# Supplementary Information

## Directed Self-Assembly of Peptide-Diketopyrrolopyrrole Conjugates – a Platform for Bio-Organic Thin Film Preparation

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## S1. General Information

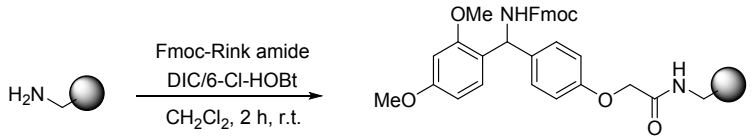
All reagents were purchased as reagent grade and used without further purification unless otherwise noted. Acetonitrile (MeCN) (HPLC grade), dichloromethane ($CH_2Cl_2$) and diethyl ether were purchased from Fisher Scientific (Hampton, NH, USA). Aminomethyl chemmetrix® (AM-CM) resin, diaion® HP20SS, and dimethylformamide (DMF) (AR grade) were purchased from Global Science (Barcelona, Spain). Acetic acid, *N,N*-diisopropylethylamine (DIPEA), *N,N'*-diisopropylcarbodiimide (DIC), *N*-methyl-2-pyrrolidone (NMP), piperidine, sodium *tert*-amyl alcohol, 2-thiophenecarbonitrile and triisopropylsilane (TIPS), were purchased from Sigma -Aldrich (St Louis, MO, USA). Trifluoroacetic acid (TFA) was purchased from Oakwood Chemical (Columbia, US). Acetic anhydride, cyclohexane, ethyl acetate (EtOAc) and potassium carbonate ($K_2CO_3$) were purchased from ECP Auckland New Zealand. (1-Cyano-2-ethoxy-2-oxoethylidenaminooxy)dimethylamino-morpholino-carbenium hexafluorophosphate (COMU), benzotriazol-1-yloxy)tripyrrolidinophosphonium hexafluorophosphat (PyBOP) and 6-chloro-1-hydroxy-1*H*-benzotriazole (6-Cl-HOBt) were purchased from AAPPTec (Louisville, KY, USA). Di-ethyl succinate and *tert*-butyl bromoacetate were purchased from AK Scientific (Union City, CA, USA). Ethyl (hydroxyimino)cyanoacetate (Oxyma) was purchased from Novabiochem® (Germany). *O*-(7-azabenzo-triazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU), 4-[(2,4-Dimethoxyphenyl)(Fmoc-amino)methyl]phenoxyacetic acid (Rink amide linker) and Fmoc-Amino acids with the following side chain protection: Fmoc-His(Trt)-OH, Fmoc-Glu(-O*t*Bu)-OH, Fmoc-Phe-OH, Fmoc-Ile-OH, Fmoc-Ser(*t*Bu)-OH, Fmoc-Thr(*t*Bu)-OH, Fmoc-Ala-OH were purchased from CS Bio(Shanghai, China). Water was purified using a Sartorius (Göttingen, Germany) arium® pro ultrapure water system. Iron chloride ($FeCl_3$) was purchased from Ajax (New Zealand). Sodium sulphate was purchased from Merck (New Zealand).

Reversed-phase high-performance liquid chromatography (RP-HPLC) analyses were performed using a Dionex Ultimate 3000 instrument (Sunnyvale, CA, USA) equipped with a 4 channel UV detector at 210, 230, 254, and 280 nm. The solvent system used was A (0.1% TFA in $H_2O$) and B (0.1% TFA in MeCN).

Peptide characterization was performed by LC-MS using ESI in positive mode on an Agilent 1120 compact LC system equipped with Agilent 6120 Quadrupole MS and a UV detector at 214 nm (Palo Alto, CA, USA). The solvent system consisted of A (0.1% formic acid in $H_2O$) and B (0.1% formic acid in MeCN).

## S2. General Methods

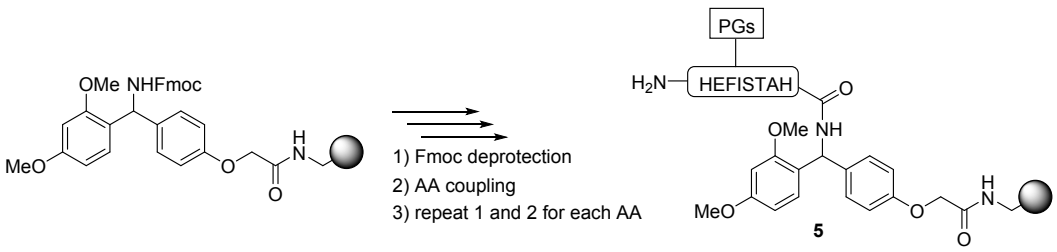
### General Method A: Attachment of Rink-amide linker to aminomethyl- Chemmatrix® resin




**Scheme S1.** Attachment of Rink amide linker to aminomethyl chemmatrix® resin.

Aminomethyl Chemmatrix® (CM) resin (149 mg, 0.1 mmol, loading 0.67 mmol/g) was swollen in $CH_2Cl_2$ (5 mL) for 15 min. The $CH_2Cl_2$ was drained from the resin and Fmoc-Rink amide (216 mg, 0.4 mmol, 4 eq.), 6-Cl-HOBt (67 mg, 0.4 mmol, 4 eq.) and DIC (62 µL, 0.4 mmol, 4 eq.) in $CH_2Cl_2$/DMF (1:4, *v/v*) were added to the resin. The reaction was agitated for 3 h at rt, then the resin was drained and was washed with DMF (3 × 5 mL). Coupling completion was confirmed by the ninhydrin test.

### General Method B: Amino acid coupling for peptide elongation

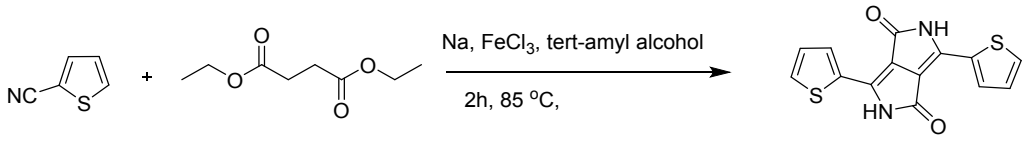


**Scheme S2.** General amino acid coupling to obtain desired peptide.

The Fmoc $N^{\alpha}$-protecting group was removed by treatment with piperidine/DMF (1:4 *v/v*, 5 mL, 2 × 10 min). The solution was drained, and the resin was washed with DMF (3 × 5 mL). The Fmoc protected amino acid (0.5 mmol, 5 eq.) and HATU (171 mg, 0.45 mmol, 4.5 eq.) were dissolved in DMF (3 mL) followed by the addition of DIPEA (174 µL, 1.0 mmol, 10 eq.). The mixture was mixed for 30 s before adding the activated amino acid to the linker-resin. The reaction mixture was stirred for 2 h at room temperature, the solution drained, and the resin was washed with DMF (3 × 5 mL). The completion of the amino acid coupling to the resin was monitored using the ninhydrin test.[1] The process is reappeared until obtaining the desired peptide sequence. The Fmoc protecting group of the final peptidyl-resin was removed to obtain free amino group for further coupling.

## General Method C: Stepwise synthesis of compound 4

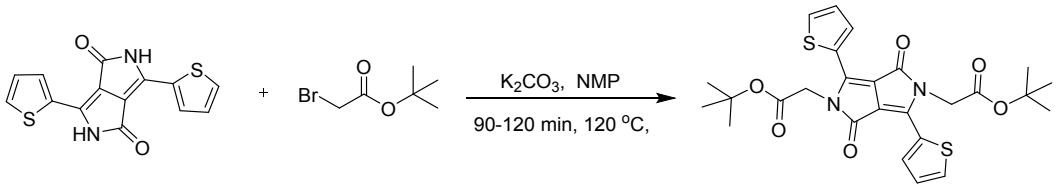
## Synthesis of 3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione, TDPP[1]




**Scheme S3.** Synthesis of TDPP.

Sodium (0.5g, 0.022mol, 3.7 eq.) was added to *tert*-amyl alcohol (10 mL) followed by a small amount of Iron (III) Chloride (5mg, 43 mmol, 0.5 eq.). The mixture was stirred vigorously for 1 hr between 95 to 102 °C until the sodium reacted. The resultant solution was cooled to 85 °C and 2-thiophenecarbinitrile (1.31g, 0.014mol, 2.3 eq.) was added. Next, di-ethyl succinate (1g, 0.006mol, 1 eq.) was added drop wise over 1 hr at 85 °C and the resultant mixture was stirred for 2 h at the same temperature. The reaction mixture was cooled to 50 °C, diluted with 10 mL methanol, slowly neutralized with 1.5 mL of glacial acetic acid and then refluxed. The reaction mixture was filtered, and the residue was washed several times with hot methanol and water. The resultant solid was dried under vacuum. A bluish red solid was obtained (1 g) and used without further purification.[1]

## Synthesis of di-tert-butyl 2,2'-(1,4-dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-2,5(1*H*,4*H*)-diyl)diacetate, Di-*t*Bu-acetyl ester-TDPP[2]

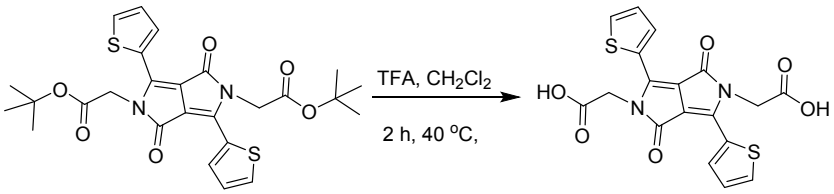



**Scheme S4.** Synthesis of di-*t*Bu-acetyl ester-TDPP.

TDPP (100 mg, 0.34 mmol, 1 eq.) was suspended in NMP (5ml) followed by the addition of anhydrous $K_2CO_3$ (506 mg, 3.66 mmol, 10.7 eq.) and the resultant mixture was heated at 120-125 °C (oil bath temperature) for 15 min. Next, a solution of tert-butyl bromoacetate (0.489 mL, 3.40 mmol, 10 eq.) in NMP (2.5 mL) was added dropwise and the resulting mixture was heated at the same temperature for 90 min. Once the reaction was completed (as verified by TLC using 100 % $CH_2Cl_2$ as eluent) the mixture was cooled to rt. The resultant mixture was poured into deionized water (25 mL) and the insoluble solid was recovered through centrifugation (3000 rpm, 15 min). The solid was washed with deionized water (25 mL), dissolved in $CH_2Cl_2$ (50 mL) and the resulting organic layer was dried over anhydrous $Na_2SO_4$. The solvent of the dried organic phase was evaporated under reduced pressure. The resulting residue was purified by column chromatography (silica gel, 35 g, heptane 100%, then step gradient of $CH_2Cl_2$ in heptane 0% to 100% to remove tert-butylbromoacetate and finally elution with $CH_2Cl_2$/EtOAc 8:2, *v/v* to recover the desired product). The desired compound was obtained as a dark reddish purple solid (112 mg, yield 64%). The product was characterised by FTIR and NMR data. FTIR (neat): ν = 2982, 2937, 2860, 1745, 1658,

1574, 1429, 1395, 1370, 1227, 1154, 1135, 1032, 846, 748, 725 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ =1.42 (s, 18H, 2 × *t*-Bu), 4.79 (s, 4H, 2 × N-C$H_2$-$CO_2$tBu), 7.26 (dd, *J* = 5.0, 4.0 Hz, 2H, H-thiophene), 7.62 (dd, *J* = 5.2, 1.0 Hz, 2H, H-thiophene), 8.75 (dd, *J* = 4 Hz, 1.0 Hz, 2H, H-thiophene) ppm; $^1C$ NMR ($CDCl_3$, 126 MHz): $\delta$ = 28.10 (6 C), 44.35 (2 C), 82.99 (2 C), 107.77 (2 C), 128.90 (2 C), 129.93 (2 C), 130.81 (2 C), 135.12 (2 C), 140.16 (2 C), 161.18 (2 C), 167.27 (2 C) ppm (Fig. S12-13). The spectroscopic data were in agreement with those reported in the literature.[2]

## Synthesis of 2,2'-(1,4-dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-2,5(1*H*,4*H*)-diyl)diacetic acid (4)[2]




**Scheme S5.** Synthesis of compound **4**.

Di-*t*Bu-acetyl ester-TDPP (100 mg, 0.19 mmol, 1 equiv.) was dissolved in $CH_2Cl_2$ (3 mL) and the resulting solution was cooled to 4 °C. Trifluoroacetic acid (0.9 mL, 11.7 mmol, 61.5 equiv.) was next added and the resulting reaction mixture was stirred for 2 h. Once the reaction was completed (as verified by TLC using $CH_2Cl_2$:EtOAc 9:1 *v/v* as eluent) the solvent was evaporated under reduced pressure and the residual TFA was azeotropically removed with toluene. The resulting solid residue was triturated and washed with cyclohexane (2 x 15 mL) and finally dried under vacuum to give compound **4** as a dark reddish purple solid (55 mg, yield 69%). The product was characterised by FTIR and NMR data. FTIR (neat): ν = 3081, 2973, 2921, 1721, 1658, 1575, 1427, 1408, 1393, 1224, 1124 ,1031, 855, 733, 728, 708, 665 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$, 400 MHz): $\delta$ = 4.79 (s, 4H, 2 × N-C$H_2$-$CO_2$H), 7.42 (dd, *J* = 4.8, 3.9Hz, 2H, H-thiophene), 8.10 (dd, *J* = 5, 0.9 Hz, 2H, H-thiophene), 8.68 (dd, *J* = 3.8, 0.9 Hz, 2H, H-thiophene) ppm (Fig. S14). The spectroscopic data were in agreement with those reported in the literature.[2]

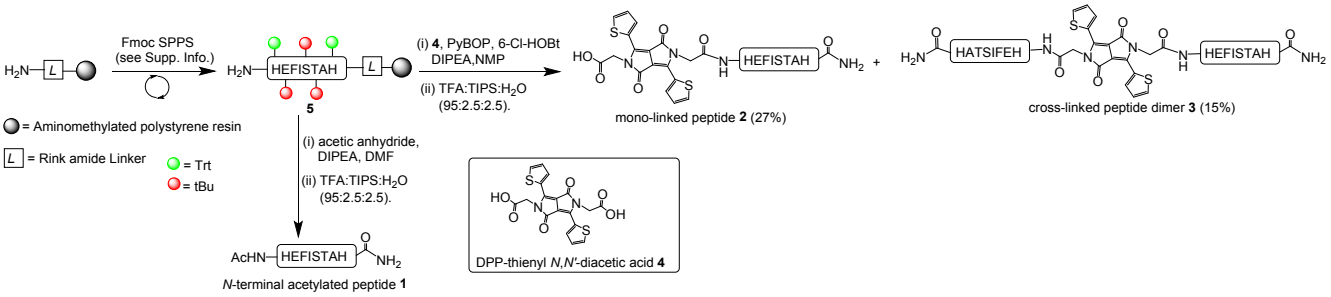
## General Method D: Global deprotection and full cleavage of peptide from resin

A cleavage cocktail of TFA/$H_2O$/TIPS (95:2.5:2.5 *v/v/v/v*, 5 mL) was added to the peptidyl resin and the mixture agitated for 1 h at rt. The cleavage mixture was drained from the resin, and the resin was further washed with an aliquot of TFA (5 mL). The solution was sparged with nitrogen to evaporate TFA, the remaining residue was triturated with diethyl ether, centrifuged and the supernatant decanted to give the crude product as a pellet. The pellet was dissolved in $H_2O$:MeCN (1:1 *v/v*) containing 0.1% TFA and a small aliquot was analysed by RP-HPLC on XTerra® C-18 column (4.6 x 150 mm, 5 µm, 125 Å; Waters) using a linear gradient of 5 – 95% B (*ca.* 3% B/min) at rt with a flow rate of 0.3 mL/min. The obtention of the desired product was determined by ES-MS. The remaining solution was lyophilized.

## General Method E: Purification of peptide conjugates

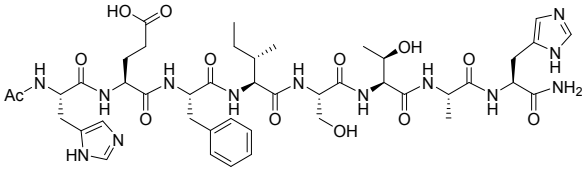
Dianion HP20SS resin (100 g) was swelled for 1 h in methanol. Later, resin was washed with MiliQ water loaded to a glass column. Beads were washed with 500 mL of $H_2O$:MeCN (1:19) (+ 0.1 % TFA), followed by loading peptide crude (mixture of 100 mg peptide crude in 2 ml of water : acetonitrile (1:19)). The acetonitrile concentration was slowly increased from 5% to 95 % and the fractions were collected followed by their analysis by RP-HPLC. The fractions containing the purified peptide were combined and lyophilized.

## S3. Experimental Section




**Scheme S6.** Synthesis of **1**-**3** using solid phase peptide synthesis.

## S3.1 Synthesis of Ac-His-Glu-Phe-Ile-Ser-Thr-Ala-His-$NH_2$ 1



**1**

Peptidyl resin **5** was synthesised using Fmoc SPPS according to **general method A** and **B**. *N*-terminus of peptidyl resin **5** was then capped with the solution of acetic anhydride:DMF (1:5 v/v, 3 mL) and DIPEA (174 µL, 5.0 mmol, 10 eq.) for 2 h. The completed peptide chain was then cleaved off the resin using **general method D** and then purified according to **general method E**. Lyophilisation yielded purified Ac-His-Glu-Phe-Ile-Ser-Thr-Ala-His-$NH_2$ **1** (yield =41%) as a white solid; $R_t$ = 9.83 min; *m/z* (ESI-MS) 982.4 ([M+H]$^+$ requires 982.5), Figure S1.

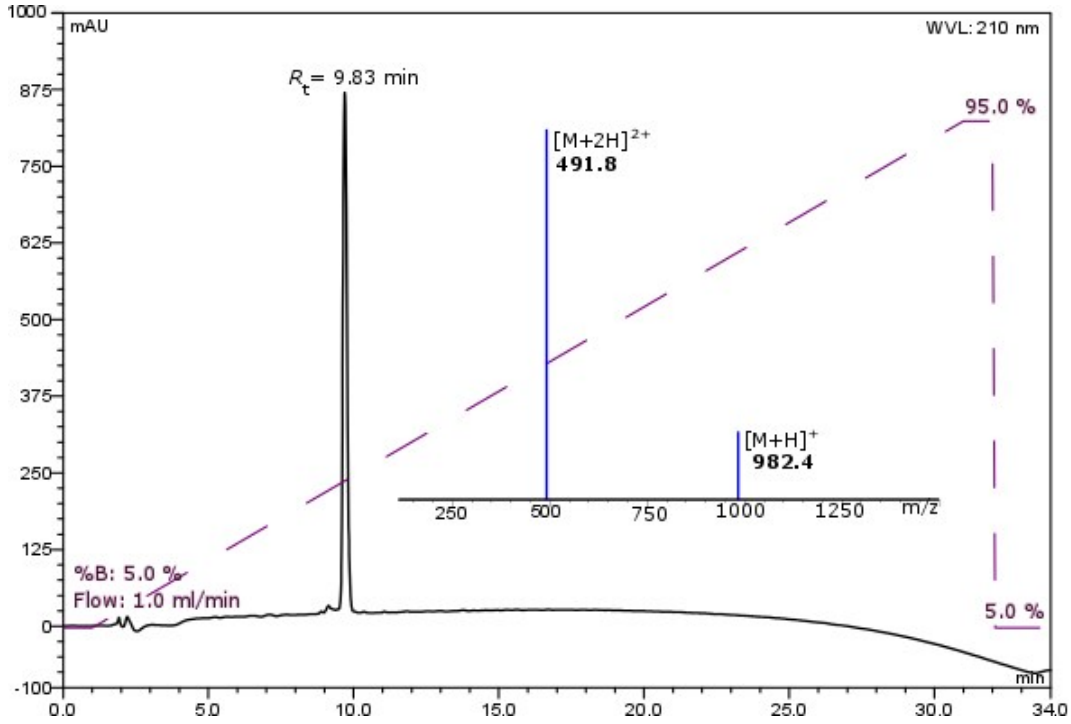
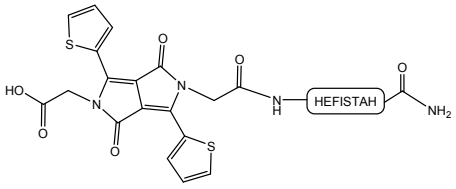
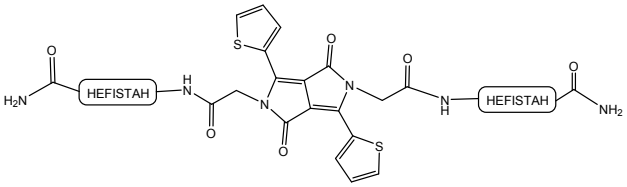


**Figure S1.** Analytical RP-HPLC and ESI-MS of purified Ac-His-Glu-Phe-Ile-Ser-Thr-Ala-His-$NH_2$ **1** (*ca.* 99% as judged by peak area of at 210 nm); XTerra® MS C18, (4.6 mm × 150 mm; 5 µm), linear gradient of 5% B to 95% B over 30 min, *ca.* 3% B per minute at rt, 1.0 mL/min.

## S3.2 Synthesis of Peptide-TDPP Conjugates 2 and 3




mono-linked peptide **2**




cross-linked peptide dimer **3**

Peptidyl resin **5** was synthesised using Fmoc SPPS according to **general method A** and **B** and compound **4** was synthesised using **general method C**. Compound **4** (84 mg, 0.2 mol, 0.2 eq.), PyBOP (210 mg, 0.4 mmol, 2 eq.), and DIPEA (76 uL, 0.45 mmol, 4.5eq.) were added to NMP (3 mL) and the resultant mixture was mixed for 10 min and then added dropwise into the resin bound peptide in NMP (500 µL) over a period of 3 h. After the addition was complete, the mixture was stirred for 24 h at room temperature. The final peptide-TDPP conjugates were cleaved from the resin according to **general method D** and crude mixture of product **2** and **3** were obtained (Figure S2). The crude mixture was purified according to **general method E** and a yield of 27 % for **2** and 15 % for **3** were obtained. Lyophilisation yielded pure **2** as a reddish solid; $R_t$ = 14.1; *m/z* (ESI-MS) 1339.3 ($[M+H]^+$ requires 1337.5), (Figure S3) and **3** as a reddish solid; $R_t$ = 12.2; *m/z* (ESI-MS) 1130.8 ($[M+H]^{2+}$ requires 1129.9), (Figure S4).

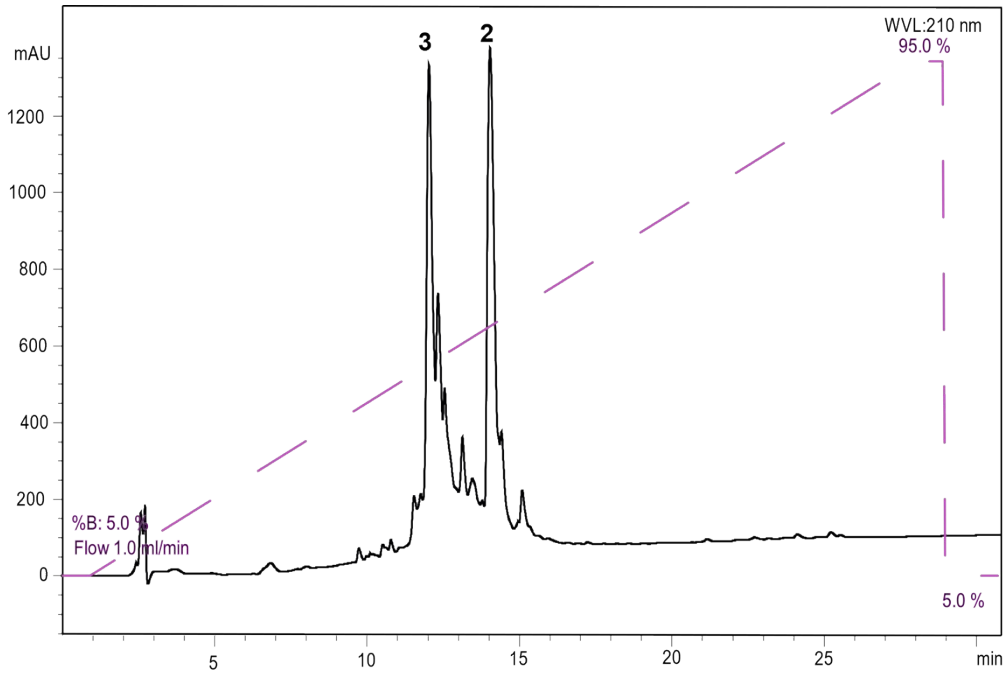
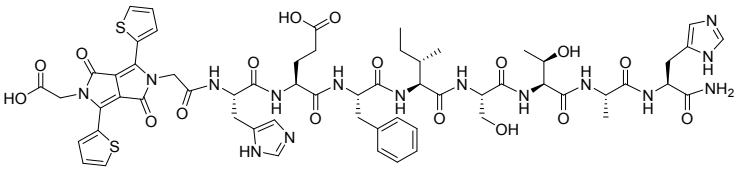



**Figure S2.** RP-HPLC trace of crude product of peptide-TDPP conjugates **2** and **3** (RP-HPLC at 210 nm); XTerra® MS C18, (4.6 mm × 150 mm; 5 µm), linear gradient of 5% B to 95% B over 30 min, *ca.* 3% B per minute at rt, 1.0 mL/min.



**2**

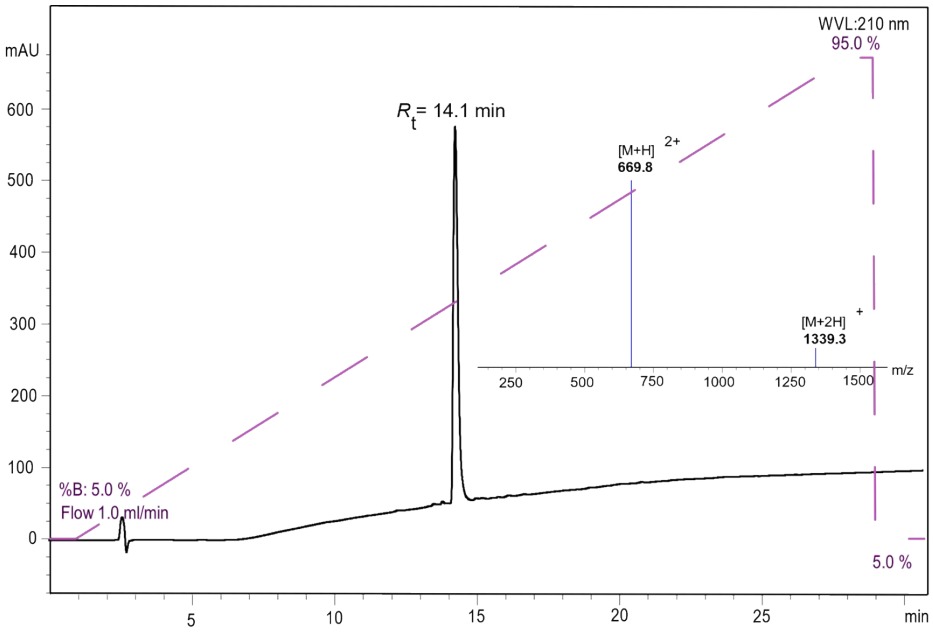
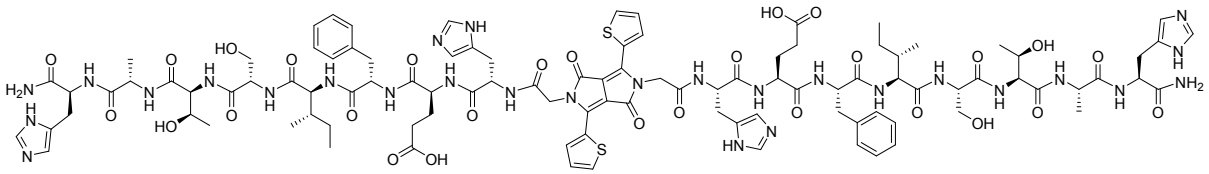



**Figure S3.** RP-HPLC and ESI-MS traces of **2**. (*ca.* 99% as judged by peak area of RP-HPLC at 210 nm); XTerra® MS C18, (4.6 mm × 150 mm; 5 µm), linear gradient of 5% B to 95% B over 30 min, *ca.* 3% B per minute at rt, 1.0 mL/min.



**3**

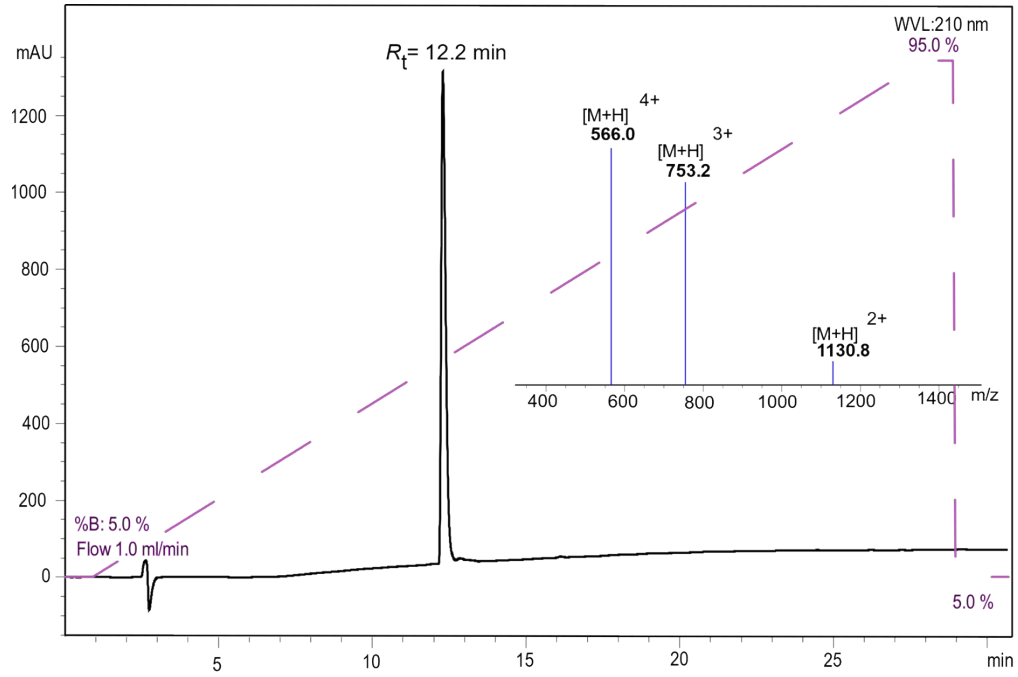



**Figure S4.** RP-HPLC and ESI-MS traces of **3**. (*ca.* 99% as judged by peak area of RP-HPLC at 210 nm); XTerra® MS C18, (4.6 mm × 150 mm; 5 µm), linear gradient of 5% B to 95% B over 30 min, *ca.* 3% B per minute at rt, 1.0 mL/min.

## S4. Hydrogel Formation

Hydrogels were prepared by mixing the lyophilized powder with Milli-Q water, followed by sonication for 1 min at room temperature.

## S5. Transmission Electron Microscopy (TEM)

Nanostructures were examined using a Technai 12 electron microscope operated at 120kV equipped with a 2Kx2K GATAN. CCD camera. Homemade carbon-coated copper grids were glow discharged 30s to render them hydrophilic. Approximately 2 μL of a sample solution was transferred to the grid, allowed to stand for 1 min and excess solution was wiped with filter paper. Next, water (2 μL) was added to the grid and kept for 15 s to remove excess peptide. Water was wiped off with filter paper. Finally, 2 μL of a 2 wt % uranyl acetate solution was applied to the grid for 30s and then the grid was blotted with a piece of filter paper and allowed to dry for 1 h at rt.

## S6. Atomic Force Microscopy (AFM)

Sample solutions at concentrations of 1 wt % were drop casted on mica and the solvent was evaporated at room temperature for 24 h. The surface topology of the samples was imaged with an Asylum Cypher ES AFM in tapping mode using silicon tips (Tap150Al-G) with a force constant 5 $nm^{-1}$ and resonance frequency of 150 kHz.

## S7. Fourier-Transformed Infrared Spectroscopy (FT-IR)

FTIR spectra of peptide hydrogels were collected using a PerkinElmer spectrum 100 FTIR spectrometer. Baseline spectra were collected with only water. Each spectrum is the average of 128 scans over the range of 4000-400 $cm^{-1}$.

## S8. Circular Dichroism (CD) Spectroscopy

The secondary structures of peptides unit were analysed using a Chirascan Dichroism spectrometer (CD) at 20 °C using a 1 mm path quartz cuvette. Each CD spectrum measurement was acquired with 1 s integrations and a step size of 1 nm over a range of wavelength from 200 to 280 nm. The reported spectrum corresponds to the average of at least 5 measurements.

## S8.1 CD spectra of thin film

The sample was prepared by diluting a 4 wt % gel to a 1 wt % viscous solution. Then 100 μL of the diluted sample was carefully transferred along the inner side wall of cuvette using micropipette to form thin film. The film was dried at rt for 3 h. The baseline spectra were collected by subtracting empty cuvette.

## S8.2 CD spectra of solution

CD spectra of solutions at 0.5 wt % were collected. Sample was prepared by diluting 4 wt % gel solution to 0.5 wt % solution. The baseline spectra were collected with water alone and then subtracted from the sample spectral data.

## S9. X-ray Diffraction

X-ray powder diffraction measurements were performed on a PANalytical Empyrean Theta-Theta diffractometer system operated in a Bragg-Brentano geometry. The system was equipped with a Cu X-ray tube and a PIXcel1D detector fitted with a monochromator. XRD analyses were conducted at room temperature over the 2θ range 5-35° using monochromated Cu Kα1 radiation (λ = 1.5418 Å, current = 40 mA, high tension = 45 kV). The samples were poured through the wall of a glass substrate and dried for 24 h. To minimise preferred orientation, samples were analysed on a rotating stage (60 RPM). Additional parameters were step size = 0.01° and dwell time = 50 s. The XRD profile of peptide samples were background subtracted with a profile of a glass substrate.

## S10. Small-Angle X-ray Scattering

SAXS experiments of gel samples were performed at the SAXS/WAXS beamline at Australian Synchrotron, Melbourne. Experiments using capillary setup. Peptide powder dissolved at 2 wt % and 1 wt % were instantly loaded into quartz capillary having 1.5 mm internal diameter and SAXS pattern were recorded for 1s. Capillary kept flowing continuously while the SAXS pattern was recorded for 1 s X-ray exposure. For each setup, the background was recorded by loading water in capillary. Each pattern shown resulted from radial integration (Scatterbrain, Australian Synchrotron) and subtraction of the background.
The SAXS intensity was fitted to a form factor corresponding to the Guinier-Porod's[3] approximation for a long thin infinite rod. The following functional form is used

$$I(q) = \frac{G}{q^s} exp\left(\frac{-q^2 R_g^2}{3-s}\right) \qquad for\ q \leq q_1$$

$$I(q) = \frac{D}{q^d} \qquad for\ q \geq q_1$$

where $q$ is the scattering variable, $I(q)$ is the scattered intensity, $R_g$ is the radius of gyration, $d$ is the Porod exponent, $s$ is a parameter that helps to model nonspherical objects ($s$ = 1 for cylinders), and $G$ and $D$ are the Guinier and Porod scale factors with the requirement of continuity of the Guinier and Porod functions given by

$$D = Gexp\left(\frac{-q_1^2 R_g^2}{3-s}\right) q_1^{(d-s)}$$

$$q_1 = \frac{1}{R_g}\left(\frac{(d-s)(3-s)}{2}\right)^{1/2}$$

The radius, $R$, for a randomly oriented thin cylinder is given by

$$R = R_g\sqrt{2}$$

The diameter or width of the cylinder is 2 x $R$.
The non-weighted data was fitted from 0.01 to 0.028 $Å^{-1}$ and the parameters obtained are summarized in the Table shown below.

| Compound, 10 mg $mL^{-1}$ | $Rg \pm error, Å$ | s | $\chi^2$ |
|---|---|---|---|
| **2** | $24.591 \pm 0.048$ | 0.905 | 0.011 |
| **3** | $21.669 \pm 0.107$ | 1.176 | 0.490 |

## S11. Fabrication of Thin Film

Thin film of **2** and **3** were successfully prepared by both drop casting and spin coating method on glass/silicon substrate.

## S11.1 Thin film by drop casting method

A sample of gel at 4 wt % concentration was diluted to 1 wt %. The diluted solution was transferred to the substrate using a pipette and water evaporated at 23 $^oC$ to yield a dry film.

## S11.2 Thin film by spin coating method

A sample gel at 4 wt % was diluted to 1 wt % and the resultant solution transferred to the substrate using pipette. The substrate was spin coated at 900 rpm for 1 min and water evaporated at 23 $^{o}$C to yield a dry film.

## S12. UV-Vis Spectroscopy and Fluorescence Spectroscopy

### S12.1 UV-Vis spectroscopy of solution

UV/Vis absorption spectra of solutions were recorded on UV-Vis spectrometer (model Shimadzu UV-3600 Plus) using a 1 cm path quartz cuvettes and water or DMSO as solvent. Sample solution was prepared at 0.05 mM concentration.

### S12.3 Fluorescence spectroscopy

Fluorescence spectra were recorded in DMSO and water using a JASCO spectrophotometer FP-8600. The absolute fluorescence quantum yield data was obtained using Edinburgh FLS980 fluorescence spectrometer.

### S12.2 UV-Vis spectroscopy of thin film

A sample of gels at 4 wt % was diluted to 1 wt % and the resultant solutions were poured through the vertically stand glass slab to fabricate a thin solution later. The resulted film were dried for 24 h and the absorption spectra collected.

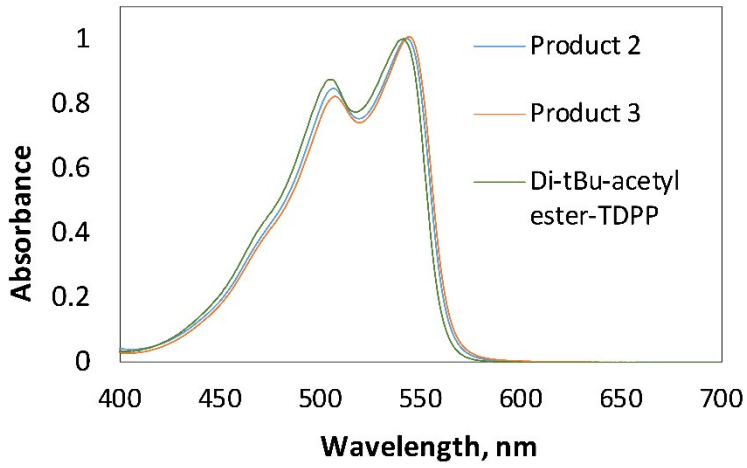



**Figure S5:** Normalised UV-Vis absorption spectra of **2**, **3** and di-*t*Bu-acetyl ester-TDPP at 0.05 mM concentration in DMSO.

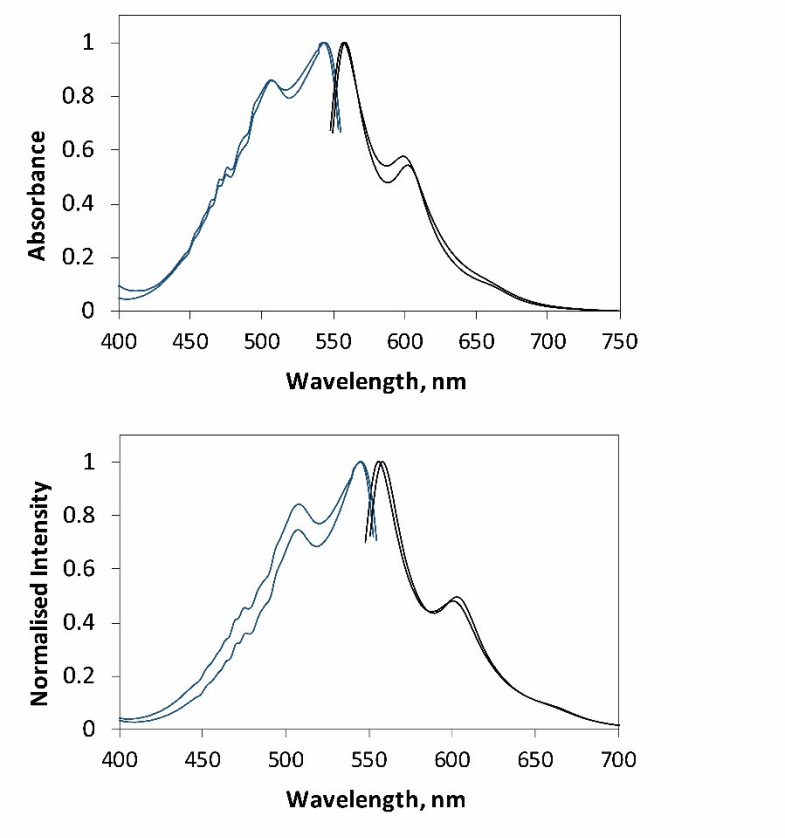



**Figure S6:** The excitation spectra in water (blue dotted line), excitation spectra in DMSO (blue solid line), emission spectra in water (black dotted line) and emission spectra in DMSO (black side line) of a solution of **2** with a concentration of 0.05 mM (Top) and the excitation spectra in water (blue dotted line), excitation spectra in DMSO (blue solid line), emission spectra in water (black dotted line) and emission spectra in DMSO (black side line) of a solution of **3** with a concentration of 0.05 mM (Bottom).

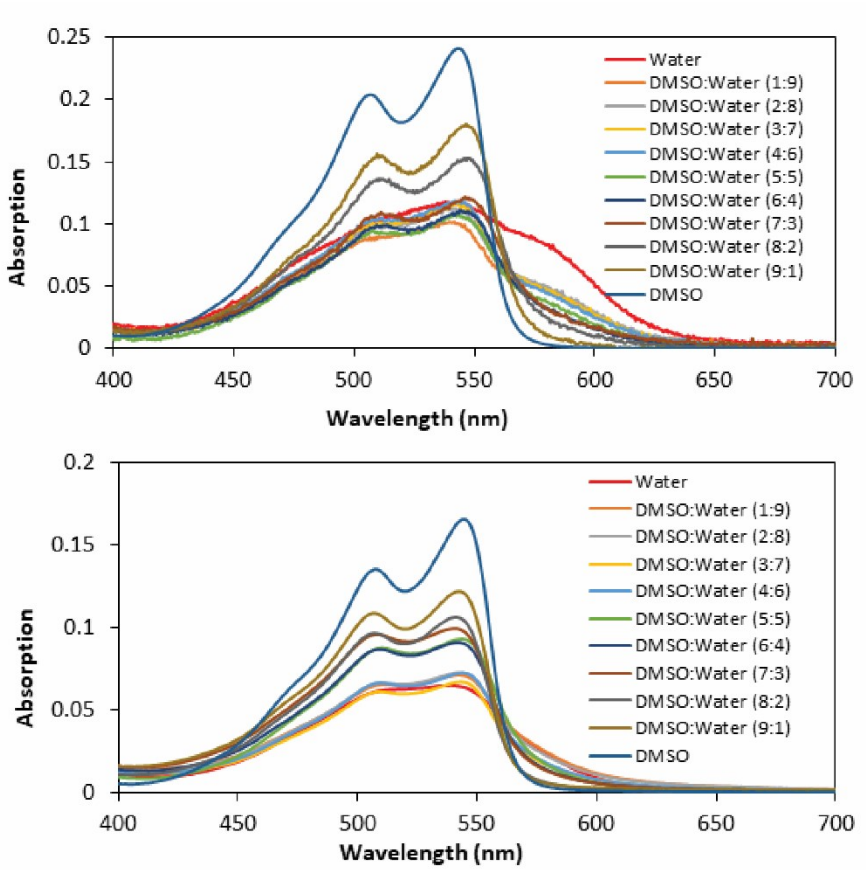



**Figure S7:** UV-Vis absorption spectra of **2** (Top) and **3** (bottom) with a concentration of 0.05 mM in different proportions of DMSO and water after 24 h of sample preparation.

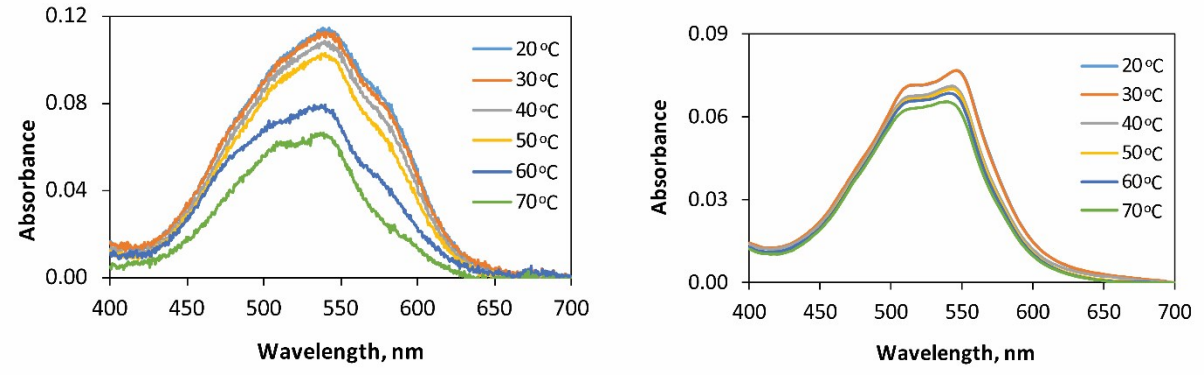



**Figure S8:** UV-Vis absorption spectra of **2** (left) and **3** (right) at 0.05 mM in water at H 7.0. The spectra were collected after keeping the samples for 24 h at 23 °C after sample preparation.

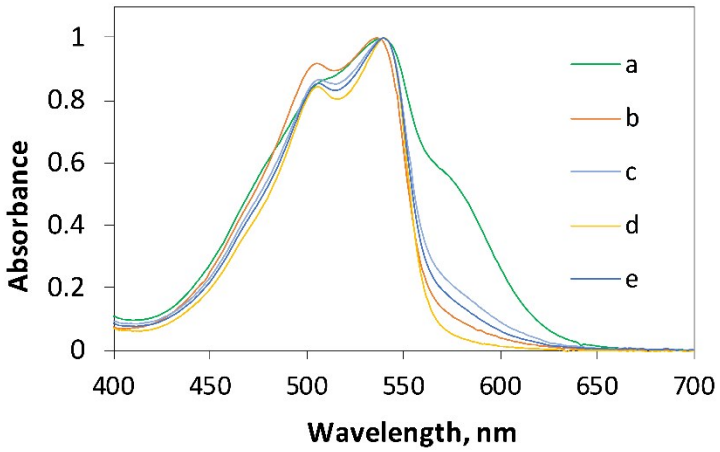



**Figure S9:** Normalised absorption spectra of **2** at 0.05 mM in water at a) pH 7 (24 hrs after sample preparation), b) pH 2 (right after lowering the pH of the previous solution), c) pH 7 (right after increasing the pH of the previous solution), d) in pH 9 (right after increasing the pH of the previous solution), e) in pH 7 (right after lowering the pH of the previous solution). The pH was adjusted by adding aliquots of HCl or NaOH aqueous solutions.

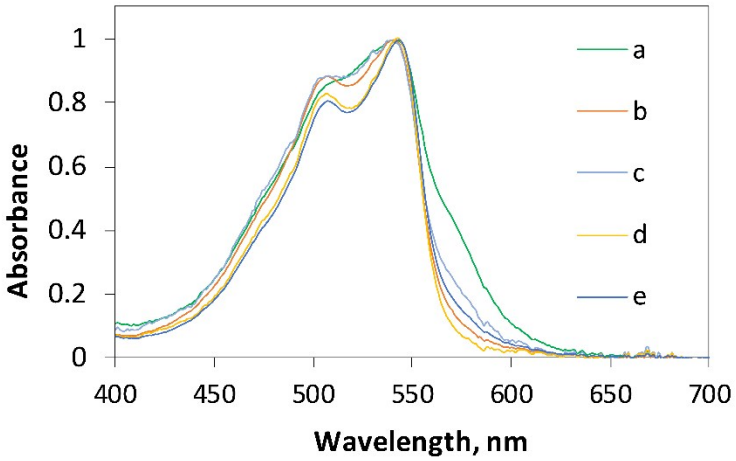



**Figure S10:** Normalised absorption spectra of **3** at 0.05 mM in water at a) pH 7 (24 hrs after sample preparation), b) pH 2 (right after lowering the pH of the previous solution), c) pH 7 (right after increasing the pH of the previous solution), d) in pH 9 (right after increasing the pH of the previous solution), e) in pH 7 (right after lowering the pH of the previous solution). The pH was adjusted by adding aliquots of HCl or NaOH aqueous solutions.

## S13. Molecular Modelling

Models were constructed using the HyperChem program. The MM+ forcefield and a Polak-Riviere (conjugate gradient) algorithm was used to energy minimize the structures formed in this program. Structures were optimized until a 0.02 Kcal/(Å mol) RMS gradient was met.

The peptide chain was first constructed in a parallel β-sheet conformation using the established database parameters of the program. The TDPP unit was separately built, the structure optimized and then manually bound to the *N*-terminus of the peptide chain. The structure of the TDPP unit in the conjugated peptide system was then optimized while keeping the peptide fragment unchanged. Four peptide strands were then manually positioned in a parallel β-sheet arrangement and the energy of the whole system was optimized.

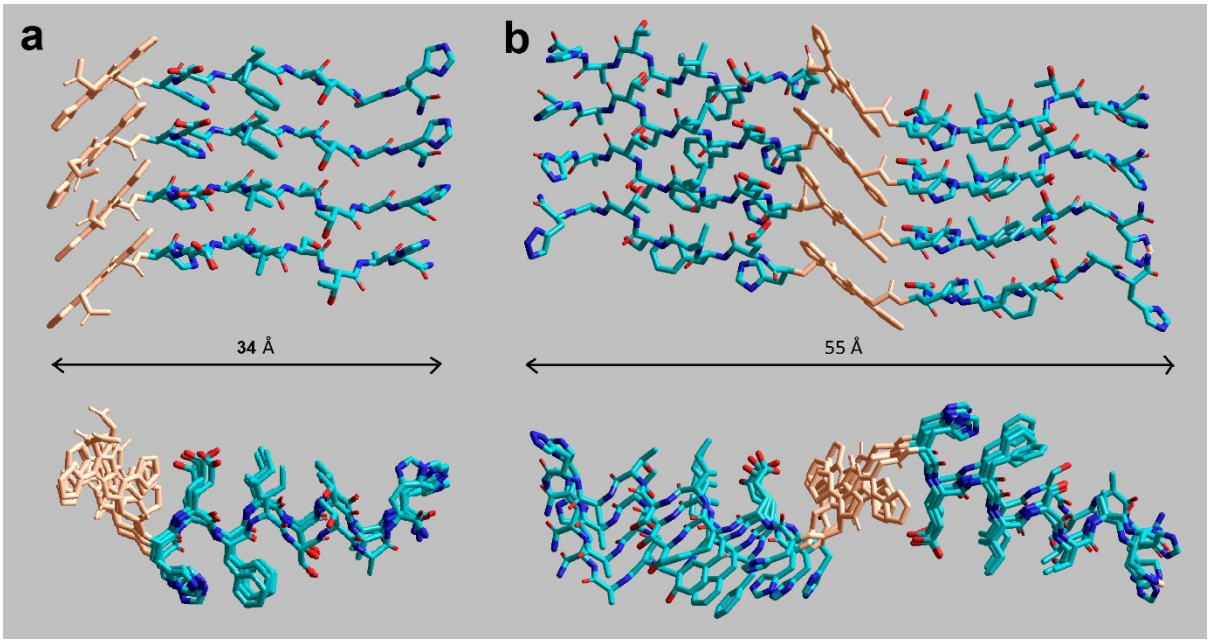



**Figure S11:** Top(top) and side (bottom) views of the minimized molecular structures of **2** (a) and **3** (b).

## S14. NMR Spectra

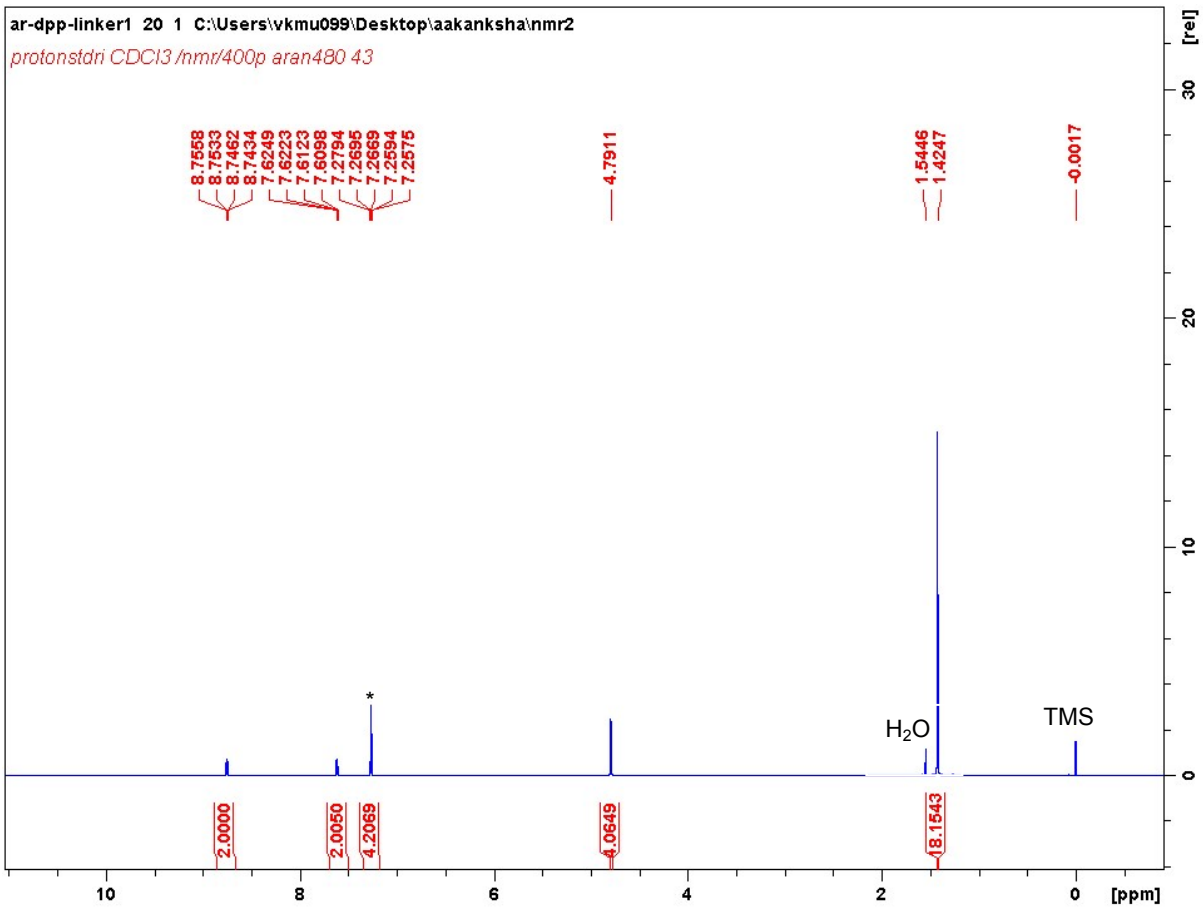



**Figure S12:** $^{1}$H NMR spectrum of compound di-*t*Bu-acetyl ester-TDPP recorded in $CDCl_3$ at 400 MHz.

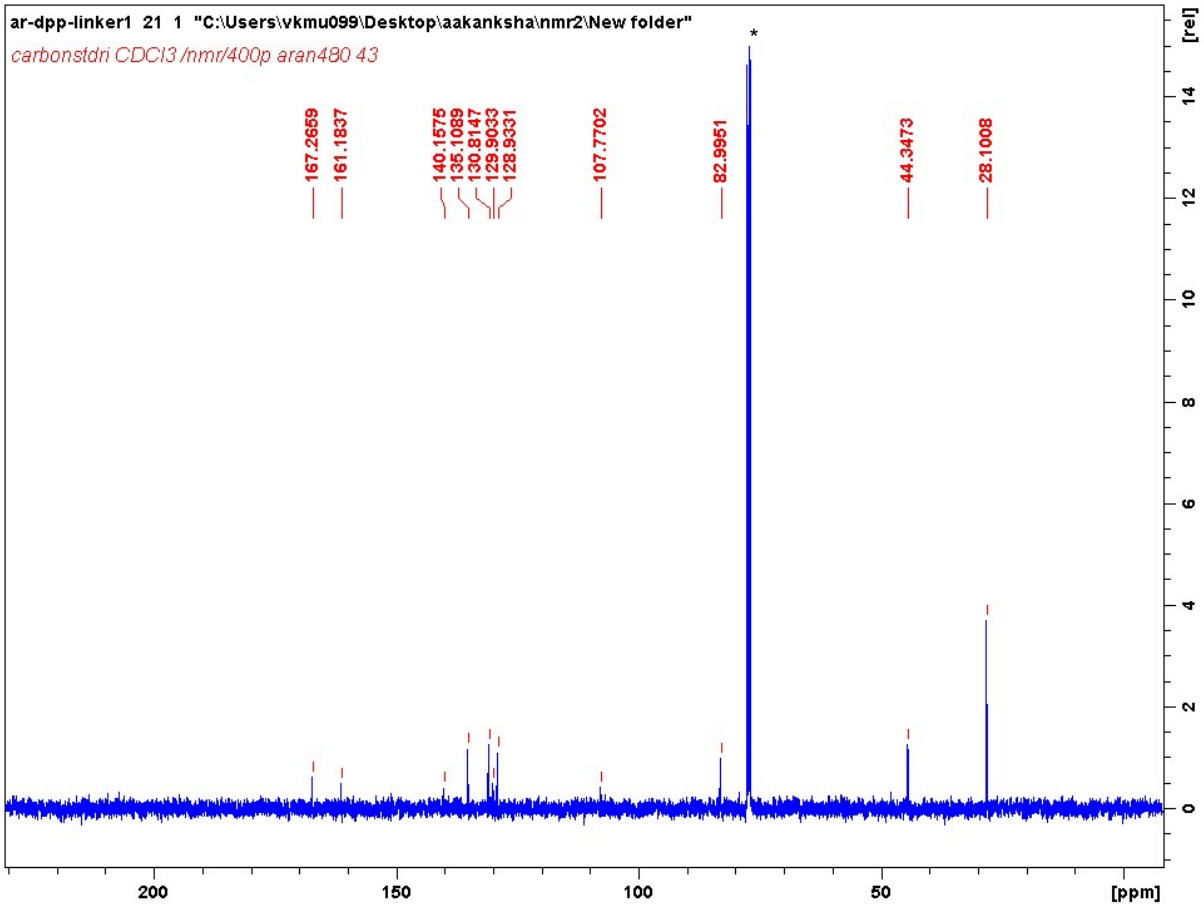



**Figure S13:** $^{1}$C NMR spectrum of compound di-*t*Bu-acetyl ester-TDPP recorded in $CDCl_3$ at 400 MHz.

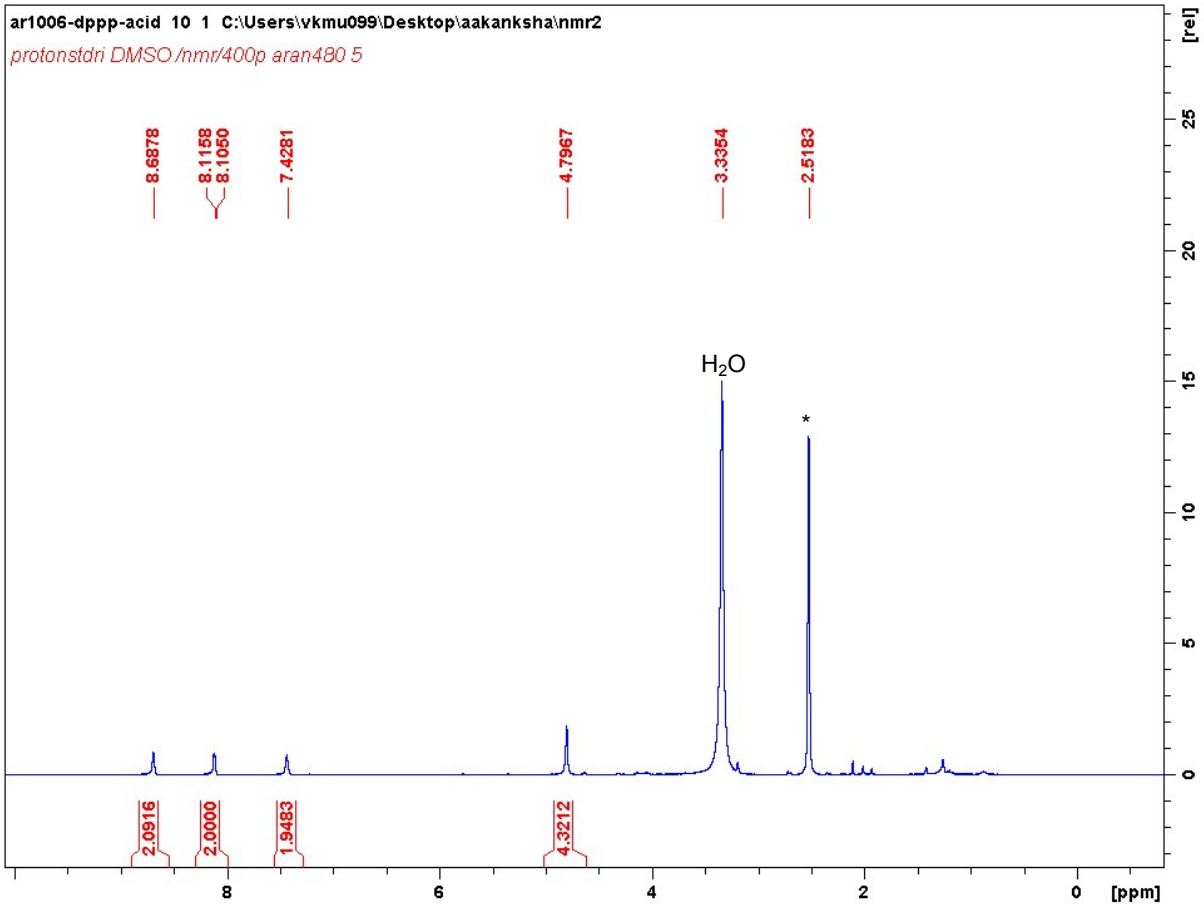



**Figure S14:** $^{1}$H NMR spectrum of compound **4** recorded in DMSO-$d_6$ at 400 MHz.

## S15. Reference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2. E. Heyer, P. Lory, J. Leprince, M. Moreau, A. Romieu, M. Guardigli, A. Roda and R. Ziessel, *Angew. Chem. Int. Ed.*, 2015, **54**, 2995-2999.
3. B. Hammouda, *J. Appl. Crystallogr.*, 2010, **43**, 716-719.