

Supporting information for the manuscript

Remarkable Impact of a Minor Structural Variation in the Chain-end on the Hierarchical Self-Assembly of a Polymeric Foldamer

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Materials and methods: Reagents and solvents were obtained from commercial sources and used after purification by literature prescribed protocols.¹ Hexamethylene-diisocyanate, Serinol, 2-octyl dodecanol, 1,4-diazabicyclo[2.2.2]octane (DABCO), Benzyl alcohol, 4-pyridine methanol, Naphthalene di-anhydride, Methyl 3,4,5-Tri hydroxy benzoate, *n*-octyl bromide, (*S*)-(+)-Citronellyl bromide and dodecanoic acid (Lauric Acid) were received from Sigma Aldrich chemical company. Hexamethylene-diisocyanate was purified by distillation under reduced pressure using Kugelrohr equipment. DABCO was recrystallized from hexane and the other reagents were used as received. Spectroscopic grade solvents were used for all physical studies. ¹H NMR experiments were performed in a Bruker DPX-500 MHz spectrometer the peak positions were calibrated using TMS as an internal standard. UV/Vis experiments were done in a Perkin Elmer Lambda 25 spectrometer equipped with a Peltier for variable temperature experiments. Emission spectra of samples were recorded in a FluoroMax-3 spectrophotometer from HORIBA Jobin Yvon. Circular Dichroism (CD) experiments were carried out in a JASCO CD spectrometer (model-J815) equipped with a peltier for temperature variation experiments. The molar ellipticity ($[\theta]$) was estimated from the obtained raw data (ellipticity (θ) in milli-degrees) by using the following equation where *C* represents the concentration in moles/ lit and *l* is the cuvette path length in cm.

$$[\theta] = \frac{\left(\frac{\theta}{1000}\right) \times 100}{C \times l}$$

Dynamic light scattering (DLS) studies were done out in Malvern instrument. FT-IR spectral measurements were carried out in a Perkin Elmer Spectrum 100FT-IR spectrometer. Transmission electron microscopy images were captured in a JEOL-2010EX machine operating at an accelerating voltage of 200 kV. Atomic force microscopy (AFM) imaging was performed in tapping mode in an Innova instrument from Bruker. Molecular weight of the polymer was evaluated in THF (1.0 mg/ ml) solvent at 30 °C with respect to poly(methyl methacrylate) (PMMA) standards in a Water's GPC machine equipped with a 515 HPLC pump, Waters 2414 RI detector and HSPgel HT 4.0/ HSPgel HT 2.5 columns connected in a series. The flow rate of the eluent was maintained as 0.6 ml/min. X-ray diffraction (XRD) was recorded on a Seifert XRD3000P diffractometer with Cu K α radiation (λ = 0.154 06 nm) and operating voltage and current of 40 kV and 30 mA, respectively.

(S)-4-((3,7-dimethyloct-6-en-1-yl)oxy)-3,5-bis(octyloxy)benzoic acid (chiral acid derivative / ESDA-1): This compound was prepared by following previous literature.² ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 7.32 (s, 2H), 5.1 (t, 1H), 4.12-4.08 (m, 2H), 4.07- 4.01 (m, 4H), 2.04-1.2 (m, 34H), 0.97-0.87 (m, 12H); HRMS (ESI): m/z calculated for C₃₃H₅₆O₅Na [M+Na]⁺ : 555.4020; found: 555.4023.

3,4,5-tris(octyloxy)benzoic acid (ESDA-2): This compound was synthesized by following previous literature.³ ¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) = 7.30 (s, 2H), 4.05-4.00 (m, 6H), 1.83-1.69 (m, 6H), 1.47- 1.43 (m, 6H), 1.30-1.24 (m, 24H), 0.87-0.85 (m, 9H).

Additional Figures:

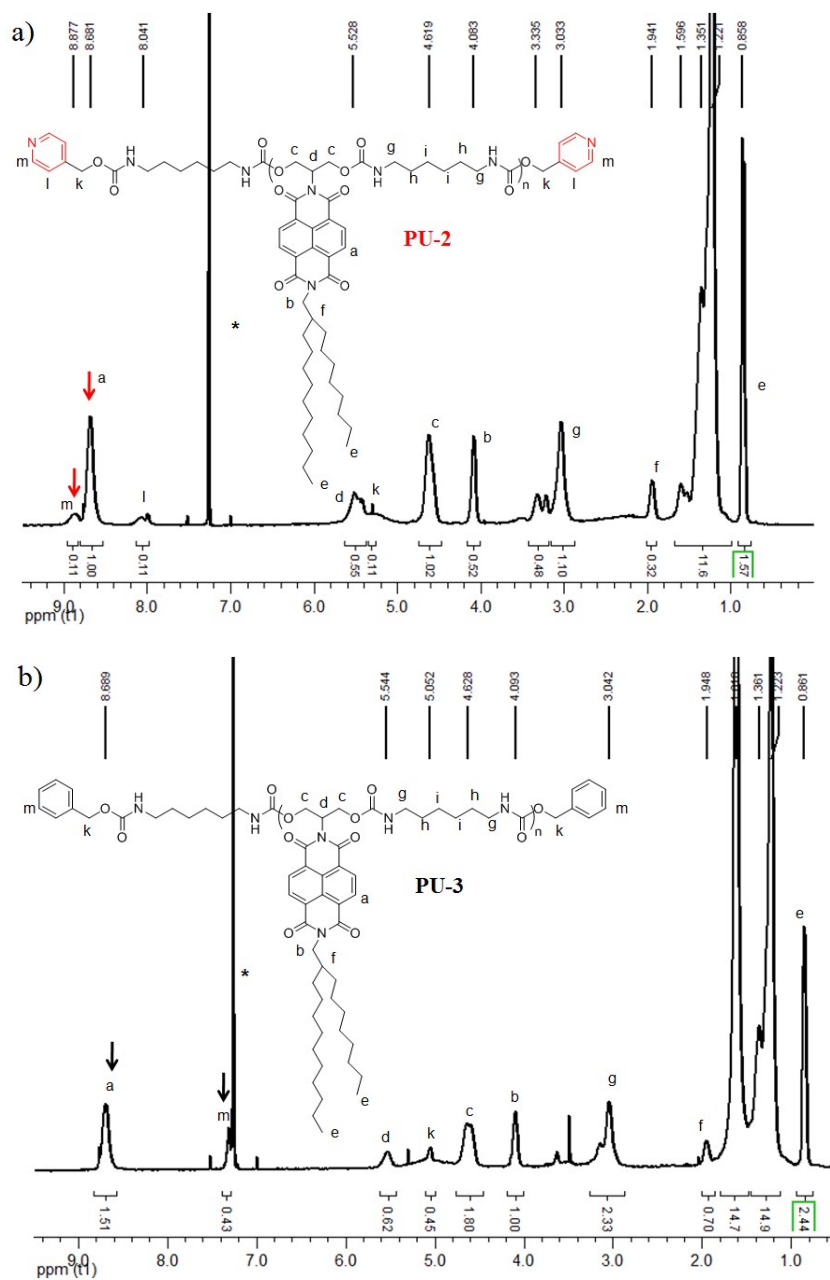


Figure S1: ¹H NMR spectra of (a) **PU-2** and (b) **PU-3** in CDCl₃ (asterisk indicates residual solvent peak).

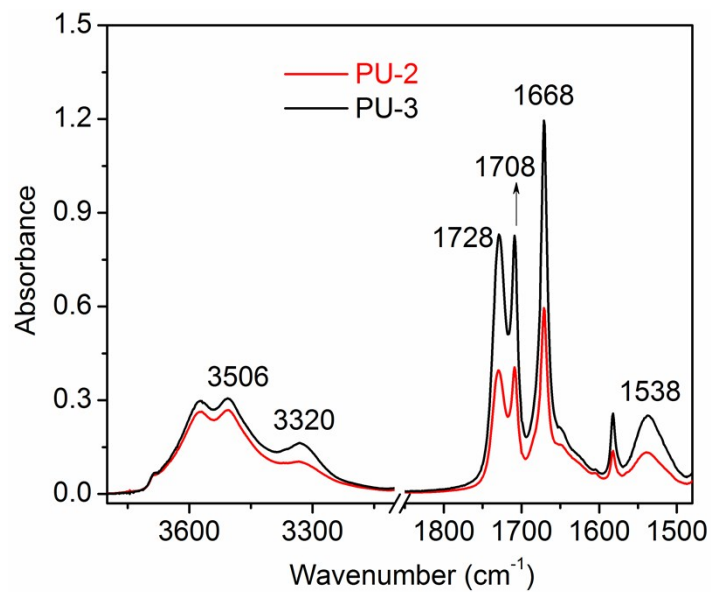


Figure S2: FT-IR spectra of **PU-2** and **PU-3** in THF (C = 5 mM).

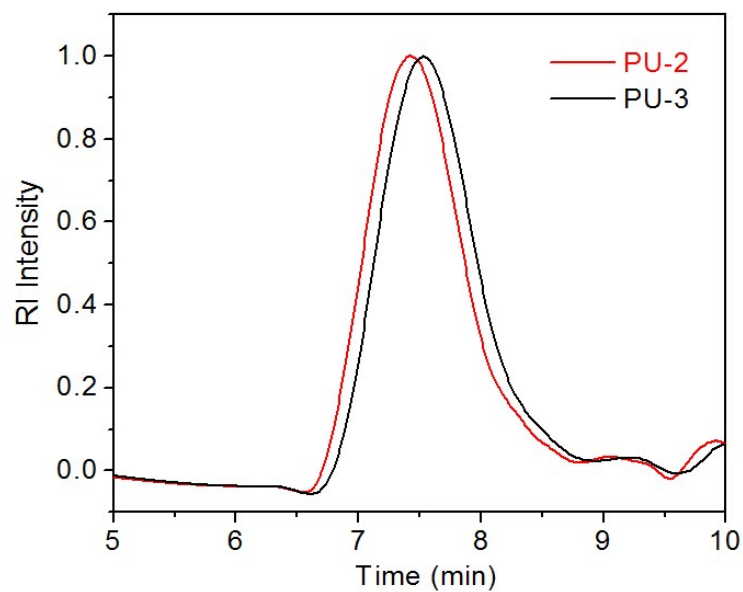


Figure S3: GPC chromatogram of **PU-2** and **PU-3** in THF.

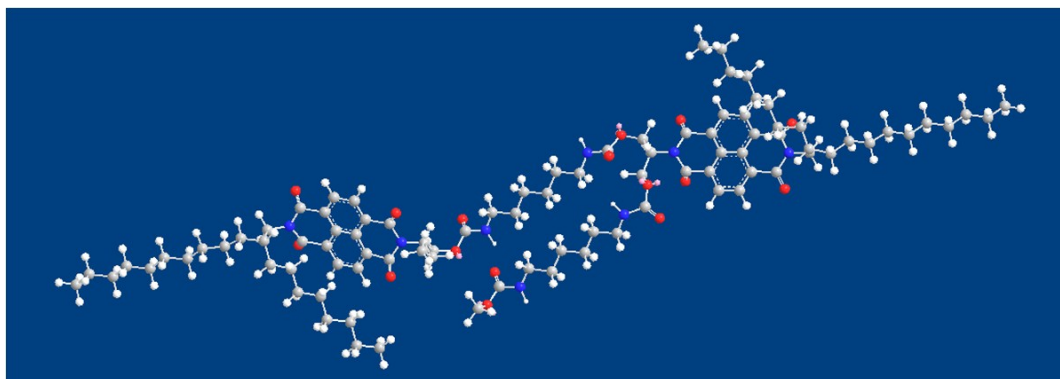


Figure S4: Energy minimized structure of repeating unit of PUs. Molecular modeling was done in Chem3D Ultra 8.0 software using MM2 for energy minimization.

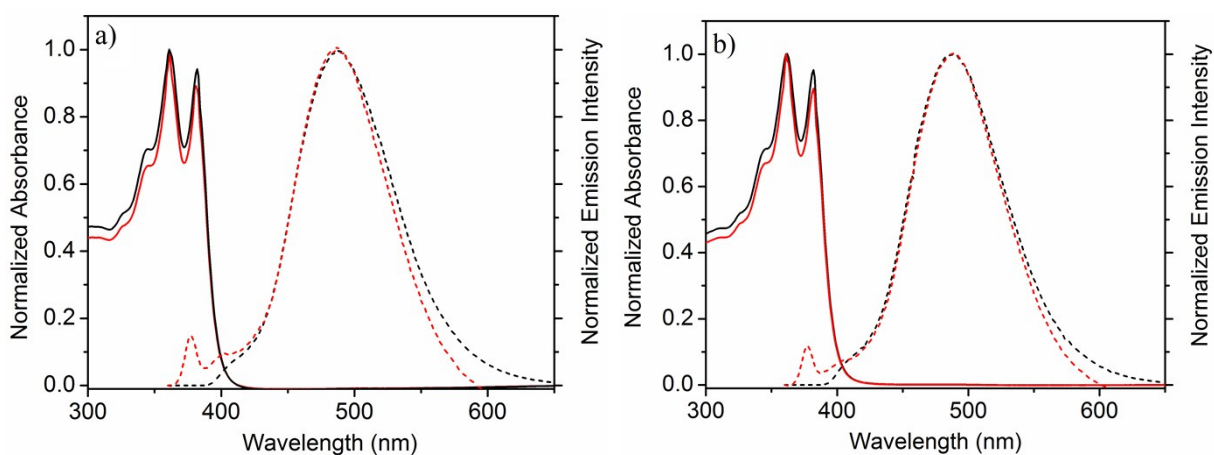


Figure S5: Intensity normalized UV-Vis absorption (solid line) and emission spectra (dotted lines) of freshly prepared MCH solution of **PU-2** (left) and **PU-3** (right) in two different concentrations (black- 10⁻⁵ M; red-10⁻⁶ M)

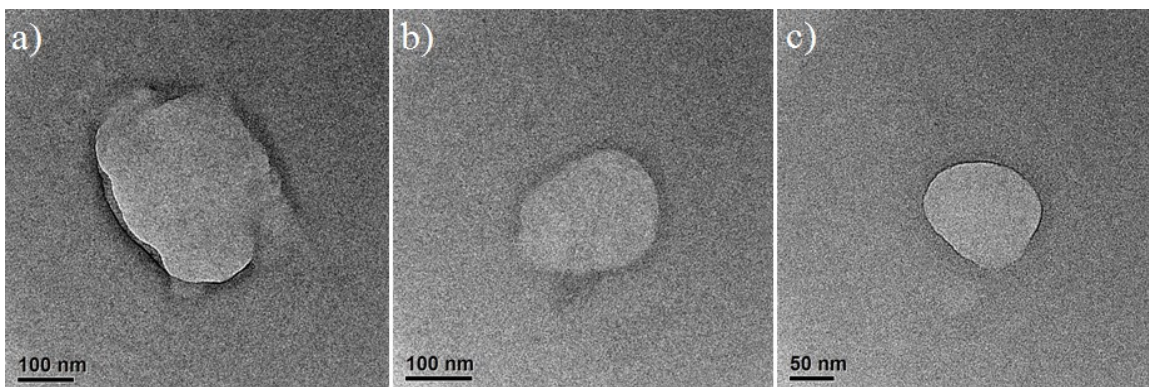


Figure S6: HRTEM images of a drop-casted sample of freshly prepared solution (or carbon coated Cu grid) of PU-3 in MCH ($C = 2.0$ mM).

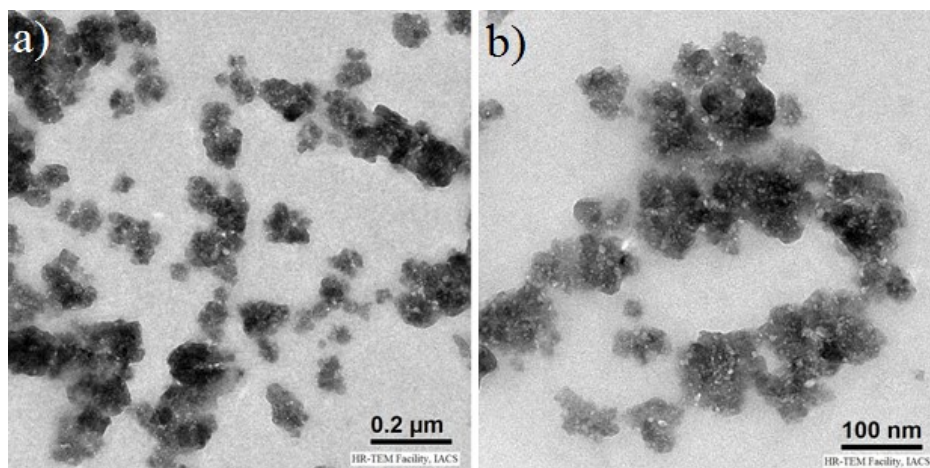


Figure S7: HRTEM image of a drop-casted sample of freshly prepared solution of PU-2 or carbon coated Cu grid) in MCH ($C = 2.0$ mM).

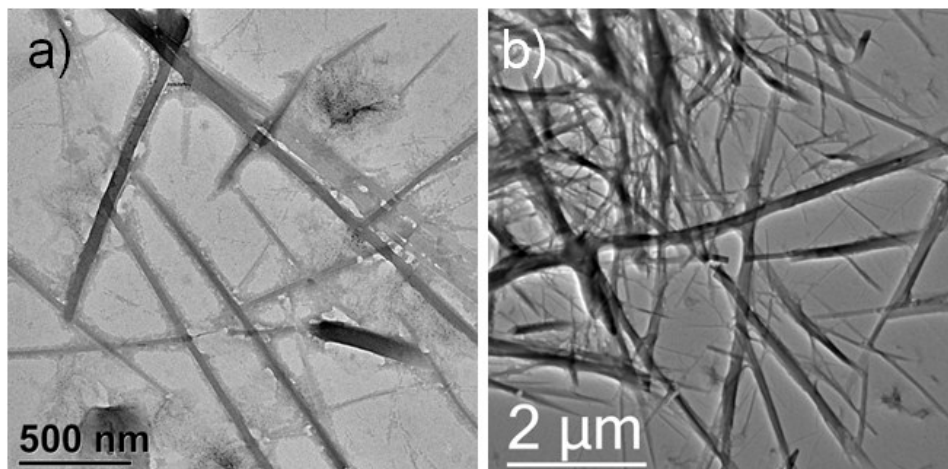


Figure S8: HRTEM images of dropcasted sample of aged (7 days) MCH solution or carbon coated Cu grid of PU-3 ($C = 2.0$ mM).

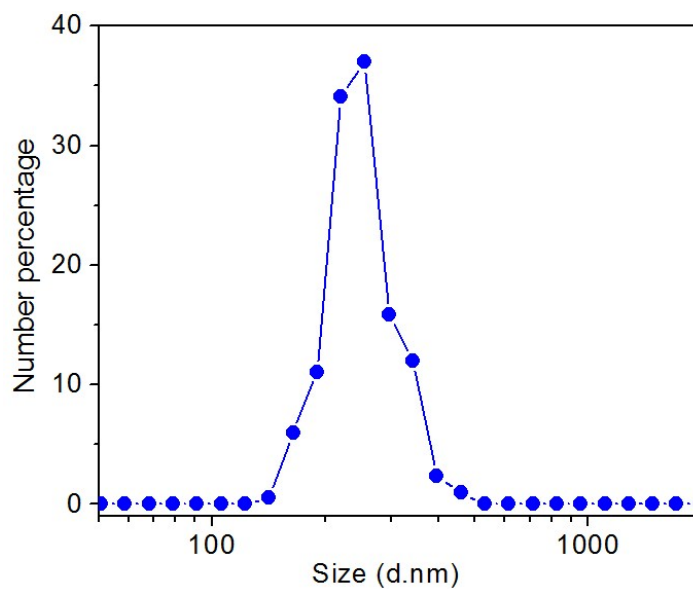


Figure S9: DLS data of the freshly prepared MCH solution PU-2 in presence of ESDA-1 ($C = 0.01$ mM).

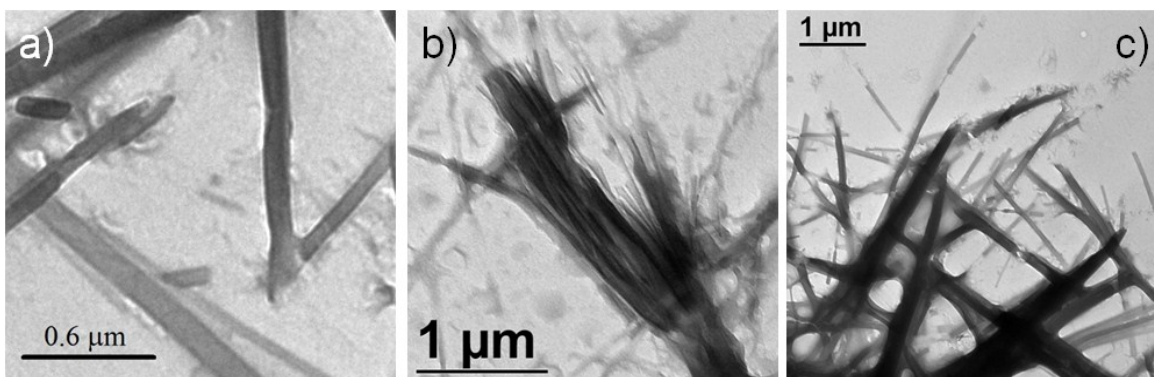


Figure S10: HRTEM images of dropcasted sample of aged (7 days) MCH solution or carbon coated Cu grid) of PU-2 in presence of ESDA-1 (C = 2.0 mM).

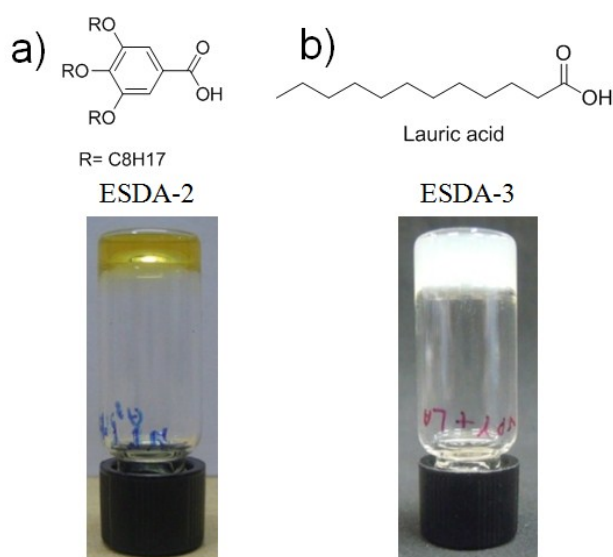


Figure S11: Images of aged (7 days) MCH solution of PU-2 in presence of (a) ESDA-2 and (b) ESDA-3 (Concentration of PU-2 = 10.0mM and ESDA = 20.0 mM).

Reference:

1. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon, Oxford, 1980.
2. M. R. Molla, A. Das, S. Ghosh, *Chem. Commun.* 2011, **47**, 8934-8936.
3. M. R. Molla, A. Das, S. Ghosh, *Chem. Eur. J.* 2010, **16**, 10084-10093.