

PROFORMA FOR APPLICATION

Discipline: **CHEMISTRY**

1. Name in full (in BLOCK LETTERS): **RUPAM JYOTI SARMA**

2. Present address:

Dr. Rupam Jyoti Sarma

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3. Date of Birth (Age as on December 31, of the previous year): 31 years (proof of age enclosed)

4. Academic qualifications (including research degrees):

Degree	University/ Institute	Year	Subjects	Percentage/CPI
B. Sc. (Chemistry)	Gauhati University	1998	Chemistry (Major), Physics, Mathematics, English	68.9
M. Sc. (Chemistry)	Gauhati University	2001	Organic Chemistry (special), Inorganic Chemistry, Physical Chemistry, Quantum Chemistry	73.2
Ph. D. (Chemistry)	Indian Institute of Technology Guwahati	2006	Chemistry	9.25

5. Details of employment and nature of duties:

Since October 2007, I have been working as Lecturer of Organic Chemistry in the Department of Chemistry, Gauhati University; duties include post-graduate teaching and research.

6. Awards and/or other recognitions received (if any):

Commonwealth Split-Site Doctoral Fellowship (2003-04): Department of Chemistry, University of Durham United Kingdom

Qualified for CSIR-Junior Research Fellowship through the combined CSIR-UGC National Eligibility Test Examination (December 2000), held by the Council of Scientific and Industrial Research and University Grants Commission India

Qualified for Graduate Aptitude Test for Engineering (GATE 2001): Percentile Score 99.17 (All India Rank 15)

7. Field of specialization: *Synthetic Organic Chemistry and Supramolecular Chemistry*

8. Research experience (Details of research work in not more than 500 words may be given, highlighting the applicant's own contributions. Indicate the institution where the work was carried out)

July 2001–October 2006: CSIR–Research Fellow in the Department of Chemistry, Indian Institute of Technology Guwahati (Ph. D. Adviser Prof. Jubaraj B. Baruah).

During the course of my doctoral studies I studied some of the aspects related to the self-assembly of substituted bis-phenols from a supramolecular perspective. From the spectroscopic and structural studies of bis-phenols we were able to discern the influence of hydrogen bond donor and acceptor groups on the self-assembly and hence on the packing of the compounds. An interesting outcome of this was our identification of the selectivity related to guest inclusion abilities of such bis-phenol assemblies, and in particular of aromatic compounds such as benzene/toluene. An important revelation was the identification of pyridyl bis-phenols as supramolecular building blocks in the construction of anion template self-assemblies. While studying the self-assembled structures of these compounds in the solid-state, we noted distinct structural and geometrical preferences of the intermolecular C–H... π interactions, and could be associated with the occurrence of polymorphs under certain conditions. In addition we found that during the self-assembly process, the pyridyl bis-phenols exhibit a unique preference for methyl and ethyl sulfate anions over hydrogen sulfate or sulfate in aqueous environments.

In the course of this work we established a simple route for the synthesis of bis-phenols and their derivatives, and subsequently revealed a useful strategy for the synthesis of substituted dibenzoxanthenes. Further we were able to show that the bis-phenols could be oxidized to the corresponding quinone methides; these compounds show interesting pH dependent optical properties and can lead to radical anions that were stabilized by delocalization (as evident from in-situ ESR studies).

Structural and spectroscopic aspects related to the self-assembly of aromatic donor-acceptor systems, particular those incorporating functionalized naphthalimide and pyromellitic diimide motifs were also studied. We made a few critical observations on the effect of stacking interactions on the charge transfer interactions between aromatic donor and acceptor systems.

Apart from this, we made key advances in the synthetic and structural aspects of transition metal carboxylate complexes, especially with regard to aqua-bridged dinuclear complexes that are structurally analogous to different aminopeptidases found in biological systems.

July 2001–October 2006: Post-Doctoral Research Associate in the Department of Chemistry, University of Geneva, Switzerland (Adviser Dr. Jonathan R. Nitschke)

The central focus of my post-doctoral work was the identification of the driving forces that operate in systems composed of multiple components capable of self-assembling under thermodynamic control, a subject that can be related to dynamic combinatorial chemistry. In this context our objective was the construction of complex structures through self-assembly of multivalent ligands in the presence of suitable templates. We could elucidate the basic rules governing the self-assembly of ligands from their corresponding subcomponents, and in the presence of copper(I) and iron(II) as templates. The construction of complex structures from complicated mixtures under thermodynamic conditions relies much on the self-sorting (or self-assembling) ability of the composite system. From our studies we found that the self-sorting ability is a consequence of two levels of reversible interactions: dynamic imine (covalent) bonds and metal-ligand (coordinative) interactions, and later disulfide linkages were also found to be compatible. This was illustrated by the perturbation of dynamic exchange between two disulfide components using the reversibility of coordinative interactions, imine exchange and both. Subsequently we were able to invoke dynamic self-sorting in complex libraries (mixtures) of ligands to select and amplify the formation of a given structure or combination of structures through the process of metal ion driven self-assembly of the library members.

9. Details of the R & D project proposed:

Project Title: Coordination-Driven Assembly and Disassembly of Peptide-Ionophores as a Strategy towards the Design of Stimuli Responsive Multicomponent Systems

Executive Summary:

The Project proposed here involves the synthesis of peptide-based crown ethers (peptide-ionophores) which will be utilized as building blocks for constructing supramolecular assemblies; in this context we also propose to explore the template driven self-assembling properties of these peptide-ionophores under various conditions. Studies have shown that the interactions between the crown ether (or polyether) motifs and ammonium (or metal) ions are quite specific and apparently serve as a design principle, as exemplified by the creation of supramolecular assemblies¹ and interlocked molecules². We also noted that the incorporation of crown (or polyether) groups into an oligomeric backbone is a simple, yet efficient approach towards the design of self-assembling systems³ such as foldamers, receptors and dendrons. With regard to the proposed work, we suggest that interactions involving the crown motif of peptide-ionophores with suitable templates can be utilized to direct the organization of small molecules into discrete supramolecular architectures that have dimensions in the nanometer scale. Notwithstanding the role of template driven self-

assembly in biological systems (e.g. tobacco mosaic virus), similar strategies can be invoked for the creation of complex architectures from systems consisting of multiple components with the aim to develop novel materials for catalytic⁴, opto-electronic⁵, liquid crystal⁶ and sensor applications⁷.

1. Chi, K.-W.; Addicott, C.; Stang, P. J. *J. Org. Chem.* **2004**, *69*, 2910-2912; Schultz, A.; Laschat, S.; Saipa, A.; Geißelmann, F.; Nimtz, M.; Schulte, J. L.; Baro, A.; Miehllich, B. *Adv. Funct. Mater.* **2004**, *14*, 163-168; Fenniri, H.; Deng, B.-L.; Ribbe, A. E. *J. Am. Chem. Soc.* **2002**, *124*, 11064-11072; Percec, V.; Cho, W.-D.; Ungar, G.; Yearley, D. J. *J. Am. Chem. Soc.* **2001**, *123*, 1302-1315
2. Leigh, D. A.; Wong, J. K.Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174-179; Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2000**, *39*, 3348-3391
3. Ghosh, S.; Ramakrishnan, S. *Angew. Chem. Int. Ed.* **2005**, *44*, 5441-5447; Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 351-360; Gruter, G.-J. M.; de Kanter, F. J. J.; Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F. J. *J. Am. Chem. Soc.* **1993**, *115*, 12179-12180; Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853-908; Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417-425
4. Vaestilae, P.; Zaitsev, A. B.; Wettergren, J.; Privalov, T.; Adolfsson, H. *Chem. Eur. J.* **2006**, *12*, 3218-3225; Murugavel, R.; Walawalkar, M. G.; Dan, M.; Roesky, H. W.; Rao, C. N. R. *Acc. Chem. Res.* **2004**, *37*, 763-774
5. Ajayaghosh, A.; Vijayakumar, C.; Varghese, R.; George, S. J. *Angew. Chem. Int. Ed.* **2006**, *45*, 456-460; Jonkheijm, P.; van der Schoot, P.; Schenning, A. P. H. J.; Meijer, E. W. *Science* **2006**, *313*, 80-83; Heoben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491-1546
6. Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Martin Tosoni, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 4832-4887 and references cited therein
7. McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537-2574; Pu, L. *Chem. Rev.* **2004**, *104*, 1687-1716; Kruppa, M.; Mandl, C.; Miltschitzky, S.; König, B. *J. Am. Chem. Soc.* **2005**, *127*, 3362-3365

Aims and Objectives of the Project

The overall objective of this Project is to study the scope of coordination (and/or template) driven self-assembly and disassembly of peptide-ionophores into complex structures such as clefts, loops (or turns) and helices. Subsequently we look forward to applying this understanding in the design and development of stimuli responsive supramolecular assemblies. In order to achieve this objective, we propose to undertake the research work in a phased manner, and by identifying suitable targets (or approaches) as outlined below:

1. Design, synthesis and characterization of crown based peptide-ionophores:

This is the initial phase of the project, and will encompass extensive organic synthesis so as to assemble the starting materials and the key building blocks for the construction of the peptide-ionophores. An important part of this work is the optimization of the different synthetic strategies that will be utilized for the synthesis of the chiral peptide fragments (as in compounds incorporating dipeptide residues). At the same time we will assess the feasibility of the various peptide-ionophore motifs towards different solvent environments, an issue that will be of prime importance so far as further investigations are concerned. It may be mentioned that apart from synthesis, the compounds prepared as part of this project will be analyzed and completely characterized.

- Utilize these peptide-ionophores as building blocks for the construction of supramolecular structures:

After successful synthesis and characterization of the building blocks and the proposed peptide-ionophores, we will study the possibility of organizing these molecules into supramolecular structures by modulating their covalent and non-covalent interactions. In this context we would like to explore the influence of specific amino acid sequences (with dipeptide, for instance) on the formation of secondary motifs such as clefts, helices, and loops. This work will require elaborate studies using IR spectroscopy, fluorescence spectroscopy, NMR spectroscopy and mass spectrometry (LC-MS), and possibly single crystal X-ray diffraction.

- To examine the effect of added template(s) on the formation of discrete nanoscale assemblies from the peptide-ionophores:

Based on the above findings, we will attempt organizing the peptide-ionophores into hierarchical structures using suitable templates, such as ammonium ions. We expect to evaluate the conditions under which these compounds can be made to self-assemble into discrete nanoscale architectures or disassemble. In either case, these processes have to be characterized completely using various techniques such as NMR, mass spectrometry, CD-ORD spectrometry, single crystal X-ray diffraction and AFM/TEM.

Research work engaged in at present: Not applicable

Importance of the Project

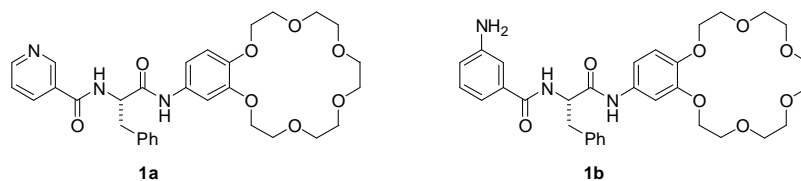
During the course of the proposed Project we seek to explore the scope of coordination (template) driven self-assembly of a few peptide-ionophores and subsequently attempt construction of complex structures through self-assembly of these compounds. The proposed work is expected to provide a model system to study intermolecular interactions (e.g. host-guest interactions) in molecules held together by non-covalent interactions; the interactions involving crown ether motifs and ammonium (or metal) ions apparently serve as a structural scaffold that bring the molecules together.

Given the crucial role played by peptide-peptide interactions in biological systems, the study of suitably designed peptidomimetic systems can have important implications on our understanding of such interactions. We imagine that the association (i.e. via self-assembly) of two or more peptide-ionophores through non-covalent interactions can result in the formation of cleft-like structures, turns and helices. As such we may explore the limits of coordination (template) driven organization of functionalized ionophores into discrete supramolecular architectures that have dimensions in the nanometer scale. Such systems are of fundamental importance in the context of the present state-of-the-art in organizing

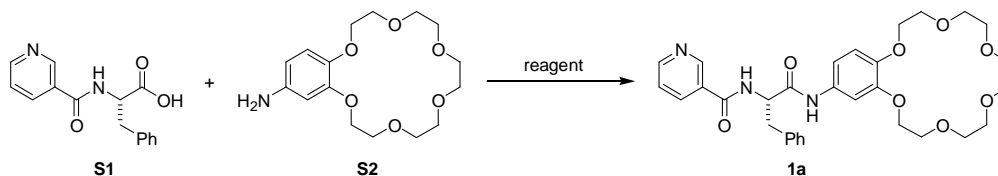
complex architectures from simple molecular components, reminiscent of macromolecular structures such as nucleic acids and enzymes that operate in biological systems. Finally, we anticipate that under suitable conditions the peptide-ionophore models proposed here can be made to self-assemble into functional materials that exhibit dynamic switching properties.

Detailed plan of action to achieve the objectives (including methodology, in 250 words):

The initial phase of this research project would involve the synthesis and characterization of a few peptide based ionophores (representative examples, **1a** and **1b**).

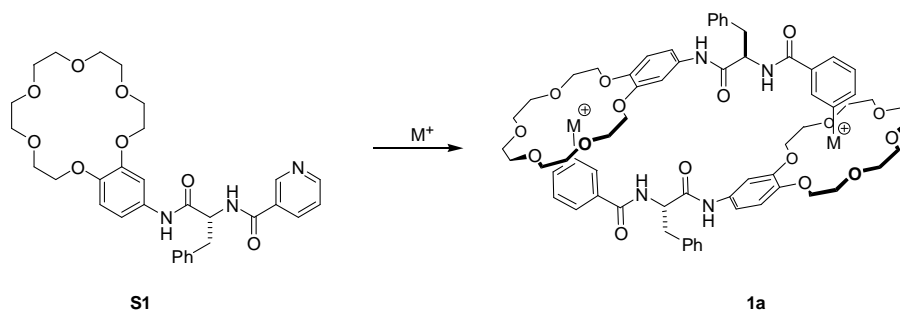


A generalized strategy for the synthesis of these compounds involves the coupling of the crown ether (**S2**) to the functionalized peptide residue (**S1**) which can be prepared from readily available starting materials (Scheme 1).



Scheme 1

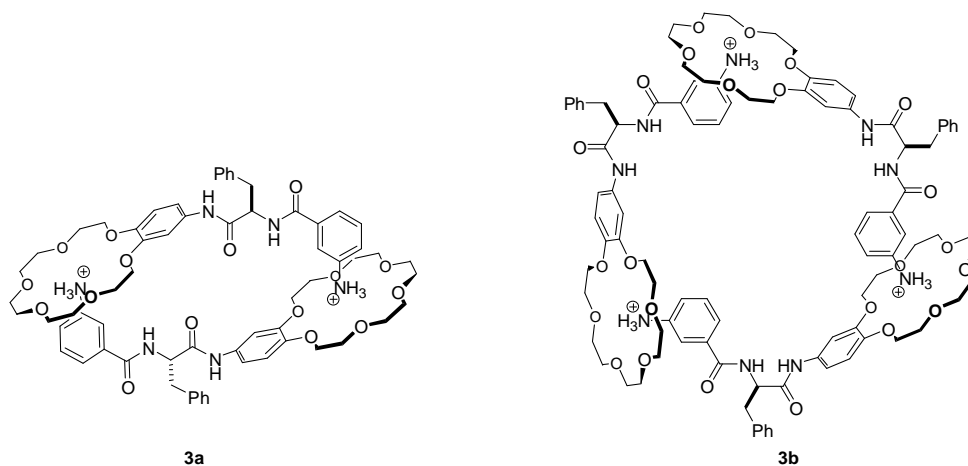
As mentioned previously, interaction of a cation with the crown motif can be utilized to direct the formation of supramolecular structures. As such the incorporation of a coordinating group (such as pyridine in **1a**) using a spacer that will provide a complementary binding site for an incoming cation.



Scheme 2

This complementary interaction involving a metal ion (M^+) and the crown unit in the presence of a coordinating group can be utilized to direct the organization of the peptide backbone as in **1a**. Under suitable conditions, compound **1a** can be expected to form

supramolecular clefts (Scheme 2), capable of encapsulating molecules or ions due to their interactions with peptide units of the backbone.



It is anticipated that the crown units will interact with the ammonium ions (upon protonation of the amino group as in **1b**) leading to the formation of discrete supramolecular structures. Apparently, protonation of the amino group of compound **1b** can lead to supramolecular clefts (such as **3a**), which should disassemble in the deprotonated state. This provides the option of possibly switching between the self-assembled supramolecular structures by regulating the protonation state of the amino group, and addition of an appropriate template. As such it is reasonable to expect that the association of multiple peptide-ionophores will lead to more complex architectures such as **3b**. In this regard, detailed analysis involving IR, NMR and mass spectrometry both in solution and in the solid-state are envisaged in order to explore the potential of this work.

Budget requirements for the Proposed Project:

Head/Items	Estimated Budget (in Rs.)			Total (in Rs.)
	1 st year	2 nd year	3 rd year	
A Project Assistant (or JRF) @ Rs.8,000/- p.m.*	96,000	96,000	96,000	288,000
B 1. Consumables **				
• Chemicals	80,000	60,000	40,000	
• Solvents (including HPLC grade)	50,000	40,000	40,000	
• NMR solvents	30,000	30,000	20,000	
• Glassware	20,000	20,000	20,000	
Total (B1)	180,000	150,000	120,000	450,000
2. Contingency***	50,000	50,000	50,000	
3. Travel expenses	20,000	30,000	30,000	
Total (B2+B3)	70,000	80,000	80,000	230,000
C Equipments (Quotations enclosed)				
• Rotary Evaporator (BIBBY STERILIN)	210,000			
• Mettler Toledo Balance	145,125			
• Normag UV lamp	59,800			
• Corning Hotware Hot-plate Stirrer	15,077			
• IKA C-MAG MS7 Hot-plate Stirrer	18,423			
• IKA C-MAG MS-4 Stirrer	17,733			
• IKA C-MAG HS4 Hot-plate Stirrer	25,875			
Total (C)	492,033			492,033
Total (A+B+C)				1,460,033

* I will be extremely grateful if sufficient funds are provided so as to accommodate a Project Assistant / JRF for implementing the Proposed Project.

** Since the proposed project involves extensive organic synthesis (involving optically pure amino acids and peptides), sufficient funds need to be allocated for procurement of starting materials/chemicals, solvents, and coupling reagents (which are expensive).

*** Apart from other contingency expenses, the work will often require Mass Spectrometry (such as LC-MS and ES-MS) and X-Ray diffraction analysis for advanced characterization. Since these facilities are not available in Gauhati University, we envisage the allocation of sufficient funds (i.e. contingency) that will enable us to access these facilities elsewhere.

10. List of publications:

- 1 R. J. Sarma, J. R. Nitschke *Self-Assembly in Systems of Subcomponents: Simple Rules, Subtle Consequences* *Angewandte Chemie International Edition* **2008**, *47*, 377-380
- 2 R. J. Sarma, S. Otto, J. R. Nitschke *Disulfides, Imines, and Metal Coordination within a Single System: Interplay between Three Dynamic Equilibria* *Chemistry- A European Journal* **2007**, *13*, 9542-9546
- 3 R. J. Sarma, J. B. Baruah *Supramolecular and Host-Guest Chemistry of Bis-Phenols and Analogues* *Crystal Growth and Design* **2007**, *7*, 989-1000
- 4 A. Karmakar, R. J. Sarma, J. B. Baruah *Structural Aspects and Properties of Salt and Inclusion Compounds of 8-Hydroxyquinoline-based Amides* *CrystEngComm* **2007**, *9*, 378-388
- 5 A. Karmakar, R. J. Sarma, J. B. Baruah *Polymorphism in an Aqua Bridged Binuclear Cobalt(II)-(2-nitrobenzoate) complex* *European Journal of Inorganic Chemistry* **2007**, 643-647
- 6 R. J. Sarma, C. Tamuly, J. B. Baruah *Synthesis and Characterisation of N-Substituted Bis-Phenols as Precursors for Unsymmetrical Triphenylmethane Cations* *Dyes and Pigments* **2007**, *72*, 75-79
- 7 R. J. Sarma, C. Tamuly, N. Barooah, J. B. Baruah *Role of π -Interactions in Solid-State Structures of a Few 1,8-Naphthalimide Derivatives* *Journal of Molecular Structure* **2007**, *829*, 29-36
- 8 A. Karmakar, R. J. Sarma, J. B. Baruah *Mechanochemical Control on Synthesis and Structures of Aqua Bridged Binuclear Nickel(II) Benzoate Complexes* *European Journal of Inorganic Chemistry* **2006**, 4673-4678
- 9 R. J. Sarma, J. B. Baruah *Hydrogen Bifluoride Mediated Hydrogen Bonded Self-Assembly of Pyridinium and Anilinium Bis-Phenols: Towards Control of C-H \cdots π Interactions* *Chemistry-A European Journal* **2006**, *12*, 4994-5000
- 10 N. Barooah, R. J. Sarma, J. B. Baruah *Metal Directed Assemblies of a Dipeptide: Formation of β -Pleated Sheets* *European Journal of Inorganic Chemistry* **2006**, 2942-2946
- 11 N. Barooah, R. J. Sarma, J. B. Baruah *Solid-State Hydrogen Bonded Assembly of Bis-(diglycyl)pyromellitic Diimide with Aromatic Guests* *CrystEngComm* **2006**, *8*, 608-615
- 12 R. J. Sarma, A. S. Batsanov, R. Katakya, J. B. Baruah *Structural Investigations on Quinone Methides for Understanding their Properties in Confined Medium* *Journal of Inclusion Phenomenon and Macrocyclic Chemistry* **2006**, *55*, 1-9

- 13 A. Karmakar, K. Deka, R. J. Sarma, J. B. Baruah *Benzoic Acid Inclusion in a Dimeric Nickel(II) complex and its Catalytic Activity* Inorganic Chemistry Communications **2006**, 9, 836-838
- 14 R. J. Sarma, J. B. Baruah *Selectivity in Guest-Host Binding in Assemblies of Bis-Phenols* CrystEngComm **2005**, 7, 608-615
- 15 R. J. Sarma, J. B. Baruah *One Step Synthesis of Dibenzoxanthenes* Dyes and Pigments **2005**, 64, 91-92
- 16 R. J. Sarma, J. B. Baruah *Synthesis and Characterisation of Bis-(3,5-dimethyl-4-hydroxyphenyl)-(aryl)methanes as Precursors for Three-State Indicators* Dyes and Pigments **2004**, 61, 39-47

11. Name of two referees conversant with applicant's work:

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Prof. S. Ramakrishnan

Department of Inorganic and Physical Chemistry,

Indian Institute of Science, Bangalore 560 012

12. Declaration:

"I hereby certify that I have not received any research grant from any funding agency as on date of application for this award."

Signature: _____

13. Forwarding note from the Head of the Organisation/Institute/University:

This is to certify that Dr. Rupam Jyoti Sarma is having a regular position in our University. The University agrees to undertake the financial and other management responsibilities for the part of the project work which will be conducted in our University. We are also aware that "No Overhead" charges will be paid to our University for carrying out this project.

Date and Place: 27-02-2008, Guwahati

Name, Signature of the Head of the University