MS36-O4 Design and fine-tuning of magnetic properties in organic salts of semiquinone radical

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Semiquinones are a class of stable organic radical anions; especially stable are ones with four electronegative substituents (Fig. 1a), which enhance delocalisation of the unpaired electron. Therefore, they are potential candidates for design of functional materials with fine-tuned magnetic properties.

Semiquinoid anions in crystals are usually stacked by π-interactions, and their magnetic properties depend on their interplanar distance. Most often, the radicals form closely bound dimers with coupled spins (type I, Fig 1c) [1,2], resulting in diamagnetic properties. However, crystal engineering can be used to enlarge the ring separation distance with equidistant-ring stacks generating antiferromagnetic [3] or paramagnetic crystals (type II, Fig 1c).

Our research has been aimed to obtain stable semiquinone systems with fine-tuned magnetic properties by crystal engineering: we varied size of substituents on the quinoid ring (Fig. 1a) and aromatic organic cations (Fig. 1b). Therefore, we varied substituents on the semiquinone ring: tetrachloro- (CA), tetrabromo- (BA) and 2,3-dicyano-5,6-dichlorosemiquinone (DDQ) were used as anions. Aromatic, approximately planar organic cations [pyridinium (py), N-methylpyridinium (N-MePY) and diquat] were used to check for possible π-interactions between cations and anions.

Crystallographic, magnetic (EPR, SQUID), electrical (impedance spectroscopy) and thermal (TG/DTA, DSC) methods were used to obtain data on structure, stability, magnetic and electrical properties of the crystalline compounds.

A pair of analogous salts, N-MePy•CA and N-MePy•BA is especially interesting: in CA salt closely bound radical dimers occur, similar to previously known K•CA•Me_2CO [1] and similar alkali salts of DDQ [2], and the crystals are diamagnetic due to spin pairing. In BA salt radicals are equdistant, similar to high-temperature polymorph of K•CA•MeCOEt [3]; due to larger interplanar distances, the crystals are paramagnetic.

To gain insight into spin coupling/decoupling and transport properties, impedance spectroscopy was done on single crystals with electrical contacts applied in the direction of stacking.

References

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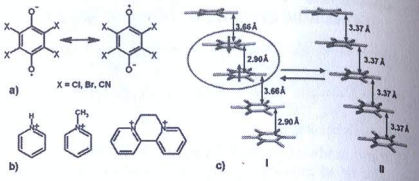

Figure 1. a) Electronic structure of semiquinone radical is between quinoid and aromatic due to an unpaired electron and negative charge delocalised throughout the ring. b) Used cations. c) Two types of stacks of quinoid rings: I dimers with coupled spins and II equidistant rings with no spin coupling.

Keywords: semiquinone radical, spin coupling, crystal engineering, magnetism, EPR spectroscopy, impedance spectroscopy