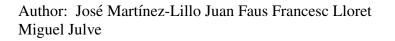
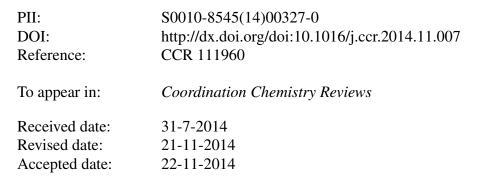
## Accepted Manuscript

Title: Towards Multifunctional Magnetic Systems through Molecular-Programmed Self Assembly of Re(IV) Metalloligands





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# ACCEPTED MANUSCRIPT

## Towards Multifunctional Magnetic Systems through Molecular-Programmed Self Assembly of Re(IV) Metalloligands

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#### Abstract

The molecular-programmed approach based on the use as ligands of tailor-made metalloligands containing stable six-coordinate rhenium(IV) as paramagnetic centers is presented in this review article. A relatively large amount of spin density is covalentdelocalized away from the rhenium to the peripheral atoms of the ligands in the case of the Re(IV) metalloligands, as shown by polarized neutron diffraction experiments and density functional theory calculations. This feature accounts for the significant through space-magnetic interactions that occur in most of its mononuclear species and more interestingly it also explains the strengthening of the magnetic interactions in the heterometallic Re(IV)-X-3d units respect to the 3d'-X-3d ones, X being a mono- or polyatomic bridging ligand. The complexing ability of the mononuclear Re(IV) species having halo- and pseudohalogeno, cyanide and dicarboxylate groups as peripheral ligands towards either fully solvated metal ion or partially blocked metal complexes allowed the rational preparation of heterometallic compounds with controlled dimensionality and interesting magnetic properties. The variety and *a priori* easy functionalization of the peripheral donors of these stable Re(IV) precursors, together with their potential bridging ability make them very promising candidates to create multifunctional molecule-based magnetic materials in a very near future.

*Keywords*: Metallosupramolecular chemistry; Rhenium(IV) complexes; Heterometallic complexes; Single-chain magnets; Single-molecule magnets.

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