Interaktsioonid, mis suunavad **molekulide ise-organiseerumist** hemikukurbituriilides ja nende kompleksides

Riina Aav

Loodusteaduskond
Keemia ja biotehnoloogia instituut

Tallinna Tehnikaülikool

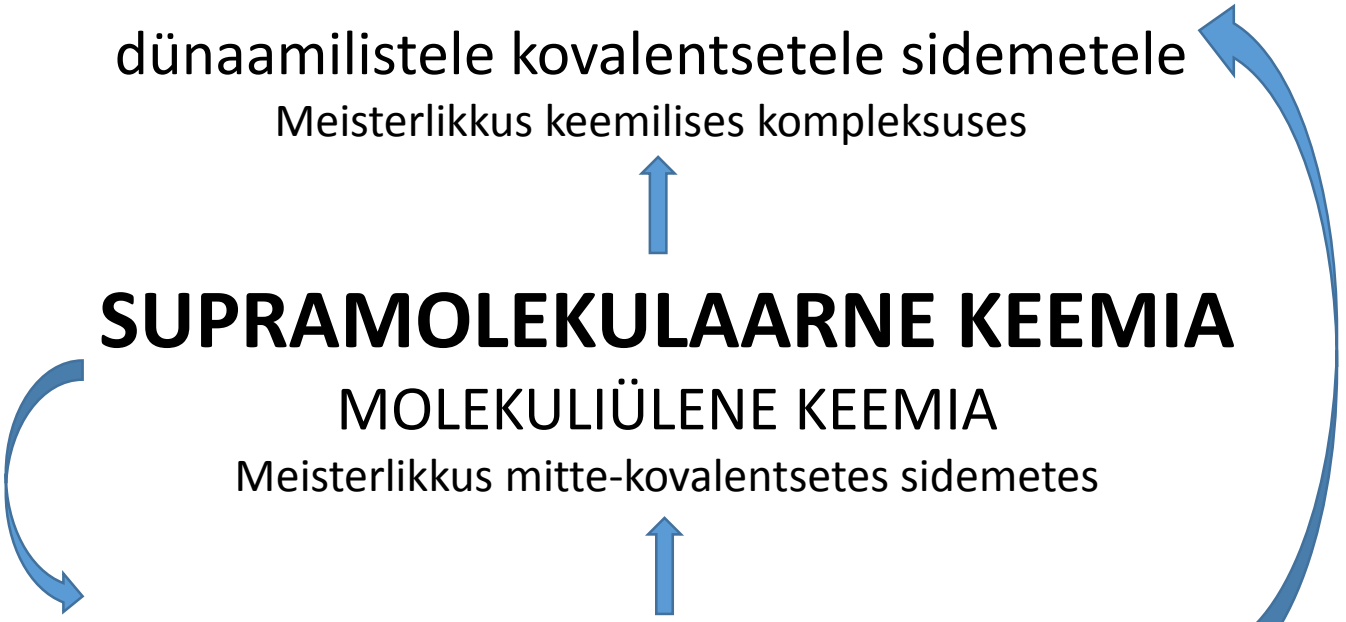
ISE-ORGANISEERUMINE

Tee keerulise ehitusega mateeriani

KOHANDUV KEEMIA

KOOSTISES DÜNAAMILINE KEEMIA tänu dünaamilistele kovalentsetele sidemetele

Meisterlikkus keemilises kompleksuses



SUPRAMOLEKULAARNE KEEMIA

MOLEKULIÜLENE KEEMIA

Meisterlikkus mitte-kovalentsetes sidemetes

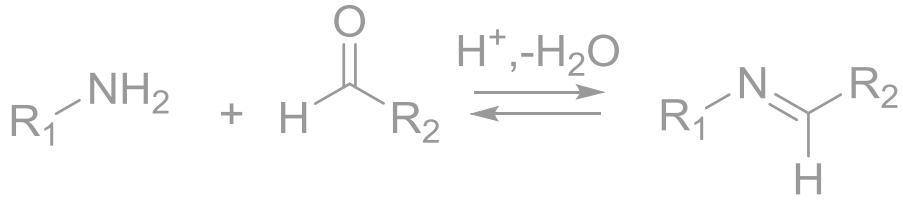
MOLEKULAARNE KEEMIA

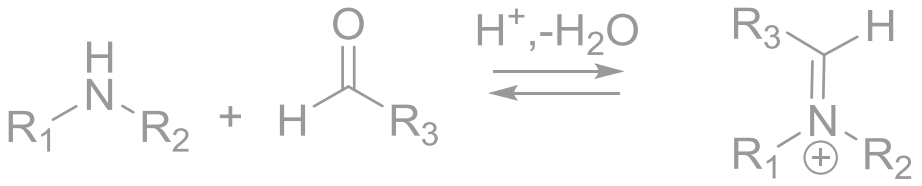
AATOMITEST MOLEKULIDENI

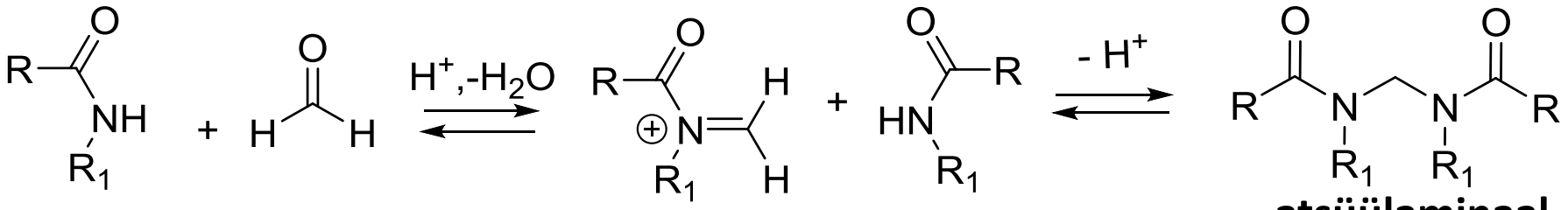
Meisterlikkus kovalentsetes sidemetes

Jean-Marie Lehn. *Angew. Chem. Int. Ed.* **2013**, 52, 2836-2850
Jean-Marie Lehn *Angew. Chem. Int. Ed*. **2015**, 54, 3276 – 3289

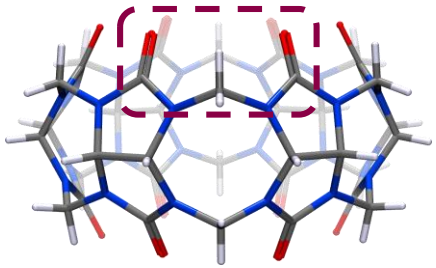
Dünaamilised kovalentsed sidemed



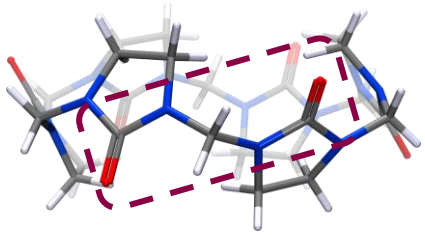




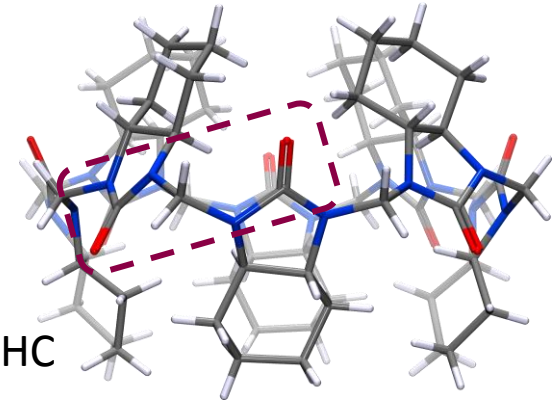
atsüülaminaal



kukurbituriil

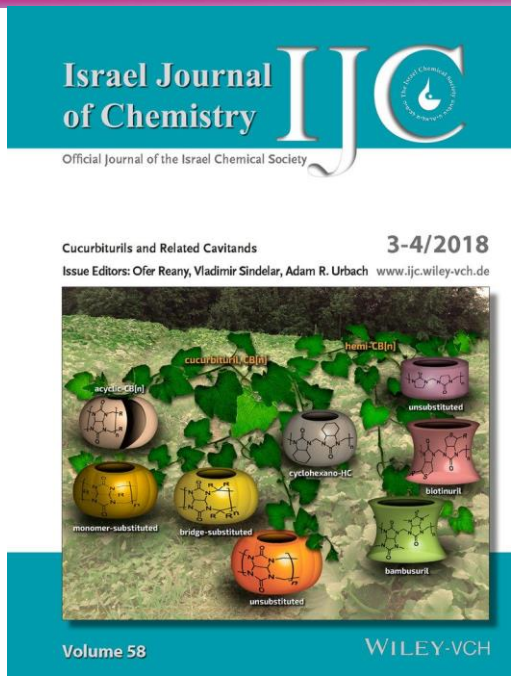


hemikukurbituriil

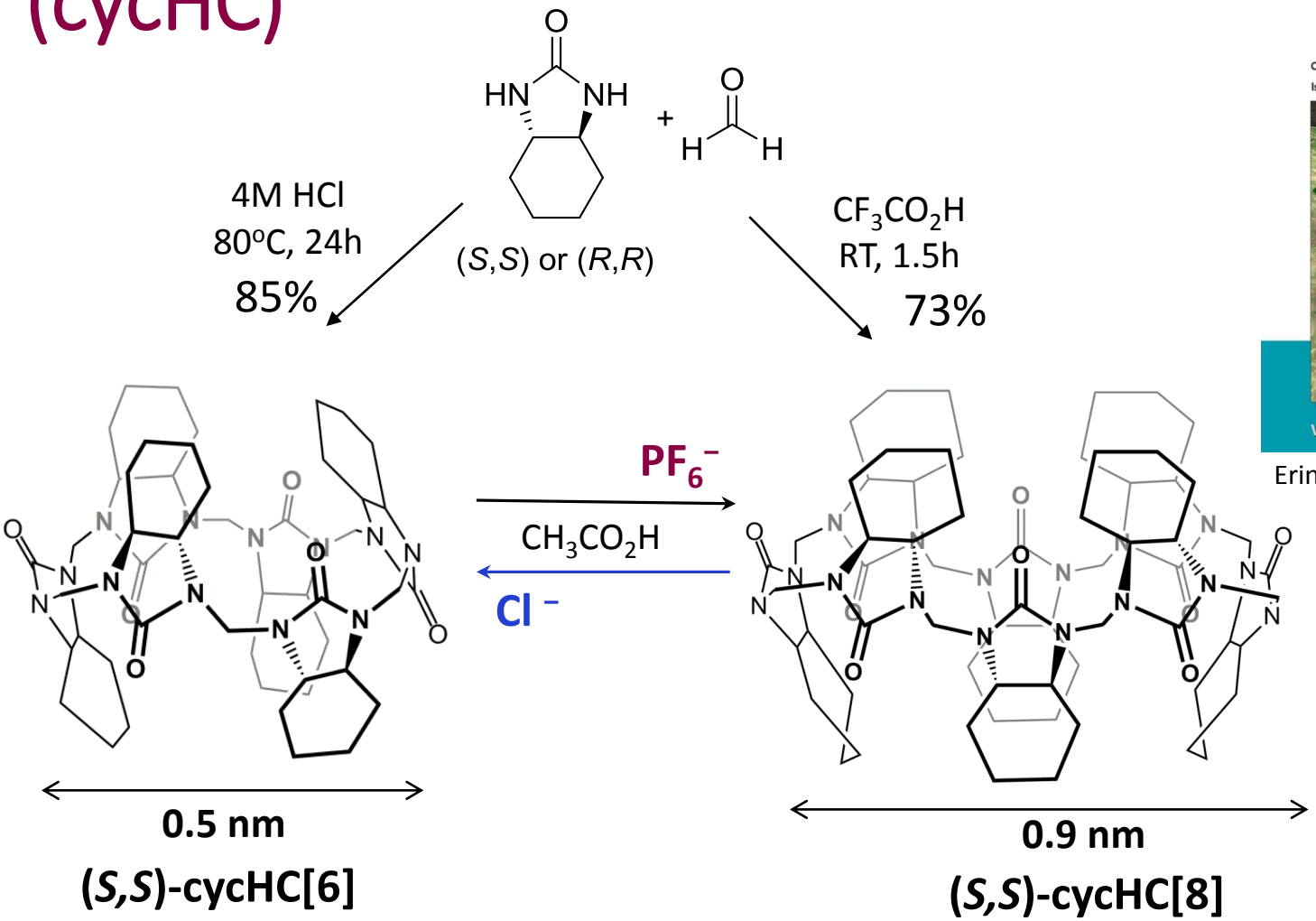


cycHC

Tsükloheksanohemikukurbituriilid (cycHC)



Erinumbri kaanepilt: Kaabel, Aav, Mid



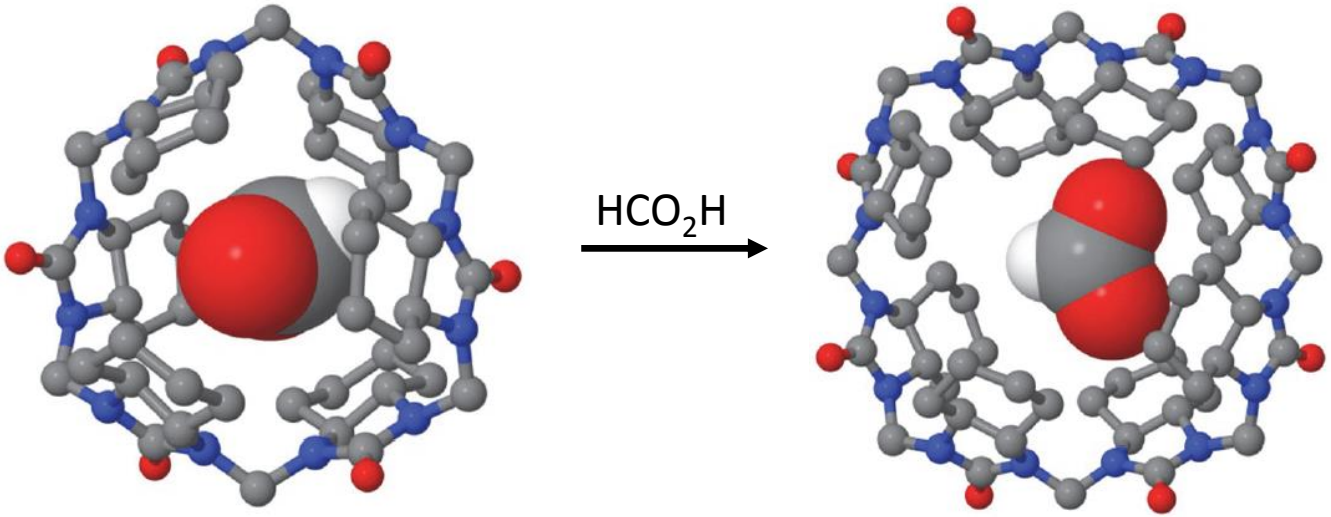
Aav et al. Org. Lett, **2013**

Prigorchenko *Chem Comm*, **2015**

Kukurbituriilide malli-põhine süntees erinumbris: Kaabel S, Aav, R *Isr. J. Chem*. **2018**

Sobiva aniooniga suluühendi teke suunab makrotsüklite vahelist tasakaalu

HCO_2^- kompleksid:



$$\Delta G = -177 \text{ kJ/mol}$$

$$4(HCO_2^-@cycHC[6]) \rightleftharpoons 3(HCO_2^-@cycHC[8]) + HCO_2^-$$

Tsüklipinget ei ole:

$$\Delta G = 1 \text{ kJ/mol}$$

$$cycHC[6] \rightleftharpoons cycHC[8]$$

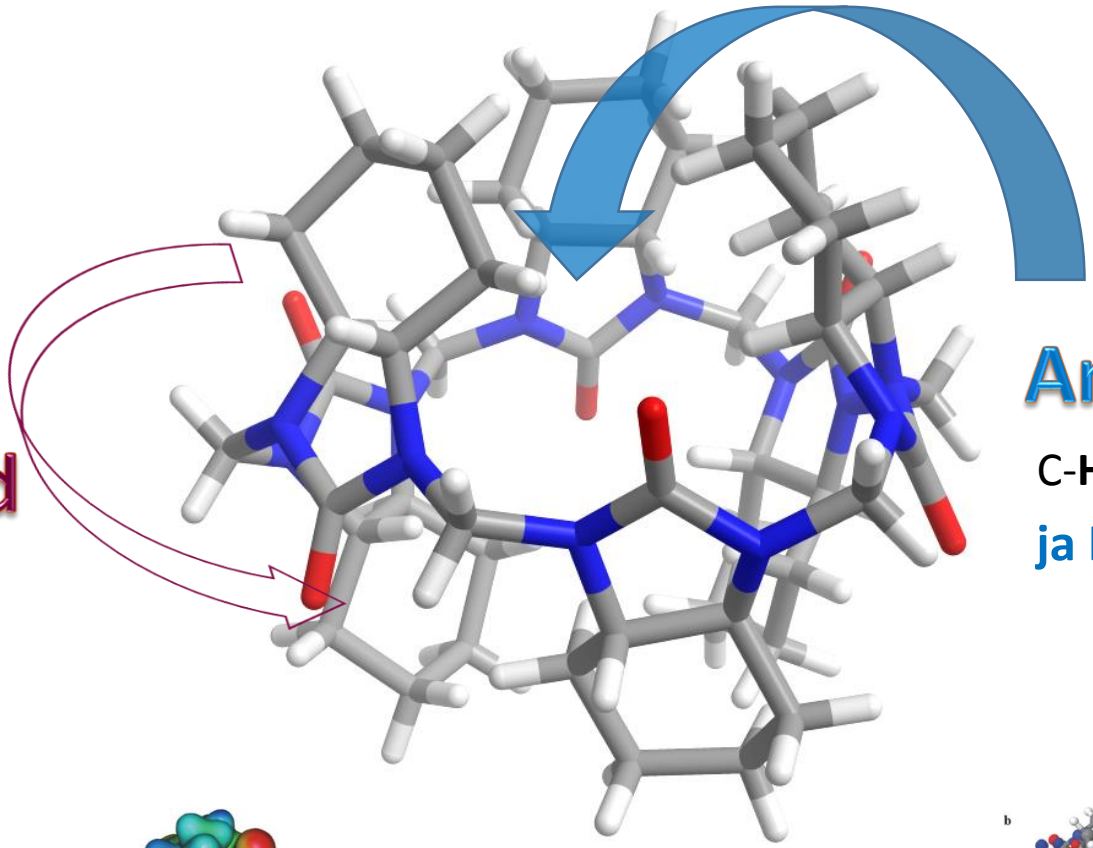
Prigorchenko *Chem Comm*, **2015**

Mitte-kovalentsed interaktsioonid

		Sideme tugevus (kJ mol^{-1})
Kovalentne side		**150 – 450**
Mitte-kovalentsed sidemed		
Elektrostaatiline interaktsioon	Ioon-ioon	200 – 300
	Ioon-dipoole	50 – 200
	Dipoole-dipoole	5 – 50
Vesinikside		4 – 120
Halogenside		10 – 150
π-π interaktsioon		0 – 50
Katioon – π interaktsioon		5 – 80
Van der Waalsi interaktsioon		< 5
Solvofoobne interaktsioon		0 – 100

S. Kaabel Doktoritöö, 2019 TTU Press doi.org/10.23658/taltech.6/2019
J. W. Steed, D. R. Turner, K. J. Wallace, Core Concepts in Supramolecular Chemistry and Nanochemistry, John Wiley And Sons, Ltd, 2007.
G. Cavallo, Chem. Rev. 2016, 116, 2478–2601.
F. Biedermann Angew. Chemie Int. Ed. 2014, 53, 11158–11171.

Tsükloheksanohemikukurbituriilide interaktsioonid



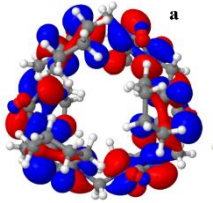
Katioonid

C=**O**---**X**$^{+}$
välisküljele

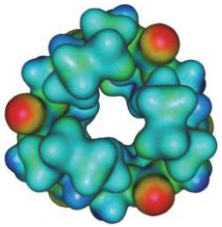
Anioonid

C-**H**---**A**$^{-}$ õõnsusesse
ja H^{+}

HOMO

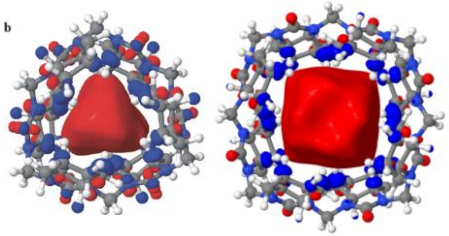


B97-D/TZVPD



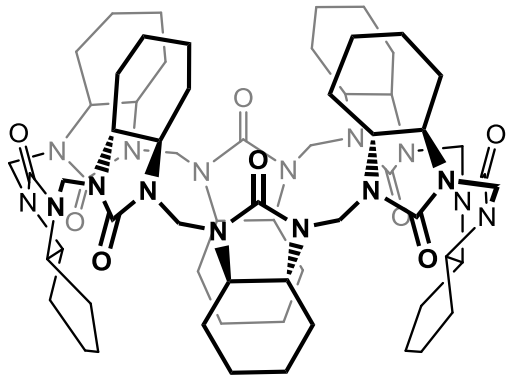
MEP

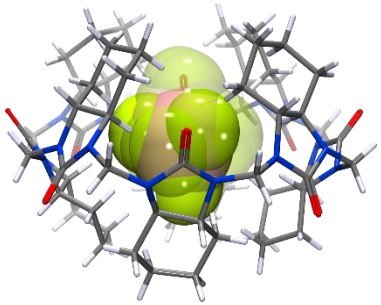
LUMO

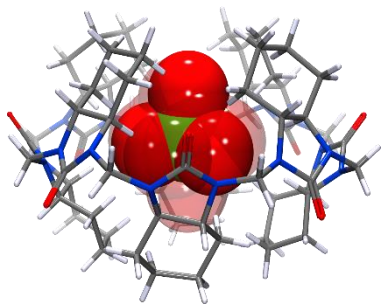


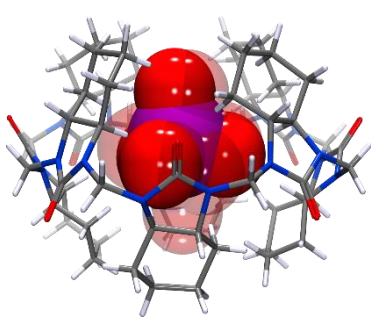
cycHC[6] cycHC[8]

(*R,R*)-cycHC[8] suluühendid anioonidega





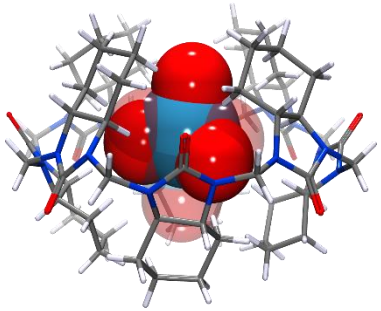


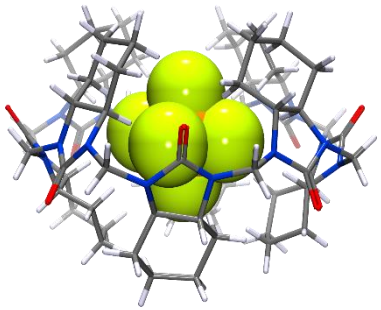


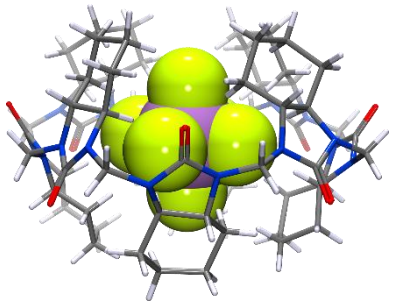
Aniooni suuruse kasv

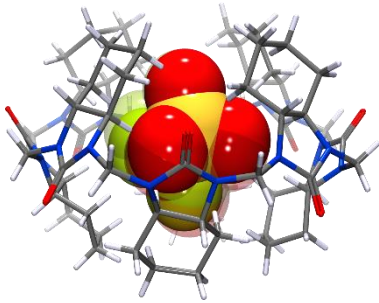
	BF_4^-	ClO_4^-	IO_4^-
K_a (MeOH) =	48 M^{-1}	470 M^{-1}	1800 M^{-1}

Õõnsus 123 Å^3,
Portaali diameeter 8.5 Å





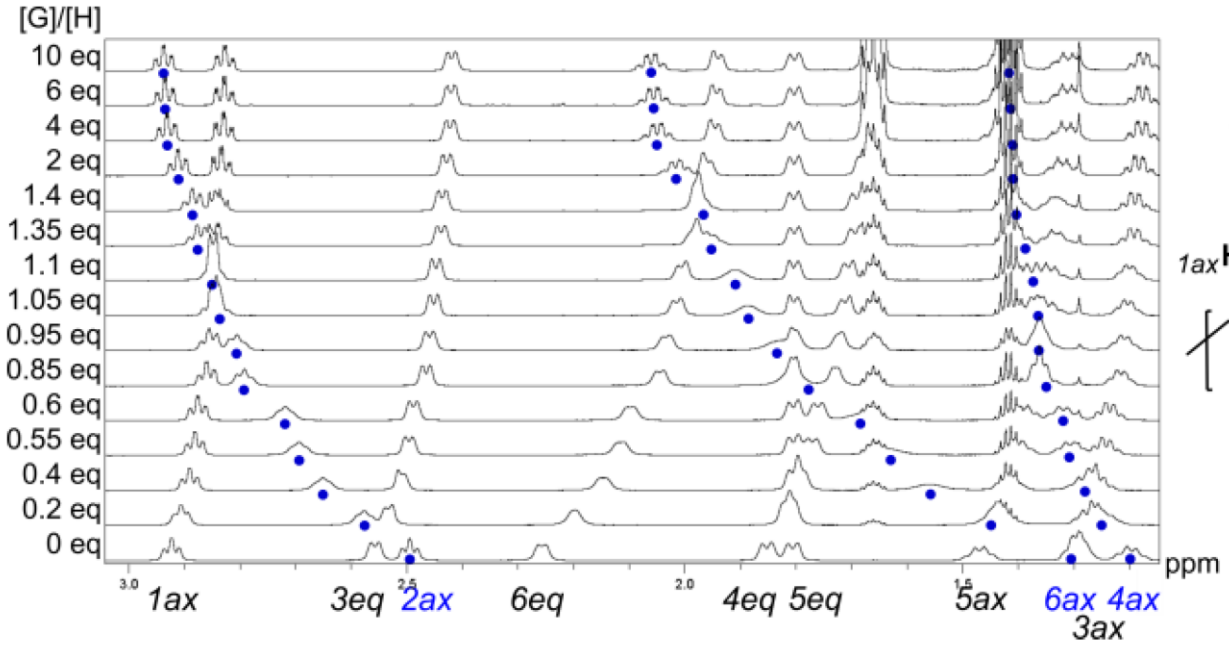


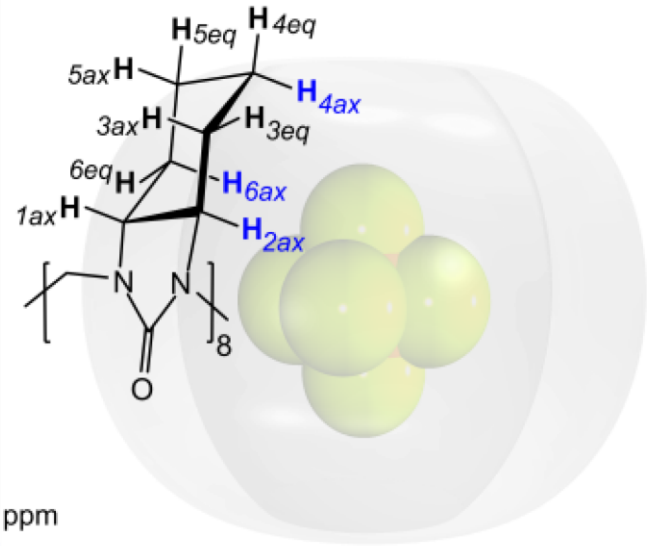


ReO_4^-	$CF_3CO_2^-$	PF_6^-	SbF_6^-	$CF_3SO_3^-$
4700 M^{-1}	K_a < 10 M^{-1}	28 000 M^{-1}	250 000 M^{-1}	39 M^{-1}

Kaabel *Chem. Sci.* **2017**, 8 (3), 2184

Komplekseerumisel tekivad C-H---A$^-$ vesiniksidemed





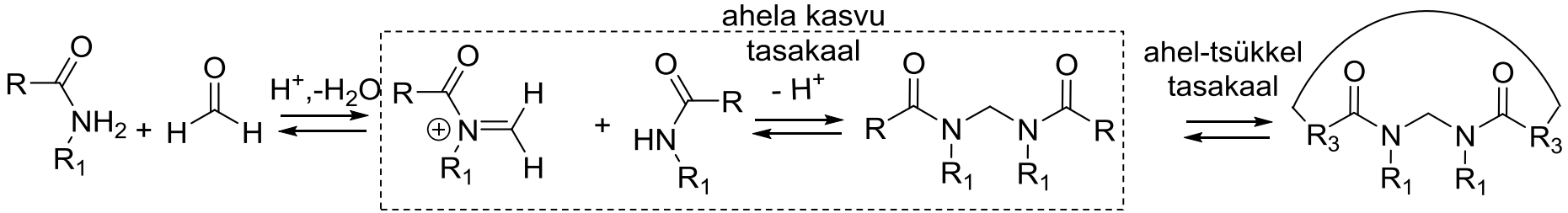
PF_6^-@cycHC[8]

	K_a (M^{-1})	$\Delta H°$ (kJ mol^{-1})	$T\Delta S°$ (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})
PF_6^-@cycHC[8]	(1.29±0.04) 10^4	-43.8±0.2	-20.4	-23.4

ITC

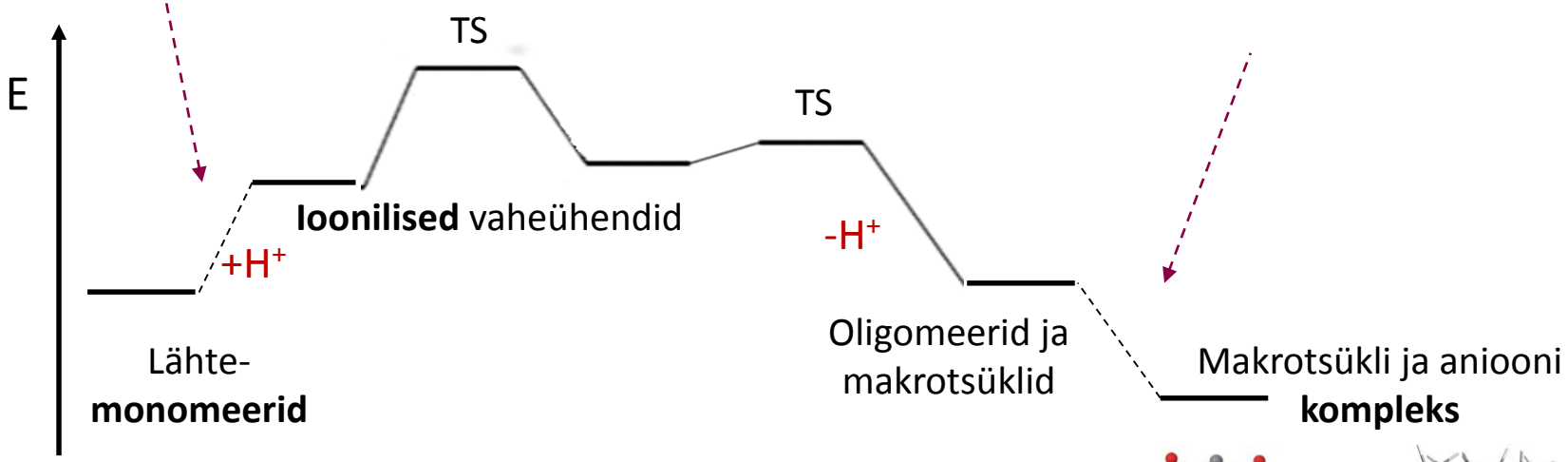
Kaabel *Chem. Sci*. **2017**, 8 (3), 2184

Dünaamiliste sidemetega hemikukurbituriilide teke

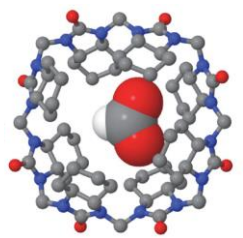


Tugev hape katalüsaatorina

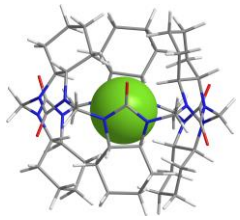
Komplekseerumine **aniooniga võimendab makrotsükli teket**



Kas mehhanokeemia soodustaks kovalentsete sidemete dünaamilisust?



HCO_2^-@cycHC[8]

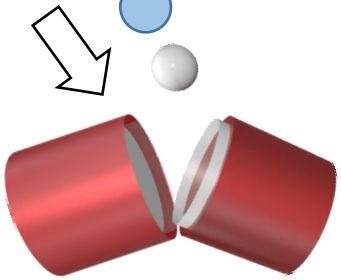


Cl^-@cycHC[6]

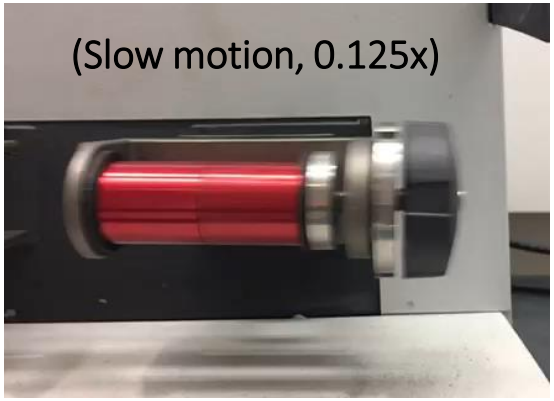
Mehhanokeemiaga hemikukurbituriilide teke

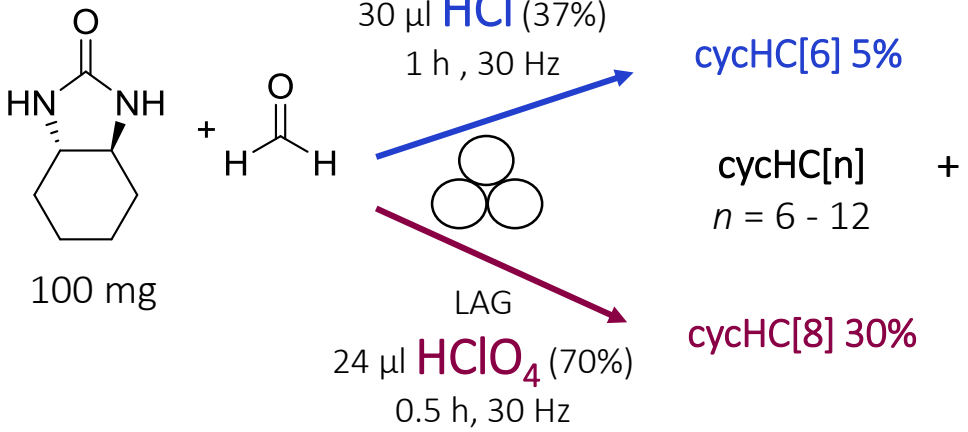
Monomeerid
100-200 mg

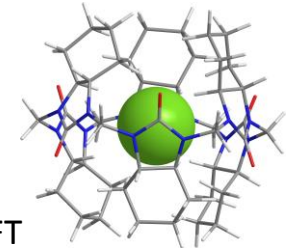
Kontsenstreeritud hape
10-30 µl



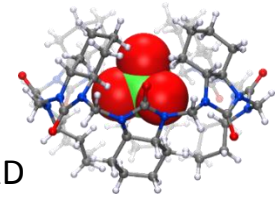
Jahvatamine







Cl^- @ cycHC[6]



ClO_4^- @ cycHC[8]

Öeren PCCP **2014**
Kaabel *Chem. Sci.* 2017

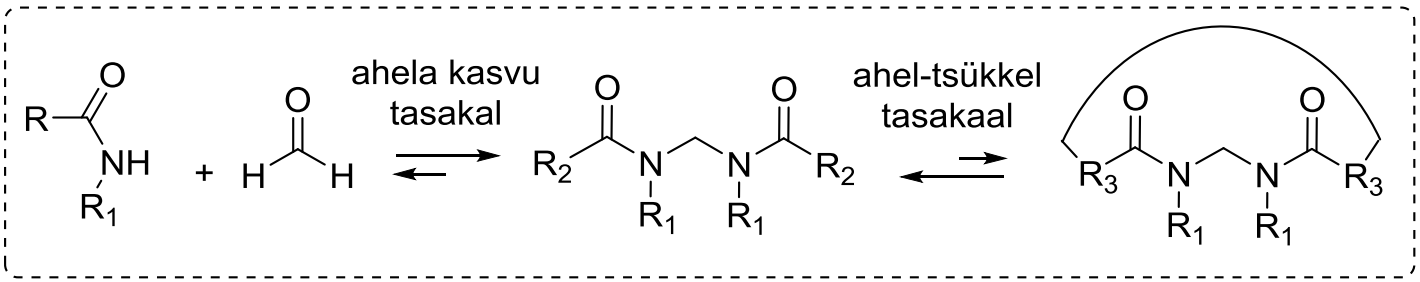
Kaabel *ACIE* **2019**

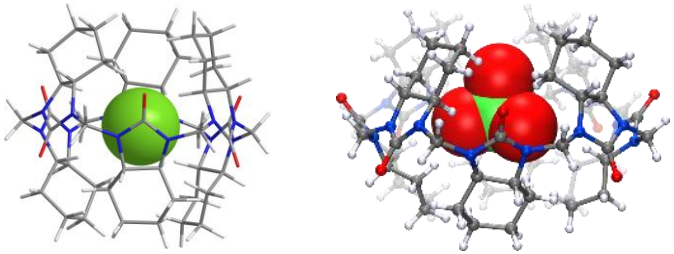
LAG - jahavatus vedeliku manulusel

Mehhanokeemiaga hemikukurbituriilide teke - jahvatus

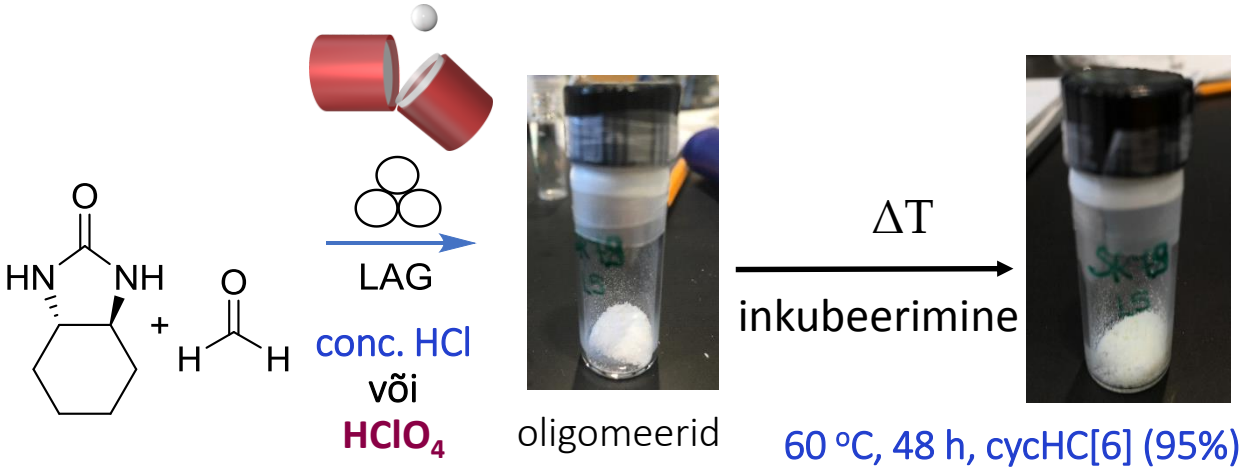
Tugeva happe kogust saab vähendada 100 korda!

Mehhaaniline aktivatsioon ei lase madala energiaga makrotsüklitel akumuleeruda





Mehhanokeemiaga hemikukurbituriilide teke – jahvatus + inkubeerimine



1. Dünaamiliste vaheühendite teke

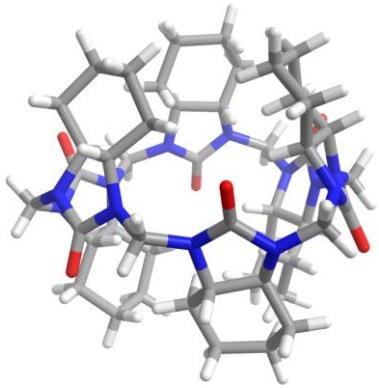
2. Ise-organiseerumine anioonse malli manulusel

Kaabel *ACIE* **2019**

Ise-organiseerumine ümber mall-molekuli

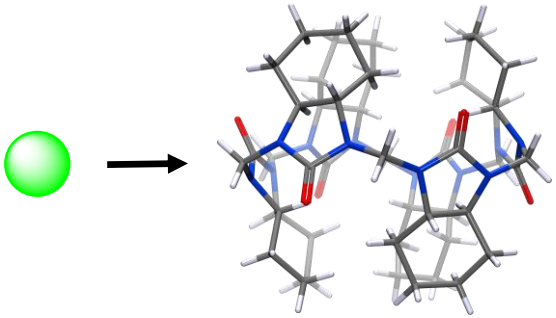
Anioonid

C-**H**---**A**$^{-}$ õõnsusesse



Katioonid

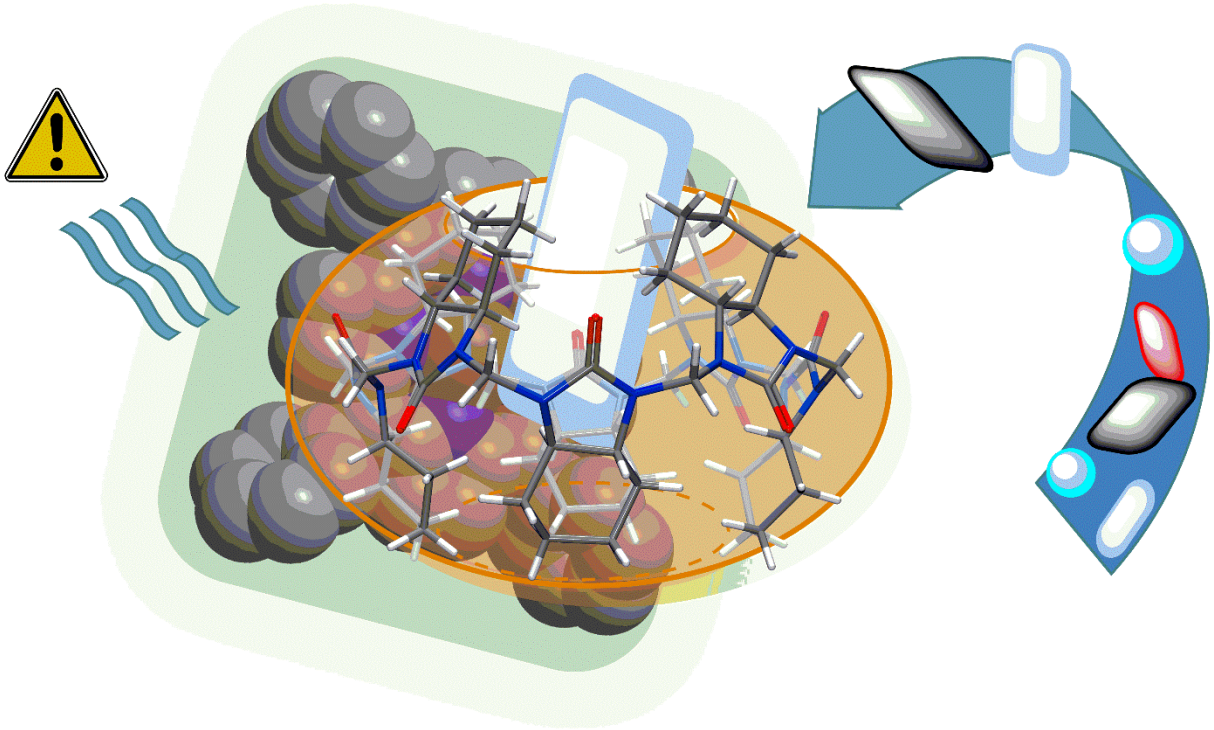
C=**O**---**X**$^{+}$
välisküljele



Suuremaid süsteeme?

Ongströmi mõõtu anioonsest mallist
nanomeeter suuruses molekulini

Ise-organiseeruvad molekulaarsed sensorid…?



https://www.project-initio.eu/

INITIO “INnovative chemIcal sensors for enanTioselective detectIon of chiral pOllutants”

Tänu!

PhD St. Elena Prigorchenko (end. Shmatova)
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PhD St. Anna Peterson
M St. Nele Konrad
M. St, Mari-Liis Ludvig
M St. Jevgenia Martõnova
Andre Roden (end M. St)
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Prof. Tomislav Friščić

Eesti Teadusagentuur
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iNitio
Innovative chemical sensors for enantioselective detection of chiral pOllutants

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