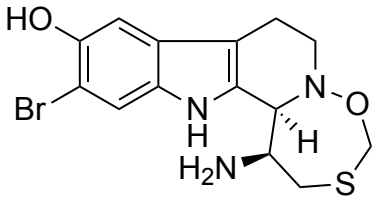
Hoe temmen we het elektron?

Jan van Maarseveen

KNCV
mensen • meningen • moleculen

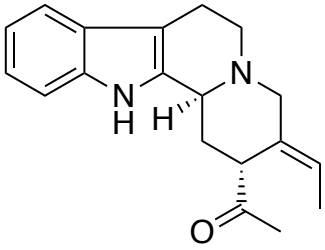
UNIVERSITY
OF AMSTERDAM

Totaalsynthese van natuurstoffen



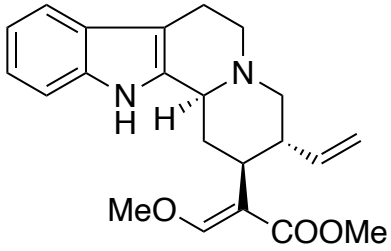
(-)-eudistomin C

J. Org. Chem., **1990**, *55*, 3998



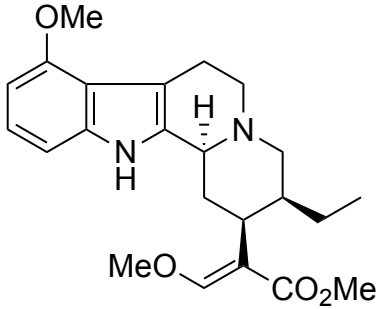
(-)-arboricine

Org. Lett., **2009**, *11*, 2579



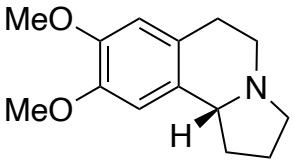
(+)-corynantheine

Chemistry, **2011**, *11*, 13680



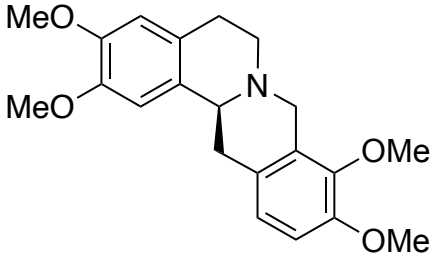
(±)-mitragynine

Chem Comm. **2012**, *48*, 1224



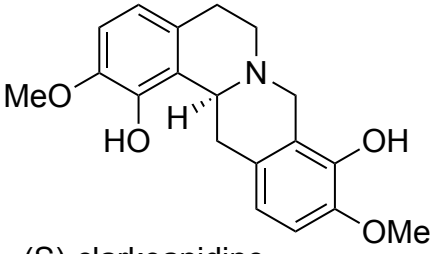
(R)-(+)-crispine A

J. Org. Chem., **2014**, *79*, 7380



(S)-norlaudanosine

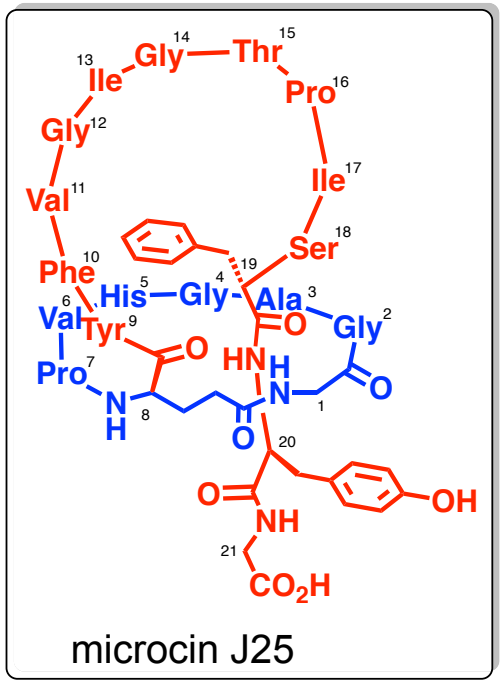
Eur. J. Org. Chem. **2016**, 3705



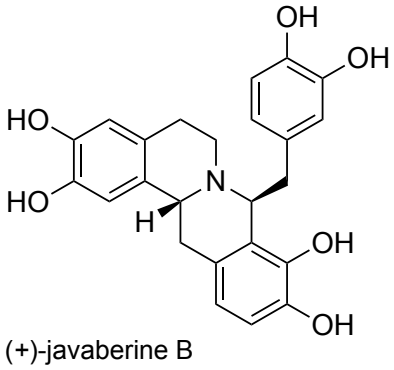
(S)-clarkeanidine

J. Org. Chem., **2018**, *83*, 15110

Lasso peptiden

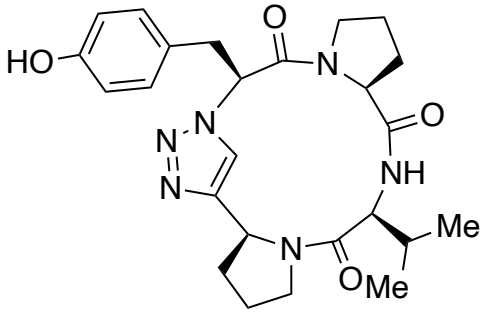


microcin J25

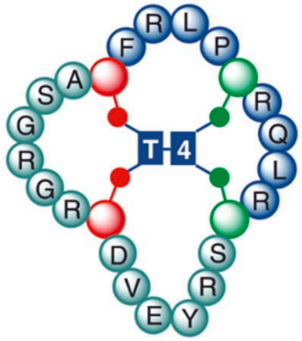


(+)-javaberine B

Eur. J. Org. Chem. **2016**, 3705



Org. Lett., **2006**, *7*, 919



Chembiochem **2018**, *19*, 1934

Dé eye-opener: Climate & Molecules (2013-2014)

- Drs. Marcel Crok (wetenschapsjournalist, auteur “de staat van het klimaat”)
- Prof. Dr. Jaap Sinnighe Damsté (NIOZ, paleogeochemicus)
- Prof. Dr Luc Lourens (RU, paleoklimatoloog)
- Prof. Dr. Bart van den Hurk (KNMI, klimatoloog)
- Dr. Caroline Katsman (KNMI, oceanoloog)
- Prof. Dr. Hein de Baar (NIOZ, geochemicus)
- Prof. Dr. Mike Jetten (RUN, microbioloog).
- Dr. Bas van Geel (UvA, paleoecoloog/paleoklimatoloog)
- Dr. Rob van Dorland (KNMI, klimatoloog, IPCC lid)
- Drs. Elmar Veerman (VPRO, hoofdredacteur “Noorderlicht”)

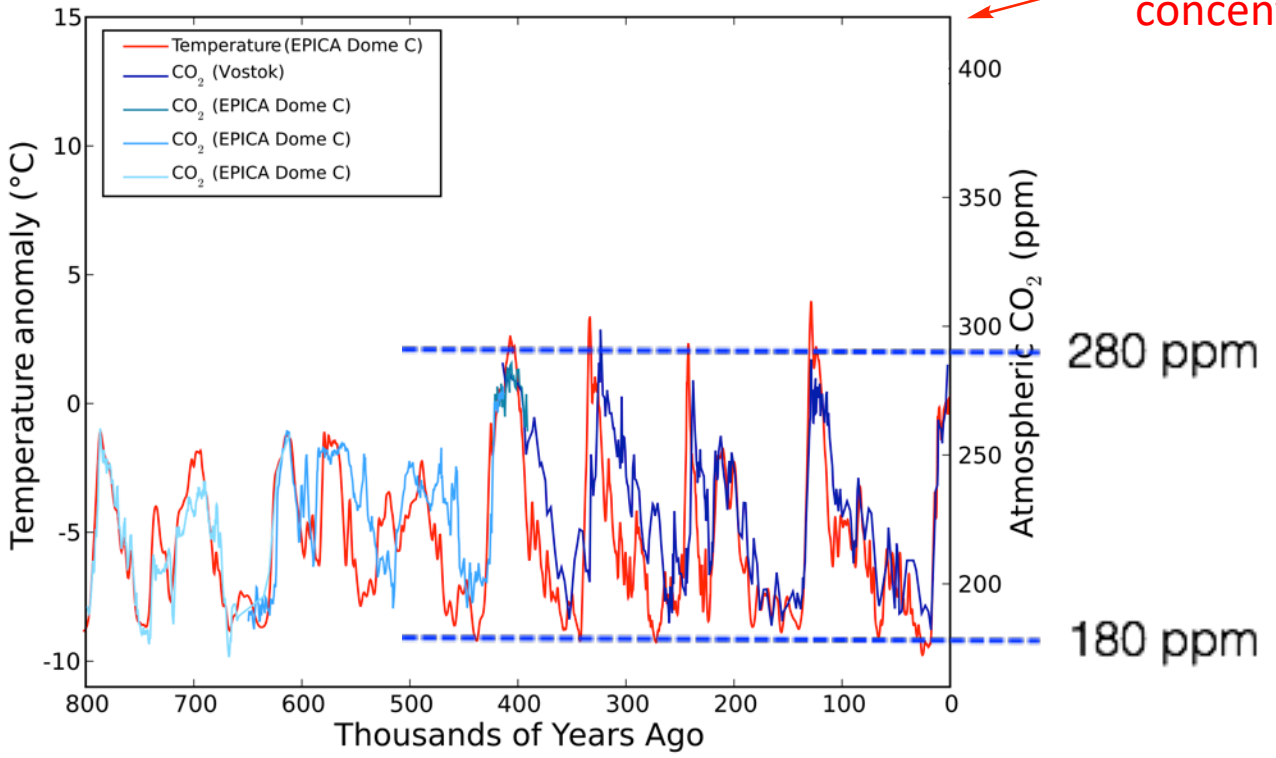
werkbezoek KNMI en NIOZ

De mensheid is het grootste experiment ooit

- De natuurlijke [CO_2] fluctueert al 800.000 jaren tussen de 180-280 ppm.
- Gedurende deze periode lieten de [CO_2] en de temperatuur een lineair verband zien.
- De afgelopen 150 jaar steeg de [CO_2] ~ 131 ppm (van 280 tot 411 ppm).

Relatie tijd en [CO_2]/temperatuur

Huidige CO_2 concentratie



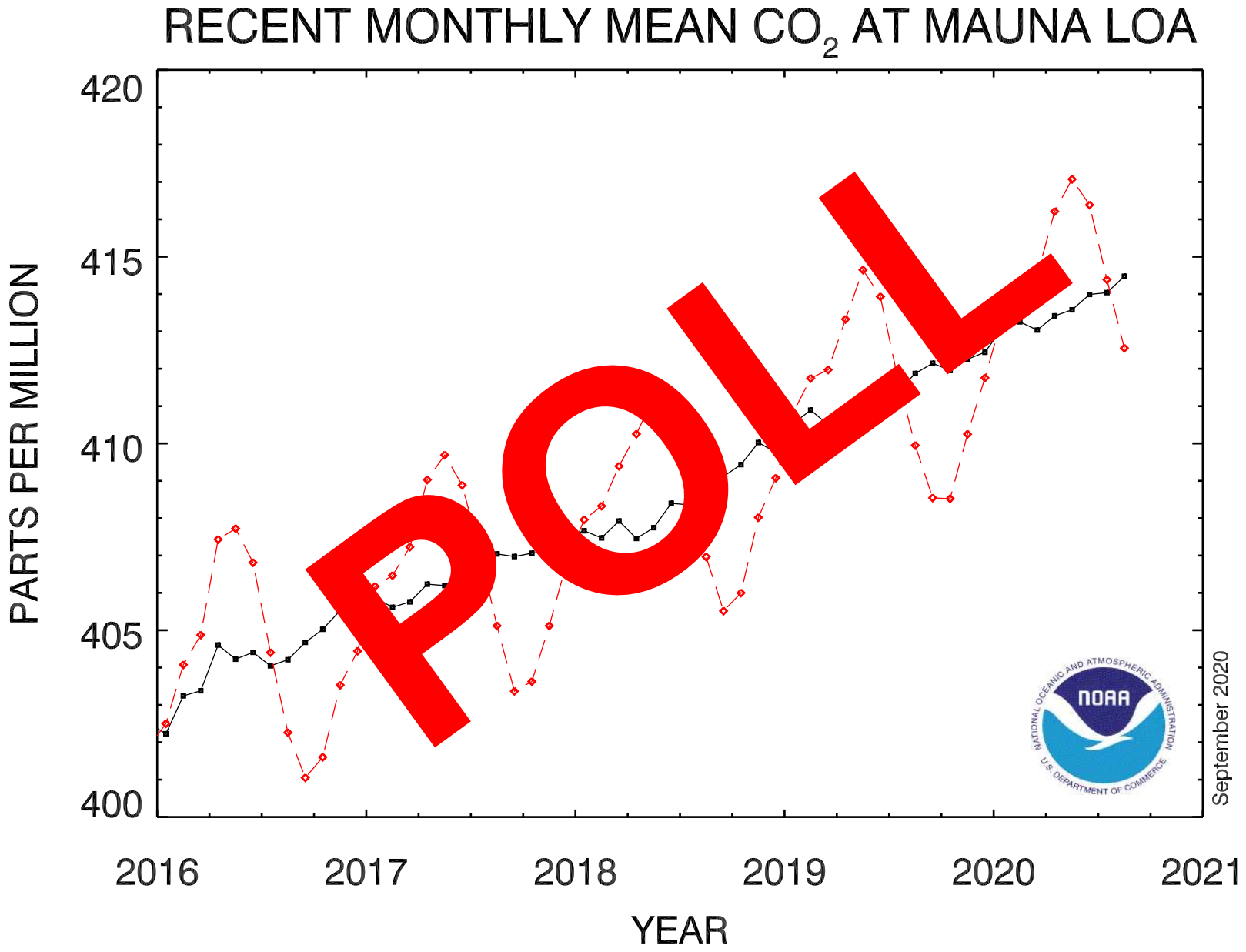
Daily CO_2

Oct. 7, 2020: **411.08 ppm**

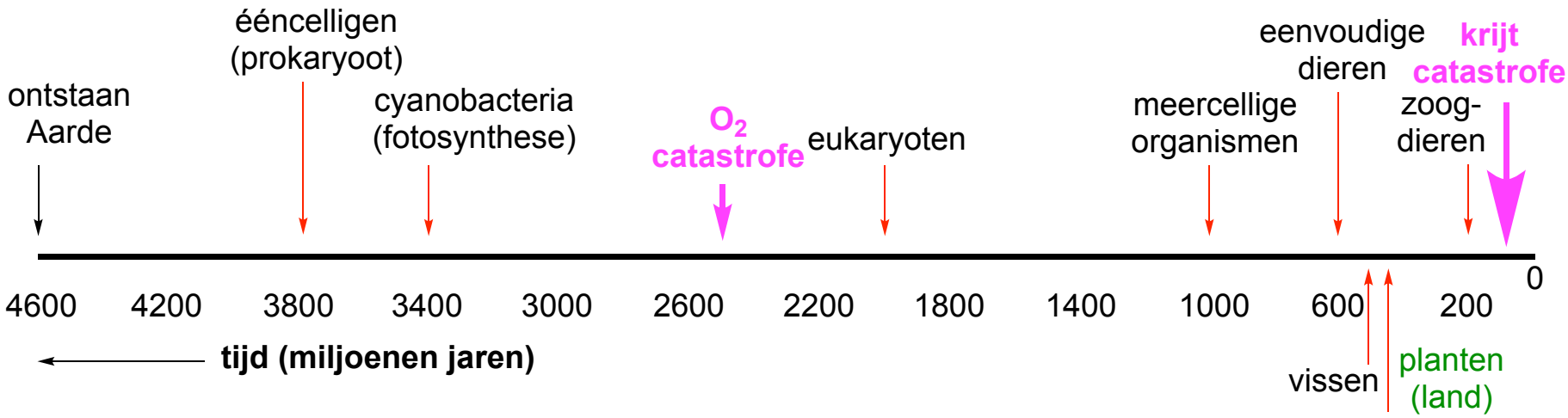
Oct. 7, 2019: **408.2 ppm**

www.co2.earth

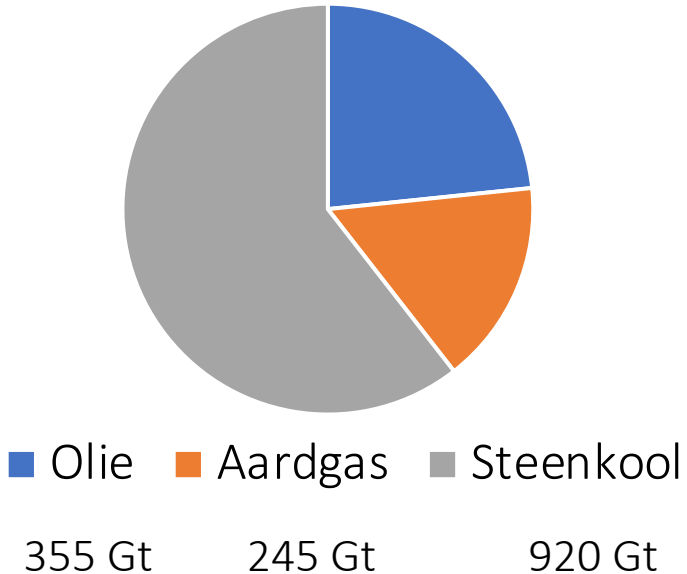
Variatie [CO_2] over 5 jaar



Fossiele brandstoffen

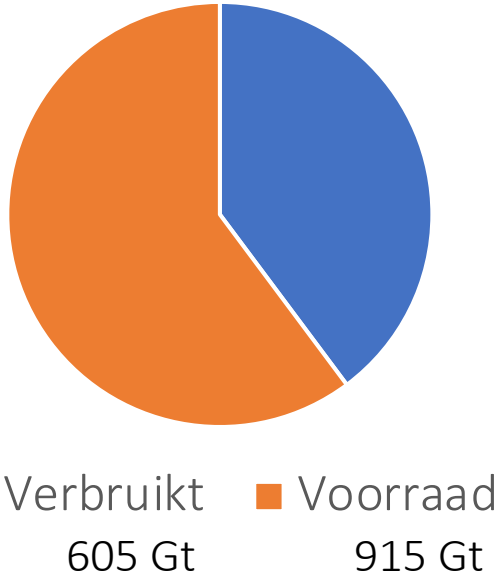


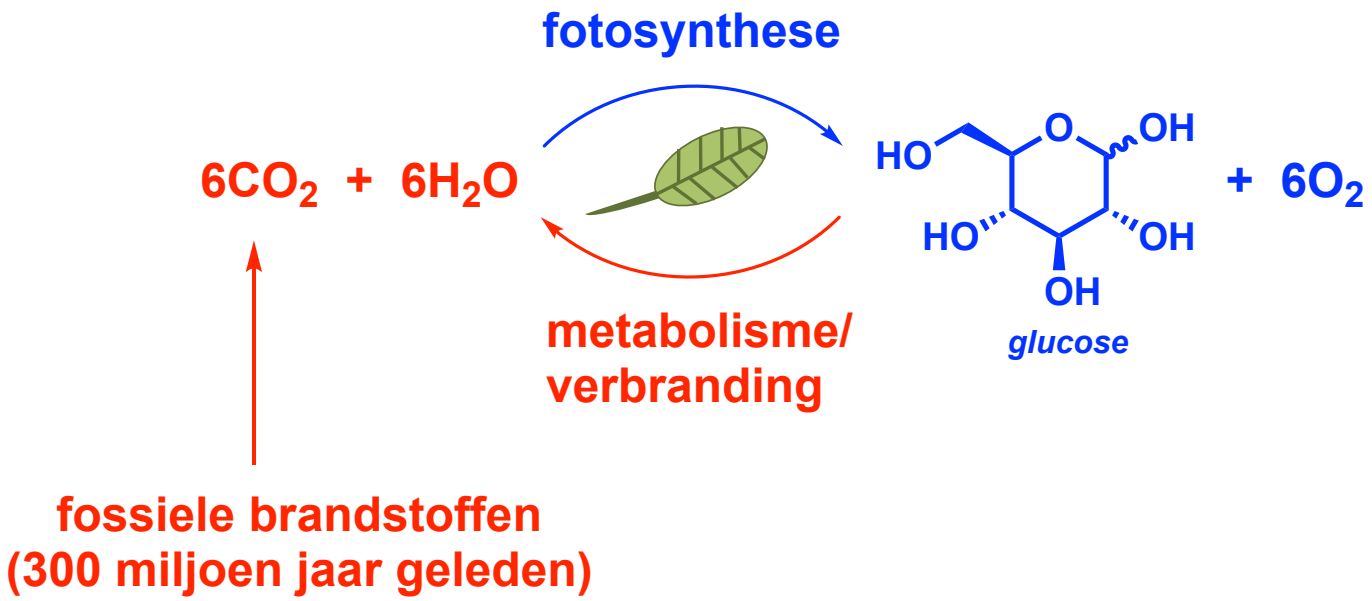
Voorraad fossiel in 1900



(totaal 1520 Gt)

Verbruikt tot op heden





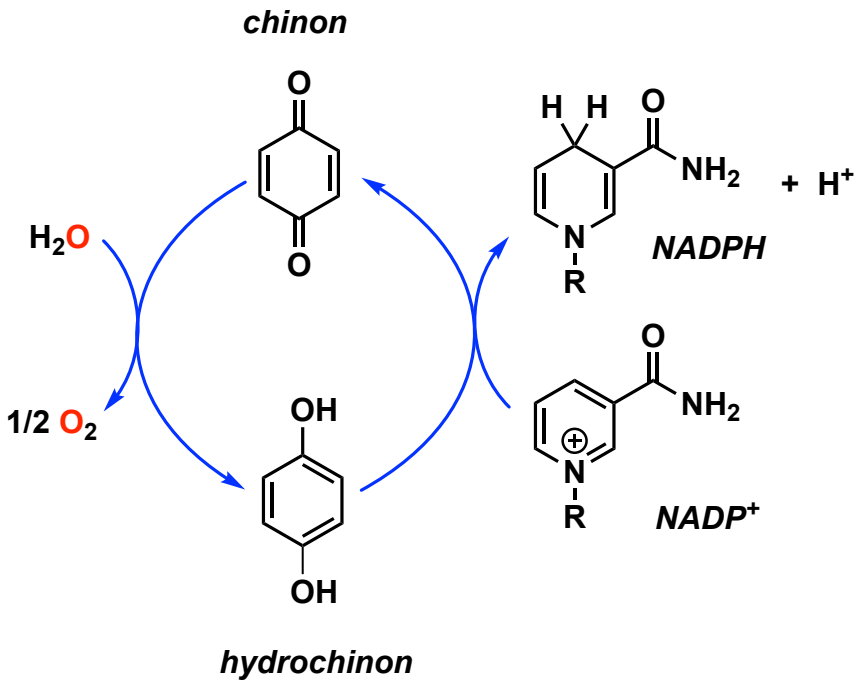
Fotosynthese komt neer op de oxidatie van water

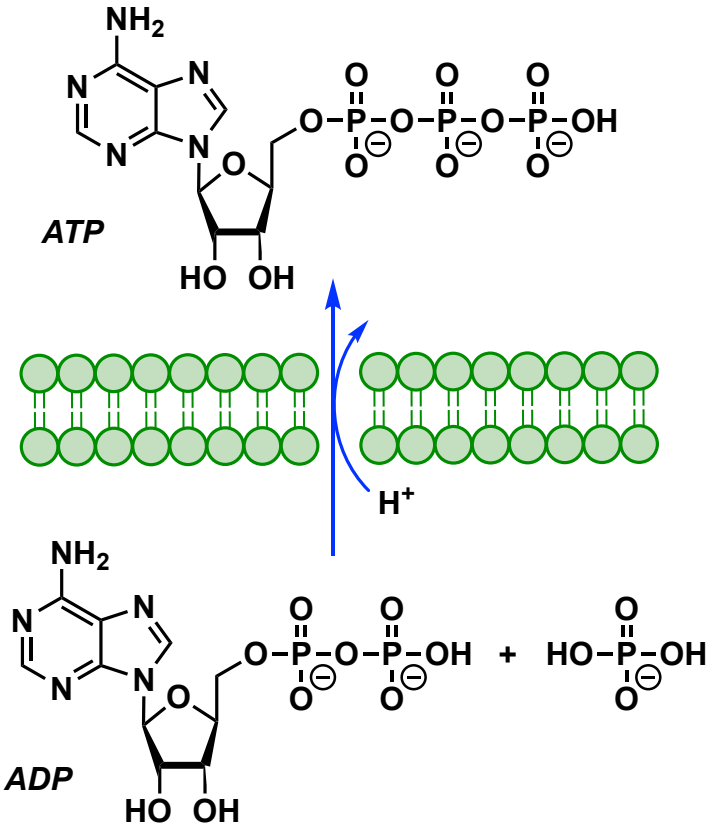
$$2\ H_2O \longrightarrow 4\ H^+ + 2\ O^{2-}$$

oxidatie: $2\ O^{2-} \longrightarrow O_2 + 4\ e^-$

$$2\ H_2O \longrightarrow 4e^- + 4\ H^+ + O_2$$

De organische chemie achter fotosynthese

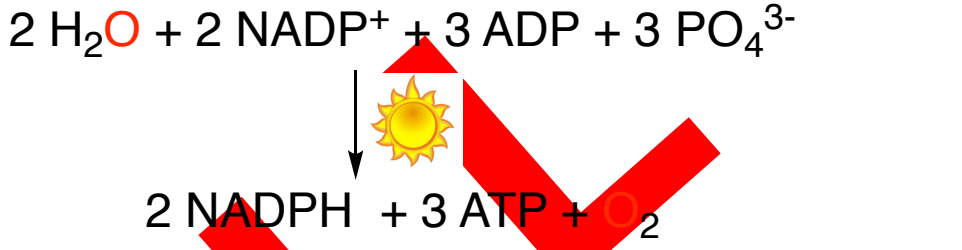




- Met de elektronen verkregen uit de wateroxidatie wordt NADPH en ATP gemaakt
- Chinonen zorgen voor het elektronentransport

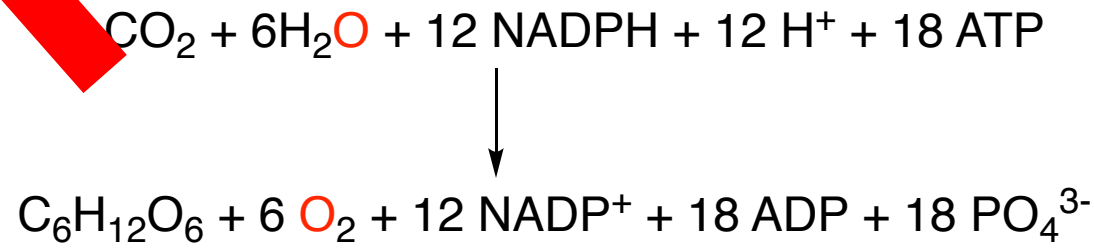
Reactievergelijkingen fotosynthese

Lichtreactie:
(H_2O oxidatie)



Donkerreactie:
(CO_2 reductie)

Overall reactie:



POLL

Chemici moeten de natuur nabootsen

Natuurlijke fotosynthese efficiency <1%

Menselijke technologie efficiency >10%

Zonne-energie (en wind)

NADP-H & ATP

Elektriciteit & Waterstof

+ H_2O

natuurlijke energiedragers en brandstoffen

menselijke energiedragers en brandstoffen

CO_2

CO_2

Glucose en andere biomoleculen (**biomassa**)

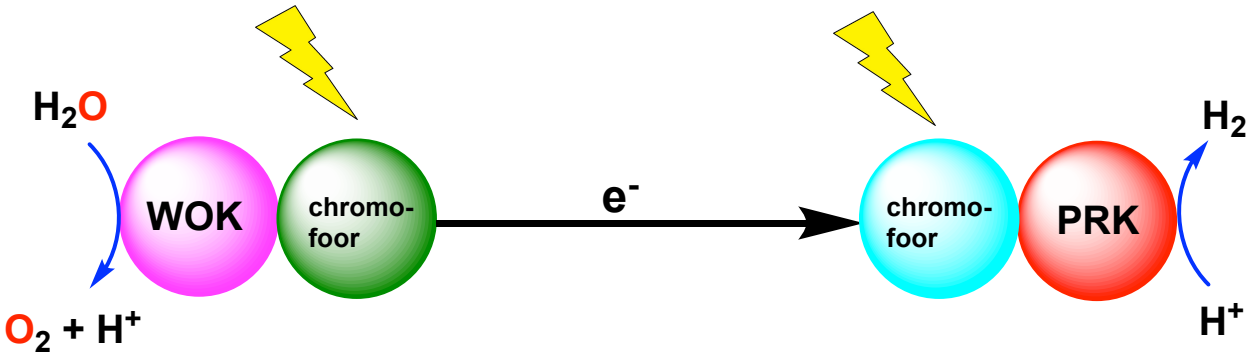
Koolstof-gebaseerde brandstoffen en producten (**synthetische brandstoffen**)

Schema: Remko Detz (TNO-ECN)

Kunstmatige fotosynthese

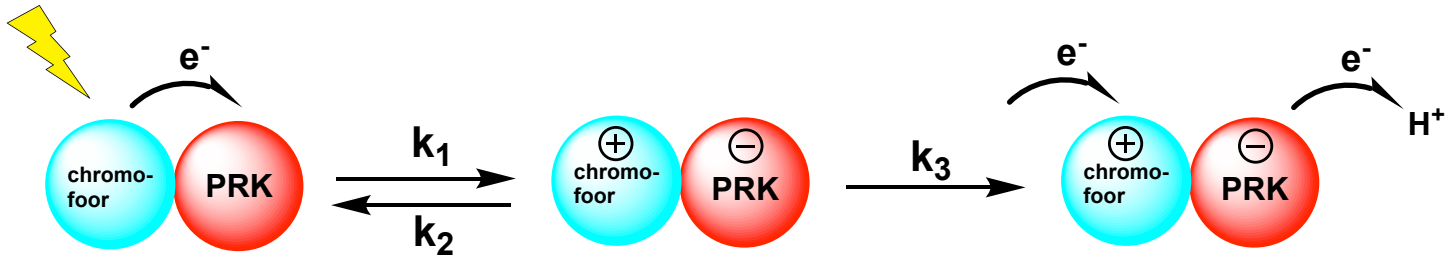
- Kleurstof (chromofoor) die fotonen absorbeert
- Ladingsscheiding
- Redoxkatalysatoren die energie van elektronen kunnen omzetten in chemische bindingen

Voorbeeld waterstoffabriek op zonlicht



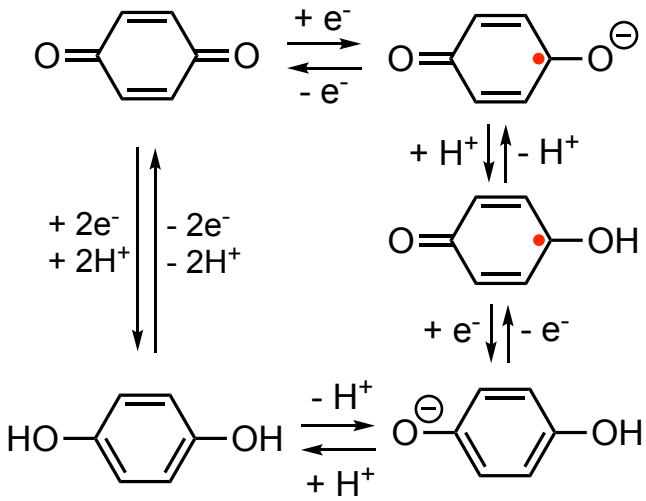
WOK = water oxidatie katalysator
PRK = proton reductie katalysator

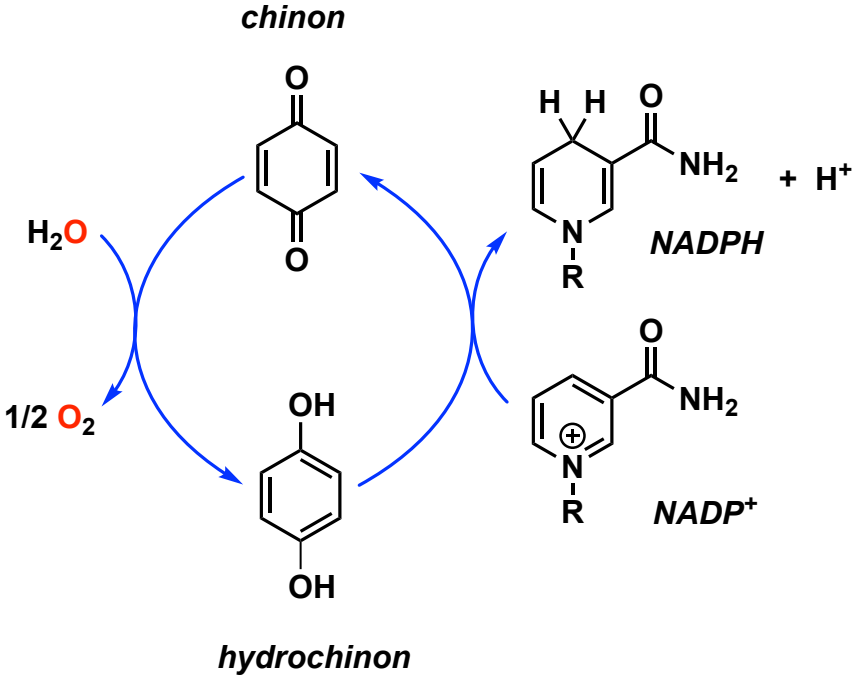
HÉT probleem: recombinatie van vrijgekomen elektron



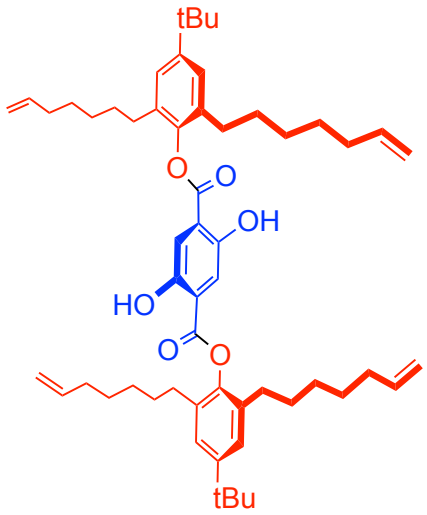
probleem: $k_2 >>> k_3$

Chinon: proton-gekoppeld elektronentransport





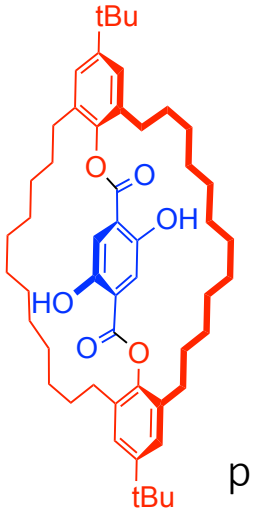
Covalente synthese van rotaxanen



1) RCM

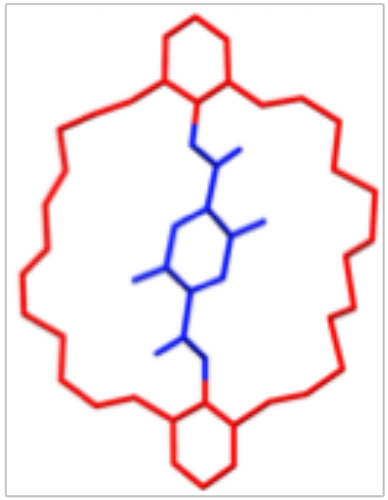
2) $Pd(C)/H_2$

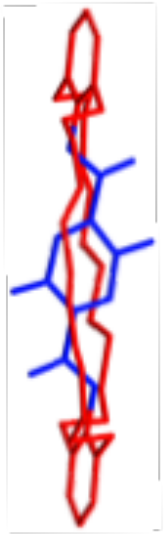
93%

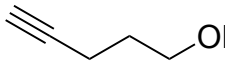


prerotaxaan

kristalstructuur

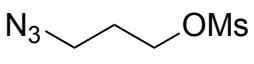






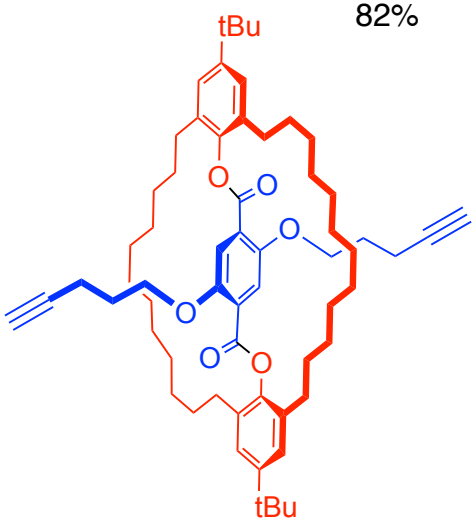
K_2CO_3, DMF,
90 °C, 20 h

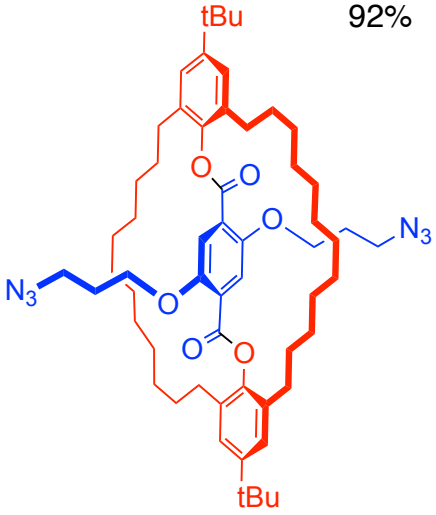
82%

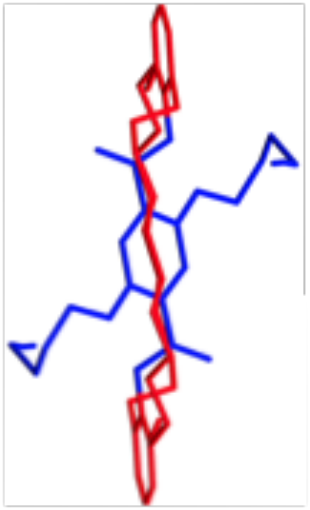


K_2CO_3, KI, DMF,
90 °C, 12 h

92%

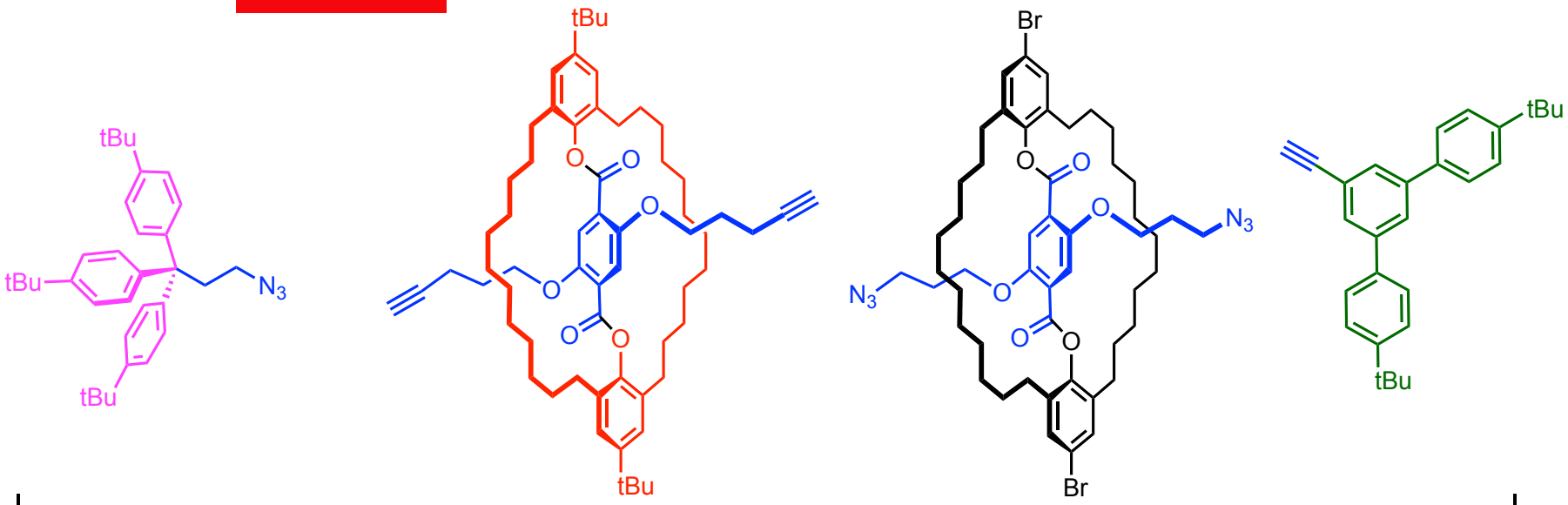


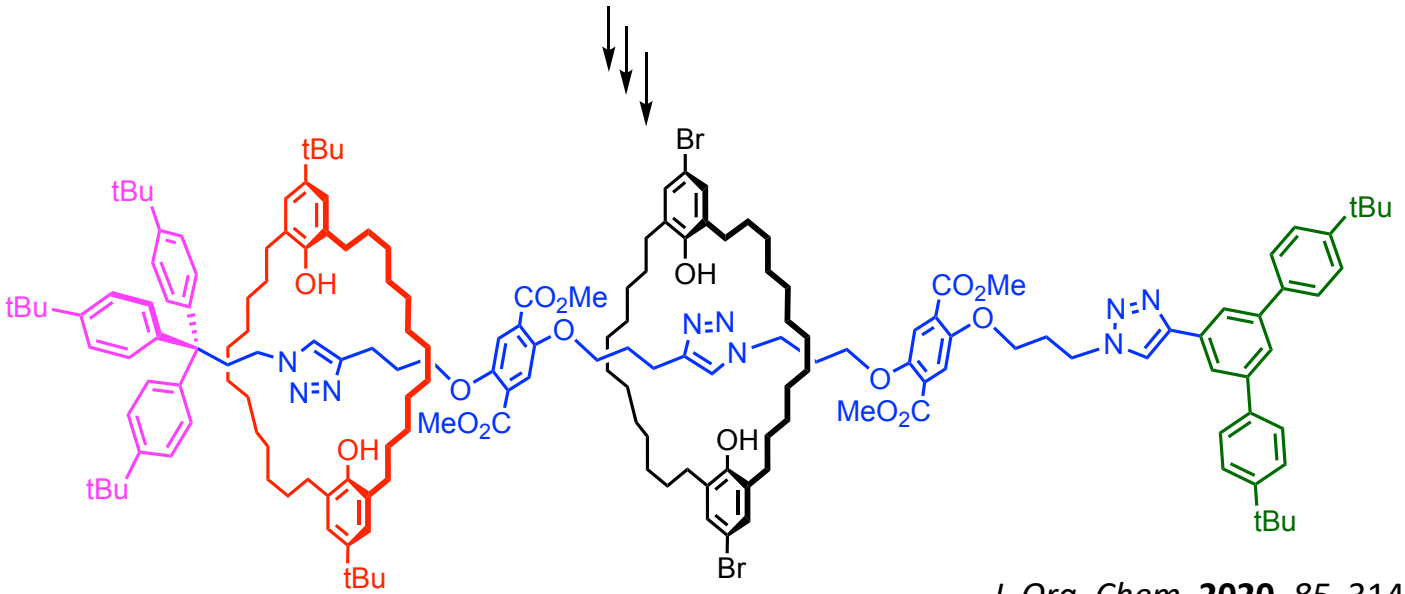




J. Org. Chem. **2020**, *85*, 3146-3159

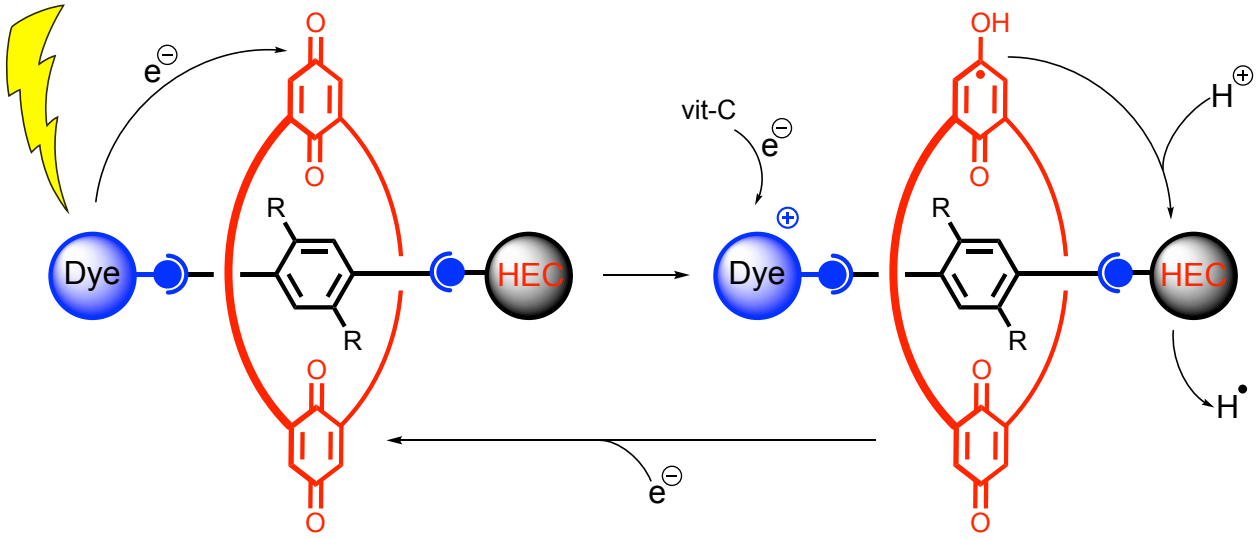
synthese van [3]-rotaxanen

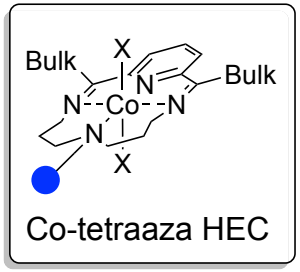




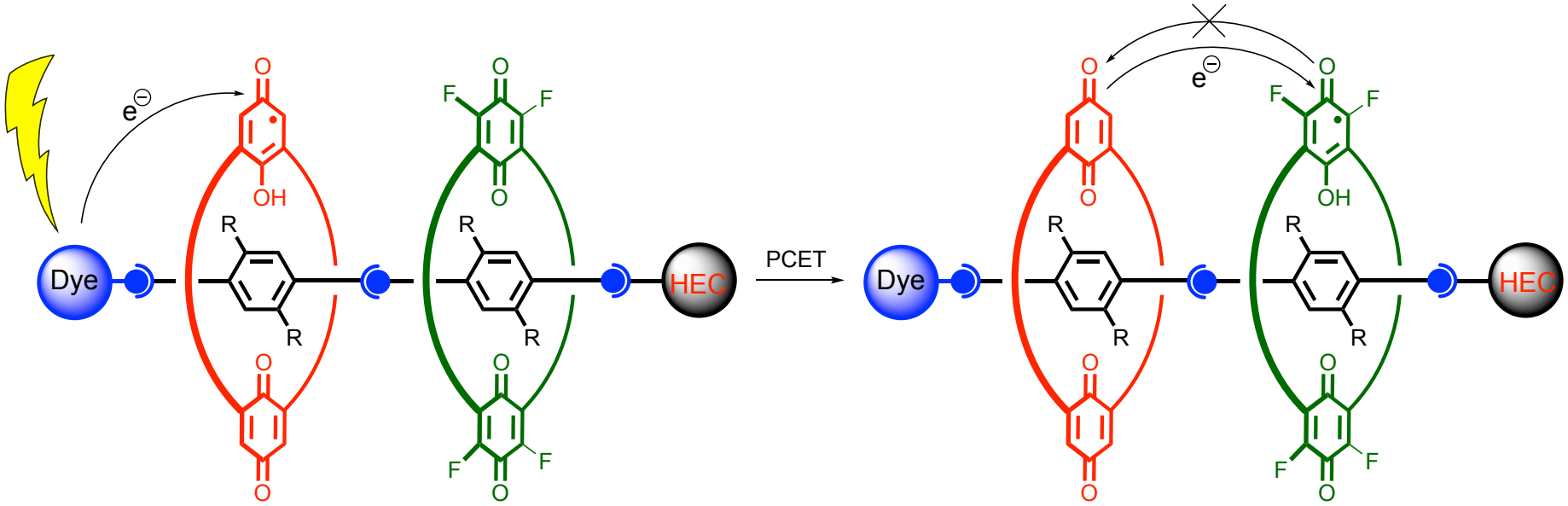
J. Org. Chem. **2020**, *85*, 3146-3159

In bewerking: ring-chinonen als elektronentaxi





Ons doel: elektronentransport in één richting



Jaap Sinnighe Damsté (NIOZ)

Remko Detz (TNO-ECN)

Joost Reek (UvA)

Gottfried Schill Luuk Steemers

Simone Pilon

Tessel Bouwens