

# Synthesis of a Series of Heavy Lanthanide(III) Monoporphyrinato Complexes with Tetragonal Symmetry

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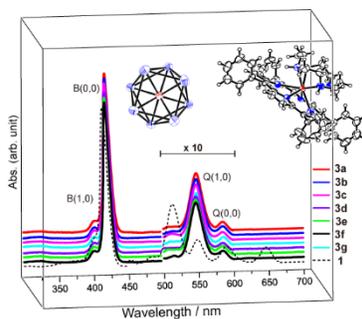
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ABSTRACT: A series of heavy lanthanide(III) and yttrium(III) monoporphyrinato complexes formulated in  $[\text{Ln}(\text{TPP})(\text{cyclen})]\text{Cl}$  ( $\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$  and  $\text{Y}$ ;  $\text{TPP} = 5,10,15,20$ -tetraphenylporphyrinato), with cyclen, 1,4,7,10-tetraazacyclododecane, as a capping ligand, has been prepared in a mild condition and studied using single crystal X-ray diffraction crystallography. The complexes exhibit B(0,0) electronic absorption band in the range of 421–423 nm, showing a bathochromic shift associated with the increase of the ionic radii of the lanthanide, as well as two peaks of Q(1,0) and Q(0,0) bands between 548–586 nm. All the complexes are isostructural, where both TPP and cyclen are coordinated to a lanthanide(III) or yttrium(III) ion giving an eight-coordinate square-antiprismatic (SAP) geometry (average skew angles are in the

range of  $43.01^\circ$ – $43.67^\circ$ ). The mean plane of the four nitrogen atoms of TPP ( $N_4^t$ ) and that of cyclen ( $N_4^c$ ) are virtually parallel with dihedral angle less than  $1^\circ$ . The lanthanide(III) or yttrium(III) ions lie between  $N_4^t$  and  $N_4^c$ . The position of the metal ion is closer to the  $N_4^t$  plane which is presumably caused by the different charges of the ligands, size of  $N_4$  square ligands and steric factor. The average Ln–N and interplanar distances ( $d_N$ ) decrease with decreasing lanthanide(III) ionic radii, showing the effect of lanthanide contraction. On the other hand, the skew angles, opening angles and N–N distances are nearly unchanged, keeping the rigid square antiprismatic geometry throughout the series.

### Synopsys



The crystal structure of lanthanide(III) monoporphyrinato complexes are rarely reported over the years. Here, a series of the complexes, formulated in  $[Ln(TPP)(cyclen)]Cl$ , which having strict four-fold symmetry axis successfully was obtained in a mild condition and crystallized in a tetragonal system with very similar lattice parameters. By varying lanthanide ions, the average Ln–N and interplanar distances ( $d_N$ ) decrease with decreasing lanthanide(III) ionic radii and gives monotonic shift to the absorption spectra.