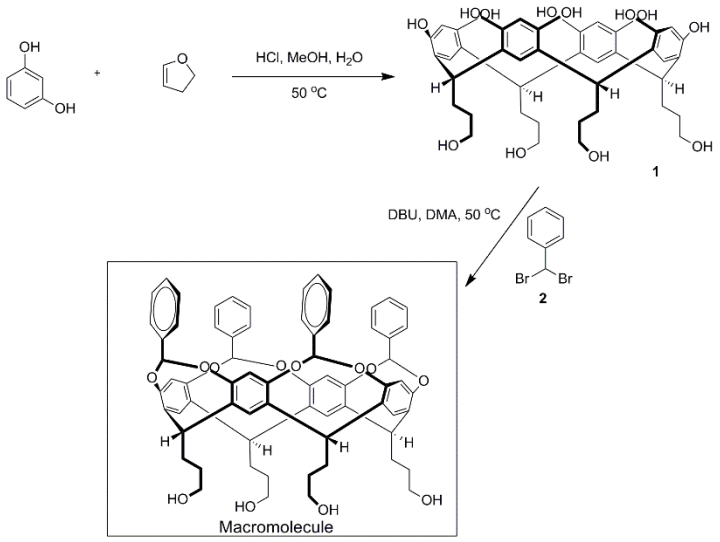
A. Title: **Water Soluble Receptor for Polyaromatic Hydrocarbon (PAH) Detection**

Dr. Rajib Choudhury, Assistant Professor of Chemistry

B. Restatement of problem researched or creative activity. The main focus of this research project was to develop a new water-soluble macrocyclic receptor built with aromatic rings. Our hypothesis was that the new macrocycle would remain moderately water-soluble due to the attached hydrophilic groups (scheme 1), whereas the inner cavity of the macrocycle would sequester Polyaromatic Hydrocarbons (PAHs). *The extent of binding would depend on the size-shape complementarity of the binding pairs as well as types of interactions, which would lead to the separation of different polyaromatic hydrocarbons in samples.*

C. Brief review of the research procedure utilized. The first aim of this research project was to synthesize a new water-soluble macromolecule. For this purpose, we have utilized resorcinarene synthesis methodology followed by bridging of resorcinarene with dibromomethyl benzene (**2**, Scheme 1).



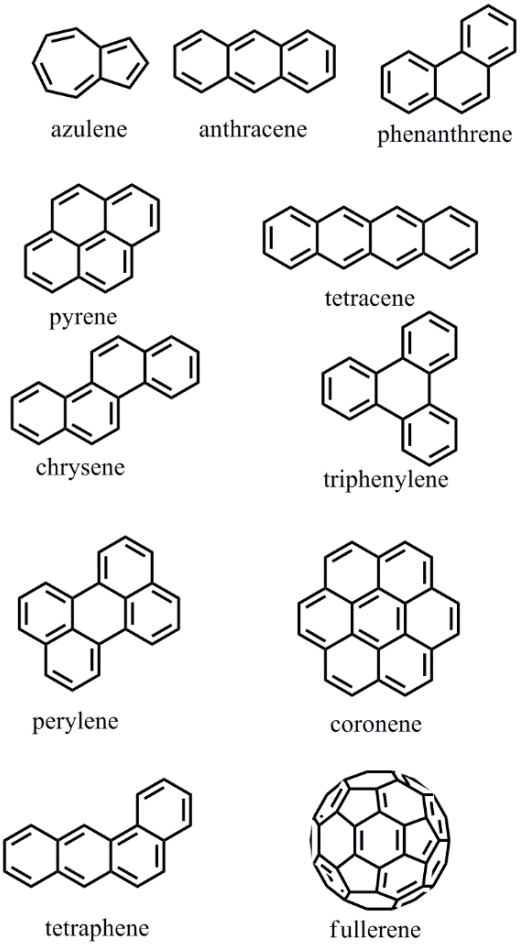
Scheme 1. Synthesis scheme for water-soluble macromolecule.

Briefly, commercially available 2, 3-dihydrofuran was coupled to resorcinol to obtain four alkyl chains attached to hydroxyl groups (-OH) (Scheme 1, compound **1**). After stirring for five days at 50 °C a mixture of macromolecules of different ring sizes was obtained. The desired macrocyclic product was extracted by repeated ultra-sonication in water followed by vacuum filtration. The size and volume of the binding pocket of the macromolecule was then increased by base catalyzed coupling of **1** with **2** (scheme 1).

Compound **1**, in presence of non-nucleophilic base DBU and solvent dimethylacetamide (DMA), was stirred with compound **2** for two days at 50 °C. The DMA was subsequently removed under reduced pressure and the residue was dried overnight under high vacuum. The residue was

dissolved in chloroform and extracted with deionized water and brine solution. The organic layer was dried quickly with anhydrous Na_2SO_4 and filtered. The volume of solution was reduced under low pressure to 20 mL and precipitated from hexane. The final compound was then characterized by UV-vis, IR, and ^{1}H NMR spectroscopy.

Next, we investigated complexation of the macrocycle with eleven Polyaromatic Hydrocarbons by molecular docking in hope of transferring the knowledge of *virtual screening* to the synthetic supramolecular host–guest systems.



Briefly, Host–guest molecular dockings were performed on a single CPU Windows-OS computer (64-bit) with 3.30 GHz processor and 8.00 GB of RAM on Vina 1.1.2 program (www.http://vina.scripps.edu/). The coordinate structures of the guests (Scheme 1) were constructed and optimized with MM2 force field. AutoDock Tools 1.5.6 was used for preparing host and guest input files in pdbqt format, which is a modified protein data bank format containing atomic charges, atom type definitions and, for ligands, topological information. During input file preparation, Gasteiger partial charges were added to each guest molecule, non-polar hydrogen atoms were merged, and torsional rotatable bonds were defined. All the single bonds were made rotatable, whereas double and triple bonds were kept as rigid (non-rotatable). All other parameters were kept at their default values. However, a rectangular box of dimension 20 × 24 × 22 Å^3 with 1.0 Å grid spacing was constructed to encompass the entire macromolecule. The exhaustiveness of each docking was kept at 8 while the seed was varied randomly as generated by the program.

D. Summary of findings.

The melting point of the macromolecule was >250 ^{o}C. FTIR study indicates presence of –OH groups (3300-3500 cm^{-1}, broad), aromatic C=C (1450-1650 cm^{-1}), and C-O groups (~950 cm^{-1}). UV-vis study in DMSO indicates presence of non-conjugated aromatic rings (λ_{max} = 280 nm). ^{1}H NMR study indicates presence of aromatic hydrogens (8.87 ppm, 7.91 ppm, 7.17 ppm, and 6.10 ppm), two types of methylene hydrogens (2.04 ppm, 1.28 ppm), and aliphatic –OH groups. All these studies suggest successful synthesis of the proposed macromolecule.

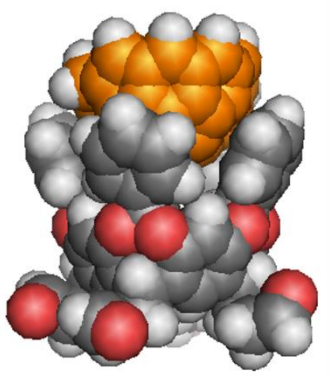


Figure 1. Docking of a fullerene molecule within the macromolecule.

The quantitative binding data suggest that the shape, size, and hydrophobicity of the PAHs are the controlling factors for binding. Azulene, having only two aromatic rings remains at the bottom of the list (-7.4 kcal/mol). Binding affinity gradually increases as the number of aromatic ring increases (table 1). The maximum binding affinity recorded was for fullerene (-12 kcal/mol; figure 1).

Molecule	**Binding affinity (kcal/mol)**
Anthracene	-7.8
Azulene	-7.4
Chrycene	-8.8
Coronene	-7.8
Perylene	-7.4
Phenanthrene	-8.4
Pyrene	-7.6
Tetracene	-8.0
Tetraphene	-8.9
Triphenylene	-8.3
Fullerene	**-12.0**

Table 1. Binding affinities of new macromolecule with PAHs.

D. Conclusions and recommendations. We have synthesized a water-soluble macrocycle capable of binding PAHs. Computational study suggests binding affinity increases as the shape and size of the PAHs become complementary to the macrocycle cavity size. This property indicates that PAHs can be extracted from aqueous solution in presence of this new macrocycle. Experimental investigations of binding affinity with a mixture of PAHs of various sizes are underway. This study will show the efficacy of this macrocycle as a pollutant removal receptor from water.