

Dithiadiazolyl radicals as building blocks for functional materials

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The 1,2,3,5-dithiadiazolyl radicals (DTDAs), $R-CNSSN^{\bullet}$, are of considerable interest due to their potential as magnetic or conducting materials. However, DTDAs tend to dimerise in the solid state via an interaction known as pancake bonding.[1] Pancake bonding between DTDAs results in spin pairing, rendering the resulting materials diamagnetic. Overcoming this dimerization interaction has been the focus of much effort, and several DTDAs that remain paramagnetic in the solid state have been characterised, with some exhibiting magnetic ordering at low temperatures.[2] This presentation will present our efforts in characterising solid-state materials containing DTDAs using a combination of X-ray diffraction experiments, computational methods and spectroscopy.

In order to better understand (and thus overcome) the pancake bonding interaction, we have turned to experimental charge density investigations.[3] An analysis of the topology of the charge density of a series of DTDAs reveals how pancake bonding differs from both covalent bonding and conventional intermolecular interactions.

We have also explored the incorporation of DTDAs into multi-component crystals, including co-crystals[4] and porous materials,[5] in order to overcome dimerisation. Co-crystal formation with DTDAs has been shown to be highly dependent on experimental conditions. Inclusion of DTDAs in porous hosts shows great potential for the development of functional materials.

Finally, we have investigated the coordination of DTDAs to metalloporphyrins, yielding at least one new material with intriguing properties. [6] It is clear that DTDAs show great potential as building blocks in the construction of molecular materials.

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[2] see D. A. Haynes, *CrystEngComm*, 2011, 13, 4793 and references therein.

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