

DESIGNING PHOTOSWITCHABLE FOLDAMERS: TOWARDS SMART DELIVERING VEHICLES

Carsten Winterboer and Stefan Hecht*

Department of Chemistry, Humboldt-Universität zu Berlin
Brook-Taylor-Str. 2, 12489 Berlin, Germany
sh@chemie.hu-berlin.de

Introduction

The reversible helix-coil transition and the tubular cavity of phenylene ethynylene foldamers^{1,2} present an ideal opportunity for the development of stimuli responsive smart materials.³ However, the stimuli, e.g. solvent composition and metal complexation, employed thus far to control the helix-coil transition in such foldamers are invasive and therefore associated with the formation of waste byproducts. Light on the other hand is perhaps the ideal stimulus since it allows for precise temporal and spatial control and is non-invasive. Hence, we've engaged in designing photoresponsive and more specifically photoswitchable, i.e. reversible, foldamer systems.⁴

Here, we present our work on the synthesis of polymeric photoswitchable systems, their photoresponsive conformational behavior, and their transporting capabilities.⁵

Results and Discussion

Our approach is based on incorporation of photochromic azobenzene moieties into the foldamer backbone such that the photoisomerization disrupts the kinked connection leading to denaturation of the helix (Figure 1).⁴

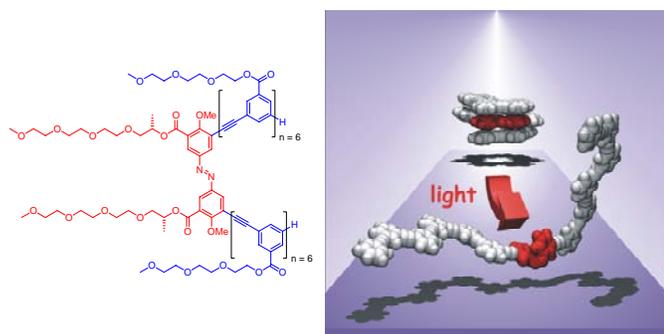


Figure 1. Prototype of a photoswitchable foldamer (left), which undergoes a light-triggered unfolding (right).⁴

While in our initial work,⁴ we could successfully demonstrate the folding transition, several drawbacks became apparent, most notably: low conversion (only 40% cis content in the photostationary state) and low loading capacity (pinene and other hydrophobic guest could be bound to the interior but only in a 1:1 ratio). To overcome these limitations, we have engaged in increasing the azobenzene photochrome content and preparing polymeric versions of our system (Figure 2).



Figure 2. Improving the design by designing polymeric photoswitchable foldamers composed of azobenzene repeat units only.

The synthesis of these backbones has been realized utilizing Pd-catalyzed cross-coupling methodology to access the polymers in their reduced and protected hydrazine forms, followed by oxidative deprotection to reveal the polyazobenzenes. Synthesis as well as structural characterization of the polymers will be presented and their folding behavior in the dark and after irradiation will be presented.

Conclusions

New synthetic protocols for the generation of azobenzene-based foldamers have been developed. The azobenzene main chain polymers have been characterized with regard to their photochemical and thermal switching behavior and the binding affinity of the respective isomeric forms to hydrophobic guests have been evaluated. The resulting materials are promising candidates for new "smart" delivering vehicles.

Acknowledgment. The authors thank Hao Yu for some initial contributions to polyazobenzene synthesis. Generous support by the German Research Foundation (DFG: SFB 658 TP B8) is gratefully acknowledged.

References

- (1) For a recent and comprehensive treatise on foldamers, see: *Foldamers: Structure, Properties, and Applications* (Eds.: S. Hecht, I. Huc), Wiley-VCH, Weinheim, **2007**.
- (2) For a review on solvophobic driven foldamer design, see: Zhao, Y.; Moore, J. S. In *Foldamers: Structure, Properties, and Applications* (Eds.: S. Hecht, I. Huc), Wiley-VCH, Weinheim, **2007**, pp. 75-108.
- (3) Hecht, S. *Small* **2005**, *1*, 26-29.
- (4) (a) Khan, A.; Kaiser, C.; Hecht, S. *Angew. Chem. Int. Ed.* **2006**, *45*, 1878-1881. (b) Khan, A.; Hecht, S. *Chem. Eur. J.* **2006**, *12*, 4764-4774.
- (5) Winterboer, C.; S. Hecht, *unpublished results*.