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Editorial items

Recent advances and applications of redox active macromolecules: Synthetic polymers and biomacromolecules

This special issue comprises selected examples of recent advances in fundamental research and applications of synthetic and biological redox active macromolecules.

In common, these macromolecules contain functional units that can be reversibly reduced or oxidized, in the main chain of the polymer or via redox centers attached to the main chain, or embedded in the macromolecular material [1]. Importantly, different redox states can reflect on significantly altered electrical, optical, mechanical or chemical properties. Well-established protocols for the immobilization of redox active macromolecules at electrochemical electrodes open novel avenues for their straightforward integration into electrochemical devices. Or particular interest in this regard is the possibility of miniaturization, enabling, for instance, the fabrication of sensing arrays, or advanced microfluidic devices. Accordingly, redox active macromolecules are highly attractive for a variety of applications in switchable electrochemical devices such as biosensors [2], biofuel cells [3,4], electrochromic displays [5,6] or batteries [7]. In addition, new applications are under continuous development in materials science, for instance related to new types of actuators [8], drug and gene delivery systems in the biomedical field [9,10] and electrochemical energy storage [11].

On the other hand redox active macromolecules represent highly attractive systems to be studied from fundamental points of view. For instance, from a mechanistic perspective, it is of pivotal importance to understand how electron transfer proceeds between the redox active macromolecule and an underlying electrochemical electrode to elucidate molecular electron transfer mechanisms [12]. As an example, redox proteins involved in biological redox cascades like the photosynthesis or the respiratory chain, to date, are being exploited in various sensing concepts, biofuel cells or applications in nanotechnology. Of particular interest are biofuel cells, where redox enzymes are linked to synthetic redox active polymers serving as wires to fuel glucose oxidase. This nicely demonstrates how novel groundbreaking technology can be designed with redox active macromolecules utilizing biological catalysis. Finally, to better understand and design redox active macromolecules, electroanalytical methods are utilized. These are under ongoing development aiming at spatial resolution towards the single molecule level, like for instance techniques like scanning electrochemical microscopy.

This special issue of European Polymer Journal is devoted to redox active macromolecules providing examples of current research in the exciting eras of both, synthetic and biological redox active macromolecules. These feature unique functional aspects which make them particularly interesting as molecular units in devices. Key applications are addressed including electrochemical sensors, nanobiodevices, and actuators with great technological relevance.

First of all appealing and upcoming new research areas are highlighted by 3 *feature* articles on recent developments. Jonckheijm et al. report on supramolecular redox protein conjugates for protein immobilization [13]. Recent advances in triggering chemical reactions by STM tip confined potentials are covered in a feature article of Elemans and de Boer [14]. The metalloprotein azurin is of particular interest in nanobiodevices which is described in the feature article of Cannistraro et al. [15].

This special issue further includes 2 *tutorials* which describe fundamental aspects of electroanalytical methods and electron transfer in nanobiodevices. Methods enabling nanoscale electrochemistry towards the single molecule level will be covered in a *tutorial* from Kranz et al. [16]. The second tutorial deals with the fundamentals of electron transfer in biomolecular electronics and is included in a tutorial from Facci and coworkers [17].

In addition 2 *reviews* are included in this special issue: Szunerits et al. review the electrochemically triggered release of drugs in a controlled manner over long-term periods utilizing various redox polymers [18]. Mathwig and Rassai elaborate on electrofluorochromic molecules and polymers including applications in sensors and displays [19].

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The issue also includes 4 *research papers* to illustrate the latest achievements in redox active macromolecules, by giving an overall idea and flavor of the research that is conducted in this area. These articles include a novel type of electrochemical glucose sensor based on a supramolecular polymer [20], poly(ferrocenylsilane)-modified microfluidic channels for switchable delay valves [21], and fundamental nano-electromechanical studies of redox-responsive ferrocene-containing polymer brushes [22] and azurin protein layers [23].

In the following a condensed summary of the individual contributions in this special edition is given.

Jonckheijm and coworkers report on redox-active host-guest supramolecular assemblies of peptides and proteins at surfaces [13]. These feature tunable reversibility making them highly attractive for the exploration of cell-interactive surfaces for biological applications. In their *feature* article various strategies to anchor bio- and redox-active peptides and proteins employing supramolecular host-guest chemistry are presented and discussed in the context of these surfaces interacting with cells.

The *feature* article of Elemans and de Boer focuses on the use of STM to induce chemical reactions at surfaces [14]. In particular they spotlight small and larger assemblies of molecules. Via local voltage pulses by the STM tip charge carriers are delivered to the surface, by applying specific bias potentials between the STM tip and the sample, or through electrochemical control over a whole surface, a variety of chemical reactions can be induced, including breaking or formation of bonds between molecules, changing redox states or trigger well-defined polymerization reactions.

Cannistraro and coworkers provide a *feature* article on the blue copper protein azurin which is of particular interest for integration in bio-optoelectronic nanodevices and biosensors [15]. Azurin reveals a very fast and efficient intramolecular electron transfer, and it shows an extraordinary robustness once adsorbed to surfaces. The feature article includes azurin electron transfer, conduction and biorecognition capability, which includes external visible light and voltage excitation.

Kranz et al. provide a fundamental *tutorial* for this special issue on electrochemical analytical techniques [16], which are essential for the study and characterization of redox active macromolecules and their comprehensive investigation in terms of function in dependence of their redox state is a fundamental prerequisite for advancing applications [Kranz]. The covered fundamental electrochemical techniques include voltammetric techniques, electrochemical impedance spectroscopy, electrochemical quartz crystal microbalance, and electrochemical scanning probe microscopies suitable for studying the electrochemical (re)activity of sample surfaces, and for determining electron transport even at the single molecule level.

Electron transfer from the electrode to a reactive species on or near its surface is pivotal for electrochemistry. Facci and Allesandrini elaborate in their *tutorial* on the key aspects of electron transfer in nanobiodevices [17]. These are considered both, from scientific and technological aspects, including fundamentals of electron transfer theory. Experimental configurations for the study of nanobiodevices are discussed and specific cases of nanobiodevices are highlighted.

Szunerits et al. *review* various strategies of electrochemically triggered release of drugs in a controlled manner over long-term periods [18]. This has been recognized as one of the most promising biomedical technologies for treatment of certain types of diseases including cancer, diabetes and chronic pain. The review includes the state of the art of materials and films devoted for electrical and electrochemical activation.

Mathwig et al. *review* electrofluorochromic molecules and polymers emphasizing their structures and functional principles and highlight specific applications [19]. Electrofluorochromic molecules have the unique property that their fluorescence changes as a function of oxidation state. This makes them interesting from a fundamental perspective as molecular dyads are designed and synthesized to tune the interplay of electrochemical and luminescent properties of molecules making them as well attractive candidates for applications in sensors and displays.

Higuchi et al. report on Co(II)-based metallo-supramolecular polymer (polyCo) as a novel matrix to immobilize glucose oxidase (GOx) for enzymatic glucose sensing [20]. Optimization of the composition and the loading of polyCo/GOx on GCE, the respective sensor revealed excellent quantification of glucose by amperometric detection. Importantly, the outstanding stability of the used metallo-supramolecular polymers implies their use as potential electrode material for a future glucose biosensor.

Vancso and coworkers report on redox control of capillary filling speed in poly(ferrocenylsilane) (PFS)-modified microfluidic channels for switchable delay valves [21]. Their method enables the reversible change of the wetting of gold-coated microchannels walls as reflected by the alteration of the capillary filling speed of water inside such modified microchannels. Strikingly, filling experiments revealed that the meniscus speed clearly depends on the redox state of the PFS film. Model calculations predicted meniscus velocities being well in agreement with the experimentally determined capillary meniscus velocity.

Nijhuis et al. investigated side chain effects in the packing structure and stiffness of redox-responsive ferrocene-containing polymer brushes with different side chain lengths prepared by surface-initiated atom transfer radical polymerization (SI-ATRP) [22]. Their results imply that brushes with short linkers between the Fc units and the polymer back bone are stiff and stand up in air up to 40 nm height. In contrast, polymers with long linkers collapse indicating that the stiffness and packing structure are affected by the length of the linkers between the Fc and polymer back bone.

Schön et al. report on electrochemical atomic force microscopy of azurin layers on gold revealing potential stimulated height changes of redox responsive Cu-azurin [23]. Interestingly the non-redox active Zn-azurin does not reveal any height changes. Consequently for Cu-azurin the observed height changes are thought to originate from conformational changes of the protein and the variation in the orientation of immobilized proteins between the oxidized and reduced states.

Altogether, this special issue shall provide an important overview of the ongoing developments in the vivid area of redox active macromolecules. related work will for sure further flourish in the coming years at an undiminished pace, as one finds

additional applications in a large range including electrochemical energy storage (batteries and supercapacitors), energy devices (biofuel cells and solar cells), sensors and biosensors, electrochromic displays, nanomedicine and microfluidics (drug delivery and actuators) and materials science.

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