Electronic Supplementary Information

Temperature-controlled helical inversion of asymmetric triphenylamine-based supramolecular polymers; difference of handedness at the micro- and the macroscopic levels

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Experimental Section

1. Materials

Unless otherwise noted, chemical reagents and solvents were purchased from commercial suppliers (Tokyo Chemical Industry (TCI) and Sigma-Aldrich) and used without further purification.

2. Instruments and Methods (Characterization)

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 300 spectrometer, and mass spectroscopy was performed on a JEOL JMS-700 mass spectrometer. A UV–visible spectrophotometer (Thermo Evolution 600) was used to obtain the absorption spectra. IR spectra were obtained using KBr pellets, in the range 400–4000 cm^{-1}, with a Shimadzu FTIR 8400S instrument. Fluorescence spectra were obtained using a RF-5301PC spectrophotometer.

2.1 AFM Observation

AFM imaging was performed with an XE-100 instrument and a PPP-NCHR 10 M cantilever (Park Systems). Samples of supramolecular polymer for AFM were prepared by spin-coating (1,500 rpm) onto freshly cleaved muscovite mica. Images were recorded in a non-contact mode in the air at RT with a resolution of 1,024 × 1,024 pixels, using moderate scan rates (0.3 Hz).

2.2 Circular Dichroism (CD) Studies

CD spectra were recorded on a Jasco J-815 CD spectrophotometer. CD spectra were recorded over the range of 280–400 nm using a quartz cell with a 1 cm path length. Scans were taken at a rate of 100 nm/min with a sampling interval of 1.0 nm and a response time of 1 s.

2.3 Self-Assembled Supramolecular Polymer Preparation

The self-assembled supramolecular polymer (**TPAs**) were used as an example to describe the preparation procedure. **TPAs** (8×10^{-5} M) were suspended in a septum-capped 5.0 mL glass vial and heated (~100 °C) until a homogeneous solution was obtained. The solution was sonicated in a bath sonicator for a few seconds and cooled to ambient temperature to afford the self-assembled supramolecular polymer.

2.4 DFT

Quantum chemical calculations were performed with the Gaussian 09 program[S1] Computations of **TPA-1** and **TPA-3** are so challenging for the full geometry optimization that the pentamers of **TPA-1** and **TPA-3** have been used in the theoretical calculations of current studies to reduce the computational cost. Unless otherwise specified, the calculations regarding **TPA-1** and **TPA-3** reported hereafter were performed out with the pentamers of **TPA-1** and **TPA-3** by employing density functional theory (DFT) Becke's three parameter hybrid functions with the nonlocal correlation of Lee−Yang−Parr (B3LYP) method in the absence of symmetry constraints. The energies include zero-point energy corrections using the B3LYP/6-31G levels of theory. Further details about the calculations are reported in the Supporting Information.

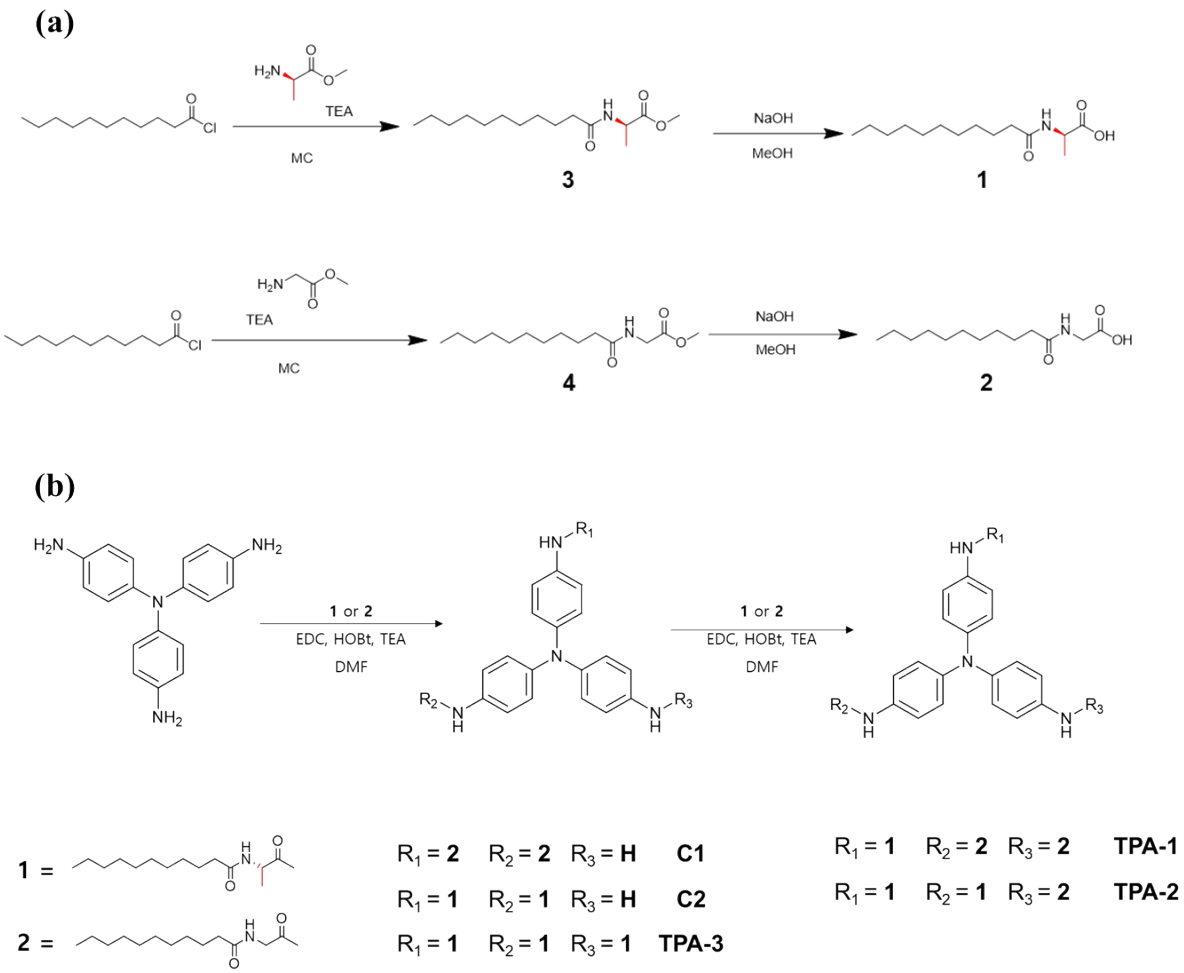
2.5 VCD

VCD and IR spectra were measured on an FT/IR-4100 spectrometer with VFT-4000 attachment (JASCO, Japan) using KBr pellets. The KBr pellet (13 mm diameter) of each sample was inserted between two BaF2 plates together with 100 um teflon spacer. The signal was accumulated by 2,000 scans (ca. 22 min) at every 90 degrees and averaged. The resolution was 4 cm^{-1}.

2.6 Linear dichroism (LD) Studies

Linear dichroism (LD) spectra were recorded on a Jasco J-815 Spectropolarimeter (150-L Type). Temperature–dependent spectra were recorded over the range of 280–500 nm using a quartz cell with a 1 cm path length. Scans were taken at a rate of 100 nm/min with a sampling interval of 1.0 nm and a response time of 1 s.

Scheme



Scheme S1. Synthetic methods for (a) **1**, **2** and (b) **TPAs**.

Supplementary Figures

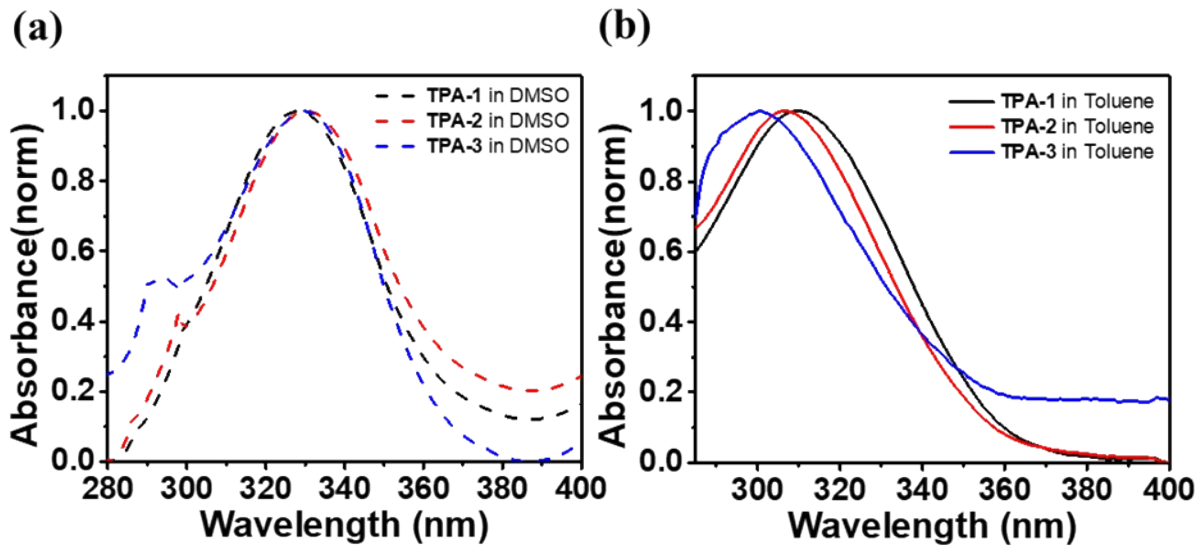


Fig. S1 UV-Vis absorption spectra of **TPA-1** (black line and black dash), **TPA-2** (red line and red dash) and **TPA-3** (blue line and blue dash) in (a) DMSO and (b) toluene at 298 K (concentrations of all samples were 8.0 x 10^{-5} M).

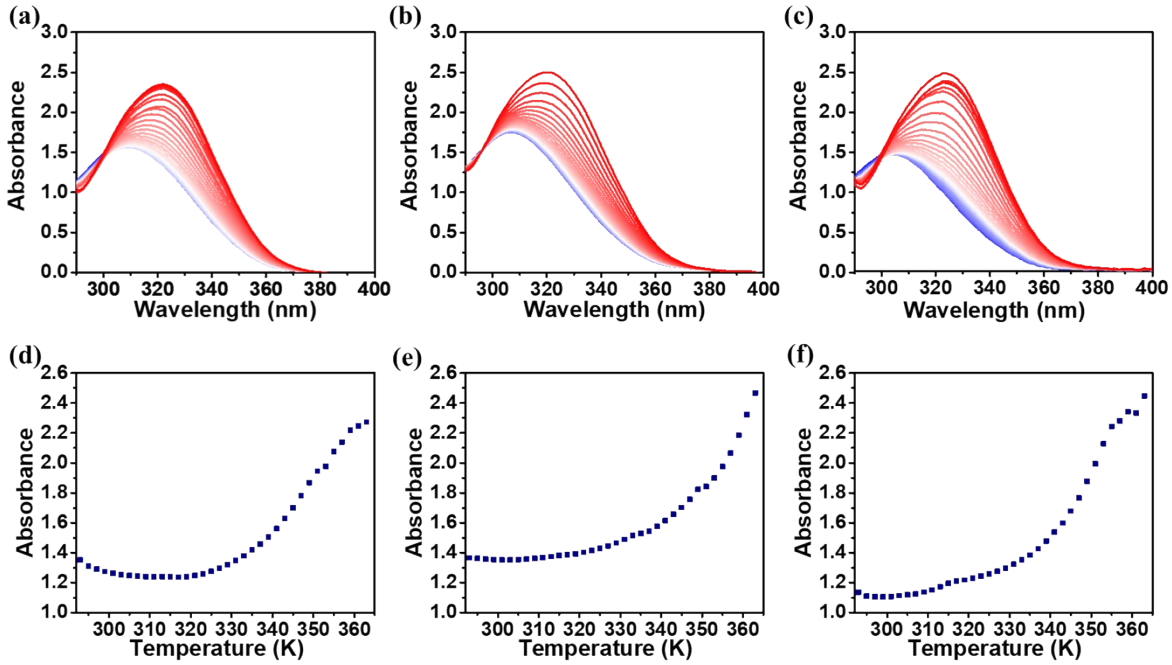


Fig. S2 Temperature-dependent electronic absorption spectra of (a) **TPA-1**, (b) **TPA-2** and (c) **TPA-3** in toluene at 8.0 x 10^{-5} M (electronic absorption spectra were measured every 2 K in the range from 293 K (blue line) to 363 K (red line)). Plots of electronic absorption intensities at the absorption maxima (λ = 320 nm) of (d) **TPA-1**, (e) **TPA-2** and (f) **TPA-3** as a function of temperatures.

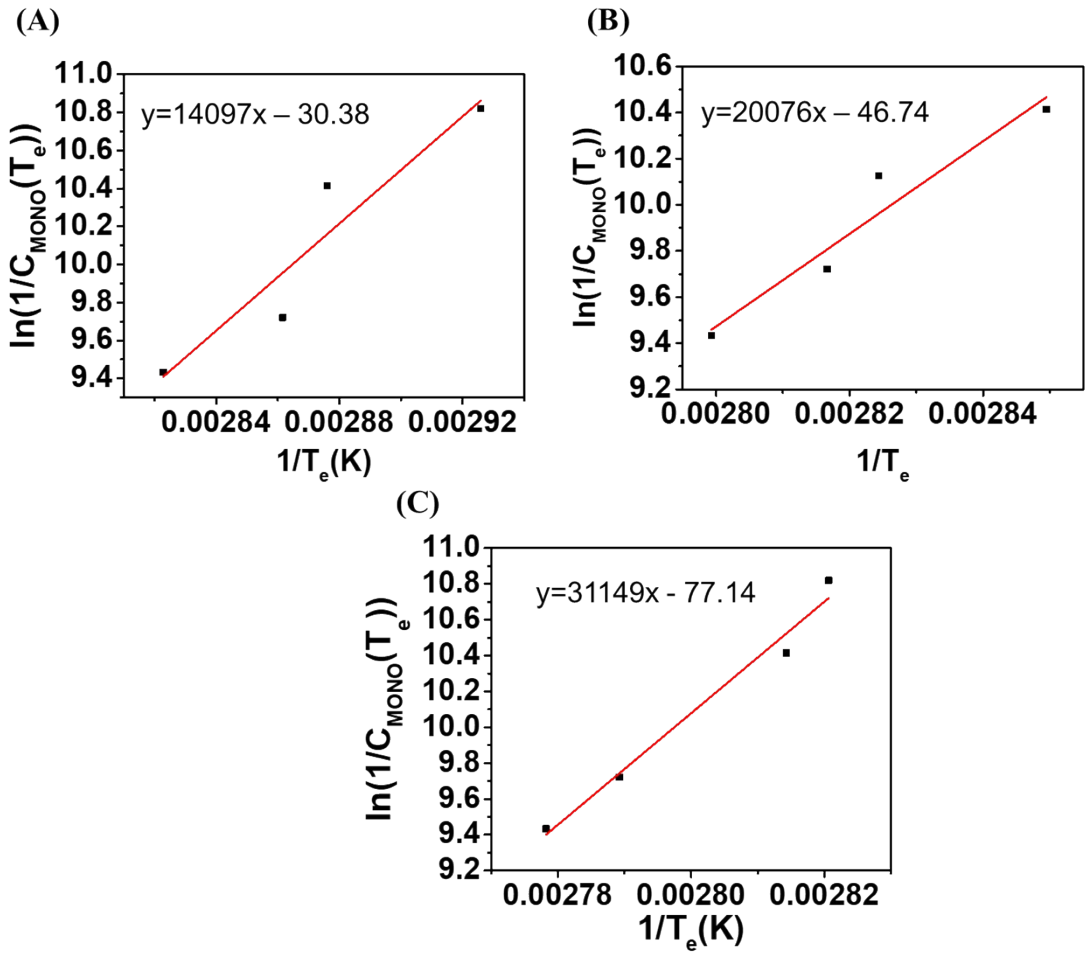


Fig. S3 Natural logarithm of the reciprocal of concentration (C_T) as a function of the reciprocal of elongation temperature T_e (van't Hoff plot) obtained through the heating experiments of (A) **TPA-1**, (B) **TPA-2** and (C) **TPA-3** in toluene under different concentrations.[S2-S5]

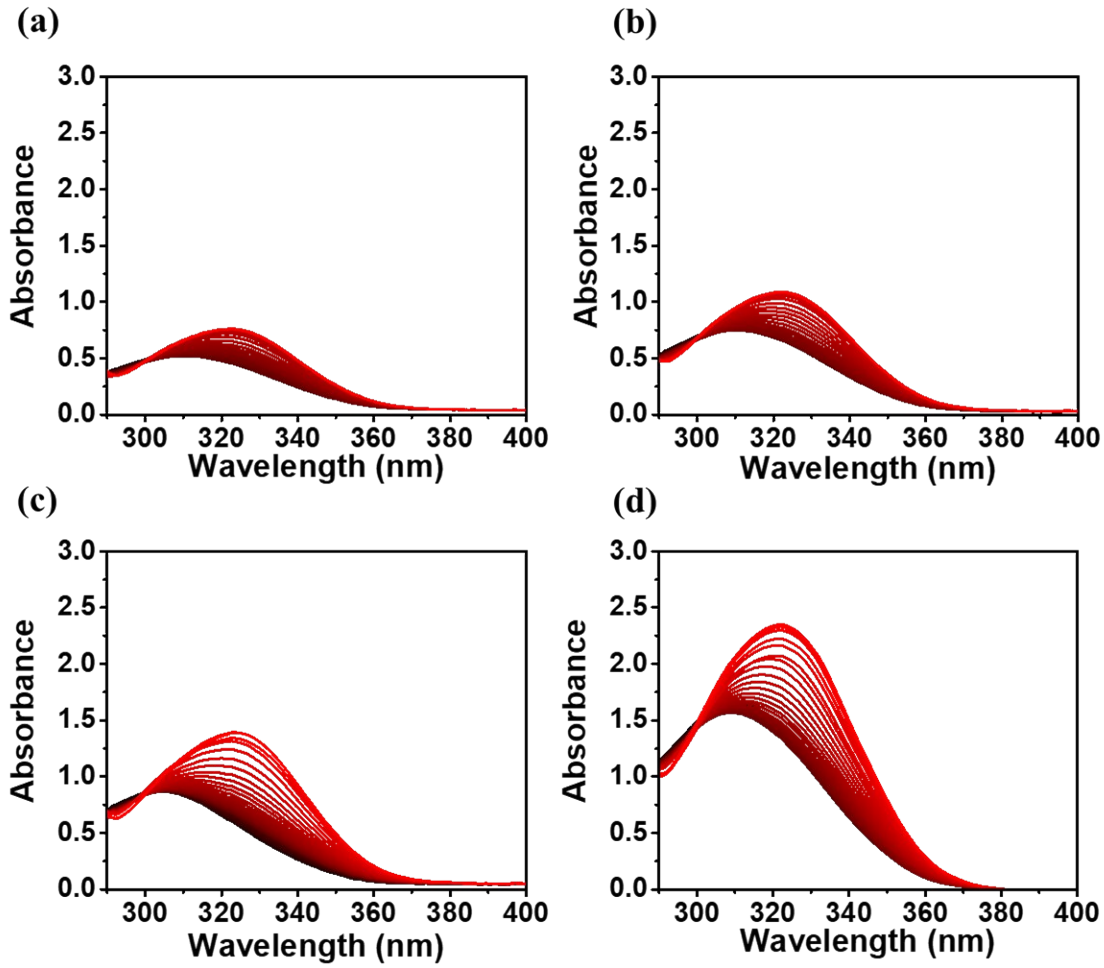


Fig. S4 Temperature-dependent UV-Vis spectra of supramolecular polymer **TPA-1** prepared at (a) 2 x 10^{-5} M, (b) 3 x 10^{-5} M, (c) 6 x 10^{-5} M, and (d) 8 x 10^{-5} M in toluene (from 293 K to 363 K).

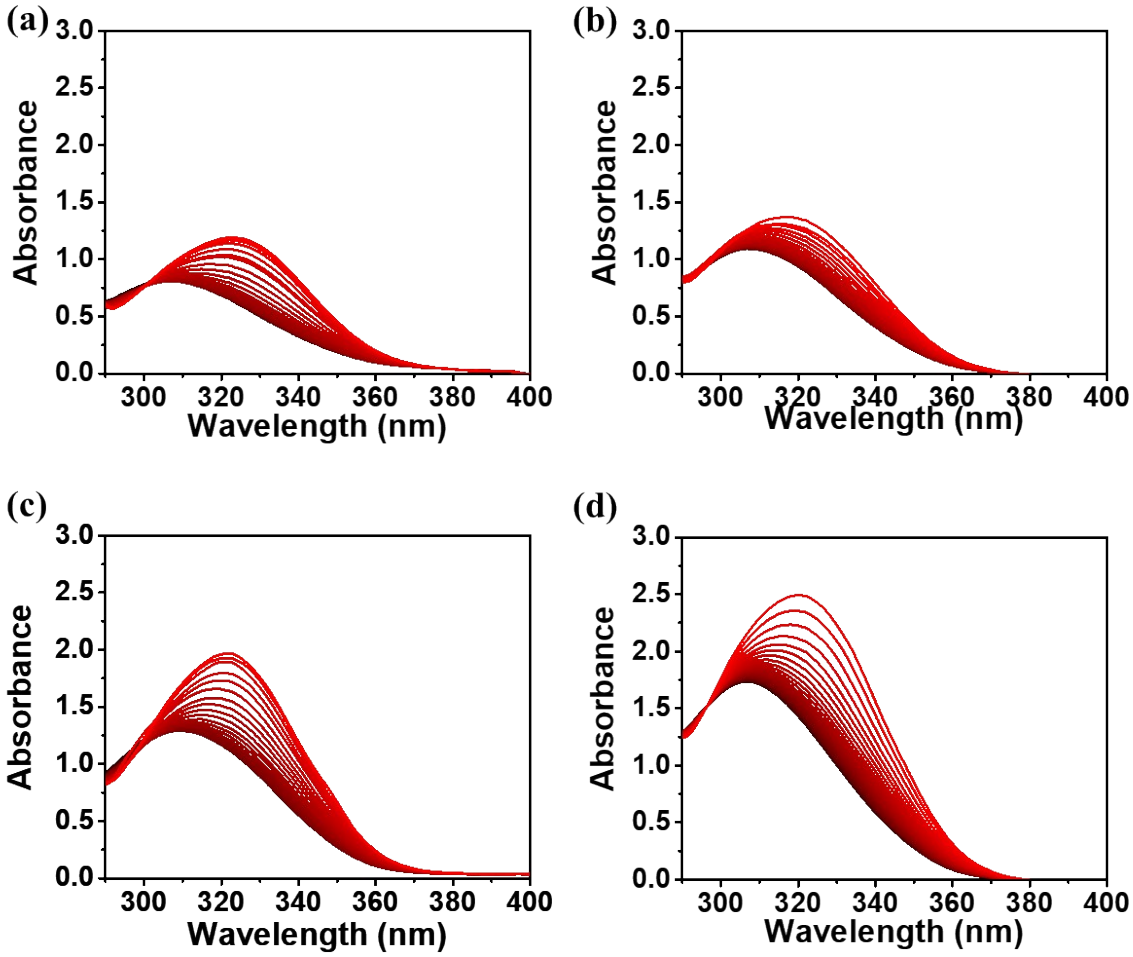


Fig. S5 Temperature-dependent UV-Vis spectra of supramolecular polymer **TPA-2** prepared at (a) 3 x 10^{-5} M, (b) 4 x 10^{-5} M, (c) 6 x 10^{-5} M and (d) 8 x 10^{-5} M in toluene (from 293 K to 363 K).

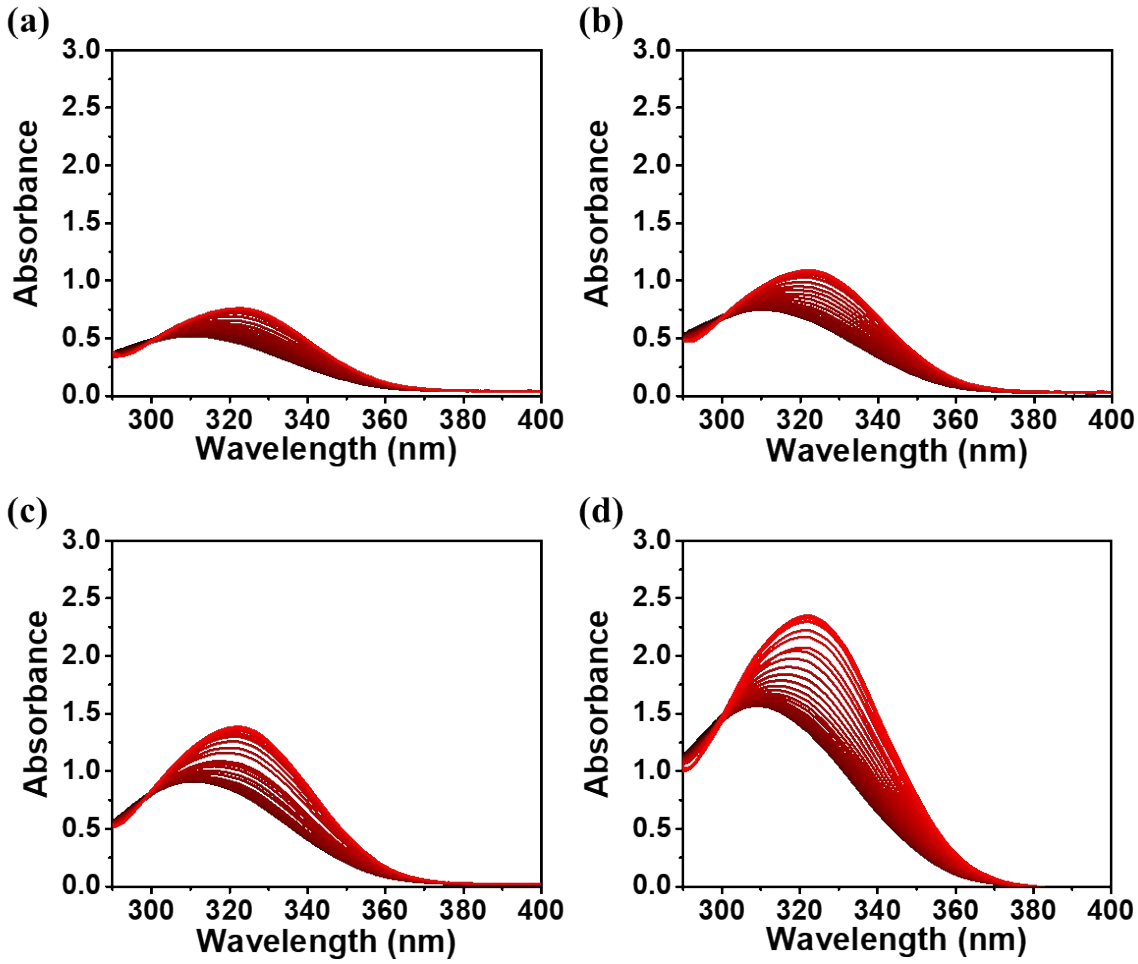


Fig. S6 Temperature-dependent UV-Vis spectra of supramolecular polymer **TPA-3** prepared at (a) 2 x 10^{-5} M, (b) 3 x 10^{-5} M, (c) 6 x 10^{-5} M, and (d) 8 x 10^{-5} M in toluene (from 293 K to 363 K).

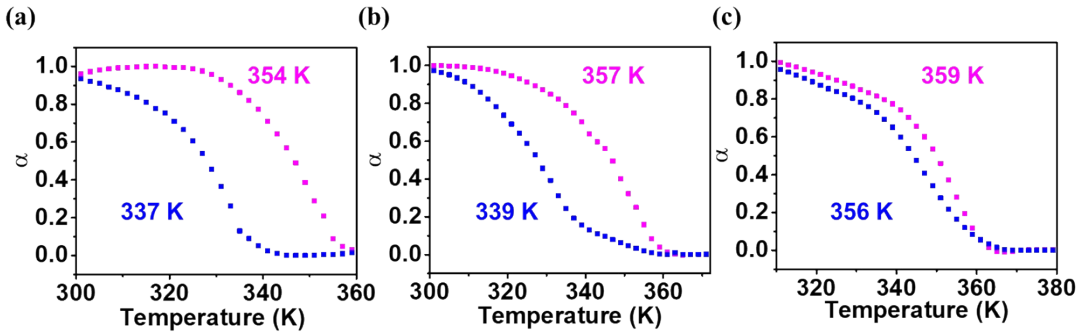


Fig. S7 Temperature-dependent degree of (a) **TPA-1**, (b) **TPA-2** and (c) **TPA-3** (α_{Agg}) calculated from the apparent absorption coefficients at λ = 320 nm observed in the cooling (blue) and heating (pink) processes in toluene.[S6, S7]

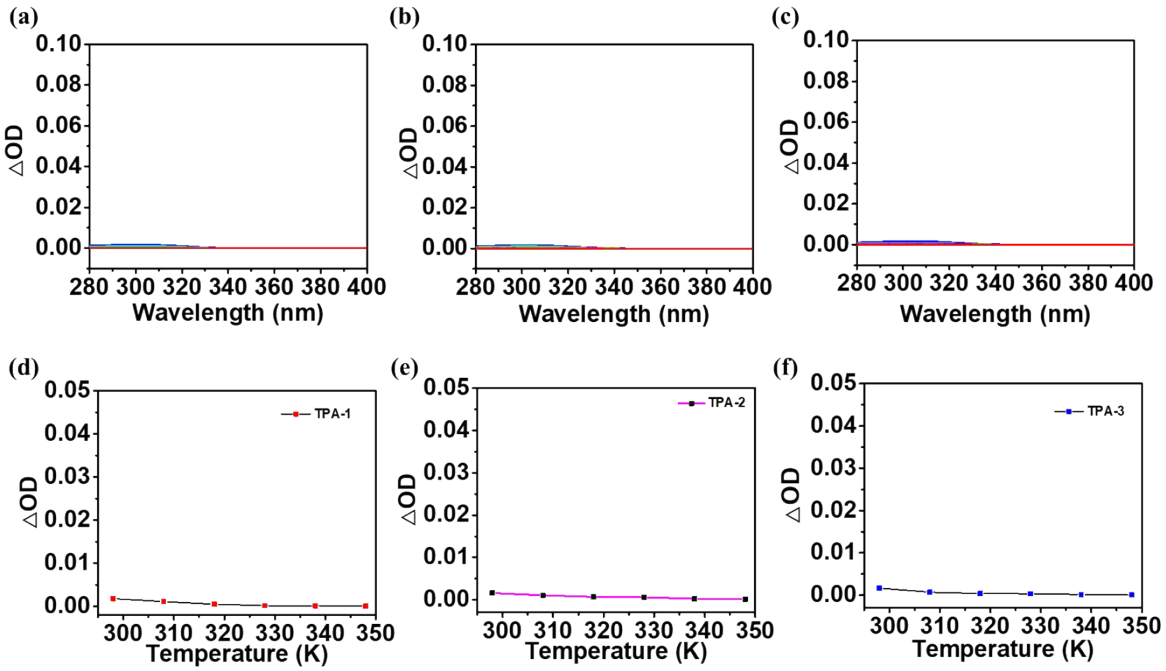


Fig. S8 Temperature-dependent LD spectra of supramolecular polymer (a) **TPA-1**, (b) **TPA-2** and (c) **TPA-3** in toluene.[S8-S10] Plot for LD intensity of (d) **TPA-1**, (e) **TPA-2** and (f) **TPA-3** against temperature.

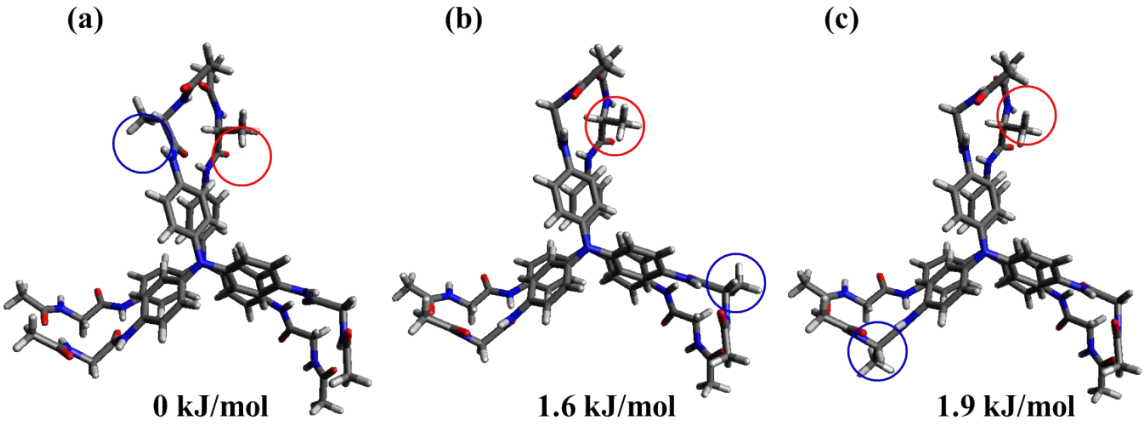


Fig. S9 DFT calculation of dimeric structures of (a) **TPA-1(AA)**, (b) **TPA-1(AG)** and **TPA-1(GA)**.

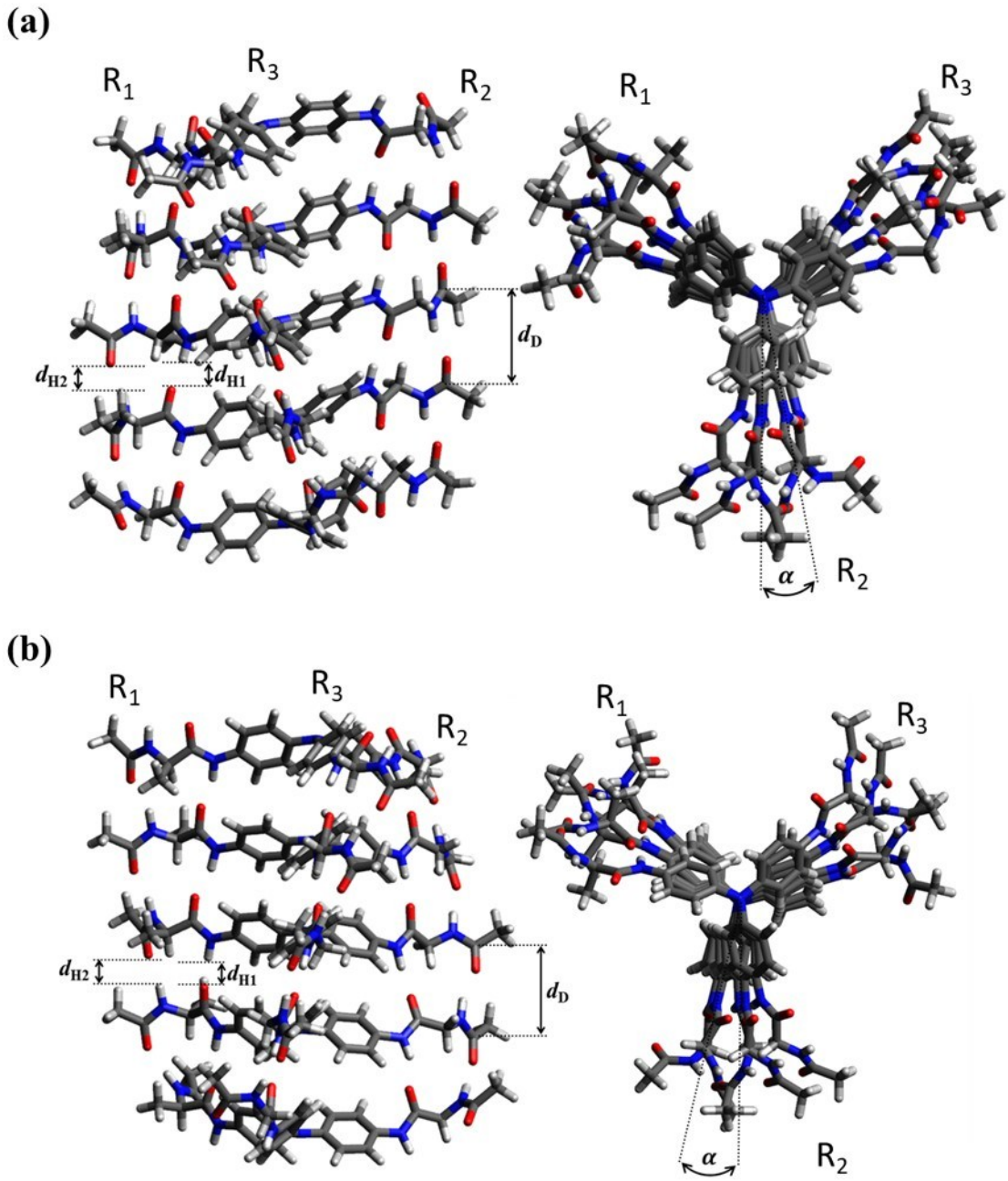


Fig. S10 Three-dimensional structures and hydrogen bond length (d_H) and interdiscotic angle (α) and interdiscotic distance (d_D) of **TPA-1(AA)** for (a) anti-parallel (2:1) and (b) parallel (3:0) conformations.

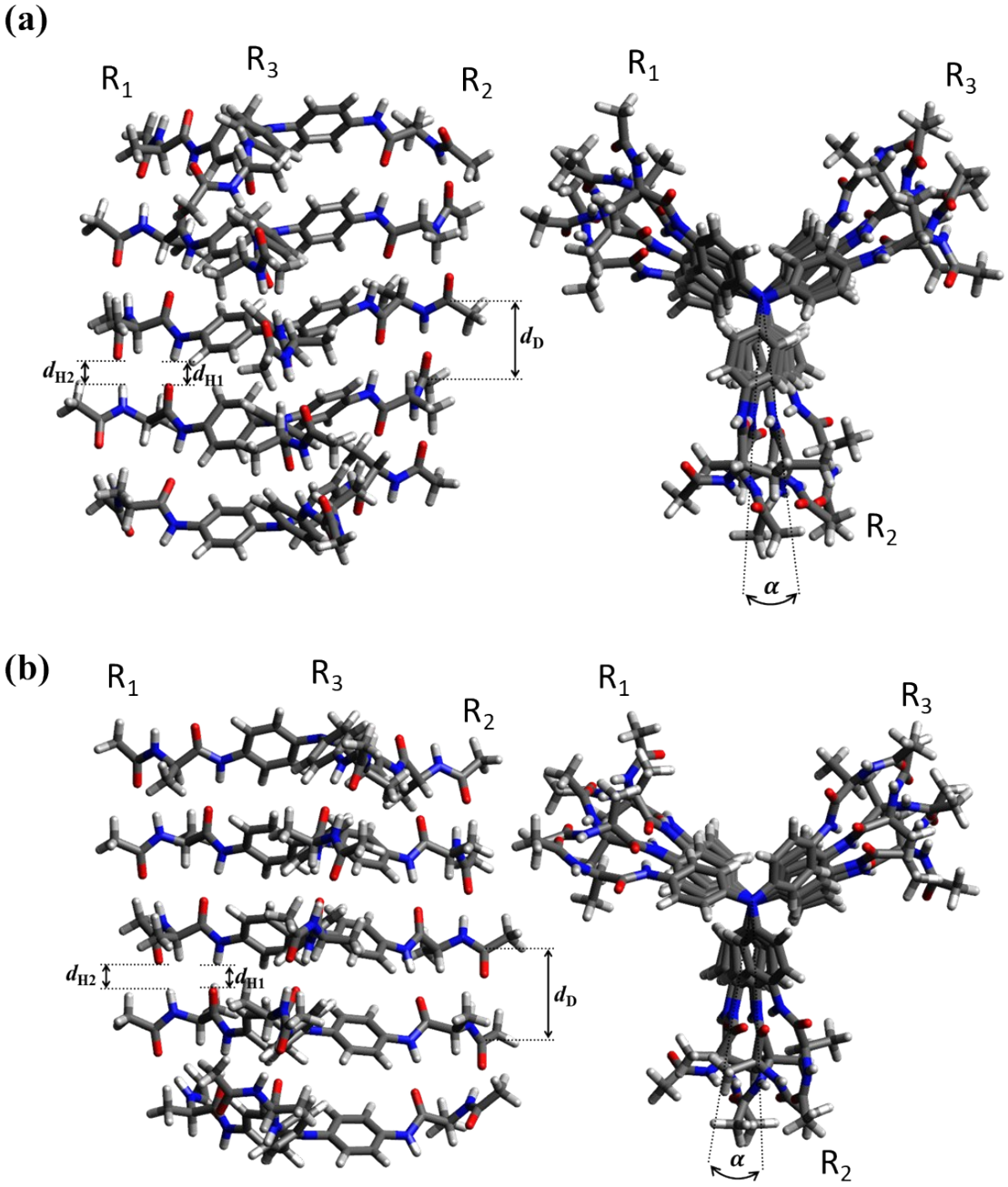


Fig. S11 Three-dimensional structures and hydrogen bond length (d_H) and interdiscotic angle (α) and interdiscotic distance (d_D) of **TPA-3(AA)** for (a) anti-parallel (2:1) and (b) parallel (3:0) conformations.

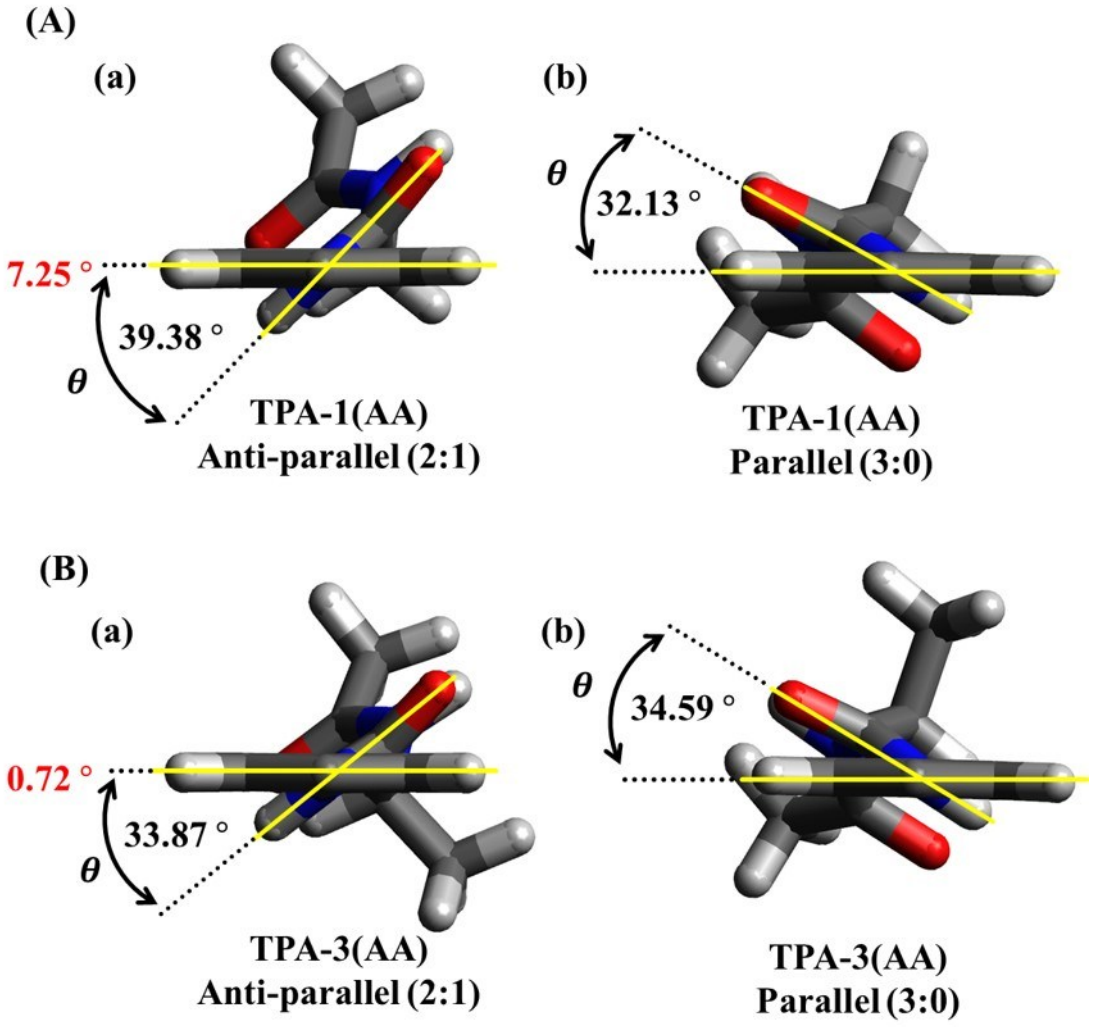


Fig. S12 Three-dimensional structures and the carbonyl-phenyl dihedral angles (θ) of monomer of (A) **TPA-1(AA)** and (B) **TPA-3(AA)** for (a) anti-parallel (2:1) and (b) parallel (3:0) conformations.

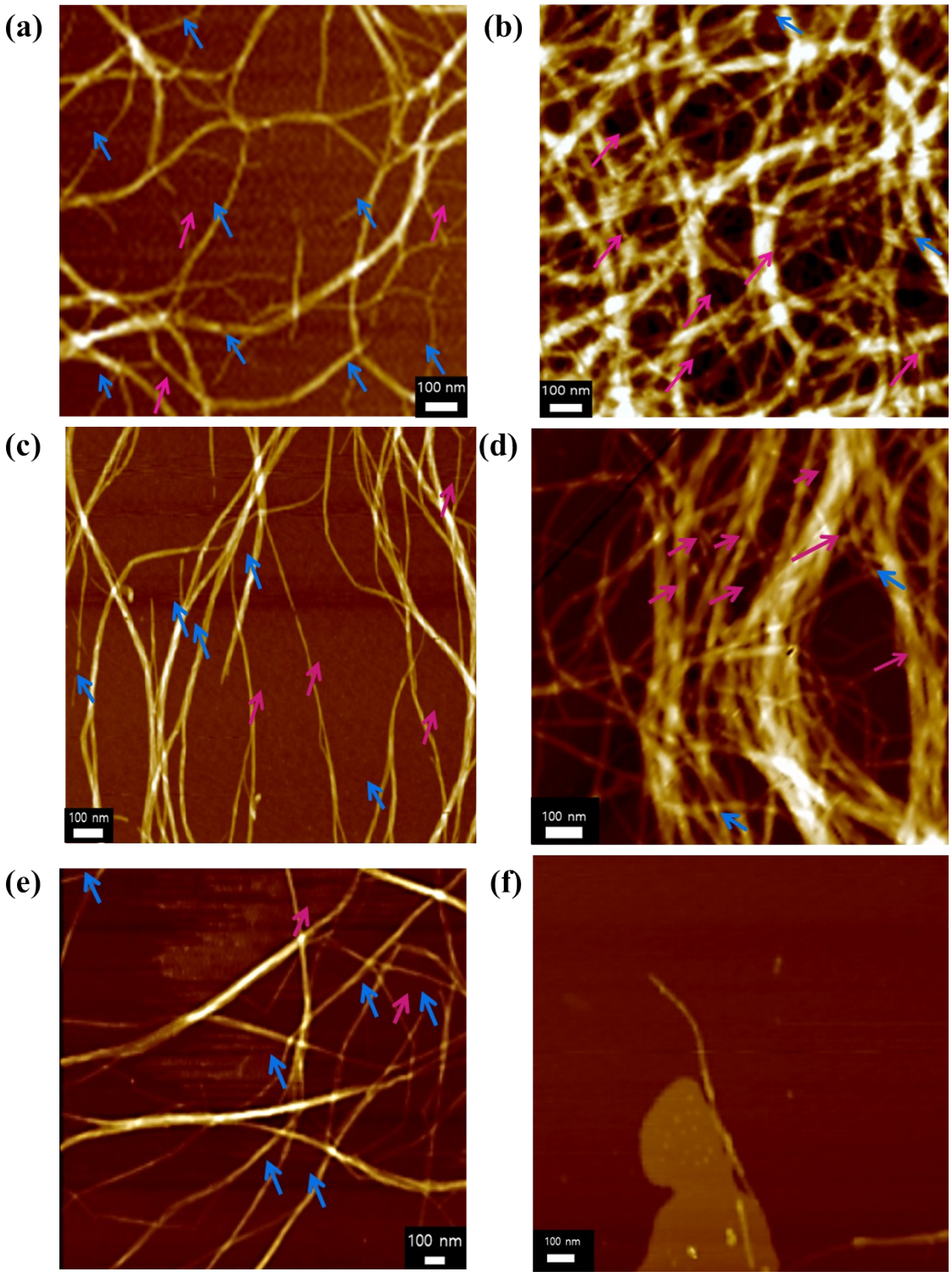


Fig. S13 AFM images of supramolecular polymers (a and b) **TPA-1**, (c and d) **TPA-2** and (e and f) **TPA-3** formed at 298 K (a, c and e) and 333 K (b, d, and f).

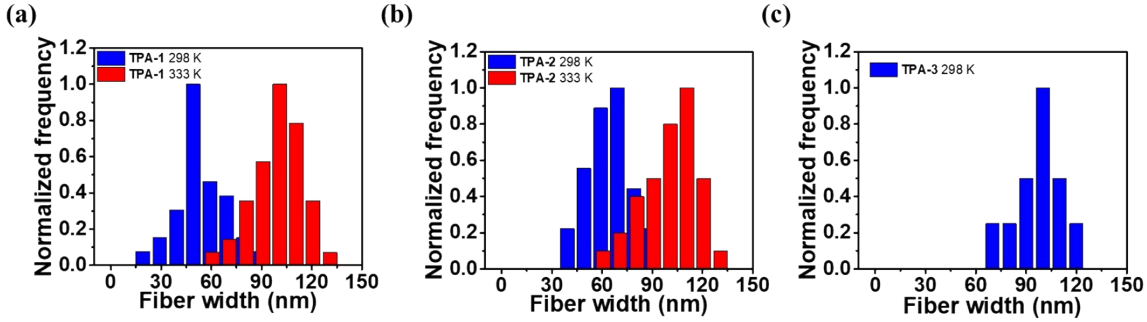


Fig. S14 Fiber width distribution of supramolecular polymers (a) **TPA-1** (b) **TPA-2** and (c) **TPA-3**.

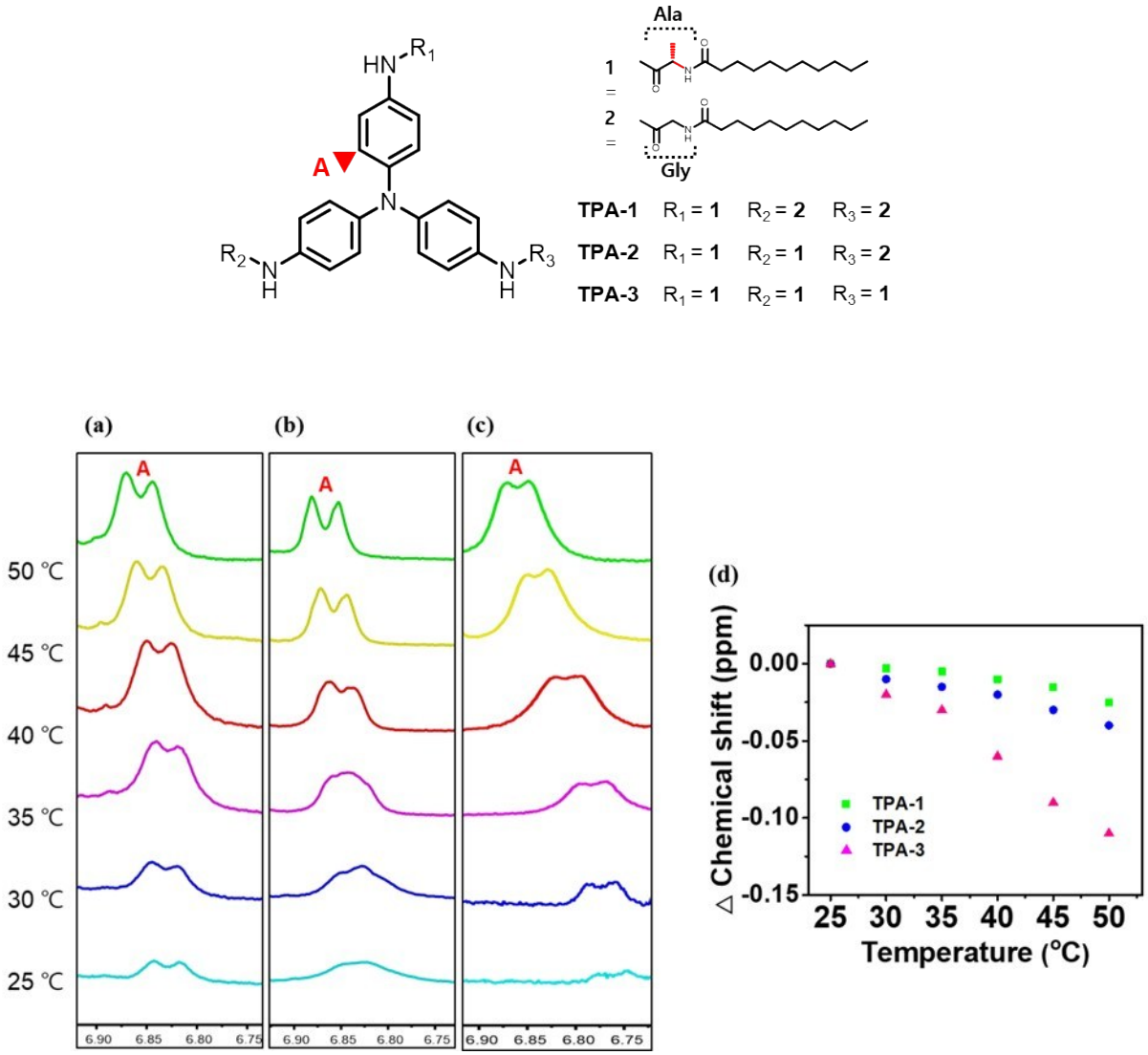


Fig. S15 Temperature-dependent ^{1}H NMR spectra of (a) **TPA-1**, (b) **TPA-2** and (c) **TPA-3** in toluene-d_8/$CDCl_3$ (3:7 v/v) (the concentration of samples was 1 x 10^{-3} M). (d) Plot for chemical shifts of the proton (A) of **TPA-1** (green), **TPA-2** (blue) and **TPA-3** (pink) as a function of temperatures.

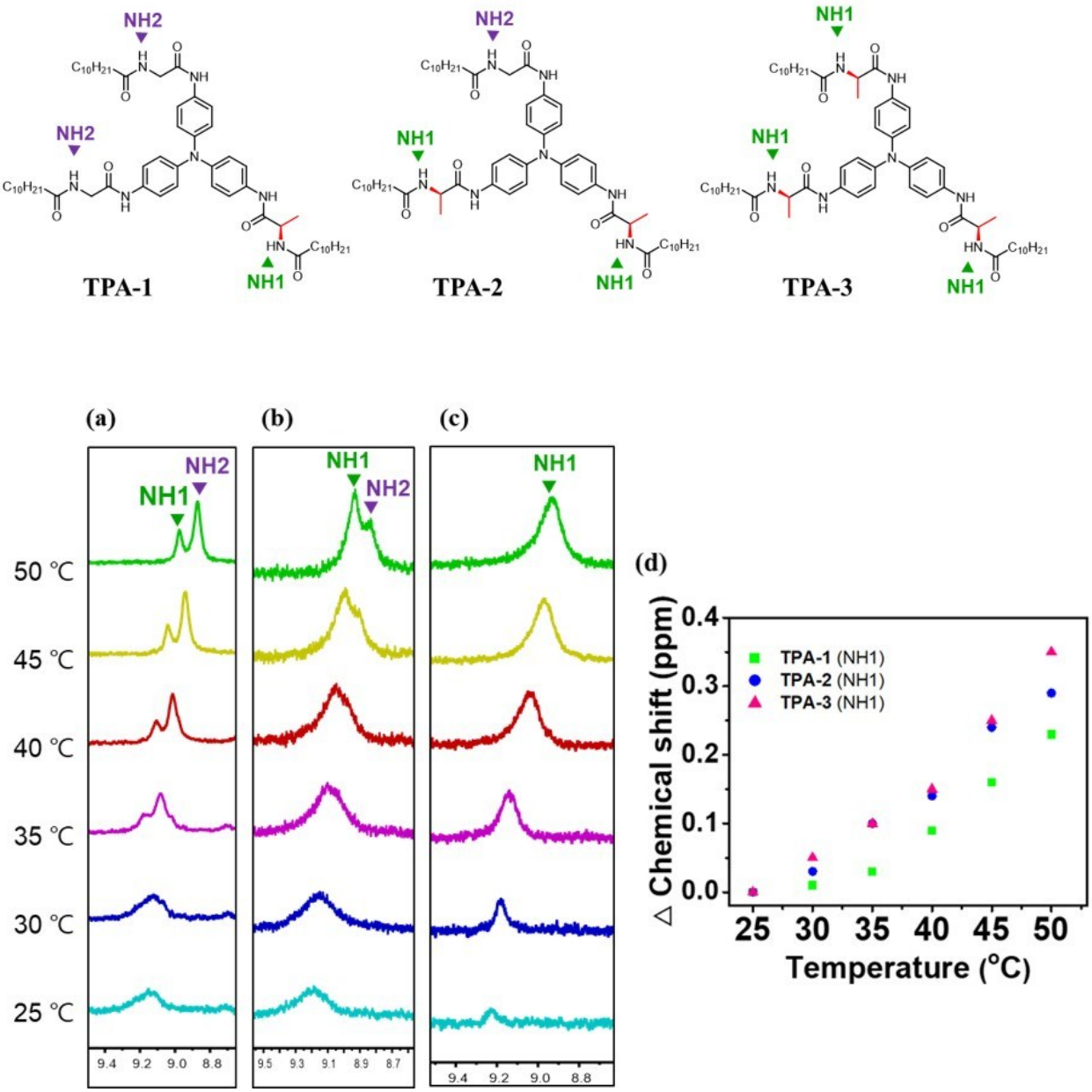


Fig. S16 Temperature-dependent ^{1}H NMR spectra of (a) **TPA-1**, (b) **TPA-2** and (c) **TPA-3** in toluene-d_8/$CDCl_3$ (3:7 v/v) (the concentration of samples was 1 x 10^{-3} M). (d) Plot for chemical shifts of the proton (NH1) of **TPA-1** (green), **TPA-2** (blue) and **TPA-3** (pink) as a function of temperatures.

Table

Table S1. Comparison of the relative energies between parallel (3:0) and anti-parallel (2:1) conformations of **TPA-1** and **TPA-3**

	TPA-1		**TPA-3**	
	Parallel (3:0)	**Anti-parallel (2:1)**	**Parallel (3:0)**	**Anti-parallel (2:1)**
Relative energy (kJ/mol)	14.76	0	14.61	0

Table S2. Calculated carbonyl-phenyl dihedral angle (θ) of **TPA-1** and **TPA-3** for parallel (3:0) and anti-parallel (2:1) conformations

		TPA-1			TPA-3		
		Parallel (3:0)	**Anti-parallel (2:1)**	**Difference**	**Parallel (3:0)**	**Anti-parallel (2:1)**	**Difference**
carbonyl-phenyl dihedral angle (θ)	**R_1**	35.08	32.09	2.99	35.72	32.96	2.76
	R_2	31.55	35.92	4.37	35.16	39.74	4.58
	R_3	32.13	39.38	7.25	34.59	33.87	0.72

Table S3. Calculated hydrogen bond length (d_H), angle (α), and interdiscotic distance (d_D) of

			TPA-1			TPA-3		
			Parallel (3:0)	Anti-parallel (2:1)	Difference	Parallel (3:0)	Anti-parallel (2:1)	Difference
Hydrogen bond length (d_H)	R_1	d_{H1}	1.76	1.78	0.02	1.76	1.78	0.02
		d_{H2}	1.87	1.89	0.02	1.88	1.89	0.01
	R_2	d_{H1}	1.77	1.78	0.01	1.76	1.76	0
		d_{H2}	1.89	1.88	0.01	1.88	1.87	0.01
	R_3	d_{H1}	1.78	1.79	0.01	1.76	1.80	0.02
		d_{H2}	1.88	1.90	0.02	1.88	1.90	0.02
Smaller interdiscotic angle (α)	R_1		9.23	9.03	0.2	9.11	8.85	0.26
	R_2		10.48	9.38	1.1	9.01	8.71	0.3
	R_3		9.61	7.93	1.68	9.10	8.33	0.77
Interdiscotic distance (d_D)	R_1		4.85	4.85	0	4.85	4.84	0.01
	R_2		4.81	4.82	0.01	4.84	4.86	0.02
	R_3		4.81	4.82	0.01	4.85	4.83	0.02

TPA-1 and **TPA-3** for parallel (3:0) and anti-parallel (2:1) conformations

Table S4. Distribution ratios of right- and left-handed helical fibers of supramolecular polymers **TPA-1**, **TPA-2** and **TPA-3** obtained at different temperatures

	Temperature [K]	Left	Right	Diameters [nm]
TPA-1	298 K	73%	27%	45
	333 K	25%	75%	90
TPA-2	298 K	55%	45%	65
	333 K	22%	78%	100
TPA-3	298 K	75%	25%	100
	333 K	-	-	100

Synthesis of Chain

Synthetic methods for **4**

Glycine methyl ester hydrochloride (3.2 g, 25.5 mmol) was dissolved in DCM (80 mL) before adding TEA (5.4 mL, 38.5 mmol). After stirring for 15 min, the solution was cooled to 0°C, and undecanoyl chloride (4 g, 19.5 mmol) was added slowly over one hour. The solution was allowed to warm to RT and was stirred overnight. HCl (10%, 10 mL) was added and the mixture was extracted with DCM (3 × 10 mL). The combined organic extracts were washed with HCl (10%, 10 mL) and brine (10 mL). The solution was dried over Na_2SO_4, filtered, and the solvent was evaporated to dryness under reduced pressure. The crude product was dried under vacuum to give **6** as a white solid in 91% yield. mp 63 – 64 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 0.86 (t, J = 6.7 Hz, 3H), 3.62 (s, 3H), 8.23 (dd, J = 8.6, 3.4 Hz, 1H), 1.24 (m, 14H), 1.48 (m, 2H), 3.81 (d, J = 5.9 Hz, 2H), 2.11 (t, J = 7.3 Hz, 2H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 173.14, 170.92, 51.95, 35.45, 31.82, 29.50, 25.64, 22.59, 14.33 ESI-MS (m/z): Calculated for $C_{14}H_{27}NO_3$ $[M+H]^+$ 258.19, Found $[M+H]^+$ 258.08.

Synthetic methods for **2**

A solution of **4** (4.5 g, 17.5 mmol) in a mixture with MeOH (100 mL) was heated to reflux. The reaction mixture was then added to aqueous 1 M NaOH.[S11, S12] After refluxing for 7 h, the organic solvents were removed in vacuo, and water (10 mL) was added. The remaining aqueous solution was acidified to pH 3 by adding 3 N HCl. The resulting precipitate was filtered and washed with water. The precipitate was dried under vacuum to give **4** as a white solid in 82% yield. mp 118 – 119 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 1.24 (m, 14H), 1.48 (m, 2H), 2.10 (t, J = 7.4 Hz, 2H), 3.72 (d, J = 5.9 Hz, 2H), 8.09 (t, J = 5.8 Hz, 1H), 12.46 (d, J = 0.9 Hz, 1H), 0.86 (t, J = 6.7 Hz, 1H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 173.14, 170.92, 51.95, 35.45, 31.82, 29.50, 25.64, 22.59, 14.33 ; ESI-MS (m/z): Calculated for $C_{13}H_{25}NO_3$ $[M+H]^+$ 243.18, Found $[M+H]^+$ 244.17.

Synthetic methods for **3**

D-alanine methyl ester hydrochloride (3.5 g, 25 mmol) was dissolved in DCM (80 mL) before adding TEA (4.8 mL, 39 mmol). After stirring for 15 min, the solution was cooled to 0°C and undecanoyl chloride (4 g, 19.5 mmol) was added slowly over one hour. The solution was allowed to warm to RT and stirred overnight. HCl (10%, 10 mL) was added and the mixture was extracted with DCM (3 × 10 mL). The combined organic extracts were washed with 10% HCl (10 mL) and brine (10 mL). The solution was dried over Na_2SO_4, filtered, and the solvent was evaporated to dryness under reduced pressure. The crude product was dried under vacuum to give **4** as a white solid in 83% yield. mp 63 – 64 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 1.48 0 (m, 2H), 2.09 (t, J = 7.3 Hz, 2H), 3.61 (s, 3H), 4.24 (p, J = 7.3 Hz, 1H), 0.86 (t, J = 6.7 Hz, 3H), 8.20 (d, J = 6.9 Hz, 1H), 1.24 (dd, J = 9.4, 3.2 Hz, 17H); ^{13}C NMR (75 MHz, DMSO-d_6) δ ppm 173.75, 172.60, 52.19, 47.87, 35.35, 31.78, 29.44, 29.26, 29.18, 29.02, 25.60, 22.57, 17.41, 14.42; ESI-MS (m/z): Calculated for $C_{15}H_{29}NO_3$ $[M+H]^+$ 271.81, Found $[M+H]^+$ 272.17.

Synthetic methods for **1**

A solution of **3** (3 g, 11 mmol) in a mixture with MeOH (50 mL) was heated to reflux. The reaction mixture was then added to aqueous 1 M NaOH.[S11, S12] After refluxing for 7 h, the organic solvents were removed in vacuo, and water (10 mL) was added. The remaining aqueous solution was acidified to pH 3 by adding 3 N HCl. The resulting precipitate was filtered and washed with water. The precipitate was dried under vacuum to give **3** as a white solid in 85% yield. We confirmed the racemization of alanine-appended **1** by HPLC with chiral columns, which resulted in the presence of pure D-alanine-appended **1**. mp 118 – 119 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 2.09 (t, J = 7.3 Hz, 2H), 4.19 (m, 1H), 8.06 (d, J = 6.5 Hz, 1H), 12.42 (dd, J = 2.2, 1.0 Hz, 1H), 1.25 (d, J = 3.3 Hz, 17H), 0.86 (d, J = 6.9 Hz, 3H), 1.48 (d, J = 5.2 Hz, 2H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 175.47, 172.46, 47.77, 35.45, 31.78, 29.45, 29.28, 29.18, 29.07, 25.65, 22.57, 17.66, 14.43; ESI-MS (m/z): Calculated for $C_{14}H_{27}NO_3$ [M+H]+ 257.20, Found [M+H]+ 257.92.

Synthesis of TPAs

Synthetic methods for **C1**

A mixture of **2** (1.67 g, 6.8 mmol), EDC (1.45 g, 7.6 mmol), and HOBt (1.02 g, 7.6 mmol) was dried in vacuo for 8 h then dissolved in DMF (50 mL). TEA (1.1 mL, 7.5 mmol) was added after the solution was cooled to 0 ℃, then, it was stirred for 1 h. To the mixed solution, tris(4-aminophenyl)amine (1.0 g, 3.4 mmol) dissolved in DMF (10 mL) was added, and it was stirred for 36 h at room temperature. The solvent was removed by evaporation. The crude product was dissolved in DCM and washed with brine three times. The solution was dried over Na_2SO_4, filtered, and the solvent was evaporated to dryness under reduced pressure. The crude material was purified by column chromatography ($CDCl_3$:MeOH = 95:5, R_f = 0.25) and concentrated under reduced pressure. The crude product was obtained and recrystallized from THF/Hexane (1:9) to give a orange solid. The orange solid was dissolved in ACN by heating at 80 ℃, and the solution was cooled to RT to afford a beige powder by recrystallization (0.7 g, 27.5%, yield). mp 190 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 6.85 (dddd, J = 65.0, 9.3, 8.7, 2.5 Hz, 12H), 8.08 (t, J = 5.7 Hz, 2H), 9.80 (s, 2H), 5.02 (s, 2H), 2.14 (t, J = 7.3 Hz, 4H), 1.49 (m, 4H), 0.85 (t, J = 6.6 Hz, 6H), 1.25 (s, 28H), 3.83 (d, J = 5.7 Hz, 4H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm173.12, 167.87, 146.24, 144.18, 133.04, 127.76, 124.10, 122.23, 120.74, 115.39, 43.00, 35.61, 31.78, 29.44, 25.67, 22.57, 14.43; ESI-MS (m/z): Calculated for $C_{44}H_{64}N_6O_4$ $[M+H]^+$ 740.75, Found $[M+H]^+$ 740.49.

Synthetic methods for **TPA-1**

A mixture of **1** (0.2 g, 0.77 mmol), EDC (0.16 g, 0.83 mmol), and HOBt (0.11 g, 0.81 mmol) was dried in vacuo for 8 h, then dissolved in DMF (40 mL). TEA (0.13 mL, 1.0 mmol) was added after the solution was cooled to 0 ℃, then, it was stirred for 1 h. To the mixed solution, **C2** (0.5 g, 0.67 mmol) dissolved in DMF (10 mL) was added, and it was stirred for 36 h at room temperature. The solvent was removed by evaporation. The crude product was dissolved in DCM and washed with brine three times. The solution was dried over Na_2SO_4, filtered, and the solvent was evaporated to dryness under reduced pressure. The crude material was purified by column chromatography ($CDCl_3$:MeOH = 95:5, R_f = 0.28) and concentrated under reduced pressure. The crude product was obtained and recrystallized from THF/Hexane (1:9) to give a orange solid. The orange solid was dissolved in ACN by heating at 80 ℃, and the solution was cooled to RT to afford a beige powder by recrystallization (0.32 g, 48%, yield). mp 200 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 9.88 (m, 3H), 1.49 (dd, J = 1.3, 0.69 Hz, 6H), 8.11 (m, 3H), 7.49 (d, J = 1.6 Hz, 6H), 6.92 (m, 6H), 2.14 (m, 6H), 3.84 (s, 4H), 0.85 (d, J = 4.2 Hz, 9H), 1.25 (s, 45H), 4.38 (m, 1H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 14.42, 18.58, 22.57, 25.68, 29.12, 29.20, 29.30, 29.44, 31.78, 35.47, 35.51, 43.06, 49.33, 120.84, 124.04, 124.10, 124.20, 134.50, 143.27, 168.04, 171.62, 172.60, 173.15; ESI-MS (m/z): Calculated for $C_{58}H_{89}N_7O_6$ $[M-H^+]^-$ 978.75, Found $[M-H]^-$ 978.69.

Synthetic methods for **C2**

A mixture of **1** (2.04 g, 7.92 mmol), EDC (1.6 g, 8.3 mmol), and HOBt (0.9 g, 6.6 mmol) was dried in vacuo for 8 h, then dissolved in DMF (50 mL). TEA (1.1 mL, 7.5 mmol) was added after the solution was cooled to 0 ℃, then, it was stirred for 1 h. To the mixed solution, tris(4-aminophenyl)amine (1.0 g, 3.4 mmol) dissolved in DMF (10 mL) was added, and it was stirred for 36 h at room temperature. The solvent was removed by evaporation. The crude product was dissolved in DCM and washed with brine three times. The solution was dried over Na_2SO_4, filtered, and the solvent was evaporated to dryness under reduced pressure. The crude material was purified by column chromatography ($CDCl_3$:MeOH = 95:5, R_f = 0.26) and concentrated under reduced pressure. The crude product was obtained and recrystallized from THF/Hexane (1:9) to give an orange solid. The orange solid was dissolved in ACN by heating at 80 ℃, and the solution was cooled to RT to afford a beige powder by recrystallization (0.8 g, 30%, yield). mp 187 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 7.40 (m, 12H), 8.02 (d, J = 7.3 Hz, 2H), 9.83 (s, 2H), 5.02 (s, 2H), 1.48 (m, 4H), 2.12 (t, J = 7.4 Hz, 4H), 0.85 (dd, J = 8.5, 4.8 Hz, 6H), 1.24 (d, J = 9.4 Hz, 34H), 4.38 (t, J = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ ppm 14.42, 18.58, 22.57, 25.68, 29.10, 29.19, 29.29, 29.44, 31.78, 35.47, 49.32, 115.37, 120.86, 122.28, 124.10, 127.58, 133.17, 134.42, 143.29, 171.60, 172.58; ESI-MS (m/z): Calculated for $C_{46}H_{68}N_6O_4$ $[M+H]^+$ 769.08, Found $[M+H]^+$ 768.53.

Synthetic methods for **TPA-2**

A mixture of **2** (0.18 g, 0.74 mmol), EDC (0.15 g, 0.78 mmol), and HOBt (0.1 g, 0.74 mmol) was dried in vacuo for 8 h, then dissolved in DMF (50 mL). TEA (0.13 mL, 1.0 mmol) was added after the solution was cooled to 0 ℃, then, it was stirred for 1 h. To the mixed solution, **C2** (0.5 g, 0.5 mmol) dissolved in DMF (10 mL) was added, and it was stirred for 36 h at room temperature. The solvent was removed by evaporation. The crude product was dissolved in DCM and washed with brine three times. The solution was dried over Na_2SO_4, filtered, and the solvent was evaporated to dryness under reduced pressure. The crude material was purified by column chromatography ($CDCl_3$:MeOH = 95:5, R_f = 0.28) and concentrated under reduced pressure. The crude product was obtained and recrystallized from THF/Hexane (1:9) to give a white solid. The orange solid was dissolved in ACN by heating at 80 ℃, and the solution was cooled to RT to afford a beige powder by recrystallization (0.32 g, 48%, yield). mp 204 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 6.90 (d, J = 8.8 Hz, 6H), 7.48 (m, 6H), 4.38 (t, J = 7.1 Hz, 2H), 3.83 (d, J = 5.7 Hz, 2H), 2.13 (q, J = 7.3, 7.2 Hz, 48H), 1.48 (m, 6H), 1.26 (d, J = 12.1 Hz, 48H), 0.84 (m, 9H), 9.89 (d, J = 10.5 Hz, 3H), 8.07 (dd, J = 10.6, 6.6 Hz, 3H) ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 14.43, 18.58, 22.57, 25.68, 29.09, 29.18, 29.27, 29.43, 31.77, 35.47, 35.61, 43.06, 49.32, 120.83, 120.86, 123.98, 124.13, 134.27, 134.45, 143.29, 168.03, 171.61, 172.59, 173.15 ESI-MS (m/z): Calculated for $C_{59}H_{91}N_7O_6$ $[M-H^+]^-$ 992.75, Found $[M-H]^-$ 993.42.

Synthetic methods for **TPA-3**

A mixture of **3** (2.75 g, 10.7 mmol), Tris(4-aminophenyl)amine (1.0 g, 3.4 mmol), EDC (3.3 g, 17.2 mmol), and HOBt (1.4 g, 10.5 mmol) was dried in vacuo for 8 h, then dissolved in DMF (50 mL) before adding TEA (4.8 mL, 34.4 mmol). The solution was stirred for 48 h at room temperature, and the solvent was removed by evaporation. The crude product was dissolved in chloroform and washed with brine three times. The solution was dried over Na_2SO_4, filtered, and the solvent was evaporated to dryness under reduced pressure. The crude material was purified by column chromatography ($CDCl_3$:MeOH = 95:5, R_f = 0.3) and concentrated under reduced pressure. The crude product was obtained and recrystallized from THF/Hexane (1:9) to give a white solid. (1.8 g, 52%, yield). ; mp 233 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 2.12 (t, J = 7.3 Hz, 6H), 4.39 (t, J = 7.1 Hz, 3H), 6.90 (d, J = 8.9 Hz, 6H), 7.49 (d, J = 8.9 Hz, 6H), 8.04 (d, J = 7.2 Hz, 3H), 9.91 (s, 3H), 0.85 (t, J = 6.6 Hz, 3H), 1.23 (m, 51H), 1.49 (dd, J = 9.5, 3.4 Hz, 6H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 14.42, 18.58, 22.57, 25.68, 29.09, 29.18, 29.28, 29.43, 31.77, 25.47, 49.33, 120.87, 124.06, 134.42, 143.29, 171.61, 172.59. HR-MS (m/z): Calculated for $C_{60}H_{93}N_7O_6$ $[M+H]^+$ 1007.7187, Found $[M+H]^+$ 1007.6835.

Analytic Data

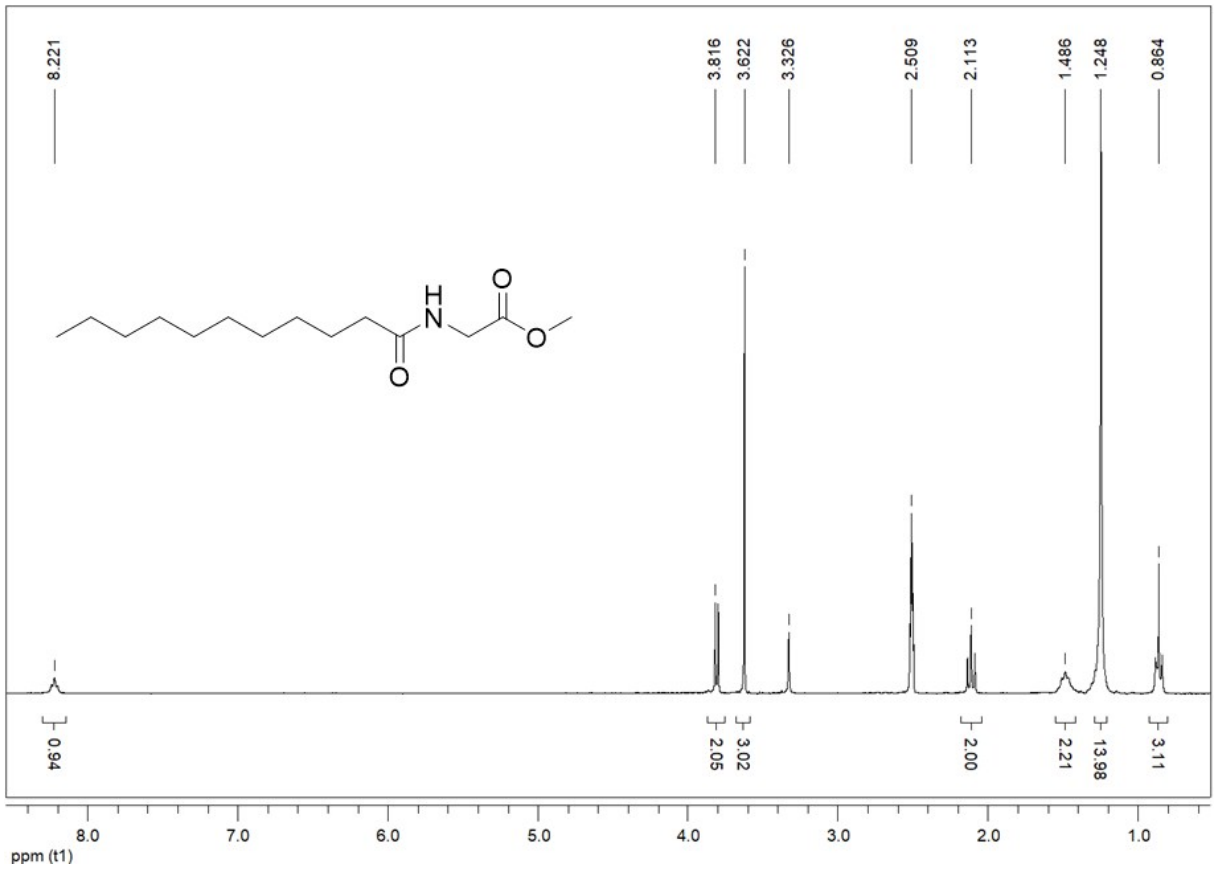


Fig. S17 ^{1}H NMR spectrum (300 MHz) of **4** in DMSO-d_6 at 25 °C.

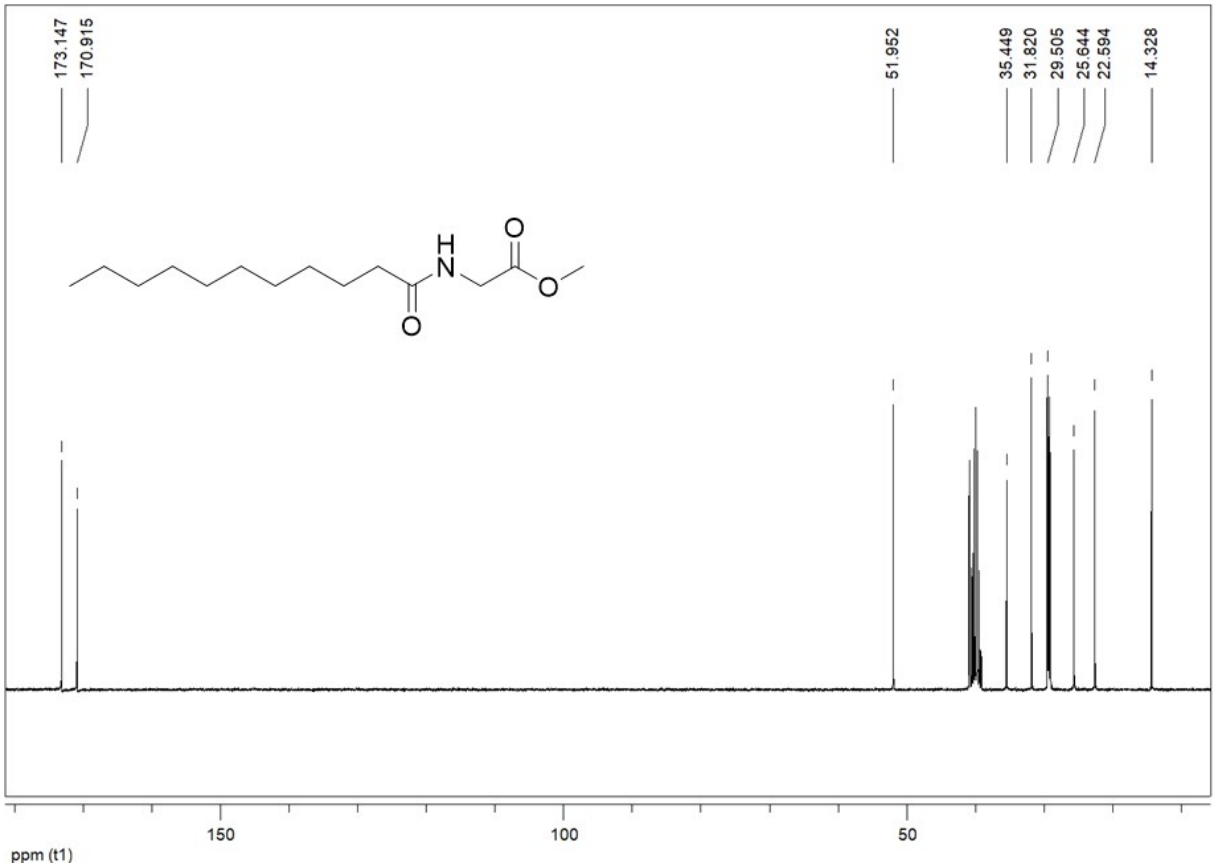


Fig. S18 ^{13}C NMR spectrum (75 MHz) of **4** in DMSO-d_6 at 25 °C.

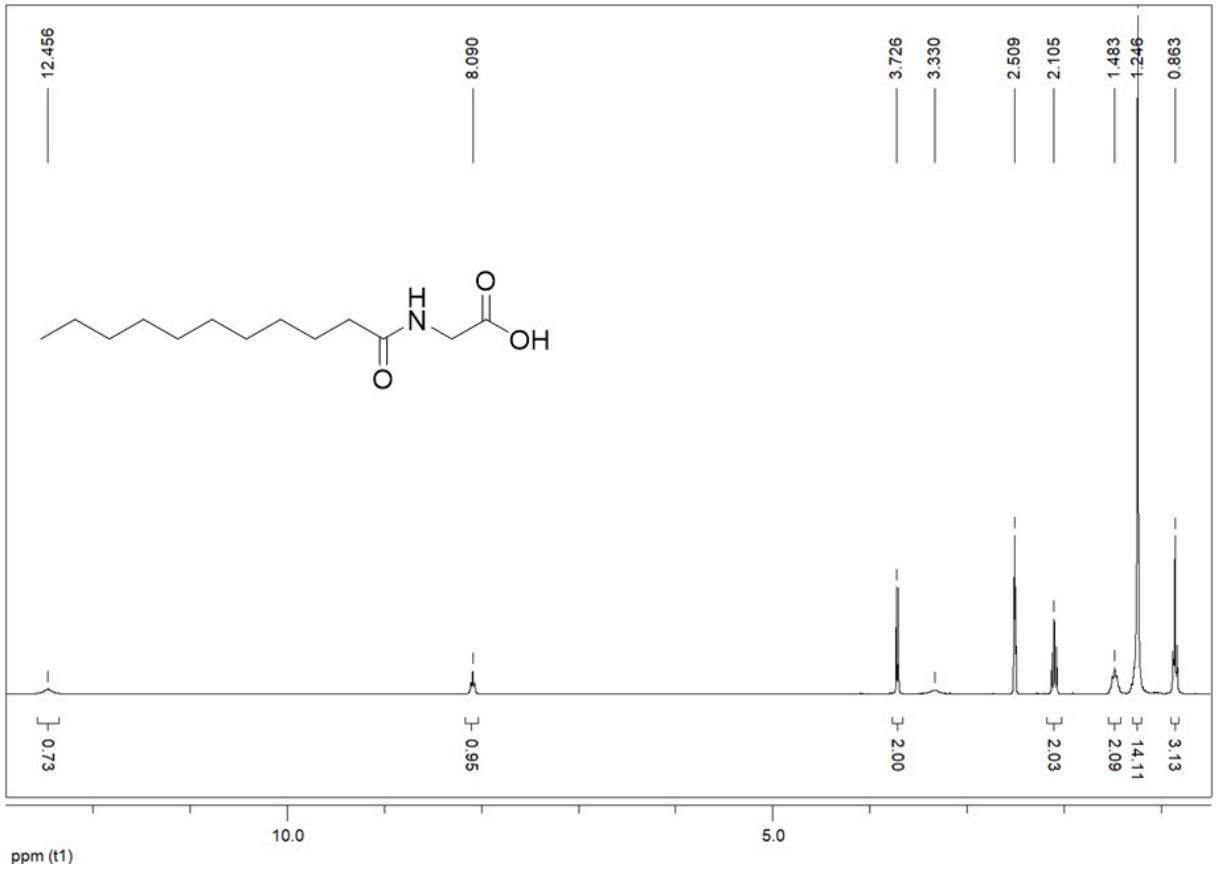


Fig. S19 ^{1}H NMR spectrum (300 MHz) of **2** in DMSO-d_6 at 25 °C.

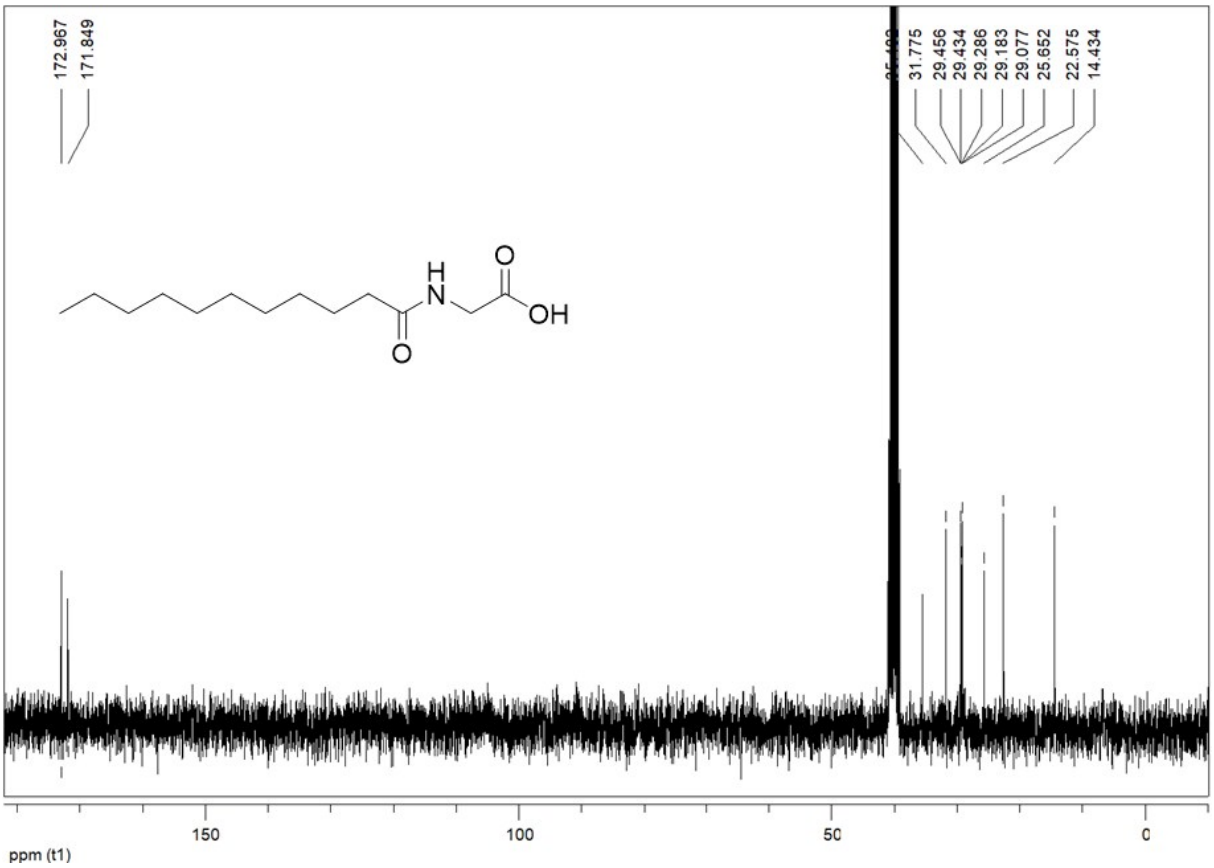


Fig. S20 ^{13}C NMR spectrum (75 MHz) of **2** in DMSO-d_6 at 25 °C.

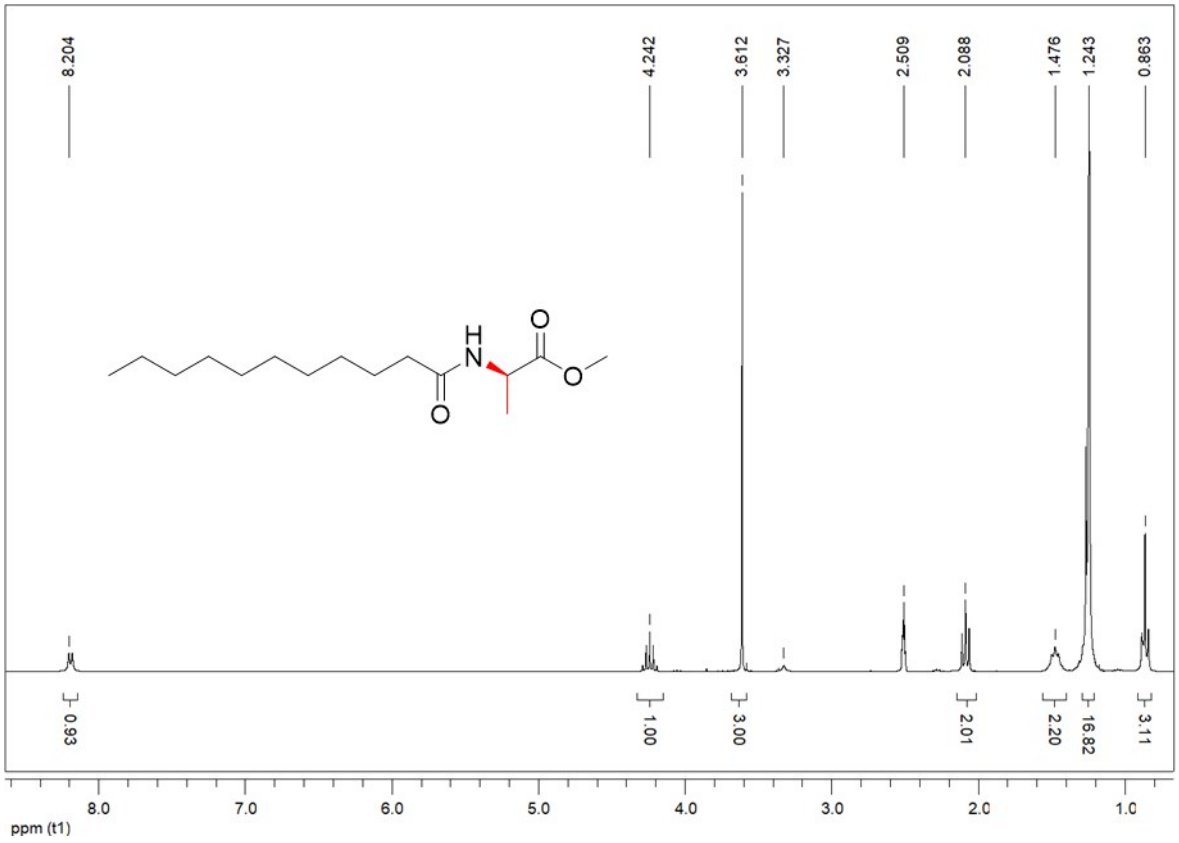


Fig. S21 ^{1}H NMR spectrum (300 MHz) of **3** in DMSO-d_6 at 25 °C.

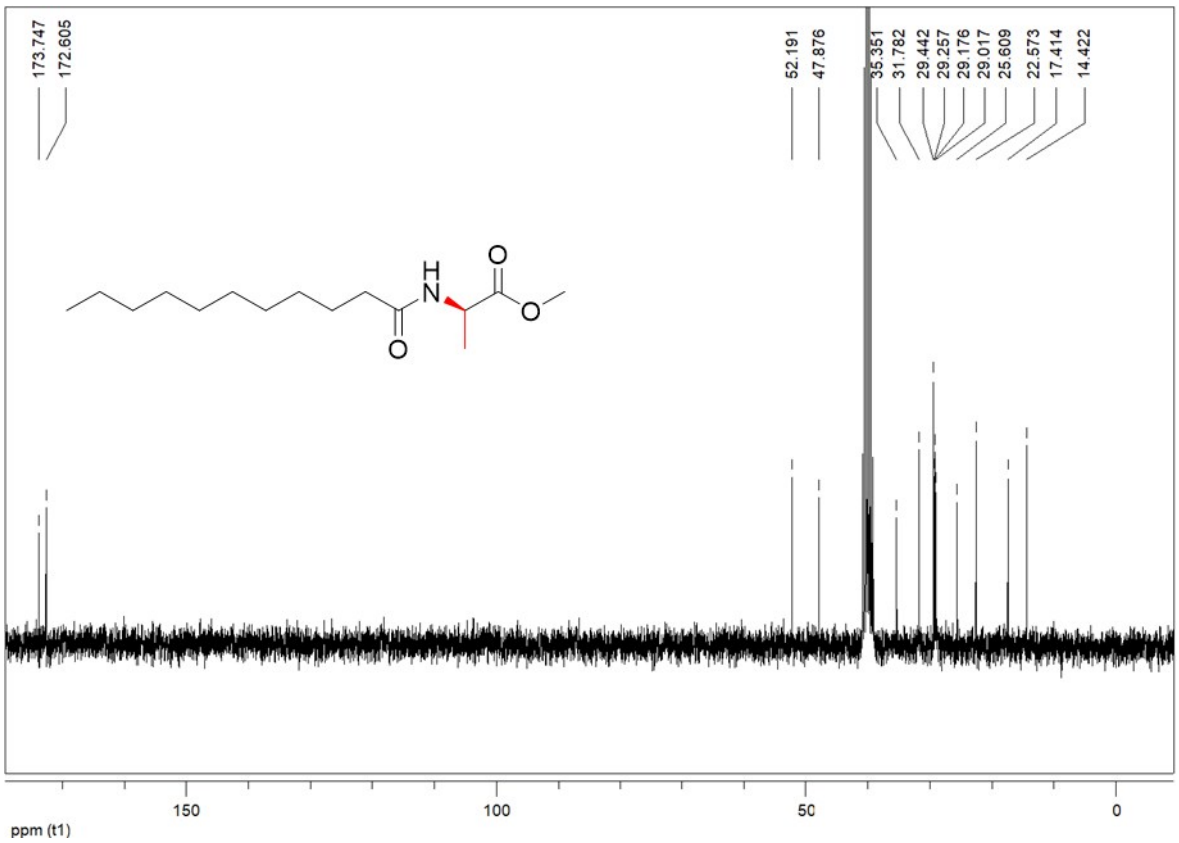


Fig. S22 ^{13}C NMR spectrum (75 MHz) of **3** in DMSO-d_6 at 25 °C.

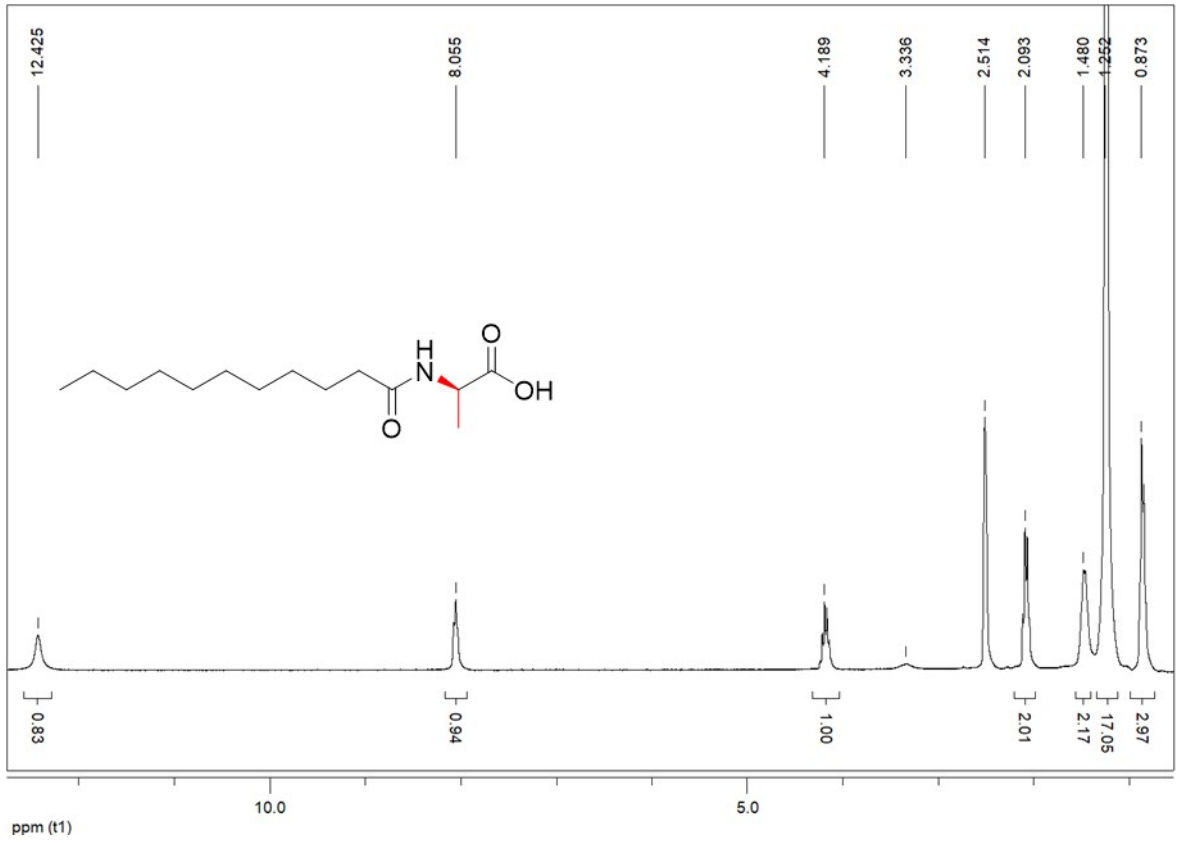


Fig. S23 ^{1}H NMR spectrum (300 MHz) of **1** in DMSO-d_6 at 25 °C.

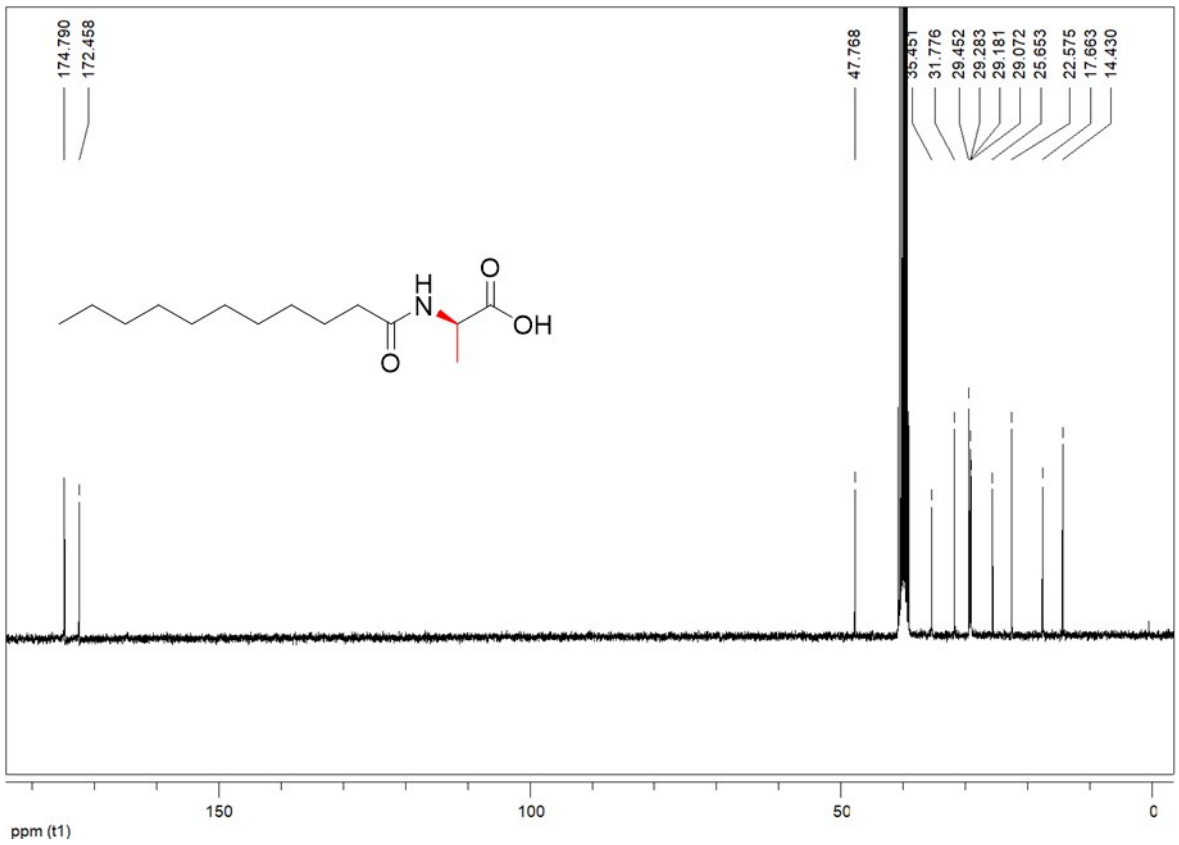


Fig. S24 ^{13}C NMR spectrum (75 MHz) of **1** in DMSO-d_6 at 25 °C.

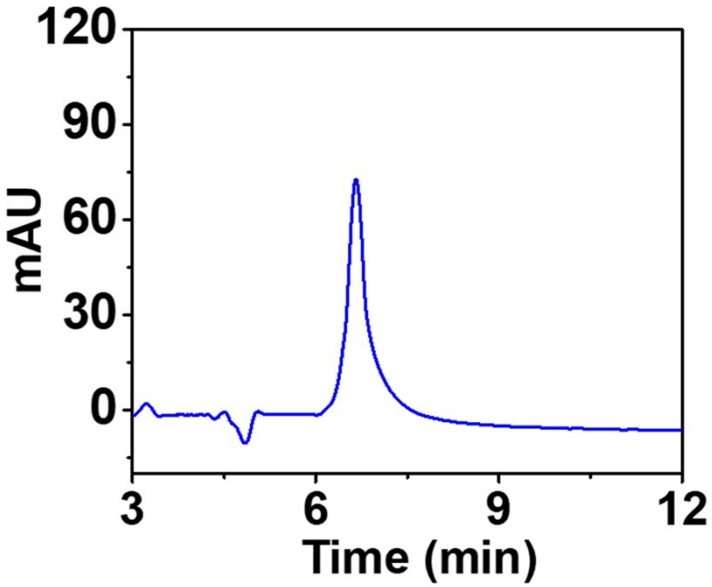


Fig. S25 HPLC chromatogram of **1** on the chiralpack IA-3 column using hexane/ethanol/trifluoroacetic acid (80/20/0.1) as mobile phase at a flow rate of 0.5 mL/min.

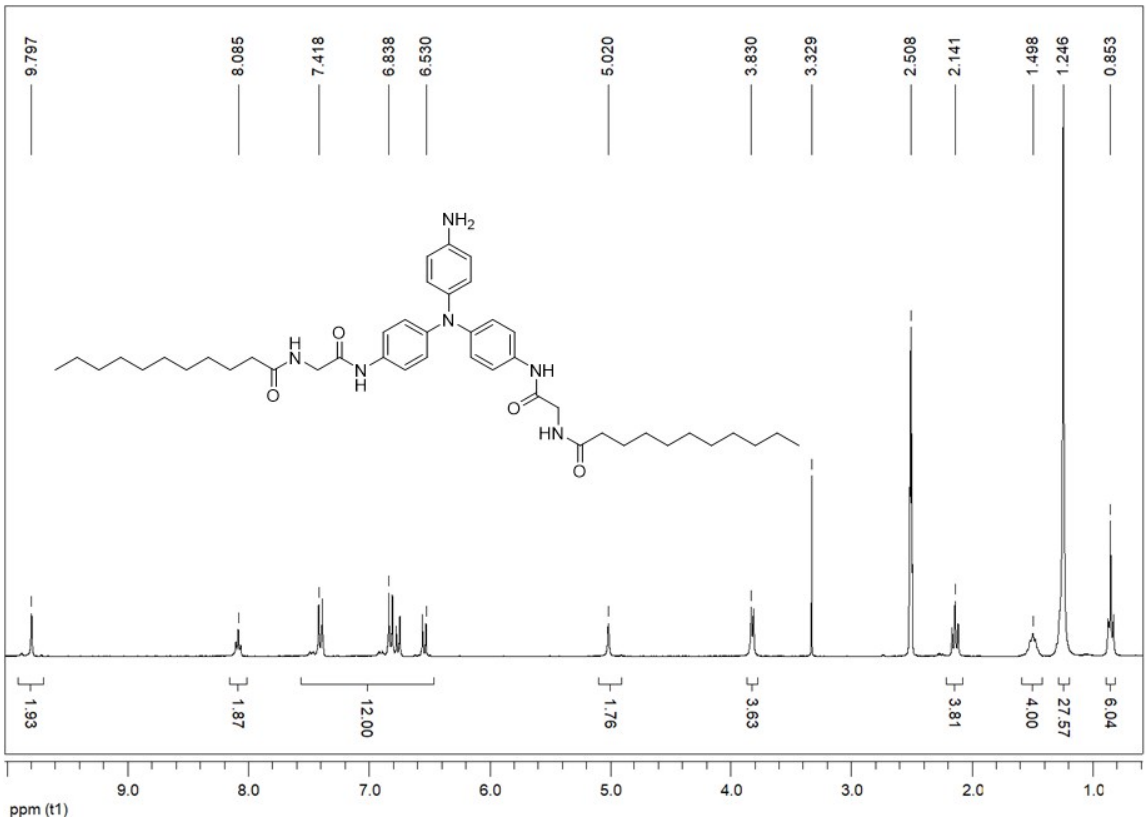


Fig. S26 ^{1}H NMR spectrum (300 MHz) of **C1** in DMSO-d_6 at 25 °C.

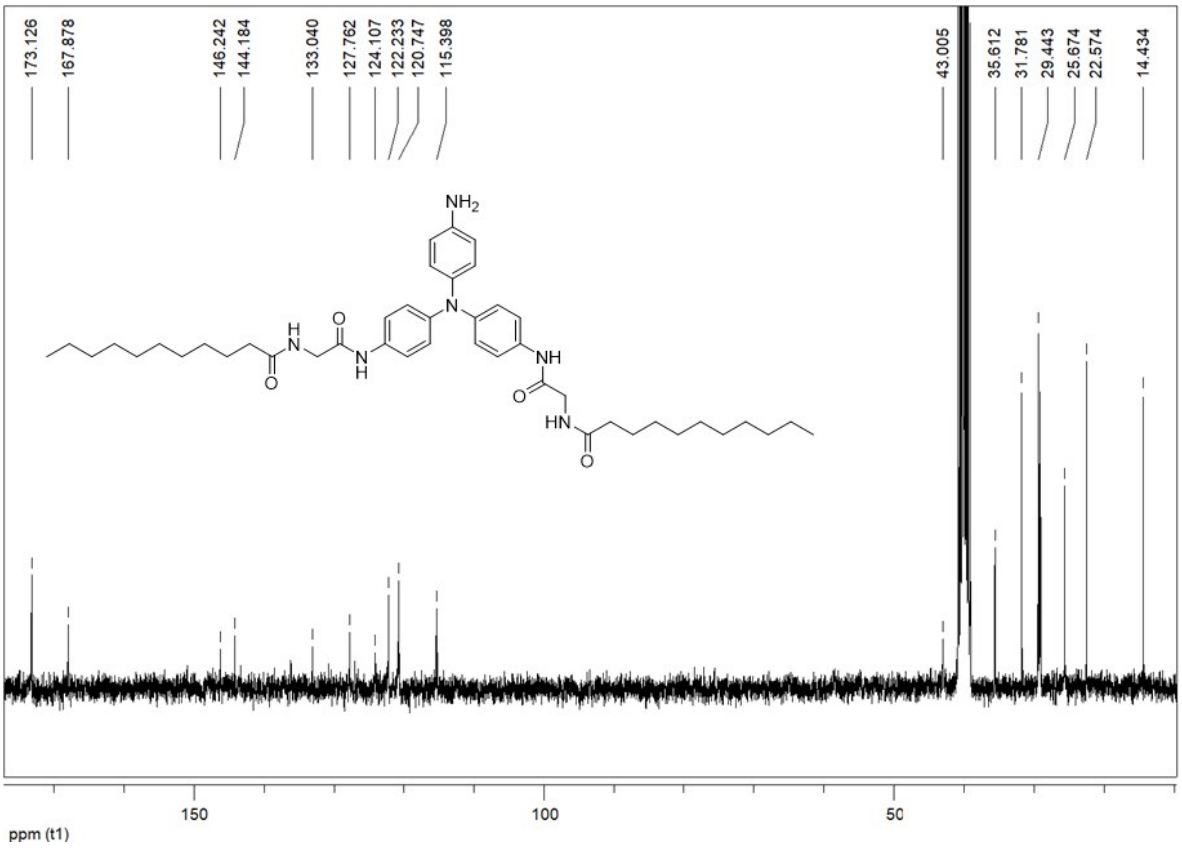


Fig. S27 ^{13}C NMR spectrum (75 MHz) of **C1** in DMSO-d_6 at 25 °C.

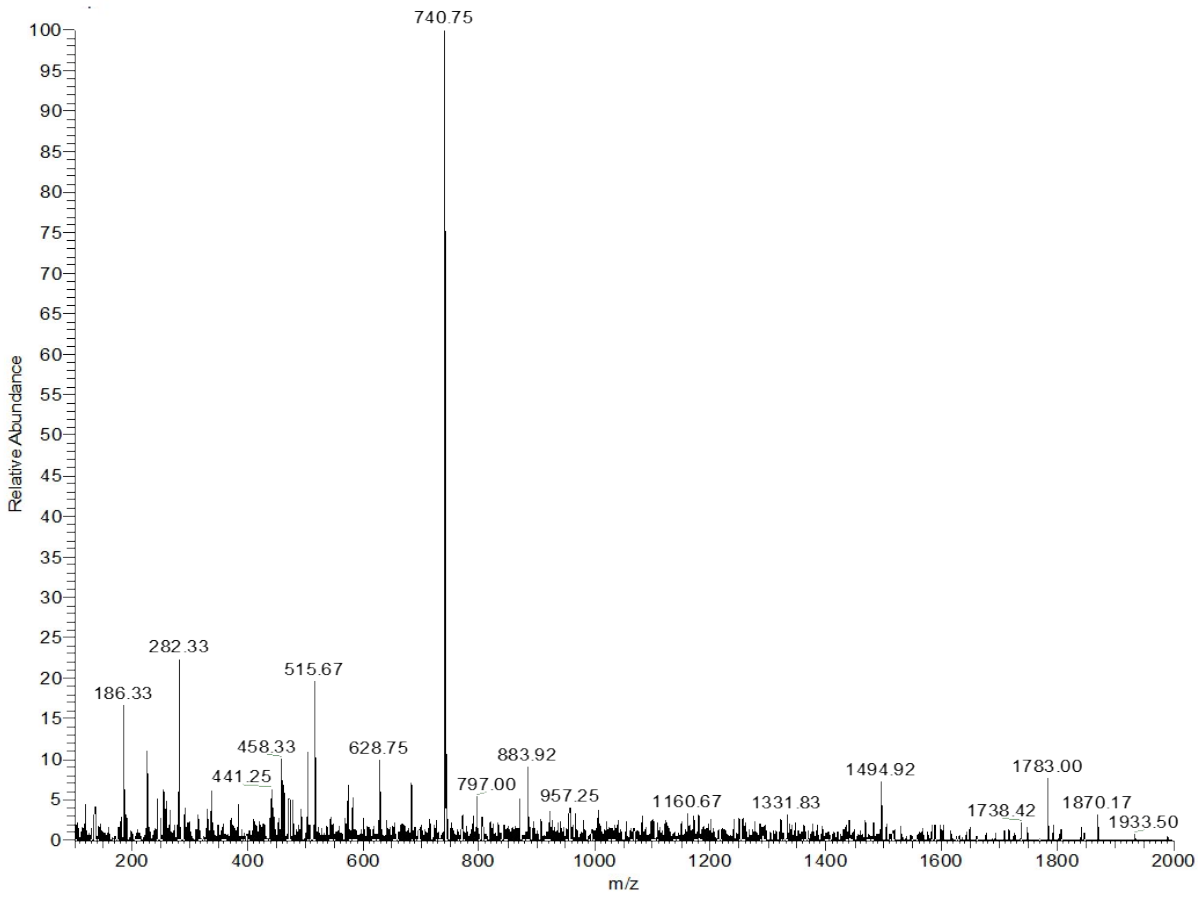


Fig. S28 ESI-Mass spectrum of **C1**.

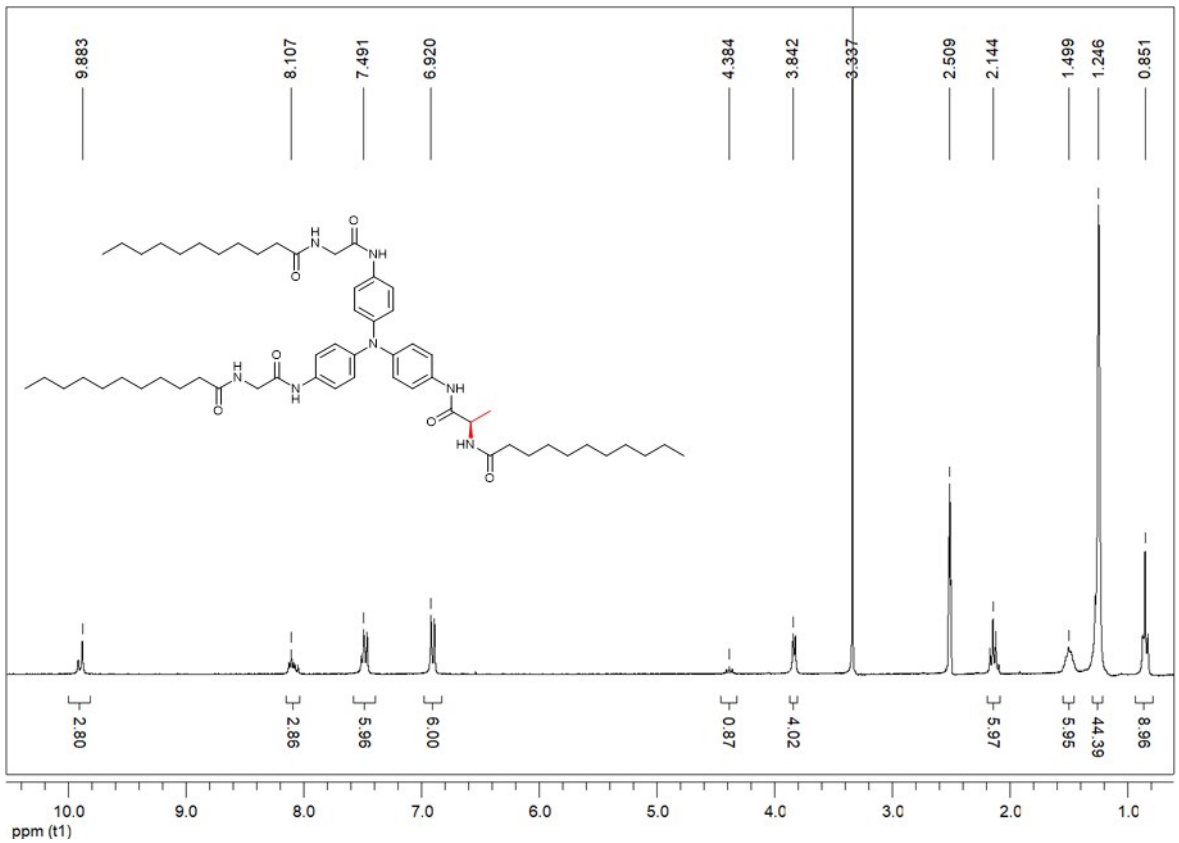


Fig. S29 ^{1}H NMR spectrum (300 MHz) of **TPA-1** in DMSO-d_6 at 25 °C.

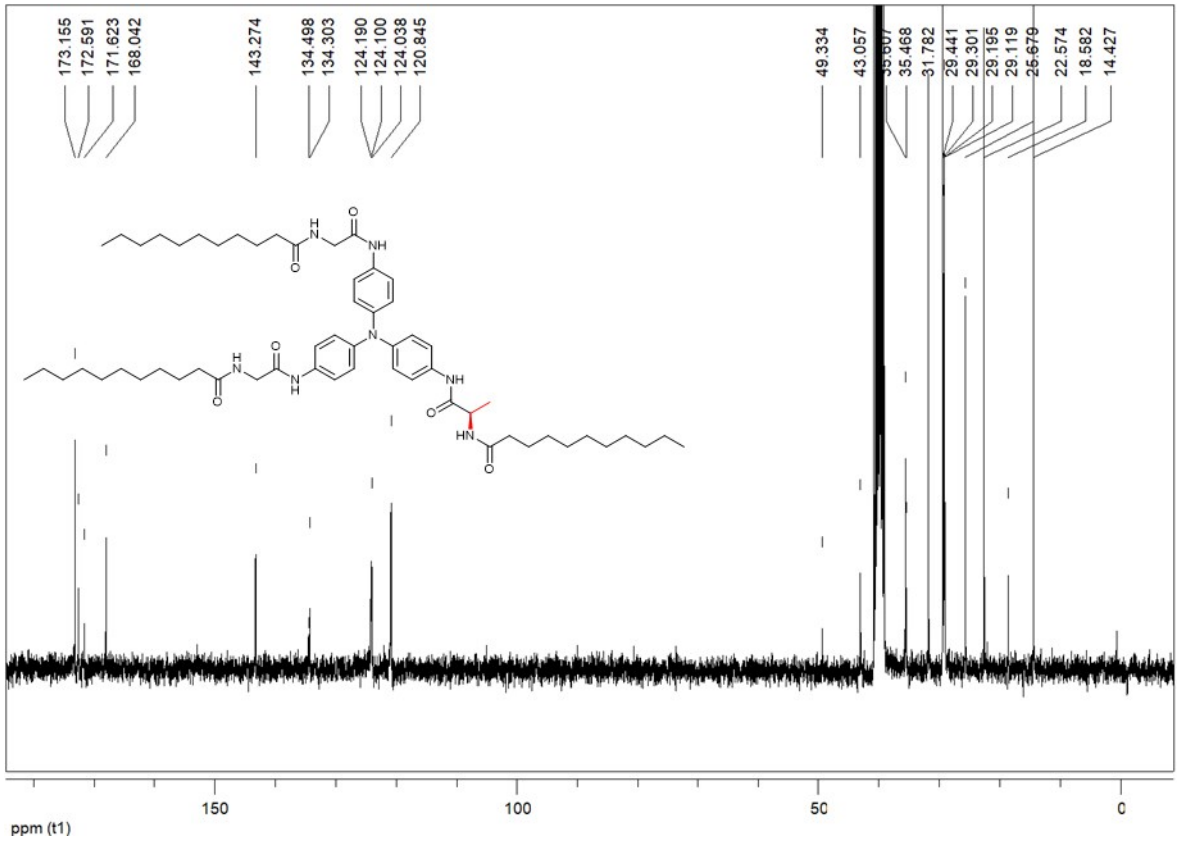


Fig. S30 ^{13}C NMR spectrum (75 MHz) of **TPA-1** in DMSO-d_6 at 25 °C.

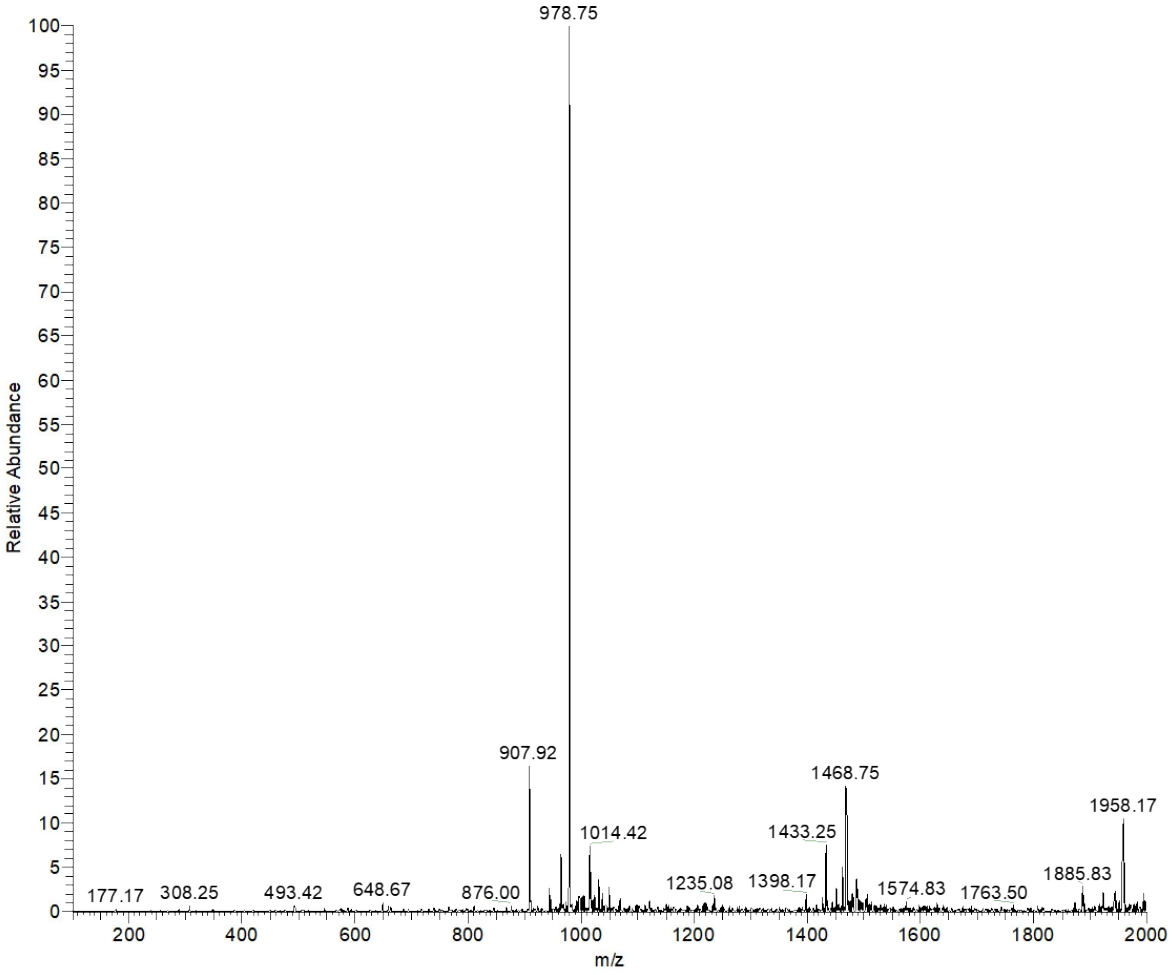


Fig. S31 ESI-Mass spectrum of **TPA-1**.

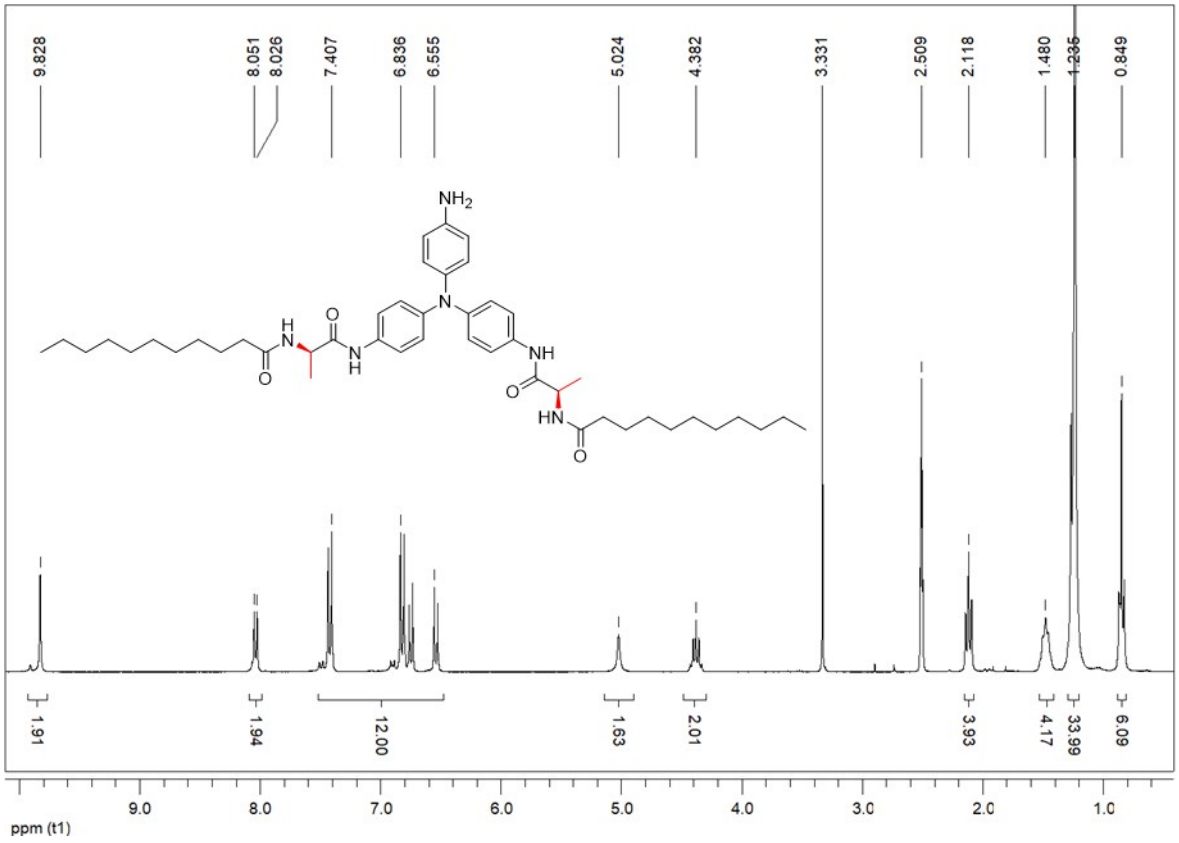


Fig. S32 ^{1}H NMR spectrum (300 MHz) of **C2** in DMSO-d_6 at 25 °C.

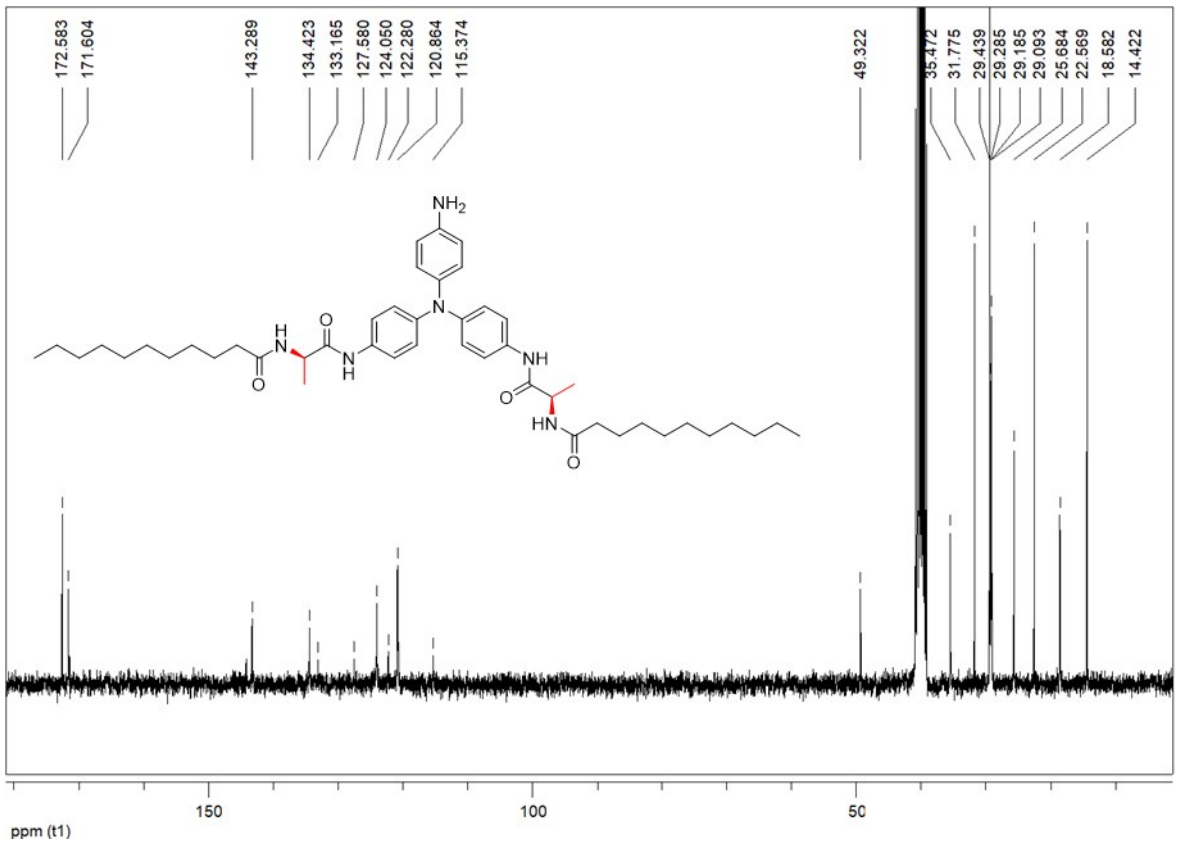


Fig. S33 ^{13}C NMR spectrum (75 MHz) of **C2** in DMSO-d_6 at 25 °C.

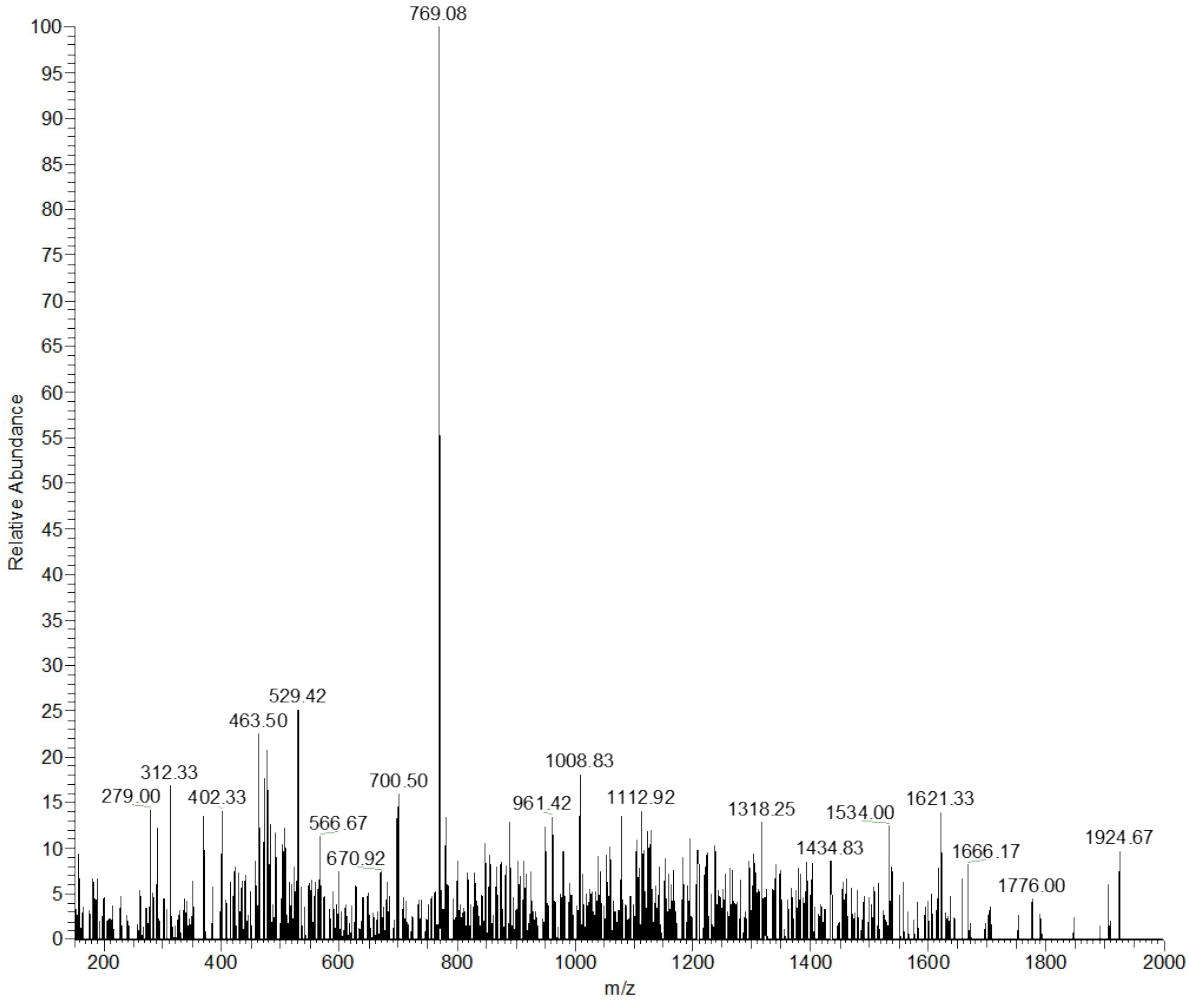


Fig. S34 ESI-Mass spectrum of **C2**.

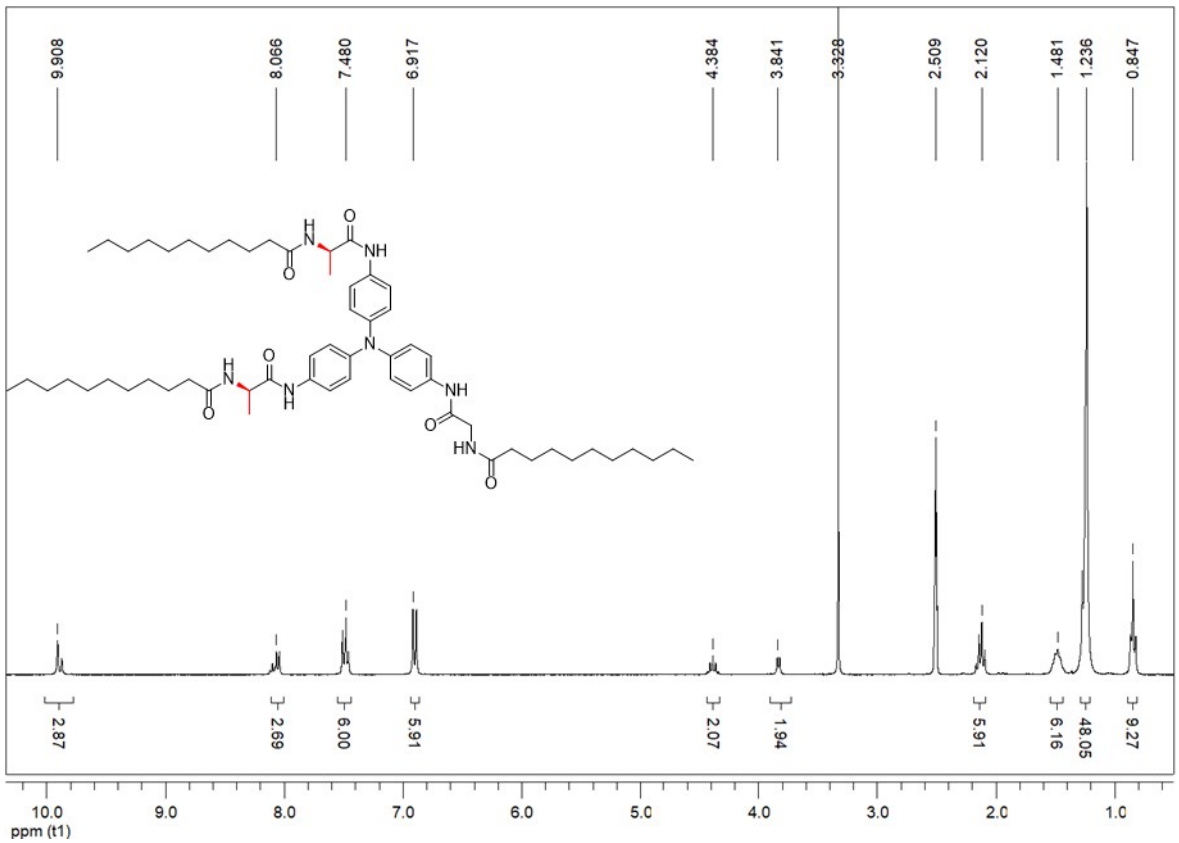


Fig. S35 ^{1}H NMR spectrum (300 MHz) of **TPA-2** in DMSO-d_6 at 25 °C.

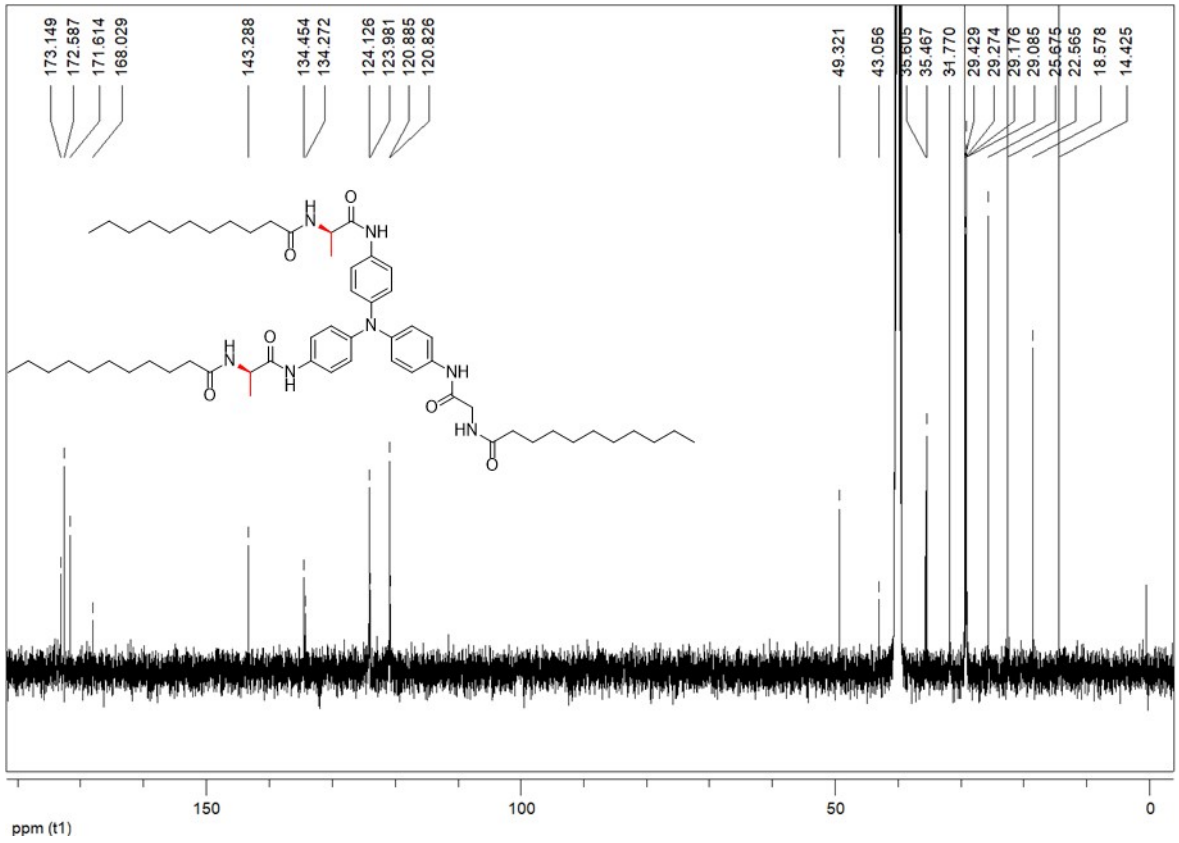


Fig. S36 ^{13}C NMR spectrum (75 MHz) of **TPA-2** in DMSO-d_6 at 25 °C.

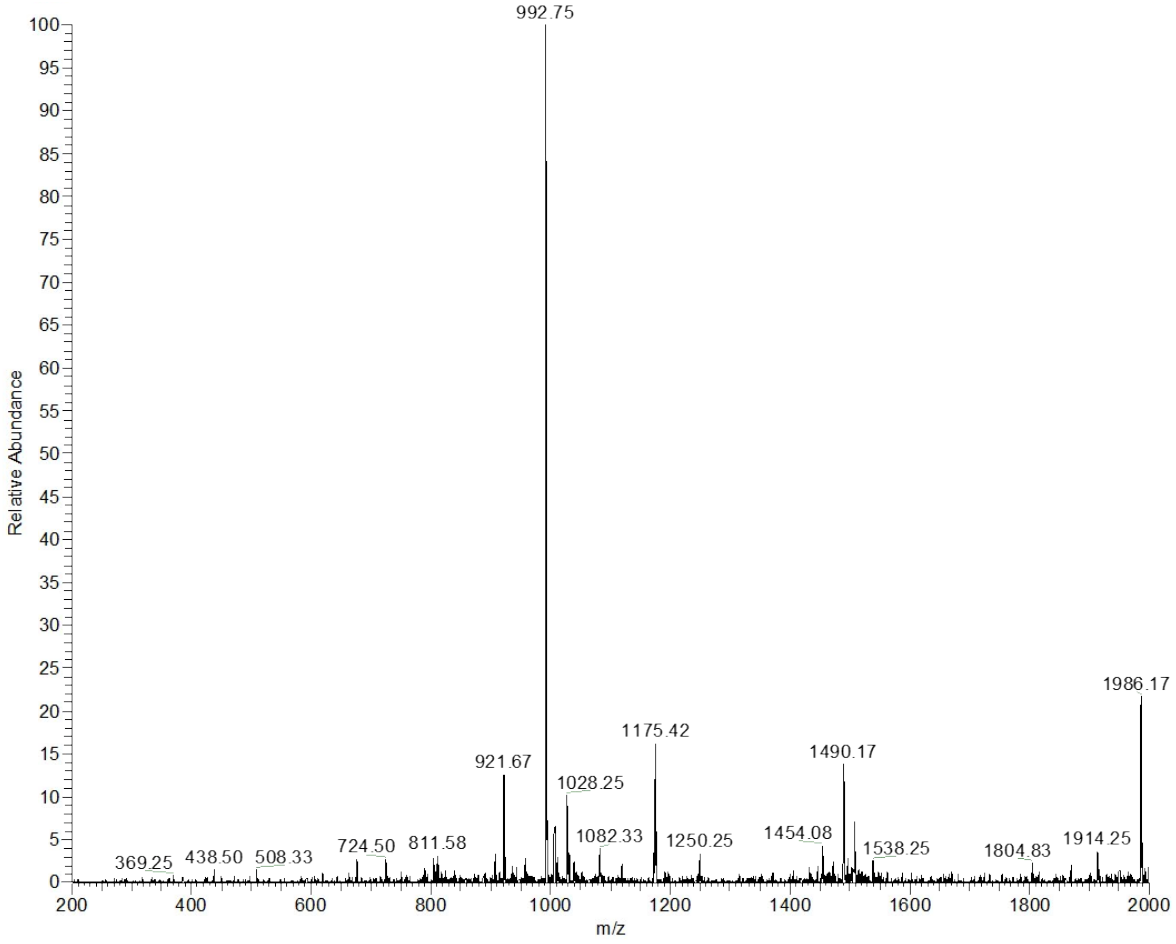


Fig. S37 ESI-Mass spectrum of **TPA-2**.

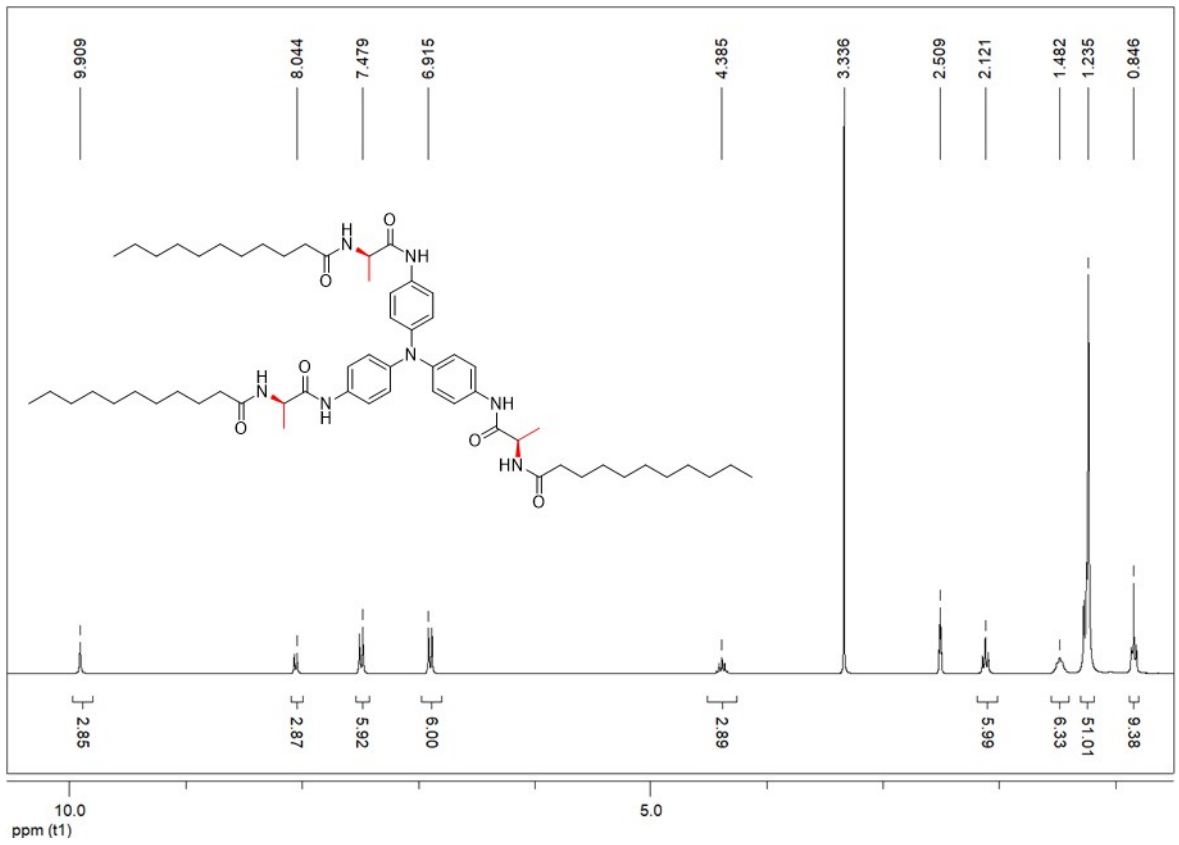


Fig. S38 ^{1}H NMR spectrum (300 MHz) of **TPA-3** in DMSO-d_6 at 25 °C.

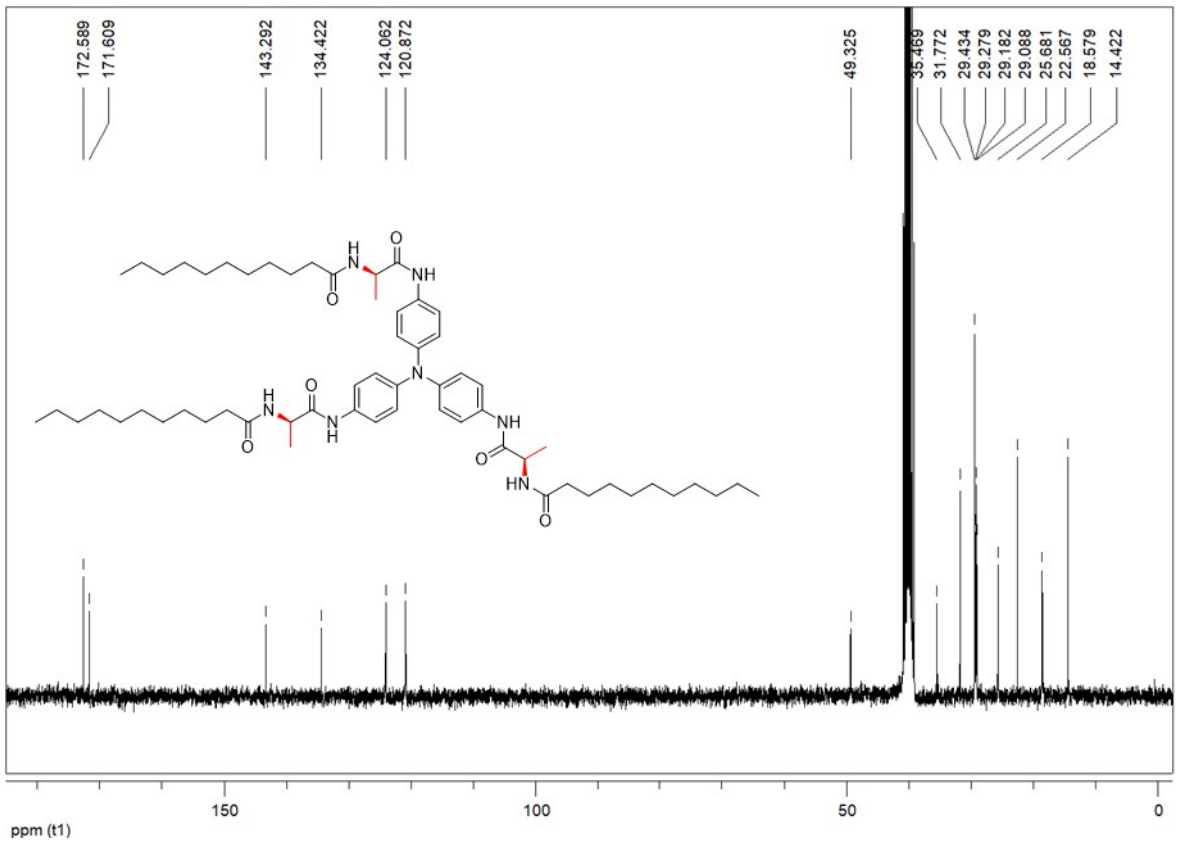


Fig. S39 ^{13}C NMR spectrum (75 MHz) of **TPA-3** in DMSO-d_6 at 25 °C.

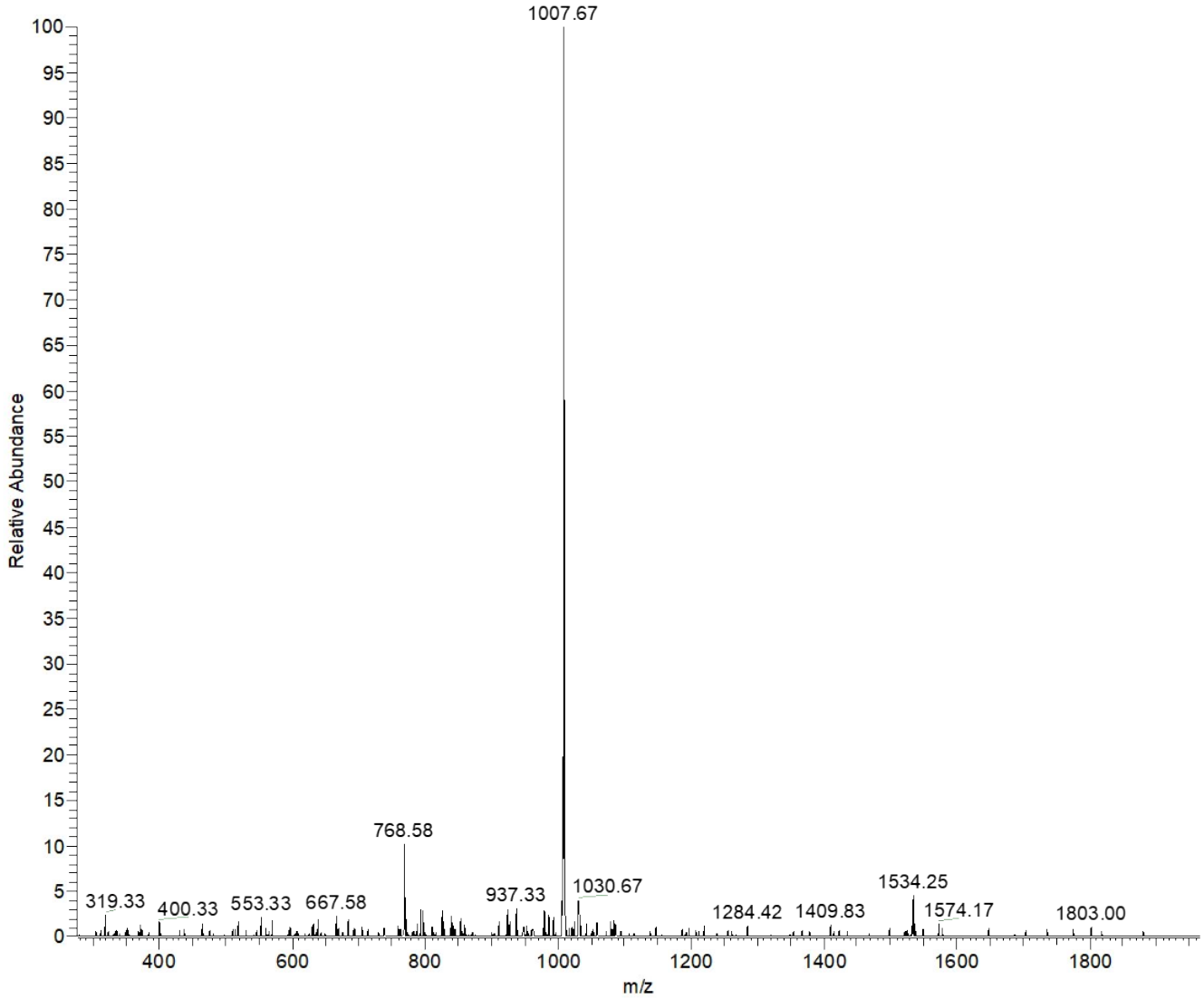


Fig. S40 ESI-Mass spectrum of **TPA-3**.

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