



## Supporting Information

### **Impact of NDI-Core Substitution on the pH-Responsive Nature of Peptide-Tethered Luminescent Supramolecular Polymers**

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## 1. General Methods

**Materials:** All chemicals were purchased from commercial sources and were used as such without any further purification. Spectroscopic grade solvents were used for all spectroscopic measurements.

**NMR Measurements:** NMR spectra were obtained with JEOL (600 MHz) Fourier transform NMR spectrometer at the Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR) and on a Bruker Avance II 400 (400 MHz) at the Institute of Organic Chemistry of the Johannes Gutenberg-University Mainz with chemical shifts reported in parts per million (ppm) with respect to TMS. Splitting patterns are designated as s (singlet), d (doublet), m (multiplet), t (triplet), q (quartet), dd (doublet of doublet) and dt (doublet of triplet).

**Mass Spectrometry:** MALDI was performed on a Bruker Daltonics Autoflex Speed MALDI TOF System (GT0263G201) Spectrometer using trans-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) and  $\alpha$ -Cyano-4-hydroxycinnamic acid (CCA) as matrix. ESI measurements were executed on an Agilent 6545QTOF-MS device at the Johannes Gutenberg-University Mainz.

**Spectroscopic Measurements:** Electronic absorption spectra were recorded on a Perkin Elmer Lambda 900 UV-Vis-NIR Spectrometer and emission spectra were recorded on Perkin Elmer LS 55 Luminescence Spectrometer. UV-Vis and emission spectra were recorded in 10 mm path length cuvettes. Circular Dichroism measurements were performed on a Jasco J-815 spectrometer and were recorded using 10 mm and 5 mm path length cuvettes. The sensitivity, time constant and scan rate were chosen appropriately.

**Fluorescence lifetime measurements:** Time-resolved decay experiments were recorded on an Horiba Delta Flex Time-Correlated Single Photon Counting (TCSPC) instrument. A 442 nm and 532 nm nano-LED with a pulse repetition rate of 1 MHz were used as light source. The instrument response function

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(IRF) was collected by using a scatterer (Ludox AS40 colloidal silica, Sigma Aldrich). For the 442 nm LED light source the instrumental full width at half maximum including detector response was 0.2 ns. The excited state decay of the sample was collected by fixing the emission wavelength. The decay was fitted to appropriate best fit multiexponential decay using IBH software (DAS6).

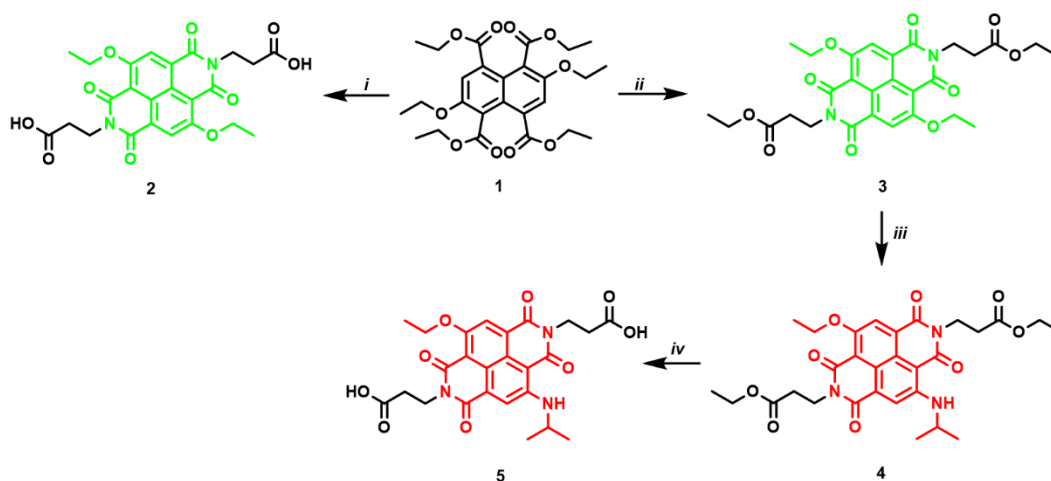
**Transmission Electron Microscopy (TEM):** TEM measurements were performed on a JEOL (JEM 3010) operated at 300 kV. Samples were prepared by placing a drop of the solution on carbon coated copper grids followed by drying at room temperature in desiccator (samples were negatively stained with uranyl acetate).

**Optical setup for imaging in Structured Illumination Microscopy (SIM) method:** The fluorescence images of supramolecular polymers were acquired using an inverted Zeiss ELYRA PS1 microscope in structured illumination mode. 488 nm (200 mW) were used for the excitation of **NDI-diOEt-cat** and 561 nm (200 mW) for **NDI-OEtIPA-cat**. 5% laser power from the objective top was used for structured illumination imaging. Imaging was performed using a Zeiss oil-immersion objective (Plan-apochromat 63x/1.40 Oil DIC M27, numerical aperture (NA) 1.40 oil). Fluorescence light was spectrally filtered with emission filters for channel I - MBS-488+EF BP 495-575/LP 750 for laser line 488 nm and for channel II - MBS- 561+EF BP 570-650/LP 750 for laser line 561 nm and imaged using a PCO edge sCMOS camera (quantum yield > 70%). Structured illumination images were processed using structured illumination analysis package for Zen software (Zeiss). Additional software was used for colour adjustment (ImageJ).

## 2. Synthetic Scheme and Procedures

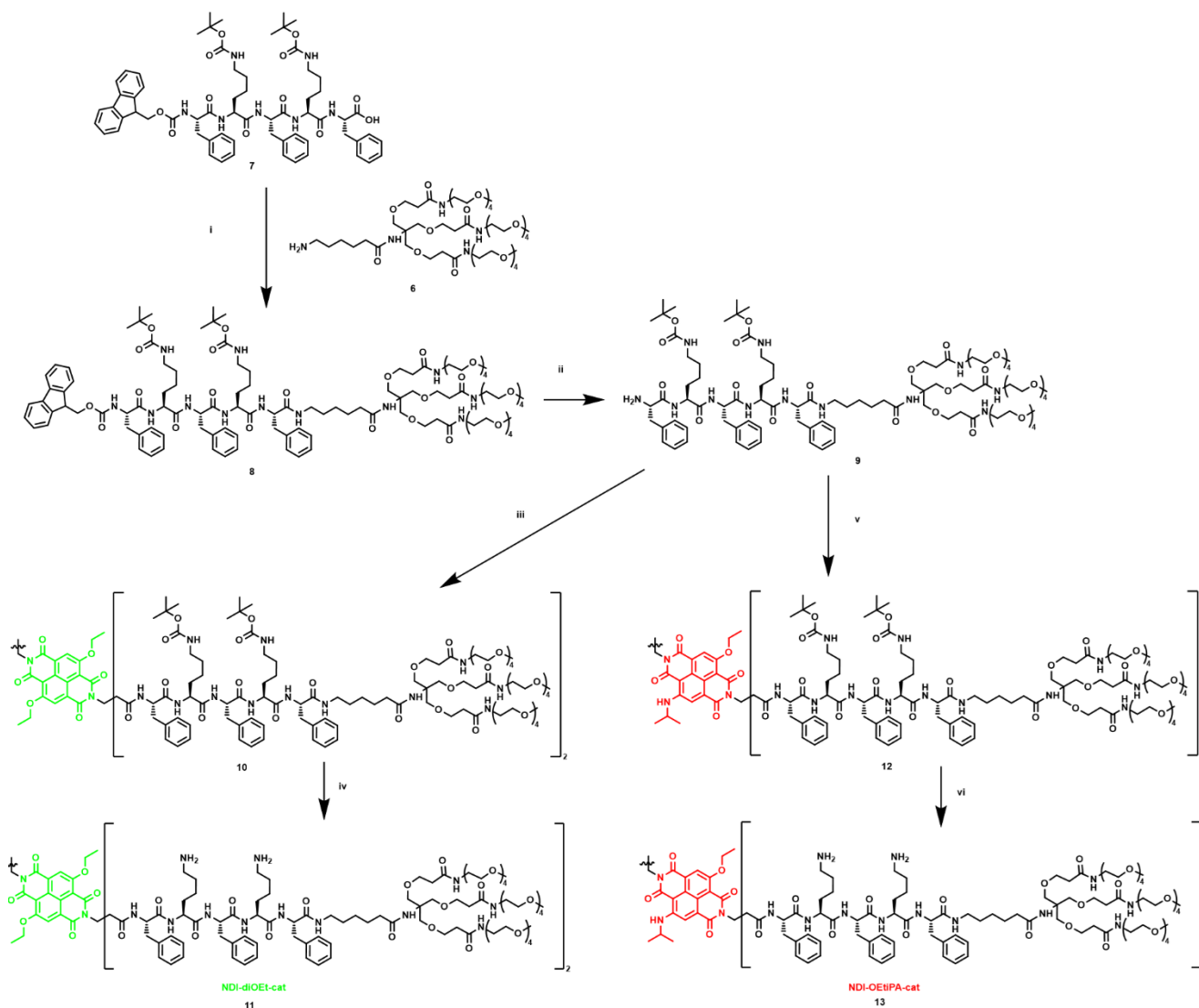
### 2.1 Synthetic Schemes

The synthetic route for the core-substituted NDI derivatives **NDI-diOEt-cat** and **NDI-OEtIPA-cat** are shown in **Scheme 1** and **2**. Compound **1** and **6** were synthesized following reported procedures.<sup>[1,2]</sup>



Scheme 1. Synthetic route for the cores **2** and **5**. *i*) 1.) **1** (1.0 eq.), 1 N KOH (excess), isopropanol, 3 d, 80 °C. 2.) 3-aminopropionic acid (3.0 eq.), AcOH, 90 °C, 2 d, 97%. *ii*) 1.) **1**, 1 N KOH (excess), isopropanol, 80 °C, 3 d. 2.) Ethyl 3-aminopropanoate, AcOH, 90 °C, 2 d, 82%. *iii*) **3** (1.0 eq.), isopropylamine (excess), CHCl<sub>3</sub>, 50 °C, 12 h, 70%. *iv*) **4** (1.0 eq.), TFA, water, 80 °C, 12 h, 83%.

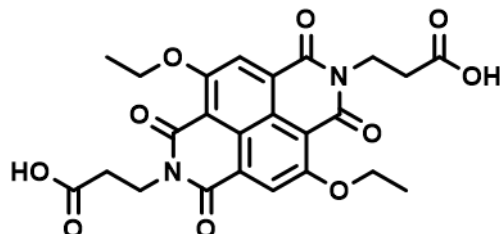
Scheme 2. Synthetic route for molecule 7



Scheme 2. Synthetic route for **NDI-diOEt-cat (11)** and **NDI-OEtPA-cat (13)**. *i*) **7** (1.3 eq.), PyBOP (1.3 eq.), HOBT (1.3 eq.), **6** (1.0 eq.), DIPEA (2.2 eq.), DMF, RT, overnight, 59%. *ii*) **8** (1.0 eq.), 10 v% piperidine in DMF, RT, 2 h, 94%. *iii*) **2** (1.0 eq.), HBTU (6.4 eq.), DIPEA (4.4 eq.), **9** (2.6 eq.), DMF, RT, 3 d, 40%. *iv*) **10** (1.0 eq.), TFA/DCM, RT, 4 h, quant. *v*) **5** (1.0 eq.), HBTU (4.0 eq.), DIPEA (3.0 eq.), **9** (2.5 eq.), DMF, RT, 2 d, 46%. *vi*) **12** (1.0 eq.), TFA/DCM, RT, 3 h, quant.

## 2.2 Synthetic Procedures

### Compound 2



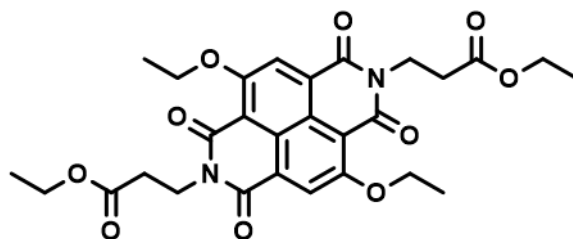
125 mg of **1** was taken in a round bottom flask and 30 mL of 1 N KOH in isopropanol was added. The reaction was refluxed at 80 °C for 3 d. The color of the reaction slowly changed from yellow to colorless. After 3 days the solvent was evaporated and the crude mixture obtained was used as such for the subsequent synthetic step. The crude mixture was suspended in 20 mL of acetic acid and 66 mg of 3-aminopropionic acid was added to it and refluxed at 90 °C. The progress of the reaction was monitored by <sup>1</sup>H-NMR spectroscopy. After completion of the reaction (2 days), it was cooled down to room temperature and excess water was added to it. The precipitate was filtered and washed with methanol to remove water and acetic acid. The precipitate was dried under ambient conditions and 120 mg of pure product was obtained as a yellow powder. Combined yield of step 1 and 2 is 97%.

**<sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K):** δ/ppm = 8.24 (s, 2H, *H*<sup>Ar</sup>), 4.45 (q, *J* = 6.9 Hz, 4H, OCH<sub>2</sub><sup>NDI</sup>), 4.21 (t, *J* = 7.9 Hz, 4H, NCH<sub>2</sub><sup>NDI</sup>), 2.58 (t, *J* = 7.8 Hz, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 1.51 (t, *J* = 6.9 Hz, 6H, CH<sub>3</sub>).

**<sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, 298 K):** δ/ppm = 172.39, 161.19, 159.51, 158.85, 125.96, 122.17, 118.55, 109.27, 65.64, 35.99, 31.96, 14.53.

**MALDI-TOF (CCA matrix, positive mode) (*m/z*):** calc. for [C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>10</sub>Na]<sup>+</sup>: 521.12, found: 521.23.

### Compound 3



1.8 g of **1** was taken in a single necked round bottom flask and 120 ml of 1 N KOH in isopropanol was added. The reaction was refluxed at 80 °C for 3 days. The color of the reaction gradually changed from yellow to colorless. The solvent was evaporated to get the crude mixture. 0.9 g of ethyl 3-aminopropanoate and 90 mL acetic acid were added to the resultant crude mixture and refluxed at 90 °C. The progress of the reaction was monitored by thin layer chromatography and NMR. After completion of the reaction (2 days), the reaction mixture was cooled down to room temperature and water was added

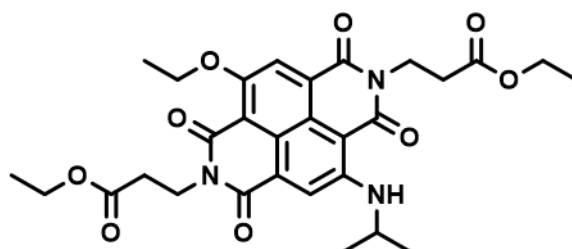
to precipitate the crude product. The obtained precipitate was filtered and washed with methanol to remove the remaining water and acetic acid. The crude mixture was purified using column chromatography with a solvent gradient ranging from 100% chloroform to 5% methanol in chloroform to get 1.67 g of pure product as a yellow solid in 82% yield.

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 298 K):** δ/ppm = 8.46 (s, 2H, H<sup>Ar</sup>), 4.53–4.47 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>, NCH<sub>2</sub>), 4.15 (q, 4H, *J* = 7.1 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.76 (t, 4H, *J* = 7.5 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 1.66 (t, 6H, *J* = 7.0 Hz, CH<sub>3</sub><sup>OEt</sup>), 1.23 (t, 6H, *J* = 7.1 Hz, CH<sub>3</sub><sup>COOEt</sup>).

**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 298 K):** δ/ppm = 171.40, 162.42, 161.11, 160.30, 127.33, 123.82, 119.95, 110.99, 66.53, 60.86, 36.61, 32.76, 29.85, 14.92, 14.30.

**MALDI-TOF (CCA matrix, positive mode) (*m/z*):** calc. for [C<sub>28</sub>H<sub>31</sub>N<sub>2</sub>O<sub>10</sub>]<sup>+</sup>: 555.20, found: 555.66.

## Compound 4



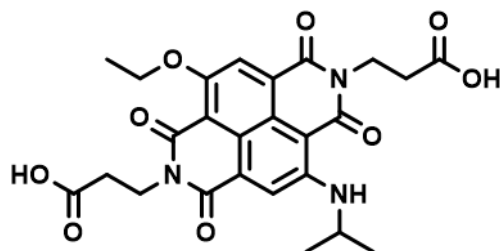
350 mg of **3** was taken in a 100 mL single necked round bottom flask and 10 mL of isopropyl amine and 20 mL of chloroform were added to it and stirred at 50 °C for 12 h. The progress of the reaction was monitored by thin layer chromatography. After completion (12 hours) of the reaction, the excess amine and chloroform was removed under reduced pressure to get the crude product. The crude mixture was purified using column chromatography with a gradient ranging from 100% chloroform to 2% methanol in chloroform to get 250 mg of pure product as a red solid in 70% yield.

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 298 K):** δ/ppm = 9.76 (d, 1H, *J* = 7.7 Hz, NH), 8.31 (s, 1H, H<sup>Ar</sup>), 8.25 (s, 1H, H<sup>Ar</sup>), 4.52–4.42 (m, 6H, CH<sub>2</sub>CH<sub>3</sub>, NCH<sub>2</sub>), 4.18–4.12 (m, 5H, CH<sub>2</sub>CH<sub>3</sub>, NHCH(CH<sub>3</sub>)<sub>2</sub>), 2.76 (t, 4H, *J* = 7.5 Hz, NCH<sub>2</sub>CH), 1.63 (t, 3H, *J* = 6.9 Hz, CH<sub>3</sub><sup>OEt</sup>), 1.41 (d, 6H, *J* = 6.4 Hz, CH<sub>3</sub><sup>iPr</sup>), 1.27–1.22 (m, 6H, CH<sub>3</sub><sup>COOEt</sup>).

**<sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>, 298 K):** δ/ppm = 171.39, 171.34, 165.89, 162.76, 162.67, 161.45, 158.09, 150.11, 127.43, 125.13, 124.33, 121.43, 120.96, 118.24, 112.22, 99.88, 66.12, 60.87, 60.82, 44.66, 36.54, 36.32, 32.88, 32.79, 29.85, 23.34, 14.95, 14.30.

**MALDI-TOF (CCA matrix, positive mode) (*m/z*):** calc. for [C<sub>28</sub>H<sub>34</sub>N<sub>3</sub>O<sub>9</sub>]<sup>+</sup>: 568.23, found: 568.11.

## Compound 5



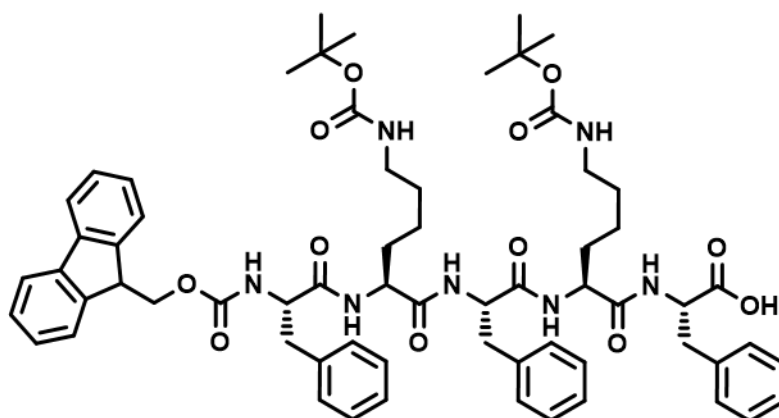
30 ml of TFA and 10 mL of water were added to 180 mg of **4** and stirred at 80 °C for 12 h. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction (12 hours), water and TFA were removed under reduced pressure to get the crude product. The crude product was washed with methanol to remove the excess water and TFA and dried under reduced pressure to get 132 mg of the pure product as a red solid in 83% yield.

**<sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K):**  $\delta$ /ppm = 12.42 (s, 2H, COOH), 9.47 (d, 1H, *J* = 7.4 Hz, NH), 7.76 (s, 1H, *H*<sup>Ar</sup>), 7.75 (s, 1H, *H*<sup>Ar</sup>), 4.25–3.96 (m, 7H, CH<sub>2</sub>CH<sub>3</sub>, NCH<sub>2</sub>, NHCH(CH<sub>3</sub>)<sub>2</sub>), 2.56 (t, 3H, *J* = 7.9 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 1.50 (t, 3H, *J* = 6.9 Hz, CH<sub>3</sub>O<sup>Et</sup>), 1.38 (d, *J* = 6.3 Hz, 6H, CH<sub>3</sub><sup>iPr</sup>).

**<sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, 298 K):**  $\delta$ /ppm = 172.39, 172.35, 164.66, 161.32, 161.10, 159.53, 156.59, 148.60, 126.20, 123.49, 122.42, 119.83, 119.07, 116.48, 110.36, 98.16, 65.08, 43.98, 35.88, 31.89, 22.68, 14.57.

**MALDI-TOF (CCA matrix, positive mode) (*m/z*):** calc. for [C<sub>25</sub>H<sub>26</sub>N<sub>3</sub>O<sub>9</sub>]<sup>+</sup>: 512.17, found: 512.49.

## Compound 7



Fmoc-protected phenylalanine (0.62 g, 1.6 mmol, 2.0 eq.) to be coupled to the 2-chlorotrityl chloride resin (0.5 g, 1.0-1.6 mmol/g capacity, 1.0 eq.) was dissolved in dry DCM and DMF (5:1, 12 mL). The dissolved amino acid was added to the reaction vessel containing the resin under an argon atmosphere followed by the addition of DIPEA (331 mg, 1.6 mmol, 2.0 eq.). The reaction mixture was shaken for 5 min. Afterwards, DIPEA (465 mg, 2.4 mmol, 3.0 eq.) was added and the reaction mixture was shaken for 1 h, treated with MeOH (1 mL/g resin) and subsequently shaken for another 15 min. The vessel was



drained and the resin was washed three times consecutively with 20 mL of DCM, DMF, DCM and MeOH. The resin was dried *in vacuo* overnight.

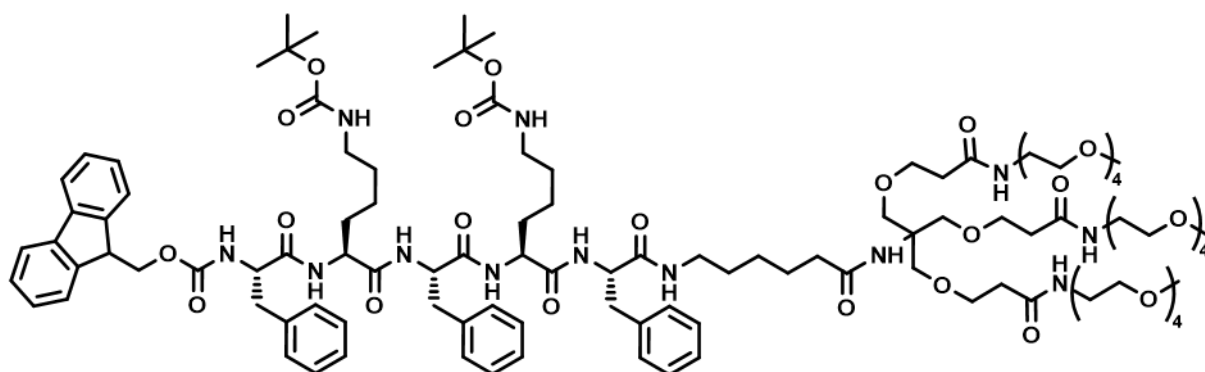
The dried beads were swollen in a 1:1 mixture of DCM and DMF for 10 min while shaking the reaction vessel. After sucking off the solution, piperidine (20 v% in DMF) was added and the vessel was shaken for 10 min. After draining of the vessel the beads were washed two times with DMF and the deprotection was repeated two times prior to the next coupling step. After the third deprotection, the resin was consecutively washed two times with DMF, DCM and DMF. Next, the resin was treated with a solution of the corresponding protected amino acid (0.4 mM, 4.0 eq.), HBTU (0.4 mM, 4.0 eq.), HOBt (0.4 mM, 4.0 eq.) and DIPEA (0.6 mM, 6.0 eq.) in DMF. After shaking for 1 h, the solution was removed and the resin was washed five times with DMF. This procedure was repeated with the corresponding amino acid for every coupling process, starting with the Fmoc deprotection on the resin. The resin was consecutively washed with DMF and DCM after the last coupling step.

In a final step, the peptide was cleaved from the resin by addition of a mixture of TFE and DCM (1:4, 18 mL). The reaction mixture was shaken for 1 h. The solution was filtrated, collected and the beads were washed two times with DCM (20 mL). The solution was concentrated under reduced pressure and slowly dropped into a solution of cold Et<sub>2</sub>O (45 mL). The obtained precipitate was centrifuged at 4350 rpm for 10 min. The supernatant was removed and the precipitate was washed with Et<sub>2</sub>O (40 mL) two times. The precipitate was dried *in vacuo* overnight to yield a colorless solid. The cleavage procedure was repeated two more times. After lyophilization, 0.81 g of a colorless amorphous solid was in 87.5% yield obtained.

**<sup>1</sup>H-NMR (400 MHz, 296 K, DMSO-*d*<sub>6</sub>):**  $\delta$  / ppm = 12.74 (s, 1H, COOH), 8.13 (d, *J* = 7.7 Hz, 1H, NH<sup>Phe/Lys</sup>), 8.04 (d, *J* = 7.9 Hz, 1H, NH<sup>Phe/Lys</sup>), 7.99 (d, *J* = 8.1 Hz, 1H, NH<sup>Phe/Lys</sup>), 7.94 (d, *J* = 8.1 Hz, 1H, NH<sup>Phe/Lys</sup>), 7.88 (d, *J* = 7.6 Hz, 2H, CH<sup>Fmoc</sup>), 7.66–7.57 (m, 3H, CH<sup>Fmoc</sup>, NH<sup>Phe/Lys</sup>), 7.44–7.37 (m, 3H, CH<sup>Fmoc</sup>), 7.34–7.09 (m, 17H, CH<sup>Phe</sup>, CH<sup>Fmoc</sup>), 6.74 (t, 1H, *J* = 5.6 Hz, CH<sub>2</sub>NH<sup>Boc</sup>), 6.70 (t, 1H, *J* = 5.7 Hz, CH<sub>2</sub>NH<sup>Boc</sup>), 4.55 (td, *J* = 5.7 Hz, 4.4 Hz,  $\alpha$ -CH), 4.44 (td, *J* = 8.1 Hz, 5.3 Hz,  $\alpha$ -CH), 4.31–4.18 (m, 3H, CHCH<sub>2</sub><sup>Fmoc</sup>), 4.16–4.08 (m, 1H,  $\alpha$ -CH), 3.94–3.81 (m, 2H,  $\alpha$ -CH), 3.12–2.67 (m, 10H, CH<sub>2</sub><sup>Phe</sup>, CH<sub>2</sub>NH<sup>Lys</sup>), 1.66–1.13 (m, 30H, CH<sub>2</sub><sup>Lys</sup>, CH<sub>3</sub><sup>Boc</sup>).

**ESI-HRMS (MeOH) (*m/z*):** calc. for [C<sub>64</sub>H<sub>79</sub>N<sub>7</sub>O<sub>12</sub>Na]<sup>+</sup>: 1160.5698, found: 1160.5685.

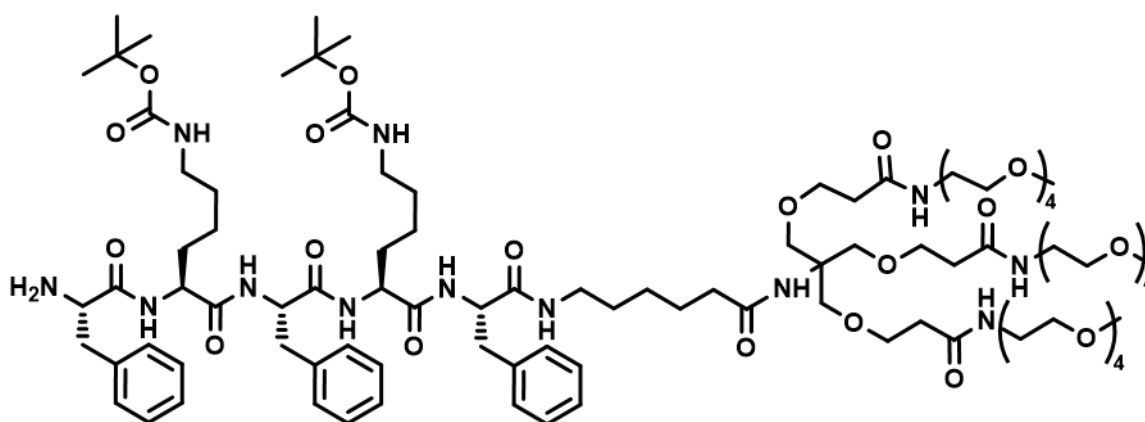
## Compound 8



**7** (508 mg, 447  $\mu\text{mol}$ , 1.3 eq.) was dissolved in DMF (peptide grade) (10 mL). PyBOP (232 mg, 447  $\mu\text{mol}$ , 1.3 eq.) and HOBt (60 mg, 447  $\mu\text{mol}$ , 1.3 eq.) were added. Next, **6** (350 mg, 343  $\mu\text{mol}$ , 1.0 eq.) followed by DIPEA (97 mg, 756  $\mu\text{mol}$ , 2.2 eq.) was added to the solution. The reaction mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the product was purified *via* SEC LH-20 in  $\text{CHCl}_3/\text{MeOH}$  2/1 and again in MeOH to give a colorless amorphous solid of 438 mg in 59% yield after drying *in vacuo*.

**$^1\text{H-NMR}$  (400 MHz, 296 K,  $\text{DMSO-}d_6$ ):**  $\delta$  / ppm = 8.08–7.99 (m, 2H,  $\text{NH}^{\text{Phe/Lys}}$ ), 7.98–7.84 (m, 8H,  $\text{NH}^{\text{Phe/Lys}}$ ,  $\text{CONH}^{\text{OEG}}$ ,  $\text{CONH}^{\text{Ahx}}$ ,  $\text{CH}^{\text{Fmoc}}$ ), 7.66–7.57 (m, 2H,  $\text{CH}^{\text{Fmoc}}$ ), 7.43–7.36 (m, 2H,  $\text{CH}^{\text{Fmoc}}$ ), 7.34–7.10 (m, 17H,  $\text{CH}^{\text{Phe}}$ ,  $\text{CH}^{\text{Fmoc}}$ ), 6.99 (s, 1H,  $\text{NHC}_q$ ), 6.80–6.64 (m, 2H,  $\text{CH}_2\text{NH}^{\text{Boc}}$ ), 4.58–4.49 (m, 1H,  $\alpha\text{-CH}$ ), 4.49–4.40 (m, 1H,  $\alpha\text{-CH}$ ), 4.31–4.04 (m, 6H,  $\alpha\text{-CH}$ ,  $\text{CHCH}_2^{\text{Fmoc}}$ ), 3.60–3.37 (m, 54H,  $\text{CH}_2\text{OCH}_2^{\text{Tris}}$ ,  $\text{CH}_2^{\text{OEG}}$ ), 3.24 (s, 9H,  $\text{CH}_3^{\text{OEG}}$ ), 3.23–3.17 (m, 6H,  $\text{NCH}_2\text{CH}_2\text{O}$ ), 3.11–2.65 (m, 12H,  $\text{NHCH}_2^{\text{Ahx}}$ ,  $\text{CH}_2^{\text{Phe}}$ ,  $\text{CH}_2\text{NH}^{\text{Lys}}$ ), 2.30 (t,  $J = 6.4$  Hz, 6H,  $\text{CH}_2\text{CH}_2\text{CO}^{\text{Tris}}$ ), 2.04 (t,  $J = 7.5$  Hz, 2H,  $\text{CH}_2\text{CO}^{\text{Ahx}}$ ), 1.65–1.08 (m, 36,  $\text{CH}_2^{\text{Ahx}}$ ,  $\text{CH}_2^{\text{Lys}}$ ,  $\text{CH}_3^{\text{Boc}}$ ).

## Compound 9

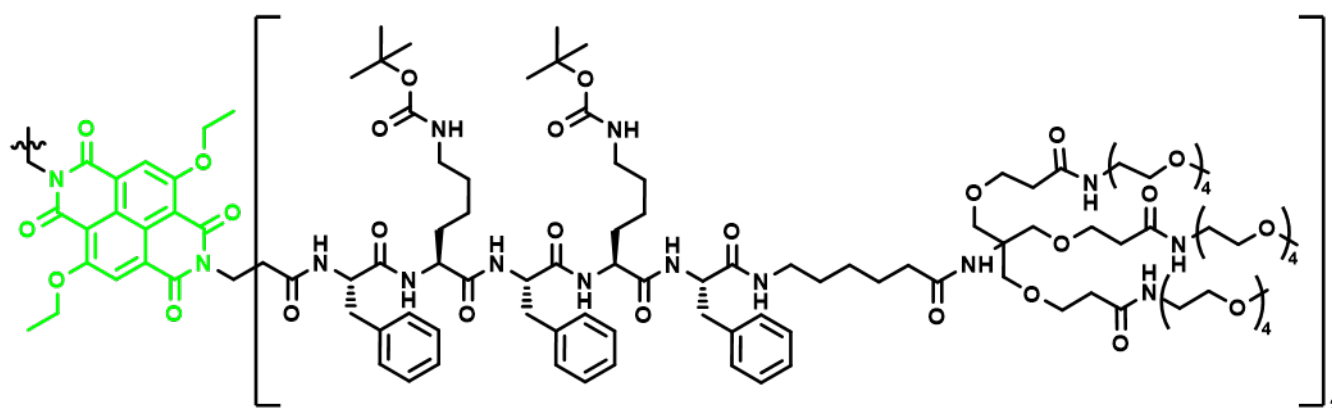


**8** (436 mg, 204  $\mu\text{mol}$ ) was dissolved in 10 v% piperidine in DMF (peptide grade) and stirred at room temperature for 2 h. The solution was concentrated under reduced pressure and purified *via* SEC LH-20 in MeOH to give a colorless amorphous solid of 369 mg in 94% yield after drying *in vacuo*.

**<sup>1</sup>H-NMR (400 MHz, 296 K, DMSO-*d*<sub>6</sub>):**  $\delta$  / ppm = 8.15–8.04 (m, 2H, NH<sup>Phe/Lys</sup>), 8.01–7.82 (m, 6H, NH<sup>Phe/Lys</sup>, CONH<sup>OEG</sup>, CONH<sup>Ahx</sup>), 7.29–7.11 (m, 15H, CH<sup>Phe</sup>), 6.98 (s, 1H, NHC<sub>q</sub>), 6.78–6.68 (m, 2H, CH<sub>2</sub>NH<sup>Boc</sup>), 4.54–4.37 (m, 2H,  $\alpha$ -CH), 4.29–4.14 (m, 2H,  $\alpha$ -CH), 3.58–3.36 (m, 55H, CH<sub>2</sub>OCH<sub>2</sub><sup>Tris</sup>, CH<sub>2</sub><sup>OEG</sup>,  $\alpha$ -CH), 3.23 (s, 9H, CH<sub>3</sub><sup>OEG</sup>), 3.22–3.14 (m, 6H, NCH<sub>2</sub>CH<sub>2</sub>O), 3.09–2.70 (m, 12H, NHCH<sub>2</sub><sup>Ahx</sup>, CH<sub>2</sub><sup>Phe</sup>, CH<sub>2</sub>NH<sup>Lys</sup>), 2.29 (t, *J* = 6.4 Hz, 6H, CH<sub>2</sub>CH<sub>2</sub>CO<sup>Tris</sup>), 2.03 (t, *J* = 7.5 Hz, 2H, CH<sub>2</sub>CO<sup>Ahx</sup>), 1.58–1.02 (m, 36, CH<sub>2</sub><sup>Ahx</sup>, CH<sub>2</sub><sup>Lys</sup>, CH<sub>3</sub><sup>Boc</sup>).

**ESI-HRMS (MeOH) (*m/z*):** calc. for [C<sub>95</sub>H<sub>158</sub>N<sub>12</sub>O<sub>28</sub>Na<sub>2</sub>]<sup>2+</sup>: 980.5548, found: 980.5539.

## Compound 10

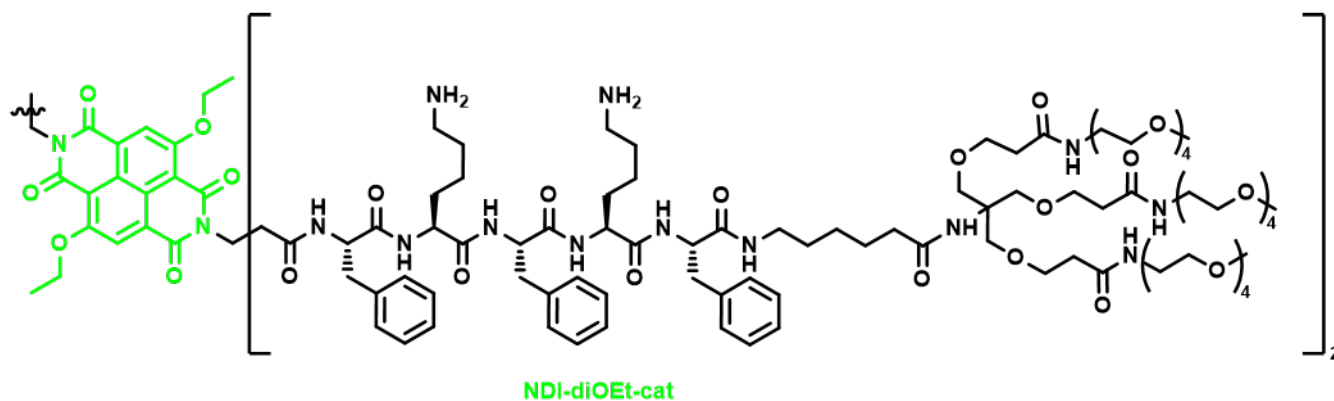


In a round bottom flask, 48 mg of HBTU, 11 mg of **2** and 11.2 mg DIPEA were suspended in 5 mL of DMF and stirred at room temperature for 30 min. After 30 min, 100 mg of **9** dissolved in 5 mL of DMF were added dropwise to the reaction mixture. The progress of the reaction was monitored by thin layer chromatography. After 3 d, DMF was removed under reduced pressure and the crude mixture was purified using size exclusion chromatography (SX-1 biobeads, chloroform) to get 42 mg of the pure product as a yellow sticky solid in 40% yield.

**<sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>OD, 298 K):**  $\delta$ /ppm = 8.42 (s, 2H, CH<sup>NDI</sup>), 7.33–7.06 (m, 30H, CH<sup>Phe</sup>), 4.55–4.05 (m, 18H,  $\alpha$ -CH, OCH<sub>2</sub><sup>NDI</sup>, NCH<sub>2</sub><sup>NDI</sup>), 3.70–3.50 (m, 108H, CH<sub>2</sub>OCH<sub>2</sub><sup>Tris</sup>, CH<sub>2</sub><sup>OEG</sup>), 3.38–3.24 (m, 30H, CH<sub>3</sub><sup>OEG</sup>, NCH<sub>2</sub>CH<sub>2</sub>O), 3.17–2.67 (m, 28H, NHCH<sub>2</sub><sup>Ahx</sup>, CH<sub>2</sub><sup>Phe</sup>,  $\epsilon$ -CH<sub>2</sub><sup>Lys</sup>, CH<sub>2</sub>N<sup>NDI</sup>), 2.43 (t, 12H, *J* = 6.0 Hz, CH<sub>2</sub>CH<sub>2</sub>CO<sup>Tris</sup>), 2.16 (t, *J* = 7.5 Hz, 4H, CH<sub>2</sub>CO<sup>Ahx</sup>), 1.78–1.18 (m, 78H, CH<sub>2</sub><sup>Ahx</sup>, CH<sub>2</sub><sup>Lys</sup>, CH<sub>3</sub><sup>Boc</sup>, CH<sub>3</sub><sup>OEt</sup>);

**MALDI-TOF (DCTB matrix, linear positive mode) (*m/z*):** calc. for [C<sub>214</sub>H<sub>334</sub>N<sub>26</sub>O<sub>64</sub>Na]<sup>+</sup>: 4318.13, found: 4319.57.

## Compound 11

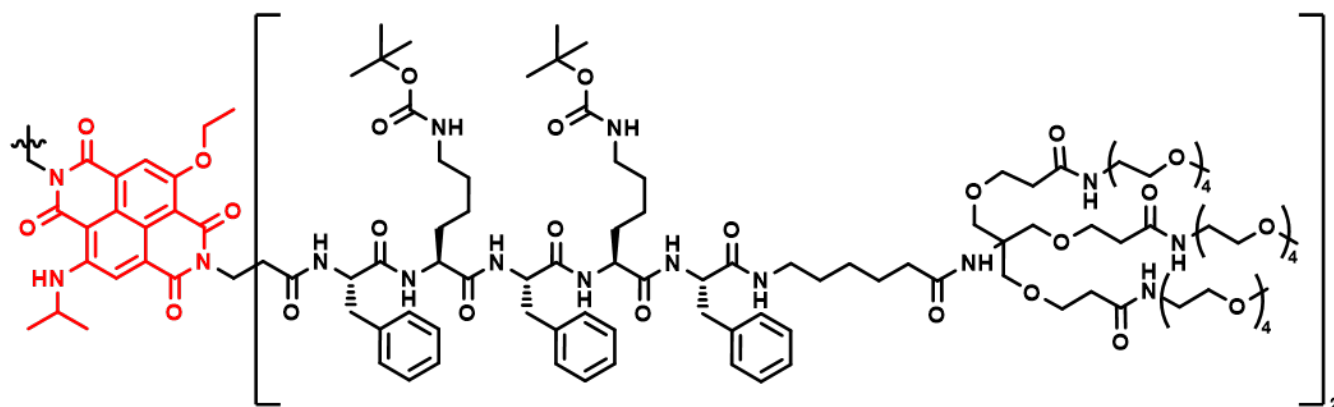


40 mg of **10** was dissolved in a 25 mL round bottom flask in 8 mL of a mixture of 1:1 TFA:DCM and stirred at room temperature for 4 h. The solvent was evaporated under reduced pressure to get 40 mg of **NDI-diOEt-cat** as a yellow solid in quantitative yields.

**<sup>1</sup>H-NMR (600 MHz, DMSO-*d*<sub>6</sub>, 298 K):**  $\delta$ /ppm = 8.35 (s, 2H, CH<sup>NDI</sup>), 8.28–8.11 (m, 4H, NH<sup>Phe/Lys</sup>), 7.98–7.80 (m, 14H, CONH<sup>Ahx</sup>, NH<sup>Phe/Lys</sup>, CONH<sup>OEG</sup>), 7.75–7.60 (m, 12H, CH<sub>2</sub>NH<sub>3</sub>), 7.28–7.09 (m, 30H, CH<sup>Phe</sup>), 6.99 (s, 2H, NHC<sub>q</sub>), 4.60–4.41 (m, 10H,  $\alpha$ -CH, OCH<sub>2</sub><sup>NDI</sup>), 4.25–4.05 (m, 8H,  $\alpha$ -CH, NCH<sub>2</sub><sup>NDI</sup>), 3.57–3.37 (m, 108H, CH<sub>2</sub>OCH<sub>2</sub><sup>Tris</sup>, CH<sub>2</sub><sup>OEG</sup>), 3.23 (s, 18H, CH<sub>3</sub><sup>OEG</sup>), 3.21–3.17 (m, 12H, NCH<sub>2</sub>CH<sub>2</sub>O), 3.09–2.67 (m, 28H, CH<sub>2</sub><sup>Phe</sup>, NHCH<sub>2</sub><sup>Ahx</sup>,  $\epsilon$ -CH<sub>2</sub><sup>Lys</sup>, CH<sub>2</sub><sup>NDI</sup>), 2.29 (t, 12H, *J* = 6.5 Hz, CH<sub>2</sub>CH<sub>2</sub>CO<sup>Tris</sup>), 2.04 (t, 4H, *J* = 7.5 Hz, CH<sub>2</sub>CO<sup>Ahx</sup>), 1.64–1.09 (m, 42H, CH<sub>2</sub><sup>Ahx</sup>, CH<sub>2</sub><sup>Lys</sup>, CH<sub>3</sub><sup>OEt</sup>);

**MALDI-TOF (DCTB matrix, linear positive mode) (*m/z*):** calc. for [C<sub>194</sub>H<sub>303</sub>N<sub>26</sub>O<sub>56</sub>]<sup>+</sup>: 3893.17, found 3894.93.

## Compound 12

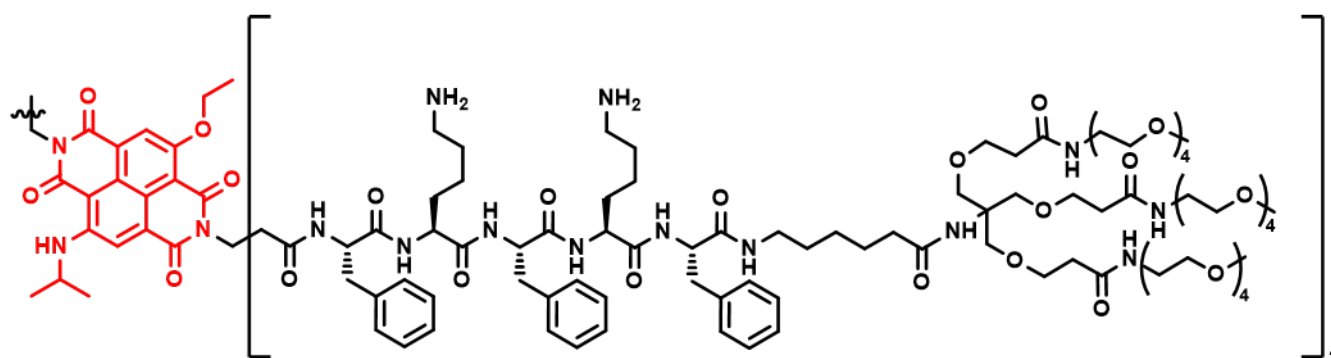


**5** (21.35 mg, 0.042 mmol, 1.0 eq.) and HBTU (63.70 mg, 0.168 mmol, 4.0 eq.) were suspended in 8 ml DMF (peptide grade). DIPEA (22.00  $\mu$ L, 0.126 mmol, 3.0 eq.) was added and the reaction was stirred at room temperature under inert atmosphere for 2 h. Compound **9** (200.00 mg, 0.104 mmol, 2.5 eq.),

dissolved in 2 ml DMF (peptide grade), was added and the solution was stirred at room temperature for 2 d. Volatiles were removed under reduced pressure and the residue was purified *via* size exclusion chromatography to get 83.50 mg of pure purple product in 46% yield. (SX-1 Bio-Beads<sup>TM</sup>-Chloroform) **<sup>1</sup>H-NMR (600 MHz, DMSO-*d*<sub>6</sub>, 298 K):**  $\delta$ /ppm = 9.70 (d, 1H, *J* = 6.8 Hz, NH<sup>iPr</sup>), 8.25–8.21 (m, 2H, NH<sup>Phe/Lys</sup>), 8.20 (s, 1H, CH<sup>NDI</sup>), 8.12 (s, 1H, CH<sup>NDI</sup>), 8.09–8.03 (m, 2H, NH<sup>Phe/Lys</sup>), 8.02–7.96 (m, 2H, CONH<sup>Ahx</sup>), 7.94–7.85 (m, 10H, NH<sup>Phe/Lys</sup>, CONH<sup>OEG</sup>), 7.85–7.80 (m, 2H, NH<sup>Phe/Lys</sup>), 7.25–7.10 (m, 30H, CH<sup>Phe</sup>), 7.00–6.96 (m, 2H, NHC<sub>q</sub>), 6.72 (t, 4H, *J* = 5.3 Hz, CH<sub>2</sub>NH<sup>Boc</sup>), 4.57–4.48 (m, 4H,  $\alpha$ -CH), 4.46–4.40 (m, 2H,  $\alpha$ -CH), 4.39–4.32 (m, 2H,  $\alpha$ -CH), 4.21–4.06 (m, 9H,  $\alpha$ -CH, NCH<sub>2</sub><sup>NDI</sup>, NCH<sup>iPr</sup>, CH<sub>2</sub><sup>OEt</sup>), 3.58–3.37 (m, 108H, CH<sub>2</sub>OCH<sub>2</sub><sup>Tris</sup>, CH<sub>2</sub><sup>OEG</sup>), 3.23 (s, 18H, CH<sub>3</sub><sup>OEG</sup>), 3.21–3.17 (m, 12H, NCH<sub>2</sub>CH<sub>2</sub>O), 3.08–2.66 (m, 28H, NHCH<sub>2</sub><sup>Ahx</sup>, CH<sub>2</sub><sup>Phe</sup>, CH<sub>2</sub>NH<sup>Lys</sup>, CH<sub>2</sub>N<sup>NDI</sup>), 2.29 (t, 12H, *J* = 6.5 Hz, CH<sub>2</sub>CH<sub>2</sub>CO<sup>Tris</sup>), 2.03 (t, *J* = 7.6 Hz, 4H, CH<sub>2</sub>CO<sup>Ahx</sup>), 1.62–1.05 (m, 81H, CH<sub>2</sub><sup>Ahx</sup>, CH<sub>2</sub><sup>Lys</sup>, CH<sub>3</sub><sup>Boc</sup>, CH<sub>3</sub><sup>iPr</sup>, CH<sub>3</sub><sup>OEt</sup>);

**MALDI-TOF (CCA matrix, positive mode) (*m/z*):** calc. for [C<sub>215</sub>H<sub>337</sub>N<sub>27</sub>O<sub>63</sub>Na]<sup>+</sup>: 4328.39, found 4328.94.

### Compound 13



**NDI-OEtIPA-cat**

Compound **12** (80 mg, 0.018 mmol, 1.0 eq.) was dissolved in 10 ml of a 1:1 mixture of TFA and DCM. The solution was stirred at room temperature for 3 h. Solvents were removed under reduced pressure and remaining TFA was co-distilled with toluene. The product was dried *in vacuo* to get 80 mg of the pure purple product in quantitative yields.

**<sup>1</sup>H-NMR (600 MHz, DMSO-*d*<sub>6</sub>, 298 K):**  $\delta$ /ppm = 9.71 (d, 1H, *J* = 7.3 Hz, NH<sup>iPr</sup>), 8.29–8.10 (m, 6H, NH<sup>Phe/Lys</sup>, CH<sup>NDI</sup>), 7.98–7.80 (m, 14H, CONH<sup>Ahx</sup>, NH<sup>Phe/Lys</sup>, CONH<sup>OEG</sup>), 7.75–7.60 (m, 12H, CH<sub>2</sub>NH<sub>3</sub>), 7.25–7.10 (m, 30H, CH<sup>Phe</sup>), 6.99 (s, 2H, NHC<sub>q</sub>), 4.60–4.42 (m, 6H,  $\alpha$ -CH), 4.40–4.34 (m, 2H,  $\alpha$ -CH), 4.30–4.05 (m, 9H,  $\alpha$ -CH, NCH<sub>2</sub><sup>NDI</sup>, NCH<sup>iPr</sup>, CH<sub>2</sub><sup>OEt</sup>), 3.57–3.37 (m, 108H, CH<sub>2</sub>OCH<sub>2</sub><sup>Tris</sup>, CH<sub>2</sub><sup>OEG</sup>), 3.23 (s, 18H, CH<sub>3</sub><sup>OEG</sup>), 3.21–3.17 (m, 12H, NCH<sub>2</sub>CH<sub>2</sub>O), 3.10–2.66 (m, 28H, CH<sub>2</sub><sup>Phe</sup>, CONHCH<sub>2</sub><sup>Ahx</sup>,  $\epsilon$ -CH<sub>2</sub><sup>Lys</sup>, CH<sub>2</sub>N<sup>NDI</sup>), 2.29 (t, 12H, *J* = 6.5 Hz, CH<sub>2</sub>CH<sub>2</sub>CO<sup>Tris</sup>), 2.04 (t, 4H, *J* = 7.5 Hz, CH<sub>2</sub>CO<sup>Ahx</sup>), 1.64–1.00 (m, 45H, CH<sub>2</sub><sup>Ahx</sup>, CH<sub>2</sub><sup>Lys</sup>, CH<sub>3</sub><sup>iPr</sup>, CH<sub>3</sub><sup>OEt</sup>);

**MALDI-TOF (DCTB matrix, linear positive mode) (*m/z*):** calc. for [C<sub>195</sub>H<sub>306</sub>N<sub>27</sub>O<sub>55</sub>]<sup>+</sup>: 3906.20, found 3907.21.

### 3. Experimental Procedure

**NDI-diOEt-cat** and **NDI-OEtIPA-cat** stock solutions ( $5 \times 10^{-3}$  M) were prepared in pH 7 water and the required volume was added to the desired pH solution to adjust the final concentration. Citric acid/sodium citrate buffer (Ca/Na<sub>3</sub>C) was used as a source of acidic pH and Tris-HCl was used as source of basic pH. TEM Samples were prepared by placing a drop of the solution on carbon coated copper grids followed by drying at room temperature in desiccator (samples were negatively stained with uranyl acetate).

### 4. Supporting Figures

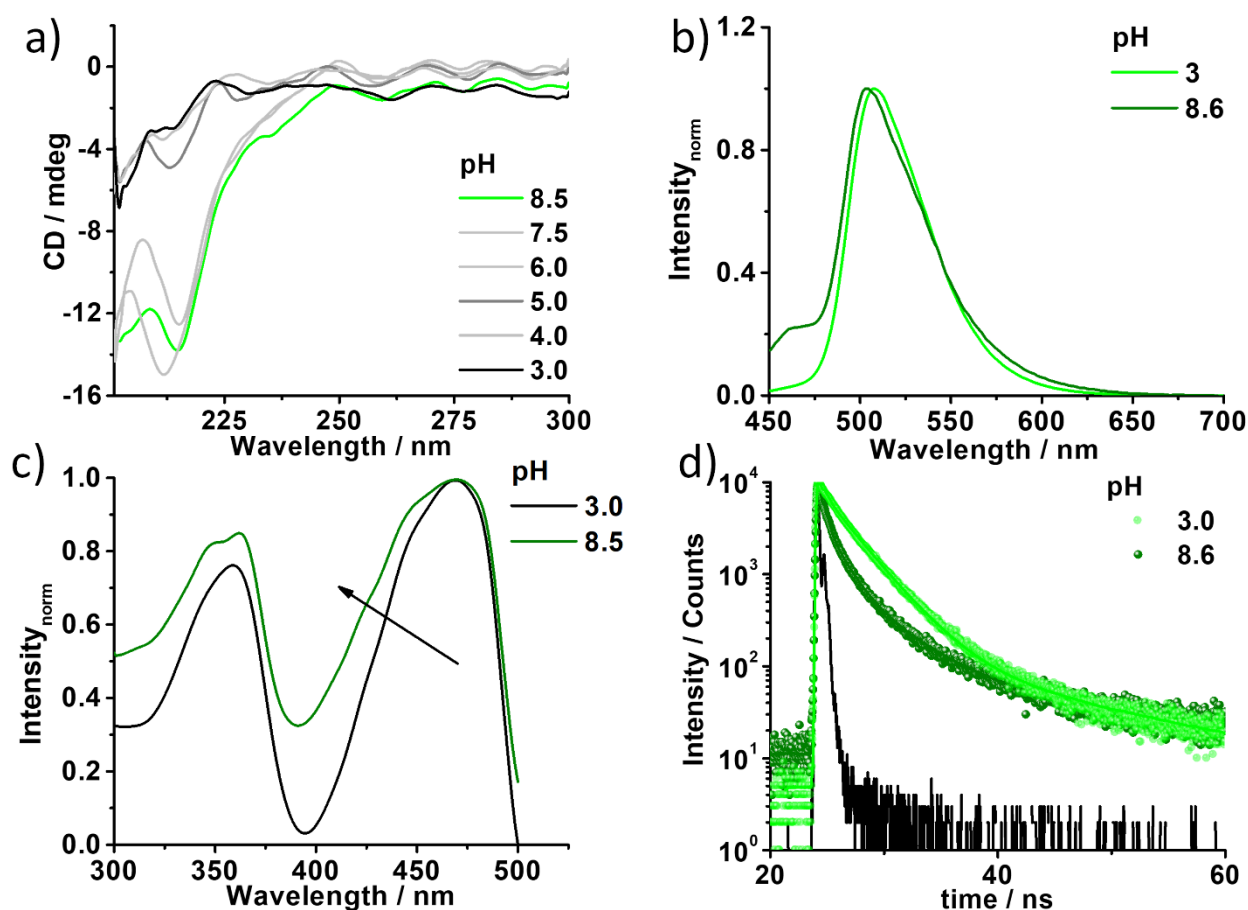


Figure SI 1. a) pH-dependent CD spectra of **NDI-diOEt-cat** from 200–300 nm showing  $\beta$ -sheet formation at pH = 3. b) Normalized emission spectra ( $\lambda_{\text{ex}} = 430$  nm) of monomeric (pH = 3) and self-assembled (pH = 8.6) **NDI-diOEt-cat** showing a slight broadening in self-assembled state. c) Excitation spectra ( $\lambda_{\text{coll}} = 510$  nm) collected for monomeric and self-assembled state of **NDI-diOEt-cat** showing slight

broadening and blue shift for self-assembled state in comparison to monomeric state. d) Time-resolved lifetime decay profile ( $\lambda_{\text{ex}} = 442 \text{ nm}$ ) shows a quenched and different lifetime for self-assembled **NDI-diOEt-cat**, compared to monomers, confirming the emissive nature of the aggregates ( $[\text{NDI-diOEt-cat}] = 5 \times 10^{-5} \text{ M}$ ,  $l = 10 \text{ mm}$ ).

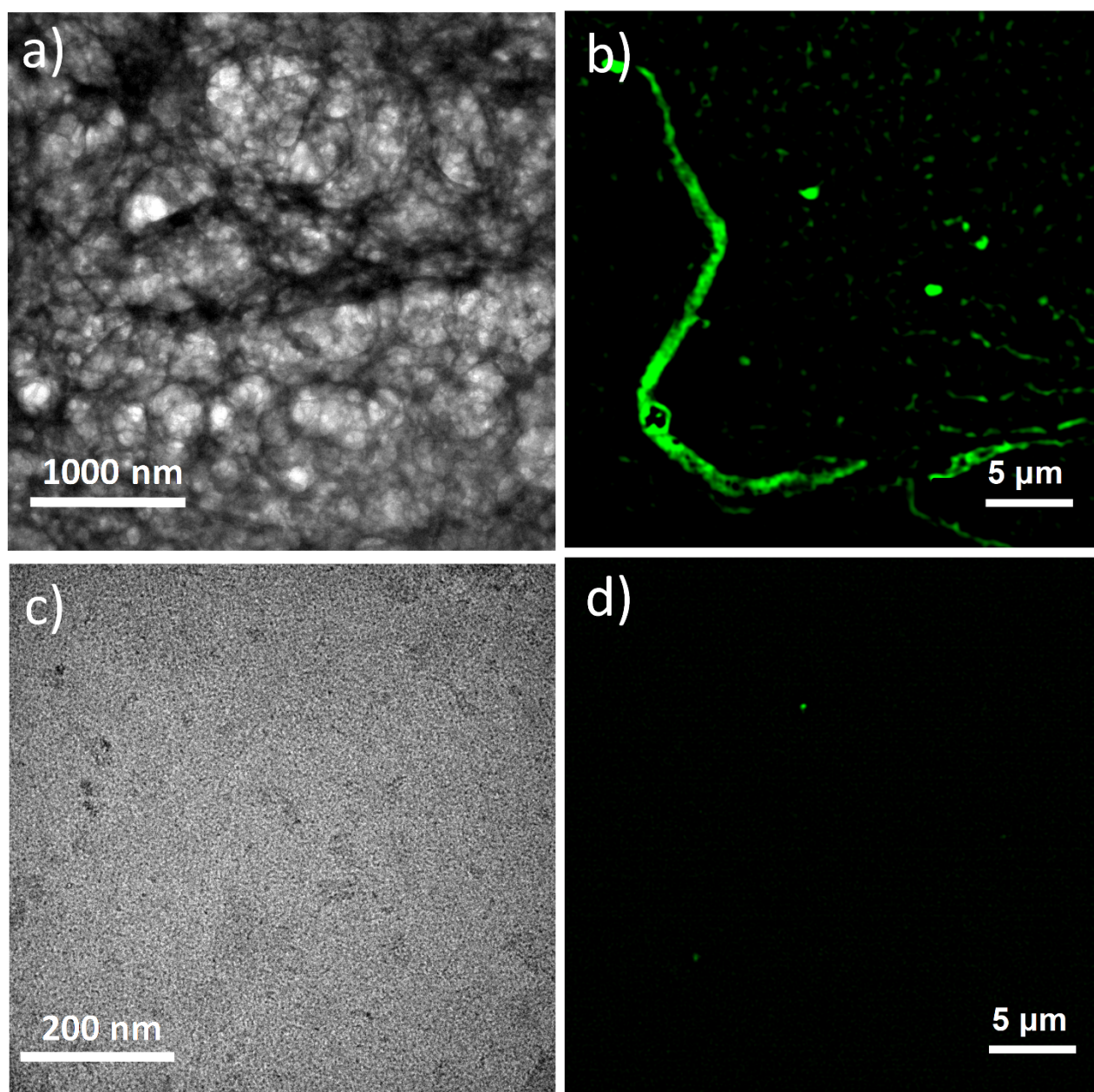


Figure SI 2. Morphological investigation of self-assembled and monomeric **NDI-diOEt-cat** obtained at different pH. TEM samples were prepared by placing a drop of the solution on carbon coated copper grids followed by drying at room temperature in desiccator, samples were stained with uranyl acetate. a) TEM and b) SIM image at pH 8.3 showing the presence of 1D supramolecular polymer. c) TEM and d) SIM image at pH 3 shows the absence of any self-assembled structures ( $[\text{NDI-diOEt-cat}] = 5 \times 10^{-5} \text{ M}$ ).

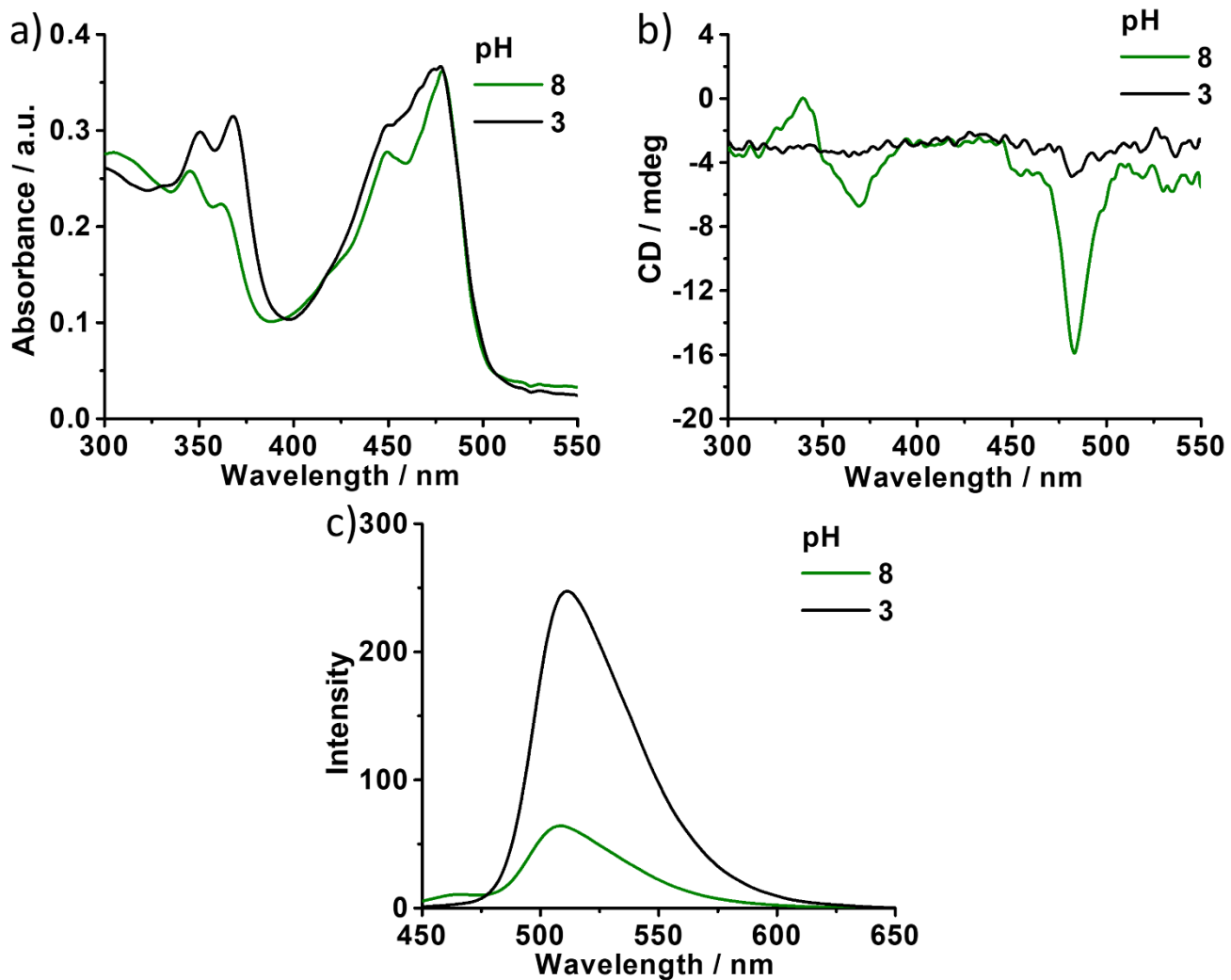


Figure SI 3. pH-induced dis-assembly of **NDI-diOEt-cat** supramolecular polymers. a) Absorption spectra, b) CD spectra, and c) emission spectra ( $\lambda_{\text{ex}} = 430 \text{ nm}$ ) ( $[\text{NDI-diOEt-cat}] = 5 \times 10^{-5} \text{ M}$ ,  $l = 10 \text{ mm}$ ).



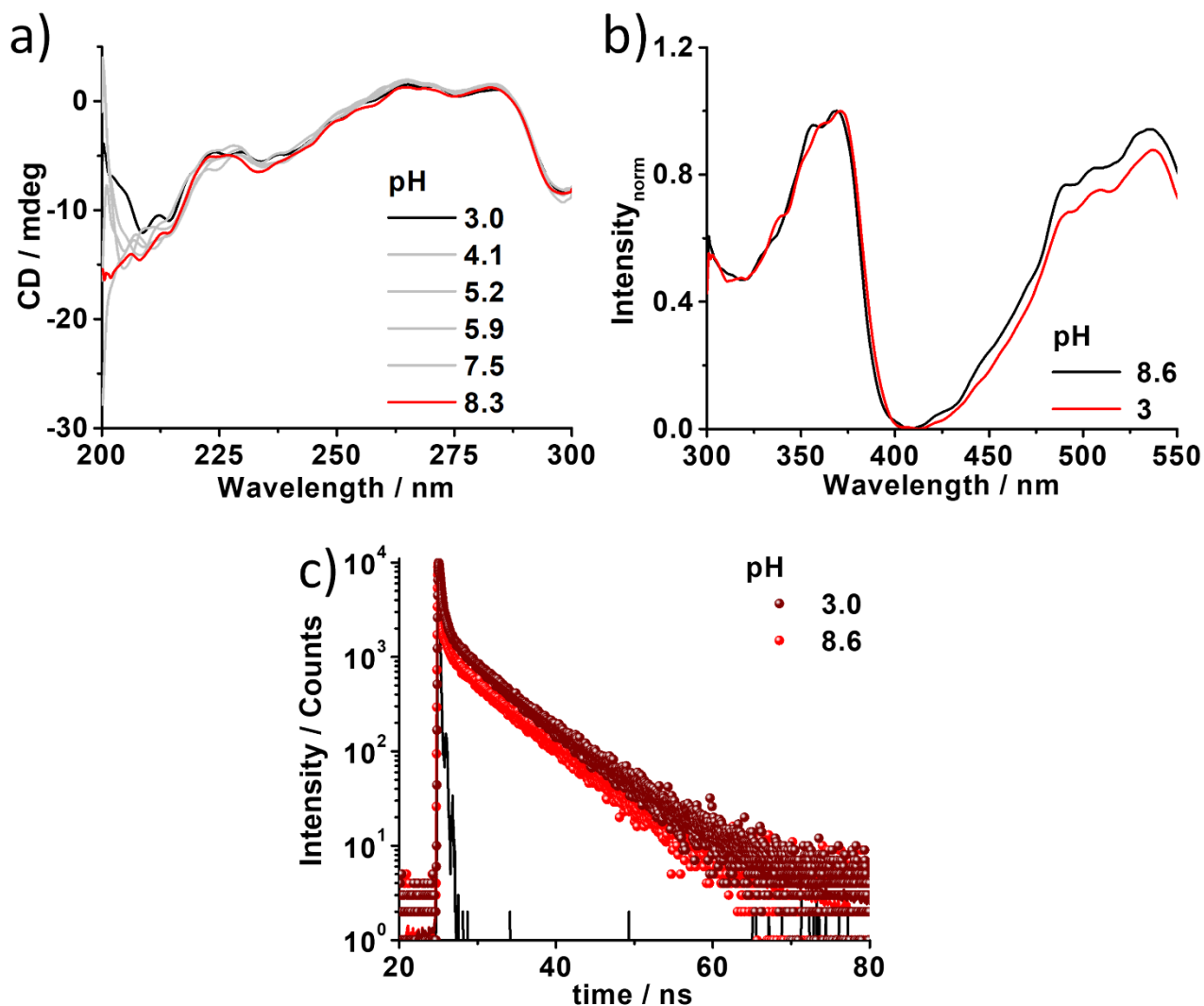


Figure SI 4. a) pH-Dependent CD spectra of **NDI-OEtIPA-cat** from 200–300 nm showing a  $\beta$ -sheet conformation of the peptide indicating its self-assembly ( $l = 2$  mm). b) Excitation spectra ( $\lambda_{\text{coll}} = 580$  nm) measured at low (pH = 3) and high pH (pH = 8.6) matches with each other which shows the emission in both the pH is coming from same species. c) Time-resolved life time decay profile showing a sharp decay due to self-assembled  $\pi$ - $\pi$  stacked NDI chromophores, which increases on going from a low pH (pH = 3) to high pH (pH = 8.6) ( $[\text{NDI-OEtIPA-cat}] = 2.5 \times 10^{-5}$  M).

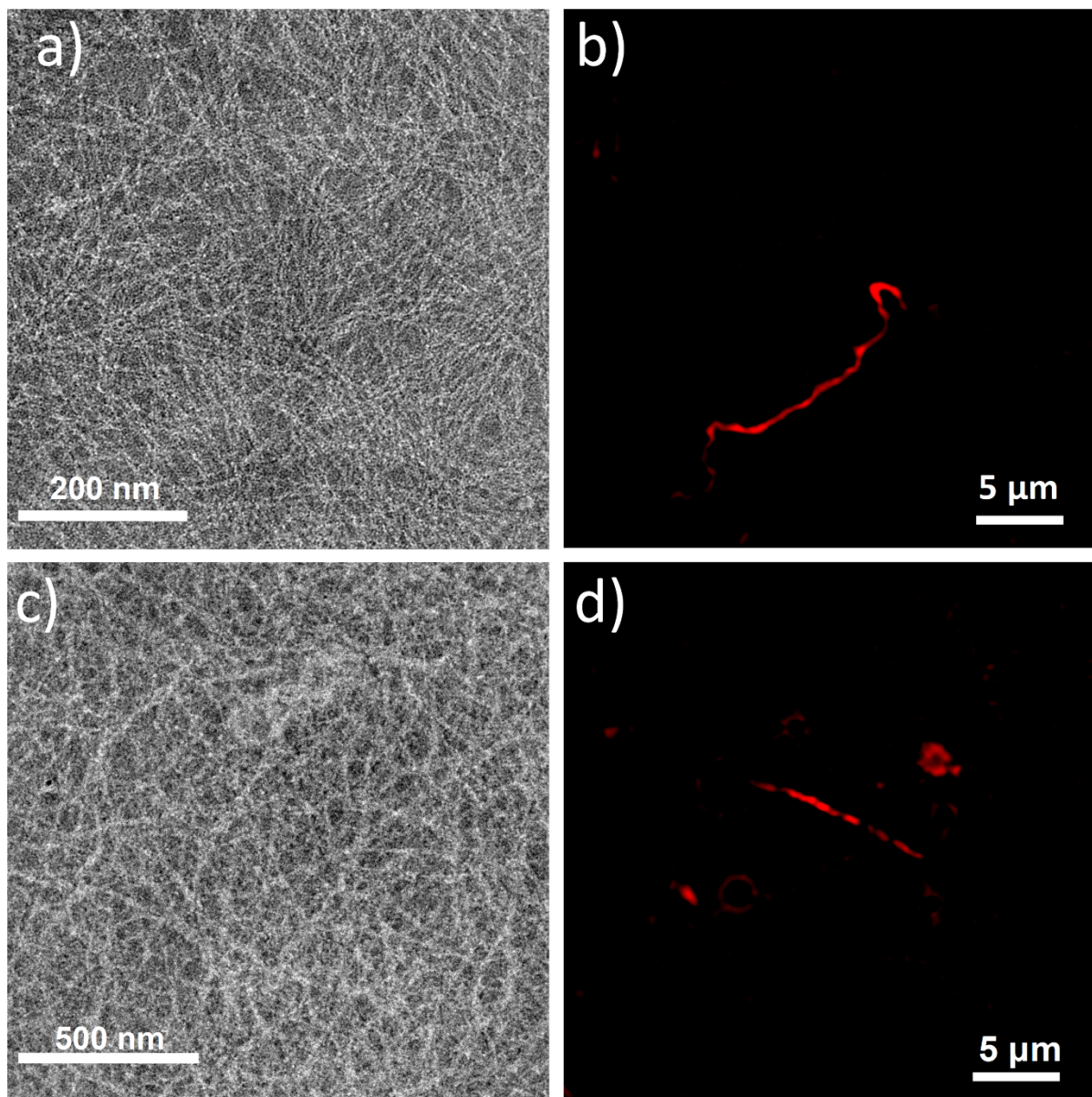


Figure SI 5. Morphological investigation of **NDI-OEtIPA-cat**. TEM samples were prepared by placing a drop of the solution on carbon coated copper grids followed by drying at room temperature in desiccator, samples were stained with uranyl acetate. TEM images at a) pH 8 and c) pH 3 and SIM image at b) pH 8 and d) pH 3 show the presence of 1D supramolecular polymers. Morphological investigations suggest **NDI-OEtIPA-cat** remains assembled at acidic and basic pH values ( $[\text{NDI-OEtIPA-cat}] = 2.5 \times 10^{-5} \text{ M}$ ).

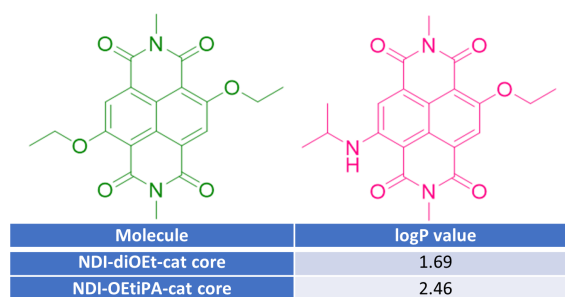


Figure SI 6. Calculated logP values using online calculation service at [www.molinspiration.com](http://www.molinspiration.com) suggests higher hydrophobicity in case of **NDI-OEtIPA-cat** than that of **NDI-diOEt-cat**. Since the peptide segments for both the molecules are same, we assume that the change in hydrophobicity should not depend on them. Hence, we have calculated the logP values using the truncated NDI core with different substitution on it.

## 5. Supporting NMR-Spectra

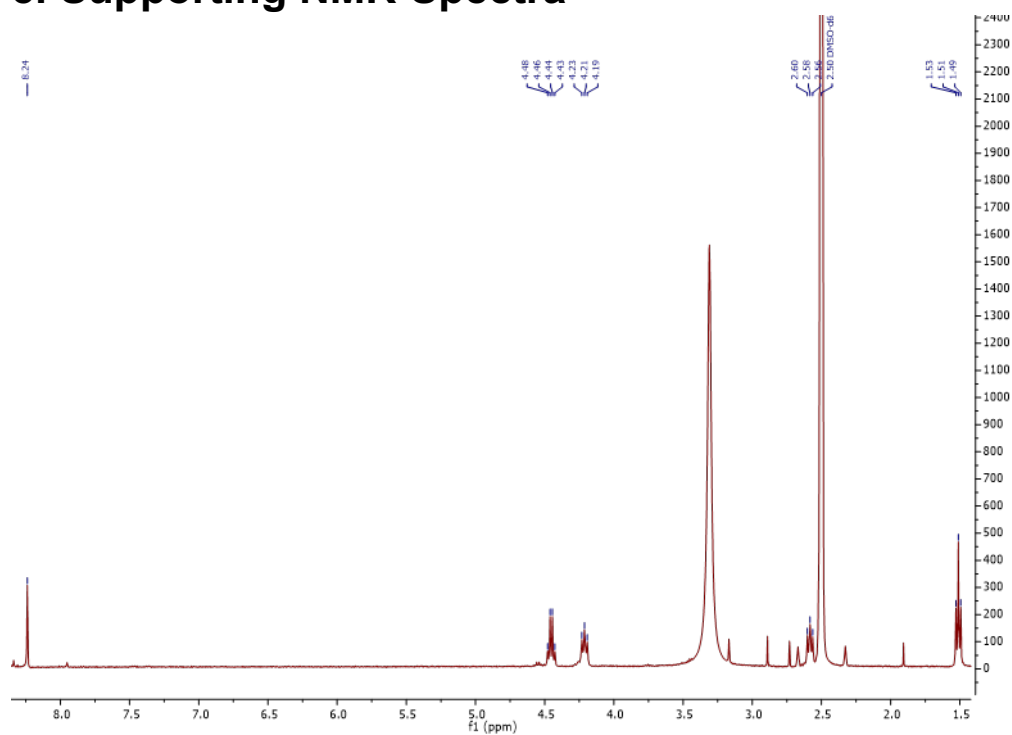


Figure SI 7. <sup>1</sup>H-NMR spectrum of **2** (400 MHz, DMSO-*d*<sub>6</sub>, 298 K).

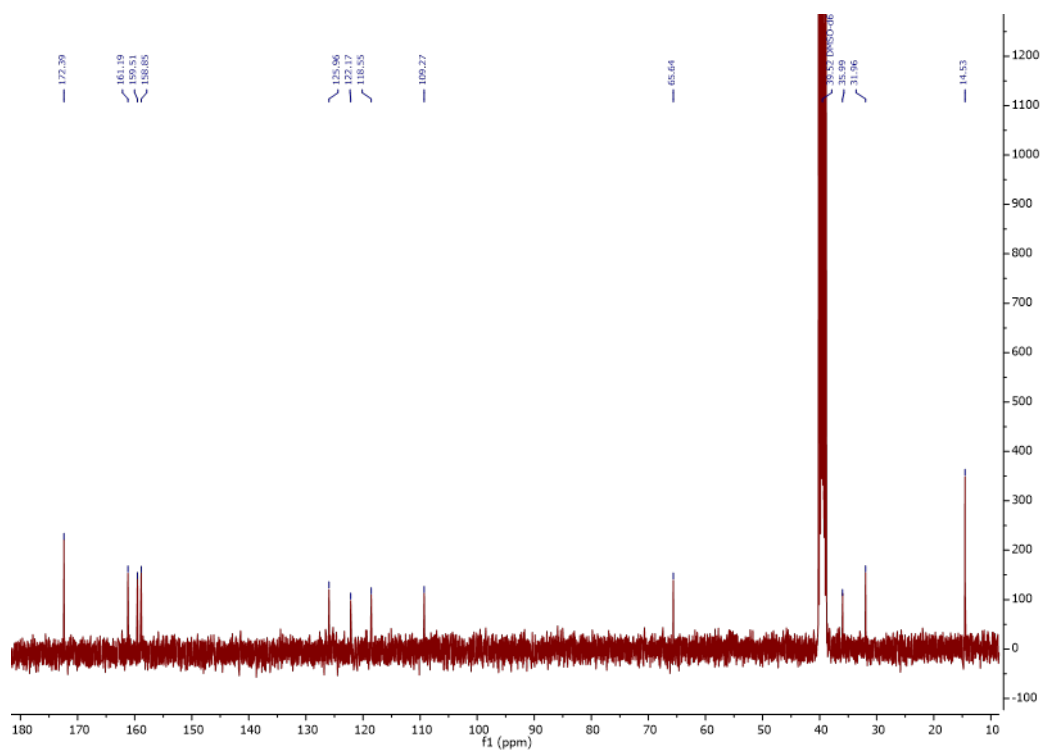


Figure SI 8. <sup>13</sup>C-NMR spectrum of **2** (100 MHz, DMSO-*d*<sub>6</sub>, 298 K).

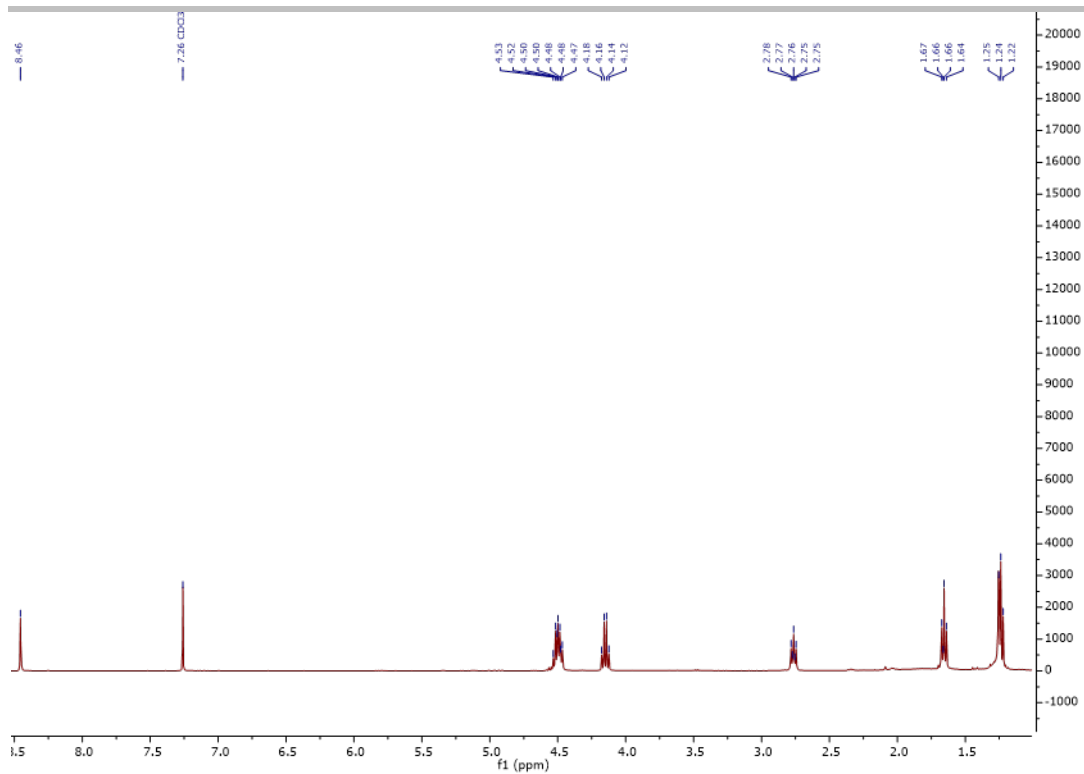


Figure SI 9.  $^1\text{H-NMR}$  spectrum of **3** (400 MHz,  $\text{DMSO-}d_6$ , 298 K).

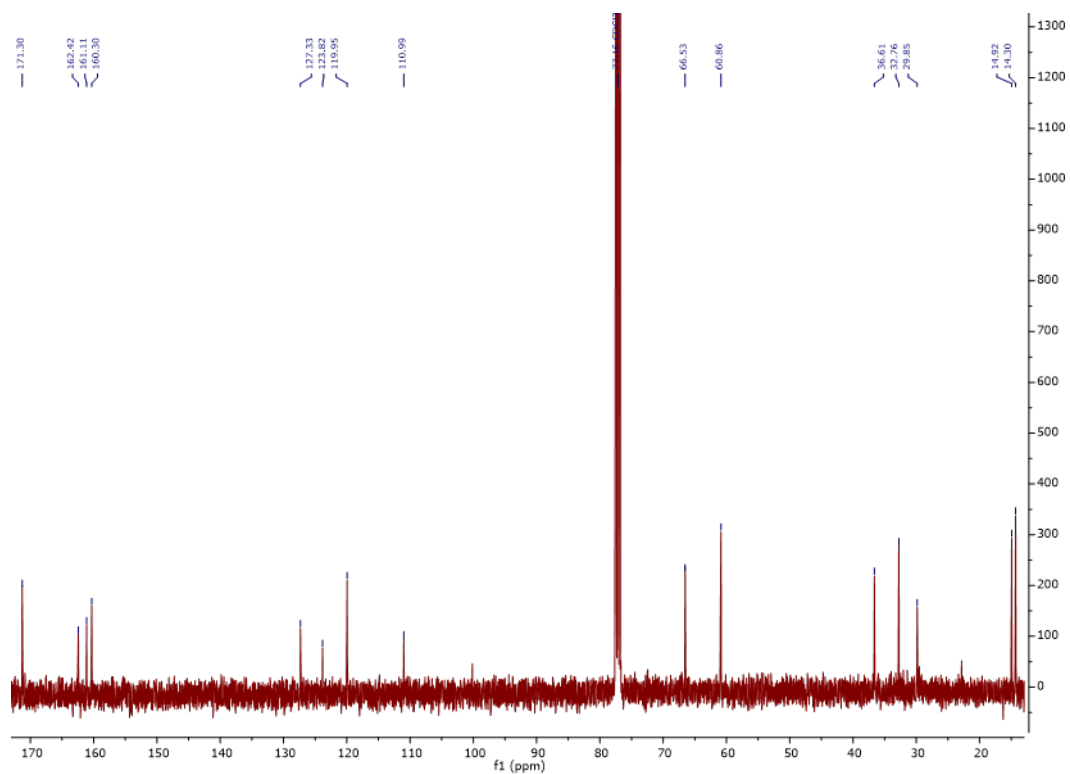


Figure SI 10.  $^{13}\text{C-NMR}$  spectrum of **3** (100 MHz,  $\text{DMSO-}d_6$ , 298 K).

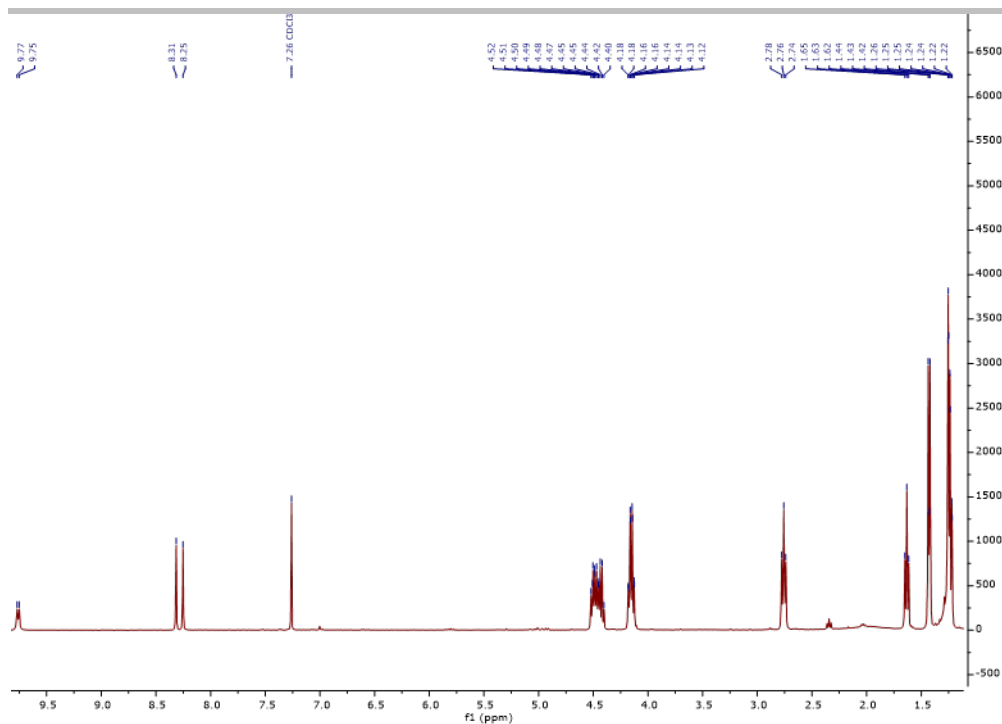


Figure SI 11. <sup>1</sup>H-NMR spectrum of **4** (400 MHz, CDCl<sub>3</sub>, 298 K).

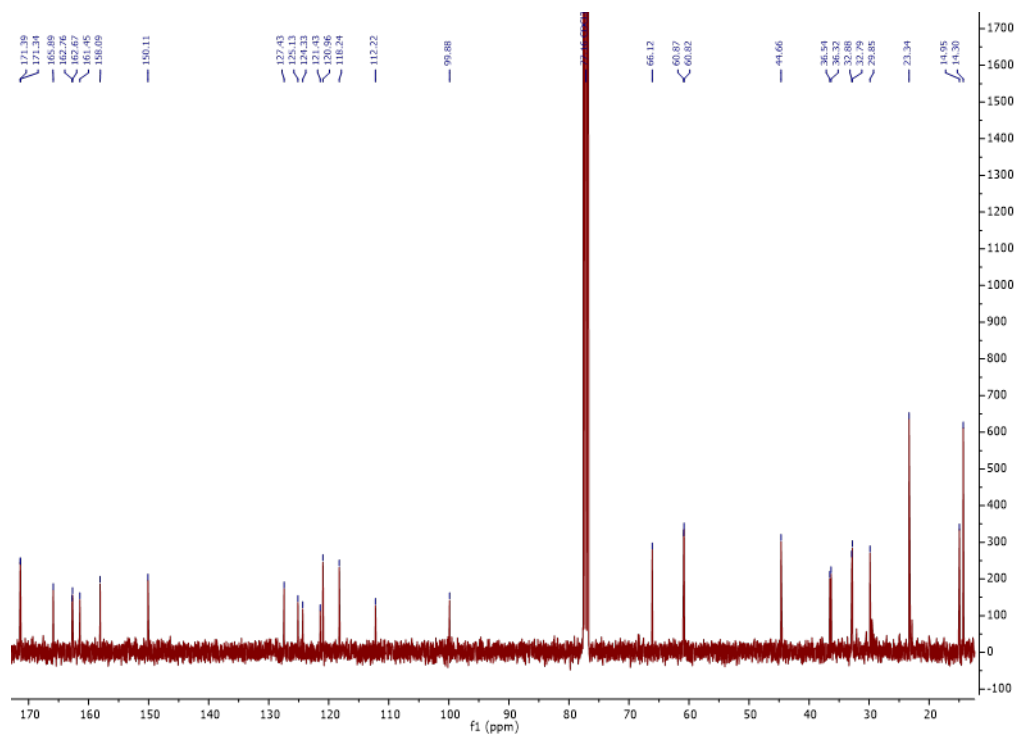


Figure SI 12. <sup>13</sup>C-NMR spectrum of **4** (100 MHz, CDCl<sub>3</sub>, 298 K).

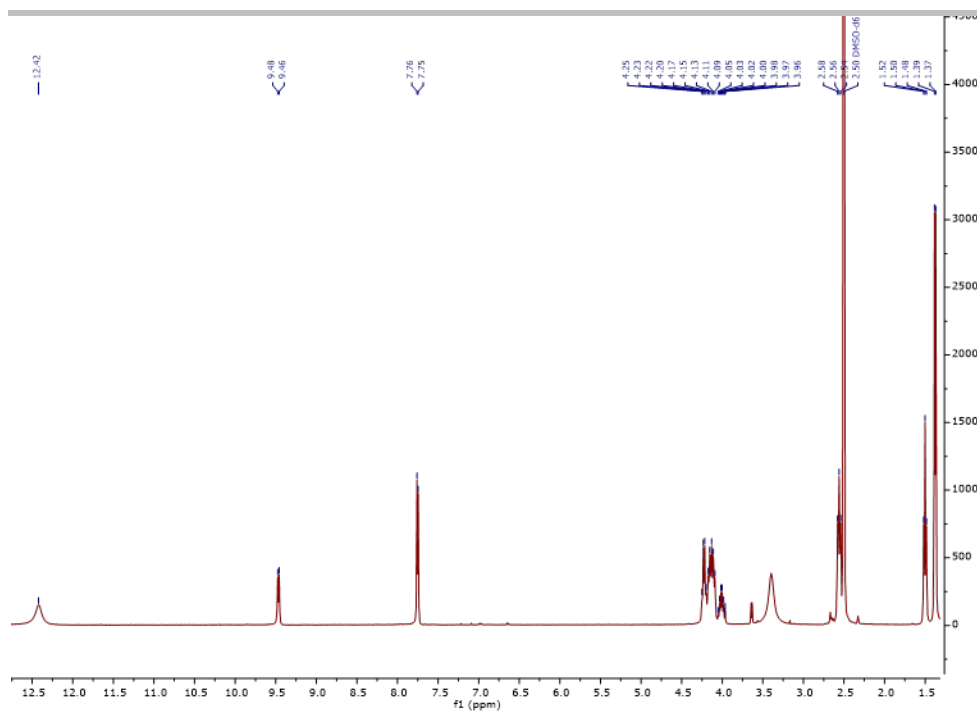


Figure SI 13.  $^1\text{H}$ -NMR spectrum of **5** (400 MHz,  $\text{DMSO-}d_6$ , 298 K).

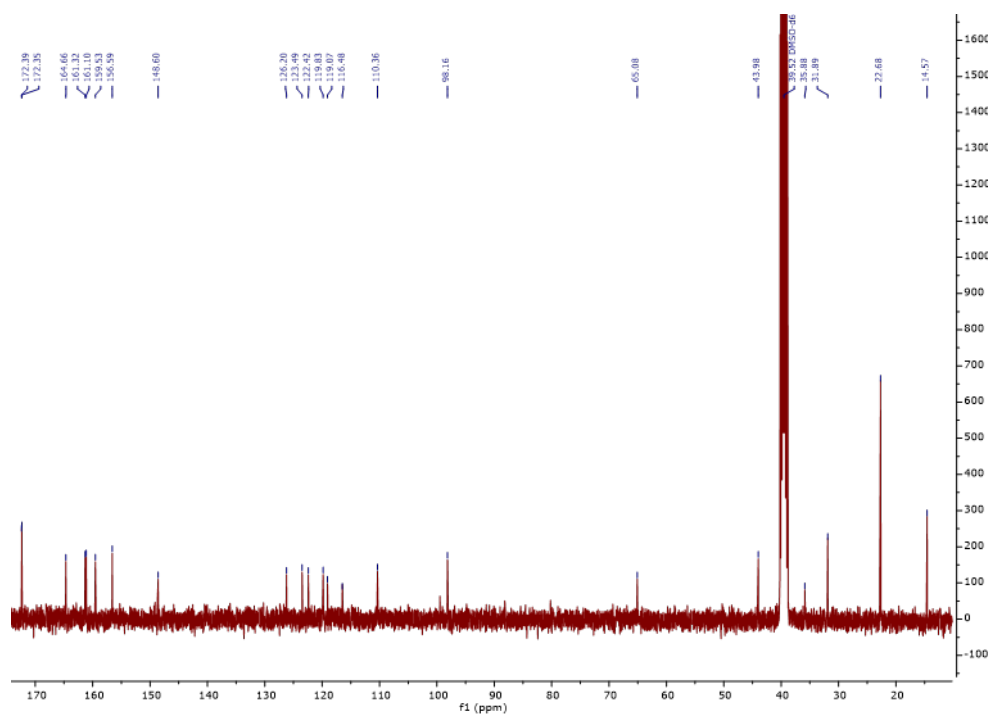


Figure SI 14.  $^{13}\text{C}$ -NMR spectrum of **5** (100 MHz,  $\text{DMSO-}d_6$ , 298 K).

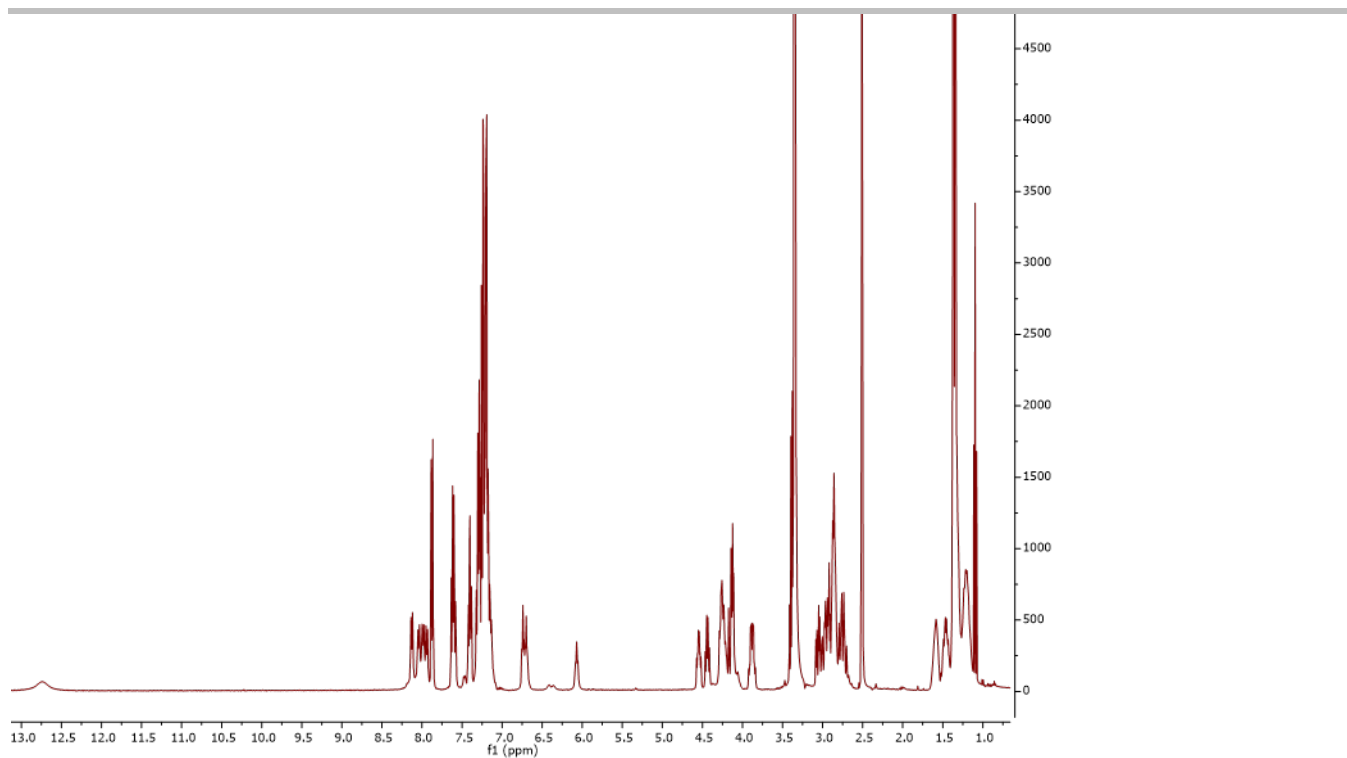


Figure SI 15.  $^1\text{H}$ -NMR spectrum of **7** (400 MHz,  $\text{DMSO-}d_6$ , 296 K).

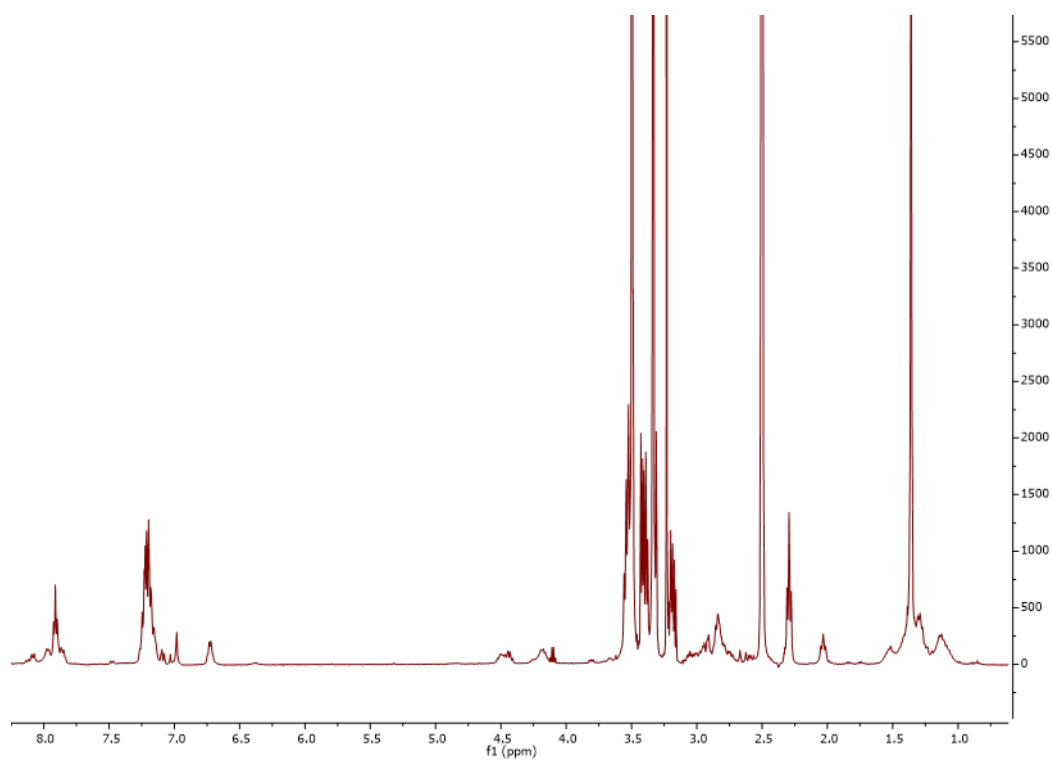


Figure SI 16.  $^1\text{H}$ -NMR spectrum of **8** (400 MHz,  $\text{DMSO-}d_6$ , 296 K).



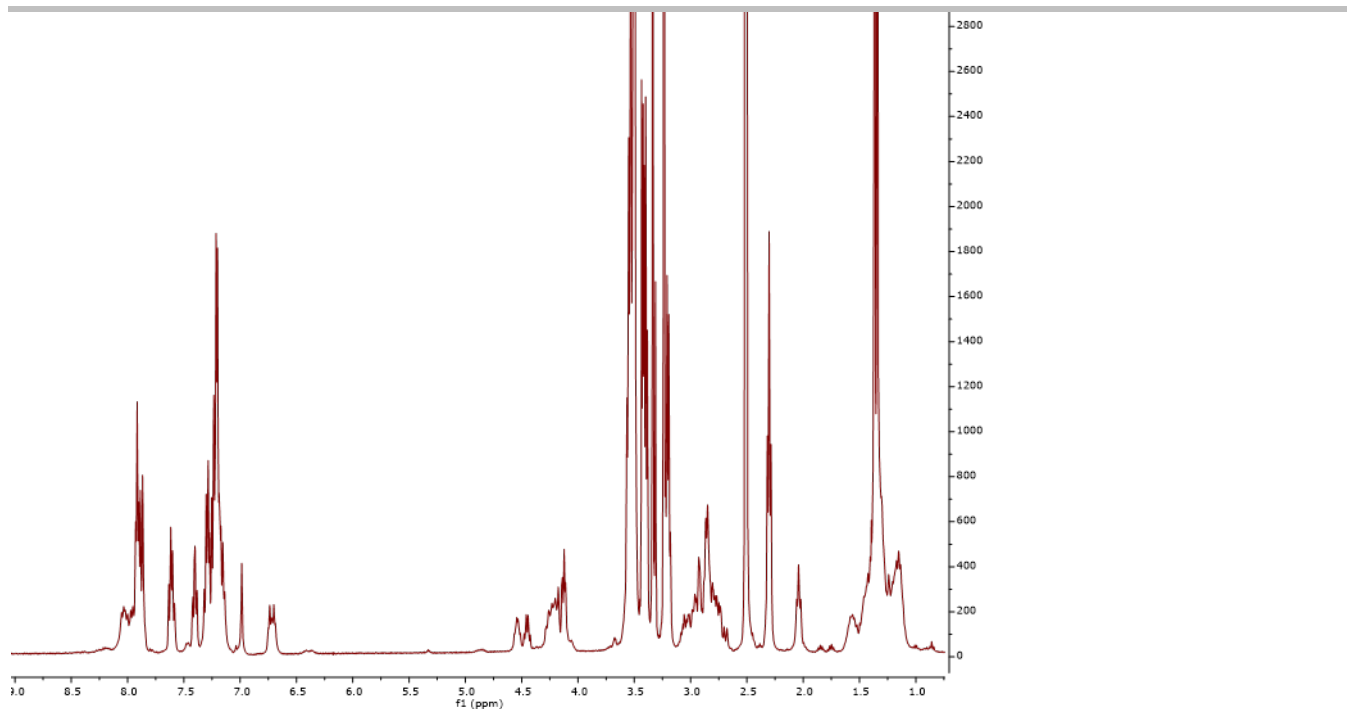


Figure SI 17.  $^1\text{H-NMR}$  spectrum of **9** (400 MHz,  $\text{DMSO-}d_6$ , 296 K).

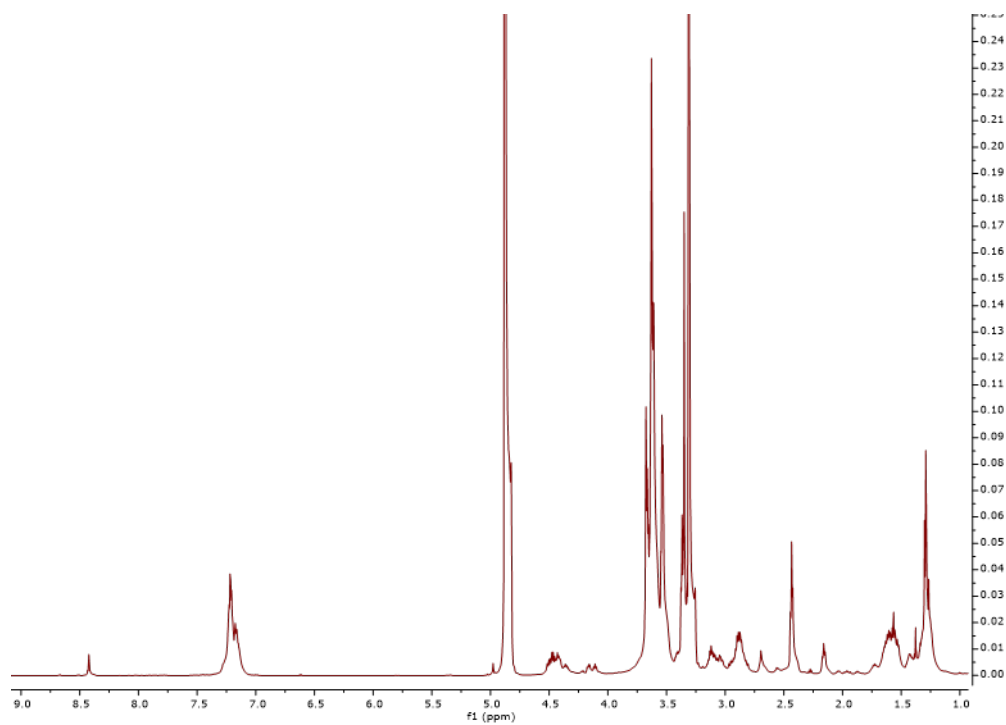


Figure SI 18.  $^1\text{H-NMR}$  spectrum of **10** (600 MHz,  $\text{CD}_3\text{OD}$ , 298 K).

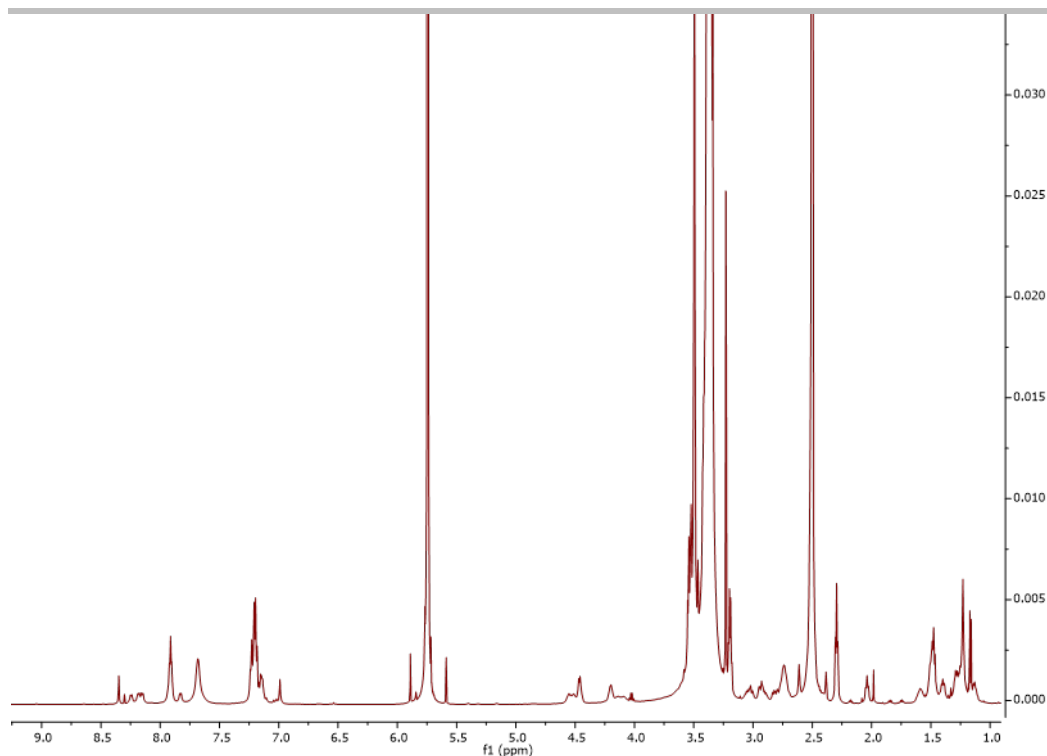


Figure SI 19.  $^1\text{H}$ -NMR spectrum of **11** (600 MHz,  $\text{DMSO-}d_6$ , 298 K).

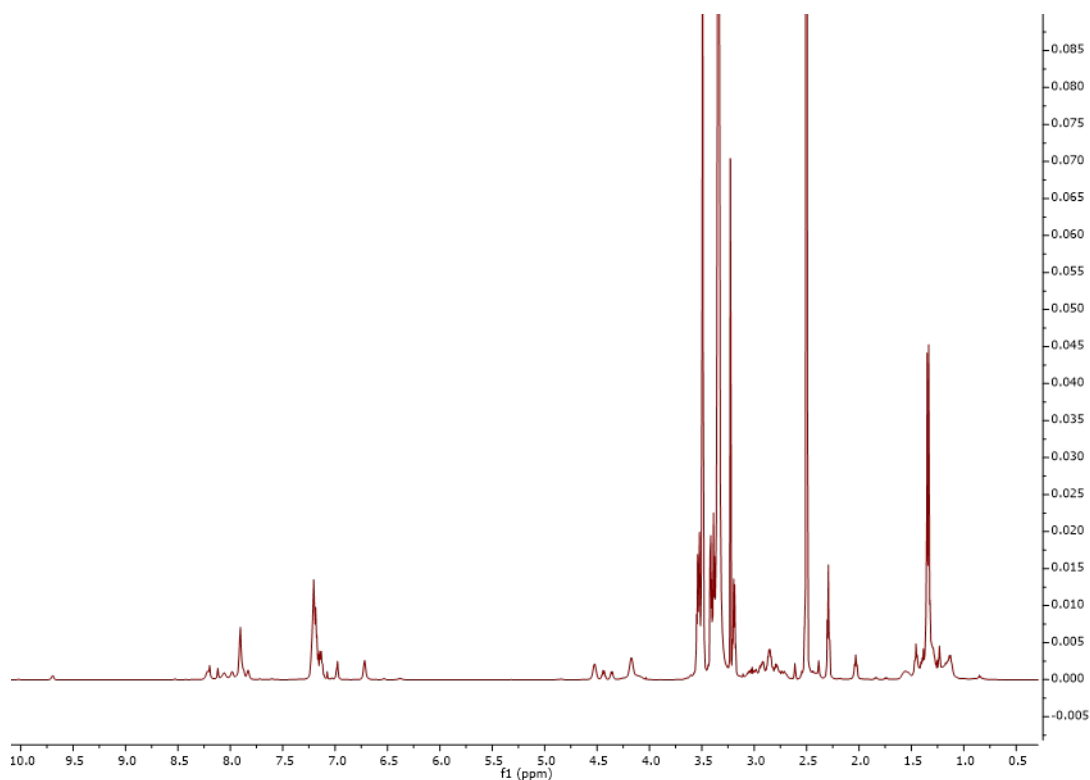


Figure SI 20.  $^1\text{H}$ -NMR spectrum of **12** (600 MHz,  $\text{DMSO-}d_6$ , 298 K).

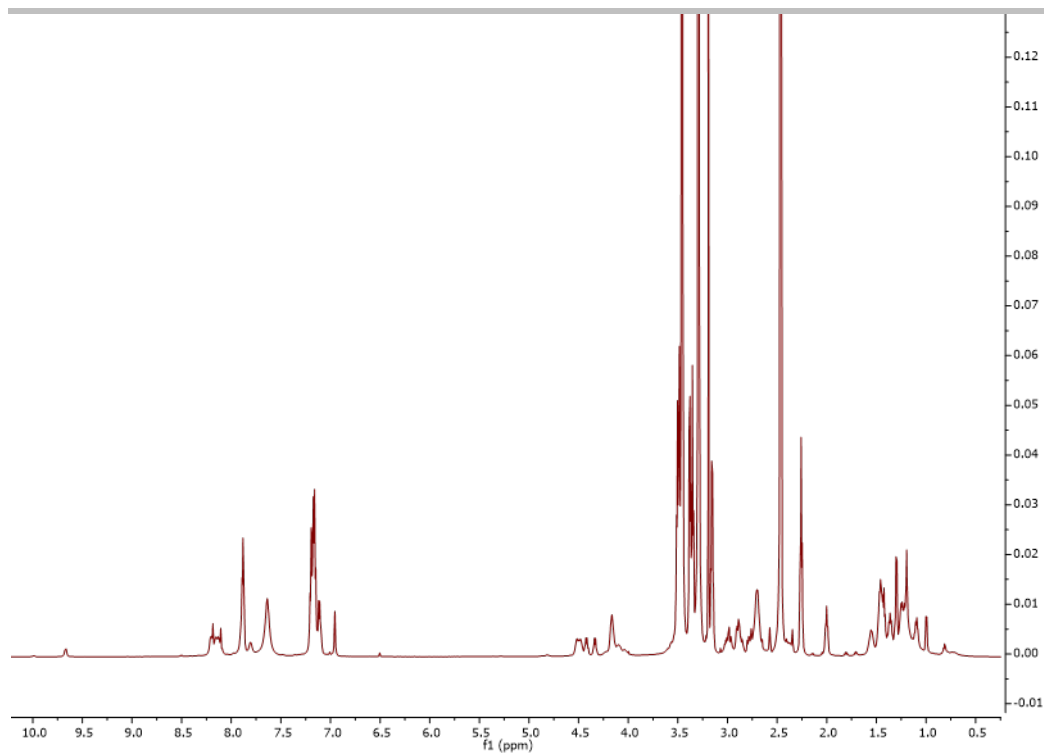


Figure SI 21.  $^1\text{H-NMR}$  spectrum of **13** (600 MHz,  $\text{DMSO-}d_6$ , 298 K).

## 6. Supporting Table

**Table S1.** Life time data of **NDI-diOEt-cat** in self-assembled state (pH 8.6) and monomeric state (pH 3.0). ( $[\text{NDI-diOEt-cat}] = 5 \times 10^{-5} \text{ M}$ ,  $\lambda_{\text{ex}} = 442 \text{ nm}$ ).

pH	$\lambda_{\text{coll}}$	$t_1/\text{ns}$	$t_2/\text{ns}$	$t_3/\text{ns}$
8.6	505	1.5	4.74	0.25
		(37.27%)	(24.50%)	(30.49%)
3.0	505	0.29	2.79	13.5
		(12.10%)	(79.76%)	(8.15%)

**Table S2.** Life time data of **NDI-OEtIPA-cat** at pH 8.6 at pH 3.0. ( $[\text{NDI-OEtIPA-cat}] = 2.5 \times 10^{-5} \text{ M}$ ,  $\lambda_{\text{ex}} = 532 \text{ nm}$ ).

pH	$\lambda_{\text{coll}}$	$t_1/\text{ns}$	$t_2/\text{ns}$	$t_3/\text{ns}$
8.6	580	0.9 (10.57%)	6.79 (61.81%)	0.1 (27.61%)
3.0	505	0.7 (12.10%)	6.66 (66.66%)	0.12 (15.61%)

## 7. References

- [1] A. Sarkar, S. Dhiman, A. Chalisehar, S. J. George, *Angew. Chem. Int. Ed.* **2017**, *56*, 13767–13771.  
[2] P. Ahlers, H. Frisch, P. Besenius, *Polym. Chem.* **2015**, *6*, 7245–7250.