

## Supporting Information

### Highly circularly polarized broad-band emission from chiral naphthalene diimide-based supramolecular aggregates

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## General information

- Microwave reactions were performed on a Biotage Initiator reactor. All the reactions were performed with power set to 300 W.
- Column chromatography was performed on a Biotage Isolera One using KP-SNAP columns and solvent gradients.
- $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a 400 MHz 4-nucleus NMR (Varian Mercury Vx) (400 MHz for  $^1\text{H}$  NMR and 100 MHz for  $^{13}\text{C}$  NMR). Proton and carbon chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) using the resonance of the deuterated solvent as internal standard.
- Matrix-assisted laser desorption/ionization-time of flight mass spectra were obtained using  $\alpha$ -Cyano-4-hydroxycinnamic acid (CHCA) and trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrices on a PerSeptive Biosystems Voyager-DE PRO spectrometer.
- DSC traces were measured on a Perkin-Elmer Pyris 1 DSC.
- IR spectra were measured on a Perkin-Elmer 1600 FT-IR.
- Electronic Circular Dichroism (ECD) spectra were measured using a J-710 CD spectrometer. Temperature dependent ECD measurement were performed on a Jasco J-815 with temperature controlled by a PTC-348WI Peltier system.
- Ultraviolet-visible (UV-Vis) absorbance spectra were recorded using a Jasco V-650 UV-Vis spectrometer with a Jasco ETCT-762 temperature controller. Fluorescence emission spectra were recorded on a Fluorolog Horiba Jobin-Yvon. The path length of the cuvettes was 1 cm for all the measurements.
- Circularly Polarized Luminescence (CPL) spectra were measured using the home-made instrument described in ref [49], using 365 nm excitation.
- Transmission Electron Microscopy was performed on a FEI company Tecnai G2 Sphera, operating at a voltage of 200 kV. For the analysis of the NDI 3 transfer to EM grids, micrographs were recorded on a CCD chip with 1024×1024 pixels. Samples were prepared as follows: 1 mM solution (supernatant of the suspension) of NDI 3 in  $\text{CHCl}_3$  (5/95 TCE/MCH) were drop cast on 400 mesh carbon film Cu TEM grids (Agar scientific) and air dried. Samples were left to dry overnight in a grid holder at room temperature and measured the day after.
- Scanning Electron Microscopy was performed with an FEI Quanta 600F instrument under high vacuum (electron beam acceleration voltage of 1 kV) without any further treatment of the sample. Samples were prepared as follows: 1 mM solution (supernatant of the suspension) of **NDI 3** in  $\text{CHCl}_3$

(5/95 TCE/MCH) were drop cast on glass cover slips (15 mm diameter) and air dried. After solvent evaporation the films were dried overnight under vacuum at room temperature.

## Experimental Procedures

### Synthesis of NMI 2

1,4,5,8-Naphthalene tetracarboxylic dianhydride (735 mg, 2.73 mmol) and (S)-3,7-dimethyl octylamine (430 mg, 2.73 mmol, 1 eq) were added in a 20 mL microwave reaction vessel. A magnetic stirrer and DMF (10 mL) were added. The glass tube was sonicated two minutes. The reaction was carried out for 5 minutes at 75 °C (power 300 W). The reaction mixture was then transferred in a flask, washing the tube with dichloromethane. The solvent was removed under reduced pressure to give a brown residue. NaOH<sub>(aq)</sub> 1 M was added to the residue, and after sonication, the insoluble residue was filtered. The filtered solution was acidified with HCl<sub>(aq)</sub> 3M until pH 5, until the formation of a precipitate. The acidic mixture was filtered and the brown solid was dried overnight in vacuo at 60 °C. 522 mg of **NMI 2** were obtained (47% yield), which was used directly in the next step without further purification.

<sup>1</sup>H-NMR (200 MHz, DMSO-d<sub>6</sub>) δ (ppm): 8.42-7.95 (dd, 4H; naphthalene core), 4.00-4.06 (m, 4H; NCH<sub>2</sub>), 1.11-1.56 (m, 10H), 0.94 (d, J = 6 Hz, 3H; CH<sub>3</sub>), 0.81 (d, J = 6.6 Hz, 6H; C(CH<sub>3</sub>)<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, 4% TFA-d in CDCl<sub>3</sub>) δ (ppm): 173.68, 163.84, 133.55, 131.93, 131.77, 131.48, 129.19, 126.02, 40.20, 39.35, 37.17, 34.97, 31.40, 28.09, 24.76, 22.77, 22.69, 19.53.

MS (MALDI-TOF, negative mode) **NMI 2 - H<sub>2</sub>O**: m/z 407.17 (calculated); 407.19 (experimental).

FT-IR (powder) wavenumber (cm<sup>-1</sup>): 1701 (s), 1651 (s), 1443 (m), 770 (s)

### Synthesis of acid appended NDI 3

4-aminobutirric acid (3 eq, 340 mg) and triethylamine (3 eq, 460 μL) were added in a 20 mL glass tube for microwave reaction. DMF (20 mL) was added and the mixture was stirred for 10 minutes. Then, the NMI 2 (1eq, 466 mg, 1.1 mmol) was added. The glass tube was sonicated for two minutes. After that, the reaction was carried out in two steps: 5 minutes at 75 °C and 20 minutes at 140 °C (power 300 W). The reaction mixture was then transferred in a flask washing the tube with dichloromethane. The solvents were evaporated and distilled water was poured into the flask. The aqueous solution was filtered and the solid dried in vacuo at 60 °C. The product was purified by chromatography (silica gel, eluent CHCl<sub>3</sub>/MeOH 95/5, R<sub>f</sub> = 0.3) to afford 233 mg of NDI 3 as off-white powder (yield 43 %).

<sup>1</sup>H-NMR (200 MHz, DMSO-d<sub>6</sub>) δ (ppm): 12.02 (s, COOH), 8.62 (s, 4H; naphthalene core), 4.08 (m, 4H; NCH<sub>2</sub>), 2.32 (m, 2H; CH<sub>2</sub>COOH), 1.89 (m, 2H; CH<sub>2</sub>CH<sub>2</sub>COOH), 1.12-1.60 (m, 10H) 0.96 (d, J = 6.3 Hz, 3H; CH<sub>3</sub>), 0.82 (d, J = 6.6 Hz, 6H; C(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm): 179.22, 167.84, 167.57, 131.41, 131.23, 131.10, 41.60, 39.30, 36.45, 35.69, 32.56, 29.13, 27.73, 27.68, 24.73.

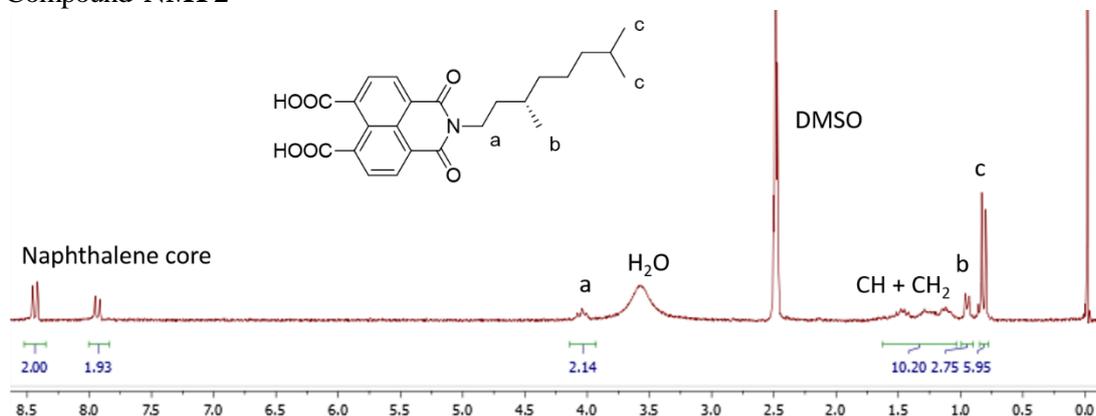
MS (MALDI-TOF, negative mode):  $m/z$  492.23 (calculated); 492.27 (experimental).

FT-IR (powder) wavenumber ( $\text{cm}^{-1}$ ): 1704 (m), 1695 (m), 1658 (s), 1338 (s), 1244 (s), 768 (s)

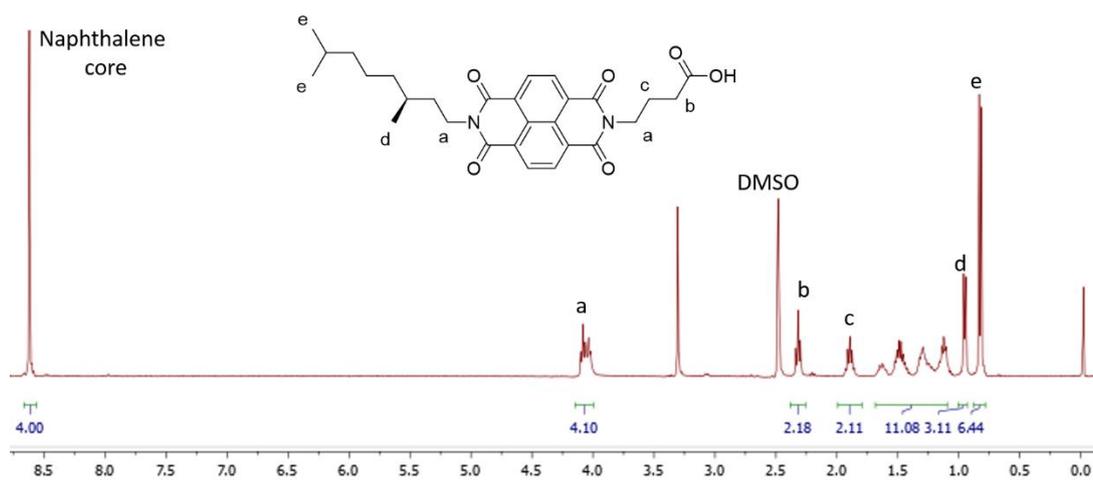
# Compounds Characterization

## $^1\text{H-NMR}$ spectra

Compound NMI 2

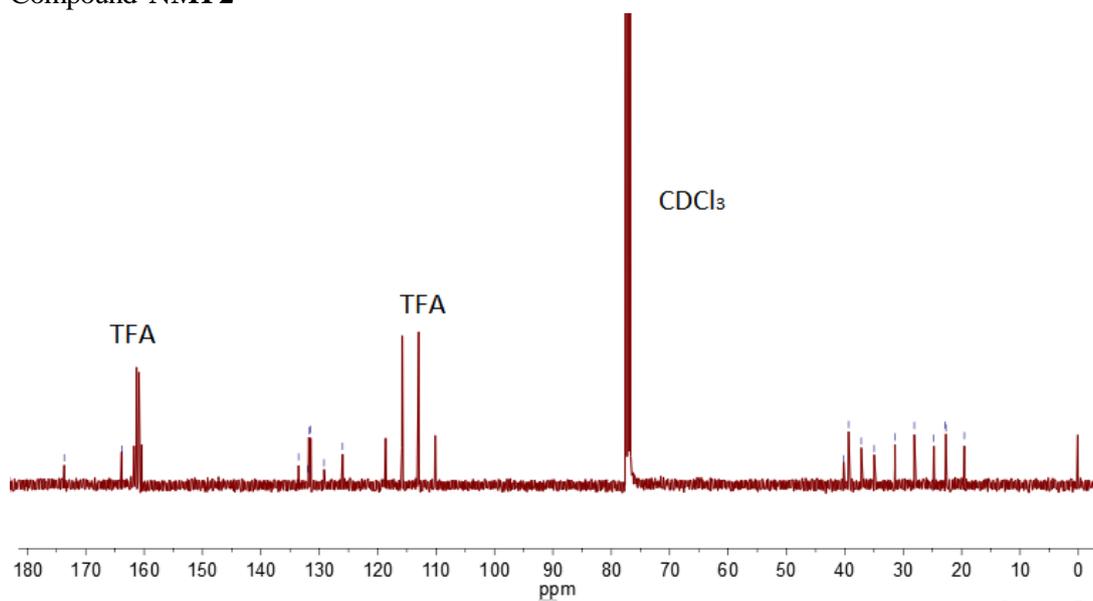


Compound NDI 3

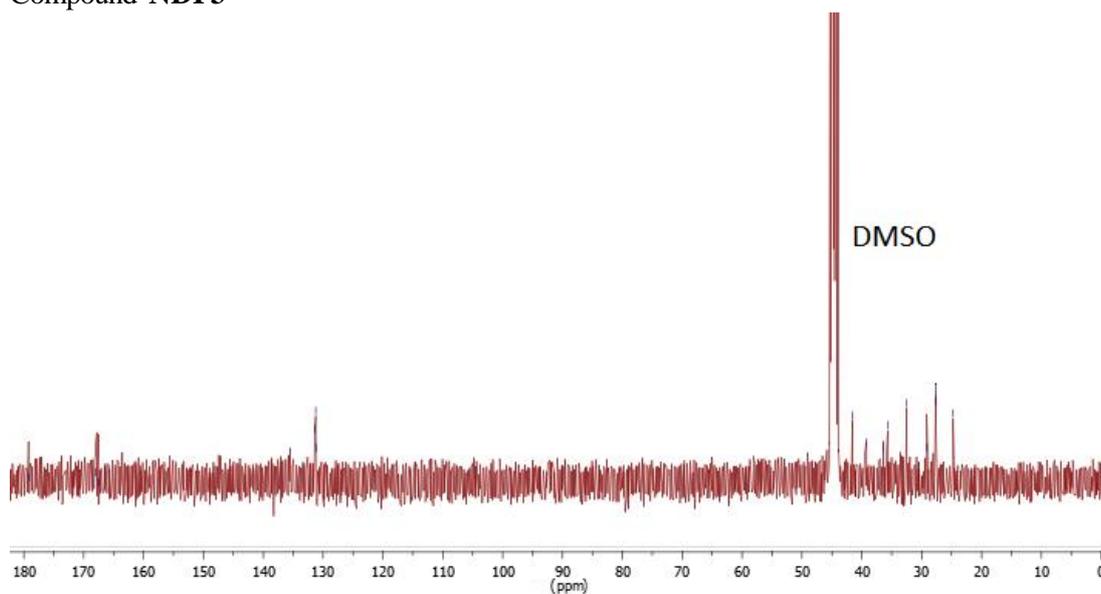


## $^{13}\text{C}$ -NMR spectra

Compound NMI 2

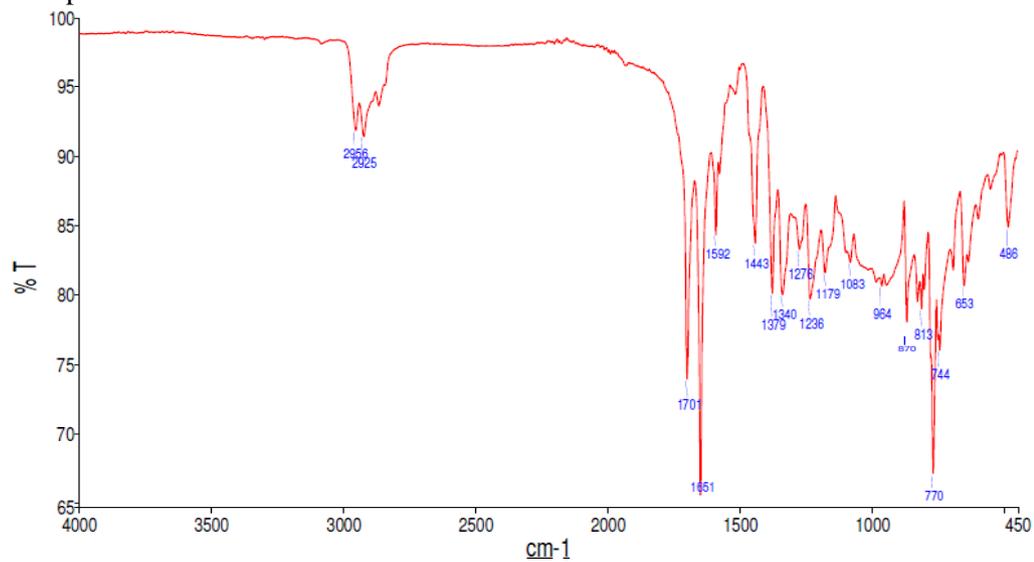


Compound NDI 3

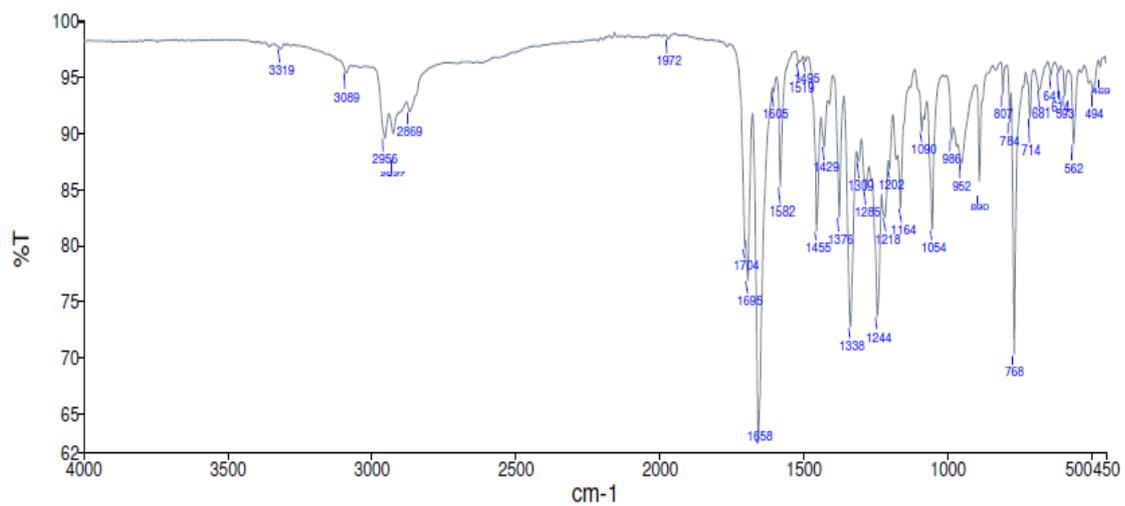


## FT-IR spectra

Compound NMI 2

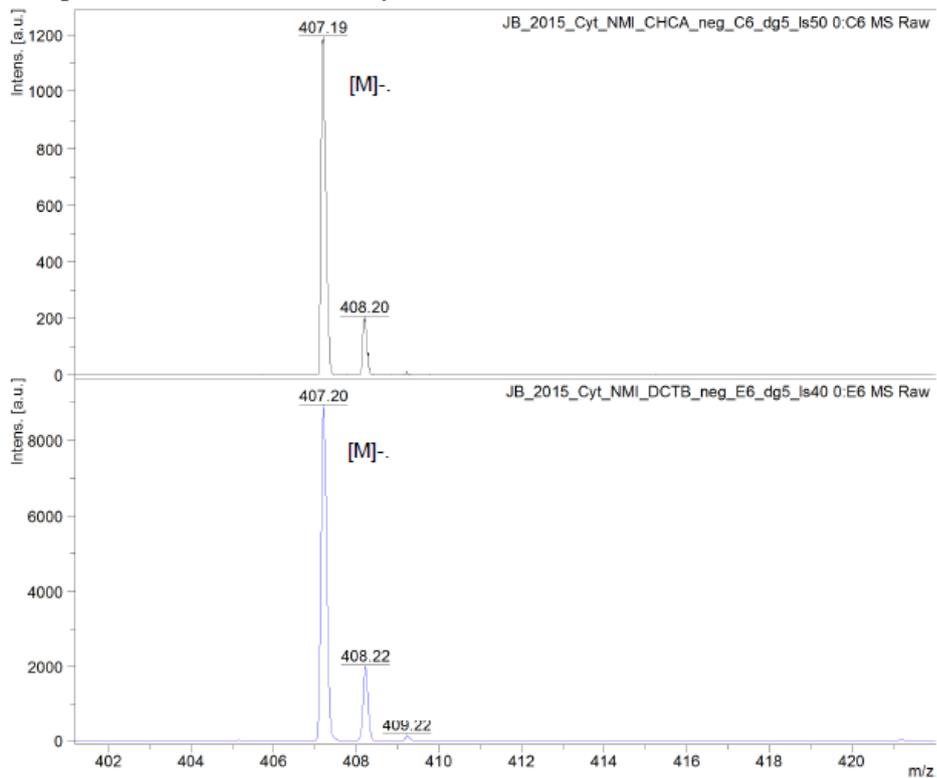


Compound NDI 3

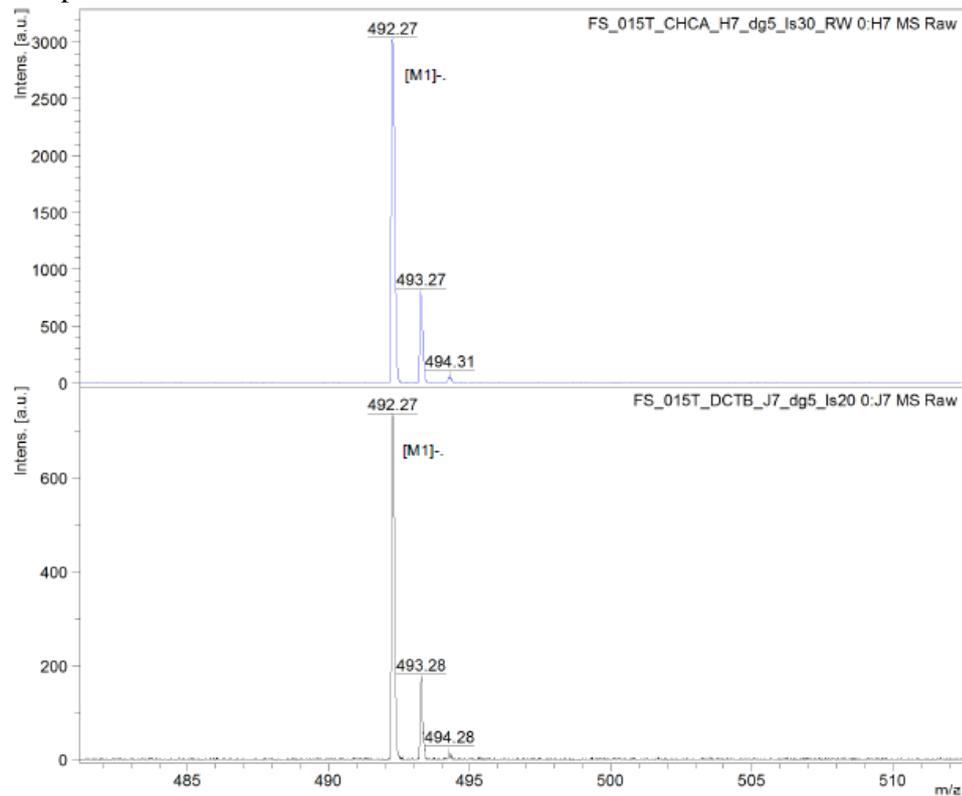


# MALDI-TOF spectra

## Compound NMI 2 – H<sub>2</sub>O (anhydride form)

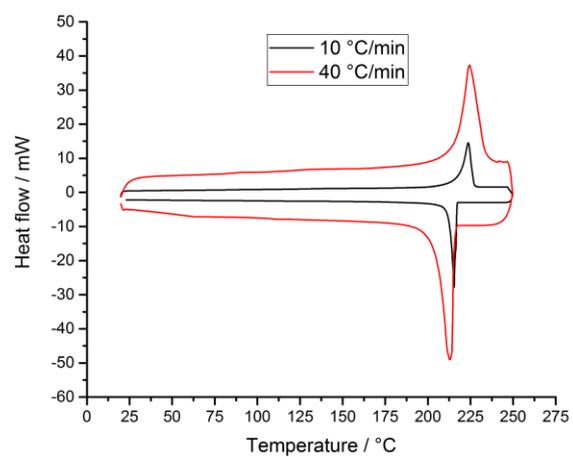


## Compound NDI 3



# Differential Scanning Calorimetry

Compound NDI 3

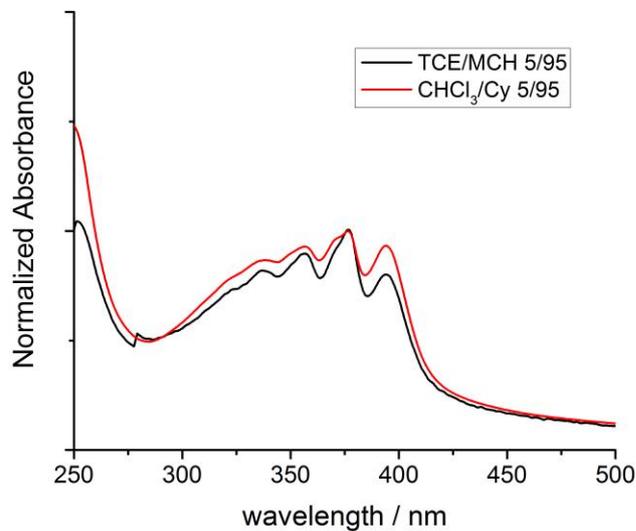


Melting point: 224 °C (10 °C/min), 224 °C (40 °C/min).

Recrystallization point: 216 °C (10 °C/min), 213 °C (40 °C/min)

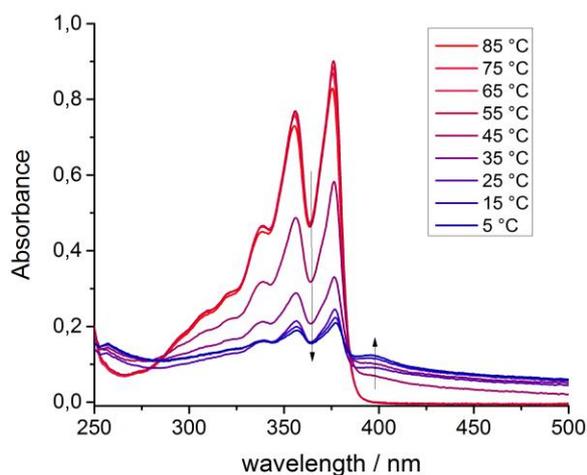
# Optical and Chiroptical Characterization

## UV-Vis spectra in different solvent mixtures



**Figure S1:** UV-Vis spectra of compound NDI **3** in the two mixtures 1,1,2,2-tetrachloroethane (TCE)/methylcyclohexane(MCH) and CHCl<sub>3</sub>/cyclohexane(Cy) 5/95,  $c = 5 \times 10^{-5}$  M.

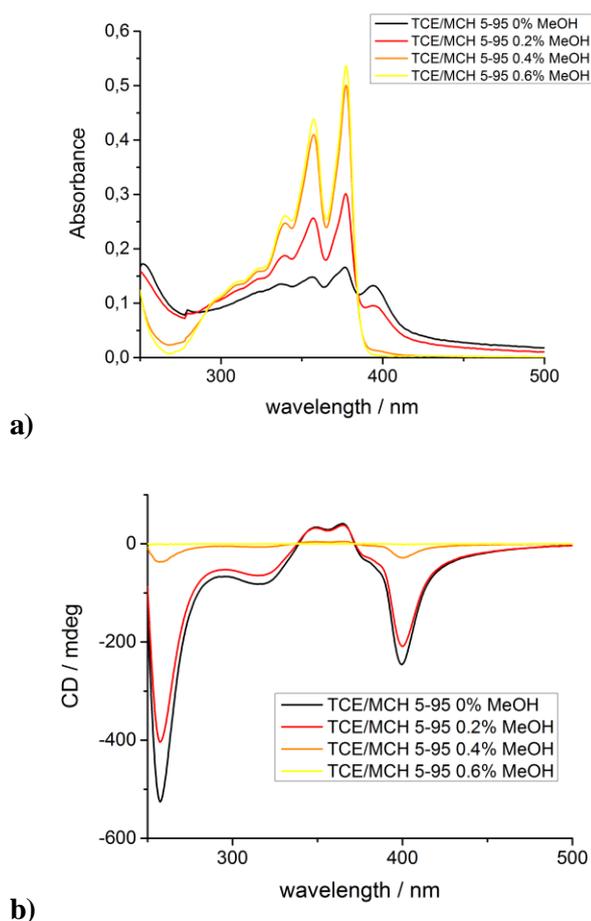
## UV-Vis spectra at variable temperatures



**Figure S2:** UV-Vis spectra of compound NDI **3** at different temperatures under cooling.

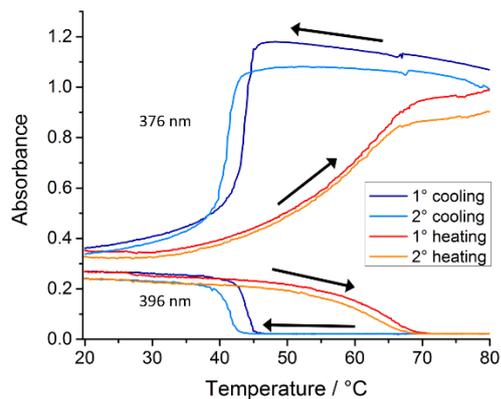
Scan rate: 100 nm/min. Each new spectrum was recorded after 10 minutes the chosen temperature had been reached. TCE/MCH 5/95,  $c = 5 \times 10^{-5}$  M.

## UV-Vis and CD experiments with MeOH addition

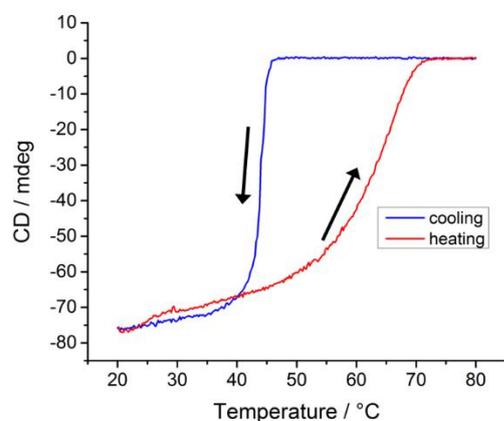


**Figure S3:** UV-Vis spectra (a) and ECD spectra (b) of the solution TCE/MCH 5/95,  $c = 5 \times 10^{-5}$  M, with increasing amount of MeOH volume percentages. The spectra were recorded 15 minutes after the addition of the volume of MeOH required. After adding 0.6% v/v of MeOH, the CD signal vanishes and the absorption band at 396 nm drops, indicating that the aggregate has completely disassembled.

## UV-Vis and CD experiments at variable temperature for a fixed wavelength



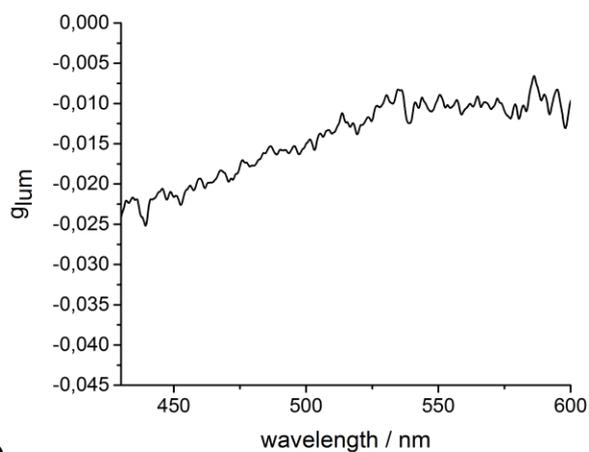
a)



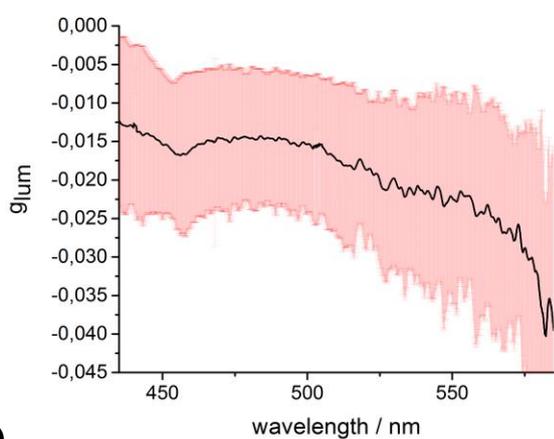
b)

**Figure S4:** Plot of absorbance (a) and CD (b) as a function of temperature upon cooling/heating cycles. The absorption was measured at 376 nm and 396 nm at the same time, the wavelengths at the maximum of the 0-0' peak of the monomer and the red-shifted peak of the aggregate, respectively. Electronic Circular Dichroism was measured at 405 nm, at the minimum of the first Cotton effect. Cooling/heating rate 60 °C/h. solution 5/95 TCE/MCH,  $c = 5 \times 10^{-5}$  M.

## Emission dissymmetry factors



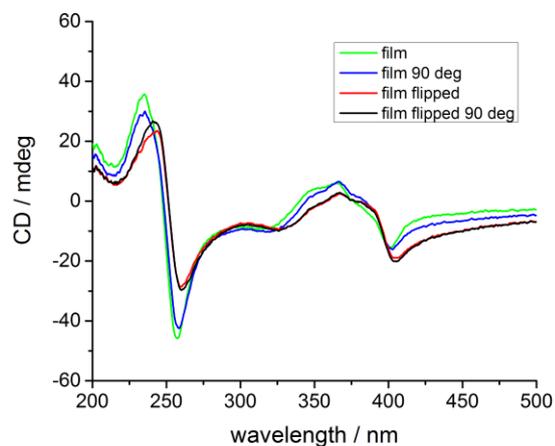
a)



b)

**Figure S5:** Plot of emission dissymmetry factors  $g_{lum}$  against wavelength for NDI 3 in  $CHCl_3$ /Cyclohexane 5/95,  $c = 5 \times 10^{-5}$  M (a), and for thin film obtained by deposition of a  $CHCl_3$  solution  $10^{-3}$  M (b). The red error bars indicate 2 standard deviations for 3 different samples.

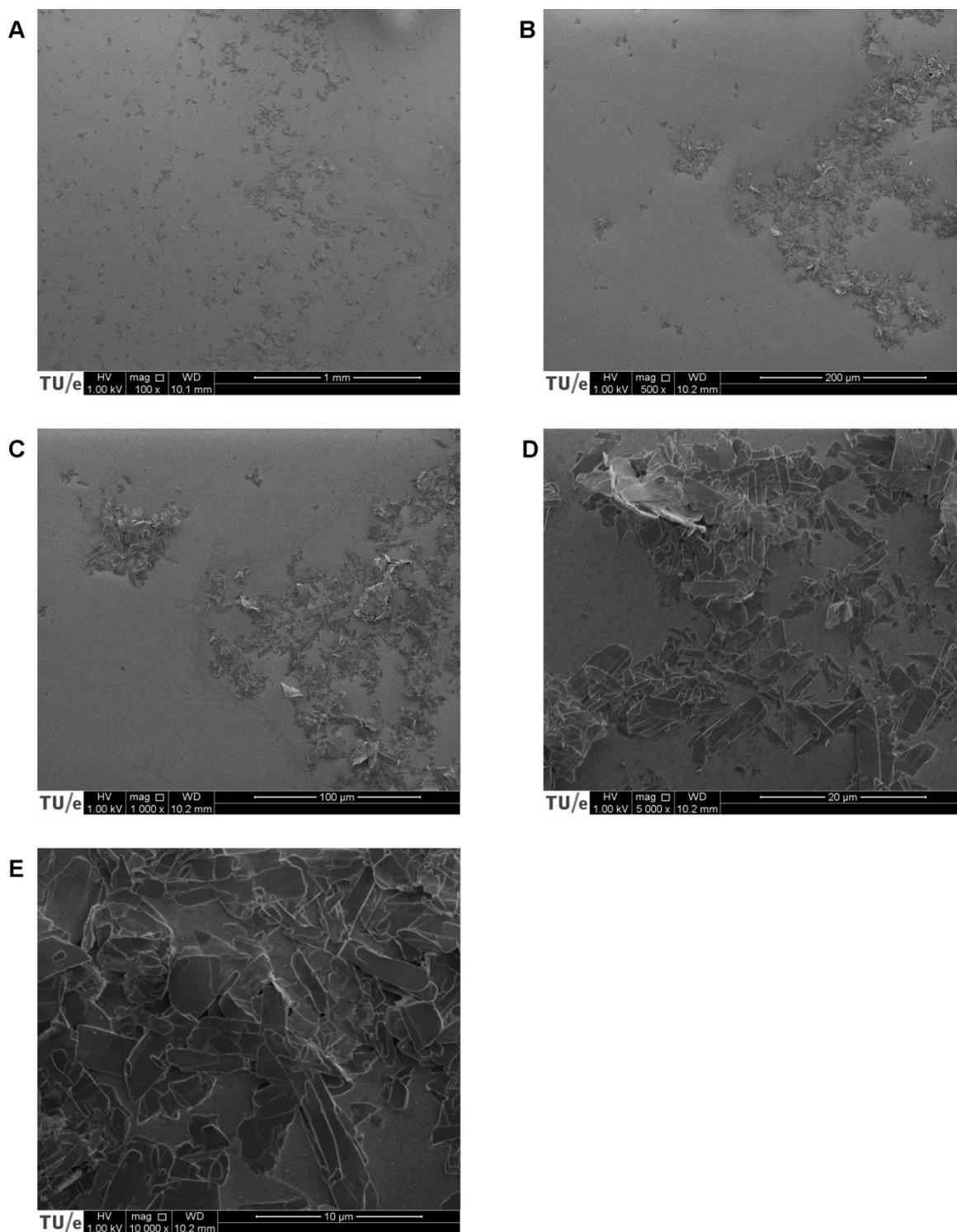
## ECD spectra of thin films



**Figure S6:** ECD spectra of the thin film obtained by consecutive depositions of concentrated solution  $\text{CHCl}_3$   $10^{-3}$  M. Spectra were recorded at different orientations, rotating the slide by  $90^\circ$  around the excitation light axis or flipping it by  $180^\circ$ , to assess homogeneity of the sample and rule out contribution from linear dichroism and linear birefringence.

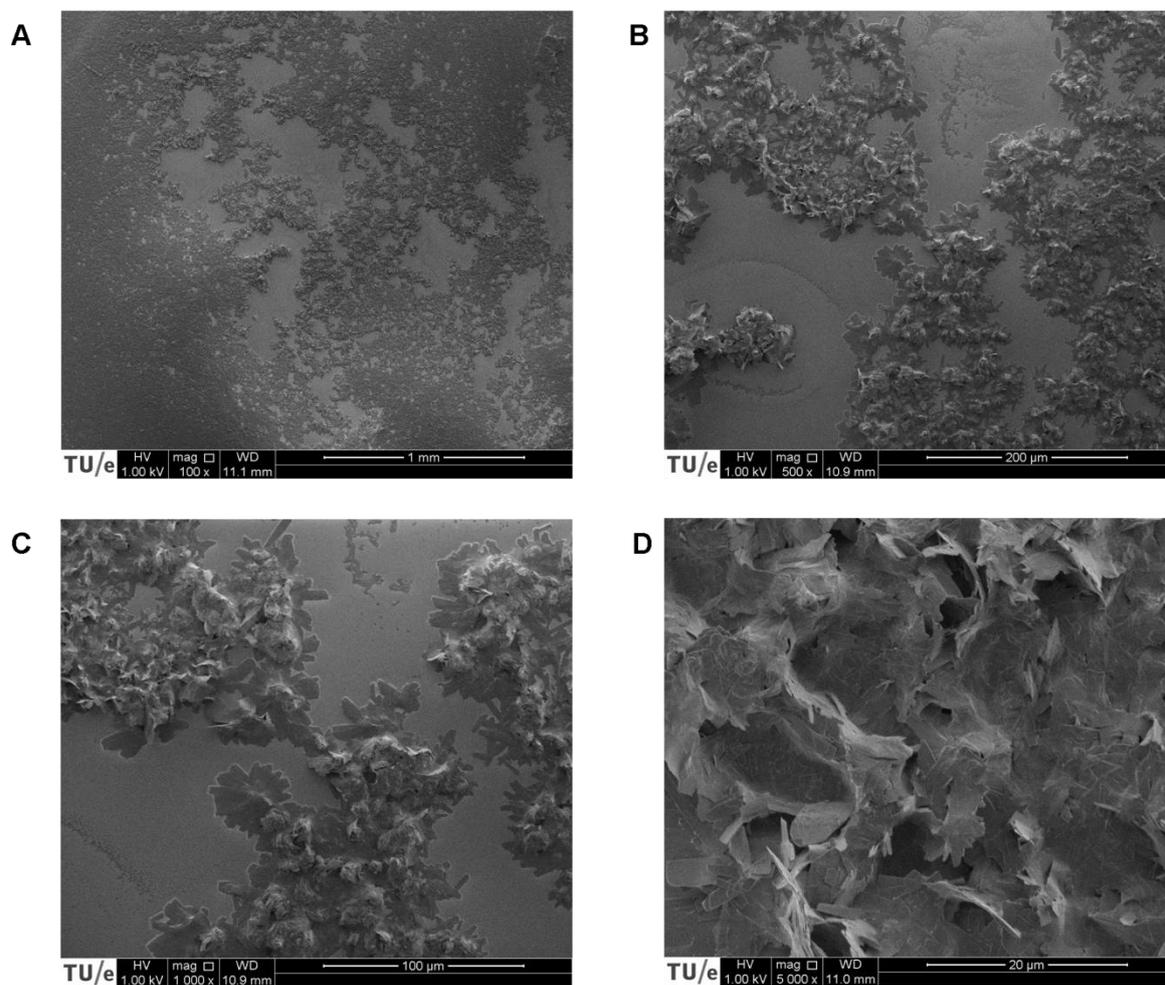
# Drop-casted Films Characterization

## Scanning Electron Microscopy on films from 5/95 TCE/MCH



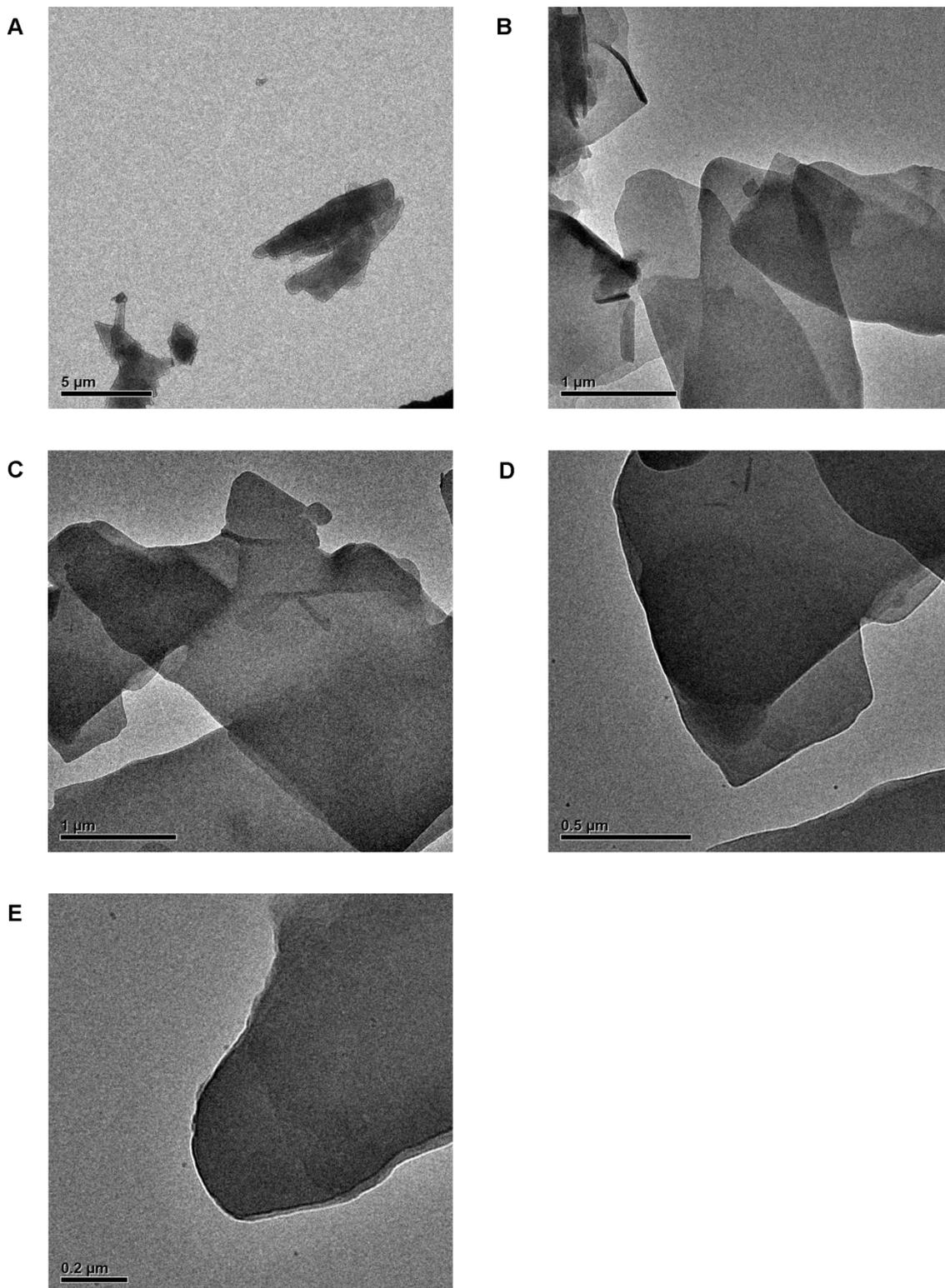
**Figure S7:** SEM micrographs of drop-casted films from nominal  $10^{-3}$  M solution of **NDI 3** in 5/95 TCE/MCH obtained at different magnifications. Scale bars (bottom right) are 1 mm (A), 200  $\mu\text{m}$  (B), 100  $\mu\text{m}$  (C), 20  $\mu\text{m}$  (D), and 10  $\mu\text{m}$  (E).

## Scanning Electron Microscopy on films from $\text{CHCl}_3$



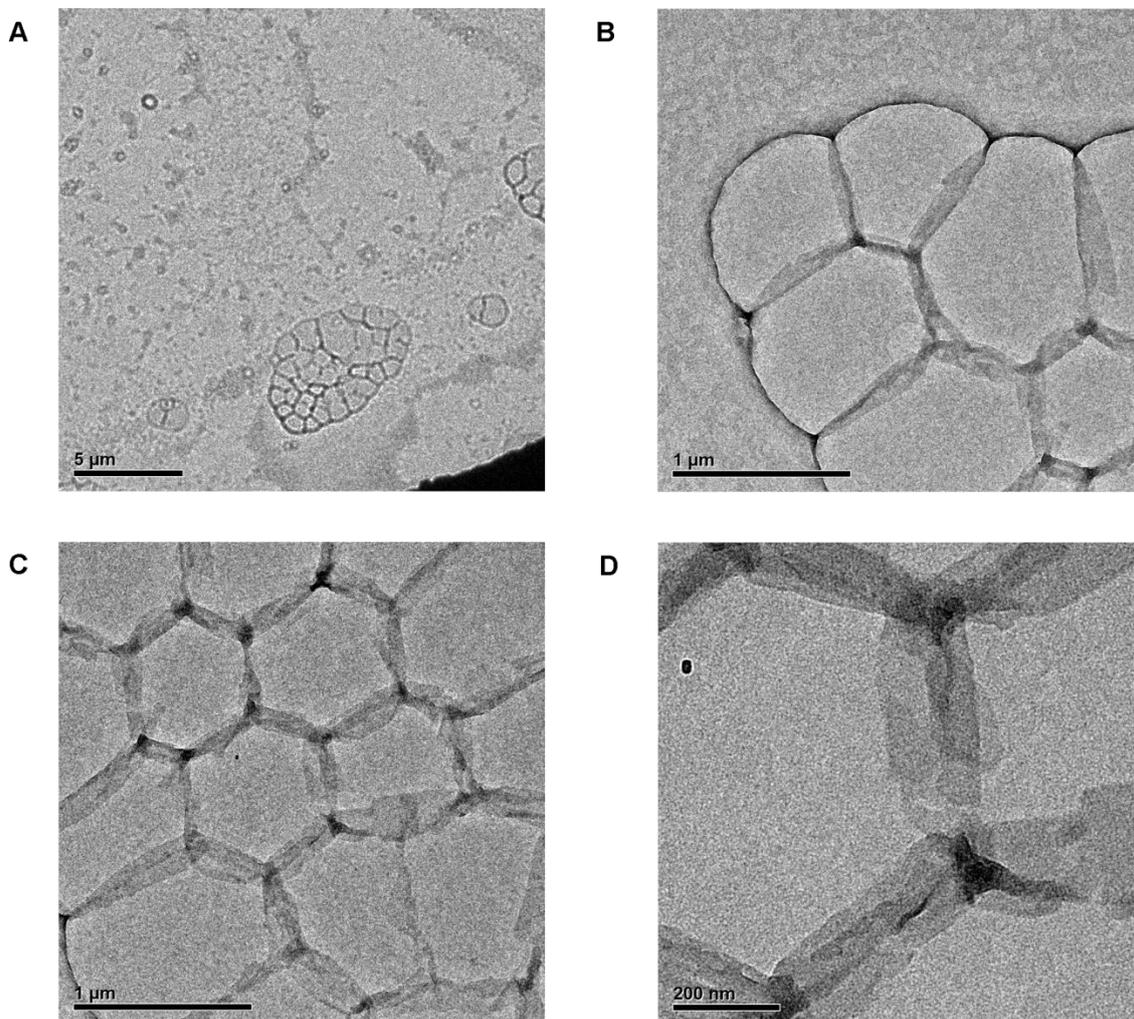
**Figure S8:** SEM micrographs of drop-casted films from  $10^{-3}$  M solution of **NDI 3** in  $\text{CHCl}_3$  obtained at different magnifications. Scale bars (bottom right) are 1 mm (A), 200  $\mu\text{m}$  (B), 100  $\mu\text{m}$  (C), and 20  $\mu\text{m}$  (D).

## Transmission Electron Microscopy on films from 5/95 TCE/MCH



**Figure S9:** TEM micrographs of drop-casted films from nominal  $10^{-3}$  M solution of **NDI 3** in 5/95 TCE/MCH obtained at different magnifications. Scale bars (bottom left) are 5 μm (A), 1 μm (B), 1 μm (C), 0.5 μm (D), and 0.2 μm (E).

## Transmission Electron Microscopy on films from $\text{CHCl}_3$



**Figure S10:** TEM micrographs of drop-casted films from  $10^{-3}$  M solution of **NDI 3** in  $\text{CHCl}_3$  obtained at different magnifications. Scale bars (bottom left) are  $5\ \mu\text{m}$  (A),  $1\ \mu\text{m}$  (B),  $1\ \mu\text{m}$  (C), and  $200\ \text{nm}$  (D).