

Supplementary Information

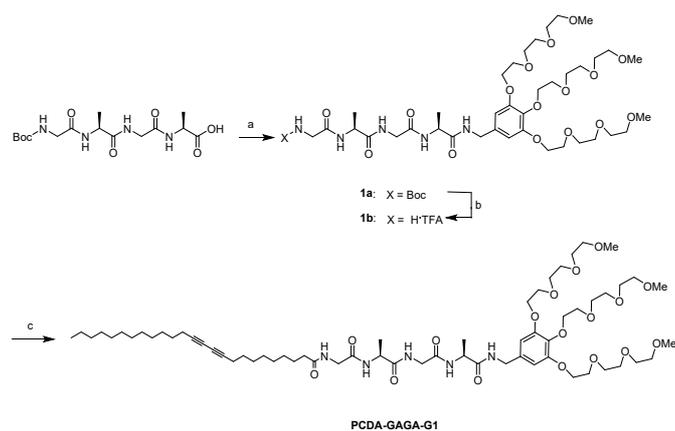
Dendronized polydiacetylenes via photo-polymerization of supramolecular assemblies showing thermally tunable chirality

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Scheme S1. Synthesis procedure for **PCDA-GAGA-G1**. Reagents and conditions: a) EDC·HCl, DiPEA, HOBT, G1-NH₂, DCM, 0~25 °C, overnight (63%); b) TFA, CH₂Cl₂, 0~25 °C, 2h (100%); c) **1b**, PCDA, EDC·HCl, DiPEA, HOBT, DCM, 0~25 °C, overnight (91%). Abbreviations: Boc = tert-butoxycarbonyl; EDC·HCl = 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride; DiPEA = diisopropylethylamine; HOBT = 1-hydroxy-1H-benzotriazole; DCM = Dichloromethane; TFA = trifluoroacetic acid.

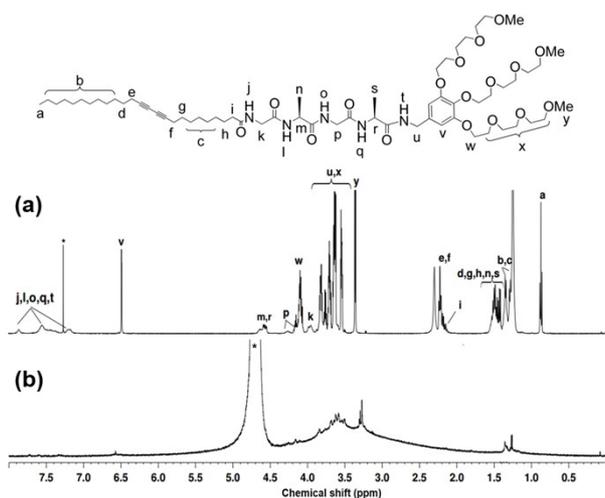


Fig. S1. ¹H NMR spectra of **PCDA-GAGA-G1** in CDCl₃ (a) and D₂O (b) at 298 K. Solvent peaks are marked with *. C = 5.0 mg·mL⁻¹

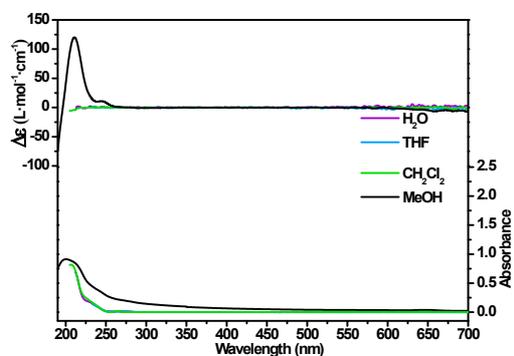


Fig. S2. CD and UV spectra of **PCDA-GAGA-G1** in different solvents at 20 °C. C = 0.2 mg·mL⁻¹.

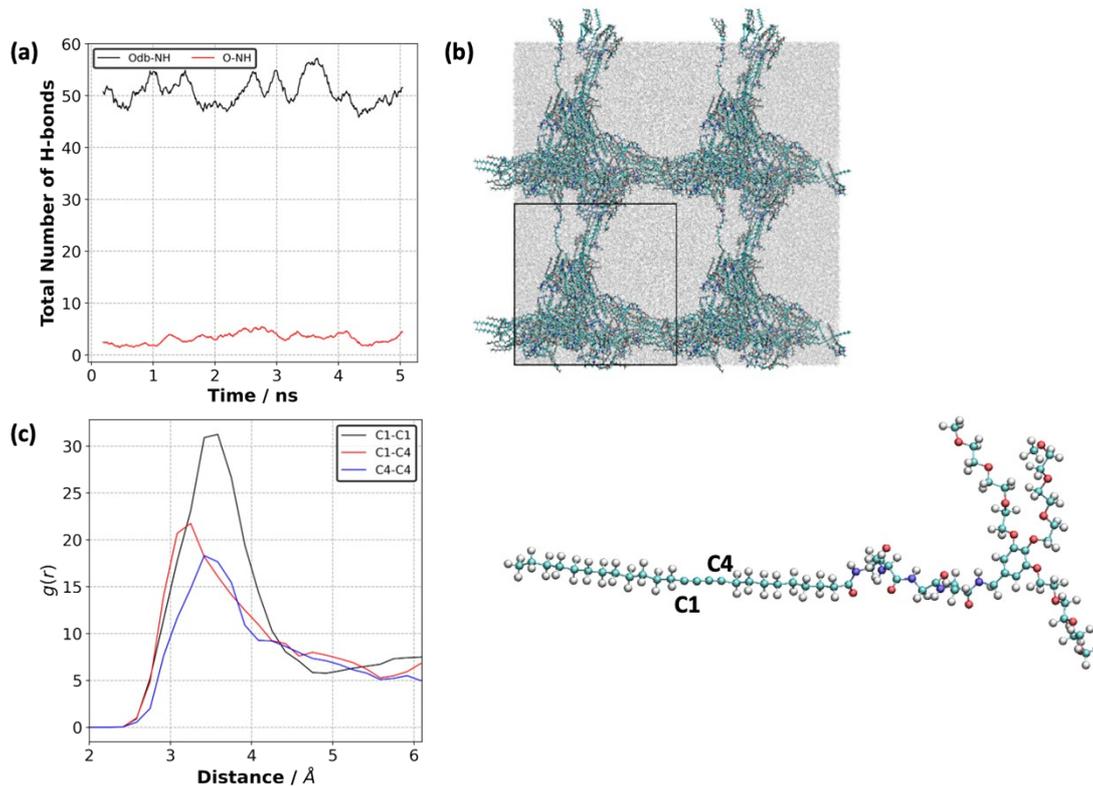


Fig. S3 (a) Total number of hydrogen bonds formed between the oxygen and nitrogen atoms of the GAGA belonging to different molecules at 25 °C. Odb and NH represent the double bonded oxygen atom to carbon atom, and nitrogen atom in the GAGA moiety, respectively. O represents the oxygen atom in the OEG moiety. (b) A snapshot (a supercell of 2x2) taken at the completion of simulations at 25 °C. The gray cloud represents the water molecules. The solid black lines represent the simulation cell boundaries. (c) Radial distribution function (RDF) plot between the first (C1) and last (C4) carbon atoms of the PDA belonging to different molecules at 25 °C.

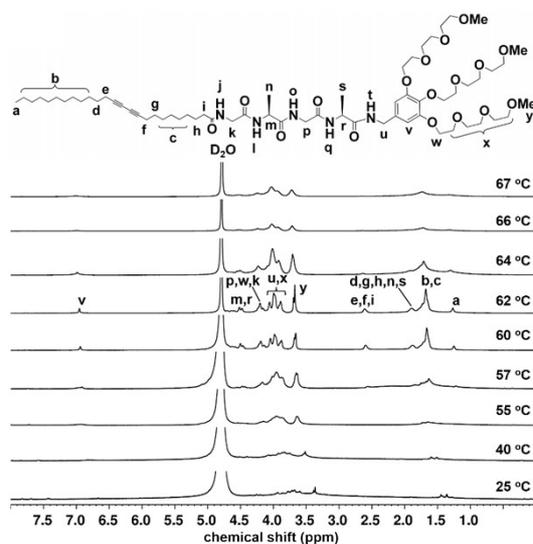


Fig. S4 ^1H NMR spectra of PCDA-GAGA-G1 in D_2O at different temperatures. $C = 5.0 \text{ mg}\cdot\text{mL}^{-1}$.

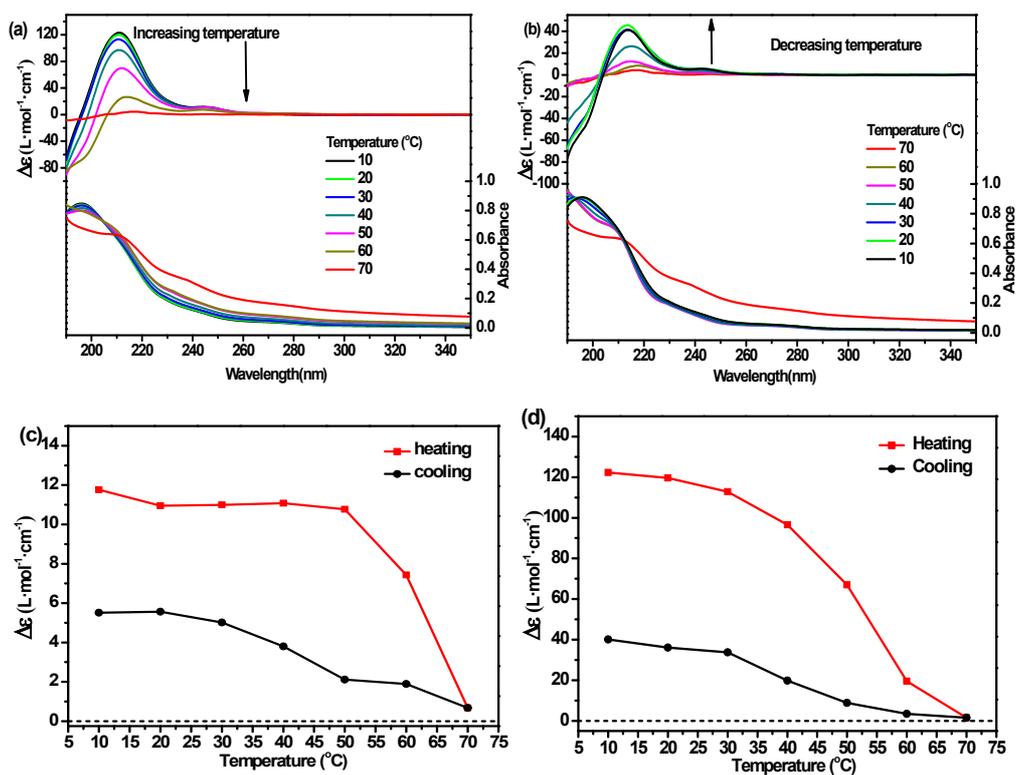


Fig. S5. UV/vis and CD spectra of PCDA-GAGA-G1 with increase (a) and decrease (b) of temperatures, as well as Cotton intensities at 244 nm (c) and 210 nm (d) of PCDA-GAGA-G1 in H_2O at different temperatures. $C = 0.2 \text{ mg}\cdot\text{mL}^{-1}$. Heating and cooling rate = $2.0 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$.



Fig. S6. Photographs of PCDA-GAGA-G1 in water ($C = 0.2 \text{ mg}\cdot\text{mL}^{-1}$) after different UV irradiation time.

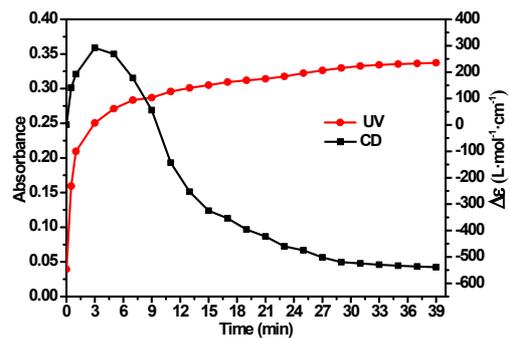


Fig. S7. Plots of signal intensities of absorbance at 646 nm and Cotton effect at 658 nm with different irradiation time. C = 0.2 mg·mL⁻¹.

1.

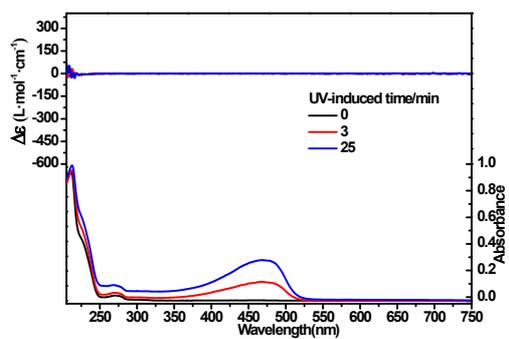


Fig. S8. UV/vis and CD spectra of the assembly of dendronized PCDA and the dendronized PDAs in HFIP, which were freezing dried from aqueous solutions. C = 0.2 mg·mL⁻¹.

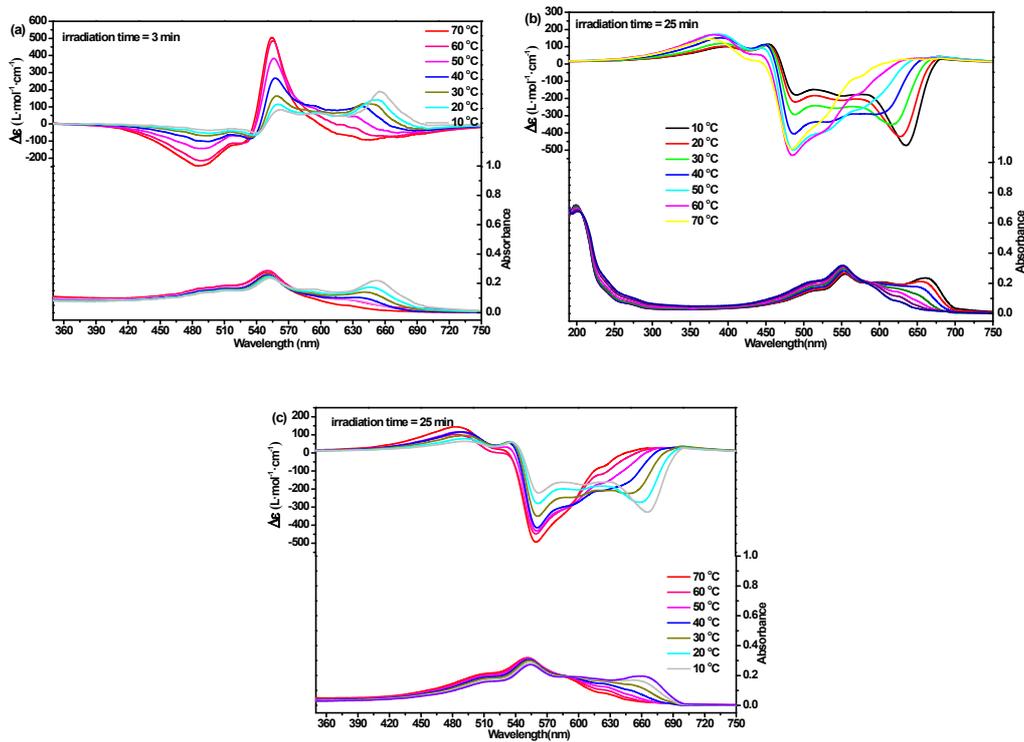


Fig. S9. CD and UV spectra of the dendronized PDAs in aqueous solutions after UV irradiation of 3 min, and temperature decreased from 70 to 10 °C (a), as well as after UV irradiation of 25 min and temperature increased from 10 to 70 °C (b), and temperature decreased from 70 to 10 °C (c). $C = 0.2 \text{ mg}\cdot\text{mL}^{-1}$. Heating and cooling rate = $2.0 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

Additional experimental details

Materials and instruments

G1-NH₂^[S1] and **Boc-Gly-Ala-Gly-Ala-OH**^[S2] were synthesized according to previous reports. Dichloromethane was distilled from CaH₂ for drying. Tetrahydrofuran was distilled from Na and LiAlH₄, respectively. Other substances were purchased from Alfa Aesar, Sigma-Aldrich or TCI and used without further purification. All synthetic steps for peptide synthesis were run under a nitrogen atmosphere. Macherey-Nagel precoated TLC plates (silica gel 60G/UV254, 0.25mm) were used for thin layer chromatography (TLC) analysis. Silica gel 60M (200-300) was used as the stationary phase for column chromatography.

NMR spectra were recorded on a Bruker AV500 spectrometer (¹H: 500 MHz; ¹³C: 125 MHz). The chemical shifts are given in ppm and referenced to residual solvent signals. High resolution MALDI-TOF-MS analyses were performed on IonSpec Ultra instruments. Circular dichroism (CD) measurements were performed on a JASCO J-815 spectropolarimeter with a thermostatically controlled 1mm quartz cell (10 accumulations, continuous scanning mode, scanning speed 500nm min⁻¹, data pitch: 0.5nm, response: 1 sec, band width: 2.0nm). UV/Vis measurements were recorded on JASCO V-750 spectrophotometer equipped with a thermostatically regulated bath. TEM images were taken on a JEOL JEM-2100F electron microscope operating at 100 kV. TEM samples were prepared by dropping the sample solution onto a carbon coated copper grid and which was then dried at room temperature.

Synthesis

Tert-butyl ((4S,10S)-4,10-dimethyl-3,6,9,12-tetraoxo-1-(3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-2,5,8,11-tetraazatridecan-13-yl)carbamate (1a): In a flask with nitrogen **Boc-Gly-Ala-Gly-Ala-OH** (1.15 g, 3.08 mmol), HOBt (4.58 g, 3.39 mmol), **G1-NH₂** (2.01g, 3.39 mmol) and DiPEA (7.96 g, 6.16 mmol) were dissolved in dry CH₂Cl₂ (50 mL) at 0 °C, and stirred for 20 min before EDC·HCl (1.18 g, 6.16 mmol) was added. The resulting mixture was stirred for 12 h at room temperature before washed thoroughly with saturated solution of NaHCO₃ and 10% KHSO₄ and dried with magnesium sulfate. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography with CH₂Cl₂/CH₃OH (40:1, v/v) to yield **1a** as a white solid (1.85g, 1.95 mmol, 63%). ¹H NMR (CDCl₃): δ (ppm) = 1.24-1.36 (m, 3H, CH₃), 1.42 (s, 9H, Boc), 1.46-1.48 (m, 3H, CH₃), 3.36-3.38 (m, 9H, CH₃), 3.53-3.56 (m, 6H, CH₂), 3.62-3.66 (m, 12H, CH₂), 3.67-3.72 (m, 8H, CH₂), 3.73-3.77 (m, 2H, CH₂), 3.80-3.86 (m, 4H, CH₂), 3.92-4.22 (m, 8H, CH₂), 4.54-4.64 (m, 1H, CH), 4.71-4.77 (m, 1H, CH), 5.85-5.98 (m, 1H, NH), 6.51 (s, 2H, Ar-H), 7.13-7.17 (m, 1H, NH), 7.29-7.61 (m, 2H, NH).

(S)-2-(2-Aminoacetamido)-N-(2-oxo-2-(((S)-1-oxo-1-((3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzyl)amino)propan-2-yl)amino)ethyl)propanamide (1b): Trifluoroacetic acid (4.45 g, 39.00 mmol) was added to a solution of **1a** (1.85 g, 1.95 mmol) in dry CH₂Cl₂ at 0 °C, and the mixture was stirred at room temperature for 3 h. The reaction was quenched by adding an excess amount of methanol. Evaporation of all solvents under vacuum afforded **1b** as a colorless oil and used without further purification (1.88 g, 1.95 mmol, 100%).

N-((4S,10S)-4,10-Dimethyl-3,6,9,12-tetraoxo-1-(3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-2,5,8,11-tetraazatridecan-13-yl)pentacosamide (PCDA-GAGA-G1): The synthesis is similar as the procedure described above for **1a** from PCDA (0.31 g, 0.82 mmol), HOBt (0.12 g, 0.90 mmol), **1b** (0.87 g, 0.90 mmol), DiPEA (0.21 g, 1.64 mmol) and EDC·HCl (0.31 g, 1.64 mmol). Silica gel chromatographic purification with CH₂Cl₂/CH₃OH (20:1, v/v) as eluent afforded the targeted compound as a white solid (0.91 g, 0.75 mmol, 91%). ¹H NMR (CDCl₃): δ (ppm) = 0.86 (t, 3H, CH₃), 1.24-1.33 (m, 26H, CH₂), 1.34-1.52 (m, 12H, CH₂ and CH₃), 2.12-2.23 (m, 6H, CH₂), 3.34-3.36 (m, 9H, CH₃), 3.52-3.54 (m, 6H, CH₂), 3.61-3.65 (m, 12H, CH₂), 3.66-3.72 (m, 6H, CH₂), 3.78-3.83 (m, 6H, CH₂), 3.94-3.97 (m, 2H, CH₂), 4.06-4.25 (m, 8H, CH₂), 4.54-4.64 (m, 2H, CH), 6.48 (s, 2H, Ar-H), 7.17-7.20 (m, 1H, NH), 7.43-7.86 (m, 5H, NH). ¹³C NMR (CDCl₃): δ (ppm) = 14.2, 19.3, 22.8, 25.6, 28.4, 28.5, 28.9, 29.0, 29.2, 29.3, 29.6, 32.0, 35.9, 43.2, 43.8, 48.9, 50.7, 59.0, 68.7, 68.8, 69.9, 70.4, 70.5, 70.6, 70.8, 71.9, 72.0, 72.3, 106.8, 134.6, 136.9, 152.5, 169.3, 172.7, 175.0. HRMS (ESI): m/z calcd for C₆₃H₁₀₇N₅O₁₇[M+H⁺] 1206.7735; found 1206.7742.

General simulation details

We used the Generalised Amber Force Field (GAFF).^[s3] to model the polymer. All-atom representation was used. The AVOGADRO software.^[s4] was used to build and geometry-optimize the initial structure of the polymer.

The initial cubic simulation cell (200 Å for each principal direction) comprised of 50 polymers and 20000 water molecules was generated by randomly packing the molecules using the freely available PACKMOL software.^[s5] A rigid water model, TIP3P water model^[s6], was used to model water via use of the SHAKE algorithm.^[s7, s8] A 50 ns simulation was performed in the the isothermal-isobaric ensemble (NPT ensemble where N, P and T represent the number of atoms, system pressure and temperature, respectively) at 25 °C and 1 atm. Following this, a 10 ns simulation was performed in the the NVT ensemble at 25 °C for and the trajectory recorded during the last 5 ns of this simulation was used for post processing.

The Nosè-Hoover thermostat^[s9, s10] and barostat,^[s9, s11] were used to control the system temperature and pressure, respectively. The long-range van der Waals (vdW) and Coulombic interactions were cut off at an inter-atomic distance of 12 Å. The contribution of long-range interactions to the electrostatic interactions were calculated via the particle-particle-particle-mesh (PPPM) algorithm.^[s12] Newton's equations of motion were time-integrated at each 1 fs. The open-access LAMMPS simulation software package (lammps.sandia.gov).^[s13] was used for MD simulations. Visual molecular dynamics (VMD) was used to visualize the trajectories generated during the MD simulations.^[s14]

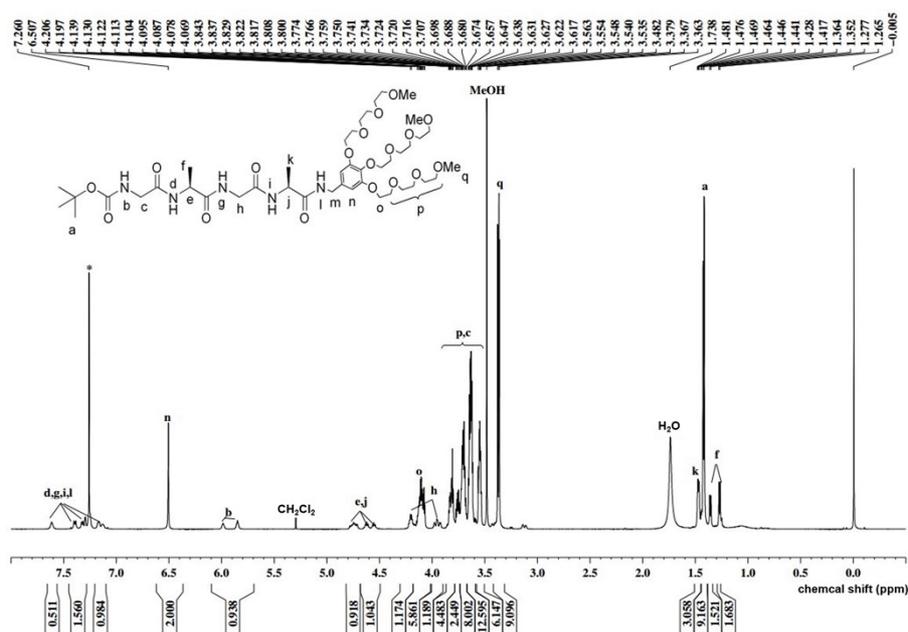


Fig. S9. ¹H NMR spectrum of **1a** in CDCl₃ at 298 K.

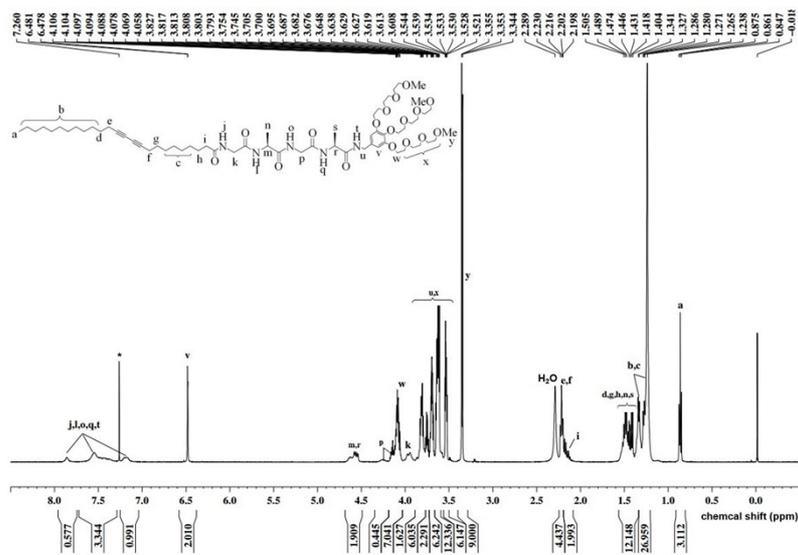


Fig. S10. ^1H NMR spectrum of PCDA-GAGA-G1 in CDCl_3 at 298 K.

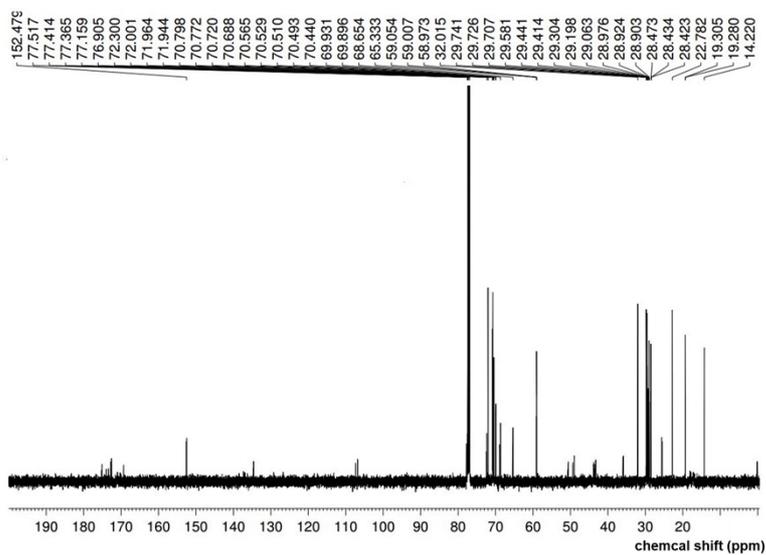


Fig. S11. ^{13}C NMR spectrum of PCDA-GAGA-G1 in CDCl_3 at 298 K.

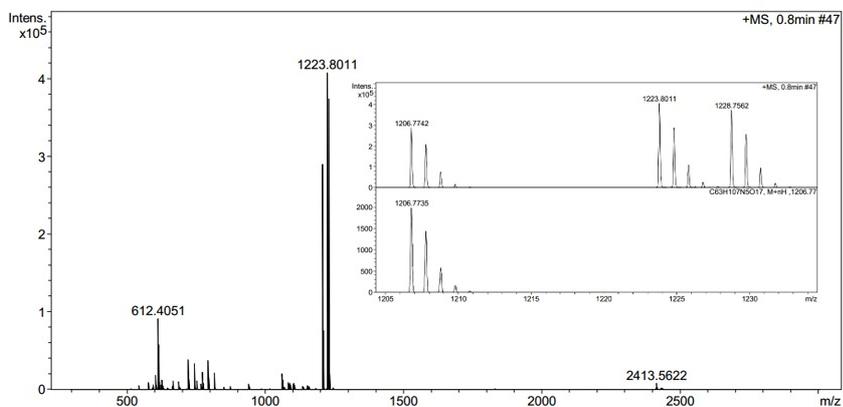


Fig. S12. ESI-MS spectrum of PCDA-GAGA-G1 (pos. mode, MeOH).

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