Electronic Supplementary Material (ESI) for ChemComm.

# Electronic Supporting Information

## Self-Organization of Amino-Acid-Derived NDI Assemblies into a Nanofibrillar Superstructure with n-Type Semiconducting Properties

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## 1. Materials and Methods

Chemicals were purchased from commercial suppliers and used as received. NMR solvents were purchased from Deutero GmbH (Germany) or Euriso-Top (France).

NMR spectra were recorded on Bruker Fourier 300 MHz (5 mm Fourier 1H/13C probe), and Bruker Avance III HD 400 MHz (5 mm BBO probe) spectrometers and referenced on solvent residual peaks. Low temperatures were obtained using Bruker BCU II external cooler. High temperatures were obtained using internal probe heater.

DLS measurement were performed with a Malvern Zetasizer Nano-S into 1 cm optical path quartz cuvettes. The molecular concentration in solution amounted to $1*10^{-6}$ M in $CHCl_3$. Before using it, the solvent was filtered multiple times with a 5 μm filter to remove suspended particles.

AFM characterization was performed with a Veeco Dimension 3100 running with a Nanoscope IV controller, in intermittent contact mode. The $CHCl_3$ solution containing aggregates were deposed by drop-casting on thermal silicon oxide ($SiO_2$), covalently functionalized with an HMDS monolayer.

The UV-Vis spectra were recorded with a Jasco V-670 spectrophotometer using 1 mm optical path quartz cuvettes. The CD spectra were recorded with Jasco J-810 spectropolarimeter using 1 mm optical path quartz cuvettes. The fluorescence spectra were recorded with an Agilent Technologies Cary Eclipse fluorescence spectrophotometer, using 1 cm optical path quartz cuvettes.

The electrical characterization was performed in air using a probe station powered by a Kethley 2636A and connected to a system that can send a pulsed flow of humid air on the sample. The aggregates were deposited from $CHCl_3$ using the drop-casting technique onto a $SiO_2/Si\ n^{++}$ substrates exposing a (230 ± 10) nm thick $SiO_2$ layer (Fraunhofer Institute for Photonic Microsystems IPMS, Dresden, Germany), pre-patterned with interdigitated gold electrodes (channel length = 2.5 μm). Before the deposition, the $SiO_2$ surface was covalently functionalized with a monolayer of hexamethyldisilazane (HMDS).

## 2. Synthesis of 1

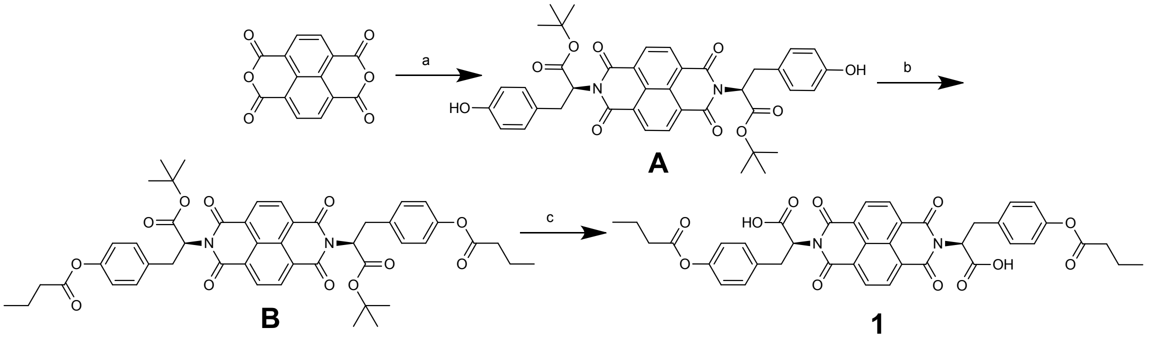


**Figure S1**: Synthesis of **1**. a) L-tyrosine tert-butyl ester, Et3N, DMF, 5 min, 140 °C in microwave reactor. b) butyryl chloride, $Et_3N$, THF, 2 h, 0 °C + 12 h, rt. c) TFA, $Et_3SiH$, $CH_2Cl_2$; 12 h, rt.

**Synthesis of A** 1,4,5,8-naphtalenetetracarboxylic acid dianhydride (200 mg, 0.745 mmol), L-tyrosine tert-butyl ester (354 mg, 1.49 mmol) and triethylamine (500 μL) were dissolved in 7 mL of dry DMF. Reaction mixture was heated under microwave irradiation (CEM Microwave reactor) for 5 min. at 140 °C. After solvent was removed under reduced pressure to give, dark brown oily residue. The latter was dissolved in 10 mL of MeCN. This solution was added dropwise under stirring to 100 mL of HCl (M=1 mol/$dm^3$). The resulting precipitate was filtered off, rinsed with 150 mL of deionized water and dried in vacuo. The pure product was isolated as an orange powder in 81,7% yield (430 mg).

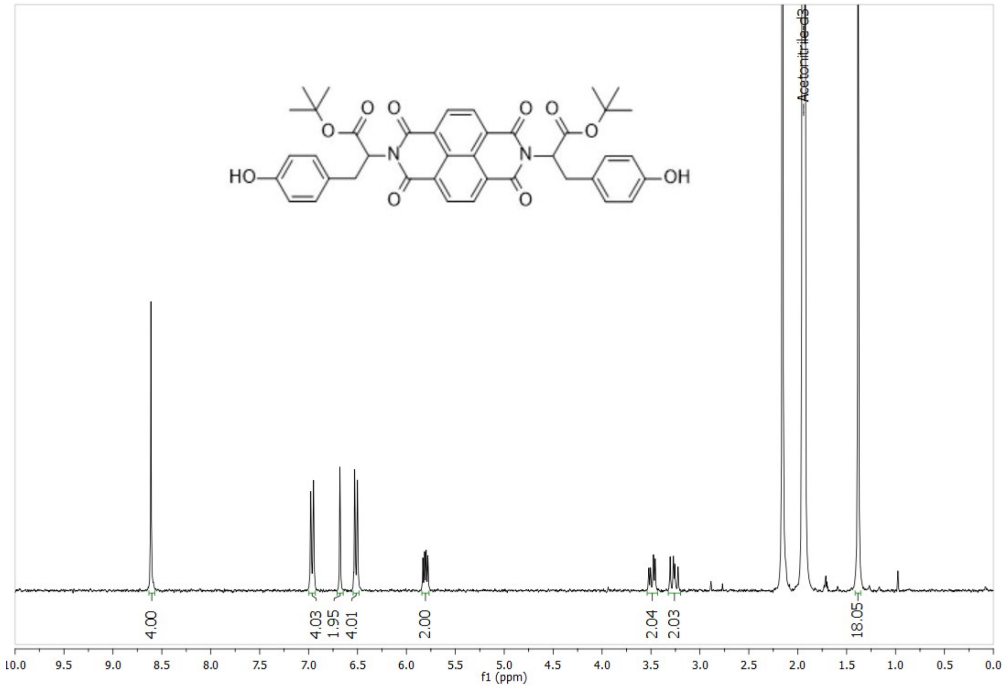


**Figure S2:** $^{1}$H NMR (300 MHz, $CD_3CN$) δ 8.61 (s, 4H), 6.96 (d, J = 8.5 Hz, 4H), 6.68 (s, 2H), 6.51 (d, J = 8.6 Hz, 4H), 5.81 (dd, J = 10.2, 5.3 Hz, 4H), 3.49 (dd, J = 14.3, 5.3 Hz, 2H), 3.26 (dd, J = 14.3, 10.2 Hz, 2H), 1.38 (s, 18H).

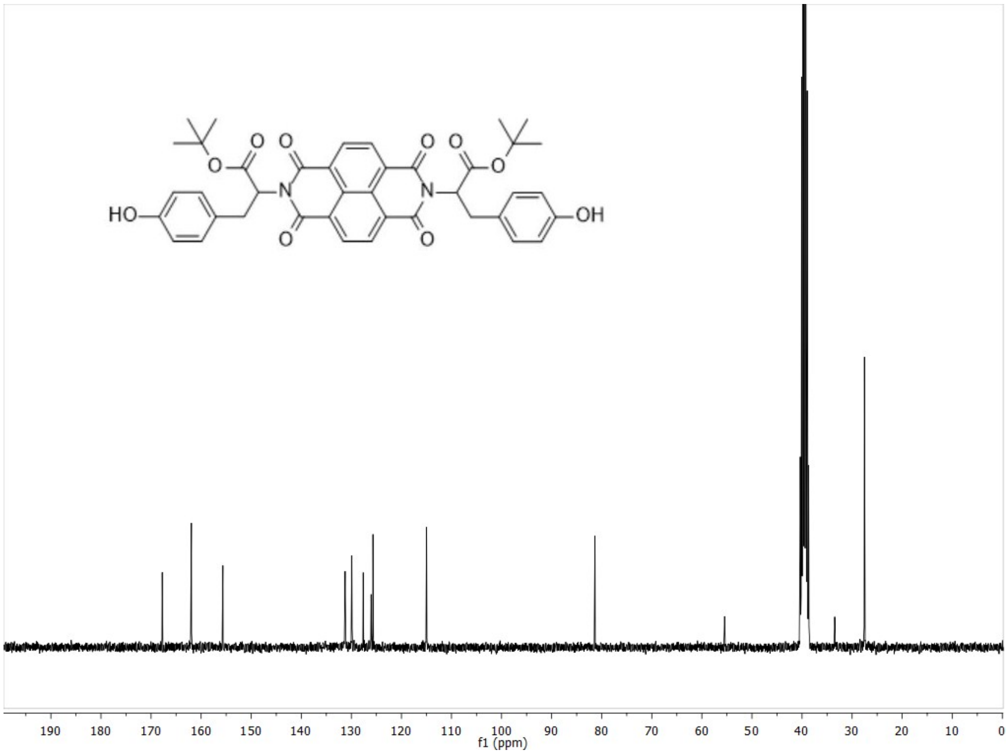


**Figure S3:** $^{13}$C NMR (75 MHz, DMSO d-6) δ(ppm): 167.76, 161.94, 155.66, 131.25, 129.92, 127.63, 126.06, 125.68, 114.98, 81.35, 55.48, 33.47, 27.54.

**Synthesis of B** To the solution of **A** (200 mg, 0.28 mmol) in dry THF (30 mL)**,** triethylamine (200 µL, 1.44 mmol) was added under Ar atmosphere. The solution was cooled down to 0 °C with ice bath and after butyryl chloride (85 mg, 0.8 mmol) was added dropwise. The mixture was stirred at this temperature for 2 h and after the stirring was continued at room temperature for 12 h. After this time, the solvent was removed under reduced pressure and the resulting paste was dissolved in 30 mL of DCM. The solution was washed with HCl (2x 25 mL M=1 mol/dm$^3$) and deionized water (2 x 25 mL), dried with anhydrous $MgSO_4$ and evaporated. Crude red product may be used in 3th step without further purification.

**B** may be also purified by 15 min sonification in n-hexane (30 ml) in about 70% purification yield, but this procedure is necessary only if **B** act as a final product.

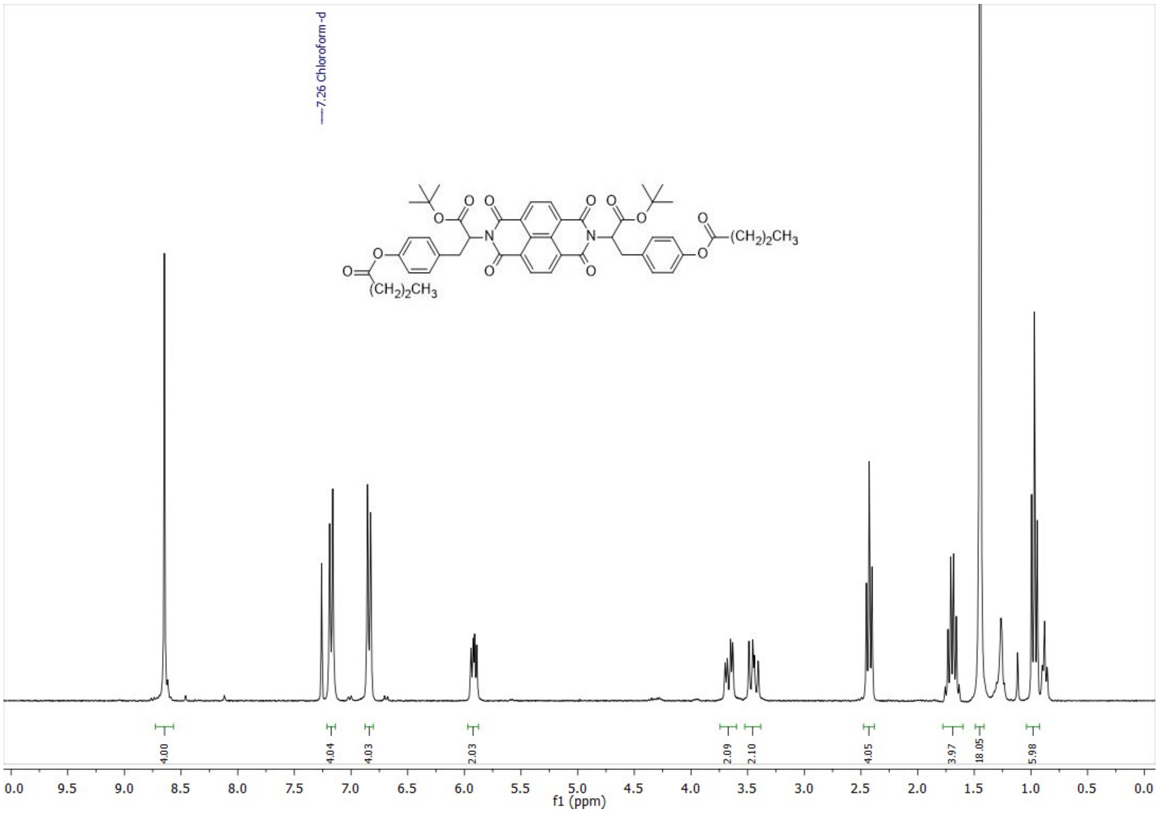


**Figure S4:** $^1$H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.65 (s, 4H), 7.17 (d, J = 8.1 Hz, 4H), 6.84 (d, J = 8.1 Hz, 4H), 5.92 (dd, J = 9.9, 5.7 Hz, 2H), 3.67 (dd, J = 14.4, 5.7 Hz, 2H), 3.45 (dd, J = 14.4, 9.9 Hz, 2H), 2.43 (t, J = 7.4 Hz, 4H), 1.70 (h, J = 7.4 Hz, 4H), 1.45 (s, 18H), 0.97 (t, J = 7.4 Hz, 6H).

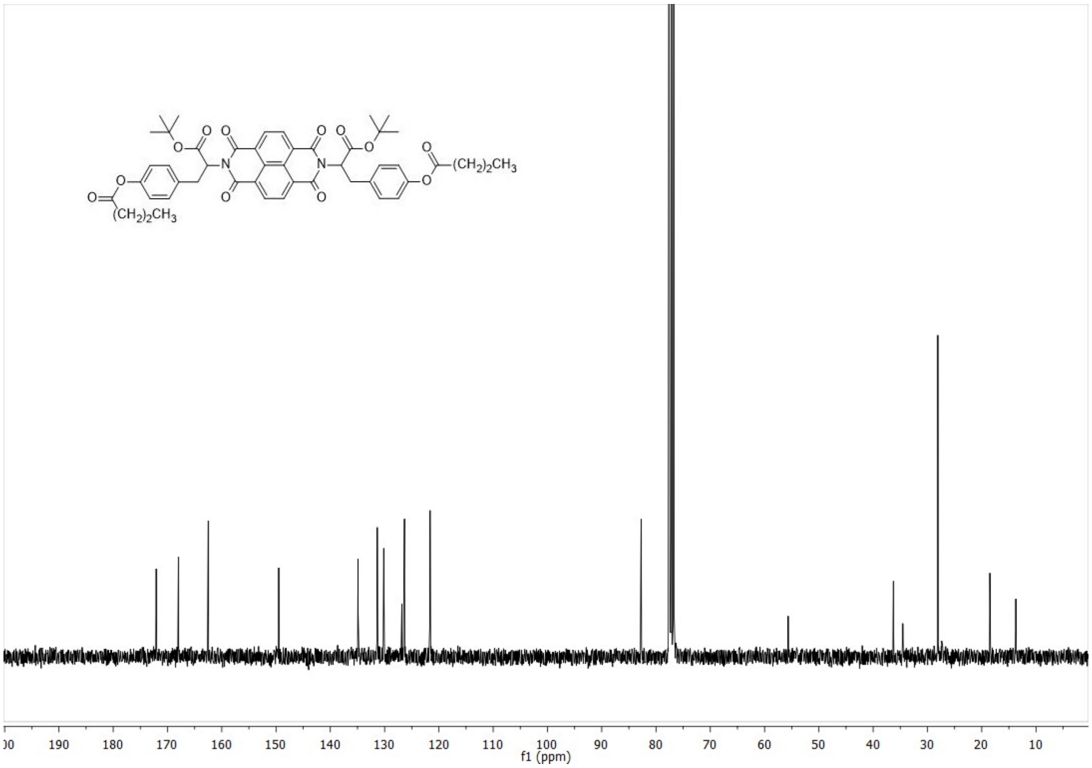


**Figure S5:** $^{13}$C NMR (75 MHz, CDCl$_3$) δ(ppm): 172.08, 167.98, 162.49, 149.51, 134.90, 131.34, 130.17, 126.83, 126.35, 121.62, 82.74, 55.65, 36.27, 34.53, 28.08, 18.50, 13.74.

**Synthesis of 1** To the solution of **B** (all obtained in 2nd step) in DCM (2 mL), trifluoroacetic acid (600 μL, 7.8 mmol) and triethylsilane (120 μl, 0.75 mmol) were added and reaction mixture was stirred at room temperature for 12 h. Afterwards, the solvents were evaporated under reduced pressure and the resulting paste was dissolved in THF (5 ml). This solution was added dropwise under vigorous stirring to 50 mL of n-haxane. The resulting precipitate was filtered off, rinsed with 25 mL of n-haxane and dried in vacuo. The pure product was obtained as pinky-red powder in overall 79 % yield (163 mg).

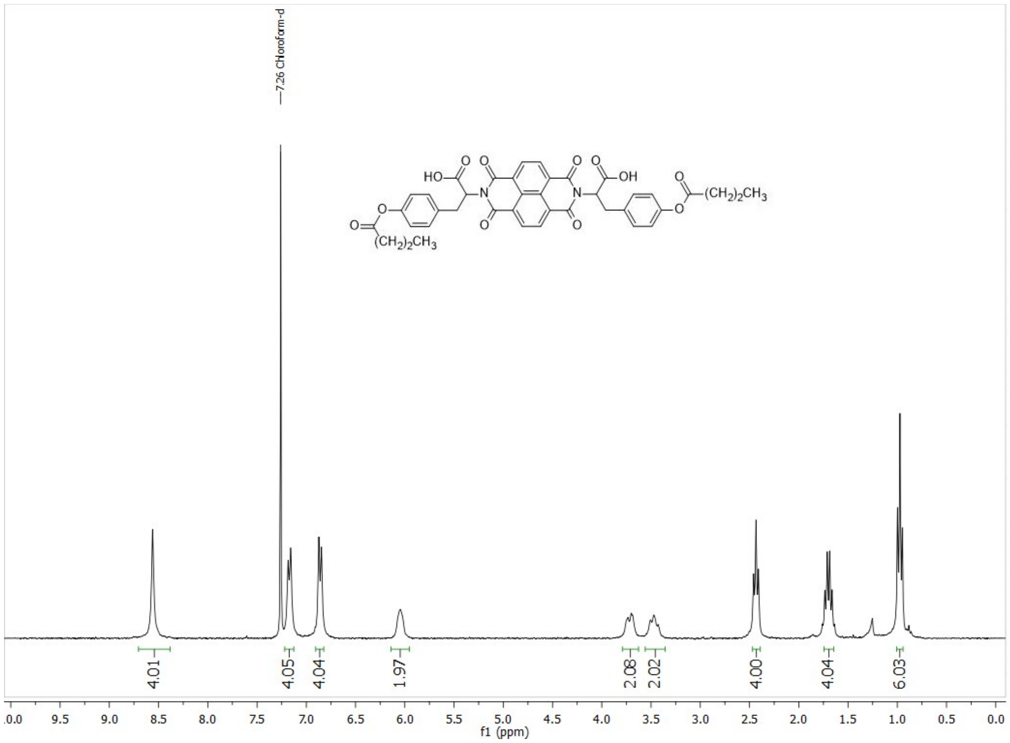


**Figure S6:** $^1$H NMR (300 MHz, CDCl$_3$) δ(ppm): 8.56 (s, 4H), 7.17 (d, J = 8.4 Hz, 4H), 6.86 (d, J = 8.4 Hz, 4H), 6.05 (bs, 2H), 3.72 (dd, J = 14.0, 5.3 Hz, 2H), 3.47 (dd, J = 14.0, 10.1 Hz, 2H), 2.44 (t, J = 7.4 Hz, 4H), 1.79 – 1.61 (m, 4H), 0.97 (t, J = 7.4 Hz, 6H).

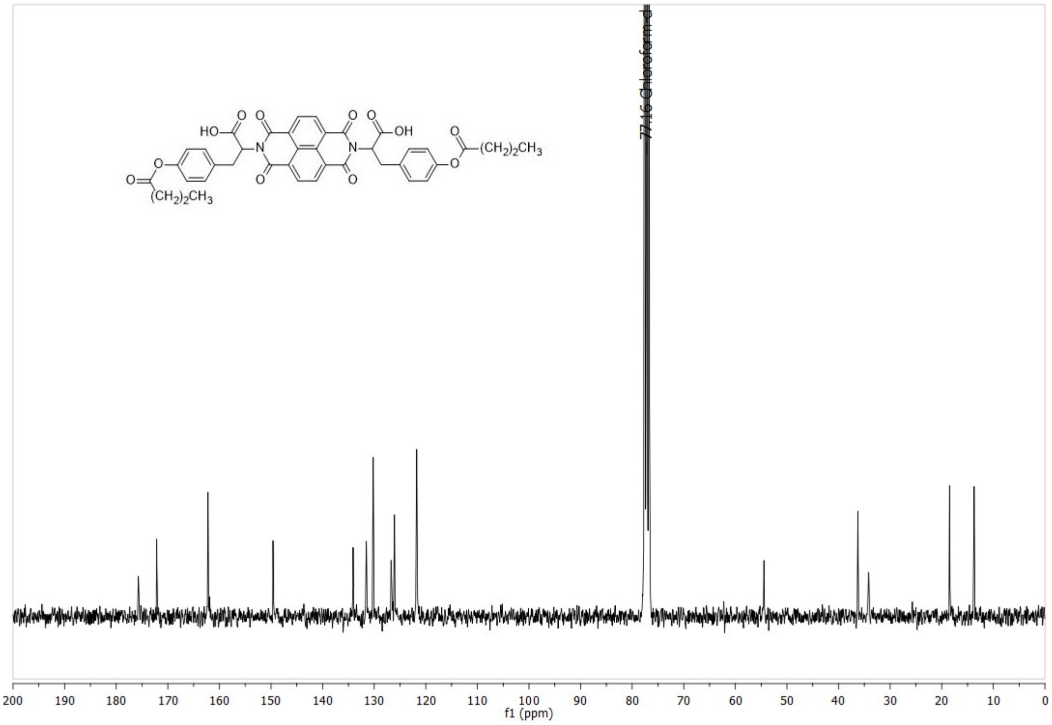


**Figure S7:** $^{13}$C NMR (75 MHz, CDCl$_3$) δ 175.71, 172.16, 162.22, 149.61, 134.09, 131.52, 130.19, 126.73, 126.07, 121.76, 77.16, 76.74, 54.46, 36.24, 34.16, 18.48, 13.72.

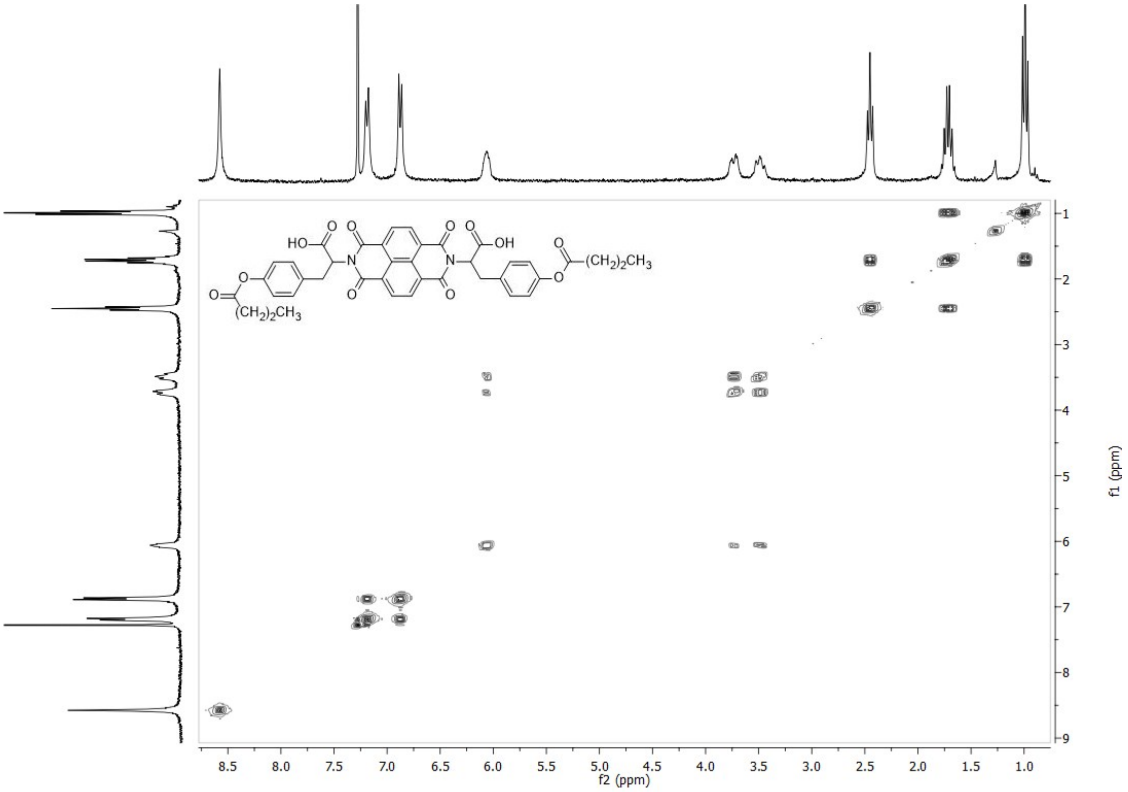


**Figure S8:** $^1$H-$^1$H COSY NMR (300 MHz $CDCl_3$)

## 3. Characterization of 1

### 3.1 NMR Data

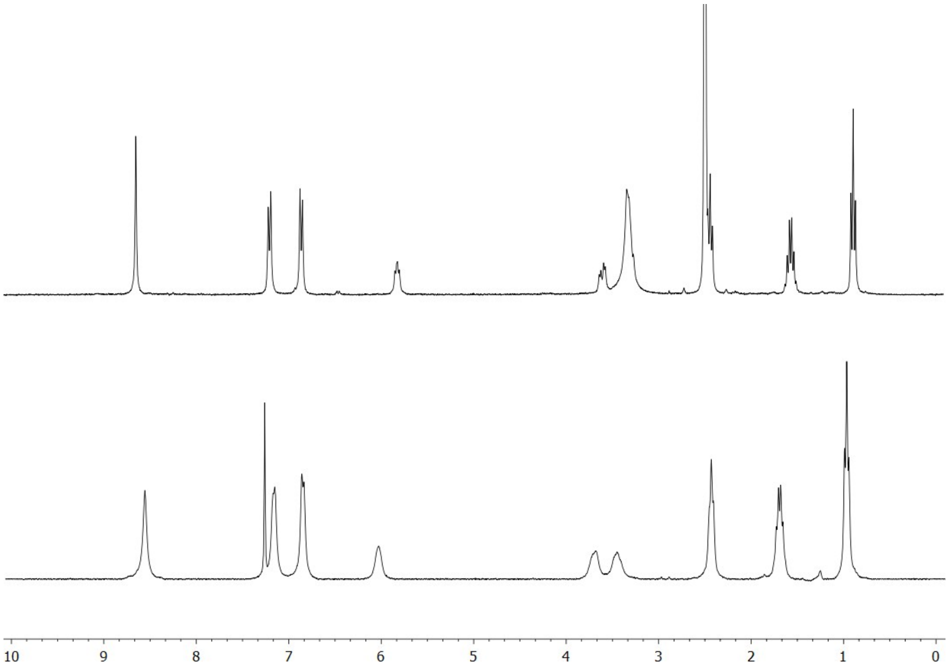


**Figure S9**: Stacked $^1$H NMR spectra (300 MHz) of **1**. Top: in DMSO d-6. Bottom: in $CDCl_3$.

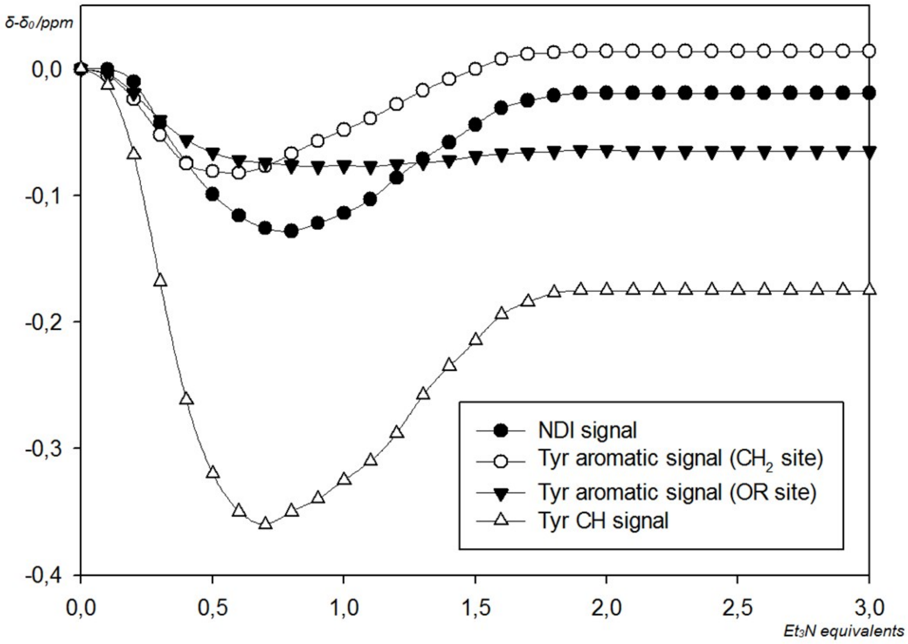


**Figure S10:** $^1$H NMR (300 MHz, $CDCl_3$) base ($Et_3N$) titration curves for four major proton signals (centre of the peak) of **1** recorded at M=0.009 mol/dm$^3$. For clarity in $\delta$-$\delta_o$ scale.

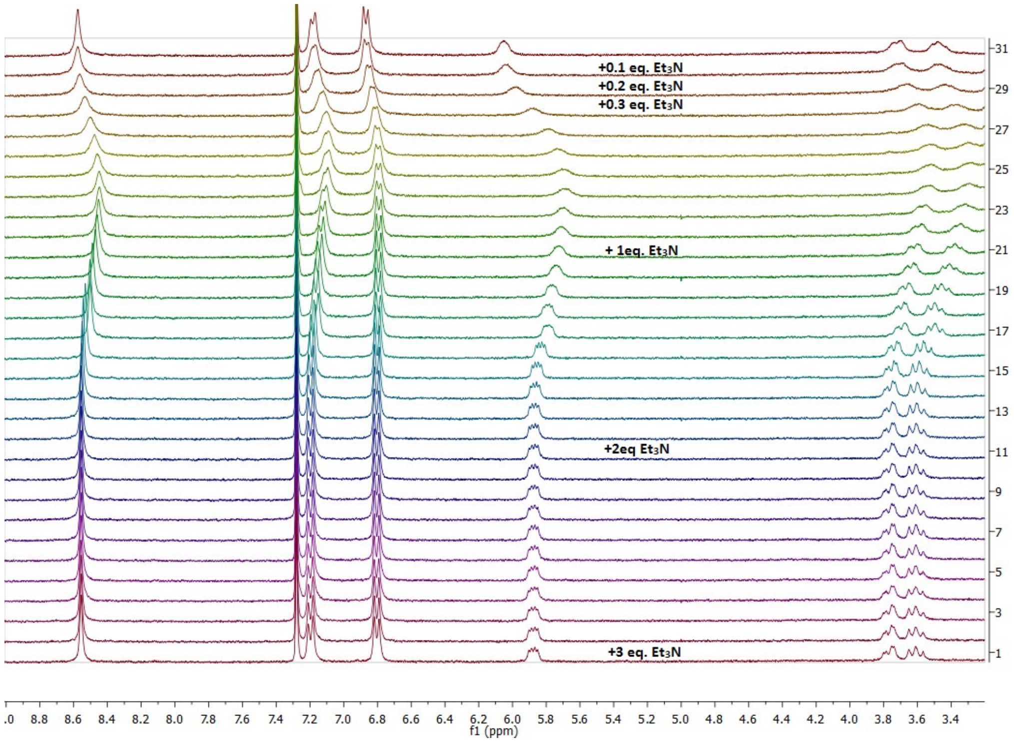


**Figure S11**: Base titration spectra (300 MHz $CDCl_3$) of **1** recorded at M=0.009 mol/dm$^3$.

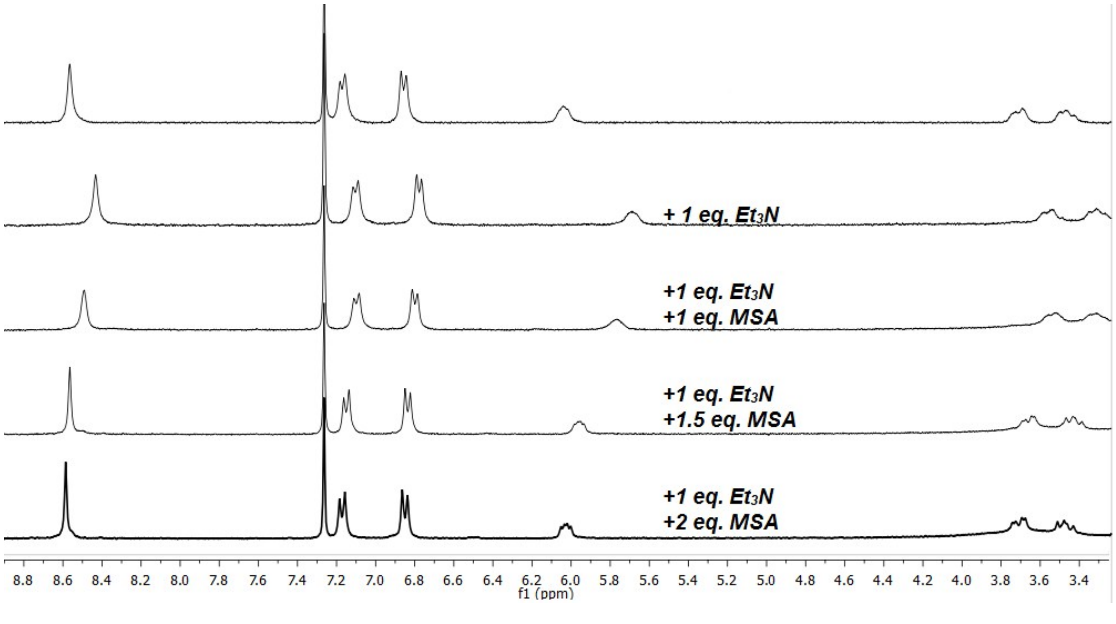


**Figure S12:** Reversible base/acid titration NMR spectra (300 MHz, $CDCl_3$) of **1** recorded at M=0.009 mol/dm$^{3.}$.

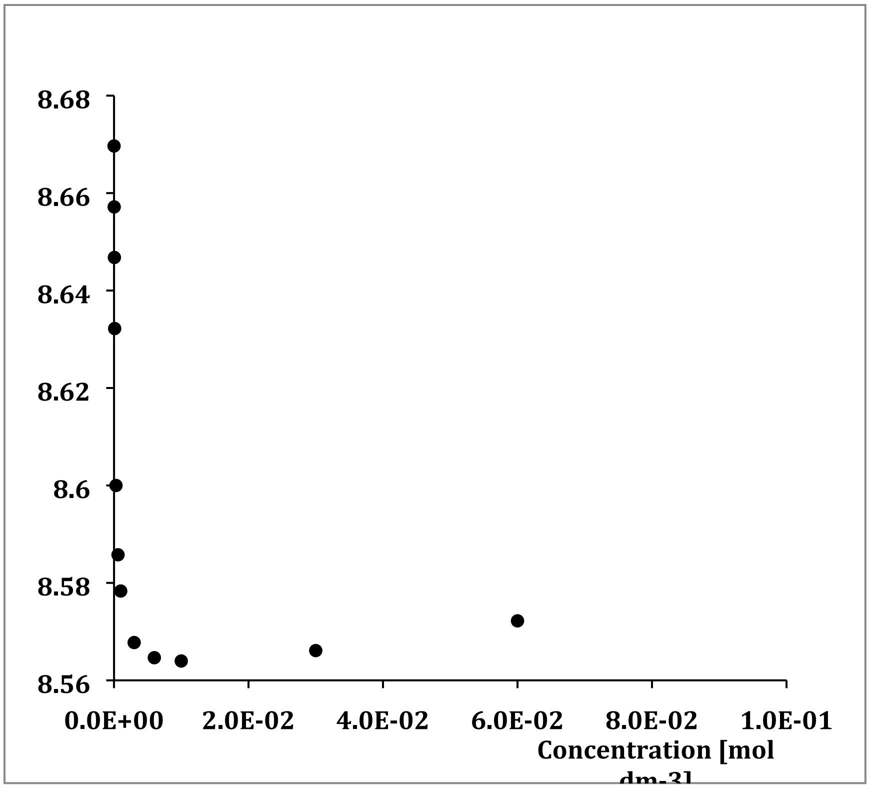


**Figure S13:** Concentration dependent NMR (300 MHz $CDCl_3$) curve of **1** (NDI signal).

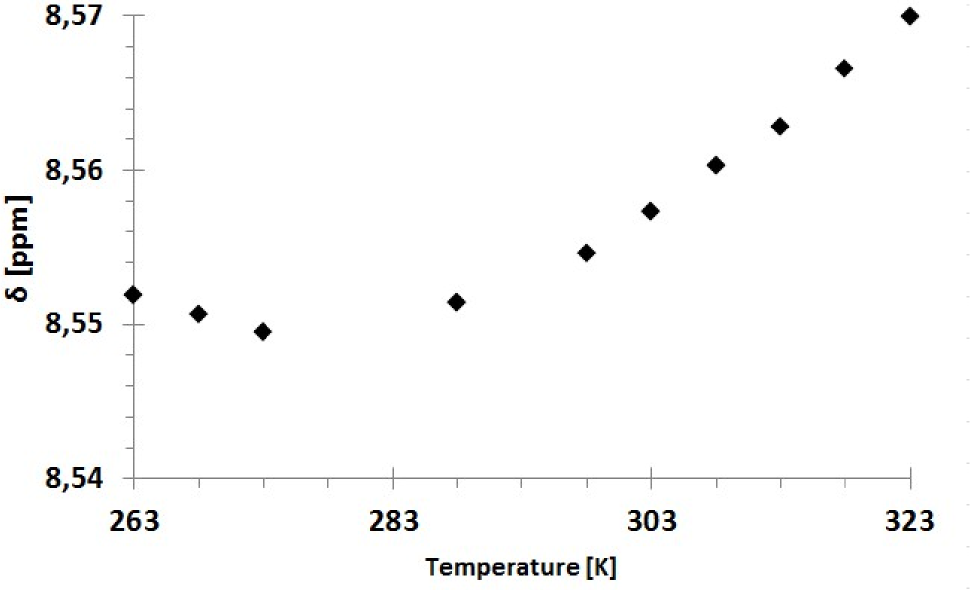


**Figure S14:** VT NMR (400 MHz $CDCl_3$) curve (NDI signal) obtained for **1**.

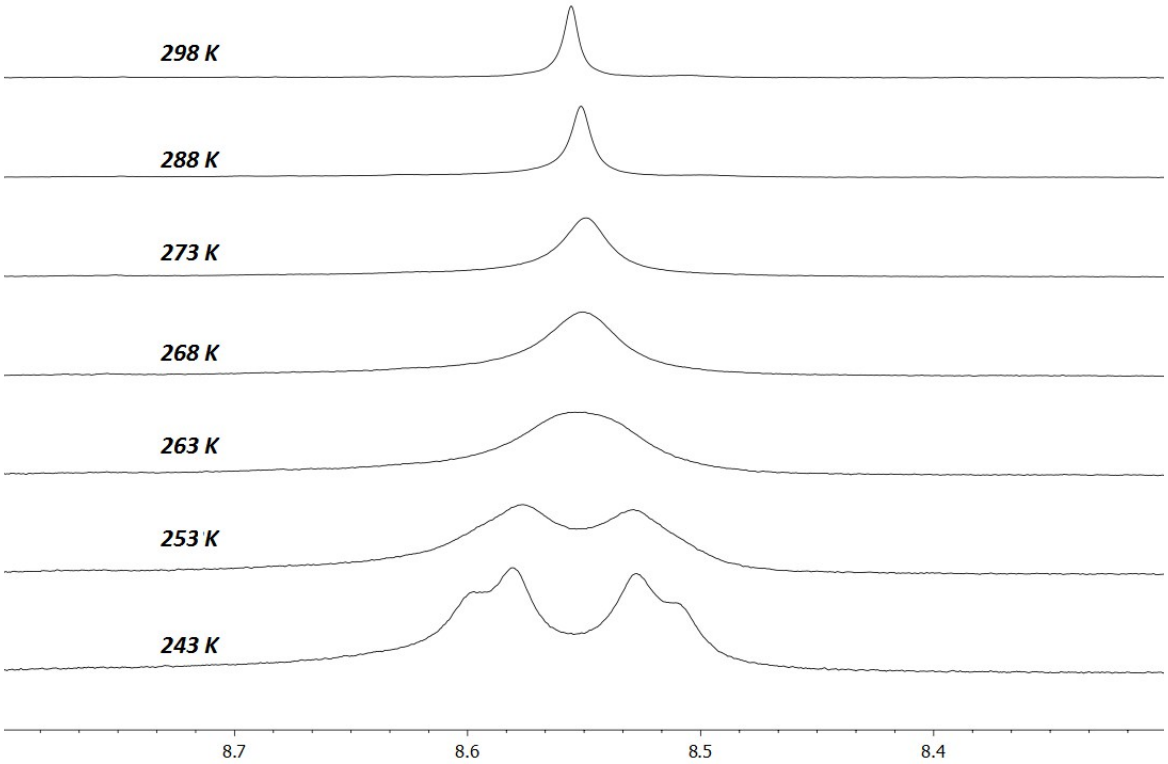
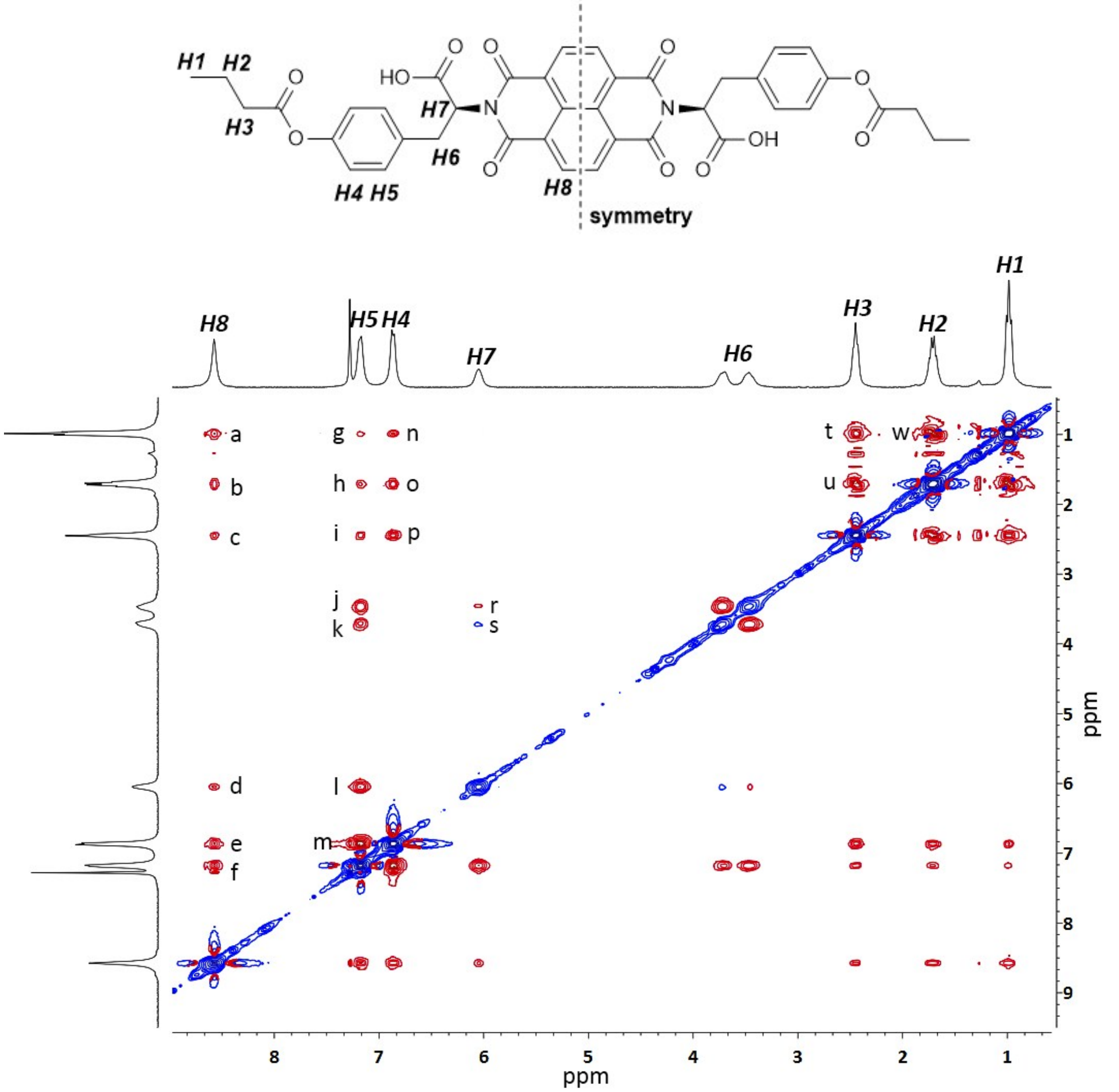


**Figure S15:** Low temperature NMR spectra (400 MHz $CDCl_3$)- of **1** (NDI signal). Integral scale was not maintained for clarity.

**Table S1.** ROESY NMR spectrum (300 MHz $CDCl_3$) of 1 with the couplings description.



| Coupling/s | Description |
|---|---|
| a, b, c | Intramolecular couplings between NDI core (***H8***) and butyryl chain (***H1,H2,H3***) confirming the *anti*-geometry of amino acid side-chains. |
| d | Intermolecular coupling between NDI core (***H8***) and α-CH (***H7***) confirming the formation of C–H···O hydrogen bonds between NDI units, which have been confirmed also with VT NMR experiments. |
| e, f | Intramolecular couplings between NDI core (***H8***) and both hydrogens from the tyrosine phenyl ring (***H4,H5***) confirming the *anti*-geometry of amino acid side-chains and intramolecular π-stacking interactions. |
| g, h, i | Weak intramolecular couplings between butyryl chain (***H1,H2,H3***) and more distant hydrogens from the tyrosine phenyl ring (***H5***) confirming the *anti*-geometry of amino acid side-chains and dynamic movements of butyryl chains. |
| j, k | Intramolecular couplings between β-$CH_2$ group (***H6***) and hydrogens from the tyrosine phenyl ring (***H5***) |

| | |
|---|---|
| l | Intramolecular coupling between α-CH group (***H7***) and hydrogens from the tyrosine phenyl ring (***H5***) |
| m | Intramolecular COSY type coupling between protons in 1,4-substituted tyrosine phenyl ring (***H4,H5***) |
| n, o, p | Intramolecular couplings between butyryl chain (***H1,H2,H3***) and neighboring hydrogens in tyrosine phenyl ring (***H4***) confirming the *anti*-geometry of amino acid side-chains and dynamic movements of butyryl chain. |
| r, s | Intramolecular COSY type coupling between α-CH (***H7***) and β-$CH_2$ groups (***H6***) |
| t, u, w | Intramolecular COSY/TOCSY type couplings between hydrogens in butyryl group (***H1,H2,H3***) |

## 3.2 Dynamic Light Scattering (DLS) characterization

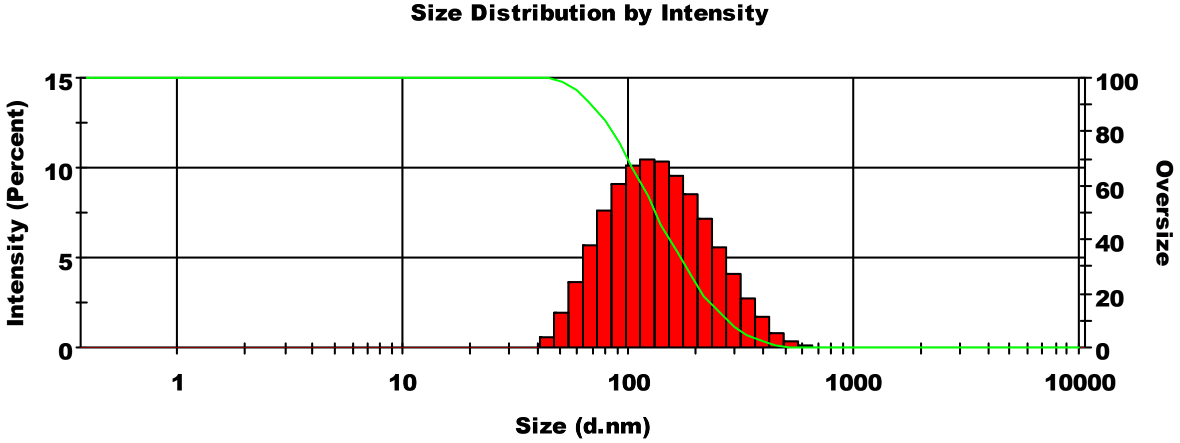


**Figure S16**: Size distribution of **1** in $CHCl_3$ $10^{-6}$ M. The spectrum shows a single peak distribution centred at 109.7 nm with a polydispersity of 0.44.

## 3.3 Atomic Force Microscopy (AFM) characterization

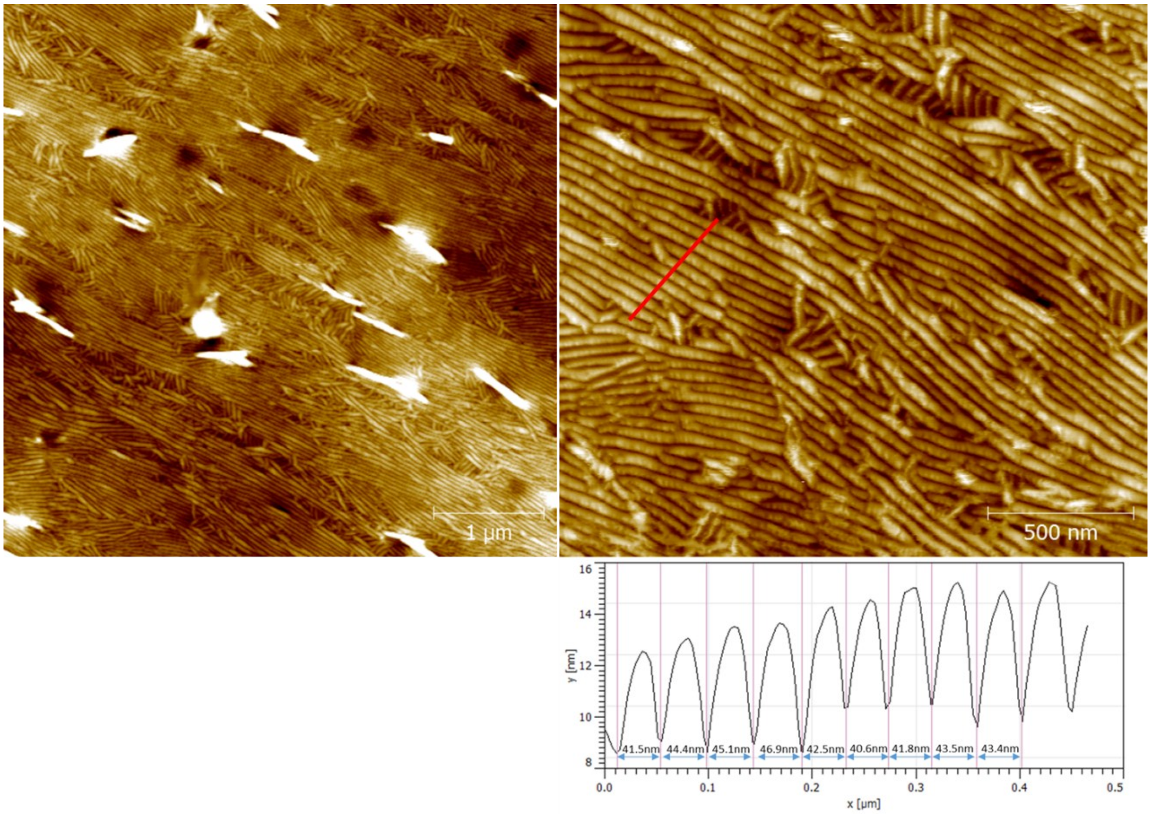


**Figure S17**: AFM topographical images, recorded in intermittent contact mode, of **1** physisorbed on $SiO_2$ and extracted topographical profile. (Image Z-scale = 20 nm)

## 3.4 Optical characterization

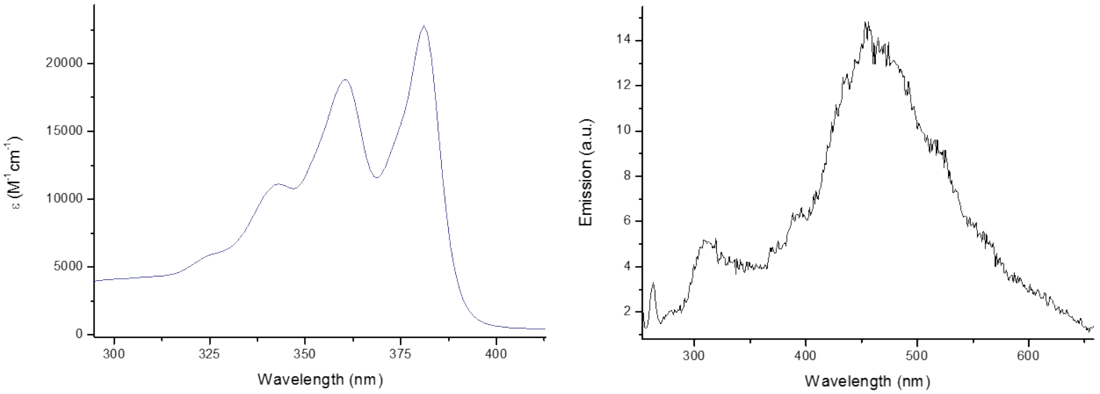


**Figure S18:** UV-Vis (left) and Fluorescence (right) spectra of **1** in $CHCl_3$ ($C = 5.8*10^{-6}$ M)

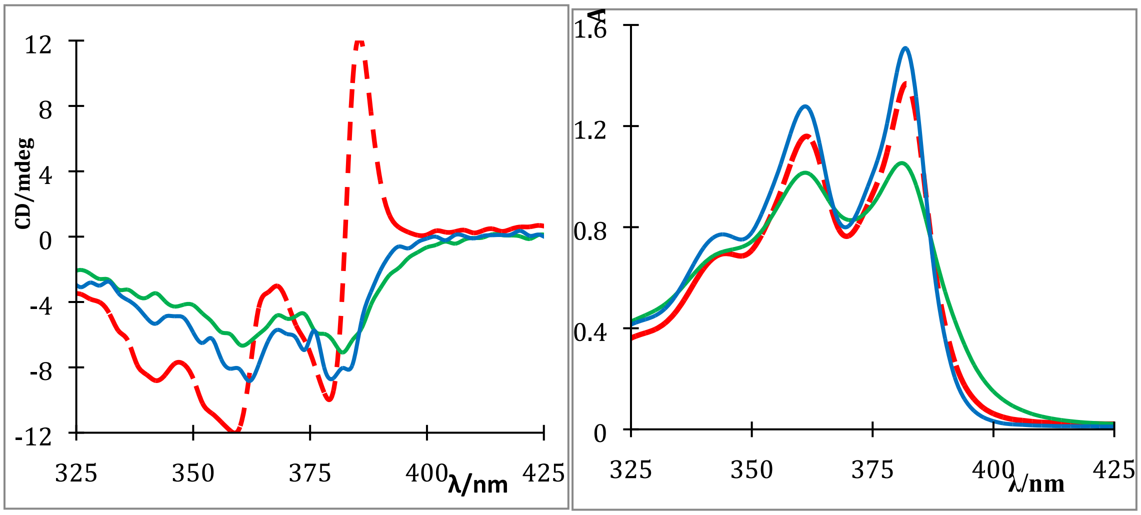


**Figure S19**. Left: CD spectra of **1** in TCE (red) and DMSO (green) solutions, and **B** in TCE solution (blue). All recorded at M= 7x10 $^{-4}$ mol/dm$^3$ and l= 1mm. Right: Corresponding absorption data.

## 3.5 Electrical characterization

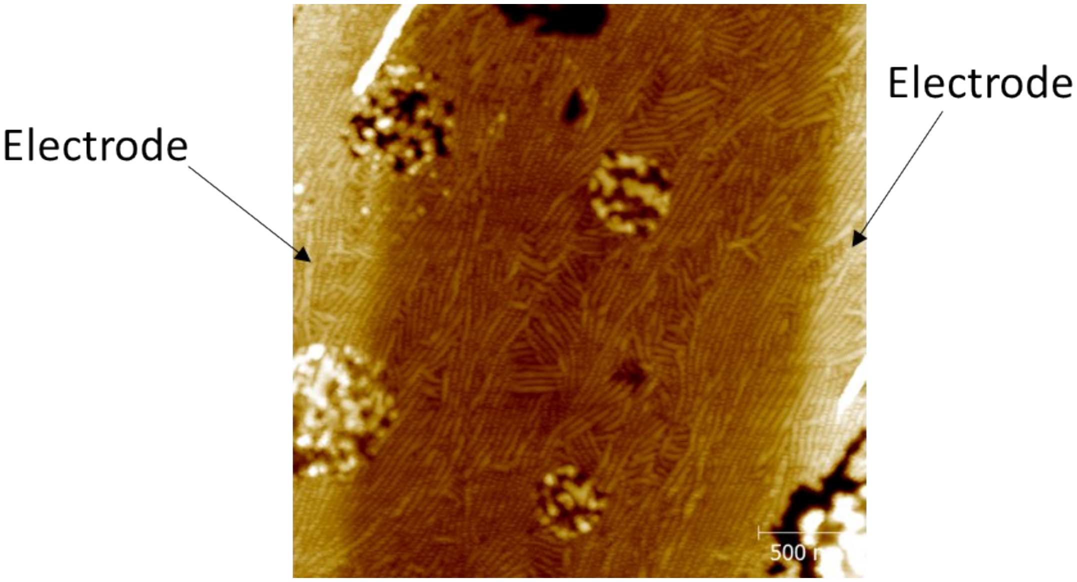


**Figure S20:** Topographical AFM image, recorded in intermittent contact mode, of **1** on SIO$_2$ pre-patterned with gold electrodes after exposure to humid environment. (Channel length = 2.5 μm, image Z-scale = 41 nm)

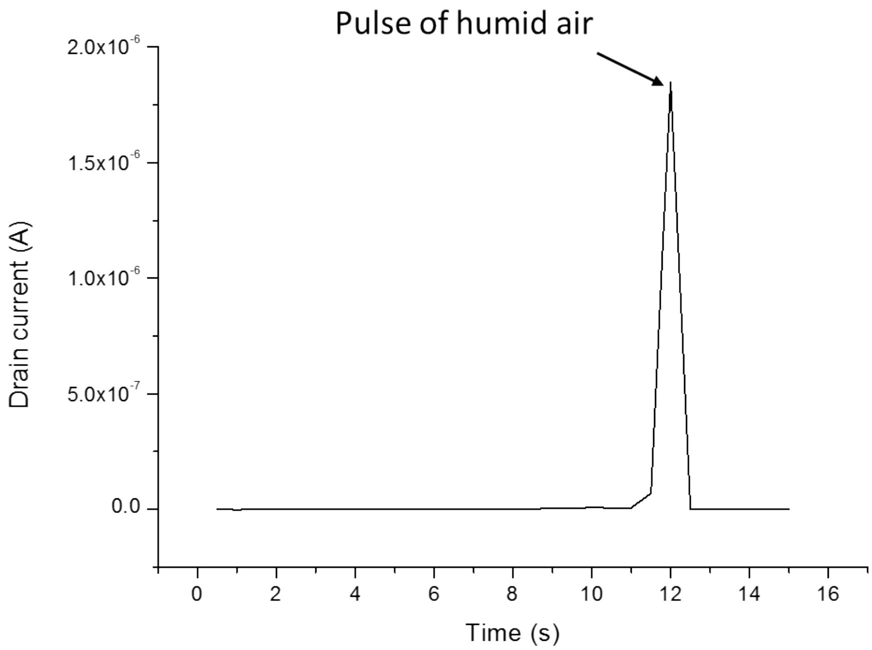


**Figure S21**: Response in drain current of **1** fibers to a pulse of humid air that flows on the sample during an I/V measurement with constant drain bias applied (Vgate = 0V, V drain = 2V).