technische universität dortmund

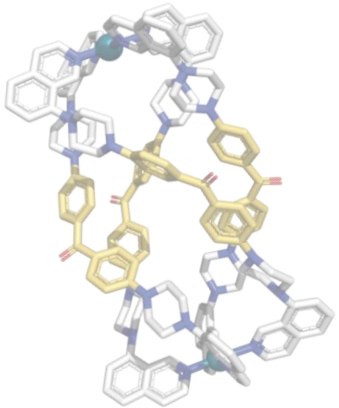
UNIVERSITÀ DEGLI STUDI DI TRIESTE

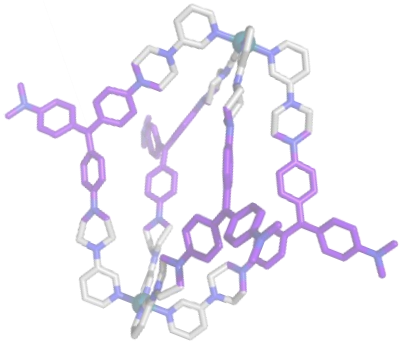
Clever Lab

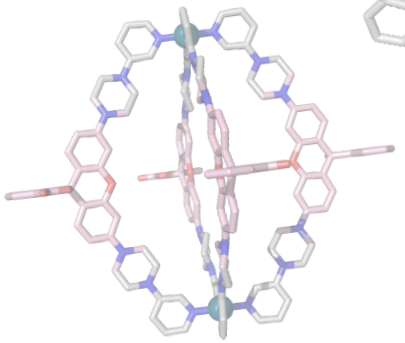
Coordination cages based on Pd(II) and banana shaped bis-pyridin ligands

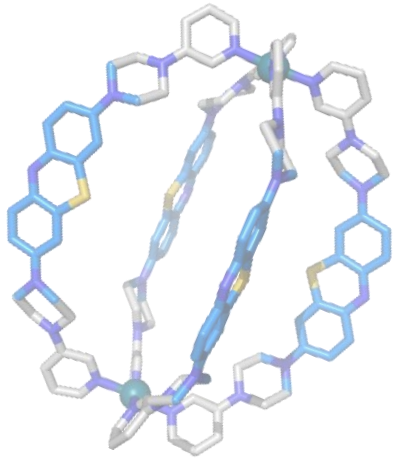
Dr. Irene Regeni

1st of December 2022





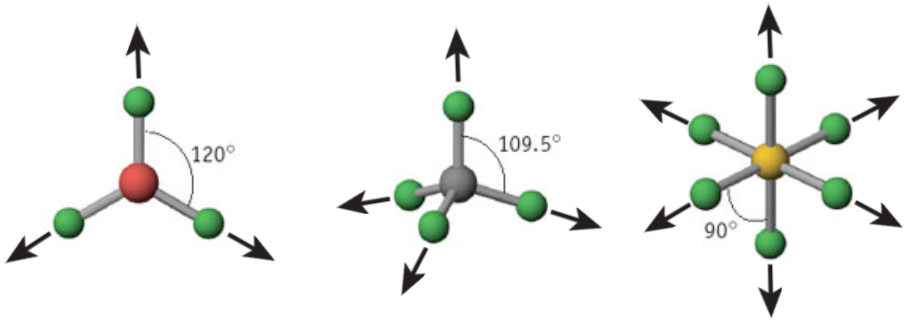




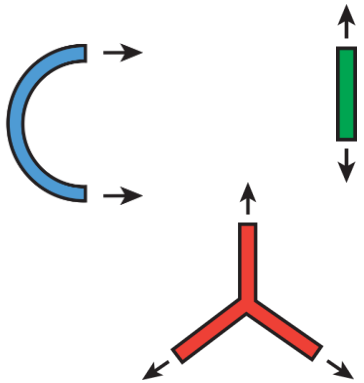
Universiteit Leiden

Metal-mediated Self-Assembly

Metal Nodes

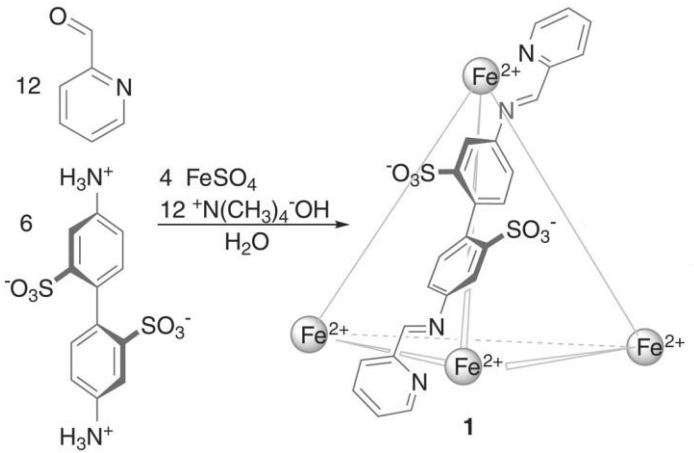


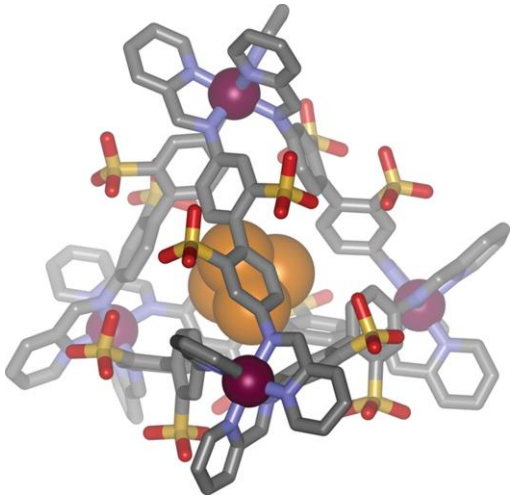
Organic Ligands



directed metal-ligand dative bonds allow control of geometry

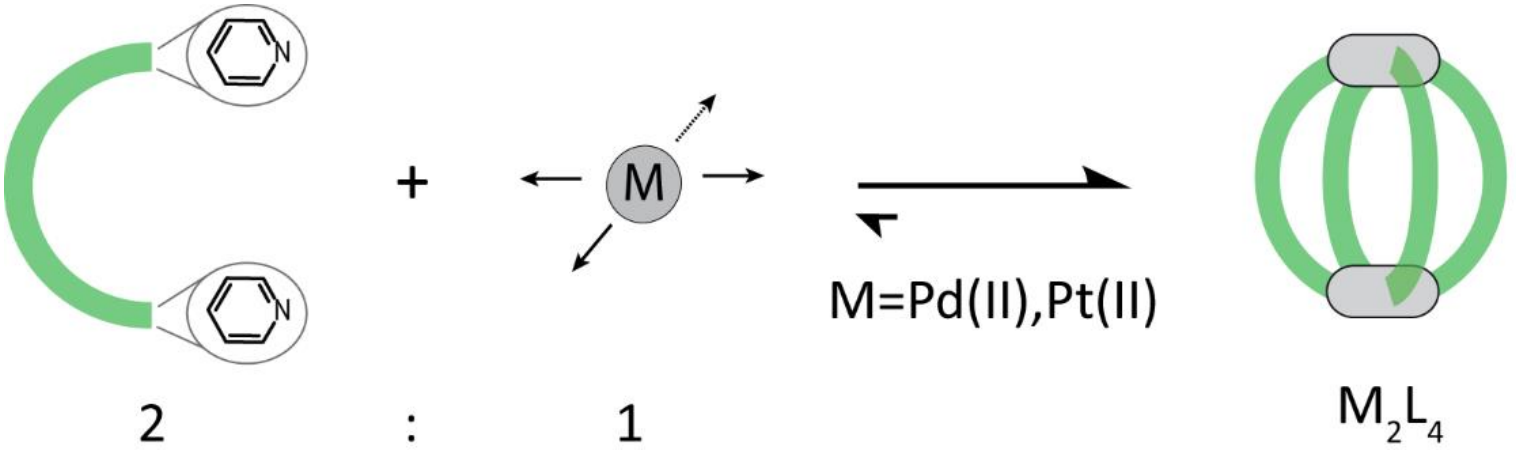
"naked ions" with chelating ligands





P. Mal, B. Breiner, K. Rissanen, J. R. Nitschke, *Science* 2009, *324*, 1697–1699

Pd(II) and banana shaped bis monodentate ligands



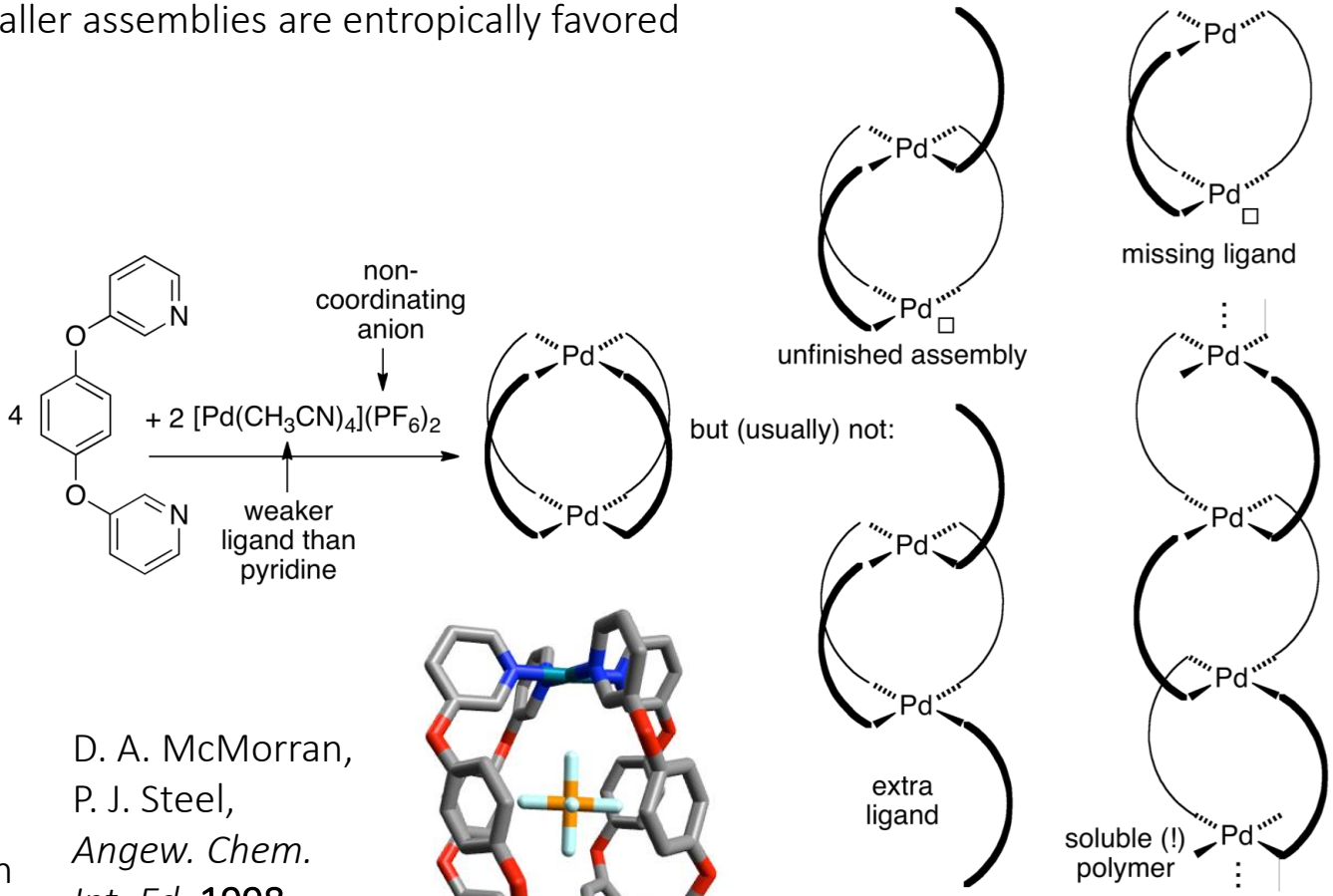
Molecular building blocks with reactive groups

Larger supramolecular objects

- Dynamic equilibrium
- Thermodynamic product
- Reversible
- Defect Free

Principle of „Maximum Site Occupancy“

- when steric and electronic conditions allow, all metal binding sites will coordinate to the maximum possible number of offered ligand donor sites → thermodynamically favored
- correct stoichiometry of metal ions and ligands
- smaller assemblies are entropically favored

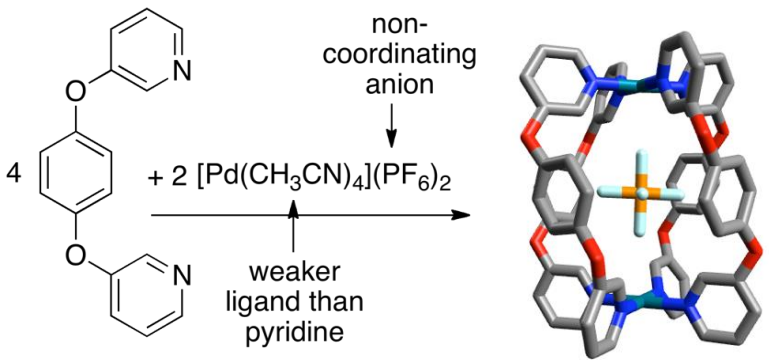


[$Pd_2Ligand_4$]

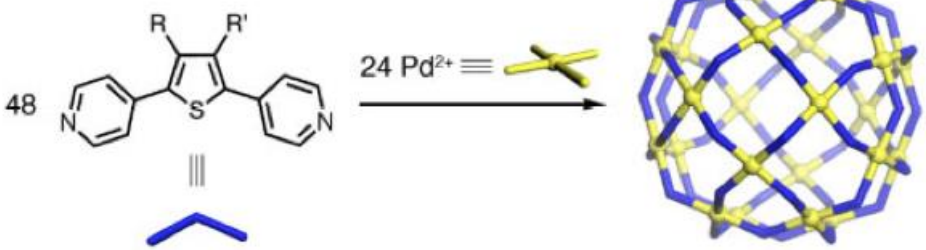
„coordination cage“

D. A. McMorran, P. J. Steel, *Angew. Chem. Int. Ed.* **1998**, *37*, 3295.

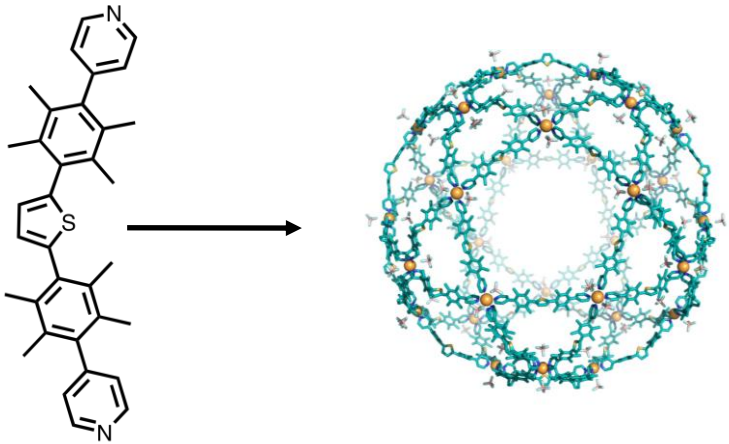
Structure Relationships



Small Rombic Cuboctaeder



$M_{30}L_{60}$ Icosidodecahedron



D. Fujita, Y. Ueda, S. Sato, H. Yokoyama, N. Mizuno, T. Kumasaka, M. Fujita, *Chem* **2016**, *1*, 91–101.

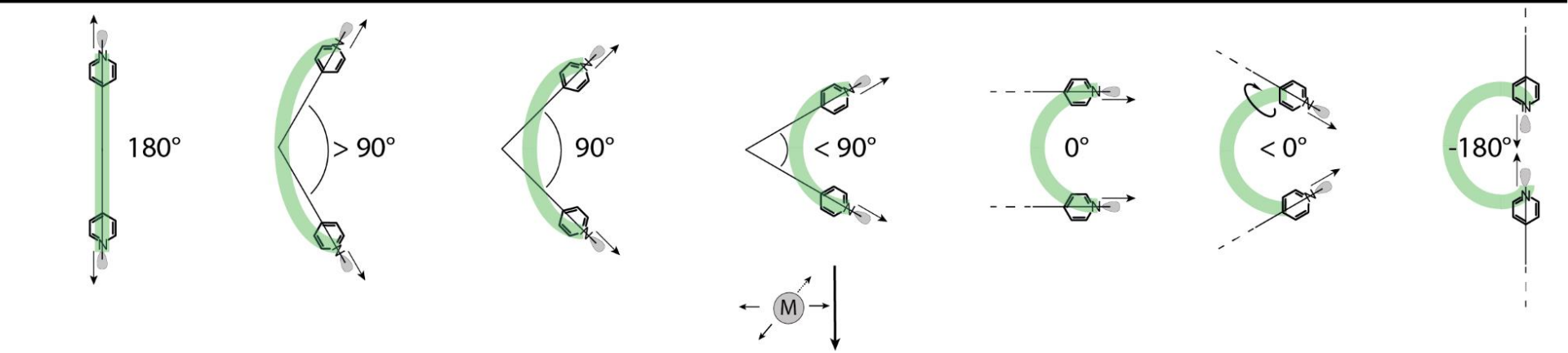
Clever

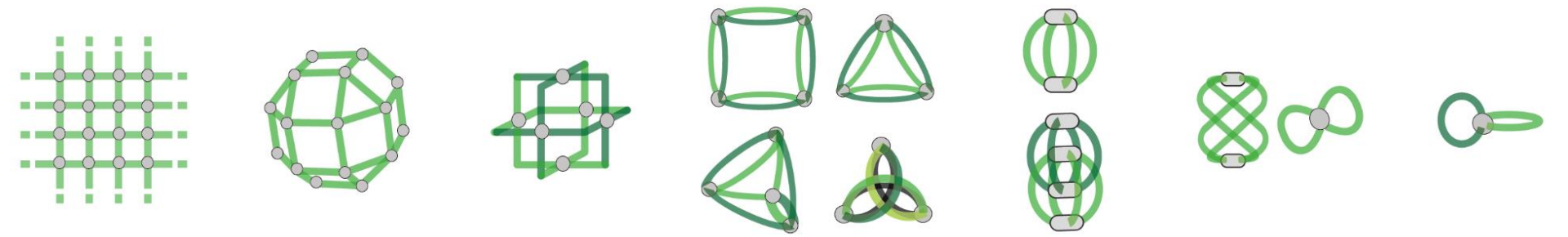
Lab

Structure Relationships

2D simplification

angle between bonding vectors





$[ML_2]_n$
Grids

$M_{12}L_{24}$, $M_{24}L_{48}$...
Spheres

M_6L_{12}
Boxes

M_3L_6, M_4L_8, M_5L_{10}
Rings, Tetrahedrons

M_2L_4, M_4L_8
Cages

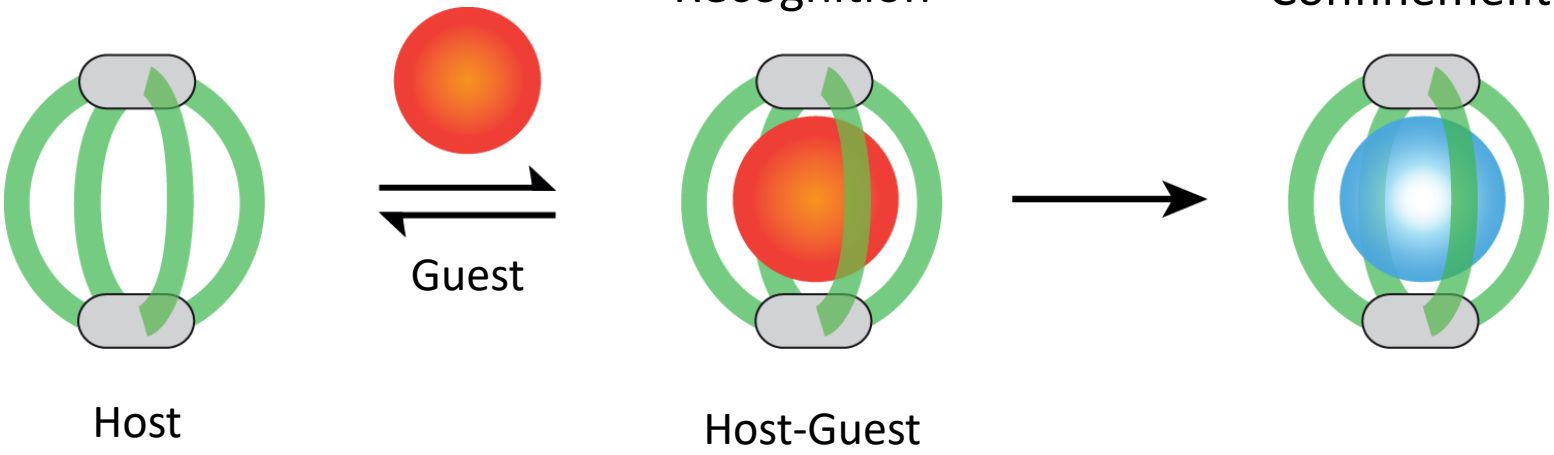
M_2L_4, ML_2
Helical Cages, *cis*-Chelates

ML_2
trans-Chelates

size of the assemblies and number of components involved

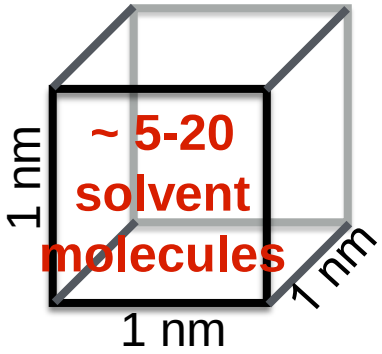
S. Saha, I. Regeni, G. H. Clever, *Coord. Chem. Rev.* **2018**, *374*, 1

Host Guest Chemistry



$$K = \frac{[HG]}{[H][G]} \ (M^{-1})$$

- NMR
- UV-Vis
- ITC
- …



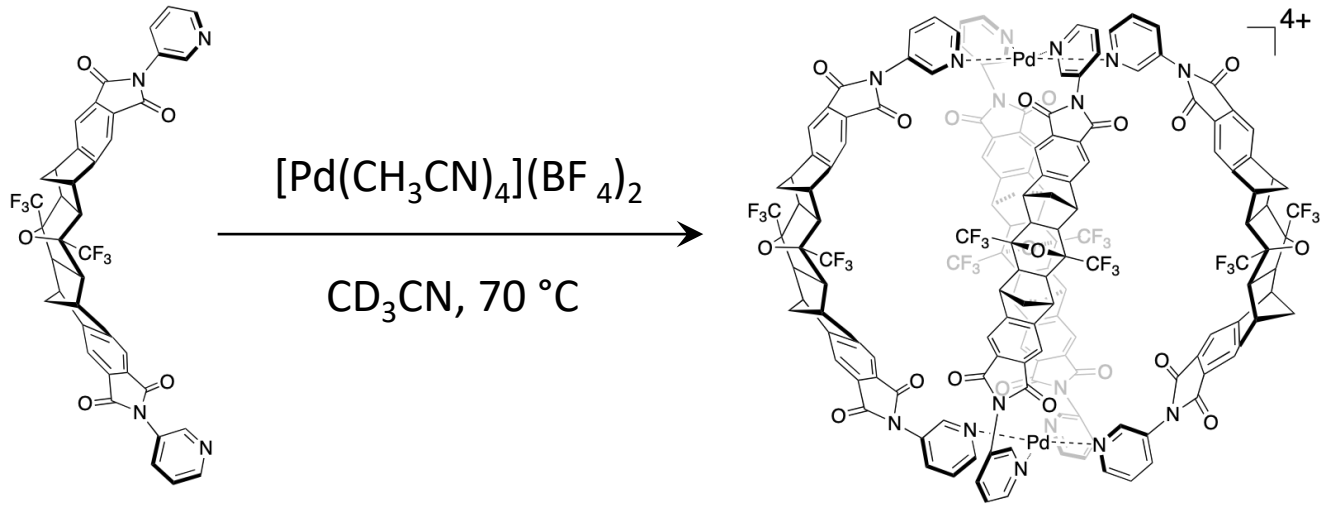
Yoctoliter (yL)
= 1 nm^3

Anion Recognition

DOI: 10.1002/anie.200902717

Inclusion of Anionic Guests inside a Molecular Cage with Palladium(II) Centers as Electrostatic Anchors**

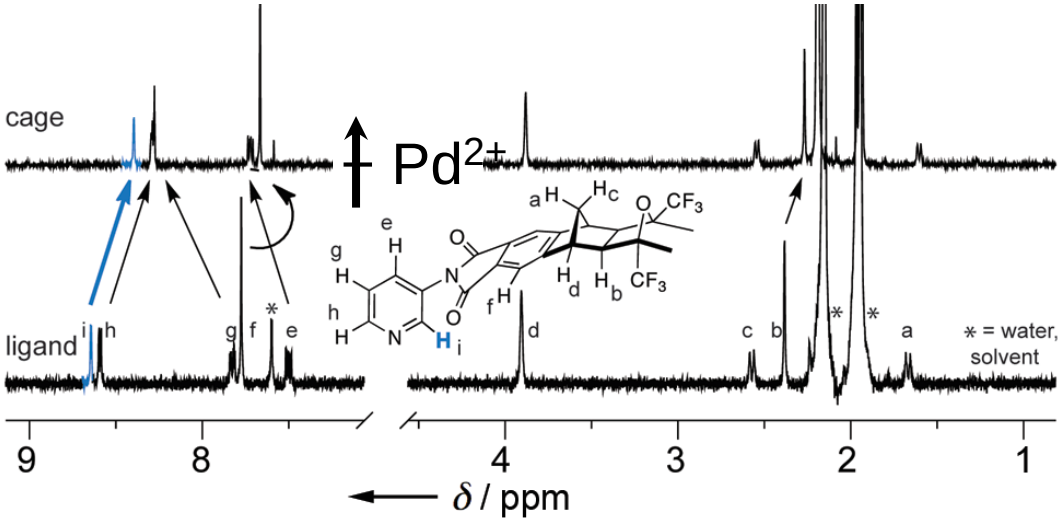
*Guido H. Clever, Shohei Tashiro, and Mitsuhiko Shionoya**

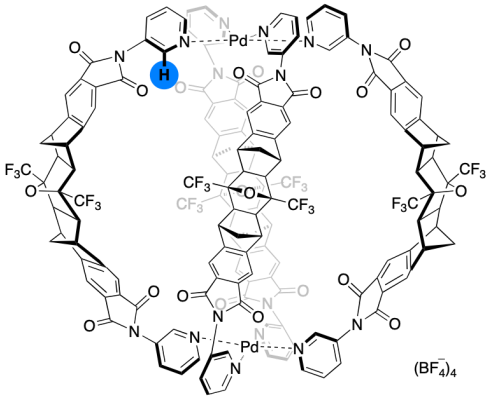


G. H. Clever, S. Tashiro, M. Shionoya, *Angew. Chem. Int. Ed.* 2009, *48*, 7010–7012.

Cage formation

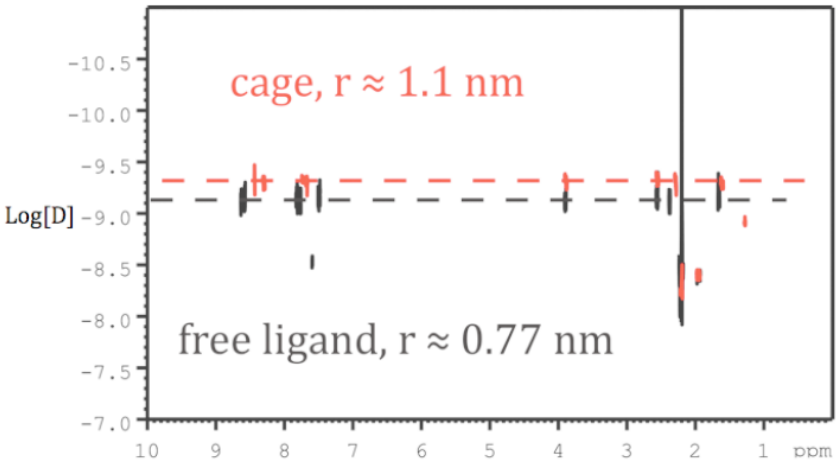
^{1}H NMR in CD_3CN





Cage forms quantitatively upon addition of appropriate amount of metal ion: L_4M_2

^{1}H DOSY NMR: Diffusion Ordered Spectroscopy



Idealized globular molecular size estimation using the Stokes-Einstein equation:

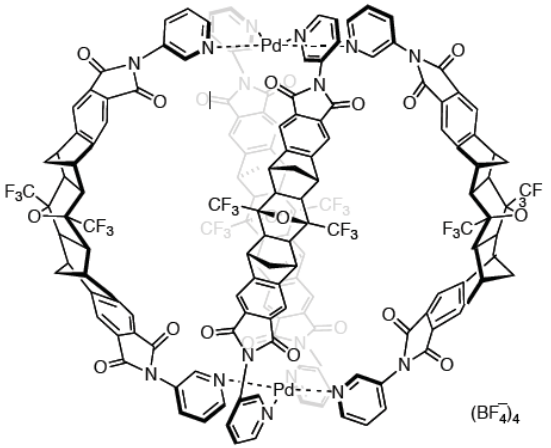
$$r = \frac{k \cdot T}{6 \cdot \pi \cdot \eta \cdot D}$$

With r = radius, k = Boltzmann const., T = Temp., η = dynamic viscosity of $CD_3CN = 3.9 \cdot 10^{-4}$ Pa/s and D = Diffusion values estimated by the DOSY experiment: $\log[D_{ligand}] \approx -9.15$, $\log[D_{cage}] \approx -9.30$

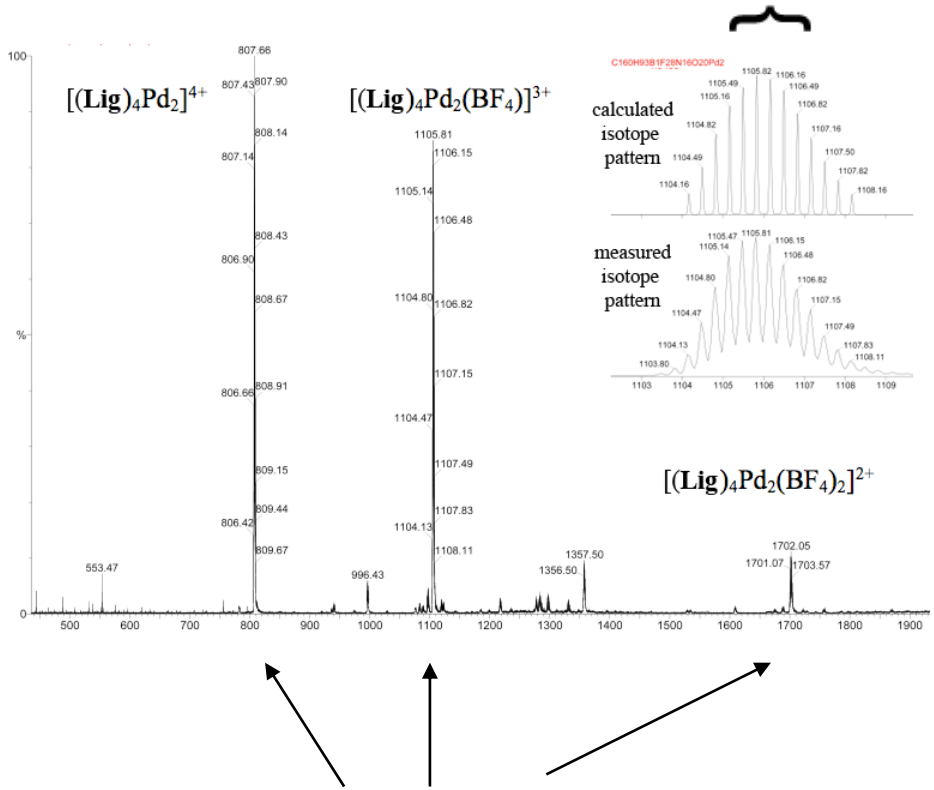
The obtained radius of 1.1 nm for cage **6** correlates well with the values from the molecular model and the x-ray structure.

Cage formation

Mass Spectrometry
Typical ESI-TOF spectra



z = 1/peak distance



all these three peaks confirm the formation of the $[(\mathbf{Lig})_4Pd_2]$ cage

In ESI mass spectra, one product often results in a series of peaks with different *m/z*.

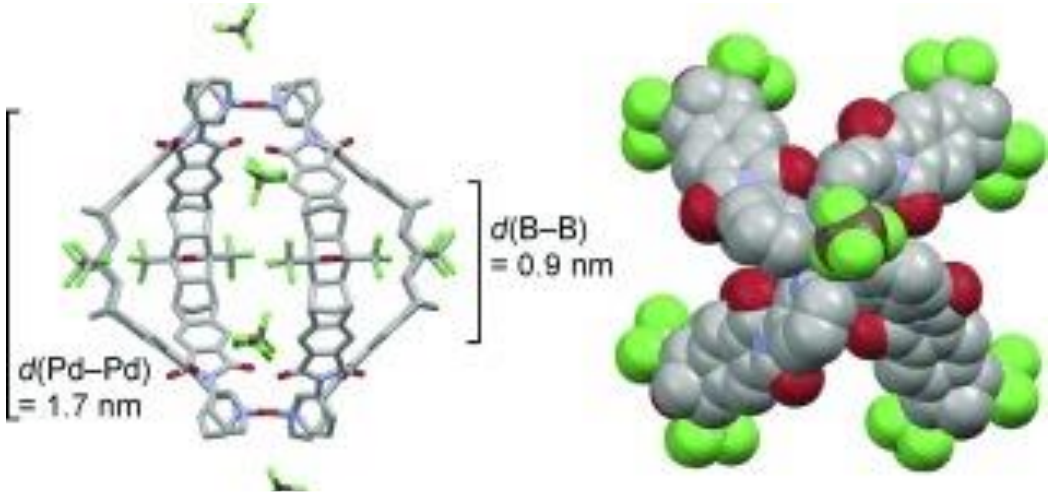
The reason for this can be:
- different protonation grade
- different number off associated counter ions
- redox processes

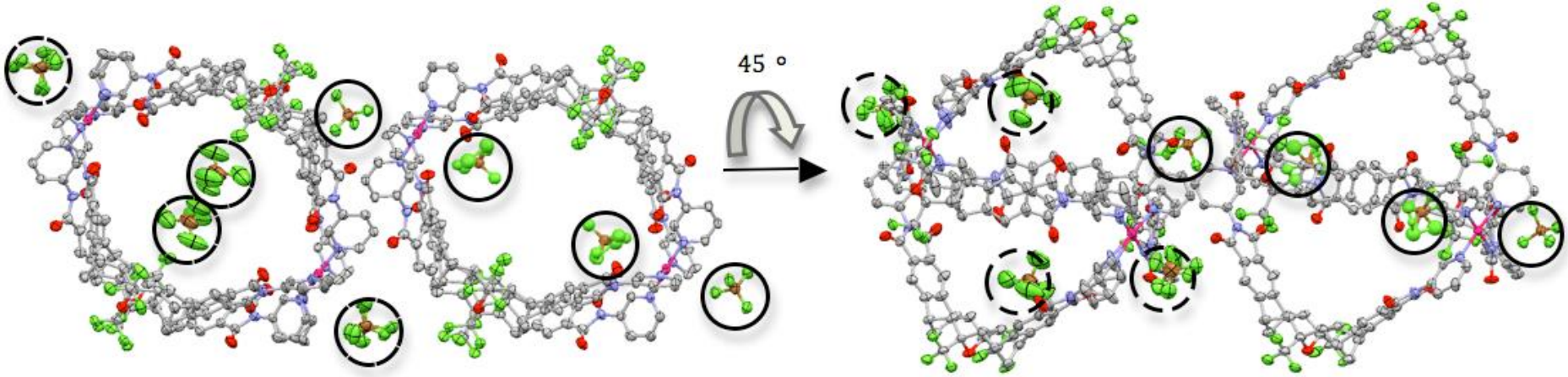
Attention: not only the charge but also the mass of additional protons or counter ions has to be considered:

m/z $[(\mathbf{Lig})_4Pd_2(BF_4)_2]^{2+}$
≠
2 x *m/z* $[(\mathbf{Lig})_4Pd_2]^{4+}$

Cage formation

X-ray crystal structure



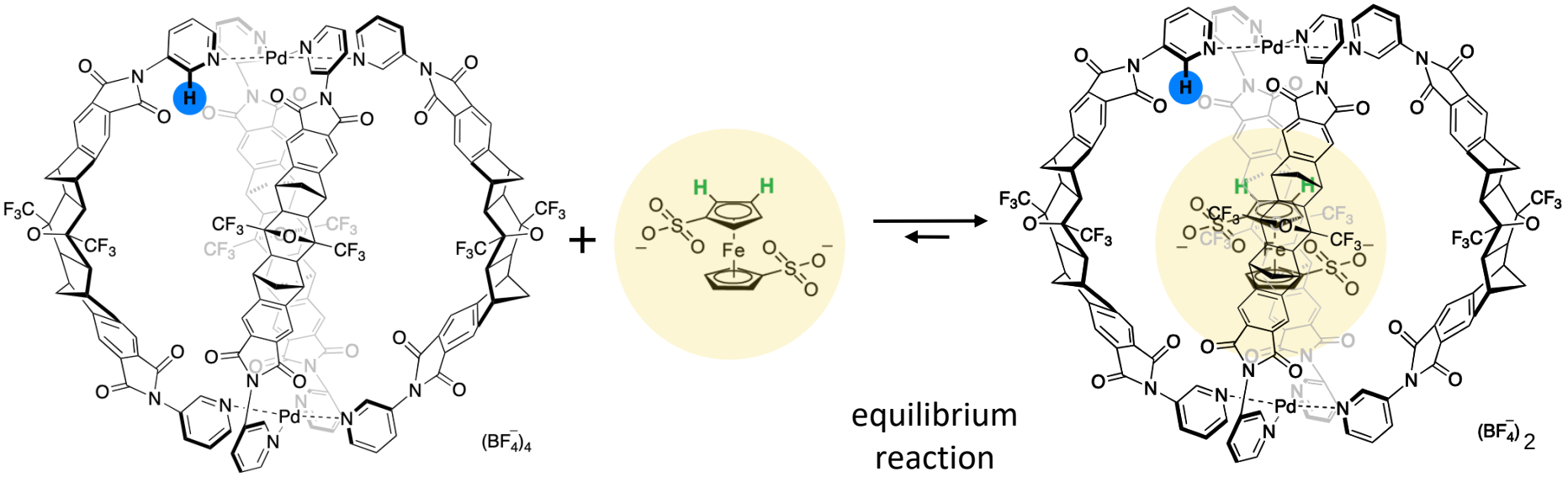


Host-Guest Interaction

Host = Self-assembled Coordination Cage

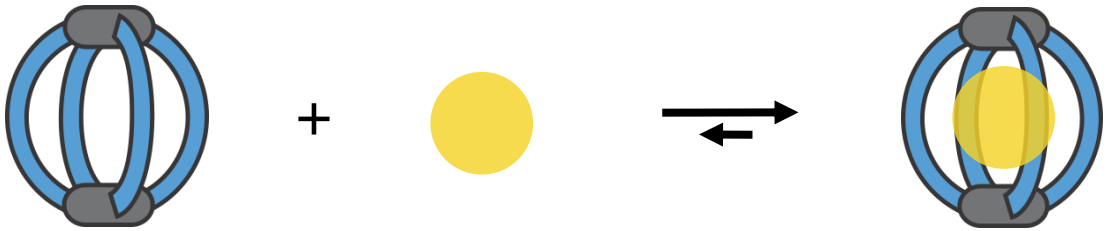
Guest = Ferrocene Bis-sulfonate

in polar solvent (MeCN)



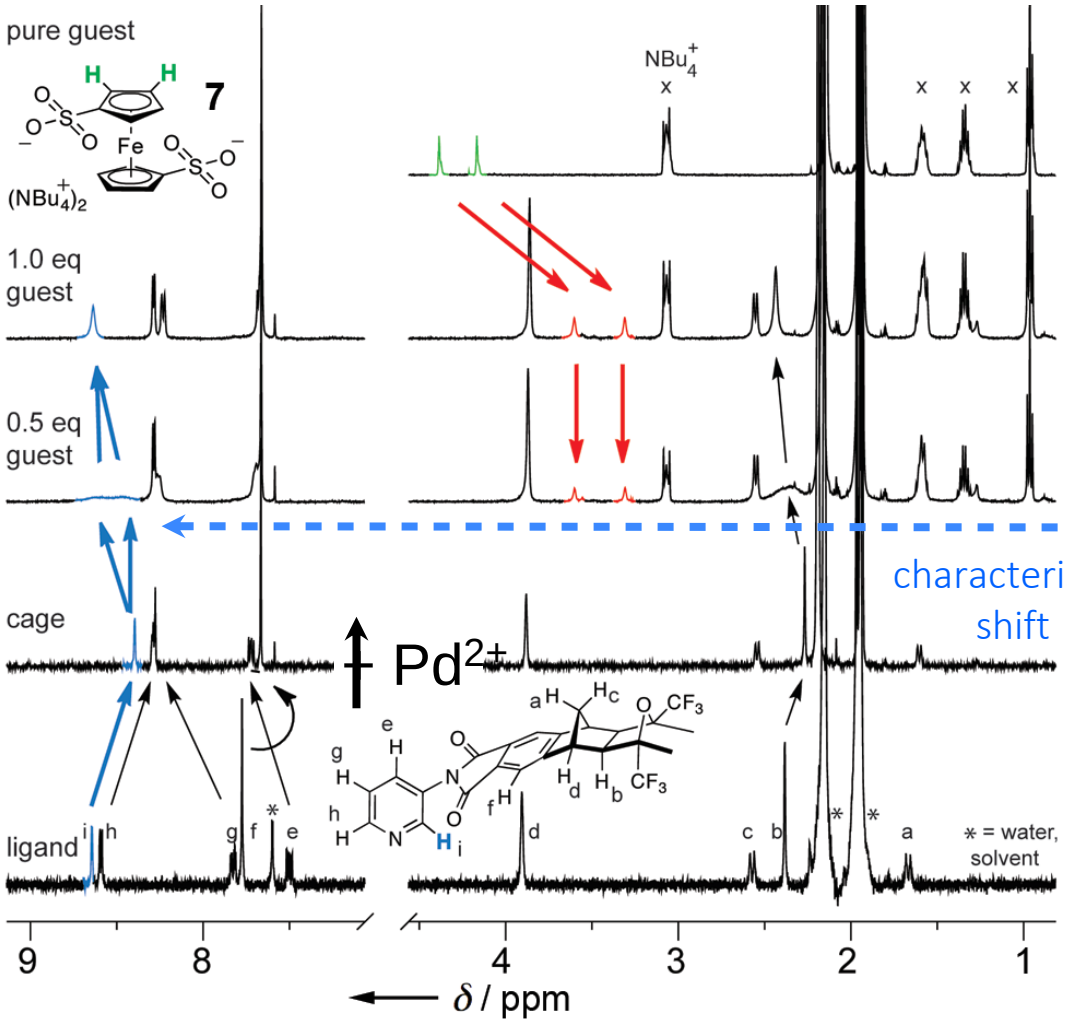
equilibrium reaction (often far on right side)

Simplified Scheme



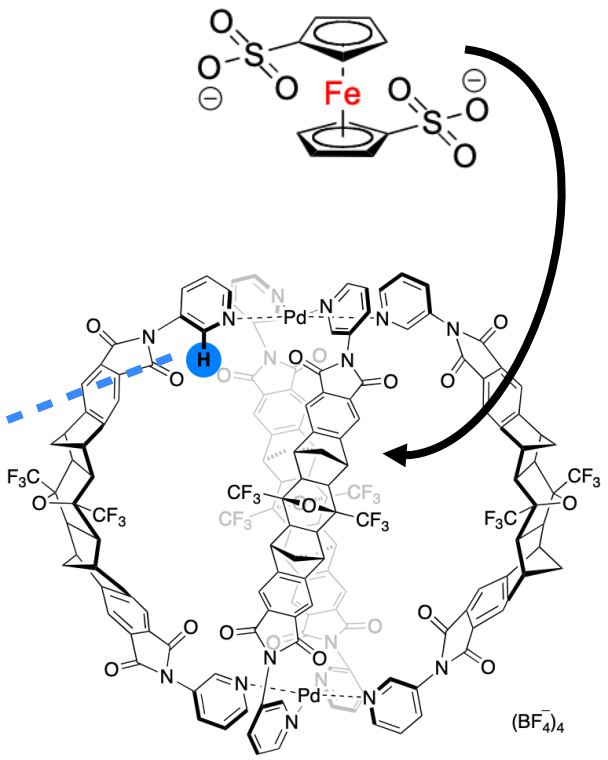
Host-Guest Interaction

NMR titration

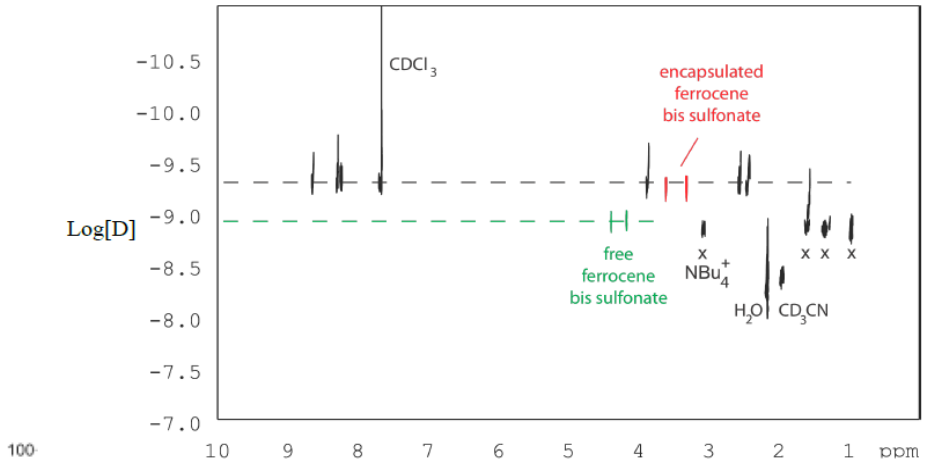


upfield shift:
typical for guest in aromatic host

characteristic shift

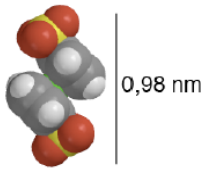


DOSY superposition of spectra of 1,1'-ferrocene bissulfonate @ Cage **6** (black: signals of cage, NBu_4^+; red: signals of encapsulated guest) and the free guest (green).

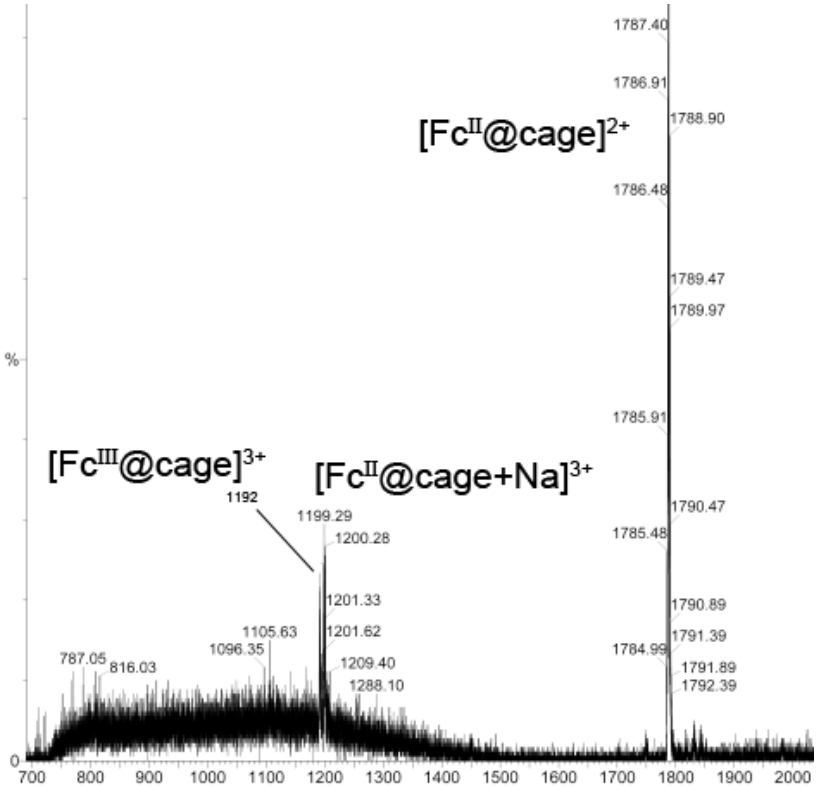


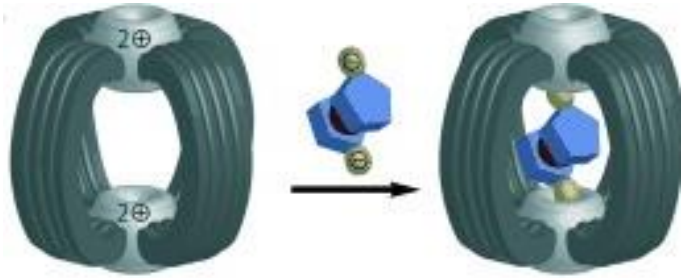
Diffusion values estimated by the DOSY experiment: $\log[D_{guest}] \approx -8.90$, $\log[D_{guest@cage}] \approx -9.30$.

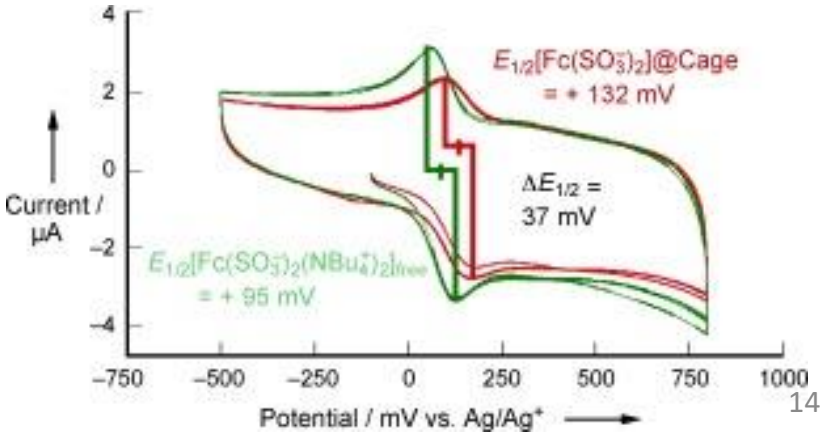
The estimated radius of the free guest, $r_{guest} \approx 0.44$ nm, is in accordance with the molecular model of 1,1'-ferrocene bissulfonate:



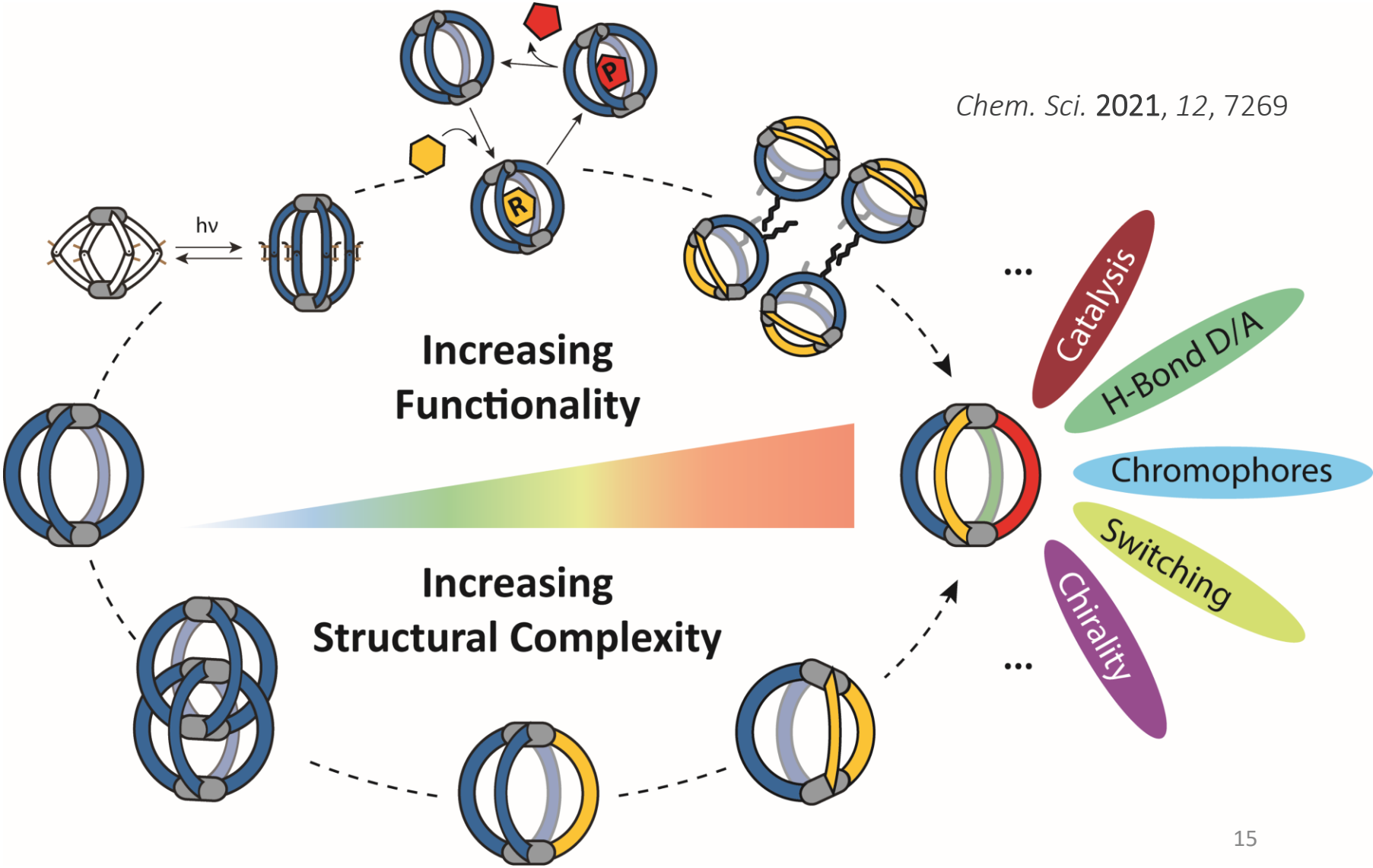
The encapsulated guest exhibits a similar diffusion coefficient as the host compound.







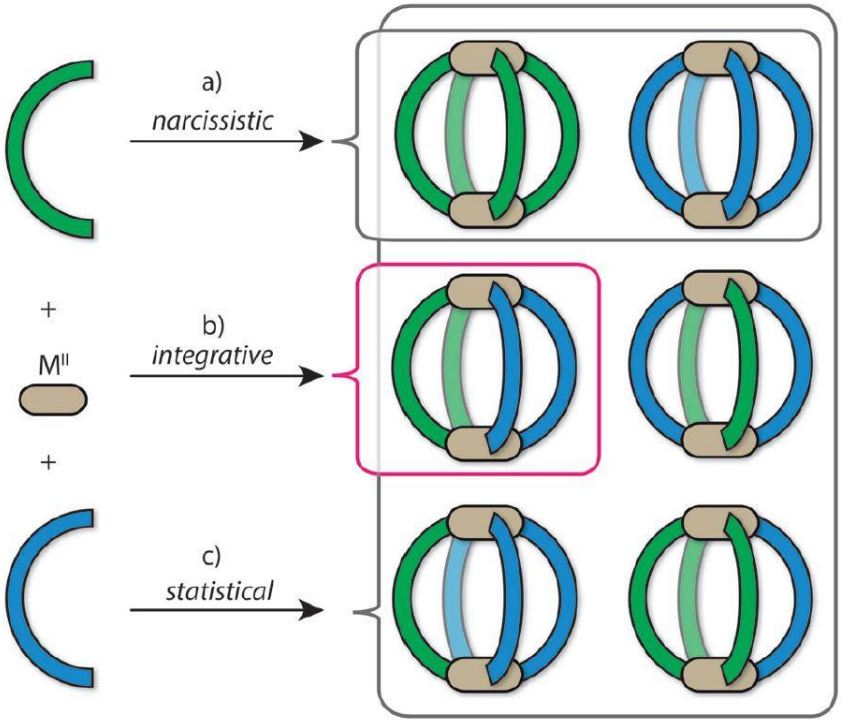
Evolution of coordination cages: Increasing the complexity



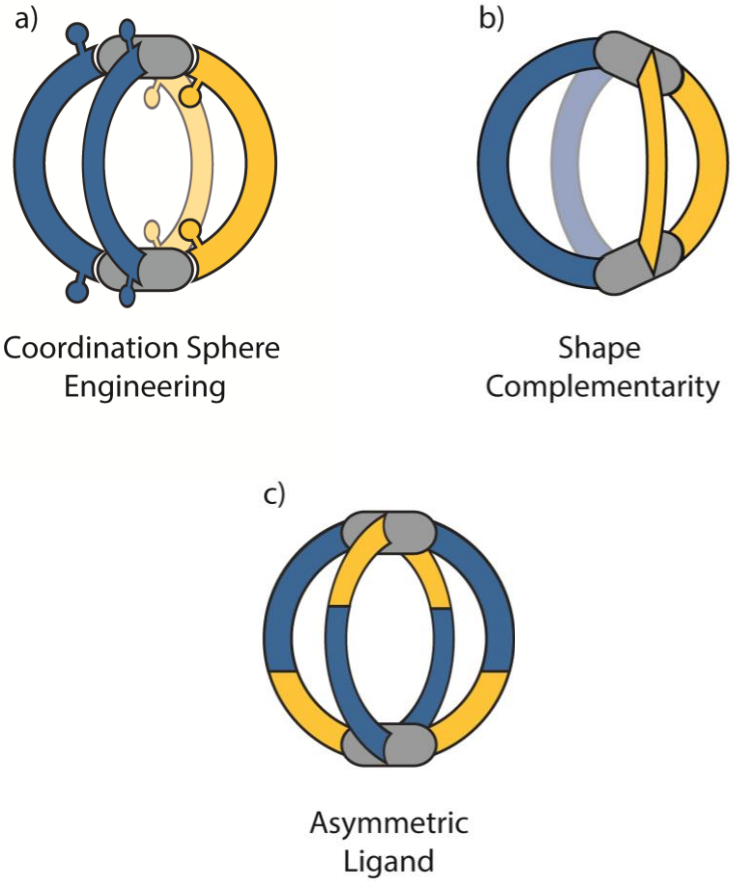
Chem. Sci. **2021**, *12*, 7269

Heteroleptic coordination cages

Self-sorting possibilities



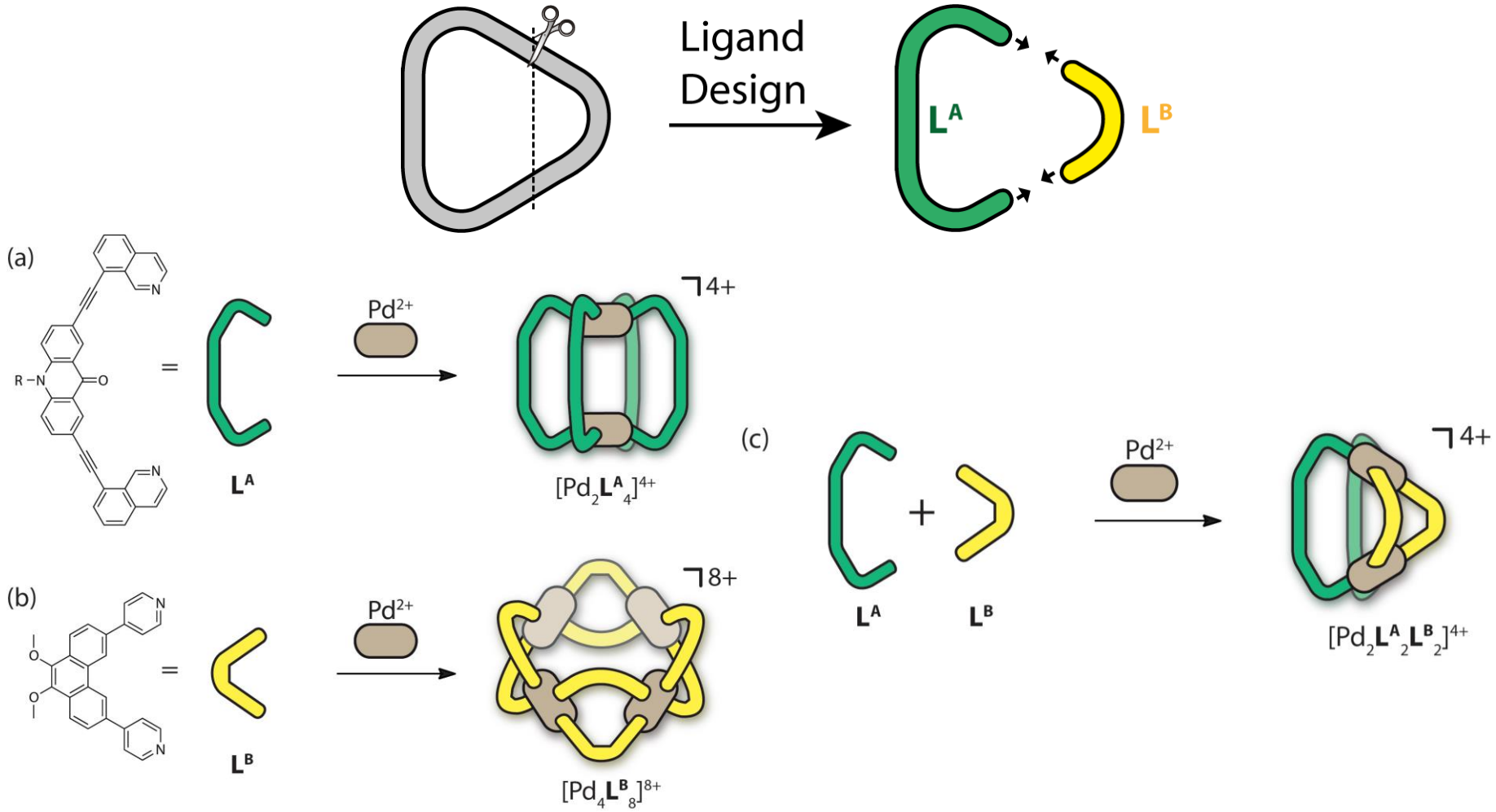
Established Strategies for integrative self-sorting



W. M. Bloch, G. H. Clever, *Chem. Commun.* **2017**, *53*, 8506–8516.

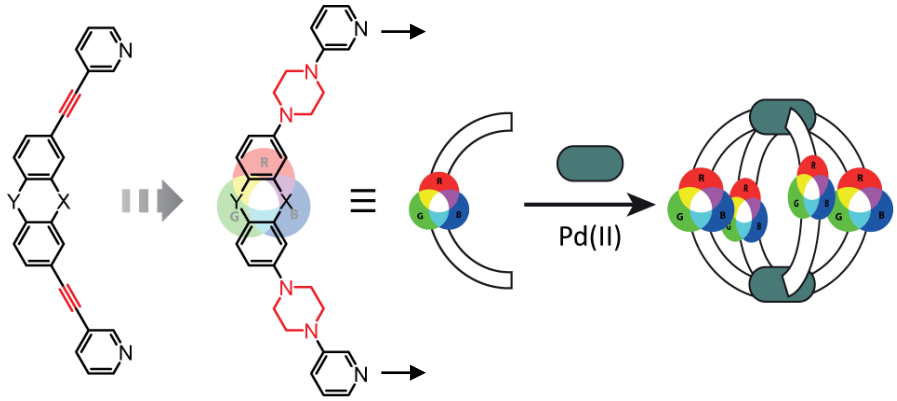
Heteroleptic coordination cages

Shape-complimentary Assembly
Directional Bonding → Bent Cages



W. M. Bloch, G. H. Clever, et al. *J. Am. Chem. Soc.* **2016**, *138*, 13750–13755

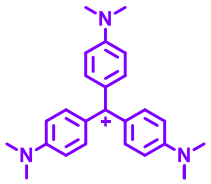
Coal-Tar Dyes-based Coordination Cages and Helicates



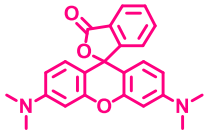
electronic structure
of the parental dye

Michler's Ketone (MK)

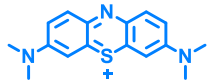
Crystal Violet (CV)



Rhodamine B (RB)



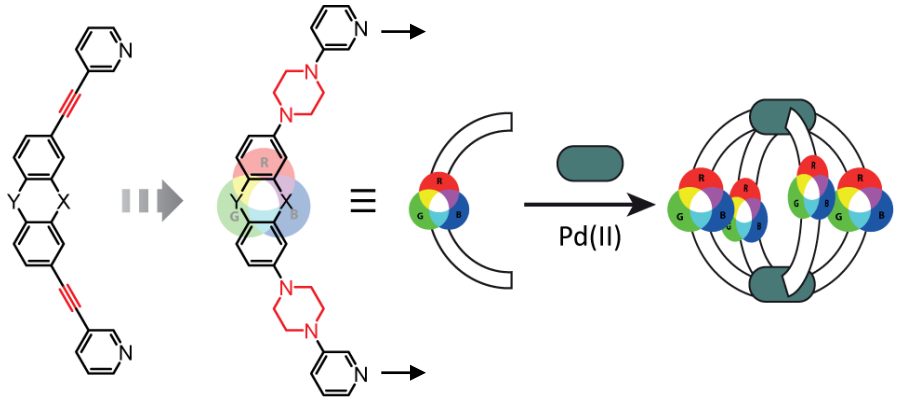
Methylene Blue (MB)



I. Regeni, B. Chen, M. Frank, A. Baksi, J. J. Holstein, G. H. Clever, *Angew. Chem. Int. Ed.* **2021**, *60*, 5673.

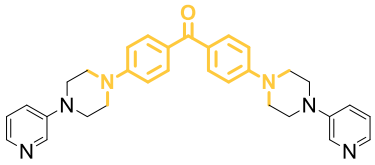
Coal-Tar Dyes-based Coordination Cages and Helicates

Clever Lab

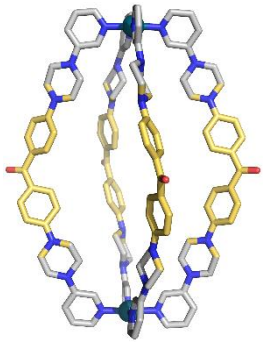


electronic structure
of the parental dye

Michler's Ketone (MK)

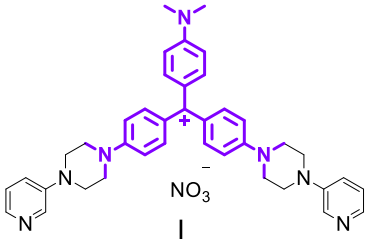


DMSO-d_6
70 °C, 2 h
Pd

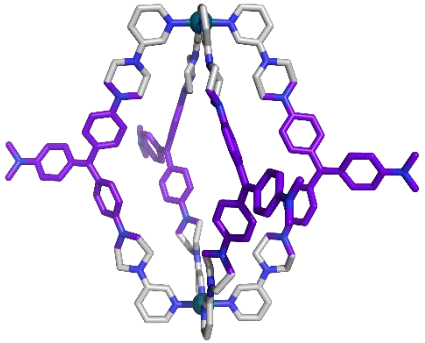


X-ray crystal structure

Crystal Violet (CV)

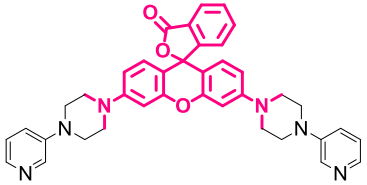


DMSO-d_6
70 °C, 2 h
Pd

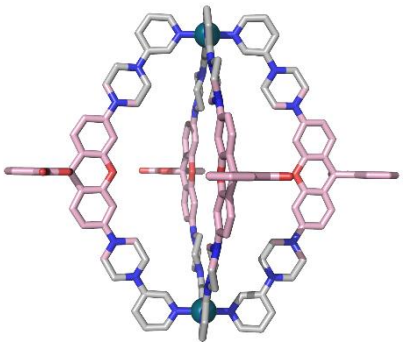


X-ray crystal structure

Rhodamine B (RB)

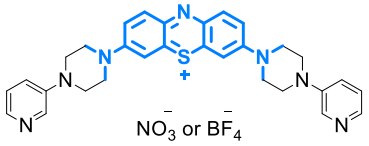


DMSO-d_6
70 °C, 2 h
Pd

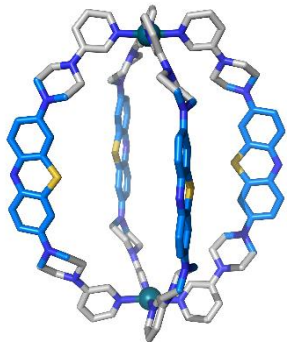


X-ray crystal structure

Methylene Blue (MB)



DMSO-d_6
70 °C, 2 h
Pd



B3LYP/def2-SV(P)

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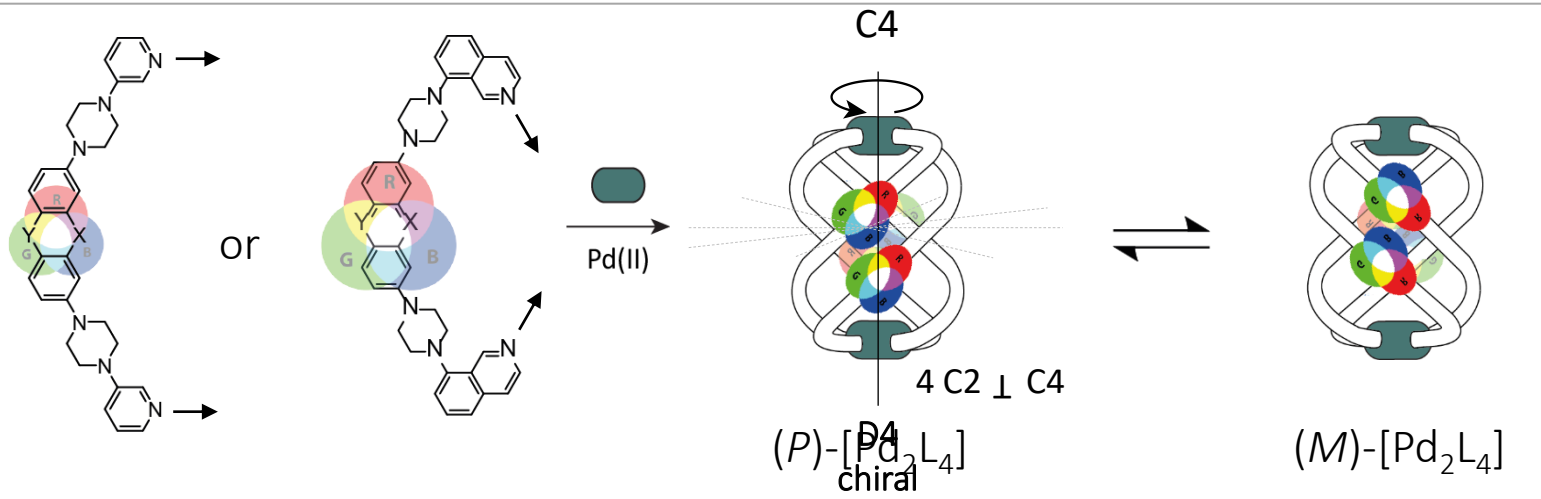
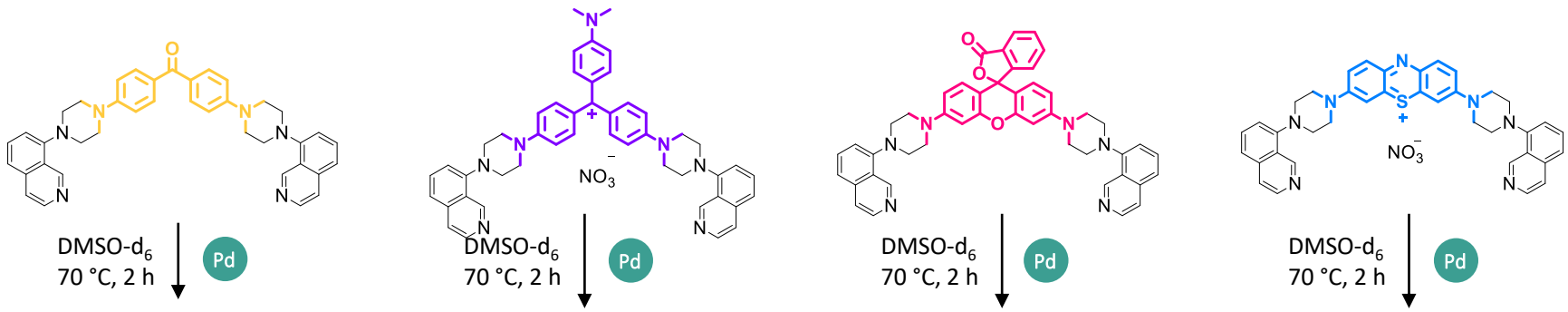
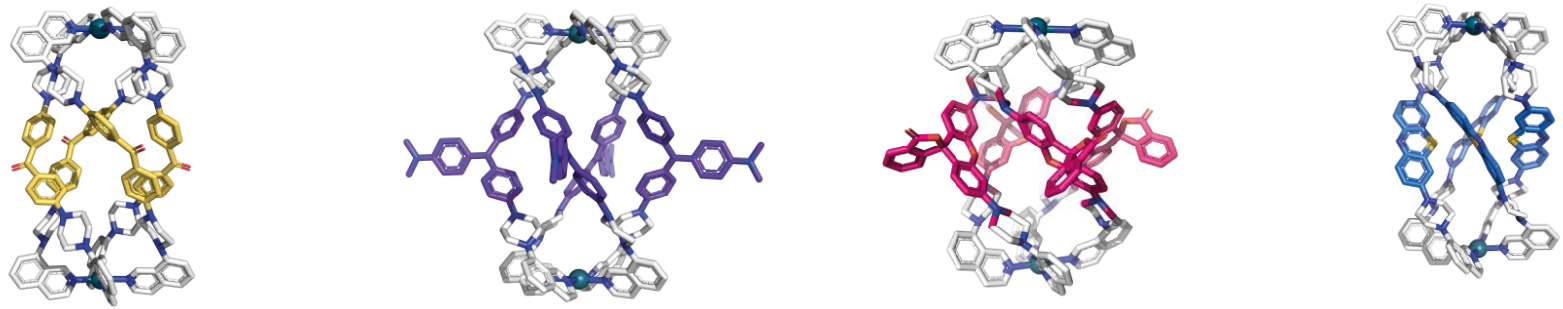
Dye-based Helicates







B3LYP/def2-SV(P) B3LYP/def2-SV(P) B3LYP/def2-SV(P) B3LYP/def2-SV(P)

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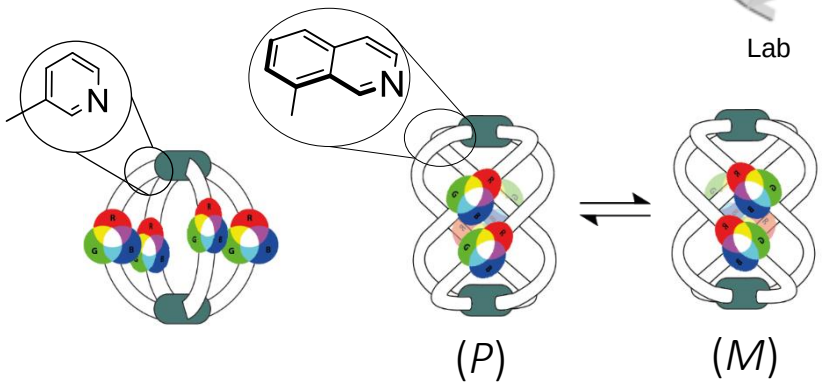
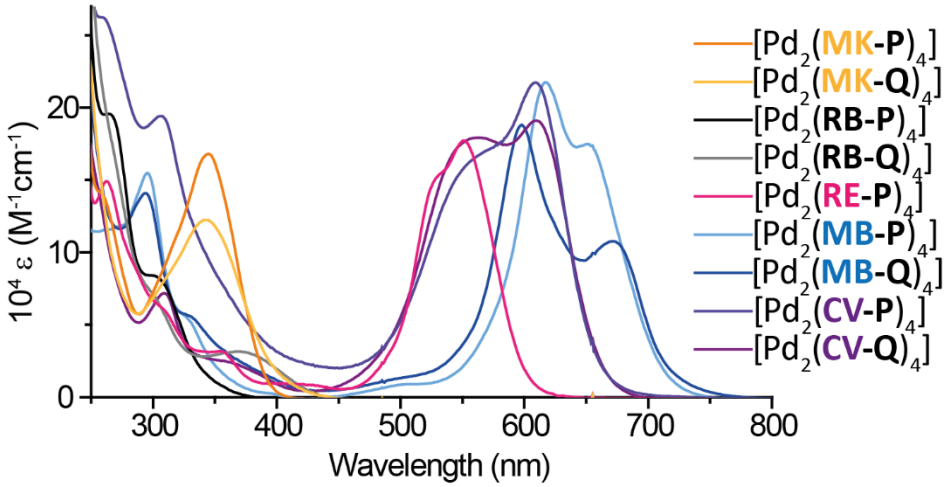
Absorption Spectra of the Dye-based Assemblies

Clever Lab

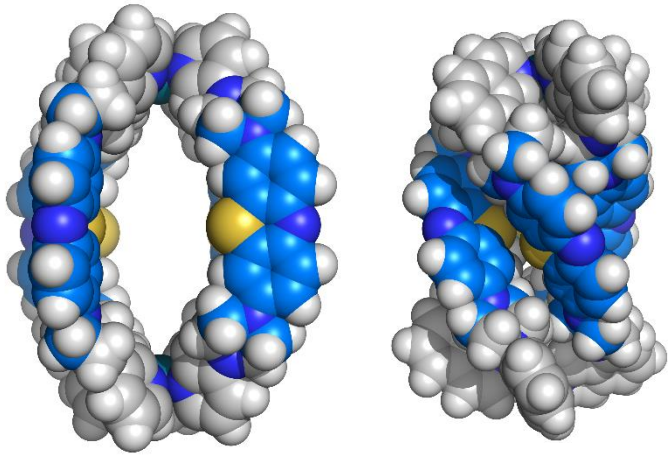


$[Pd_2(\mathbf{DYE\text{-}P})_4]$ $[Pd_2(\mathbf{DYE\text{-}Q})_4]$



Cage solutions in DMSO. In the picture concentration of 0.7 mM of cage (2.8 mM ligand concentration)

Space-filling view of B3LYP/def2-SV(P) models



$[Pd_2(\mathbf{MB\text{-}P})_4]$ (*M*)-$[Pd_2(\mathbf{MB\text{-}Q})_4]$

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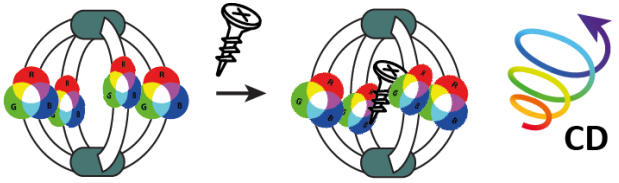
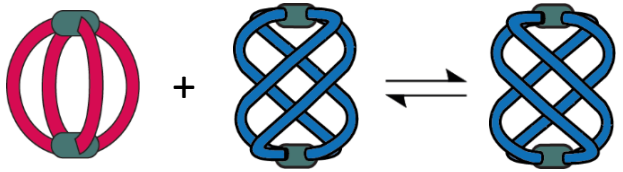
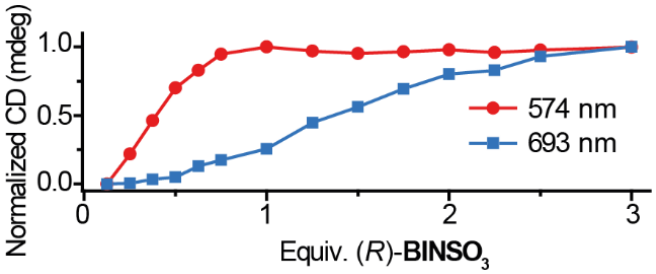
Chiral Induction from Small Molecule to Cage

Clever Lab

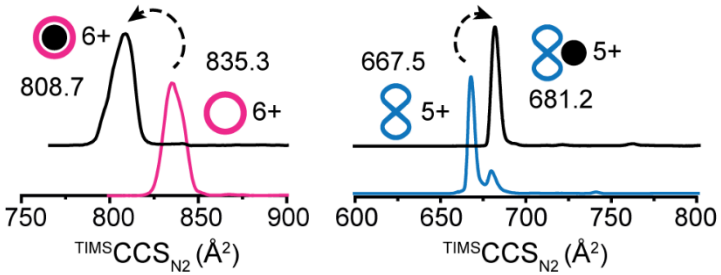


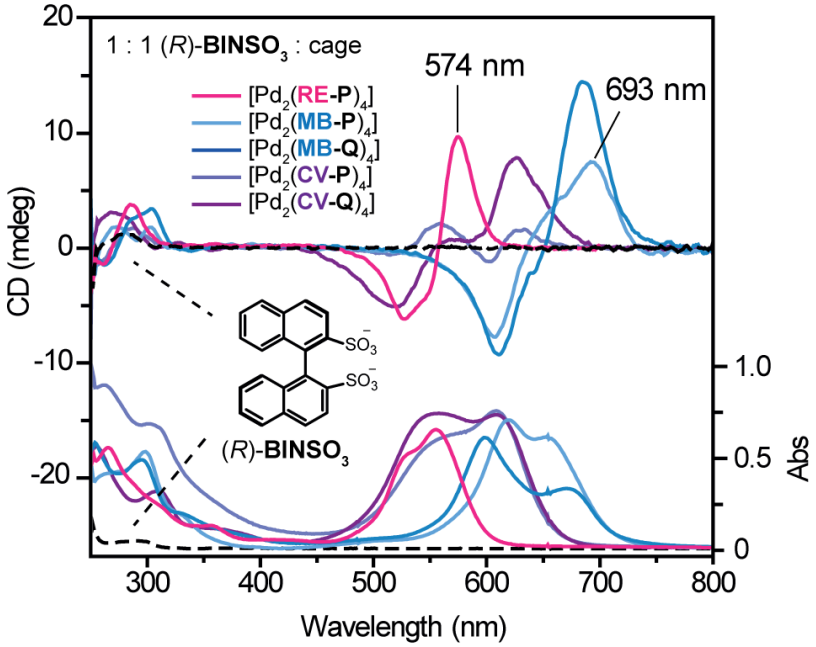


$[Pd_2(RE\text{-}P)_4]$ $[Pd_2(MB\text{-}Q)_4]$

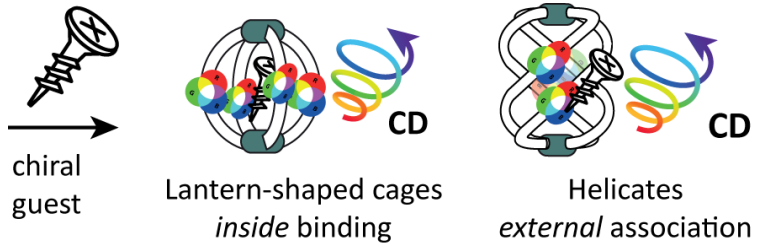


Ion Mobility





Sample conditions: 18.7 µM cage and 18.7 µM guest in DMSO. T = 25 °C.



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Domande?