

Optical Switching of Hierarchical Self-Assembly: Towards “Enlightened” Materials**

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- chirality
- gels
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Continuing device miniaturization aiming to fabricate features at the scale of few nanometers has led to the development of bottom-up approaches that involve rational manipulation as well as the self-assembly of atomic/molecular building blocks. In order to generate periodic and defect-free structures in a highly parallel fashion, directed self-assembly^[1] mediated by noncovalent interactions offers some significant advantages.^[2] Incorporation of responsive units capable of changing supramolecular organization ultimately will lead to the development of dynamic devices^[3] useful for actuation, sensing, data storage, and computing. Arguably, light represents perhaps the most attractive external stimulus, and Nature has made use of light-responsive systems to power and regulate biological systems. While photosynthesis efficiently harvests and converts solar energy into chemical energy, vision as well as light-triggered development (photomorphogenesis) and motion (photomovement) represent important mechanisms that alter biological functions in response to exposure with (sun)light. These fundamental biological processes are based on the initial interaction of light with a suitable chromophore causing a cascade of biochemical transformations and therefore enabling photoregulation in living systems.

Photochromic molecules^[4] have been extensively investigated over the years, primarily due to their potential in optical memories. While such traditional applications rely on the reversible change of optical properties in the bulk, conformational and electronic changes upon switching have also been used to affect structure and function at the molecular level (Figure 1).^[5] For example, the large structural reorganization accompanying the classical *E/Z* photoisomerization of azobenzene derivatives has been explored to control peptide conformation,^[6] degree of π -conjugation,^[7] binding affinity,^[8] catalytic activity,^[9] and molecular motion^[10] amongst others. On the other hand, electronic changes between the ring-opened and ring-closed forms of Irie's diarylethene photoswitches have inspired the design of dual-mode switching devices involving additional redox,^[11] magnetic,^[12] or emissive functions.^[13] In addition, chiral optical switches have great promise in creating directional molecular rotors.^[2,4b-c] However, the use of structural changes in such photochromic building blocks to affect their self-assembly behavior and therefore modulate macroscopic properties has previously only rarely been explored.^[14-17] Here, a significant recent advance in this area enabling the optical switching of the liquid-gel phase transition by modulating molecular self-assembly behavior is highlighted.

Recently, van Esch, Feringa, and co-workers have described low-molecular-weight gelators^[18] based on a chiroptical switch with appended hydrogen-bonding units that allows for photocontrol of chirality on the molecular as well as the supramolecular level.^[19] Their system consists of dithienylcyclopentene cores with pendant (*R*)-1-phenylethylamine-derived amides as gelation scaffold (Figure 2). Gels of the open form (**O**) obtained at temperatures below 0 °C in toluene and above the critical gelation concentration (CGC = 1.8 mM) show strong circular dichroism (CD) in the aromatic absorption range due to exciton coupling within the aggregates. Aggregation locks **O** into one chiral conformation (*P*) leading to the formation of right-handed (*P*-helical) fibers as independently evidenced by transmission electron microscopy (TEM). Photochemical ring closure in the gel state induced by UV irradiation (313 nm) retains chirality to yield the closed form (**C**) in large diastereomeric excess

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[**] Generous support by the Sofja Kovalevskaja Program of the Alexander von Humboldt Foundation sponsored by the Federal Ministry of Education and Research and the Program for Investment in the Future (ZIP) of the German Government is gratefully acknowledged. In the title, the word “enlightened” is used in a provocative way to highlight the interaction of light with molecules to afford photoresponsive (more popularly called “smart”) materials.

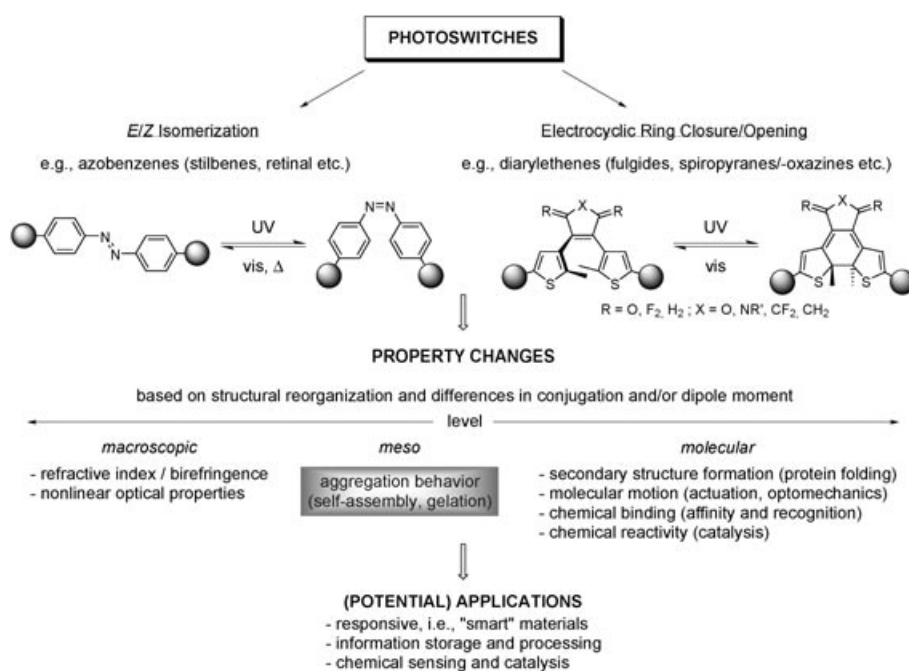


Figure 1. Photochromic molecules:^[4] Switching between two (independently) addressable states leads to reversible property changes from the molecular to the macroscopic level with potential applications in a variety of areas. This article highlights recently achieved photocontrol of aggregation behavior (gray box).

(96% *de*). In solution however, due to the rapid equilibrium between the two helical forms of **O**, no CD effect is detected and no stereochemical preference (0% *de*) during ring closure is observed.

Covalent-bond formation during the concerted photochemical reaction not only causes an optical transcription of supramolecular chirality into molecular chirality but also leads to subtle structural changes that affect the self-assembly behavior of **C**. The gels of **C** obtained by irradiation in the aggregated state are metastable and hence a heating/cooling cycle affords thermodynamically stable gels with fibers of the opposite handedness, that is, *M* helicity. The observed helix reversal is presumably caused by oppos-

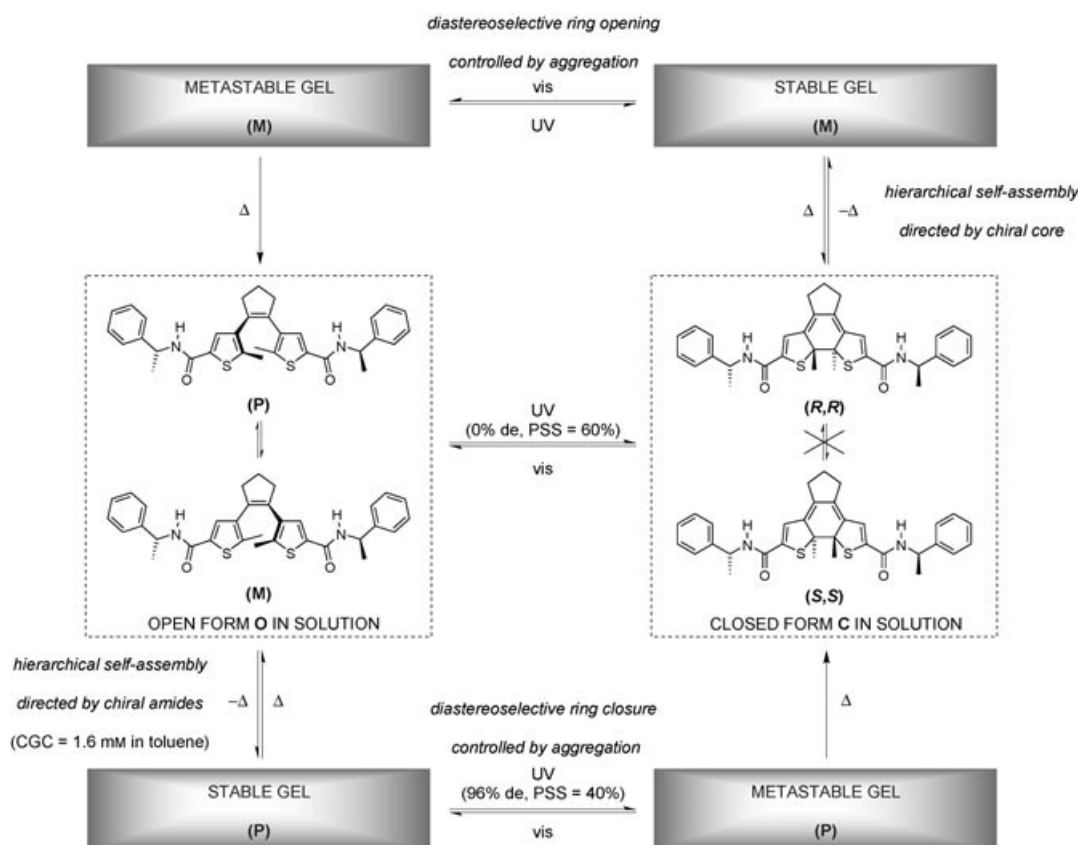


Figure 2. Four-state chiroptical switching cycle by van Esch and Feringa:^[19a] Combining hierarchical self-assembly with diastereoselective ring-closure/opening processes allows for reversible transcription of supramolecular into molecular chirality. CGC = critical gelation concentration, *de* = diastereomeric excess, PSS = photostationary state, UV = ultraviolet light (313 nm), vis = visible light (> 460 nm).

ing directing effects of the chiral amide units in **O** as compared to the central methyl groups of the planarized photo-switch in **C**. In order to close the four-state switching cycle, irradiation of the closed form's stable gel using visible light (>460 nm) leads to ring opening and retranslates molecular into supramolecular chirality. The obtained gel is again metastable and can be transformed into the original gel of the opened form by heating and cooling.

It should be noted that both metastable gel states are only accessible via diastereoselective photochemical ring closure and closure processes in the aggregates of **O** and **C**, respectively, induced by irradiation with light of the appropriate wavelength. Both stable gel states are conveniently populated by an orthogonal thermal input via heating/cooling cycles. Due to the well-separated absorption spectra of the diarylethene, and hence addressability of both switching states **O** and **C** as well as the significant fatigue resistance,^[5] the photochemical reactions are fully reversible and the sequential transformations described above can be repeated without noticeable degradation. Previous systems^[14] based on azobenzene-derived switches show similar effects, such as inversion of chirality, yet they suffer from limited addressability due to overlapping absorption spectra as well as thermal instability of the *Z* form.

This work impressively illustrates several important design aspects, most notably the utility of covalent-bond formation to freeze-in specific conformations caused by supramolecular organization and the advantage of reversible structural changes within photochromic compounds to direct hierarchical self-assembly. The system described above allows one to repeatedly cycle between four distinct switching states that can easily be read out due to different (chiro)optical properties, and therefore offers potential for the development of memory systems. Furthermore, controlling diffusion processes in the gels by means of advanced optics, such as holographic grating techniques, offers a new way to reversibly pattern substrates.^[20] Last but not least, the work of van Esch and Feringa should facilitate the design of "smart" functional materials, which respond to external stimuli by subtle structural reorganization at the molecular level leading to significant changes in their macroscopic properties mediated by noncovalent interactions. Thus, in line with the appealing name of this journal: *small (changes) will have a big impact*.

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