Supporting Information for the communication

# Controllable Supramolecular Polymerization via Chain-growth Mechanism

Deep Sankar Pal, Haridas Kar and Suhrit Ghosh*

Indian Association for the Cultivation of Science, Polymer Science Unit, 2A and 2B Raja S. C. Mullick Road, India-700032
Email: psusg2@iacs.res.in

Materials and methods: Reagents were received from Sigma Aldrich Chemical Co., Tokyo Chemicals Industries or local suppliers and used without further purification. Solvents were purchased from commercial sources and purified by reported protocol.[1] Spectroscopy grade solvents were used for physical studies. ^{1}H NMR experiments were performed in a Bruker DPX-500 MHz spectrometer and the peak positions were calibrated using TMS as an internal standard. UV/Vis studies were done in a Perkin Elmer Lambda 25 spectrometer equipped with a Peltier for variable temperature experiments. Mass spectrometric data were acquired by an electron spray ionization (ESI) technique on a Q-tof-micro quadruple mass spectrometer. DLS was done using a Malvern instrument with a scattering angle of 173°. Circular Dichroism (CD) experiments were carried out in a JASCO CD spectrometer (model-J815) equipped with a peltier for temperature dependent experiments. For transmission electron microscopy (TEM) imaging, a solution of NDI-1 in MCH at a given concentration was drop-casted on a copper grid and dried at room temperature for 12 h before capturing images in a JEOL-2010EX machine operating at an accelerating voltage of 200 kV. FT-IR spectra were recorded in a Perkin Elmer Spectrum 100FT-IR spectrometer using a CaF_2 cell (path length=1.0 mm) with a scan rate = 2 cm^{-1} /sec. Since the concentration of the samples was rather low, number of scans was set to 256. For better visualization of the desired peaks by avoiding the solvent cut off, the range of the scan was narrowed down to 3300-2900 cm^{-1}(for OH stretching) and 1800 - 1600 cm^{-1}(for carbonyl stretching) in two independent spectral measurements. AFM images were recorded in a Bruker Innova machine.

Synthesis: Synthesis of NDI-2 was reported by us elsewhere.[2] Synthesis of NDI-1 is depicted in Scheme S1.
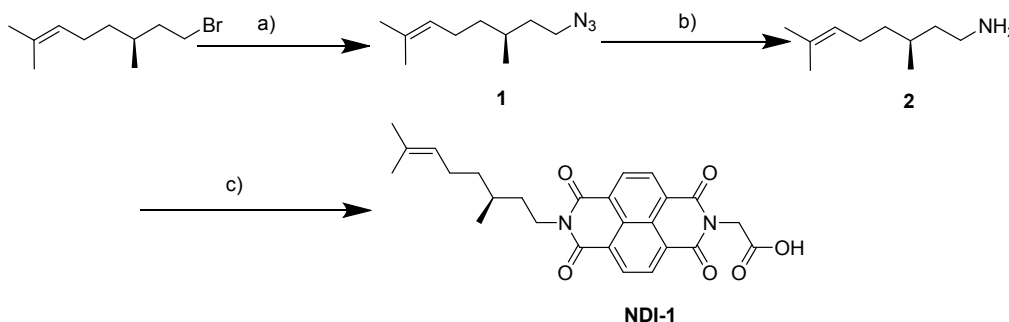
a) NaN$_3$, dry DMF, 90°C, 12h; b) LiAlH$_4$, dry THF,r.t., 12h; c) NDA, glycine, dry DMF, 120°C, 12h

Scheme S1: Synthesis of NDI-1

Compound 1: A solution of (*S*)-citronellyl bromide (2.6 g, 11.8 mmol) was stirred with 5.8 g of sodium azide in 50 ml of DMF at 90 °C overnight. Heating was stopped, the reaction mixture was allowed to cool to rt, and then was diluted with 150 ml water. The product was extracted with 50 ml ethyl acetate and the organic layer was subsequently washed with (3 x 50) ml water, dried over Na$_2$SO$_4$ and solvent was evaporated to yield the desired compound **1** which was used for next step without further purification. Yield= 1.8g (85 %); ^{1}HNMR (CDCl$_3$, 500MHz, TMS): δ (ppm) = 5.10-5.07 (1H, m), 3.33-3.24 (2H, m), 2.04-1.95 (2H, m), 1.69-1.208 (10H, m), 0.995(3H, J = 6.4Hz).

Compound 2: A suspension of lithium aluminium hydride (1.13g, 30 mM) in anhydrous THF was added drop-wise to compound **1**(1.8 g, 10 mM) in THF. After the addition was completed, the reaction mixture was stirred for 12 h at rt. Then the reaction mixture was cooled in an ice bath ad was hydrolyzed by the addition of 20% Rochelle salt solution (about 2.5-3 mL/g LAH) and a granular precipitate was formed which was filtered and washed thoroughly with ethyl acetate. The filtrate was washed with 6 N H$_2$SO$_4$ until the organic phase became clear; the acidic solution was adjusted to pH 11 with KOH and extracted 5 times with ethyl acetate. The organic phase was washed with sat. NaCl solution and dried over Na$_2$SO$_4$ and

evaporated. Yield=1.2g (77%); (CDCl$_3$, 400MHz, TMS): δ (ppm) = 5.10-5.07 (1H, m), 2.76-2.65 (2H,m), 2.04-1.95 (2H, m),1.69-1.21 (10H, m), 0.99 (3H, J = 6.4Hz).

NDI-1: 1,4,5,8 Naphthalene-tetracarboxylic di-anhydride (1.5 g, 5.59 mM), glycine (0.42g, 5.59 mM) and compound **2** (0.87g, 5.59 mM) were taken in a reaction flask and dry DMF (20 mL) was added to it and the reaction mixture was stirred for 12 h at 120 °C under N$_2$ atmosphere. After cooling to room temperature, the solution was placed in the refrigerator for 30 min while the product precipitates out from the solution. The precipitate was filtered, and washed with MeOH several times. The product was further purified by column chromatography using silica gel as stationary phase and 4% MeOH in CH$_2$Cl$_2$ as eluent to afford NDI-1 as a light brown solid (0.6 g, 23 %). mp= 298 °C, UV/Vis (THF): λ_{max} (ε) = 359 nm (33,432 M^{-1}cm^{-1}), 379 nm (41,653 M^{-1}cm^{-1}). HRMS (ESI): m/z calc for C$_{26}$H$_{26}$N$_2$O$_6$ [M + H]$^+$: 463.1869; found : 463.1864. ^{1}HNMR ((CD$_3$)$_2$SO), 400MHz, TMS) : δ (ppm)=13.22 (1H, b), 8.74-8.69 (4H, m), 5.09 (1H, b), 4.77 (2H, s), 4.10-4.08 (2H, m), 2.01-1.97 (2H, m), 1.723-1.012(10H, m), 0.995(3H, J=6.4Hz). ^{13}C NMR (CDCl$_3$, 100 MHz, TMS): δ (ppm) = 169.0, 162.5, 162.3, 130.9, 130.6, 130.5, 126.9, 126.3, 126.1, 125.4, 124.5, 41.4, 38.4, 36.3, 34.0, 32.1, 30.0, 25.4, 24.8, 19.4, 17.5.

Preparation of the meta-stable monomer: Nature of H-bonding of the carboxylic acid group in NDI-1/ NDI-2 was found to be greatly dependent on the solvent and concentration (Fig. S1). In THF (C = 5 x 10^{-4} M), the FT-IR spectrum indicated free carboxylic acid without any signature of H-bonding. At the same concentration in CHCl$_3$, NDI-1 formed a dimer by inter-molecular H-bonding (state A, Figure S1). An aliquot (24 µl) was transferred to a separate vial and dried by gentle heating to remove residual CHCl$_3$. The solid residue was dissolved in MCH (2.0 ml) and heated with shaking to give a homogeneous solution of NDI-1 (6x10^{-6} M, 2 ml). FT-IR and UV/Vis spectra (see main text) suggested formation of extended polymer chain (let's say state C) and J-aggregation among the NDI, possibly by breaking of the dimer (closed H-bonding) followed by adopting the open chain conformation due to enhanced π-stacking propensity of NDI. Now when the stock solution in CHCl$_3$ was prepared at five times dilute condition (1 x 10^{-4} M), the FT-IR spectrum was found to be distinctly different and indicated that the carboxylic acid groups were intra-molecularly H-bonded with the carbonyl of the imide ring (state B, Fig. S1). An aliquot (120 µl) of this stock solution was transferred to a seperate vial, 2.0 ml MCH was added and CHCl$_3$ was removed by gentle heating to have a homogeneous solution (6x10^{-6} M). It showed identical FT-IR spectra to that of the state B in CHCl$_3$ indicating existence of the trapped NDI monomer in which the carboxylic acid remains H-bonded with carbonyl oxygen of the neighbouring imide group. Note that assignment of the various H-bonded states in the FT-IR spectra (Fig S1) is consistent with previous literature[3] on FT-IR spectra of H-bonded and non-bonded COOH group. Following a similar procedure, intra-molecularly H-bonded monomeric NDI could also be isolated in cyclohexane which was characterized by the UV/Vis and FT-IR spectra (Fig. S11). ^{1}H NMR spectrum (Fig. S12) in this case confimred complete removal of the CHCl$_3$ in the monomer solution in cyclohexane.

Preparation of NDI-1$_{Seed}$: A J-aggregated polymeric solution of NDI-1 in MCH (6x10^{-6} M) (prepared by above mentioned method) was sonicated for 20 minutes for breaking long fibrillar network into short objects. UV/Vis studies confirmed lack of complete disassembly to monomeric state while DLS, AFM and TEM studies confirmed generation of fragmented short objects which were used as seed for initiating supramoleular polymerization.

Concentration/ temperature dependent UV/Vis study: Solution of NDI-1 in MCH (0.008 mM/0.006 mM) was prepared following the above mentioned protocol and transferred to a quartz cuvette and heated by a peltier device at 358K for 15 minutes prior to the experiment. The solution was subjected to a cooling/ heating cycle and absorption at a single wavelength (390 nm) was monitored as function of temperature (358 K to 298 K at 1 K/min or 0.1 K/min) by Perkin-Templab software connected to the UV/Vis machine. Mole fraction of aggregates (α_{agg}) at different temperature was estimated using the following equation (1).

$$\alpha_{(agg)} = \frac{A(T) - A(\min)}{A(\max) - A(\min)} -----(1)$$

Where A (max), A (min) and A (T) stand for band (390 nm) intensity maximum, minimum and at the recording temperature. While the curves appeared to be non-sigmoidal in nature and indicated cooperative pathway, a significant hysteresis was observed between the cooling and heating curves indicating kinetic influence even at a slow cooling rate. Therefore thermodynamic parameters were not obtained from these curves by fitting them to well known equations.

AFM Study: 10 µl of the NDI-1$_{Seed}$ solution (0.006 mM, 2.0 ml) was dropcasted on a silicon wafer and dried at room temperature for 12 h before capturing images. NDI-1$_{Seed}$ solution (0.006 mM. 2 ml) in MCH (60 µl) was added to NDI-1$_{Mono}$ solution (0.006mM, 2 ml). 10 µl of the solution was dropcasted on a silicon wafer at intervals of 2min, 6 min and 14 min. Samples were dried at room temperature for 12 h before capturing images.

Calculation of Instantaneous rate: From Fig 3a, the value of apparent polymerization rate between 4-5 min were calculated for different concentration of seed using the following equation:

$$Rate = \frac{[C]_{t_2} - [C]_{t_1}}{t_2 - t_1}$$

Log value of the rates were computed in Origin 8.0. In Origin 8.0 log of [NDI-1$_{seed}$] was calculated and plotted against log value of rates which showed a linear relationship suggesting first order reaction.[4]
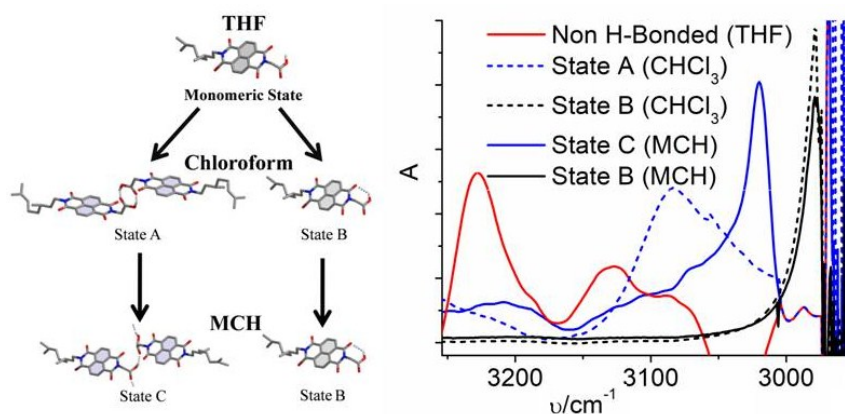
Additional Figures

Fig S1. Various modes of H-bonding of the COOH group of NDI-1 (left) depending on the solvent and solution preparation methods and their FT-IR spectra (right) (selected region). In THF, the peak due to OH stretching appears at 3225 cm^{-1} indicating non-H bonded COOH group. In CHCl$_3$ (state A) it appears at 3090 cm^{-1} indicating H-bonded dimer while in the same solvent for state B it appears at below 3000 cm^{-1} indicating strong intra-molecular H-bonding. The spectra in MCH (state C) shows the peak at 3020 cm^{-1} suggesting open chain H-bonding.
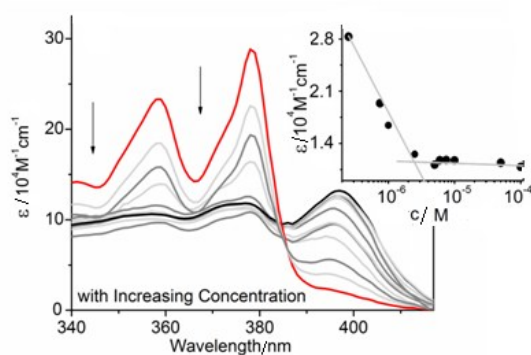
Fig S2. Concentration dependent absorption spectral changes (arrows indicate spectral change with increasing concentration) of NDI-1 in MCH at rt. Inset- the vatiation of the molar extinction coefficient at 378 nm (*l*=1cm) as a function of concentration; the inflection point indicates CAC.

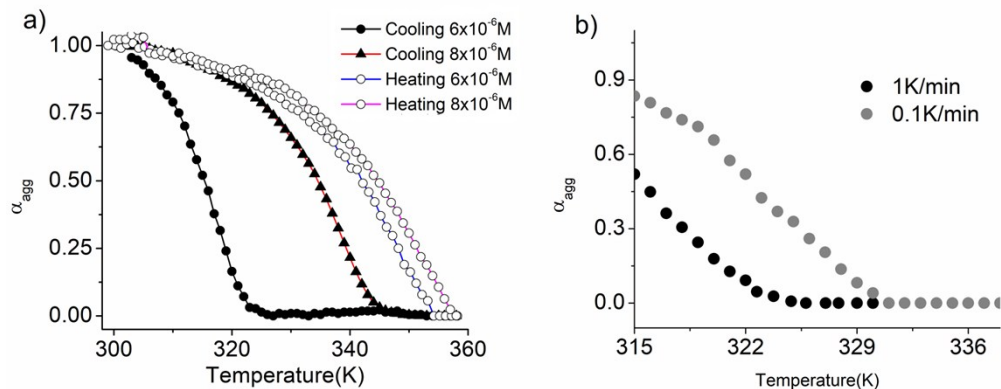**Fig S3.** (a) Temperature-dependent variation in α_{agg} of NDI-1 in MCH observed during the cooling and heating processes at a rate of 1.0 K min^{-1} in two different concentrations. (b) Comparison of cooling curves of NDI-1 in MCH (C = 6 x 10^{-6}M) at two different cooling rates. It shows even at 0.1 K/min, the onset of aggregation is at ~330 K while the heating curves (a) show α_{agg} > 0.8 at that temperature indicating significant kinetic influence on supramoleular polymerization.
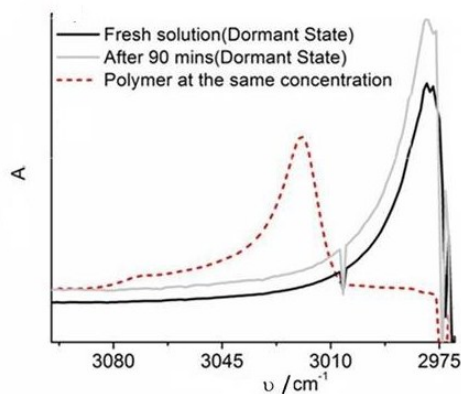
Fig S4. FTIR spectra (selected region) of NDI-1 dormant molecules (c=6x10^{-6}M) in MCH together with that of the J-aggregate at the same concentration.
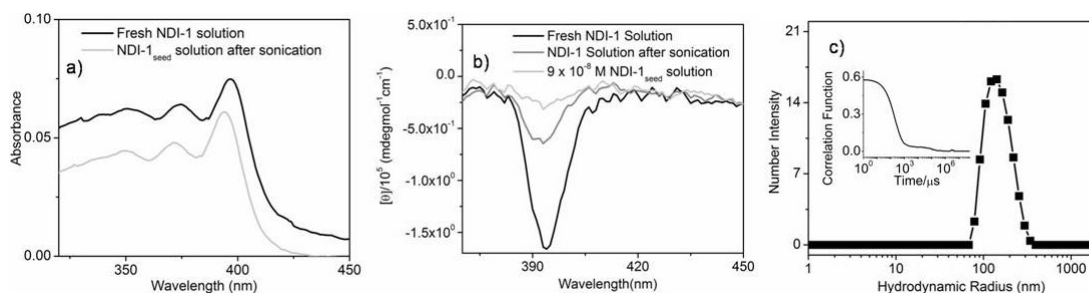
Fig S5. a) UV/Vis and b) CD spectra of NDI-1$_{seed}$ (6x10^{-6}M, l=1 cm) in MCH together with those of the J-aggregate before sonication. c) DLS of NDI-1$_{Seed}$ (c=6x10^{-6}M) solution together with the correlation curve (inset) in MCH after sonication.
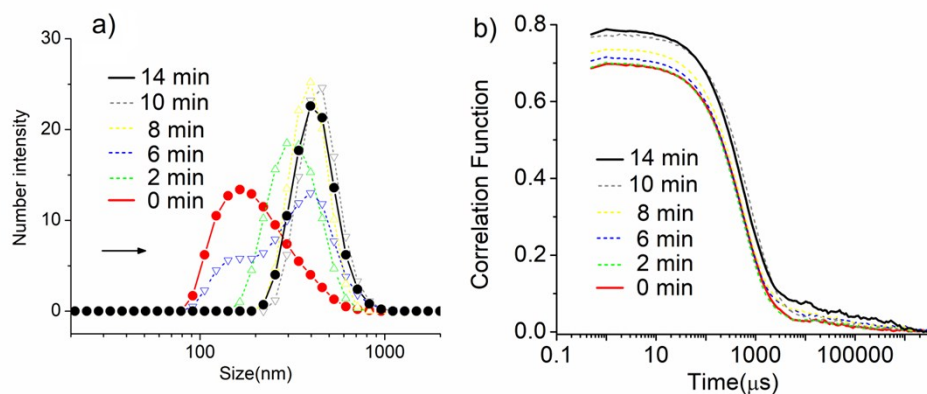
Fig S6. (a)- Time dependent change in particle size distribution monitored by DLS after addition of NDI-1$_{Seed}$ in NDI-1$_{Mono}$ (c=6x10^{-6}M) ([NDI-1$_{Mono}$]/[NDI-1$_{Seed}$]$_0$ = 34) solution in MCH. (b)- Corresponding DLS correlation functions.
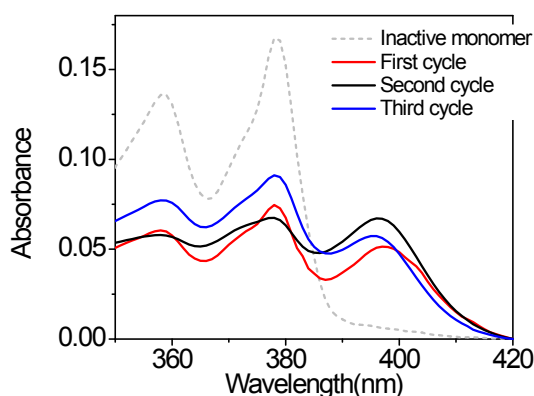

Fig S7. UV/Vis absorption spectra of NDI-1$_{Mono}$ and NDI-1 polymer at the end of first, second and third cycle of living supramolecular polymerization. C = 6 x 10^{-6} M, l= 1.0 cm. It can be noticed that the intensity of the J-band slightly increases in the second cycle compared to the first cycle which may be related to more efficient seeding. In the second cycle, the supramolecular polymer prepared in the first cycle was used as the seed while in the first cycle sonication-induced fragments of spontaneously assembled J-aggregates were used as the seed.
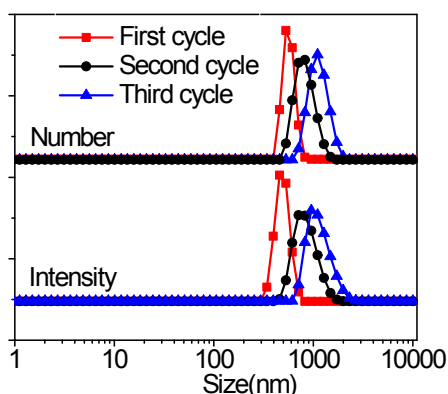

Fig S8. Comparison of number (top) and intenisty (bottom) average DLS profiles during living supramoleular polymerization of NDI-1 in MCH after each cycle.
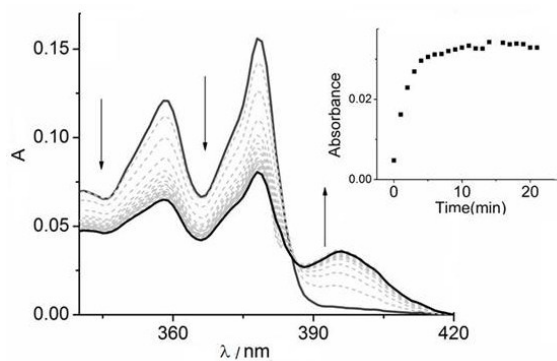
Fig S9. Time dependent change (indicated by arrow) in the UV/Visible spectra after addition of NDI-1$_{Seed}$ in NDI-2$_{Mono}$ solution in MCH ([NDI-2$_{Mono}$]/[NDI-1$_{Seed}$]$_0$ = 34) (c=6x10^{-6}M, l=1 cm). Insets show change in the absorbance intensity at 393 nm as a function of time c).
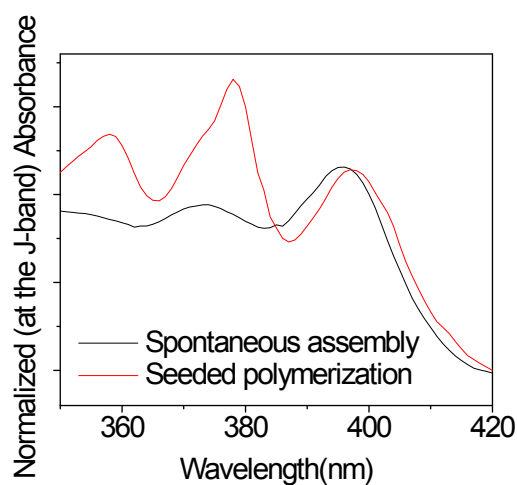

Fig S10. Normalized (at the λ_{max} of the J-band) UV/Vis spectra of NDI-1 aggregate in MCH prepared under two different conditions. C = 6 x 10^{-6} M, l= 1.0 cm.

Table S1. Kinetic data of the seeded supramolecular polymerization of NDI-1 at 298 K in MCH (6 x 10^{-6} M)

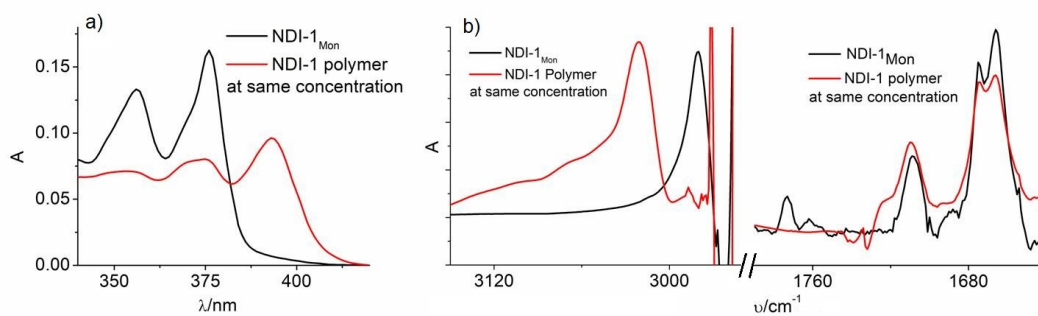| NDI-1$_{Seed}$	NDI-1$_{Mono}$/NDI $_{Seed}$	M$_\infty$	Kc*
(M)		(M)	(min^{-1})
0.90 x 10^{-7}	67	2.377	0.0862
1.35 x 10^{-7}	45	2.707	0.1622
1.80 x 10^{-7}	34	2.616	0.2295
2.25 x 10^{-7}	27	3.086	0.3196

Fig S11. a) UV/Vis and b) FTIR spectra of NDI-1$_{Mon}$ and spontaneously assembled J-aggregates of NDI-1 in cyclohexane (c = 6 x 10^{-6} M, l=1cm).
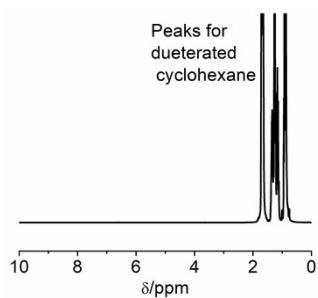
S6

Fig S12. ^{1}H NMR spectrum of NDI-1$_{Mon}$ in dueterated cyclohexane (c = 6 x 10^{-6} M). Due to very low concentration of the sample, no peaks could be detected. Intense peaks in the region of δ = 0-2 ppm appear due to residual cyclohexane in C6D12. Absence of a peak at δ= 7.26 ppm confirms absence of any residual chloroform in the sample.

References

1.   D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, *2nd Ed*., Oxford: Pergamon **1980**.
2.   M. R. Molla and S. Ghosh, *Chem. Eur. J.*, 2012, **18**, 1290.
3.   J. T. Balmer and M. F. Shurvell, *J. Phys. Chem.*, 1973, **77**, 256.
4.   S. Ogi, K. Sugiyasu, S. Manna, S. Samitsu and M. Takeuchi, *Nat. Chem.*, 2014, **6**, 188.