

Radical building block approach to three-dimensional magnetic exchange networks

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Pyridine-bridged bisdithiazolyl (BP) radicals are among a class of stable radical building blocks towards the design of molecular magnetic materials. Through resonance stabilization and the steric influences resulting from their beltline substituents, BP radicals have been shown to afford self-assemblies that generate three-dimensional magnetic networks through pairwise exchange interactions.[1,2] To this end, the *N*-methyl-4-phenylpyridine-bridged bisdithiazolyl radical (PhBPMe) has been synthesized, crystallizing in two phases: the α -phase in the trigonal space group $P3_121$ and the β -phase in the orthorhombic space group $Pca21$. In the crystal structure of the β -polymorph, radicals assemble into corrugated herringbone arrays of slipped π -stacks, from which the beltline substituents restrict radical-radical close contacts to within two-dimensional motifs. However, in the α -phase, these substituents contribute to the arrangement of π -stacks into spiral motifs about 3_1 axes that propagates radical-radical interactions in three dimensions (Figure 1). Variable temperature magnetic susceptibility measurements on the β -phase indicate strong antiferromagnetic coupling while weaker but predominantly antiferromagnetic interactions are observed in the α -phase. Moreover, a three-dimensional antiferromagnetic state ordering below 8 K is observed for the α -phase (Figure 1). This presentation will discuss the selective isolation of each crystalline phase along with their corresponding magnetic behaviour, as analyzed with high temperature series expansion methods and further supported through density functional theory broken symmetry calculations.

[1] L. Beer, Chem. Mater. **16**, 1564 (2004)

[2] N.J. Yutronkie, Inorg. Chem. **58**, 419 (2019)

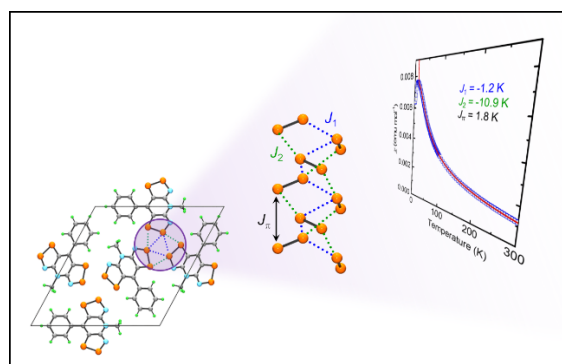


Figure 1 : (left) Unit cell projection of α -PhBPMe down the π -stacking axis and (middle) view of the interstack interactions along one of the spiral motifs. (right) Plot of the magnetic susceptibility as a function of temperature for α -PhBPMe.