

## Formation of chiral heteronuclear $\text{Lu}^{\text{III}}$ assemblies by ion pair formation.

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### Streszczenie

Cationic  $\text{Ln}^{\text{III}}$  complexes with the chiral macrocycle **L**,  $(P)$ - $[\text{LnL}_{RRRRRR}]^{3+}$ , interact with anionic  $\text{Ln}^{\text{III}}$  tris(dipicolinate) complexes,  $[\text{Ln}'(\text{dpa})_3]^{3-}$ , forming tight hydrogen-bonded ion pairs in solution. Formation of these pairs has been documented by the DFT calculations, and a strong paramagnetic shift of the signals of the diamagnetic cation interacting with the paramagnetic anion was observed. This ion pair interaction leads to spectral enantiodifferentiation of the  $\Lambda$ - $[\text{Ln}'(\text{dpa})_3]^{3-}$  and  $\Delta$ - $[\text{Ln}'(\text{dpa})_3]^{3-}$  enantiomers of the anionic complex. Although no Pfeiffer effect was observed for the  $(P)$ - $[\text{LnL}_{RRRRRR}]^{3+}$  diastereomers of the cationic complex, the  $(M)$ - $[\text{LnL}_{RRRRRR}]^{3+}$  diastereomers induce CD signals in the anionic  $[\text{Ln}'(\text{dpa})_3]^{3-}$  partner. These spectra indicate a Pfeiffer effect, i.e. a shift of equilibrium between the  $\Lambda$ - $[\text{Ln}'(\text{dpa})_3]^{3-}$  and  $\Delta$ - $[\text{Ln}'(\text{dpa})_3]^{3-}$  enantiomers. This effect arises from the ion pair interaction between the anionic complex  $[\text{Ln}'(\text{dpa})_3]^{3-}$  and the intact cationic complex as well as between  $[\text{Ln}'(\text{dpa})_3]^{3-}$  and **L**. The protonated macrocycle  $(\text{H}_3\text{L}_{RRRRRR})^{3+}$  forms highly insoluble salts with  $[\text{Ln}'(\text{dpa})_3]^{3-}$ . These supramolecular compounds are formed by the reaction of **L**, acids and  $[\text{Ln}'(\text{dpa})_3]^{3-}$  anions. The same product can also be formed by the reaction of  $(M)$ - $[\text{LnL}_{RRRRRR}]^{3+}$  with three equivalents of dipicolinic acid. The model structure of  $(\text{H}_3\text{L}_{RRRRRR})[\text{Ln}'(\text{dpa})_3]$  corresponds with a linear polymer with alternate cationic macrocycles and anionic  $[\text{Ln}'(\text{dpa})_3]^{3-}$  complexes interacting through charge interactions and multiple hydrogen bonds.

### Adres publiczny

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