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Name of Scholar: **Ishfaq Ahmad Rather**

Name of Supervisor: **Dr. Rashid Ali**

Name of Department: **Chemistry**

Topic of Research: **Design, synthesis and applications of functionalized calix[4]pyrroles**

Findings

The thesis entitled "Design, synthesis and applications of functionalized calix[4]pyrroles" consists of seven chapters and deals with the design, synthesis and diverse applications (anion binding, sensing, adsorption, and transmembrane ion transport) of functionalized calix[4]pyrroles (C4Ps), being regarded as emergent supramolecular functional materials. Chapter I deals with historical background, various synthetic strategies and diverse applications of functionalized C4Ps. Chapter II deals with the green synthesis of diverse functionalized dipyrromethanes (DPMs) and C4Ps in respectable yields by utilizing a deep eutectic solvent of *N*,*N'*-dimethyl urea (DMU) and L-(+)-tartaric acid (TA) in the ratio of 7:3 at 70-80 ^{o}C. Chapter III, Part A deals with facile synthesis of new one-walled *meso*-substituted phenylboronic acid functionalized C4P and its utilization in the electrochemical sensing of dopamine and catechol. The phenylboronic acid functionalized C4P modified glassy carbon electrode (GCE) was observed to reveal exceptional stability and reproducibility in the electrochemical sensing of dopamine with a nM level limit of detection as low as 15 nM and linear correlation in the concentration range of 0.165-2.302 µM. The Part B of Chapter III deals with the application of one-walled phenylboronic extended C4P in the adsorption of paracetamol from simulated water. The isotherm modeling inferred the Freundlich model to appropriate the equilibrium data, with high Langmuir adsorption capacity (479.30 mg g^{-1} at 298 K). The $\Delta H°$ (–53.98 kJ mol^{-1}) along with a drop in adsorption capacity with temperature implied the process to be exothermic. The kinetics was in accord with the pseudo-second order model specifying electrostatic interactions. Chapter IV, Part A deals with synthesis and anion binding studies of *meso*-substituted one-walled phthalimide-based C4P (*m*-PC4P) through UV-Vis spectroscopy and time-dependent density functional theory (TD-DFT). The *m*-PC4P displayed higher anion binding affinities in comparison to the parent C4P system, due to the additional weak CH-anion interactions besides four NH-hydrogen bonds of the C4P framework. The Part B of Chapter IV deals with the application of *m*-PC4P in the adsorption of NO_3^- ion from aquatic phase. The *m*Pth-C4P demonstrated excellent adsorption competence (> 91%) within 16 min from a [NO_3^-] of 20 mg L^{-1}, which translates into a good pseudo-second order rate constant value of 0.026 g mg^{-1} min^{-1}. Freundlich model was the best fit model pointing out multilayer adsorption with high Langmuir adsorption capacity (239.30 mg g^{-1} at 298 K). Chapter V, Part A deals with the synthesis and anion binding investigation of one-walled *meso*-cyanophenyl functionalized C4P. Notably, the UV-Vis absorbance titrations performed in CH_3CN solvent, revealed significantly higher anion binding of cyanophenyl one-walled C4P receptor in comparison to the simple C4P, thereby endorsing the involvement of electron deficient cyanophenyl moiety in anion recognition event through anion-π interactions. Part B of Chapter V deals with the anion-binding studies of one-walled *meso*-phenylboronic acid functionalized C4Ps with halides, linear anions, and trigonal/tetrahedral oxoanions. Overall, the anion binding affinity of C4P receptor holding boronic acid moiety at *meta*-position of phenyl ring *w.r.t. meso*-position of C4P has been found higher than those of C4P receptor holding same moiety at *para*-position of phenyl, presumably due to more cooperative NH and OH hydrogen bonding interactions. Chapter VI deals with the selective chemodosimetric detection and quantification of hydrazine, by means of *β*-dicyanovinyl substituted C4P sensor using UV-Vis spectroscopy. It allows the sensing of hydrazine with a LOD of 1.3 mg/L and a linear response on the 10-1000 µM range. Chapter VII, Part A deals with the synthesis and anion binding studies of trifluorophenyl/phthalimide extended C4Ps and naphthalenediimide (NDI) bridged *bis*-C4Ps systems. In terms of binding stoichiometry, a 1:1 binding mode has been observed and higher anion binding affinities have been observed in these novel two-walled/*bis*-C4P systems in comparison to simple/one-walled C4Ps reported in the literature. This is probably due to involvement of complementary anion-π and CH-anion interactions, which assists preliminary NH-hydrogen bonding interactions of C4P framework in binding a particular anion. Among *cis/trans*-isomers of two trifluorophenyl C4Ps, *cis*-isomer offer higher anion binding affinity in comparison to *trans*-isomer due to more cooperative effect of NH-hydrogen bonding and anion-π interactions. Part B of Chapter VII deals with chloride ion transport of two walled trifluorophenyl/phthalimide C4P receptors across lipid bilayer. When measured across bilayer lipid membrane (EYPC-LUVs⊃HPTS), the more active two walled trifluorophenyl C4P transporter offered EC_{50} value of 0.39 µM and Hill coefficient of n~1, indicating the involvement of one receptor molecule in catalyzing ion transport process. Detailed ion-transport mechanistic studies on more active ion transporter have revealed that ion transport occurs through Cl^-/NO_3^- antiport mode.