

Supporting Information

Supramolecular polymerization and bulk properties relationship in ester-functionalized *N*-annulated perylene-3,4,9,10-tetracarboxylic diimides

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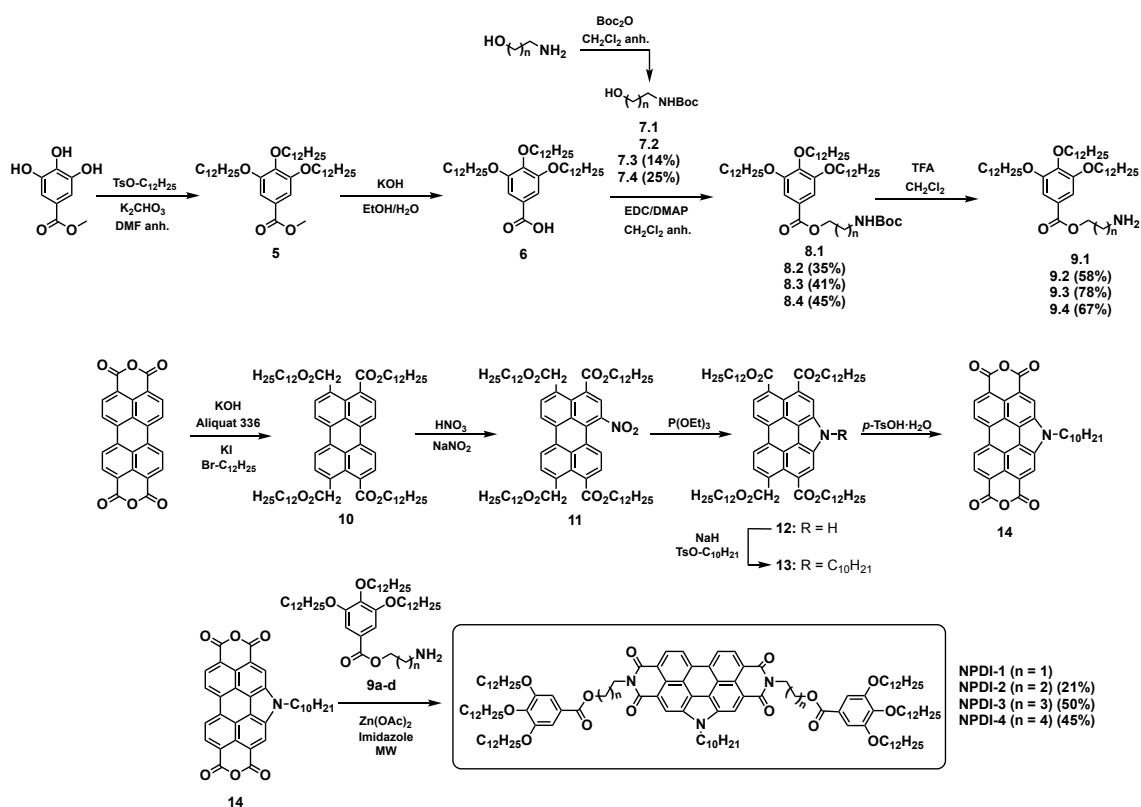
1. Materials and methods

All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230–240 mesh or Scharlau 60, 230–240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminium-coated Merck Kieselgel 60 F254 plates. Matrix-assisted laser desorption/ionization (MALDI) high resolution mass spectra (HRMS) were recorded on a MALDI Bruker daltonics Ultraflex TOF/TOF spectrometer. DCTB was used as matrix. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 MHz spectrometer (^1H : 300 MHz; ^{13}C : 75 MHz) at 298 K. Deuterated solvents were used as internal standards. Coupling constants (J) are quoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Fourier Transform Infrared Spectroscopy (FT-IR) spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer.

UV-Vis absorption spectra were registered on a Jasco-V630 spectrophotometer equipped with a Peltier thermoelectric temperature controller. Circular dichroism (CD) measurements were performed in a Jasco-J1500 spectrophotometer equipped with a Peltier thermoelectric temperature controller (Jasco MCB-100 model). The spectra were recorded in the continuous mode between 750 and 220 nm, with a data pitch of 0.2 nm, a DIT of 1 s, and a bandwidth of 2 nm. 1 cm and a 1 mm path-length quartz cuvettes (Hellma) with screw cap were used. Emission spectra was recorded in a Jasco FP8300. The thermodynamic parameters associated to the supramolecular polymerization mechanism were derived by applying the Matlab® script built up to execute the one-component equilibrium model published by ten Eikelder and coworkers.^{S1} To attain accurate values for the thermodynamic parameters, global fittings using four cooling curves, corresponding to four different concentrations of the monomer species, were performed. Fluorescence spectra were recorded on a JASCO FP-6300 fluorescence spectrometer at low sensitivity for the J aggregates and medium for the H ones.

Atomic force microscopy (AFM) was performed on a SPM Nanoscope IIIa multimode microscope working on tapping mode with a TESPSS tip (Veeco) at a working frequency of ~235 kHz. Differential scanning calorimetry (DSC) data were collected on a DSC Q2000 equipment from TA instruments, calibrated with an indium standard. The samples were weighed into aluminium pans and hermetically sealed. The samples were initially heated 20 °C above their melting point and then subjected to two cooling/heating cycles with a rate of 10 K min⁻¹. Hereafter, a second measurement was performed with similar conditions with a heating/cooling rate of 2 K min⁻¹. The data presented are the second heating and/or cooling cycle. Polarized optical microscopy (POM) images were recorded upon placing samples between two glass substrates and imaged using a Nikon Xfinity1 Lumenera microscope with 4x, 16x and 25x magnification. Two crossed linear polarizers were used to image the samples under polarized light. The samples were heated using a Linkam heating stage mounted in the POM set-up. Bulk small angle X-ray scattering (SAXS) was performed on a Ganesha 300XL instrument from SAXSLab. The flight tube and sample holder are all under vacuum in a single housing, with a GeniX-Cu ultra-low divergence X-ray generator. The source produces X-rays with a wavelength (λ) of 0.154 nm and a flux of 1×10^8 ph s⁻¹. Scattered X-rays were captured on a 2-dimensional Pilatus 300K detector with 487 × 619 pixel resolution. The sample-to-detector distance was 0.084 m (WAXS mode) or 0.48 m (MAXS mode). The instrument was calibrated with diffraction patterns from silver behenate. The results are listed below.

2. Synthetic details and characterization



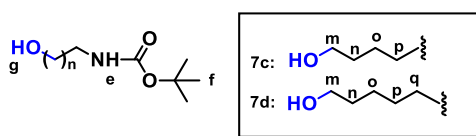
Scheme 1. Synthetic route for the preparation of the reported NPDIs **2-4**.

Compounds **5-14**^{S2,S3} and NPB **1**^{S4} were prepared according to previously reported synthetic procedures and the same amounts were used.

Synthesis of the N-BOC protected aminoalcohols **7.3** and **7.4**.

The corresponding aminoalcohol (4-amino-1-butanol or 5-amino-1-pentanol; 11.24 mmol) is dissolved in anhydrous CH_2Cl_2 (40 mL) under Ar atmosphere. After that, di-*tert*-butyl decarbonate (1.91 g, 11.24 mmol) is added in a mixture of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1:1) (20 mL) at 0 °C. The mixture is stirred for 24 h at room temperature. After this time, the reaction mixture is washed with HCl 1 M (2 x 20 mL) and H_2O (2 x 20 mL). The organic layer is dried over MgSO_4 , filtered and the solvent is removed in vacuo, obtaining **7** as a colourless oil. The product thus obtained is utilized in the next synthetic step without any further purification.

Compounds **7**



7.3 ($n = 3$): (yield: 14%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , 298 K) δ (ppm): 4.87 (1H, H_e , s), 3.57 (2H, H_m , t, $J = 6.0$ Hz), 3.22 (1H, H_g , s), 3.07 (2H, H_p , s), 1.51 (4H, $\text{H}_{n,o}$, t, $J = 3.4$ Hz), 1.37 (9H, H_f , s). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ (ppm): 156.34, 79.16, 62.06, 40.34, 29.70, 28.43, 26.54. FT-IR: 3573.16, 3428.29, 3351.36, 2929.03, 2872.28, 1687.39, 1529.89, 1453.44, 1392.64, 1366.75, 1279.62, 1252.46, 1169.79, 1106.54, 1057.87, 1021.07, 651.57, 628.17 cm^{-1} . HRMS (MALDI-TOF) m/z : calculated for $\text{C}_9\text{H}_{19}\text{NO}_3$: 189.1400, found: 212.1250 [$\text{M}+\text{Na}$].

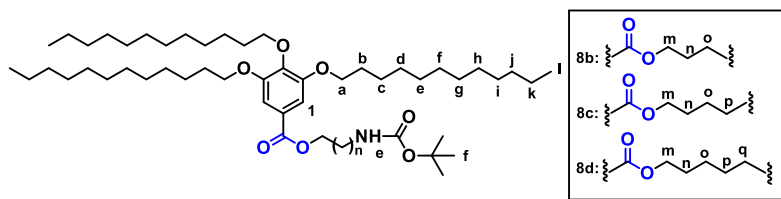
7.4 ($n = 4$): (yield: 25%). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , 298 K) δ (ppm): 4.67 (1H, H_e , br), 3.58 (2H, H_m , t, $J = 6.84$ Hz), 3.07 (2H, H_q , t, $J = 6.90$ Hz), 2.34 (1H, H_g , br), 1.58 – 1.31 (15H, $\text{H}_{n,p,f}$, m). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , 298 K) δ (ppm): 157.01, 79.19, 67.85, 62.53, 60.51, 40.61, 32.32, 30.11, 28.44, 23.14. FT-IR: 631.76, 757.95, 781.07, 867.26, 953.09, 1013.10, 1052.48, 1168.69, 1250.15, 1273.35, 1365.47, 1391.64, 1454.86, 1477.68, 1525.06, 1686.30, 2864.40, 2933.52, 2975.34, 3338.14. HRMS (MALDI-TOF) m/z : calculated for $\text{C}_{10}\text{H}_{21}\text{NO}_3$: 203.1521, found: 204.1588 [$\text{M}+\text{H}$].

Synthesis of the trialkoxybenzoate esters **8**.

A mixture of EDC (1.1 eq) and DMAP (1.1 eq) is added in the solid state over a solution of **6** (989 mg, 1.47 mmol) in anhydrous CH_2Cl_2 (10 mL) under Ar atmosphere and 0 °C. After stirring for 15 min, a solution of **7** (1.1 eq) in anhydrous

CH₂Cl₂ (10 mL) is added dropwise at 0 °C. The reaction is then stirred for 24 h at room temperature. After this time, the crude is washed with HCl 1 M (2 x 20 mL), NaOH 2 M (2 x 20 mL) and H₂O (2 x 20 mL). Then, the organic layers are dried over MgSO₄, filtered and dried in vacuo, obtaining product **8** as a pale brown solid. The product thus obtained is utilized in the next synthetic step without any further purification.

Compounds 8



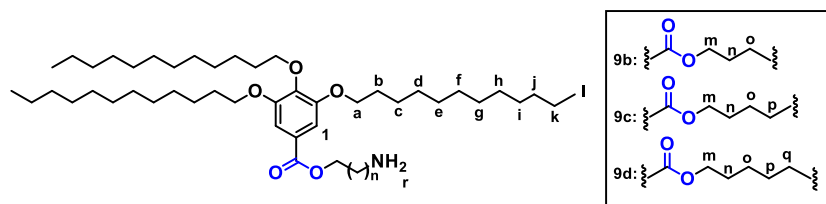
8.2 (n = 2): (35%). ¹H-RMN (300 MHz, CDCl₃, 298K) δ (ppm): 7.21 (s, 2H, H₁), 5.23 (s, 1H, H_e), 4.33 (t, 2H, H_m, J = 6.09 Hz), 4.01 - 3.92 (m, 8H, H_{a,o}), 3.22 (m, 2H, H_n), 1.92 (m, 2H, H_b), 1.81 - 1.51 (m, 4H, H_{c,d}), 1.48 - 1.10 (m, 14H, H_{e-k}), 1.47 (s, 9H, H_f), 0.83 (m, 9H, H_i). ¹³C-RMN (75 MHz, CDCl₃) δ (ppm): 152.9, 142.6, 124.7, 108.2, 77.6, 77.2, 76.8, 73.6, 69.3, 62.5, 32.0, 31.7, 30.4, 29.7, 29.5, 28.5, 26.2, 22.8. FT-IR: 3403.10, 2981.41, 2936.56, 1807.79, 1757.20, 1690.06, 1807.79, 1757.20, 1690.06, 1515.57, 1477.48, 1458.83, 1395.43, 1307.41, 1255.05, 1211.765, 1168.40, 1114.66, 1062.22, 996.22, 950.46, 913.27, 866.10, 842.93, 775.79, 736.24, 703.38, 662.79, 518.2 cm⁻¹. HRMS (MALDI-TOF) m/z: calculated for C₅₁H₉₃NO₇: 831.7005, found: 831.7788 [M]⁺.

8.3 (n = 3): (41%). ¹H-NMR (300 MHz, CDCl₃, 298 K) δ (ppm) 7.22 (2H, H₁, s), 4.63 (1H, H_e, s), 4.29 (2H, H_m, t, J=6.46 Hz), 3.99 (6H, H_a, t, J=6.42 Hz), 3.17 (2H, H_p, c, J=6.42 Hz), 1.85 - 1.66 (8H, H_{b,n}, m), 1.66-1.53 (2H, H_o, m), 1.52 - 1.44 (6H, H_c, m), 1.43-1.39 (9H, H_f, m), 1.33-1.20 (48H, H_{d-k}, m), 0.85 (9H, H_i, t, J = 6.40 Hz). ¹³C-NMR (75 MHz, CDCl₃) δ (ppm): 166.47, 156.03, 152.89, 142.51, 124.91, 108.09, 79.17, 73.54, 69.26, 64.64, 63.01, 40.31, 32.00, 30.41, 29.80, 29.78, 29.74, 29.72, 29.65, 29.49, 29.45, 29.41, 28.46, 26.24, 26.18, 26.15, 25.86, 22.73, 14.14. FT-IR: 3383.72, 2921.85, 2852.79, 1715.68, 1586.30, 1500.29, 1465.65, 1429.22, 1388.70, 1365.26, 1332.38, 1246.80, 1214.00, 1171.98, 1111.97, 1034.94, 864.31, 764.47, 721.39 cm⁻¹. HRMS (MALDI-TOF) m/z: calculated for C₅₂H₉₇NO₇: 845.71, found: 845.7181 [M]⁺.

8.4 (n = 4): (45%). ¹H-RMN (300 MHz, CDCl₃, 298K) δ (ppm): 7.23 (2H, H₁, s), 4.55 (1H, H_e, br), 4.29 (2H, H_m, t, J = 7.08 Hz), 4.00 (6H, H_a, t, J = 6.49 Hz), 3.13 (2H, H_a, m), 1.78 (8H, H_{b,n}, m), 1.60 - 1.45 (4H, H_{o,p}, m), 1.42 (9H, H_f, s), 1.38 - 1.15 (48H, H_{d-k}, br), 0.88 (9H, H_i, t, J = 6.36 Hz). ¹³C-RMN (75 MHz, CDCl₃, 298K) δ (ppm): 166.91, 156.42, 153.11, 142.43, 125.01, 108.54, 79.25, 73.63, 96.42, 64.86, 40.63, 32.12, 30.54, 29.90, 29.82, 29.80, 29.76, 29.74, 29.67, 29.50, 29.49, 29.47, 29.42, 28.59, 28.50, 23.41, 22.82, 14.22. FT-IR: 524.68, 575.14, 721.27, 765.11, 865.03, 1004.20, 1040.09, 1114.29, 1173.57, 1214.67, 1244.69, 1333.68, 1365.34, 1389.02, 1429.58, 1465.99, 1500.28, 1586.64, 1716.79, 2853.22, 2922.46, 3402.81. HRMS (MALDI-TOF) m/z: calculated for C₅₃H₉₇NO₇: 859.7265, found: 859.8257 [M]⁺.

Synthesis of aminoesters 9. General procedure.

Trifluoroacetic acid is added dropwise over a solution of **8** (515 mg, 0.61 mmol) in CH₂Cl₂ (10 mL). After stirring 2h at room temperature, the crude is washed with H₂O. The organic layer is then dried over MgSO₄, filtered and dried in vacuo, obtaining product **9** as a pale brown solid. The product thus obtained is utilized in the next synthetic step without any further purification.



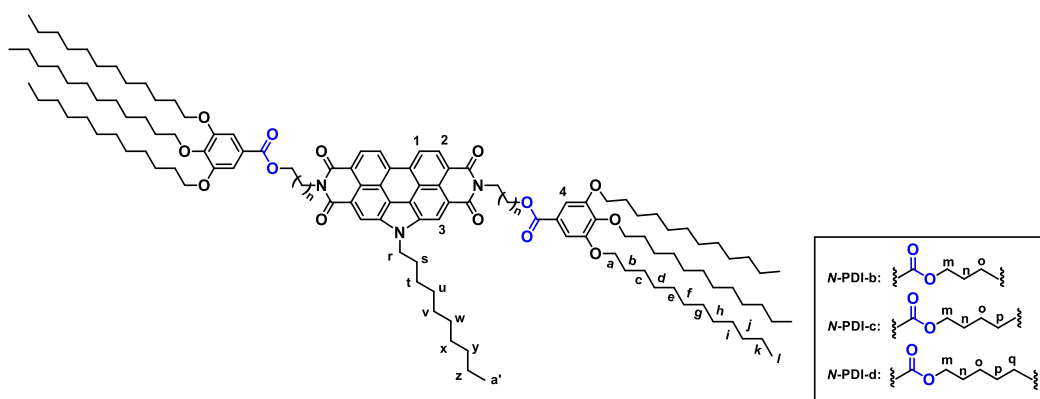
9.2 (n = 2): (58%). ¹H-RMN (300 MHz, CDCl₃, 298 K) δ(ppm): 7.20 (s, 2H, H₁), 4.44 (t, 2H, H_m, J = 5.85 Hz), 4.04 - 3.93 (m, 8H, H_{a+n}), 3.18 (t, 2H, H_r, J = 6.32 Hz), 2.35-2.21 (m, 2H, H_o), 1.86-1.65 (m, 8H, H_b), 1.53 - 1.18 (m, 54H, H_{c-k}), 0.88-0.84 (m, 9H, H_i). ¹³C-RMN (75 MHz, CDCl₃) δ (ppm): 166.9, 153.1, 143.0, 124.0, 108.3, 77.6, 77.2, 76.7, 73.7, 69.4, 61.5, 32.1, 30.6, 29.9, 29.5, 26.3, 22.8, 14.2. FT-IR: 2920.37, 2852.02, 1712.10, 1587.80, 1532.63, 1500.12, 1466.83, 1430.60, 1384.07, 1335.48, 1214.93, 1116.27, 1061.97, 1007.67, 862.90, 759.20, 722.23, 577.23, 544.32, 513.50 cm⁻¹. HRMS (MALDI-TOF) m/z: calculated for C₄₆H₈₅NO₅: 731.6165, found: 732.6506 [M]⁺.

9.3 (n = 3) (78%). ¹H-NMR (300 MHz, CDCl₃, 298 K) δ (ppm): 8.29 (2H, H_r, s), 7.21 (2H, H₁, s), 4.31 (2H, H_m, s), 3.99 (6H, H_a, t, J=6.42 Hz), 3.07 (2H, H_p, s), 1.94 - 1.85 (4H, H_{n,o}, m), 1.85 - 1.73 (6H, H_b, m), 1.49-1.42 (6H, H_c, m), 1.33 - 1.20 (48H, H_{d-k}, m), 0.85 (9H, H_i, t, J = 6.34 Hz). ¹³C-NMR (75 MHz, CDCl₃) δ (ppm): 166.55, 152.98, 142.71, 124.57, 108.17, 73.62, 69.35, 63.83, 39.63, 32.04, 30.47, 29.86, 29.83, 29.77, 29.71, 29.57, 29.48, 26.25, 26.19, 25.97, 24.34, 22.81, 14.22. FT-IR: 3448.37, 2953.98, 2918.16, 2849.92, 1705.80, 1587.07, 1502.02, 1467.25, 11429.68, 1387.75, 1335.77, 1252.61, 1217.01, 1117.33, 1012.07, 763.43, 721.19 cm⁻¹. HRMS (MALDI-TOF) m/z: calculated for C₄₇H₈₇NO₅: 745.6689, found: 746.6628 [M+H]⁺.

9.4 (n = 4): (67%). ¹H-RMN (300 MHz, CDCl₃, 298K) δ (ppm): 7.21 (2H, H₁, s), 4.55 (1H, H_r, br), 4.30 (2H, H_m, t, J = 7.08 Hz), 3.99 (6H, H_a, t, J = 6.49 Hz), 3.02 (2H, H_q, m), 1.78 (6H, H_{n-p}, m), 1.60 – 1.45 (6H, H_b, m), 1.42, 1.38 – 1.15 (48H, H_{d-k}, br), 0.88 (9H, H_l, t, J = 6.36 Hz). ¹³C-RMN (75 MHz, CDCl₃, 298K) δ (ppm): 166.92, 153.15, 142.48, 125.08, 108.51, 79.28, 73.65, 96.48, 64.87, 40.63, 32.12, 30.54, 29.90, 29.82, 29.80, 29.76, 29.74, 29.67, 29.50, 29.49, 29.42, 28.50, 23.41, 22.82, 14.21. FT-IR: 3448.47, 2953798, 2918.56, 2849.92, 1705.80, 1587.07, 1502.02, 1467.25, 11429.68, 1387.75, 1335.78, 1252.61, 1217.01, 1117.45, 1012.07, 763.43, 721.89 cm⁻¹. HRMS (MALDI-TOF) m/z: calculated for C₄₈H₈₉NO₅: 759.6741, found: 760.6838 [M+H]⁺.

Synthesis of N-annulated perylendiimides 2-4.

In a microwave vial, dihydride **14** (50 mg, 0.09 mmol), the corresponding aminoester **9** (2.2 eq), zinc acetate (1 eq) and imidazole (500 mg, 7.344 mmol) are added. After performing 3 Ar/vacuo cycles, the mixture is reacted under microwave radiation for 35 min (165 °C). After this time, the crude is extracted with CH₂Cl₂ and washed with H₂O, dried over MgSO₄ and dried in vacuo. The final NPDI is purified by column chromatography (silica gel, CH₂Cl₂), obtaining the final product as a waxy, red compound. This compound is redissolved in the minimum amount of CH₂Cl₂ and precipitated with methanol, yielding a red powder as a final product.



NPDI-2 (n = 2): (21%). ¹H-RMN (300 MHz, CDCl₃, 298 K) δ (ppm): 8.76 (s, 2H, H₃), 8.70 (d, 2H, H₂, J = 8.02 Hz), 8.65 (d, 2H, H₁, J = 8.3 Hz), 7.22 (s, 4H, H₄), 4.79 (t, 2H, H_r, J = 6.75 Hz), 4.52 (m, 8H, H_{m,o}), 3.93 – 3.80 (m, 12H, H_a), 2.41-2.30 (m, 4H, H_n), 2.19-2.07 (m, 2H, H_s), 1.75-1.60 (m, 12H, H_b), 1.40 – 1.19 (m, 124H, H_{b-j}, y H_{t-z}), 0.90-0.78 (m, 21H, H_{a,i}). ¹³C-RMN (75 MHz, CDCl₃) δ (ppm): 166.4, 165.0, 163.6, 152.8, 142.2, 134.5, 132.6, 125, 124.4, 123.6, 122.1, 121.4, 119.2, 118.7, 108.1, 77.5, 77.0, 76.6, 73.3, 69.1, 63.3, 32.0, 30.4, 29.7, 29.5, 29.2, 26.1, 22.7, 14.2. FT-IR: 721.46, 763.08, 804.29, 1122.40, 1219.54, 1335.16, 1398.71, 1443.07, 1467.44, 1601.82, 1662.37, 1693.20, 2851.43, 2920.23 cm⁻¹. HRMS (MALDI-TOF) m/z: calculated for C₁₂₆H₁₉₃N₃O₁₄: 1972.4584, found: 1972.446 [M]⁺.

NPDI-3 (n = 3): (50%). ¹H-NMR (300 MHz, CDCl₃, 298 K) δ (ppm): 8.71 (2H, H₁, s), 8.59 (4H, H_{2,3}, s), 7.26 (4H, H₄, s), 4.78 (2H, H_r, t, J = 6.75 Hz), 4.43 (8H, H_{m,p}, s), 4.00 (12H, H_a, t, J = 6.55 Hz), 2.19-2.06 (2H, H_s, m), 2.05-1.95 (8H, H_{n,o}, m), 1.86-1.61 (12 H, H_b, m), 1.51-1.15 (122 H, H_{c-k,t-z}, m), 0.92-0.77 (21H, H_{l,a'}, m). ¹³C-NMR (75 MHz, CDCl₃) δ (ppm): 166.55, 164.88, 163.64, 152.88, 142.42, 134.45, 132.26, 127.33, 125.03, 124.11, 123.53, 122.04, 121.40, 121.26, 118.98, 118.46, 108.13, 73.56, 69.27, 64.82, 40.55, 32.04, 32.02, 31.88, 31.68, 30.44, 29.84, 29.80, 29.74, 29.69, 29.53, 29.49, 29.46, 29.29, 27.28, 26.67, 26.21, 26.18, 25.11, 22.78, 22.70, 14.21, 14.15. FT-IR: 2955.33, 2921.66, 2852.06, 1691.98, 1660.89, 1601.09, 1466.34, 1431.77, 1379.32, 1360.13, 1333.44, 1310.63, 1255.33, 1218.96, 1120.43, 804.24, 761.94, 740.57, 721.52, 619.15 cm⁻¹. HRMS (MALDI-TOF) m/z: calculated for C₁₂₈H₁₉₇N₃O₁₄: 2000.4885, found: 2001.4770 [M+H]⁺.

NPDI-4 (n = 4): (45%). ¹H-RMN (300 MHz, CDCl₃, 298K) δ (ppm): 8.75 (2H, H₁, s), 8.62 (4H, H_{2,3}, m), 7.24 (4H, H₄, s), 4.79 (2H, H_r, t, J = 7.73 Hz), 4.36 (8H, H_{m,q}, t, J = 6.87 Hz), 3.98 (12H, H_a, t, J = 6.50 Hz), 2.13 (2H, H_s, m), 1.93 (12H, H_{n-p}, m), 1.83 – 1.58 (12H, H_b, m), 1.52 – 1.14 (122H, H_{c-k,t-z}, m), 0.85 (21H, H_{l,a'}, m). ¹³C-RMN (75 MHz, CDCl₃, 298K) δ (ppm): 166.63, 164.98, 163.74, 125.92, 142.43, 134.57, 127.42, 125.15, 124.19, 123.66, 122.12, 121.48, 121.40, 119.13, 118.56, 108.13, 73.60, 69.30, 65.08, 32.08, 32.06, 31.91, 30.48, 29.87, 29.84, 29.78, 29.73, 29.56, 29.53, 29.50, 29.32, 28.71, 28.11, 27.32, 26.24, 26.21, 23.79, 22.84, 22.82, 22.73, 14.24, 14.19. FT-IR: 721.46, 763.08, 804.29, 1122.40, 1219.54, 1335.16, 1398.71, 1443.07, 1467.44, 1601.82, 1662.37, 1693.20, 2851.43, 2920.23 cm⁻¹. HRMS (MALDI-TOF) m/z: calculated for C₁₃₀H₂₀₁N₃O₁₄: 2028.5109, found: 2029.5068 [M+H]⁺.

3. NMR spectra

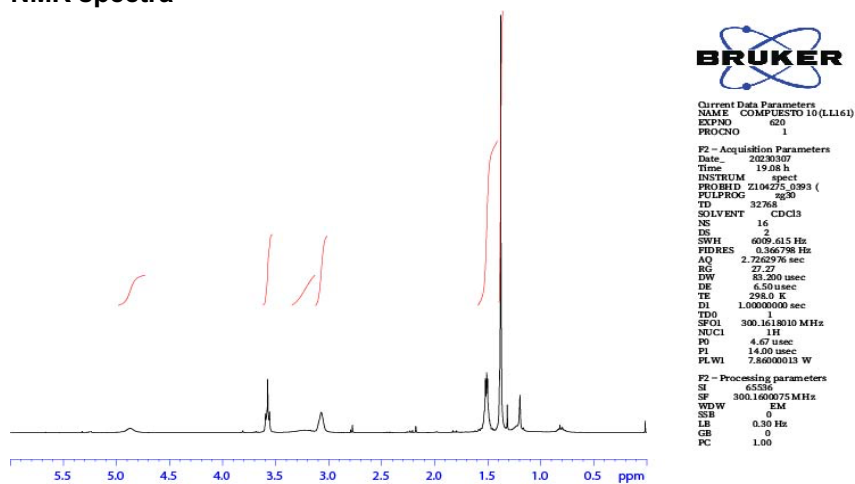


Figure 1: ^1H NMR spectra (CDCl_3 , 300 MHz, 298 K) of compound 7.3.

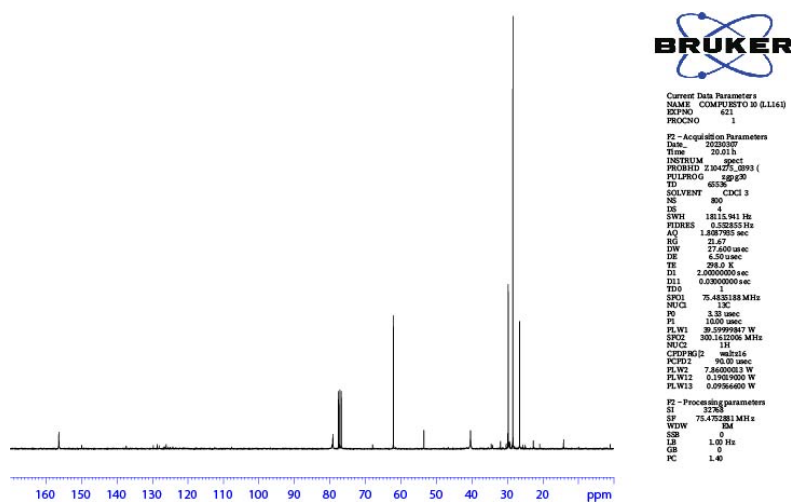


Figure 2: ^{13}C NMR spectra (CDCl_3 , 75 MHz, 298 K) of compound 7.3.

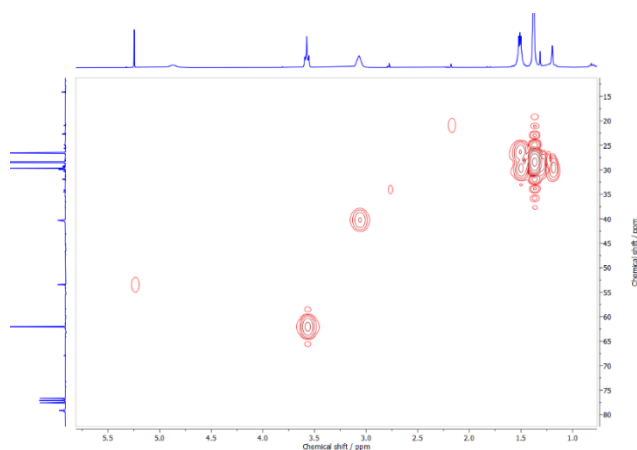
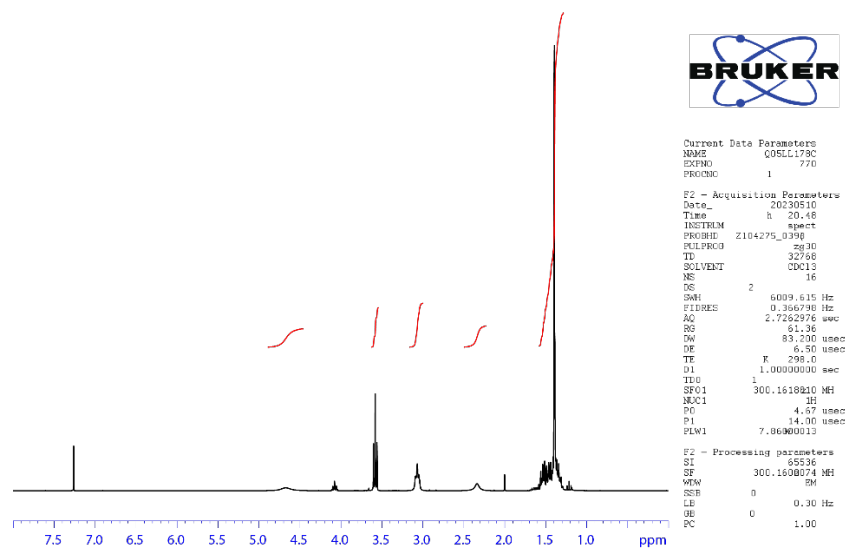
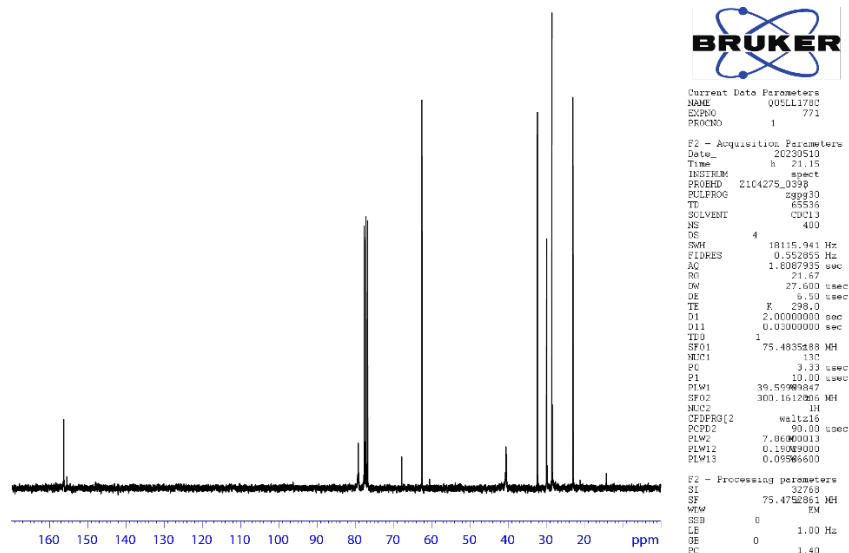


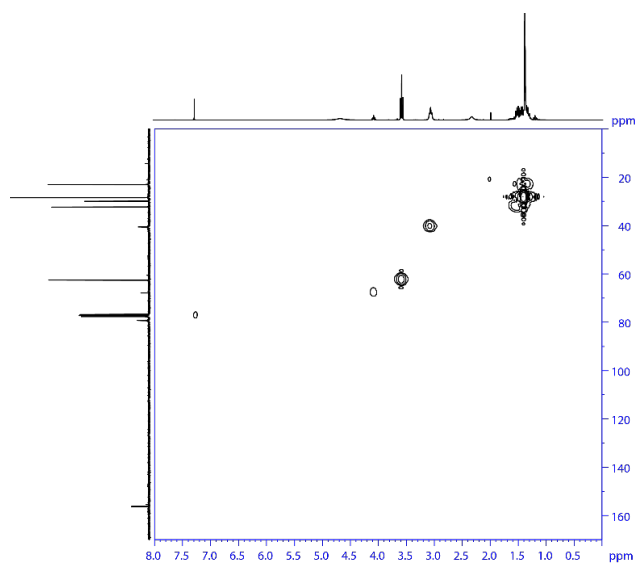
Figure 3: ^1H , ^{13}C HMQC spectra (CDCl_3 , 298 K) of compound 7.3.



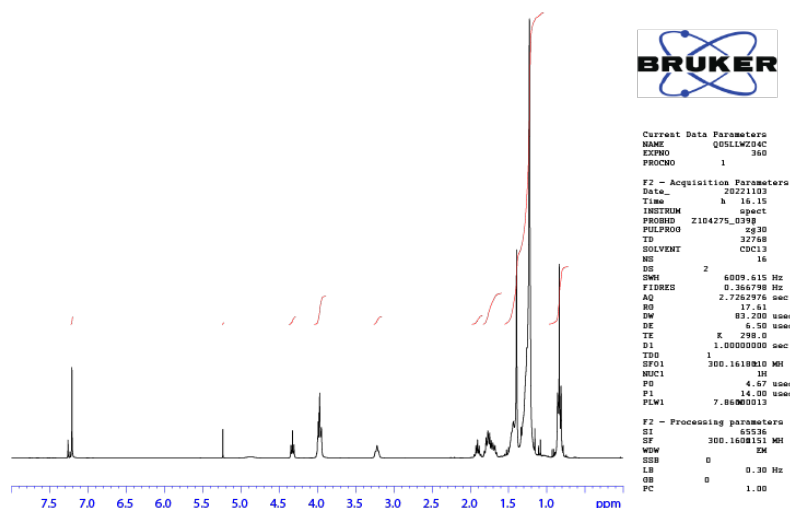
^1H NMR spectra (CDCl_3 , 300 MHz, 298 K) of compound **7.4**.



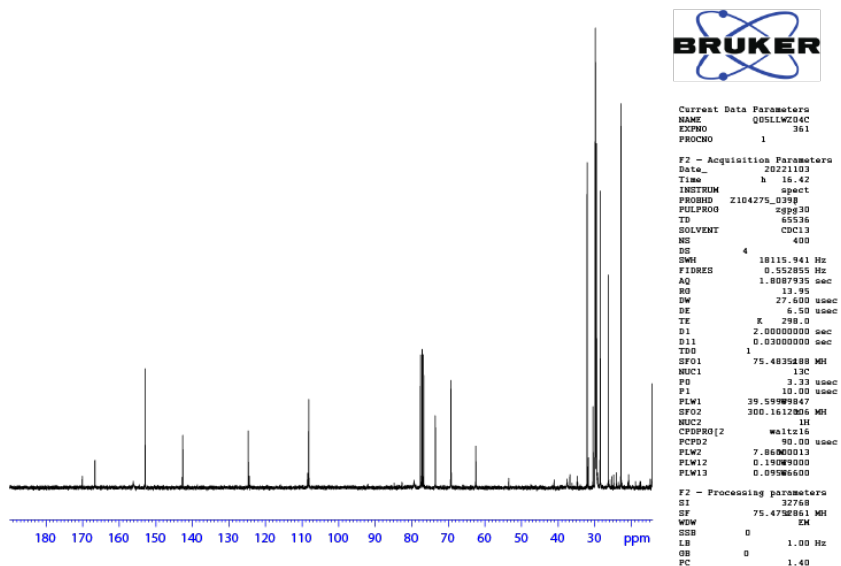
^{13}C NMR spectra (CDCl_3 , 75 MHz, 298 K) of compound **7.4**.



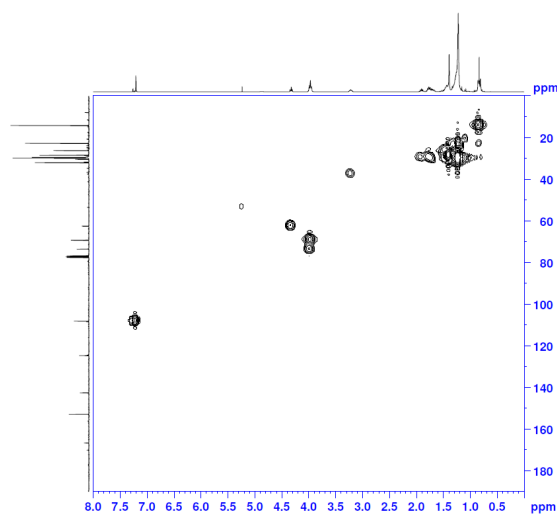
^1H , ^{13}C HMQC spectra (CDCl_3 , 298 K) of compound **7.4**.



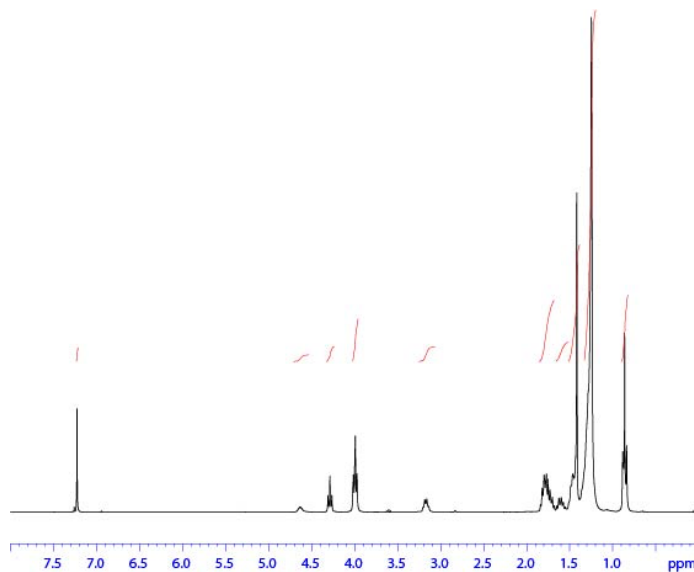
^1H NMR spectra (CDCl_3 , 300 MHz, 298 K) of compound **8.2**.



^{13}C NMR spectra (CDCl_3 , 300 MHz, 298 K) of compound **8.2**.



^1H , ^{13}C HMQC spectra (CDCl_3 , 298K) of compound **8.2**.

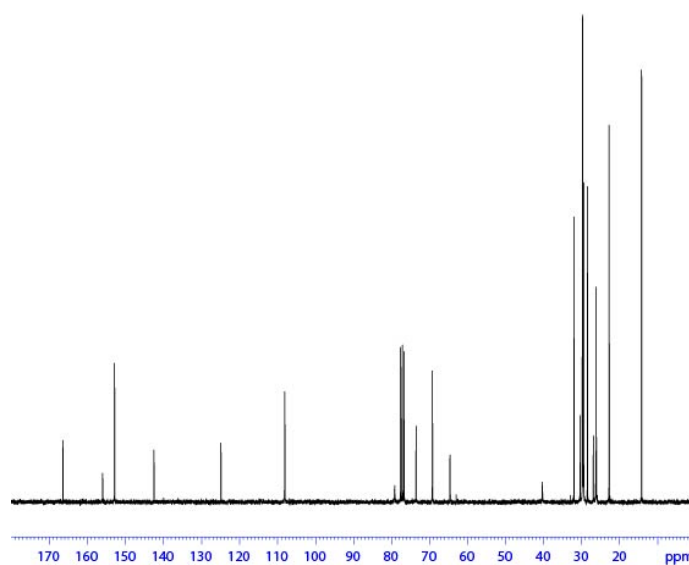


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¹H NMR spectra (CDCl₃, 300 MHz, 298 K) of compound **8.3**.

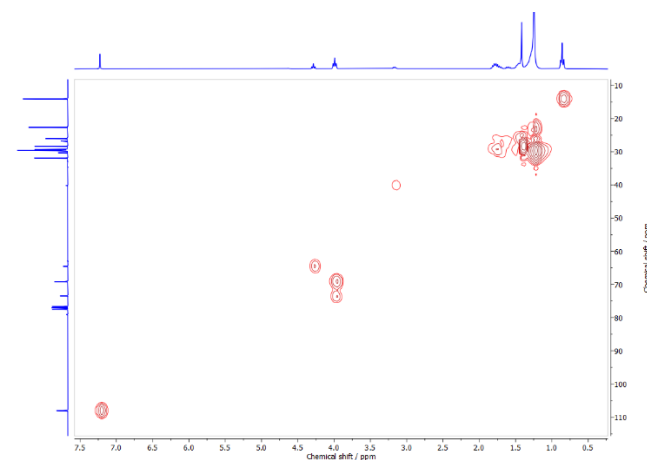


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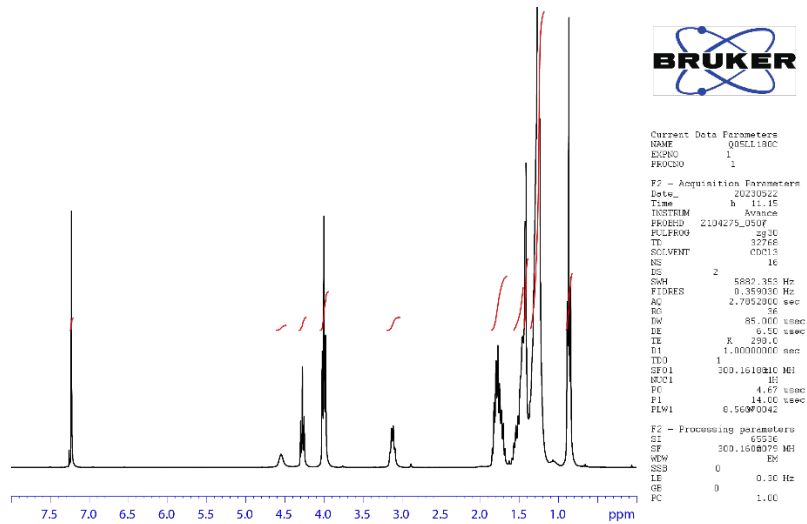
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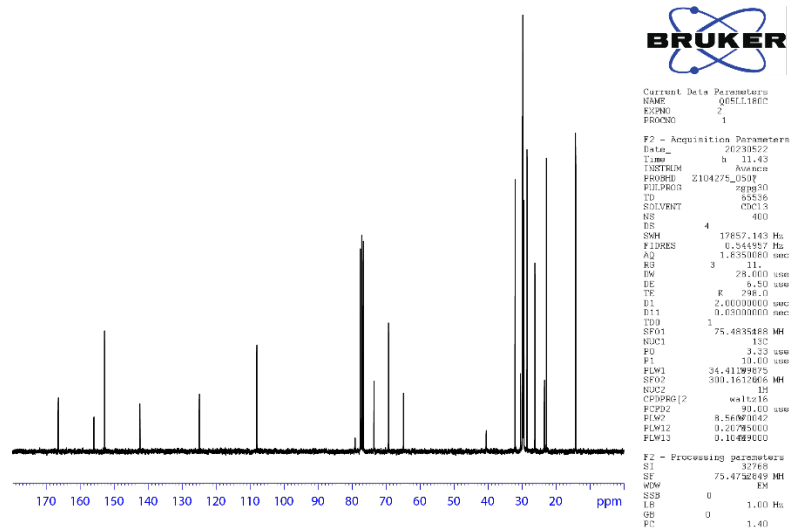
¹³C NMR spectra (CDCl₃, 75 MHz, 298 K) of compound **8.3**.



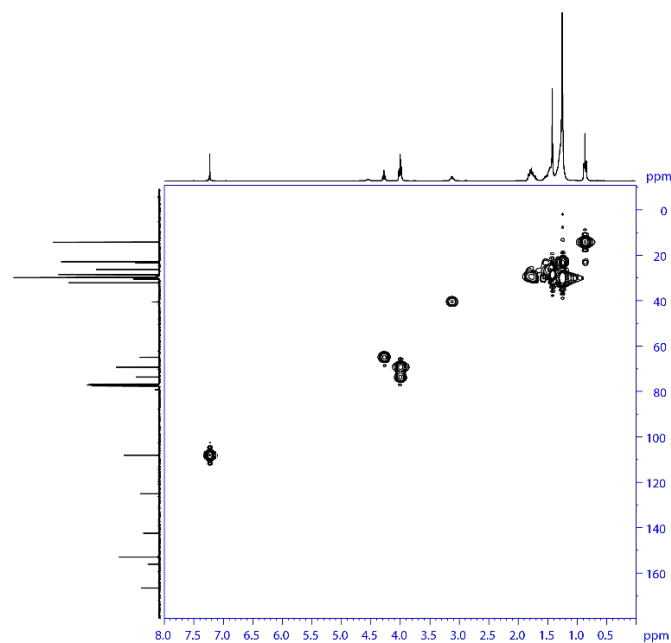
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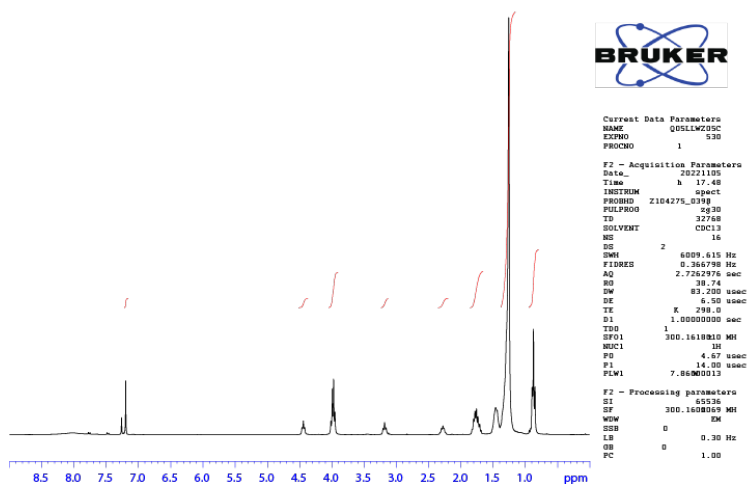
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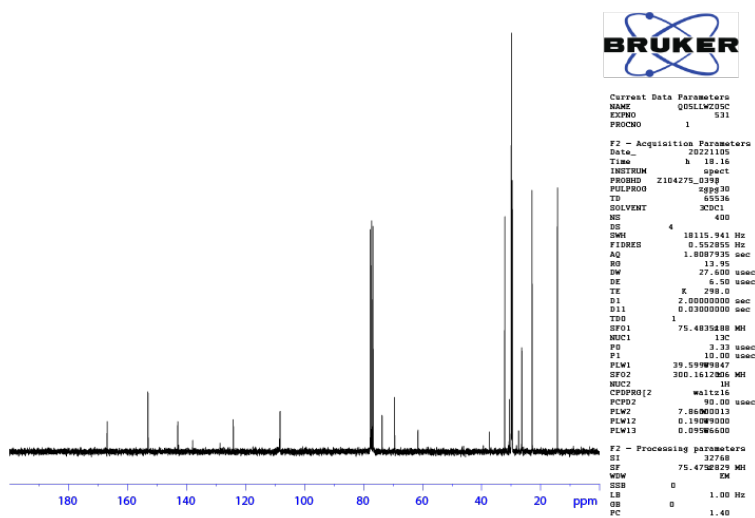
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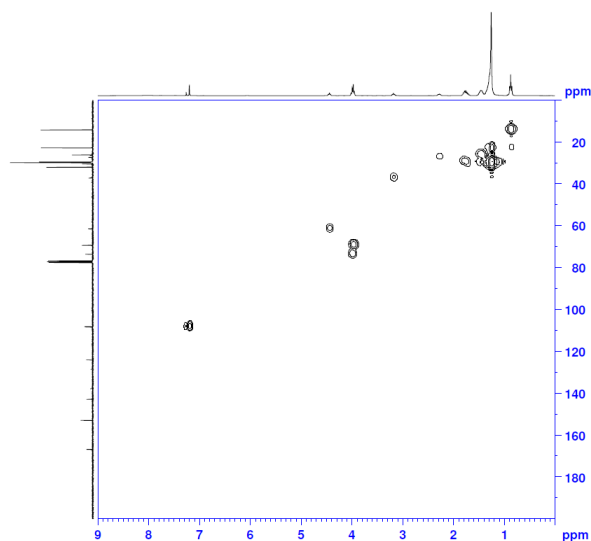
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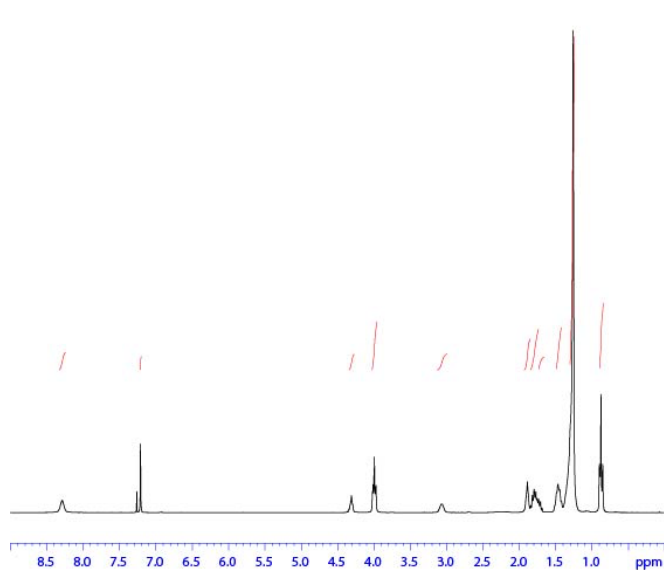
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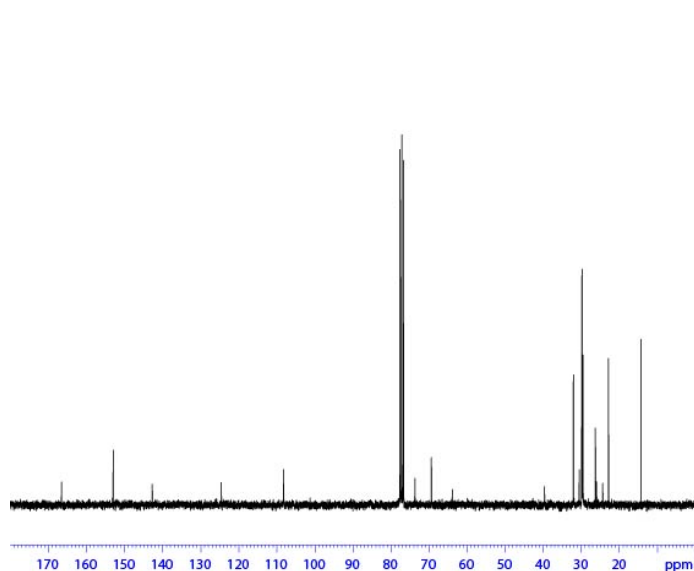
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¹H-NMR spectra (CDCl₃, 300 MHz, 298 K) of compound **9.3**.



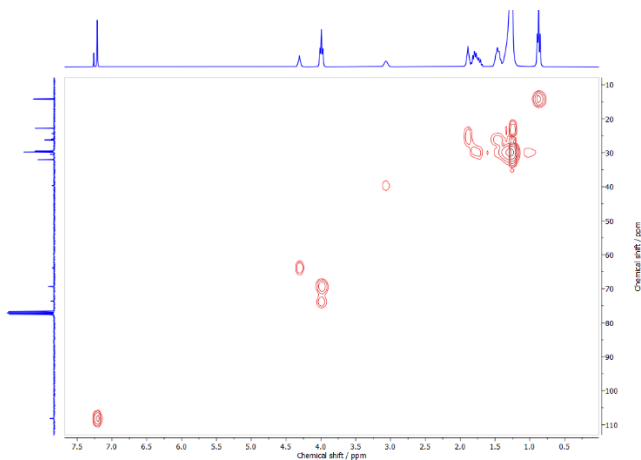
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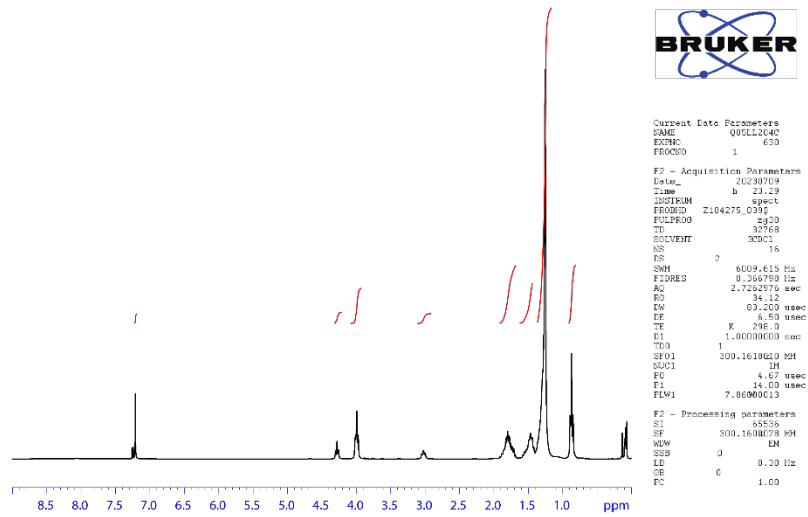
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NUC2      1H
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PLW13    0.10419000 W

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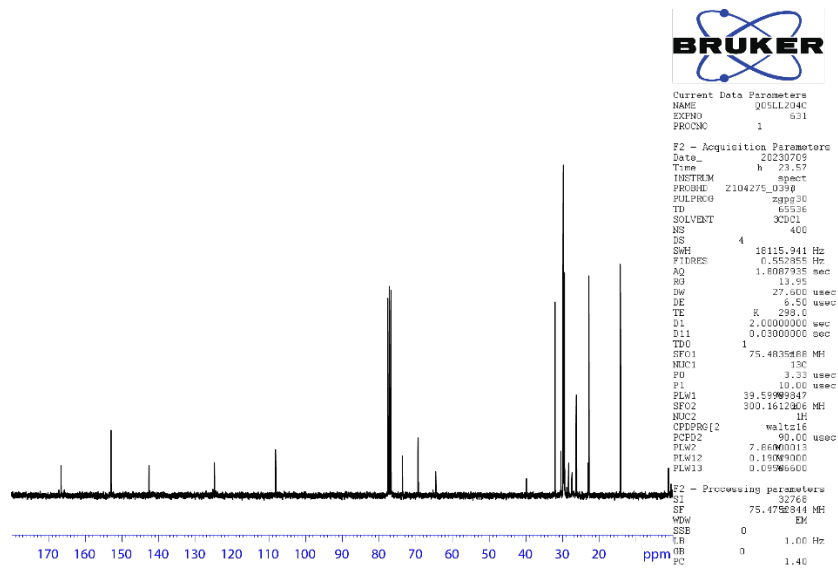
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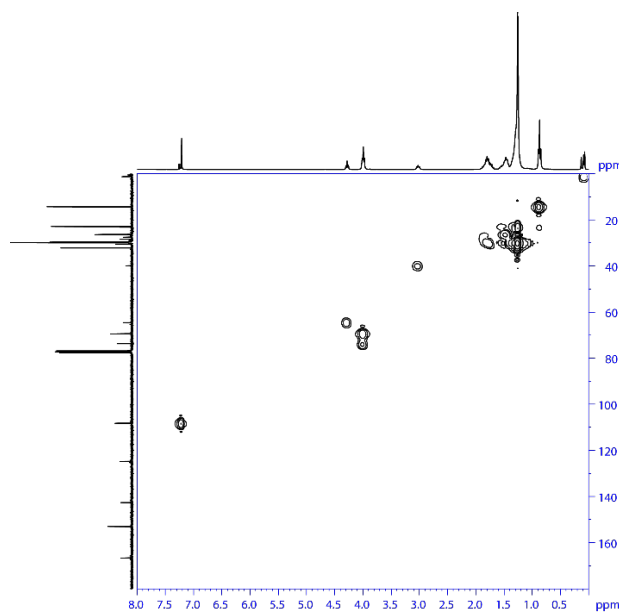
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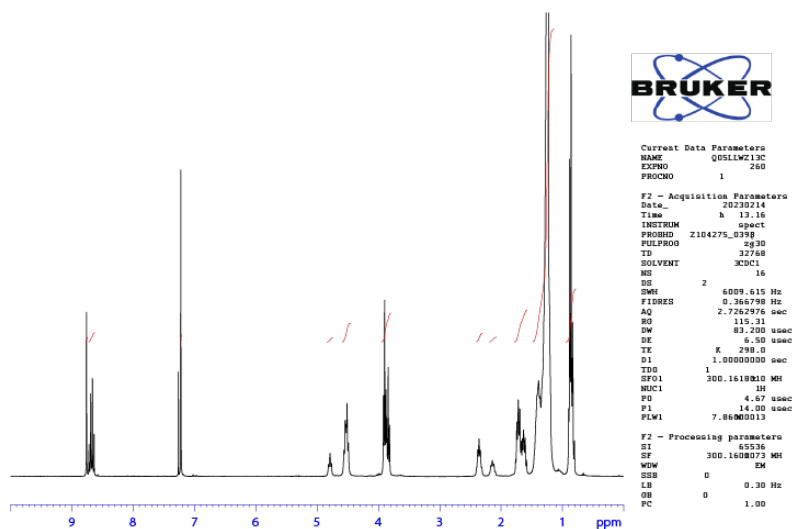
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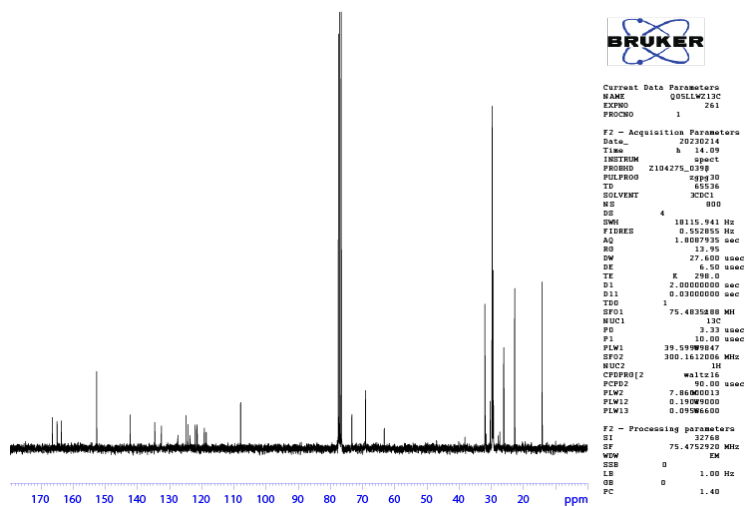
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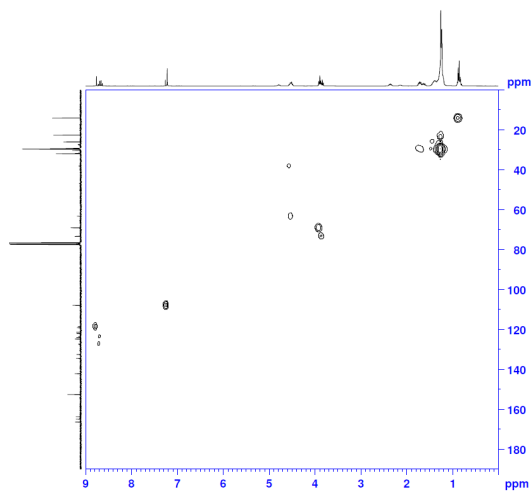
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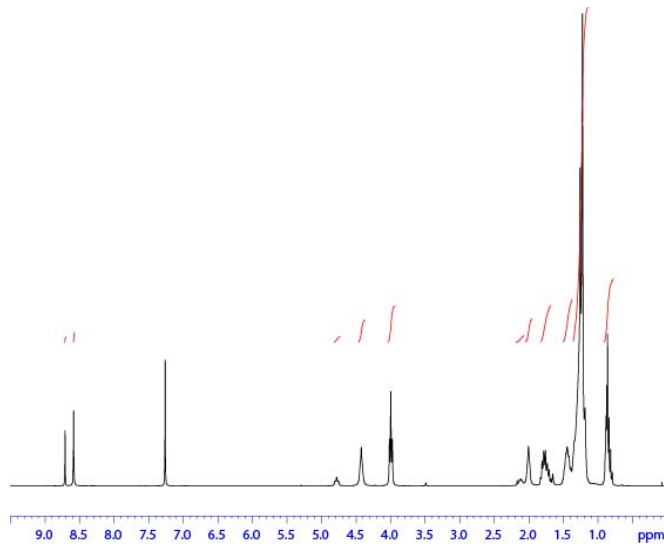
¹H NMR spectra (CDCl₃, 300 MHz, 298 K) of NPDI 2.



¹³C NMR spectra (CDCl₃, 300 MHz, 298 K) of NPDI 2.

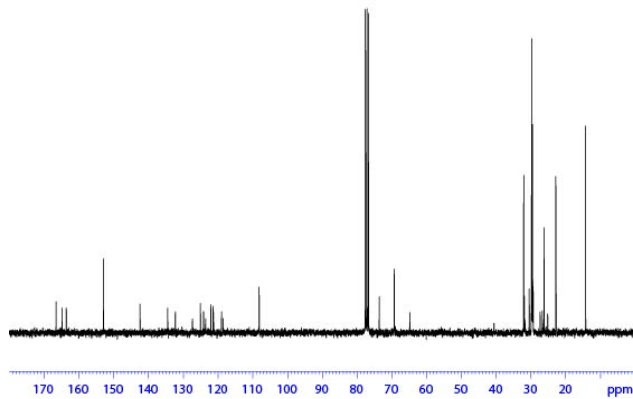


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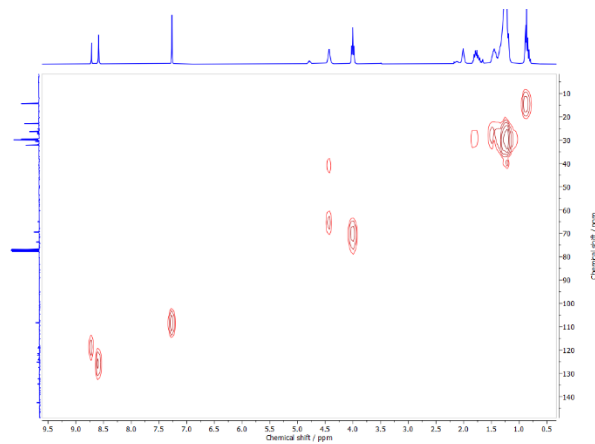
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 TD0 1
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¹H NMR spectra (CDCl₃, 300 MHz, 298 K) of NPDI 3.

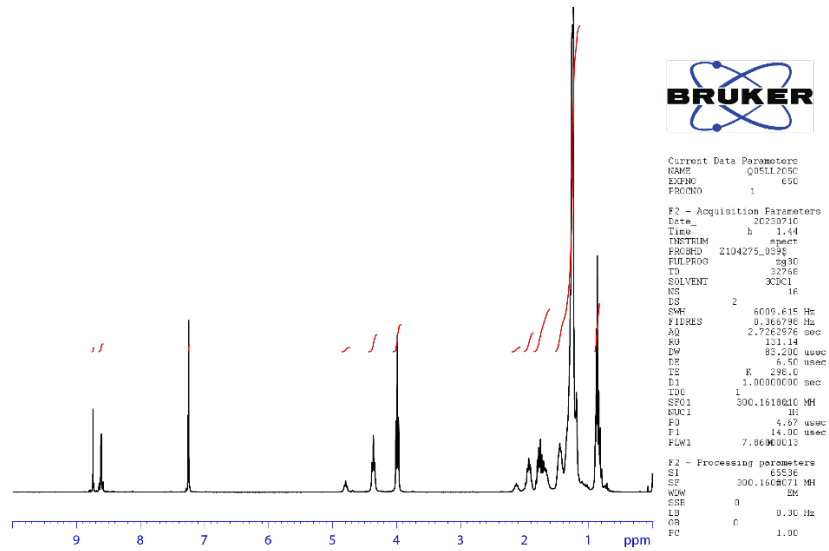


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 NUC2 1H
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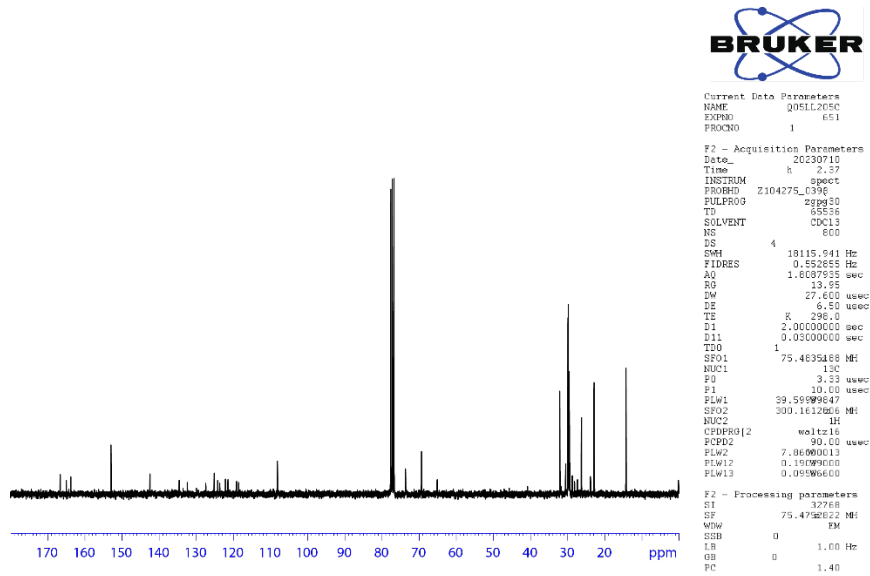
¹³C NMR spectra (CDCl₃, 75 MHz, 298 K) of NPDI 3.



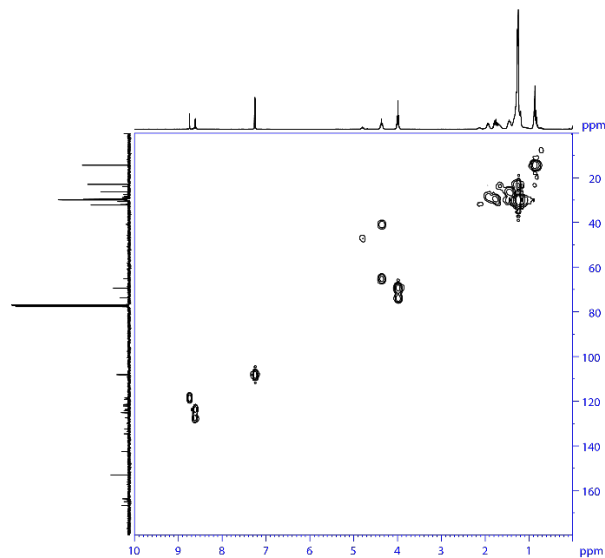
¹H, ¹³C HMQC spectra (CDCl₃, 298 K) of NPDI 3.



¹H NMR spectra (CDCl₃, 300 MHz, 298 K) of NPDI 4.



¹³C NMR spectra (CDCl₃, 75 MHz, 298 K) of NPDI 4.



¹H, ¹³C HMQC spectra (CDCl₃, 298 K) of NPDI 4.

4. Supplementary Figures

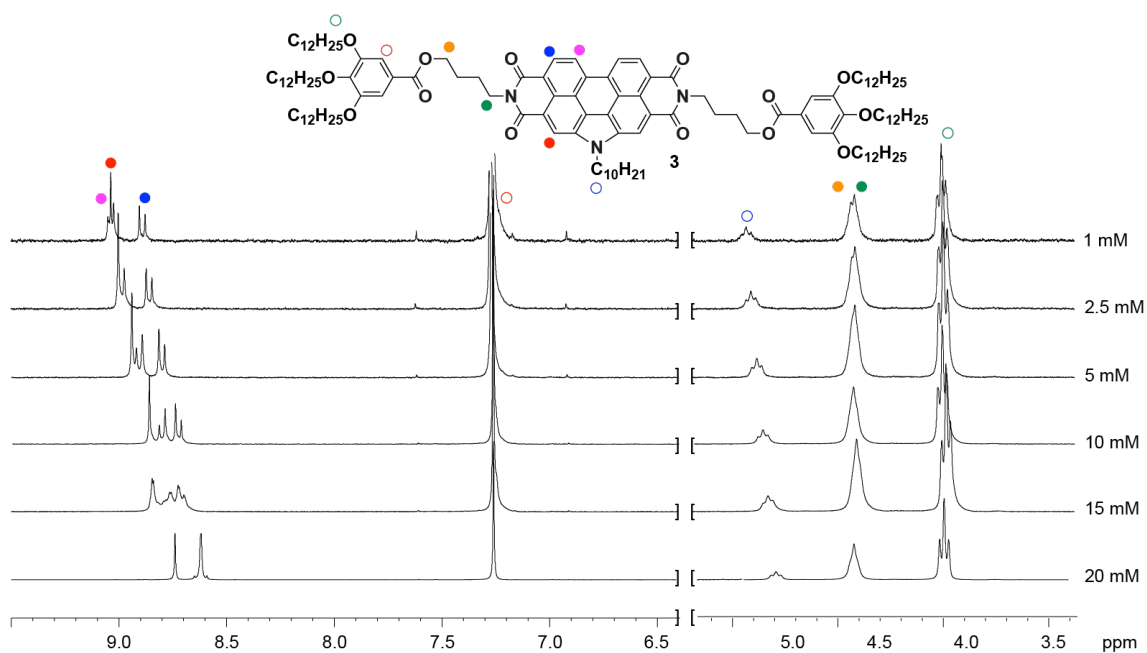


Figure S1. Partial ^1H NMR spectra of **3** recorded at different concentrations showing the aromatic and some of the aliphatic protons (CDCl_3 , 298 K, 300 MHz)

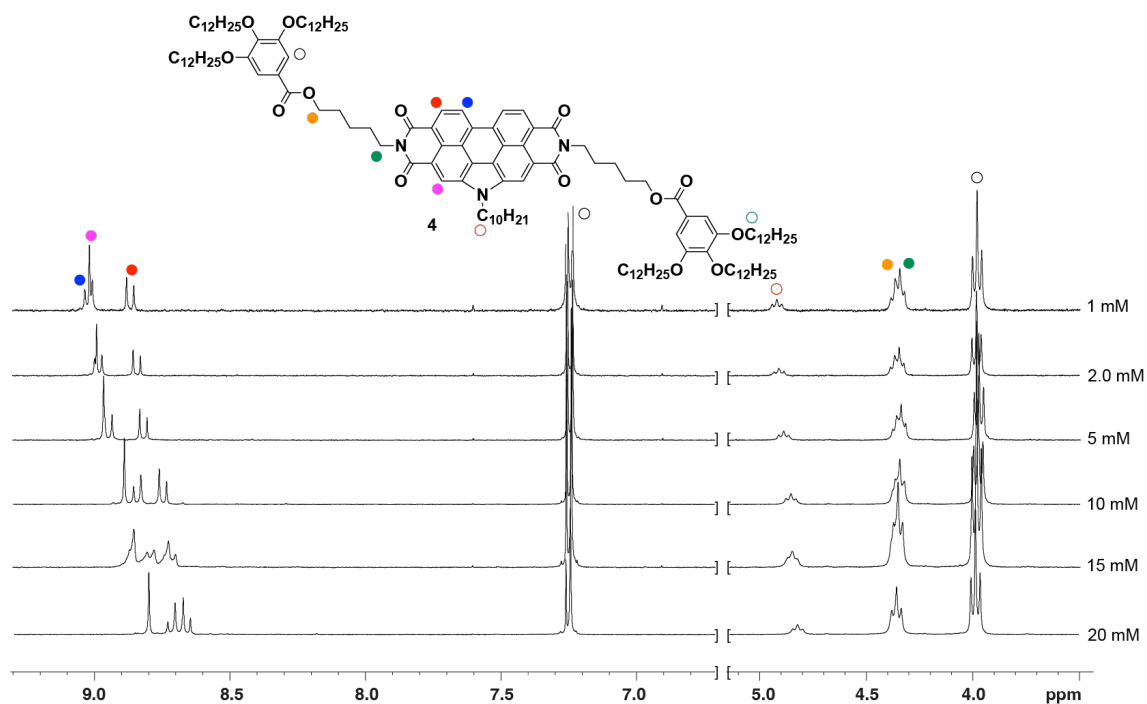


Figure S2. Partial ^1H NMR spectra of **4** recorded at different concentrations showing the aromatic and some of the aliphatic protons (CDCl_3 , 298 K, 300 MHz).

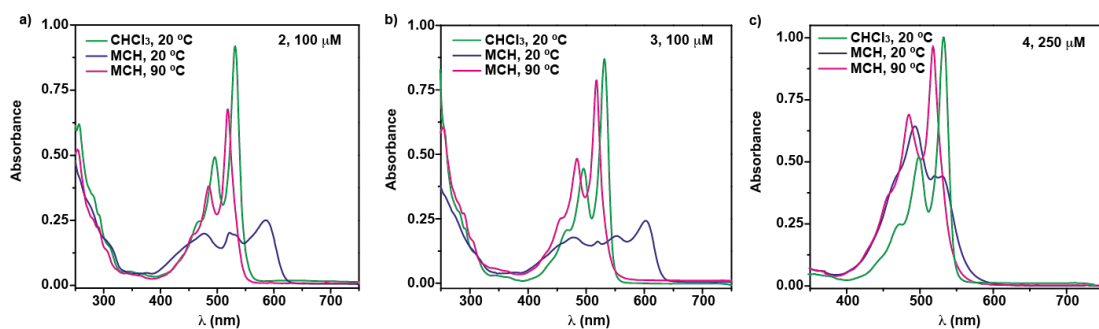


Figure S3. UV-Vis spectra of NPDIs **2** (a), **3** (b) and **4** (c) in different solvents and temperatures (pathlength: 1mm).

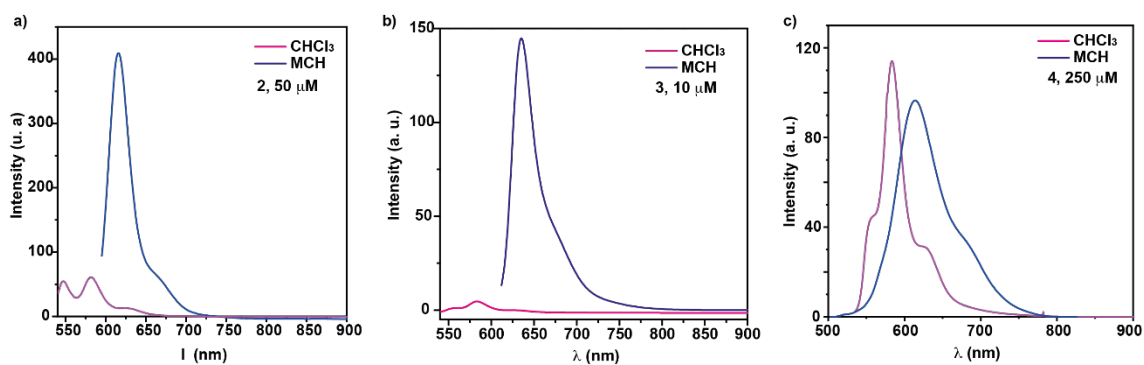


Figure S4. Emission spectra of NPDIs **2** (a), **3** (b) and **4** (c) in different solvents; ($\lambda_{\text{ex}} = 531$ nm for CHCl₃, $\lambda_{\text{ex}} = 602$ nm for **2** and **3** in MCH, $\lambda_{\text{ex}} = 596$ nm for **4** in MCH).

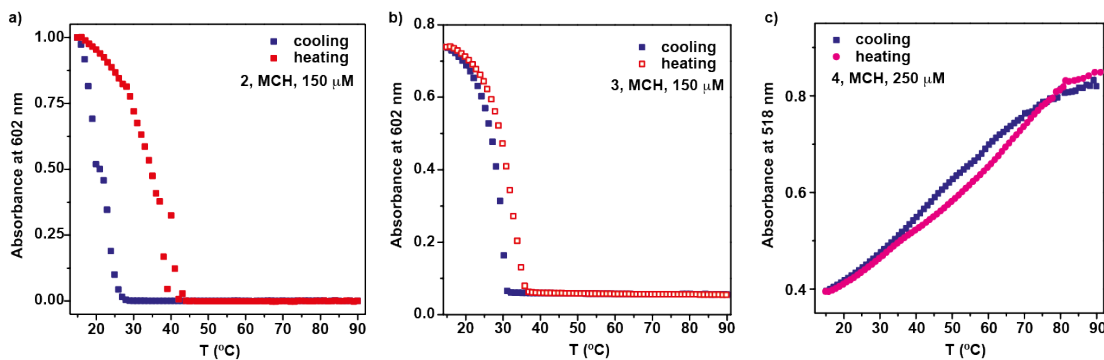


Figure S5. Heating and cooling curves for NPDIs **2** (a), **3** (b) and **4** (c) in MCH (1 K min⁻¹, pathlength: 1mm).

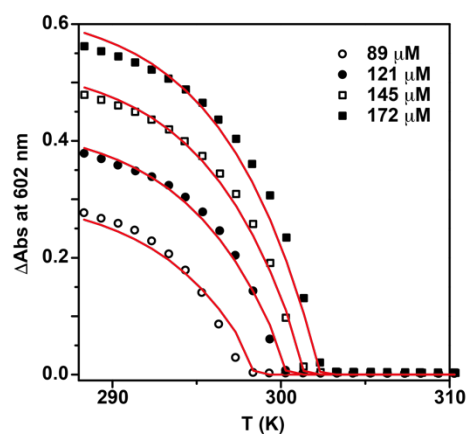


Figure S6. Zoomed plot of the variation of absorbance at $\lambda = 602$ nm versus temperature for **3** at a cooling rate of 1 Kmin⁻¹. The red traces depict the fitting of the equilibrium (EQ) model to the experimental curves.

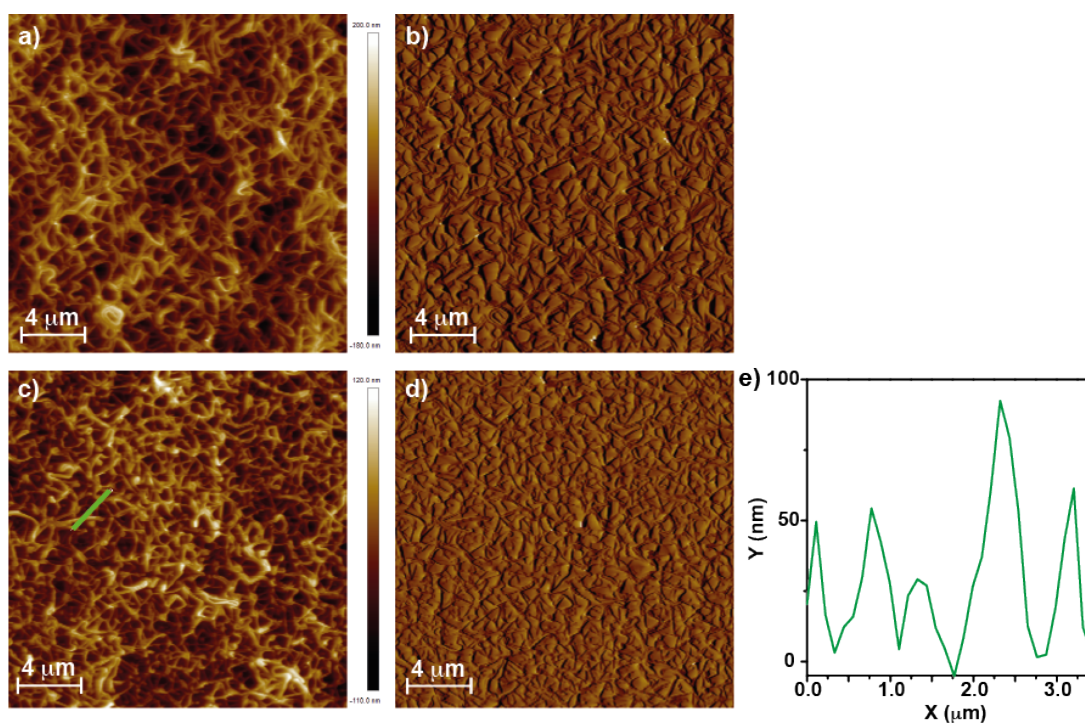


Figure S7. Height (a, c) and phase (b, d) AFM images of the supramolecular polymers formed upon self-assembly of **2** in MCH ($c_T = 150$ μ M, spin-coated, HOPG as surface). Panel (e) shows the height profile along the green line in panel (c).

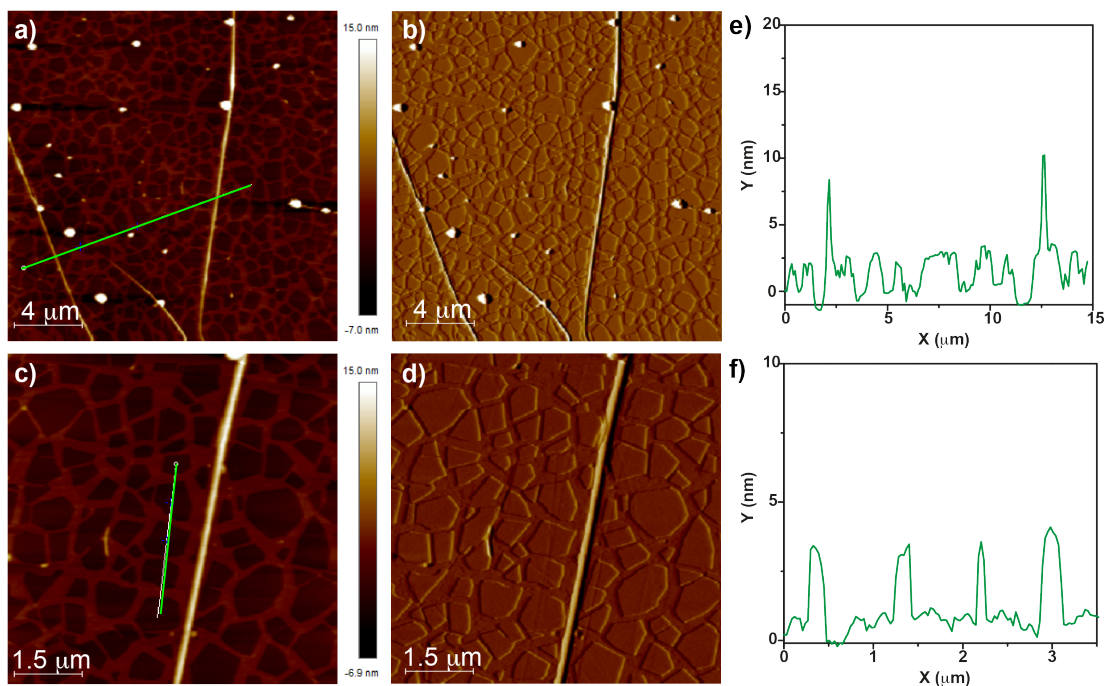


Figure S8. Height (a, c) and phase (b, d) AFM images of the supramolecular polymers formed upon self-assembly of **3** in MCH ($c_T = 150 \mu\text{M}$, HOPG as surface). Panels (e) and (f) show the height profile along the green lines in panels (a) and (c).

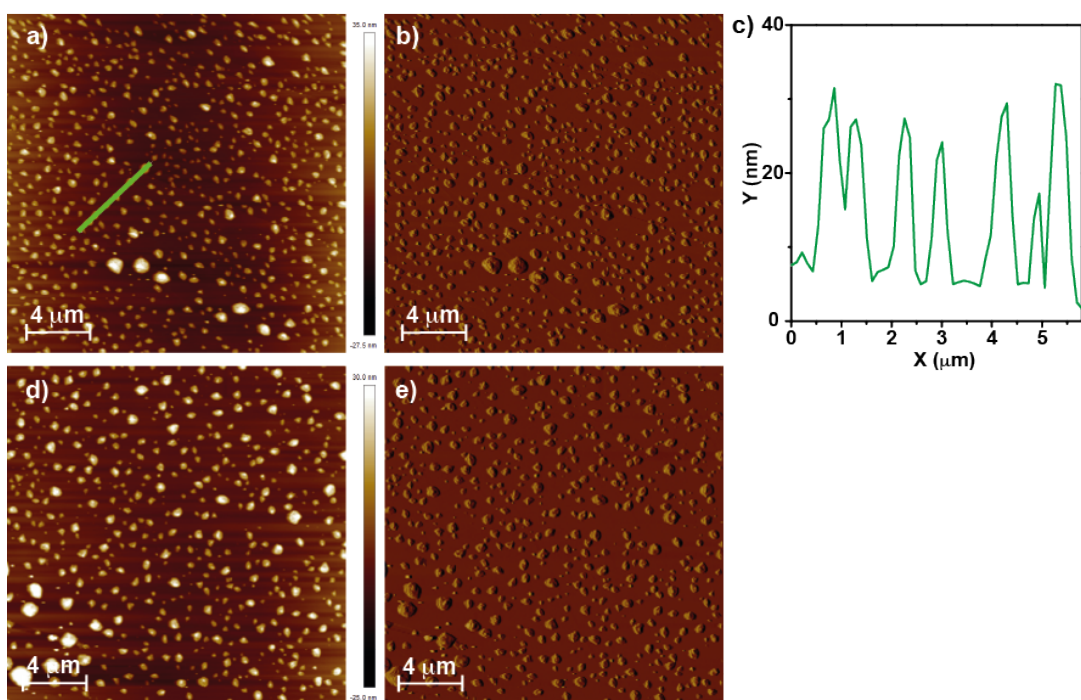


Figure S9. Height (a, d) and phase (b, e) AFM images of the supramolecular polymers formed upon self-assembly of **4** in MCH ($c_T = 200 \mu\text{M}$, spin coated, HOPG as surface). Panel (c) shows the height profile along the green line in panel (a).

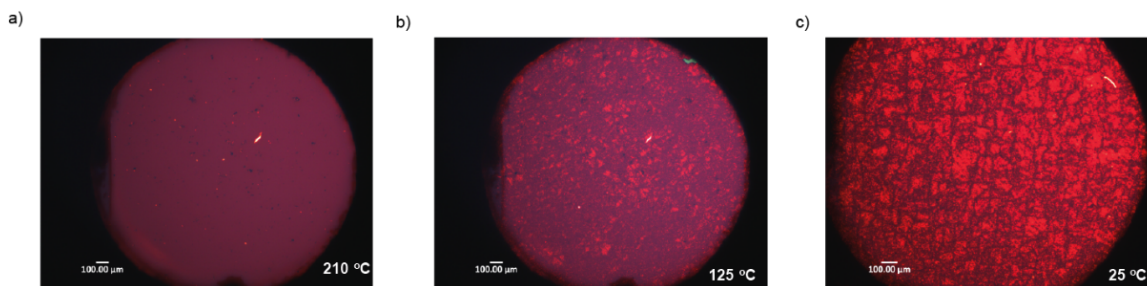


Figure S10. POM images of NPDI 1 at a) 210 °C, b) 125 °C and c) 25 °C obtained upon cooling from the isotropic melt (5 K min⁻¹).

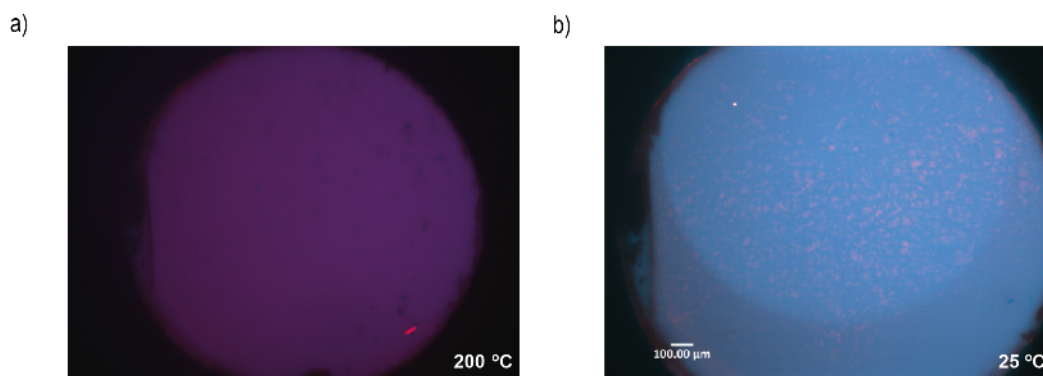


Figure S11. POM images of NPDI 2 at a) 200 °C and b) 25 °C (5 K min⁻¹).

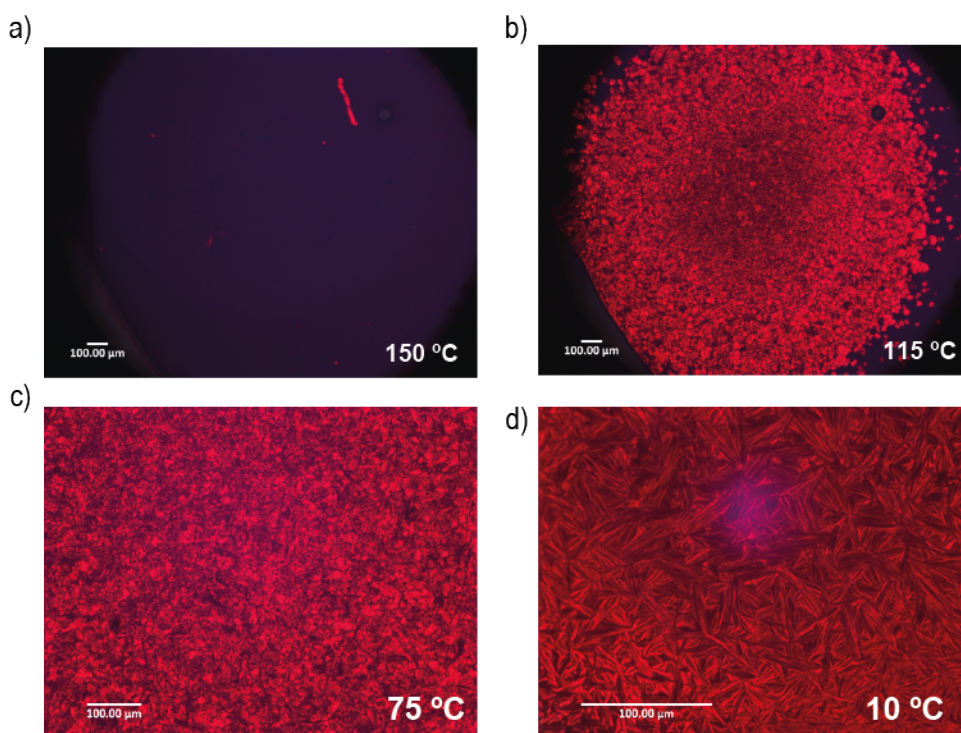


Figure S12. POM images of NPDI 3 at a) 150 °C, b) 115 °C, c) 75 °C and d) 10 °C obtained upon cooling from the isotropic melt (5 K min⁻¹).

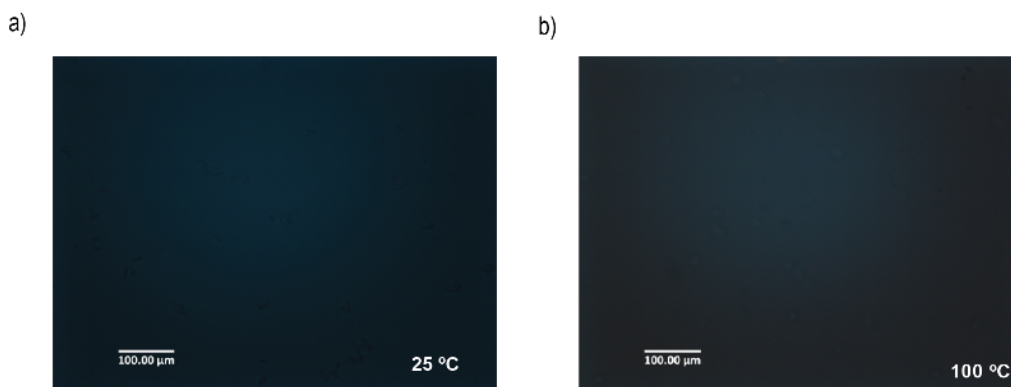


Figure S13. POM images of NPDI 4 at a) 25 °C and b) 105 °C (5 K min⁻¹).

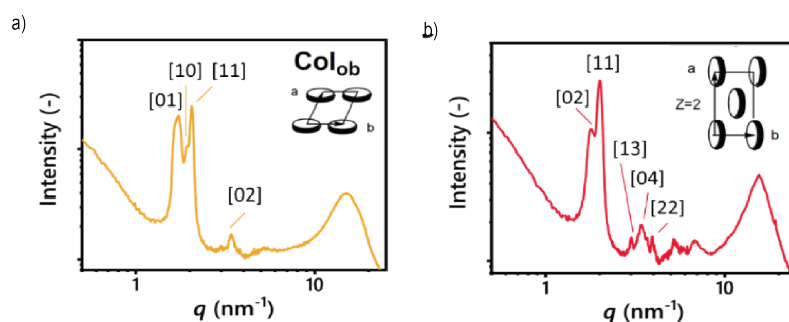


Figure S14. 1D transmission scattering profiles of NPDI 3 showing the morphologies at a) 75 °C and b) -10 °C.

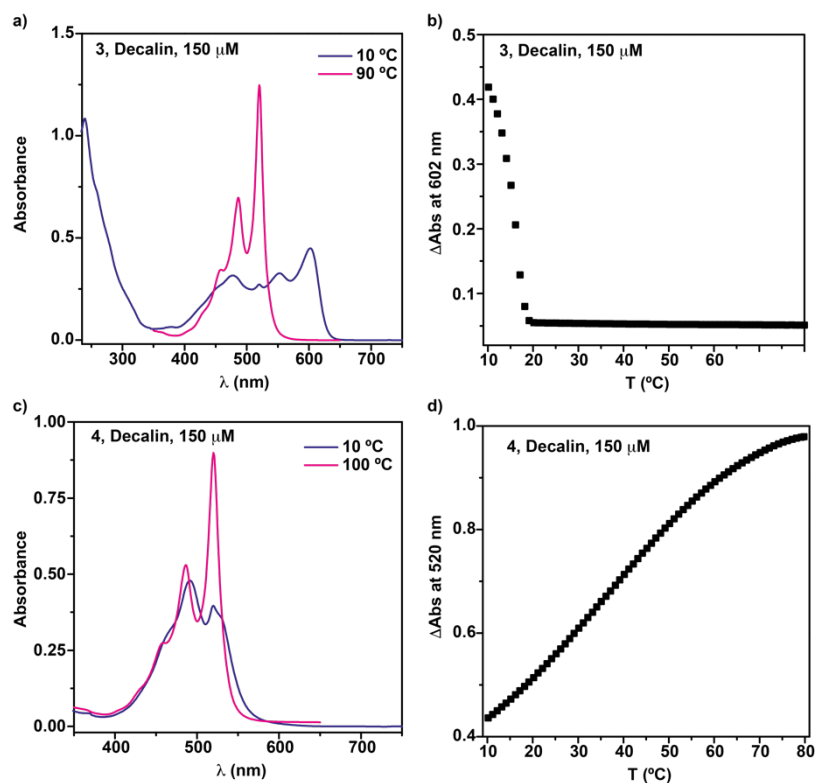


Figure SM1. (a and c) UV-Vis spectra at different temperatures of NPDI 3 (a) and 4 (c) in decalin as solvent; (b and d) cooling curves of NPDI 3 (b) and 4 (d) in decalin at a scan rate of 1K/min ($c_T = 150 \mu\text{M}$).

Table S1. Summary of data obtained from SAXS studies.

Name	# C-atoms in spacer (-)	Observed phase	Lattice parameters
Even			
1	2	LC (120 °C) = Col _{obl} (P2m)	a = 3.4 nm b = 3.9 nm γ = 86°
		C = Col _h	a = 3.2 nm
3	4	LC (115 °C) = Col _{obl} (P2m)	a = 3.5 nm b = 3.9 nm γ = 69°
		LC (75 °C) = Col _{obl} (P2m)	a = 3.5 nm b = 3.8 nm γ = 68°
		C = Col _{obl} (C2/m)	a = 3.5 nm b = 7.1 nm γ = 82°
Odd			
2	3	Col _h	a = 3.3 nm
4	5	Col _h	a = 4.6 nm

Table S2. Detailed explanation of the Miller Planes belonging to each peak. Peak positions (q) are taken from the SAXS spectra, observed domain spacing is calculated using the equation $d = 2\pi/q$.

Name	Peak position (nm ⁻¹)	Observed domain spacing (nm)	Calculated domain spacing (nm)	Miller Indices
1 (LC – 120 °C)	1.61	3.90	3.90	[010]
	1.84	3.41	3.41	[100]
	2.35	2.67	2.66	[110]
	3.08	2.04	1.95	[020]
	3.66	1.72	1.71	[200]
3 (LC – 115 °C)	1.71	3.67	3.67	[010]
	1.92	3.27	3.27	[100]
	2.07	3.04	3.05	[110]
	3.42	1.84	1.84	[020]
3 (LC – 75 °C)	1.78	3.53	3.53	[010]
	1.94	3.24	3.24	[100]
	2.06	3.05	3.01	[110]
	3.00	2.09	2.04	[110]
	3.50	1.80	1.76	[020]
3 (C – -10 °C)	1.79	3.51	3.51	[020]
	2.02	3.11	3.11	[110]
	3.01	2.09	2.08	[130]
	3.46	1.82	1.76	[040]/[200]
	3.72	1.69	1.65	[220]

5. References

- (S1) ten Eikelder, H. M. M.; Markvoort, A. J.; de Greef, T. F. A.; Hilbers, P. A. J. An equilibrium model for chiral amplification in supramolecular polymers. *J. Phys. Chem. B* **2012**, *116*, 5291–5301.
- (S2) (a) Greciano, E. E.; Matarranz, B.; Sánchez, L. Pathway Complexity Versus Hierarchical Self-Assembly in N-Annulated Perylenes: Structural Effects in Seeded Supramolecular Polymerization. *Angew. Chem. Int. Ed.* **2018**, *57*, 4697–4701. (b) Dorca, Y.; Naranjo, C.; Ghosh, G.; Gómez, R.; Fernández, G.; Sánchez, L. Unconventional Chiral Amplification in Luminescent Supramolecular Polymers Based on Trisbiphenylaminetricarboxamides. *Organic Materials* **2020**, *2*, 41–46. (c) Naranjo, C.; Dorca, Y.; Ghosh, G.; Gómez, R.; Fernández, G.; Sánchez, L. Chaincapper effect to bias the amplification of asymmetry in supramolecular polymers. *Chem. Comm.* **2021**, *57*, 4500–4503.
- (S3) Gupta, R. K.; Pathak, S. K.; Pradhan, B.; Rao, D. S. S.; Prasad, S. K.; Achalkumar, A. S. Self-assembly of luminescent N-annulated perylene tetraesters into fluid columnar phases. *Soft Matter* **2015**, *11*, 3629–3636; b) Gupta, R. K.; Rao, D. S.; Prasad, S. K.; Achalkumar, A. S. Columnar Self-Assembly of Electron-Deficient Dendronized Bay-Annulated Perylene Bisimides. *Chem. Eur. J.* **2018**, *24*, 3566–3575.
- (S4) Martínez, M. A.; Doncel-Giménez, A.; Cerdá, J.; Calbo, J.; Rodríguez, R.; Aragón, J.; Crassous, J.; Ortí, E.; Sánchez L. Distance Matters: Biasing Mechanism, Transfer of Asymmetry, and Stereomutation in N-Annulated Perylene Bisimide Supramolecular Polymers. *J. Am. Chem. Soc.* **2021**, *143*, 13281–13291.