ADVANCED FUNCTIONAL MATERIALS

Rational Design of Conjugated Polymer Supramolecules with Tunable Colorimetric Responses

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Polydiacetylenes (PDAs), a family of highly π-conjugated polymers, have unique characteristics associated with their ability to self-assemble. Disruption of the extensively delocalized enyne backbones of molecularly ordered PDA sidechains induces a blue-to-red color change, which has been elegantly applied in the design of chemosensors. Recently, colorimetrically reversible PDAs have received significant attention, not only to gain a better understanding of the fundamentals of PDA chromism, but also to develop methodologies to overcome limitations associated with their colorimetrically irreversible counterparts. In this article, recent progress made in the field of colorimetrically tunable (reversible, stable, or sensitive) PDAs is described. Major emphasis is given to rational design strategies developed in our group. Relevant mechanistic investigations, a diagnostic method to test colorimetric reversibility, as well as future challenges in this area will be also discussed.

1. Introduction

Conjugated polymers have been extensively investigated as novel functional materials owing to their intriguing optical and electrical properties associated with extensively delocalized π-electron networks and intrinsic conformational restrictions.[1–5] Especially interesting are stimulus-induced changes that take place in the electronic absorption and emission properties of these substances, which have been elegantly applied to the design of efficient chemosensors.[6–17] Thus, a variety of conjugated polymers have been constructed which undergo color and fluorescence transitions upon environmental perturbation.

Among the conjugated polymers reported to date, polydiacetylenes (PDAs) are unique in several respects.[18–45] First, these polymers can be prepared from supramolecularly assembled crystalline or semicrystalline states of diacetylene (DA) monomers. Conventional solution-based chemical approaches typically employed for the preparation of conjugated polymers do not yield PDAs efficiently. Second, PDAs are produced by UV or γ-irradiation of self-assembled DAs without the need for chemical initiators or catalysts (Scheme 1). Thus, the resulting polymers are not contaminated with unwanted by-products. Third, PDAs are readily prepared in aqueous solution in the form of nanostructured liposomes, vesicles and wires, properties that enable them to be employed as matrices for biosensing. Finally, nanostructured PDAs undergo a blue-to-red color change in response to heat (thermochromism),[23,46,47] organic solvents (solvatochromism),[48–52] mechanical stress (mechanochromism),[53–56] and ligand-receptor interactions (affinochromism).[57–69]

The majority of PDA-based chemosensors, reported thus far, function in an irreversible fashion. Accordingly, the blue-to-red color change that takes place when an external stimulus is applied is not reversed when the external stimulus is removed. PDA systems displaying colorimetric reversibility, especially in aqueous solution, are exceptionally rare. During the course of investigations aimed at developing PDA-based chemosensors[18,49] and colorimetrically reversible PDA supramolecules,[57,70,71] we found that strong headgroup interactions in the PDAs are required in order to bring about complete colorimetric reversibility during repeated heating–cooling cycles. In addition, we observed that strong headgroup interactions make the PDA supramolecules more stable to thermal stimulation.[72] In contrast, colorimetrically sensitive polymers are obtained when DA monomers, having weak headgroup interactions, are transformed to PDAs.[73] Thus, we are now able to control not only the colorimetric reversibility but also the colorimetric temperature window of PDA sensor systems by manipulating the headgroup interactions.

In this Feature Article, an overview is presented of recent achievements in studies of PDA systems that display reversible thermochromism and extreme colorimetric stability. Major emphasis is given to investigations we have conducted with these systems. Mechanistic investigations of PDA thermochromism using in-situ FT-IR and electronic absorption spectroscopic analysis, a diagnostic method for differentiation of the colorimetric reversibility, and future challenges in this area are also described.

2. Chromisms of Polydiacetylene Supramolecules

2.1. Thermochromism

One of the fascinating features of PDAs is the brilliant blue-to-red color transition that takes place upon stimulation, such as heat,

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DOI: 10.1002/adfm.200801074

