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Molecular design and engineering of biomimetic, bioinspired and biologically derived materials

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Arthi Jayaraman

Arthi Jayaraman holds the position of Professor in the Departments of Chemical and Biomolecular Engineering and Materials Science and Engineering at the University of Delaware. She currently also serves as an Associate Editor of *Macromolecules*. She received her B.E (Honors) degree in Chemical Engineering from Birla Institute of Technology and Science, Pilani, India in 2000. She received her Ph.D. in Chemical and Biomolecular Engineering

from North Carolina State University in 2006, and from 2006–2008 she conducted her postdoctoral research in the Department of Materials Science and Engineering at the University of Illinois-Urbana Champaign. In August 2008 she joined the faculty of the Department of Chemical and Biological Engineering at University of Colorado at Boulder and held the position of Patten Assistant Professor till 2014. In August 2014 she joined the Chemical and Biomolecular Engineering faculty at the University of Delaware with a joint appointment in Materials Science and Engineering. Her research expertise lies in the development of theory and simulation techniques and application of these techniques to study polymer nanocomposites and solutions and to design macromolecular materials for biological applications. She has been awarded the Saville Lectureship at Princeton University (2016), the AIChE COMSEF division young investigator award (2013), the ACS PMSE division young investigator recognition (2014), a University of Colorado Provost Faculty Achievement Award (2013), a Department of Energy (DOE) Early Career Research Award (2010), and the University of Colorado outstanding undergraduate teaching award (2011) and graduate teaching award (2014) in Chemical and Biological Engineering.



Amish Patel

Amish Patel received his Bachelors in Chemical Engineering from the Indian Institute of Technology – Bombay in 2001 and his Doctorate in Chemical Engineering from the University of California – Berkeley in 2007. After completing postdoctoral fellowships in the Department of Chemistry at the University of California – Berkeley, and in the Department of Chemical and Biological Engineering at Rensselaer Polytechnic Institute, Amish

joined the Chemical and Biomolecular Engineering department at the University of Pennsylvania, where he is currently an Associate Professor. His research strives to achieve a molecular-level understanding of solvation and transport in aqueous and polymeric systems, with applications ranging from predicting protein interactions to designing advanced materials for water purification and renewable energy. To study these biological, nanoscopic, and polymeric systems, the Patel group uses statistical mechanics and liquid state theory in conjunction with the development and use of novel molecular simulation techniques. For his research and teaching, Amish has received the NSF CAREER award (2017), the Sloan Research Fellowship in Chemistry (2017), the OpenEye Outstanding Junior Faculty Award from the Computers in Chemistry division of the American Chemical Society (2018), the Distinguished Teaching Award by Penn's AIChE Student Chapter (2018), the Camille Dreyfus Teacher-Scholar award (2019), and the Van Ness Award Lectureship from Rensselaer Polytechnic Institute (2019).

Molecular design and engineering of organic and inorganic materials that are bioinspired, biomimetic and/or biologically derived is an area of active research in a broad range of disciplines both in the physical sciences (*e.g.*, physics, chemistry, biology) as well as in engineering (*e.g.*, chemical engineering, biomedical engineering, materials engineering). This collection of experimental and computational studies in the form of papers and mini-reviews highlights some of the exciting new and recent work in this research area, covering various topics within this field, spanning therapeutics and antimicrobial materials design, biomimetic polymer design, controlling nanostructure within bioinspired/biomimetic polymeric materials, behavior at organic-inorganic interfaces relevant to biomaterials, materials capable of highly specific biomacromolecular recognition, new models and computational techniques, *etc.*

Biomimetic (organic) materials, specifically copolymers and their nano- and microstructures are the focus of articles by Perry and Sing (DOI: 10.1039/C9ME00074G) and by Vogt *et al.* (DOI: 10.1039/C9ME00101H). Perry and Sing describe their collaborative work using experiments and theory to study electrostatically-driven liquid-liquid phase separation, also known as ‘complex coacervation’, for a series of model polyampholytic polypeptides with increasing blockiness. They show that these polypeptides undergo complex coacervation when sequences have a certain number of closely placed like-charges along the chain and as the blockiness along these chains increases they observe a larger two-phase region. Vogt and coworkers present experiments with hydrogels generated from a statistical protein-mimetic copolymer of hydroxyethyl acrylate and *n*-octadecyl acrylate (HEA-ODA) wherein the crystallization of the ODA provides a simple route to manipulate the structure within the hydrogels. The hydrogel nanostructure is demonstrated to control the structure of water molecules confined at supercooled temperatures without the use of fluorinated hydrophobic moieties.

The hydrophobic effect plays an important role in stabilizing diverse biomaterials and biomolecular assemblies. Two articles in this collection focus on elucidating aspects of multifaceted hydrophobic interactions. Ashbaugh and coworkers (DOI: 10.1039/C9ME00076C) study the aqueous assembly of bowl-shaped supramolecular hosts assisted by their *n*-alkane guests. As the length of the guest chain is increased, the hosts are able to dimerize, initially with each host containing its own guest. Interestingly, the authors find that methylating the host entrance leads to the destabilization of the two guest-two host dimer configuration, and results in a non-monotonic progression from monomeric, to dimeric, to monomeric, to dimeric complexes with increasing guest chain length. Using atomic force microscopy, Abbott and coworkers (DOI: 10.1039/D0ME00016G) characterize the thermodynamic signatures of hydrophobic interactions between several judiciously chosen homogeneous and heterogeneous self-assembled monolayer (SAM) surfaces. In particular, the authors find that the temperature dependence of hydrophobic interactions is inverted when 40% of the methyl head-groups in the SAM surface are replaced by polar amine (or guanidinium) groups, but not when a similar substitution is performed using the cationic ammonium groups.

Hybrid materials (*e.g.*, composites, inorganic-organic interfaces) that are relevant for biomaterials or biomimicry are highlighted in studies by Pfaendtner *et al.* (DOI: 10.1039/C9ME00158A) and Lee *et al.* (DOI: 10.1039/C9ME00148D). Lee, Riggleman and coworkers study polymer infiltration in dense assemblies of nanoparticles as a model system to design and manufacture bio-inspired nanocomposites that mimic nacre's architecture. They use a combination of experiments and simulations to elucidate solvent-driven infiltration of polymers (SIP) into nanoparticle packings formed on top of glassy polymer films which leads to the formation of the nanocomposite structure. Pfaendtner and coworkers probe the fundamental mecha-

nism of medical implant fouling *via* nonspecific adsorption of non-collagenous bone matrix proteins (NCPs) onto a newly implanted interface. They describe the thermodynamic forces underlying the adsorption of a commonly occurring NCP, osteocalcin, onto mineral and metal oxide surfaces.

Multiple contributions in this collection demonstrate how molecular modeling and coarse-grained simulations serve as a valuable tool in the molecular-level design of biologically relevant materials. Deshmukh and coworkers (DOI: 10.1039/C9ME00173E) have developed transferable coarse-grained (CG) models of the twenty standard amino acids, which can be used to perform molecular dynamics (MD) simulations of proteins and peptides. Nangia and coworkers (DOI: 10.1039/C9ME00177H) are interested in using molecular simulation methods to help *in vitro* and *in vivo* characterization of tight junction macroassemblies where molecular-level precision is essential for understanding nature's design principles for biomimetic applications. In their article, they have used their recently developed protein association energy landscape (PANEL) method to mine the interaction data of amino acid residue contacts from millions of geometries *via* exhaustive sampling of the interaction states of claudin, a protein active in the blood-brain barrier.

Theory and simulations are also highlighted in the mini-review by Dzubiella and co-workers (DOI: 10.1039/C9ME00106A) where they present recent theoretical and computational efforts to design “nanoreactors” that are relevant for engineering highly selective, programmable “colloidal enzymes”. Specifically, they summarize computational efforts to calculate reaction rates of surface-catalyzed bimolecular reactions in stimuli-responsive nanoreactors in terms of the key material design parameters like polymer permeability, reactant partition ratio, *etc.* Another mini-review by Neoh (DOI: 10.1039/C9ME00175A) describes recent work in the design of anti-cancer chemotherapeutics and antimicrobials through sugar-mediated targeted delivery strategies that

capitalize on the unique metabolic features of cancer cells and bacteria for improved drug/antimicrobial efficacy.

We thank the authors for their valuable contributions to this themed collection, and hope that

readers appreciate these articles and learn from them as much as we have.