

## Biomaterial Interfaces Division

### Room B117-119 - Session B12+AS+HC+SS-MoM

#### Energy Transfer and Light Induced Phenomena in Biologic Systems

**Moderators:** **Morgan Alexander**, University of Nottingham, UK, **Tobias Weidner**, Aarhus University, Denmark

10:40am **B12+AS+HC+SS-MoM-8 Electrochemically Conducting Lipid Bilayers: Q-Lipid-Containing Membranes Show High in-Plane Conductivity Using a Membrane-on-a-Chip Setup**, *U. Ramach*, TU Wien, Austria; *J. Andersson*, IST Austria; *Markus Valtiner*, TU Wien, Austria

The light-driven reactions of photosynthesis as well as the mitochondrial powersupply are located in specialized membranes containing a high fraction of redox-active lipids. In-plane charge transfer along such cell membranes is recurrently thought to be facilitated by the diffusion of redox lipids and proteins.

Using a membrane on-a-chip setup, we show here that redox-active model membranes can sustain surprisingly high currents (mA) in-plane at distances of 25 nm. We also show the same phenomenon in free-standing monolayers at the air-water interface once the film is compressed such that the distance between redox centers is below 1 nm. Our data suggest that charge transfer within cell walls hosting electron transfer chains could be enabled by the coupling of redox-lipids via simultaneous electron and proton in-plane hopping, similar to conductive polymers. This has major implications for our understanding of the role of lipid membranes, suggesting that Q-lipid-containing membranes may be essential for evolving the complex redox machineries of life.

[1] U. Ramach, J. Andersson, R. Schöfbeck and M. Valtiner, *Science* 26 (2), 2023.

11:00am **B12+AS+HC+SS-MoM-9 Light Responsive Cyclic Peptide Polymer Nanomaterials**, *O. Atoyebi*, *M. Beasley*, *W. Maza*, *M. Kolel-Veetil*, *A. Dunkelberger*, **Kenan Fears**, US Naval Research Laboratory

Cyclic peptides are capable of self-assembling into supramolecular peptide nanostructures, via hydrogen bonding along the backbone of the peptide rings. To improve upon this molecular architecture, we designed and synthesized cyclic peptide polymers by covalently linking the cyclic peptides into a linear polymer chain, and demonstrated the conformation of the polymer chain could be transitioned from an unfolded state into rigid, peptide nanorods by varying solution pH. Here we present an alternate way to control the self-assembly via photo-isomerization. We capitalize on azobenzene's photo-actuable nature using a di-carboxylic acid azobenzene to covalently crosslink the cyclic peptide rings into a linear cyclic peptide polymer via terminal amines present in the ring. Self-assembly of the cyclic peptide nanotube occurs by exposing the polymerized cyclic peptide to ultraviolet radiation causing a trans- to -cis transition of the azobenzene and thus assembling the cyclic peptide nanotube. Furthermore, we fluorescence donor/acceptor pairs can be displayed from these materials, at highly controlled separation distances, to alter the optical response of these materials as a function of polymer conformation.

11:20am **B12+AS+HC+SS-MoM-10 Programmable Biomimetic Light-Harvesting Systems based on Strong Coupling of Synthetic Peptides and Dye-Functionalised Polymer Brushes to Plasmon Modes**, *Graham Leggett*, University of Sheffield, UK

Excitation transfer in molecular photonic materials is dominated by incoherent hopping processes; consequently, exciton diffusion lengths are short (~10 nm) placing severe constraints on device design. A grand challenge for the past two decades has been to discover how to achieve efficient long-range transfer of excitation in molecular systems. We have developed a new approach to the design of materials for solar energy capture that combines biomimetic design, inspired by structures used in photosynthesis, with strong light-matter coupling.

Photosynthetic pigment-protein light-harvesting antenna complexes (LHCs) from plants and bacteria are strongly coupled to the localised surface plasmon resonances (LSPRs) in arrays of metal nanostructures leading to the formation of macroscopically extended excited states. Modelling of data indicates that the coupling results from linear combinations of plasmon and exciton states. For example, wild-type and mutant LH1 and LH2 from *Rhodobacter sphaeroides* containing different carotenoids yield different coupling energies; the methods of synthetic biology enable strong light-matter coupling to be programmed.

However, proteins are not suitable for putative applications of molecular photonic materials. Instead, we have designed programmable biomimetic pigment-peptide and pigment-polymer antenna complexes, in which surface-grafted peptide and polymer scaffolds organise excitons within localised surface plasmon resonances to achieve strong light-matter coupling. In these systems, delocalised excited states (plexitons) extend across at least 1000s of pigments. In synthetic peptide and protein systems, we find that the plasmon mode couples to states not seen under weak-coupling, providing evidence for the formation of macroscopically-extended excited states that facilitate coherent transfer of excitation across long distances. In pigment-polymer systems, the dye concentration in the film can be increased to ~2M, significantly exceeding the concentration of chlorophyll in biological light-harvesting complexes, by optimisation of the polymer grafting density and the dye-scaffold coupling chemistry. Fitting of spectra for these plexitonic antenna complexes yields Rabi energies up to twice as large as those achieved with biological LHCs. Moreover, synthetic plexitonic antenna complexes display pH- and temperature-responsiveness, enabling active control of strong plasmon-exciton coupling via regulation of the polymer conformation.

These biomimetic quantum-optical brush systems offer great promise for the design of new types of molecular photonic device.

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