X International Voevodsky Conference "Physics and Chemistry of Elementary Chemical Processes" (VVV-2022)

2022 Novosibirsk 05-09 Sep 2022

MAGNETIC MATERIALS BASED ON SANDWICH LANTHANIDE COMPLEXES WITH PHTHALOCYANINES

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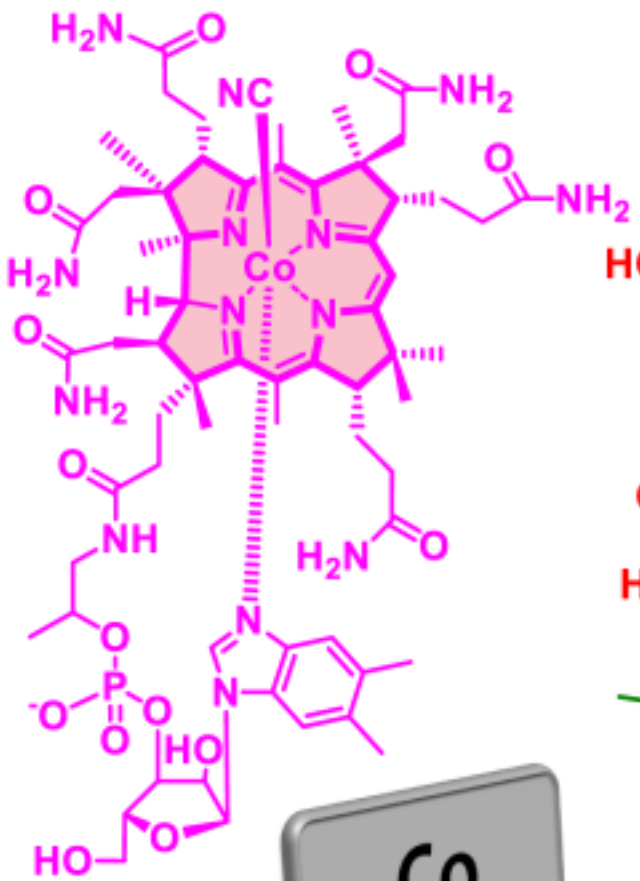
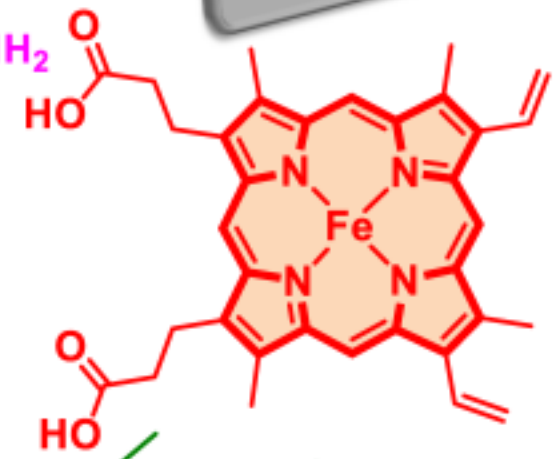
In Memoriam – Brilliant Chemist, Professor Larisa Tomilova - 1947-2021

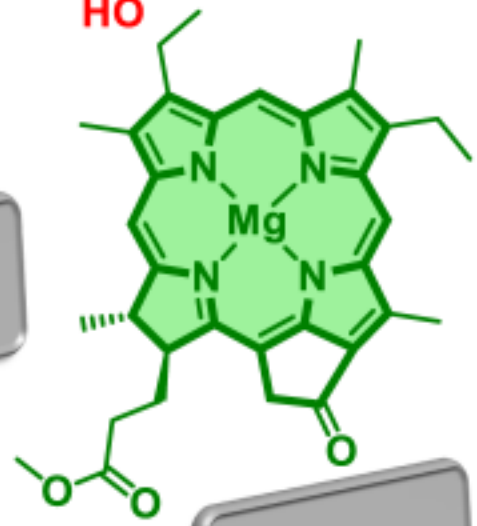
Natural porphyrins



Co

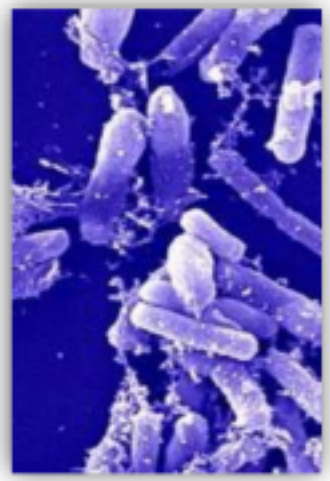


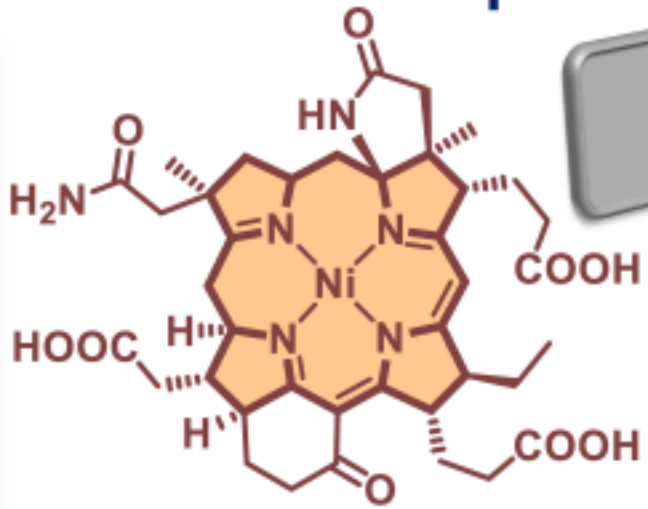
Fe



Mg

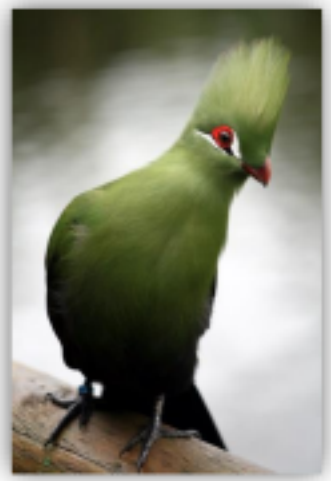
Exotic examples

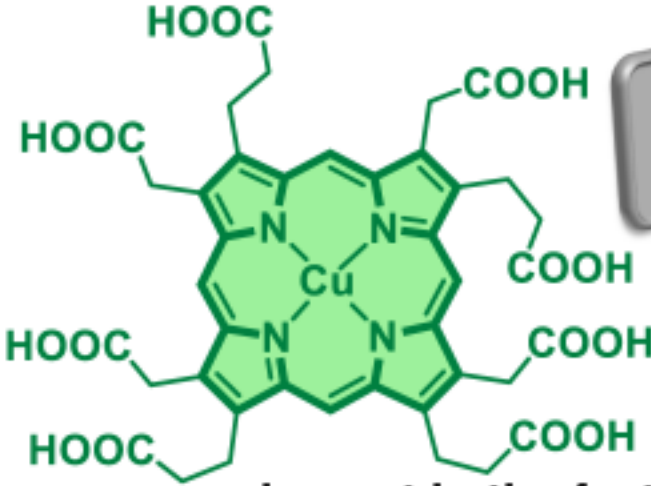




Ni

Factor F430 – a component of the enzymatic system of methanobacteria

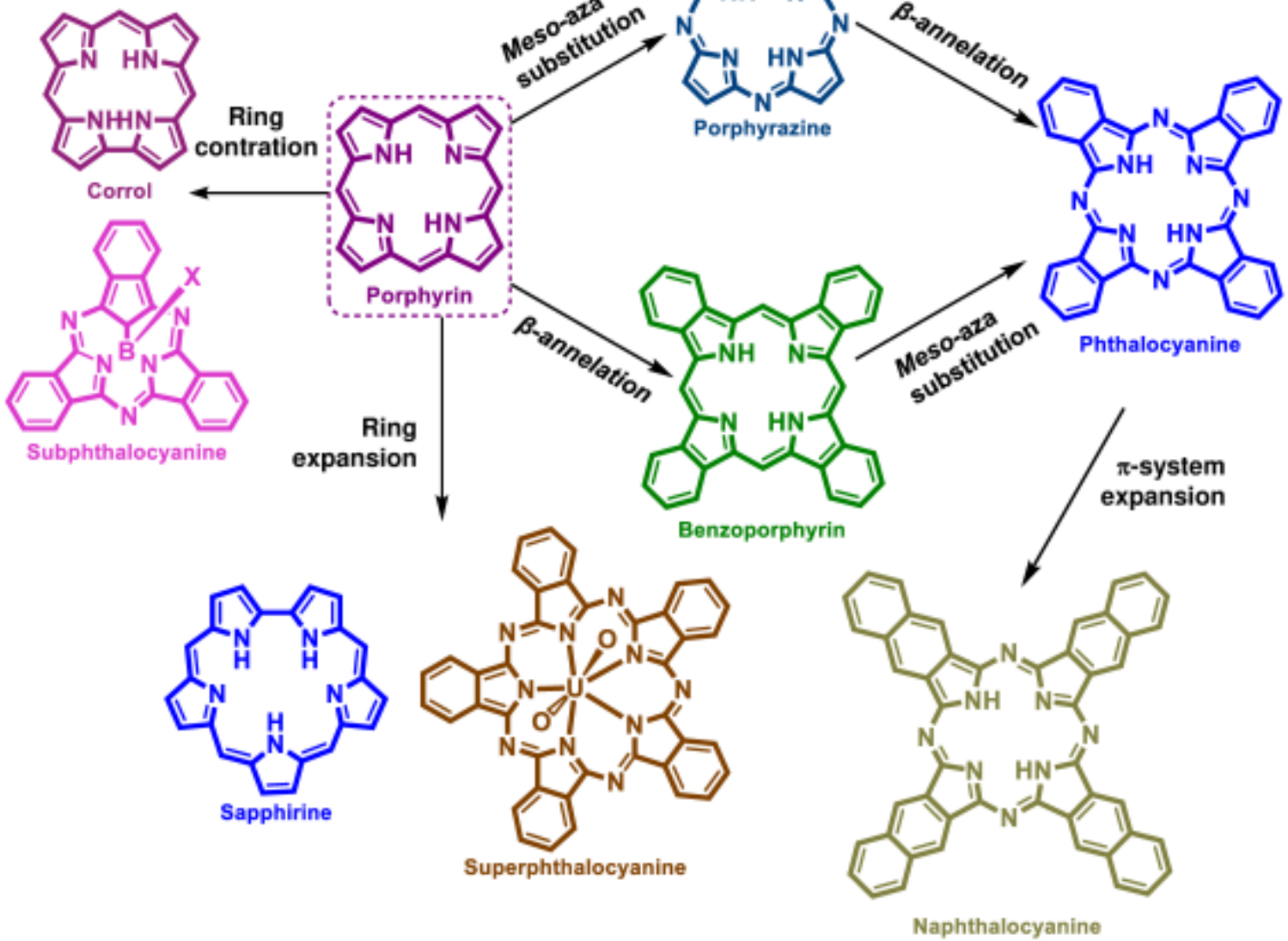


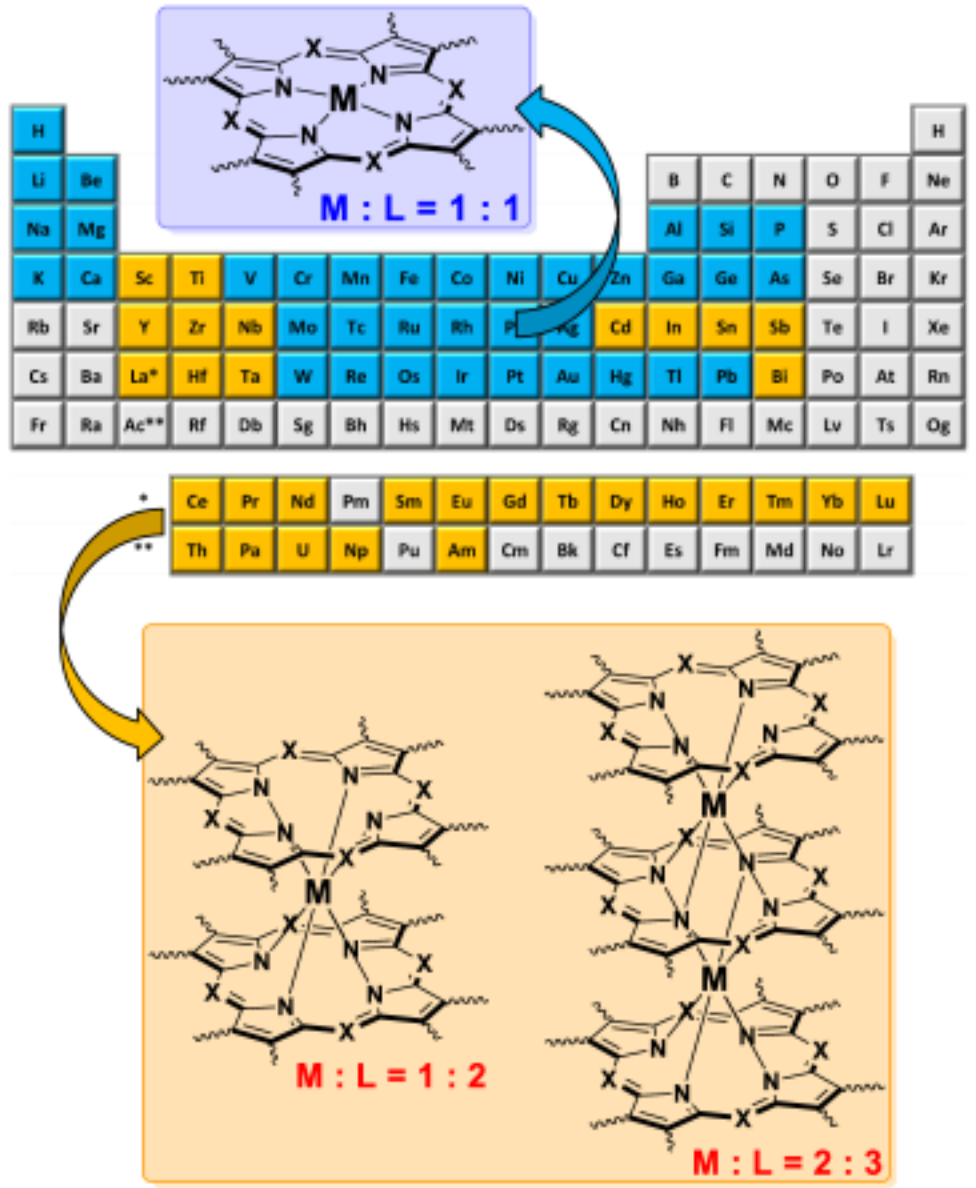


Cu

Turacoverdine - a green pigment in the feathers of banana birds

Synthetic porphyrinoids: structural and functional diversity throughout core modification



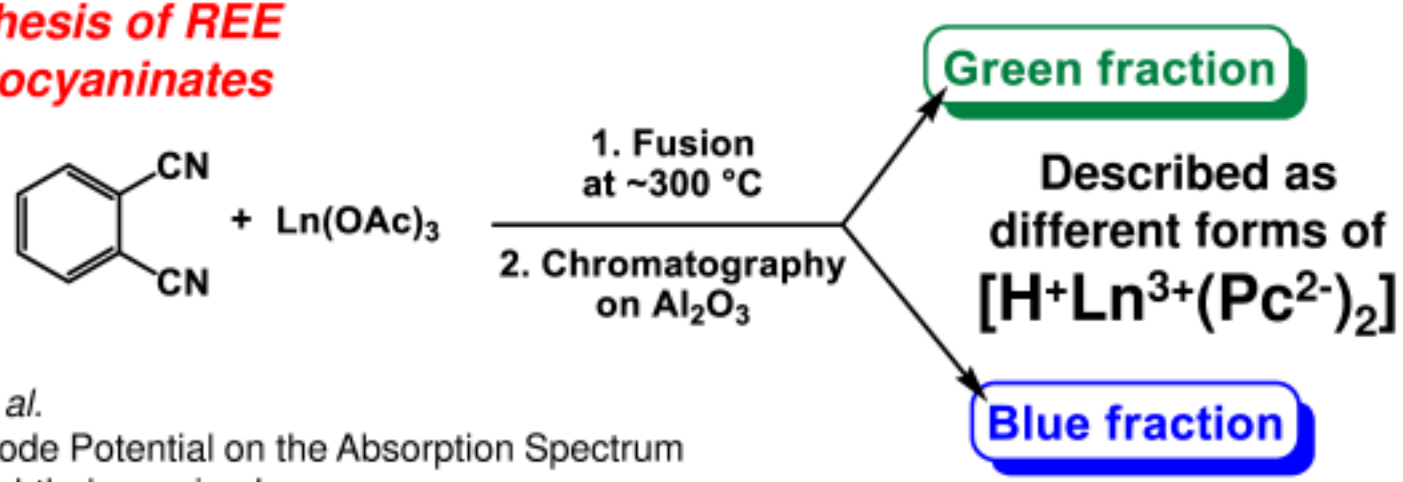


Milestones in the history of sandwich Pc's

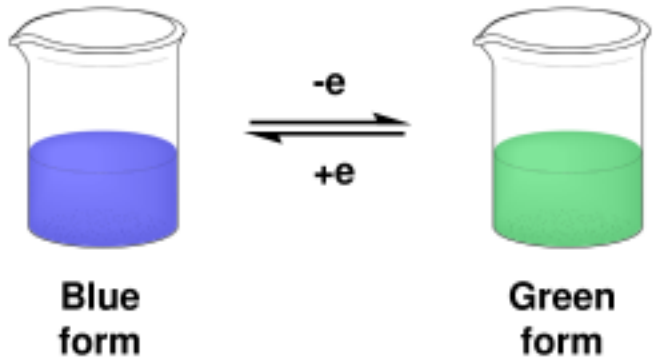
Template reaction between phthalonitrile and $Ln(OAc)_3$

•Kirin I. S. *et al.*
Formation of Unusual Phthalocyanines of the Rare-Earth Elements
Russ. J. Inorg. Chem. **1965**, *10*, 1065

First synthesis of REE bisphthalocyaninates



•Moskalev P. N. *et al.*
Effect of the Electrode Potential on the Absorption Spectrum of a Rare-Earth Diphthalocyanine Layer
Opt. i Spektrosk. **1970**, *29*, 414



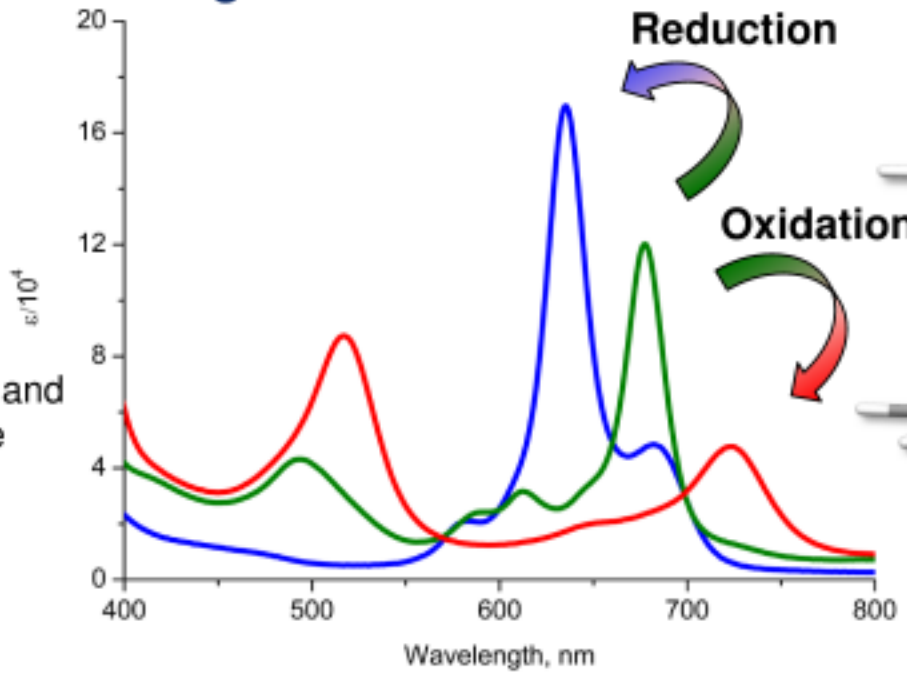
Either acid-base equilibrium or redox-process?

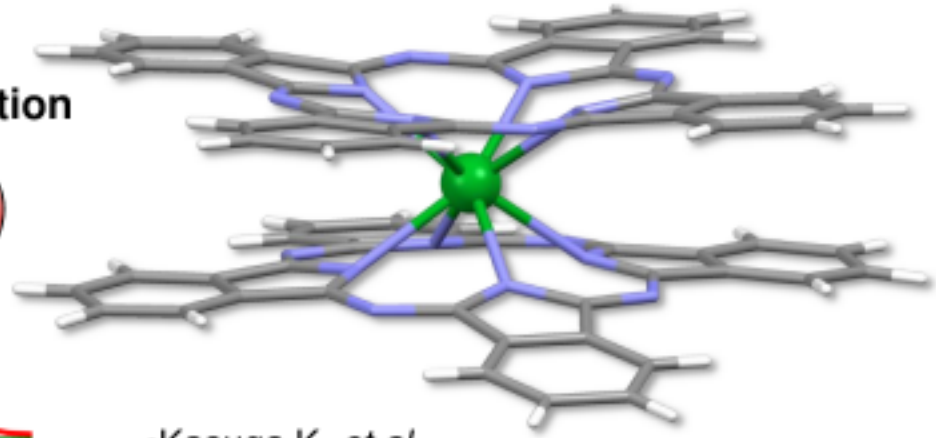
Milestones in the history of sandwich Pc's

Nature of green and blue forms of $LnPc_2$

•Corker G. A. *et al.*
An Explanation of the Electrochromism of Lutetium Diphthalocyanine
J. Electrochem. Soc. **1979**, *126* (8), 1339

•Chang A. T. *et al.*
Preparation and Characterization of Oxidized and Reduced Forms of Lutetium Diphthalocyanine
Inorganica Chim. Acta **1981**, *53*, L241





•Kasuga K. *et al.*
Structure of bis(phthalocyaninato)neodymium(III)
J. Am. Chem. Soc. **1980**, *102* (14), 4835

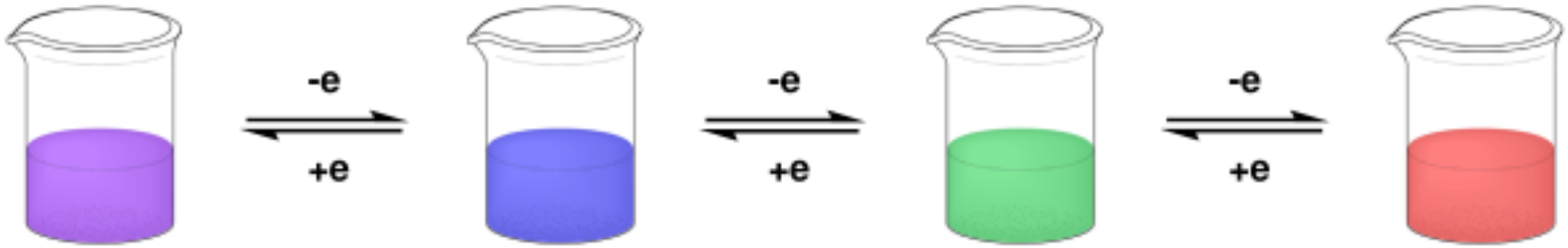
Redox-process is responsible for electrochromism

$[(Pc^{2-})Ln(Pc^{\bullet 3-})]^{2-}$
ESR signal
g=2.002

$[Ln(Pc^{2-})_2]^{-}$
ESR silent

$[(Pc^{2-})Ln(Pc^{\bullet -})]^{0}$
ESR signal
g=2.0033

$[Ln(Pc^{\bullet -})_2]^{+}$
ESR silent

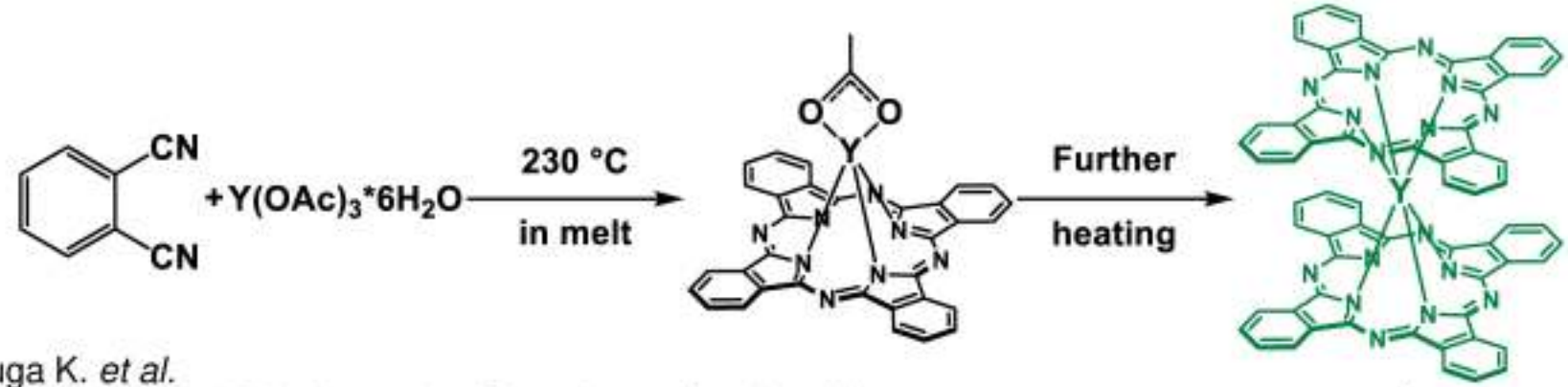


Violet form | **Blue form** | **Green form** | **Red form**

•De Cian A. *et al.*
Synthesis, Structure, and Spectroscopic and Magnetic Properties of lutetium(III) Phthalocyanine Derivatives: $LuPc_2 \cdot CH_2Cl_2$ and $[LuPc(OAc)(H_2O)_2] \cdot H_2O \cdot 2CH_3OH$
Inorg. Chem. **1985**, *24* (20), 3162

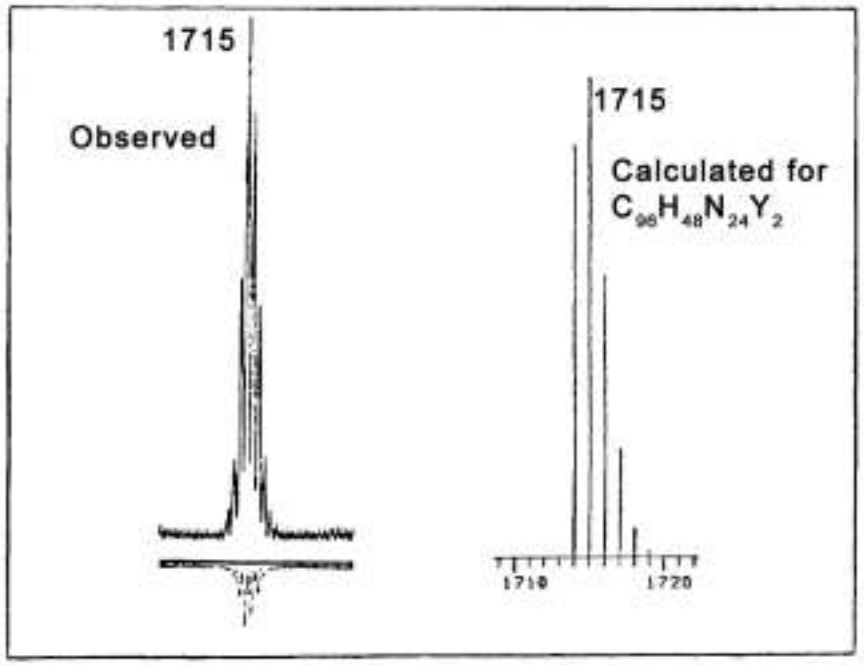
Milestones in the history of sandwich Pc's

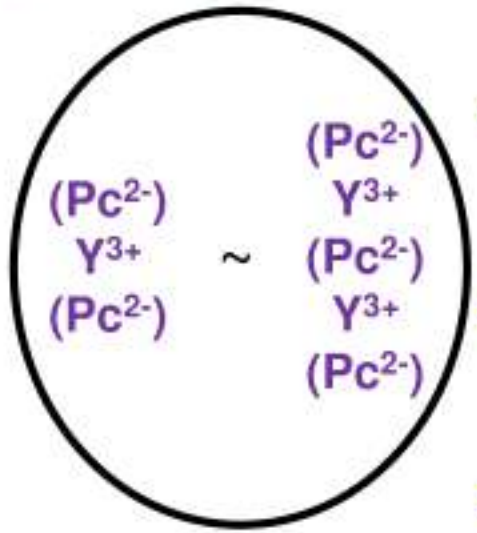
One more blue form isolated in template synthesis of $LnPc_2$



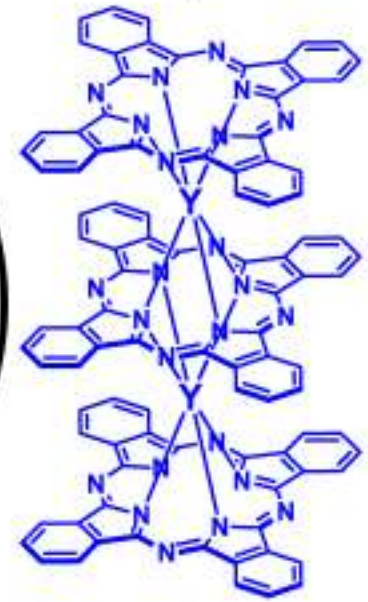
•Kasuga K. *et al.*
Preparation of New Phthalocyanine Complexes of yttrium(III) and Some Lanthanoid(III) Ions
Chem. Lett. **1986**, *2* (7), 1095

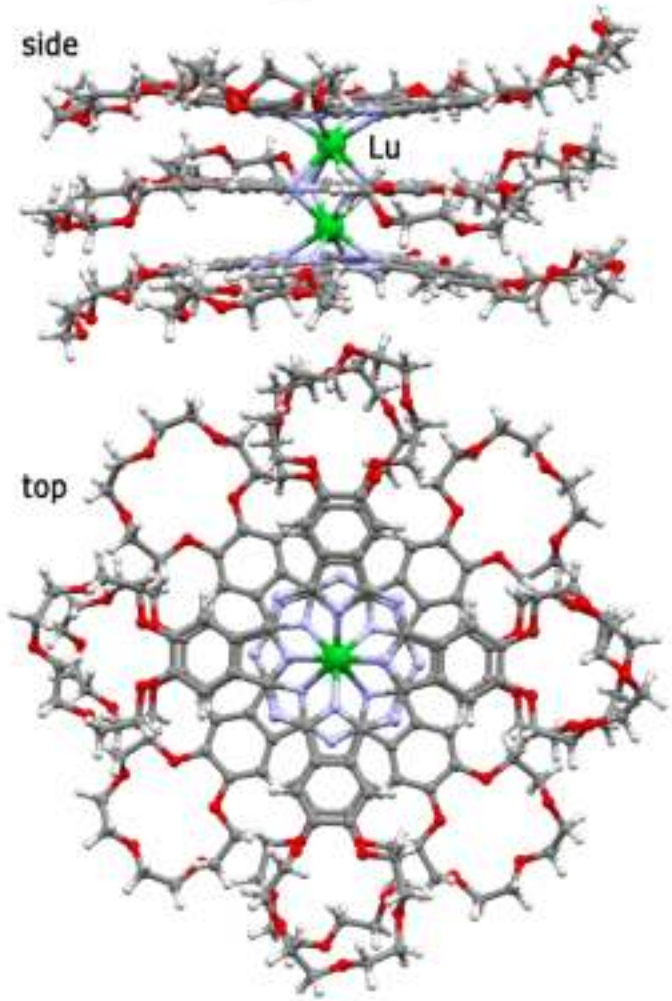
First evidence of REE triple-decker phthalocyaninate





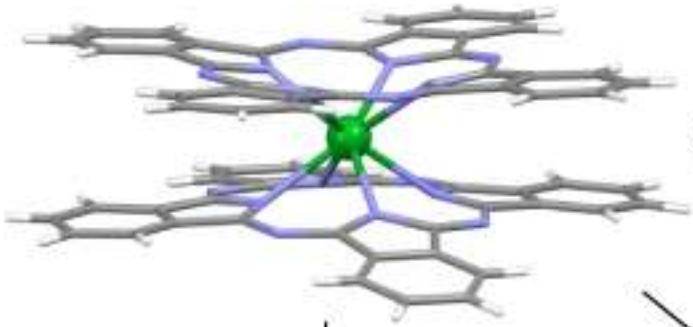
Further heating





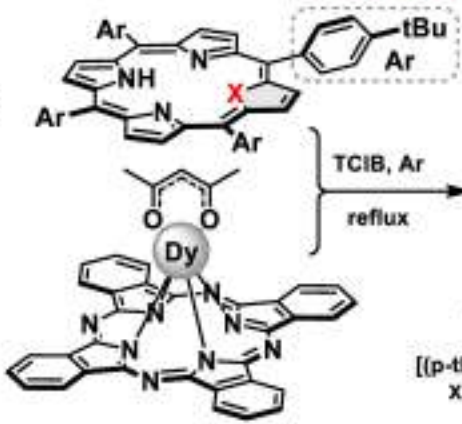
•Troyanov C. I. *et al.*
Crystal structure of tristetra(15-crown-5) phthalocyaninatodilutetium(III)
Doklady Chem. **1999**, *367* (5), 192

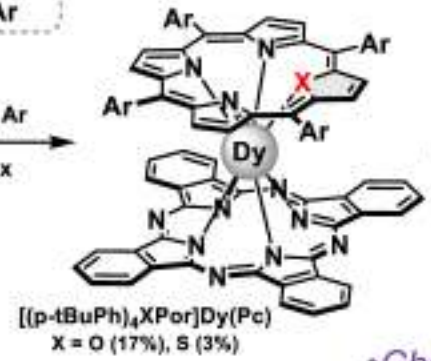
From prototypical double-decker to sophisticated sandwiches



Complexes with core-modified ligands

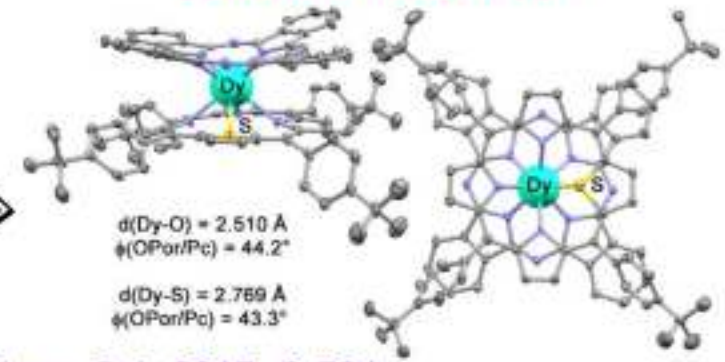
Oxa- and thia-porphyrins





[(p-tBuPh)$_4$XPor]Dy(Pc)
X = O (17%), S (3%)

Largest anisotropy in Dy(III) sandwich tetrapyrrols

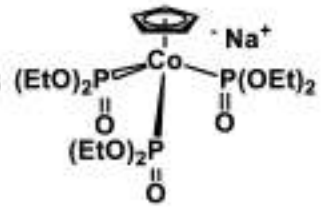


•*Chem. Sci.*, **2015**, *6*, 594

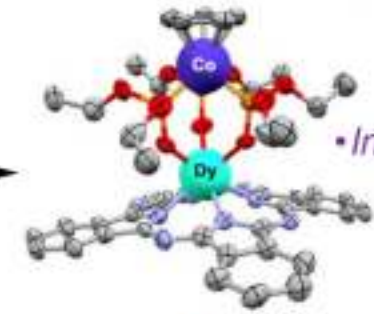
Sandwiches with non-tetrapyrrlic ligands

•*Chem. Commun.*, **2015**, *51*, 5986

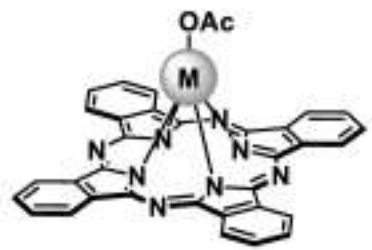
Sandwiches with axial metalloligands



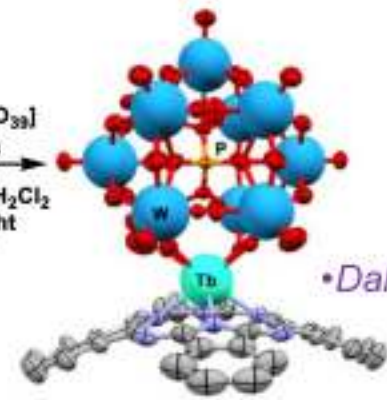
CH$_3$CN, MeOH, 100 °C



•*Inorg. Chem.*, **2013**, *52*, 6407



(NBu$_4$)$_4$H$_3$[PW$_{11}$O$_{39}$]
NBu$_4$Br, NEt$_3$
CH$_3$CH, MeOH, CH$_2$Cl$_2$
50 °C, overnight

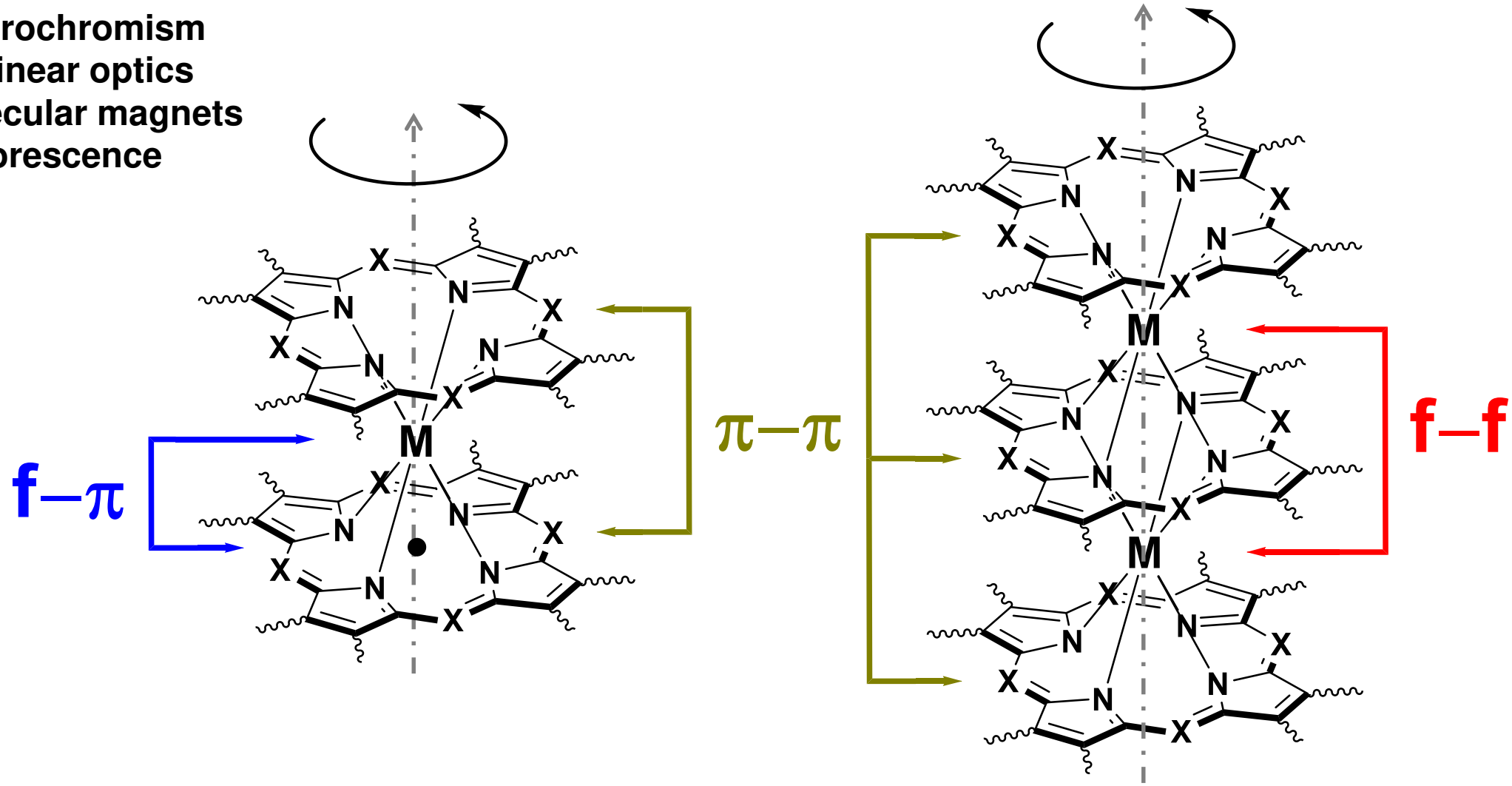


•*Dalton Trans.*, **2020**, *49*, 16638

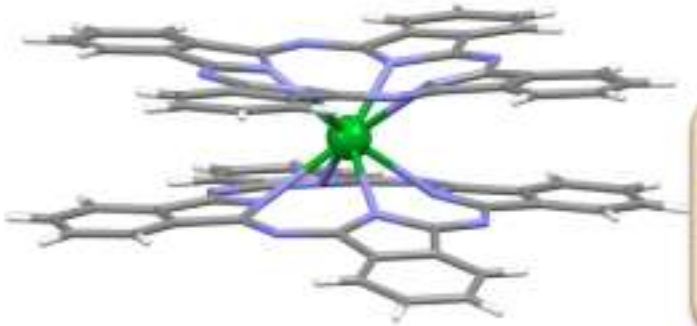
Electronic interactions in sandwich complexes

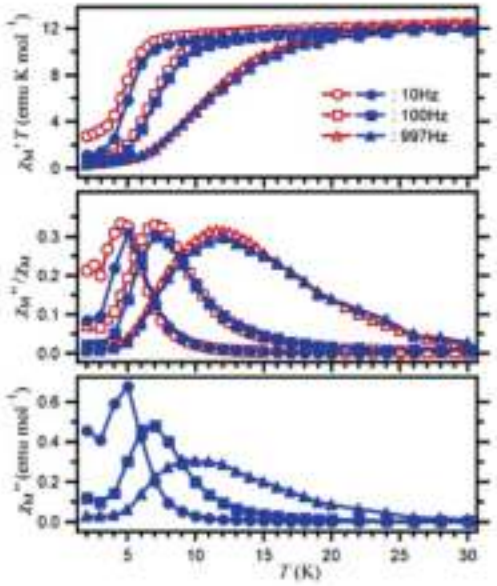
- electrochromism
- nonlinear optics
- molecular magnets
- f-fluorescence

etc.



Early years timeline of single molecule magnets





Transition-metal SMMs

Polynuclear SMMs

Mn_{12} Mn_4 Mn_8 Mn_{84} Mn_{19} Mn_6

Single-ion SMMs

Fe Co

1993 2003 2006 2007 2011

Single-ion SMMs

$LnPc_2$

Tb_2Cu_2 Dy_3 Dy_4 Dy_5

Polynuclear SMMs

N_2^{3-} / Dy_2, Tb_2

Lanthanide SMMs (4*f* / 3*d*-4*f*)

•Ishikawa, N. et al.
Lanthanide Double-Decker Complexes Functioning as Magnets at the Single-Molecular Level.
J. Am. Chem. Soc. **2003**, *125* (29), 8694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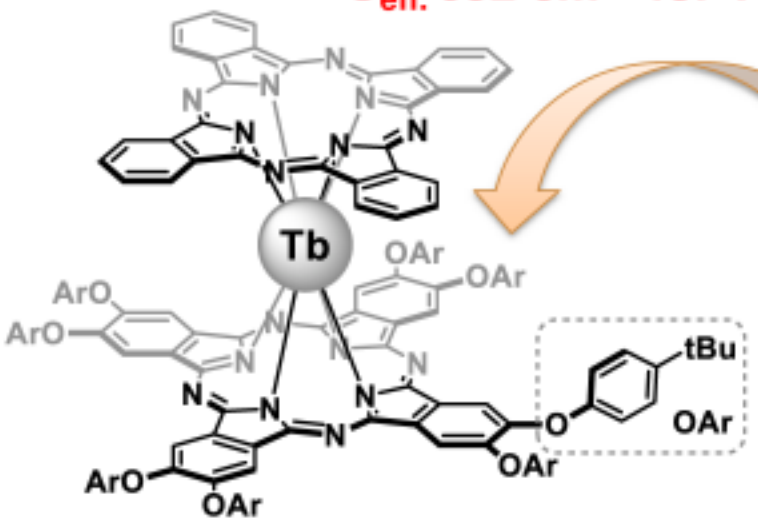
Review

Single-molecule magnetism of tetrapyrrole lanthanide compounds with sandwich multiple-decker structures

Hailong Wang[a], Bing-Wu Wang[b], Yongzhong Bian[a], Song Gao[b,*], Jianzhuang Jiang[a,*]

Why is molecular magnetism still studied on examples of lanthanide sandwiches with tetrapyrrolic ligands?

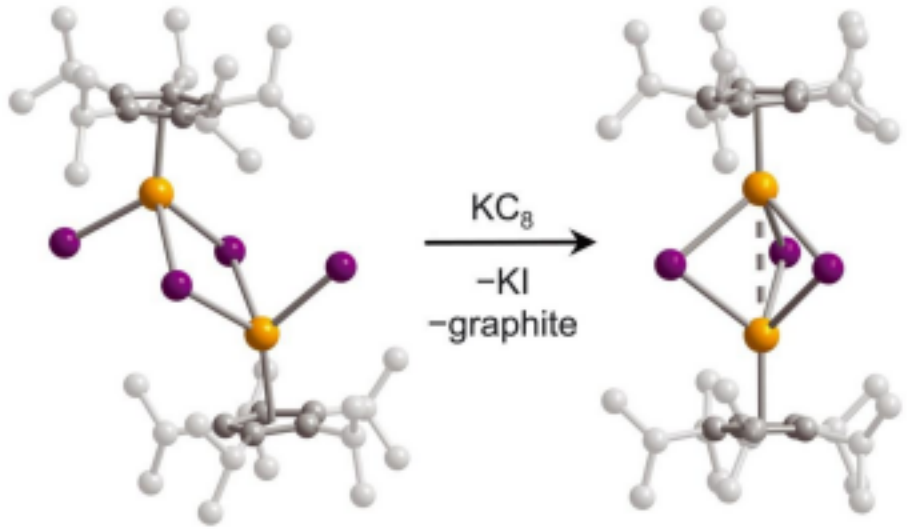
$U_{eff.}$ 652 cm^{-1} for Tb



Phthalocyanine-based sandwiches

- Relatively facile synthesis
- Stable towards aerobic conditions, moisture and high temperatures
- Highly soluble
- Easily processable, forming crystals, thin films, hybrid materials, etc.

$U_{eff.}$ 1383(45) cm^{-1} for Tb, 1631(25) cm^{-1} for Dy



$(Cp^{iPr5})_2Ln_2I_4$
Ln = Y, Gd, Tb, Dy

$(Cp^{iPr5})_2Ln_2I_3$ (1-Ln)
Ln = Y, Gd, Tb, Dy

•Ganivet, C. R.; Ballesteros, B.; de la Torre, G.; Clemente-Juan, J. M.; Coronado, E.; Torres, T.

Influence of Peripheral Substitution on the Magnetic Behavior of Single-Ion Magnets Based on Homo- and Heteroleptic Tb(III) Bis(Phthalocyaninate).

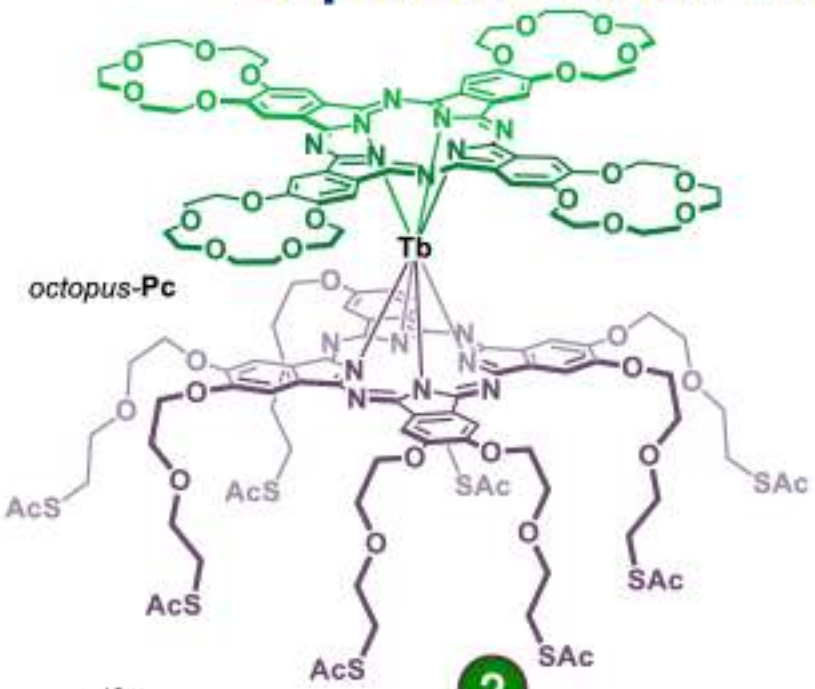
Chem. Eur. J. **2013**, *19* (4), 1457–1465
DOI: 10.1002/chem.201202600.

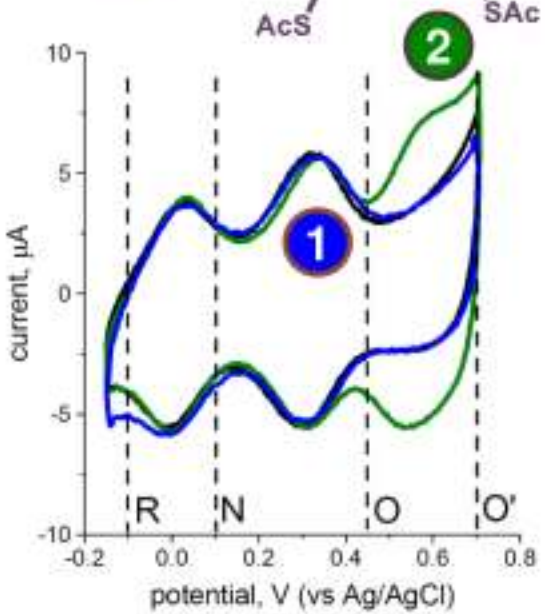
•Gould, C. A.; McClain, K. R.; Reta, D.; Kragskow, J. G. C.; Marchiori, D. A.; Lachman, E.; Choi, E.-S.; Analytis, J. G.; Britt, R. D.; Chilton, N. F.; Harvey, B. G.; Long, J. R.

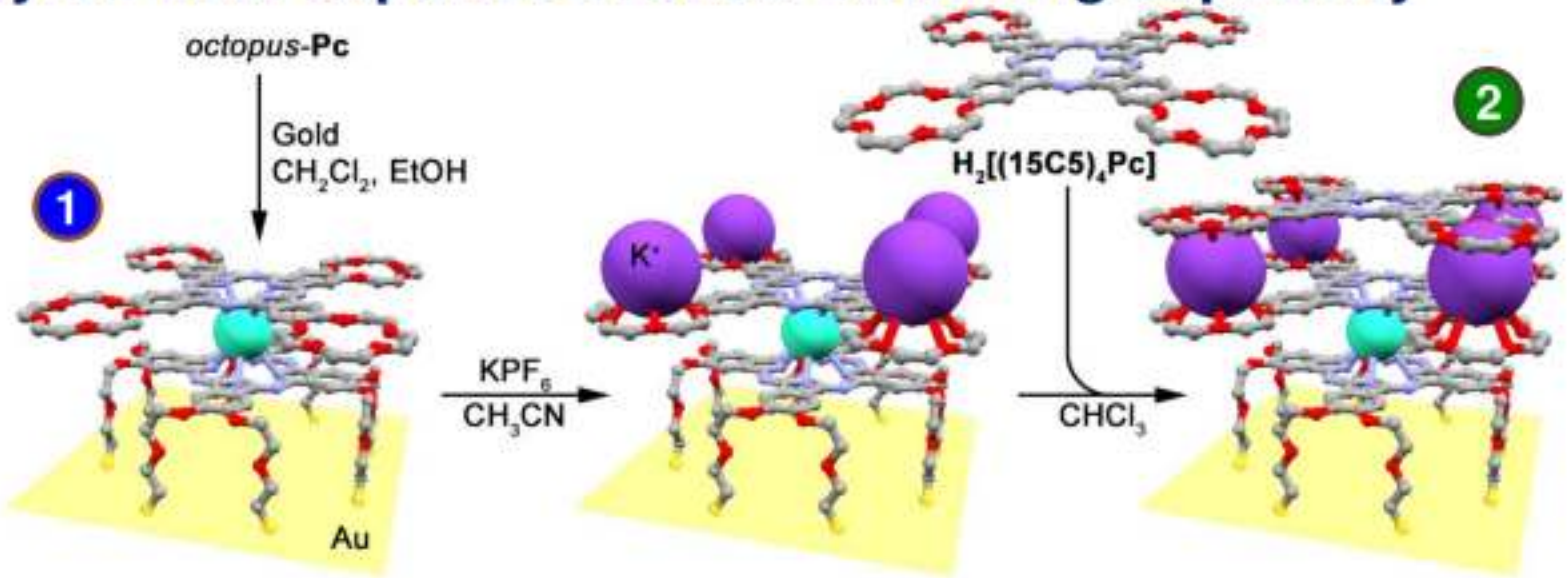
Ultrahard Magnetism from Mixed-Valence Dilanthanide Complexes with Metal-Metal Bonding.

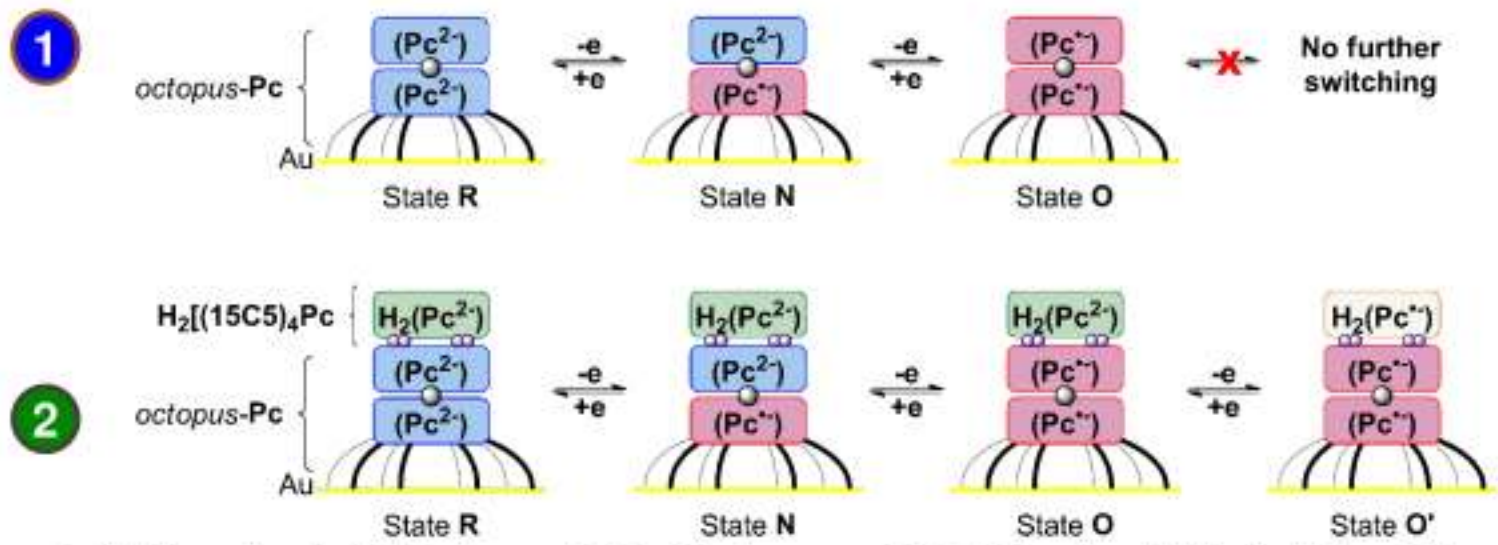
Science **2022**, *375* (6577), 198–202
DOI: 10.1126/science.abl5470.

Octopus-type crown-bisphthalocyaninate anchor for bottom-up assembly of supramolecular bilayers with expanded redox-switching capability



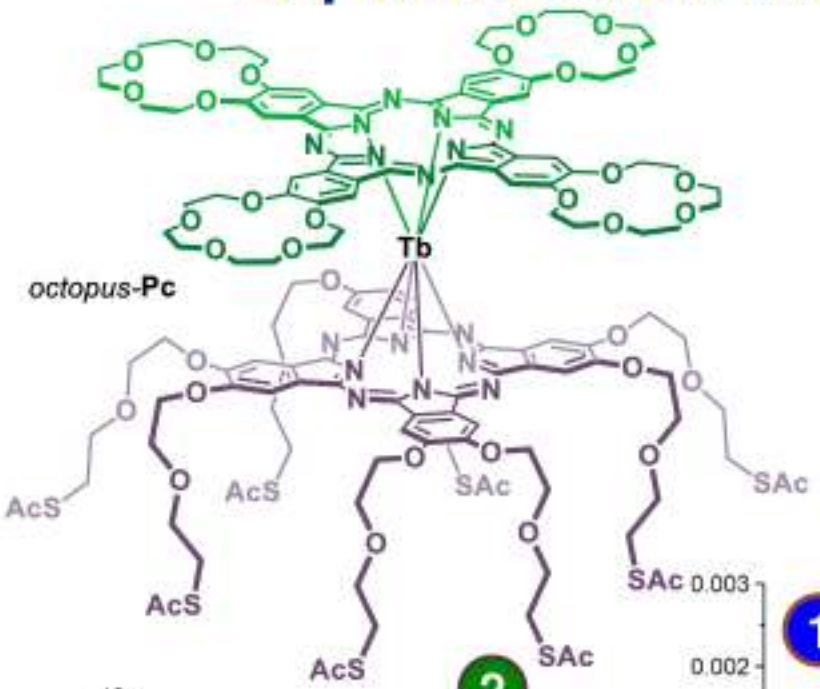


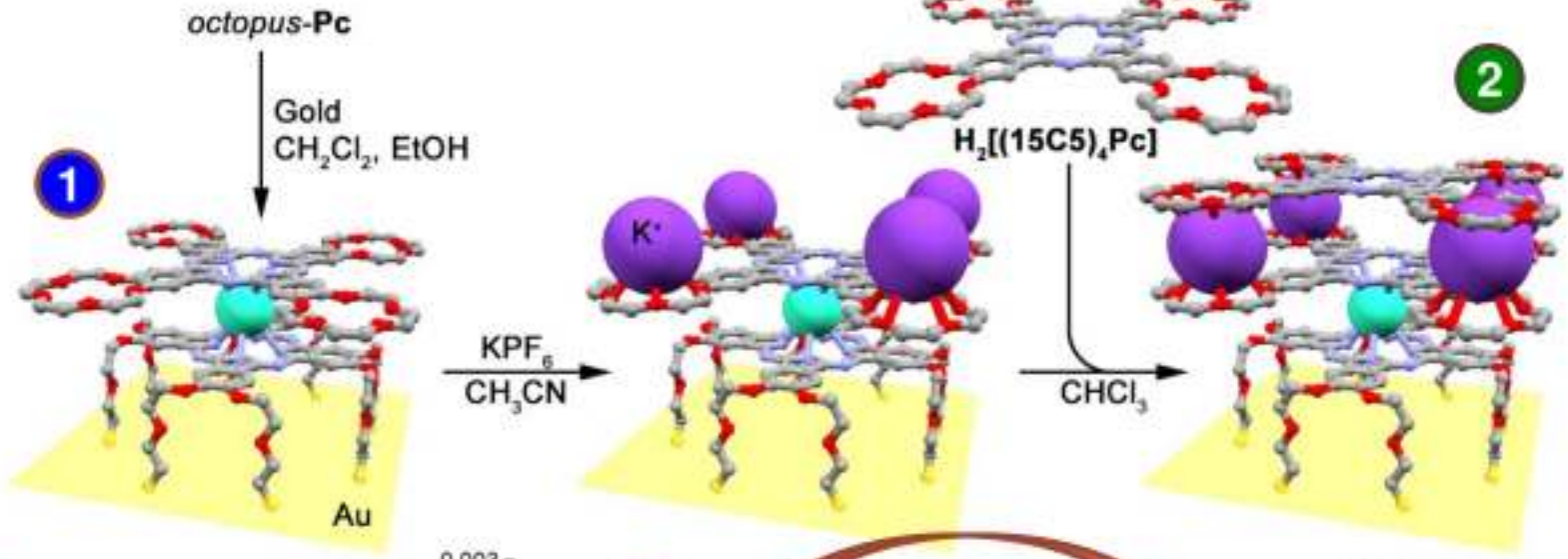


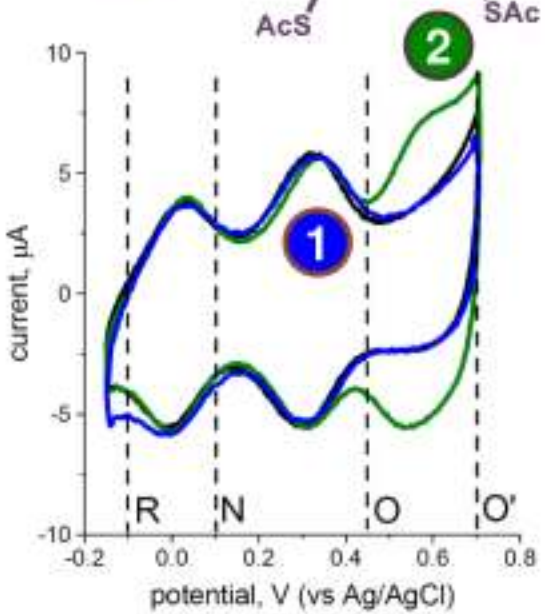


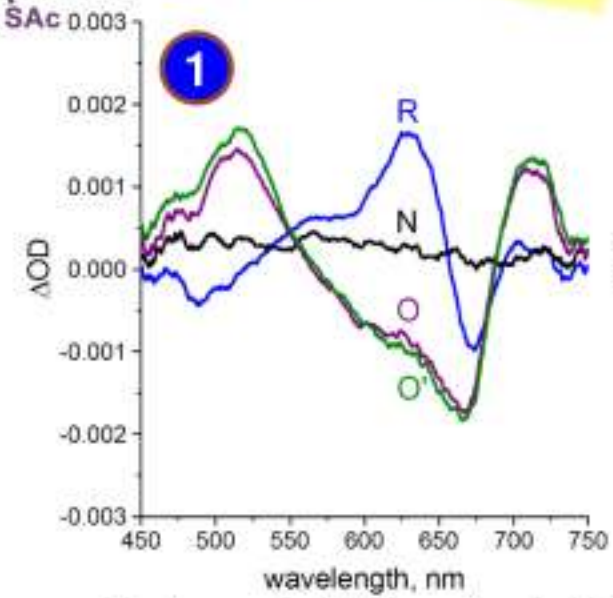
•Shokurov, A. V.; Yagodin, A. V.; Martynov, A. G.; Gorbunova, Y. G.; Tsivadze, A. Y.; Selektor, S. L. *Small* **2021**, 2104306

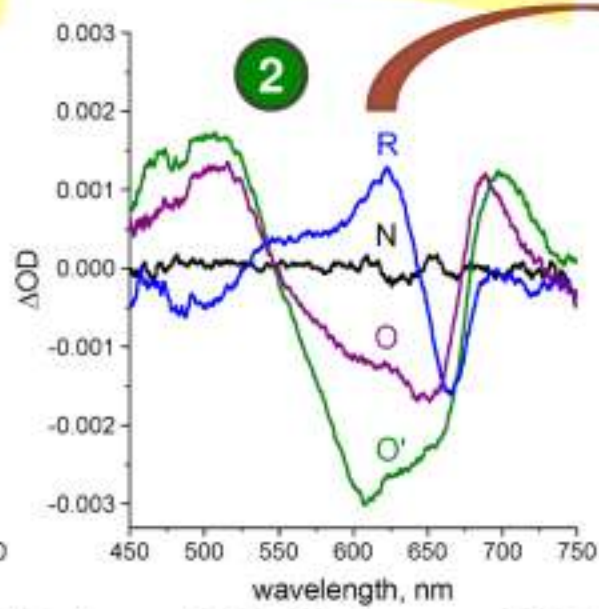
Octopus-type crown-bisphthalocyaninate anchor for bottom-up assembly of supramolecular bilayers with expanded redox-switching capability



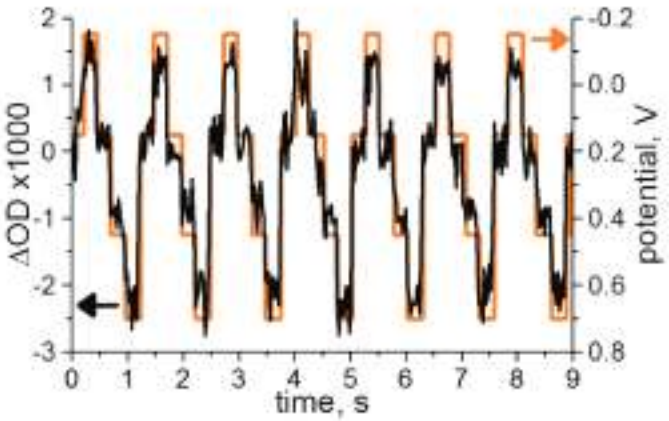








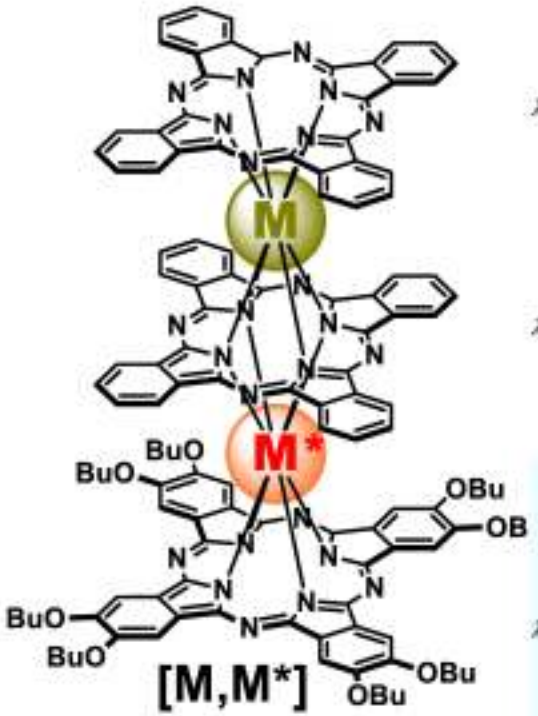
Reversibility and reproducibility

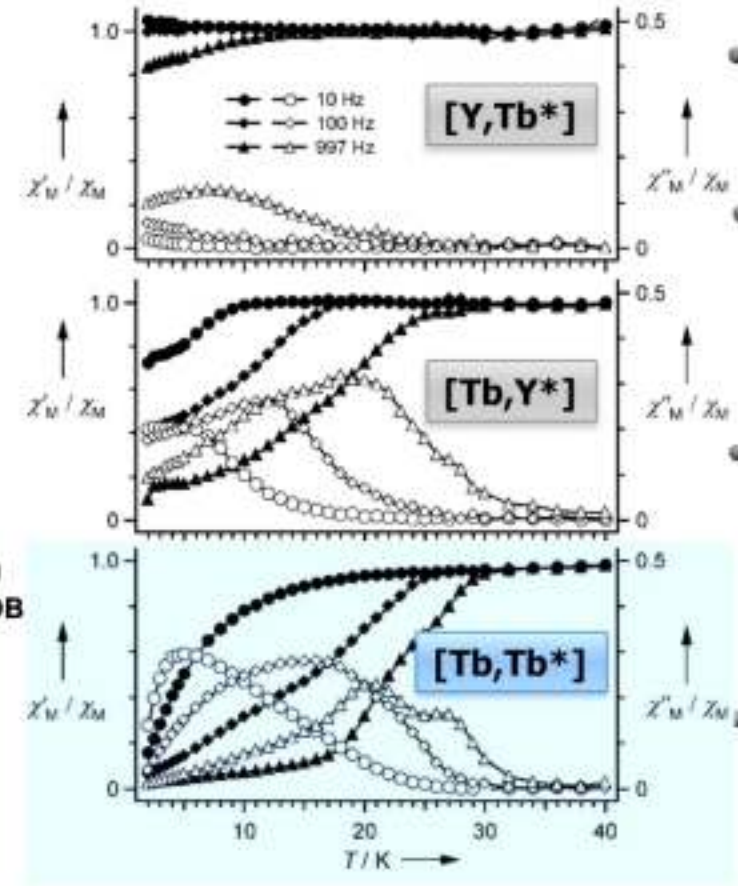


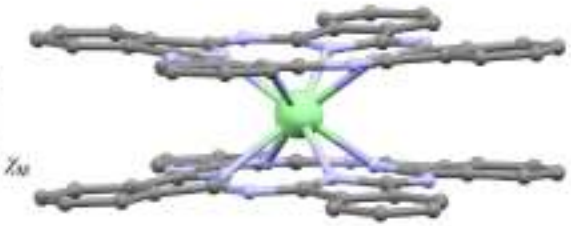
•Shokurov, A. V.; Yagodin, A. V.; Martynov, A. G.; Gorbunova, Y. G.; Tsivadze, A. Y.; Selektor, S. L. *Small* **2021**, 2104306

Triple-decker complexes as multinuclear SMM

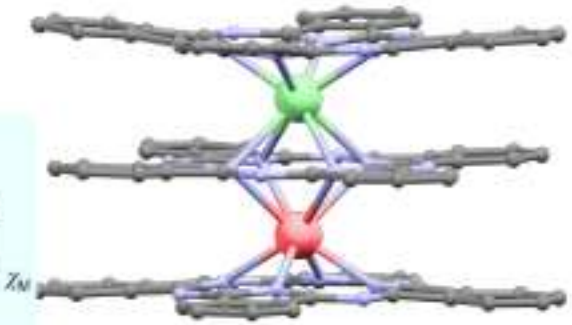
•<u>Heteronuclear</u> complexes are single-ion field-induces SMMs due to QTM in contrast to double-decker complexes which reveal SMM behavior in zero dc field





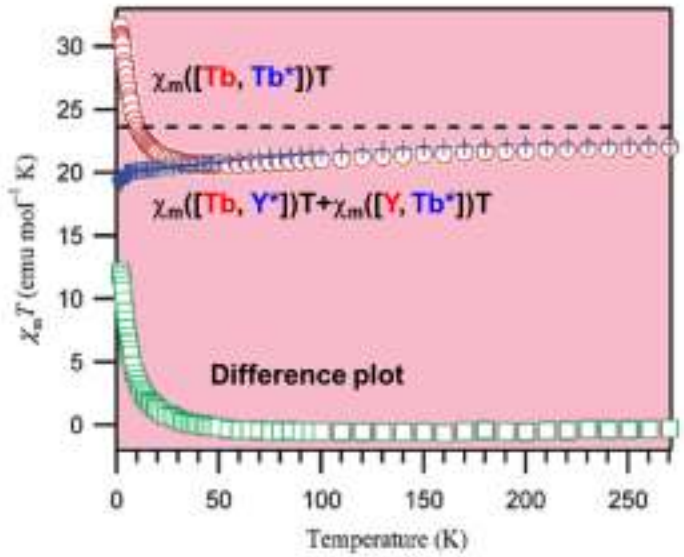


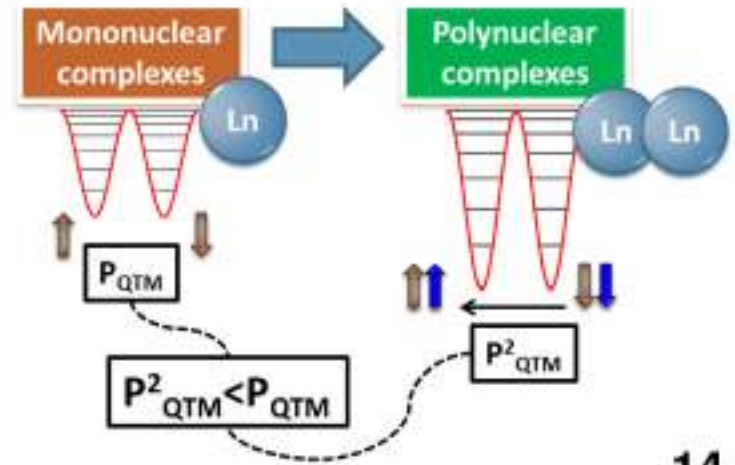
Ln-N bonds are equivalent
Tb^{3+} ion symmetry = D_{4h}



Ln-N^{out} are shorter by ~0.3Å than Ln-N^{inner}
Tb^{3+} ion symmetry = C_{4v}

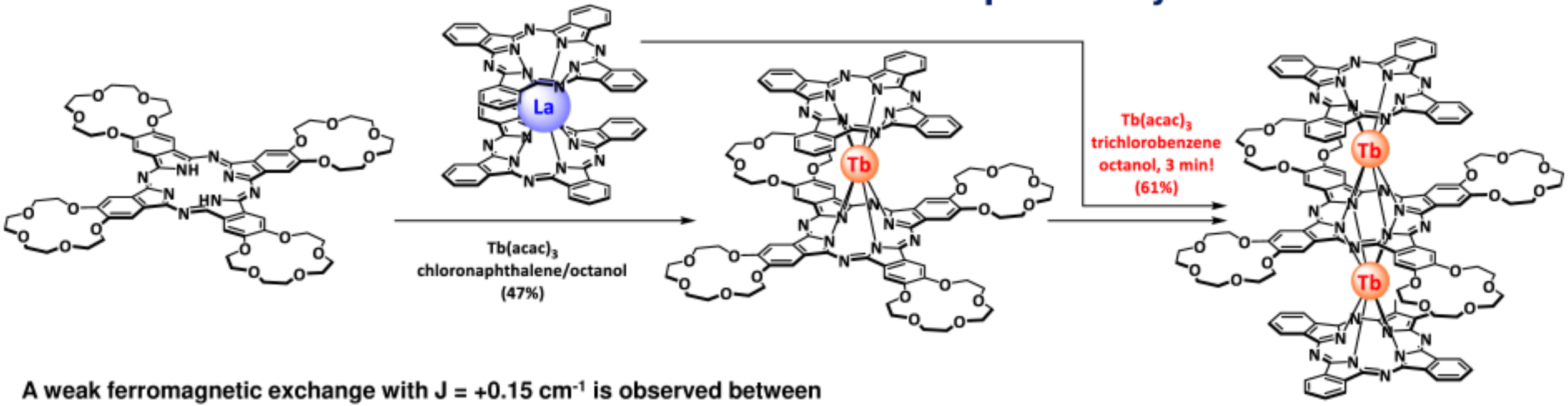
•<u>Homonuclear</u> complexes are SMM in zero field due to suppress of QTM via ferromagnetic Tb…Tb interactions





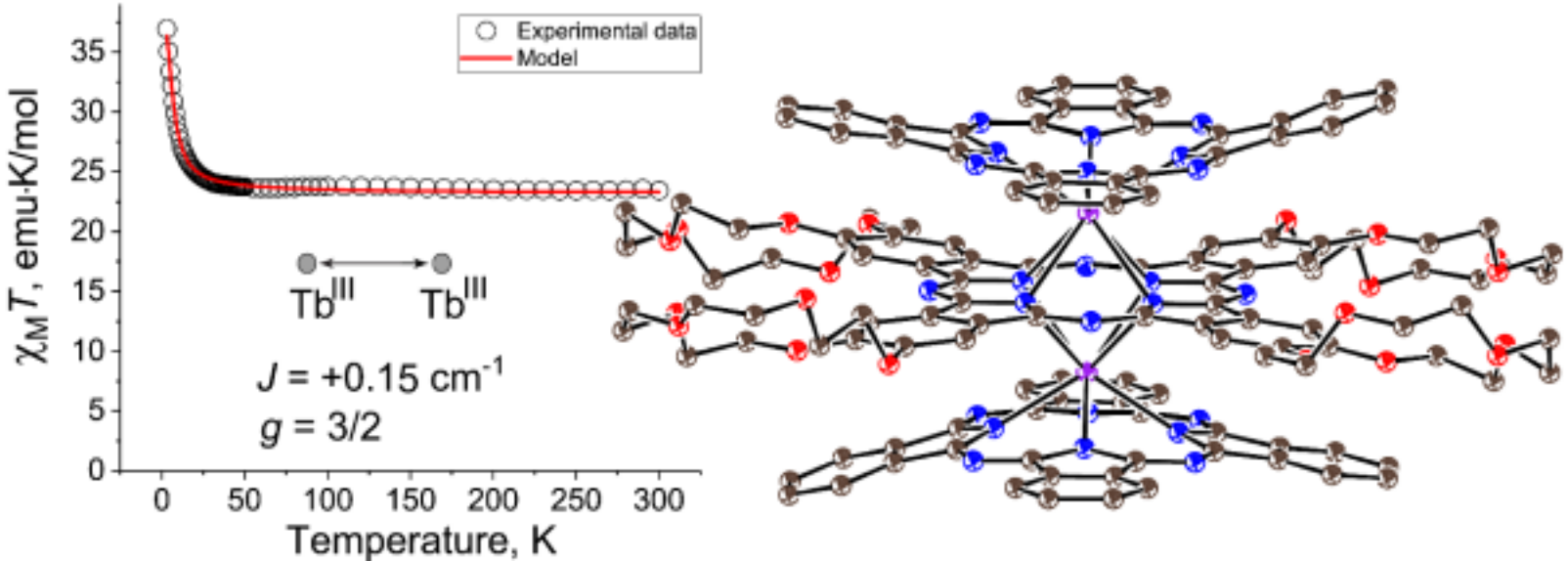
•Ishikawa, N. et al.
The Effect of the f–f Interaction on the Dynamic Magnetism of a Coupled $4f^8$ System in a Dinuclear Terbium Complex with Phthalocyanines.
Angew. Chemie Int. Ed. **2005**, *44* (5), 731

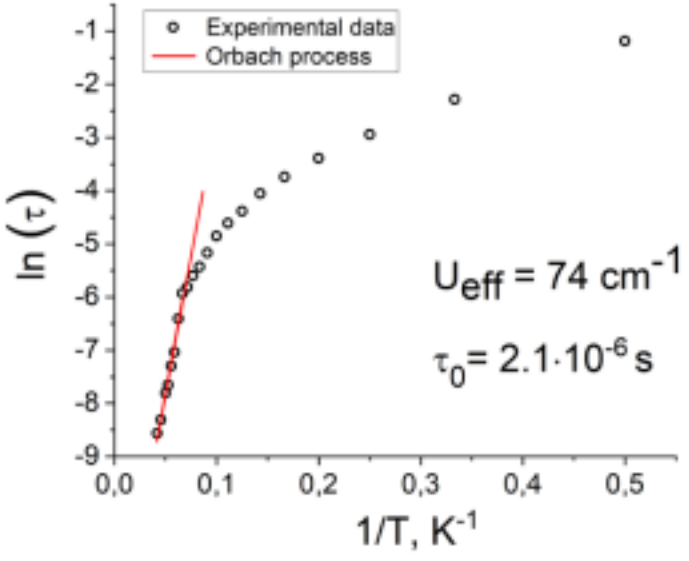
SMM behavior of crown-substituted trisphthalocyaninates



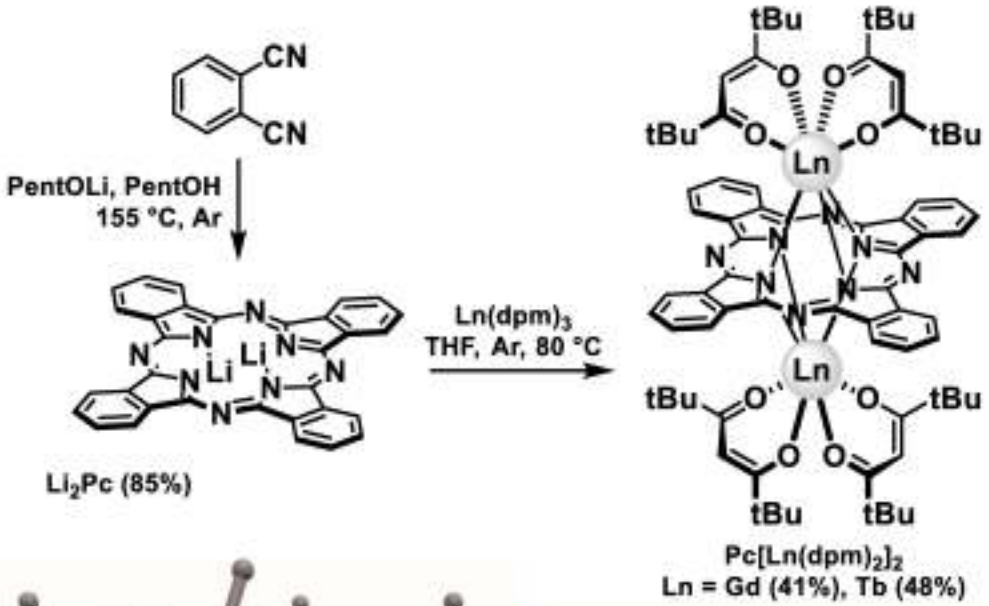
A weak ferromagnetic exchange with J = +0.15 cm^{-1} is observed between the spins of the two terbium ions. At T< 35K the terbium spins are ordered in parallel and the $\chi_M T$ value increases from 23.3 to 37.0 emu K/mol.

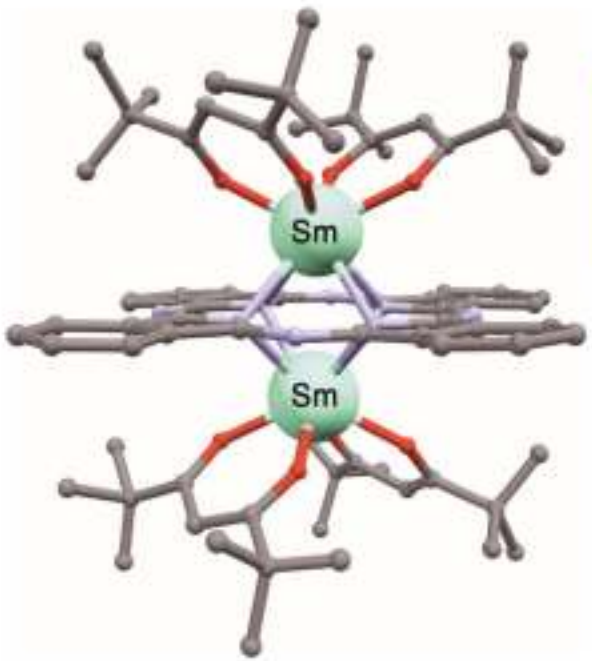
At the same time, the compound is a single molecule magnet with the barrier U_{eff} = 74 cm^{-1} or 105 K.





“Inverted” sandwich – one Pc ligand between two Ln metal centers





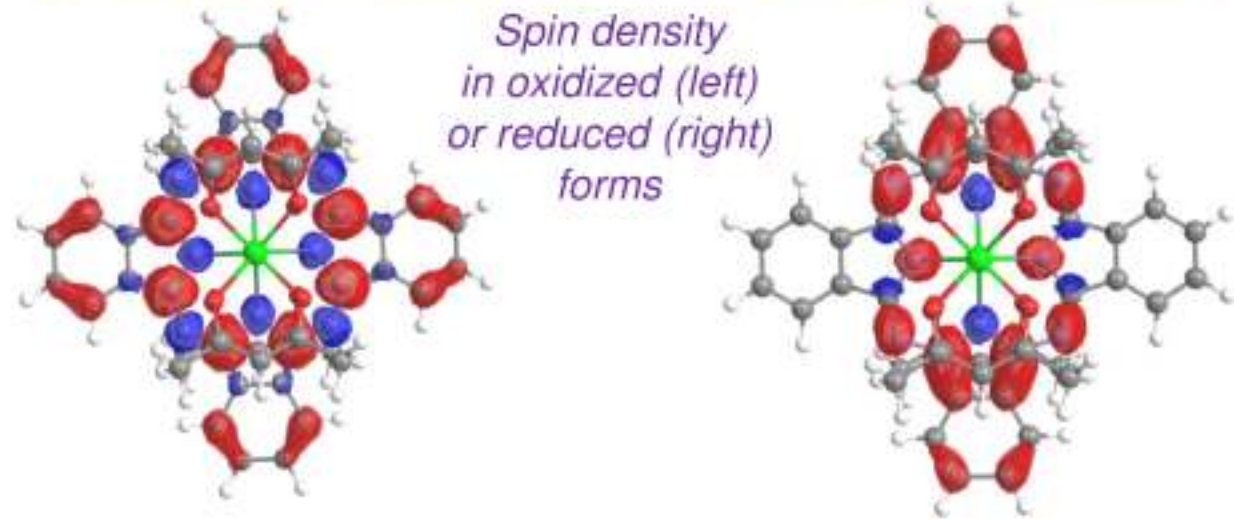
•First report on exchange interaction between Ln ions

•Maeda, A.; Sugimoto, H.

Intramolecular Exchange Interaction between Two Rare-Earth Ions.

J. Chem. Soc. Faraday Trans. 2 **1986**, *82* (11)

Phthalocyanine ligand can be a reservoir for one additional spin center due to oxidation or reduction

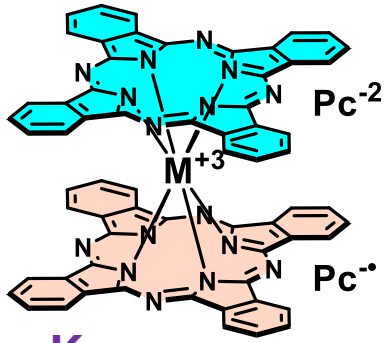


Spin density in oxidized (left) or reduced (right) forms

Complex undergoes demetallation upon reduction

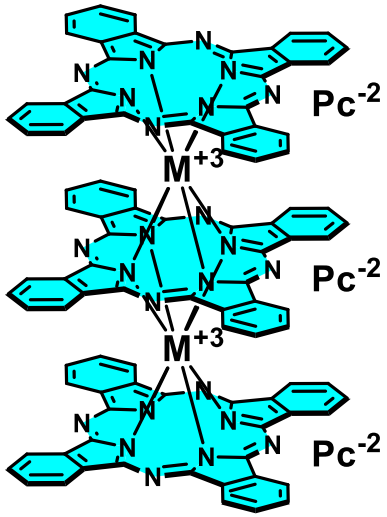
$$Pc[Tb(dpm)_2]_2 \xrightarrow[o\text{-dichlorobenzene}]{Co(Cp^*)_2} H_2Pc{\bullet}Co(Cp^*)_2{\bullet}C_6H_4Cl_2$$

Can we introduce more than three decks and more than two lanthanide ions in sandwich complexes?

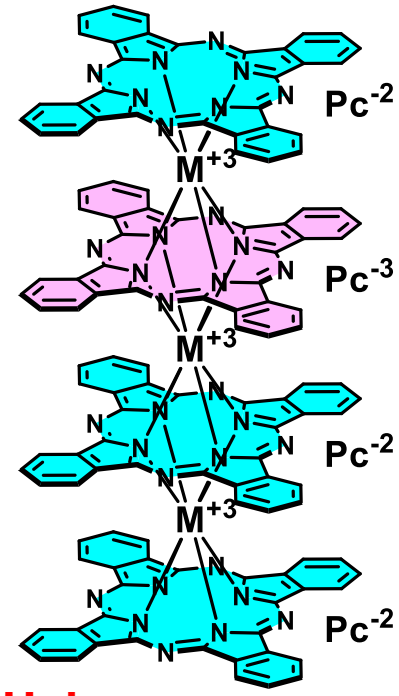


Known
Stable

Electrostatic limitation



Known
Stable



Unknown

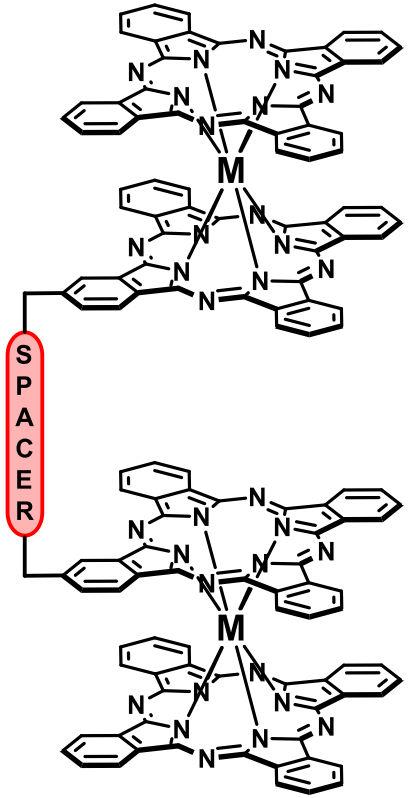
Only few reports on highly reduced sandwich complexes, including

•Konarev, D. V.; Khasanov, S. S.; Batov, M. S.; Martynov, A. G.; Nefedova, I. V.; Gorbunova, Y. G.; Otsuka, A.; Yamochi, H.; Kitagawa, H.; Lyubovskaya, R. N.

Effect of One- and Two-Electron Reduction of Terbium(III) Double-Decker Phthalocyanine on Single-Ion Magnet Behavior and NIR Absorption.

Inorg. Chem. **2019**, *58* (8), 5058

How to overcome electrostatic limitation?



Spacers:

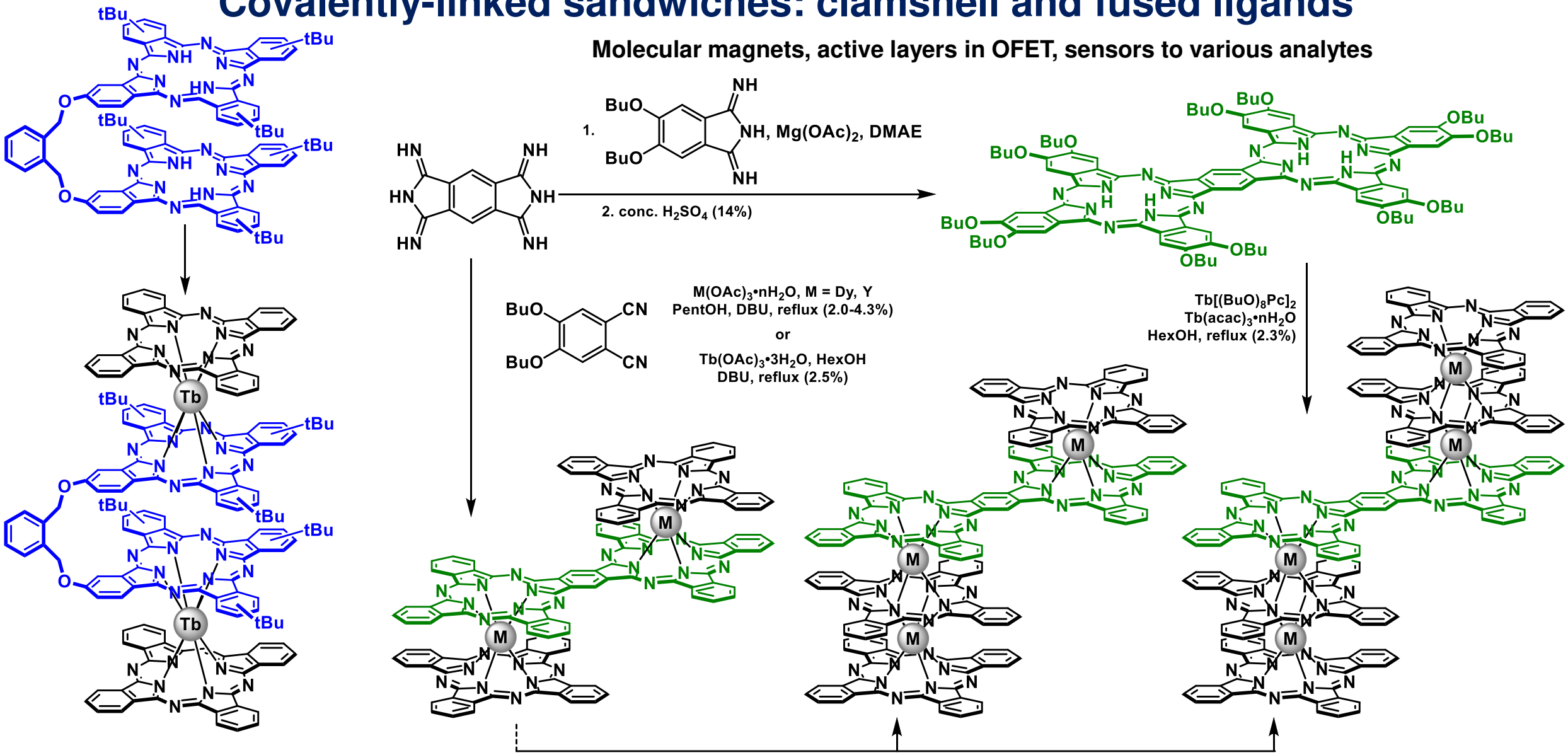
-covalent

-coordination

-supramolecular

Covalently-linked sandwiches: clamshell and fused ligands

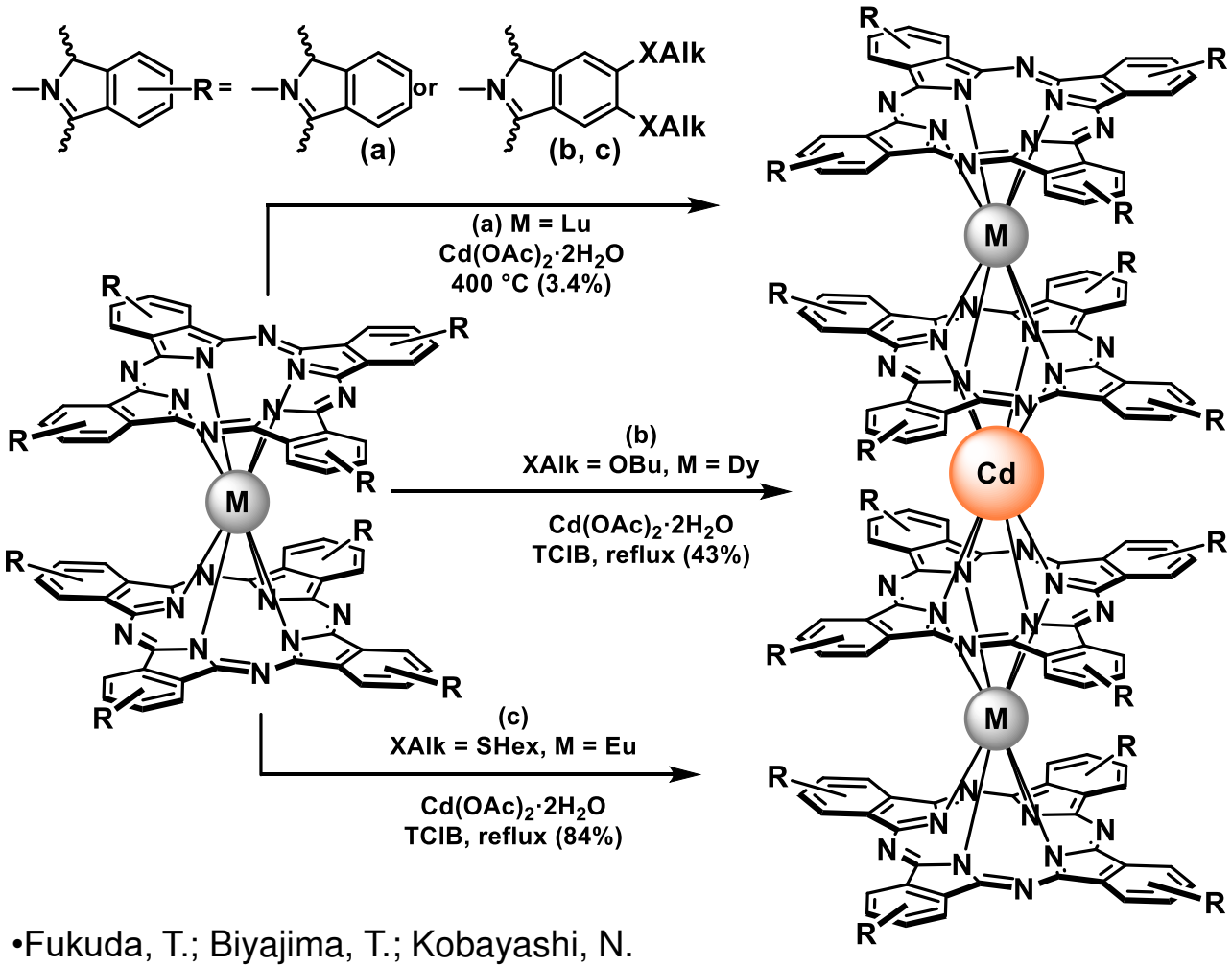
Molecular magnets, active layers in OFET, sensors to various analytes

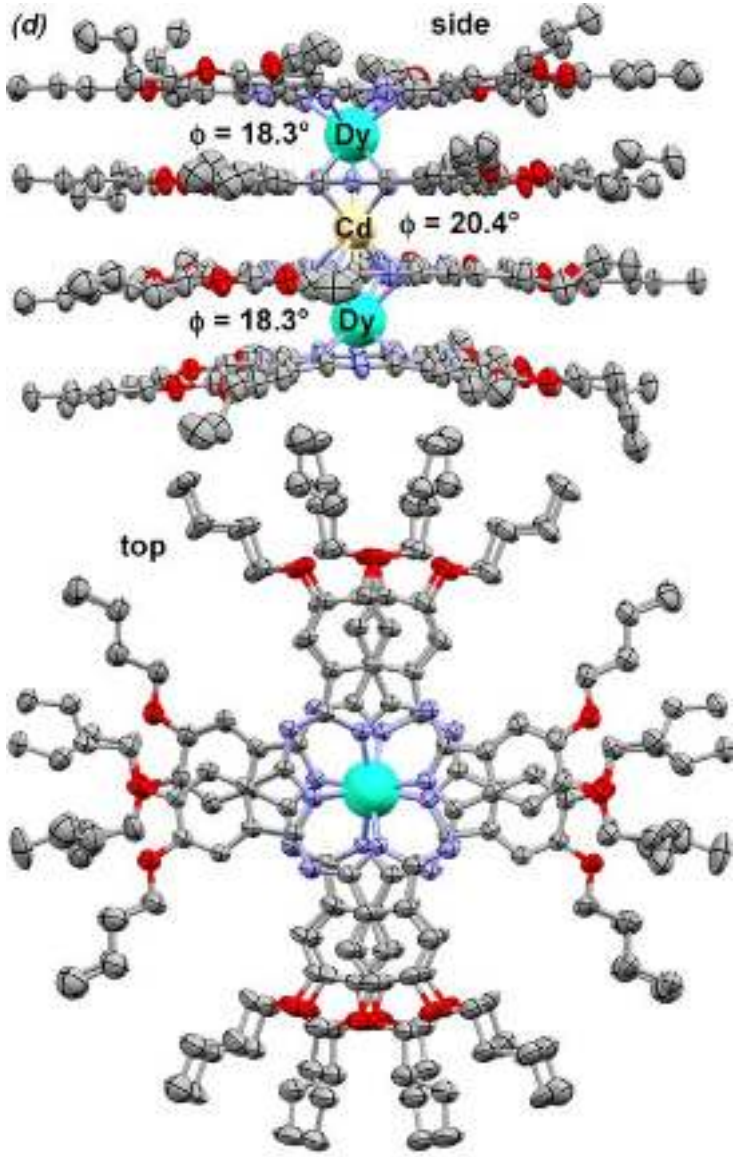


•Pushkarev, V. E. et al.
Chem. Eur. J. **2012**, *18* (29), 9046

•Wang, K. et al.
Chem. Eur. J. **2013**, *19* (34), 11162

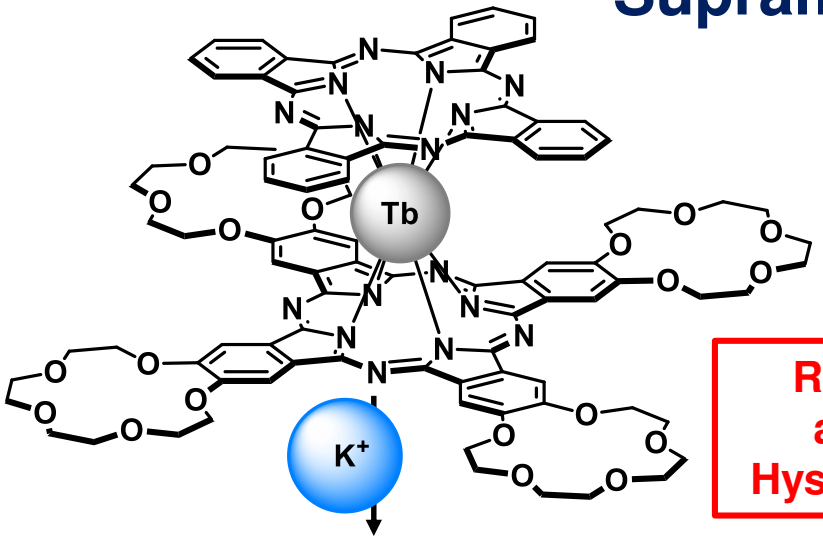
Coordination bonds linking double-deckers into multidecker sandwiches



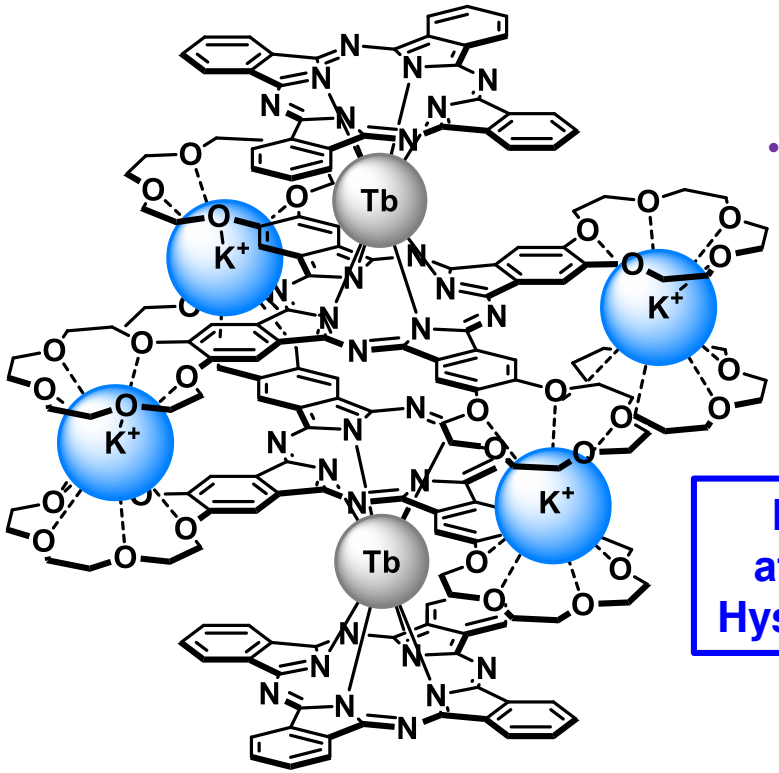


•Fukuda, T.; Biyajima, T.; Kobayashi, N.
A Discrete Quadruple-Decker Phthalocyanine.
J. Am. Chem. Soc. **2010**, *132* (18), 6278

Supramolecular assembling of sandwiches

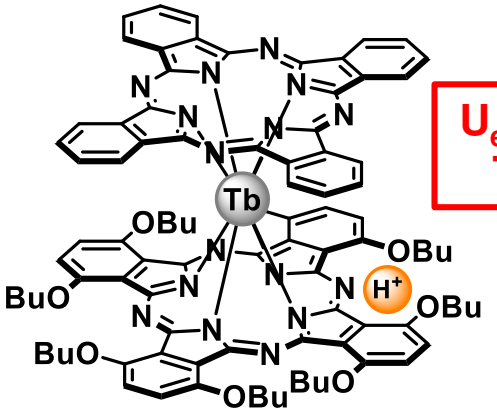


Relaxation time at 2K 1.07 ms
Hysteresis up to 7K



•*Chem. Eur. J.* **2018**, *24* (17), 4320

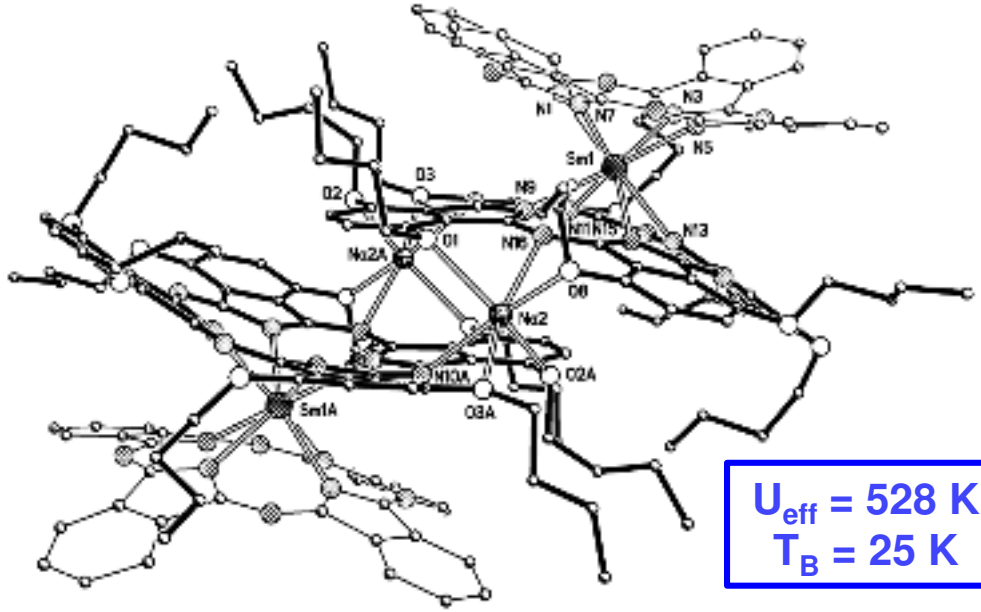
Relaxation time at 2K 1.01•10^3 ms
Hysteresis up to 15K



U_{eff} = 180 K
T_B = 2 K

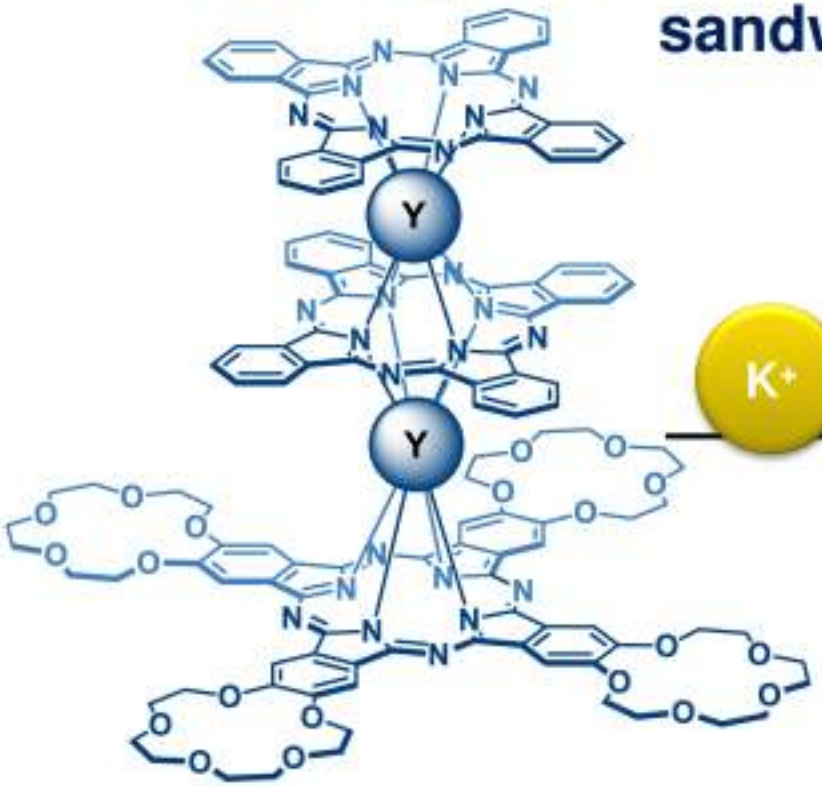
•*Chem. Eur. J.* **2018**, *24* (32), 8066

NaOH, MeOH



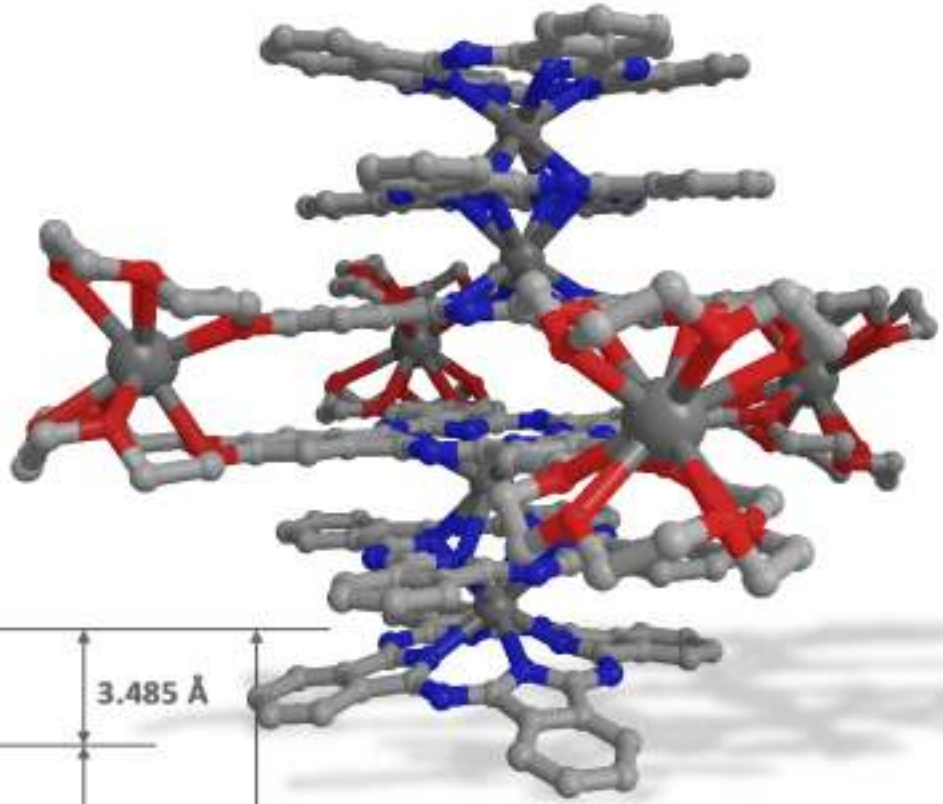
U_{eff} = 528 K
T_B = 25 K

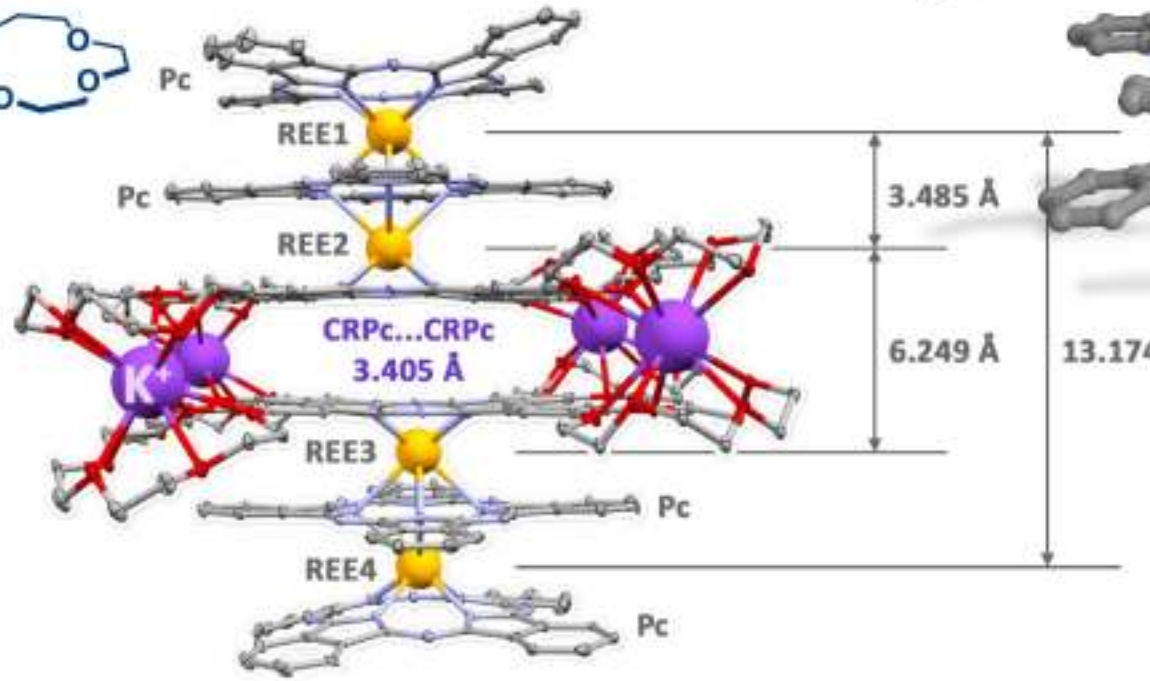
First example of structurally-characterized supramolecular dimer based on sandwich REE crown-phthalocyaninate



K^+

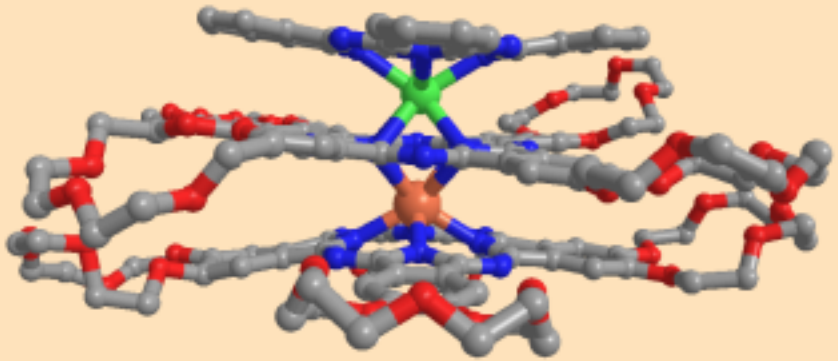
Slow diffusion of $KBPh_4$ in CH_3CN into the solution of complex in $CHCl_3/CH_3CN$

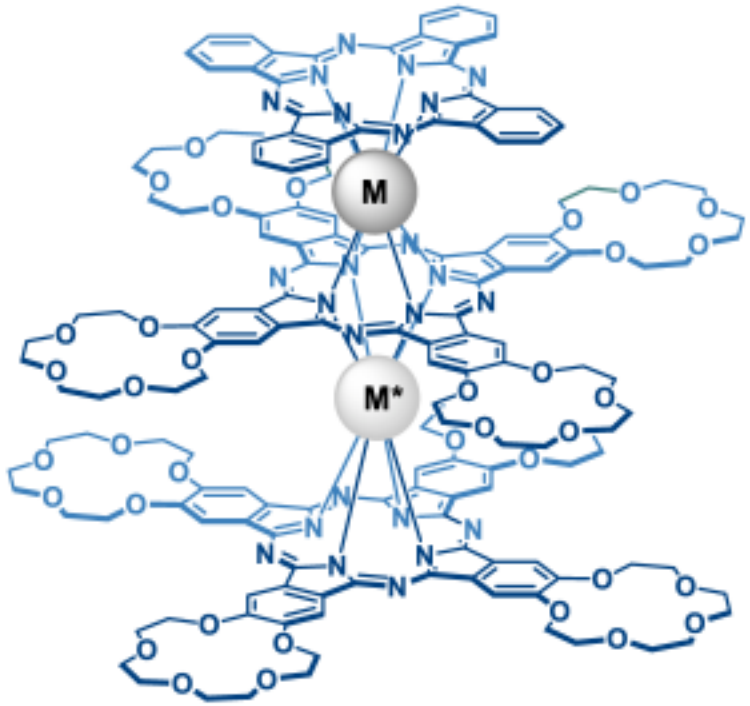




Inorganic Chemistry **2020**, *59* (13), 9424–9433

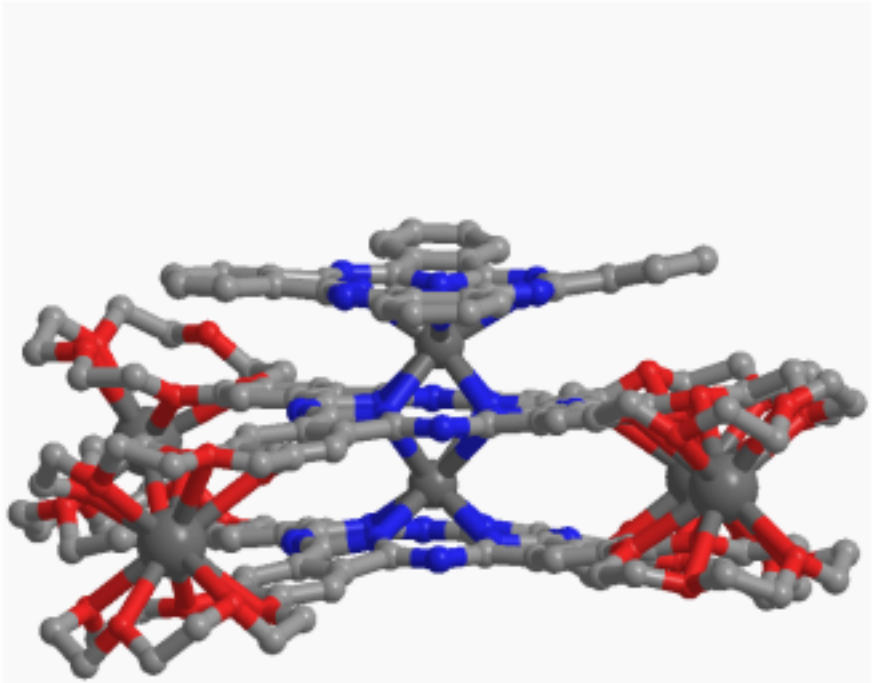
Heteroleptic crown-substituted tris(phthalocyaninates) as dynamic supramolecular scaffolds with switchable rotational states





M* = M = Tb: U_{eff} 223 K (zero dc)
M* = Y, M = Tb: U_{eff} 169 K (1500 Oe dc)
M* = Tb, M = Y: U_{eff} 130 K (1500 Oe dc)

Dalton Transactions **2016**, *45* (22), 9320–9327

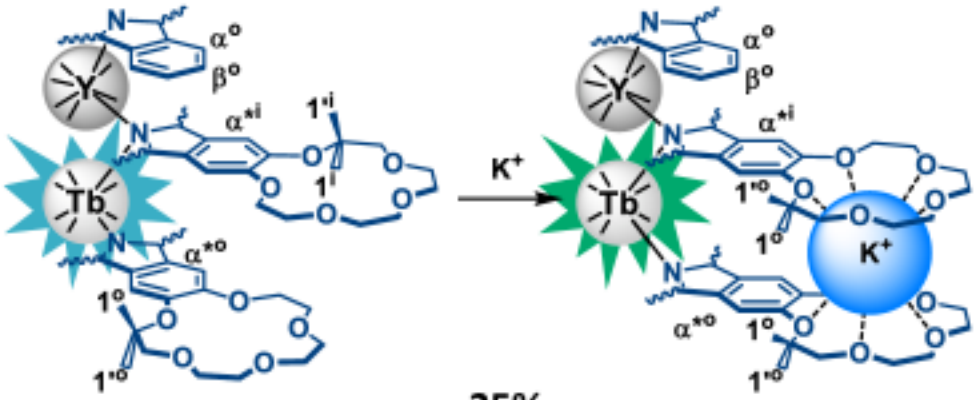


Inorganic Chemistry **2016**, *55* (18), 9258–9269

Slow diffusion of $KBPh_4$ in acetone to solution of complex in mixture of$CHCl_3$ and acetone

Inorganic Chemistry **2021**, *60* (12), 9110–9121

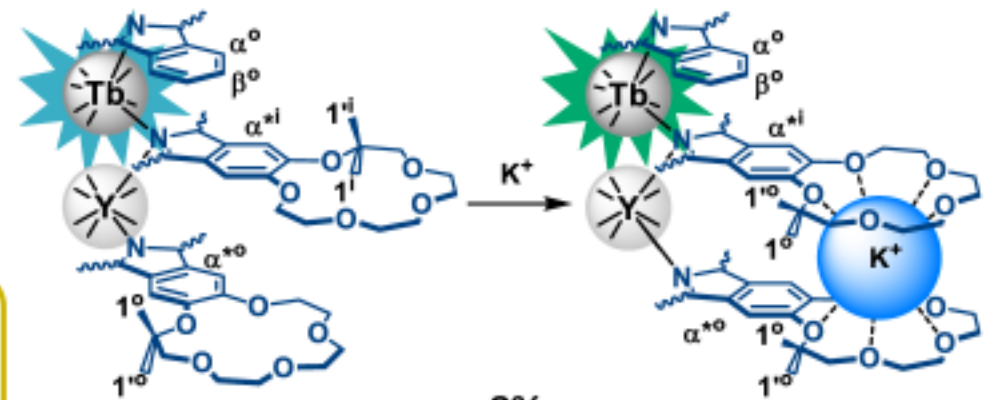
Heteroleptic crown-substituted tris(phthalocyaninates) as dynamic supramolecular scaffolds with switchable magnetic properties



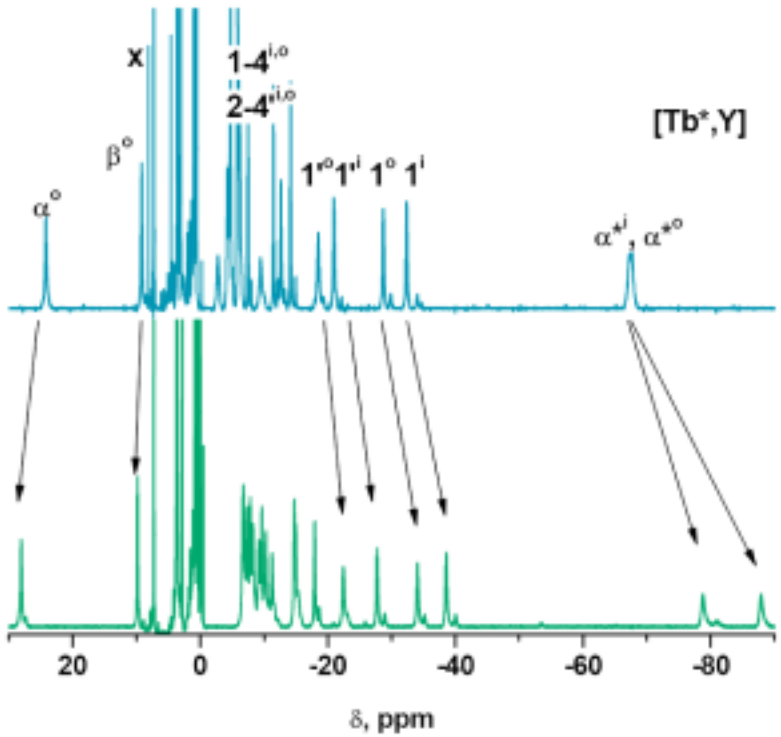
χ_{ax}=8.41·10^{-31} → 25% increase → χ_{ax}=1.06·10^{-30}

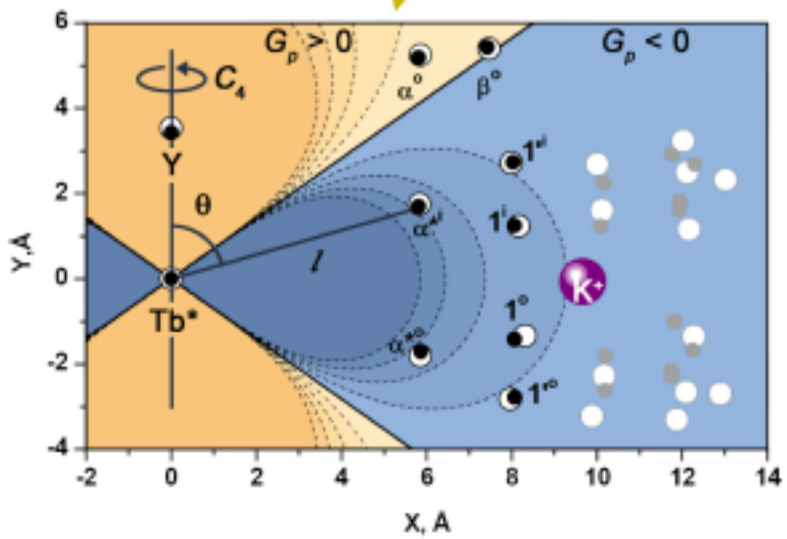
$$\Delta\delta_k \approx \frac{\chi_{ax}}{12\pi}\cdot\frac{(3\cos^2\theta_k - 1)}{r_k^3}$$

X

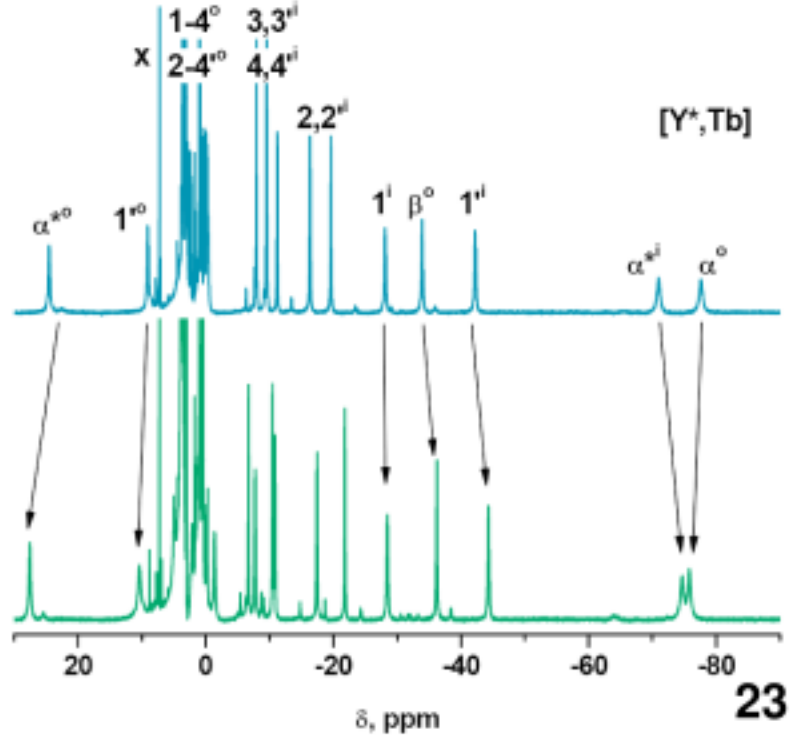


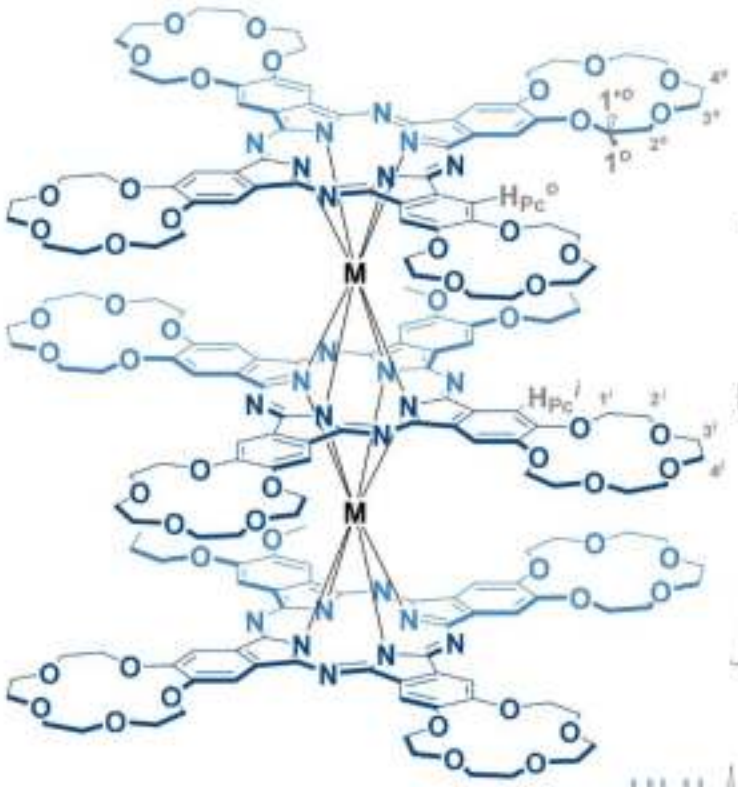
χ_{ax}=8.98·10^{-31} → 8% increase → χ_{ax}=9.64·10^{-31}





Inorganic Chemistry **2021**, *60* (12), 9110–9121





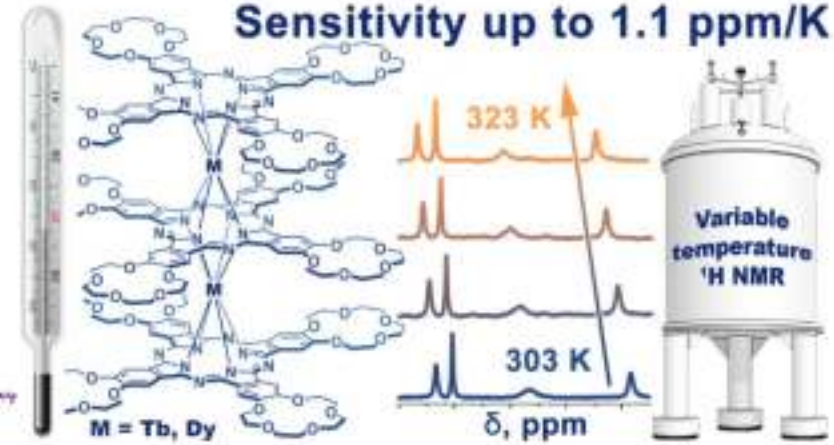
Why anisotropy is important?

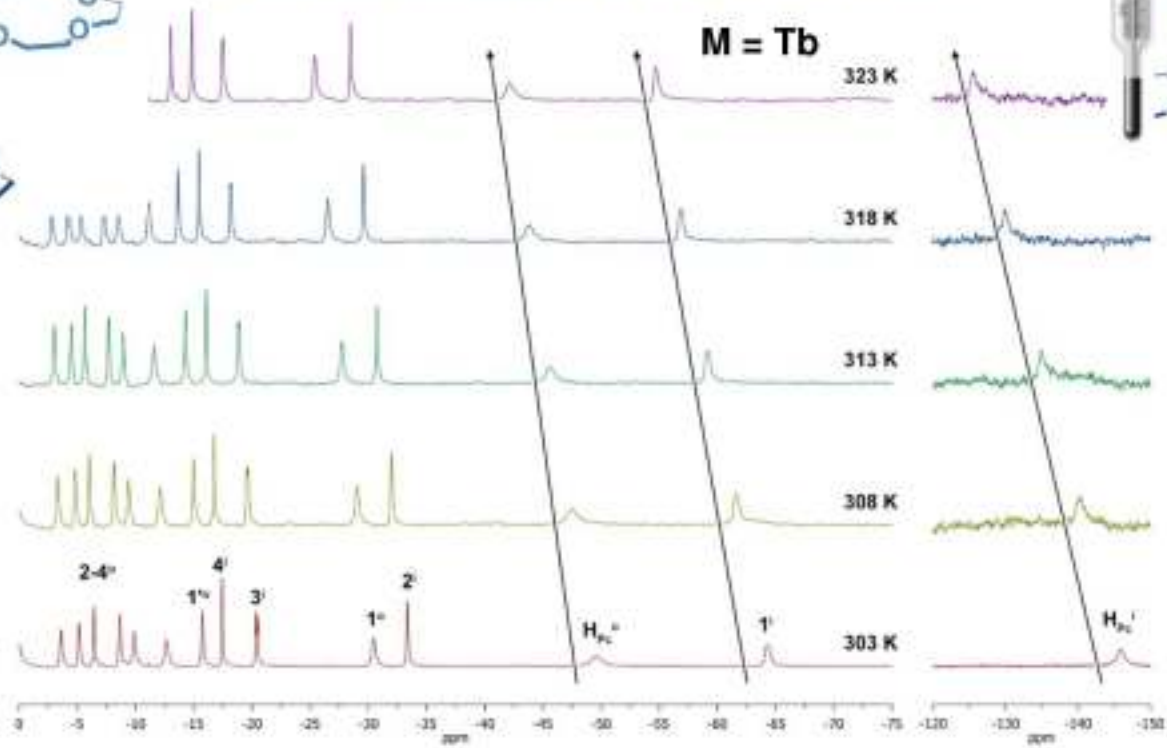
•Magnetic properties of lanthanides manifested at ambient conditions

•Babailov, S. P.; Polovkova, M. A.; Kirakosyan, G. A.; Martynov, A. G.; Zapolotsky, E. N.; Gorbunova, Y. G.

NMR Thermosensing Properties on Binuclear Triple-Decker Complexes of Terbium(III) and Dysprosium(III) with 15-Crown-5-Phthalocyanine.

Sensors Actuators A Phys. **2021**, *331*, 112933





M = Tb

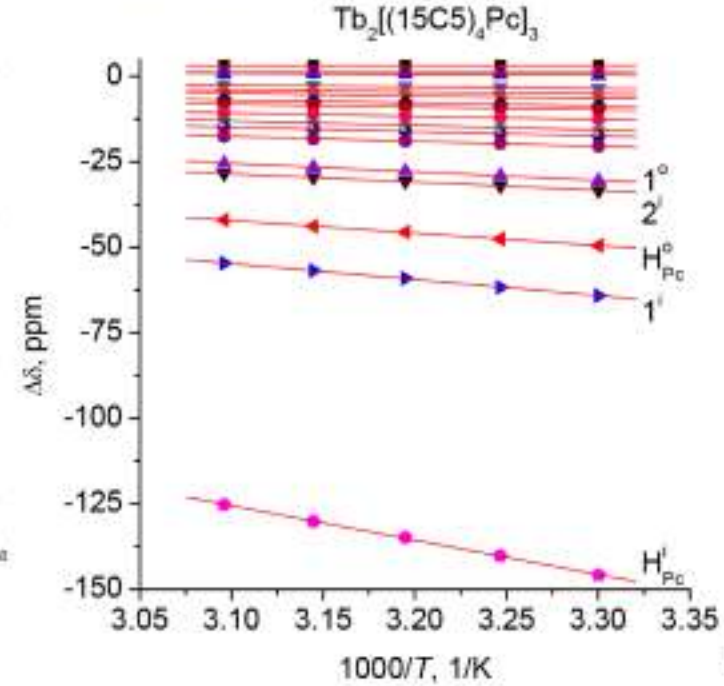
χ_{ax}=8.60·10^{-31} m^{-3}

∂δ/∂T = 1.10 ppm/K

M = Dy

χ_{ax}=4.42·10^{-31} m^{-3}

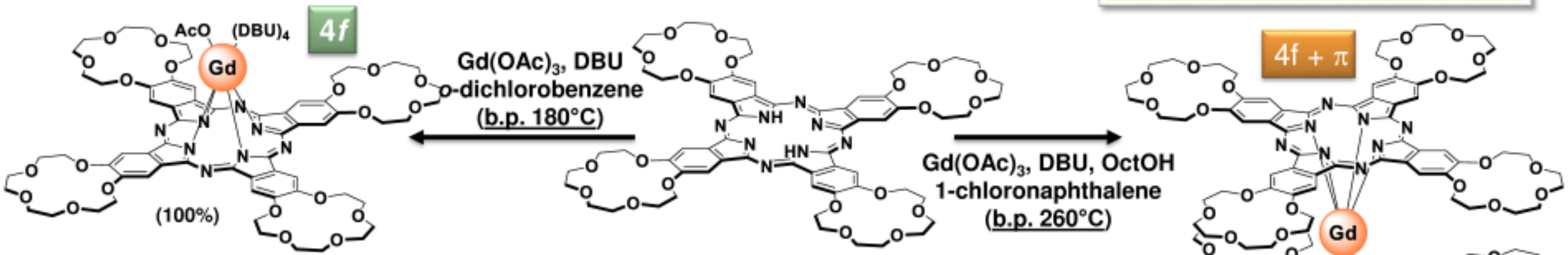
∂δ/∂T = 0.55 ppm/K



•*J. Porphyr. Phthalocyanines* **2022**, *26* (04), 334–339 •*Polyhedron* **2022**, *219*, 115792

Gadolinium complexes in magnetic resonance imaging

•Magnetic properties of lanthanides manifested at ambient conditions



STUDY OF RELAXATION CHARACTERISTICS* OF GADOLINIUM COMPLEXES

Monophthalocyanate $[(15C5)_4Pc]Gd(OAc)(DBU)_4$

•The complex forms stable aqueous solutions in a wide concentration range.

-The relaxivity of the complex (r_1 19 s^{-1} mM^{-1} at 1T) exceeds the relaxivity of Omniscan (3.9 s^{-1} mM^{-1} at 1 T) used in clinical practice

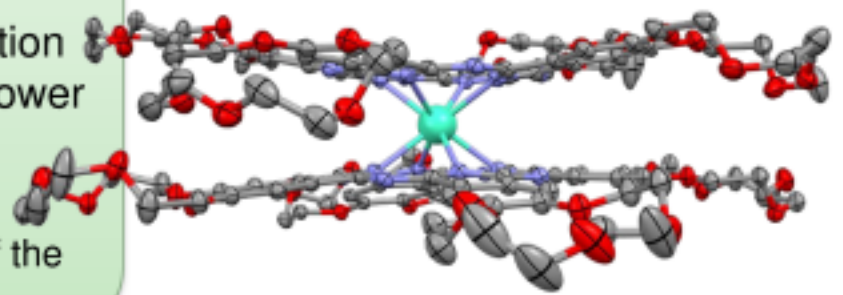
Double-decker complex $Gd[(15C5)_4Pc]_2$

•Low solubility in water, solutions in water/DMSO mixture are unstable due to aggregation

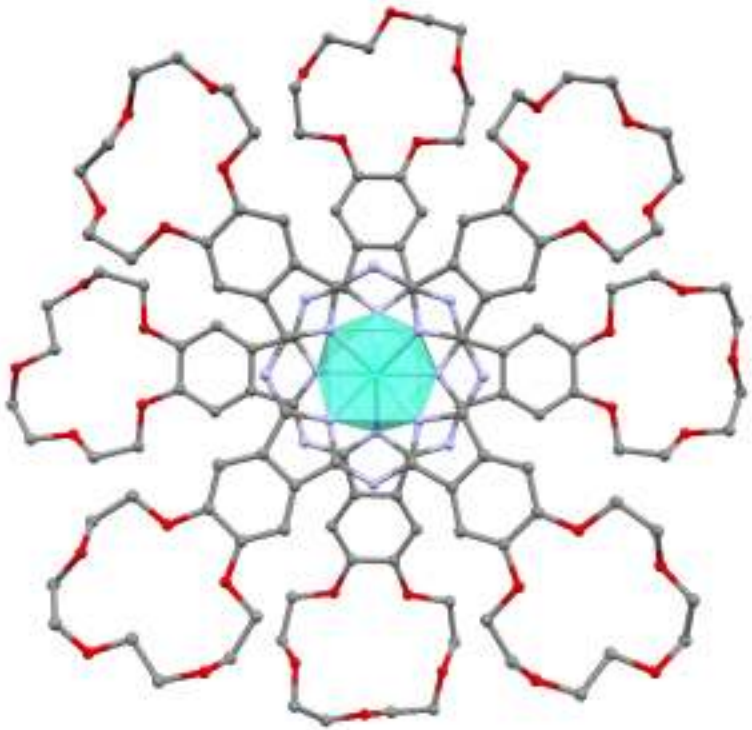
•Sixteen times lower relaxivity in comparison with monophthalocyanine because of lower availability of gadolinium ion for the solvent molecules.

*Relaxation characteristics were measured in the laboratory of photochemical radical reactions of the ITC SB RAS by Dr. Yurkovskaya A.V. and Dr. Zhukov I.V.

X-ray structure

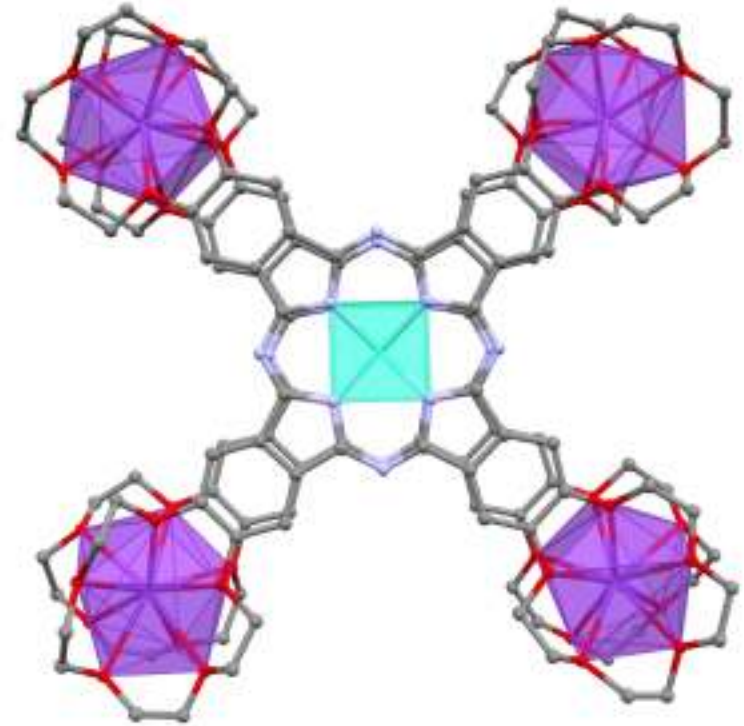


Crown-substituted gadolinium bisphthalocyaninate as a molecular switcher



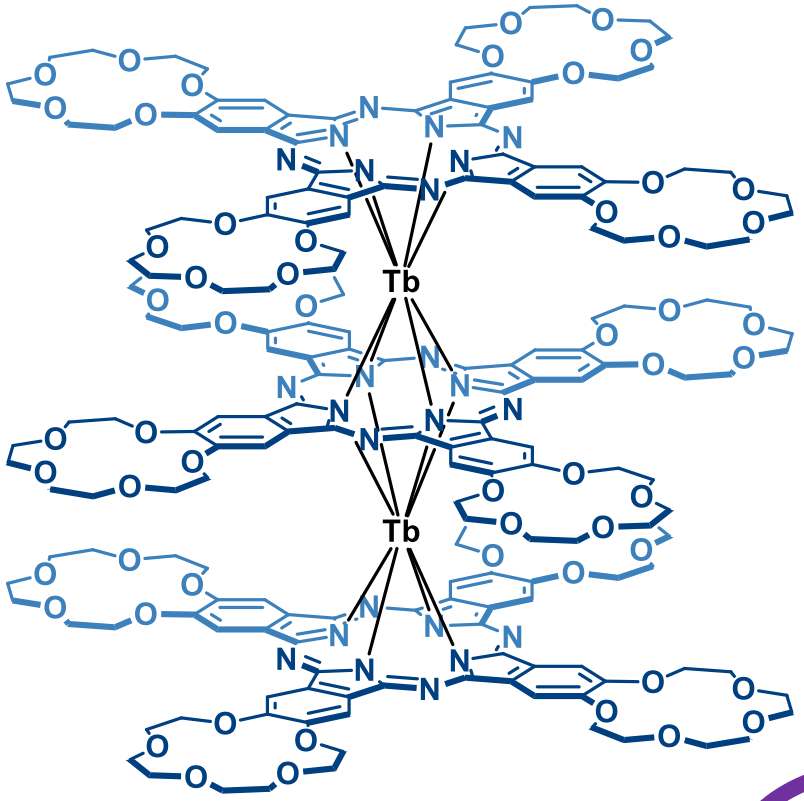
$Gd[(15C5)_4Pc]_2$

Intercalation of K^+ ions switches coordination polyhedron from SAP to SP without formation of supramolecular polymers



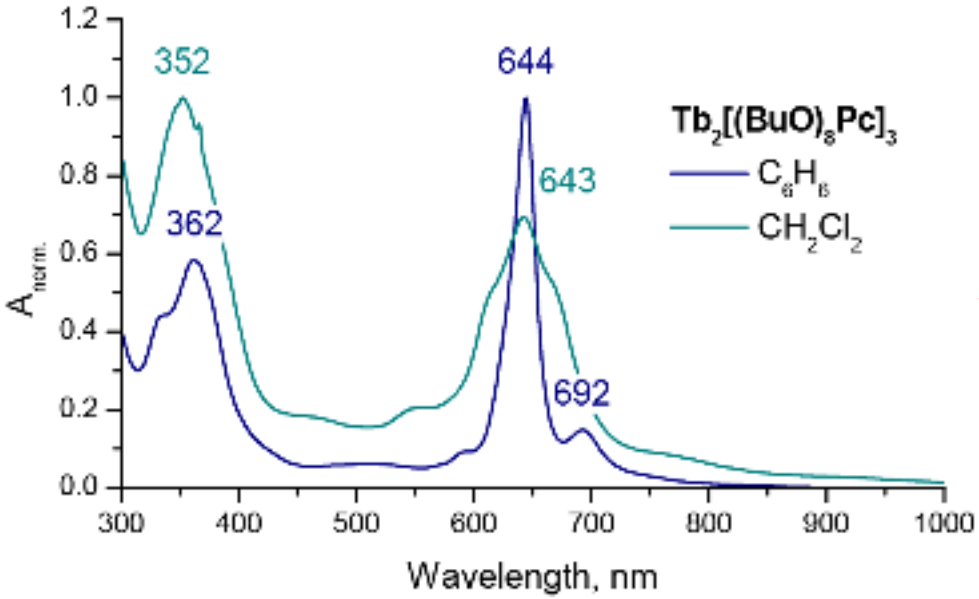
$Gd[(15C5)_4Pc]_2 \cdot 4K^+$

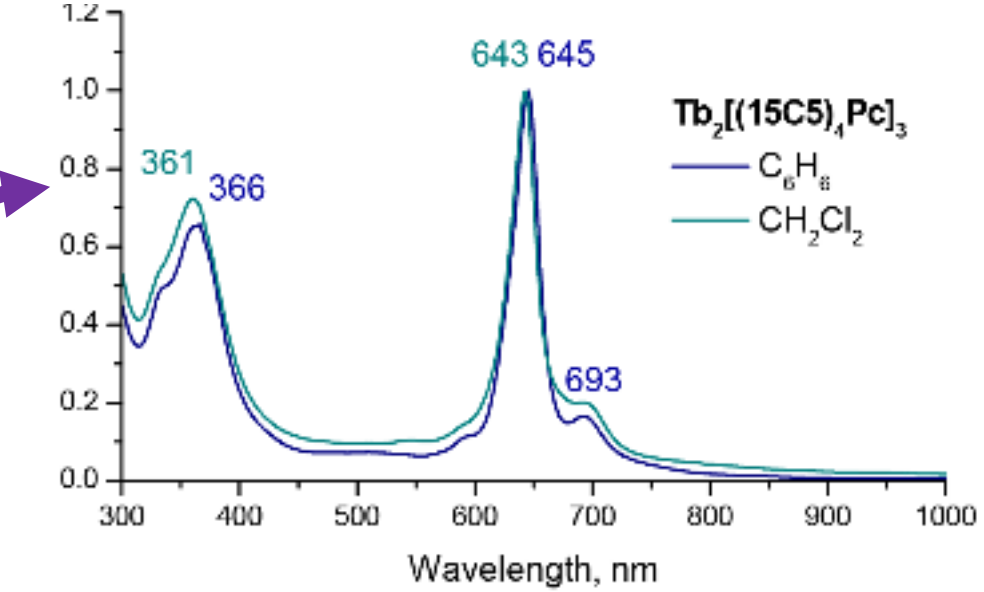
Solvatochromic behavior of crown- *vs.* butoxy-substituted triple-decker complexes in aliphatic and aromatic solvents



$Tb_2[(15C5)_4Pc]_3$

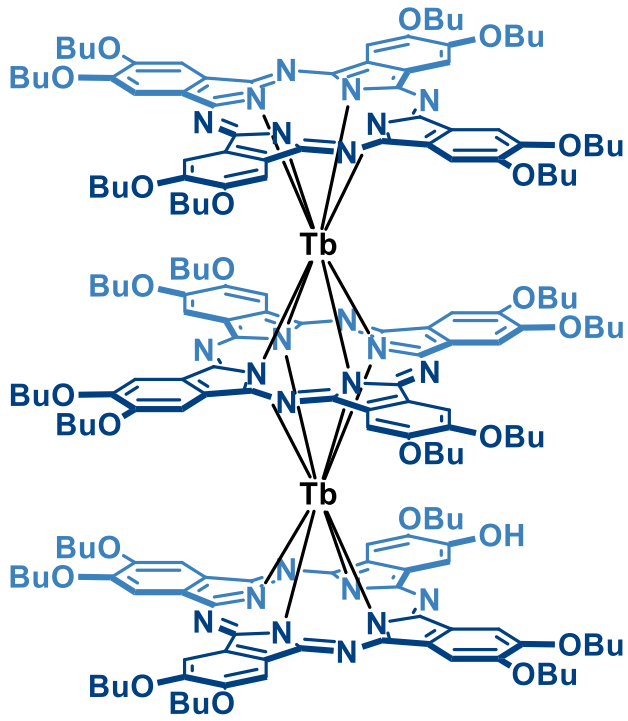
•Complex is <u>not</u> solvatochromic





$Tb_2[(BuO)_8Pc]_3$

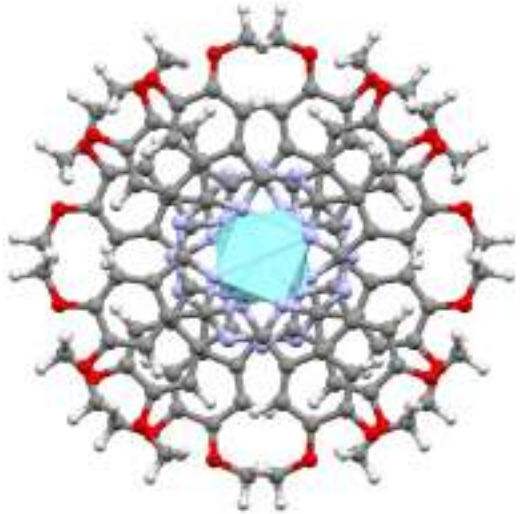
•Complex is solvatochromic

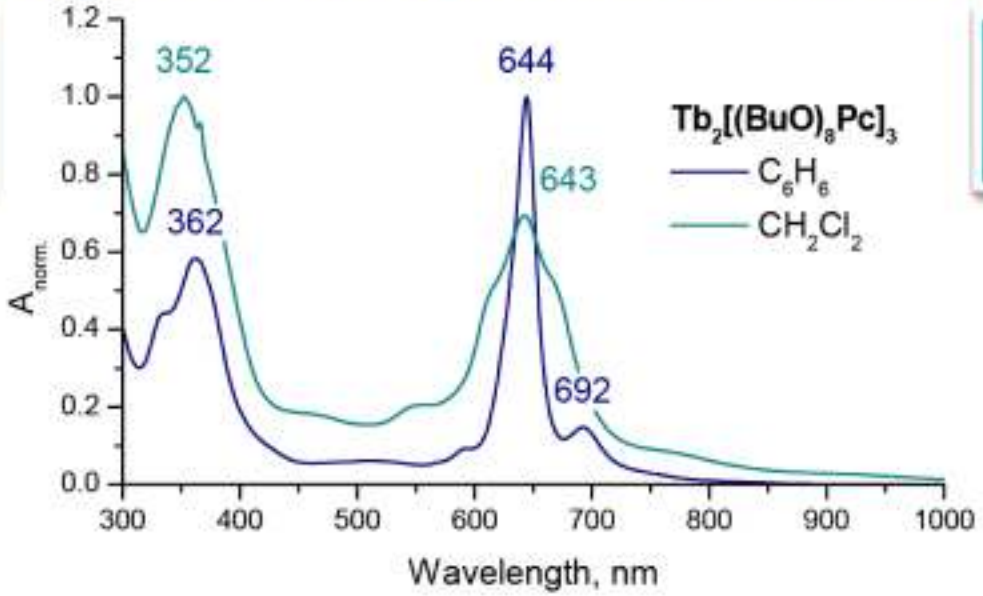


•Martynov A.G., Polovkova M.A., Gorbunova Yu.G., Tsivadze A.Yu. *Molecules*, 2022, *submitted*

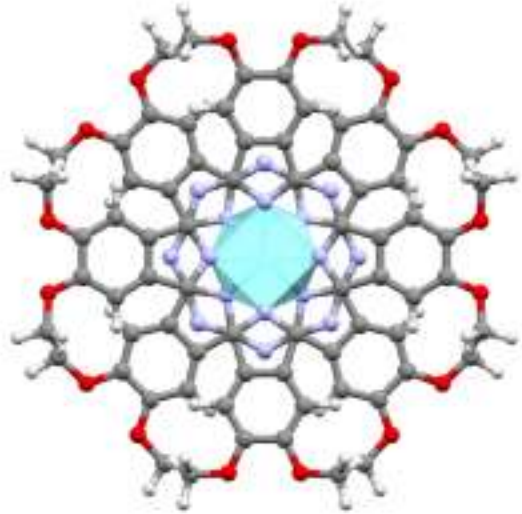
Solvatochromic behavior of crown- *vs.* butoxy-substituted triple-decker complexes in aliphatic and aromatic solvents

Staggered conformation



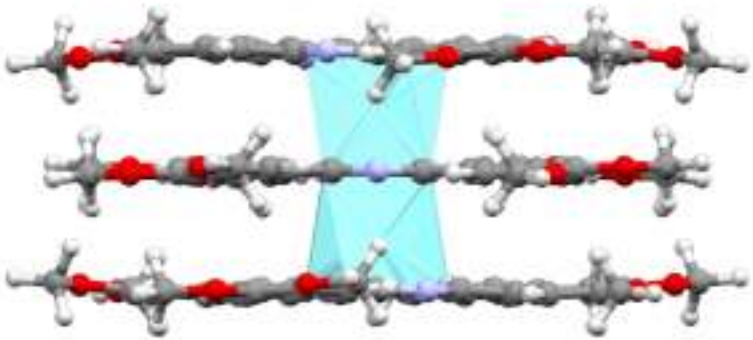


Gauche conformation

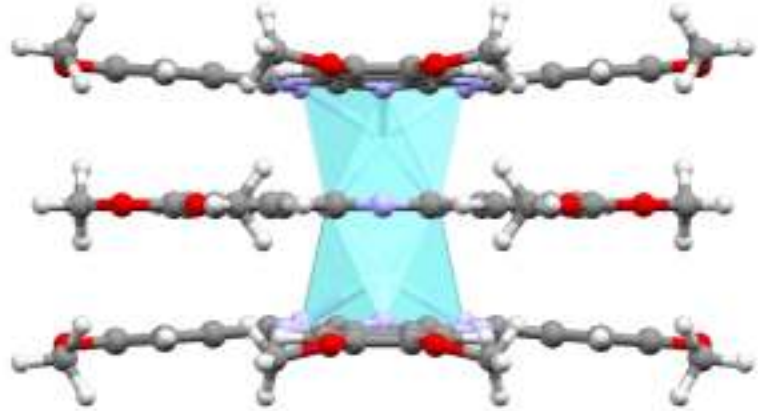


SOLVENT-INDUCED

CONFORMATIONAL SWITCHING



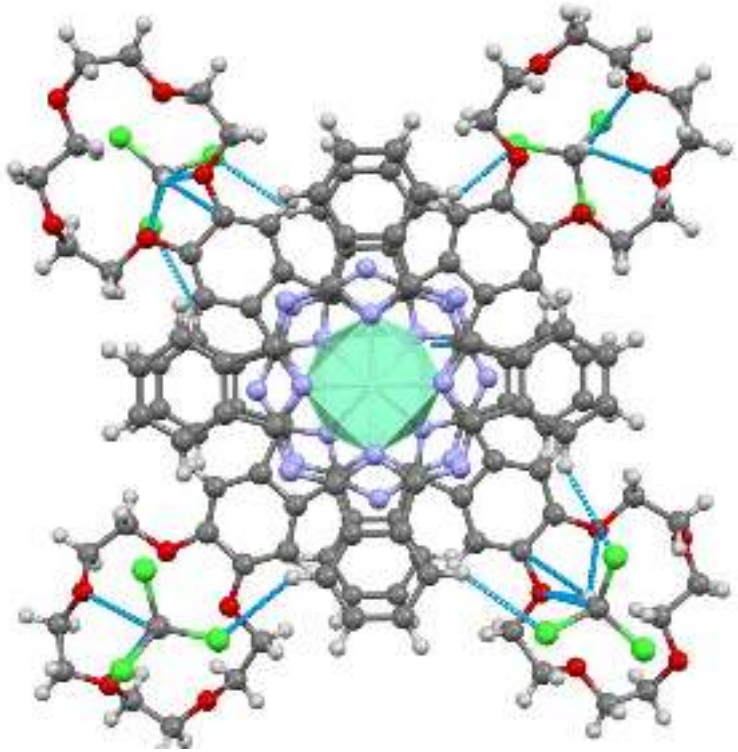
Observed for BuO-substituted complex, but not for 15C5-substituted triple-decker



•Martynov A.G., Polovkova M.A., Gorbunova Yu.G., Tsivadze A.Yu. *Molecules*, 2022, *submitted*

Solvation can stabilize conformational states

•*Eur. J. Inorg. Chem.* **2007**, 4800–4807.

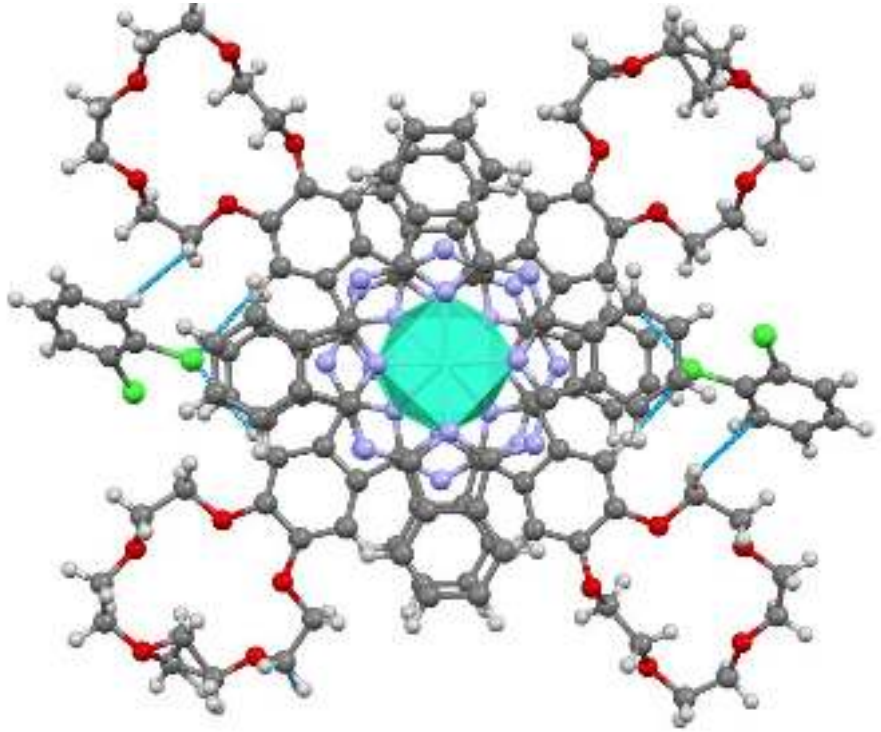


(Pc)Sm[(15C5)$_4$Pc]Sm(Pc)
– solvate with chloroform

Weak $Cl_3CH\ldots O^{crown}$ contacts

Crowns are <u>needed</u> to stabilize
staggered conformation in chlorinated alkanes

•**THIS WORK!**



(Pc)Tb[(15C5)$_4$Pc]Tb(Pc)
– solvate with *o*-dichlorobenzene

Weak $Cl\ldots CH^{(Pc)}$ contacts

Crowns are <u>not needed</u> to stabilize
staggered conformation in aromatic solvents

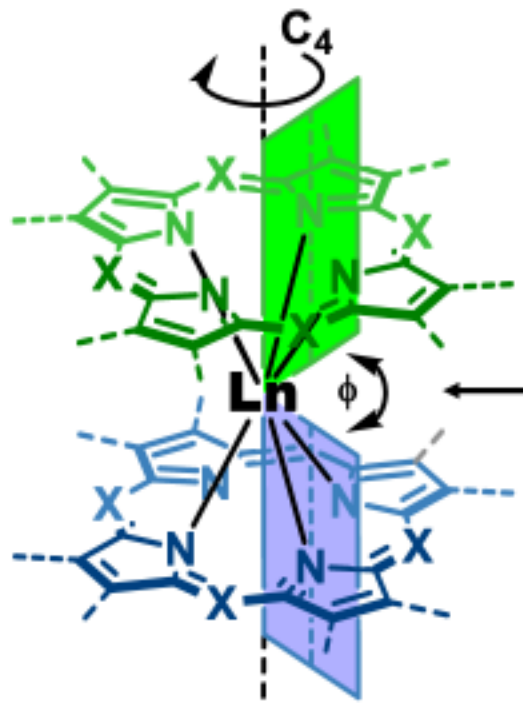
Sandwich lanthanide complexes – multitools for studies of molecular magnetism

Static control *Vs.* Dynamic control

Nature of ligands

Metal center

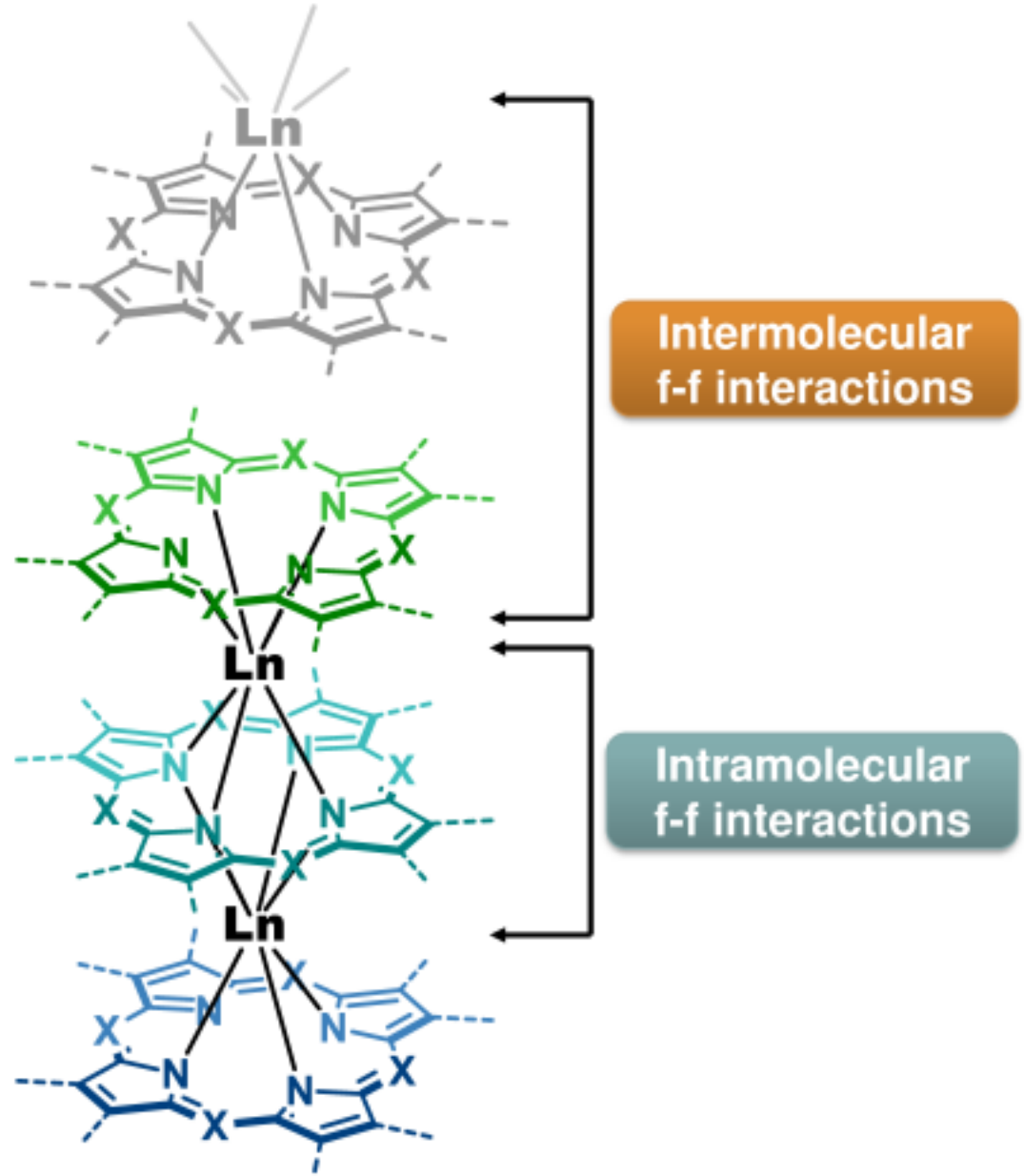
Redox-state of ligands



f → 45° (SAP)

Skew angle

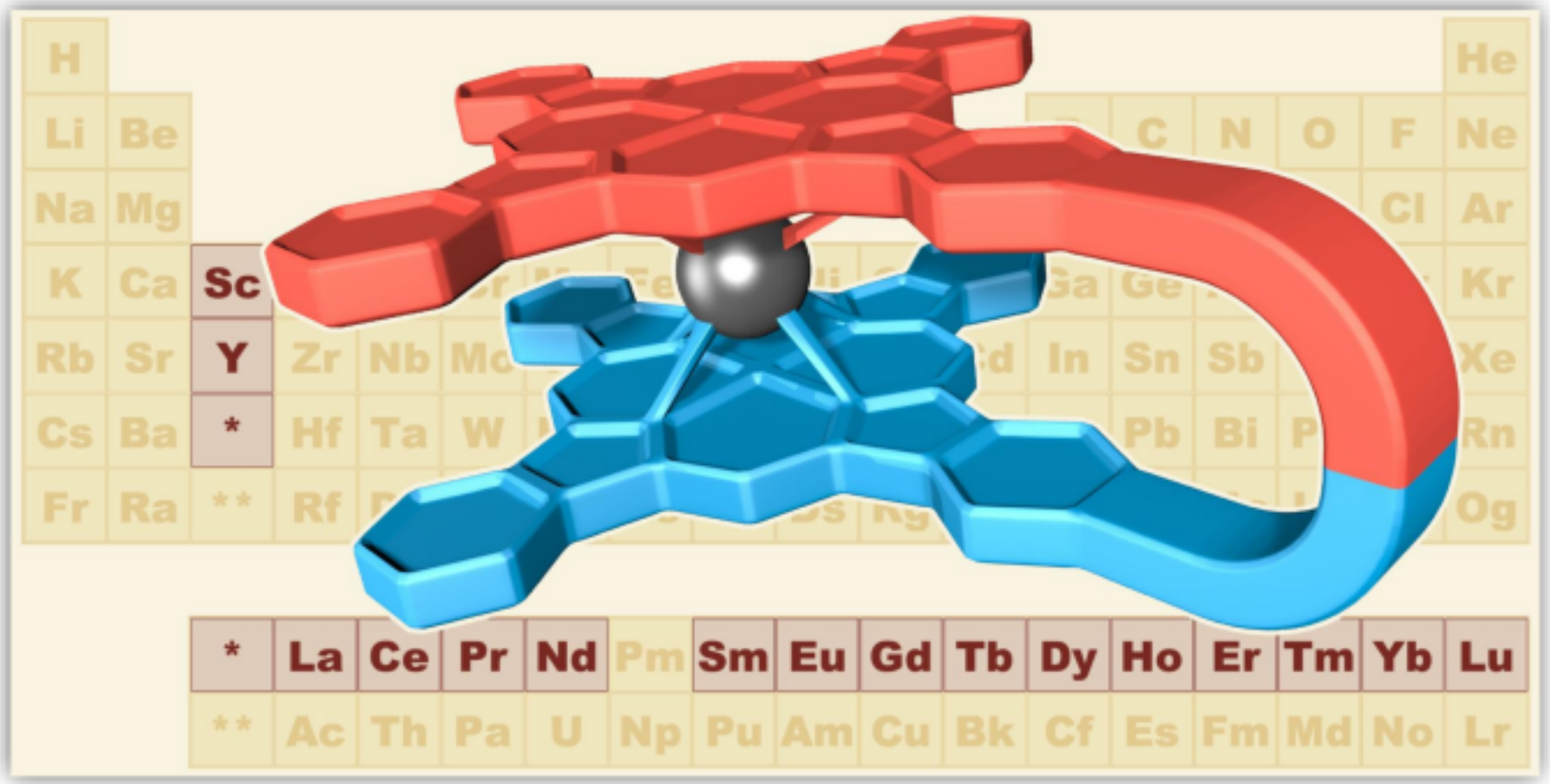
f → 0° (SP)



Intermolecular f-f interactions

Intramolecular f-f interactions

THANK YOU FOR ATTENTION!



The work was supported by the Ministry of Science and Higher Education of Russia
(grant agreement No. 075-15-2020-779).