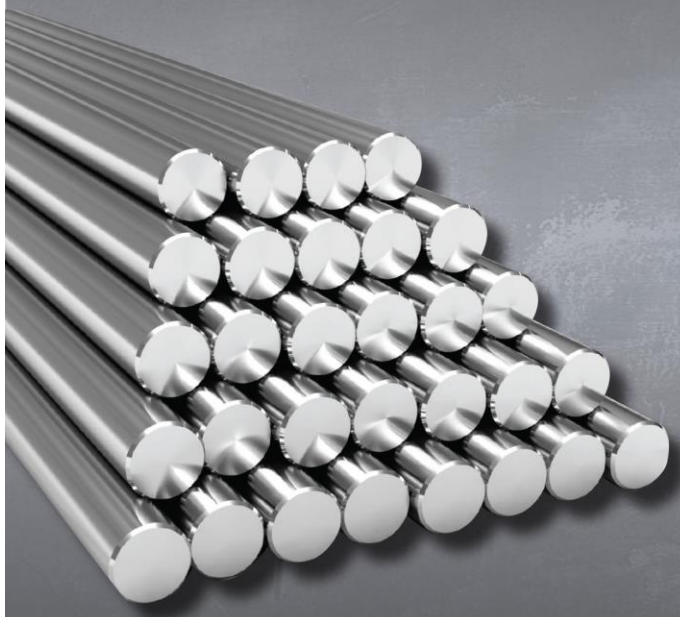
259th OMICS International Conferences

International Conference on

Smart Materials & Structures

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June 15 -17, 2015 Las Vegas, USA



Exploring the Fusion of Intelligence with Materials

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Center for Exploitation of Solar Energy &
Department of Chemistry, University of Copenhagen

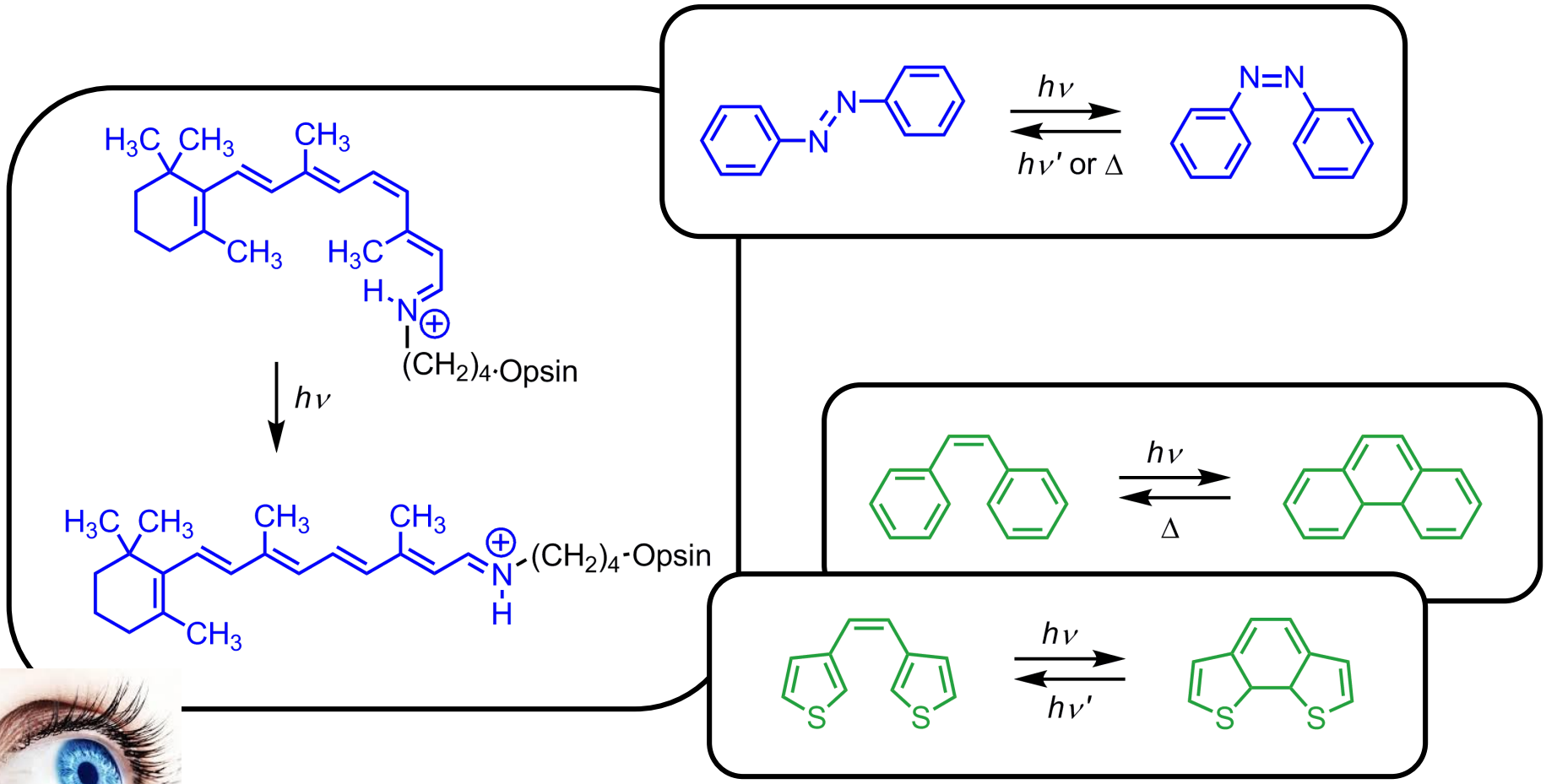
From Light-Controlled Molecular Electronics Devices to Solar Energy Storage Materials

Mogens Brøndsted Nielsen



Smart Materials & Structures, Las Vegas, 15-17.6

Photoswitches





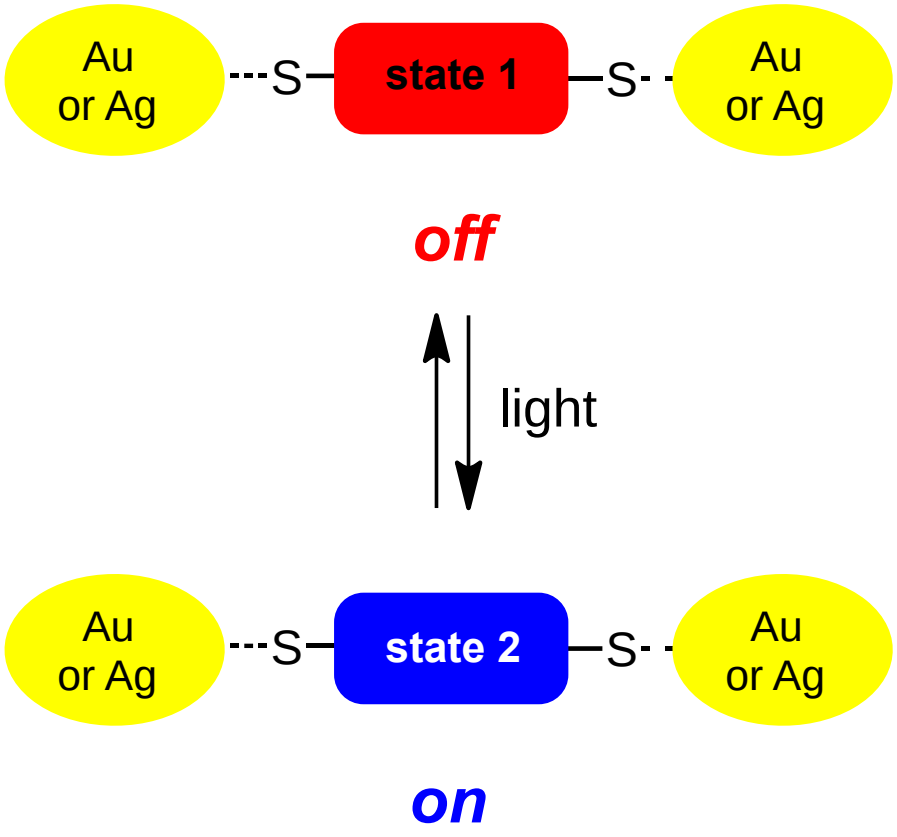
Cis-trans isomerizations

Electrocyclic reactions

… changes in conjugation

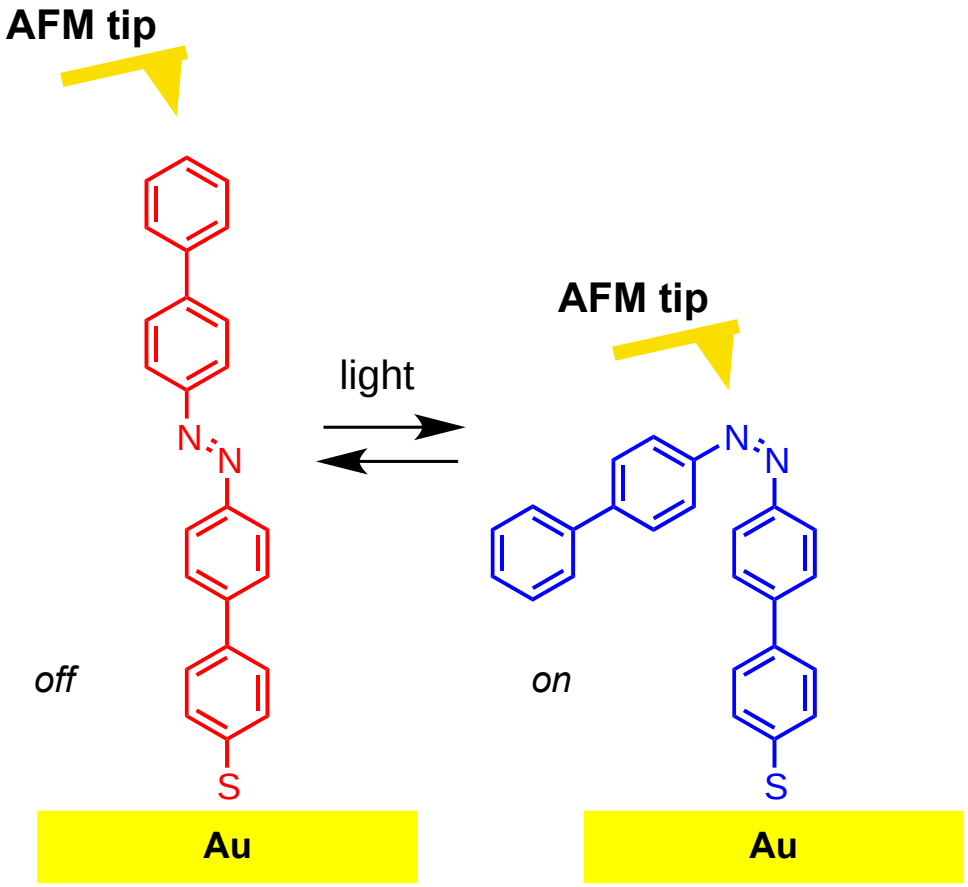


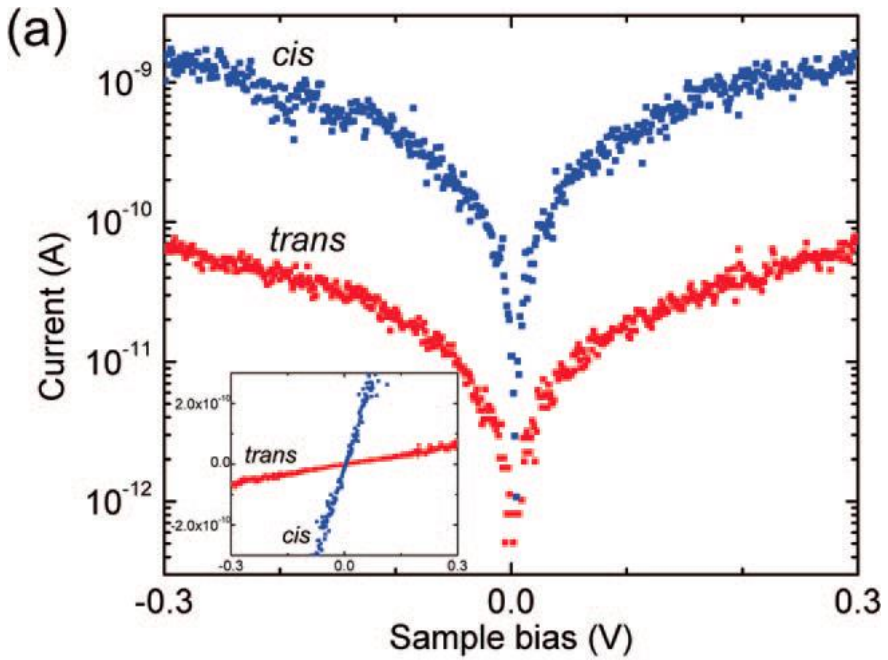
Photoswitches for Molecular Electronics

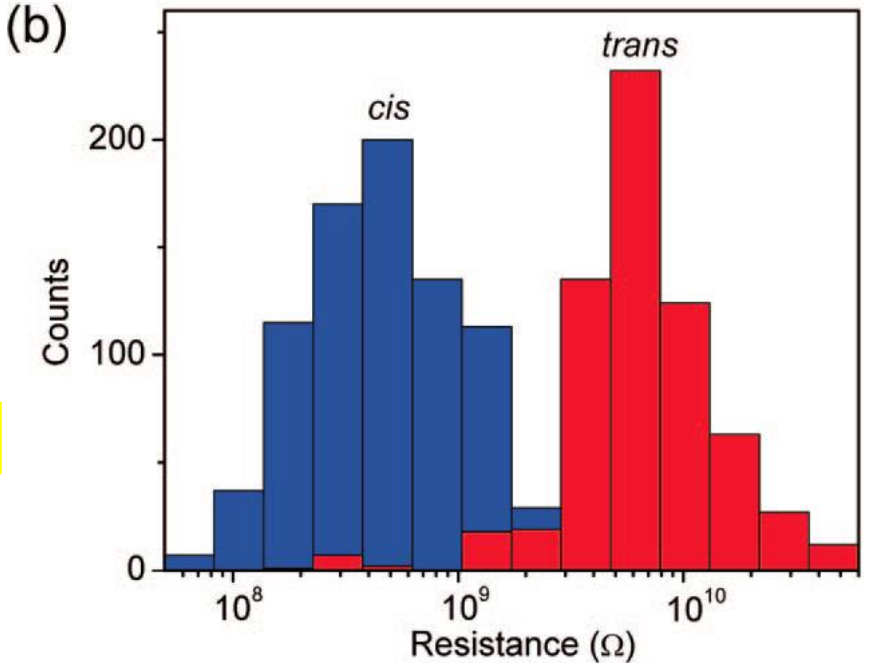




Conducting Probe AFM Measurements

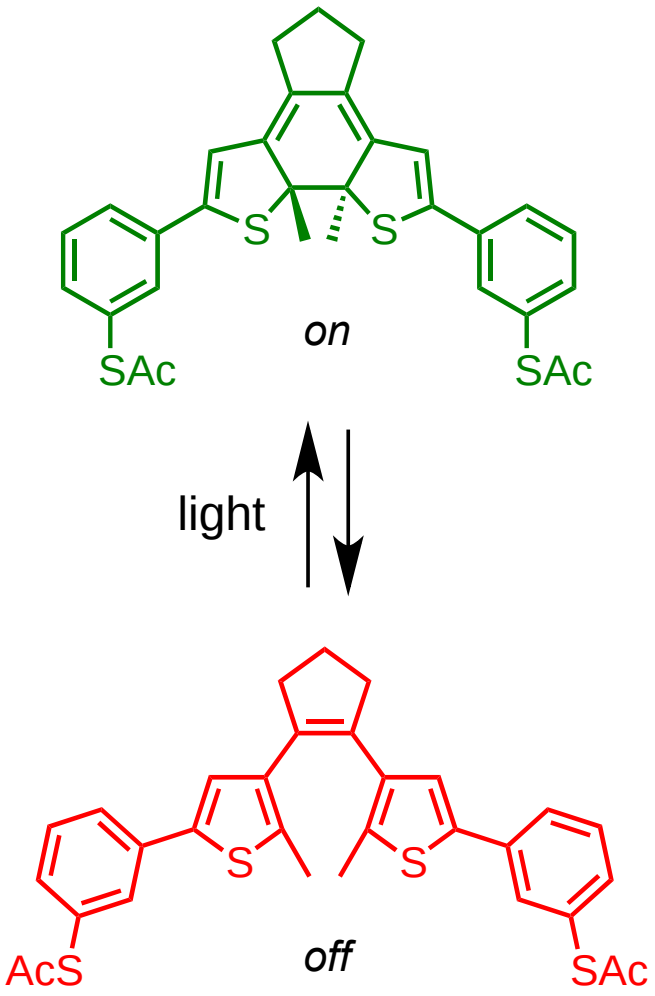


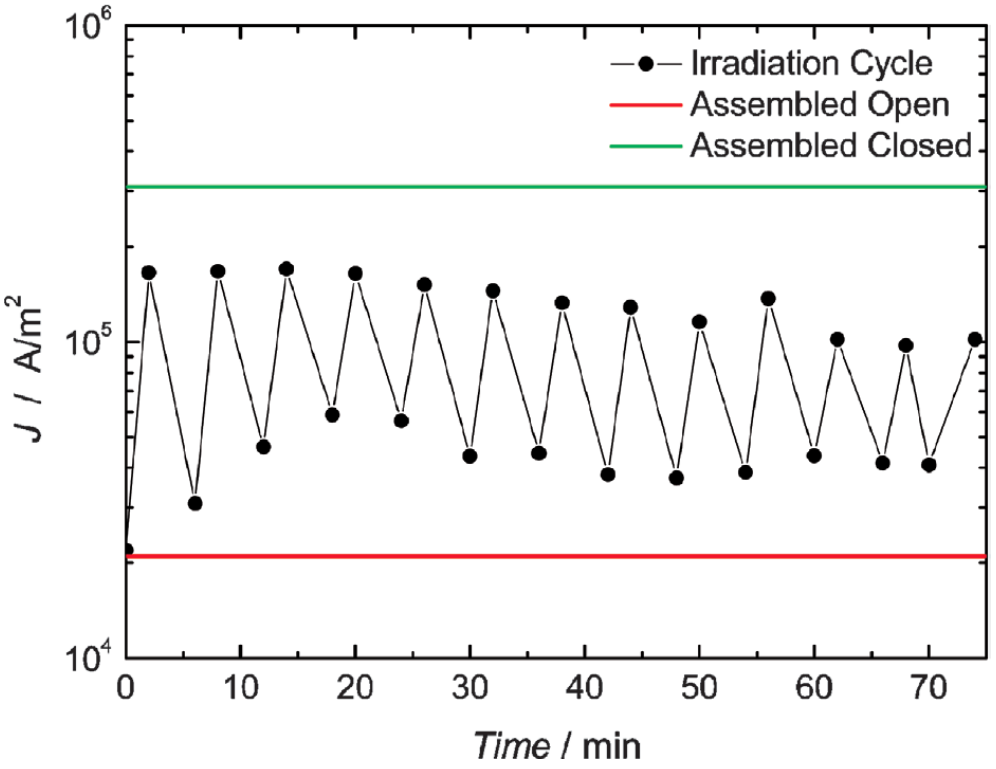




J. M. Mativetsky, G. Pace, M. Elbing, M. A. Rampi, M. Mayor, P. Samorì, *J. Am. Chem. Soc.* **2008**, *130*, 9192-9193.

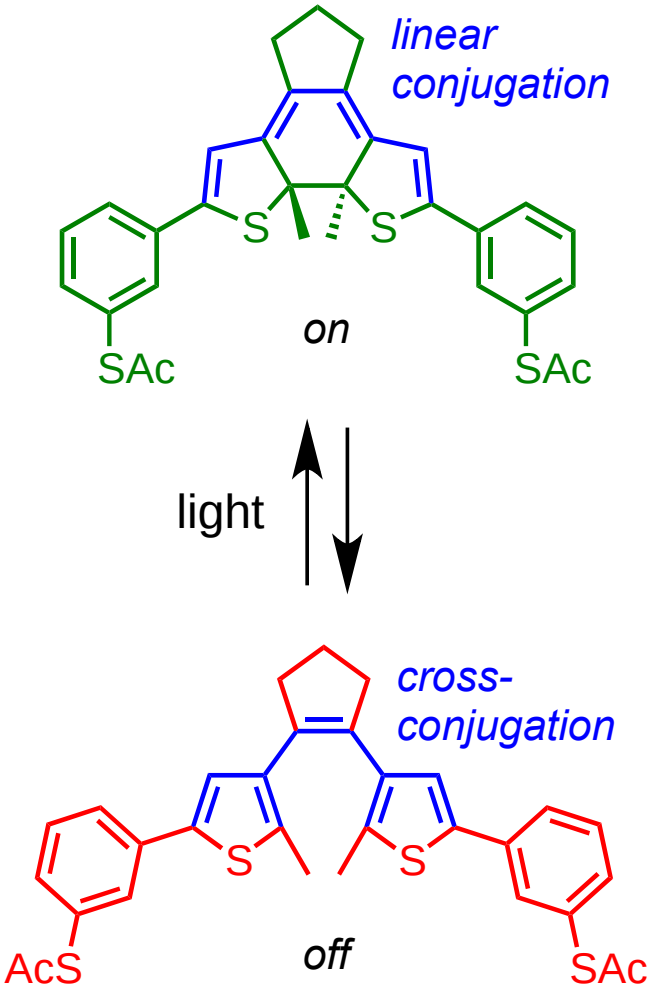
Dithienylethene Photoswitch

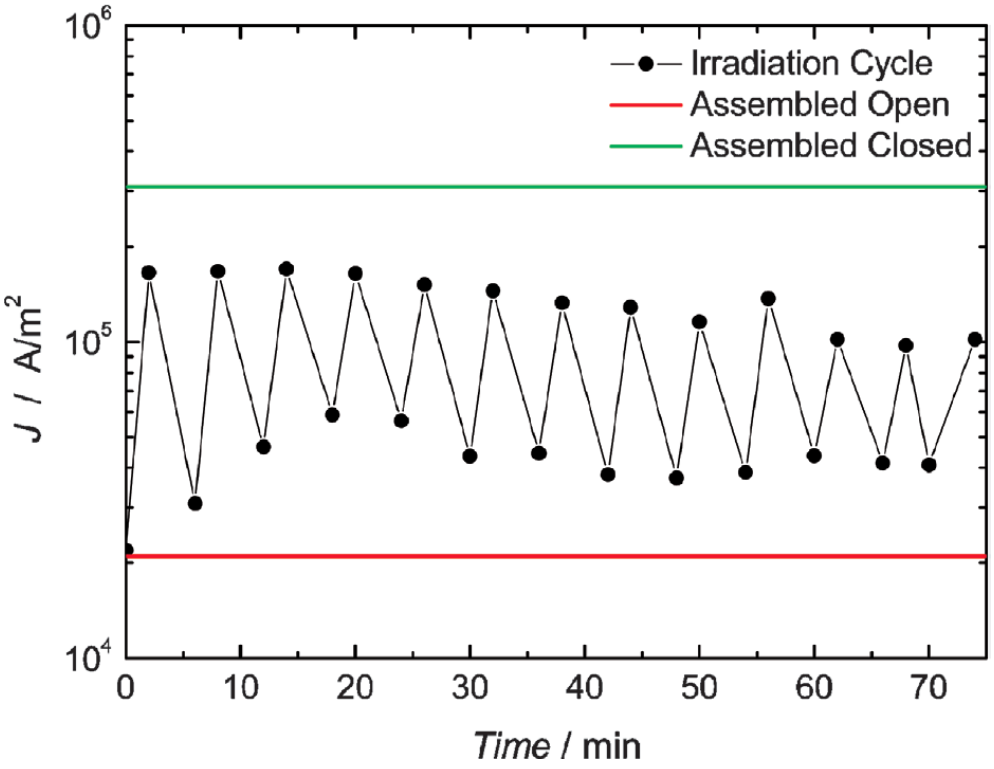




A. J. Kronemeijer, H. B. Akkerman, T. Kudernac, B. J. van Wees, B. L. Feringa, P. W. Blom, B. de Boer, *Adv. Mater.* **2008**, *20*, 1467-1473.

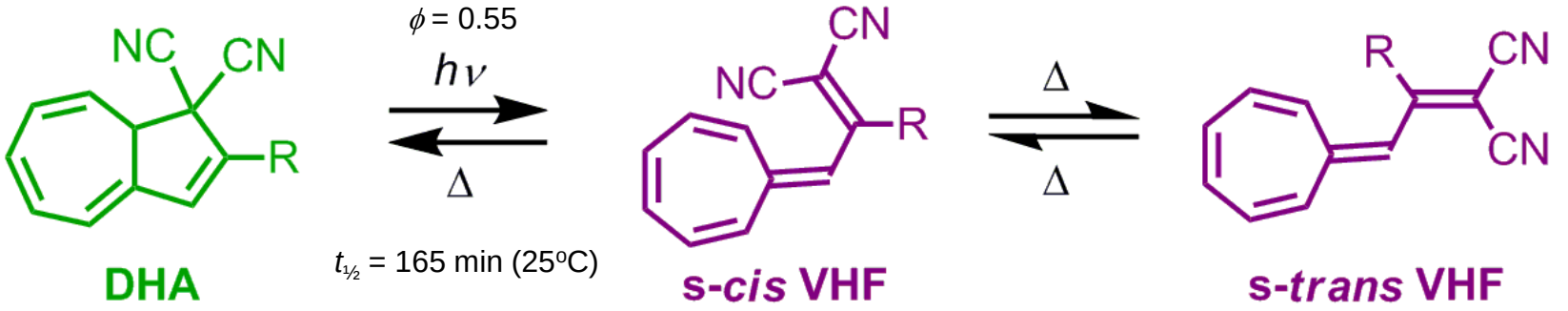
Dithienylethene Photoswitch





A. J. Kronemeijer, H. B. Akkerman, T. Kudernac, B. J. van Wees, B. L. Feringa, P. W. Blom, B. de Boer, *Adv. Mater.* **2008**, *20*, 1467-1473.

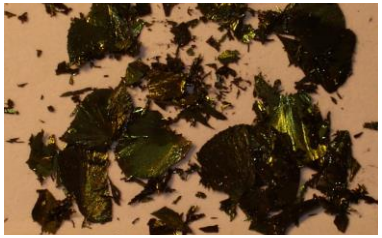
Dihydroazulene (DHA) / Vinylheptafulvene (VHF) Photoswitch

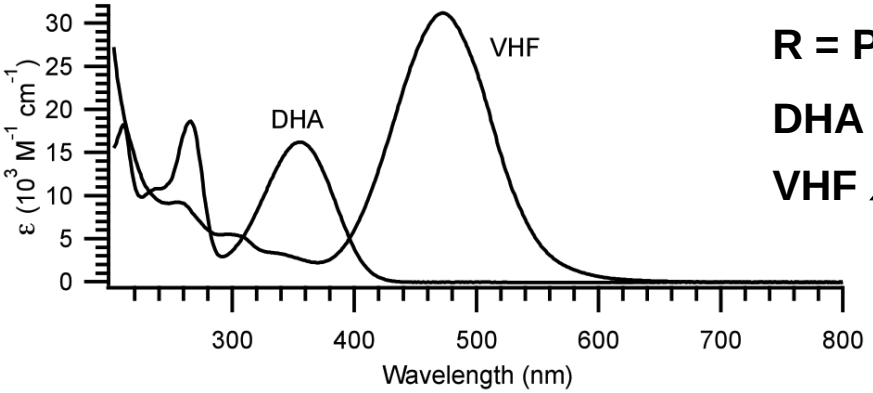












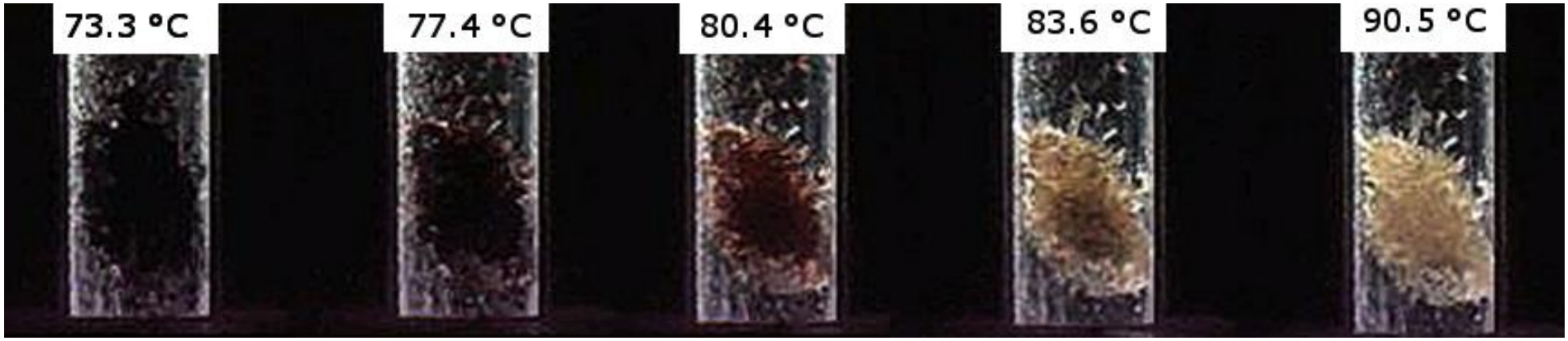
R = Ph:

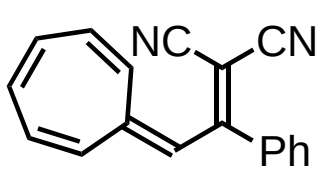
DHA λ_{max} 353 nm

VHF λ_{max} 470 nm

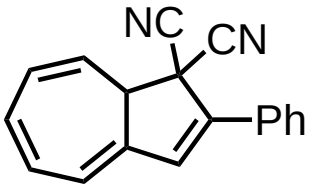
(solvent: MeCN)

Thermal Conversion of VHF Crystals

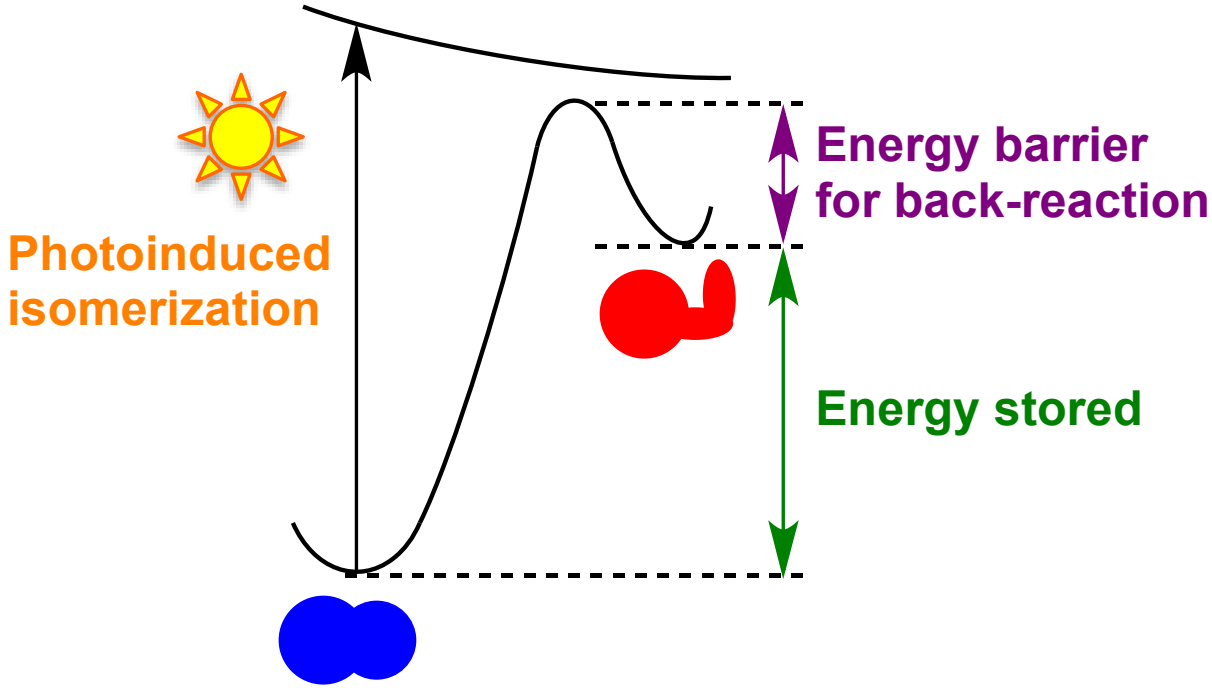


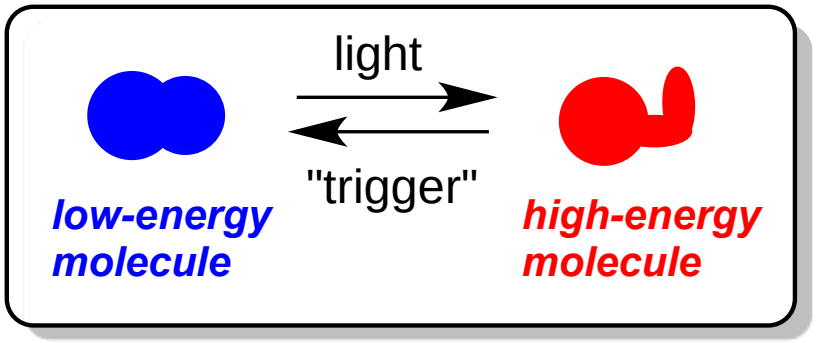




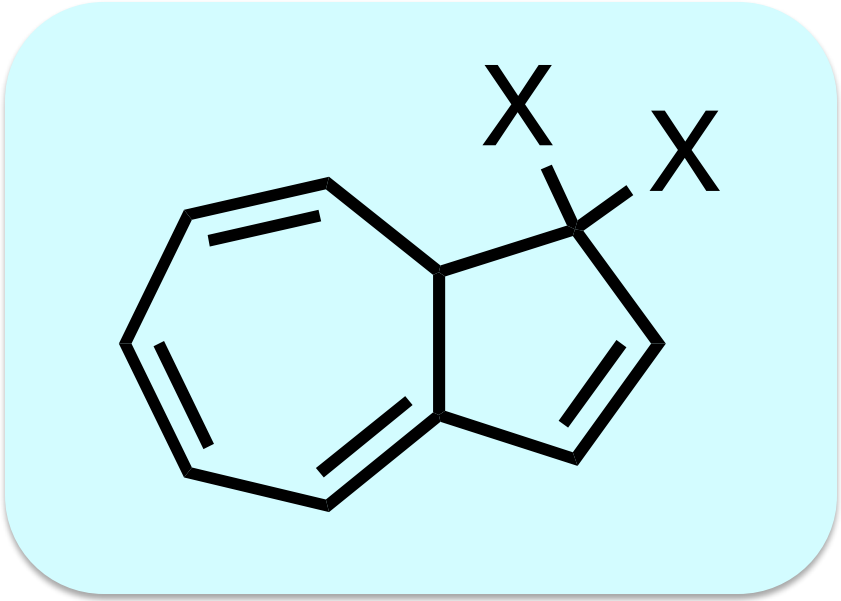


Solar Energy Storage Using Photoisomerization





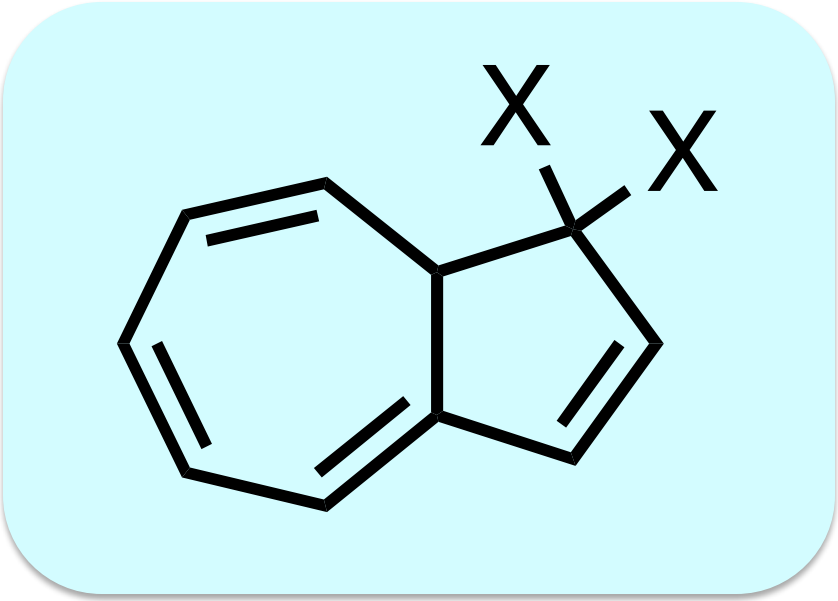
… Slow switching


X
X

Tuning of switching events?

- fast or slow

Many positions available
for substitution



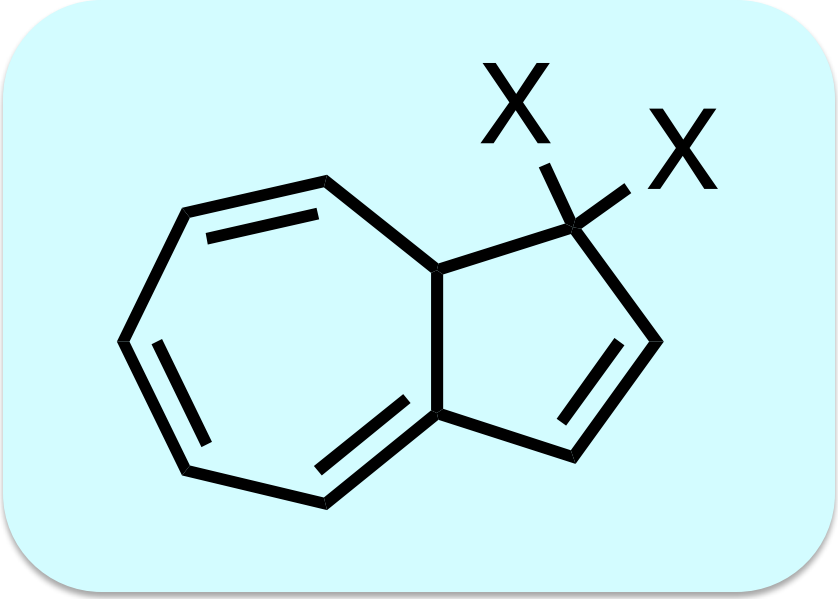
Tuning of switching events?

- fast or slow

Many positions available for substitution

Synthetic protocols for functionalization?

Can the core be used as substrate for further reactions?



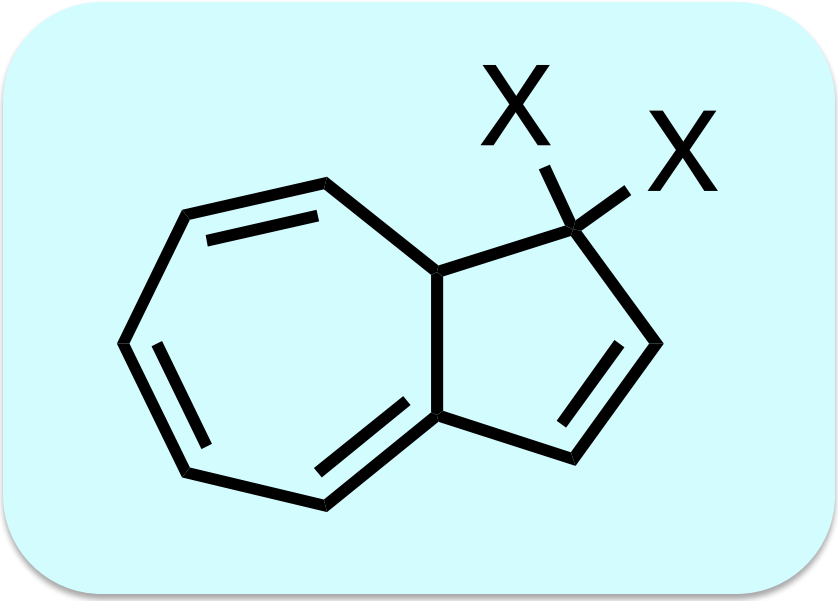
Tuning of switching events?

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many positions available for substitution

Synthetic protocols for functionalization?

Can the core be used as substrate for further reactions?



Switch for molecular electronics?

- Incorporation of electrode ”alligator clips”



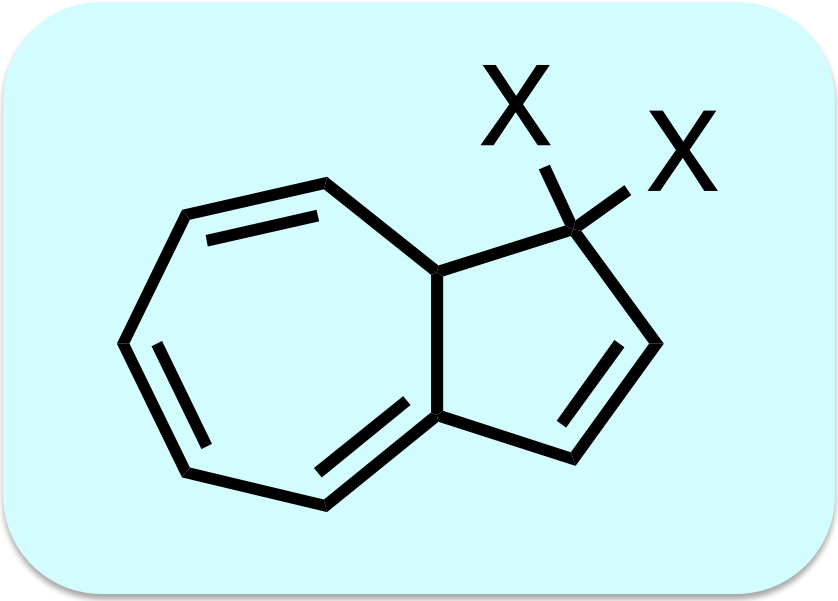
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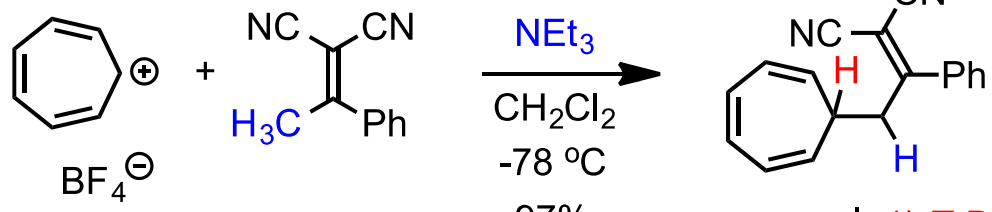
- Incorporation of electrode ”alligator clips”

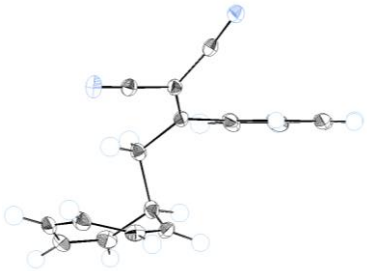


Solar energy storage?

Only photoactive in one direction but can we control the heat release?

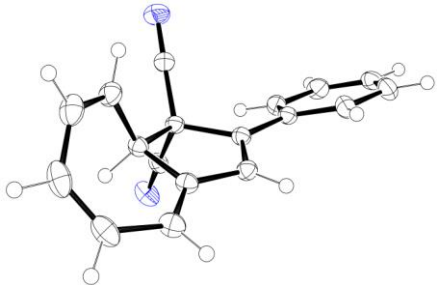
DHA Synthesis

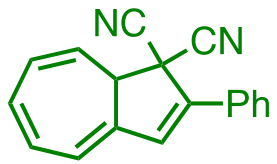




1) $TrBF_4$
CH_2ClCH_2Cl
2) Et_3N, PhMe

$Tr^{\oplus} = Ph_3C^{\oplus}$

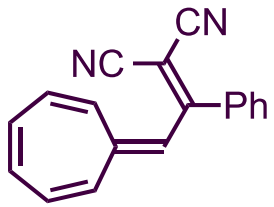




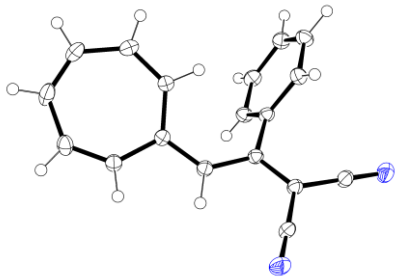
DHA

3) heat

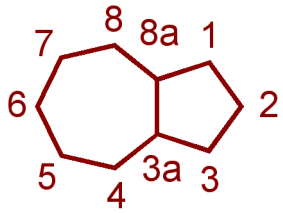
86%



VHF

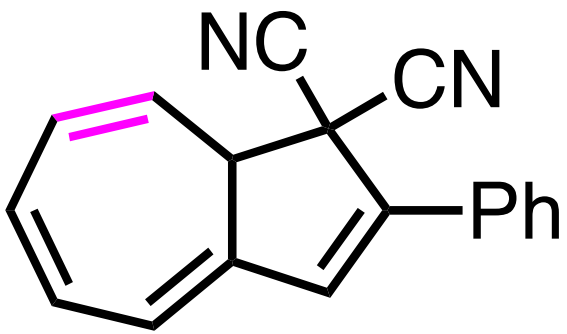


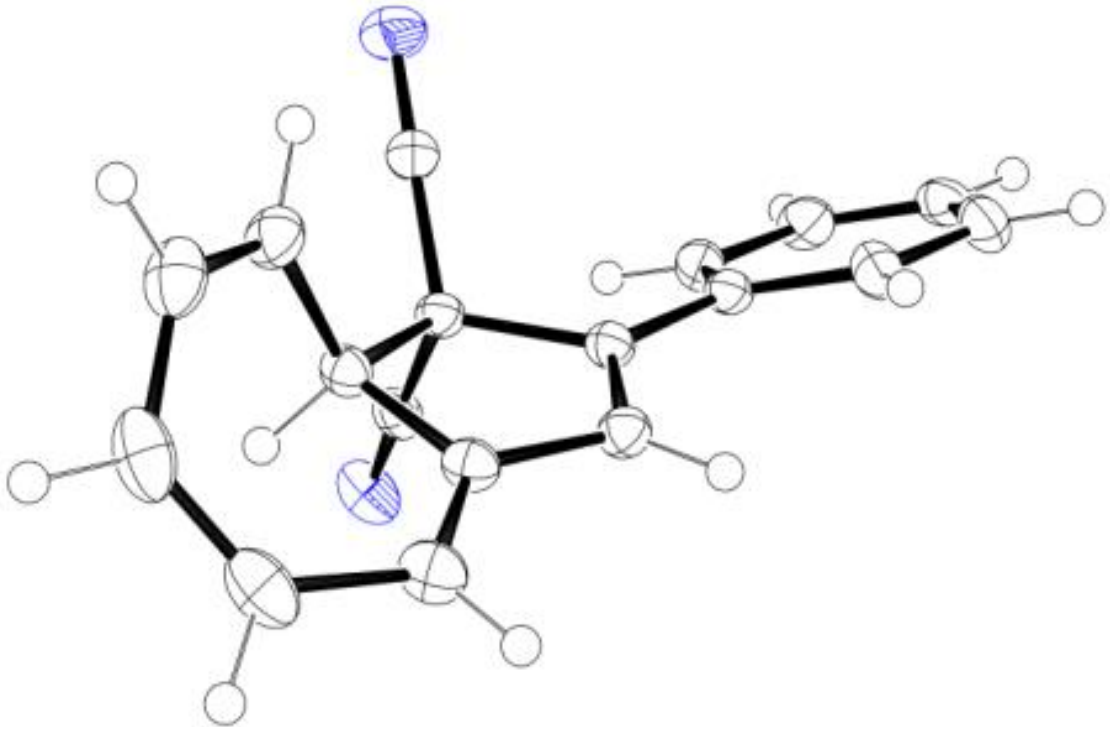
optimized to 15 g scale



… method allows ready incorporation of an aryl group at position 2

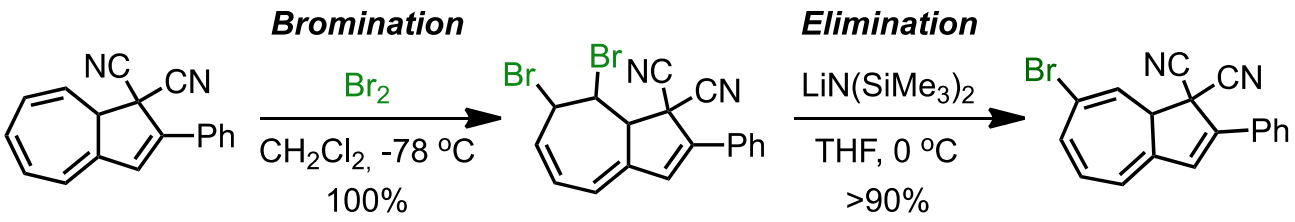
S. L. Broman, S. L. Brand, C. R. Parker, M. Å. Petersen, C. G. Tortzen, A. Kadziola, K.Kilså, M. B. Nielsen, *ARKIVOC* **2011**, *ix*, 51-67.


NC
CN
Ph



Regioselective Functionalization of DHA

Bromination – Elimination – Cross-coupling protocol

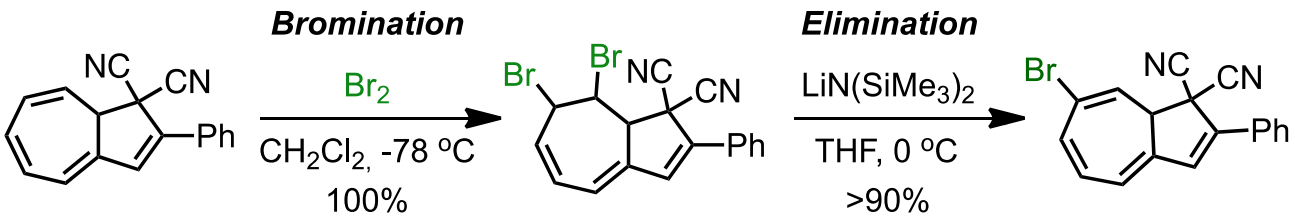


S. L. Broman, M. Å. Petersen, C. Tortzen, A. Kadziola, K. Kilså, M. B. Nielsen, *J. Am. Chem. Soc.* **2010**, *132*, 9165-9174.

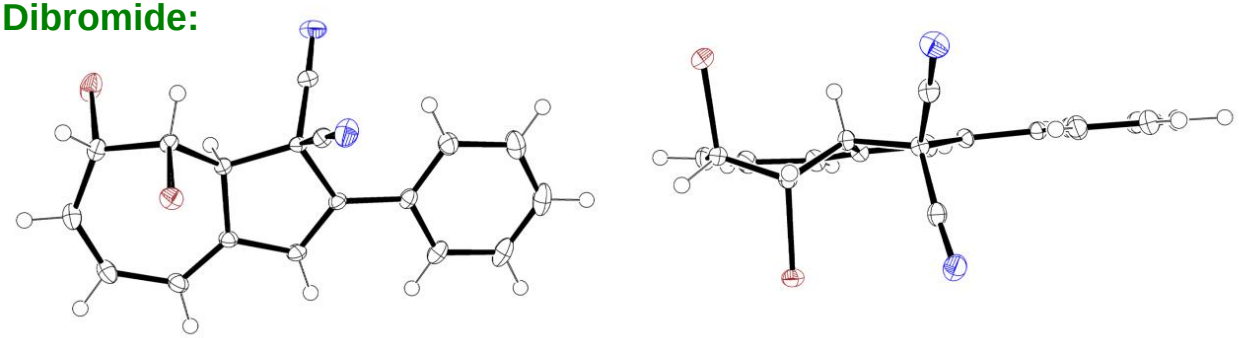
M. Å. Petersen, S. L. Broman, A. Kadziola, K. Kilså, M. B. Nielsen, *Eur. J. Org. Chem.* **2011**, 1033-1039.

Regioselective Functionalization of DHA

Bromination – Elimination – Cross-coupling protocol



Dibromide:

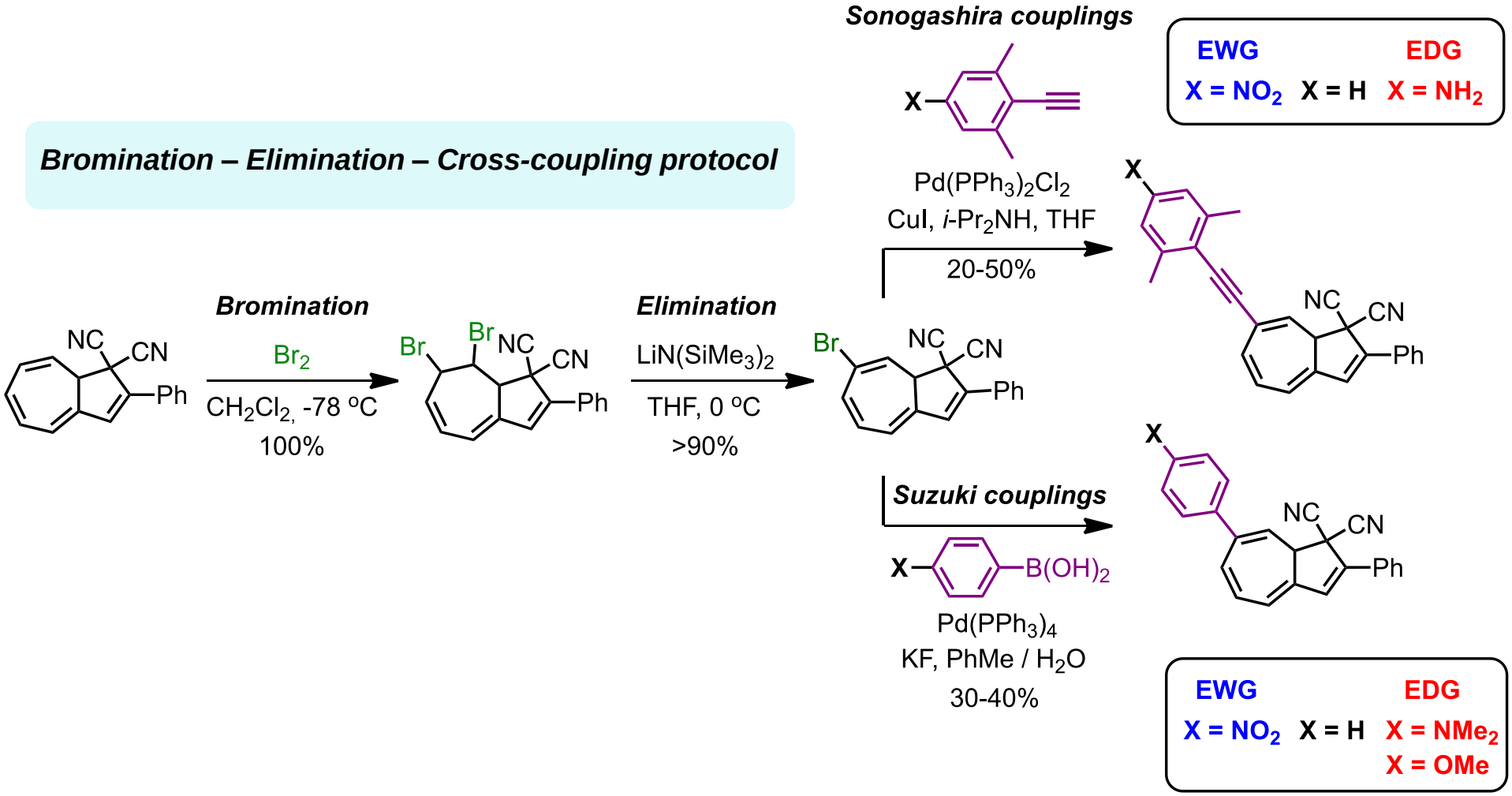


S. L. Broman, M. Å. Petersen, C. Tortzen, A. Kadziola, K. Kilså, M. B. Nielsen, *J. Am. Chem. Soc.* **2010**, *132*, 9165-9174.

M. Å. Petersen, S. L. Broman, A. Kadziola, K. Kilså, M. B. Nielsen, *Eur. J. Org. Chem.* **2011**, 1033-1039.

Regioselective Functionalization of DHA

Bromination – Elimination – Cross-coupling protocol



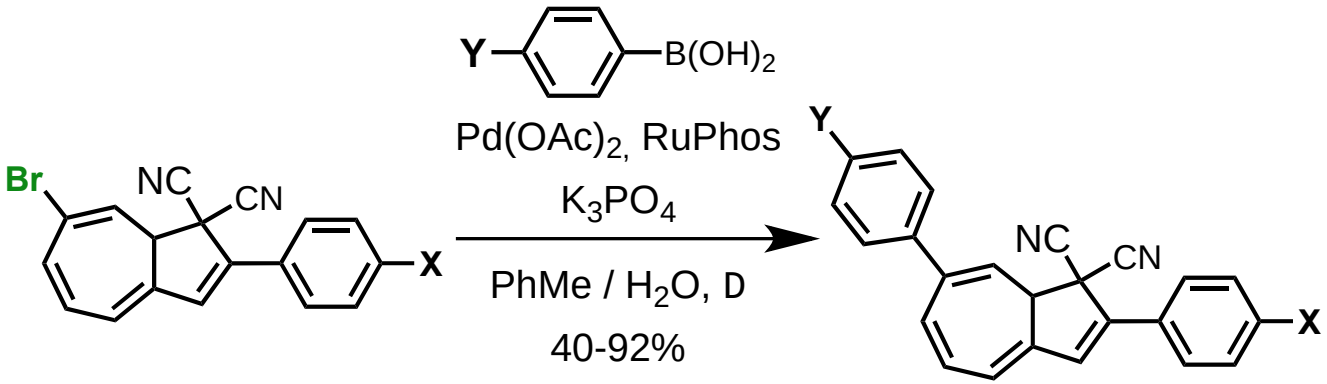
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M. Å. Petersen, S. L. Broman, A. Kadziola, K. Kilså, M. B. Nielsen, *Eur. J. Org. Chem.* **2011**, 1033-1039.

EWG = electron-withdrawing group

EDG = electron-donating group

Expanding and Optimizing the Protocol

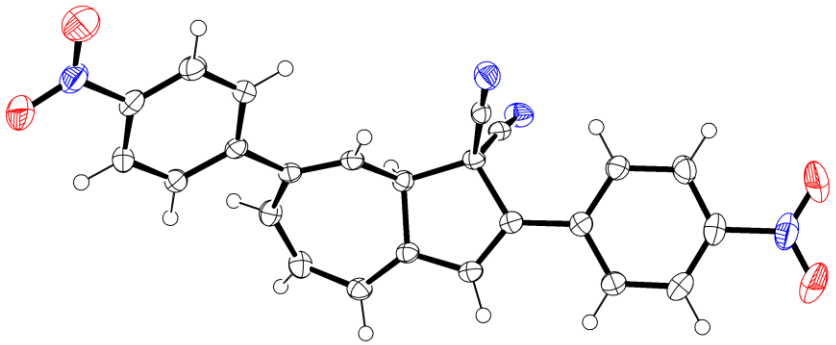


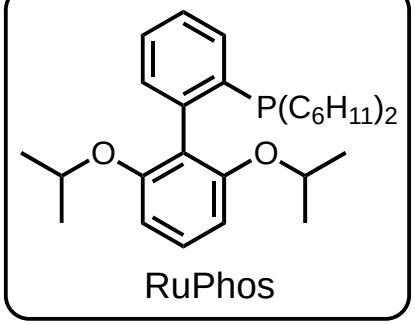
(a few exceptions < 10%)

X	Y
NO_2	NO_2
CN	CN
Br	SO_2t-Bu
SMe, S*t*-Bu	SO*t*-Bu
H	Br
Me	SMe, S*t*-Bu
Ph	H
C_6H_4OMe	Me
NMe_2	OMe
	NMe_2
	NH_2

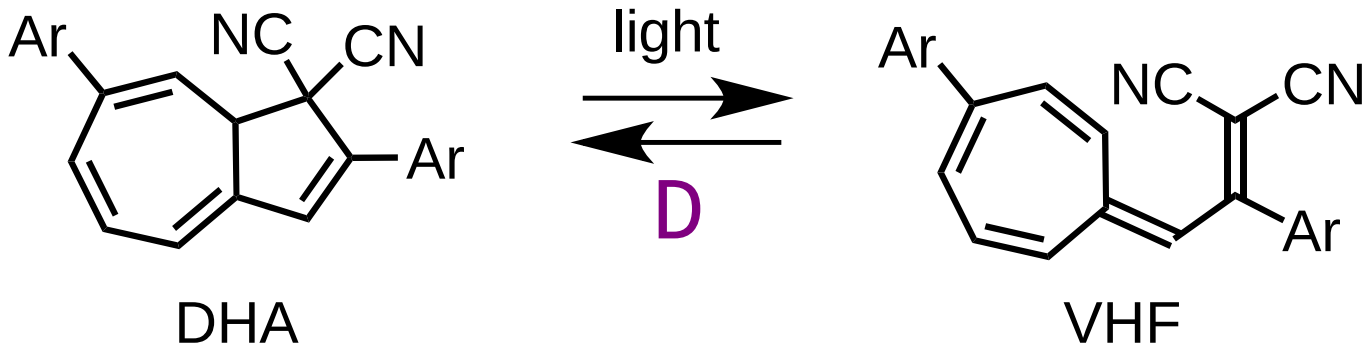
28 different combinations

X = Y = NO_2:





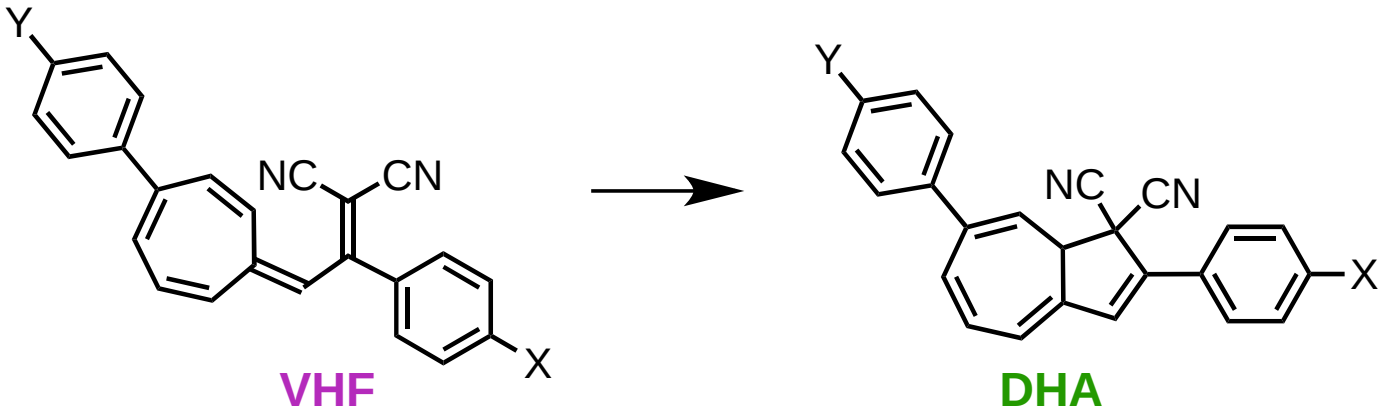
S. L. Broman, M. Jevric, M. B. Nielsen, *J. Org. Chem.* **2014**, *79*, 41-64.

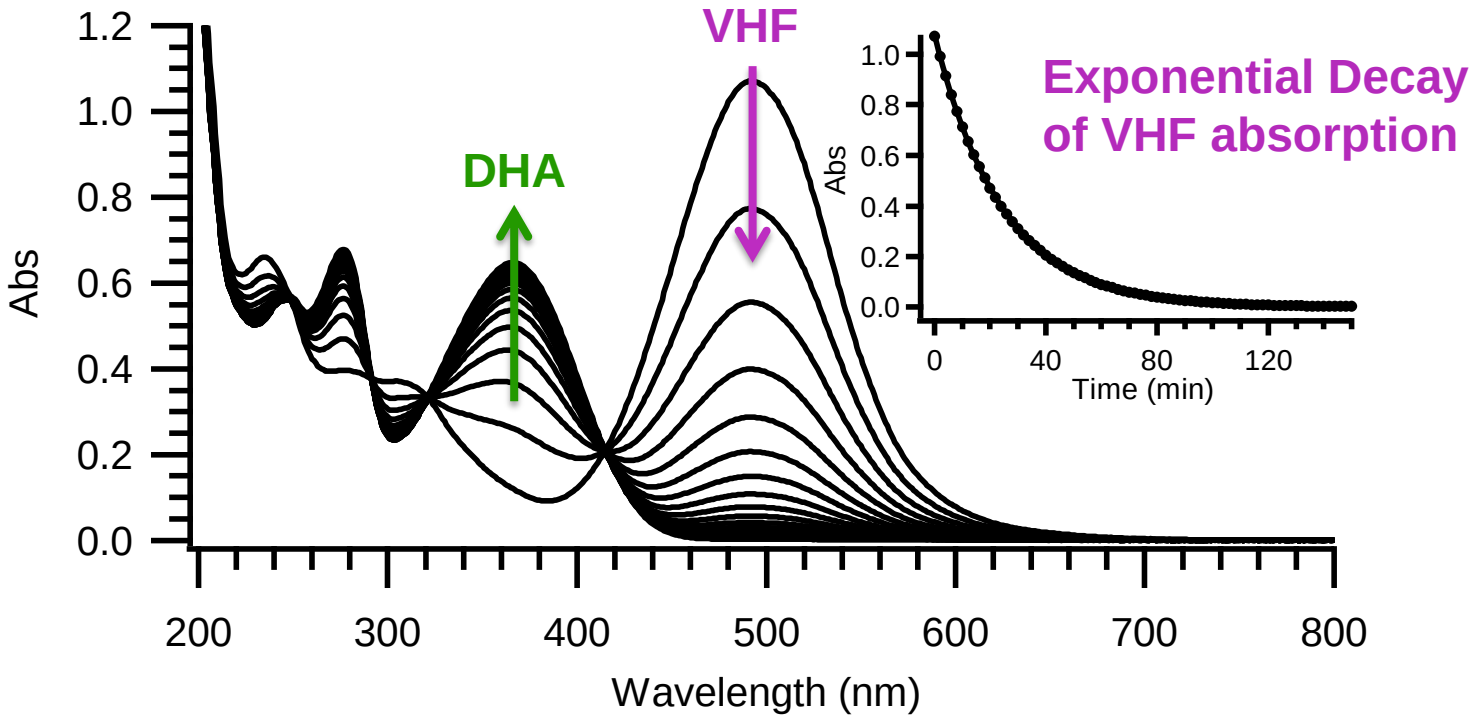


DHA VHF

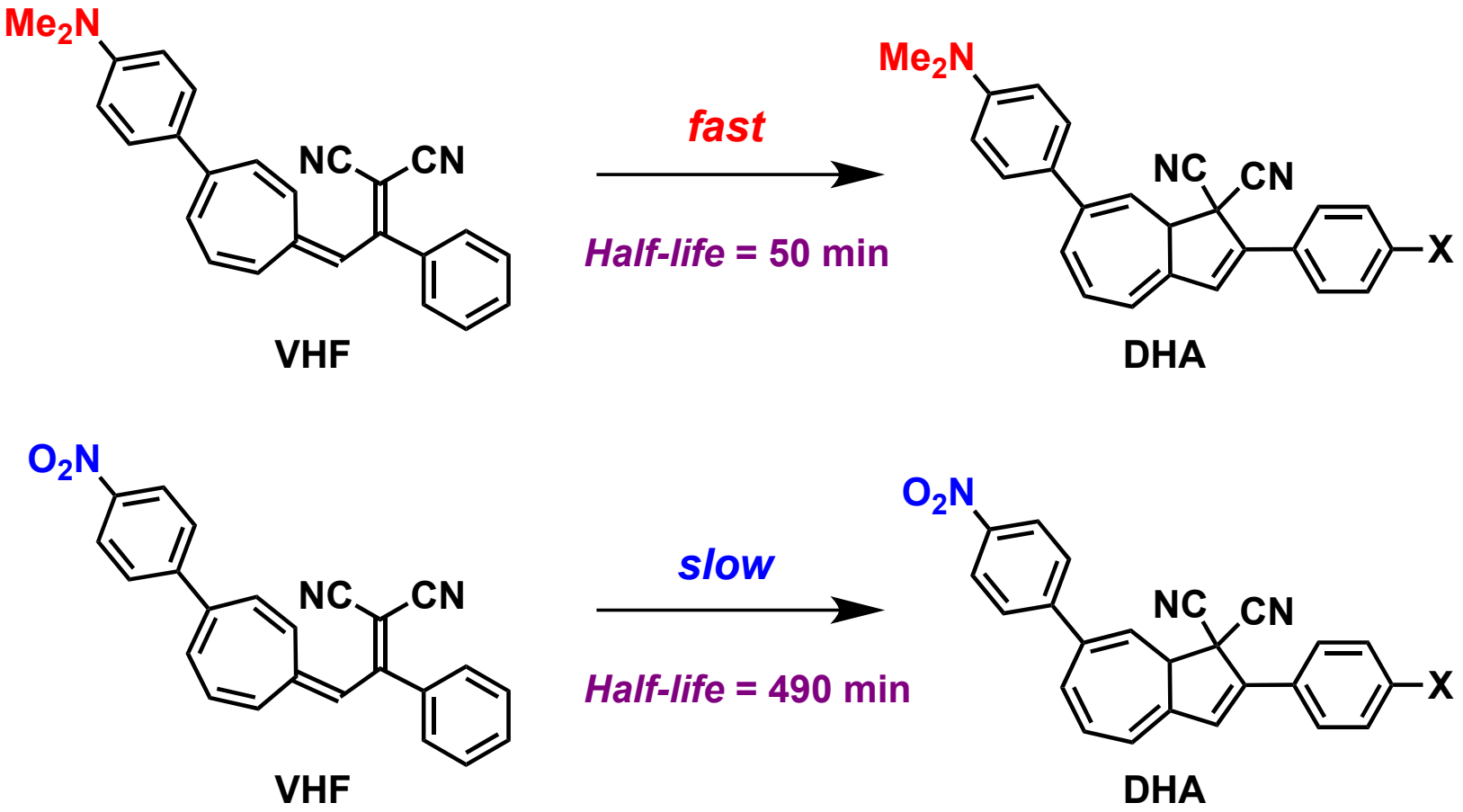
How fast is the ring-closure reaction?

Kinetics Easily Followed by Absorption Spectroscopy





Ring-Closure Reactions in MeCN at Room Temperature

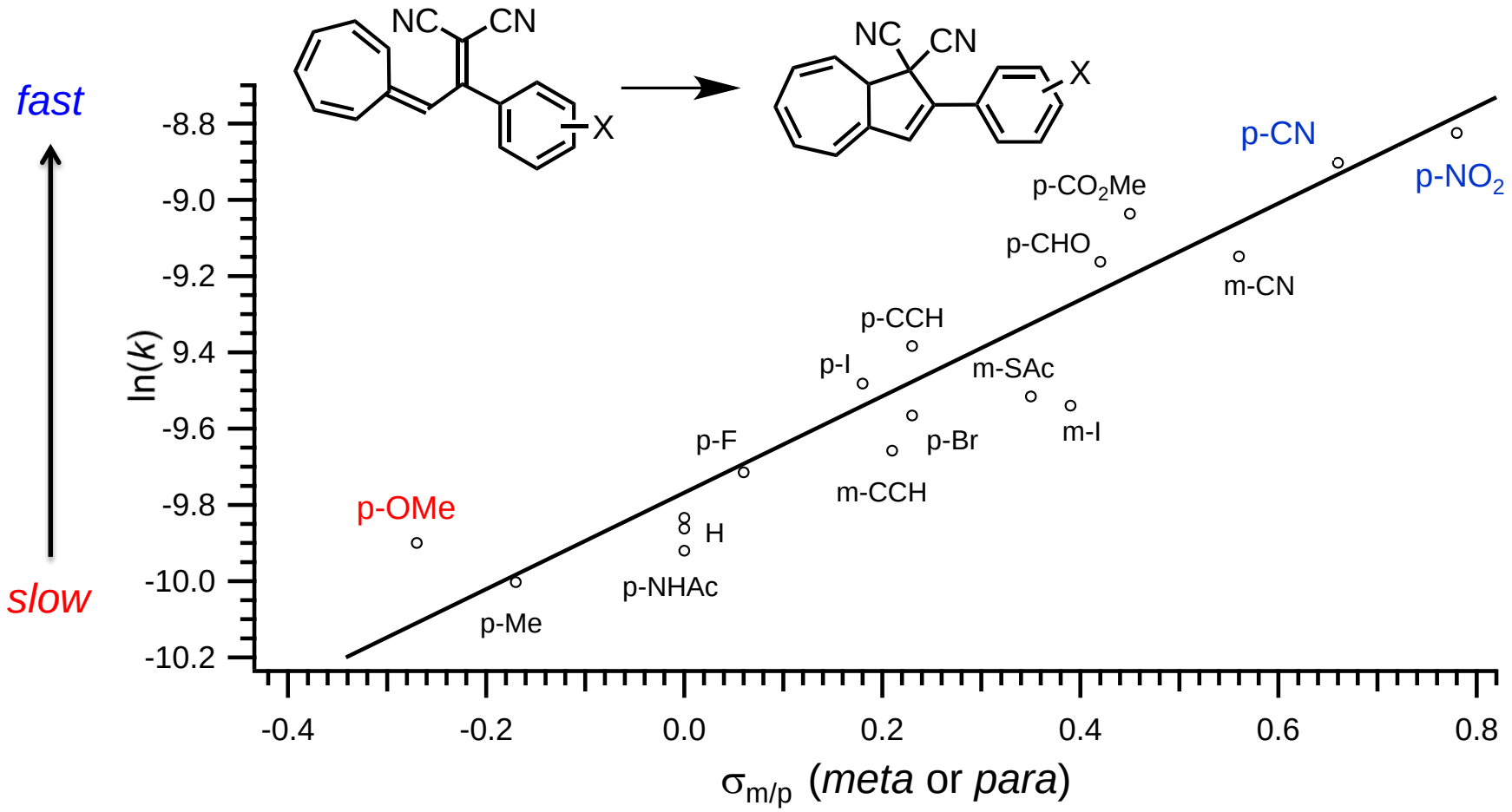


Electron-donating group at the seven-membered ring enhances the ring-closure

S. L. Broman, M. Jevric, M. B. Nielsen, *Chem. Eur. J.* **2013**, *19*, 9542-9548.

VHF Ring-Closure – Hammett Correlation

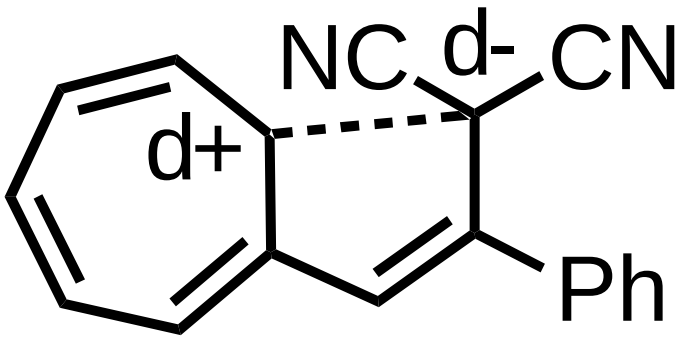
- Effect of changing the aryl group at the vinylic position



Electron-withdrawing group at vinylic position ring enhances the ring-closure

S. L. Broman, M. Jevric, M. B. Nielsen, *Chem. Eur. J.* **2013**, *19*, 9542-9548.

Polar Transition State



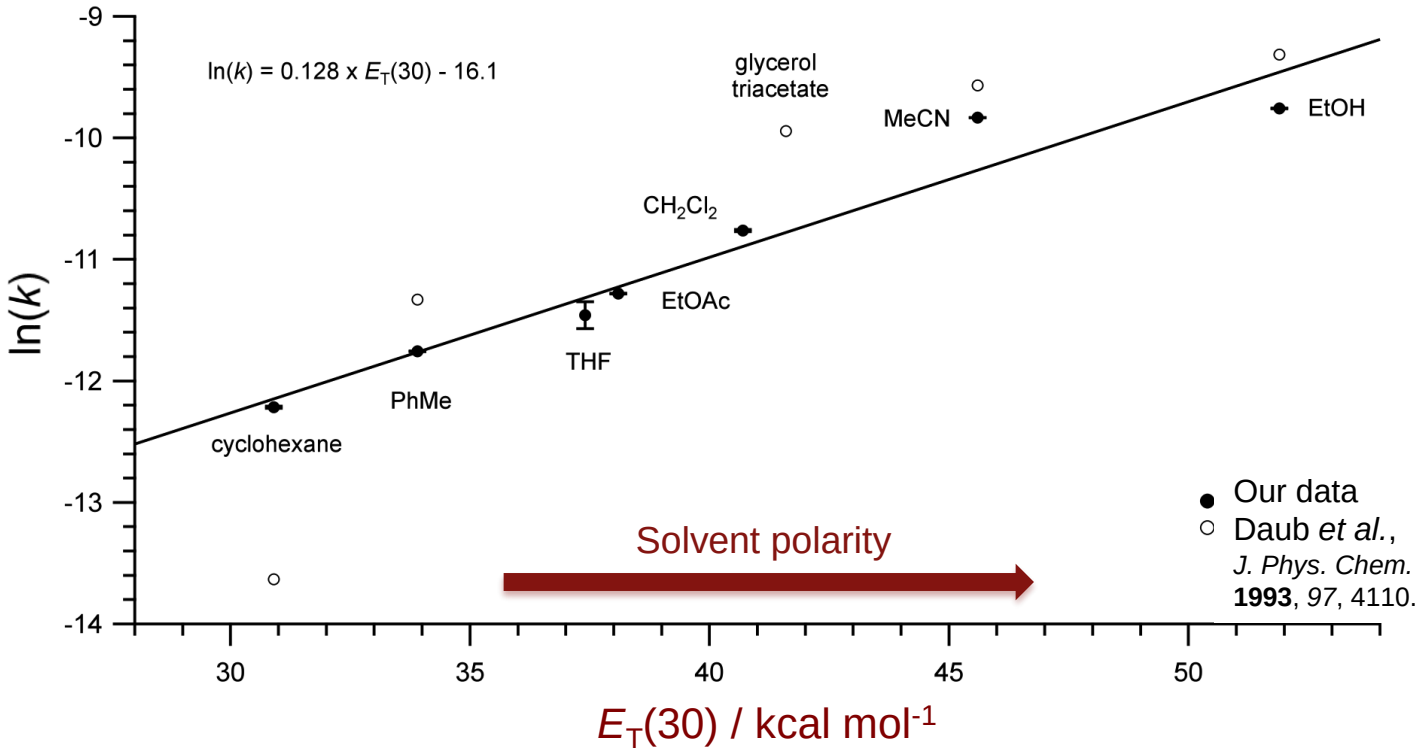
Electron-donating group at the seven-membered ring enhances the ring-closure

Electron-withdrawing group at vinylic position ring enhances the ring-closure

Calculations reveal a change in dipole moment between VHF and the transition state of ca. 4 Debye

O. Schalk, S. L. Broman, M. Å. Petersen, D. V. Khakhulin, R. Y. Brogaard, M. B. Nielsen, A. E. Boguslavskiy, A. Stolow, T. I. Sølling, *J. Phys. Chem. A.* **2013**.

Solvent Effects – Further Support for Polarized TS



S. L. Broman, S. L. Brand, C. R. Parker, M. Å. Petersen, C. G. Tortzen, A. Kadziola, K.Kilså, M. B. Nielsen, *ARKIVOC* **2011**, *ix*, 51-67.

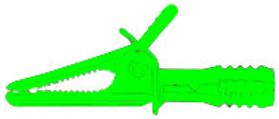


Molecular Switch for Molecular Electronics

Au or Ag – S – **DHA** – S – Au or Ag

heat ⇕ light

Au or Ag – S – **VHF** – S – Au or Ag



Me–S–R

Au

weak contact

S–R

Au

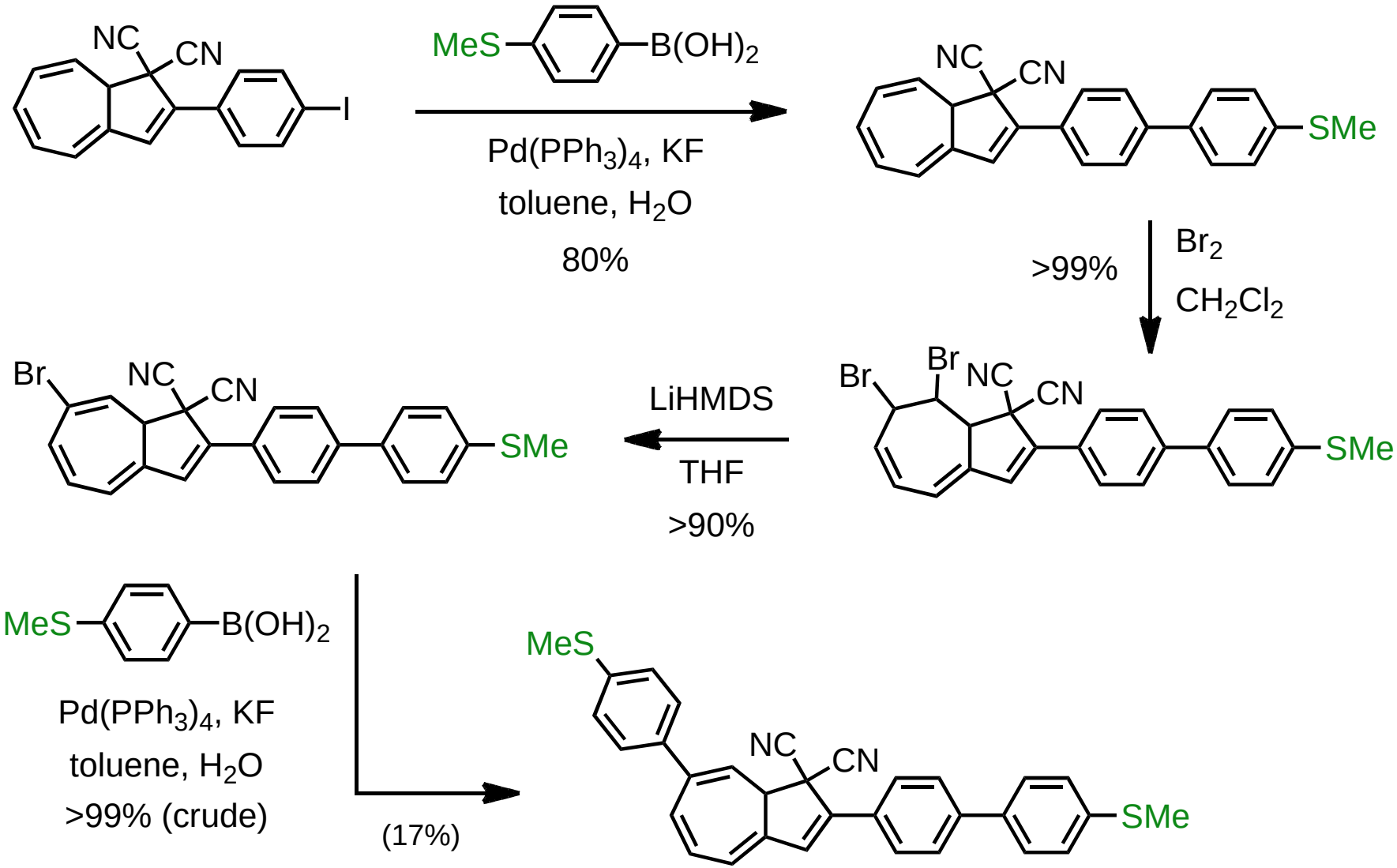
strong contact

S–R

Ac

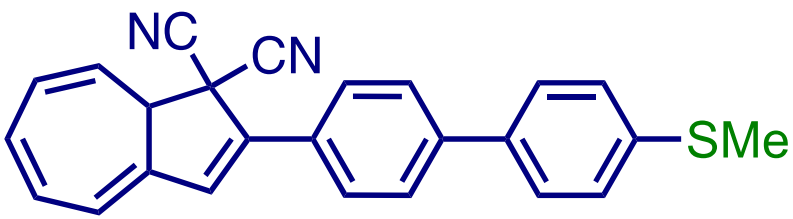
cleavable protecting group

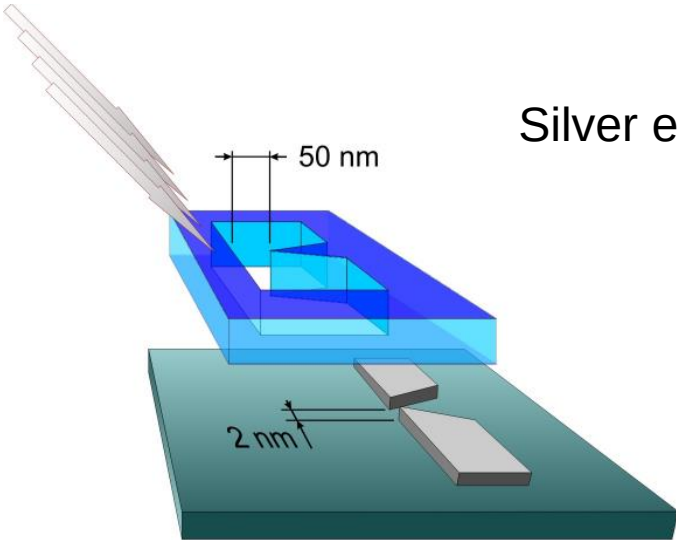
Incorporation of Methylthio End-Groups – ”Alligator Clips”



S. L. Broman, S. Lara-Avila, C. L. Thisted, A. D. Bond, S. Kubatkin, A. Danilov, M. B. Nielsen, *Adv. Funct. Mater.* **2012**, *22*, 4249-4258.

Molecular Electronics: Single-Molecule Junction (4 K)





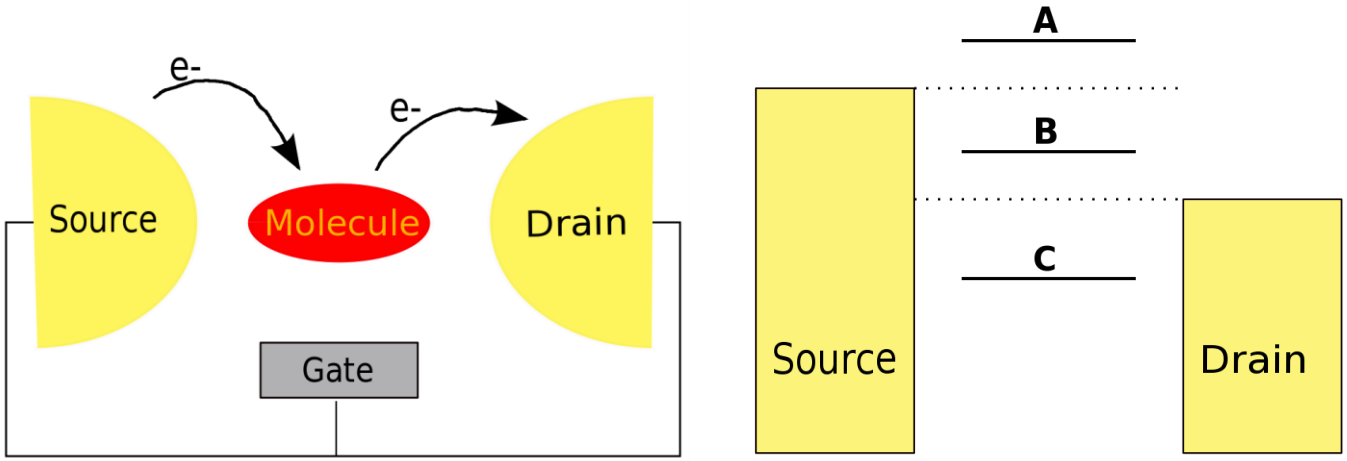
Silver electrodes

1) **Sublimation of silver**
2) **Sublimation of molecules**
3) **Molecules land on substrate at 4 K**
4) **Surface diffusion is activated at 30-60 K**
5) **Cooling back to 4 K after capture of molecule**

Samuel Lara-Avila, Andrey Danilov, Sergey Kubatkin, Chalmers University of Technology

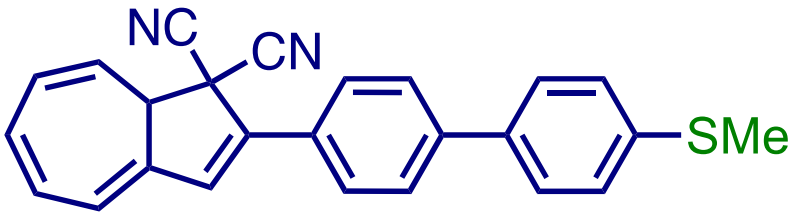
Department of Chemistry

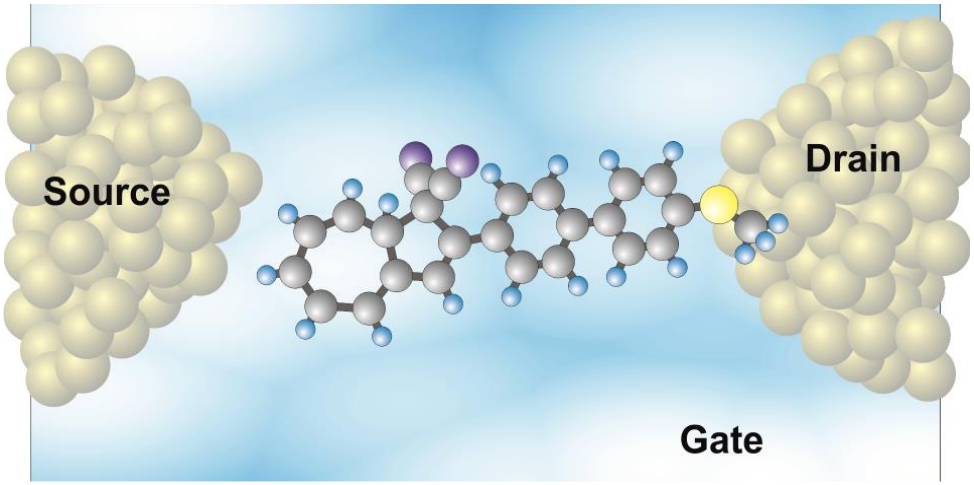
The Single Electron Transistor



- The structure: a gate, two electrodes, and a molecule
- Coulomb Blockade Regime
- Well defined transport
- The transport can be controlled by V_{SD} (bias potential) and V_G (gate potential)

Molecular Electronics: Single-Molecule Junction (4 K)



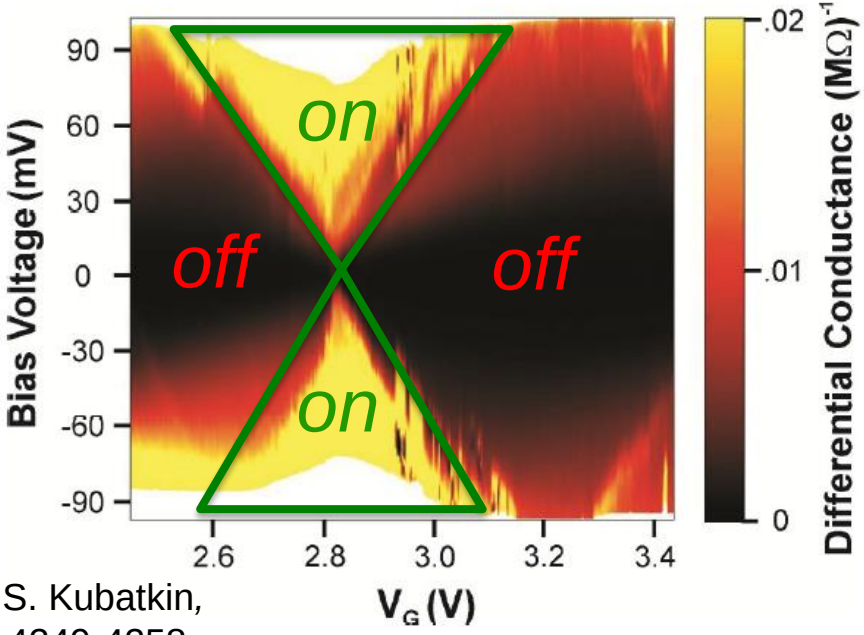


Stability plot:
A set of differential conductance curves taken at different gate voltages

Coulomb blockade diamonds

The molecule is weakly coupled to electrode

- electron hopping mechanism

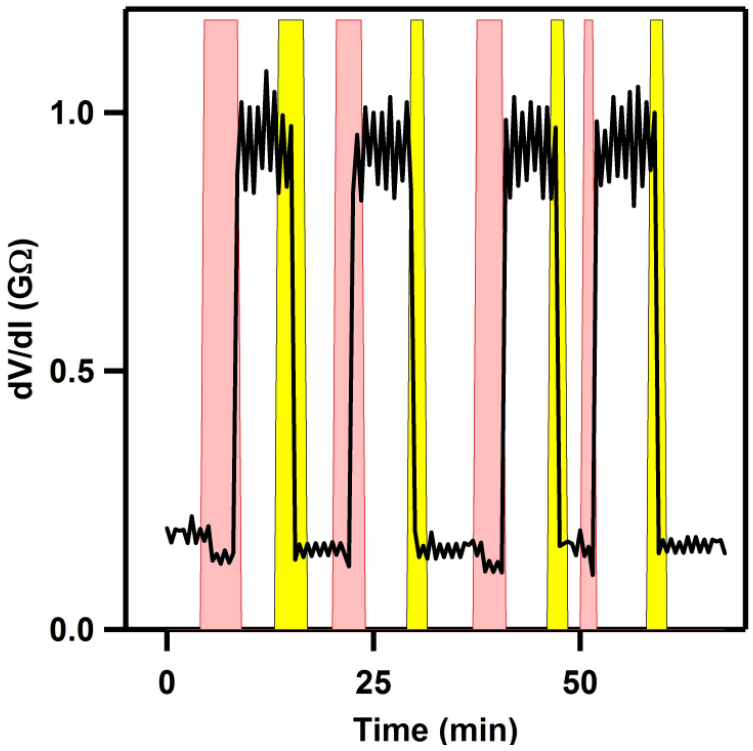


S. L. Broman, S. Lara-Avila, C. L. Thisted, A. D. Bond, S. Kubatkin, A. Danilov, M. B. Nielsen, *Adv. Funct. Mater.* **2012**, *22*, 4249-4258.

Reversible Switching at Gate Potential of 2.6 V

Increase of temperature from 4 to 25 K

Light



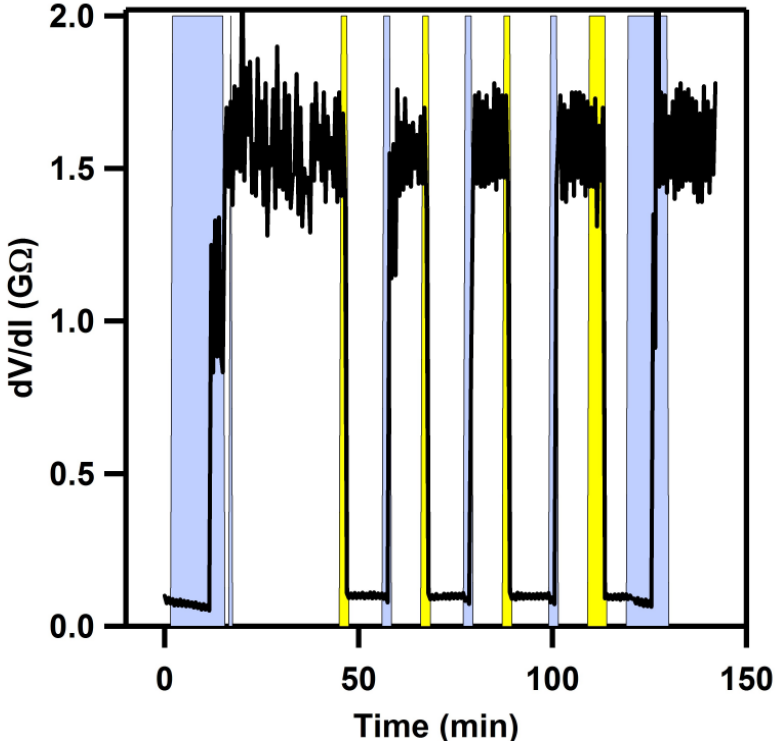


DHA (*off*)

VHF (*on*)

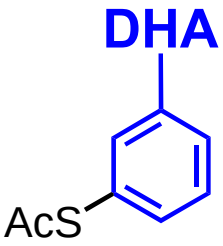
Increase of bias voltage from 25 to 80 mV

Light

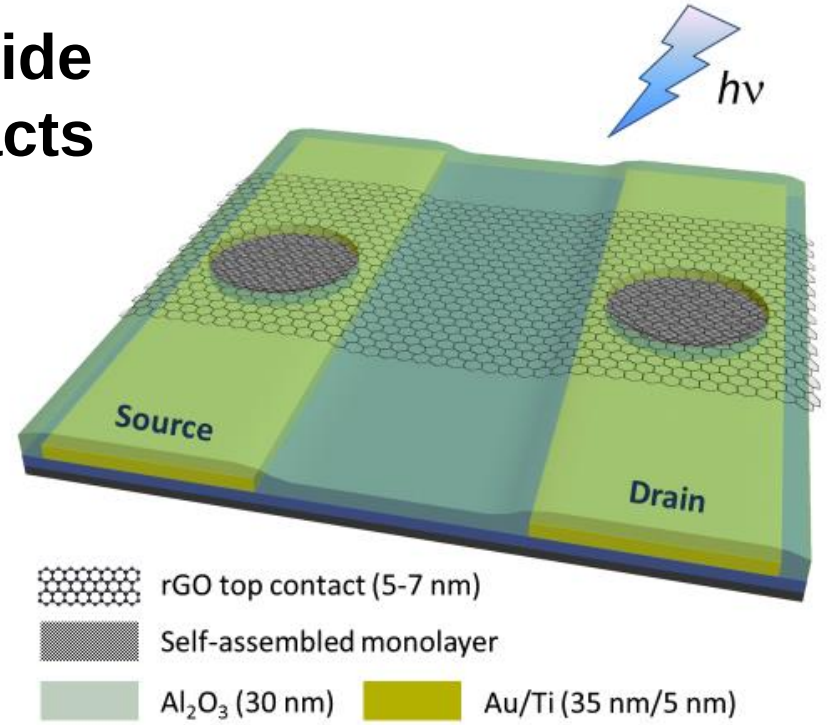


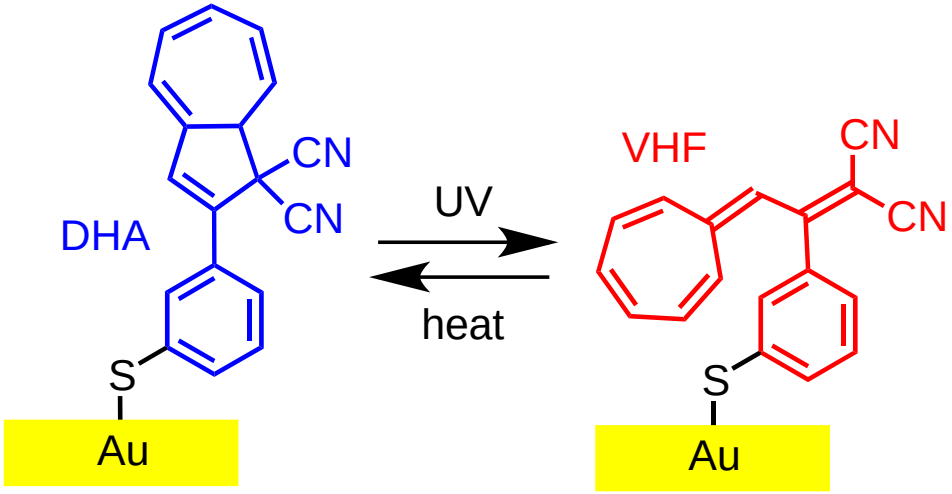
S. L. Broman, S. Lara-Avila, C. L. Thisted, A. D. Bond, S. Kubatkin, A. Danilov, M. B. Nielsen, *Adv. Funct. Mater.* **2012**, *22*, 4249-4258.

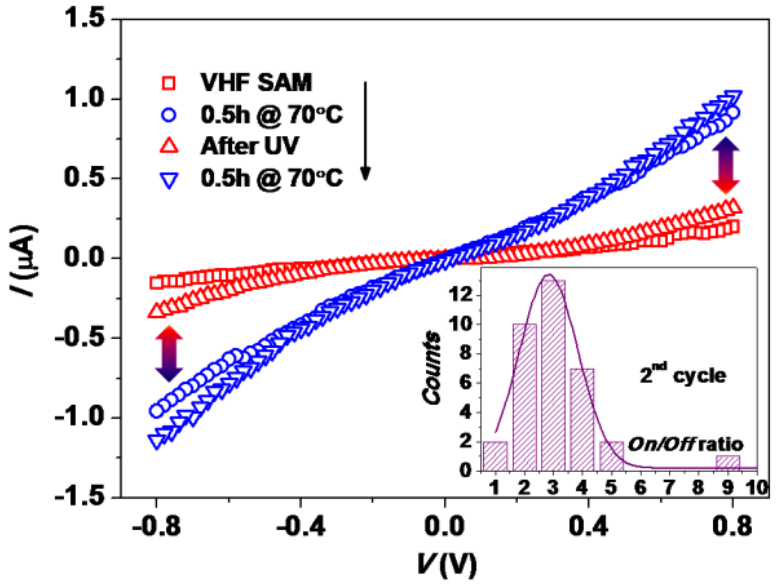
Ultrathin Reduced Graphene Oxide Films as Transparent Top-Contacts



meta-configuration
to avoid quenching
of photoactivity



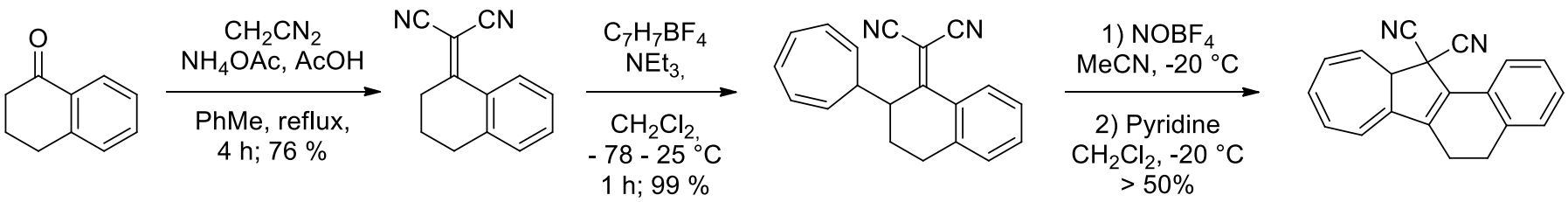


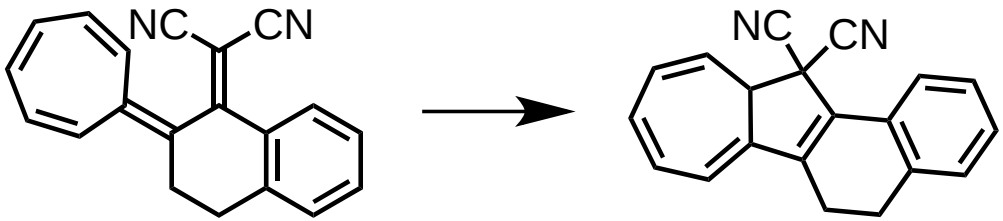


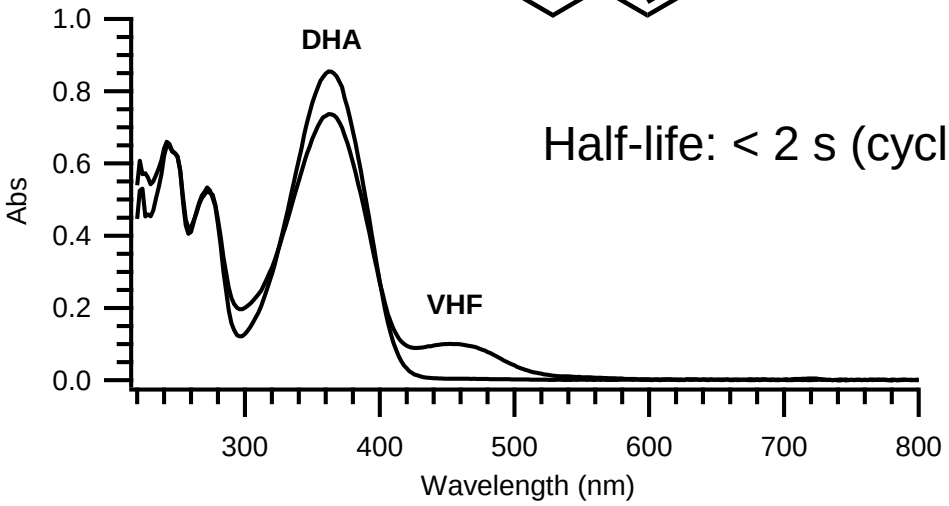
Adv. Mater. **2013**, *25*, 4164-4170.

Collaboration with Tao Li, Kasper Nørgaard, Bo W. Laursen

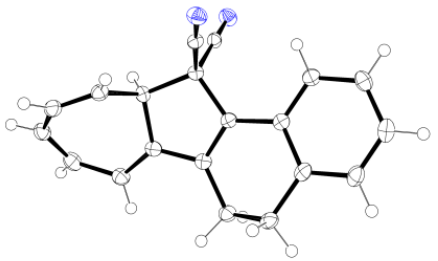
Ultrafast Ring-closure of VHF in Locked *s-cis* Conformation





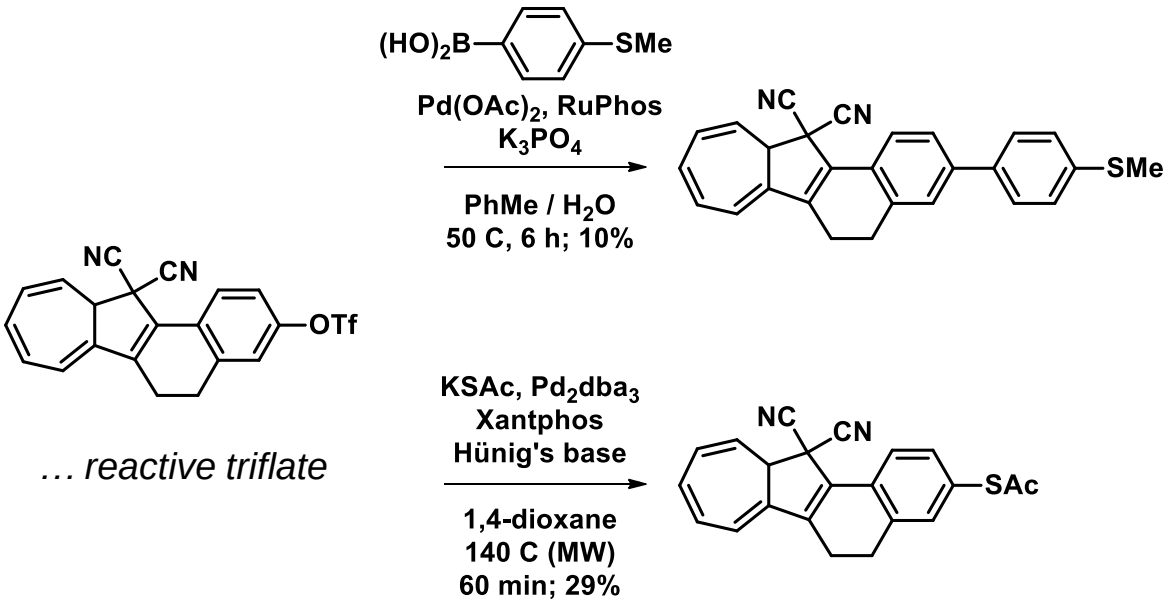


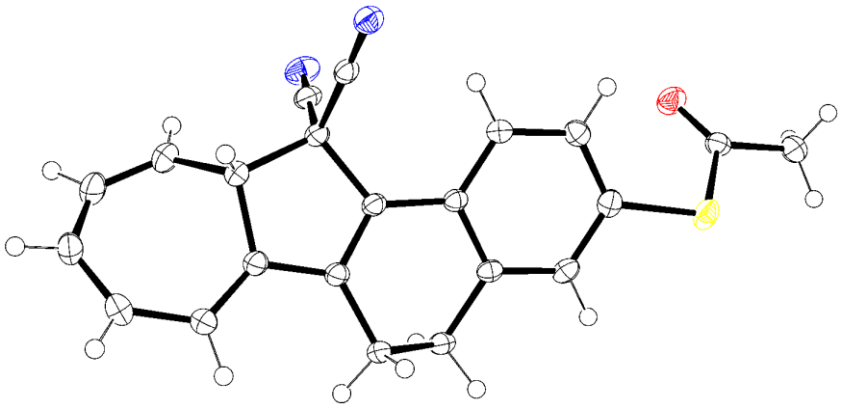
Half-life: < 2 s (cyclohexane)

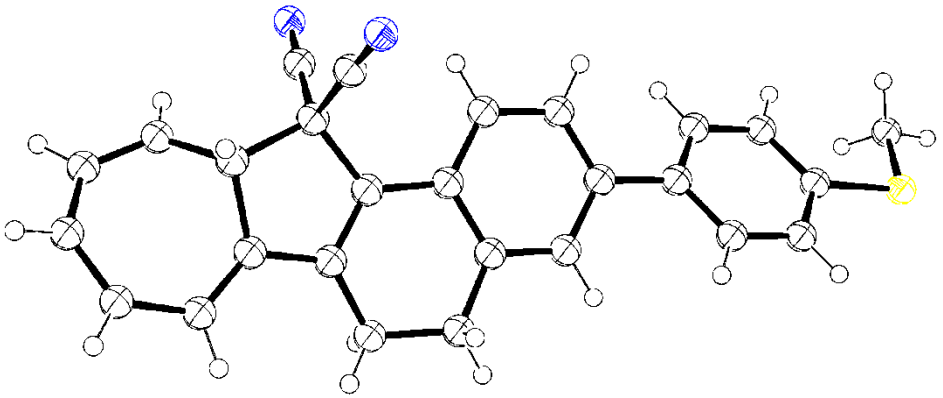


S. L. Broman, J. Daub, M. B. Nielsen *et al.*, *EurJOC*, In press

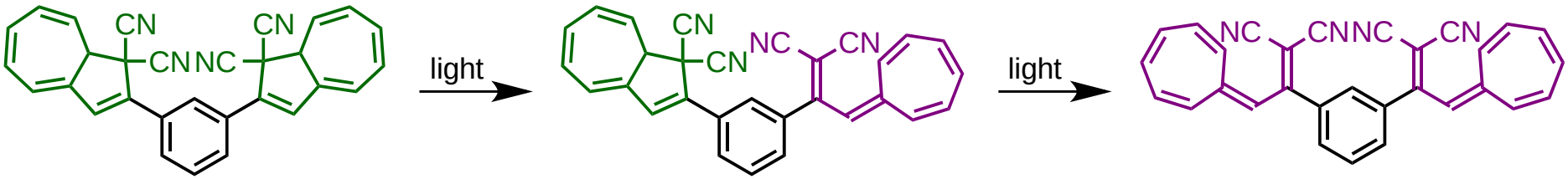
Incorporation of Anchoring Groups

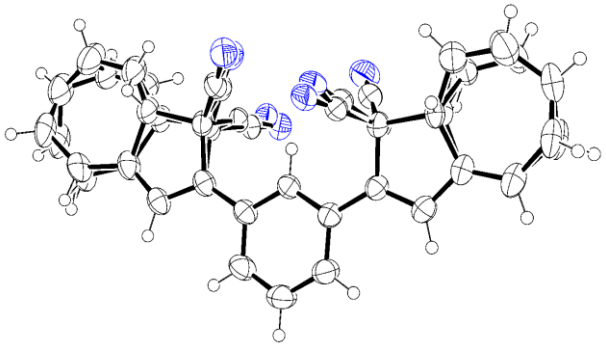




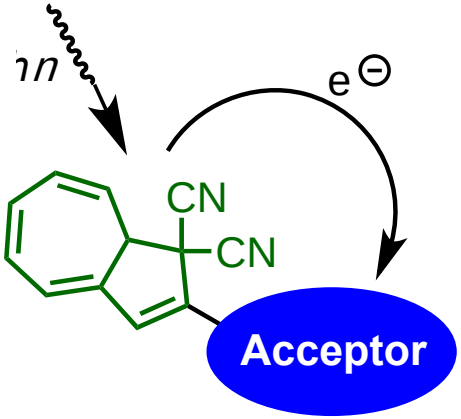


DHA Double Switch – Stepwise Ring-Openings





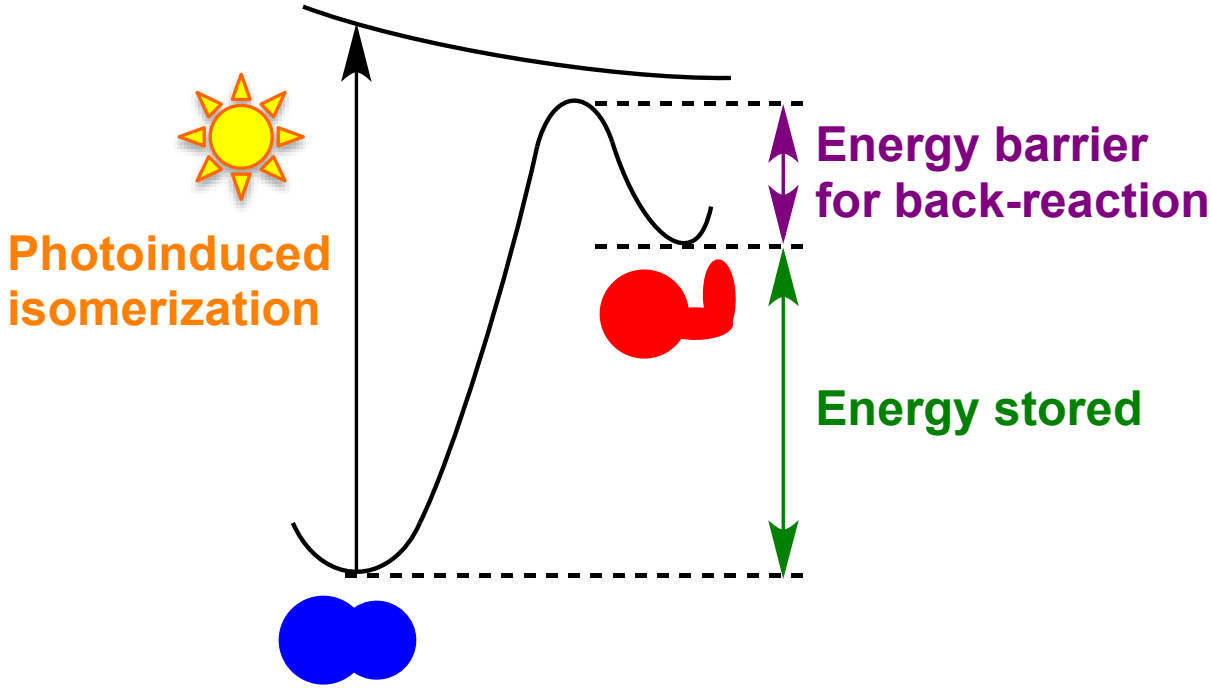
… quenching of photoactivity by nearby electron acceptor

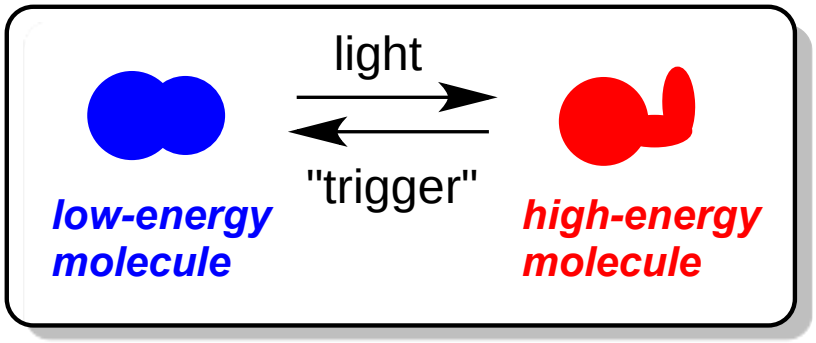




A.U. Petersen, S.L. Broman, S.T. Olsen, A.S. Hansen, L. Du, A. Kadziola, T. Hansen, H.G. Kjaergaard, K.V. Mikkelsen, M.B. Nielsen, *Chem. Eur. J.* **2015**, *21*, 3968-3977.

Solar Energy Storage Using Photoisomerization





… Material with energy density of 1 MJ / kg

- Heat release of 1 MJ can be used to bring 3 L of water from room temperature to the boiling point

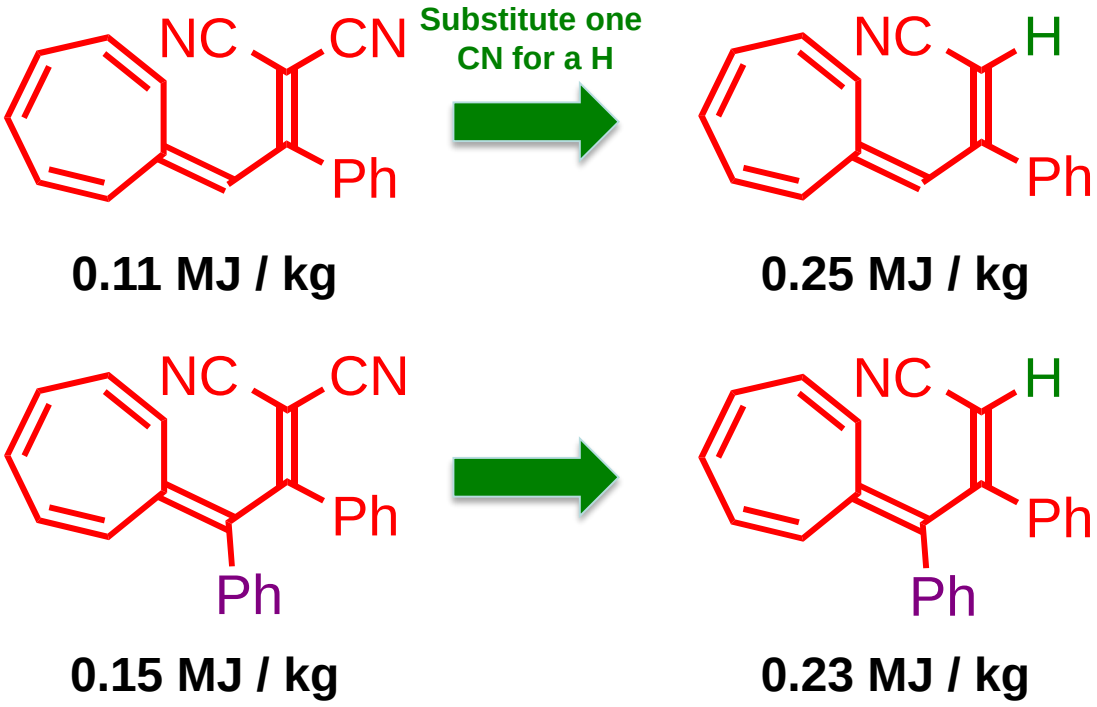
- Harvesting light during the day and releasing heat during the night:

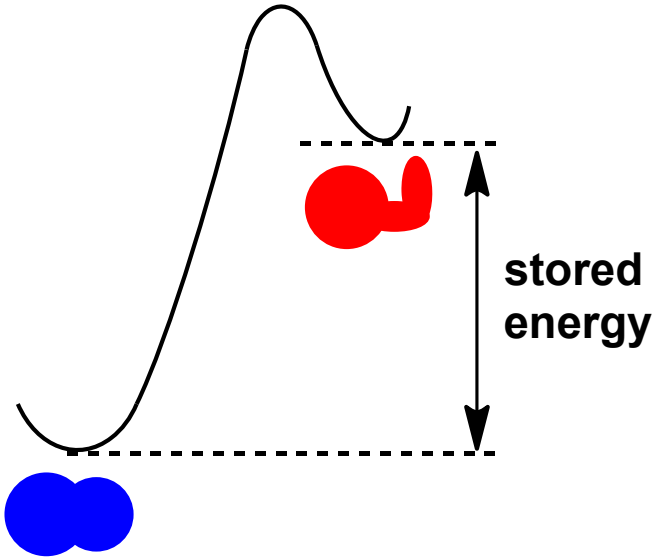
  - maintaining 1 m^3 at 19 ^oC with outside temperature of -6 ^oC requires ca. 3 kg of solar battery (when using foam insulation)

T. R. Kucharski, Y. Tian, S. Akbulatov, R. Boulatov, *Energy Environ. Sci.* **2011**, *4*, 4449-4472.

M06-2X
(vacuum)

Energy Storage



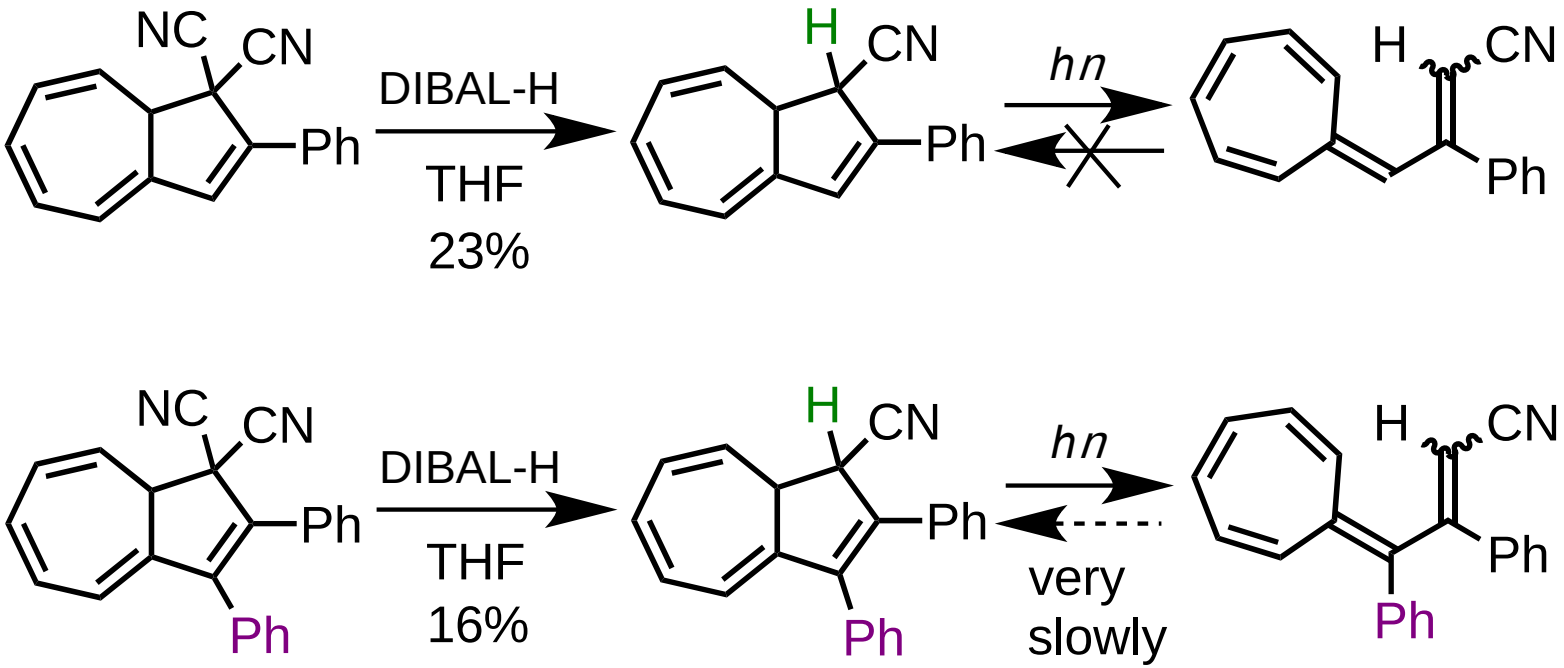


By minor structural variations we can double the energy density!

S.T. Olsen, J. Elm, F.E. Storm, A.N. Gejl, A.S. Hansen, M.H. Hansen, J.R. Nikolajsen, M.B. Nielsen, H.G. Kjaergaard, K.V. Mikkelsen, *J. Phys. Chem. A* **2015**, *119*, 896-904.

M. Cacciarini, A.B. Skov, M. Jevric, A.S. Hansen, J. Elm, H.G. Kjaergaard, K.V. Mikkelsen, M.B. Nielsen, *Chem. Eur. J.* **2015**, *21*, 7454-7461.

Reductive Decyanations



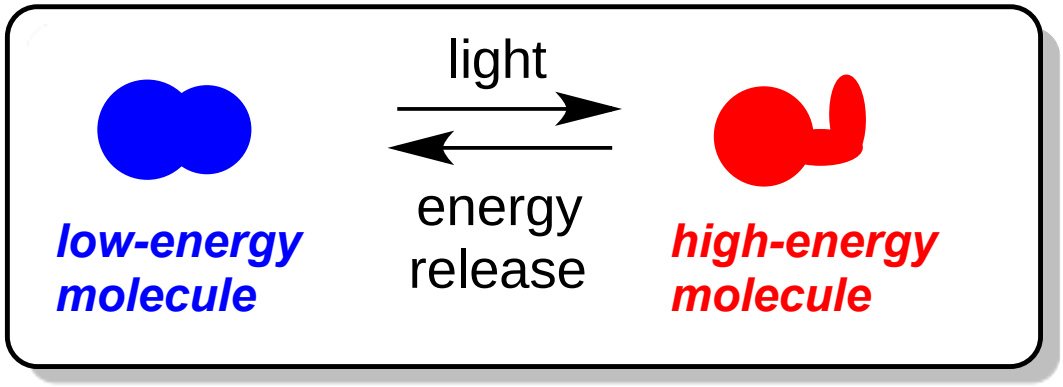
VHF of this DHA:
Half-life of 14 s

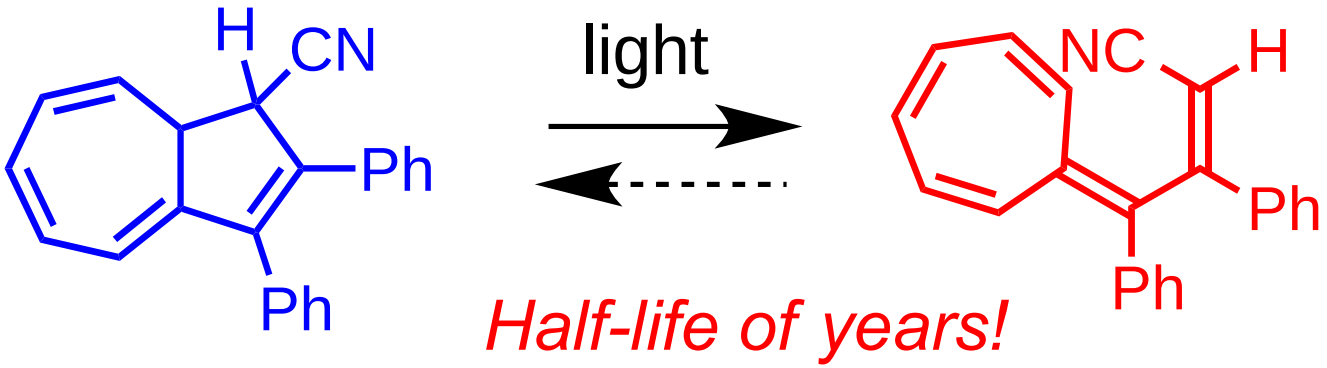
TS calculations:
$\Delta G^{\ddagger}$ = 125.7 kJ/mol

Half-life >10 years at rt

M. Cacciarini, A.B. Skov, M. Jevric, A.S. Hansen, J. Elm, H.G. Kjaergaard, K.V. Mikkelsen, M.B. Nielsen, *Chem. Eur. J.* **2015**, *21*, 7454-7461.

Halting the Energy-Releasing Back-Reaction

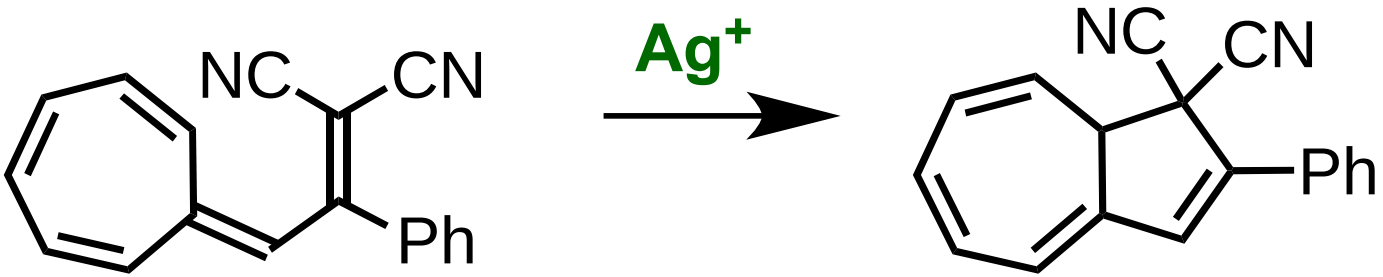




… We are currently working on triggering the energy release by a catalyst

Chem. Eur. J. **2015**, *21*, 7454-7461.

Triggering the Ring-Closure



Effect of Ag^+ on the thermal ring-closure reaction of VHF:

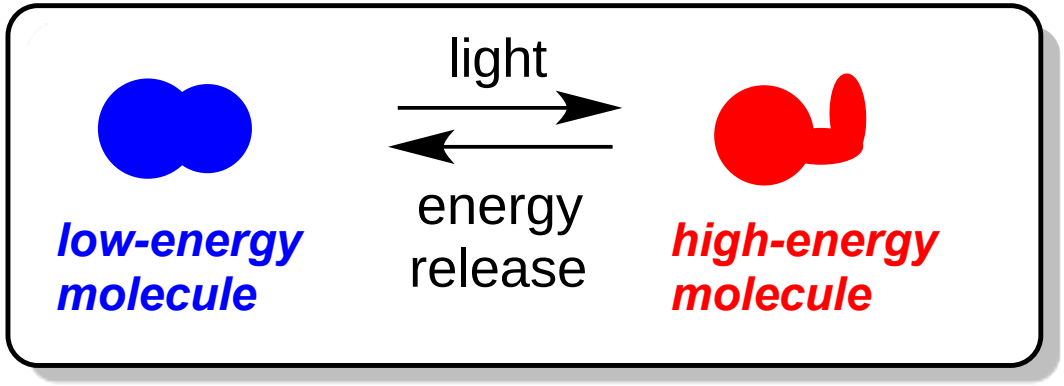
Eq AgOTf	0	0.1	0.5	1	10	25	100	150	250	
Half-life	597	556	406	317	71	33	13	10	9	min

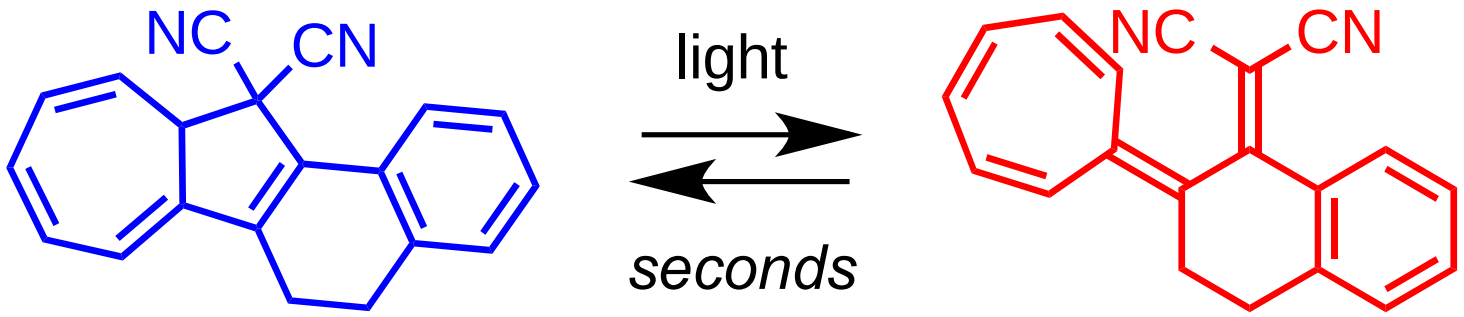
Solvent: 1,2-dichloroethane

C. R. Parker, C. G. Tortzen, S. L. Broman, M. Schau-Magnussen, K. Kilså, M. B. Nielsen, *Chem. Commun.* **2011**, *47*, 6102-6104.

The Other Extreme: A Very Fast Photoswitch

Light-Harvesting followed by Immediate Energy Release





EurJOC, In press.

Conclusions

- Efficient synthetic protocol for functionalization of the dihydroazulene/ vinylheptafulvene system in its seven-membered ring:

  ”addition – elimination – cross-coupling protocol”

- Tuning of switching events by ***donor-acceptor substitution*** and ***solvent polarity***

- Light-triggered ***conductance switching*** in single-molecule dihydroazulene/vinylheptafulvene junctions

- Minor structural changes can increase the ***energy storage capacity*** and the heat release from **seconds to years**

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Kasper Fjelbye
Anders Bo Skov

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Prof. Bo W. Laursen
Assoc. Prof. Kasper Nørgaard
Assoc. Prof. Anders Kadziola
Prof. Andrew Bond
Dr. Jonas Elm
Stine T. Olsen

Chalmers University of Technology

Prof. Sergey Kubatkin
Dr. Andrey Danilov
Dr. Samuel Lara-Avila

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The Carlsberg Foundation

The Villum Kann Rasmussen Foundation

Danish-Chinese Center for Nanoelectronics

University of Copenhagen
– Center for Exploitation of Solar Energy