Invited Lecture

Crystal Engineering of Radical-Radical Cocrystals

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In 1928 Heisenberg proposed that bulk (ferro)magnetic order would only ever be achieved in systems containing heavy atoms (i.e. metals, their oxides, nitrides etc) [1]. Indeed, the first observation of bulk ferromagnetism in an organic radical was not observed until 1991, albeit at 0.6 K [2]. Since then approaches to develop new organic magnets with higher ordering temperatures have been explored. In 1993 Peter Day suggested that magnetic ordering in organic materials would not occur above room temperature [3] and, while ordering temperatures up to 70 K have been achieved [4], radical magnetism at room temperature continues to be elusive.

Our research has recently focussed on the cocrystallization of radicals to afford radical-radical cocrystals as potential routes to organic ferrimagnets [5,6]. The current study explores the cocrystallization of dithiadiazolyl (DTDA, E = S, Fig. 1) and diselenadiazolyl (DSDA, E = Se, Fig 1) radicals with TEMPONE [6]. This presentation reports recent experimental and computational studies on the relative energetics of DTDA…O-N< *vs* DTDA…O=C< interactions, reflected in competing regions of O^{d-} for TEMPONE (Fig. 1(inset)) [7].

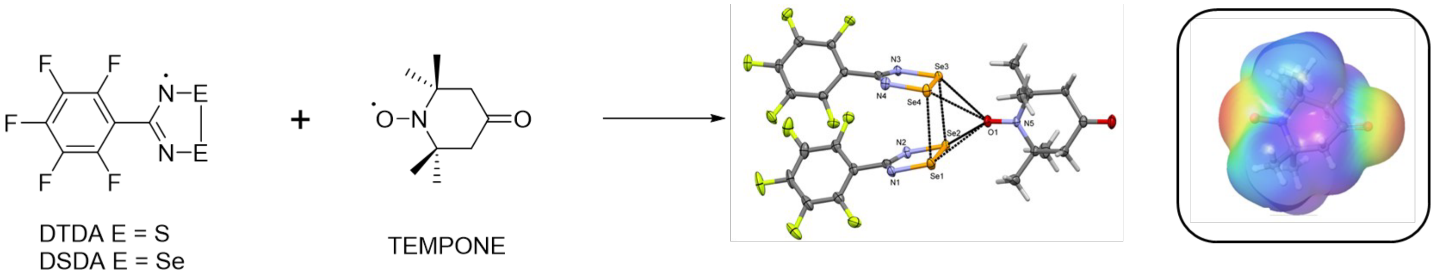

Figure 1. Reaction of the DTDA and DSDA radicals with TEMPONE afford the 2:1 cocrystals [DTDA]$_2$[TEMPONE] and [DSDA]$_2$[TEMPONE]; inset: molecular electrostatic potential for TEMPONE.

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