Supporting Information for

To Assemble or Fold ?

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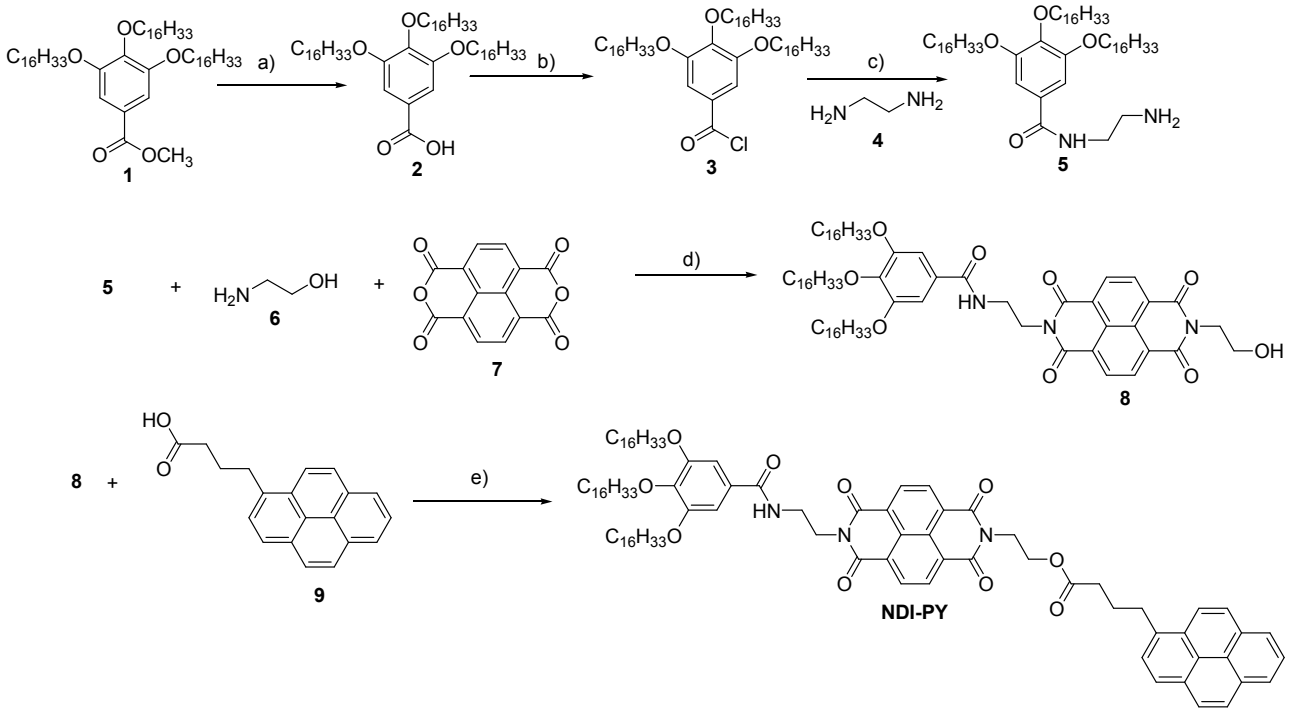
Materials and Methods: 1-Pyrenebutyric acid was purchase from Sigma Aldrich. Solvents and reagents were purchased from commercial sources and purified by standard methods.[1] For UV-vis studies, spectroscopic grade solvents were used and spectra were recorded in a Perkin Elmer Lambda 25 spectrometer. FT-IR spectra were obtained in Perkin Elmer Spectrum 100FT-IR spectrometer. TEM images were taken in JEOL-2010EX machine operating at an accelerating voltage of 200KV. ^{1}H NMR spectra were recorded on a Bruker DPX-400 MHz NMR spectrometer and calibrated against TMS. Dynamic light scattering (DLS) and static light scattering (SLS) measurements were obtained from BI-200SM goniometer (Ver.2.0). Variable temperature DLS studies were carried out in Malvern instrument equipped with a temperature controlled experimental set up. XRD data was recorded on a Seifert XRD3000P diffractometer with Cu Kα radiation (a = 0.15406 nm) and voltage and current of 40 kV and 30 mA, respectively. Variable-temperature fluorescence spectroscopy was performed in a Fluorolog-3 spectrophotometer from HORIBA Jobin Yvon with an external temperature controller. MALDI-TOF experiment was done in Ultraflextreme mass spectrometer (Bruker Daltonics) equipped with Bruker smartbeam II 355 nm Nitrogen laser using dithranol as matrix. Before the experiment, the instrument was calibrated using an external standard calibration mixture composed of bradykinin 1-7, bradykinin 2-9, angiotensin I, angiotensin II, Substance P, bombesin, adrenocorticotropic hormone clip 1–17, and clip 18–39, and somatostatin 28 from the Bruker Daltonics.

Synthesis and Characterization:

Synthesis of the compound **NDI-PY** was achieved in few steps following the synthetic protocol as outlined in **Scheme S1**. The compound has been characterized by ^{1}H NMR, ^{13}C NMR, UV-visible, and MALDI-TOF. Synthesis of **1**[2] has been described by us before..



a) KOH, EtOH/H_2O, 100 ^oC, 91% b) $SOCl_2$, CH_2Cl_2, rt, c) NEt_3, 0 ^oC-rt, 74%, d) DMF, 140 ^oC, 38%, e) EDC, HOBt, DIEA, 0 ^oC -rt, 54%.

Scheme S1: Synthetic scheme for preparation of compound **NDI-PY**.

3,4,5-tris(hexadecyloxy)benzoic acid [3] (2): A solution of compound **1** (5.5 g, 6.52 mmol) in 27 mL ethanol was added with aqueous KOH solution (3.80 g in 27 mL) and the reaction mixture was stirred at 100 °C for 8 h. The reaction was stopped, cooled to room temperature and solution was poured slowly into a solution of concentrated HCl (5 mL) in ice-cold water (125 mL). A white precipitate came out, which was filtered and washed with distilled water and dried under vacuum to get the crude product as a white powder (5.0 g, 92%) which was used for the next step without further purification. M.P. = 78 °C- 80 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) = 7.18 (s, 2H), 4.05-3.98 (m, 6H), 1.82-1.79 (m, 6H), 1.48-1.45 (m, 6H), 1.31-1.25 (m, 72H), 0.89-0.86 (m, 9H). MALDI-TOF: *m / z* calcd for $C_{57}H_{108}N_2O_4H$ [*M* + Na]$^+$: 865.76; found: 865.79.

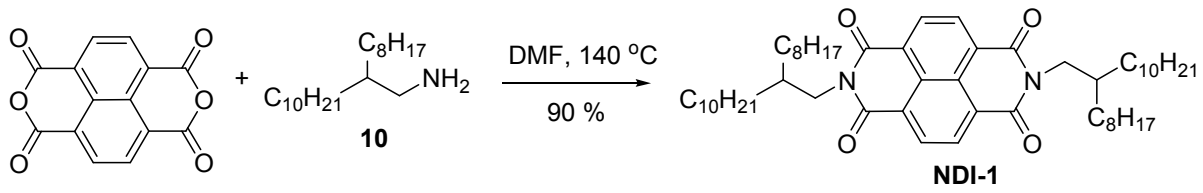
N-(2-aminoethyl)-3,4,5-tris(hexadecyloxy)benzamide (5): [4] Compound **2** (6.5 g, 7.66 mmol) was dissolved in dry dichloromethane (25 mL) and added with few drops of dry N, N-dimethylformamide. To this solution, freshly distilled thionyl chloride (28 mL) was added dropwise for 30 minutes. After the addition was over the reaction mixture was stirred at room temperature for 12 h. The reaction was stopped and excess thionyl chloride was removed by

distillation and dried under vacuum to achieve the crude product (**3**) as a white waxy-material with complete conversion as checked from TLC. The product was not characterized and purified at this stage and was taken to the next step as such. A solution of compound **3** (1.5 g, 1.74 mmol) in dry dichloromethane (10 mL) was added dropwise for 2h to an ice-cold flask containing ethylene diamine (**4**) (8 mL) and triethylamine (2.0 mL). After the addition was over the reaction mixture was stirred at rt for 24 h. Then it was diluted with 25 mL dichloromethane and the solution was washed with H_2O (3 x 30 mL), saturated $NaHCO_3$ solution (1 x 30 mL), and brine (1 x 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to get the crude product which was purified by column chromatography using silica gel as stationary phase and 2% MeOH in $CHCl_3$ as eluent to obtain the desired product as white solid (1.15 gm, 74 %). M.P. = 65 °C- 67 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) = 6.87 (s, 2H), 4.01-3.94 (m, 6H), 3.62 (br, 2H), 3.10 (br, 2H), 1.74-1.70 (m, 6H), 1.44-1.33 (m, 6H), 1.28-1.25 (m, 72H), 0.88 (t, J = 9.2 Hz, 9H); MALDI-TOF: m/z calcd for $C_{57}H_{108}N_2O_4Na$ $[M + Na]^+$: 907.82; found: 908.11.

Compound 8: Compound **5** (1.0 g, 1.13 mmol), 2-aminoethanol (**6**) (69 mg, 1.13 mmol) and 1,4,5,8-naphthalenetetracarboxylic bis-anhydride (**7**) (303 mg, 1.13 mmol) were taken together with dry DMF (15 mL) and heated at 140 °C for 18 h under N_2 atmosphere. The solution was cooled to rt and placed in the refrigerator for 2 h. The brown precipitate obtained was filtered and collected. The filtrate was added with MeOH (1 mL) to obtain a brown precipitate which was mixed with the first fraction and the combined solid was purified by column chromatography using silica gel as stationary phase and 0.5% MeOH in $CHCl_3$ as eluent to obtain the desired product as orange solid (400 mg, 38 %). M. P. 152 - 154 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.76 (s, 4H), 6.89 (s, 2H), 6.67 (br, 1H), 4.54 (t, J = 5.2, 2H), 4.47 (t, J = 5.4, 2H), 4.02 – 3.93 (m, 8H), 3.88 (t, J = 5.6, 2H) 1.82 - 1.69 (m, 6H), 1.48 - 1.41 (m, 6H), 1.28 - 1.25 (m, 72H), 0.87(t, J = 6.8, 9H); MALDI-TOF: m/z calcd for $C_{73}H_{115}N_3O_9H$ $[M + H]^+$: 1178.87; found: 1179.10; UV-visible ($CHCl_3$): λ_{max} (ε) = 381 (22178), 361 (17799), 342 (10398), 325 (5760) 267 (9133) M^{-1} cm^{-1}.

Compound NDI-PY: Compound **8** (150 mg, 0.13 mmol), **9** (53 mg, 0.19 mmol), EDC (67 mg, 0.35 mmol), HOBT (45 mg, 0.33 mmol) and DIEA (0.1 mL, 0.61 mmol) were taken together in a round bottom flask along with 6.0 mL dry CH_2Cl_2 and stirred at 0 °C for 15 min under N_2 atmosphere for 12 h. After the reaction, CH_2Cl_2 was evaporated and the solid was taken with MeOH (3 x 5 mL) and centrifuged to obtain light pink colored crude product which was purified by column chromatography using silica gel as stationary phase and 0.5 %

MeOH in $CHCl_3$ as eluent to obtain the desired product as sticky reddish brown solid. (100 mg, 54 %).^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.71 (s, 4H), 8.43 (d, J = 7.6, 1H), 8.20 (d, J = 7.6, 1H), 8.10 (d, J = 7.2, 1H), 8.00-7.94 (m, 4H), 7.75 (d, J = 9.6, 1H), 7.67-7.63 (m, 1H), 6.85 (s, 2H), 6.62 (br, 1H), 4.61 (br, 2H), 4.56 (br, 2H), 4.19 (br, 2H), 4.00 – 3.93 (m, 6H), 3.71 (br, 2H), 3.02 (t, J = 8, 2H), 2.49(t, J = 6.8, 2H), 2.07-2.03 (m, 2H), 1.82-1.67 (m, 6H), 1.50 – 1.33 (m, 6H), 1.28-1.25 (m, 72H), 0.89 – 0.86 (m, 9H); ^{13}C NMR ($CDCl_3$, 300 MHz): 173.54, 167.50, 163.52, 162.92, 153.05, 141.03, 135.31, 131.26, 130.67, 130.46, 129.03, 129.78, 128.22, 129.54, 127.06, 126.86, 126.77, 126.13, 125.65, 125.09, 124.09, 124.88, 124.76, 124.53, 122.67, 105.26, 73.54, 69.23, 61.57, 39.88, 34.29, 32.01, 31.52, 30.28, 29.77, 26.23, 22.78, 14.20; UV-visible ($CHCl_3$): λ_{max} (ε) = 382 (22764), 360 (22210), 344 (46073), 330 (32947), 315 (18389), 278 (50072), 268 (37554) M^{-1} cm^{-1}; MALDI-TOF: m / z calcd for $C_{93}H_{129}N_3O_{10}Na$ $[M + Na]^+$: 1470.95; found: 1470.91.



Scheme S2: Synthesis of **NDI-1**

Compound NDI-1: Naphthalene bis-anhydride (NDA) (540 mg, 2.01 mmol) and the branched amine **10** (1.2 g, 4.02 mmol) were mixed with dry DMF (10 ml) in a reaction flask and the mixture was stirred at 140 °C under inert atmosphere for 12 h. The stirring was stopped and the reaction mixture was allowed to cool to rt while the desired product precipitated out from the medium as light yellow solid. It was filtered and the solid product was washed several times with MeOH to remove DMF and other polar impurities. Subsequently, it was washed several times with hexane to remove any nonpolar impurity. The crude was dried under vacuum to get the desired product as light yellow solid. As from TLC and NMR the product appeared to be pure, it was used as such for the control experiment without further purification. Yield = 90%. M. P. 55-58 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ (ppm) = 8.75 (4H, s); 4.13 (4H, d); 1.98(1H); 1.5-1.2 (32 H); 0.86(6H, t). HRMS (ESI): m/z calc for $C_{54}H_{86}N_2O_4Na$ $[M + Na]^+$: 849.6486; found: 849.6479.

Experimental Procedures:

Solution preparation: A stock solution of **NDI-PY** was made in $CHCl_3$ (2.0 mM). Measured volume of the aliquot was taken in a vial and the solvent was evaporated. A thin red film

obtained was dissolved in equal volume of MCH to make the final concentration = 2.0 mM. The solution was allowed to equilibrate for 1h at room temperature before any physical studies.

UV-visible studies: Solution of **NDI-PY** in MCH (2.0 mM) was prepared as mentioned above. The sample was transferred to a quartz cuvette of 0.1 cm path-length and UV was recorded at 25 °C. For the control experiment, a stock solution of **NDI-1** and **PY** was made separately in $CHCl_3$ (2.0 mM). Measured volume of the aliquots from the two solutions were mixed in a vial and the $CHCl_3$ was evaporated to obtain a thin film which was dissolved in equal volume of MCH to make a final concentration of 2.0 mM which was transferred to a 0.1 cm path-length cuvette for recording the UV data. For the dilution experiment, a solution of **NDI-PY** (10.0 mM) in MCH was diluted with measured volume of MCH and the CT-band was monitored as a function of dilution. CT-band intensity at 525 nm was plotted as a function of concentration.

For variable temperature experiments, solution of **NDI-PY** (0.4 mM, 0.2 mL) in MCH was taken in a 0.1 cm cuvette and the sample was heated from 25 ^oC to higher values with an external temperature controller and spectral measurements were carried out at different temperature intervals. After the desired temperature was reached, 10 min equilibrium time was provided before each measurement. Charge-transfer band at 525 nm was plotted as a function of temperature.

Photoluminescence (PL) studies: A solution of **NDI-PY** (0.4 mM) in MCH was transferred to a PL cuvette with a path-length of 1.0 cm. The sample was heated from 20 ^oC to higher values with an external temperature controller and spectral measurements were carried out at different temperature. The solution was excited at 337 nm and the slit was maintained at 2.5 nm.

FT-IR studies: A solution of **NDI-PY** (2.0 mM) in MCH was placed between two NaCl windows (path length = 0.2 mm) and spectral measurements (scan range = 4000-400 cm^{-1}, resolution = 0.5 cm^{-1}) were carried out in the transmittance mode.

Transmission Electron Microscopy (TEM) studies: Solution of **NDI-PY** in MCH (0.4 mM) at room temperature was drop casted on a copper grid. The samples was left open to the atmosphere for 12 h (to allow MCH to evaporate) prior to imaging.

Dynamic Light Scattering (DLS) studies: Experiment was carried out with 1.0 mL solution of **NDI-PY** (0.4 mM) in MCH. The scattering angle was fixed at 90 ^oC. For variable temperature studies, a solution of **NDI-PY** in MCH (0.4 mM) was heated from 25 ^oC to higher temperature and the spectral measurements were carried out at different temperature.

Each time after the desired temperature was reached the sample was allowed to stand for 5 minutes before taking the measurement.

Static Light Scattering (SLS) studies: For SLS, the same solution prepared for DLS was used and measurements were done at different scattering angles (30, 45, 60, 90 and 120 °C), keeping the concentration same to determine the radius of gyration (R_g) from partial Zimm plot using the following equation.[2]

$I^{-1} = C(1 + R_g^2 q^2 /3)$

$I = I'.\text{Sin}\theta$, where I' is intensity of scattered light, θ is the angle of scattered light, C is a constant, R_g is the radius of gyration and q is the magnitude of the scattering wave vector; $q = 4\pi n.\sin(\theta/2)/\lambda o$ (n is the refractive index of the of the liquid and λo is the wavelength of light in vacuum). From this plot the R_g is determined from the slope.

MALDI-TOF Experiment: A saturated solution of dithranol was prepared in $CHCl_3$:MCH (2:8) ratio and mixed in 1:1 ratio with a solution of **NDI-PY** (2.0 mM) in MCH. The mixture was spotted on the MTP 384 MALDI target plate. Mass spectra were acquired in reflectron mode with an acceleration voltage of 22 kV. Approximately 500 laser shots were accumulated for each spectrum.

Powder X-Ray diffraction studies: A solution of **NDI-PY** (2.0 mM, 1.0 mL) in MCH was drop-casted repeatedly on a glass slide to make a thick red film and was air dried for 24 h. Data was recorded with this sample from 0.5° to 30 ° with sampling interval of 0.02 ° per state.

Additional figures

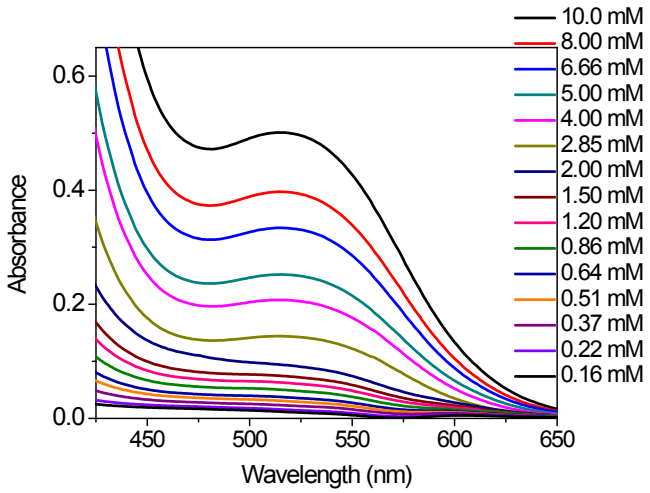


Fig S1: Effect of concentration on the CT-band intensity of **NDI-PY** in MCH; path length = 0.1 cm.

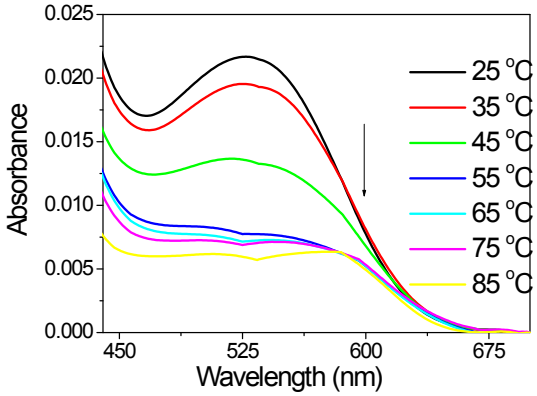


Fig S2: Effect of temperature on the CT-band intensity of **NDI-PY** in MCH in presence of 5% MeOH. Concentration = 0.4 mM; path length = 0.1 cm.

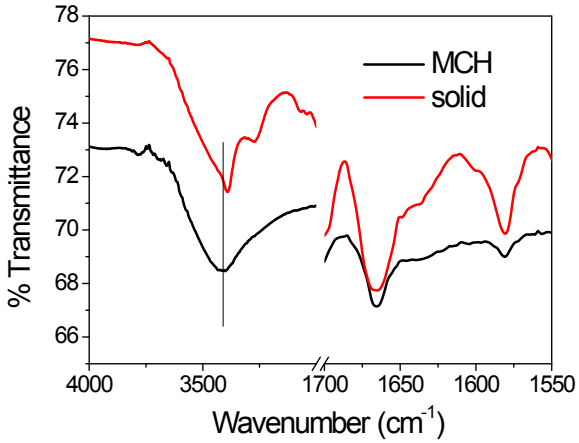


Fig S3: Selected region of the FT-IR spectra of **NDI-PY** in solid state and MCH solution (Concentration = 2.0 mM). Peaks at 1666 and 1580 cm^{-1} correspond to H-bonded amide-I and amide-II respectively. Broad peak at 3410 cm^{-1} corresponds to the NH- stretching of the amide.

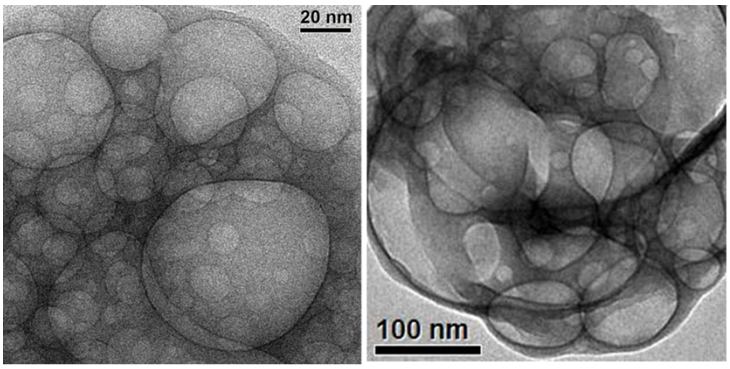


Fig S4: TEM images (collected from various sections of the grid) of the reverse vesicle formed by **NDI-PY** in MCH. Concentration = 0.4 mM

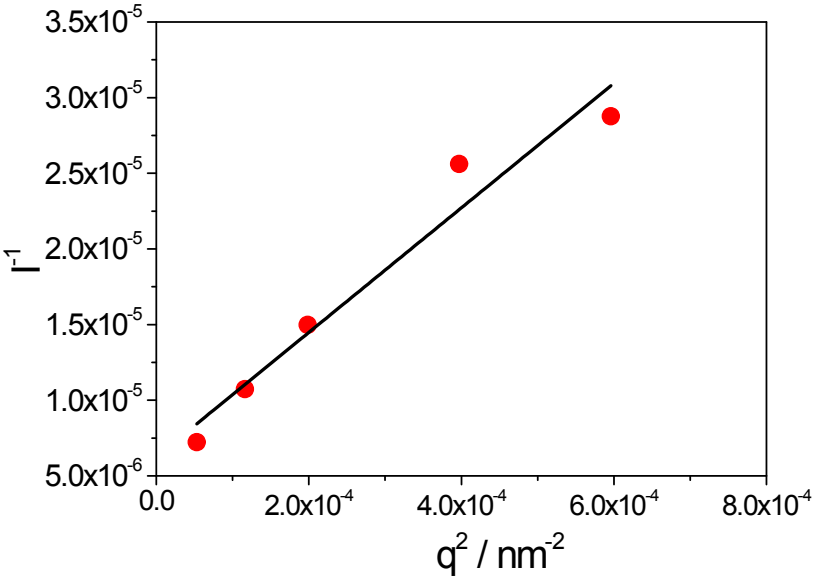


Fig S5: Partial Zimm plot obtained for **NDI-PY** in MCH. Concentration = 0.4 mM. R_g was determined from the slope using the equation described in the experimental procedure.

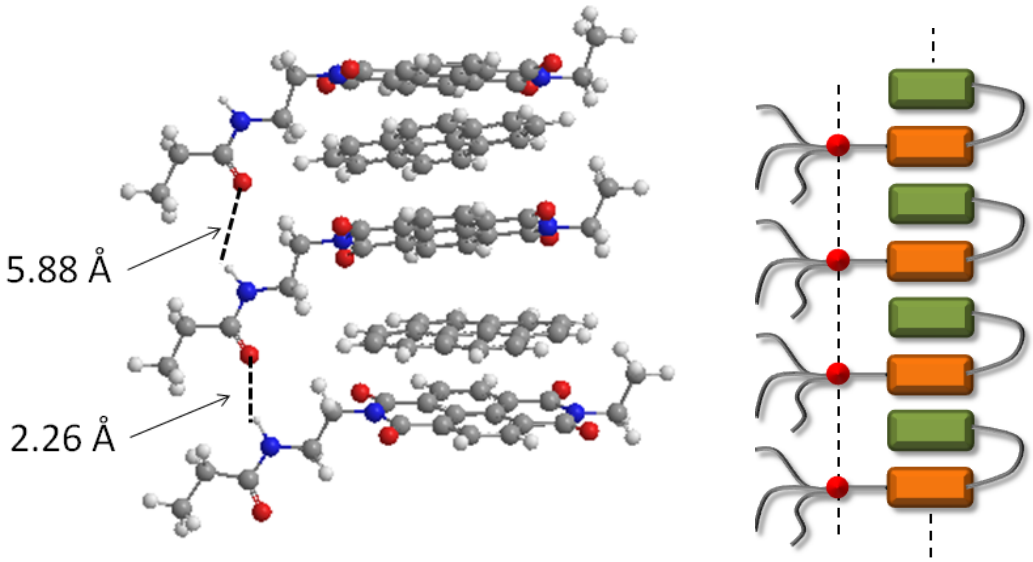


Fig S6: *Left*- Energy minimized structure of the pyrene inserted amide functionalized acceptor stack showing in this arrangement it is not possible that all the amide groups are within close proximity (~ 2.0 Å) to be involved in H-bonding and thus it eliminates extended stacking of the folded structure with --DADADAD-- sequence as shown in the right. Molecular modeling was done in Chem3D Ultra 8.0 using MM2 for energy minimization.

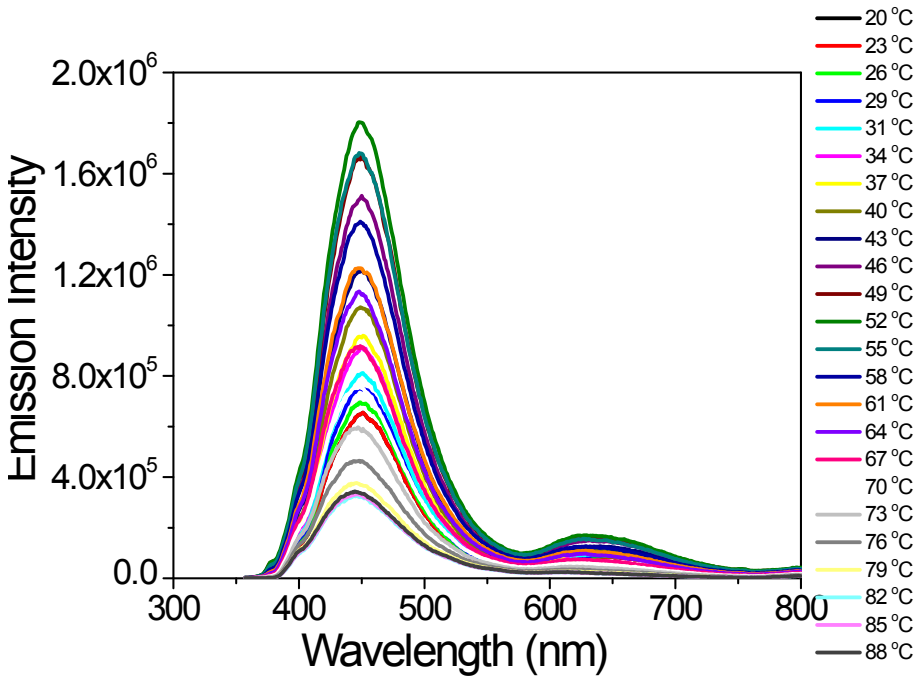


Fig S7: Variable-temperature photoluminescence spectra of **NDI-PY**. Concentration = 0.4 mM; λ_{ext} = 337 nm, slit = 2.5 nm.

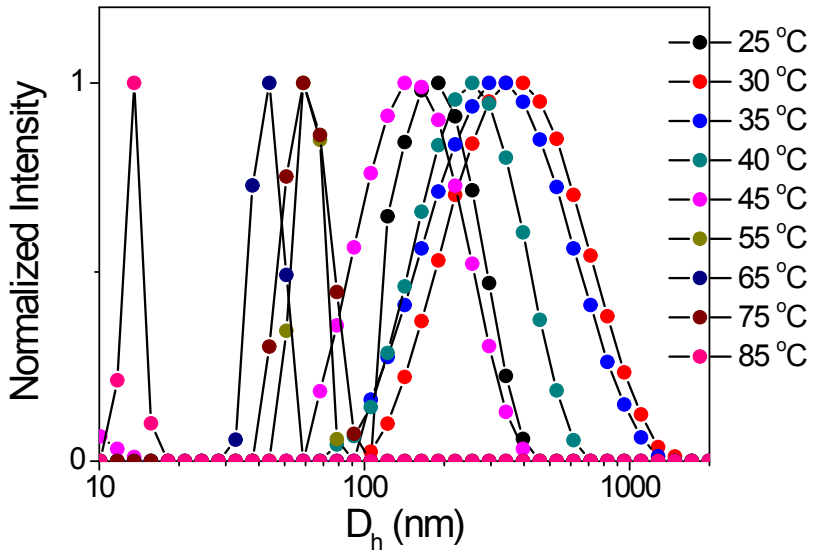


Fig S8: Variable-temperature DLS data for **NDI-PY** in MCH showing change in particle size with increasing temperature. Concentration = 0.4 mM.

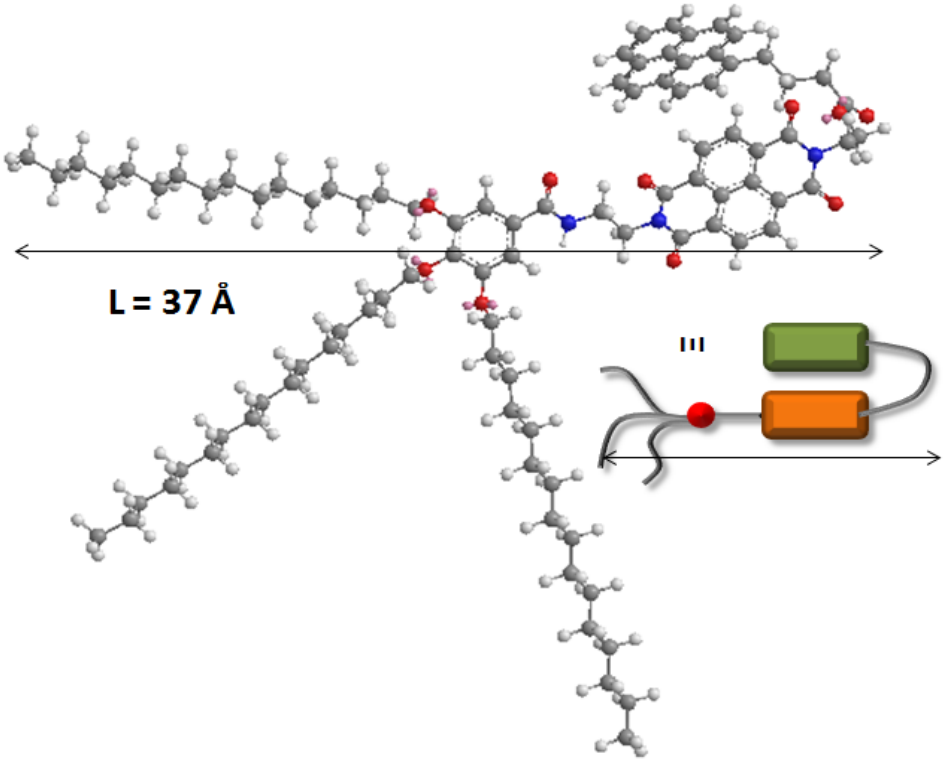


Fig S9: Energy minimized folded structure of **NDI-PY**. Molecular modeling was done in Chem3D Ultra 8.0 using MM2 for energy minimization.

References:

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