

Dithiadiazolyl radicals as building blocks for molecular materials

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27 de Septiembre de 2018

Seminario de Física Nuclear

13:00 p.m.

The 1,2,3,5-dithiadiazolyl radicals (DTDA), $R\text{-CNSSN}\cdot$, are of considerable interest due to their potential as building blocks for materials with interesting magnetic or conducting properties. These radicals are thermally and kinetically stable, but frequently dimerise in the solid state, rendering them diamagnetic. [1] We have explored the incorporation of DTDA into multi-component crystals, including co-crystals and porous materials, in order to overcome dimerisation.

The potential of co-crystallisation as a means of overcoming dimerisation in DTDA, via the introduction of a strong supramolecular synthon on the co-crystal former, has been probed. [2] A number of co-crystals have been characterized, and experimental charge density studies [3] as well as computational investigations have shed some light on the nature of the dimerisation interaction in these co-crystals.

As part of this study, we have investigated the coordination of DTDA to metalloporphyrins. An interesting coordination polymer of 4-(4'-pyridyl)-1,2,3,5-dithiadiazolyl and cobalt(II) tetraphenylporphyrin has been characterised. [4] Investigations using EPR and UV-visible spectroscopy indicate that a number of othermetalloporphyrin-DTDA complexes form in solution.

The inclusion of DTDA in porous materials has also been investigated: PhDTDA has been included in a metallocyclic host constructed by reacting CuCl_2 with 1,3-bis(imidazolyl-1-ylmethyl)-2,4,6-trimethylbenzene [5]. The radical is included in the host as a monomer, via a single-crystal to single-crystal process, and is stable in the host under ambient conditions. It is clear that DTDA show great potential as building blocks in the construction of molecular materials.

[1] see D. A. Haynes, *CrystEngComm*, 2011, 13, 4793 and references therein. [2] C. Alan, D. A. Haynes, C. M. Pask, and J. M. Rawson, *CrystEngComm*, 2009, 11, 2048; S. W. Robinson, D. A. Haynes and J. M. Rawson, *CrystEngComm*, 2013, 15, 10205. [3] S. Domagała, K. Kościński, S. W. Robinson, D. A. Haynes and K. Wozniak, *Cryst. Growth Des.*, 2014, 14, 4834; S. Domagała and D. A. Haynes, *CrystEngComm*, 2016, 18, 7116. [4] D. A. Haynes, L. J. van Laeren and O. Q. Munro, *J. Am. Chem. Soc.*, 2017, 139, 14620. [5] V. I. Nikolayenko, L. J. Barbour, A. Arauzo, J. Campo, J. M. Rawson and D. A. Haynes, *Chem. Commun.*, 2017, 53, 11310.