Translating the action of molecular motors to supramolecular polymers

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RESEARCH HIGHLIGHT

Translating the action of molecular motors to supramolecular polymers

Magda M. J. Dekker | **Ghislaine Vantomme**

Institute for Complex Molecular Systems and Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

Correspondence
Ghislaine Vantomme, Institute for Complex Molecular Systems and Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, Eindhoven, 5600 MB The Netherlands.
Email: g.vantomme@tue.nl

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The amplification of asymmetry from the molecular level to the macroscopic scale is an intriguing mechanism operative in natural systems to control complex functions. Inspired by nature, strategies for transferring chiral information across length scales in purely synthetic systems have been investigated.[1,2] Thereof, chiral molecules are embedded into well-defined ordered supramolecular structures with the dynamics of noncovalent interactions leading to the amplification effect. However, it remains a challenge to achieve precise and noninvasive modulation of chirality in these systems as it requires to control molecular motion at the nanoscale.

Recently, Feringa and co-workers reported on this topic with a novel water-soluble supramolecular polymer composed of light-driven molecular motors.[3] Within this supramolecular polymer, the intrinsic chirality of the molecular motor is transferred to the nanofibers, and the chirality and morphology of the polymer are governed by the rotation of the motor. As depicted in Figure 1A, molecular motor M1 displays four states with different inherent chiralities and geometries, through which the morphology and chirality of the supramolecular polymer can be regulated. First studied in methanol, the rotation of the molecular motor showed to be a four-step unidirectional rotary cycle process featuring two photochemical isomerizations, each followed by a thermal helix inversion (THI), similar to other first-generation molecular motors.[4] Subsequent experiments revealed that the stable (*P,P*)-*cis* isomer forms uniform helical fibers of micrometer length in aqueous media.

Next, the rotation of the molecular motor was studied within the supramolecular polymers and followed by circular dichroism and UV-vis absorption spectroscopy. In contrast to methanol, experiments performed in water showed the appearance of the metastable (*M,M*)-*trans* isomer. Due to stabilization of the metastable (*M,M*)-*trans* isomer by the supramolecular fibers, the standard Gibbs free energy of activation of THI increased from 78.8 kJ mol^{-1} in methanol to 85.0 kJ mol^{-1} in water, and at the same time increasing the lifetime of the motor from 12.4 s to 2.6 min (Figure 1B). In addition, the chirality and morphology changes of the assemblies during rotation of the motor were explored. The stable (*P,P*)-*cis* isomer formed helical fibers, which transformed into micelles after irradiation to reach the stable (*P,P*)-*trans* isomer. Subsequent irradiation for 10 min led to the formation of worm-like fibers after reaching a photostationary state of 32/68 unstable (*M,M*)-*cis*/stable (*P,P*)-*trans* isomers. Finally, the 360° rotation of the motor was completed by irradiation in a water/THF 7/3 mixture, followed by warming the sample for THI and the stable (*P,P*)-*cis* helical fibers were recovered demonstrating a unique multistate supramolecular system in water with light-controllable properties. Furthermore, the emission of the four different states was studied by fluorescence spectroscopy. While the monomeric state had no emission, all four supramolecular states in water showed distinct fluorescence spectra, thereby displaying multistate light-controllable aggregation induced emission.[5]

Overall, this study nicely presents a novel photochemically tunable multistate dynamic supramolecular system in water. The present work is a step forward in the efforts to make light-controllable chiroptical materials with exciting applications in opto-electronic devices.

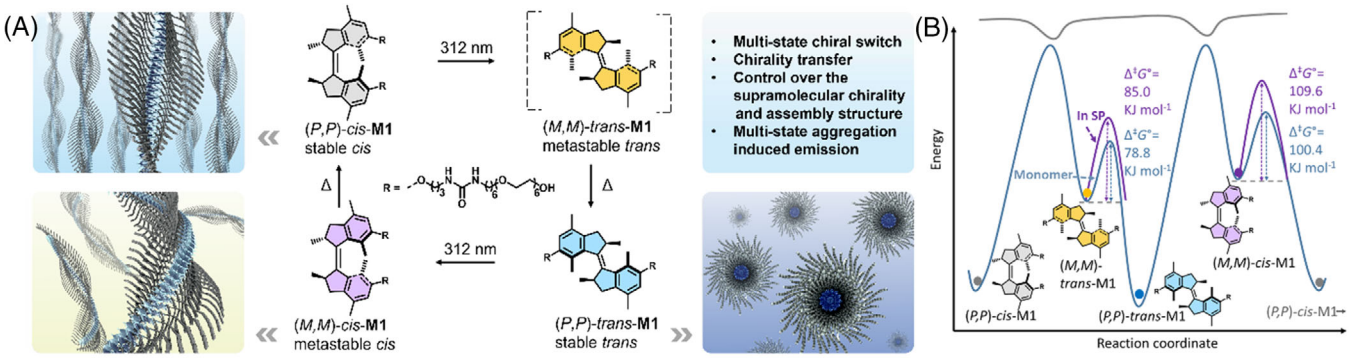

FIGURE 1 (A) Structures of molecular motor M1 and illustration of multistate rotation, isomers with distinct chirality and the corresponding assembly structures. (B) Energy diagram of the rotation of molecular motor M1 in methanol (blue trace) and water (purple trace); SP: supramolecular polymer[3]

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

There are no new data associated to this article.

ORCID

Ghislaine Vantomme https://orcid.org/0000-0003-2036-8892

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