

Metal-Containing Polymers and Networks with Redox-Active Quinoid Bridging Ligands

Cu^{II}-p-Hydroquinonate Polymers and Nanoscale 3D Metal Aggregates

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Introduction

Bose-Einstein condensation is a well-known phenomenon for certain supercooled gases (e.g., superfluid ⁴He), but not abundant in solid-state chemistry. However, when certain solid materials are exposed to a magnetic field, an ensemble of $S_z = 1$ triplet states is generated which can be regarded as a gas of bosonic particles carrying a magnetic moment. One way to prepare such solids is to create an array of antiferromagnetically coupled dimers of $S_z = \frac{1}{2}$ ions.

The intradimer coupling constant J_{intra} has to meet two requirements:

- It needs to be significantly stronger than any interdimer coupling constant.
- It has to be small enough to allow for the use of laboratory-scale magnetic instrumentation to moderate the spin gap to such an extent that the $S_z = 1$ state is adopted by a significant number of spin pairs.

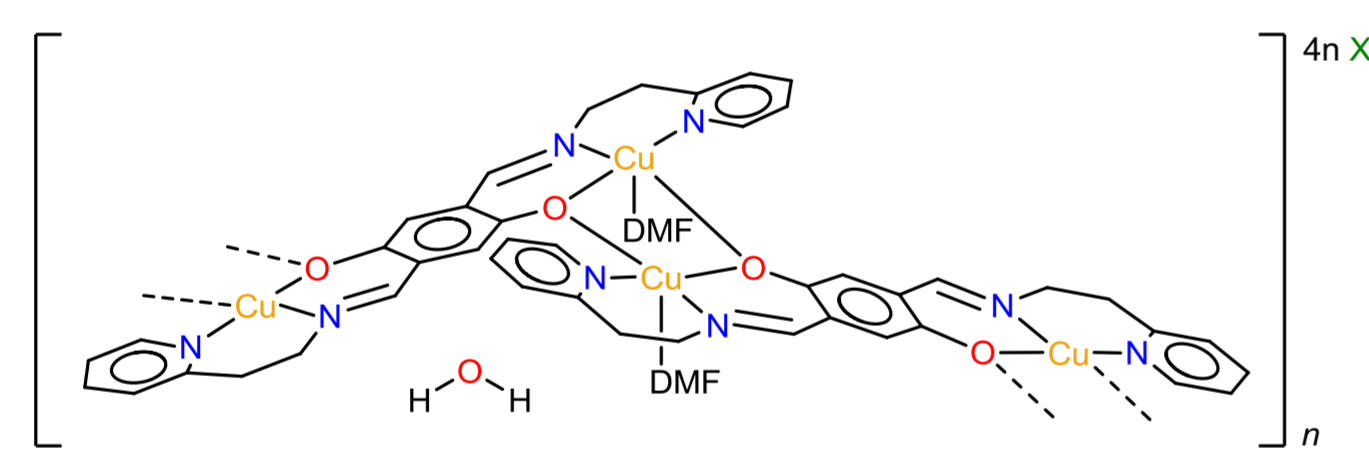
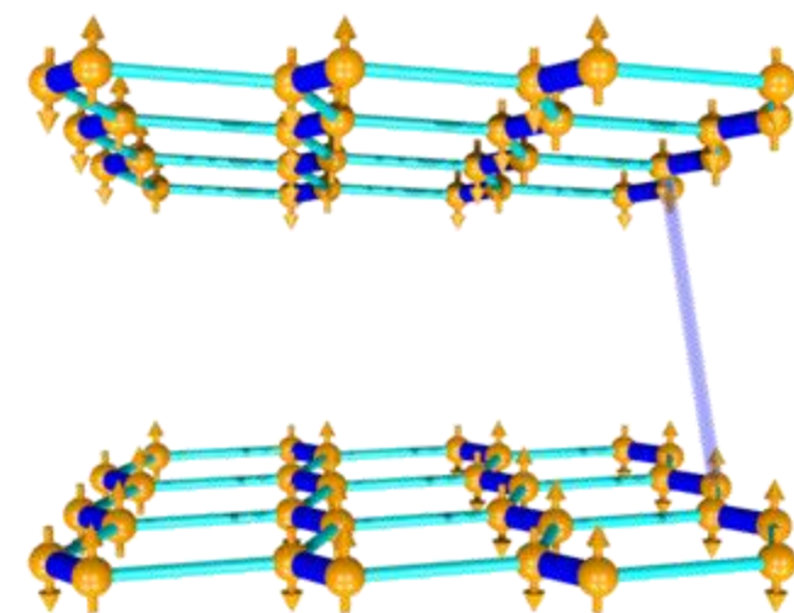
Following a “molecules-to-materials” approach, our group has recently prepared the Cu^{II} -*p*-hydroquinonate polymer **1**, which exhibits unique cooperative magnetic properties as well as a rich solid-state chemistry.^[1,2,3]

- Cu^{II} ions have been chosen as spin carriers, because they show the desired overall spin of $S_z = \frac{1}{2}$ while spin-state crossover cannot occur.
- Ditopic *para*-hydroquinonate ligands lead to intradimer coupling constants J_{intra} of the desired strength.

Cu^{II} -*p*-Hydroquinonate Polymers

Cooperative Magnetic Behavior and Crystal-to-Crystal Transformations

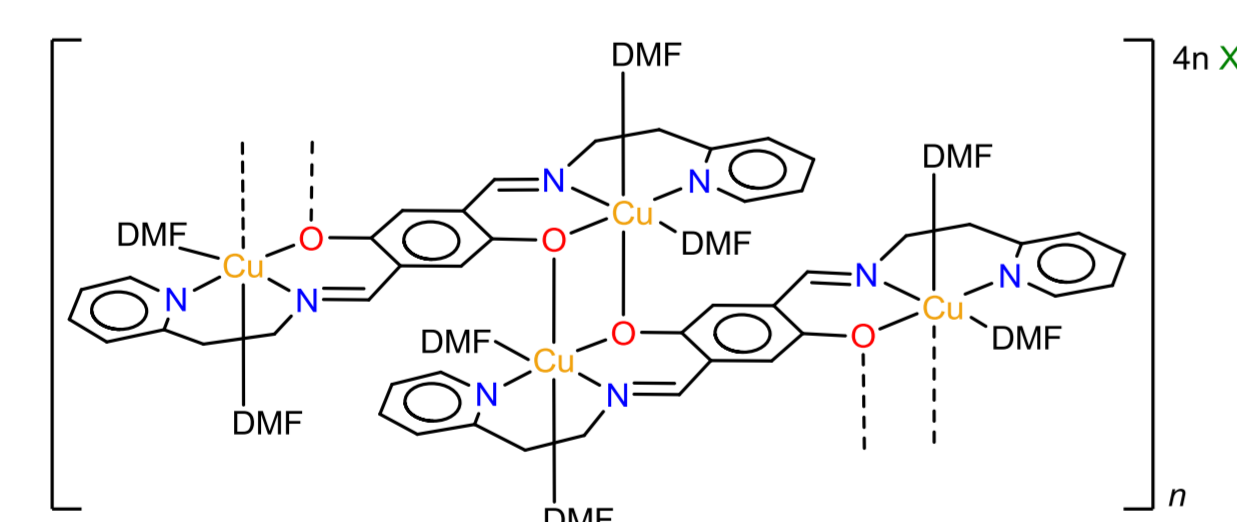
Distorted honeycomb network of spin-spin interactions in **1** (from DFT calculations).



2*: X = CF₃SO₃⁻

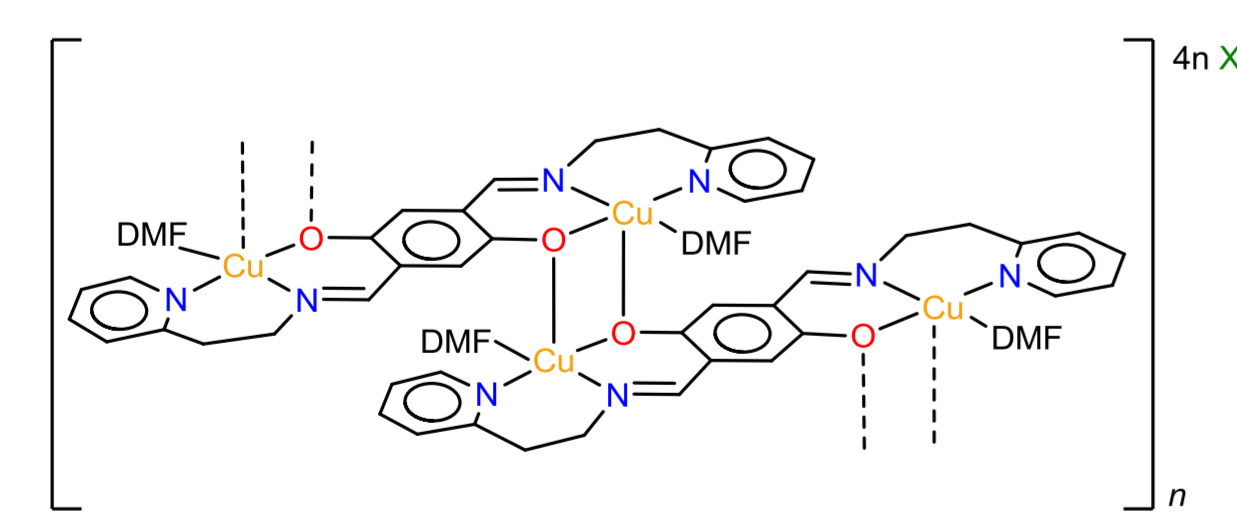
r.t. humid air -4n DMF

r.t. DMF vapor +4n DMF



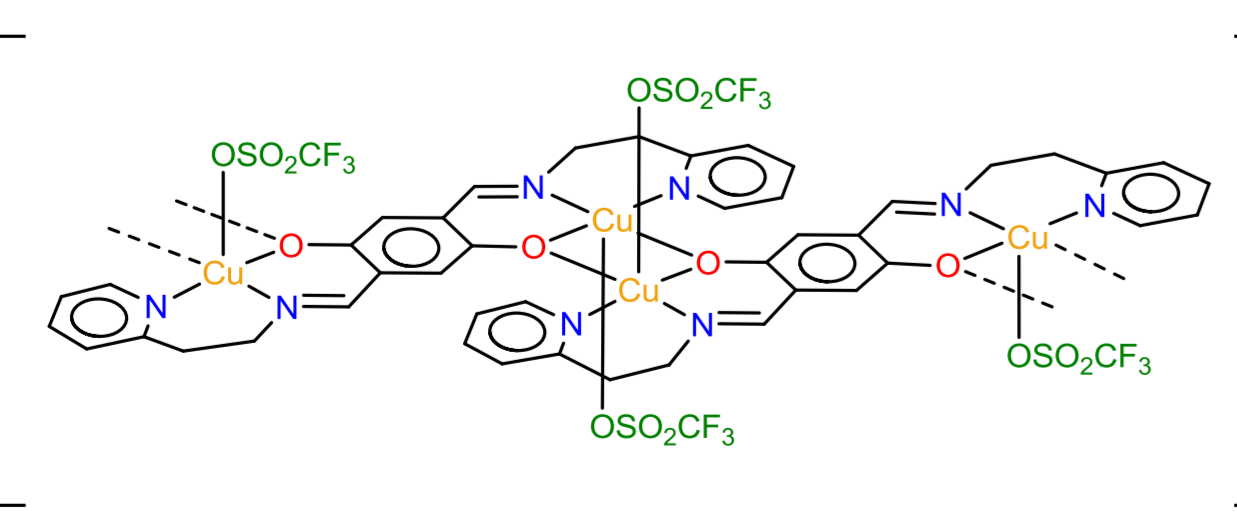
1: X = CF₃SO₃⁻

100 °C -4n DMF



2: X = CF₃SO₃⁻

220 °C -4n DMF

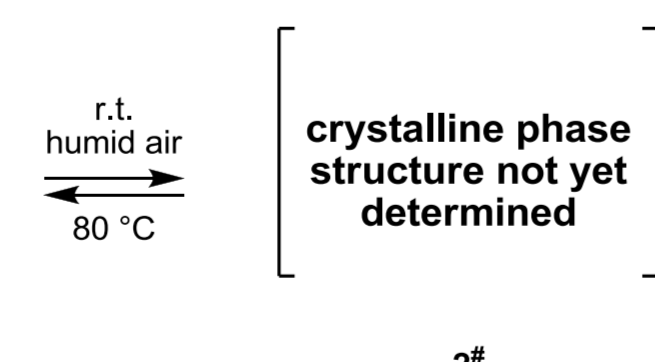


3

- Loss of ancillary DMF donors induces a series of crystal-to-crystal transformations.

- Different crystal structures are established when the conversion is carried out at high (cf. **2**) or low temperatures (cf. **2***); co-crystallized H₂O also influences the crystal structures (cf. **2**, **2***, **2#**).

- The main coupling pathways and the dominant coupling constants are decisively different in **1**, **2**, and **3**.



A top-down approach to new well-defined coordination polymers is highly promising.

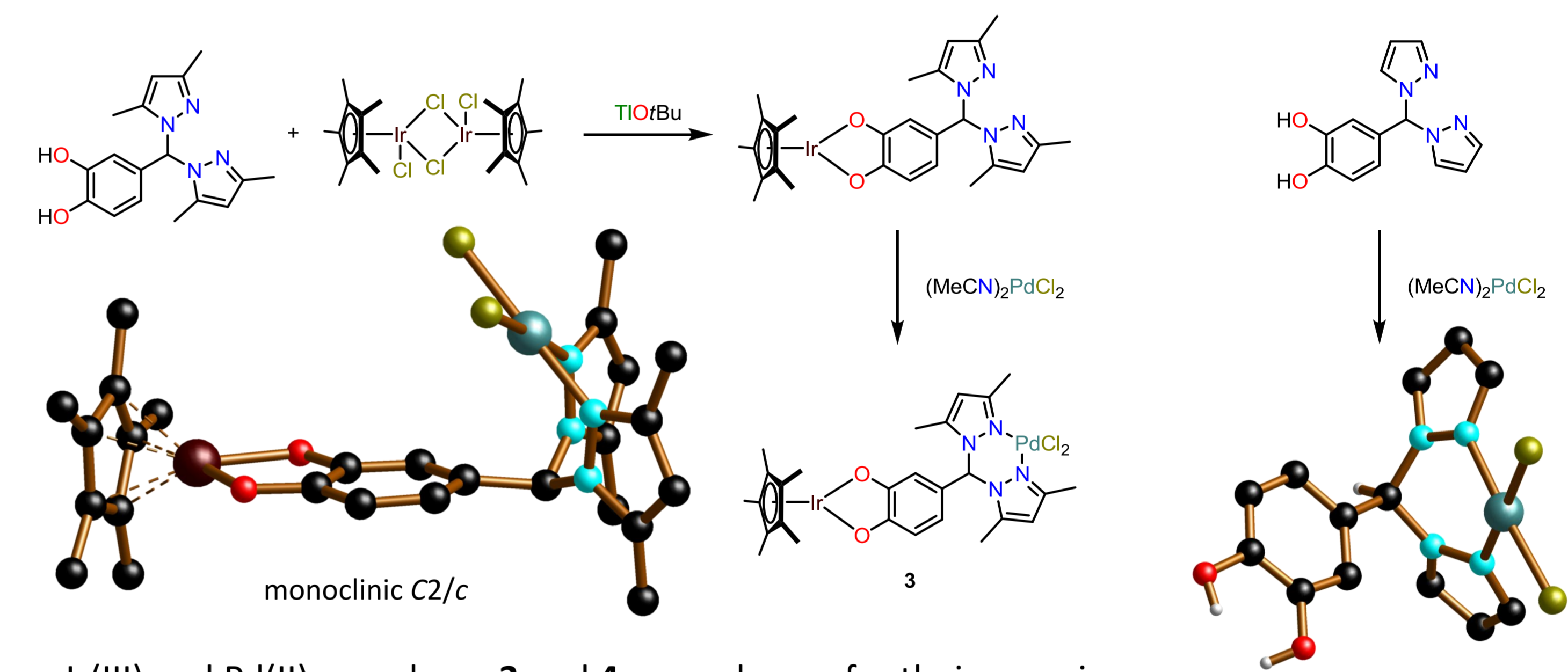
In the area of three-dimensional (3D) networks we are also focusing on compounds in which multiple (hetero)metal centers are bridged by redox-active ligands. *ortho*-Quinones equipped with additional donor groups (e.g., [O,O]/[N,N] mixed-donor linkers) are well suited to synthesize 3D networks after three of these ditopic ligands have been assembled around a metal center. The additional spatially separated donor groups can extend the network in all three dimensions by coordination of further metal ions. Model systems are used to evaluate synthetic methods.

Bis(pyrazol-1-yl)methane donors were chosen in the present case because:

- They form stable complexes with a variety of (transition) metals.
- Steric demand and donor strength can be varied over a broad range.
- The ligand properties of bis(pyrazol-1-yl)methanes on the one hand and *ortho*-quinones on the other are sufficiently different to ensure selective complexation.

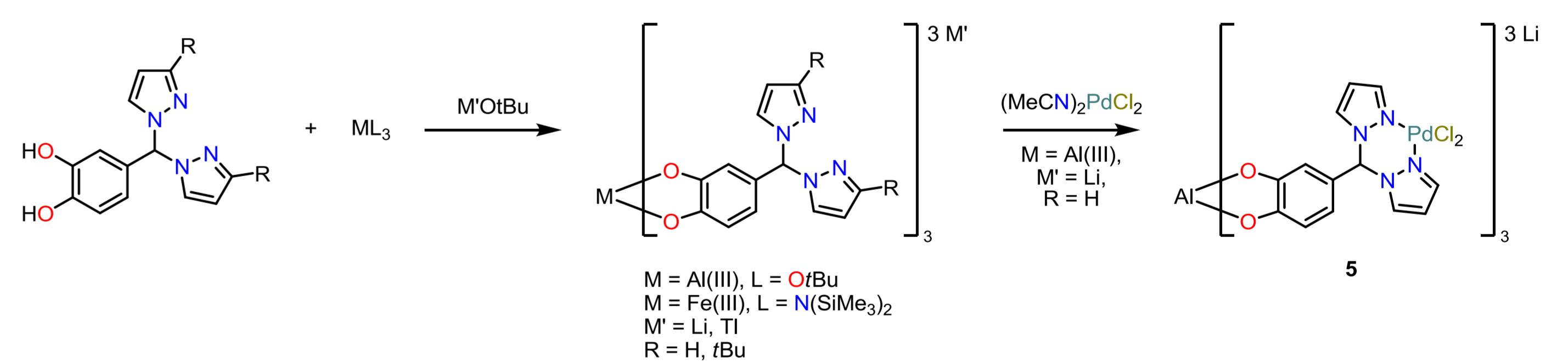
Nanoscale 3D Transition Metal Aggregates

Synthesis and Structure of Model Systems

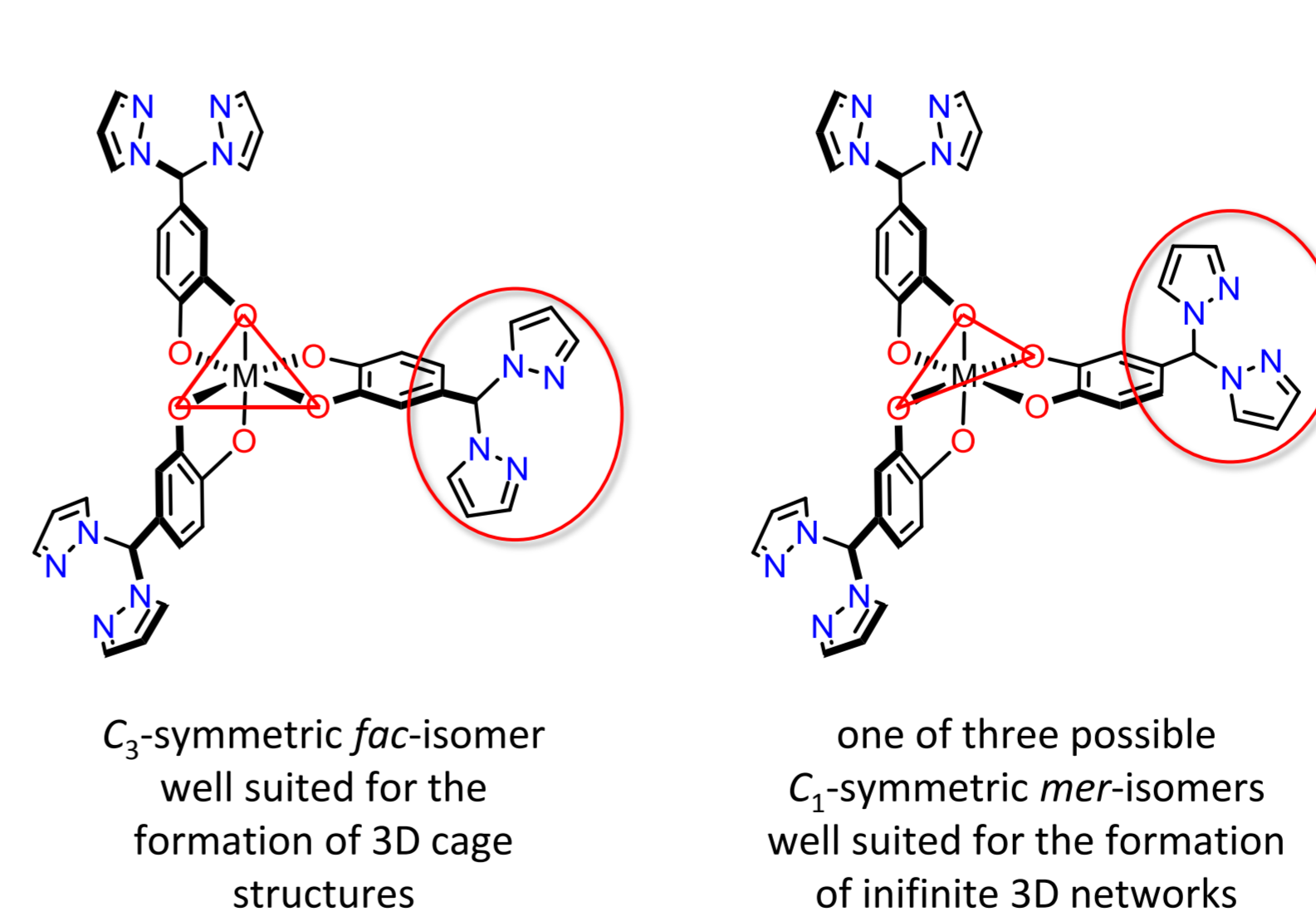


- Ir(III) and Pd(II) complexes **3** and **4** were chosen for their superior solubility and diamagnetism, which make characterization easy.^[4]
- The highly selective introduction of metal ions is facile.
- With these synthetic routes available, a formation of oligonuclear species can be attempted.

Synthesis of Three-Dimensional Networks



- Only microcrystalline precipitates were obtained.
- R = H derivatives are poorly soluble.
- Structure determination from X-ray powder diffraction data for **5** is ongoing.



C_3 -symmetric *fac*-isomer well suited for the formation of 3D cage structures

one of three possible C_1 -symmetric *mer*-isomers well suited for the formation of infinite 3D networks

- NMR spectroscopy (only one signal set) on the M = Al(III) derivative suggests rapid interconversion between *fac*- and *mer*-isomers.
- According to force-field calculations, the interconversion proceeds either via a *Ray-Dutt* or a *Bailar* twist.
- Formation of either cage structures or infinite networks is most likely depending on solvent, temperature, metal ion, etc.

[1] T. Kretz, J. W. Bats, S. Losi, B. Wolf, H.-W. Lerner, M. Lang, P. Zanello, M. Wagner *Dalton Trans.* **2006**, 4914.
 [2] Y. Tsui, A. Brühl, K. Removic-Langer, V. Pashchenko, B. Wolf, G. Donath, A. Pikul, T. Kretz, H.-W. Lerner, M. Wagner, A. Salguero, T. Saha-Dasgupta, B. Rahaman, R. Valenti, M. Lang *J. Magn. Magn. Mater.* **2007**, *310*, Part 2, 1319.
 [3] N. H. Phan, I. Halasz, I. Opahle, E. Alig, L. Fink, J. W. Bats, P. T. Cong, H.-W. Lerner, B. Sarkar, B. Wolf, H. O. Jeschke, M. Lang, R. Valenti, R. Dinnebier, M. Wagner *Cryst. Eng. Comm.* **2011**, *13*, 391.
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