

Supporting Information

Synthesis and Self-Assembly of a C₃-Symmetric Benzene-1,3,5-Tricarboxamide Anchored Naphthalene Diimide Disc

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1. General Methods

NMR Measurements: NMR spectra were recorded with a Bruker AVANCE 400 (400 MHz) Fourier transform NMR spectrometer with chemical shifts reported in parts per million (ppm) with respect to TMS. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; m, multiplet.

FT-IR Measurements: Solution state IR measurements were performed on a Perkin-Elmer Spectrum GX series with a resolution of 4 cm⁻¹. Caesium Fluoride cells with a spacer of 2 mm were used. The solutions for the IR measurements were prepared in Tetrachloroethane (TCE) and Methylcyclohexane (MCH) which were gently warmed and sonicated for making the solutions homogeneous and clear. Solid state Infrared spectra were recorded using a

Bruker IFS 66 v/S spectrometer. The samples were prepared by using KBr pellets made by using KBr from local commercial suppliers.

Optical Measurements: Electronic absorption spectra were recorded on a Perkin Elmer Lambda 900 UV-Vis-NIR Spectrometer. Circular Dichroism (CD) spectra and temperature dependent UV-Vis spectra were recorded on a Jasco J-815 spectrometer where the sensitivity, time constant and scan rate were chosen appropriately. The temperature dependent measurements were performed with a CDF-426S/15 Peltier-type temperature controller with a temperature range of 263-383 K and adjustable temperature slope.

Dynamic light scattering Experiments (DLS): The measurements were carried out using a Nano ZS (Malvern UK) employing a 532 nm laser at a back scattering angle of 173° . The samples were measured in a 10 mm glass cuvette.

Atomic Force Microscopy (AFM): AFM measurements were performed on a Veeco diInnova SPM operating in tapping mode regime. Micro - fabricated silicon cantilever tips doped with phosphorus and with a frequency between 235 and 278 kHz and a spring constant of 20- 40 Nm^{-1} were used. The samples were prepared by drop casting a solution of **C₃-NDI** on a glass substrate and dried under high vacuum at room temperature.

Field Emission Scanning Electron Microscopy (FE-SEM): FE-SEM measurements were performed on a NOVA NANO SEM 600 (FEI) by drop casting the solutions on glass substrate followed by drying under high vacuum at room temperature and was operated with an accelerating voltage of 5 kV.

Transmission Electron Microscopy (TEM): TEM measurements were performed on a JEOL, JEM 3010 operated at 300 kV. Samples were prepared by placing a drop of the solution on carbon coated copper grids followed by drying at room temperature. The images were recorded with an operating voltage of 300 kV. In order to get a better contrast, the samples were stained with uranyl acetate (1 wt % in water) before the measurements.

XRD Measurements: Small angle XRD patterns were recorded in Siefert XRD instrument using Cobalt (Co) source ($\theta = 0.4^\circ - 60^\circ$).

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF): MALDI-TOF spectra were obtained on a Brukerdaltonics autoflex (ST- A2130) MALDI- TOF mass spectrometer with α - cyano- 4- hydroxycinnamic acid matrix in reflector mode.

Molecular Modelling Calculations: Geometry optimizations were carried out at HF/6-31G level of theory using Gaussian-09 suite of programs.^[S1] The molecules were visualized using Visual Molecular Dynamics.^[S2]

2. Synthesis and Characterization

The starting materials used for synthesizing various compounds were obtained from commercial suppliers. The moisture sensitive reactions were performed under an atmosphere of argon. DMF was dried by distillation under vacuum and dried on 3 Å molecular sieves activated at 180 °C. Analytical thin layer chromatography was carried out on Merck silica gel 60. Column chromatography was carried out on silica gel (100-200 mesh).

Compounds **1** and **3** were synthesized according to methods reported in literature.^[S3,S4]

Unsymmetric Naphthalene diimide Derivative (4). 2.22 g (3.96 mmol) of **1** and 0.82 g (3.96 mmol) of **3** were mixed with 1, 4, 5, 8-Naphthalenetetracarboxylic dianhydride (**2**) (0.99 g, 3.69 mmol) in 4 ml of dry DMF and was stirred under argon atmosphere at 110 °C for 16 hours. The unsymmetric diimide was obtained along with the symmetrical diimide derivatives. The hydrophobic symmetric digallic derivative was removed by washing with hexane, while **4** along with the symmetrical protected *p*-phenylenediamine derivative were collected as the precipitate. The mixture was then subjected to a chloroform wash where the symmetrical di-Boc derivative precipitated and the desired compound **4** was collected in the filtrate. It was then dried under vacuum and purified using column chromatography (silica gel, 100-200 mesh) in 2% methanol in chloroform followed by size exclusion chromatography (CHCl₃, SX-3). Yield = 47%; ¹H NMR (400 MHz, CDCl₃): δ 8.84 (s, 4H, NDI ArH), 7.59 (d, J = 8.4 Hz, 2H, ArH), 7.26 (d, J = 8.4 Hz, 2H, ArH), 6.63 (s, 1H, -NH), 6.52 (s, 2H, ArH), 4.06-3.99 (m, 6H, -OCH₂), 1.55 (s, 9H, -C(CH₃)₃), 1.9-0.8 (57H, alkyl H); ¹³C NMR (100 MHz, CDCl₃): δ 163.2, 163.2, 153.9, 139.4, 138.8, 131.6, 129.6, 129.2, 129.1, 127.3, 127.2, 119.2, 106.9, 71.9, 67.6, 39.6, 39.4, 29.9, 28.5, 28.1, 24.9, 22.9, 22.8, 22.7, 19.8, 19.7; FT-IR (KBr): ν (cm⁻¹) = 3447, 3365 (Amide -NH stretch), 1675 (Amide -C=O stretch), 1524 (Amide (II) band); M.P. 240 °C-242 °C.

Unsymmetric Naphthalene diimide amine (5). 1.29 g (1.29 mmol) of **4** in 50 ml dry DCM was added drop wise to a mixture of Trifluoroacetic acid (TFA) (11.1 ml) and dry DCM (10 ml) and stirred at 0 °C under argon atmosphere. The ice bath was then removed after 1.5 hours and the reaction mixture was allowed stirring at room temperature for an additional 3

hours. An extraction was done with 2 M NaOH/CHCl₃ after which the organic layer was dried on Na₂SO₄ and evaporated to get the deprotected product. Yield = 99%; ¹H NMR (400 MHz, CDCl₃): δ 8.83 (s, 4H, NDI ArH), 7.5 (d, J = 8.8 Hz, 2H, ArH), 6.84 (d, J = 8.8 Hz, 2H, ArH), 6.51 (s, 2H, ArH), 4.1-3.97 (m, 6H, O-CH₂), 1.9-0.8 (57H, alkyl H); ¹³C NMR (100 MHz, CDCl₃): δ 163.4 163.2, 153.9, 147.2, 138.7, 131.5, 129.2, 127.3, 127.2, 127.0, 115.8, 106.9, 71.9, 67.6, 45.9, 39.5, 39.3, 37.7, 37.5, 36.4, 30.0, 29.9, 29.8, 28.1, 24.9, 22.8, 22.7, 19.8, 19.7; HRMS (APCI): m/z calcd for C₅₆H₇₅N₃O₇: 906.5605, found: 906.5698 [M]⁺; FT-IR (KBr): ν (cm⁻¹) = 3463, 3374 (-NH stretch); M.P. 172 °C-174 °C.

C₃-NDI: 0.08 g (0.3 mmol) of **6** was taken in 2 ml of dry DCM and stirred at 0 °C for 10 minutes under argon atmosphere. To this, a mixture of triethylamine (0.22 ml, 1.61 mmol) and the deprotected amine **5** (1.15 g, 1.28 mmol) in 5 ml of dry DCM was added drop wise. The resultant mixture was allowed to warm to room temperature and the stirring was continued for 11 hours after which it was refluxed for additional 2 hours to ensure the completion of the reaction. The reaction mixture was cooled to room temperature and was dried under vacuum. The unreacted amine **5** was removed by an ethyl acetate wash as the filtrate, while **C₃-NDI** was collected as the residue. The residue was further purified by a silica gel column chromatography (100-200 mesh, 2% methanol in chloroform, 1% TFA) and size exclusion chromatography (CHCl₃, SX-3) to get the pure compound in 46.8% yield. The compound was obtained as a sticky solid after the column chromatography, which on re-precipitation in methanol followed by drying in vacuum converted into a beige colour powder. ¹H NMR (400 MHz, CDCl₃, 2% (v/v) TFA): δ 9.65 (s, 3H, NH), 9.19 (s, 3H, BTA core ArH), 8.92 (s, 3H, NDI ArH), 8.12 (d, J = 8.8 Hz, 2H, ArH), 7.46 (d, J = 8.8 Hz, 2H, ArH), 6.55 (s, 2H, ArH), 4.2-4.15 (m, 6H, -OCH₂), 4.0-3.99 (m, 12H, alkyl H), 1.9-1.14 (54H, alkyl H); ¹³C NMR (100 MHz, CDCl₃, 2% (v/v) TFA) (Figure S1) : δ 165.9 (3C, 1), 163.7, 163.6 (4C, 10, 16), 153.8 (2C, 19), 138.0 (1C, 20), 135.0 (3C, 2) 132.2 (2C, 12), 131.5 (3C, 17), 131.1 (1C, 3), 129.9, 127.3, 127.1 (6C, 11, 14, 15), 129.5 (2C, 13), 127.0 (2C, 4, 7), 122.2 (4C, 5, 6, 8, 9), 106.6 (2C, 18), 73.3 (1C, 21), 67.9 (2C, 30), 39.5 (1C, 22), 39.4 (2C, 31), 37.6 (1C, 24), 37.5 (2C, 33), 37.0 (1C, 25), 36.3 (2C, 34), 30.0 (1C, 23), 29.9 (2C, 32), 28.1 (3C, 27, 36), 24.8 (6C, 26, 35), 22.8 (1C, 29), 22.7 (2C, 38), 19.7 (2C, 28), 19.6 (4C, 37); MALDI-TOF MS: m/z calcd for C₁₇₇H₂₂₅N₉O₂₄:2862.73, found: 2885.74 [M+Na]⁺; HRMS (FAB): m/z calcd for C₁₇₇H₂₂₅N₉O₂₄: 2862.7316, found: 2880.6462 [M+H₂O]⁺; FT-IR (KBr): ν (cm⁻¹) = 3361, 3482 (Amide -NH stretch), 1675 (Amide -C=O stretch), 1538 (Amide (II) band); M.P. 256 °C.

3. Supporting Figures

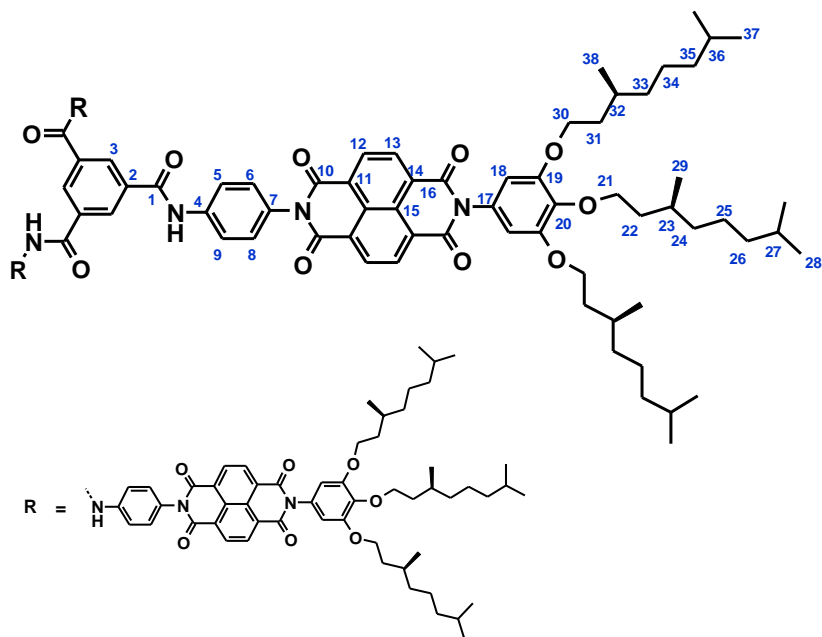


Figure S1. Molecular structure of **C3-NDI** with numbered carbons for ^{13}C assignment.

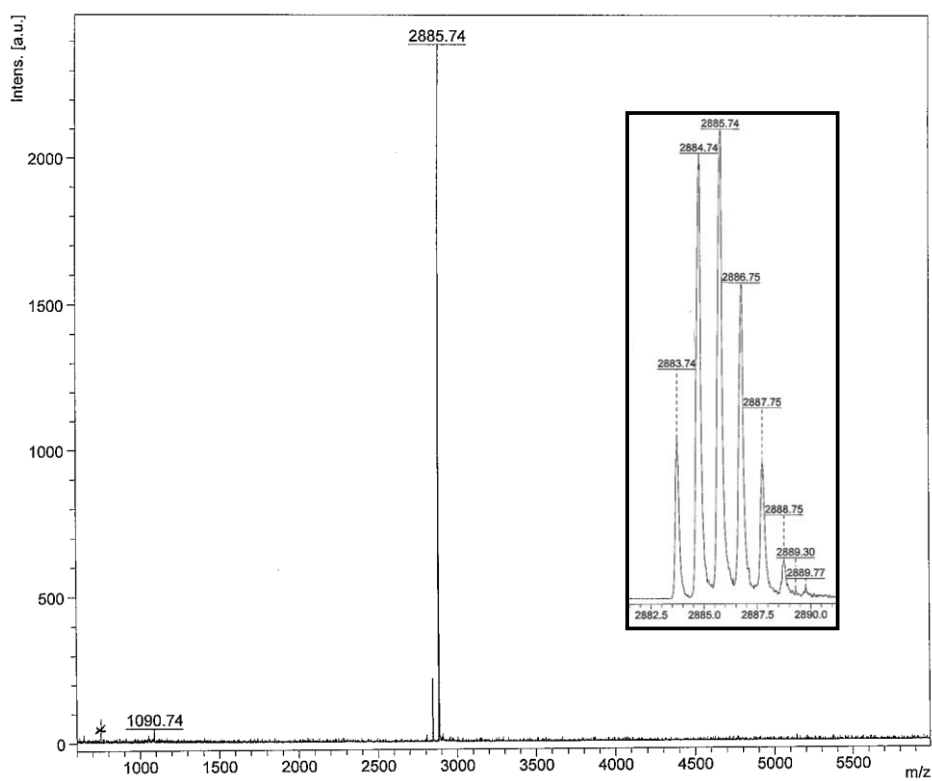


Figure S2. MALDI-TOF mass spectrum of **C3-NDI**; inset shows the isotopic pattern of the $[\text{M}+\text{Na}]^+$ peak.



Figure S3. Photograph of a gel of **C₃-NDI** ($c = 5$ mg/ml) formed in toluene.

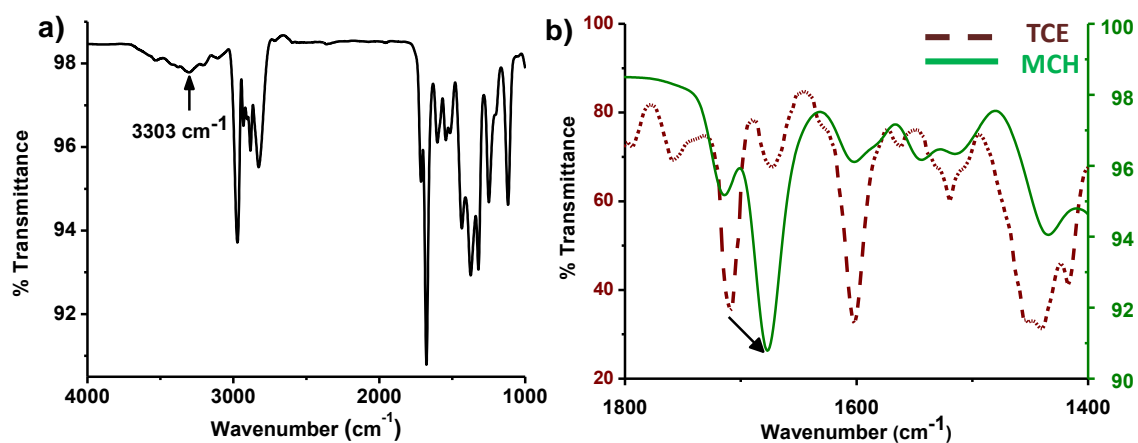


Figure S4. FT-IR spectra of **C₃-NDI** (10^{-3} M) in solution phase as a proof of intermolecular hydrogen bonding: a) IR spectrum in MCH and b) Comparative solution state IR spectra in TCE and MCH showing the differences in the C=O stretch.

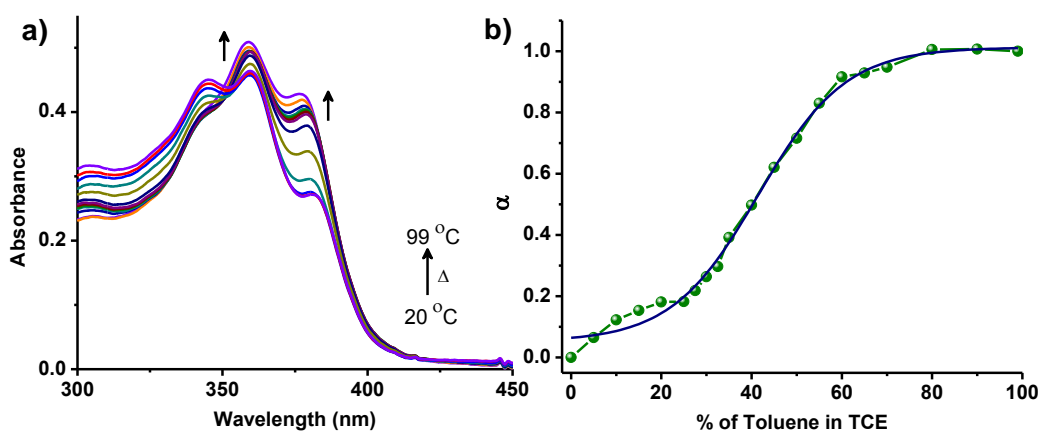


Figure S5. Chiroptical properties of **C₃-NDI** in toluene/TCE solvent mixtures ($c = 10^{-5}$ M):
a) Temperature dependent absorption spectra of **C₃-NDI** in 80% toluene in TCE. b) green curve: Plot of the fraction of aggregation (α) versus the solvent composition obtained by probing the absorbance at 378 nm; blue curve: sigmoidal fit.

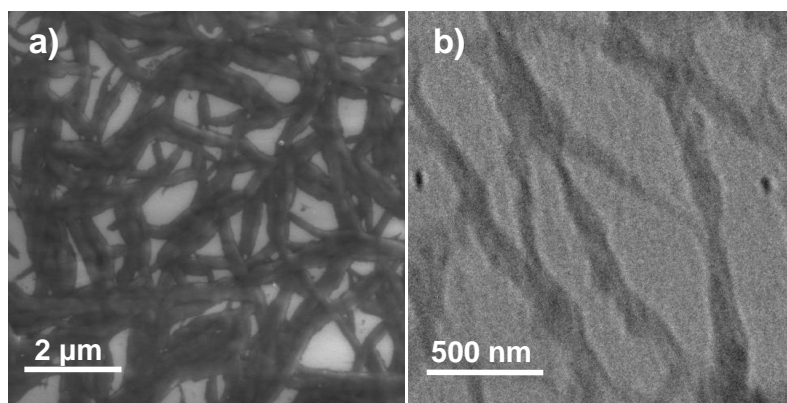


Figure S6. Additional microscopic images of **C₃-NDI** self-assembly in toluene/TCE (90/10 v/v) solvent mixtures: a) FE-SEM ($c = 10^{-4}$ M) and b) TEM ($c = 5 \times 10^{-5}$ M).

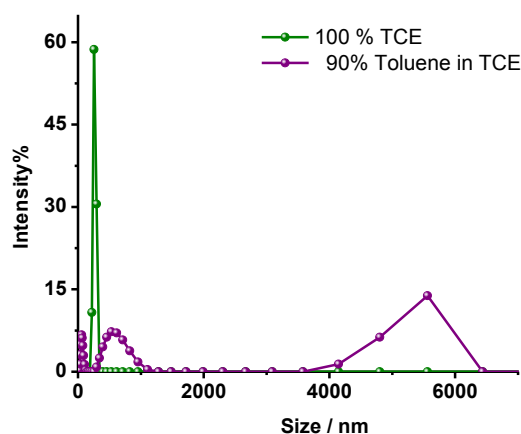


Figure S7. Dynamic light scattering (DLS) studies of **C₃-NDI** (10^{-4} M) in TCE and toluene/TCE (90/10 v/v) solvent mixtures.

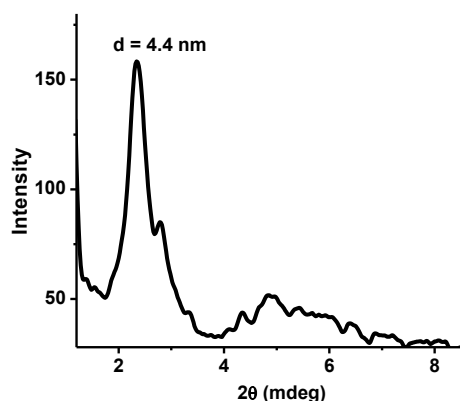


Figure S8. X-Ray diffraction profile of a film of a toluene gel ($C = 5$ mg/mL) of **C₃-NDI** drop-casted on a glass substrate.

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