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Hyperconjugation-induced chromism in linear responsive polymers†

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Responsive polymers, undergoing changes in light absorption and emission properties in response to stimuli, have been extensively investigated as key smart materials. Here, we report the nature underlying the optical and spectroscopic responses in linear polydiacetylenes, responsive conjugated polymers well-known for a blue-to-red transition upon specific stimuli. By means of a theoretical strategy mimicking entire empirical treatments, we reveal that hyperconjugation between the side chain and conjugated backbone signals their response: the first understanding at the electronic state level, unlike molecular conformational arguments prevailing since topochemical polymerization was discovered by Wegner in 1972. We provide quantitative exploration of (i) the thermochromic response, and (ii) applied functions showing reversible and irreversible chromism. The present work should lead to a new angle for polydiacetylene-based materials design from the hyperconjugation perspective.

Introduction

Responsive polymer materials exhibit changes in their optical and/or physical characteristics in response to external stimuli such as physical (heat, pressure, current, *etc.*), chemical (pH, organic solvent, *etc.*), and biological (ligand–receptor interaction) inputs.^{1–7} Because of this property, responsive polymer materials have been extensively used for a variety of applications, such as smart surfaces, sensors, actuators, bio-imaging, drug delivery, and biomimetic crystallization.^{8–14} Among the responsive polymer materials investigated, polydiacetylenes (PDAs) have gained special attention owing to their unique optical properties associated with the presence of extensively delocalized π -electrons in their backbone.^{1,15} As PDAs are prepared by photopolymerization of self-assembled diacetylene (DA) monomers, they possess alternating ene–yne motifs in their polymer backbone and typically display an intense blue color with strong absorption at 600–640 nm. When blue-colored PDAs are subjected to various types of environmental stimuli, they undergo a blue-to-red colorimetric transition reflected by shifted absorption at 500–550 nm. The optical change of PDAs can be readily observed by the naked eye and accompany photoluminescence changes,¹⁶ from non-fluorescence to fluorescence. These features (colorimetric transition and fluorescence “turn on”) make PDAs promising for use in sensing applications.

The first report by D. Charych and co-workers in 1993, which demonstrated that PDAs can serve as specific influenza-virus sensors,² has stimulated many recent efforts to develop new sensors based on PDAs. It has been reported that a wide range of chemical and biochemical (*e.g.*, volatile organic solvents,¹⁷ gases,¹⁸ ions,¹⁹ surfactants,²⁰ biotoxins,²¹ carbohydrates,^{22,23} nucleotides²⁴ and explosives²⁵) and physical (*e.g.*, temperature,^{26,27} mechanical strain,²⁸ and electric current²⁹) stimuli promote colorimetric and fluorometric transitions. However, despite prolific empirical efforts to develop stimuli-responsive PDAs, few reports have described the mechanism of colorimetric transitions in PDAs. Experimental (microscopic and spectroscopic) approaches^{30–32} and theoretical investigations^{33–35} have been employed to unravel the mechanism underlying the response characteristics of PDAs. However, the previous mechanisms for chromatic transitions are still controversial and remain uncertain. In this contribution, we use multiscale and classical molecular dynamics (MD) simulations and quantum mechanical (QM) computations, allowing us to fully elucidate the nature of the responsive characteristics of PDAs. Several crucial contributions are derived from this study. Firstly, we show that the colorimetric transition in PDAs is associated with a gating phenomenon of electrons in the main polymer chain through hyperconjugation. This electro-gating action induced by rotation of side chains results in reduced delocalization of π -electrons along the PDA backbone. Secondly, we point out the origin of chromic reversibility, being connected to the relative energy of the blue and red states, and thus provide a design rule for infusing reversible function into PDAs. Thirdly, we investigate the validity of the models previously proposed for the colorimetric transition. We confirmed that the model mechanisms suggested in the literature were found to be

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