

## CPP 24: Focus: Mechanoresponsive Molecules and Materials - organized by Kerstin Blank and Robert Göstl

Time: Tuesday 10:45–13:00

Location: H14

### Invited Talk CPP 24.1 Tue 10:45 H14

**Mechanochemical activation of Cu-NHC-complexes : molecular design, force-measurements and application in polymer materials** — •WOLFGANG H BINDER<sup>1</sup>, MICHEL BIEWEND<sup>1</sup>, PHILIPP MICHAEL<sup>1</sup>, MARTIN BEYER<sup>2</sup>, and MATTHEW SAMMON<sup>2</sup> — <sup>1</sup>Martin-Luther University Halle-Wittenberg, Institute of Chemistry, Chair of Macromolecular Chemistry — <sup>2</sup>Leopold-Franzens-Universität Innsbruck, Institut für Ionenphysik und Angewandte Physik

Understanding rupture of single chemical bonds is an important aspect in chemistry, physics and biology, as many bonds form and reform reversibly, imparting dynamic properties into a molecule or the material it is embedded into (eg. DNA-replication, protein-assembly). However, rupture of covalent bonds can also be induced by molecular force when acting on a chemical bond, enabling bond breaking by distortion. We here report on a metal-complex designed to be activated by molecular force, transmitted via bound polymer chains acting as molecular handles. We will discuss the chemical nature of the metal-complex acting as a mechanophoric system, followed by considerations to measure the molecular force by AFM. Designed cyclic mechanophores enable to discriminate true disruptive events from purely thermal induced debonding events. The use of molecular networks to efficiently transmit force onto the labile mechanochemical bonds will be discussed in view of force-detection in polymeric materials. References: Chem. Soc. Rev. 2011, 40, 2359; MRC, 2018, 0, 1800376; Angew. Chem., Int. Ed. 2015, 54, 13918; Angew. Chem. Int. Ed. 2015, 54, 2556.

### 15 min. break

### Invited Talk CPP 24.2 Tue 11:30 H14

**Mechanoradicals in collagen or: Why playing soccer hurts** — •FRAUKE GRÄTER<sup>1,2</sup>, CHRISTOPHER ZAPP<sup>1,2</sup>, AGNIESZKA OBARSKA-KOSINSKI<sup>1</sup>, CSABA DADAY<sup>1</sup>, and REINHARD KAPPL<sup>3</sup> — <sup>1</sup>HITS, Heidelberg, Germany — <sup>2</sup>Interdisciplinary Center for Scientific Computing, Heidelberg University, Germany — <sup>3</sup>Medical Center of Saarland, Homburg, Germany

Polymers subjected to mechanical stress - be it a shoe sole or rubber band - generate mechanoradicals by undergoing homolytic bond scission. The existence, nature and mode of action of mechanoradicals formed in protein materials under physiological levels of loading, are fully unknown. I will present our recent results on mechanoradicals in collagen. Electron-paramagnetic resonance (EPR) spectroscopy of stretched rat tail tendon fascicles in conjunction with atomistic Molecular Dynamics simulations of collagen I model fibrils show that the radicals form by bond scission in the direct vicinity of crosslinks along the fiber. Radicals then migrate to the adjacent clusters of aromatic residues where they are stabilized. They finally convert into hydrogen peroxide, a key redox signaling molecule. Our work proposes protein mechanoradicals as a yet undiscovered source of oxidative stress, with potential links to processes such as pain sensation and inflammation. Being exposed to extreme loads, collagen I evolved as a radical sponge, a defense against mechano-oxidative damage.

### CPP 24.3 Tue 12:00 H14

**Joint experimental and computational design of tunable molecular photoswitches based on Hemithioindigo compounds** — •MARTIN LEA, BARNEY LEWIS, MICHAEL STANFORTH, VASILIOS STAVROS, and REINHARD J. MAURER — University of Warwick, Coventry, United Kingdom

The ability to reversibly modify the properties of a material in response to external stimuli is fundamental for the design of novel functional materials. Being able to manufacture and control this ability at the molecular level could lead to the realization of the next generation of

nanomaterials for sensors and optoelectronics. Achieving an understanding of how chemical modifications can be used to augment or even inhibit switching will enable intuitive component design for the fabrication of tailor-made, light responsive materials and interfaces.

An emerging class of photoswitching molecules are Hemithioindigos (HTIs). HTIs exhibit exciting photoisomerization properties which can be tuned through means of chemical functionalization. Here we present a joint first-principles-based computational and spectroscopic experimental study on the influence functional groups have upon the key design parameters of HTIs that enable the switching capabilities. These design parameters include spectral properties and the thermodynamic stability of the equilibrium compounds, but also parameters that capture the ground - and excited - state landscapes that determine the photodynamics. On the basis of our findings, we propose molecules with a propensity for successful switching in different applications.

### CPP 24.4 Tue 12:15 H14

**How mechanical properties of coiled coils depend on the oligomerization state: comparing dimers and trimers using molecular dynamics simulations** — •ANA BERGUES-PUPO, REINHARD LIPOWSKY, KERSTIN BLANK, and ANA VILA VERDE — Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

Coiled-coils (CCs) are ubiquitous motifs in many proteins of the cytoskeleton, extracellular matrix and also in bio-engineered materials. The study of their mechanical response is crucial to understand their function and to tune their properties for specific applications. The relationship between CC sequence-structure and mechanics at the molecular level is however not fully understood. Here, we investigate different aspects of CC topology in the mechanical response under shear stress by means of molecular dynamics simulations: we compared a dimer and a trimer CC of similar sequence composition and also look at the effect of amino acids mutations and single helix stability in the mechanical response of the trimer.

The trimeric coiled coil is mechanically more stable than the dimer. The molecular mechanisms of deformation are also different: trimer exhibits irreversible helix unfolding, while unfolding/refolding assisted sliding is observed for the dimer. Interestingly, this increase on stability is almost unaffected by mutations on the hydrophobic and charged amino acids of the trimer. These interactions are known to be determinant for the thermodynamic stability. On the other hand, the mechanical strength of the trimer considerably increases if helical strength is increased such that single helix unfolding is prevented.

### Invited Talk CPP 24.5 Tue 12:30 H14

**The challenges and opportunities of polymer mechanochemistry** — •ROMAN BOULATOV — University of Liverpool, Liverpool, UK

Polymer mechanochemistry is an emerging field at the interface of chemistry, materials science, physics and engineering. It aims at understanding and exploiting unique reactivities of stretched polymer chains. Macromolecules or their segments become stretched in bulk polymers under mechanical loads or when polymer solutions are sonicated or flow rapidly through abrupt contractions. Increasing amount of empirical data suggest that mechanochemical phenomena are widespread wherever polymers are used. In the past decade, empirical mechanochemistry has progressed enormously, from studying fragmentations of commodity polymers by simple backbone homolysis to demonstrations of self-strengthening and stress-reporting materials and mechanochemical cascades using purposefully designed monomers. Progress in developing the conceptual foundation of mechanochemistry has been more limited. I'll discuss this progress and the outstanding challenges facing polymer mechanochemistry.