixture was allowed to come at room temperature. Then it was acidified with 15 mL of acidic water (2N HCl). Brown colored precipitate was obtained which was filtered through Buchner funnel and it was further washed with methanol. Further purification was performed by column chromatography using silica gel (100-200 mesh) as a stationary state and 1.5 % methanol in dichloromethane as eluent to get the desired product as pale white sticky solid. Yield= 0.600 g (Yield-24%); ^{1}H NMR ($CDCl_3$, 500MHz, TMS): δ (ppm) = 8.771 (4H, s), 5.001 (2H, s), 4.127 (2H, d), 1.985 (1H, s), 1.290-1.210 (32H, m), 0.88 (6H, t). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ (ppm) = 171.78, 163.22, 162.65, 131.59, 131.19, 127.28, 126.99, 126.09, 45.24, 41.33, 36.77, 32.02, 31.84, 30.14, 29.76, 29.73, 29.68, 29.47, 29.42, 26.58, 22.82, 22.79, 14.23. HRMS (ESI): m/z for $C_{36}H_{48}N_2O_6$ [M + Na] calc: 627.7858; found: 627.8315.

NDI-2: 3-Aminopropanoic acid (0.108 g, 0.0012 mole), napthalenetetracarboxylic dianhydride (0.326 g, 0.0012 mole) and compound **3** (0.362 g, 0.0012 mole) were taken in dry N, N-dimethylformamide (DMF) (5 mL) and the reaction mixture was stirred at 140 ^{o}C in inert atmosphere along with triethylamine (0.123 g, 0.0012 mole) for 18 h. The heating was stopped and the reaction mixture was allowed to come at room temperature. Then it was solubilized in 20 mL ethyl acetate and the organic layer was washed by 3 x 15 mL of acidic water (2N HCl) and brine solution (2 x 15mL). Further purification was performed by column chromatography using silica gel (100-200 mesh) as a stationary state and 1.0 % methanol in dichloromethane as eluent to get the desired product as pale white sticky solid. Yield= 0.120 g (Yield-20%); ^{1}H NMR ($CDCl_3$, 400MHz, TMS): δ (ppm) = 8.794 (4H, s), 4.541(2H, t), 4.134 (2H, d), 2.853 (2H, t), 1.978 (1H, s), 1.373-1.217 (32H, m), 0.88 (6H, t). ^{13}C NMR ($CDCl_3$, 400 MHz, TMS): δ (ppm) = 175.50, 163.26, 162.92, 131.35, 131.19, 127.05, 126.93, 126.41, 45.20, 36.77, 36.42, 32.25, 32.05, 32.02, 31.83, 30.14, 29.76, 29.73, 29.69, 29.47, 29.42, 26.58, 22.82, 22.79, 14.24. HRMS (ESI): m/z for $C_{37}H_{50}N_2O_6$ [M + Na] calc: 641.3249; found: 641.3249.

NDI-3: 4-Aminobutyric acid (0.166g, 0.0016 mole), napthalenetetracarboxylic dianhydride (0.432 g, 0.0016 mole) and compound **3** (0.479 g, 0.0016 mole) were taken in dry N, N-dimethylformamide (DMF) (5 mL) and the reaction mixture was stirred at 140 ^{o}C in inert atmosphere along with triethylamine (0.123 g, 0.0012 mole) for 18 h. The heating was stopped and the reaction mixture was allowed to come at room temperature. Then it was solubilized in 20mL ethyl acetate and the organic layer was washed by 3 x 15 mL of acidic water (2N HCl) and brine solution (2 x 15mL). Further purification was performed by column chromatography using silica gel (100-200 mesh) as a stationary state and 1.0 % methanol in dichloromethane as eluent to get the desired product as pale white sticky solid. Yield= 0.130 g (Yield-15%); ^{1}H NMR ($CDCl_3$, 400MHz, TMS): δ (ppm) = 8.765 (4H, s), 4.294(2H, t), 4.128 (2H, d), 2.505 (2H, t), 2.114 (2H, t), 1.978 (1H, s), 1.373-1.217 (32H, m), 0.88 (6H, t). ^{13}C NMR ($CDCl_3$, 400 MHz, TMS): δ (ppm) = 177.74, 177.62, 163.29, 162.11, 131.25, 131.16, 126.93, 126.89, 126.56, 45.18, 40.07, 36.76, 36.42, 32.05, 32.02, 31.83, 31.73, 31.47, 30.14, 29.76, 29.73, 29.68, 29.47, 29.42, 26.58, 22.81, 22.79, 14.24. HRMS (ESI): m/z for $C_{38}H_{52}N_2O_6$ [M + H] calc: 633.3904; found: 633.3915

Preparation of dormant monomer

At first, a 2.0 mM stock solution of NDI-1/NDI-4 in $CHCl_3$ was prepared. 100 µL of that solution was transferred to a separate vial and further diluted by adding 1.0 mL $CHCl_3$. One drop of methanol was added to it and was mixed properly. Then the solution was kept open for overnight at RT to allow slow evaporation. The solid residue obtained was again dissolved in 100 µL $CHCl_3$ and an aliquot of 75 µL solution was added to 1.5 mL decane to make the final concentration of the solution 0.1 mM. Then the solution was heated at 70-80 ^{o} C temperature for half an hour to evaporate the $CHCl_3$. After cooling at 25 ^{o}C, UV/Vis, FT-IR and fluorescence spectra were recorded and spectra indicate monomeric nature.

Spontaneous aggregation

75 µL of 2.0 mM stock solution of NDI-derivatives in $CHCl_3$ was transferred to a vial. Then solvent was evaporated and solid residue was obtained. That residue was dissolved in 1.5 mL decane by strong heating. After cooling for 15 min, UV/Vis, FT-IR and fluorescence spectra are recorded to probe the nature of the spontaneously assembled state.

Supramolecular polymerization by DBU/DMAP

1.0 mM stock solution of DBU/DMAP in $CHCl_3$ was made. From that, an aliquot was transferred to another vial, solvent was removed and measured amount of decane was added to make a solution of DBU/DMAP in decane with 0.1 mM concentration. Then the dormant monomer (0.1 mM, 1.5 mL) was prepared by above mentioned procedure. Then required amount of 0.1 mM decane solution of DBU/DMAP was added to the NDI-1_{mono}/ NDI-4_{mono} solution in decane and the supramolecular polymerization at 25 ^{o}C was monitored by UV/Vis spectroscopy. Mole fraction of aggregates at different time was determined using the following equation (1)

$$\alpha_{\text{agg}} = \frac{A(t) - A(\min)}{A(\max) - A(\min)} \text{ – } (1)$$

where *A* (max), *A* (min) and *A* (t) stand for maximum and minimum absorbance of the band at 376 nm and absorbance at the particular time t.

AFM study

10.0 μl of the sample solutions in decane (0.1 mM, 1.5 ml) were drop casted on a mica surface and dried at room temperature for 12 h before capturing images.

Additional figures:

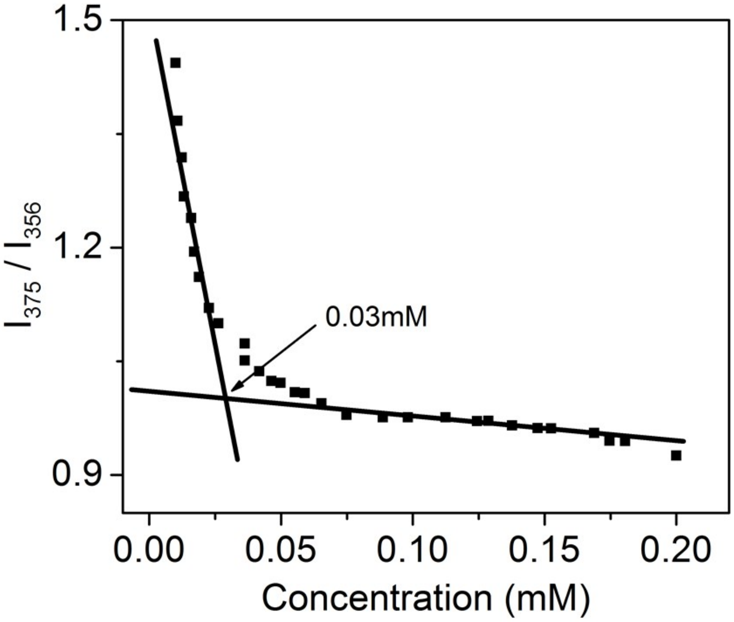


Figure S1. Determination of Critical Aggregation Concentration (CAC) of NDI-1 in decane by UV/Vis spectroscopy (Data obtained by performing dilution experiment from 0.2 mM to 0.01 mM).

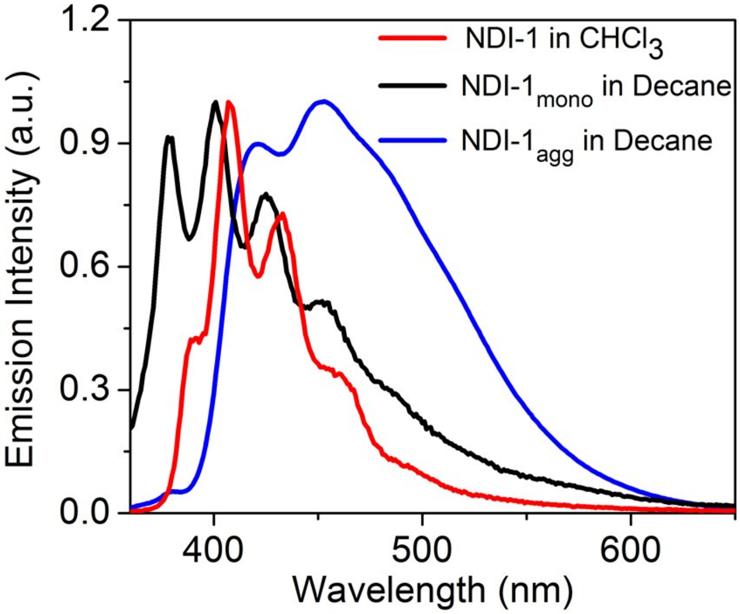


Figure S2. Solvent dependent fluorescence spectra of NDI-1 in monomeric and aggregated state [slit-5; λ_{ex}= 340 nm; *C* = 1 x 10^{-4} M].

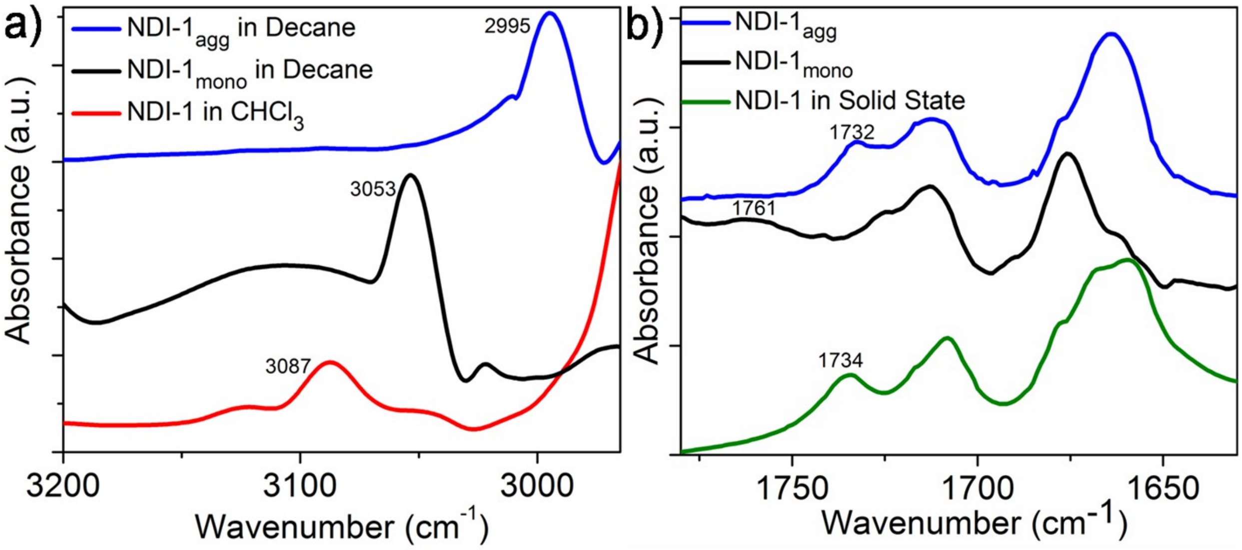


Figure S3. FT-IR spectra (a, b- different region) of different states of NDI-1 in solution (C = 10^{-4} M) or in solid state.

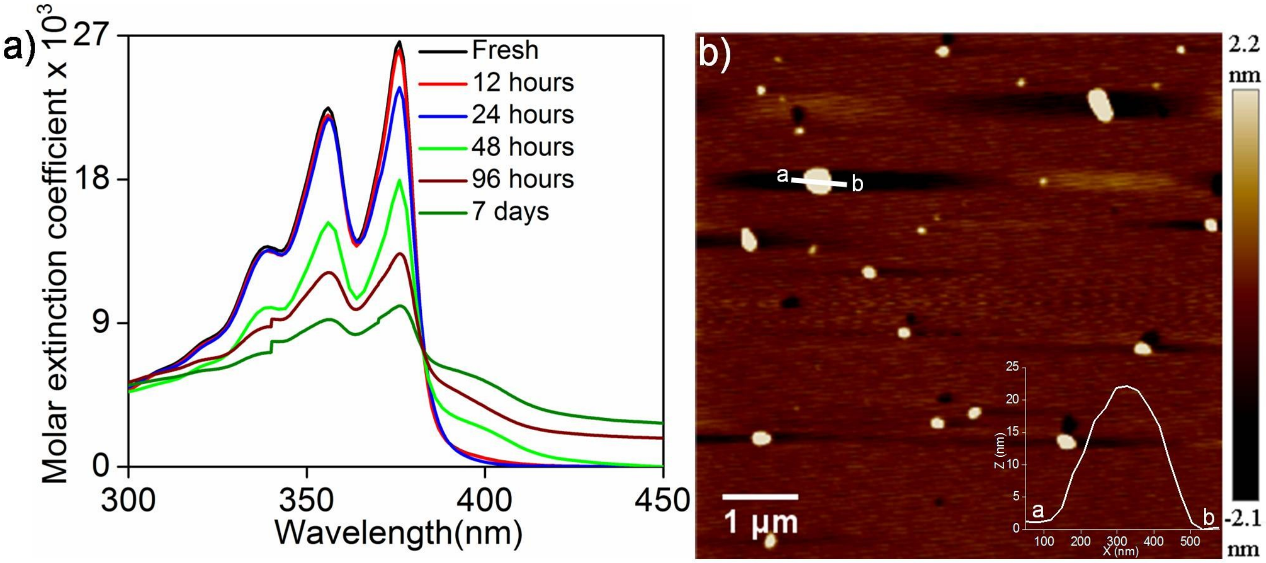


Figure S4. a) Time-dependent change in the UV/Vis spectra of NDI-1_{mono} in decane. [l = 1 cm; C = 1 x 10^{-4} M]; b) AFM image of the sample prepared by taking aliquot from the NDI-1_{mono} solution (decane) after seven days waiting time. Inset shows height profile across a-b.

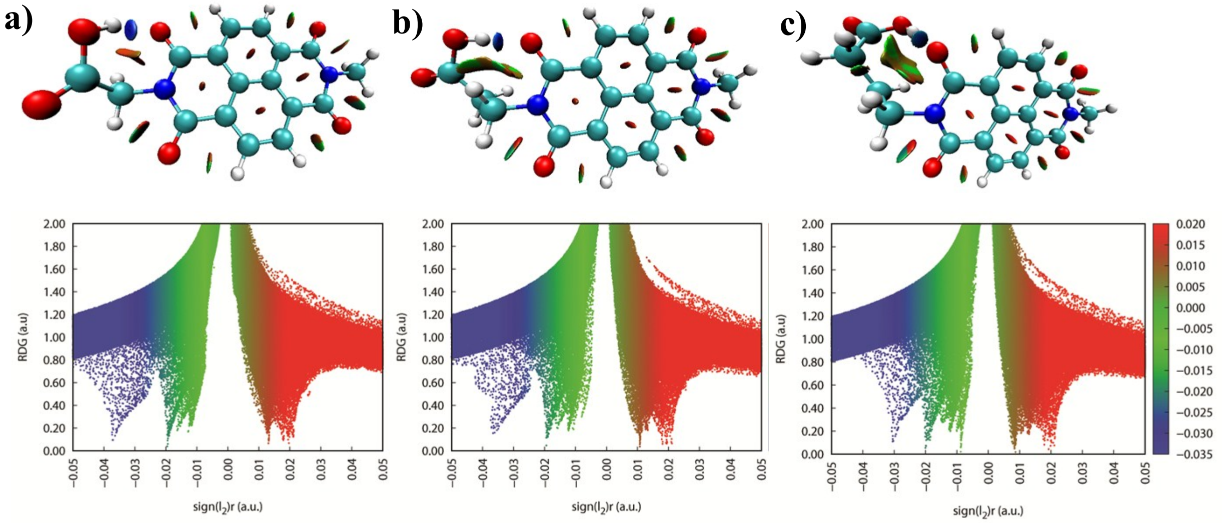


Figure S5. Non-covalent interaction plot for intra-molecularly H-bonded cyclic structure of NDI-1(a), NDI-2 (b) and NDI-3(c), in the top showing the RDG isosurface plot with an gradient isosurfaces (s = 0.5 au) and lower side represents the plot of RDG versus the electron density multiplied by the sign of the second Hessian Eigen value. Different colour codes are used to represent the interaction strength with respect to the values of sign(λ_2)ρ. Large negative values represented by blue colour for strong attractive interactions (H-Bonding), green colour for weaker interaction like Van der Waals interactions and red colour for the repulsive interactions.

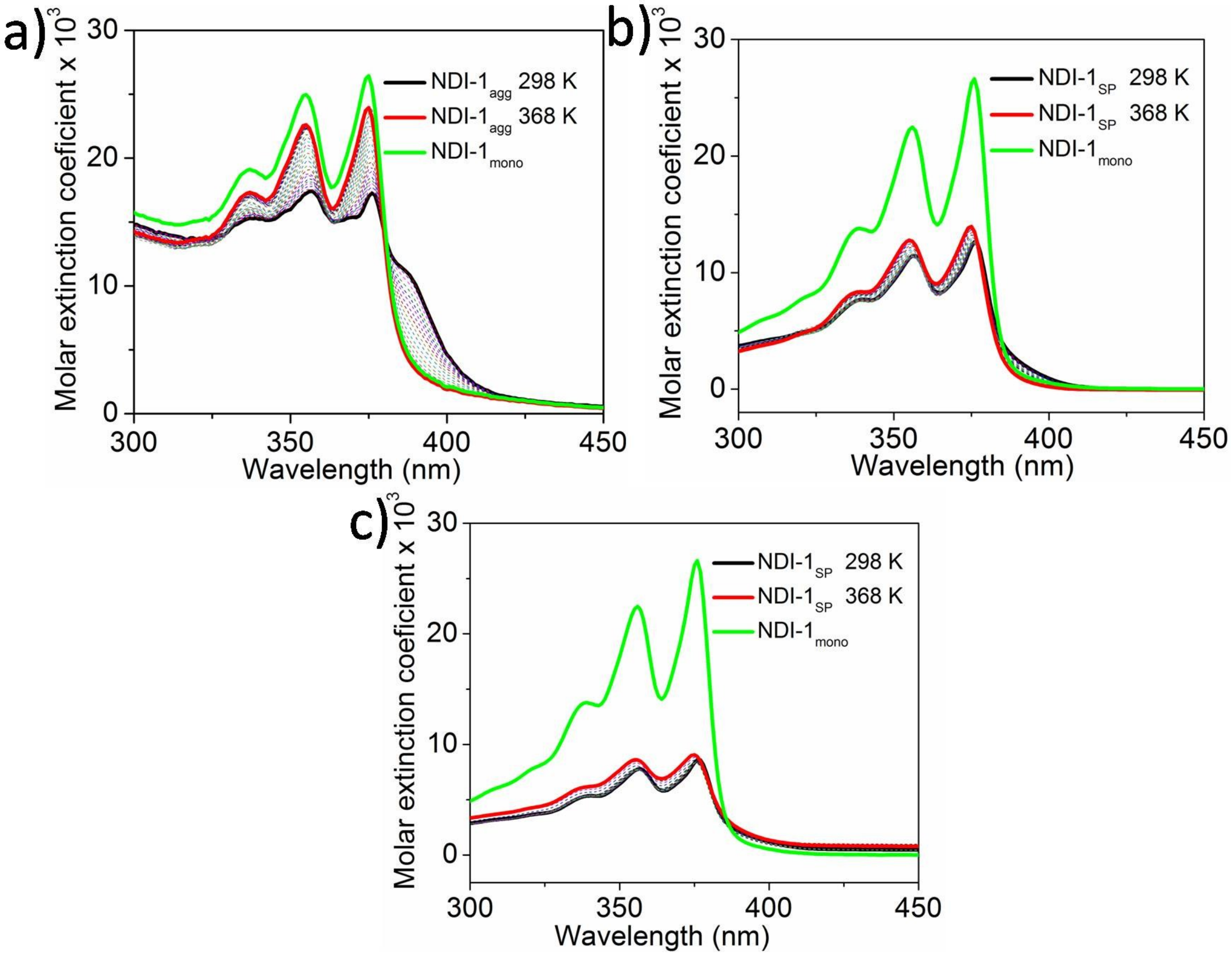


Figure S6. Variable temperature (heating) UV-Vis spectra of a) NDI-1$_{agg}$ and b, c) NDI-1$_{SP}$ (b-DMAP triggered polymer; c-DBU triggered polymer) in decane. [*l* = 1 cm; *C* = 1 x 10^{-4} M];

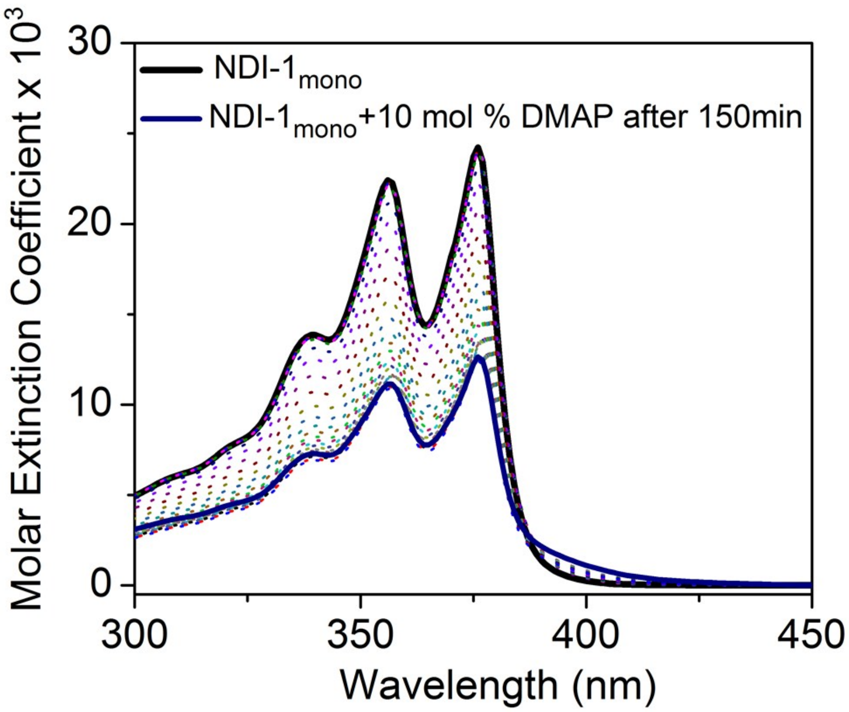


Figure S7. Time dependent UV-Vis spectra during SROP of NDI-1_{mono} in presence of 10 mole % DMAP [l = 1 cm; C = 1 x 10^{-4} M].

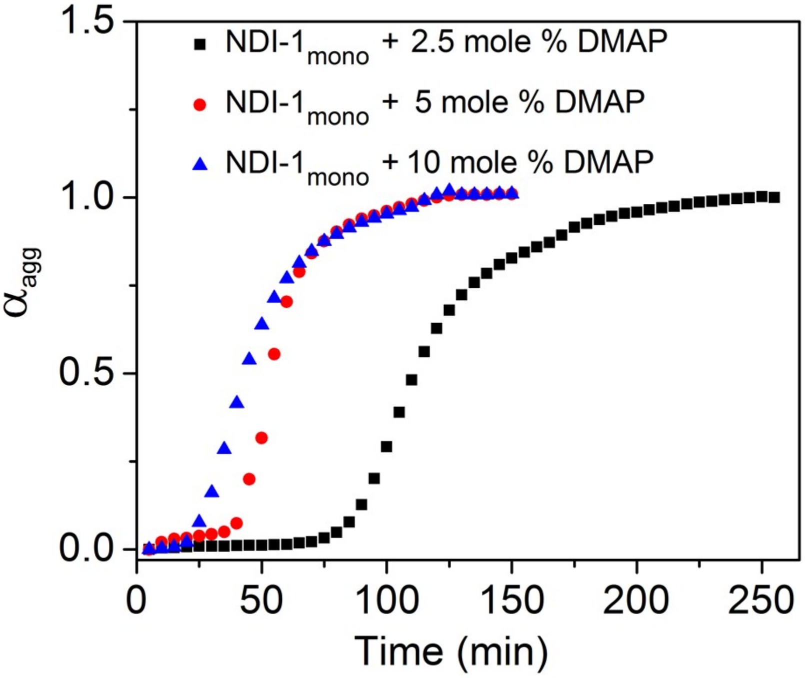


Figure S8. Plots of degree of polymerization of NDI-1_{mono} vs. time in presence of different mole % of DMAP.

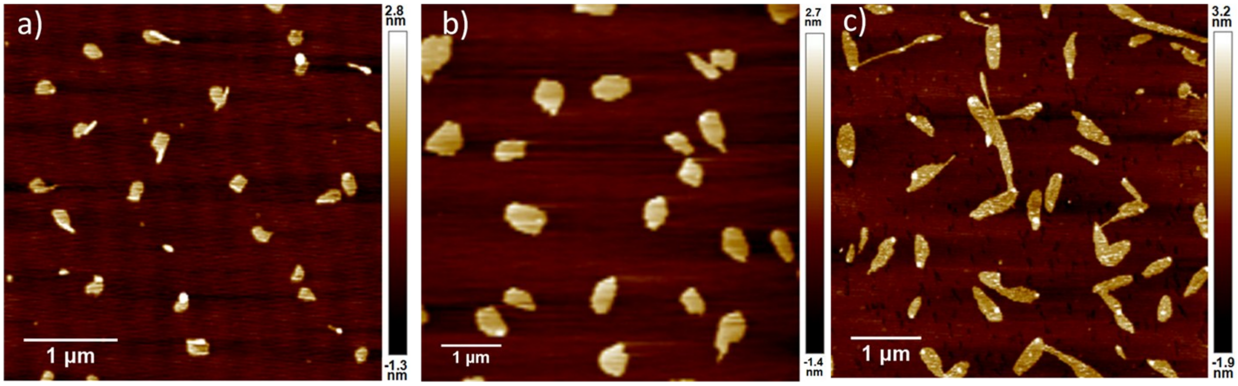


Figure S9. AFM images of NDI-1_{SP} in presence of (a) 2.5 (b) 5.0 and (c) 10 mole % DMAP. In all cases, samples were drop casted on the mica surface at end of polymerization [$C = 1 \times 10^{-4}$ M].

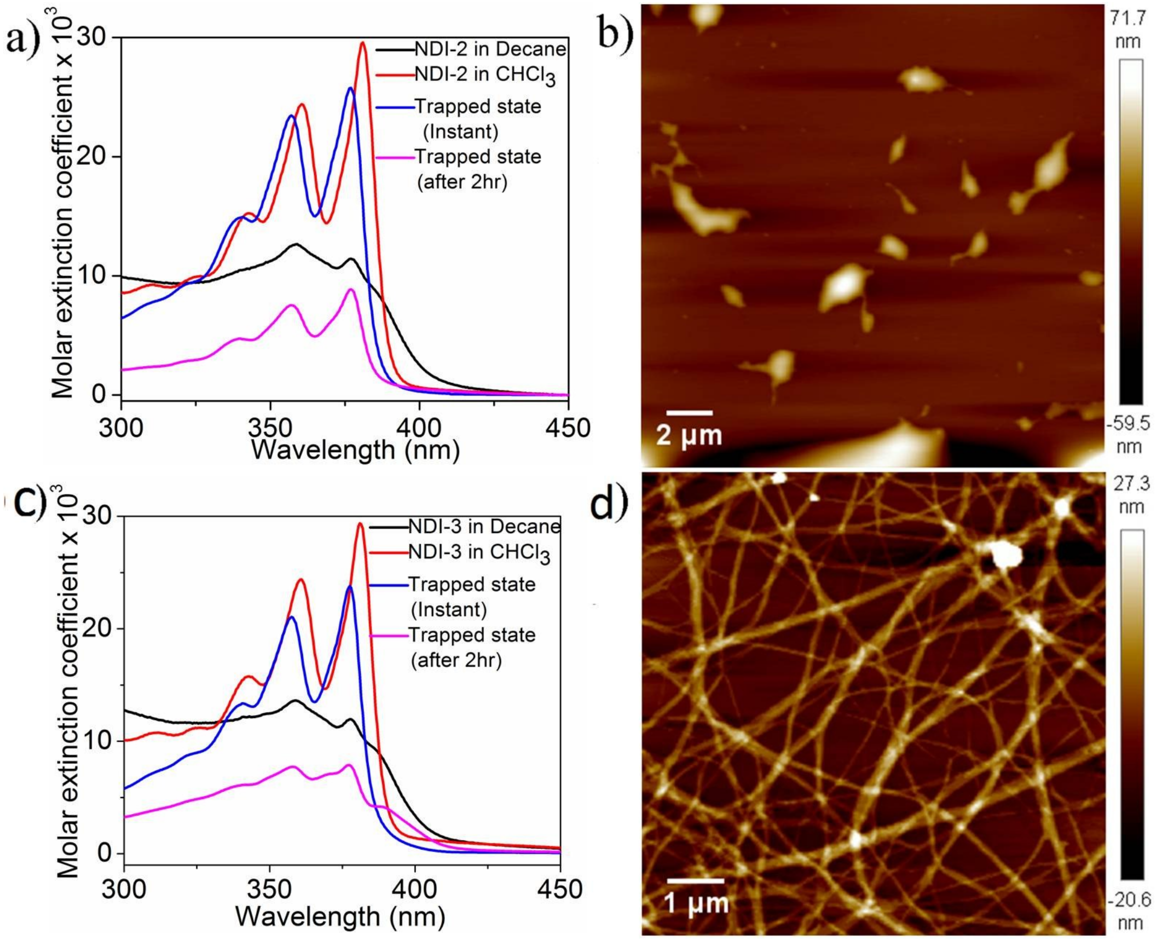


Figure S10. a, c) UV-Vis spectra of NDI-2, NDI-3 in different conditions. Red- monomeric state in good solvent $CHCl_3$; Black-aggregated state by spontaneous self-assembly in decane; blue- Transient monomeric state in decane by trapping the active monomer in dormant state by following monomer preparation method described for NDI-1; pink- aggregated state by self-polymerization/ aggregation from the trapped monomeric state after 2 h at rt in the absence of any base. b, d) AFM images of aggregation formed from trapped state of NDI-2, NDI-3 in decane.in presence of 10 mole % DMAP [l = 1 cm; C = 1 x 10^{-4} M].

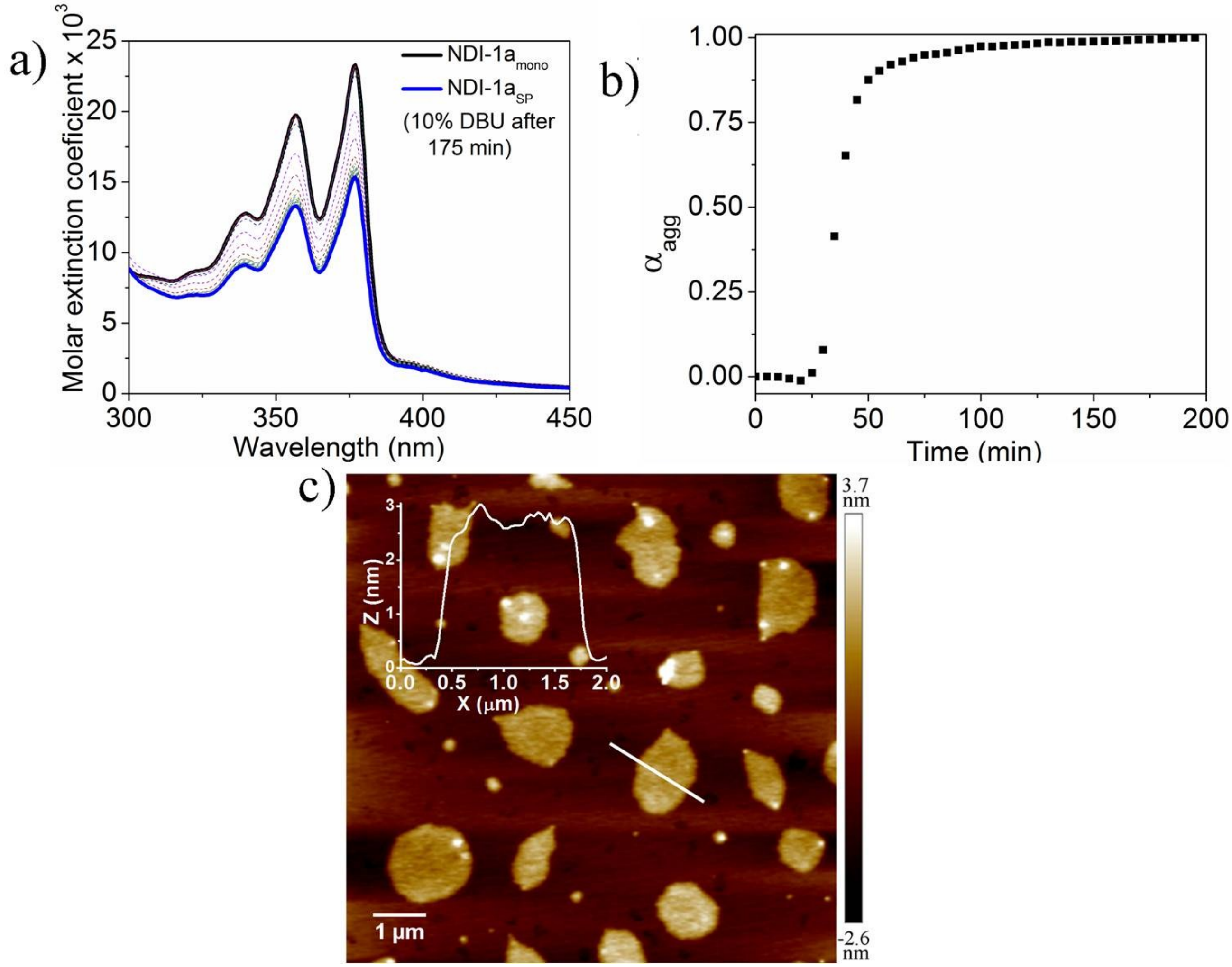


Figure S11. a) Time dependent UV-Vis spectra during SROP of NDI-4_{mono} in presence of 10 mole % DMAP; b) Plot of α_{agg} vs. time and c) AFM image of the final product produced by supramolecular polymerization of NDI-4_{mono} in presence of 10 mole % DMAP [l = 1 cm; C = 1 x 10^{-4} M].

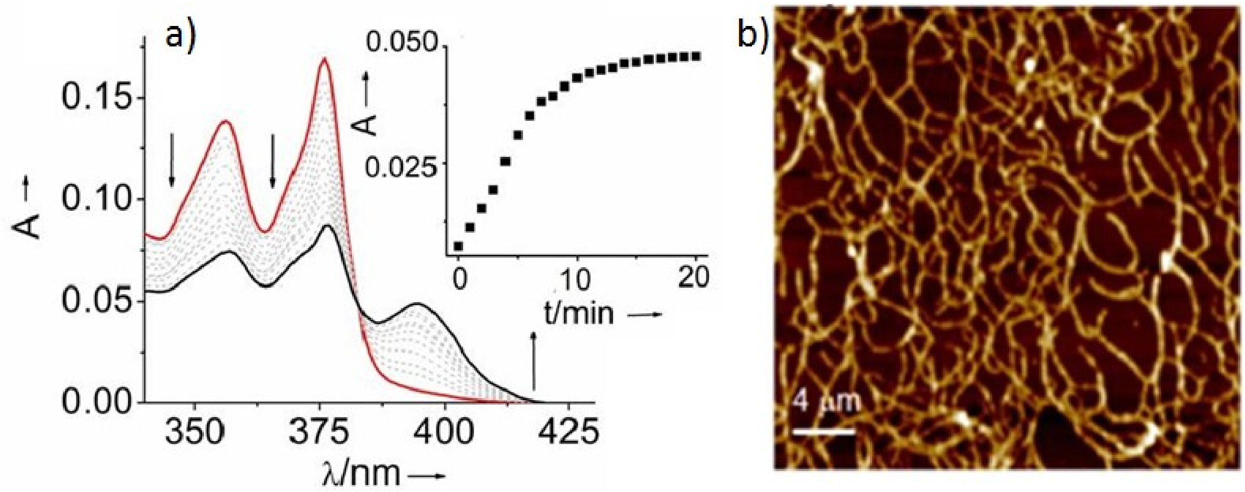


Figure S12. a) UV/Vis and spectra of NDI-4_{mono} (red line) and its change as a function of time after addition of NDI-4_{seed} (monomer/ seed = 34, l = 1.0 cm, T = 298 K). Inset shows the variation of the absorbance at 393 nm in the UV/Vis spectra; b) AFM image of the supramolecular polymer of NDI-4 prepared by seeded supramolecular polymerization of NDI-4_{mono} instead of base triggered SROP. C = 5 x 10^{-6} M; solvent- MCH. Reprinted with permission from (Ref. 7); Copyright (2018) The Royal Society of Chemistry.

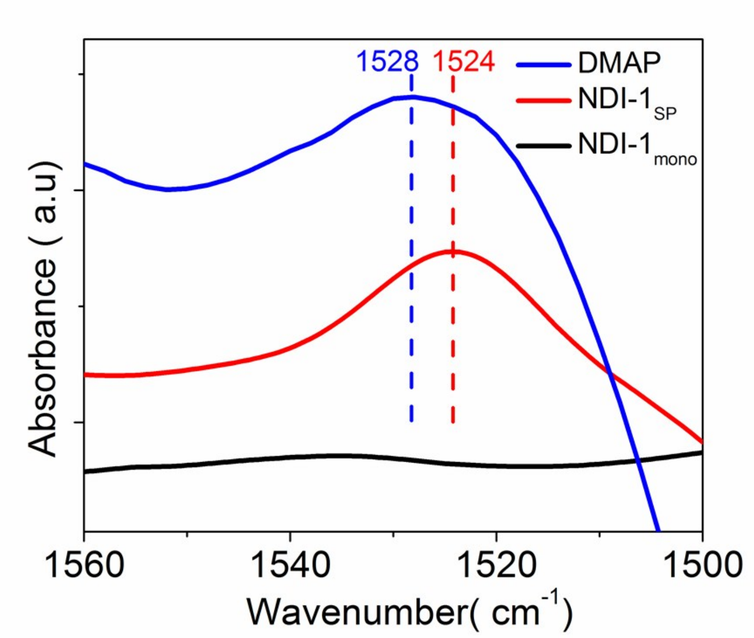


Figure S13. FT-IR spectra (selected region) of DMAP, NDI-1_{mono} and an aliquot taken from the polymerization (with 10 % DMAP) mixture [C = 1 x 10^{-4} M] 3 h after addition of the base. The peak at 1528 cm^{-1} correspond to the C=N stretching frequency of DMAP which shifts to 1524 cm^{-1} indicating its involvement in H-bonding.[2]

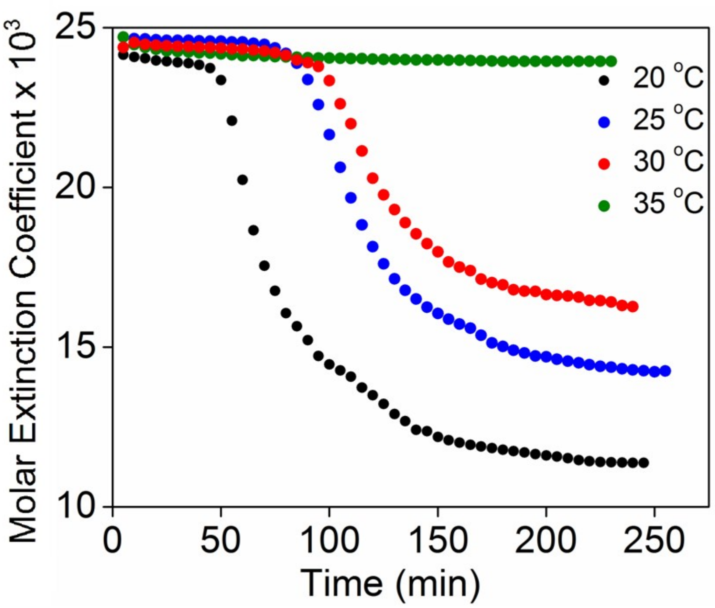


Figure S14. Variation of absorbance at 377 nm in the UV/Vis spectra of NDI-1_{mono} in decane (0.1 mM) after addition of 2.5 % DMAP at different temperatures.

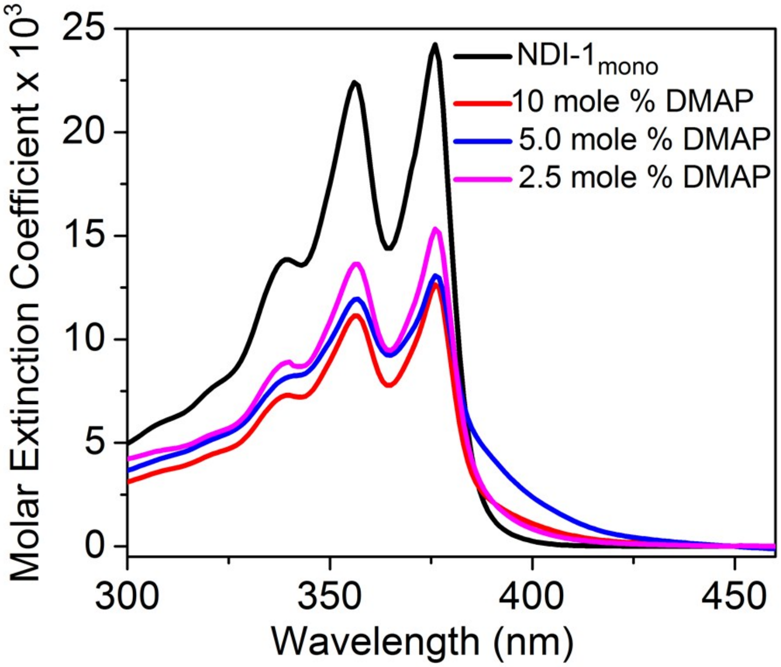


Figure S15. UV-Vis spectra of SPs of NDI-1 in presence of different mole % DMAP at the end of polymerization [l = 1 cm; C = 1 x 10^{-4} M]. Slightly reduced intensity of the absorption bands going from 2.5 to 5 mole % DMAP possibly indicates higher monomer conversion.

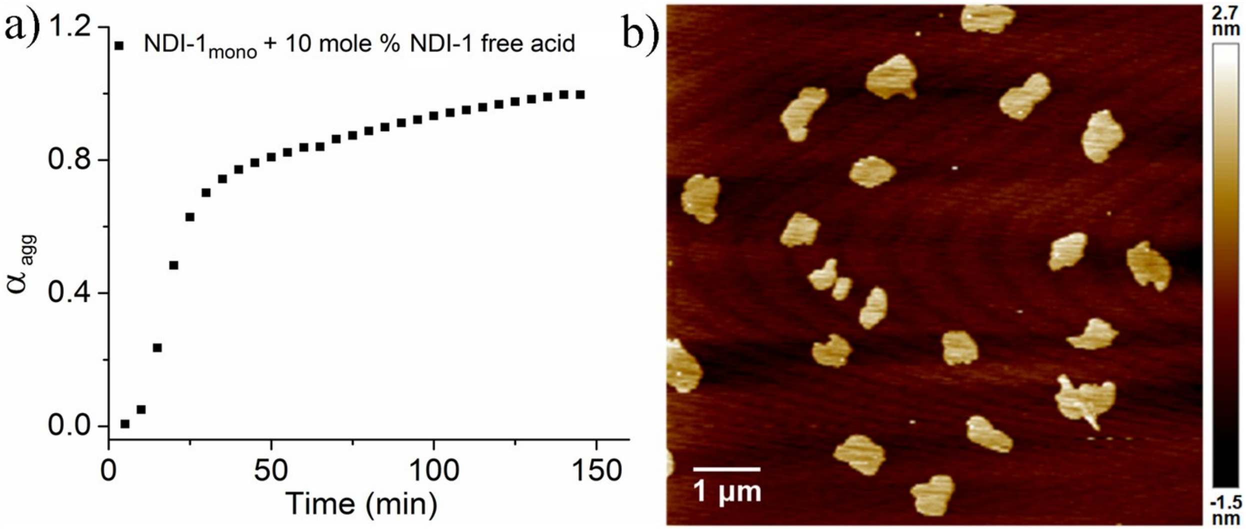


Figure S16. (a) Plot of α_{agg} vs. time and (b) AFM image of the final product produced by supramolecular polymerization of NDI-1_{mono} in presence of 10 mole % free NDI-1 acid [$C = 1 \times 10^{-4}$ M].

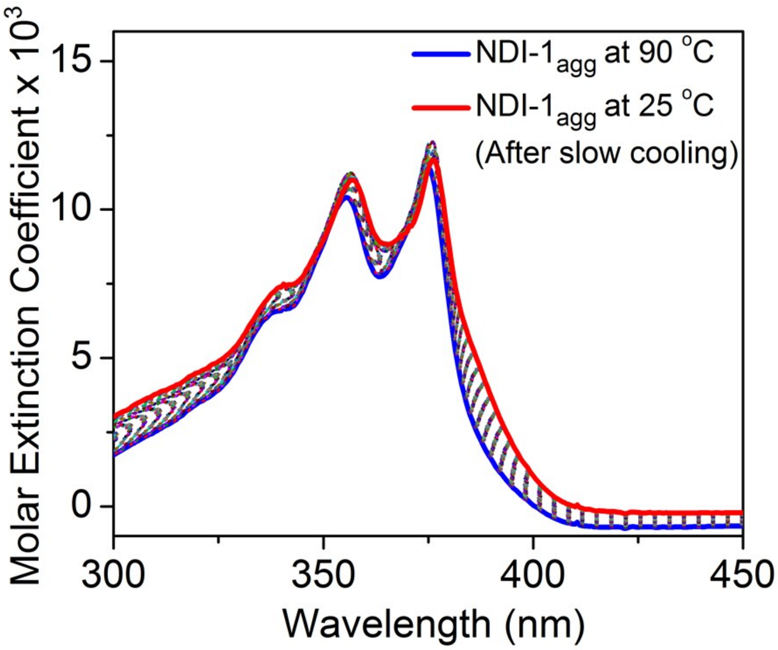


Figure S17. UV-Vis spectra of NDI-1_{agg} after slow cooling from 90 °C to 25 °C [Cooling rate = 1K/min; l = 1 cm; $C = 1 \times 10^{-4}$ M]. The spectral changes indicate when heating the initially formed irregular aggregate converts to the thermodynamically stable product which is even stable at 90 °C and then does not go back to the kinetic state after cooling. For the UV/Vis spectra of the spontaneously aggregated species see Figure 1

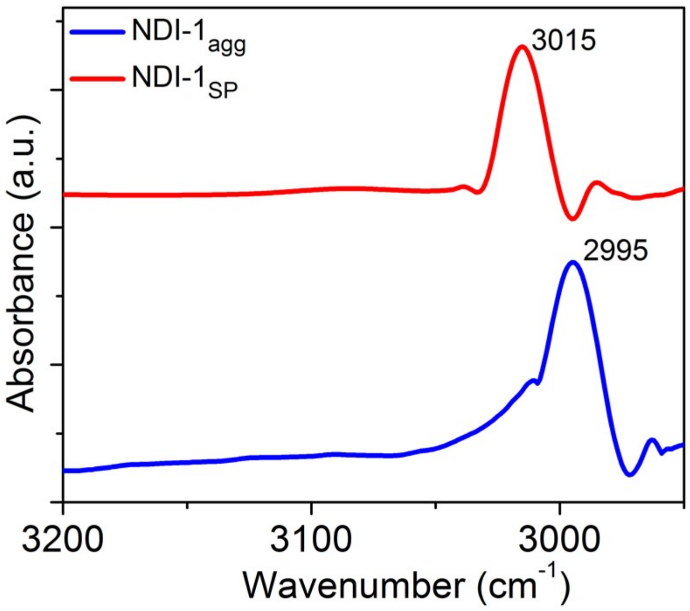


Figure S18. FT-IR spectra (selected region) of NDI-1_{agg} and NDI-1_{SP} [C = 1 x 10^{-4} M].

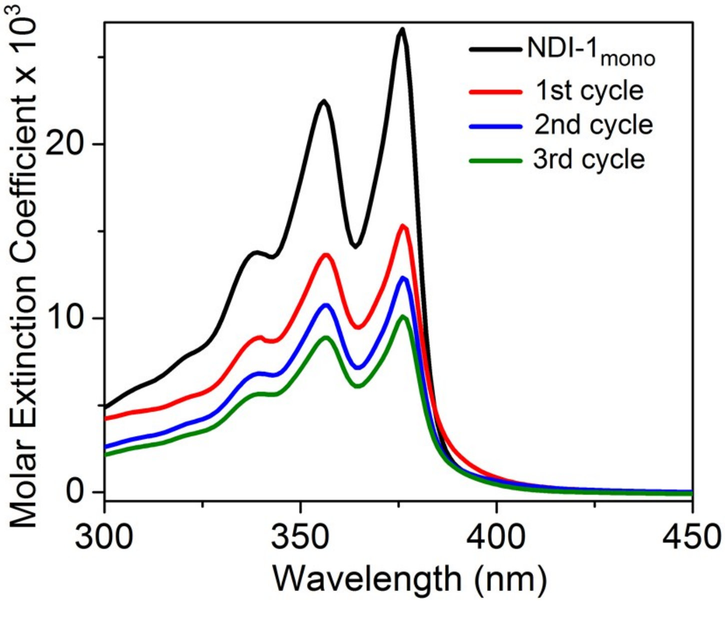


Figure S19. UV-Vis spectra of NDI-1_{SP} after each cycle during living SROP. [1st cycle in presence of 2.5 mole %; l = 1 cm; C = 1 x 10^{-4} M, subsequent two cycles initiated by NDI-1_{SP} as the macro-initiator**]**

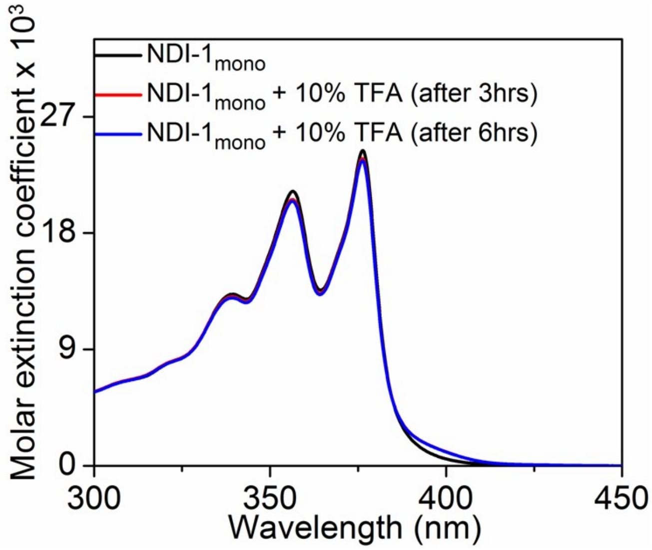


Figure S20. a) UV/Vis spectra of NDI-1mono in decane at different time after addition of 10 % TFA [l = 1 cm; C = 1 x 10^{-4} M; T= 25 °C].

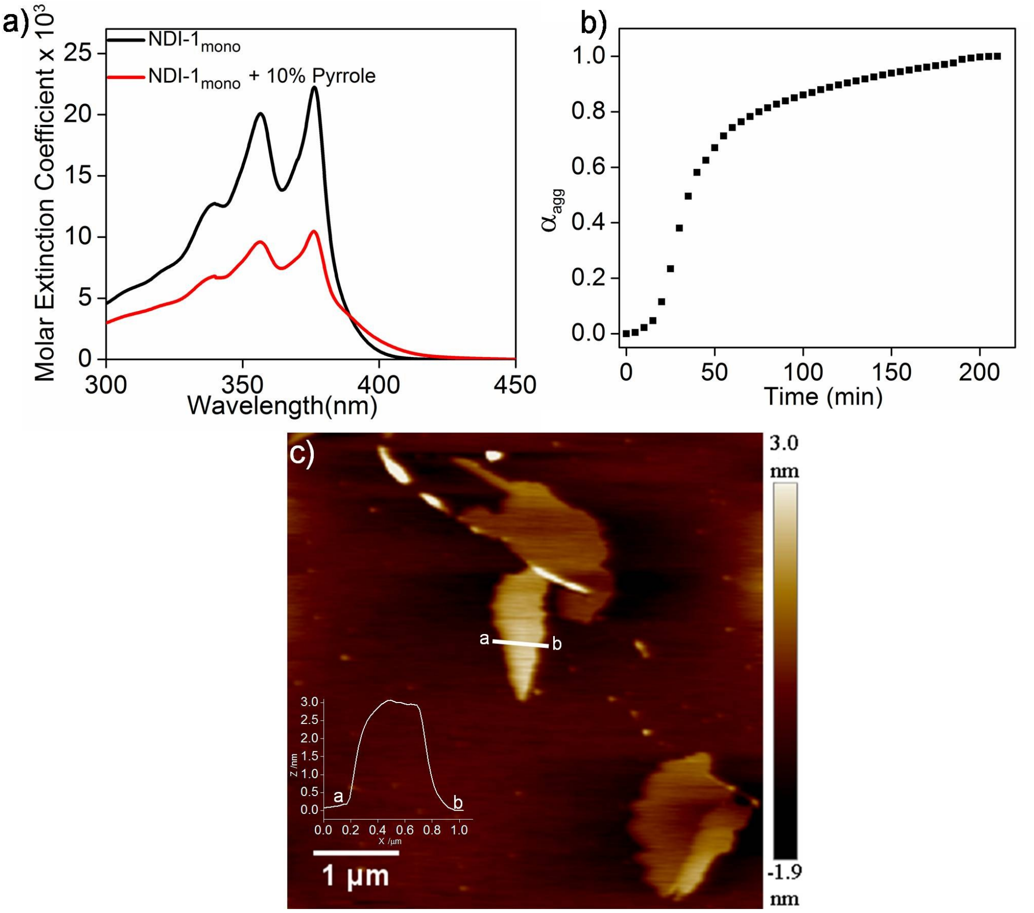


Figure S21. a) UV/Vis spectra of NDI-1mono in decane and the corresponding supramolecular polymer (spectrum was recorded after 210 min) synthesized by 10 mole % pyrrole; b) Plot of

α_{agg} vs. time during the pyrrole triggered SROP. α_{agg} was calculated using the change in absorbance at 377 nm as a function of time; c) AFM image of the final product produced by SROP of NDI-1_{mono} in presence of 10 mole % pyrrole [l = 1 cm; C = 1 x 10^{-4} M; T= 25 °C].

References

1. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, *2nd Ed*., Oxford: Pergamon **1980.**
2. T. Mondal and S. Ghosh, *Polym. Chem*., 2016, **7,** 6735-6743.