Dynamic Covalent Self-Assembly of Bi- and Tripodal Architectures

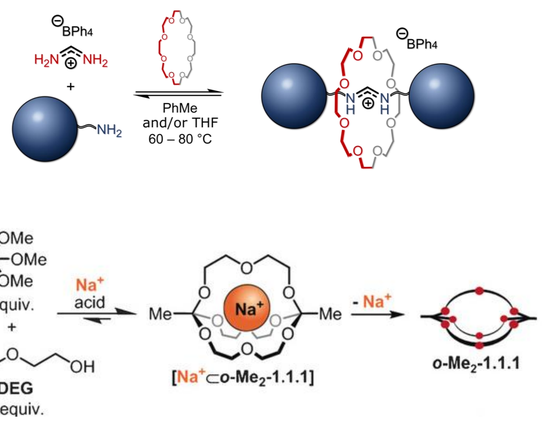
Yevhenii Shchukin†*, Oleg Borodin†, Jana Koenigsdorff† and Max von Delius†

† University of Ulm, Institute of Organic Chemistry, Albert-Einstein-Allee 11, 89081 Ulm, Germany

*yevhenii.shchukin@uni-ulm.de, www.deliusgroup.net

1. Introduction

In **dynamic covalent chemistry** (**DCvC**), special functional groups can undergo interconversion by continuous forming and breaking of covalent bonds. Due to its unique properties – mild reaction conditions, stimuli responsiveness and adaptive behaviour, DCvC has found application in the discovery of new drugs, material science and supramolecular chemistry. [1,2]



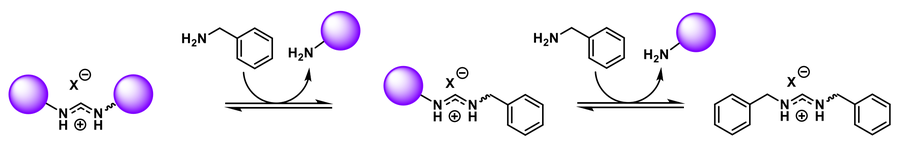
Previous results

We have demonstrated the possibility of using underexplored amidinium exchange reaction to form a mechanically interlocked architectures ([2]rotaxanes).[3] Herein, we would like to expand the scope of solvents, amines and influence of anions on the kinetics and outcome of **amidinium exchange**.

Since the discovery of exchange of *O,O,O*-orthoesters with alcohols in our group, numerous cryptates and cryptands have been synthesized.[4,5] By modifing the diols with bulky substituents, we aim to achieve the synthesis of **carceplexes** with kinetically entrapped cations inside the cavity.

2. Amidinium Exchange: Bipodal Molecular Architectures

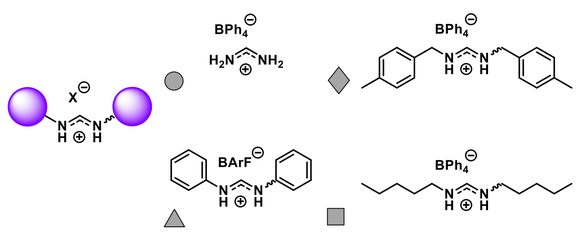
Amidinium exchange

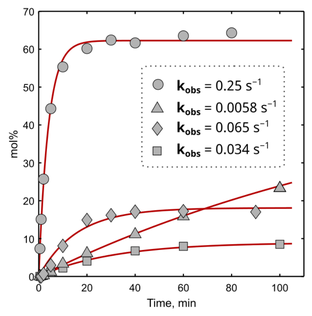


Solvents scope

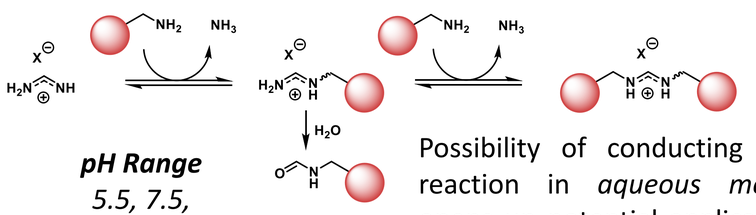
DMSO, MeCN, Alcohols, pyridine, THF, EtOAc, THF/H_2O

Amines scope





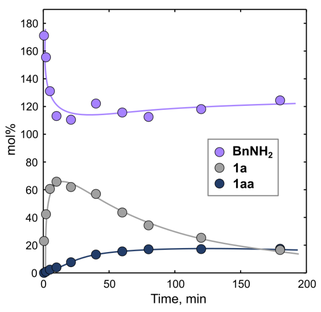
Amidinium exchange in water



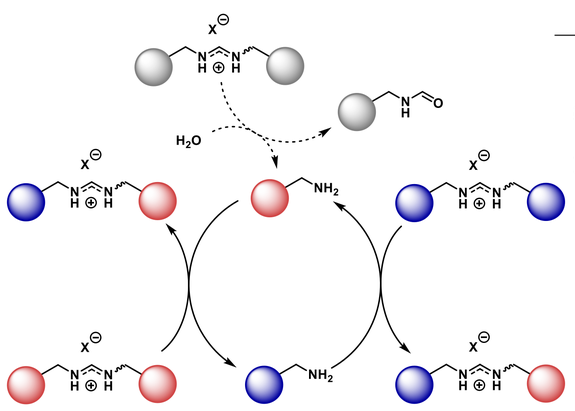
pH Range

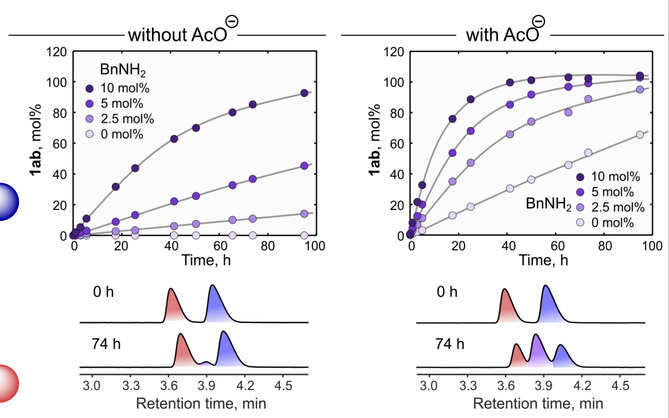
5.5, 7.5, 9.5, 11.5

Possibility of conducting the reaction in *aqueous media* opens up potential application of amidinium exchange in *drug delivery* or *out-of-equilibrium systems.*

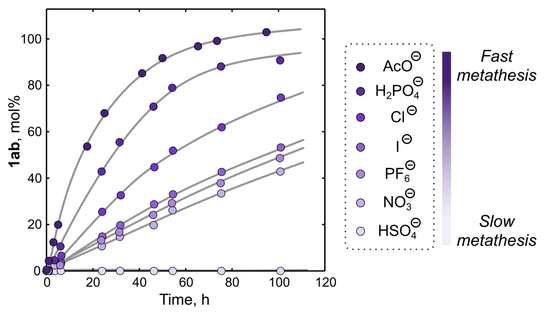


Amidinium metathesis

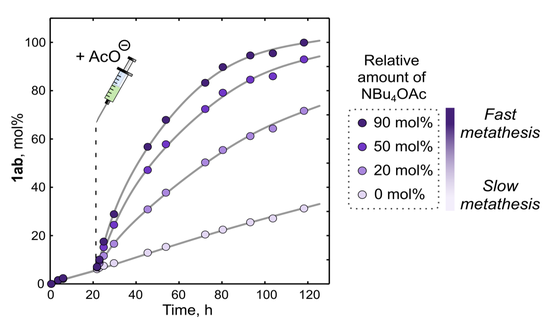




Anion scope



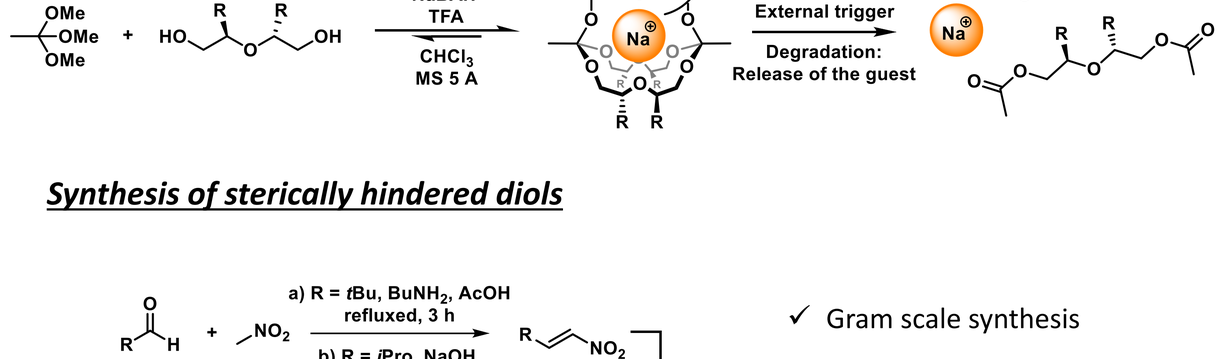
Infuence of AcO^- amount



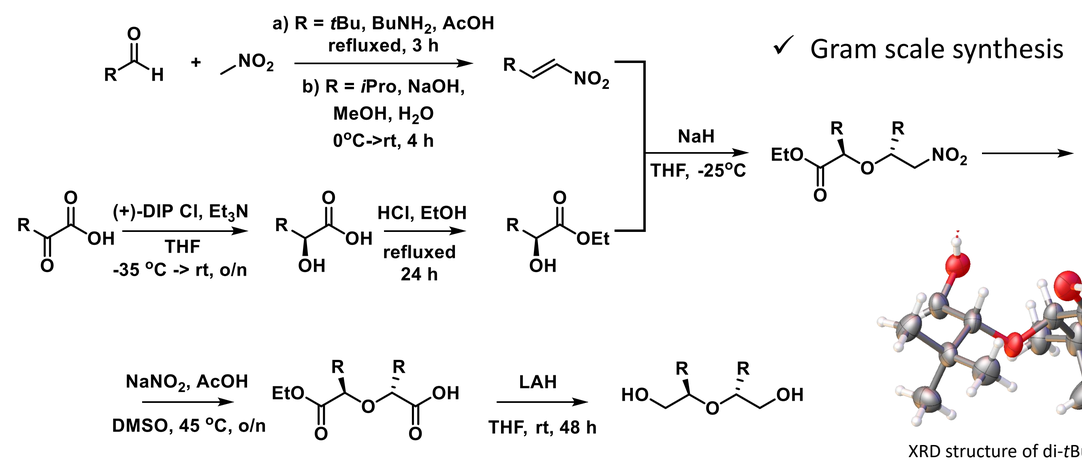
Borodin, O., Shchukin, Y., Schmid, J., von Delius, M., *manuscript submitted.*

3. Orthoester Exchange: Tripodal Molecular Architectures

Main goal: self-assembly of carceplex



Synthesis of sterically hindered diols



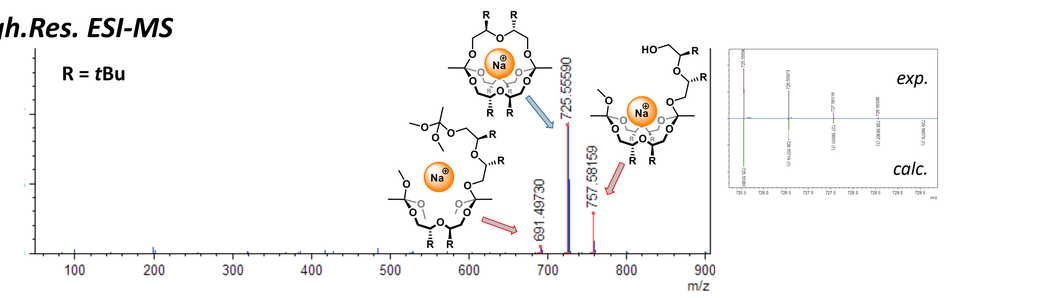
✓ Gram scale synthesis

XRD structure of di-*t*Bu-diol

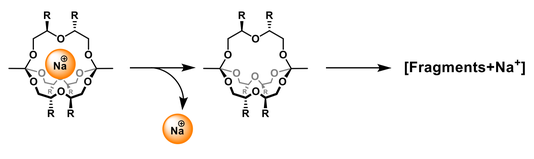
Synthesis of carceplexes and preliminary characterization of its stability

High.Res. ESI-MS

R = *t*Bu



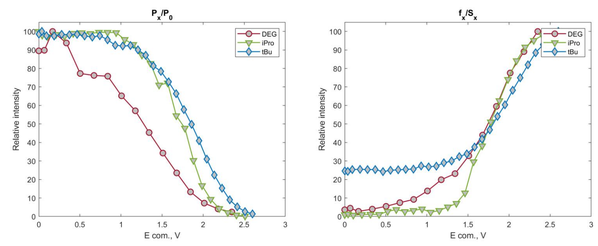
High.Res. ESI-MS/MS



Charged, Detectable

Neutral, Not detectable

Charged, Detectable



P_0 – total intensity of parent ion at 0 Volts;
P_x – total intensity of parent ion (incl. isotopes) at x Volts;
S_x – total intensity of all ions at x Volts;
f_x – total intensity of all fragment at x Volts ($f_x = S_x - P_x$);

4. Outlook

- Investigate the possibility of using amidinium exchange reaction towards anion sensing, kinetically gated chemical networks and the self-assemblies of micelles and vesicles;
- Further optimization of the reaction conditions towards the synthesis of carceplexes, followed by its application in active ion transport.

[1] Herrmann, A., *Chem. Soc. Rev.* **2014**, *43*, 1899–1933
[2] Jin, Y., Wang, Q., Taynton, P., Zhang, W., *Acc. Chem. Res.* **2014**, *47*, 1575–1586.
[3] Borodin, O., Shchukin, Y., Robertson, C. C., Richter, S., von Delius, M. *J. Am. Chem. Soc.* **2021**, 143, *40*, 16448–16457
[4] Brachvogel, RC., Hampel, F., von Delius, M. *Nat Commun* **2015** *6*, 7129
[5] Shyshov, O., Brachvogel, R., Bachmann, T., Srikantharajah, R., Segets, D., Hampel, F., Puchta, R., von Delius, M. *Angew.Chem.Int.Ed.* **2017**, *56*, 776 – 781

Acknowledgements:
We are grateful to the European Research Council for financial support.

#StandWithUkraine