

A Report of Summer Internship

**Synthesis of a Photoresponsive Azobenzene based
Bistable Molecular Switch**

Submitted by
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Belonging to
Material Science and Engineering
Dual Degree (B.Tech+M.Tech)
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This is to certify that the project work entitled “Synthesis of a Photoresponsive Azobenzene based Molecular Switch” is a bonafide record of research work carried out by **Md Zibran Khan (2352002)**, a student of National Institute of Technology Patna, during the period 3rd June 2024 – 8th August 2024 under the guidance of **Dr. Suvankar Dasgupta**, Assistant Professor, Department of Chemistry, National Institute of Technology, Patna.

I wish him all the success in his career and future endeavours.

Dr. Suvankar Dasgupta

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Acknowledgement

With immense pleasure, I, Md Zibran Khan present “Synthesis of a Photoresponsive Azobenzene based Bistable Molecular Switch” the summer internship report . I wish to thank all the people who gave me unending support.

I express my profound regards to my supervisor Dr. Suvankar Dasgupta, Assistant Professor, who helped me in the preparation of this report.

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Chapter 1: Introduction

1.1. Rotaxanes

Rotaxanes are a category of mechanically interlocked molecules distinguished by a dumbbell-shaped component that threads through a macrocyclic ring. The stability of this configuration is upheld by the inclusion of large stopper groups positioned at the extremities of the dumbbell, effectively inhibiting the ring from detaching. The unique structure of rotaxanes enables fascinating dynamic characteristics, allowing the ring to move along the length of the dumbbell.

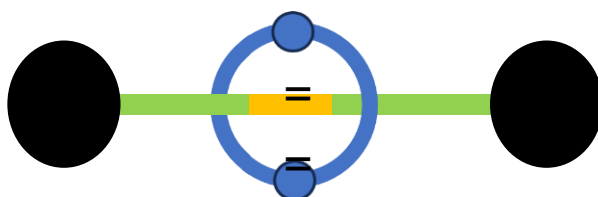


Figure 1.1. Cartoonic representation of a [2]rotaxane.

1.2. Molecular Switches

Molecular switches are defined as systems that can undergo transition reversibly between two or more stable states, when exposed to external stimuli such as light, pH, or chemical agents. These switches are essential for the development of molecular devices as they control the behavior and properties of the molecular system. In the context of rotaxanes and pseudorotaxanes, the movement of the macrocyclic ring along the dumbbell can act as a switching mechanism, leading to significant changes in the molecule's properties.

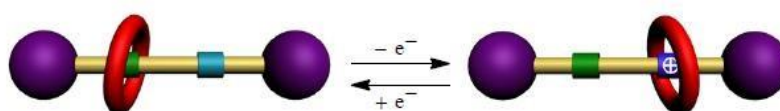


Figure 1.2. Cartoonic representation of a rotaxane-based molecular switch.

1.3. Photoresponsive Molecular Switches

In a supramolecular system, the polymers are well-organized assemblies of monomeric units based on highly directional and reversible noncovalent interactions, hydrogen bonding, π - π stacking, host-guest interaction. It can undergo transition reversibly between two or more stable states through homopolymerization of light-activated monomers.

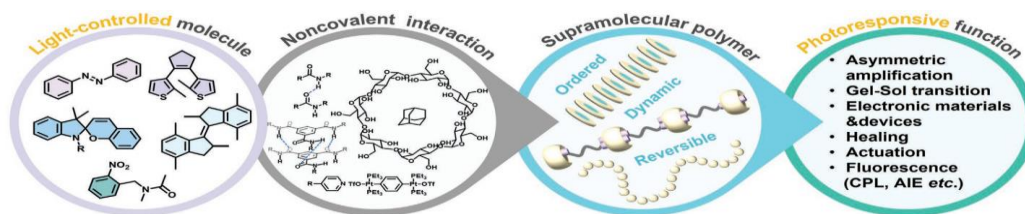


Figure 1.3. Illustration of the construction of supramolecular polymers from light-responsive molecules.

1.4. Azobenzene

Azobenzenes are the most extensively used photoswitches in supramolecular polymers. In solution, irradiation of trans(E)-isomers with UV light induces the geometric isomerization around the N=N double bond, resulting in cis(Z)-isomers (**Figure 1.4**).¹ The lengths of trans- and cis-azobenzene units are 9 and 6 Å along with Trans-azobenzenes with nearly zero dipole moment, while cis-isomers have larger dipole moments.

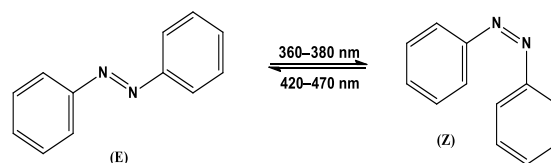


Figure 1.4. Cis-Trans form of Azobenzene.¹

1.4. Diarylethene

Diarylethenes are particular derivatives of stilbene (**Figure 1.5**).^{2,3} the double bond is embedded in a ring structure, cis/trans isomerization is prevented. Instead, the ring-opened form of diarylethenes undergoes a photocyclization upon irradiation, forming a more rigid ring-closed form, and in an equal amount of (R,R)- and (S,S)-enantiomers

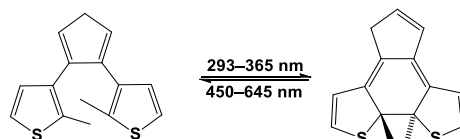


Figure 1.5. Open/Closed form of Diarylethene.^{2,3}

1.6. Stilbenes

Stilbene is a configurational switch that undergoes trans to cis isomerization around the double bond upon UV irradiation (**Figure 1.6**).⁴ the regular stilbenes usually induces

cyclization to give dihydrophenanthrene, which is then further oxidized to phenanthrene as a side product.

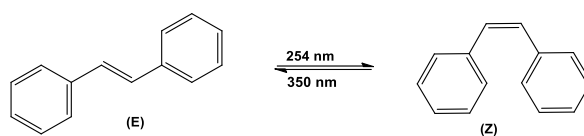


Figure 1.7. Cis-Trans form of Stilbenes.⁴

Stiff-stilbenes⁵ show a relatively rigid structure and can undergo reversible isomerization, avoiding cyclization, the cis isomer of stiff-stilbenes is usually thermally stable.

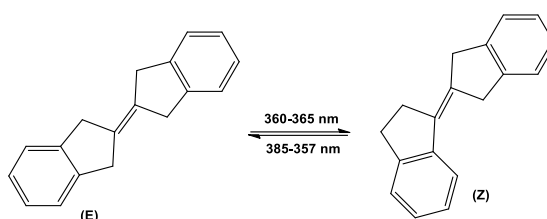


Figure 1.7. Cis-Trans form of Stiff-stilbene.⁵

1.8. Spiropyran

Spiropyrans undergo a reversible cleavage of the C-O bond upon irradiation and have a ring-closed form “spiropyran” and a ring-opened zwitterionic isomer “merocyanine” (**Figure 1.8**).^{6,7} The protonated merocyanine is able to release and re-capture H⁺, acting as photoacids, which can be used to control conductivity and reversible assembly of supramolecular systems. The massive difference in dipole moment, acidity, and electronic structure of spiropyran and merocyanine enable the corresponding materials to have significantly different properties.

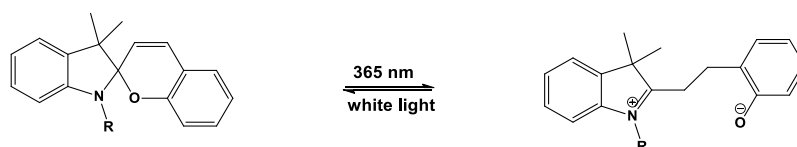


Figure 1.7. Open/Closed form of Spiropyran.^{6,7}

1.9. Hydrazone-based switches

Hydrazone-based switches can undergo E/Z isomerization around the C=N bond.^{8,9} When activated with chemicals or light, phenyl-quinolinyl hydrazine and bis-phenyl hydrazine with electron-withdrawing and donating groups are bistable switches with outstanding

stability. Along with that bis-phenyl hydrazone shows excellent configurational switching and fluorescence ON/OFF toggling in the solid-state.

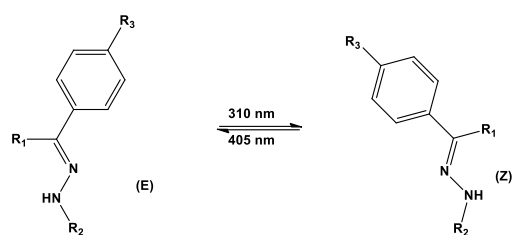


Figure 1.9. E/Z isomerization of Hydrazone-based Switches.^{8,9}

Chapter 2: Literature Survey

2.1. Photo-Controlled Supramolecular Polymerization

It is the pictorial representation (**Figure 2.1**) how the photoresponsive monomer, in which photoresponsive moiety serves as the “core” or “side chain” of monomers, and as a ligand. This process has 3 steps:- i) photo-induced supramolecular polymerization, ii) deformation, and iii) disassembly of photoresponsive polymers, including the photocontrol of morphology and length.

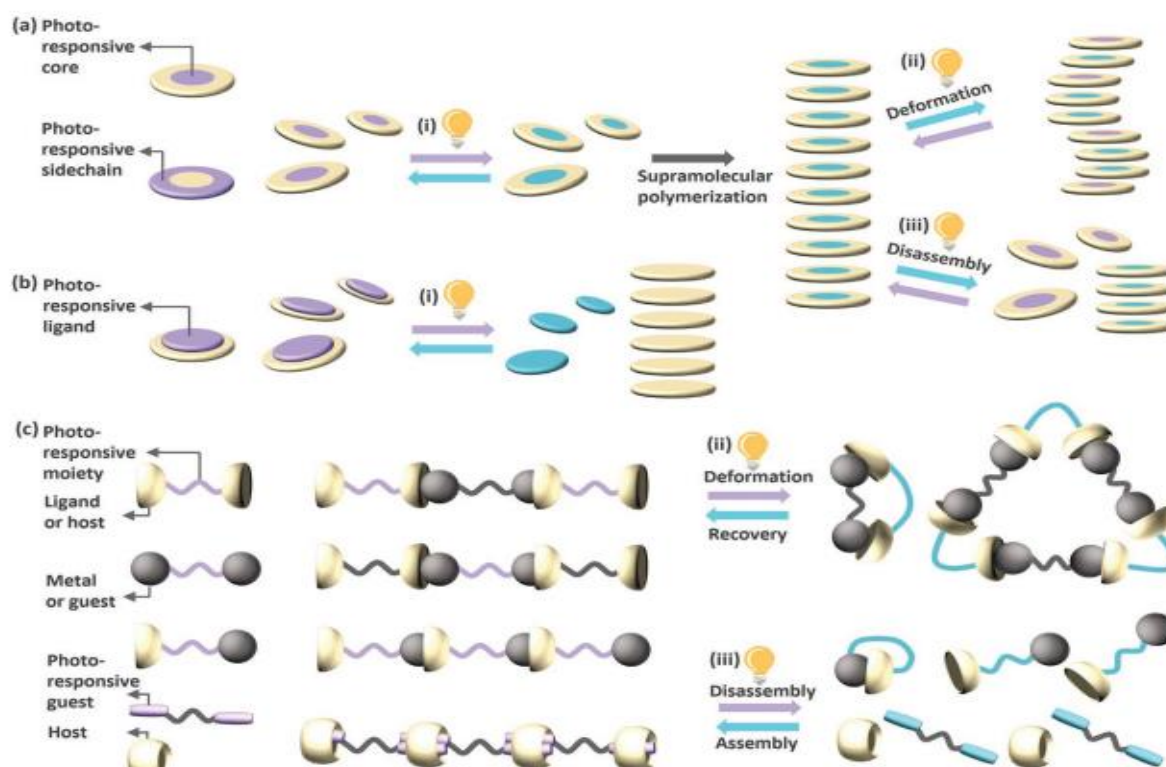


Figure 2.1. Photo-Controlled Supramolecular Polymerization.

2.2. Photo-Induced Supramolecular Polymerization

The light-induced steric changes of azopyridine-based ligands (**Figure 2.2a**),¹⁰ such as stilbazole and phenylazopyridine led to different binding affinity with metal–porphyrins. Here, trans-phenylazopyridine derivative exhibited higher binding strength with zinc porphyrins than cis-isomer. Upon irradiation, trans-phenylazopyridine switches to the cis-isomer and thus releases the free zinc porphyrin monomers to allow further cooperative self-assembly (**Figure 2.2b**).¹⁰

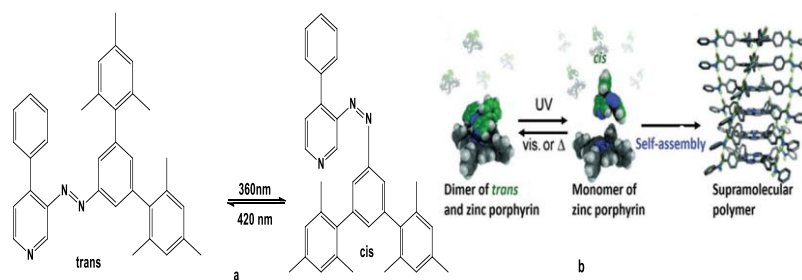


Figure 2.2. a) Cis-Trans form of phenylazopyridine b) Assembly-Disassembly of phenylazopyridine.¹⁰

A photoresponsive supramolecular polymer based on stiff-stilbene bis-ureas, in which both isomers are thermally stable. The cis-form is “locked” for self-assembly by an intramolecular hydrogen bond, and serves as an inactive monomer. Upon irradiation, the cis is unlocked to trans, forming intramolecular hydrogen bonds, and the compound assembles. **(Figure 2.3a).**¹¹ At a higher concentration, a solution of cis could induce in situ gelation upon irradiation with 385 nm light. The reverse gel–sol transition was carried out by irradiating with 365 nm light **(Figure 2.3b).**¹¹

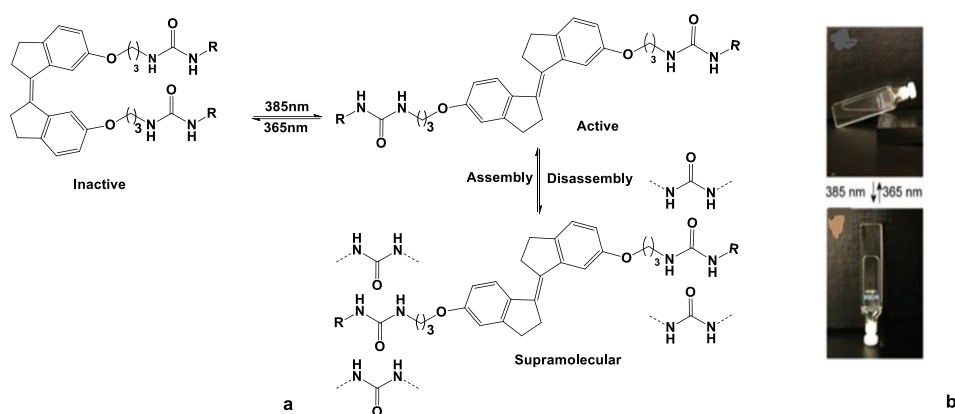


Figure 2.3. a) Polymerization of stiff-stilbene bis ureas. b) Sol-gel transition of stiff-stilbene.¹¹

2.4. Photocontrol of Morphology and Length of Supramolecular Polymers

A photoresponsive supramolecular system based on stiff-stilbene bipyridyl ligand “E/Z form” and organoplatinum(II) complexes “m” in **(Figure 2.4a)**.¹² Upon irradiation with 360 nm light, the supramolecular polymer disassembled and reassembled to cyclic oligomers with an (E)/(Z) ratio of 47/53. The reversible transformation between linear supramolecular polymers and cyclic oligomers can be achieved by irradiating with 387 and 360 nm light, respectively. **(Figure 2.4b)**¹².

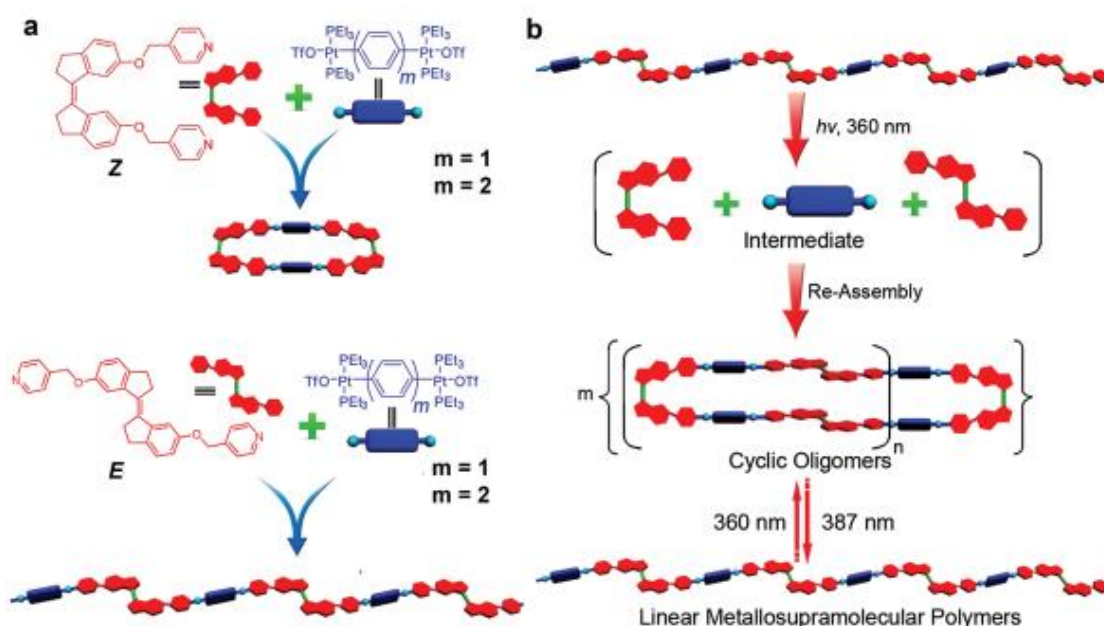


Figure 2.4. a) Polymerization of stiff-stilbene bipyridyl. b) Change in morphology of stiff-stilbene bipyridyl.¹²

E-stilbene-bridged bis(β -CD) host **I** forms a supramolecular dimer with pyridinium-adamantyl derivative **II** as a guest **(Figure 2.5a)**¹³. Whereas Z-isomer and guest **II** form linear supramolecular polymer. **(Figure 2.5b)**¹³. Nanofiber of **Z** and **II** complexes of 350nm in length, while **E** and **II** form small objects with a size ≈ 30 nm. with **II** is thrice than the one of **Z** with **II** due to cooperative effect.

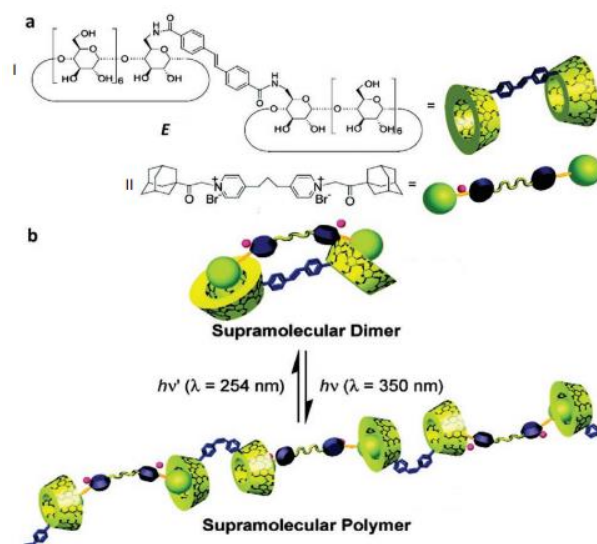


Figure 2.5. a) Host guest interaction **I** and **II**. b) Change in morphology of polymer complex upon UV radiation¹³.

A co-assembly of alkyl benzene-1,3,5-tricarboxamide **I** monomers and photoresponsive acyl hydrazine-based BTA monomers that acts as an intercalator **E** or chain **Z** capper in the supramolecular polymer (**Figure 2.6a**).¹⁴ Upon irradiation with 310 nm light, the intercalated **E** transforms to **Z** acting as a chain capper, as a consequence of chain length decrease, a sol-to-gel transition was completed after 15 min UV light irradiation. The supramolecular polymer sol was recovered by heating at 90 °C or irradiating with 405 nm light and subsequent re-equilibrating for 2 h.

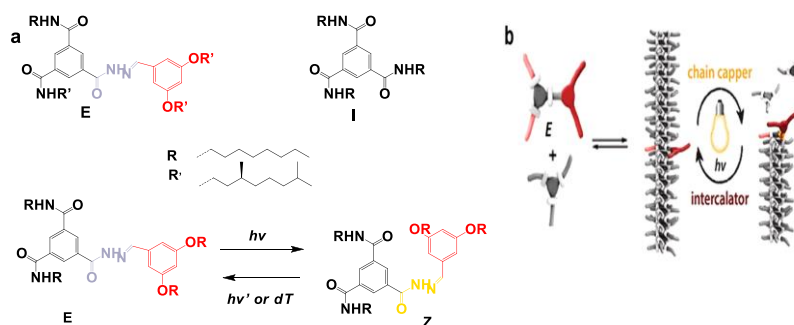


Figure 2.6. a) Co-assembly of alkyl benzene-1,3,5-tricarboxamide **I** monomers and acyl hydrazine-based BTA monomers b) Change in morphology upon UV radiation.¹⁴

2.7. Photo-Induced “Depolymerization” of Supramolecular Polymers

A supramolecular homopolymer, in which the photoresponsive monomer was designed based on a BTA core with three identical amino acid wedges. UV-irradiation on polymer resulted in a dominant amount of (Z,Z,Z) and (Z,Z,E), leading to the disruption of the supramolecular polymer due to the less efficient stacking as a result of the planar structure of the (Figure 2.7a).¹⁵ The supramolecular homopolymer orthogonally responded to multiple stimuli: light, pH, ionic strength, and temperature. (Figure 2.7b).¹⁵

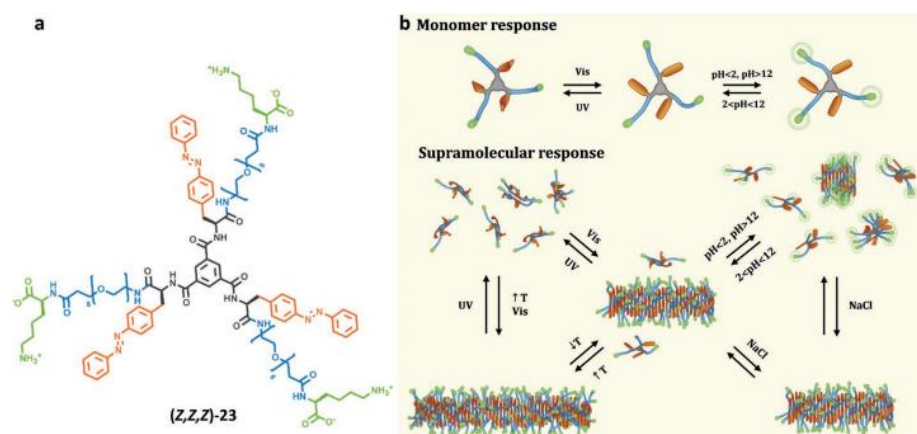


Figure 2.7. a) The supramolecular polymer in Z,Z,Z. b) Stimuli using light, PH, ionic etc¹⁵.

The host–guest complexation of β -CD derivatives and the guest containing E-azobenzene and viologen moiety; another is the metal–ligand coordination of ethylenediamine palladium(II) nitrate and bipyridine moiety in β -CD derivatives (Figure 2.8).¹⁶

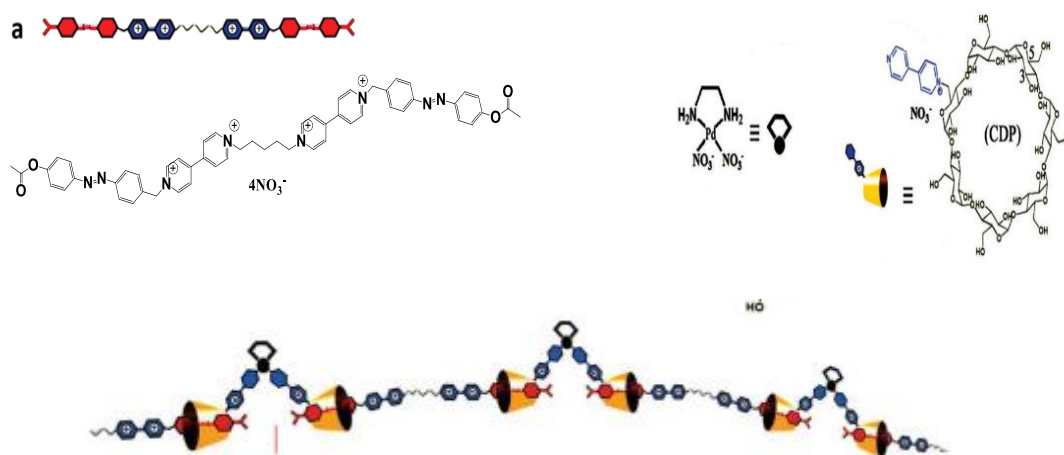


Figure 2.8. Molecular structure and cartoon presentation of the guest and host¹⁶.

The viscosity of the supramolecular polymer decreases upon irradiation with UV light, suggesting the disassembly of the supramolecular polymer

2.9. Photoresponsive Functions of Supramolecular Polymers

A photoresponsive supramolecular polyelectrolyte based on lanthanide ions **IV**, bis-pyridinedicarboxylic acid ligand **III**, and cationic diarylethene derivative **I/II** (**Figure 2.9a**).¹⁷ Ring-opened diarylethene displays a bright red emission, upon irradiation with UV light, the conversion from open to its ring-closed form, meanwhile the luminescence of open form was quenched after irradiation with UV light. The absorption band at 294nm gradually decreased with an peak of two bands at 380nm and 615nm.

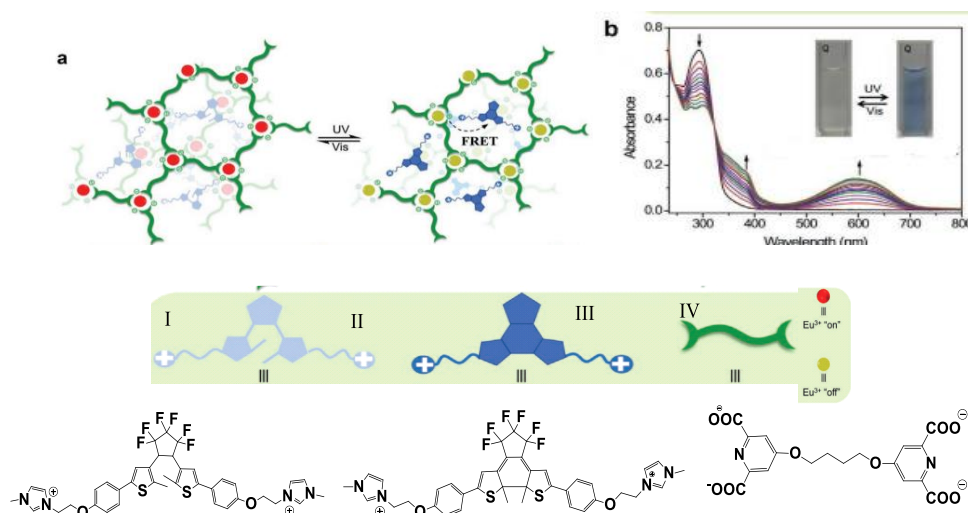


Figure 2.9. a) Polymerization of diarylethene derivatives, b) Absorption spectrum of supramolecular complex¹⁷.

This is used for a high level of security, as both the luminescent and quenched QR code were invisible under daylight and red pattern is visible under excitation of 294nm, and removed under 300nm (**Figure 2.10**).¹⁷

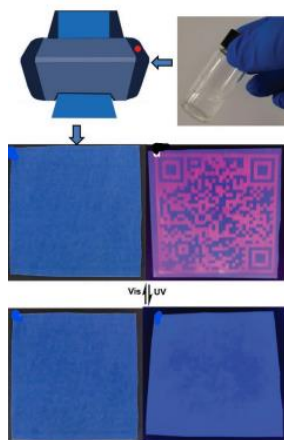


Figure 2.10. Diarylethene derivatives used for a high level of security¹⁷.

Two kinds of photoresponsive hydrogen-bonded rosettes **IV** and **V** composed of three trans-azobenzene-appended melamines **I** and three barbiturates **II** or cyanurate **III** respectively (**Figure 2.11**).¹⁸ The hydrodynamic diameter of **IV** to be 7.8 nm, while an average hydrodynamic diameter of 52 nm was determined for **V** aggregates at 20 °C in cyclohexane. The temperature sensitivity suggests that the **V** aggregates are assembled through aromatic stacking of hydrogen-bonded rosettes while **IV** remains have unfavourable morphology.

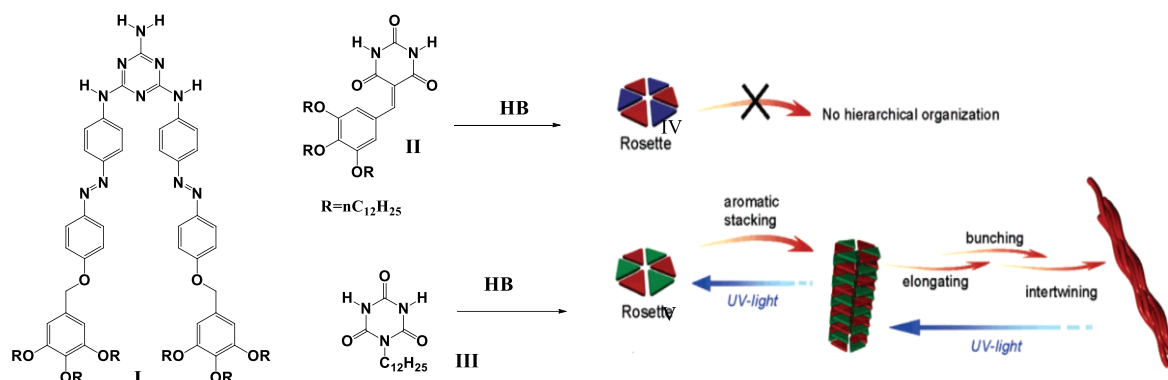


Figure 2.11. Schematic illustration of assembly and disassembly of **I** with barbiturates **II** or cyanurates **III**.¹⁸

Irradiating the **V** aggregates with UV light leads to a decrease of the hydrodynamic diameter, reaching nearly single rosette size (8 nm) at PSS with the amount of cis-isomer reaching 36% as well as gel-sol transition also take place (**Figure 2.12**).¹⁸ The gel state was also recovered by keeping the solution in dark for 48h.

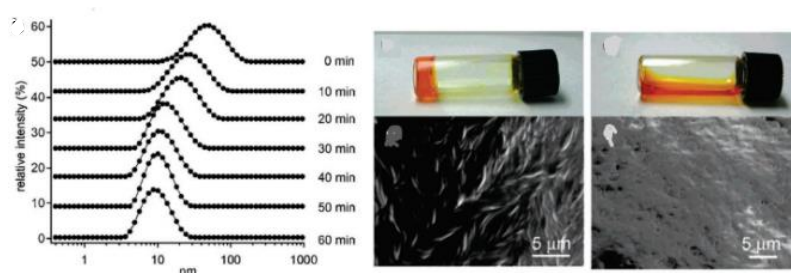


Figure 2.12. Irradiating **V** with UV light leads to gel-sol transition¹⁸.

The device was made up of prepatterned metallic electrodes with a solution of disk-shaped triarylamine (**Figure 2.13a**)¹⁹ in nanotrenches (**Figure 2.13b**).¹⁹ Before irradiation, the conductance of the circuit is around a few nanosiemens a few cationic radicals produced

upon irradiation with white light, as a result, the device conductance increased to several tens of millisiemens, resistance also decreases as temperature decreases.

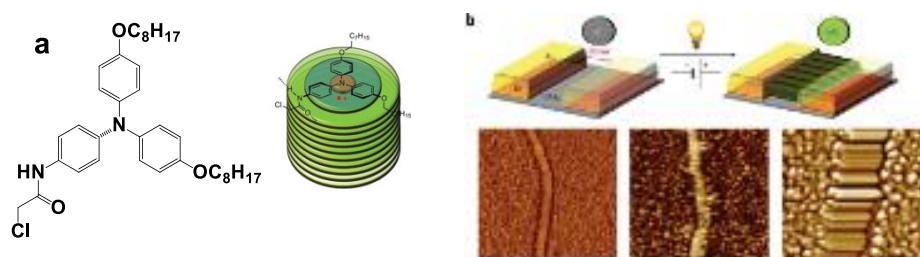


Figure 2.13. **a)** Molecular structure of triarylamine derivatives **b)** Light induced fiber between gold/nickel electrodes.¹⁹

Chapter 3: Work Description

3.1. Objective

We aim to develop a [2]rotaxane-based molecular switch that includes a [23]crown ether and investigate its metastability upon the addition of various halide anions, as well as under the influence of DBU and TFA.

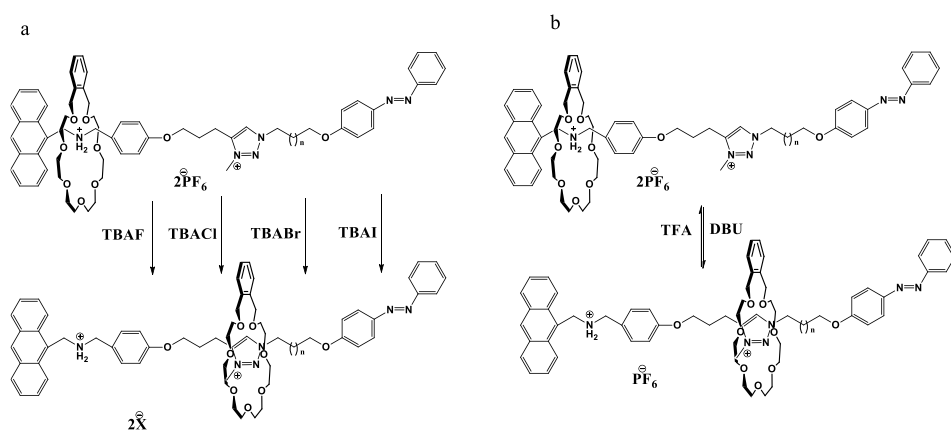
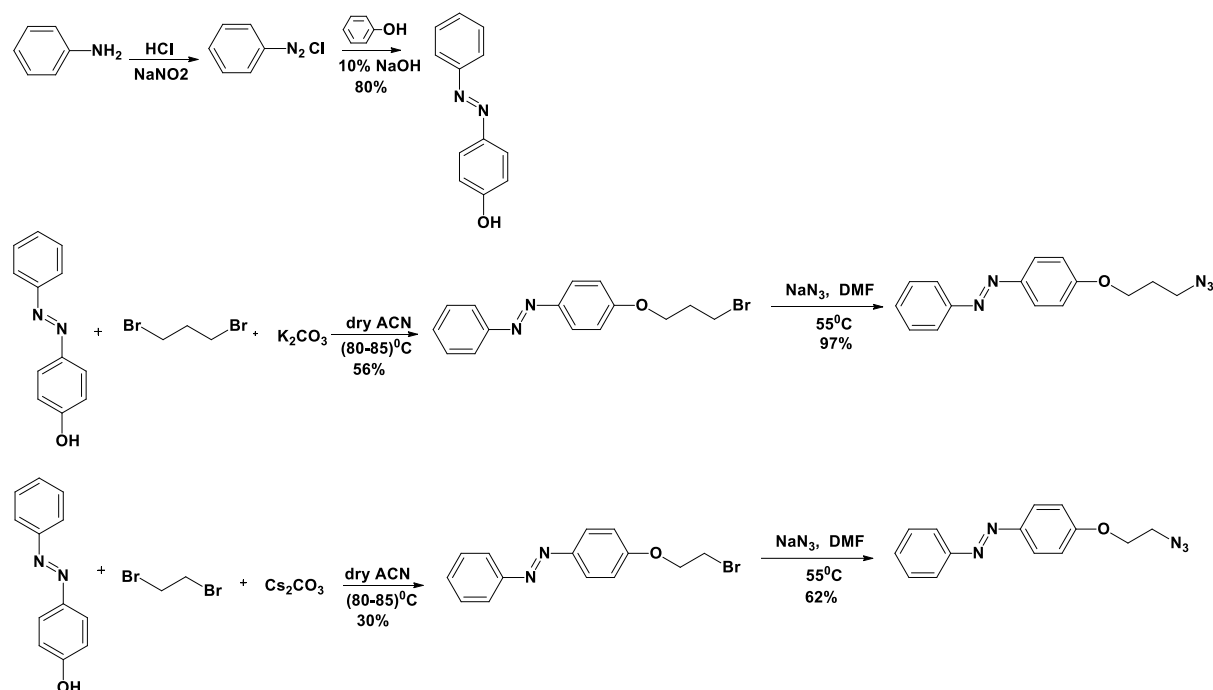


Figure 3.1. (a) Action of halide anion on [2]rotaxane-based molecular switch that includes a X23C7 ring, (b) Action of DBU and TFA on [2]rotaxane-based molecular switch that includes a X23C7 ring.

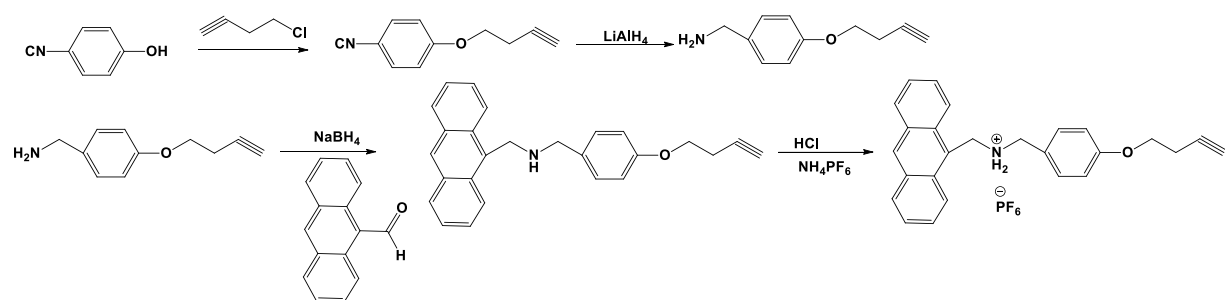
3.2. Reaction Scheme

Step 1



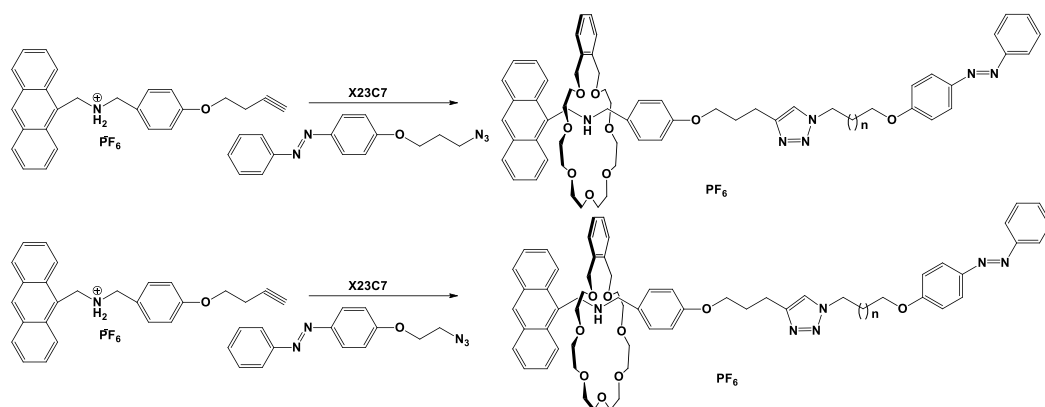
In first step, prepared the axle portion of supramolecular complex that contained azobenzene part . By using the Diazonium method, prepared a diazonium chloride salt, subsequently Phenoletic reaction give rise to 4-hydroxyazobenzene. Further addition of Br and azide reaction on later (for both 2 and 3carbon chain), lead to our desire product.

Step 2



In this step, 4-cynphenol undergoes S_N^2 reaction with 5-chloro-1-pentyne, subsequently reduction with $LiAlH_4$ give rise to primary amine. Using Dean Stark apparatus it undergoes Imine condensation with PyCHO , further reaction with HCl lead to the formation of chloride salt and in the presence of NH_4PF_6 , the obtained product is salt of PF_6 .

Step 3



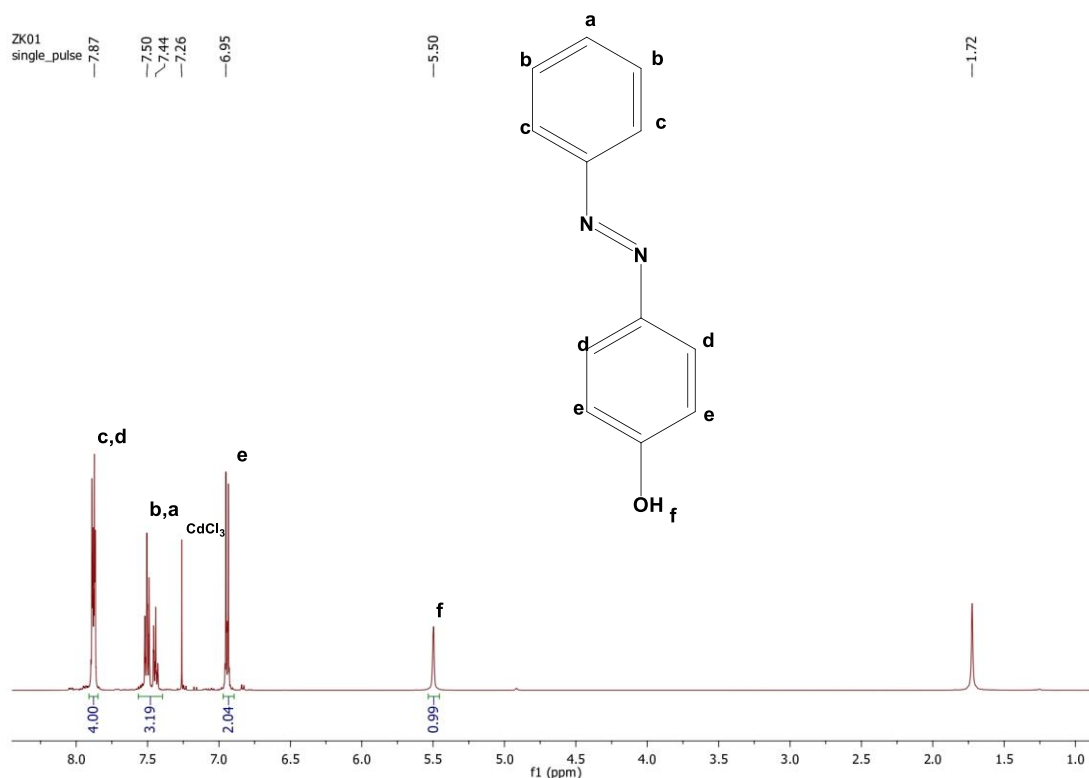
In third step, by using Click reaction over rotaxane having anthracene and tert-butyl benzene and X23C7 as a macrocycle yield to an supramolecular complex which shows stimulation on exposing halides anion and TFA and DBU.

3.3. Experimental Section

a) Synthesis of 4-hydroxyazobenzene

To synthesize 4-hydroxyazobenzene, 1 ml of aniline was placed in a 100 ml conical flask along with added 4-5 ml HCl keeping the solution at 0°C. Subsequently, 740.90 mg of sodium nitrite was added while stirring, after 20 min the reaction mixture is filtered out, followed by the addition of phenol and 10% solution of NaOH solution. Keep it for dry in indirect sunlight. The final yield of the product is 1.70g, leading to an estimated reaction yield of around 80%.

¹H NMR (500 MHz, CDCl₃, RT): δ ppm = 7.87 (m, 4H, Ar), 7.50-7.44 (m, 3H, Ar), 6.95 (m, 2H, Ar), 5.50 (s, 1H, OH).

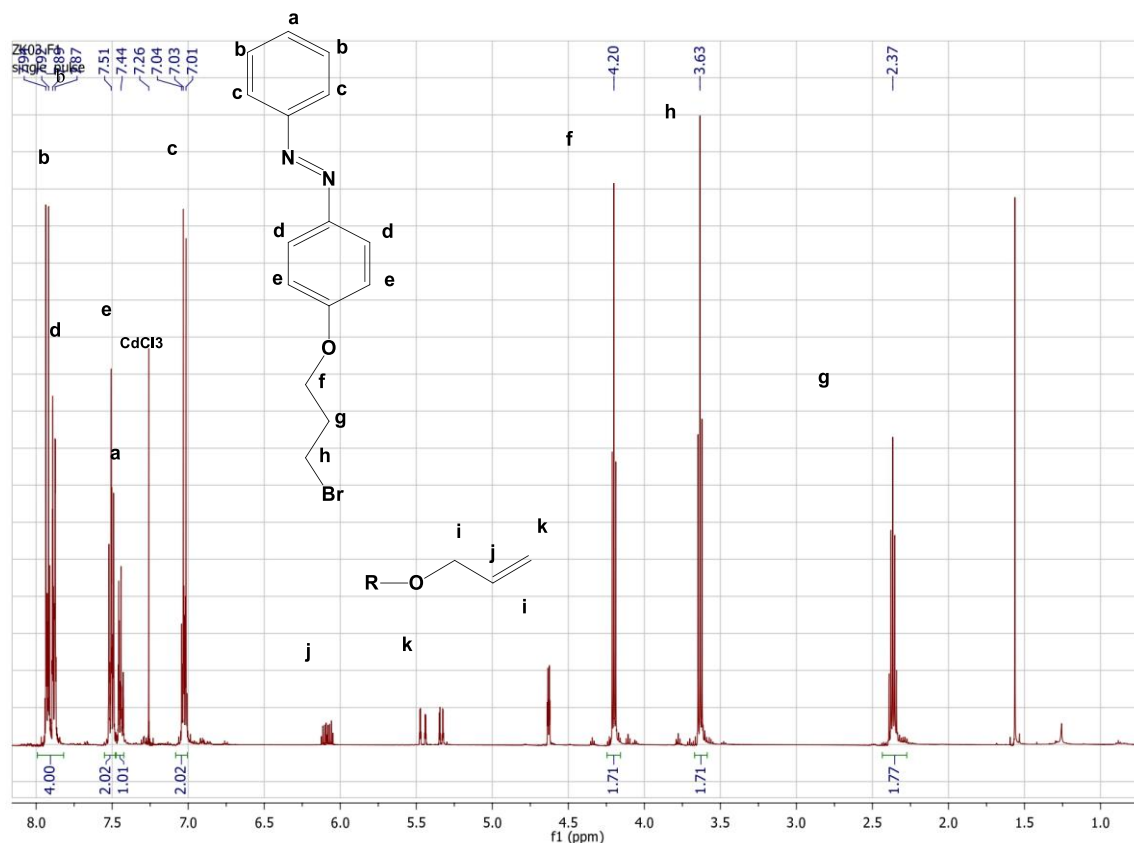


b) Addition of 1,3-dibromopropane on 4-hydroxyazobenzene

For adding 1,3-dibromopropane, 250mg of 4-hydroxyazobenzene was placed in a 100 ml 2 neck RBF under a nitrogen environment. Subsequently, 348.54mg of K₂CO₃ and Dry ACN were added, followed by the addition of 381.87mg of 1,3-dibromopropane. Keep it for refluxing and heating at 80°C for 36 hrs. The product purification process includes column chromatography utilizing a (0-2)% EA-Hexane solvent for seven iterations, TLC analysis

performed using 5% EA-Hexane. The final yield of the purified product is 225.1mg, leading to an estimated reaction yield of around 56%.

^1H NMR (500 MHz, CDCl_3 , RT): δ ppm = 7.94-7.87 (m, 4H, Ar), 7.51-7.44 (m, 3H, Ar), 7.04-7.01 (m, 2H, Ar), 4.20 (s, 2H, CH_3), 3.63 (s, 2H, CH_3), 2.37 (s, 2H, CH_3).

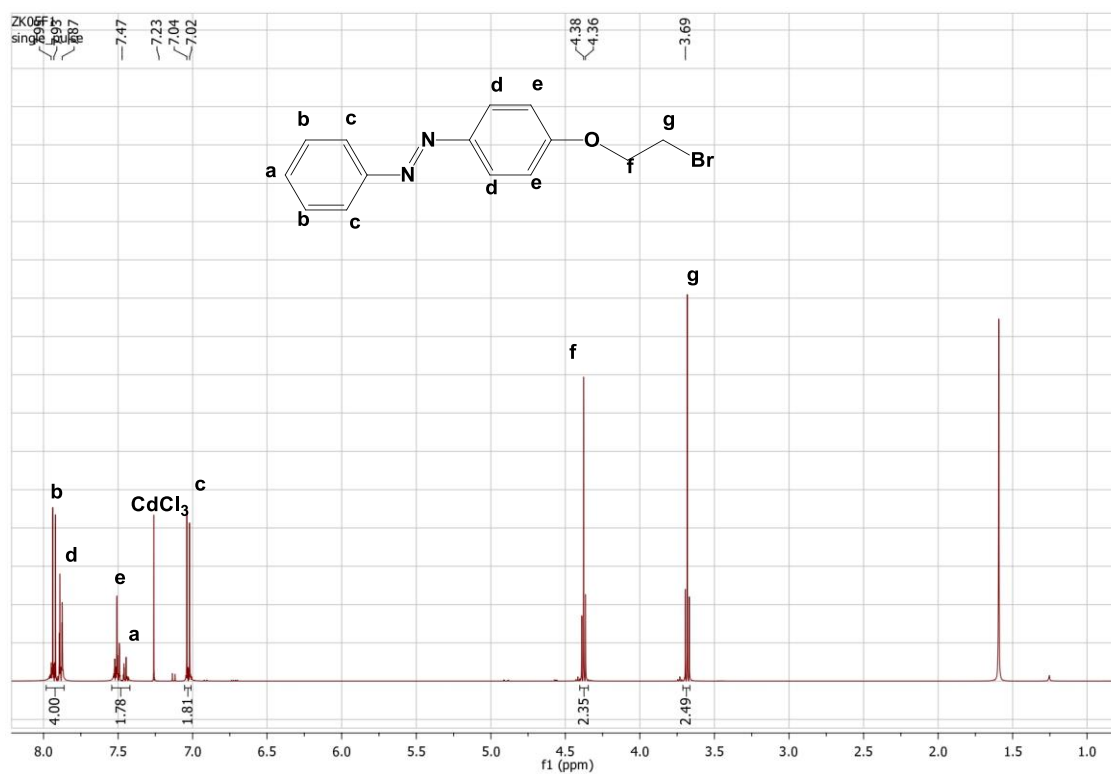


c) Addition of 1,2-dibromoethane on 4-hydroxyazobenzene

For adding 1,2-dibromoethane, 500mg of 4-hydroxyazobenzene was placed in a 100 ml 2 neck RBF under a nitrogen environment. Subsequently, 1.64g of Cs_2CO_3 and Dry ACN were added, followed by the addition of 710.67mg of 1,2-dibromopropane. Keep it for refluxing and heating at 80°C for 36hrs. After analysing the aliquot the reaction was not proceeded thus we added 1.64g of Cs_2CO_3 , 710.67mg of 1,2-dibromopropane and 83.73mg of KI for 12hrs. The product purification process includes column chromatography utilizing a (0-1.5)% EA-Hexane solvent for three iterations, TLC analysis performed using 5% EA-Hexane

The final yield of the purified product is 224.4mg, leading to an estimated reaction yield of around 30%.

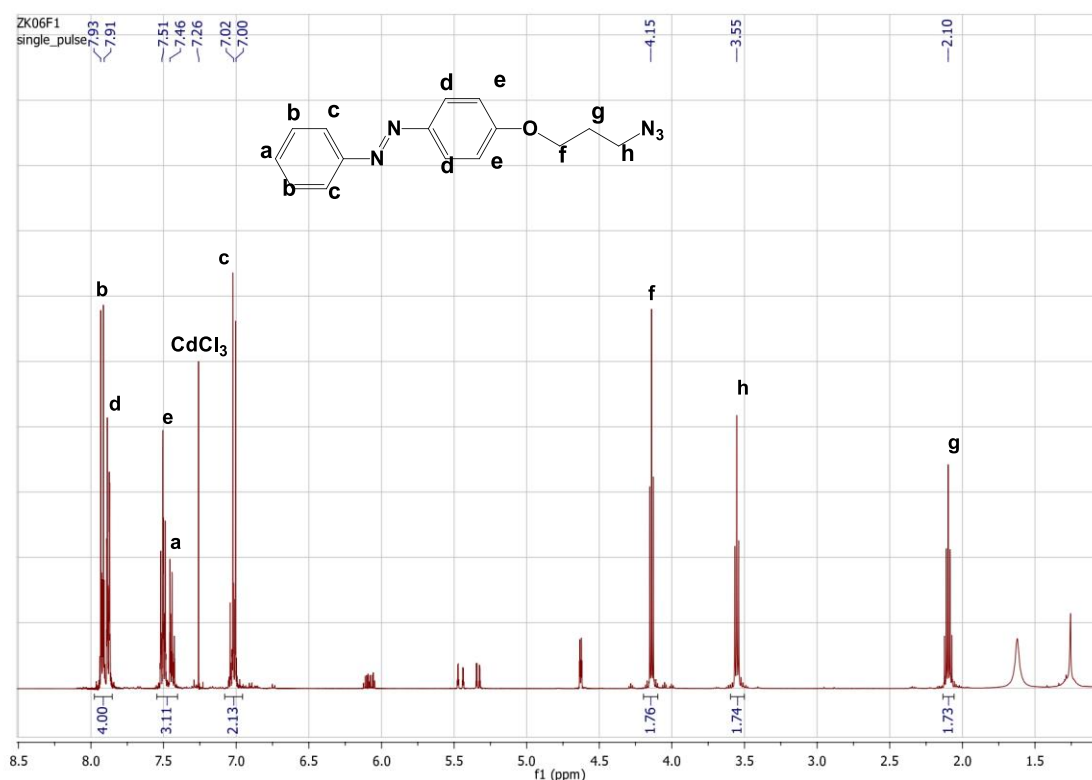
^1H NMR (500 MHz, CDCl_3 , RT): δ ppm = 7.93 (m, 4H, Ar), 7.47 (m, 3H, Ar), 7.02 (m, 2H, Ar), 4.38 (s, 2H, CH_2), 3.69 (s, 2H, CH_2).



d) Addition of NaN₃ on (E)-1-(4-(3-bromopropoxy)phenyl)-2-phenyldiazene

For azide reaction of (E)-1-(4-(3-bromopropoxy)phenyl)-2-phenyldiazene, 225.0mg of (E)-1-(4-(3-bromopropoxy)phenyl)-2-phenyldiazene was placed in a 100 ml 2 neck RBF under a nitrogen environment. sat 55°C for 24hrs. The final yield of the product is 191.9mg, leading to an estimated reaction yield of around 97%.

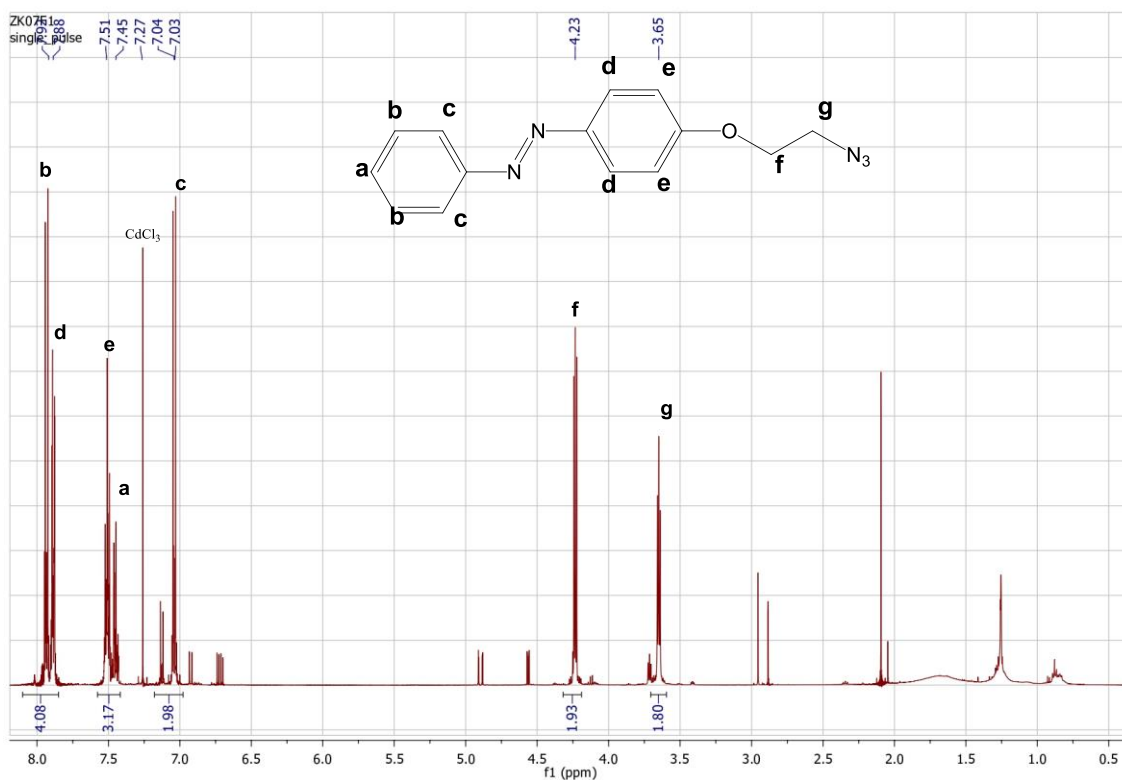
¹H NMR (500 MHz, CDCl₃, RT): δ ppm = 7.94-7.91 (m, 4H, Ar), 7.51-7.46 (m, 3H, Ar), 7.02-7.00 (m, 2H, Ar), 4.15 (s, 2H, CH₂), 3.55 (s, 2H, CH₂), 2.10 (s, 2H, CH₂).



e) Addition of NaN_3 on (E)-1-(4-(2-bromoethoxy)phenyl)-2-phenyldiazene

For all reaction of (E)-1-(4-(2-bromoethoxy)phenyl)-2-phenyldiazene, 225.0mg of (E)-1-(4-(2-bromoethoxy)phenyl)-2-phenyldiazene was placed in a 100 ml 2 neck RBF under a nitrogen environment. Subsequently, DMF were added, followed by the addition of 91.53mg of NaN₃. Keep it for refluxing and heating at 55°C for 24hrs. The final yield of the product is 191.9mg, leading to an estimated reaction yield of around 97%.

¹H NMR (500 MHz, CDCl₃, RT): δ ppm = 7.92-7.88 (m, 4H, Ar), 7.51-7.45 (m, 3H, Ar), 7.04-7.03 (m, 2H, Ar), 4.23 (s, 2H, CH₃), 3.65 (s, 2H, CH₃).



Chapter 4: Conclusion

- ✓ My internship has been a valuable and enriching experience that has deepened my understanding of supramolecular chemistry and molecular machines.
- ✓ This is my 1st internship, during this period, I went through many articles which discussed about how we are evolving ourselves from one period to other.
- ✓ Like for sensors we are shifting ourselves from **electrical resistance and capacitance to chemical stimulation**.
- ✓ Through my research project, I gained hands-on experience with various techniques such as **setting up a chemical reaction, monitoring a chemical reaction with TLC and purification using a column chromatography**.
- ✓ This project has not only honed my research skills but also instilled in me a deeper appreciation for the potential applications of supramolecular chemistry in addressing real-world challenges.
- ✓ During this internship, I also learned how to draw various structures using **ChemDraw software**, , read many **research articles** prepared my own internship **report**, prepare references using **Mendeley software**.
- ✓ Overall, I enjoyed a lot, and completely enjoyed this summer break. This internship has been a rewarding experience that has shaped my understanding and provided approach to scientific research. I am confident that the skills and knowledge gained during this internship will serve me well in my future endeavours.

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