Spatially organized π -electron rich foldamers

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CERTIFICATE OF EXAMINATION

This is to certify that the dissertation titled "**Spatially organized π-electron rich foldamers**" submitted by Ms. ARYA AJITH (Register No: MS14118) for the partial fulfilment of BS-MS dual degree programme of Indian Institute of Science Education and Research Mohali, has been examined by the thesis committee duly appointed by the institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Raj kumar Roy (Supervisor)	Dr. Sugumar Venkataramani (Committee member)	Dr. Sanchita Sengupta (Committee member)

Date:

DECLARATION

The work presented in this dissertation has been carried out by me under the guidance of Dr. Raj Kumar Roy at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Arya Ajith
(Candidate)
Date :

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Raj Kumar Roy
(Supervisor)

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Arya Ajith.

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List of abbreviations

DAN	-	Dialkoxynaphthalene
NDI	-	Naphthalene diimide
CuAAc	-	Copper(I)-catalyzed azide–alkyne [3+2] cycloaddition
DFT	-	Discrete fourier transform
Mn	-	Number average molecular weight
Mw	-	Weight average molecular weight
PDI	-	Poly dispersity index
DMAP	-	4-dimethylaminopyridine
AcCl	-	Acetyl chloride
DMF	-	Dimethylformamide
DCM	-	Dichloromethane
K_2CO_3	-	Potassium carbonate
THF	-	Tetrahydrofuran
DBTDL	-	Dibutyltin dilaurate
DMSO	-	Dimethysulfoxide
KBr	-	Potassium bromide
Nm	-	Nanometer
mM	-	millimolar
^{1}H NMR	-	Proton NMR
TLC	-	Thin layer chromatography

ABSTRACT

The field of foldamer chemistry was inspired from the investigation of natural biological systems in which covalent and non-covalent molecular interactions between specific units in their sequence assist folding into a well-defined three-dimensional structure of higher order architectures. Recreating this feature on synthetic systems would not only allow reproducing biological functions but also developing new functions that suitable for our technological needs. In this work, we mainly focused on foldamer designing and synthesis of a π-electron rich polymer in which conformational preferences can be induced through different non-covalent and covalent interactions. The target polymer mainly consists of Dialkoxy naphthalene units, a potential candidate to facilitate charge transport through space when confined those units into a well-organized foldameric system. All other structural features of the backbone are meant to assist the folding process. The major outcome of the work is a functionalized polymer backbone with an optimized spacer chain length, having the potential to adopt higher order architectures.

1. Introduction

1.1 Foldamers

Foldamers are synthetic molecules carrying strong tendency to adopt a specific well defined conformation such as helices, sheets etc. They are widely used in diverse fields including molecular scale electronics[1], protein mimicking[2-8], molecular recognition[9-11], self-assembly[12-13], photo induced electron and energy transfer[14] etc. Similar to highly ordered bio-macromolecules (proteins, DNA etc.), the folding process is aided by different moieties interacting non-covalently. H-bonding[15], π-stacking[16], metal-ion interactions[17], charge-transfer complexation[18] etc. are such interactions to stabilize the entropically unfavourable folded state. Some of them are discussed in the following sections.

H-bonding: As we see in protein secondary structures like α-helix and β-sheets, intramolecular hydrogen bonds offer several conformational order to synthetic molecules as well. For example, in a reported the π-folded molecular junction depicted in figure 1, the presence of the 2, 6-pyridinedicarboxamides promotes a sigmoidal conformation because of the favourable intramolecular hydrogen-bonding interactions along with π-stacking[1]

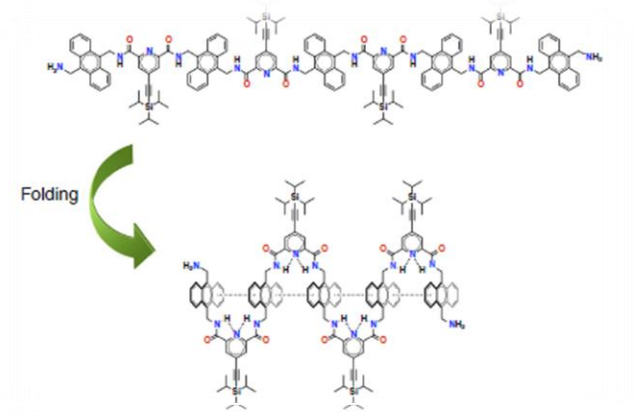


Figure 1. Anthracene based π-folded molecular junction in which folding is assisted by intramolecular H-bondings. (Adopted from reference 1)

***π*-stacking:** The overall polarization of the aromatic π-electron cloud is predicted in such a way that a partially positive-charged σ-framework around the periphery of the molecule is sandwiched between two partially negatively-charged π-electron clouds (Figure 2a). So, a neutral, non-substituted aromatic molecules, such as benzene, naphthalene etc. would prefer

to interact in electrostatically favourable T-shaped (Figure 2d) or off-centred (Figure 2c) stacking geometries. Face-centred (Figure 2b) is difficult to attain due to the repulsion offered by partially negatively-charged π-electron clouds[20]. Here comes the role of substituted aromatic species. By the substitution of electron withdrawing groups in the periphery, the quadruple moment of the polarization can be reversed to yield an electron deficient aromatic core. So when associating with strongly electron-withdrawing substituents, relatively electron-rich aromatics prefer to stack in an alternating face-centred geometry[21].

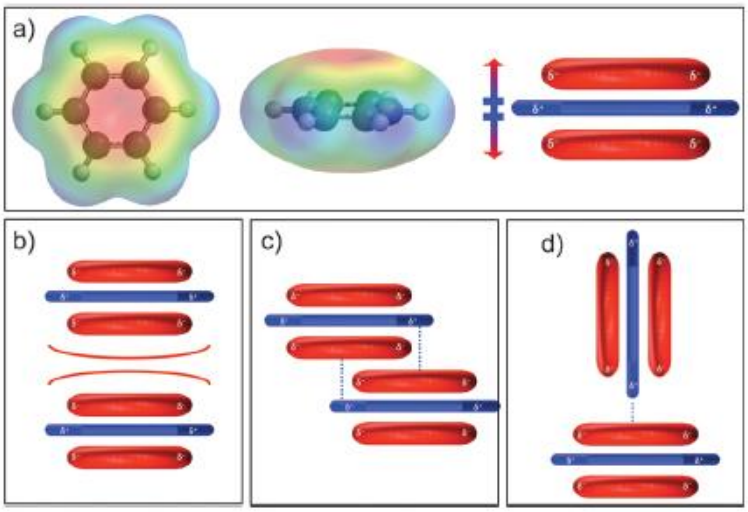


Figure 2. (a) Electrostatic potential map of benzene with cartoon depicting the localization of σ and π electron clouds (b) Repulsion offace-centered stacking of benzene. (c) Possible off-centered stacking ofbenzene. (d) Preferred T-shaped interaction of benzene (Adopted from the reference **21**)

Solvophobic interaction: Aromatic interactions are strongly solvent dependent. In weakly interacting (nonpolar) solvents, the electrostatic force between electron rich and electron deficient species dominates, whereas in strongly interacting polar solvents solvophobic effect dominates over the other. For example, in aqueous environment (highly polar) aromatic molecules prefer to stack in a face centred manner, thereby decreasing the surface area in contact with water. In short, the stacking pattern exhibited by aromatic molecules in solution is an interplay between electrostatic forces and solvophobic interactions[21]

1.2 Donor-Acceptor charge transfer mediated folding

There exist arrays of foldamers that exploit interactions between aromatic units to drive their assembly in predictable fashion. It was already demonstrated that the relatively electron-rich DAN and relatively electron-deficient NDI associate in solution[22]. Based on this observation, the first aromatic foldamer operating in water was invented by linking DAN and NDI units in an alternating fashion with flexible peptide linkers[22]. Along with that, the folding is also assisted by solvophobic interaction in water. Meanwhile, the aggregation and precipitation of aromatic π-electron rich molecule in water is prevented by the glutamic acid residues chosen to link the aromatic units together.

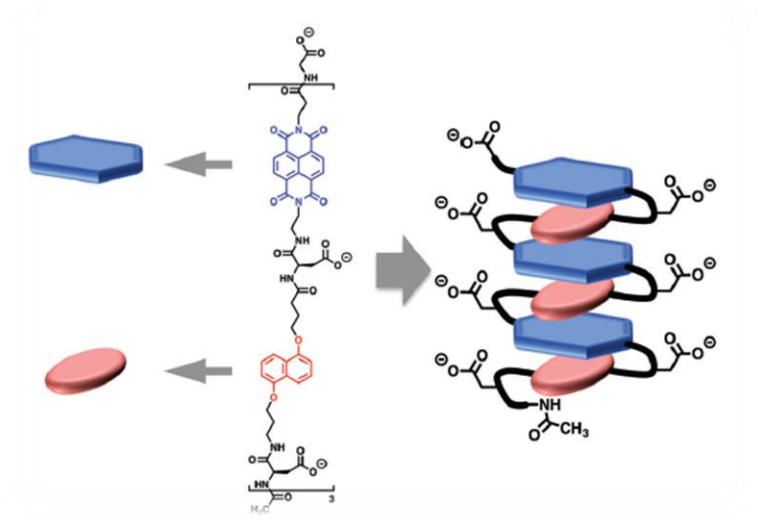


Figure 3. Molecular structure and cartoon diagram of folded conformation of Lokey's first aromatic foldamer (Adopted from the reference **22)**

1.3 Click reactions for post-polymerization modifications

The basic concept of click chemistry is binding two molecular building blocks together in a facile, selective, high-yield reaction under mild water-tolerant conditions with no or little byproducts which can be removed by non-chromatographic methods[22]. In other words click reactions are thermodynamically-favored reactions that lead specifically to one product. Among those reactions fulfil these criteria, Cu-catalyze dazide/alkyne cycloaddition (CuAAC), the metal free alternatives such as Diels–Alder cycloaddition and thiol-based reactions are the most employed in the polymer field.

Copper(I)-catalyzed azide–alkyne [3+2] cycloaddition (CuAAC): The non-catalysed cycloaddition reactionbetween azides and alkynes to yield 1,2,3-triazoles are called huigen's cycloaddition[23]. The major drawbacks of this kind of reactions are the lack of selectivity between 1, 4 and 1, 5-disubstitution products, slower kinetics and high reaction temperature. All these drawbacks can be overcome by adding a metallic species into the reaction medium. Cu(I) is commonly used for the purpose even if other metals such as Ru, Ni, Pt, Pd are there[24,25] (Figure 6). So called, Cu (I)-catalyzed azide/alkyne cycloaddition (CuAAC) has been extensively investigated as a ligation tool for synthesizing and modifying many different polymeric structures.

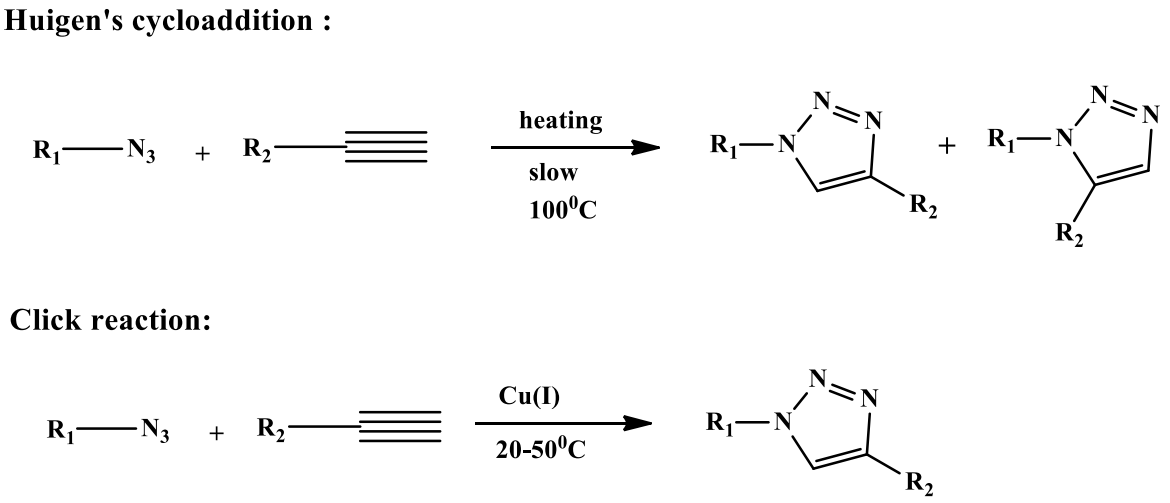


Figure 4. Azide-Alkyne cycloaddition

1.4 Our approach

In this work, we have undertaken the study of the specific noncovalent covalent interactions that occur between aromatic units, particularly in the study of 1, 5-dialkoxynaphthalene (DAN) and 1,4,5,8-naphthalenetetracarboxylic acid diimide (NDI) units in the construction of foldamers. Here, the electron-deficient aromatic acceptor NDI molecules act as an external folding agent for the polymer backbone made up of electron-rich aromatic donors (DAN) through a donor-acceptor mediated charge transfer. The electrostatic potential surface maps of these two molecules reveal the polarization of the aromatic core and periphery (Figure 5a). In DAN, due to the electron-donating alkoxy groups in periphery the

core is sufficiently electron rich. Similarly, due to electron withdrawing imide carbonyl groups, NDI is having a highly electron deficient aromatic core (Figure 5b.). Therefore, an alternating, face-centred alignment is predicted for these two complementary aromatic molecules n solid state as well as in solution[26].

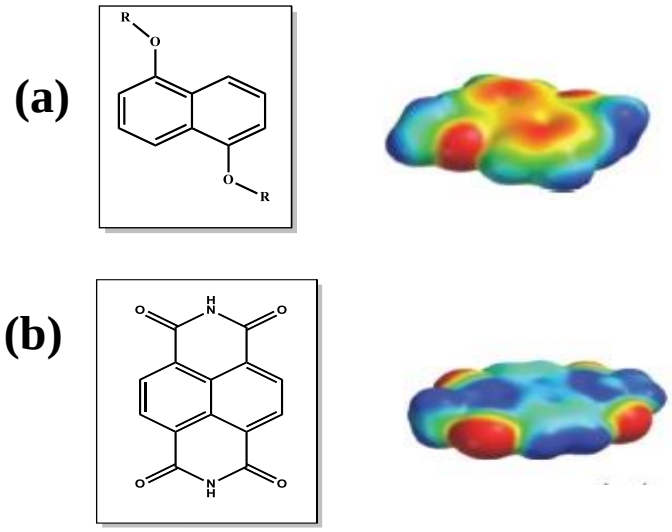


Figure 5. Molecular structures and electrostatic potential surfaces calculated for (left) NDI and (right) DAN using DFT (B3LYP/6-31G*) as implemented in Spartan (Wavefunction, Inc.). (Adopted from the reference **22**)

Since charge transfer interactions are weak and noncovalent in nature, there exist a dynamic equilibrium between folded and random state conformations. It can be driven towards the folded by facilitating covalent intermolecular crosslinkings between special moieties occupied at fixed length along the polymer backbone.

1.5 Design of the folded structure

In this work our primary focus was on synthesising a π-electron rich polymer (Figure 6) composed of electron rich DAN units capable of fold in to a well defined foldamer. Here we chose chelidamate ester as linker and 2-carbon spacer length. The chelidamic ester linker is substituted with propargyl group, thereby giving a reactive handle for intramolecular crosslinking.

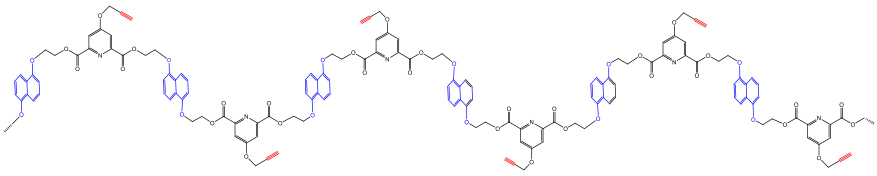


Figure 6. Molecular structure of target polymer with C-2 spacer chain length

In general, those donor-containing polymers are preferred to stay as a random-coil-like structure. Here we predict a disordered trans conformation around the ethyl linkages. While acceptor molecules (NDI) introduced into the system, conformational changes occur in a predictable fashion. The most sensible conformation which can be adopted by the target polymer is a one-dimentional pleated one which is actually triggered by alternating face centred stacking of NDI moieties in between the repeating naphthalene units. (Figure 7)

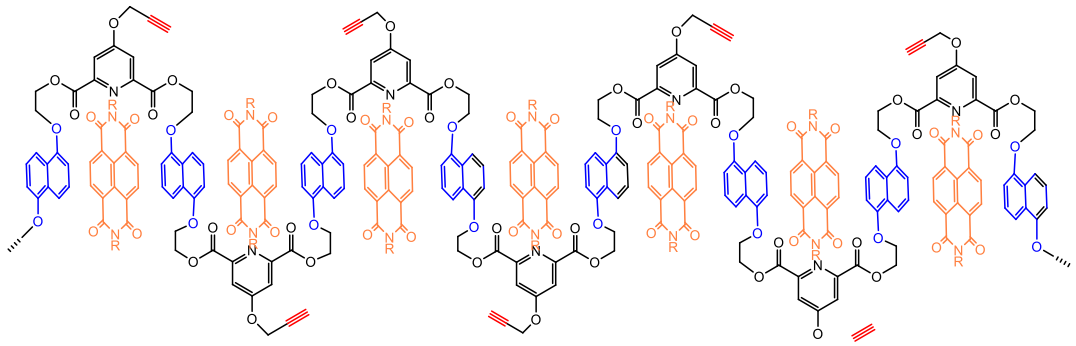


Figure7. Folding of the target assisted by NDI derivatives

At this stage, the alternate propargyl groups come closer so that they can crosslink each other with the aid of an external crosslinker. CuAAc is a very promising click reaction between terminal alkynes and azide substituents. So if we introduce a diazide crosslinker into our system of weakly folded charge transfer complex, the folded state will be locked covalently via triazole ring formation throughout the polymer chain (Figure 7). By choosing the diazide crosslinker wisely, different chemical and physical properties of the foldamer can be controlled. In Figure 7, the crosslinking is depicted with meta-disubstituted crosslinker. If we use para instead, the final foldamer is expected to have larger cavity size and lesser compactness.

Finally acceptor will be removed out of the system, the folded state persists due to strong intramolecular crosslinks as depicted in Figure8

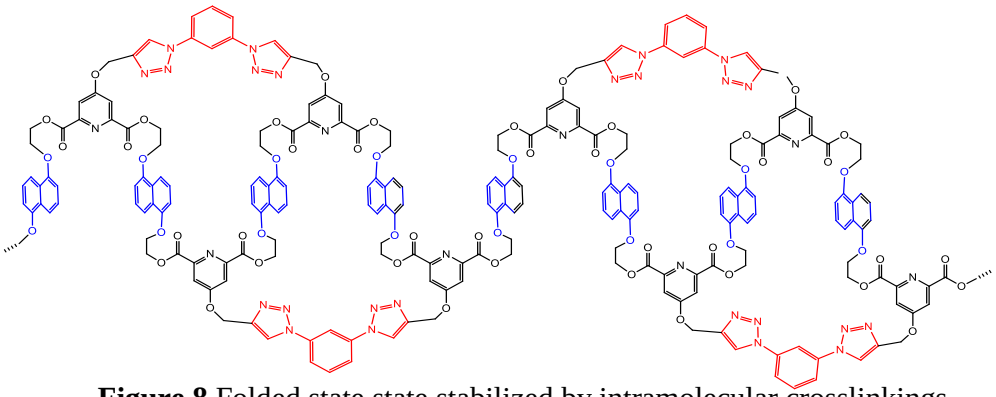


Figure 8. Folded state state stabilized by intramolecular crosslinkings

1.6 Gel permeation chromatography

Gel permeation chromatography is an inevitable analytical technique in polymer chemistry for characterizing the complete molecular weight distribution of a polymer. It helps in determining several important parameters including number average molecular weight (Mn), weight average molecular weight (Mw), Z weight average molecular weight (Mz) and molecular weight distribution (PDI). These measurable values has significant effects in the end-use properties of a polymer include tensile strength, hardness, softening temperature, melt viscosity, Brittleness, elastomer relaxation, Stress-crack resistance, flex life, impact strength etc. GPC is based on behaviour of polymer molecules in solution.

2. Results and discussions

2.1 C-2 spacer polymer:

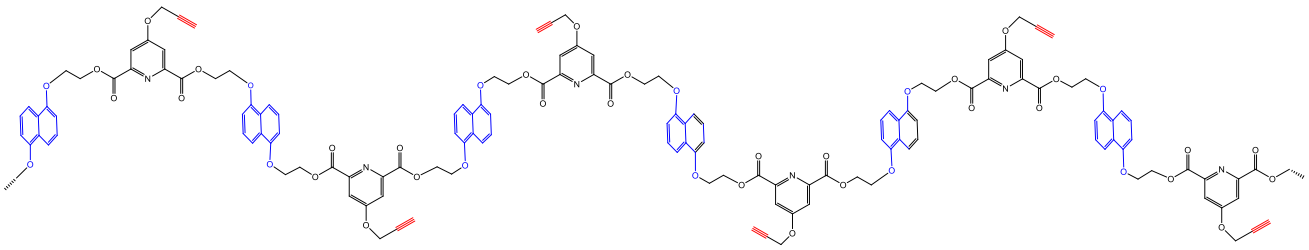
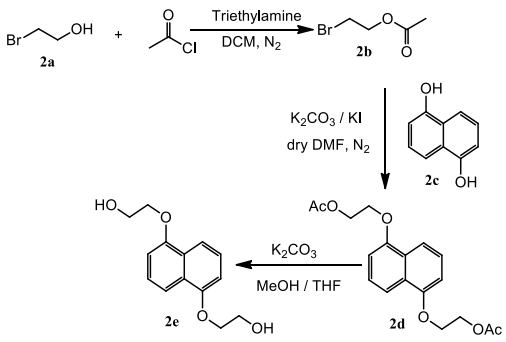


Figure 9: Molecular structure of C-2 spacer polymer

The C-2 spacer polymer is made up of repeating DAN units, connected through a chelidamic ester-based linker functionalized with propargyl group with a fixed spacer chain length 2.

We commenced our project with the aim of synthesizing monomer candidates yield C-2 spacer polymer by using transesterification. Acetylation of 2-bromo ethanol was carried out following the optimization table 1 shown to obtain product ethyl bromoacetate (2b) with better yield. This was followed by coupling 2b with 1,5-dihydroxy naphthalene (2c) and further hydrolysis by following the optimization table 2 to obtain 2e with good yields.



Scheme 1. Synthesis of monomer A (2e)

Table 1. Optimization table for acetylation of 2-bromoethanol

Entry No.	Reagent	Base	Yield(%)
1.	Acetic anhydride	Pyridine	54
2.	Acetic anhydride	DMAP	60
3.	Acetyl chloride	Triethylamine	79

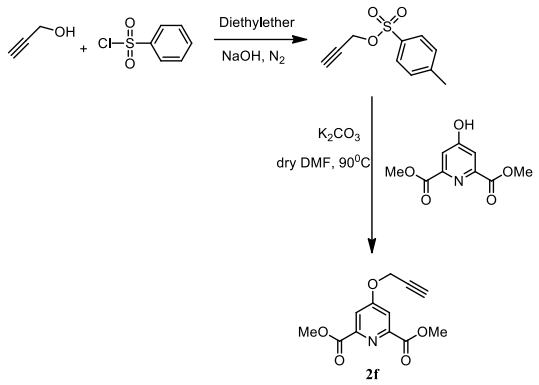
The acetylation of 2-bromoethanol was carried out by varying the reagent and base. It was observed that maximum yield obtained when AcCl was used as the reagent and triethylamine as the base.

Table 2. Optimization table for 2-bromoethanol-1,5-dihydroxy naphthalene coupling

Entry No.	Reaction condition	Solvent	Yield(%)
1.	100^0C, 72 hr	Acetonitrile	35
2.	60^0C, 12 hr	DMF	65

Electrophilic substitution of 1,5-dihydroxy naphthalene with 2-bromoethanol was carried out by varying solvent and reaction condition. Fastest reaction kinetics was observed in DMF. In DMF, time and temperature requirements were minimal.

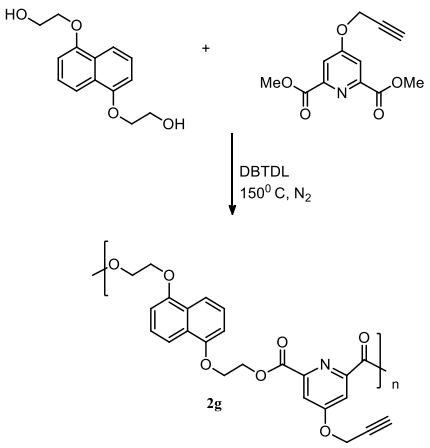
Then we moved on to the chelidamic ester-based 2nd monomer. Methylation of chelidamic acid was done to prepare chelidamic ester.



Scheme 2. Synthesis of monomer B (**2f**)

Propargyl alcohol was tosylated with tosyl chloride to yield propargyl tosylate. This was followed by the electrophilic substitution of chelidamic ester with propargyl tosylate to yield monomer B (2f) by following scheme 2.

Finally, the target polymer with spacer chain length 2 was synthesized by performing melt transesterification of the two monomers at molten state with the use of lewis acid catalyst DBTDL. Polymerization was carried out in two stages. At first, oligomerization takes place for monomers in molten state under continuous purging of N_2, later the polymerization was completed by distillation using kugelrohr.



Scheme 3. Melt transesterification of monomer A and monomer B

Solubility of the polymer was checked and found to be insoluble in most of the common organic solvent systems. A partial solubility was observed in DMSO. Then low molecular weight species were removed out of the system by continuous precipitation from DMSO by adding bad solvent methanol.

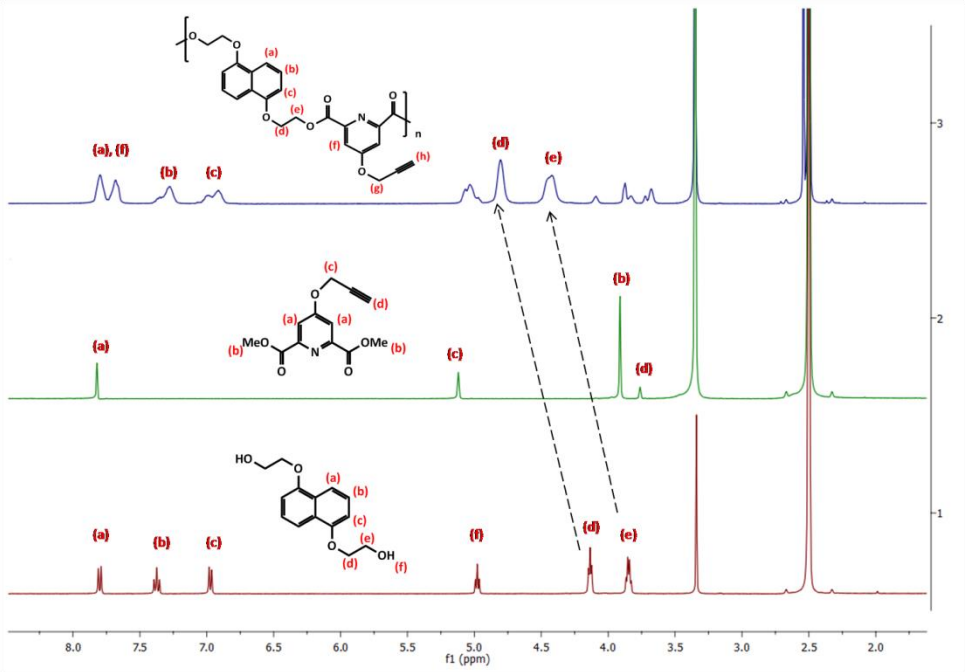
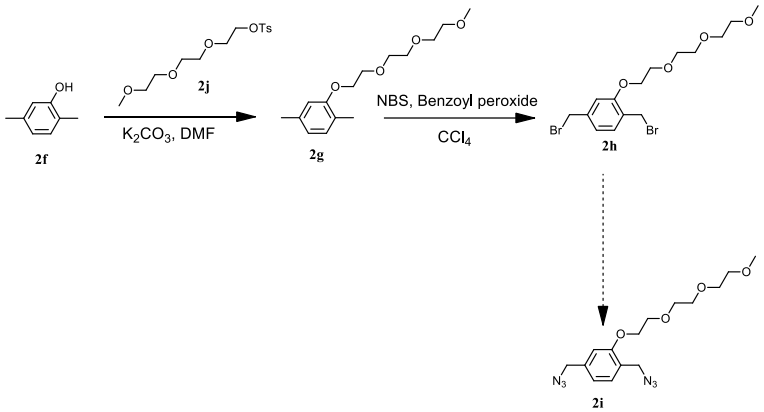


Figure 10. ^{1}HNMR spectrum of C-2 spacer polymer recorded in $(CD_3)_2SO$

While looking at the ^{1}H NMR spectrum of C-2 spacer polymer, **(e)** and **(d)** protons were found to be shifted towards downfield with the progress of polymerization. This indicates the transesterification happened to respective monomers. Propargyl group and terminal group protons were not clearly identified due to overlap with the solvent peaks.

However, to proceed further the polymer should be dissolved completely in a suitable organic solvent. From this moment, we started to investigate more on polymer solubility and ways by which it could be enhanced. So a new intramolecular crosslinker diazide substituted with a long oxy ethyl chain has been proposed along with the following synthetic scheme.



Scheme 4. Proposed synthetic route of diazide crosslinker

2,5-Xylenol (2f) was substituted with a long oxy ethyl chain by coupling it with tosylated 3,6,9-Trioxadecanol (2j). But the brominated product couldn't be isolated from column chromatography. Because it ended up with multiple spots in TLC along with the reactants, which were too close and so the product was unable to be purified by column chromatography.

The next alternative solution that we have tried was a polymer chain length optimization. A C-2 spacer oligomer was synthesized, by minimizing the reaction time. The ^{1}H NMR spectrum of the oligomer is shown in Figure 11. C-2 spacer oligomer was characterized using ^{1}HNMR and the solubility in DMSO was satisfactory.

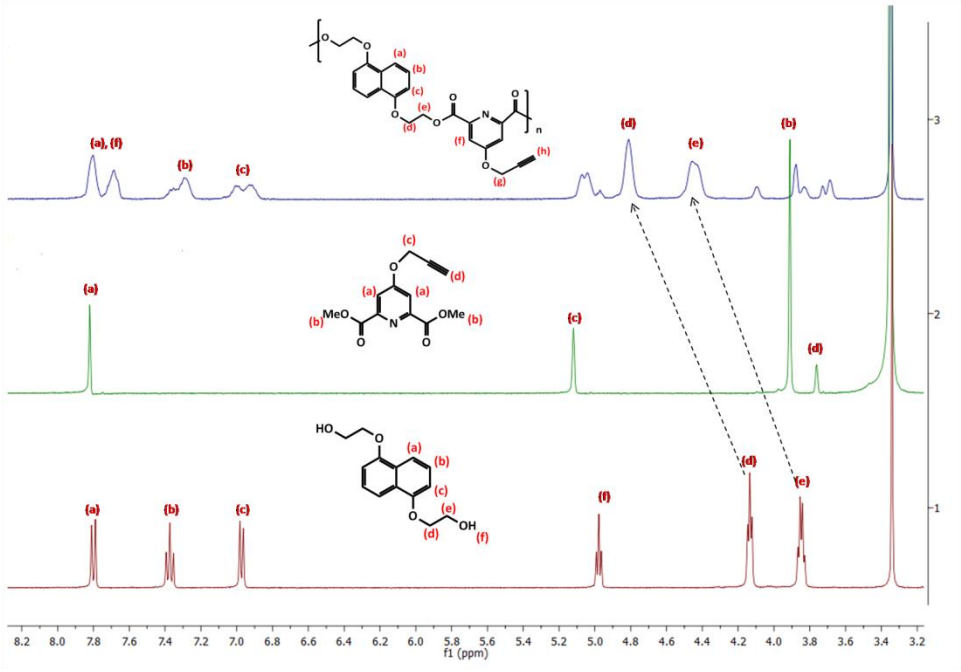


Figure 11. ^{1}HNMR spectrum of C-2 spacer oligomer recorded in $(CD_3)_2SO$

2.2 C-4 spacer polymer:

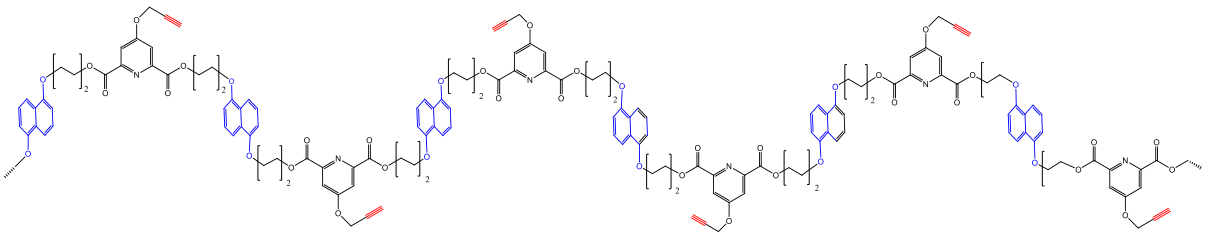
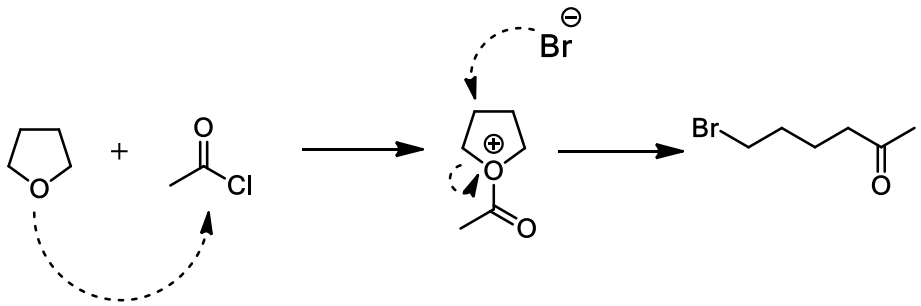


Figure 12. Molecular structure of C-4 spacer polymer

A new polymer was designed and synthesized with the aim of solubility enhancement in organic solvents. The infrastructure of the new polymer is similar to that of the previous one except that the spacer chain length has increased to 4. Synthesis of the C-4 spacer polymer was more or less similar to that of C-2 spacer, except the synthesis of butyl bromoacetate. It was synthesized from anhydrous THF through a ring opening mechanism.



Scheme 5. Mechanism behind the synthesis of butyl bromoacetate from THF and AcCl

This was followed by the synthesis of monomer A and monomer B of C-4 spacer and further polymerization

As we have expected, the melt transesterification product seems to have enhanced solubility in many organic solvents and solvent mixtures. Especially, chloroform and THF found to be the potential candidates.

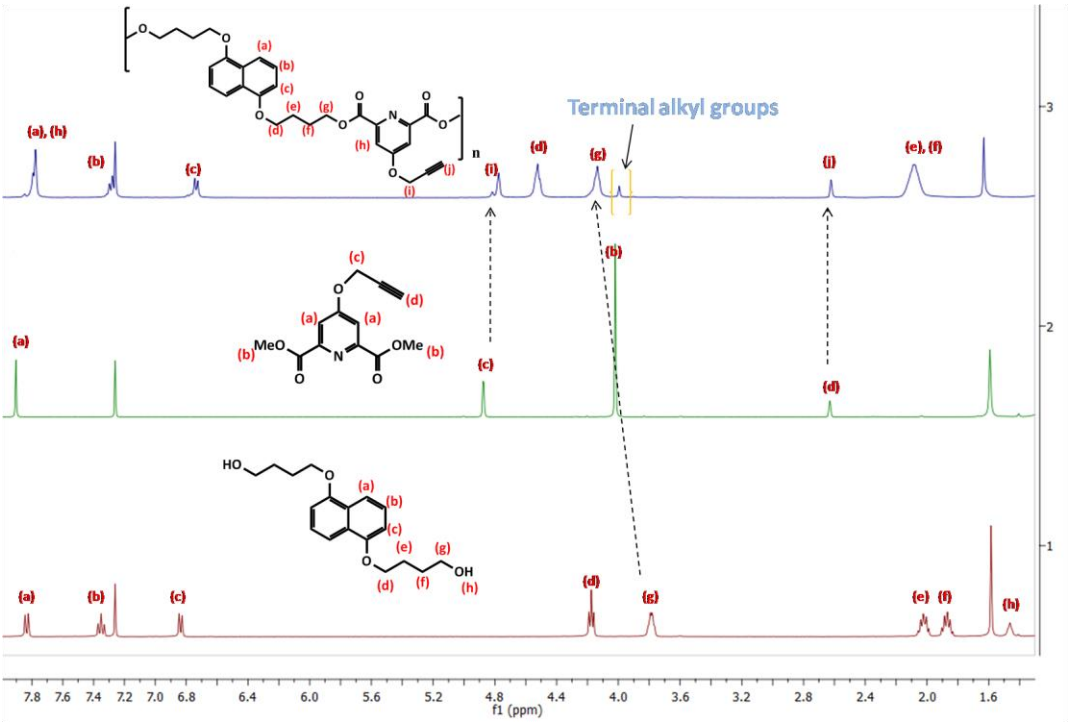


Figure 12. ^{1}H NMR spectrum of C-4 spacer polymer recorded in $CDCl_3$

^{1}H NMR of C-4 spacer clearly depicts the transesterification polymerization of respective monomers via the downfield shift of alkyl protons, especially the **(g)** protons occupied right next to the ester linkages. All the peaks are clearly visible due to its complete solubility in $CDCl_3$. Peak of terminal groups is identified at 3.9 ppm, so that it can be further used for a rough estimation of polymer length. Also, it's evident that propargyl group survives the trans esterification. It will be further used as a reactive handle for some post polymerizational modifications.

From gel permeation chromatography, the **no. average molecular weight (Mn)** of C-4 spacer polymer was found to be **4063 g/mol.** Also the molecular weight distribution or **poly dispersive index (PDI)** was found to be **1.67.** From, the value of no. average molecular weight the polymer length was roughly estimated to be 8.

3. Summary and outlook

The major objective of our work was to synthesize a polymer candidate made up of π-electron rich aromatic donor moieties which have the potential to undergo effective charge transfer complex formation with a complimentary aromatic acceptor. Since the previously designed target polymer exhibits poor solubility, many modifications had to be done to the polymer backbone to enhance the solubility. A benzylic diazide substituted with a long alkyl chain has been designed, which might have the ability to crosslink the terminal alkynes located in the polymer backbone. But, multiple side reactions lead to the formation of unwanted compounds of similar polarity. So the desired product couldn't be isolated using column chromatography. Then we moved on to a polymer chain length optimization by controlling the reaction time. The oligomer was found to be well soluble in DMSO. Parallel to that a C-4 spacer polymer soluble in many organic solvents was also synthesized. Both the C-2 spacer oligomer and C-4 spacer polymer will be subjected to charge transfer complex based folding studies in near future

4. Experimental section

4.1 Materials

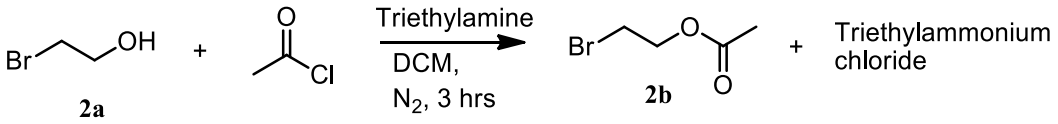
All the reagents and solvents were commercial grade purchased from Sigma Aldrich, TCI and avra. Solvents like DCM, methanol, THF, acetonitrile and DMF, and toluene were dried in the lab using standard reflux and distillation techniques. Reactions were monitored using TLC plate (Merck) and visualized with short UV (254 nm) rays. Anhydrous sodium sulphate was used to dry organic extracts and solvents were removed by rotary evaporation under reduced pressure.

4.2 Measurements

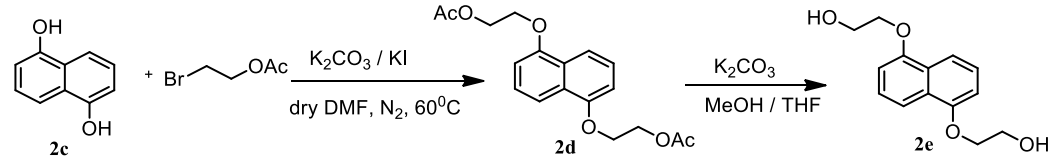
1H and ^{13}C NMR spectra were recorded in Avance-III, Brucker Biospin at 400 MHz and 100 MHz spectrometers, respectively with TMS as standard at room temperature. All the coupling constants were reported in Hz. $CDCl_3$, DMSO-d_6 were the solvents used for the above. Column chromatography was done using silica gel (100-200) mesh.

4.3 Synthesis

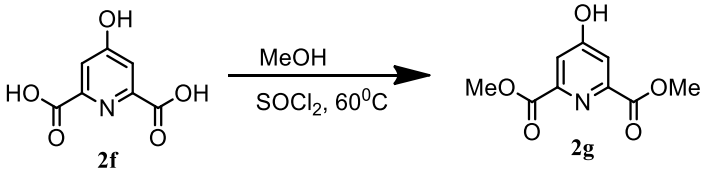
Ethyl bromoacetate: To a stirred solution of 10 g (80 mmol) of 2-bromoethanol in 90 mL of anhydrous dichloromethane at room temperature under N_2 was added a solution of 8.6 mL (9.4 g, 120 mmol) of acetyl chloride in 90 mL of anhydrous DCM, dropwise over 10 min, followed by addition of 11.1 mL (8.1 g, 80 mmol) of triethylamine via syringe over 2 min. Stirring was continued at room temperature for 3 h. The reaction mixture was diluted with 200 mL of DCM and the resulting solution was washed with 200 mL of H_2O, 200 mL of saturated aqueous $NaHCO_3$, 200 mL of H_2O, dried (Na_2SO_4), and concentrated in vacuo, to yield the crude product as a yellow liquid. This material was distilled under reduced pressure using kugelrohr to yield 10.4 g (77%) of ester as a colorless liquid[27]. Characterization was done using ^1H NMR



1,5-Bis(2-hydroxyethoxy)naphthalene (monomer A): In a double necked R.B. flask 1,5-Dihydroxynaphthalene(2c) (1.5 g, 9.38 mmol) was taken in dry DMF (25 mL) along with 2-bromo ethyl acetate(7 g, 41.9 mmol) and KI. N_2 was purged directly through one of the necks for 30 min. Then activated K_2CO_3 (6.48 g, 46.89 mmol) was added and the contents were refluxed for 12 hrs at 60^0C. After the reaction was complete, DMF was removed using vacuum pump and the contents were poured in alkaline (5% NaOH) water. The residue formed was filtered and dried to get compound 2d, which was then directly used for the next step without further purification. Compound 2d was taken with K_2CO_3 (3.0 g) in a mixture of dry MeOH (15 mL) and dry THF (15 mL) and stirred for 12 h at 50 ^{0}C. Then, the solvents were removed, and the residue poured in basic (5% NaOH) water. The precipitate formed was filtered and purified using column chromatography. Compound 2e was collected in 5% methanol in ethyl acetate.[28]

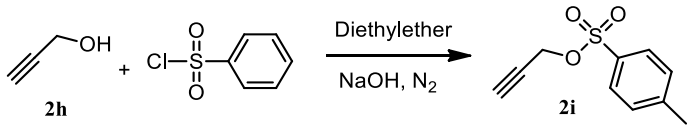


Dimethyl chelidamate ester: To a solution of chelidamic acid (2 g, 10.9 mmol) in MeOH (80 mL), $SOCl_2$ (1.95mL) was added slowly. The mixture was refluxed overnight. Then the solvent methanol was removed in vacuo. Extraction was done using ethyl acetate and water. The organic part was dried over Na_2SO_4 and solvents were removed in vacuum.[29]

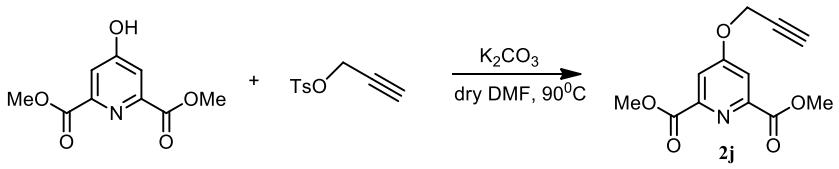


Propargyl tosylate: Around bottom flask was equipped with a mechanical stirrer was charged with 5mL(86 mmol) of propargyl alcohol, 21.3 g (112 mmol) of tosyl chloride and 90 mL of diethyl ether under N_2. Then NaOH pellets was added in 6 portions. The mixture was continuously stirred overnight at room temperature. The suspension was poured into cold water and the resulting aqueous layer was extracted with ether (2x25 mL). The ether layer

was dried over Na_2SO_4 and concentrated. Pure propargyl tosylate obtained by drying under high vacuum.[30]

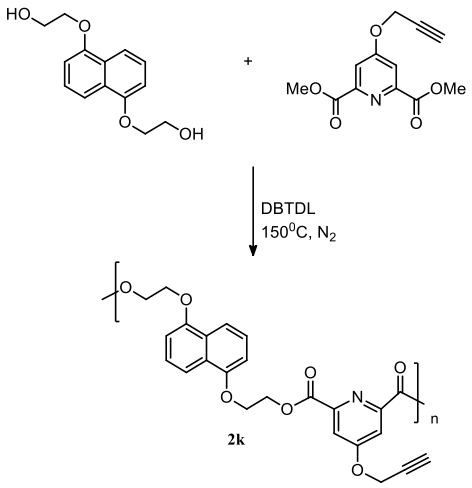


4-(Prop-2-yn-1-yloxy)pyridine-2,6-diyl)dimethanol (Monomer B) : Dimethyl chelidamate was taken in a round bottom flask along with activated K_2CO_3. Then propargyl tosylate and dry DMF were added using a syringe under N_2. Then the mixture was refluxed at 90^0C for 4 hrs. Stirring was continued overnight. The reaction mixture was poured into ice cold water and the precipitate formed was separated using ethylacetate. The organic layer was concentrated by rotary evaporation. The above step was repeated two times. The solid product obtained finally was dried using vacuum pump and recrystalized to get the final compound as white solid.[31]

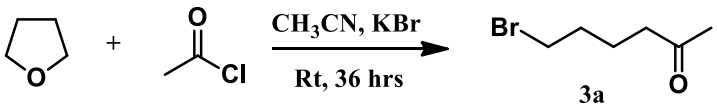


Melt transesterification:

In a 10mL round bottom flask monomer A (0.500 g, 2.01 mmol) and monomer B (0.502 g, 2.01 mmol) was taken in exactly 1:1 equivalent. Then a lewis acid catalyst DBTDL (0.050 g, 0.080 mmol) was added to the flask. N_2 was purged directly into the flask. Stirring at 160^0C was continued till the stirring bar get stick into the walls. Polymerization was completed in a kugelrohr and the condensation by-products were removed fully under 70^0C and very low pressure(less than 5 mmHg). The polymer then dissolved in 2mL DMSO by ultra sonication and heating and poured drop wise into excess methanol equipped with a stirring bar. Then the solid was filtered out from methanol and dissolved again in DMSO and repeated the above procedure few times. The solid product was dried completely using vacuum pump.

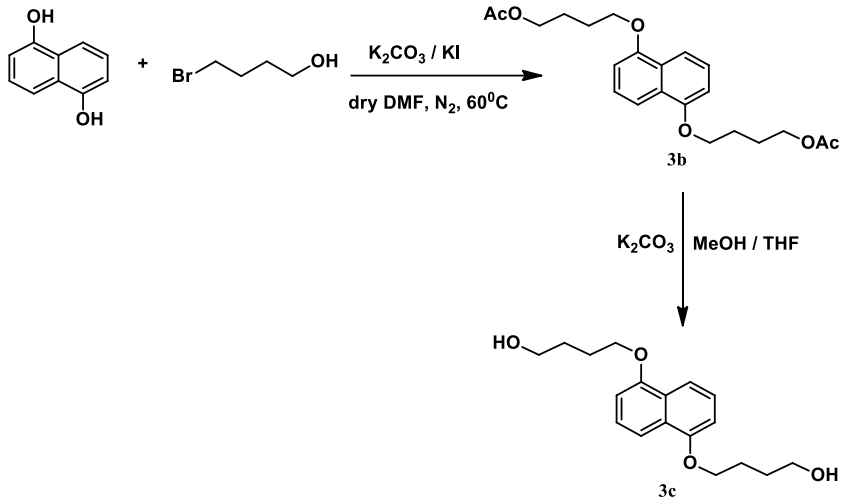


Butyl bromoacetate: In a double-necked round bottom flask, KBr (21.2 g, 178.1 mmol), anhydrous THF (12.2 mL, 134.7 mmol), and CH_3CN (150 mL) were taken. A N_2 baloon was used keep the atmosphere inert. The whole setup was kept in ice bath while adding acetyl chloride (CH_3COCl) (11 mL, 154.15 mmol) drop wise. Then the mixture was stirred at room temperature for 36 hrs. After the completion of reaction, the solvent was removed, and dissolved in ethyl acetate. In a separation funnel, the organic part was washed several times with water, and $NaHCO_3$ solution (to neutralize) and dried over Na_2SO_4. The crude product was then distilled under reduced pressure (90^0C, 15 mm Hg) using kugelrohr to yield 24 g (91.8 %) of butyl bromoacetate(3a)as a colorless liquid[32]. Characterization was done using ^{1}H NMR



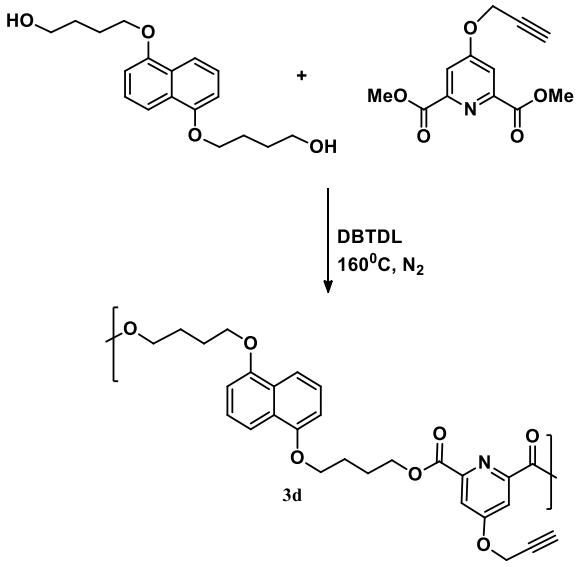
1, 2-Bis(4-hydroxybutoxy)naphthalene(Monomer A): In a double necked R.B. flask 1,5-Dihydroxynaphthalene(2c) (1.5 g, 9.38 mmol) was taken in dry DMF (25 mL) along with butyl bromoacetate (3a) (7 g, 41.9 mmol) and KI. N_2 was purged directly through one of the necks for 30 min. Then activated K_2CO_3 (6.48 g, 46.89 mmol) was added and the contents were refluxed for 12 hrs at 60^0C. After the reaction was complete, DMF was removed using vacuum pump and the contents were poured in alkaline (5% NaOH) water. The residue formed was filtered and dried to get compound 3b, which was then directly used for the next step without further purification.Compound 3b was taken with K_2CO_3 (3.0 g) in a mixture of dry MeOH (15 mL) and dry THF (15 mL) and stirred for 12 h at 50 ^{0}C. Then, the solvents were removed, and the residue poured in basic (5% NaOH) water. The precipitate formed was filtered and purified using column

chromatography. Compound 3c was collected in 5% methanol in ethyl acetate with a yield of 87% [28].



Melt transesterification:

Monomer A (3c) (0.500 g, 1.81mmol) and monomer B (2j) (0.450 g, 1.81 mmol) was taken in exactly 1:1 equivalent in a 10 mL flask. Then a lewis acid catalyst DBTDL (0.045 g, 0.072 mmol) was added to the flask. N_2 was purged directly into the flask. Stirring at 160^0C was continued till the stirring bar get stick into the walls. The flask then moved tokugelrohr to complete the polymerization under 70^0C and very low pressure(less than 5 mmHg). The polymer then dissolved in 2mL $CHCl_3$ and precipitated by adding methanol (a bad solvent). This was continued for few times. The solid product was dried completely using vacuum pump.



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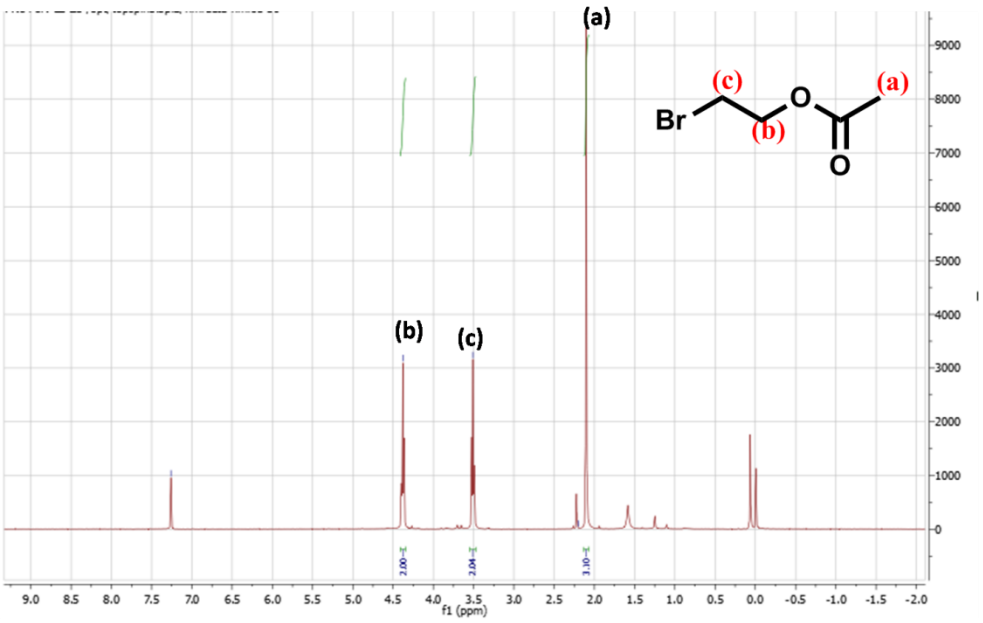
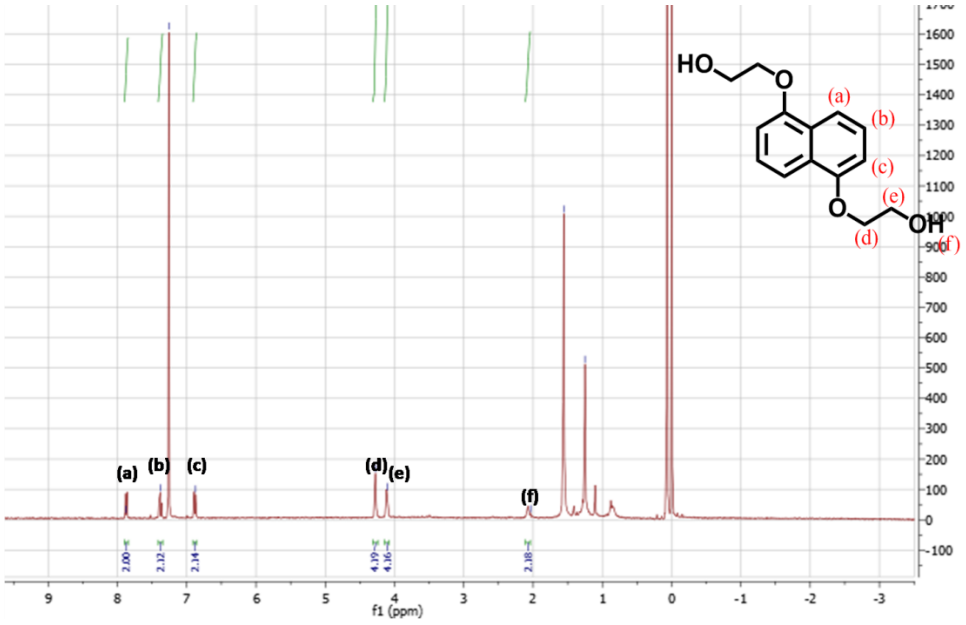
Appendix

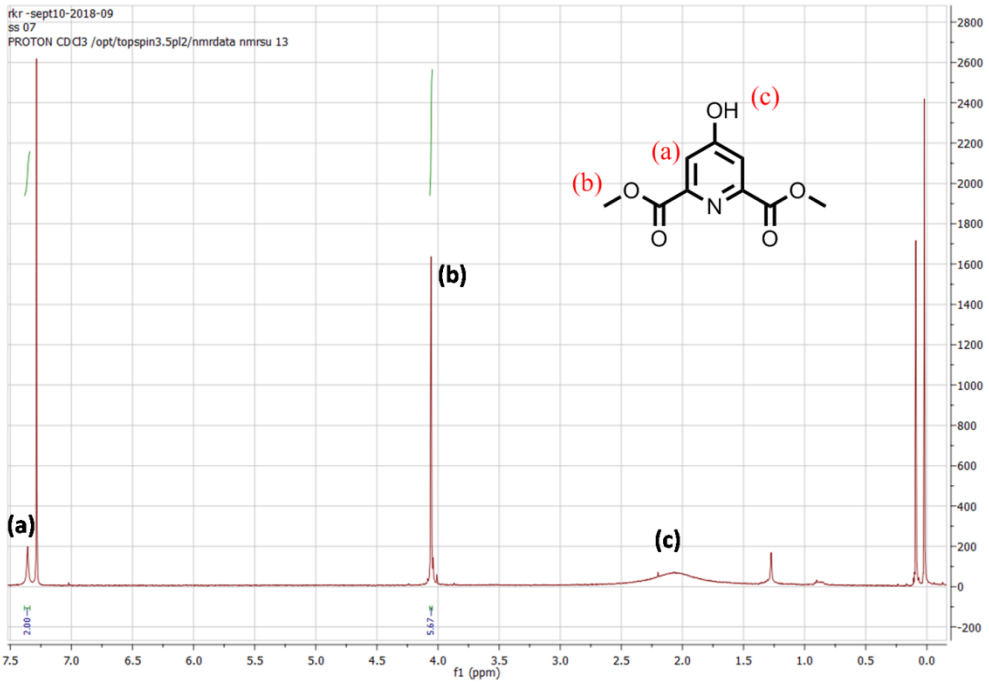
Ethyl bromoacetate (2b), ^{1}H NMR, $CDCl_3$



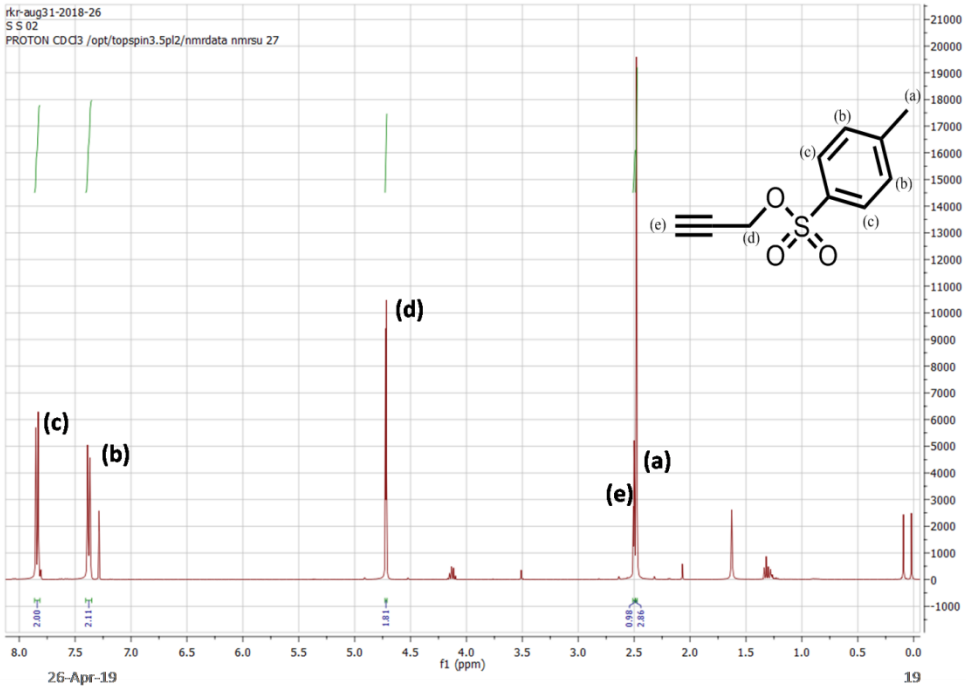
1,5-Bis(2-hydroxyethoxy)naphthalene (2e), ^{1}H NMR, $CDCl_3$



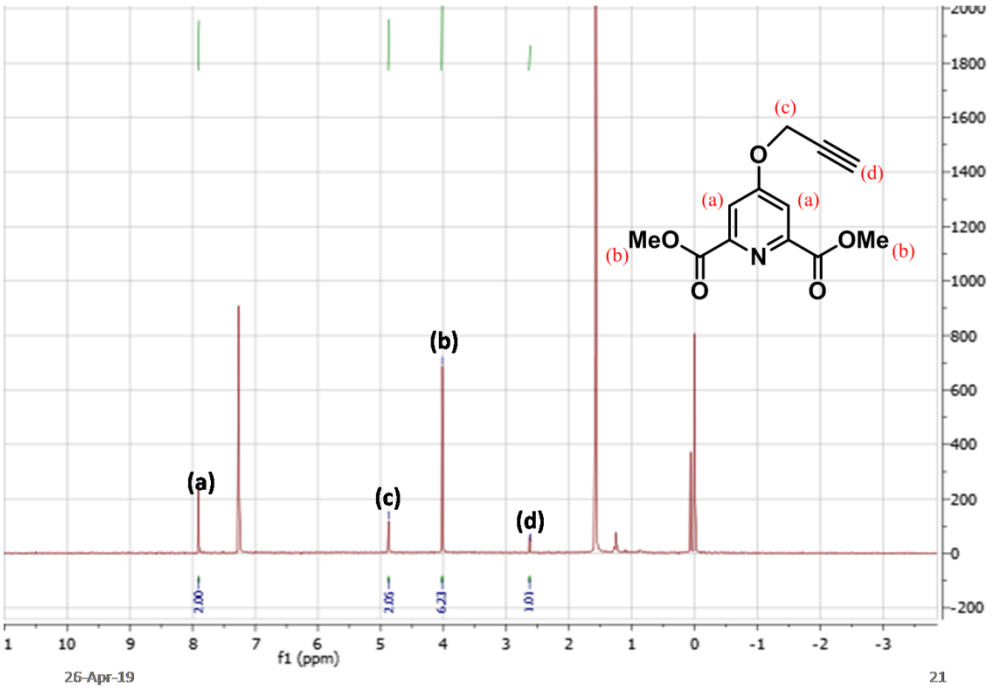
Dimethyl chelidamate ester (2g), ^{1}H NMR, $CDCl_3$



Propargyl tosylate (2i), ^{1}H NMR, $CDCl_3$



4-(Prop-2-yn-1-yloxy)pyridine-2,6-diyl)dimethanol (2j), ^{1}H NMR, $CDCl_3$



1,2-Bis(4-hydroxybutoxy)naphthalene (3c), ^{1}H NMR, $(CD_3)_2SO$