Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPLEMENTARY INFORMATION

Folding of aromatic polyamides into a rare intrachain β-sheet type structure and further reinforcement of secondary structure through host-guest interactions

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1. Materials

Chelidamic acid, 5-hydroxy isophthalic acid, pyrene, propargyl alcohol, 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), 4-dimethylaminopyridine (DMAP), Poly (ethylene glycol) methyl ether with average Mn of 550 (MeO-PEG_{550}-OH), 1,1,2,2-tetrachloroethane (TCE), Tosyl chloride, NaSH, hexamethylphosphoramide (HMPA), N-Methyl-2-pyrrolidone (NMP), all the deuterated solvents, etc. were purchased from Sigma Aldrich. KOH, NaOH, thionyl chloride, sodium azide, $CuSO_4$, Na-ascorbate, K_2CO_3, etc., and all the common organic solvents were purchased from both TCI Chemicals and Avra and were used without further purification. Solvents like DCM, methanol, THF, HMPA, and NMP were dried, using standard drying procedures and distilled using standard distillation set up while HMPA and NMP were distilled using kugelrohr apparatus. Purification of products was carried out by column chromatography using silica gel of mesh size of both 100-200 µm and 60-120 µm. Thin-layer chromatography (TLC) was carried out on pre-coated plates. UV light (254 nm) and ninhydrin stain were used for nitrogen-containing compounds for visualization.

2. Methods

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Biospin Avance III FT-NMR 400 MHz spectrometer, with tetramethylsilane (TMS) as an internal standard at room temperature. NMR data were processed using Mestre Nova software. UV-Vis spectral measurements were carried out with Agilent Cary 60 UV-Vis spectrophotometer using 1 cm path length quartz cuvettes. Temperature-dependent absorption spectra of samples were measured using Agilent Cary 60 UV-Vis spectrophotometer equipped with a single-cell Peltier accessory. The single-cell Peltier was used in the temperature range of 25^{o}C to 100^{o}C. The steady-state emission studies were performed using FL Solution software with the Hitachi F7000 fluorescence spectrophotometer. The temperature-dependent fluorescence of samples was measured using a temperature-controlled cuvette holder for the Hitachi F7000 spectrophotometer (Luma 40) from Quantum Northwest. The Luma 40 was used in the temperature range of 25^{o}C to 100^{o}C. GPC measurements were carried out with Malvern Omnisec instrument having refractive index (RI) detector using Shodex GPC KD-806M column with DMF with 0.01 M LiBr as eluent at 35^{o}C with a flow rate of 0.7 mL/min and PMMA as standard for all the samples. The results were analyzed by using Omnisec software. The sample peaks were analyzed for M_n, M_w, and Đ using the conventional calibration method. Hydrodynamic radii were estimated using dynamic light scattering (DLS) measurements on a Malvern Zetasizer Nano ZS90 instrument. All the data were plotted in Origin 2018 software. Molecular structures and reaction schemes were drawn using Chemdraw Professional 15.0 software.

3. Computational studies

In order to gain insights into the various factors such as intramolecular H-bonding, π-stacking interactions which control the relative stability between the helical and βsheet-like structure of the aromatic oligoamides we have designed a few model aromatic polyamides by varying their π-surface area as well as amide linkages. The monomer units of such model aromatic polyamides are shown in **Figure S1**. Polyamides formed from A1 unit will have naphthalene 1,5-linkage whereas polyamides formed from A2 and A3 units will have pyrene 2,7 and 1,6-linkages respectively. The A2 and A3 units are linkage isomers of the same monomeric compounds.

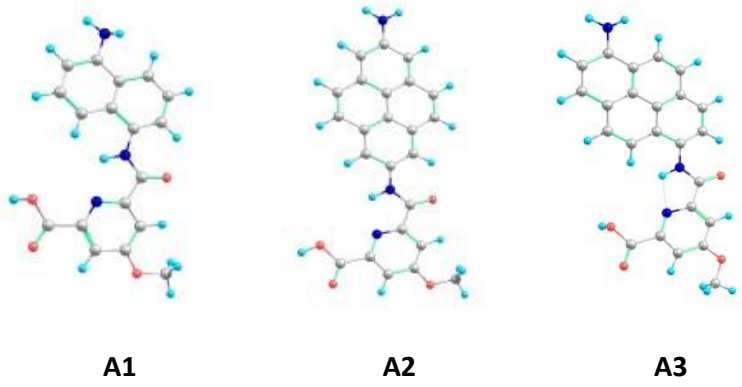


Figure S1: Monomer units of model aromatic polyamides

To compare the stability of the helical and the βsheet-like structures of the aromatic oligoamides formed by the above monomers (A1, A2, and A3) we have considered the hexamer units for both conformers for all three monomers as shown in **Figure S2**. All these structures were optimized using Gaussian 9 software[1], employing the M06-2X,[2] functional with the 6-31G* basis set.[3] The nature of stationary points was confirmed by frequency calculations. The solvent effects were incorporated by applying the CPCM solvation model4 and the dielectric properties of $CHCl_3$ were used for solvent calculations. The relative zero-point corrected energies (in kcal/mol) calculated at M062X/6-31G* level of theory are given within parentheses.

The helical structure of the hexamer for the naphthalene-linked oligoamide (1a) is 45.7 kcal/mol more stable than the βsheet-like structure (1b) for the same oligoamide. The higher stability of the helical structure is due to the presence of twelve intramolecular H-bonding interactions between the amide N-H and the pyridine nitrogen atom. The stability gained due

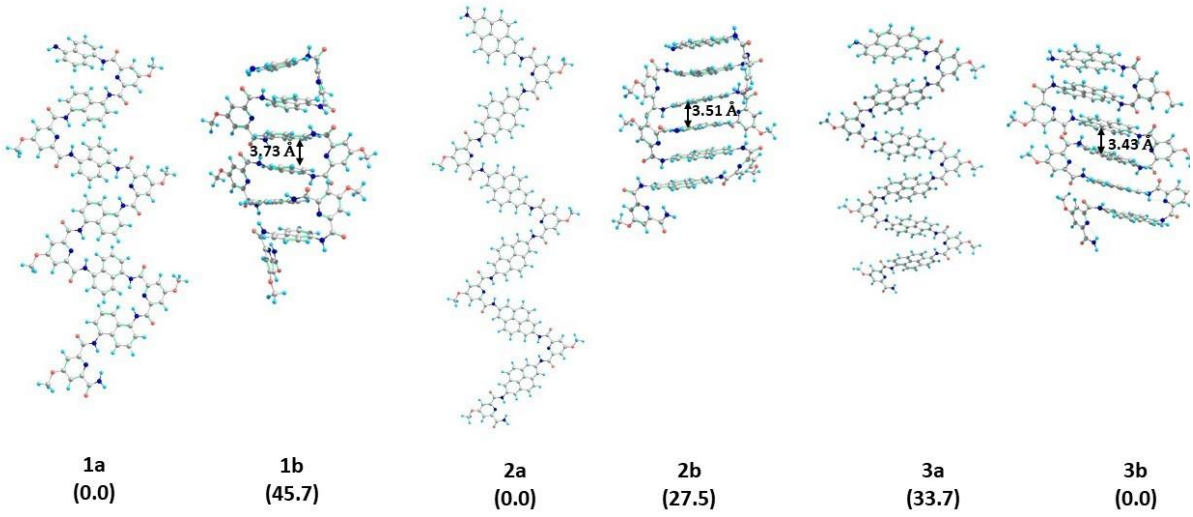
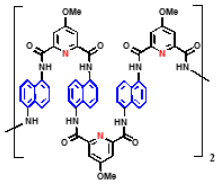
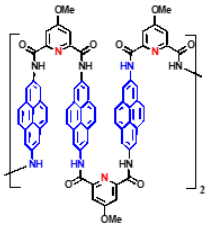
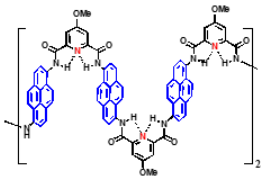
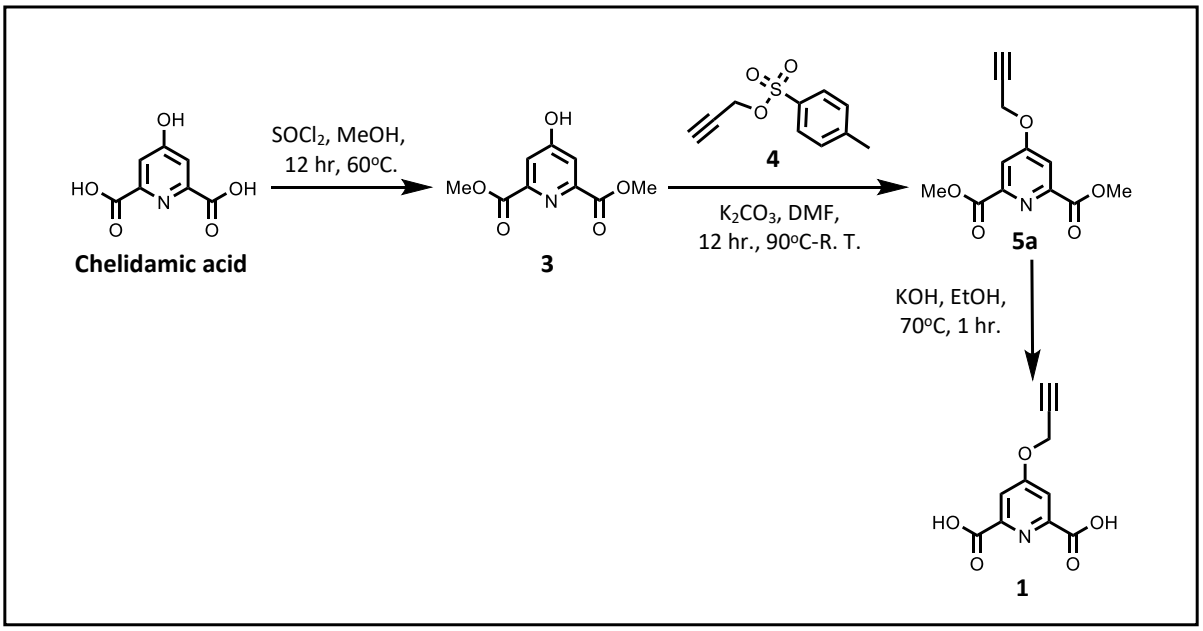


Figure S2*: Structures of helical and β-sheet conformations of hexamers formed by monomer A1 (1a and 1b), by monomer A2 (2a and 2b) and by monomer A3 (3a and 3b).*

to the presence of π-stacking interactions in 1b can not compensate for the absence of H-bonding interactions in it. When we replace the naphthalene diamine with pyrene diamine as a larger π-surface motif, the difference in energy between the helical (2a) and βsheet-like structure (2b) decreases from 45.7 kcal/mol to 27.5 kcal/mol. This suggests that the introduction of pyrene-based linkers increases the π-stacking interactions which reduce the energy gap between the 2a and 2b, however, the helical structure, 2a remained the preferred conformer for this system too. When we use a different linkage isomer as a monomeric unit (A3) to construct the hexamer, we observed that the βsheet-like structure (3b) becomes 33.7 kcal/mol more stable than the helical conformer, 3a. The reversal of stability between the helical and βsheet-like structures for this system arises due to the retention of one of the H-bonding interactions in the βsheet-like structure. It is also observed that the average π-stacking distance decreases from 3.51 Å to 3.43 Å while going from 2b to 3b suggesting a reinforcement of the π-stacking interactions due to the intramolecular H-bonding interaction remained in the 3b. Thus, it can be concluded that both intramolecular H-bonding and π-stacking interactions are necessary to stabilize the βsheet-like structure.

π-surface and amide-linkage	**Energy of helical structure** (in kcal/mol)	**Energy of β-sheet like structure** (in kcal/mol)	**Average π-stacking distances in β-sheet like structure (in Å)**
A1 	0.0	45.7	3.73
A2 	0.0	27.5	3.51
A3 	33.7	0.0	3.43

4. <u>Synthetic scheme for the preparation of dicarboxylic acid monomer</u> (1)



Scheme S1: *Synthetic scheme of propargyl bearing dicarboxylic acid monomer (**1**).*

Compound 3 [4]

To Chelidamic acid (2.5 gm, 13.65 mmol), dry MeOH (100 ml) was added under nitrogen atmosphere and the resulting suspension was cooled to 0°C in an ice bath. Thionyl chloride (2.5 ml, 33.58 mmol) was carefully added to the reaction mixture and the whole setup was placed at 60°C and stirred overnight. After completion of the reaction, all the solvents were removed under reduced pressure. The residue was then added to cold water (20 ml) and extracted with chloroform (100 ml × 3). The organic layer was collected, combined, and passed through anhydrous Na_2SO_4. After the removal of organic solvents under reduced pressure, the pure product (**3**) was obtained as a white solid (yield: 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 2H, Ar-**H**), 4.06 (s, 6H, -OC**H$_3$**).

Propargyl tosylate (4) [5]

To Propargyl alcohol (3 gm, 53.51 mmol), Tosyl chloride (14 gm, 70.28 mmol), and diethyl ether (60 ml) was added under nitrogen atmosphere and the reaction mixture was cooled in an ice bath. NaOH pellets (12 gm, 0.28 mol) were added to the solution in 6 portions at 0°C under vigorous stirring. The solution was stirred overnight at room temperature. The suspension was then poured into cold water (40 ml) and extracted with diethyl ether (30 × 3 ml). The organic layer was collected, combined, and passed through anhydrous Na_2SO_4. After the removal of organic solvents under reduced pressure, pure propargyl tosylate was obtained as a yellow liquid (yield: 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, 2H, Ar-**H**, *o*-SO_2OCH_2-), 7.38 (d, 2H, Ar-**H**, *p*-SO_2OCH_2-), 4.72 (s, 2H, -OC**H$_2$**CCH), 2.50 (t, 1H, -OCH_2CC**H**), 2.48 (s, 3H, -OSO_2ArC**H$_3$**).

Compound 5a [6]

To a suspension of compound **3** (4 gm, 16.05 mmol) and K_2CO_3 (5 gm, 36.81 mmol) in dry DMF (100 ml), propargyl tosylate (**4**) (4.78 ml, 27.62 mmol) was added under nitrogen atmosphere. The mixture was heated at 90°C for 4 hours and stirred overnight at room temperature. The reaction mixture was filtered to remove excess K_2CO_3 and the filtrate was poured (dropwise) into cold water with vigorous stirring. The resulting precipitates were filtered, washed several times with water, and dried under the vacuum. The residue was purified by recrystallization using a mixture of solvent (chloroform: hexane = 1:3) to afford product **5a** as a white solid (yield: 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 2H, Ar-**H**), 4.90 (d, 2H, -OC**H$_2$**CCH), 4.05 (s, 6H, -OC**H$_3$**), 2.65 (t, 1H, -OCH_2CC**H**).

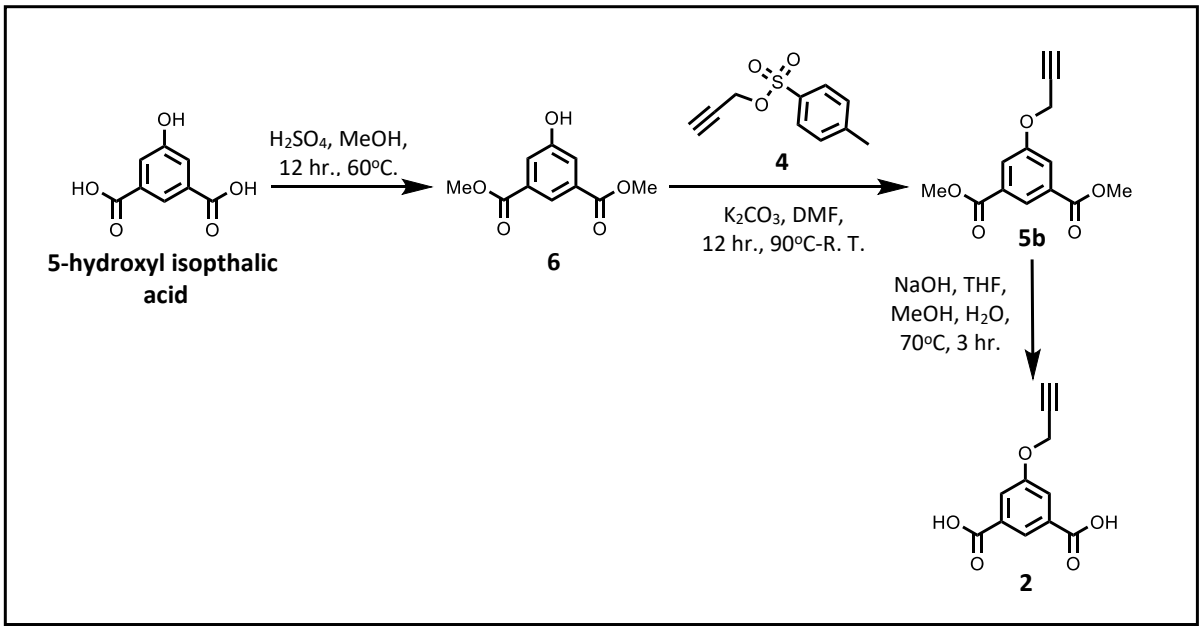
Compound 1 [7]

To a hot mixture of Compound **5a** (300 mg, 1.20 mmol) in EtOH (9 ml), solid KOH (269.33 mg, 4.8 mmol) was added. The mixture first changed to a clear solution and then became viscous. The reaction mixture was heated at 70°C for 1 hour. After completion of the reaction, all the solvents were evaporated under reduced pressure and the residue was dissolved in water, followed by the addition of dilute HCl. The resulting precipitates were filtered, washed with water, and dried under the vacuum. The pure product (**1**) was obtained as a pale-yellow solid (yield: 80%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (s, 2H, Ar-**H**), 5.11 (d, 2H, -OC**H$_2$**CCH), 3.75 (t, 1H, -OCH_2CC**H**).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.82, 165.71, 150.30, 114.46, 80.30, 80.26, 78.19, 56.88.

5. <u>Synthetic scheme for the preparation of dicarboxylic acid monomer</u> (2)



Scheme S2: *Synthetic scheme of propargyl bearing dicarboxylic acid monomer (**2**).*

Dimethyl 5-hydroxyisophthalate (6) [8]

To 5-hydroxy isophthalic acid (10 gm, 54.91 mmol), dry MeOH (100 ml) was added under a nitrogen atmosphere and the resulting suspension was cooled to 0°C in an ice bath. Conc. H_2SO_4 (5 ml) was slowly added to the reaction mixture and the whole setup was refluxed for 12 hours. After completion of the reaction, all the solvents were removed under reduced pressure. The residue was then added to water (70 ml) and extracted with ethyl acetate (100 ml × 3). The combined organic layer was washed with 10% aq. $NaHCO_3$ (100 ml), water (70 ml), brine (50 ml) and passed through anhydrous Na_2SO_4. After the removal of organic solvents under reduced pressure, the pure product (**6**) was obtained as a white solid (yield: 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (t, 1H, Ar-**H**), 7.80 (d, 2H, Ar-**H**), 3.97 (s, 6H, -OC**H$_3$**).

Compound 5b [6]

To a suspension of dimethyl 5-hydroxyisophthalate (**6**) (4 gm, 16.11 mmol) and K_2CO_3 (5 gm, 36.81 mmol) in dry DMF (100 ml), propargyl tosylate (**4**) (4.78 ml, 27.62 mmol) was added under nitrogen atmosphere. The mixture was heated at 90°C for 4 hours and stirred overnight at room temperature. The reaction mixture was filtered to remove excess K_2CO_3 and the filtrate was poured (dropwise) into cold water with vigorous stirring. The resulting precipitates were filtered, washed several times with water, and dried under the vacuum. The residue was purified by recrystallization using a mixture of solvent (chloroform: hexane = 1:3) to afford product **5b** as a white solid (yield: 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (t, 2H, Ar-**H**), 7.85 (d, 2H, Ar-**H**), 4.90 (d, 2H, -OC**H$_2$**CCH), 4.05 (s, 6H, -OC**H$_3$**), 2.65 (t, 1H, -OCH$_2$CC**H**).

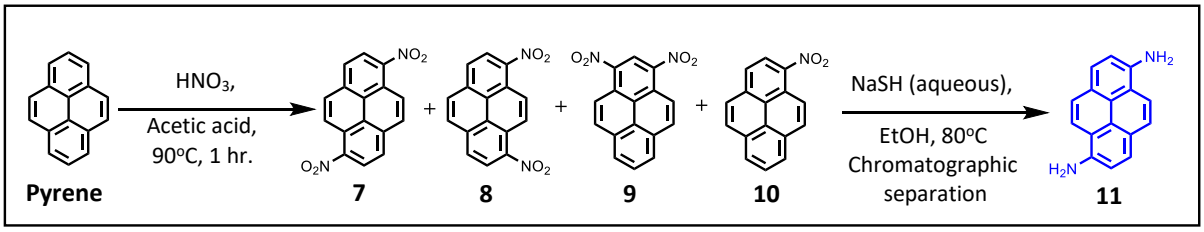
Compound 2 [9]

To a mixture of Compound **5b** (500 mg, 2.02 mmol) in THF (4 ml), H_2O (4 ml), and MeOH (4 ml), solid NaOH (403.2 mg, 10.08 mmol) was added. The reaction mixture was stirred at 70°C for 3 hours. After completion, THF and MeOH were evaporated from the reaction mixture. 1 (N) HCl (15 ml) was added to the residue. The resulting white precipitates were filtered, washed with water, and dried under the vacuum. The desired product (**2**) was obtained as a pale-yellow solid (yield: 85%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.36 (s, 2H, Ar-COO**H**), 8.12 (t, 1H, Ar-**H**), 7.72 (d, 2H, Ar-**H**), 4.96 (d, 2H, -OC**H$_2$**CCH), 3.65 (t, 1H, -OCH$_2$CC**H**).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.76, 157.76, 133.08, 123.34, 120.05, 79.45, 79.41, 79.12, 56.39.

6. <u>Synthetic scheme for the preparation of pyrene-1,6-diamine</u> (11)



Scheme S3: *Synthetic scheme of diamine monomer (**11**).*

Pyrene-1,6-diamine (11) [10]

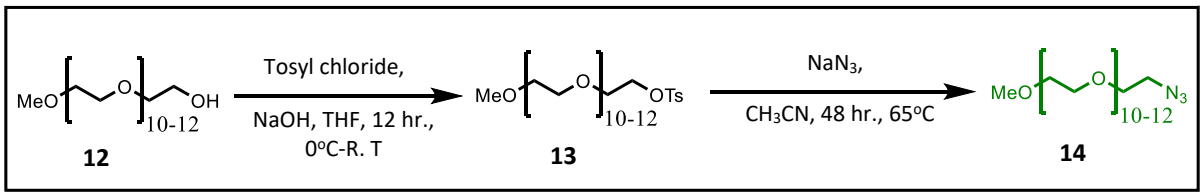
To pyrene (2.5 gm, 12.36 mmol), glacial acetic acid (25 ml) was added and the reaction mixture was stirred at 90°C. A mixture of HNO_3 (1.9 ml) and glacial acetic acid (5 ml) was added slowly and the yellow suspension was stirred at 90°C for 1 hour. The reaction mixture was cooled to room temperature and the resulting precipitates were filtered, washed with MeOH, and dried under the vacuum. The crude product contains a mixture of 1,6-dinitropyrene (**7**), 1,8-dinitropyrene (**8**), 1,3-dinitropyrene (**9**) and 1-nitropyrene (**10**).

Nitropyrenes thus obtained were suspended in EtOH (25 ml) and an aqueous solution of NaSH (9 gm, 0.16 mol) was added to the mixture. The solution was refluxed for 3 hours, followed by the addition of H_2O (25 ml) and the whole reaction mixture was allowed to cool. The resulting precipitates were filtered and dried under a vacuum. Column purification was done using ethyl acetate/hexane as the eluent to get the desired product (**11**) as a yellow solid (yield: 32%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.80 (d, 2H, Ar-**H**), 7.74 (d, 2H, Ar-**H**), 7.68 (d, 2H, Ar-**H**),), 7.26 (d, 2H, Ar-**H**), 5.93 (d, 4H, Ar-N**H$_2$**).

^{13}C NMR (101 MHz, DMSO-d_6) δ 142.78, 127.09, 125.48, 124.34, 123.06, 117.27, 116.61, 113.39.

7. Synthetic scheme for the preparation of PEG_{550} monomethyl ether azide (14)



Scheme S4: *Synthetic scheme of PEG_{550} monomethyl ether azide (**14**).*

PEG_{550} monomethyl ether tosylate (13) [11]

To a mixture of MeO-PEG_{550}-OH (**12**) (10 gm, 18.18 mmol) in THF, aqueous NaOH (2.18 gm, 54.54 mmol) solution (10 ml) was added. The reaction mixture was placed in an ice bath and the contents were allowed to cool down. Then Tosyl chloride (5.2 gm, 27.27 mmol) solution in THF was added slowly and the reaction mixture was stirred overnight at room temperature. After completion, the organic layer was separated and the aqueous layer was extracted with diethyl ether (50 ml × 3). The combined organic layer was washed with 10% aq. NaOH solution (30 ml) and passed through anhydrous Na_2SO_4. After the removal of organic solvents under reduced pressure, the pure product (**13**) was obtained as a light-yellow liquid (yield: 82%).

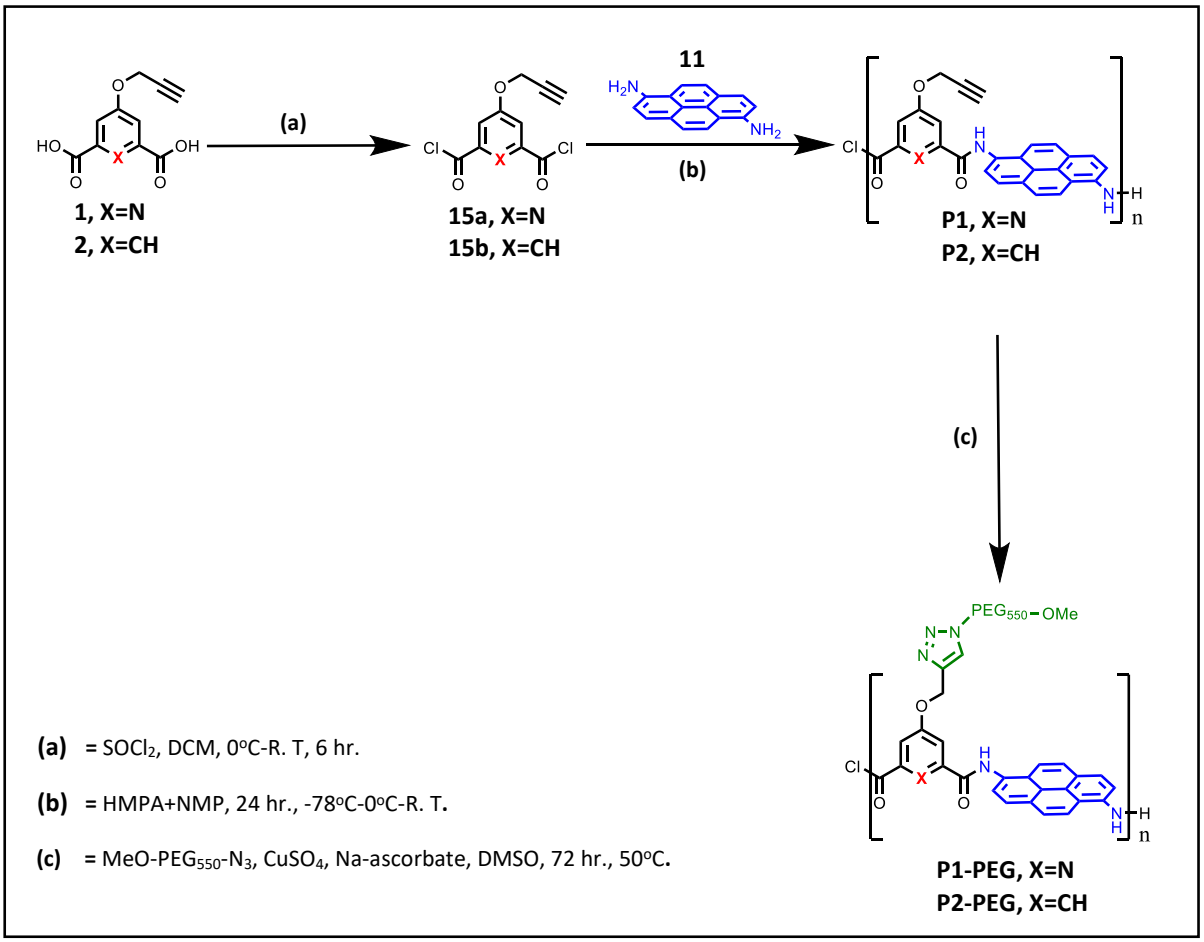
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 2H, -OSO_2**ArH**CH_3), 7.33 (d, 2H, -OSO_2**ArH**CH_3), 4.13 (t, 2H, -SO_2OC**H_2**CH_2O-), 3.73 – 3.48 (m, C**H_2** s of PEG skeleton), 3.35 (s, 3H, -CH_2OC**H_3**), 2.43 (s, 3H, -OSO_2Ar**CH_3**).

PEG_{550} monomethyl ether azide (14) [11]

To a mixture of PEG_{550} monomethyl ether tosylate (**13**) (4 gm, 3.46 mmol) and sodium azide (1 gm, 13.84 mmol), dry acetonitrile (100 ml) was added under nitrogen atmosphere. The whole setup was placed at 65°C and stirred for 2 days. After completion of the reaction, all the solvents were removed under reduced pressure and the residue was poured into water and extracted with DCM (70 ml × 3). The organic layer was collected, combined, and passed through anhydrous Na_2SO_4. After the removal of organic solvents under reduced pressure, the pure product (**14**) was obtained as a yellowish liquid (yield: 67%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 3.60 (t, 2H, -NC**H_2**CH_2O-), 3.57 – 3.38 (m, C**H_2** s of PEG skeleton), 3.24 (s, 3H, -CH_2OC**H_3**).

8. Synthesis of pyrene based Polymers and post-polymerization modification with PEG_{550} monomethyl ether azide



Scheme S5: *Synthetic scheme of aromatic polyamides (precursor polymer) and their post-polymerization modification.*

In situ preparation of acid chloride from dicarboxylic acid (15a or **15b)**

To dicarboxylic acid (**1** or **2**) (104 mg, 0.47 mmol), dry DCM (8 ml) was added under nitrogen atmosphere and the resulting suspension was cooled to 0°C in an ice bath. Thionyl chloride (0.2 ml, 2.26 mmol) was added dropwise over 10 mins, followed by the addition of DMF (2 drops). The reaction mixture was stirred at room temperature for 6 hours. Excess thionyl chloride and all the solvents were removed under reduced pressure. Assuming quantitative transformation to acid chloride, the remaining solids were directly used for the next step (polymerization).

General synthetic procedure for the preparation of precursor polymers (P1 or **P2)**

To pyrene-1,6-diamine (**11**) (110 mg, 0.47 mmol), dry HMPA (2 ml), and dry NMP (1 ml) was added under nitrogen atmosphere and the whole setup was placed at -78°C to chill the reaction mixture and in this process, the solution in the flask was frozen. DCM solution of the acid chloride (**15a** or **15b**) (0.47 mmol), prepared from corresponding dicarboxylic acid (**1** or **2**), was transferred to the chilled reaction mixture through a cannula. The -78°C bath was

immediately replaced by an ice-water bath. The reaction mixture was stirred at 0°C for 6 hours, followed by 24 hours stirring at room temperature. After completion, DCM was removed from the reaction mixture under reduced pressure and the residue was slowly poured into cold water. The resulting precipitates were filtered, washed with acetone, and dried under vacuum. The dried solids were dissolved in a minimum volume of DMSO and precipitated in chloroform to remove unreacted starting materials, very low molecular weight species (small oligomers), etc. The remaining solids were filtered and washed with diethyl ether. This process was repeated 3 times and the remaining solids were dried under a vacuum to get the desired polymer (**P1** or **P2**) as a bright yellow solid.

P1 (yield: 73%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.83 (s, 2H, Ar-N**H**CO-), 8.24-8.5 (m, 8H, Ar (Pyrene)-**H**), 8.06 (s, Ar-**H**, *o*-OCH2-), 5.24 (d, 2H, -OC**H$_2$**CCH), 3.82 (t, 1H, -OCH$_2$CC**H**).

^{13}C NMR (101 MHz, DMSO-d_6) δ 163.11, 151.35, 131.85, 129.66, 128.11,127.76, 126.15, 125.80, 124.79, 79.35, 56.62.

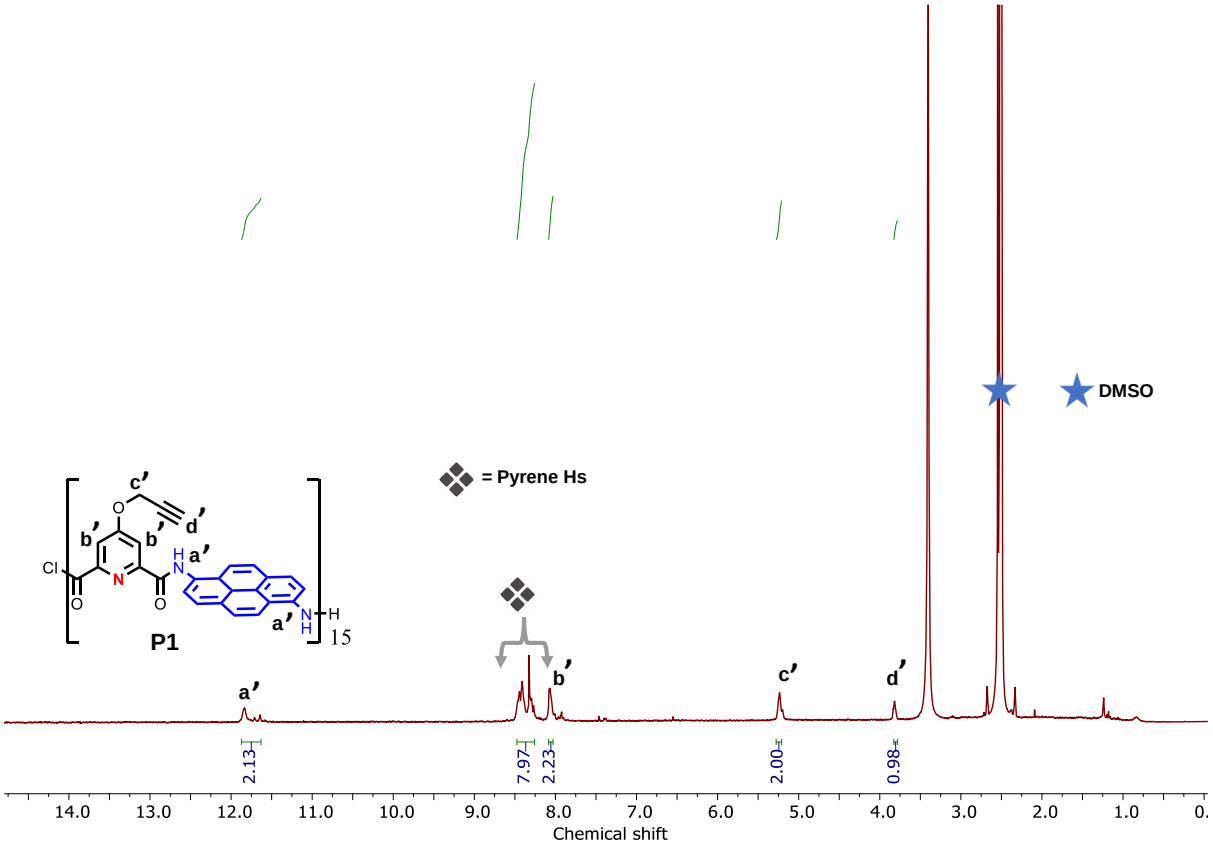


Figure S3: *^{1}H NMR spectra of polymer (**P1**) recorded in DMSO-d_6 at room temperature.*

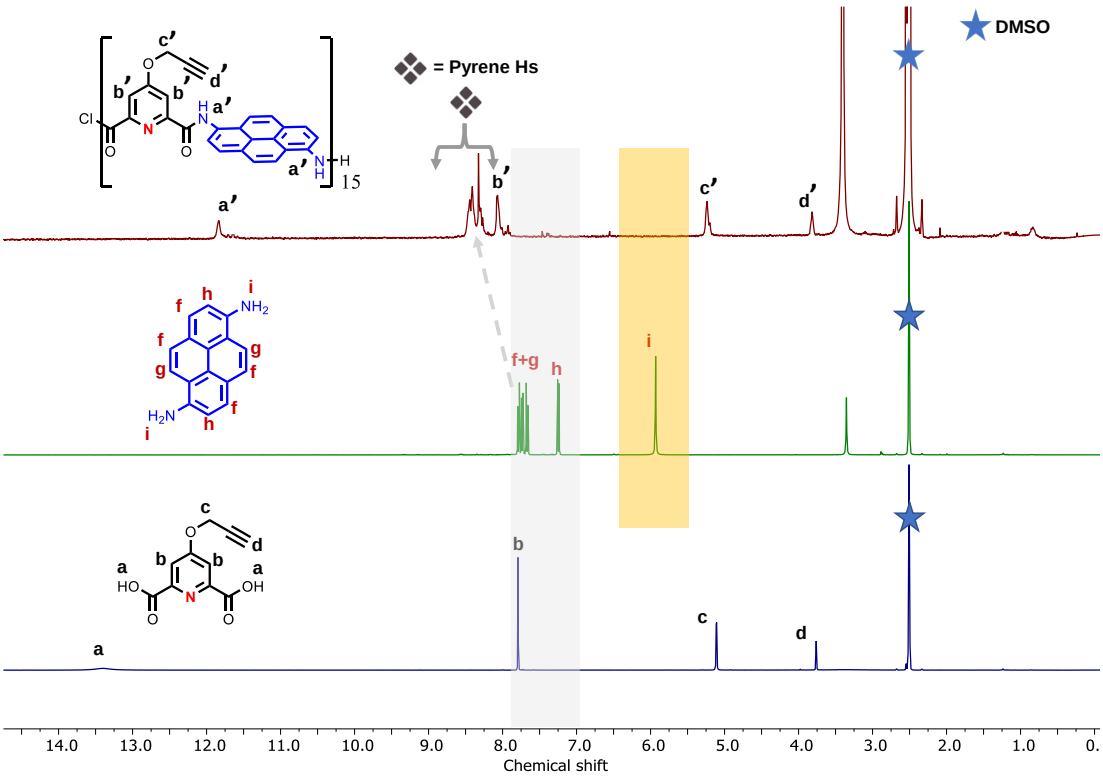


Figure S4: *Stack plot ^{1}H NMR spectra of dicarboxylic acid* ***(1)*** *(bottom), pyrene-1,6-diamine (**11**), precursor polymer (**P1**) (top) (recorded in DMSO-d_6 at room temperature).*

P2 (yield: 70%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.06 (s, 2H, Ar-N**H**CO-), 8.66 (s, 1H, Ar-**H**, *p*-OCH_2-), 8.22-8.44 (m, 8H, Ar (Pyrene)-**H**), 8.06 (s, 2H, Ar-**H**, *o*-OCH_2-), 5.11 (d, 2H, -O**CH_2**CCH), 3.75 (t, 1H, -O**CH_2**CCH).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.08, 157.93, 136.68, 132.36, 129.47, 127.74, 126.32, 125.90, 125.60, 124.95, 79.40, 56.69.

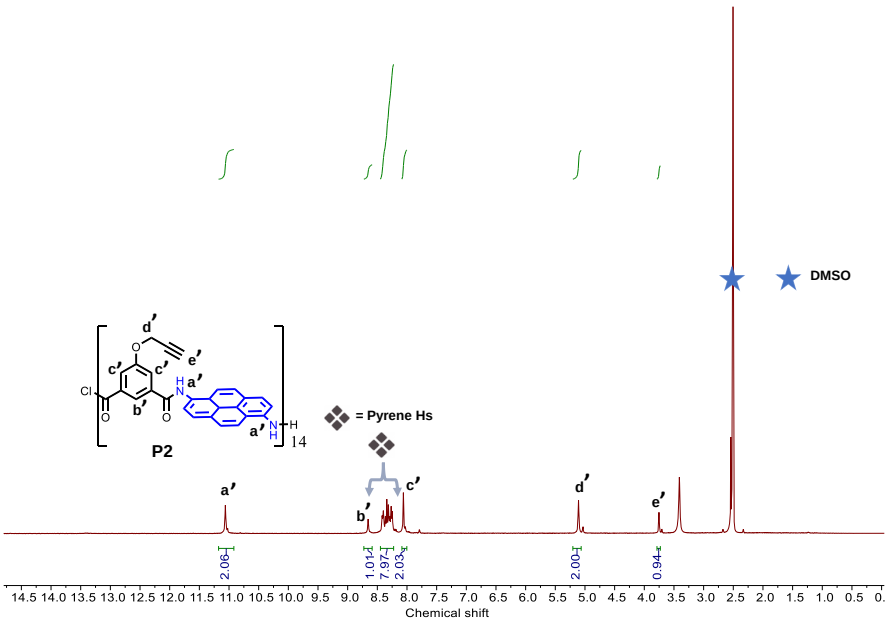


Figure S5: *^{1}H NMR spectra of polymer (**P2**) recorded in DMSO-d_6 at room temperature.*

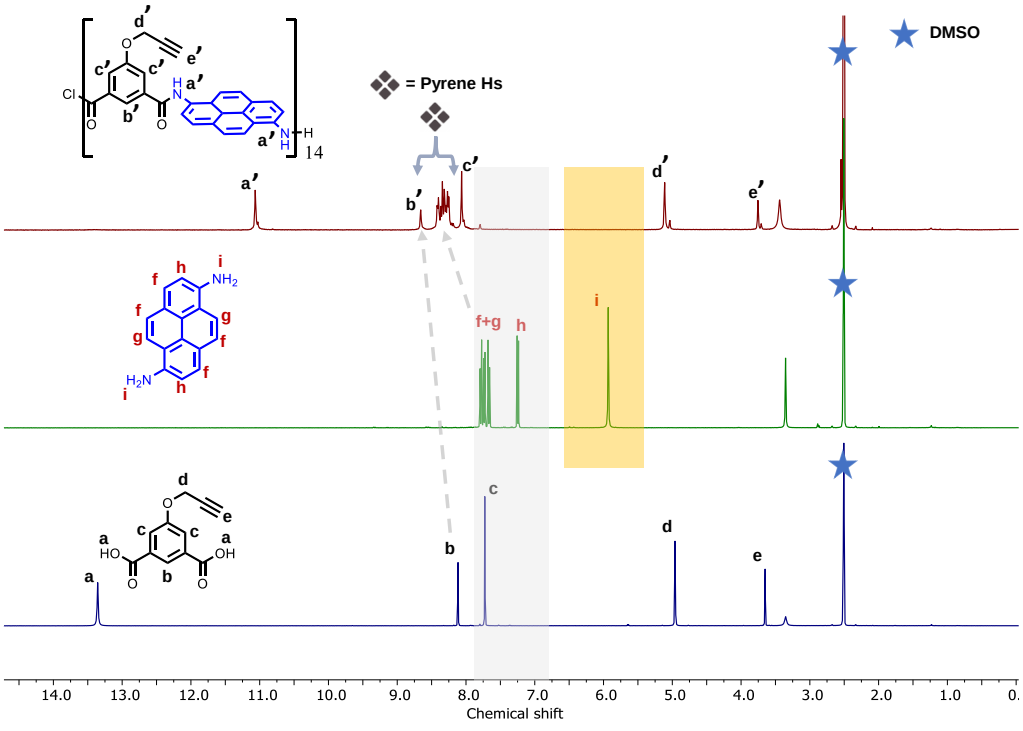


Figure S6: *Stack plot ^{1}H NMR spectra of dicarboxylic acid **(2)** (bottom), pyrene-1,6-diamine (**11**), precursor polymer (**P2**) (top) (recorded in DMSO-d_6 at room temperature).*

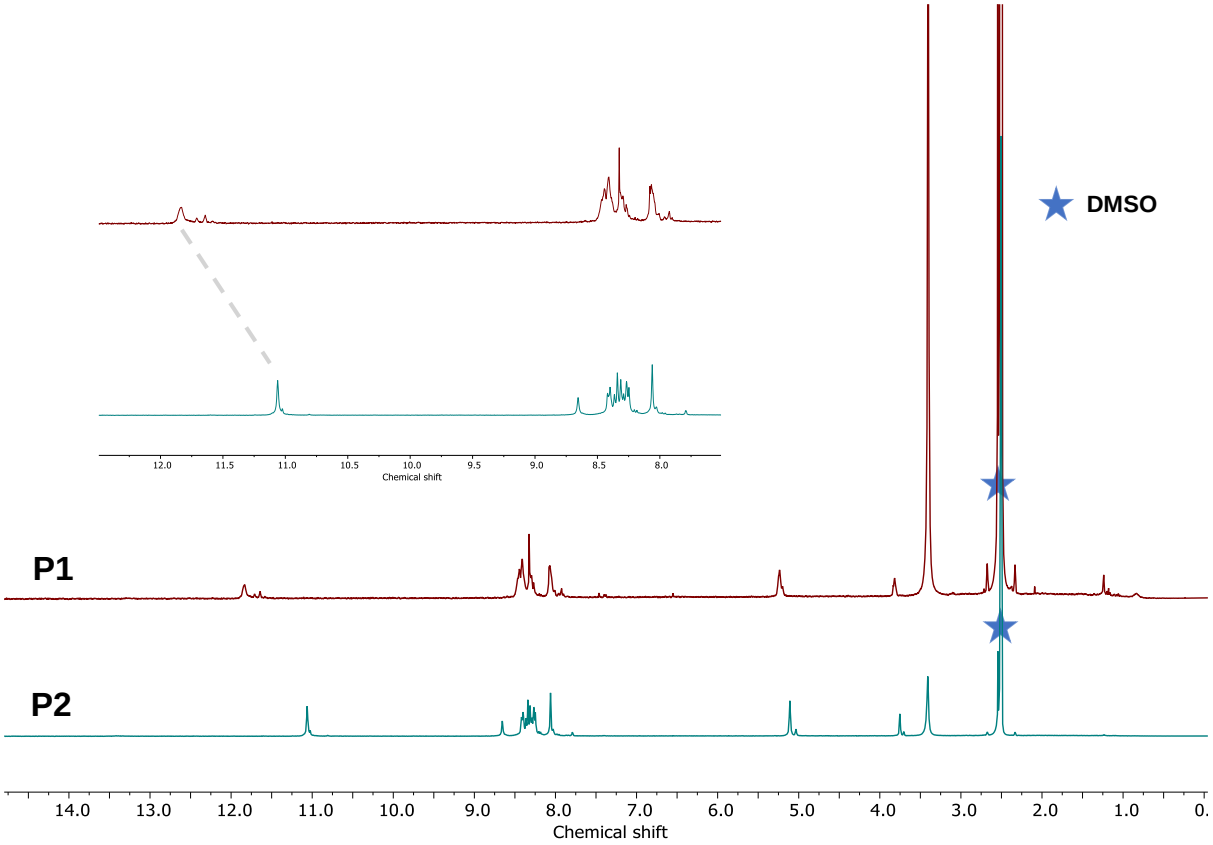


Figure S7: *Stack plot ^{1}H NMR spectra of precursor polymers,* ***P2*** *(bottom) and* ***P1*** *(top). Amide protons of* ***P1*** *showed an almost 0.7 ppm downfield with respect to* ***P2*** *amide protons. NMR spectra was recorded in DMSO-d_6 at room temperature.*

Post polymerization modification (Azide-yne click reaction) of precursor polymers with PEG_{550} monomethyl ether azide

To a mixture of parent polyamide (**P1** or **P2**) (49 mg, 0.12 mmol, w.r.t to repeat unit) and PEG_{550} monomethyl ether azide (**14**) (200 mg, 0.35 mmol), DMSO (3 ml) was added and the reaction mixture was purged with nitrogen for 30 mins to remove dissolved oxygen from the solution. Sodium ascorbate (9 mg, 0.05 mmol) (dissolved in 30 µL of H_2O) and $CuSO_4.5H_2O$ (6 mg, 0.02 mmol) (dissolved in 20 µL of H_2O) was added simultaneously under nitrogen atmosphere and the content was stirred at 50°C for 3 days. After completion, the reaction mixture was added to diethyl ether to remove DMSO. The resulting precipitates were washed with methanol and diethyl ether respectively. This process was repeated a few times and the remaining solid was dried under a vacuum to get the desired product (**P1-PEG** or **P2-PEG**) as a dark yellow solid.

P1-PEG (yield: 45%)

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.81 (s, 2H, -N**H**CO-), 7.67-8.61 (11H, triazole ring; Ar (Pyrene)-**H**; Ar (Pyridine)-**H**), 5.55 (2H, -OC**H₂**CCH-), 4.56 (2H, -NC**H₂**CH_2O-), 3.83 (2H, -NCH_2C**H₂**O-), 3.38-3.54 (m, C**H₂** s of PEG skeleton), 3.20 (s, 3H, -OC**H₃**).

^{13}C NMR (101 MHz, DMSO-d_6) δ 163.06, 151.32, 131.79, 129.62, 128.01, 126.05, 124.72, 71.70, 70.20, 70.01, 69.11, 58.47, 49.99.

P2-PEG (yield: 47%)

^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.04 (s, 1H, -N**H**CO-), 8.60 (s, 1H, Ar-**H**, *p*-OCH$_2$-), 8.10-8.41 (11H, triazole ring; Ar (Pyrene)-**H**; Ar-**H**, *o*-OCH$_2$), 5.47 (2H, -OC**H$_2$**-), 4.61 (2H, -OC**H$_2$**CCH-), 3.87 (2H, -NCH$_2$C**H$_2$**O-), 3.40-3.57 (m, C**H$_2$** s of PEG skeleton), 3.21 (s, 3H, -OC**H$_3$**).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.10, 157.97 136.70, 132.42, 129.42, 127.56, 126.29, 125.57, 71.71, 70.21, 70.02, 69.19, 58.48, 49.98.

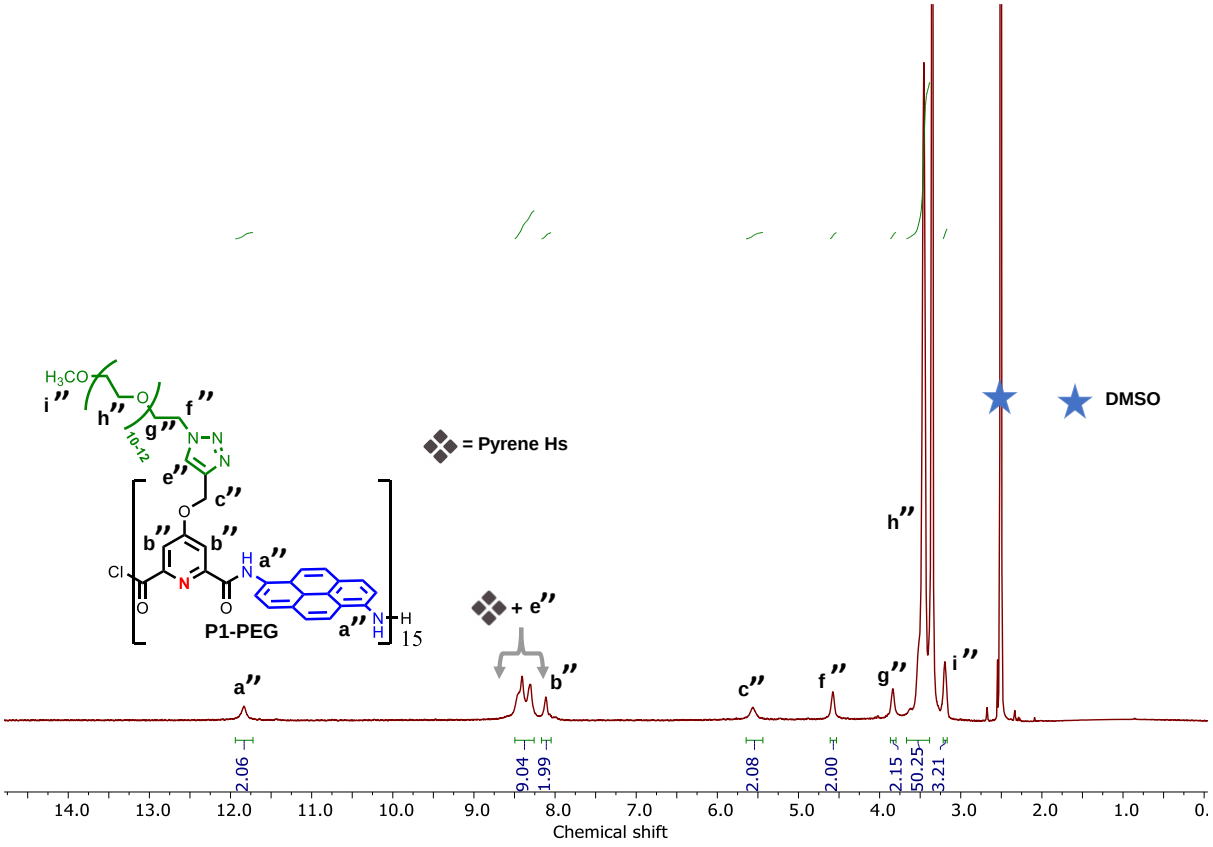


Figure S8: *^{1}H NMR spectra of polymer (**P1-PEG**) was recorded in DMSO-d$_6$ at room temperature.*

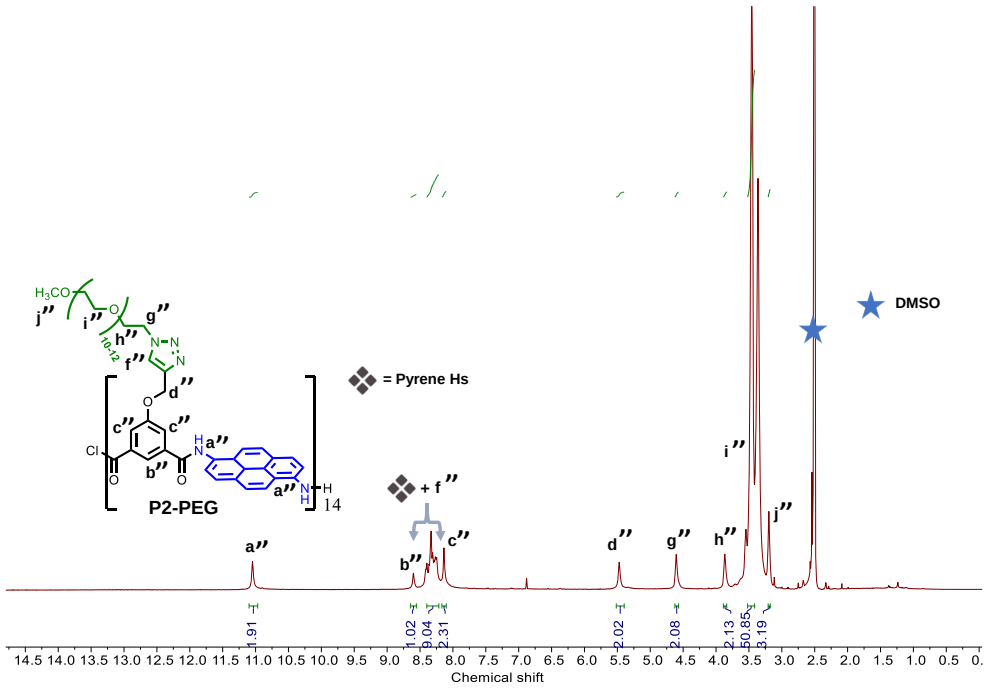


Figure S9: *^{1}H NMR spectra of polymer (**P2-PEG**) was recorded in DMSO-d_6 at room temperature.*

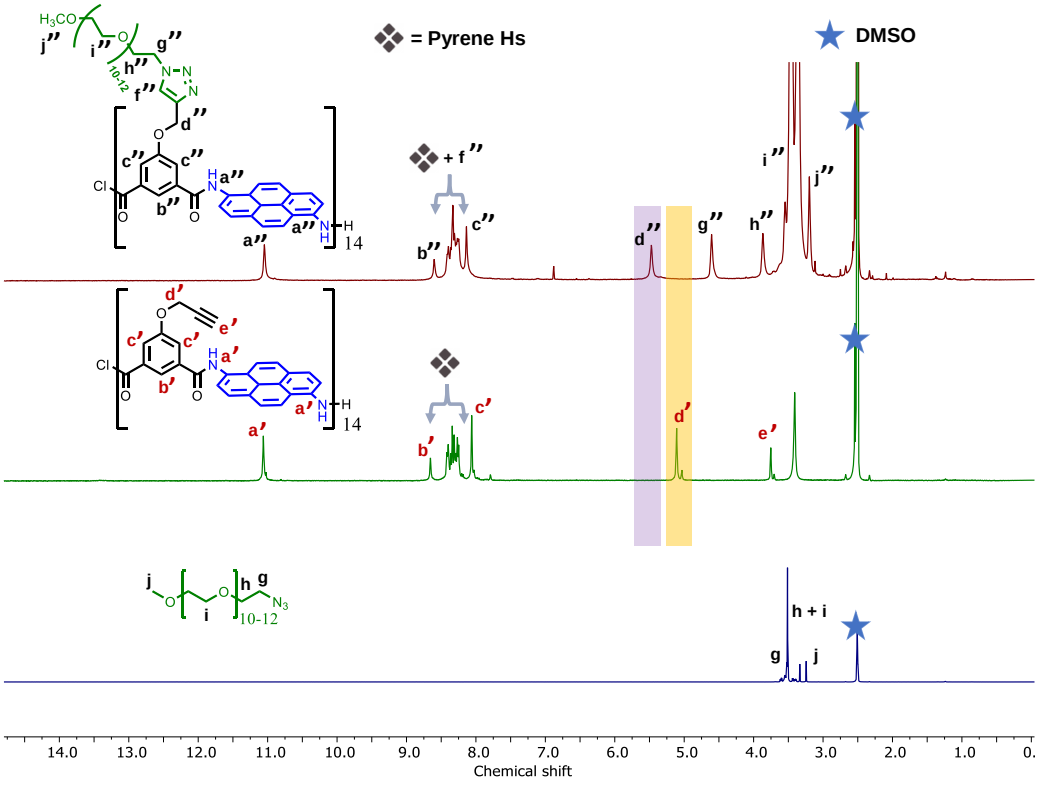


Figure S10: *Stack plot ^{1}H NMR spectra of MeO-PEG$_{550}$-N$_3$ (**14**) (bottom), precursor polymer (**P2**), and periodically grafted polymer chain (**P2-PEG**) (top). NMR spectra were recorded in DMSO-d_6 at room temperature*

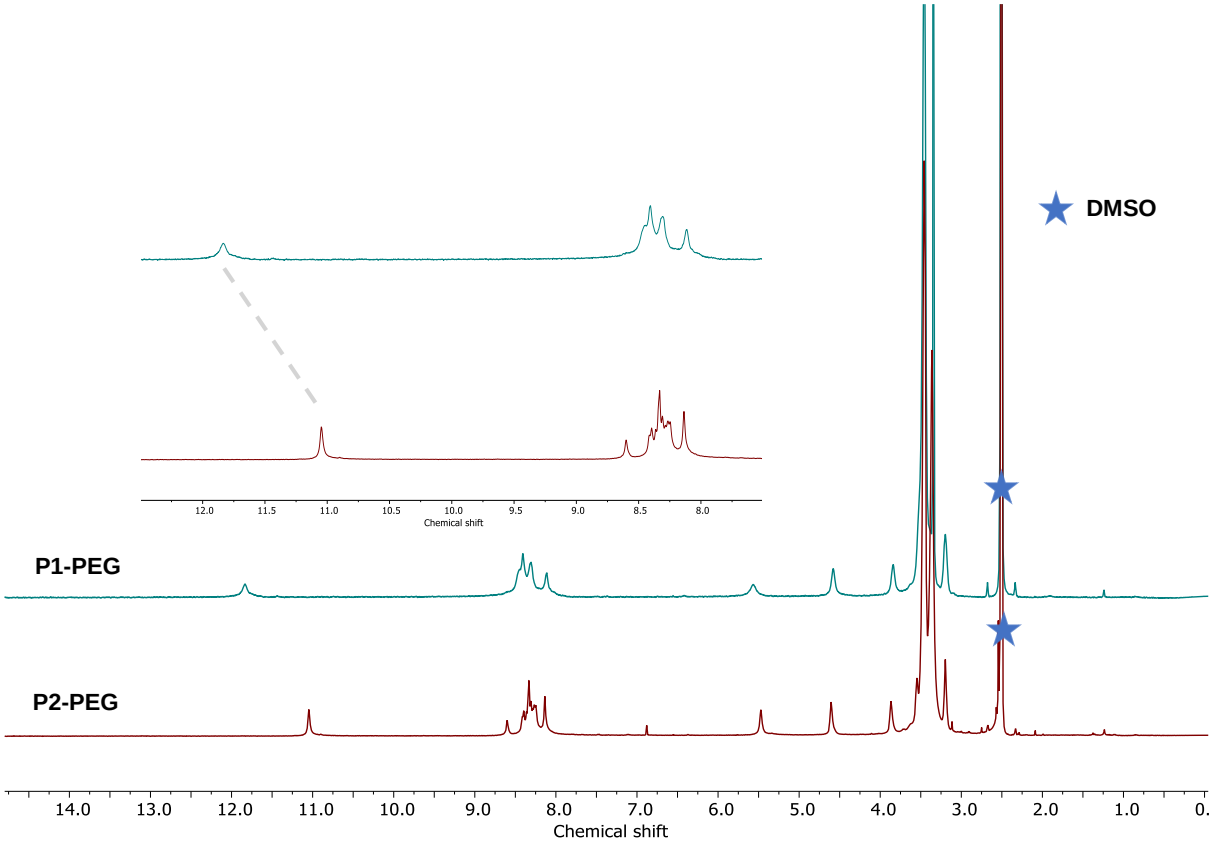


Figure S11: *Stack plot ^{1}H NMR spectra of **P2-PEG** (bottom) and **P1-PEG** (top). The difference in chemical shift between the amide protons of **P2-PEG** and corresponding **P1-PEG** remained the same as that between **P1** and **P2**. NMR spectra were recorded in DMSO-d_6 at room temperature.*

Table S1: *Solubility of polymers in common organic solvents*

Polymer	Solubility in micromolar concentration				
	DMSO	DMF	CHCl3	TCE	THF
P1	Y	partially	N	N	N
P2	Y	N	N	N	N
P1-PEG	Y	Y	Y	Y	N
P2-PEG	Y	Y	Y	Y	N

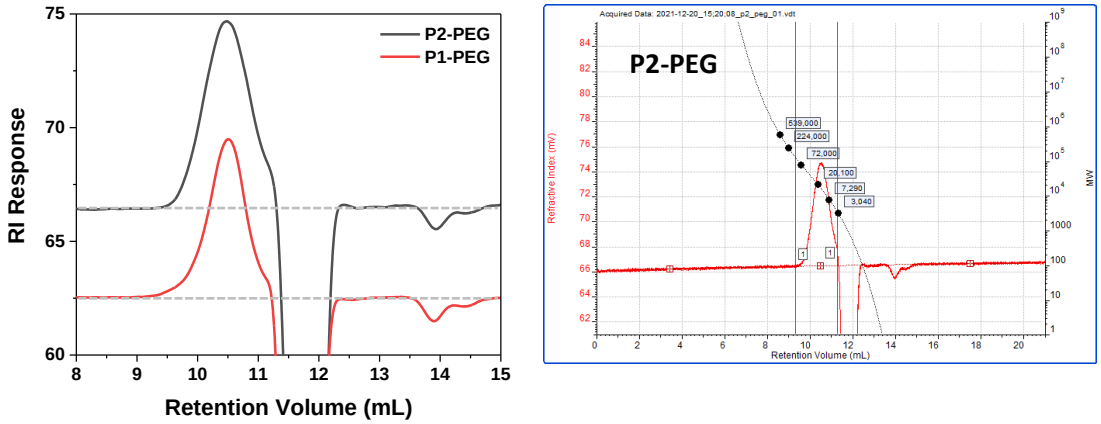
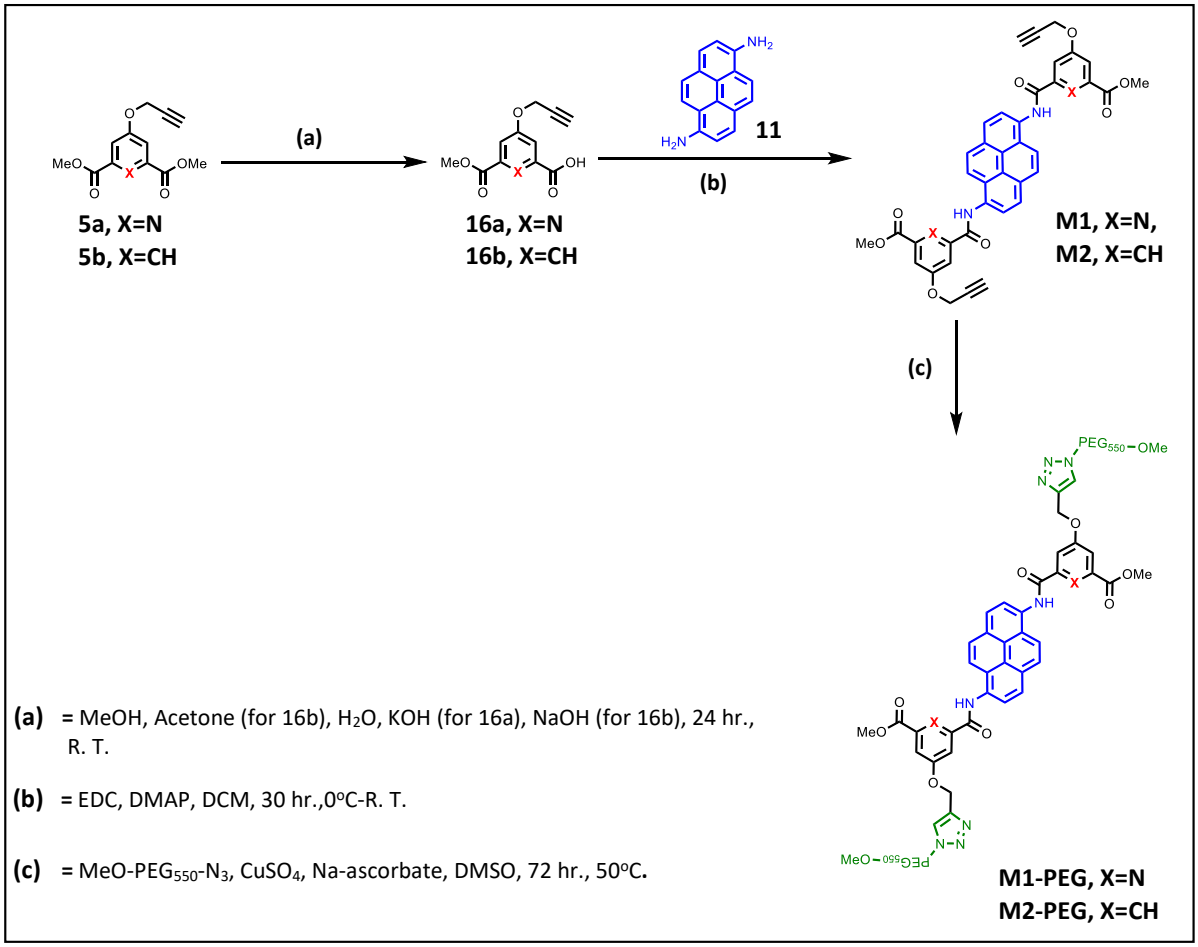


Table S2: *Table containing weight average (M_w), number average (M_n) molecular weight, and polydispersity index (Đ) of the polymers*

Polymer	M_w	M_n	Đ
P1-PEG	21,457	15,203	1.41
P2-PEG	20,408	13,872	1.47

9. Synthesis of model compounds



Scheme S6: *Synthetic scheme of model compounds.*

Compound 16a [12]

To a mixture of **5a** (1 gm, 4.02 mmol) in MeOH (10 ml), solid KOH (225 mg, 4.02 mmol) was added and the reaction mixture was stirred at room temperature for 16 hours. After completion of the reaction, all the solvents were evaporated under reduced pressure. The residue was added to water (20 ml) and extracted with DCM (25 ml × 4). The aqueous layer was then acidified to pH 1 using 1(N) HCl and the resulting precipitates were extracted with DCM (25 ml × 4). The combined organic layer was passed through anhydrous Na_2SO_4 and evaporated under reduced pressure. Column purification was done using ethyl acetate as the eluent to get the desired product (**16a**) as a white solid (yield: 73%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.55 (s, 1H, Ar-COO**H**), 7.80 (q, 2H, Ar-**H**), 5.11 (d, 2H, -OC**H$_2$**CCH), 3.91 (s, 3H, Ar-COOC**H$_3$**), 3.76 (t, 1H, - OCH$_2$CC**H**).

Compound 16b

To a mixture of **5b** (628.2 mg, 2.53 mmol) in acetone (4 ml) and MeOH (2 ml), solid NaOH (101 mg, 2.53 mmol) was added and the reaction mixture was stirred at room temperature for 24 hours. After completion of the reaction, all the solvents were evaporated under reduced

pressure. The residue was added to water (12 ml) and extracted with DCM (13 ml × 4). The aqueous layer was then acidified to pH 1 using 1(N) HCl and the resulting precipitates were extracted with DCM (13 ml × 4). The combined organic layer was passed through anhydrous Na_2SO_4 and evaporated under reduced pressure. Column purification was done using ethyl acetate as the eluent to get the desired product (**16b**) as a white solid (yield: 65%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.43 (s, 1H, Ar-COO**H**), 8.12 (t,1H, Ar-**H**), 7.75 (ddd, 2.6, 1.5 Hz, 2H, Ar-**H**), 4.98 (d,2H, -OC**H$_2$**CCH), 3.89 (s, 3H, Ar-COOC**H$_3$**), 3.66 (t,1H, -OCH$_2$CC**H**).

M1

To a mixture of **16a** (100 mg, 0.43 mmol), pyrene-1,6-diamine (**11**) (49 mg, 0.21 mmol), and DMAP (5 mg, 0.043 mmol), dry DCM was added under nitrogen atmosphere and the resulting solution was cooled to 0^{o}C in an ice bath. EDC (200 mg, 1.28 mmol) (dissolved in dry DCM) was added dropwise over 10 mins and the reaction mixture was stirred at room temperature for 30 hours. The resulting precipitates were filtered, washed multiple times with DCM, and dried under vacuum to afford **M1** as a dark yellow solid (yield: 62%). **M1** was insoluble in common deuterated organic solvents. It was taken to the next step without further characterization.

M2

To a mixture of **16b** (100 mg, 0.43 mmol), pyrene-1,6-diamine (**11**) (49 mg, 0.21 mmol), and DMAP (5 mg, 0.043 mmol), dry DCM was added under nitrogen atmosphere and the resulting solution was cooled to 0^{o}C in an ice bath. EDC (200 mg, 1.28 mmol) (dissolved in dry DCM) was added dropwise over 10 mins and the reaction mixture was stirred at room temperature for 30 hours. The resulting precipitates were filtered, washed several times with DCM, and dried under vacuum to afford **M2** as a yellow solid (yield: 70%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.05 (s, 2H, Ar-N**H**CO-), 8.42 (s, 2H, Ar-**H**, *p*-OCH$_2$-), 8.37 (d, 2H, Ar (Pyrene)-**H**), 8.26 (s, 4H, Ar-**H**, o-OCH$_2$), 8.19 (d, 2H, Ar (Pyrene)-**H**), 8.08 (s, 2H, Ar (Pyrene)-**H**), 7.80 (s, 2H, Ar (Pyrene)-**H**), 5.05 (d, 4H, -OC**H$_2$**CCH), 3.95 (s, 6H, Ar-COOC**H$_3$**), 3.72 (t, 2H, -OCH$_2$CC**H**).

M1-PEG

To a mixture of **M1** (20 mg, 0.03 mmol) and PEG$_{550}$ monomethyl ether azide (**14**) (38 mg, 0.066 mmol), DMSO (2 ml) was added and the reaction mixture was purged with nitrogen for 30 mins to remove dissolved oxygen from the solution. Sodium ascorbate (9 mg, 0.047 mmol) (dissolved in 30 µL H_2O) and $CuSO_4.5H_2O$ (6 mg, 0.024 mmol) (dissolved in 20 µL H_2O) was added simultaneously under nitrogen atmosphere and the mixture was stirred at 50^{o}C for 3 days. After completion, the solution was added to diethyl ether to remove DMSO. The resulting precipitates were washed with methanol and diethyl ether respectively. This process

was repeated a few times and the remaining solids were dried under a vacuum to get the desired product (**M1-PEG**) as a sticky dark yellow solid (yield: 52%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.21 (s, 2H, Ar-N**H**CO-), 8.73 – 7.72 (m, 14H, triazole ring; Ar (Pyrene)-**H**; Ar (Pyridine)-**H**), 5.49 (d, 4H, -OC**H$_2$**CCH-), 4.58 (t, 4H, -NC**H$_2$**CH$_2$O-), 4.01 (t, 4H, -NCH$_2$C**H$_2$**O-), 3.84 (s, 6H, Ar-COOC**H$_3$**), 3.44-3.55 (C**H$_2$** s of PEG skeleton), 3.23 (s, 3H, -OC**H$_3$**).

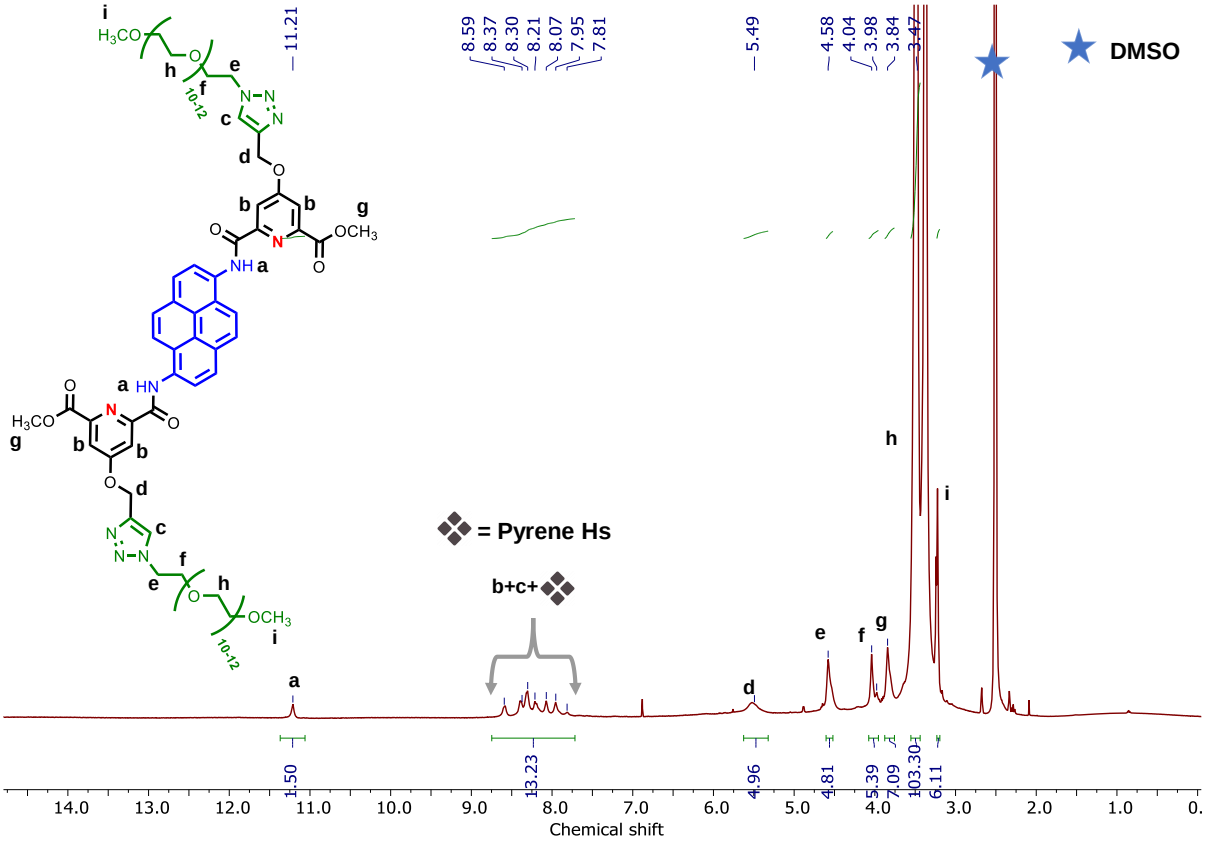


Figure S12: *^{1}H NMR spectra of model compound (**M1-PEG**) was recorded in DMSO-d_6 at room temperature.*

M2-PEG

To a mixture of **M2** (20 mg, 0.03 mmol) and PEG_{550} monomethyl ether azide (**14**) (38 mg, 0.066 mmol), DMSO (2 ml) was added and the reaction mixture was purged with nitrogen for 30 mins to remove dissolved oxygen from the solution. Sodium ascorbate (9 mg, 0.047 mmol) (dissolved in 30 µL H_2O) and $CuSO_4.5H_2O$ (6 mg, 0.024 mmol) (dissolved in 20 µL H_2O) was added simultaneously under nitrogen atmosphere and the mixture was stirred at 50^{o}C for 3 days. After completion, the solution was added to diethyl ether to remove DMSO. The resulting precipitates were washed with methanol and diethyl ether respectively. This process was repeated a few times and the remaining solids were dried under a vacuum to get the desired product as a sticky dark brown solid (yield: 60%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.02 (s, 2H, Ar-N**H**CO-), 8.37 (d, 4H, Ar-**H**, *p*-OCH_2-, Ar (Pyrene)-**H**), 8.30 – 8.11 (m, 10H, triazole ring; Ar (Pyrene)-**H**; Ar-**H**, *o*-OCH_2), 7.84 (s, 2H, Ar

(Pyrene)-**H**), 5.39 (d, 4H, -OC**H₂**CCH-), 4.58 (t, 4H, -NC**H₂**CH₂O-), 3.94 (s, 6H, Ar-COOC**H₃**), 3.84 (t, 4H, -NCH₂C**H₂**O-), 3.43-3.60 (C**H₂** s of PEG skeleton), 3.22 (s, 3H, -OC**H₃**).

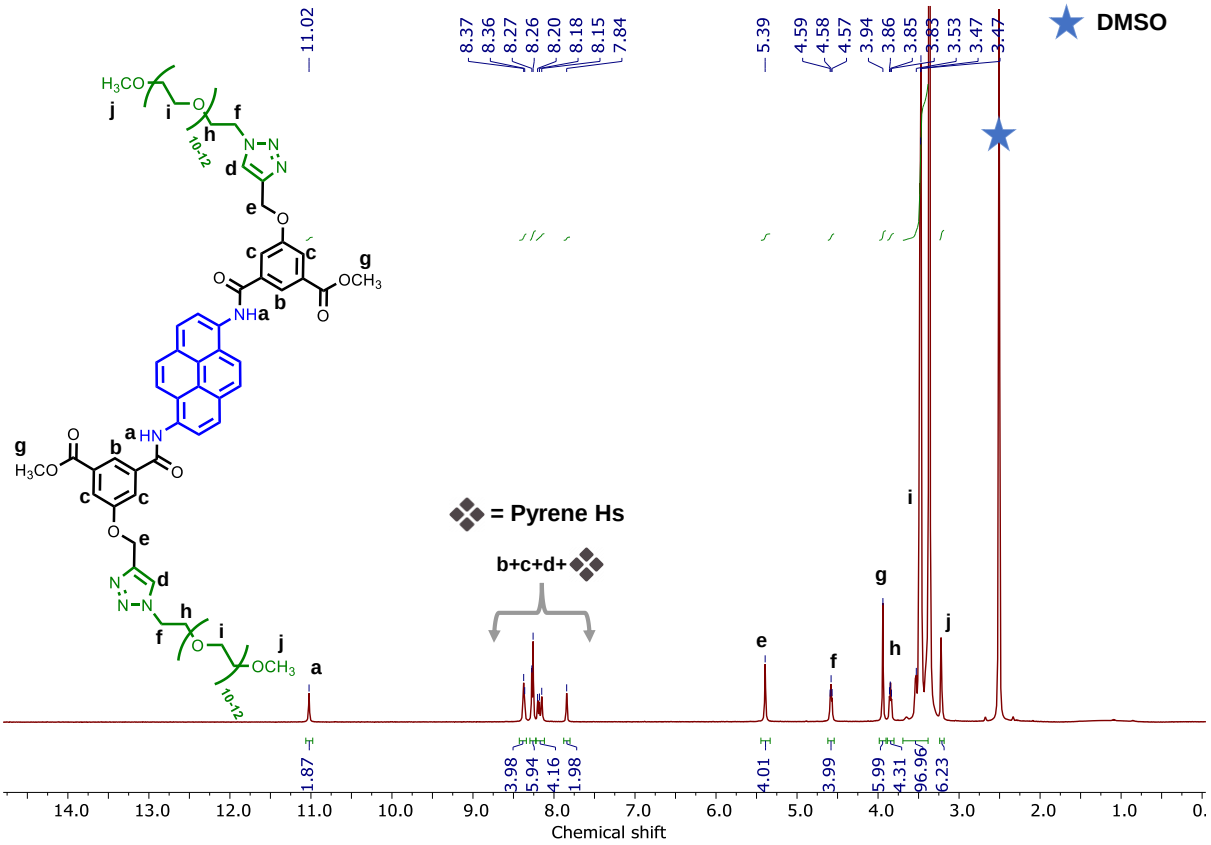


Figure S13: *^{1}H NMR spectra of model compound (**M2-PEG**) was recorded in DMSO-d_6 at room temperature.*

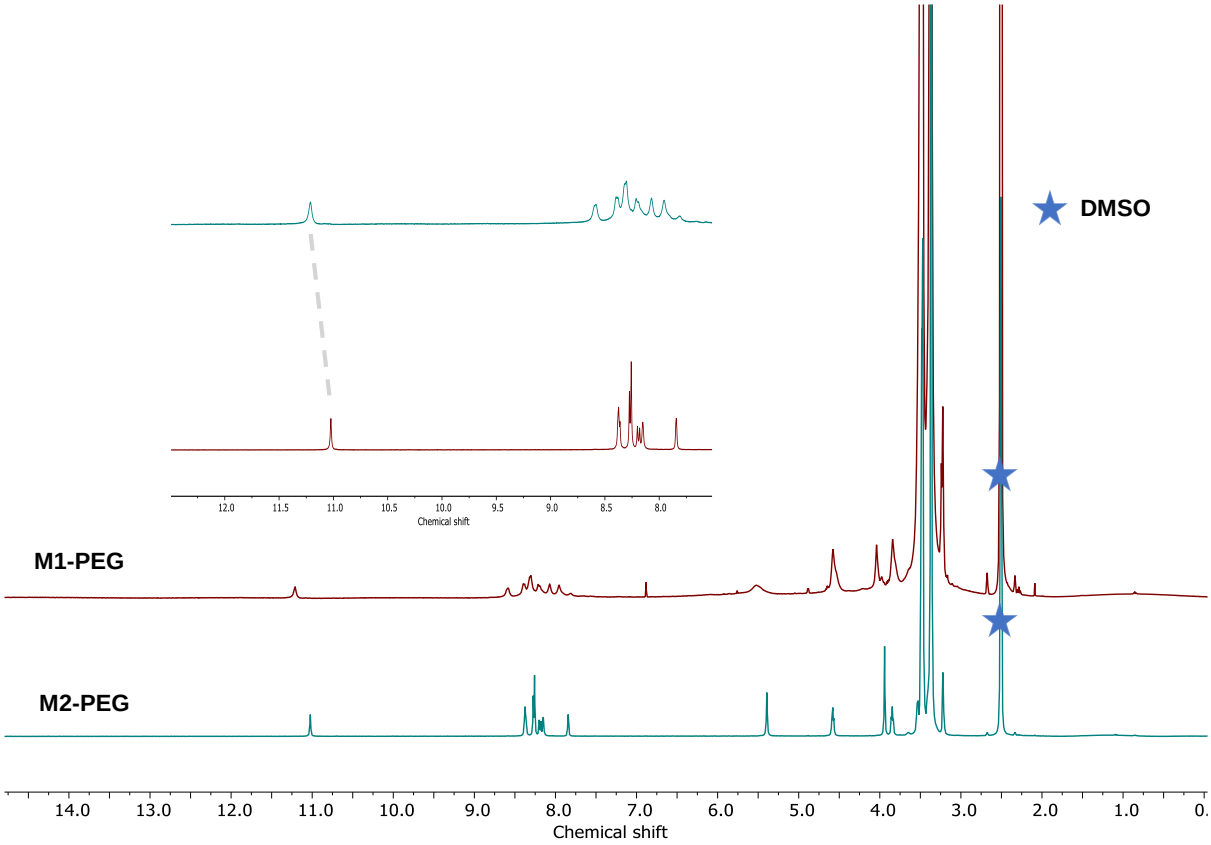


Figure S14: *Stack plot ^{1}H NMR spectra of model compounds,* ***M2-PEG*** *(bottom) and* ***M1-PEG*** *(top). Amide protons of* ***M1-PEG*** *showed an almost 0.25 ppm downfield shift with respect to* ***M2-PEG*** *amide protons. NMR spectra were recorded in DMSO-d_6 at room temperature.*

10. Comparison with the model compound

Two model compounds M1-PEG and M2-PEG relevant to the polymer P1-PEG and P2-PEG respectively were prepared for this folding study. As shown in Figure 1, the model compound M2-PEG cannot form any intramolecular H-bonding however, the model compound M1-PEG can form one intramolecular H-bonding. As similar to those polymers, due to the intramolecular H-bonding of the amide proton with the adjacent pyridine unit (Figure 1), the ^{1}H NMR signal of the amide proton in M1-PEG exhibit a substantial downfield shift in comparison with the other model compound (M2-PEG) devoid of such intramolecular H-bonding (Figure S10). However, as shown in Figure S11, the extent of the downfield shift of the amide proton for the model compound ($\Delta\delta$ = 0.25 ppm) was significantly lower in comparison with the polymers (Figure S11, $\Delta\delta$ = 0.75 ppm). In this regard, the extent of the downfield shift often provides information regarding the strength and occurrence of the H-bond. For example, the amide proton involving 3 centers H-bond (-CONH is surrounded by two H-bond acceptors) generally shows more downfield shift than the amide proton experiencing 2 centers H-bond. In this example, amide protons from both the polymer (P1-PEG) and related model compound (M1-PEG) experience 2 centers H-bonding (similar strength). So, the origin of a higher extent downfield shift of the polymer could be due to H-bond interactions being further strengthened by the intrachain π-stacking interactions available in the polymeric structure, which indicates cooperativity.

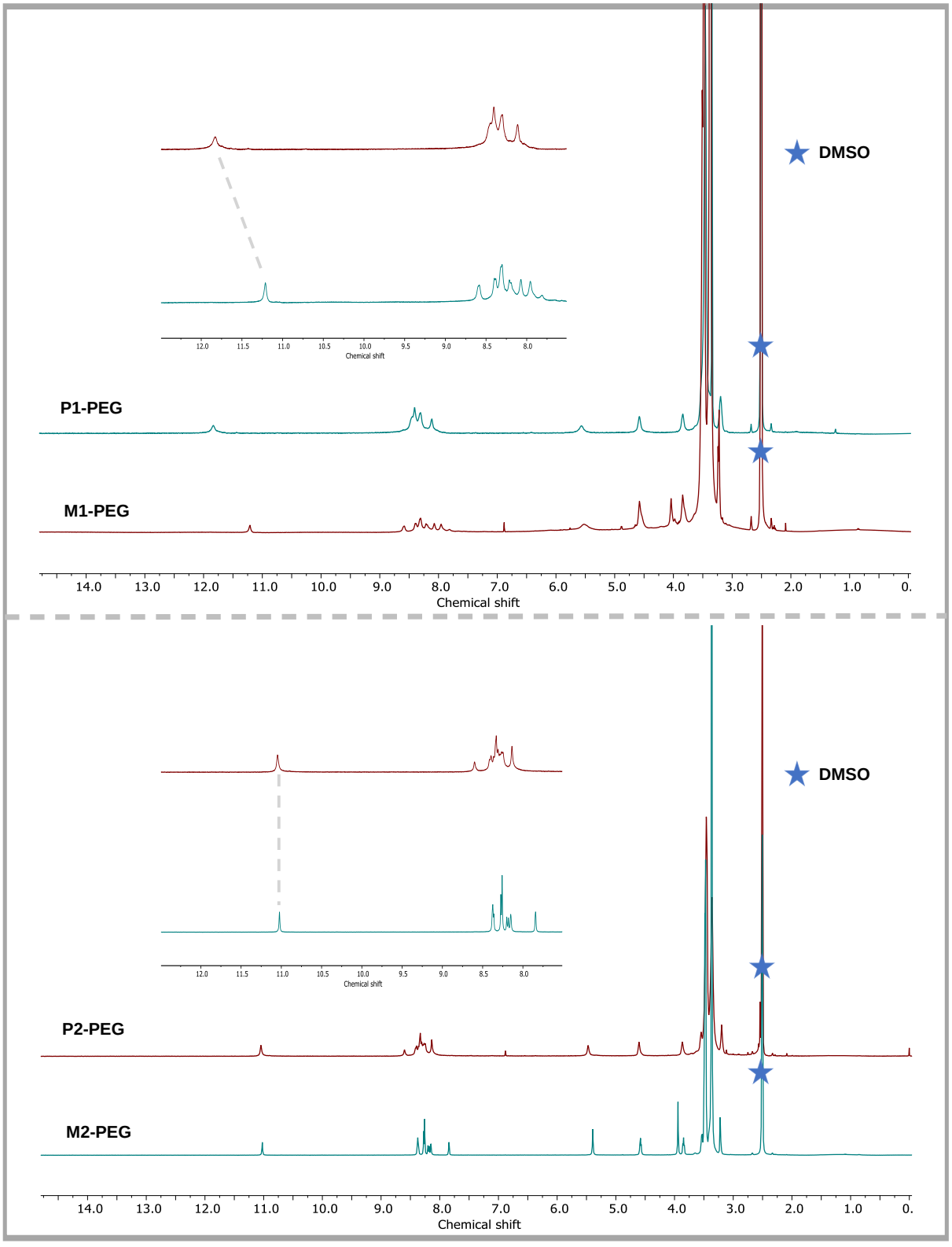


Figure S15: *Stack plot ^{1}H NMR spectra of model compounds with periodically grafted polymers, (**a**) **M1-PEG** (bottom) with **P1-PEG** (top) and (**b**) **M2-PEG** (bottom) with **P2-PEG** (top). The extent of the downfield shift of the amide proton for the polymers (0.75 ppm) was more than the model compounds (0.25 ppm). NMR spectra were recorded in DMSO-d_6 at room temperature.*

Single chain behavior of the polymer in dilute solutions:

Dynamic Light Scattering studies:

We performed the DLS experiments at various concentrations of polymers (P1-PEG & P2-PEG) in 1,1,2,2-tetrachloroethane with and without the guest molecules. The solvents were filtered through a PTFE membrane prior to making the solutions.

As shown in Figure S16 (below), an aggregate formation (intermolecular) beyond 50 µM concentration was observed. However, upon dilution, from 25 µM onwards, the particle sizes were substantially lower and remains nearly the same on further dilution to 12.5 µM. Additionally, the dimension of the polymer chain at lower concentrations reflects a single polymer chain. Although the folding studies were performed at a much lower concentration (6.25 µM), we were unable to retrieve DLS data at concentrations below 12.5 µM as the count rate was too low to get reliable data. Nevertheless, the DLS studies clearly reveal that indeed the polymer chains are at a single molecular level in our experimental concentration. Interestingly, the similarity of the molecular weight of those two polymers (P1-PEG & P2-PEG) as estimated by SEC analysis was also reflected in their hydrodynamic diameter measured by using DLS analysis.

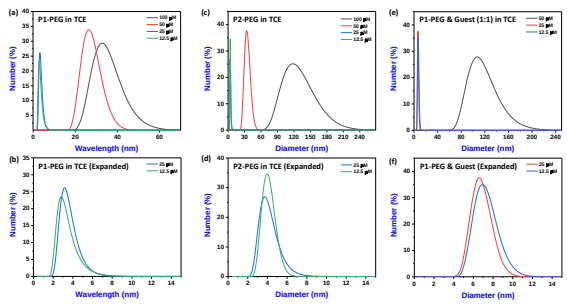


Figure S16: *Size of the polymer chains estimated by using DLS studies; (a) P1-PEG in TCE recorded at different concentrations; (b) single-chain behavior of P1-PEG in TCE ≤ 25 µM; (c) P2-PEG in TCE recorded at different concentrations; (d) single-chain behavior of P1-PEG in TCE ≤ 25 µM;(e) Host-guest complex of P1-PEG & Naphthalene (1:1) in TCE recorded at different concentrations; (f) P1-PEG & Naphthalene (1:1) in TCE ≤ 25 µM.*

Table S3: *The size of those polymer chains at various concentrations has been shown below*

Polymer	Guest	Concentration (µM)	Size (nm)
P1-PEG	No	50	26.94 ± 3.95
P1-PEG	No	25	3.41± 0.78
P1-PEG	No	12.5	3.16 ± 0.87
P1-PEG	Yes (1:1)	25	6.648 ± 0.84
P1-PEG	Yes (1:1)	12.5	7.06 ± 0.99
P2-PEG	No	50	34.30 ± 4.25
P2-PEG	No	25	3.96 ± 0.84
P2-PEG	No	12.5	4.016 ± 0.56

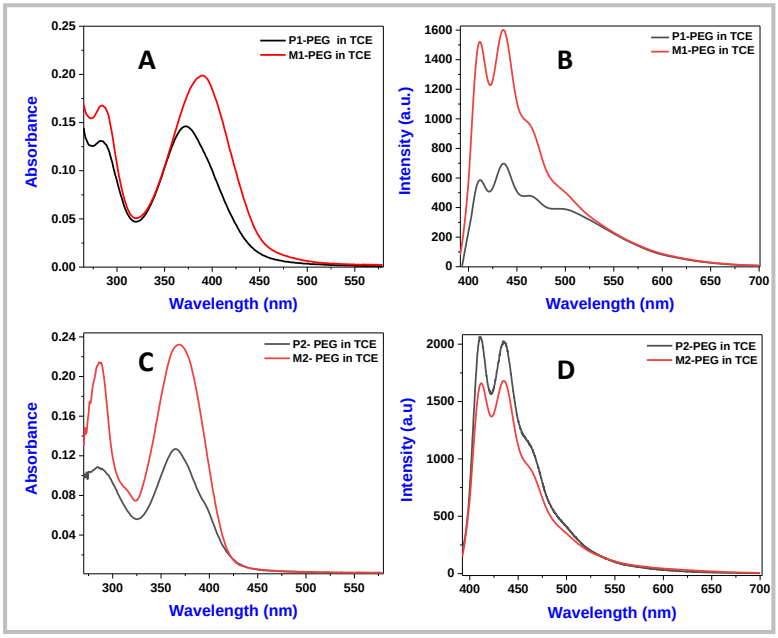


***Figure S17**: A comparison of photophysical properties between the polymers and related model compounds, solutions were prepared in TCE at 6.25 µM. Absorption spectra (**A**) and emission spectra (**B**) of **P1-PEG** and **M1-PEG**; Absorption spectra(**C**) and emission spectra (**D**) of **P2-PEG** and **M2-PEG**.*

11. Computed UV-VIS Spectra

We have computed and compared the absorption spectra of the model (4) and the trimer model (5) of the polymer (P1-PEG) having π-stacking interactions using Time-Dependent Density Functional Theory (TDDFT) at M06-2X/6-31G* level of theory as shown in **Figure S18**. We have found that the characteristic peak observed at 362.7 nm in the TDDFT absorption spectrum for model (4) shifts to 345.1 nm for the π-stacked trimer model (5) of P1-PEG polymer. The 17.6 nm blue-shift in the computed absorption spectra due to the formation of the π-stacked structure confirms the formation of the H-aggregate structure.

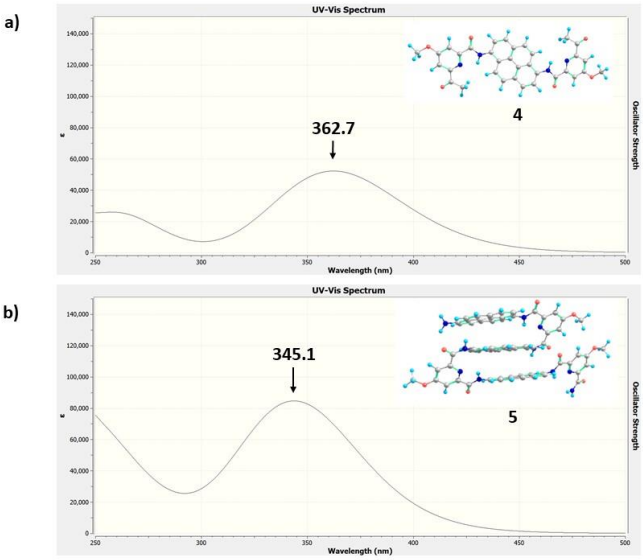


***Figure S18**: Comparison of computed absorption spectra of **a**) model compound (**4**) and **b**) the trimer model of **P1-PEG** polymer. The calculations are done at M06-2X/6-31G* level of theory.*

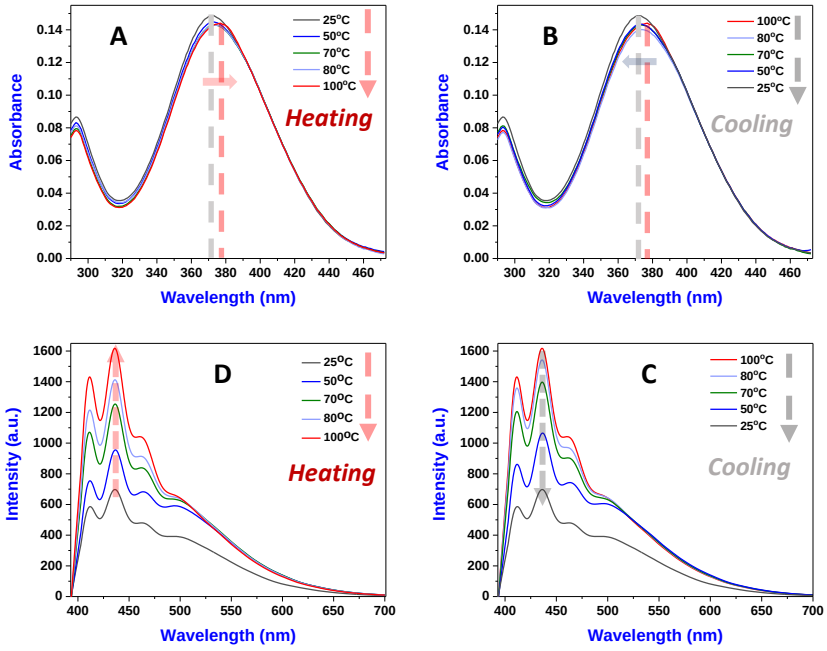


***Figure S19:** Temperature-dependent photophysical studies of the folded polymer chain (**P1-PEG**); Arrows indicate the spectral changes upon increasing or decreasing the temperature (**A**) UV-Visible studies (heating-cycle), (**B**) UV-Visible studies (cooling-cycle), **(C)** Fluorescence studies (heating-cycle). **(D)** Fluorescence studies (cooling-cycle). [solvent: TCE, concentration: 6.25 µM].*

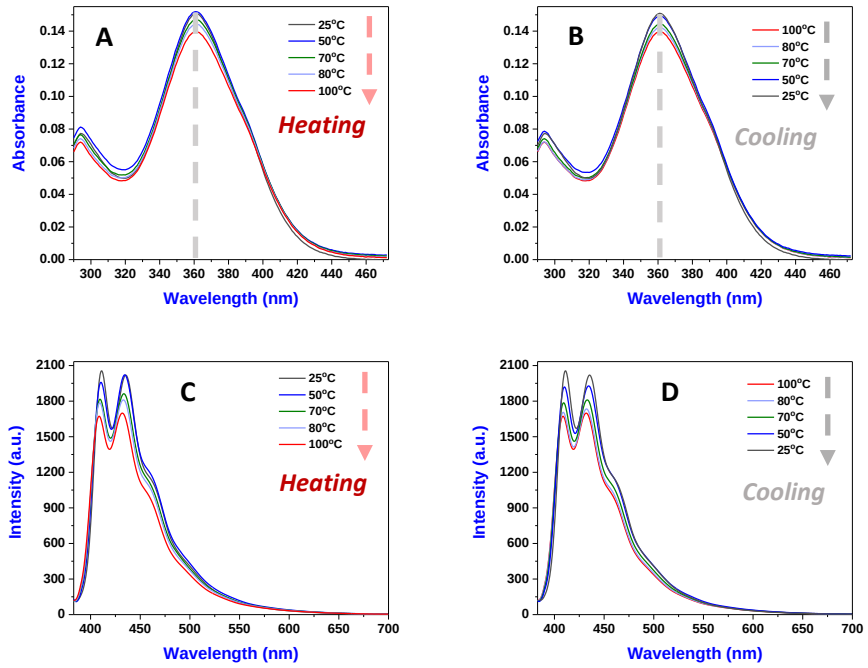


Figure S20: *Temperature-dependent photophysical studies of the folded polymer chain (**P2-PEG**); Arrows indicate the spectral changes upon increasing or decreasing the temperature (**A**) UV-Visible studies (heating-cycle), (**B**) UV-Visible studies (cooling-cycle), **(C)** Fluorescence studies (heating-cycle). **(D)** Fluorescence studies (cooling-cycle). [solvent: TCE, concentration: 6.25 µM].*

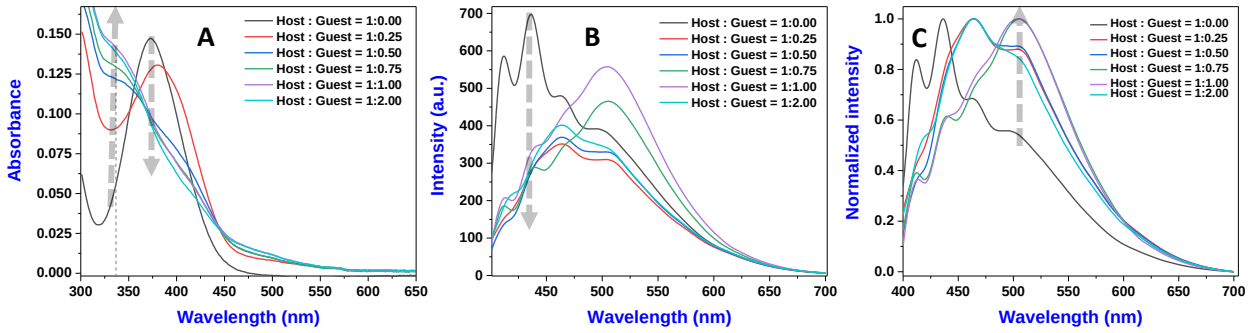


Figure S21*: Host-guest complexation (**P1-PEG**) assisted folding probed by UV-Visible and Fluorescence spectroscopy. Arrows indicate the spectral changes upon increasing the guest molecules (naphthalene) in the **P1-PEG** (TCE) at 6.25 µM. Titration experiments monitored by using UV-Visible spectroscopy (**A**); Fluorescence spectroscopy (**B**) and normalized emission spectra of the same (**C**).*

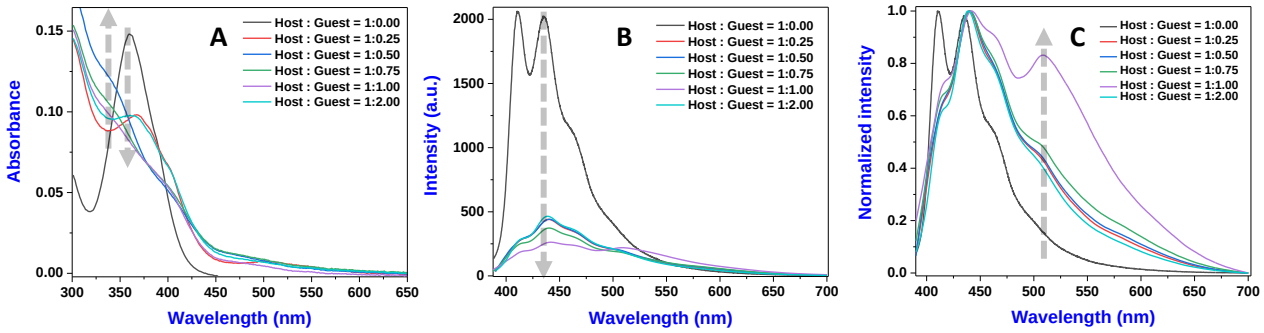


Figure S22**: Host-guest complexation assisted folding probed by UV-Visible and Fluorescence spectroscopy. Arrows indicate the spectral changes upon increasing* the guest molecules (naphthalene) in the ***P1-PEG (*TCE*) *at 6.25 µM. Titration experiments were monitored by using UV-Visible spectroscopy (**A**); Fluorescence spectroscopy (**B**) and normalized emission spectra of the same (**C**).*

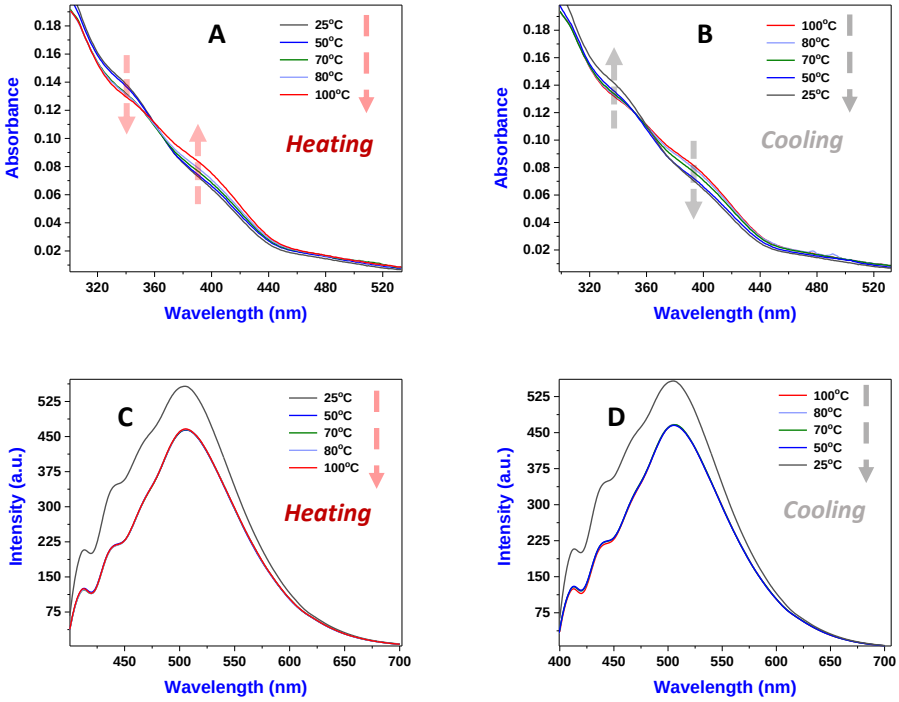


***Figure S23:** Temperature-dependent photophysical studies of the host-guest complex (**P1-PEG** & **Naphthalene**) mediated folded polymer chain; Arrows indicate the spectral changes upon increasing and decreasing the temperature (**A**) UV-Visible spectra (Heating cycle), (**B**) UV-Visible spectra (Cooling cycle), (**C**) Emission spectra (Heating cycle), (**D**) Emission spectra (Cooling cycle),The Host-guest complex was stable up to 100°C and little disturbance (decrease in absorbance at 333 nm and increase in absorbance at 390 nm) was visualized. [solvent: TCE, concentration: 6.25 µM].*

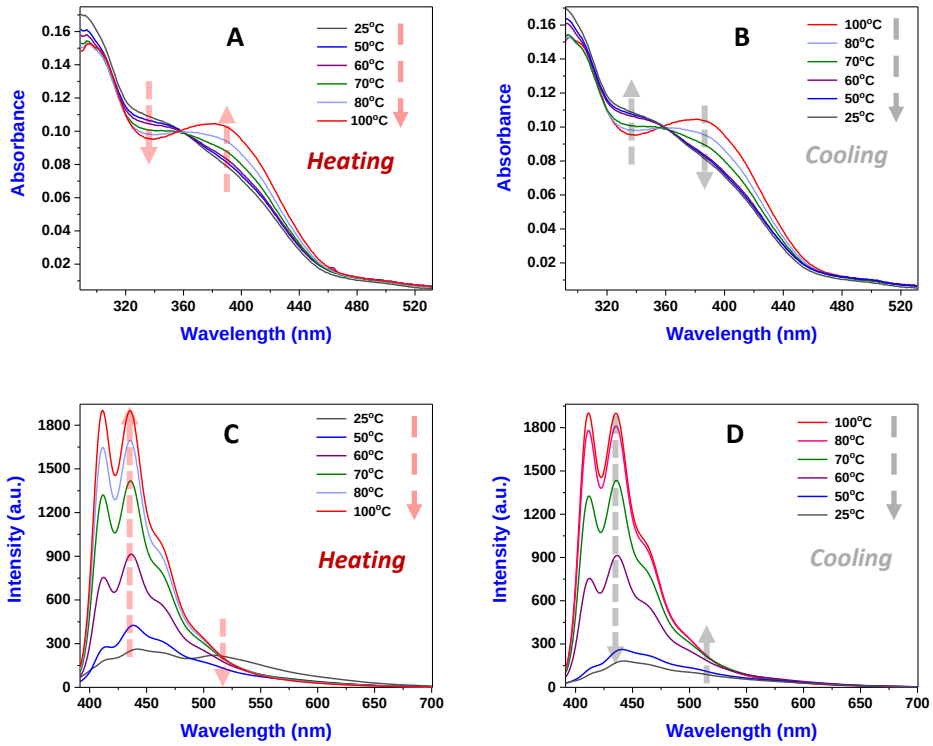


Figure S24: *Temperature-dependent photophysical studies of the host-guest complex (**P2-PEG** & **Naphthalene**) mediated folded polymer chain; Arrows indicate the spectral changes upon increasing and decreasing the temperature (**A**) UV-Visible spectra (Heating cycle), (**B**) UV-Visible spectra (Cooling cycle), (**C**) Emission spectra (Heating cycle), (**D**) Emission spectra (Cooling cycle). [solvent: TCE, concentration: 6.25 µM].*

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