



DCS, IISER KOLKATA presents,

SCBFM 2018

Supramolecular Chemistry in Biology and Advanced Functional Materials

ABSTRACT BOOK

29 MARCH – 30 MARCH ,
TRC AUDITORIUM (2ND FLOOR)

CONTENTS

❖ Abstracts for Lectures

❖ Posters Abstracts



ABSTRACTS FOR LECTURES

Probing the Thermodynamics of Protein-nanoparticle Interaction by Second Harmonic Light Scattering in Solution

Puspendu K. Das

Dept. of Inorganic and Physical Chemistry

Indian Institute of Science

Bangalore 560012

pkdas@ipc.iisc.ernet.in

Gold nanoparticle surface provides a biocompatible vehicle for delivery and release of a protein or peptide based therapeutic at a targeted site. Understanding the interaction of proteins with gold nanoparticle surface and the forces that stabilize such interaction are imperative in achieving nanoparticle based transport of drugs and therapeutics. Although interaction of proteins with nanoparticles are known since 1977, detailed mechanistic and quantitative information are missing. We have studied adsorption of two proteins, alcohol dehydrogenase (ADH) and lysozyme on nanogold surface using the incoherent second harmonic light scattering (SHLS) technique. The second harmonic light intensity scattered from gold nanoparticles in aqueous buffer solution is high due to strong surface polarization and is easily detectable. When ADH is added in small quantities to the solution, it gets adsorbed on the surface and forms a protein corona and consequently the SHG intensity decreases as a function of protein concentration. The normalized second harmonic intensity decay is fitted to a modified Langmuir type isotherm to get the binding constant (K_a), free energy change (ΔG^0), and the number of adsorbed protein molecules (n_{ads}) on the surface. The enthalpy of adsorption (ΔH^0) and entropy change (ΔS^0) are obtained in a temperature variation SHLS experiment at nanomolar concentrations which is not possible to obtain by any other technique at such low concentrations. From the measurements we conclude that ADH is physisorbed on the gold surface. The number of adsorbed protein molecules varies with the size of the gold nanoparticle as expected, but a quantitative analysis was not known (and I believe is not obtainable!) from proteomic studies. To look at some of the quantities by other techniques, we employ dynamic light scattering (DLS) and fluorescence spectroscopy albeit in different concentrations and compare the results. While the story for ADH is unravelled, the story of lysozyme adsorption on gold nanosurface is both

qualitatively and quantitatively different from that of ADH. I will also present the results for lysozyme in the talk.

Stimuli-Responsive Materials: Bottom-Up Control of Material Properties by De Novo Molecular Design

Jarugu Narasimha Moorthy

Department of Chemistry, IIT Kanpur, Kanpur 208016

E-mail: moorthy@iitk.ac.in

The properties of bulk organic materials are determined by organization of their constituents molecules. Implicit in it is the fact that the structures of organic molecules that make up the bulk materials crucially control the properties of the latter. We believe that ‘organic structure is quintessential to control both reactivity as well as molecular organization, and hence the properties of materials’.

I will exemplify how organic compounds may be maneuvered by a diligent design to control photoreactivity^[1] and molecular self-assembly to develop functional materials.^[2] As to the latter in particular, I will present our very recent de novo approaches to the development of stimuli-responsive 2D metal-organic framework nanosheets (MONs).^[3]

References:

1. (a) Moorthy, J. N.; Mandal, S.; Parida, K. *Org. Lett.*, **2012**, 14, 2438. (b) Moorthy, J. N.; Mandal, S.; Mukhopadhyay, A.; Samanta, S. *J. Am. Chem. Soc.*, **2013**, 135, 7872. (c) Mukhopadhyay, A.; Maka, V.; Moorthy, J. N. *Eur. J. Org. Chem.* **2015**, 1403. (d) Mukhopadhyay, A.; Maka, V.; Moorthy, J. N. *Photochem. Photobiol. Rev. C* **2016**, 29, 73.
2. (a) Seth, S.; Savitha, G.; Moorthy, J. N. *J. Mater. Chem. A* **2015**, 03, 22915. (b) Seth, S.; Savitha, G.; Moorthy, J. N. *Inorg. Chem.* **2015**, 54, 6829. (c) Chandrasekhar, P.; Mukhopadhyay, A.; Savitha, G.; Moorthy, J. N. *Chem. Sci.* **2016**, 07, 3085. (d) Chandrasekhar, P.; Savitha, G.; Moorthy, J. N. *Chem. Eur. J.* **2017**, 23, 7297.
3. (a) Chandrasekhar, P.; Mukhopadhyay, A.; Savitha, G.; Moorthy, J. N. *J. Mater. Chem. A* **2017**, 5, 5402. (b) Mukhopadhyay, A.; Maka, V.; Savitha, G.; Moorthy, J. N. *Chem* (Cell Press), **2018**, ASAP.

Exploring new amphiphilic polymer architectures

S. Ramakrishnan

Department of Inorganic and Physical Chemistry

Indian Institute of Science, Bangalore

Amphiphilic polymers have been long been investigated for the variety of morphologies that can be formed in water; specifically, to explore the possibility of utilizing these as carriers of drugs, dyes and other contrast agents for applications in biological contexts. Over the past decade, we have examined a variety of different amphiphilic architectures; our focus has been largely to understand the morphological features that such systems could develop in the bulk phase, specifically in the context of generating microphase separated morphologies at very small length scales.

In the talk, I shall first briefly describe some our efforts in this direction, while emphasizing some of the recent results concerning a special class of amphiphilic polymeric hydrogels gels that exhibit a gel-to-sol transition in response to both shear and temperature; such systems hold the potential of serving as injectable reservoirs for thermally-sensitive therapeutics, which need to be incorporated within the gels at relatively low temperatures and also can be injected by exploiting the shear-induced gel-to-sol transition.

A Journey to the Centre of Ribonuclease A

Tanmaya Pathak

Department of Chemistry

Indian Institute of Technology Kharagpur, Kharagpur 721302, India

tpathak@chem.iitkgp.ernet.in

Abstract

The members of the ribonuclease (RNase) superfamily are involved in a multitude of activities in addition to their normal catalytic activities. The activities of the members of the RNase superfamily are crucially dependent on their ability to cleave the intranucleotide phosphate linkage of RNAs, which is termed ribonucleolytic activity. These life-sustaining proteins are often associated with different physiological irregularities, which are also attributed to their enzymatic activities. The design of inhibitors of the ribonucleolytic activity of proteins is expected to have an indirect effect on their purported biological activities. The homology of these proteins with ribonuclease A (RNase A) permits its use as a model system in the development of inhibitors.[1] In fact, RNase A has been extensively used as a model system for designing inhibitors for the ribonuclease superfamily although the structural variations of inhibitors are limited. A wide variety of modified nucleosides[2] are being synthesized and studied for their inhibitory activities against RNase A. The lecture will highlight our approaches to design inhibitors of RNase A.[3]

References

- [1] (a) Marshall, G. R.; Feng, J. A.; Kuster, D. J. *Biopolymer*, **2008**, *90*, 259. (b) Cuchillo, C. M.; Nogues, M. V.; Raines, R. T. *Biochemistry*, **2011**, *50*, 7835.
- [2] Pathak, T. *Chem. Rev.* **2002**, *102*, 1623.
- [3] (a) Maiti, T. K.; De, S.; Dasgupta, S.; Pathak, T. *Bioorg. Med. Chem.* **2006**, *14*, 1221. (b) Debnath, J.; Dasgupta, S.; Pathak, T. **2009**, *17*, 6491. (c) Leonidas, D. D.; Dasgupta, S.; Pathak, T.; Zographo, S. E.; Oikonomakos, N. G. *J. Med. Chem.* **2009**, *52*, 932. (d) Debnath, J.; Dasgupta, S.; Pathak, T. *Bioorg. Med. Chem.* **2010**, *18*, 8257. (e) Samanta, A.; Dasgupta, S.; Pathak, T. *Bioorg. Med. Chem.* **2011**, *19*, 2478. (f) Debnath, J.; Dasgupta, S.; Pathak, T. *Chem. Eur. J.* **2012**, *18*, 1618. (g) Datta, D.; Samanta, A.; Dasgupta, S.; Pathak, T. *Bioorg. Med. Chem.* **2013**, *21*, 4634. (h) Datta, D.; Dasgupta, S.; Pathak, T. *ChemMedChem* **2014**, *9*, 2138. (i) Datta, D.;

Dasgupta, S.; Pathak, T. *ChemMedChem* **2016**, *11*, 620. (j) Datta, D.; Mondal, P.; Dasgupta, S.; Pathak, T. *ChemistrySelect* **2017**, *2*, 2106.

Molecular Interaction Driven Assembly of Amphiphilic Polymers and Proteins

Suhrit GHOSH

Professor, Polymer Science Unit, Indian Association for the Cultivation of Science,
Kolkata INDIA-700032; Email: psusg2@iacs.res.in

Abstract: Amphiphiles are prominent synthetic systems explored for wide-ranging mesoscopic structures with close relevance in nanotechnology and biomedicine. However in majority examples, their immiscibility driven aggregation does not endow precision in important structural parameters including size, morphology or functional group display. In contrast, directional molecular interactions (primarily H-bonding) form the basis of structural evolution and functional perfection of biomacromolecules such as enzymes, DNA or RNA in which alteration in the sequence of a single amino acid or mismatch in one base-pair could make vital contribution to the overall structure and function.

We have recently introduced assembly of supramolecularly engineered amphiphilic macromolecules (SEAM) ^[1-2] with precise internal order. In these systems, a supramolecular structure directing unit (SSDU) has been appended with a hydrophilic coil-like polymer. The SSDU is made of a H-bonding functional group (hydrazide/ amide) and a NDI-chromophore. By synergistic H-bonding and aromatic interaction, the SSDU pre-assembles and thus the subsequent step, involving hydrophobic association of the wedge, becomes a function of the first step (dictated by molecular interaction). Therefore the mesoscopic structure can be regulated by the distinct nature of the molecular interaction involved in the first step by fully ignoring the packing parameters. Consequently, two amphiphilic block copolymers having identical chemical structure and same hydrophobic/ hydrophilic balance organize to form distinctly different assemblies (polymersome or cylindrical micelle) depending on the nature of the single H-bonding functional group (hydrazide or amide) of the SSDU. So prominent is the motivation for self-selection that in a mixture of two such polymers, self-sorting can be noticed although they differ merely by a *SINGLE* H-bonding functional group. Recently, we have established that the design can be extended to wide-ranging polymers including charged polymers and the same rule applies. In fact, the hydrophilic polymer, when replaced with a protein, still the SSDU could direct highly stable (no denaturation upto 90 °C) nano-structured assembly of the supramolecularly engineered protein (SEP) without disrupting its enzymatic activity.^[3] Co-assembly of thermo-responsive SEAM with SEP provides unique opportunity

to thermo-regulated enzymatic activity. In depth isothermal calorimetric (ITC) studies ^[4] reveal prominent entropy motivation in highly stable self-assembly of the SEAMs/ SEB having merely 4-6 wt % hydrophobic content. The presentation will highlight recent results from our group in this area.

References

1. A. Das and S. Ghosh, *Macromolecules* **2013**, *46*, 3939-3949.
2. P. Pramanik, D. Ray, V. K. Aswal and S. Ghosh, *Angew. Chem. Int. Ed.* **2017**, *56*, 3516-35202.
3. A. Sikder and S. Ghosh, *Unpublished results*.
4. P. Dey, P. Rajdev, P. Pramanik and S. Ghosh, *Manuscript submitted*.

Assisted pi-stacking: a strong synergy between weak interactions

Dr. Debanshu Chaudhuri

Indian Institute of Science Education and Research, Kolkata

dchaudhuri@iiserkol.ac.in

A pair of weak non-covalent interactions that strengthen each other synergistically can be an important tool in supramolecular chemistry, because of its ability to predispose a molecular self-assembly towards a specific pathway. We report assisted pi-stacking, a synergistic association between regular aromatic pi-stacking and a much weaker non-covalent interaction that is characterized by an exceptional strength and thermal stability, unprecedented among the strongest known pi-stacking interactions. We investigate the nature of assisted pi-stacking in a naphthalene diimide (NDI) foldamer, where it is responsible for the unusual stabilization of the folded conformer. A selective termination of the weaker secondary interaction causes a spontaneous disruption of the assisted pi-stacking state, validating the synergistic nature of the interaction. A similar assisted pi-stacking interaction motif, when incorporated in a monomeric NDI, drives its self-assembly in a non-aggregating solvent medium. Such strong synergistic interactions are great tools to exercise pathway control in molecular self-assembly, and can also find potential use in supramolecular catalysis by stabilizing the transition state.

References:

1. A. Rahim, P. Saha, K. K. Jha, N. Sukumar and B. K. Sarma, *Nat. Commun.*, **2017**, 8, 78.
2. M. M. J. Smulders, A. P. H. J. Schenning and E. W. Meijer, *J. Am. Chem. Soc.*, **2008**, 130, 606.
3. T. E. Kaiser, V. Stepanenko and F. Würthner, *J. Am. Chem. Soc.*, **2009**, 131, 6719.
4. S. Ogi, K. Sugiyasu, S. Manna, S. Samitsu and M. Takeuchi, *Nat. Chem.*, **2014**, 6, 188.
5. Y. Zhao, Y. Domoto, E. Orentas, C. Beuchat, D. Emery, J. Mareda, N. Sakai and S. Matile, *Angew. Chem. Int. Ed.*, **2013**, 52, 9940.

Colloidal Engineering: Beyond Molecular Self-Assembly

Nonappa

*Department of Applied Physics,
Aalto University School of Science, Finland
nonappa@aalto.fi*

Molecular self-assembly relies on various non-covalent interactions between well-defined molecular-level building blocks. However, at higher length scale utilization of such supramolecular interactions in the self-assembly of nanoparticles (organic/inorganic) is challenging, due to aggregation tendencies, polydispersity and difficulties in controlling the directionality of the building blocks. In nature, biological particles, such as virus capsid self-assemblies are inspirational examples for sub-unit based hierarchical structure formation. They represent one of the fascinating examples for genetic economy, efficiency and error-free structure formation. In this presentation, I will show how to control the synthesis of nanoparticles at atomic precision and their self-assembly to obtain hierarchical superstructures (Figure 1).¹ The special emphasis will be on free-standing 2D nanosheets with one nanoparticle thick layer (2.5 nm) and their bending to hollow spherical capsids with a monolayer thick shell.^{2,3} Further, the importance of monodisperse building blocks for designing chiral plasmonic polarizers will be discussed.^{4,5}

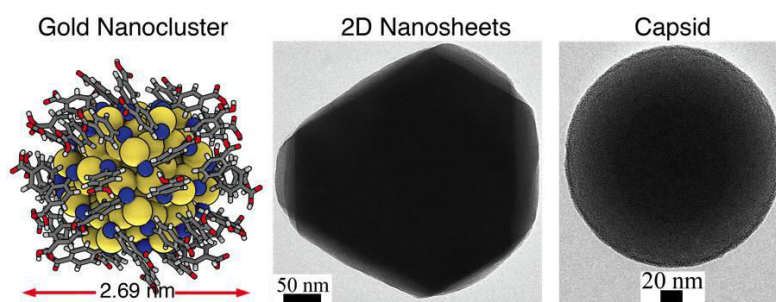


Figure.1 Self-assembly of atomically precise gold nanocluster to 2D nanosheets and spherical capsids.

References:

- [1] Nonappa, T. Lahtinen, J. S. Haataja, H. Häkkinen, O. Ikkala. *Angew. Chem. Int. Ed.* **2016**, 55, 16035-16038.
- [2] Nonappa, J. S. Haatja, J. V. I. Timonen, S. Malola, P. Engelhardt, N. Houbenov, M. Lahtinen, H. Häkkinen, O. Ikkala. *Angew. Chem. Int. Ed.* **2017**, 56, 6473-6477.

- [3] Nonappa, O. Ikkala. *Adv. Funct. Mater.* **2017**, 1704328.
- [4] A. Chakraborty, A. C. Fernandez, A. Som, B. Mondal; G. Natarajan, G. Paramasivam, T. Lahtinen, H. Häkkinen; Nonappa, T. Pradeep. *Angew. Chem. Int. Ed.* **2018** (*manuscript accepted*).
- [5] V. Lisjström, A. Ora, J. Hassinen, H. Rekola, Nonappa, M. Heilala, V. Hynninen, J. Joensu, R.H. A. Ras, P. Törma, O. Ikkala, M. A. Kostiainen. *Nat. Commun.* **2017**, 8, Article number : 671.

Prying into Prion: Electrostatic Modulation in Binding, Misfolding and Assembly

Samrat Mukhopadhyay

Centre for Protein Science, Design and Engineering

, Department of Biological Sciences and Department of Chemical Sciences

Indian Institute of Science Education and Research (IISER), Mohali,

Email: mukhopadhyay@iisermohali.ac.in

Prion diseases are a class of deadly neurodegenerative diseases such as Creutzfeldt-Jakob disease, Gerstmann-Sträussler-Scheinker disorder and fatal familial insomnia. The causative agent of prion diseases is known to be proteinaceous infectious particles comprising aggregates of a misfolded membrane-anchored protein, namely the prion protein (PrP). The critical step in the pathogenesis is found to involve a profound conformational switch from a largely α -helical normal cellular form (PrP^C) to a predominantly β -sheet-rich protease-resistant scrapie form (PrP^{Sc}). A line of evidences indicates that the interaction of PrP with the anionic lipid headgroups of the membrane surface may play an important role in the conformational conversion of PrP^C to PrP^{Sc}. Using a diverse array of biophysical and biochemical tools, we have been able to establish the role of intrinsically disordered N-terminal segment of PrP in the deadly lipid membrane mediated conformational conversion process. Our results demonstrate that the membrane-induced conformational change is mediated by the electrostatic interaction between anionic headgroup of lipids and the disordered segment of PrP that leads to misfolding and oligomerization on the lipid membrane. Our studies provide a compelling evidence of membrane-induced misfolding and assembly of PrP. I will also discuss our new results on the interaction of the intrinsically disordered N-terminal segment PrP with the distinct types of conformation-specific oligomers of the amyloid- β peptide that is linked to Alzheimer's disease.

Synthetic Molecular Machineries for Transmembrane Chloride Transport

Pinaki Talukdar

Indian Institute of Science Education and Research Pune, India.

Email: ptalukdar@iiserpune.ac.in

The transport of ions across liposomal membranes is regulated by natural proteins embedded within the lipid bilayer.¹ Controlled and selective transport of ions by these proteins is essential for living cells to maintain the ionic homeostasis which is essential for cell proliferation, hormone secretion, signal transduction and cell survival. Dysregulated transport of sodium, potassium, calcium, and chloride is known to induce apoptosis in cells.² Thus, immense attention is given to the design and develop biomimetic systems capable of transporting a specific type of ions across the lipid membranes. We have developed unimolecular chloride channels by functionalizing cyclo-oligo-(1→6)-β-D-glucosamines with pentabutylene glycol chains. The ion transport activity of these derivatives was tuned by varying oligomericity.³ The *N*¹,*N*⁴-dicyclohexylfumaramide, a significantly small-molecule, was demonstrated to form of self-assembled chloride channels.⁴ A bis(ketal) protected mannitol-derivative formed supramolecular channels involving its free hydroxyl groups.⁵ The channel displayed hopping-mediated chloride transport across the lipid bilayer. Based on hydrogen bond network of hydroxyl groups, observed in the solid state structure of the mannitol derivative, a bis(dihydroxyl) based system was designed which also formed selective chloride channels.⁶ The effect of artificially transported chloride ions perturbed the cellular chloride homeostasis and induced apoptotic cell death. Considering this interesting finding, artificial chloride transport systems can be useful for targeting cancer.

References:

1. (a) Jentsch, T. J.; Hubner, C. A.; Fuhrmann, J. C. *Nat. Cell Biol.*, **2004**, 6, 1039. (b) Bose, T.; Cieslar-Pobuda, A.; Wiechec, E. *Cell Death Dis.*, **2015**, 6, e1648.
2. (b) Duran, C.; Thompson, C. H.; Xiao, Q.; Hartzell, C. *Annu. Rev. Physiol.* **2010**, 72, 95. (b) Benz, R.; Hancock, R. E. W. *J. Gen. Physiol.* **1987**, 89, 275. (c) Yu, S. P.; Canzoniero, L. M. T.; Cho, D. W. *Curr. Opin. Cell Biol.* **2001**, 13, 405.
3. Saha, T.; Roy, A.; Gening, M. L.; Titov, D. V.; Gerbst, A. G.; Tsvetkov, Y. E.; Nifantiev, N. E.; Talukdar, P. *Chem. Commun.* **2014**, 50, 5514-5516.
4. Roy, A.; Biswas, O.; Talukdar, P. *Chem. Commun.* **2017**, 53, 3122-3125.
5. Saha, T.; Dasari, S.; Tewari, D.; Prathap, A.; Sureshan, K. M.; Bera, A. K.; Mukherjee, A.; Talukdar, P. *J. Am. Chem. Soc.* **2014**, 136, 14128-14135.

6. Saha, T.; Gautam, A.; Mukherjee, A.; Lahiri, M.; Talukdar, P. *J. Am. Chem. Soc.* **2016**, *138*, 16443-16451.

Self-Assembly of Renewable Nano-sized Triterpenoids

Braja Gopal Bag,^{*} Subhajit Das, Sk Nurul Hasan, Abir Chandan Barai, Subrata Ghorai, Chhabi Garai, Saikat Kumar Panja, Sanjit Santra

Department of Chemistry and Chemical Technology
Vidyasagar University, Midnapore 721 102, West Bengal, India.
Email: braja@mail.vidyasagar.ac.in

Plant metabolites may serve as a significant renewable alternative to fossil and petroleum resources for a sustainable future. Among various plant secondary metabolites, terpenoids constitute the most numerous and structurally diverse group of natural products having more than

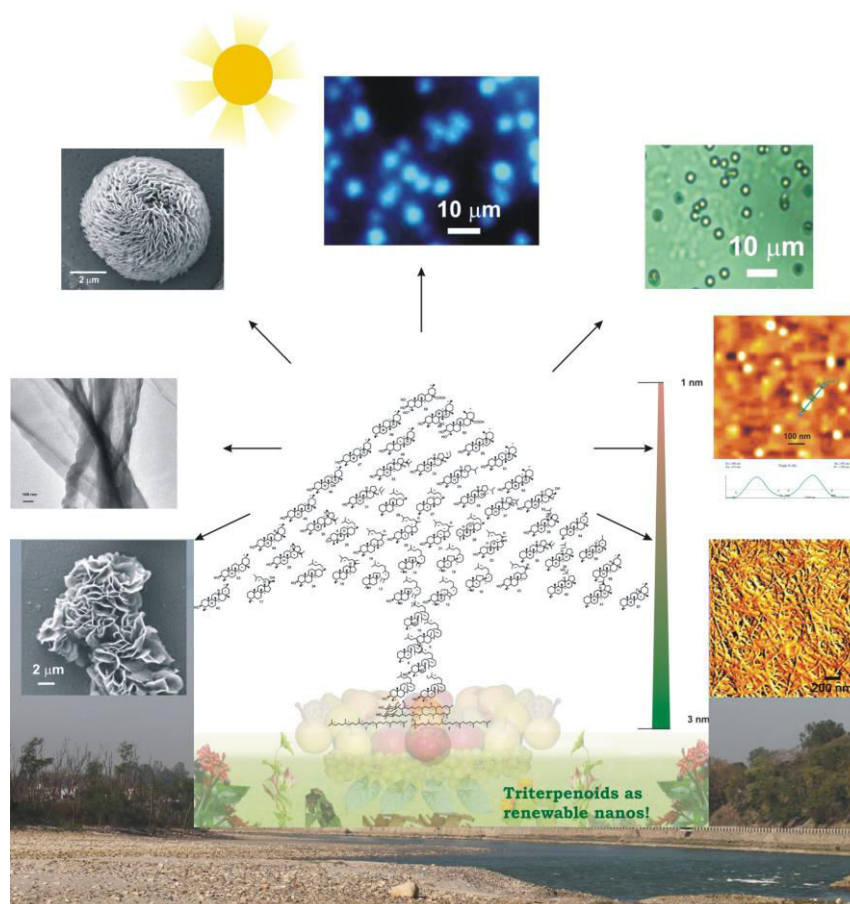


Fig. 1: Spontaneous self-assembly renewable nano-sized triterpenoids

300 ring systems. Computations carried out by us on sixty representative triterpenoids have revealed that all the triterpenoids are nanometer long having varied rigid and flexible lengths (Figure 1).¹⁻⁹

The triterpenoids isolated from plants such as arjunolic, betulinic, oleanolic, glycyrrhetic and ursolic acids and betulin self-assembled in the liquids at low concentrations affording self-assembled nano- to micro-sized architectures such as helical fibers, vesicles, spheres, etc. The self-

assemblies were capable entrapping fluorophores including the anticancer drug doxorubicin. Recent results will be presented in the perspective of green, renewable and nanos.

References

1. B.G. Bag, R. Majumdar, *Chem. Rec.* **2017**, 17, 841-873.
2. R. Majumdar, B.G. Bag, *ChemistrySelect*, **2018**, 3, 951-957.
3. B.G. Bag, Sk N. Hasan, P. Pongpamorn, N. Thasana, *ChemistrySelect*, **2017**, 2, 6650-6657.
4. B.G. Bag, S. Das, Sk N. Hasan, A.C. Barai, *RSC Advances*, **2017**, 7, 18136 – 18143.
5. B.G. Bag, R. Majumdar, *RSC Advances*, **2014**, 4, 53327-53334.
6. B.G. Bag, S.S. Dash, *RSC Advances*, **2016**, 6, 17290-17296.
7. B.G. Bag, S.S. Dash, *Langmuir*, **2015**, 31, 13664-13672.
8. B.G. Bag, K. Paul, *Asian J. Org. Chem.* **2012**, 1, 150-154.
9. R. Majumdar, S. Tantayanon, B.G. Bag, *Chem. Asian J.*, **2016**, 2406.

Smart Molecules that Break Bad Supramolecular Assembly in Body: Supramolecular Terminators

Dr. Bhubaneswar Mandal

Laboratory of Peptide and Amyloid Research,

Department of Chemistry,

Indian Institute of Technology Guwahati

Email : bmandal@iitg.ernet.in

Abstract

Although supramolecular association and dissociation of biological molecules drive life processes, sometimes self-assembly of some biological macromolecules may be fatal. More than thirty diseases are known that are caused by the aggregation or supramolecular association of various peptides generated by the misregulation of protein homeostasis. For example, Alzheimer's disease (AD), a common age-related human neurodegenerative disorder, is caused by aggregation of Amyloid- β ($A\beta$) peptide. Pathological investigations revealed the existence of numerous plaques (bad supramolecular association) in the Alzheimer's patients' brain composed of $A\beta$ peptides, derived from amyloid precursor proteins (APPs). Similarly, another age-related disorder, type II diabetes (T2DM) is caused by the supramolecular association of Amylin peptide. These diseases have no cure yet. Therefore, we need to design such a smart molecule that can bind to those bad supramolecular associations in the body, restricts their growth and disrupts them to facilitate excretion. Design of such molecules is challenging as one needs to play with the same supramolecular interactions by which the aggregations are formed but exerting opposite effect. However, we could find four different types of such constructs and termed them as supramolecular terminators. The first class of terminator molecules is formed by embedding an anthranilic acid in relevant peptide sequences (β -sheet breaker α/β hybrid peptides, BSBHps) that can be recognized by the bad supramolecular associations (BDAs). We have demonstrated that such constructs indeed can inhibit and disrupt BDAs associated with AD¹ and T2DM². The second class of the supramolecular terminators contains β -breaker di-peptides (BBDPs). These constructs align with the BDAs, co-assemble with them, transform their covalent as well as

supramolecular architecture by a cascade of predestined chemical reactions, and finally destroy the BDAs. The third type of terminators is formed by mimicking the “paratope” part of an antibody, and we have termed them as synthetic paratope. Such synthetic paratopes wrap A β monomers and small soluble oligomers, stops further aggregation, and help in their excretion. The fourth type of terminator constructs is prepared by mimicking the action of the enzyme α -secretase. We have designed a peptide-small molecule conjugate that gets recognized by the A α sequence and cut it at the α -secretase cleavage site favouring non-toxic pathway of APP processing. We have demonstrated that such well-designed peptide-conjugates are capable of inhibition of amyloid formation of A β peptide. Also, they disrupt preformed toxic fibrillar aggregates into nontoxic species in vitro. Such peptides may be useful for designing novel drugs against various amyloidoses including Alzheimer’s disease, Parkinson’s disease and diabetes type II. Recent advancements in this direction will be discussed in the SCBFM 2018.

References:

1. Ashim Paul, Krishna Chaitanya Nadimpally, Tanmay Mondal, Kishore Thalluri, and Bhubaneswar Mandal*, "Inhibition of Alzheimer’s Amyloid- β Peptide Aggregation and its Disruption by a Conformationally Restricted α/β Hybrid Peptide", *Chemical Communications*, **2015**, 51, 2245-2248.
2. Ashim Paul, Sourav Kalita, Sujan Kalita, Piruthivi Sukumar and Bhubaneswar Mandal*, "Disaggregation of Amylin Aggregate by Novel Conformationally Restricted Aminobenzoic Acid containing α/β and α/γ Hybrid Peptidomimetics", *Scientific Reports* (Nature Publishing Group) :7, 40095; doi: 10.1038/srep40095 (2017).

Extremely stretchable and tough self-healing hydrogels

Agniva Dutta, Supriya Maity and Rajat K. Das*¹

¹*Materials Science Centre, Indian Institute of Technology, Kharagpur*

Contact: rajat@matsc.iitkgp.ernet.in

Hydrogels have great potential for applications in fields such as tissue engineering¹, drug delivery and actuation. However, most of the hydrogels are brittle. They do not possess simultaneously a high mechanical strength and toughness (stretchability) that could enormously expand the scope of these applications. Combining these two properties is not trivial as they typically are mutually exclusive². During the past decade or so, one of the main approaches towards tackling this problem has been to introduce efficient energy dissipation pathways³ through combination of a highly stretched and densely cross-linked network (providing stiffness) with a flexible, lightly cross-linked network (providing stretchability). In the present work, we have synthesized a reasonably tough, stiff and extremely stretchable physical hydrogel by polymerizing acrylamide in aqueous medium, in absence of any cross-linker, and only in the presence of small amount of chitosan, a naturally available biopolymer. Although these hydrogels contain ~ 85 % water, they can be stretched up to 30 times their original length (Figure 1A and 1B) compared to a physical gel of polyacrylamide (PAAm), which can only withstand a stretching of 3 times its original length. The composite physical hydrogels possess toughness as much as 80 times higher than that of parent PAAm hydrogel. They can also withstand a compressive strain of 95% without fracture and recover their original shape after removal of the strain (Figure 1C-E). These gels exhibit pronounced hysteresis during loading-unloading cycle indicating the presence of effective energy dissipation mechanism contributing to toughness. When a strip of the gel is cut into two pieces and the two halves kept pressed together at elevated temperature, the gels self-heal and recover up to 25% of the initial toughness and 65% of original extensibility. These results and their implications will be discussed in this presentation.

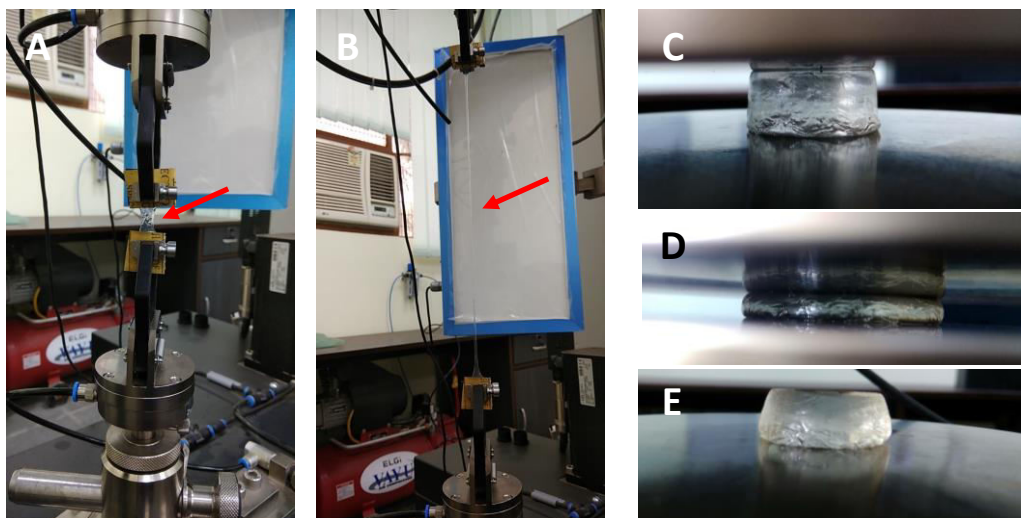


Figure 1. Uniaxial tensile testing experiment with composite gel (A and B). A: initial state, B: ~ 3000% strain. Red arrow indicates gel position. C-E: Photographs demonstrating how the composite gels can sustain high compression. C: before compression, D: under compression, E: after removing compression.

Reference

- [1] Das, R. K., Gocheva, V., Hammink, R., Zouani, O. F., Rowan, A. E. Stress-stiffening mediated stem cell commitment switch in soft responsive hydrogels. *Nat. Mater.* **2016**, 15, 318-325.
- [2] Ritchie, R. O. The conflicts between strength and toughness. *Nat. Mater.* **2011**, 10, 817-822.
- [3]. Sun, J-Y. *et al.* Highly stretchable and tough hydrogels. *Nature* **2012**, 489, 133–136.

Dual pH- and Thermo- Responsive Alternating Copolymer with Unusual Fluorescence Behaviour

Biswajit Saha, Kamal Bauri, Priyadarsi De*

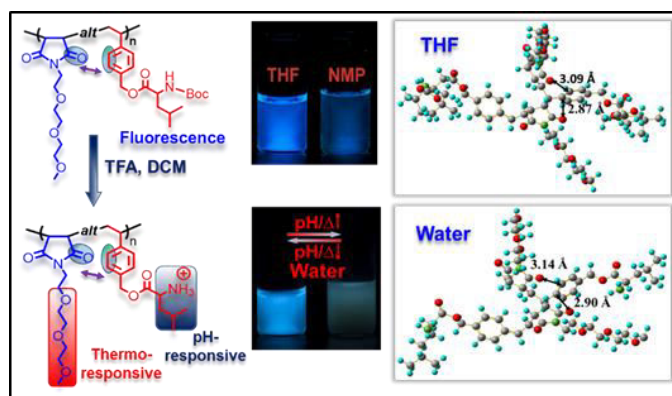
Polymer Research Centre,

Department of Chemical Sciences,

Indian Institute of Science Education and Research Kolkata

e-mail address : p_de@iiserkol.ac.in

In recent years, the intrinsic emission from nonconventional macromolecular luminogens without classic conjugated chromophores¹ have drawn increasing interests owing to their fundamental importance and promising applications. Also, stimuli-responsive polymers (especially pH and or temperature) have been developed for various interesting applications. Amalgamation of the fluorescence property of unorthodox macromolecular luminogens with “smart” stimuli-responsiveness in a single polymer system will give a new class of polymeric material with diversified functions.² Herein, we report a new approach for the synthesis of a novel dual pH- and thermo- responsive fluorescent alternating copolymer devoid of conventional fluorophore moiety based on a sequence-specific copolymer of Boc-protected leucine appended styrenic monomer and *N*-substituted maleimide monomer bearing diethylene oxide side-chain. The reversible-addition fragmentation chain transfer (RAFT) polymerization ensured the alternate placing of the monomer unit throughout the polymer chain, which was confirmed by ¹³C NMR spectroscopy and MALDI-TOF-MS. The as-synthesized alternating copolymer exhibits a bright-blue fluorescence in organic solvents. After expulsion of Boc group, the resultant copolymer showed dual pH- and thermo-responsive behaviour and retained its luminescence property in organic solvents as well as in water. Interestingly, the fluorescence activity of the copolymer has shown to be very sensitive towards pH and temperature. The origin of the fluorescence in the copolymers was ascertained by density functional theory (DFT), where we observed that the “through-space” π - π interaction between the benzene ring and the neighbouring carbonyl group of maleimide unit is responsible for the unexpected fluorescence into the alternating copolymer.



References :

- 1) Yan, J. J.; Wang, Z. K.; Lin, X. S.; Hong, C. Y.; Liang, H. J.; Pan, C. Y.; You, Y. Z. *Adv. Mater.* **2012**, *24*, 5617
- 2) Saha, B.; Bauri, K.; Bag, A.; Ghorai, P. K.; De, P. *Polym. Chem.* **2016**, *7*, 6895

Self-assembled luminescent metal nanoclusters and its incorporation in soft organic scaffold to furnish hybrid organo-nano material

Balamurugan Kuppan* and Uday Maitra

The Department of Organic Chemistry,

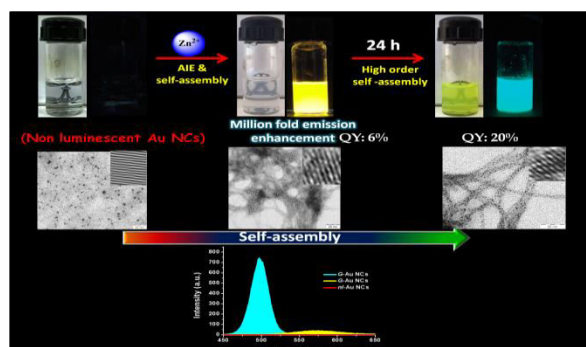
Indian Institute of Science, Bangalore

bala_04thapa@yahoo.com

Hybrid materials comprised of soft organic material and nanoparticles are gaining attention in research profoundly in the recent years. The materials' application diversifies when the nano component of the material happens to be luminescent. Luminescent nano species we are interested are metal nanoclusters and the organic soft scaffold is bile acid derived metallohydrogel. In brief, luminescent metal nanoclusters (NCs) possess ultra-small size (< 2 nm) that bridges the gap between nanoparticles and molecules. Applications of this spreads widely in the field of bioimaging, biosensing, catalysis, LED, *etc.* We have developed a facile protocol for instant room temperature synthesis of luminescent metal NCs (Au, Ag and Cu) in aqueous media using a short thiol molecule.

We have largely focused on Au NCs, as it shows extensive self-assembly and AIE mediated emission color tuning. During the course of emission energy tuning the Au NCs transforms from non self-assembled, non luminescent to disordered yellow emitting assemblies to highly ordered green emitting 1-D assemblies.¹ Later we have developed a simple protocol to synthesize blue emitting species from this green emitting one using acid as the only reagent. Subsequently, these are incorporated in the metallohydrogel to increase its luminescence stability. Detailed analysis of photophysical, TEM, lifetime, and zetapotential studies have aided us in understanding the mechanism and role of self-assembly in tuning of emission energy. Excited state dynamics associated with the ligand have been understood through time resolved photoluminescence studies.

The outcome of these organic-inorganic hybrid materials is such that they provide a synergistic stability between NCs and hydrogels. Successful fabrication of such hybrid luminescent materials with detailed understanding of the systems paves way towards directing these materials to application in various scientific fields.



Keywords: Nanoclusters, bile acid, metallohydrogel, luminescent

References:

1. B. Kuppan and U. Maitra, *Nanoscale* 2017, **9**, 15494.

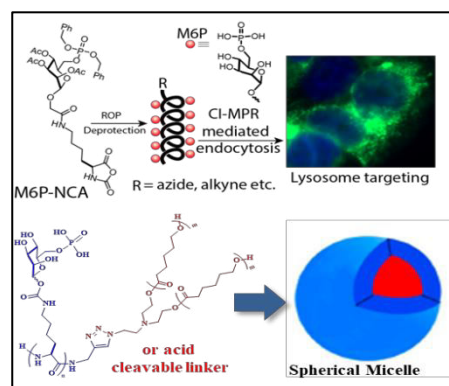
Mannose-6-Phosphate Functionalized Glycopolypeptide (M6P-GP) for Lysosome Targeting

Basudeb Mondal

Indian Institute of Science Education and Research, Kolkata

Abstract:

The ubiquitous expression of the mannose-6-phosphate receptor on the majority of human cells makes it a valid target in the quest to deliver therapeutics selectively to the lysosome. In this work end-functionalized polyvalent mannose-6-phosphate glycopolypeptides (M6P-GPs) with high molecular weights (up to 22 kDa) have been synthesized via NCA polymerization. These synthetic M6P-GPs were



found to display minimal toxicity to cells in vitro and show exceptional selectivity for trafficking into lysosomes in various cell lines. Comparison of the cellular uptake behaviour of M6P-GP and the corresponding mannose-GP polymer reveals that incorporation of the phosphate moiety at the 6-position of mannose completely alters its trafficking behavior and becomes exclusively lysosome specific. We also demonstrate that trafficking of M6P-GPs in mammalian cells is likely associated with the CI-MPR receptor pathway. In addition, as demonstrated by us and others, amphiphilic glycopolypeptides can be self-assembled into vesicles, micelles, and nanorods. These self-assembled nanostructures synthesized from M6P-glycopolypeptide can be used to encapsulate therapeutics or lysosomal storage enzymes for targeting and delivering them exclusively to lysosomes.

References:

- [1] Kornfeld, S. *Annu. Rev. Biochem.* **1992**, *61*, 307–330.
- [2] Das, S.; Parekh, N.; Mondal, B.; Sen Gupta, S. *ACS Macro Lett.* **2016**, *5*, 809–813.
- [3] Pati, D.; Das, S.; Patil, N. G.; Parekh, N.; Anjum, D. H.; Dhaware, V.; Ambade, A. V.; Sen Gupta, S. *Biomacromolecules* **2016**, *17*, 466–475.
- [4] Pati, D.; Kalva, N.; Das, S.; Kumaraswamy, G.; Sen Gupta, S.; Ambade, A. V. *J. Am. Chem. Soc.* **2012**, *134*, 7796–7802.
- [5] Huang, J.; Bonduelle, C.; Thevenot, J.; Lecommandoux, S.; Heise, A. *J. Am. Chem. Soc.* **2012**, *134*, 119–122.

- [6] Kramer, J. R.; Rodriguez, A. R.; Choe, U. J.; Kamei, D. T.; Deming, T. J. *Soft Matter***2013**, 9, 3389–3395.
- [7] Das, S.; Sharma, D. K.; Chakrabarty, S.; Chowdhury, A.; Sen Gupta, S. *Langmuir***2015**, 31, 3402–3412.



ABSTRACTS FOR POSTERS



Tuning of Excited State Intramolecular Proton Transfer Processes in Sugar Functionalized Hydrogel for the Detection of Cancer Cell

Santu Maity and Jhuma Ganguly

Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur,
Howrah-711103, India

E-mail: santumaity77@gmail.com and jhumaiest@gmail.com

A biopolymeric hydrogel using functionalized 2-(benzo[d]thiazol-2-yl)phenol with chitosan has been synthesized which exhibits excited state intramolecular proton transfer (ESIPT) in both gel and solution phase. The ESIPT process in the hydrogel can be easily identified by UV-Vis and fluorescence spectroscopic techniques. The ‘keto-enol’ tautomers behave quite different under UV-irradiation. From the DFT study, it is evident that O-H bond length in enol form is greater for more stable planar structure, suggesting the enhanced possibility of a proton migration in this form. Moreover, it is observed that the H-N_T bond distance is remarkably shorter as compared to the corresponding H-N_C bond length. Therefore, it is more feasible for the hydrogen atom of the phenolic –OH group to migrate to the nitrogen of HBT moiety, i.e. N_T. The fluorescence lifetime of the hydrogels are found to increase remarkably in gel phase compared to its aqueous solution.

The self-healing property of the hydrogel is based on the dynamic chemistry. Upon placing two pieces of hydrogel close together in moisture saturated air, can heal spontaneously within 1 h. Since, the hydrogel is constituted through the dynamic imine linkage between amino groups of chitosan and aldehyde groups of the cross-linker, the polymeric gel on the wound surfaces keep moving and recross-link together. Thus, it results in the recovery and regeneration of the imine bonds continuously in the hydrogel network on molecular level. Rheological step-strain measurements under varying strain at room temperature are also performed to quantify the self-healing property in the hydrogel. Besides, cell imaging study suggests that the MCF 7 cell line shows much higher binding efficiency as compared to the Vero cells. Therefore, the hydrogels can be effective in sensing of cancer cell.

References

1. O. Chaudhuri, L. Gu, D. Klumpers, M. Darnell, S. A. Bencherif, J. C. Weaver, N. Huebsch, H. Lee, E. Lippens, G. N. Duda, D. J. Mooney, *Nat. Mater.*, 2016, **15**, 326–334.

2. S. Maity, A. Datta, S. Lahiri and J. Ganguly, *RSC Adv.*, 2015, **5**, 89338–89345.
3. S. Maity, A. Datta, S. Lahiri and J. Ganguly, *RSC Adv.*, 2016, **6**, 81060-81068.
4. S. Maity, A. Chatterjee, N. Chakraborty and J. Ganguly, *New J. Chem.*, 2018, Accepted Manuscript, **DOI**: 10.1039/C7NJ04178K.

Hybrid nanostructured materials from bile salt derived supramolecular gels

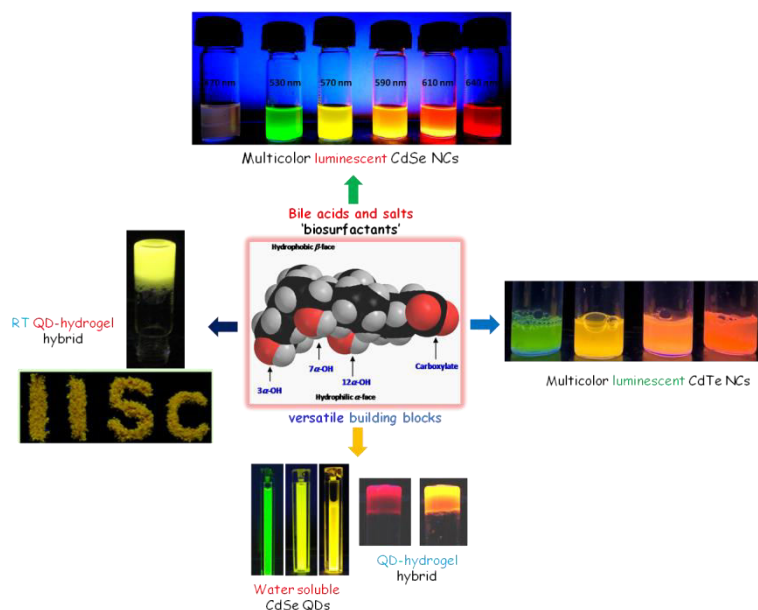
Ajay Kumar, Sayantan Chatterjee and Uday Maitra*

Department of Organic Chemistry, Indian Institute of Science, Bangalore- 560012

ajayk8039@gmail.com

sayantan.iisc@gmail.com

During the past two decades, molecular gels, semiconductor nanocrystals (NCs) and gel-QD composites have become burgeoning fields in scientific research as they have many applications in biological and material sciences. There is an ever-growing interest in these areas because the entangled fibrous network of the gel in the nano-regime can act as a soft template in the synthesis of nanoparticles (NPs) and also in many other applications such as tissue engineering, catalysis, *etc.*^{1,2} Bile acids/salts are known for over a century, and have attracted considerable attention in recent years for applications in supramolecular chemistry. Our group has recently explored bile salts which form hydrogels in the presence of various metal ions. The nano-fibrillar networks of the metal cholates hydrogels have been used as unique soft templates for the synthesis of a variety of metal and metal sulfide NPs. New bile salt derived cadmium precursors (cadmium deoxycholate) were explored for efficient synthesis of high-quality CdSe and CdTe NCs.³ The high thermal stability of these salts allowed us to fine tune the synthesis of the NCs at high temperatures while maintaining the monodispersity, crystallinity and reproducibility. We have also shown that hydrophobically coated CdSe QDs can be dispersed in an aqueous phase using cationic micelles without any exchange of surface ligands and subsequently incorporated them in a hydrogel network.⁴ Additionally, a one step, *in situ*, room temperature synthesis of yellow luminescent CdSe QDs was achieved in a metallohydrogel derived from a bile salt, resulting in a QD-gel hybrid.⁵ We also describe the successful isolation of the luminescent CdSe QDs from the gel followed by their re-dispersion in an organic solvent using suitable capping ligands. We believe that in future these hybrid materials have potential applications in biology, optoelectronics, sensors, non-linear optics and material science.



References:

1. Chakrabarty, U. Maitra and A.D. Das, *J. Mater. Chem.*, 2012, **22**, 18268.
2. F. R. Llansola, B. Escuder and J. F. Miravet, *J. Am. Chem. Soc.*, 2009, **131**, 11478.
3. A. Chakrabarty, S. Chatterjee and U. Maitra, *J. Mater. Chem. C*, 2013, **1**, 2136.
4. S. Chatterjee and U. Maitra, *Nanoscale*, 2016, **8**, 14979. .
5. S. Chatterjee and U. Maitra, *Nanoscale*, 2017, **9**, 13820.

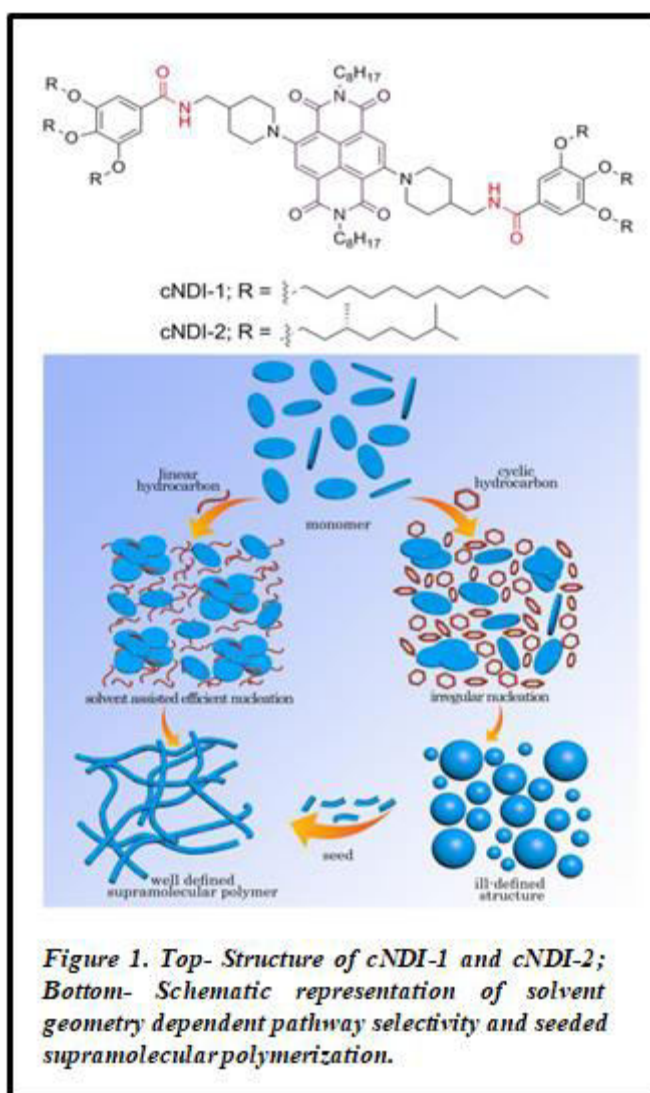
Solvent Geometry Regulated Pathway Selection and Seeded Supramolecular Polymerization

Goutam Ghosh, Haridas Kar and Suhrit Ghosh*

Polymer Science Unit, Indian Association for the Cultivation of Science, Kolkata

Email: psusg2@iacs.res.in

Directional molecular interactions such as H-bonding and others though endow an internal order in supramolecular polymers of diverse π -systems, controlling their growth mechanism and the mesoscopic structure remains an uphill task. Recently, we have shown core-substituted naphthalene-diimide derivatives (cNDI-1/ cNDI-2) although exhibit similar J-aggregation in cyclic as well as linear hydrocarbon solvents, gelation was noticed only in linear alkanes (dodecane, decane, heptane, hexane) in contrast to free flowing solution in their cyclic analogs (methylcyclohexane, hexane). Investigation of mechanistic pathway by variable temperature UV/Vis studies indicated highly cooperative self-assembly pathway in linear hydrocarbon (Decane) due to the direct participation of linear alkanes in the nucleation process by favorable mixing with the peripheral alkyl chains whereas ill-defined polymerization was noticed in Methylcyclohexane (MCH) because of inefficient nucleation owing to geometry mismatch. Morphology studies revealed the formation 1D fibrillar structure in decane whereas in MCH



irregular particles were produced indicating an off-pathway aggregation. We have explored this solvent geometry regulated pathway selection for controllable supramolecular polymerization by a chain growth mechanism. Fibrillar structure produced in decane was sonicated to small seeds which were used as initiator for controlled supramolecular polymerization of the off-pathway aggregate in MCH. By this method it was possible to synthesize supramolecular polymers with controllable chain length (by varying monomer/seed ratio) and low polydispersity. Chiral seed produced from cNDI-2 was successfully utilized to generate helical supramolecular from the meta-stable off pathway aggregate of achiral cNDI-1 in MCH. The presentation will highlight precise solvent geometry effect on nucleation and thermodynamic properties of supramolecular polymerization and elucidate the impact on controlled seed-initiated supramolecular polymerization.

Reference

1. H. Karf, **G. Ghosh†**, S. Ghosh, "Solvent geometry regulated supramolecular assembly of an amine substituted naphthalene diimide" *Chem. Eur. J.* **2017**, 23, 10536 – 10542 († equal contribution)
2. **G. Ghosh**, S. Ghosh, " Solvent Dependent Pathway Diversity and Seeded Supramolecular Polymerization" (Manuscript to be submitted)

Engineering peptide based sealants to facilitate faster blood-clotting

Snehasish Ghosh¹, Sanchita Mukherjee², Chiranjit Dutta¹, Kasturee Chakraborty², Paramita Gayen², Somnath Jan², Dhananjay Bhattacharyya^{3*} and Rituparna Sinha Roy^{2*}

¹Department of Chemical Sciences,

Indian Institute of Science Education and Research, Kolkata

²Department of Biological Sciences

Indian Institute of Science Education and Research, Kolkata

³Computational Science Division,

Saha Institute of Nuclear Physics, Kolkata.

E-mail address: sg12rs027@iiserkol.ac.in

Abstract

Self-assembled peptide based functional biomaterials are promising tools for biomedical applications. In our study, we have engineered isopeptide bond stabilized fibrin-inspired nanoscale peptide based sealants which can facilitate faster blood clotting than natural fibrin. These sealants are stabilized by lysine-aspartate ionic interactions and also by N ϵ (γ -glutamyl)lysine isopeptide bond mediated covalent interaction. Each peptide based sealant is having two complementary peptides to facilitate lysine-aspartate ionic interactions and designed isopeptide bond mediated interactions. Computational studies have shown energetically favourable peptide assemblies in designed sealants 1-3. Sealants 2 and 3 facilitate clot formation like natural fibrin in presence of transglutaminase enzyme and blood corpuscles.

Ex-vivo studies with blood corpuscles reveal that sealant 2 and 3 are having superior hemostatic activities than fibrin. Designed sealants feature mechanical properties and biocompatibility as evidenced by AFM and cell based studies. Such nature-inspired sealants might be potentially translated into clinics to promote efficient blood clotting to handle traumatic coagulopathy and impaired blood clotting (ref: **Snehasish Ghosh et. al. *Sci. Rep.*, 2017, 7, 6509**)

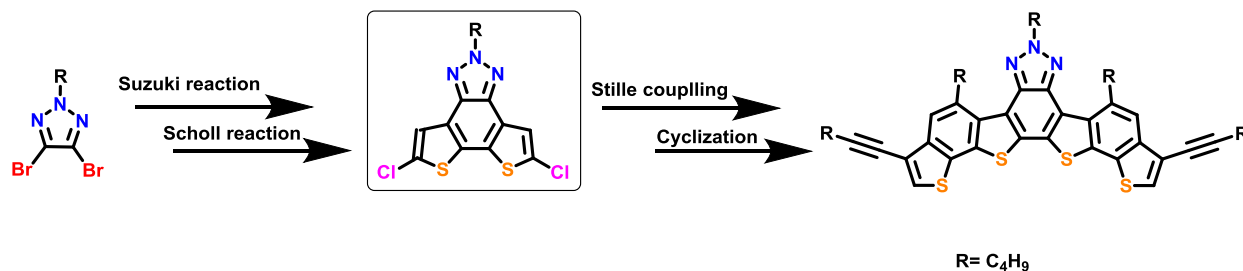
Dithieno-benzotriazole: An old precursor for new ladder type heterocyclic donor acceptor fused acene.

Abhijeet R. Agrawal, Sanjio S. Zade*

Department of Chemical Sciences,
Indian Institute of Science Education and Research, Kolkata.

Abstract

Novel and facile synthesis of triazole and thiophene fused heteroacene has been developed. In the present case oxidative cyclodehydrogenation by Scholl reaction of thiophene substituted triazole is followed by unexpected formation of chlorinated dithieno-benzotriazole. Crystal structure analysis reveals the importance of this molecule in crystal bending studies. This molecule is a novel precursor for easy and effective construction of longer acenes having all *syn* oriented thiophene. A ladder type of donor acceptor heptacene has been synthesized having all *syn* orientation of the thiophene units. This fused aromatic acene can also be subjected to various chemical transformations to generate diverse molecules with potential applications in π -conjugated materials for organic electronics.



References :

- 1) Arroyave F. A.; Richard C. A.; Reynolds J. R. *Org. Lett.* **2012**, *14*, 6138–6141.
- 2) Ni J. S.; Yen Y. C.; Lin J. T. *Chem. Commun.* **2015**, *51*, 17080—17083.
- 3) Ni J. S.; Yen Y. C.; Lin J. T. *J. Mater. Chem. A* **2016**, *4*, 6553–6560

Designed pH-responsive molecular transporters for enabling enhanced siRNA delivery

Abhijit Biswas,^{#,1} Chiranjit Dutta,^{#,1} Kasturee Chakraborty,^{#,2} Sanchita Mukherjee,^{#,2} Paramita Gayen,² Somnath Jan,² Dhananjay Bhattacharyya^{*,3} and Rituparna Sinha Roy^{*,2}

¹Department of Chemical Sciences, IISER Kolkata

²Department of Biological Sciences, IISER Kolkata

³Computational Science Division, Saha Institute of Nuclear Physics, Kolkata.

Abstract

Cell-penetrating peptidebased molecular transporters have gained significant importance for intracellular delivery of functional siRNA. The cellular internalization pathway of CPP-cargo complex is determined by the size, charge and concentration of CPP-cargo complexes and cell types used for the study and mainly occur by endocytic pathways and suffer from endosomal entrapment. The endosomal entrapment and inefficient release of cargo from endosome prevents high yield cytosolic delivery of functional siRNA. To overcome these challenges, we have designed peptide based molecular transporters having Arg-(L/D)His-Arg moiety in the sequence and evaluated their physicochemical properties and gene silencing efficacies. pH-sensitive residue, histidine exhibits proton sponge effect in endosomal acidic environment and facilitates the release of entrapped CPP-cargo complexes to the cytosol. Interestingly, histidine-rich molecular transporters demonstrate significant gene silencing like commercial transfection agent hiPerfect and we anticipate such molecular transporters might be translated to clinics for developing next-generation siRNA based nanotherapeutics.

Vesicular self-assembly of Nano-sized Terpenoids

Abir C. Barai, Subrata Ghorai, Subhajit Das, Sk Nurul Hasan, Saikat Kr. Panja,

Chhabi Garai, Sanjit Santra, Braja Gopal Bag*

Department of Chemistry and Chemical Technology

Vidyasagar University, Midnapore 721 102, West Bengal, India

Email: braja@mail.vidyasagar.ac.in

Study of the spontaneous self-assembly of molecules yielding vesicles are of tremendous interest in recent years due to its application in the areas of targeted drug delivery, medical implants, tissue engineering, gene therapy, theranostics, magnetic resonance imaging, etc.^{1,2} Vesicular self-assemblies of molecules from renewable resources are of special significance because of their availability in renewable supply, low toxicity and biodegradability. Among various plant metabolites, study of the self-assembly of terpenoids have gained significant interest during the last decade. Terpenoids are a large and structurally diverse group of natural products containing multiple of C₅ (isoprene) units. They are categorized by the number of C₅ units as: hemi- (one C₅ unit), mono- (C₁₀; two C₅ units), sesqui- (C₁₅; three C₅ units), di- (C₂₀; four C₅ units), sester- (C₂₅; five C₅ units), tri- (C₃₀; six C₅ units), and so on.³ Herein we report the spontaneous self-assembly properties of several terpenoids yielding vesicles in aqueous binary solvent mixtures. The vesicular self-assemblies were capable of entrapping various fluorophores including the anticancer drug doxorubicin.^{4,5,6,7,8,9} The entrapped drug could be released at physiological pH making these vesicular self-assemblies useful as prospective drug delivery vehicle.

References

1. P. Moitra, K. Kumar, P. Kondaiah, S. Bhattacharya, *Angew. Chem. Int. Ed.*, 2014, 53, 111
2. T. Shimizu, M. Masuda, H. Minamikawa, *Chem. Rev.*, 2005, 105, 1401.
3. B. G. Bag, A. C. Barai, Sk N. Hasan, S. Das, C. Garai, S. Ghorai, S. K. Panja *Prayog. Ras.*, 2017, 1, 61.
4. B. G. Bag, R. Majumdar, *Chem. Rec.*, 2017, 17, 841.
5. B. G. Bag, R. Majumdar, S. K. Dinda, P. P. Dey, G. C Maity, V. A. Mallia, R. G. Weiss, *Langmuir*, 2013, 29, 1766.
6. B. G. Bag, R. Majumdar, *RSC Adv.*, 2014, 4, 53327.
7. B. G. Bag, K. Paul, *Asian J. Org. Chem.*, 2012, 1, 150.
8. B. G. Bag, S. Das, S. N. Hasan, A. C. Barai, *RSC Adv.*, 2017, 7, 18136.
9. B. G. Bag, A. C. Barai, K. Wijesekera, P. Kittakoop, *ChemistrySelect*, 2017, 2, 4969.

Functional Group Display and Shape Regulation in H-Bonding Promoted Supramolecular Assembly of π -Amphiphiles and Impact on Multivalent Binding

Amrita Sikder,^aDebes Ray,^bVinod K Aswal,^b and Suhrit Ghosh^{*a}

^aPolymer Science Unit

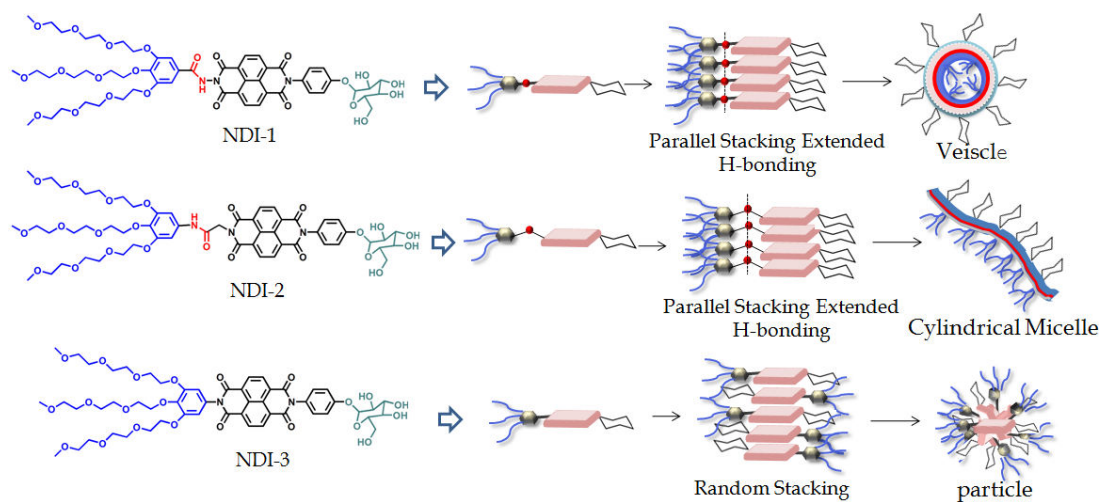
Indian Association for the Cultivation of Science Kolkata

E-mail: amrita1.chem@gmail.com

^bSolid State Physics Division

Bhabha Atomic Research Centre, Mumbai

Amphiphiles are prominent synthetic systems explored for wide-ranging nanostructures with close relevance in nanotechnology and biomedicine. Our recent results show contrasting supramolecular assembly of the twin bola-shape unsymmetrical π -amphiphiles, both having the naphthalene-diimide (NDI) chromophore connected to a non-ionic and anionic head groups in opposite arms, but differ only in the location of the hydrazide group, placed either at the non-ionic or anionic arm of the NDI chromophore. H-bonding among the hydrazides, compensating electrostatic and steric factors, promotes unidirectional alignment and monolayer vesicles leading to a contrasting surface functional group display (depending on the location of the hydrazide group) and consequently enzyme inhibition activity.¹ Subsequent studies demonstrate the possibilities of precisely tuning the size and surface charge density of such vesicles by systematic variation of the structure of the ionic head groups.² Most recently, H-bonding regulated functional group display has also been verified³ by the glycol-cluster effect exhibited by sugar-functionalized similar π -amphiphiles (Scheme 1). For example, NDI-1, virtue of H-bonding, exhibits unidirectional assembly producing unsymmetric membrane leading to effective display of the sugar moieties at the vesicular surface which enables much efficient binding with ConA compared to NDI-3 that lacks any H-bonding group. Interestingly, NDI-2, consisting of amide as the H-bonding group rather than hydrazide as in NDI-1, shows cylindrical micellar structure, attributed to difference in H-bonding motifs between amide and hydrazide. The difference in structure between NDI-1 and NDI-2 shows strong impact on binding with ConA; NDI-2 appears much better than NDI-1 due to the flexibility of an open chain cylindrical structure than a vesicle. Highlights of these results will be described in the presentation.



Scheme.1: Schematic presentation of H-bonding regulated supramolecular assembly of glucose containing unsymmetricbola-shape π -amphiphiles.

Reference:

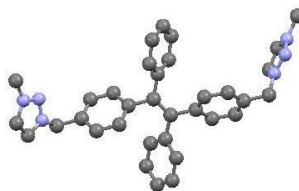
1. A. Sikder, A. Das, and S. Ghosh, *Angew. Chem. Int. Ed.* **2015**, 54, 6755–6760.
2. A. Sikder, D. Ray, V. K. Aswal and S. Ghosh, *Langmuir* **2018**, 34, 868-875.
3. A. Sikder, D. Ray, V. K. Aswal and S. Ghosh, Unpublished results.

Detection and differentiation of DNA and RNA with a novel AIE bioprobe

*Sk. Atiur Rahaman, Subhajit Bandyopadhyay**

Indian Institute of Science Education and Research (IISER) Kolkata

Tetraphenylethene (TPE) units are known to display aggregation induced emission (AIE) properties.¹ A TPE based molecule with two appended methylimidazolium units were synthesized. The presence of the cationic moieties enhances its solubility tremendously in the aqueous media and alter the solvent dependent aggregation properties of this molecule. This molecule interacts with double stranded DNA and RNA with unique emissive features. The synthesis, aggregation induced fluorescence properties, and the fluorescence behavior of this molecule in the presence of nucleic acids will be presented and discussed.



Reference :

[1] Tang, B. Z et.al. Chem. Soc. Rev., 2011, **40**, 5361–5388.

Antibacterial Activity of Side-Chain Amino Acid Based Cationic Polymers and Morphological Switching of Treated Bacterial Cell

Ishita Mukherjee,^a Anwesha Ghosh,^b Punyasloke Bhadury^b and Priyadarsi De^{a,*}

^a Department of Chemical Sciences

^b Department of Biological Sciences

Indian Institute of Science Education and Research Kolkata.

Synthetic polymer based antimicrobial materials have been reported in the literature to demolish conventional antibiotic resistant microorganisms.^{1,2} Although these antibacterial polymers replicate the properties of antimicrobial peptides (AMPs), their effect on the bacterial cell morphology has not been studied comprehensively. To investigate the morphological switching of bacterial cell in the presence of antimicrobial polymer, herein we have synthesized side-chain amino acid based cationic polymers. These polymers exhibited efficient antibacterial activity against Gram-negative (*E.coli*) as well as Gram-positive (*B.subtilis*) bacteria. Drastic morphological switching from rod shape to spherical shape of *E.coli* cells was observed by field emission scanning electron microscopy (FE-SEM) analysis during cell wall disruption through polymer treatment, whereas *B.subtilis* cell structure and size remain unchanged, but stacked to each other after polymer treatment (Figure 1). Using side-chain leucine pendant cationic polymer, the bacterial growth inhibitory property in Luria Broth media was proved by the absence of exponential phase of bacterial growth curve of *E.coli*.

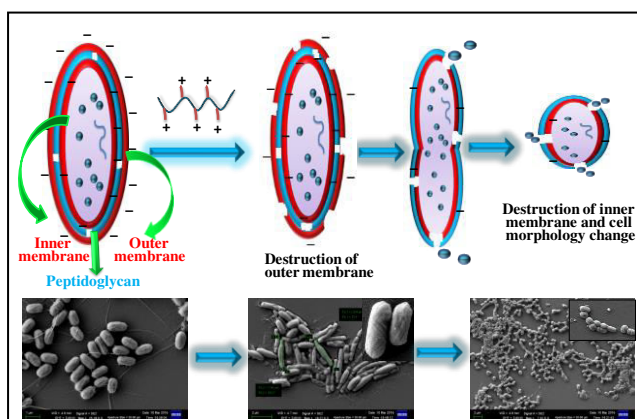


Figure 1

KEYWORDS: Antimicrobial peptides (AMPs), Zone of inhibition, Gram-positive and Gram-negative bacteria, morphological switching

***Corresponding Authors: Priyadarsi De (p_de@iiserkol.ac.in)**

References :

- (1)Oda, Y.; Kanaoka, S.; Sato, T.; Aoshima, S.; Kuroda, K. *Biomacromolecules***2011**, *12*, 3581–3591.
- (2)Engler, A. C.; Tan, J. P. K.; Ong, Z. Y.; Coady, D. J.; Ng, V. W. L.; Yang, Y. Y.; Hedrick, J. L.*Biomacromolecules***2013**, *14*, 4331–4339.

AminoAcid-based Biocompatible Polymeric Fluorescent Probe for Selective Sensing and Removal of Hg^{+2} Ion from Aqueous Media

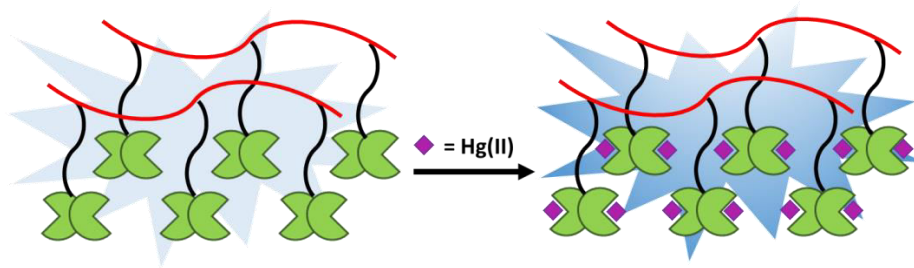
Neha Choudhury and Priyadarsi De*

Polymer Research Centre, Department of Chemical Sciences,

Indian Institute of Science Education and Research Kolkata

e-mail address: p_de@iiserkol.ac.in

Exposure to mercury ions can damage human brain, the nervous system, the endocrine system, and other biological systems, due to its high toxicity.¹ Thus, simple and convenient sensors are needed, which can meet the requisite conditions such as rapid detection, sufficient sensitivity, and minimal or no interference to protect the environment from the metal ion toxicity.² To serve this purpose, we sought to develop a tryptophan-based water-soluble polymeric sensor for the fluorometric detection of Hg^{+2} in aqueous media via reversible-addition fragmentation chain transfer (RAFT) polymerization. In presence of several metal ions, the probe can selectively sense Hg^{2+} ion with a 4-fold enhancement of the fluorescence. In addition, this tryptophan-based polymeric probe is able to sense ppb levels of Hg^{+2} with higher selectivity in an aqueous environment and can remove the toxic metal through the formation of irreversible 1:2 polymer- Hg^{+2} complex. The *in vitro* cytotoxicity study confirmed the excellent biocompatibility of the resultant polymer. Furthermore, the intracellular detection of Hg^{2+} ions was achieved by virtue of fluorescence confocal microscopy.



References :

1. P. B. Tchounwou, W. K. Ayensu, N. Ninashvili, D. Sutton, *Environ. Toxicol.*, **2003**, *18*, 149–175.
2. G. Chen, Z. Guo, G. Zeng, L. Tanga, *Analyst*, **2015**, *140*, 5400–5443.

Multi-Stimuli Responsive Assembly of Alternating Donor-Acceptor Supramolecular Copolymer

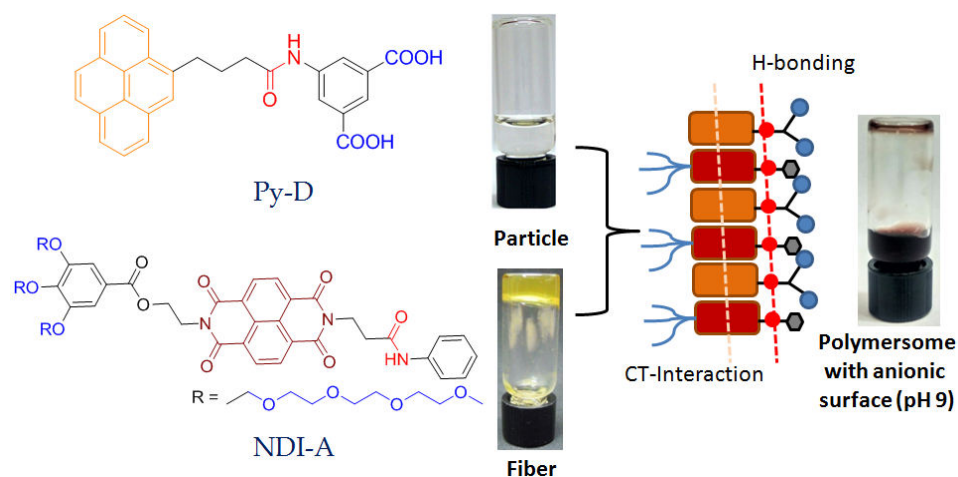
Saptarshi Chakraborty, Amrita Sikder and Suhrit Ghosh*

Polymer Science Unit, Indian Association for the Cultivation of Science,
Kolkata-700032, India

E-mail: saptarshi431@gmail.com

Abstract

Charge-transfer (CT)-interaction driven alternating assembly between aromatic Donor(D) and Acceptor(A) π -systems although is well known for a long time, their weak binding affinity in majority examples hinders hierarchical assembly. We have recently reported the possibility of alternating supramolecular copolymerization by H-bonding assisted D-A interaction.¹ This particular alternating copolymerization strategy has now been successfully extended to aqueous domain with newly synthesized water soluble D and A building blocks (Scheme 1). Py-D and NDI-A forms micelle and meta-stable fibrillar gel, respectively, while their 1:1 mixture exhibits highly stable alternating supramolecular copolymerization and assembles to multi-stimuli responsive polymersome in water. As both the D and A components contain a single amide group and unsymmetric in nature, the H-bonding driven alternating copolymer had distinct two phases; one displaying the carboxylic acid group (coming from Py-D) and the other displaying the non-ionic wedge (coming from NDI-A). In the resulting membrane, the carboxylic acid groups were found to be displayed on the outer surface (confirmed by highly negative zeta potential in basic pH where the carboxylic acid groups remain as salt) which is attributed to (i) less electro-static repulsion and/ or (ii) propensity of the H-bonded chain to bend in a particular direction. It was reflected in very effective binding with an enzyme Chymotrypsin and inhibition of its activity comparable to the best reported values in the literature. The polymersome showed collapse either at higher temperature beyond the lower critical solution temperature of the assembled non-ionic wedge and also under acidic pH. Uniquely disassembly was also observed under reducing environment which generated the NDI radical anion and thereby destroyed the D-A interaction, leading to the triggered release of the entrapped guest molecules. The presentation will focus on design, structure and multi-stimuli responsiveness assembly of these alternating supramolecular copolymers.



Scheme 1. Structure of the donor-acceptor building blocks and their alternating copolymerization motif leading to formation of polymersome from (micelle + fiber)

Reference:

1. A. Sikder, B. Ghosh, S. Chakraborty, A. Paul and S. Ghosh, *Chem. Eur.J.* **2016**, 22, 1908-1913.
2. S. Chakraborty and S. Ghosh, *Unpublished results*.

Luminescent lanthanide hydrogels and their application in (bio)analyte sensing

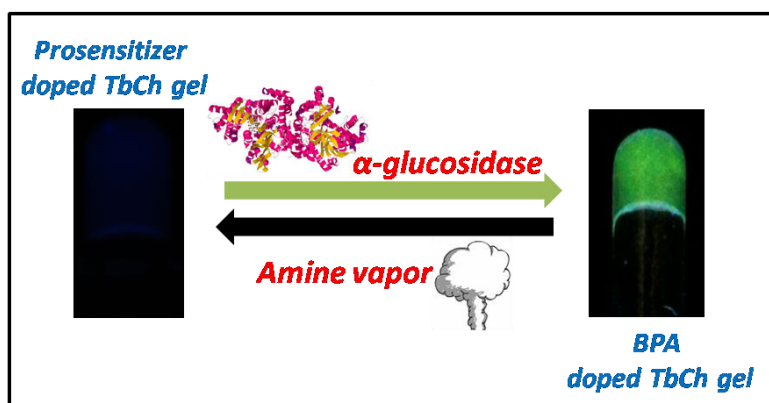
Dipankar Bhowmik, Shruthi Sakthivel & Uday Maitra

The Department of Organic Chemistry

Indian Institute of Science, Bangalore

shruthisakthivel@gmail.com

Luminescent lanthanides have intrinsic low molar absorptivities. This problem can be addressed by complexing the lanthanide ion with suitable chelating ligands, which improves the luminescence properties drastically. However, the design of such systems often involves careful planning and laborious synthetic steps. It is therefore desirable to have a simpler way to sensitize lanthanides with high efficiency. It was observed in our group that doping micro molar concentration of 2,3-dihydroxy naphthalene (DHN) in terbium cholate (TbCh) hydrogel resulted in enhanced luminescence. Recently, we also discovered that several biphenyl derivatives could also sensitize Tb(III) in TbCh gels. We have used such sensitized luminescence in developing a simple strategy involving a luminescence *turn-on* response for the rapid detection of a biologically important enzyme - α -glucosidase and a luminescence *turn-off* response for detecting hazardous amine vapours in TbCh gel. Increasing luminescence was observed on addition of α -glucosidase to a α -DHN-glucoside (prosensitizer) doped TbCh gel, making it an effective method for the enzyme detection and quantification. The luminescence enhancement was due to the release of free DHN (sensitizer) upon enzyme action. This detection method showed good selectivity in the presence of other closely related enzymes and prosensitizers. When the same TbCh gel doped with 4-biphenyl carboxaldehyde was exposed to various amine vapours, quenching was observed. Interestingly, the quenching was only selective to amine and nitro compounds. In addition, appreciable quenching was observed even at low ppm levels of the analyte. Further, we have simplified this detection method by using a low-cost, user-friendly paper based approach using TbCh gel coated paper discs/strips for easy detection of the analytes.

**References:**

1. Banerjee, S.; Ramesh, K.; Bhowmik, S.; Maitra, U. *Soft Matter* **2011**, *7*, 8207-8215.
2. Bhowmik, S.; Maitra, U. *Chem. Commun.* **2012**, *48*, 4624-4626
3. Gorai, T.; Maitra, U. *ACS Sens.* **2016**, *1*, 934-940.

Supramolecular Polymerization in Aqueous Media Utilizing pH induced Conformational Modulation of Monomers

Shubhra Kanti Bhaumik and Supratim Banerjee*

Department of Chemical Sciences, IISER Kolkata

Abstract:

In this study, the host-guest interaction between small bifunctional monomers and cucurbit[8]uril (**CB[8]**) is being utilized for the formation of supramolecular polymers in aqueous media. **CB[8]** is a water-soluble macrocyclic host which can form ternary complexes by encapsulating two guest molecules simultaneously¹. We

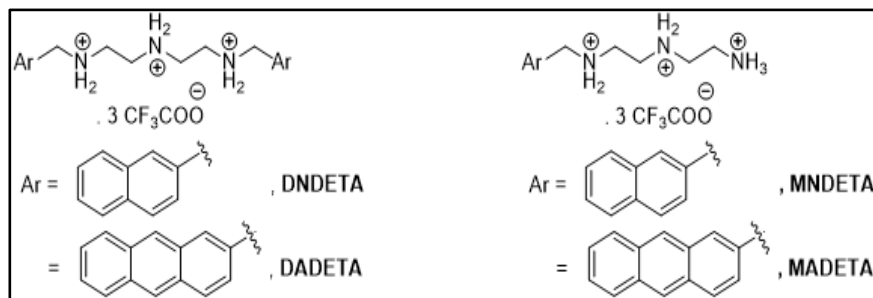


Fig 1: Structures of DNDETA, DADETA, MNDETA and MADETA

have designed naphthalene- and anthracene-based monomers, **DNDETA** and **DADETA** (Fig 1) for this purpose. Due to the presence of diethylenetriamine as the linker in their structures, the monomers undergo conformational modulation depending on the pH of the medium² (Fig

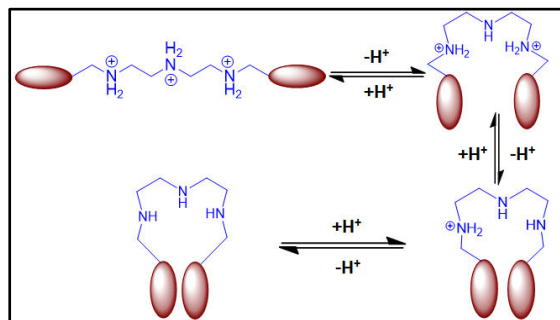


Fig 2: pH-induced conformational variation of bi-functional monomers

2). For example, at basic pH values (>8), they adopt a “bent” conformation whereas an “open” conformation results in acidic pH (Fig 2). The “open” conformation is capable of forming linear supramolecular polymers in the presence of **CB[8]** (Fig. 3). Monofunctional monomers, **MNDETA** and **MADETA** (Fig 1) have also

been synthesized as model compounds. Binding studies as well as the binding stoichiometry of

mono- and bi-functional monomers with **CB[8]** are currently being investigated at different pH values employing absorption and fluorescence spectral studies. This type of supramolecular polymers having cationic backbone are also promising as sensing probes for biologically relevant anionic analytes.

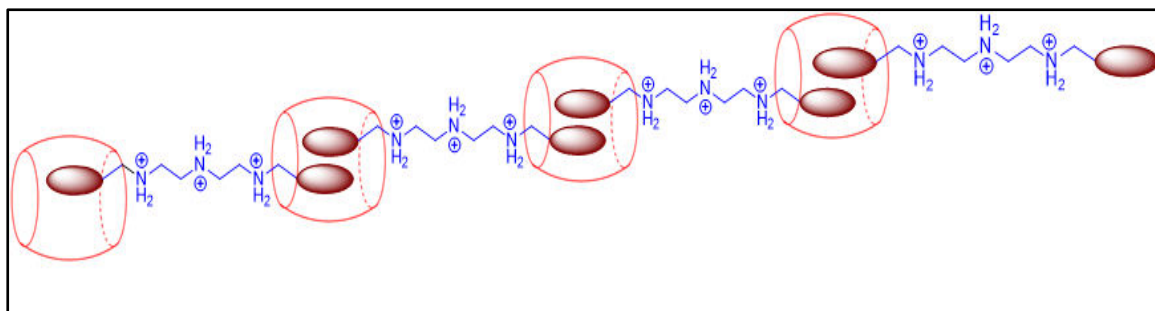


Fig 3: Representation of the formation of a linear supramolecular polymer at low pH

References:

1. K. Kim, N. Selvapalam, Y. H. Ko, K. M. Park, D. Kim, J. Kim, *Chem. Soc. Rev.* **2007**, 36, 267 – 279.
2. T. Hirai, Y. Tokitoh, Y. Shiraishi, *Org. Lett.* **2006**, 17, 3841 – 3844.

Water Soluble Alternating Polyperoxides Derived from Poly(ethylene glycol) Substituted Styrenic Monomers with thermal degradation

Sourav Mete, Priyadarsi De*

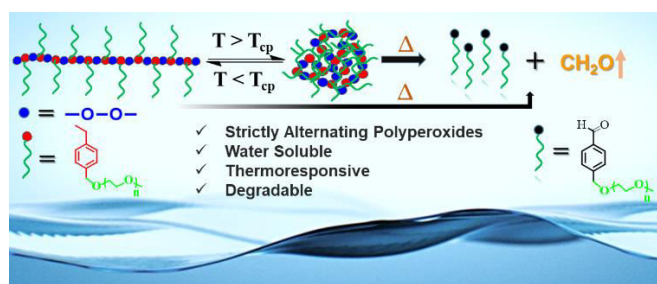
Polymer Research Centre and Centre for Advanced Functional Materials

Department of Chemical Sciences

Indian Institute of Science Education and Research Kolkata.

* *Corresponding author E-mail: p_de@iiserkol.ac.in*

4-vinylbenzyl methoxypoly(oxyethylene) ether (PEGSt) and molecular oxygen react at 50 °C under high pressure in presence of radical initiator gives water soluble alternating polyperoxides. NMR spectroscopy and FT-IR have been used to confirm the alternating copolymer structure of peroxy (-O-O-) bonds in the main chain. This class of polymers are unique due to their highly exothermic decomposition, in contrast to common polymers which generally degrade endothermically. Polyperoxides find application as auto combustible fuel, polymeric thermal macroinitiator, dismantlable adhesive, curatives in coating and moulding compositions, drug delivery carrier, etc. Highly exothermic degradation of polyperoxides have been investigated by differential scanning calorimetry (DSC)¹ and the degradation products have been characterized by electron impact mass spectroscopy (EI-MS). The rate of polymerization (R_p) was calculated from the slope of the oxygen consumption against time plot. The synthesised polymers show thermoresponsiveness at variable temperature, which can be tuned by varying the chain length of ethylene oxide moiety in the side chain and incorporation of methyl methacrylate in the side chain. The cloud point of the polymer was measured by UV-vis spectroscopy and dynamic light scattering (DLS).² At the end we established that the obtained polyperoxides can be used as a free radical initiator for the polymerization of vinyl monomer like *N,N*-dimethylacrylamide (DMA) in organic medium.



References:

- (1) Pal, S; Das, A; Maiti, S; De, P. Synthesis and characterization of a biodegradable polymer prepared via radical copolymerization of 2-(acetoacetoxy)ethyl methacrylate and molecular oxygen *Polym. Chem.*, **2012**, 3, 182-189.
- (2) Pal, S.; De, P. Water soluble polyperoxides from 2-(2-methoxyethoxy)ethyl methacrylate: influence of molecular oxygen on thermoresponsive properties and thermal degradation *Chem. Commun.* **2012**, 48, 4229-4231.

The Molecular Toplogy and Supramolecular Chemistry

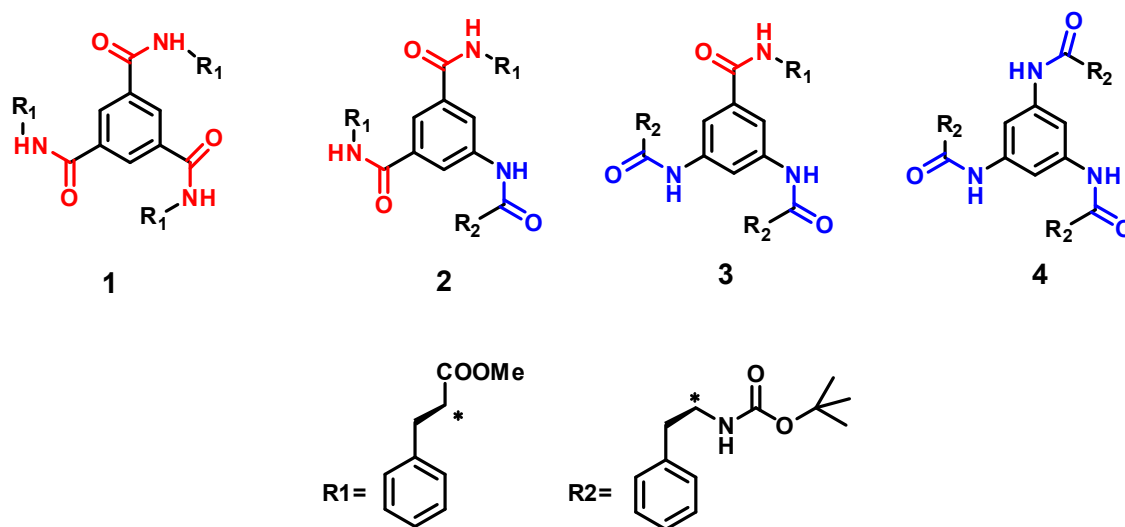
Supriya Sasmal, Santu Bera and Debasish Haldar*

Department of Chemical Sciences

Indian Institute of Science Education and Research Kolkata

E-mail: deba_h76@iiserkol.ac.in

The topochemical arrangement of small molecules that can modulate the physical properties of a supramolecular system may have potential as futuristic materials.¹ Herein we report how the self-assembly of benzene tricarboxamide (BTA) derivative depends on the direction of amide bond (NH-CO) attached with central benzene ring. The C=O (1) and N-centered (4) BTA where the entire three amides bond directed to similar direction, give fiber like morphology. The BTA derivative of isophthalic acid (2) where two amides bonds are same direction and other one to different direction, gives vesicle morphology. The BTA derivative of 3, 5 diamino benzoic acid (3) where the direction of amide bonds are just opposite to 2, gives spherical like morphology. We show this phenomenon is true until there is no introduction of side chain-core interaction. After heating cooling and sonication in toluene, 1 gives semi gel. 2 and 3 do not show any kind of gelation property. But 4 form gel.



References:

1. Bera, S.; Haldar, D. A rechargeable self-healing safety fuel gel. *J. Mater. Chem. A*. 2016, 4, 6933-6939.

Mopping up the Oil, Metal, and Fluoride Ions from Water

Tanmay Das and Debasish Haldar.

Department of Chemical Sciences,

Indian Institute of Science Education and Research Kolkata.

E-mail: deba_h76@yahoo.com.

The recycle, cleaning, and reuse of water are highly important for environmental remediation.¹ This issue is addressed by creating a fluorescent zwitterionic spirocyclic Meisenheimer complex (**1**) with high chelating propensity for toxic metals using low-cost starting materials and a one-pot synthesis technique.² The resulting material is able to detect fluoride up to 12.8 ppb level and remove 82% aqueous fluoride from 1000 mL of 100 ppm fluoride solution in a single contact. The material demonstrates rapid kinetics and is capable of dropping the toxic metal ion (Pb/Hg/Cd) concentration below 0.2 ppb within 10 min. A resin-free, precipitation-free, and reusable technique has been developed for the removal of toxic metal ions and fluoride from extremely polluted water.³ Moreover, utilizing its extreme hydrophobicity, polystyrene sponges have been coated with the Meisenheimer complex to mop up oil spill and organic solvents from a biphasic mixture.

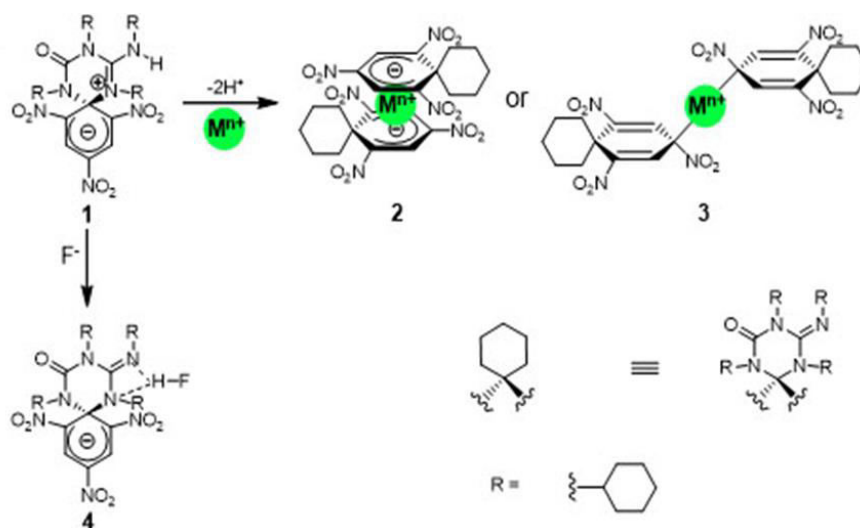


Figure 1. Possible mode of binding of **1** with different metal ion and fluoride anion.

References :

[1] Veldkamp, T. I. E.; Wada, Y.; de Moel, H.; Kummu, M.; Eisner, S.; Aerts, J. C. J. H.; Ward, P. J.

Changing mechanism of global water scarcity events: Impacts of socioeconomic changes and

inter-annual hydro-climatic variability. *Global Environmental Change* **2015**, 32, 18-29.

[2] Das, T.; Pramanik, A; Haldar, D. On line Ammonia Sensor and Invisible Security Ink by Fluorescent ZwitterionicSpirocyclic Meisenheimer Complex. *Sci. Rep.* **2017**, 7, 40465.

[3] Das, T.; Haldar, D. Mopping up the Oil, Metal, and Fluoride Ions from Water.ACS Omega 2017, 2, 6878–6887.