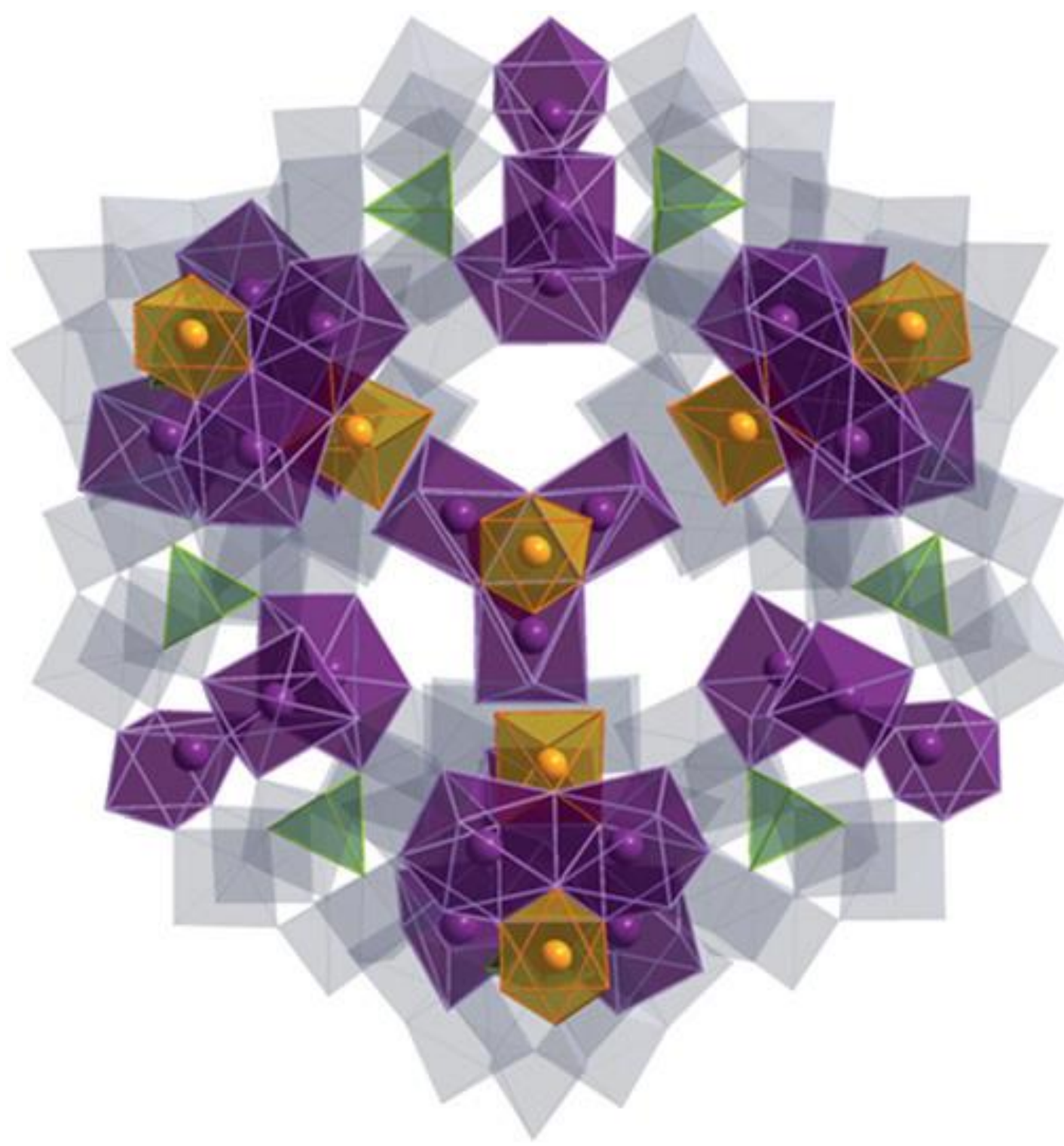
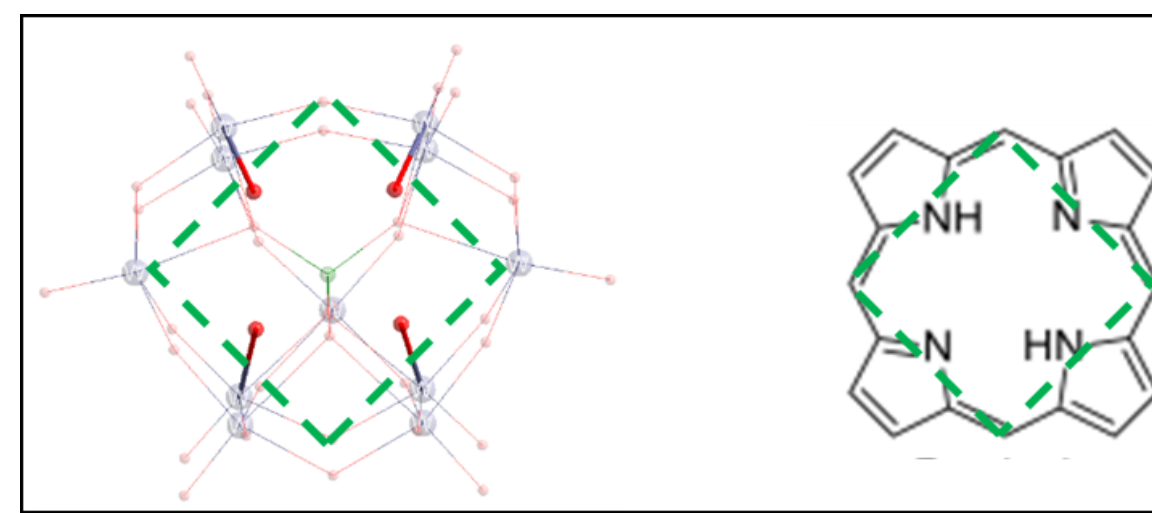


## POM-Based MRI Contrast Agents (CAs)

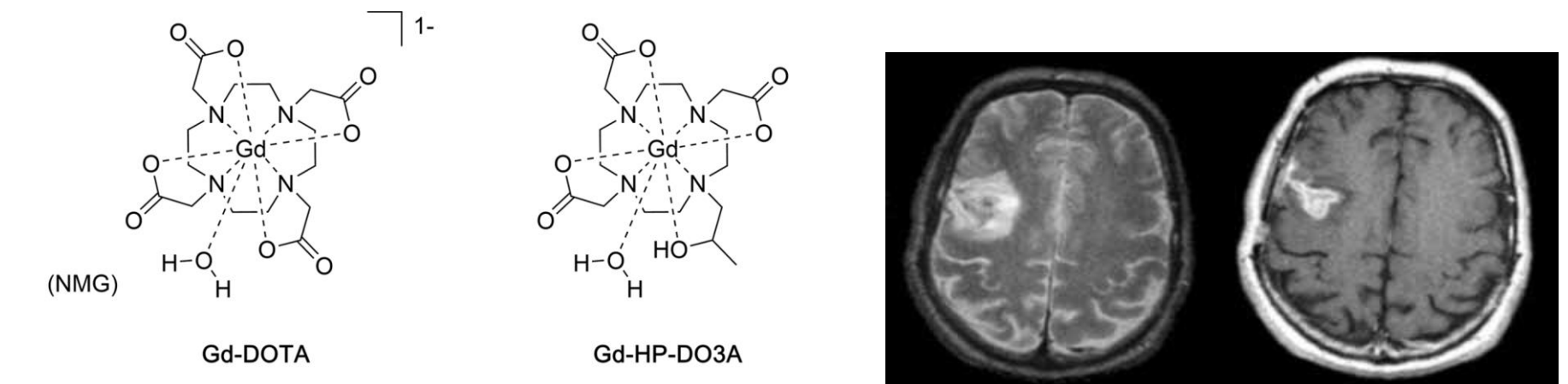
Polyoxometalates (POMs) are anionic clusters composed of early transition metal-oxygen clusters. When integrated with 3d,4f or combined 3d-4f metals at lacunary sites they yield diverse molecular structures with unique electronic properties. These properties play a crucial role in catalysis, magnetism and material science. Paramagnetic metal containing polyoxometalates serves as an inorganic analogue of MRI contrast agents, intended for non-human applications. Their efficacy is evaluated using Nuclear Magnetic Resonance (NMR) technique, measuring their ability to enhance longitudinal and transverse relaxation of nearby water molecules, known as Paramagnetic Relaxation Enhancement (PRE)<sup>1-2</sup>.



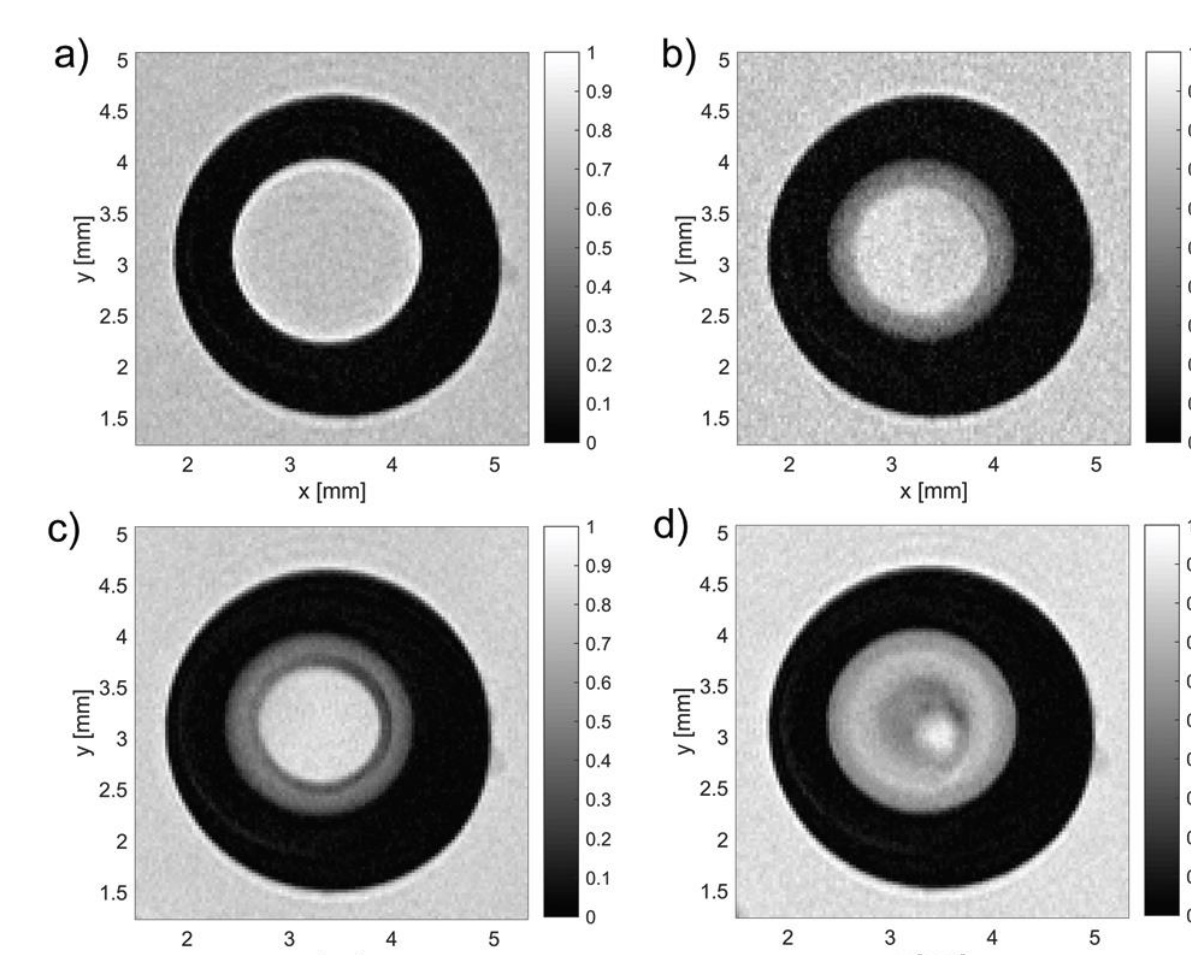
$[(\text{GeW}_6\text{O}_{24})_2\text{RE}^{\text{III}}_3(\text{OH})_3(\text{H}_2\text{O})_6(\text{Co}^{\text{II}}_2\text{RE}^{\text{III}}_3(\text{OH})_2)_6(\text{OH})_6)_6]^{56-}$   $\{\text{RE}_{30}\text{Co}_6\}$   
RE = Dy, Gd, Eu, Y;  $\text{WO}_6$  octahedra gray,  $\text{GeO}_4$  tetrahedra green,  $\text{CoO}_6$  orange,  $\text{DyO}_x$  purple; (DOI: 10.1002/anie.201504663)



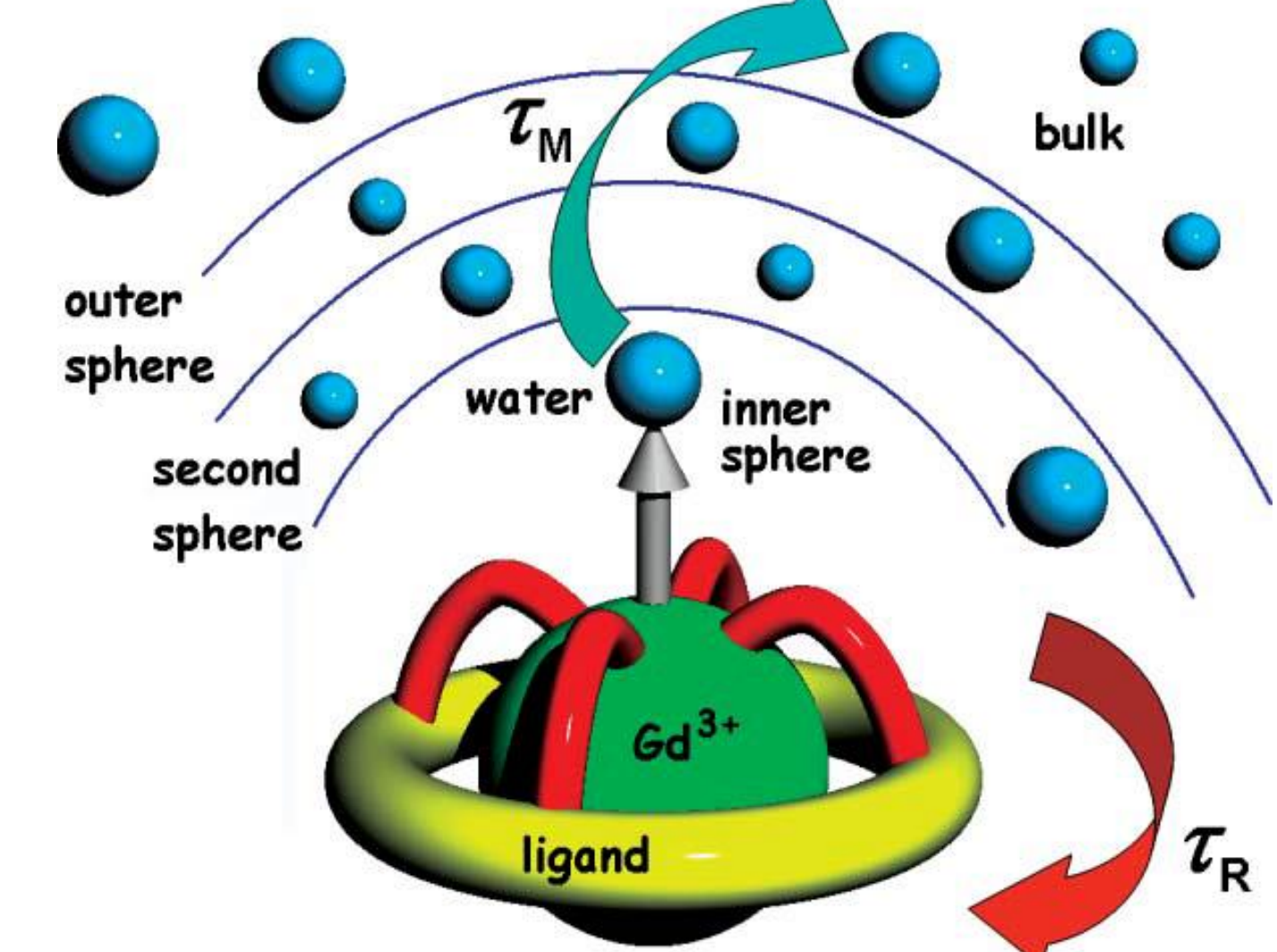
Analogy of monolacunary POM ligand  $[\text{GeW}_{11}\text{O}_{39}]^{8-}$  with porphyrin



Structures of commercially approved clinical MRI contrast agents, MR image of brain before and after CAs; DOI: 10.1021/acs.chemrev.8b00363



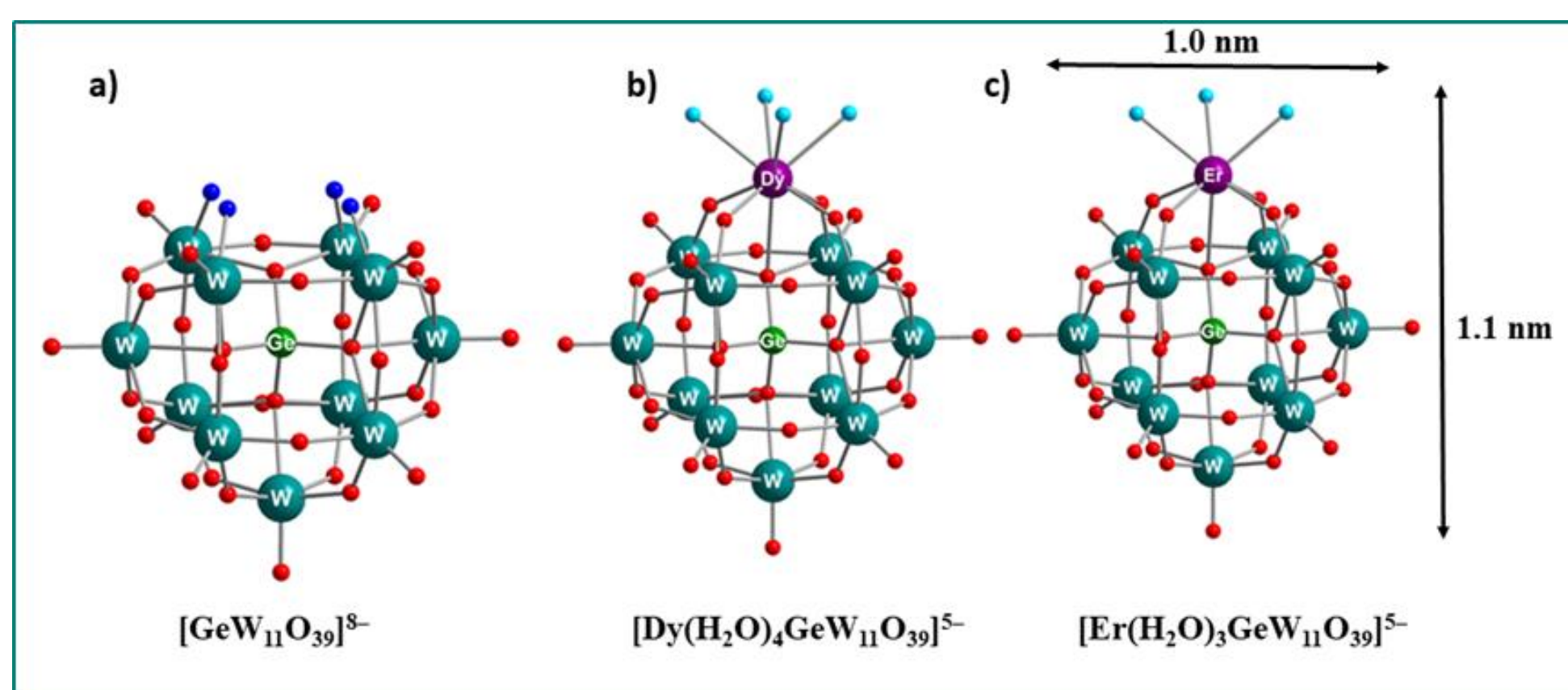
Axial MR image during an in situ dead end membrane filtration of skimmed milk ( $\text{Gd}_{30}\text{Co}_6$  added to enhance the MRI Contrast)



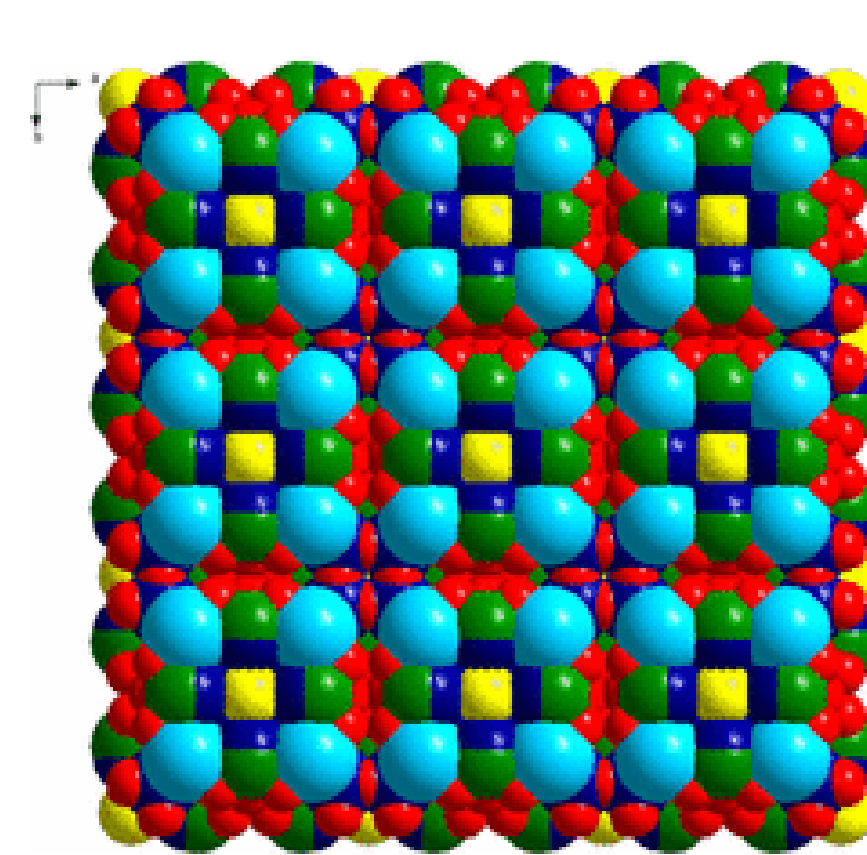
Representation of CAs in solution; DOI: 10.1039/b719704g

## Mononuclear Potential MRI Contrast Agents

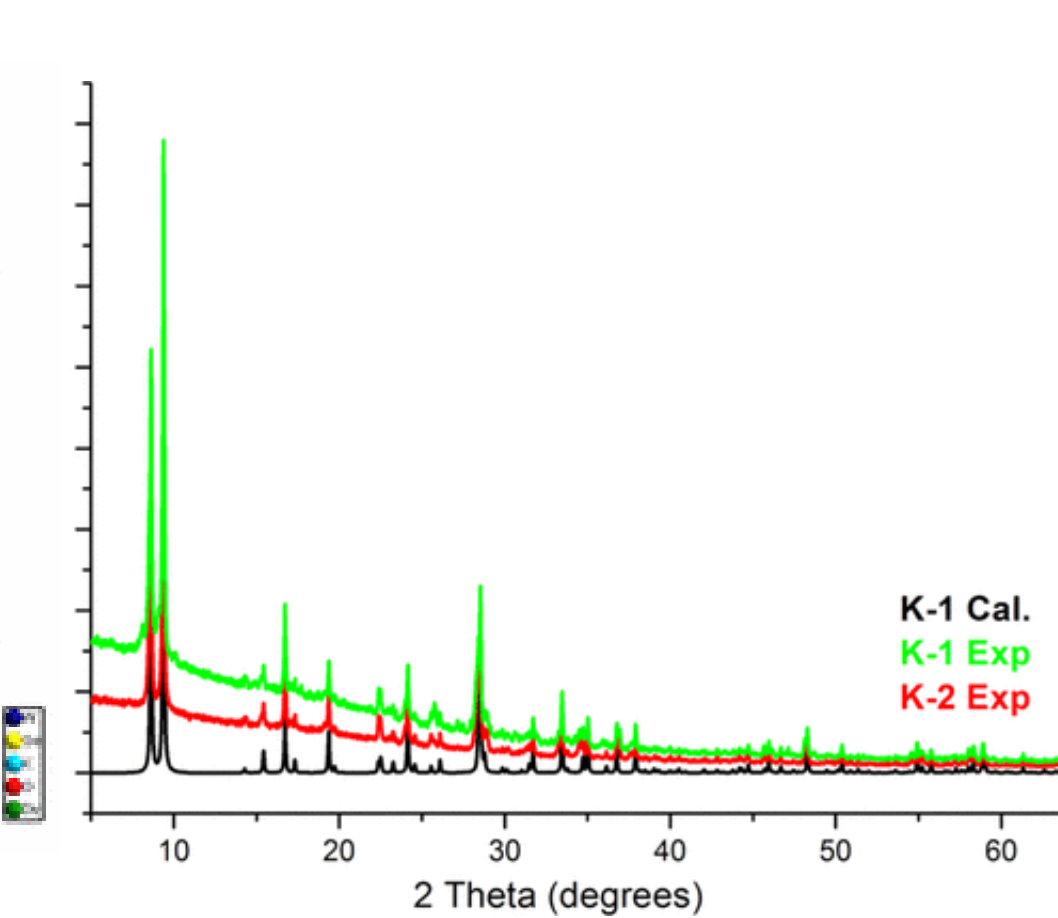
Two monolanthanide-containing polyanions based on monolacunary Keggin germanotungstates  $[\text{Ln}(\text{H}_2\text{O})_n\text{GeW}_{11}\text{O}_{39}]^{5-}$  ( $\text{Ln} = \text{Dy}, \text{Er}$ ,  $n = 4, 3$ ) have been synthesized in simple one-pot synthetic procedure and compositionally characterized in solid state by single-crystal X-ray diffraction, powder X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, and elemental analysis.



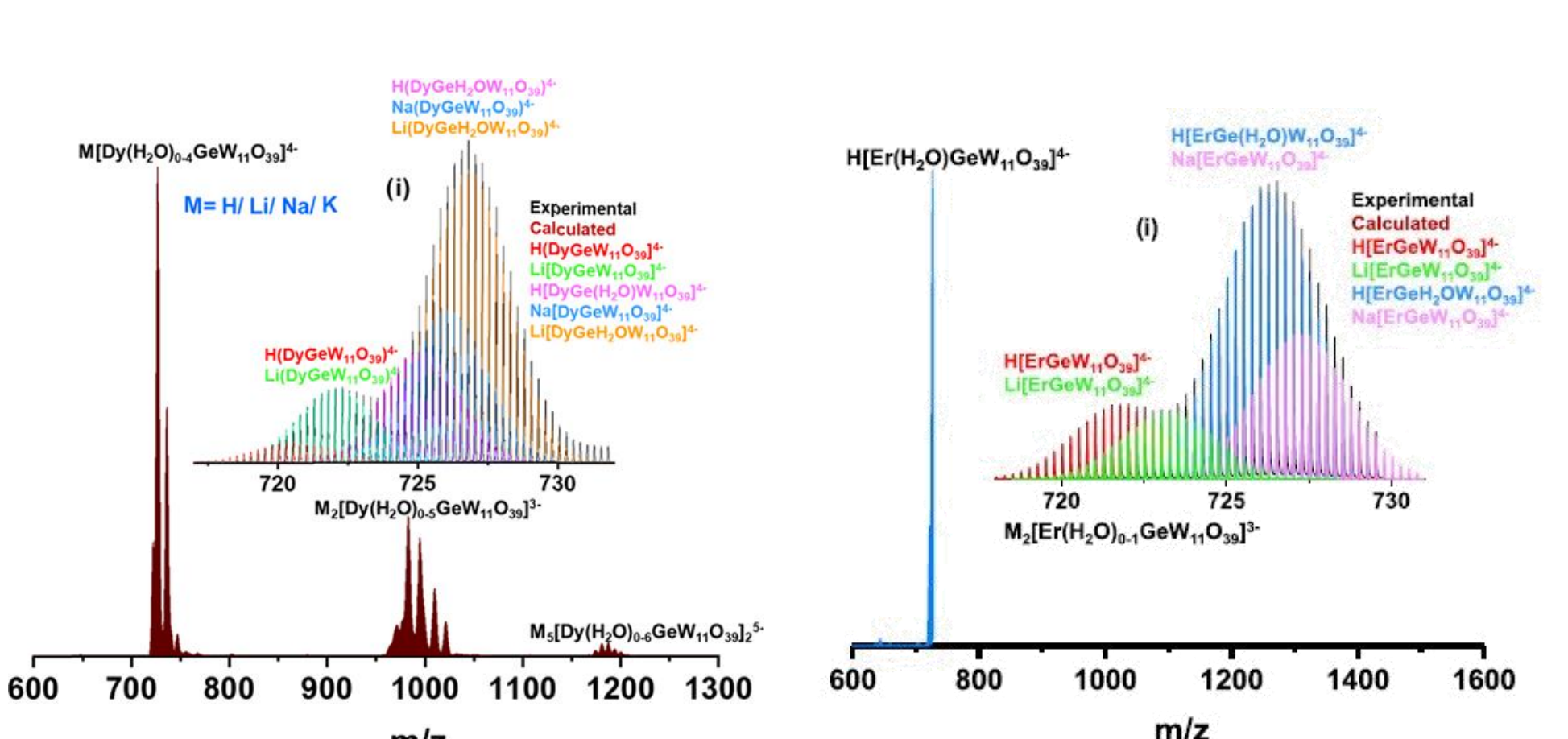
Ball and stick representation of (a) Keggin POM ligand (b)  $(\text{Dy}-\text{W}_{11})$ , (c)  $(\text{Er}-\text{W}_{11})$   
Colour code: O= Red, Aqua= Turquoise, Four oxoligands that coordinate to paramagnetic metal ions = Dark blue



Crystal packing arrangements



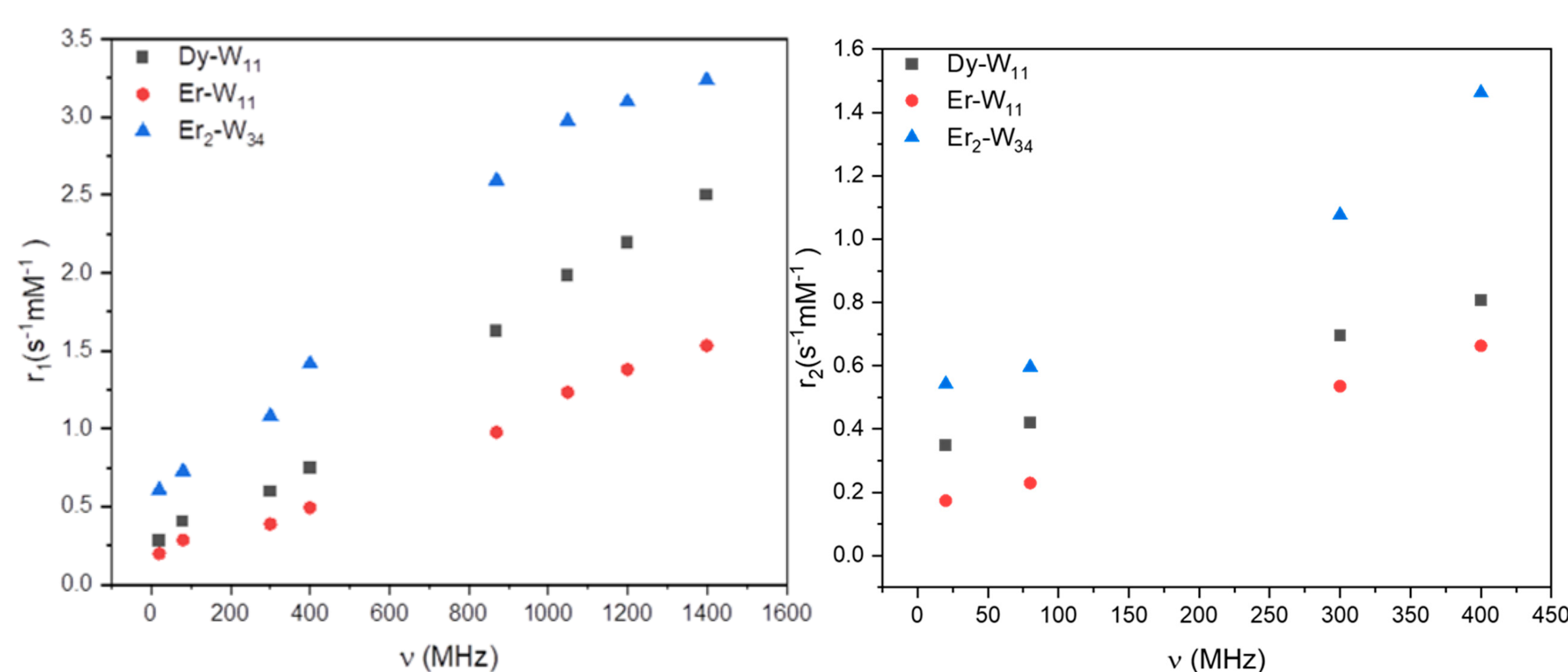
PXRD studies



Electrospray ionization mass spectrometry (ESI-MS)

## Water $^1\text{H}$ Relaxation Measurements

To investigate the Paramagnetic Relaxation Enhancement (PRE) of the POMs ( $\text{Dy}-\text{W}_{11}$ ), ( $\text{Er}-\text{W}_{11}$ ) and ( $\text{Er}_2-\text{W}_{34}$ ), longitudinal and transverse relaxivity measurements were performed at NMR Larmor frequencies from 20 MHz to 1.4 GHz.

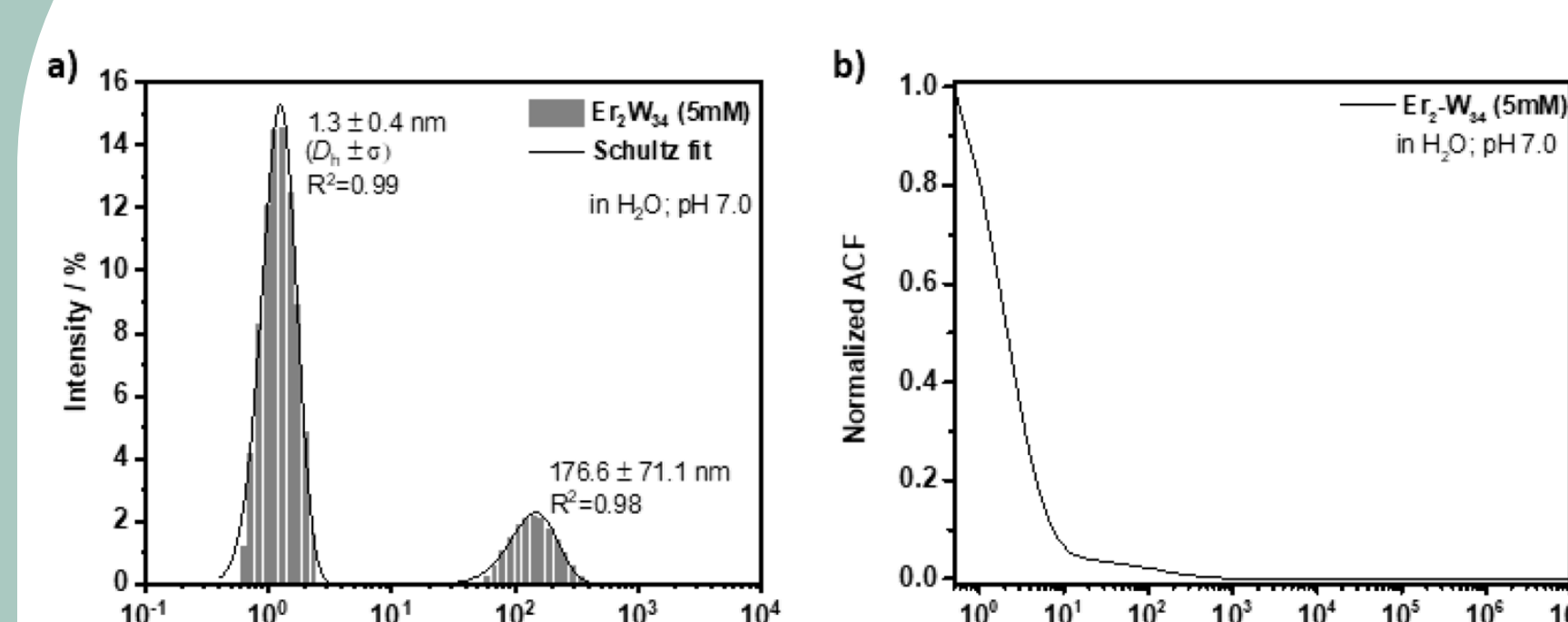


longitudinal relaxivities  $r_1$  and transverse relaxivities  $r_2$  of  $^1\text{H}$  of water with POM metal clusters ( $\text{Dy}-\text{W}_{11}$  and  $\text{Er}-\text{W}_{11}$ , and  $\text{Er}_2-\text{W}_{34}$ ) as a function of the Larmor frequency  $\nu$

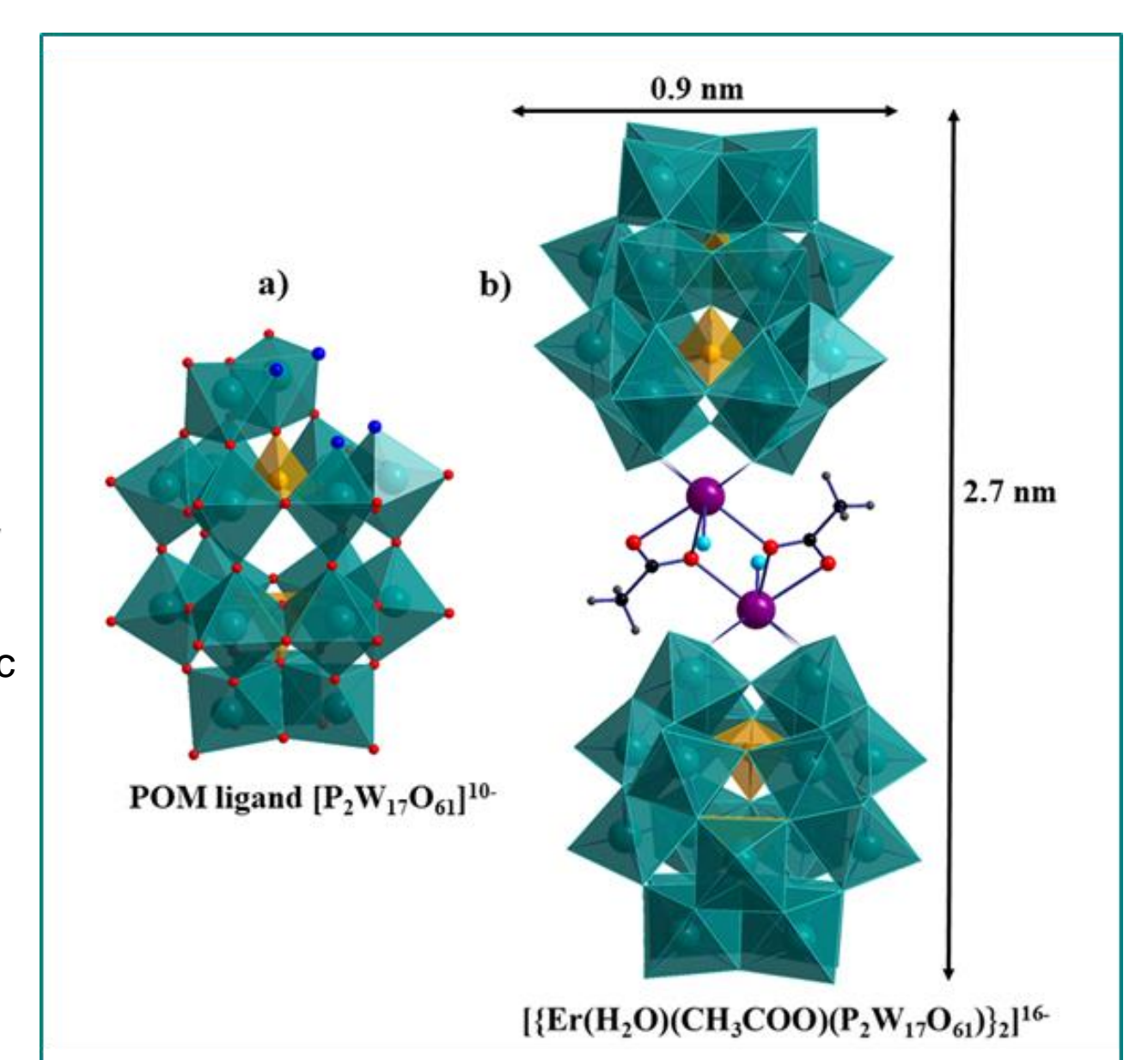
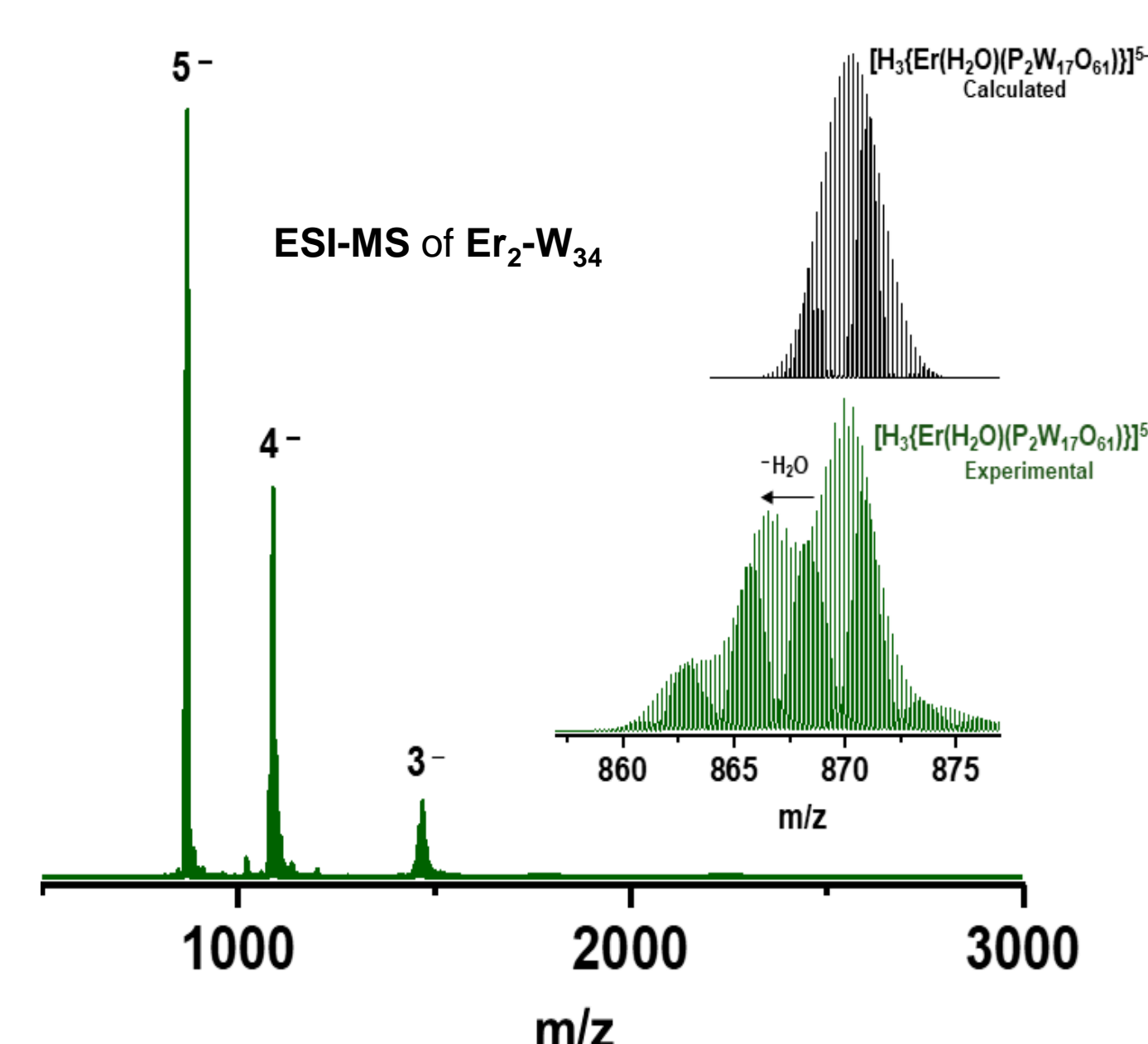
## Conclusion

The high anisotropic electronic ground state of the paramagnetic lanthanide ions in the molecules provides very short electronic relaxation times in the  $^1\text{H}$  relaxation measurements so it can perform as an efficient MRI CAs at intermediate to ultra-high magnetic fields.

## Dinuclear Potential MRI Contrast Agents



DLS analysis on  $\text{Er}_2-\text{W}_{34}$  (5 mM) at pH 7.0 in water. (a) Hydrodynamic diameter of  $\text{Er}_2-\text{W}_{34}$ . (b) Corresponding normalized autocorrelation function.



(a) Ligand (b)  $\text{Er}_2-\text{W}_{11}$ . Color code: O= red; aqua ligand = turquoise, four oxo ligands that coordinate to Er metal ions = dark blue,  $\text{WO}_6$  octahedral = teal,  $\text{PO}_4$  tetrahedra = yellow, Er = violet, C = black, H = grey.

A dinuclear erbium(III) substituted sandwich-type POM ( $\text{Er}_2-\text{W}_{34}$ ) has been isolated from a simple one-pot synthetic procedure and characterized it in the solid as well as in the solution state.