

CLICKAMERS AND CLICKATES AS VERSATILE BUILDING BLOCKS IN MACROMOLECULAR AND SUPRAMOLECULAR CHEMISTRY

Marie-Anne Berlin, Marc Ostermeier, Robert M. Meudtner, Christian Limberg,* and Stefan Hecht*

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

Introduction

Synthetic chemists have increasingly been inspired by Nature and its astonishing variety of marvelous yet functional structures. Natural design principles include covalent conformational preferences, which restrict backbone conformation, as well as non-covalent interaction, for example metal ion coordination, as efficient means to generate well-defined architectures. However, as synthetic chemistry cannot rely on biological machinery for the generation of molecular structures, it is dependent on efficient synthetic methodology to prepare the desired target molecules. One of the most notable synthetic advances has been “click chemistry”, which although being a general concept introduced by Sharpless¹ is usually restricted to the Cu-catalyzed 1,3-dipolar cycloaddition of azides and terminal alkynes.^{2,3} This particular reaction has had a tremendous impact on synthetic materials chemistry and has been the topic of several reviews.⁴

A few years ago, our group has engaged into a program aiming at utilizing the 1,2,3-triazole moiety, which is formed in the click reaction, as a structure directing building block.⁵ Our design has been inspired by the work of Lehn and coworkers, who have utilized the 2,2'-bipyridine “helicity codon” to design architectures, which can interconvert between compact helical and extended grid-like structures in the presence of coordinating metal ions.⁶ Our key building blocks, 2,6-bis(1-phenyl-1,2,3-triazol-4-yl)pyridines (BTPs), are efficiently derived via click chemistry from 2,6-diethynylpyridines and phenyl azides carrying various substituents. We could show that BTPs show a strong preference to adopt a kinked *anti,anti* conformation in solution and in the solid state.^{5a} Coordination of transition metal ions leads to formation of complexes with different stoichiometry, i.e. $M(\text{BTP})_{1,3}$, which have been fully characterized and show some promising luminescent, magnetic, and catalytic properties.^{5a,7} Incorporation of the BTP motif into linear strands afforded helically folding oligomers^{5b} and polymers,^{5c} which could be crosslinked by metal ions to yield metallosupramolecular gels.^{5c} Recently, we could also utilize the conformational transformation in BTP derivatives to switch between different 2D self-assembled structures on graphite surfaces.^{5d}

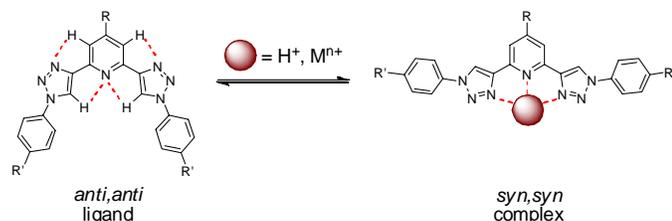


Figure 1. Conformational preferences 2,6-bis(1-phenyl-1,2,3-triazol-4-yl)pyridines (BTPs) in the absence or presence of metal ions.⁵

Here, we present our most recent work on both a detailed thermodynamic investigation of the BTP coordination chemistry by isothermal calorimetry (ITC) as well as the synthesis, coordination and self-assembly behavior of functional BTP-containing structures based on (metallo)porphyrins.⁷

Results and Discussion

BTPs carrying different substituents in the central pyridine as well as terminal phenyl moieties were investigated with regard to their coordination behavior to various transition metal ions, in particular Fe(II). ITC was used to monitor the thermodynamics of the binding process.⁷ A linear free energy relationship between the complexation enthalpies and the electronic structure of the substituents (R and R') was found. Importantly, the determined

complexation constants were similar to terpyridine yet the exchange dynamics were significantly accelerated. This suggests that BTPs might be beneficial for the design of rapidly equilibrating metallosupramolecular polymers.⁹ Furthermore, several new transition metal complexes with varying stoichiometry could be characterized by single crystal X-ray crystallography.⁷

To utilize the structure-directing ability of the BTP scaffold, more functional entities were prepared. For example, BTPs were attached to a (metallo)porphyrin core via click chemistry utilizing alkynylated (metallo)porphyrins. The system was rendered amphiphilic by introducing polar and chiral oligoethyleneglycol side chains.⁸ The aggregation behavior of the system was investigated using various optical techniques as well as X-ray diffraction at a synchrotron source.¹⁰ Importantly, the influence of metal coordination on the self-assembly behavior of these systems has been studied.

The results of these investigations will be detailed as well as future directions of this research theme discussed.

Conclusions

Click chemistry has been utilized to prepare BTP-containing (macro)molecules. The strong conformational preferences of the BTP scaffold that undergo dramatic changes when metal coordination takes place thereby enable the design of responsive materials.

Acknowledgment. Support by ERA Chemistry (Project “SurConFold”) is gratefully acknowledged.

References

- (1) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2001**, *40*, 2004.
- (2) (a) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 2596. (b) Tornøe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057.
- (3) Please note that the non-catalyzed, thermal [4+2] cycloaddition reactions of various 1,3-dipoles have been pioneered by Huisgen, see: Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry* (Ed.: A. Padwa), Wiley, New York, **1984**, pp. 1.
- (4) (a) Lutz, J.-F. *Angew. Chem. Int. Ed.* **2007**, *46*, 1018-1025. (b) Binder, W. H.; Sachsenhofer, R. *Macromol. Rapid Commun.* **2007**, *28*, 15. (c) Fournier, D.; Hoogenboom, R.; Schubert, U. S. *Chem. Soc. Rev.* **2007**, *36*, 1369.
- (5) (a) Meudtner, R. M.; Ostermeier, M.; Goddard, R.; Limberg, C.; Hecht, S.; *Chem., Eur. J.* **2007**, *13*, 9834; (b) Meudtner, R. M.; Hecht, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 4926; (c) Meudtner, R. M.; Hecht, S. *Macromol. Rapid Commun.* **2008**, *29*, 347; (d) Piot, L.; Meudtner, R. M.; El Malah, T.; Hecht, S.; Samori, P. *Chem. Eur. J.* **2009**, in press.
- (6) For a review, see: (a) Huc, I.; Cuccia, L. In *Foldamers: Structure, Properties, and Applications* (Eds.: S. Hecht, I. Huc), Wiley-VCH, Weinheim, **2007**, pp. 1. For coordination-triggered extension and use in dynamic molecular devices, see: (b) Barboiu, M.; Lehn, J.-M. *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5201.
- (7) Unpublished results.
- (8) Khan, A.; Kaiser, C.; Hecht, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 1878.
- (9) U. S. Schubert, *Metal-Containing & Metallo-Supramolecular Polymers & Materials*, ACS symposium series 928.
- (10) In collaboration with A. Thünemann (BAM).