CHRISTOU research group

Transition Metal and Lanthanide Molecular Clusters: Syntheses, Properties and Nanoscience Applications

Acknowledgements

Distinguished and Drago Professor George Christou's Research Group is a synthetic, bioinorganic and physical inorganic group. Our main research interests are in metal-oxo coordination chemistry, focused on the synthesis and characterization of polynuclear metal-oxo clusters (complexes with more than two metal centers) with relevance to such areas as molecular nanoscience, catalysis, supramolecular chemistry, and molecular magnetism.

"There's plenty of room at the bottom."
Richard Feynman

Synthesis: Aerobic conditions in solution, various temperatures, crystallization techniques, and organic synthesis for complex ligands, where necessary.

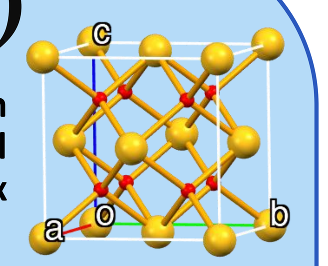
Characterization: FT-IR, paramagnetic NMR, UV-vis spectroscopy, electrochemistry, SQUID magnetometry, X-ray crystallography, EPR spectroscopy, Mössbauer spectroscopy, and DFT calculations, some of them with expert collaborators

MOLECULAR NANOPARTICLES (MNPs)

Molecular Nanoparticles = molecular clusters with the same structure as a bulk metal oxide, and greater than 1 nm in size.

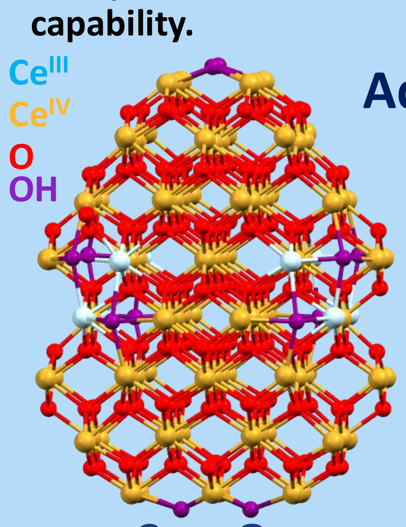
Cerium Dioxide (CeO_2)

Cerium dioxide (ceria, CeO_2) exhibits the fluorite lattice and has been extensively employed in a wide range of fields such as in industrial catalysis and biomedical applications owing to its Ce^{3+}/Ce^{4+} redox capability.



CeO_2 unit-cell

Ce^{III} Ce^{IV} O OH



$Ce_{100}O_{167}$
2.40 nm
Russell-Webster, B. *et al. Angew. Chem. Int. Ed.*, **2021**

Advantages of a Molecular Approach

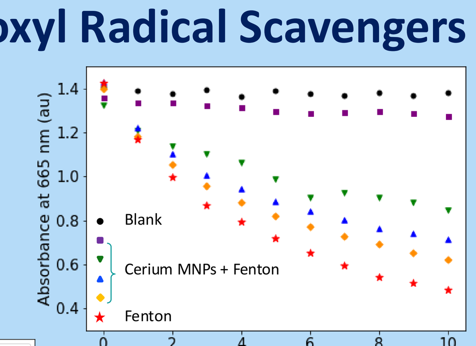
1. Monodispersity – single-size from each synthesis
2. Crystallinity – highly ordered arrays of identical molecules
3. Structural characterization to atomic resolution using single-crystal X-ray diffraction (SC-XRD)

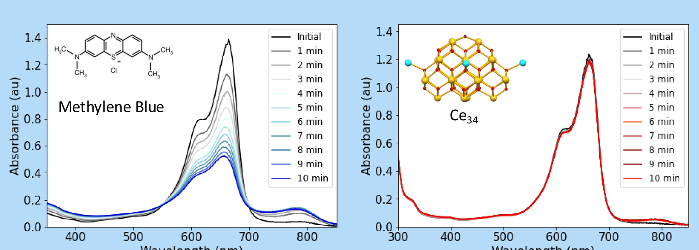
Cerium Dioxide MNPs as Hydroxyl Radical Scavengers

The Fenton Reaction:

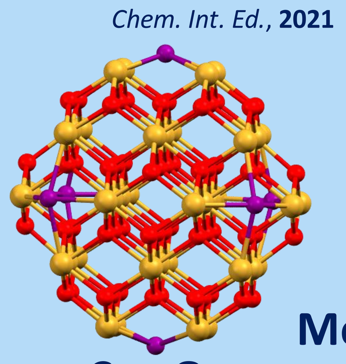
$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \cdot OH + OH^-$$

The characteristic peak of Methylene Blue (MB) decreased at a slower rate in the presence of cerium MNPs

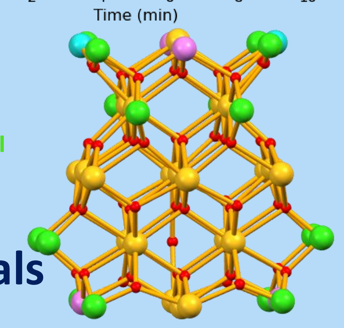




$Ce_{38}O_{62}$
1.20 nm
Mitchell, K. J. *et al. Nature Commun.*, **2017**, *8*, 1445.



Ce^{III} Ce^{IV} Mn^{III} O



$Ce_{23}Mn_{20}$
1.10 nm

Models of Nanoparticle-supported 3d Metals

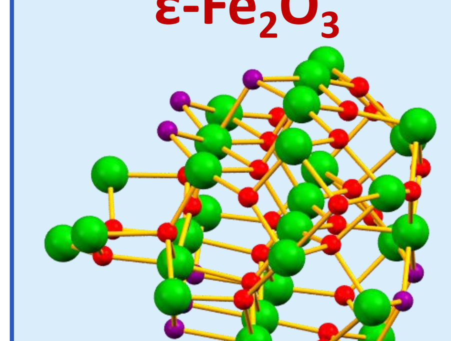
3d transition metals (e.g., Ti, Co, Fe, Ni) have been placed on the surfaces of Ce MNPs as molecular models of 3d metals on ceria nanoparticles

Das Gupta, S. *et al. Inorg. Chem.*, **2022**

Magnetic Iron Oxides

Iron oxides are important materials with variety of applications, e.g., magnetic storage, catalysts, and biomedical applications. Our group has synthesized and characterized MNPs of magnetic iron oxides, ε-Fe_2O_3, γ-Fe_2O_3 and MFe_2O_4 spinels (M = Co^{II}, Ni^{II}, Mg^{II}), as a bottom-up approach to the synthesis of ultra-small nanoscale magnets

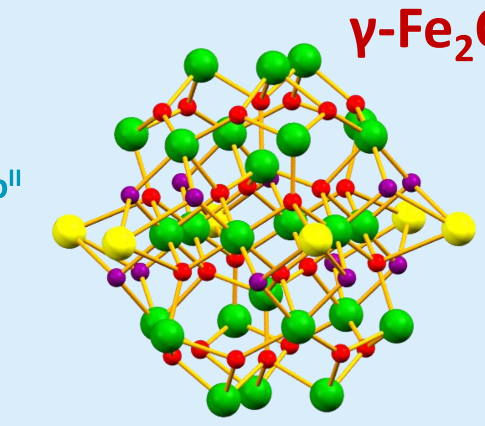
ε-Fe_2O_3



Fe_{29}
Singh, A. *et al.* In preparation

Fe^{III} Ln^{III} Co^{II} Fe^{III}/Co^{II} O OH

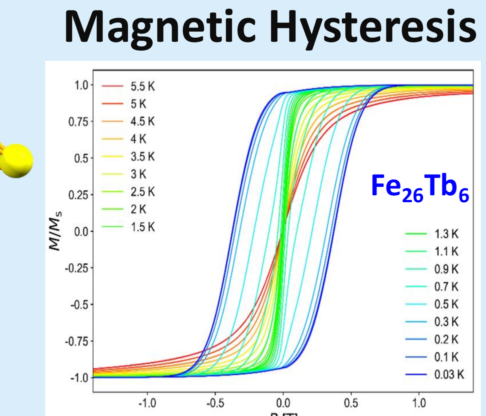
γ-Fe_2O_3



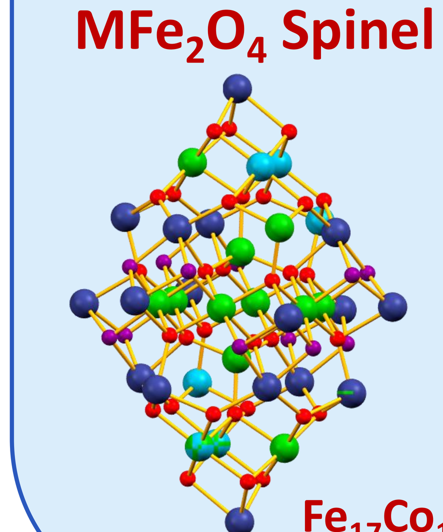
$Fe_{26}Ln_6$
Ln = La, Tb

Ligands are omitted for clarity

Magnetic Hysteresis

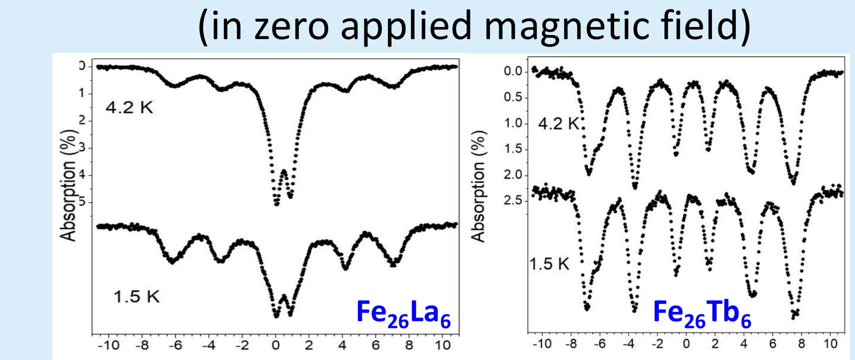


MFe_2O_4 Spinel



$Fe_{17}Co_{17}$
Singh, A. *et al.* In preparation

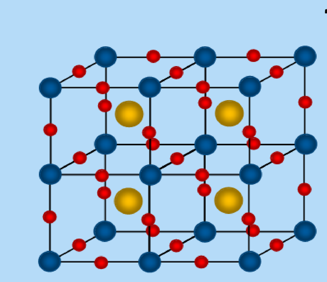
^{57}Fe Mössbauer Spectra
(in zero applied magnetic field)



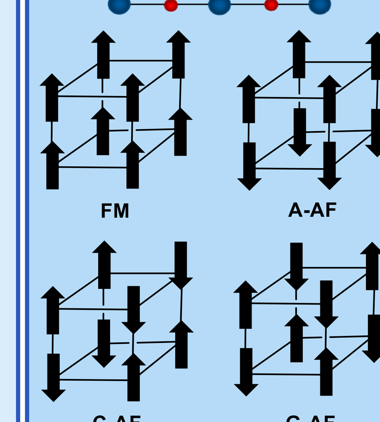
6-line spectrum indicates that $Fe_{26}La_6$ and $Fe_{26}Tb_6$ are single-molecule magnets at low temperature, showing the minimum size for γ-Fe_2O_3 nanoparticles to exhibit magnetic behavior

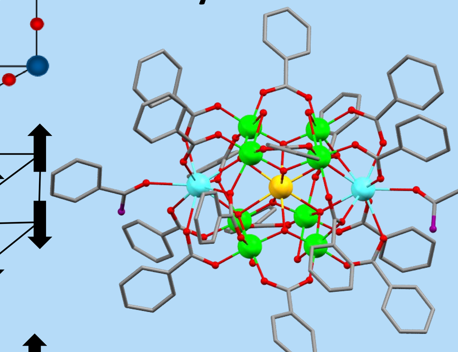
Singh, A. Sanakis, Y. et al, in preparation

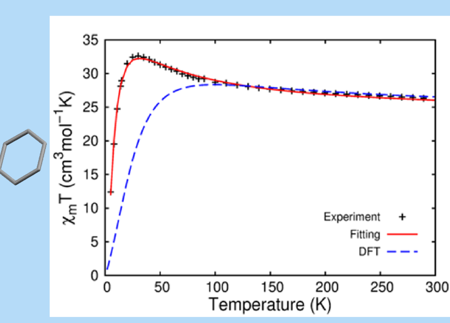
$LnMnO_3$ Perovskites

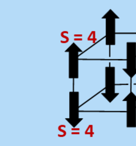


Perovskite manganites ($AMnO_3$) exhibit important and diverse magnetic properties, with nanoscale modifications being a key area of study based on Mn ion spin alignment.





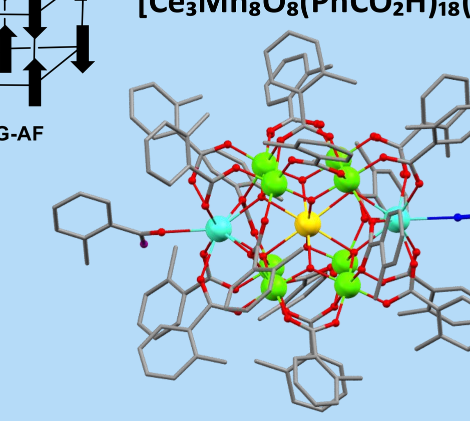


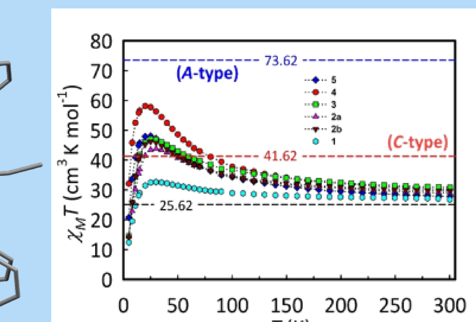


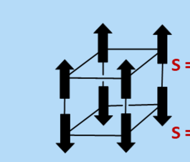
C-type AF: Four S = 4
$\chi_M T$ = 40 cm^{3}mol^{-1}K
(g = 2.0)
or $\chi_M T \approx$ 38 cm^{3}mol^{-1}K
(g = 1.95)

[$Ce_3Mn_8O_8(PhCO_2H)_{18}(PhCO_2H)_2$] (1)

Ce^{III} Ce^{IV} Mn^{III} O OH N

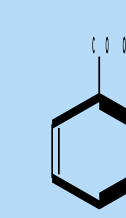




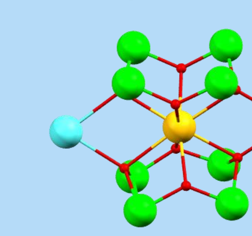


A-type AF: Two S = 8
$\chi_M T$ = 72 cm^{3}mol^{-1}K
(g = 2.0)
or $\chi_M T \approx$ 68 cm^{3}mol^{-1}K
(g = 1.95)

[$Ce_3Mn_8O_8$(Me-PhCO_2)$_{18}$(Me-PhCO_2H)(MeCN)] (4)



X = H (1), -Cl(2), -CH_3(3), -CH_3 (4), -Br (5)



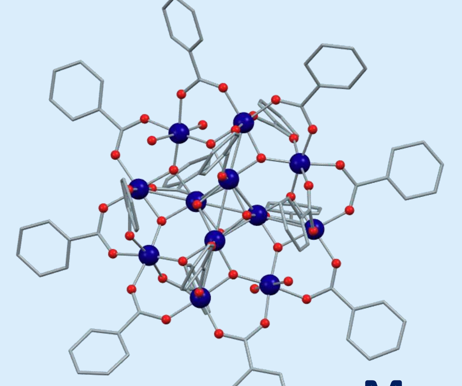
Core structure

Introducing -Cl, -Br, or -CH_3 substituents at the 2-position of benzoic acid as seen in complex (4) causes a distinct change in the magnetic properties of the compounds, switching the ground state from C-type AF to A-type AF ground state.

Thujis, A. E. *et al.*, *Nat Commun.*, **2017**, 8, 500

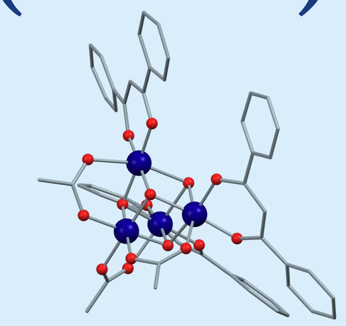
Cao, T. S. *et al.*, *Polyhedron*, **2020**, *176*, 114275

Single-Molecule Magnets (SMMs)



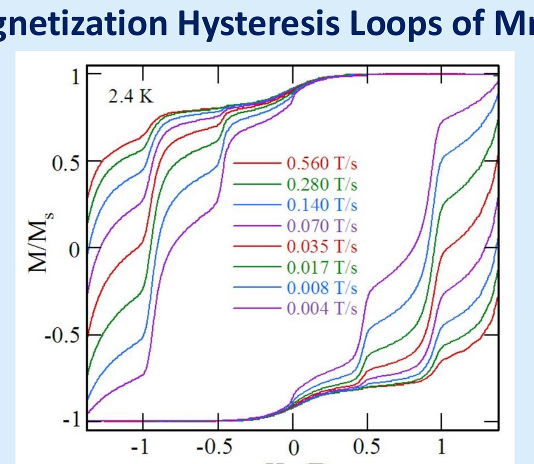
Mn_{12}
Boyd, P.D.W. *et al. J.Am.Chem.Soc.*, **1988**, *110*

SMMs are ultra-small nanoscale permanent magnets below a certain 'blocking temperature'. They have been proposed for high-density classical information storage, spintronics, and new quantum information technologies.



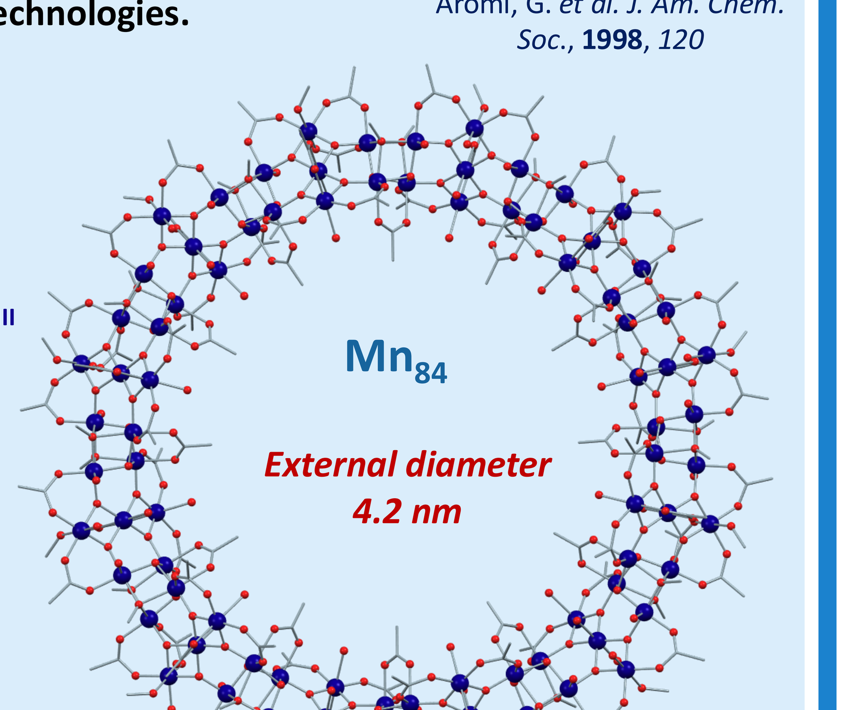
Aromi, G. *et al. J. Am. Chem. Soc.*, **1998**, *120*

Magnetization Hysteresis Loops of Mn_{12} SMM



Chakov, *et al. Inorg.Chem.*, *2005*, *44*

Mn^{III} O N C



Giant SMM Molecules

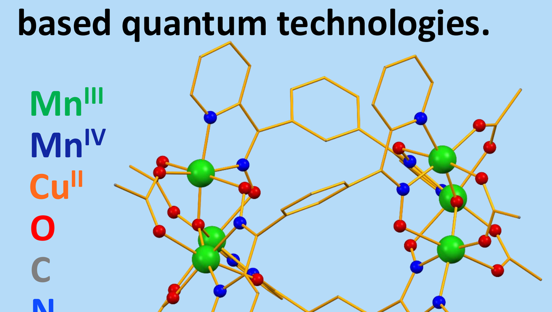
Giant molecules (>30 metal centers) display both quantum and classical properties, such as the giant Mn_{84} torus. These are the largest Mn/O clusters and SMMs to date.

Tasiopoulos, A. *et al. Angew. Chem.*, **2004**, *43*

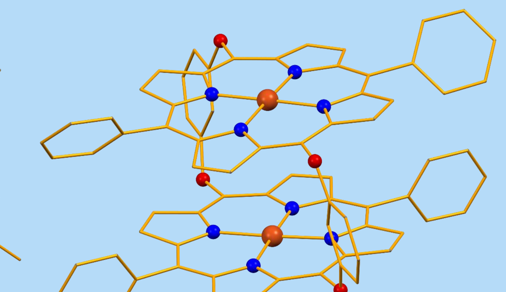
Supramolecular Aggregates

Supramolecular aggregates of molecules are ordered systems of molecular subunits that retain their intrinsic properties. In the Christou group, we utilize a variety of magnetic molecules as supramolecular subunits linked together through covalent bonds. Magnetic subunits chosen vary from SMMs to spin (S) = ½ molecules for use as components of spin-based quantum technologies.

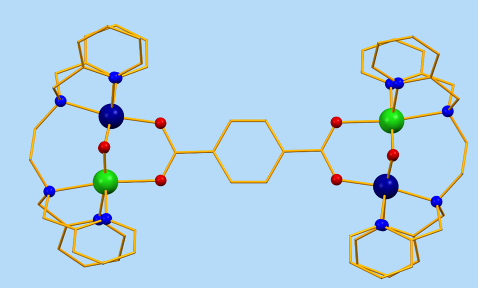
Mn^{III} Mn^{IV} Cu^{II} O C N



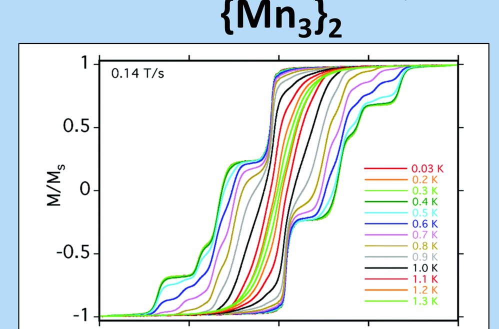
{Mn_3}$_2$



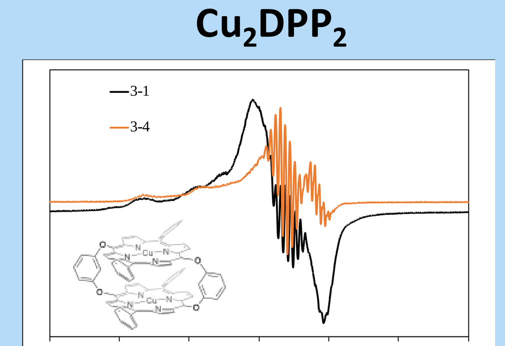
Cu_2DPP_2



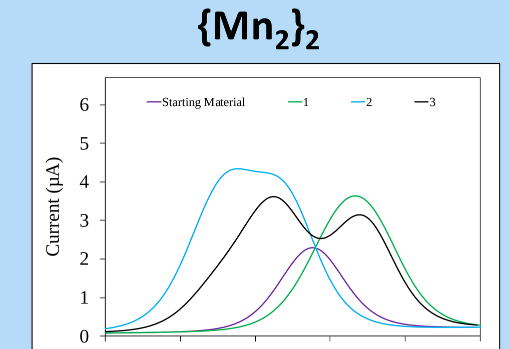
{Mn_2}$_2$



Magnetization Hysteresis
Ghosh, T. *et al.* Phys. Chem. Chem. Phys., **2021**, 23, 8854



Electron Paramagnetic Resonance (EPR)
Diodati, A. *et al.* In Preparation.



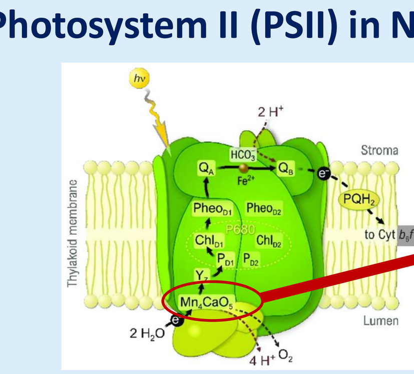
Differential Pulse Voltammetry (DPV)
Diodati, A. *et al.* In Preparation.

Based on the magnetic subunit used and the method of covalent linkage, the quantum properties can be adjusted. In the case of SMMs, quantum tunneling of magnetization can be observed in the hysteresis at low temperature. Quantum properties and interactions between magnetic subunits can be measured through EPR and DPV techniques, respectively.

Bioinorganic Chemistry

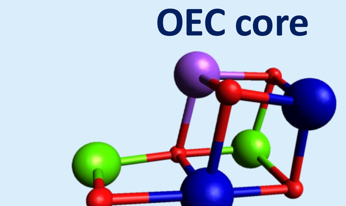
The oxygen-evolving complex (OEC) in plants and cyanobacteria is a Mn_4Ca-oxo complex that undergoes a light-induced oxidation reaction to split water molecules into oxygen gas, protons, and electrons.

Photosystem II (PSII) in Nature



Björn, L. O. *Oxygen* **2022**, *2* (3), 337

OEC core

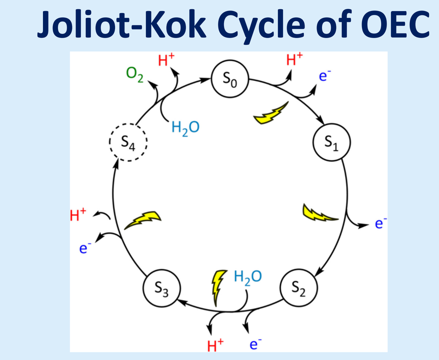


Mn_4CaO_5
Zhang, C. et al. *Science* **2015**, *348* (6235), 690–693

$$2\,H_2O \xrightarrow{h\nu} O_2 + 4H^+ + 4e^-$$

Mn^{III} Mn^{IV} Ca^{II} O

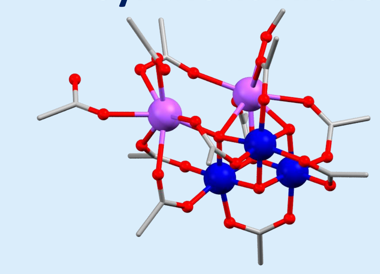
Joliot-Kok Cycle of OEC



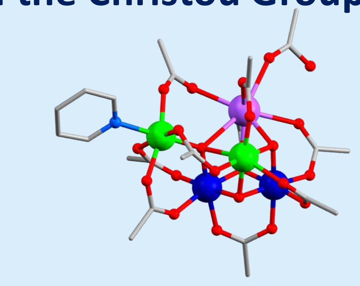
Malcomson, T. et al. *J. Photochem. Photobiol. B: Biol.* **2024**, *257*, 112946

Synthetic Analogues of the OEC from the Christou Group

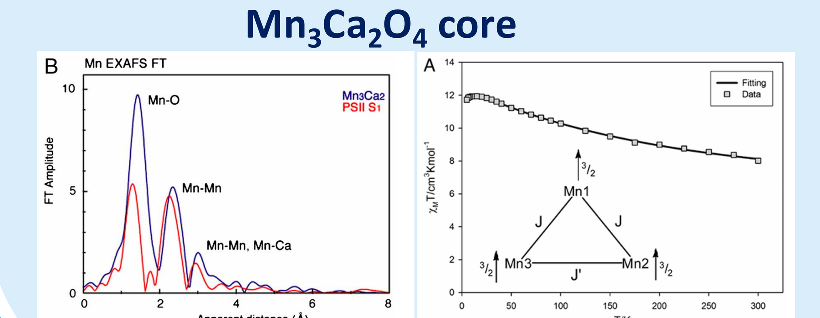
Mn^{III} Mn^{IV} Ca^{II} O C N



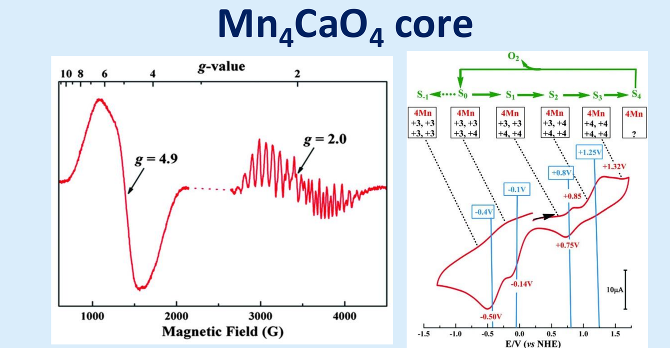
$Mn_3Ca_2O_4$ core



Mn_4CaO_4 core



Mukherjee, S. et al. *PNAS*, **2011**, *109* (7), 2257–2262



Zhang, C. et al. *Science* **2015**, *348* (6235), 690–693