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**Fine-tuning of magnetic properties in semiconductive 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, which enhance delocalisation of the unpaired electrons. 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 [1,2], which result in diamagnetic properties. However, in smartly designed crystals the distance can be increased, so stacks with equidistant rings will appear, which may be antiferromagnetic [3] or paramagnetic.

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, N-methylpyridinium and diquat) were used to check for possible π-interactions between cations and anions. The goal of our research was design novel stable (in air, at room temperature) semiquinone systems with fine-tuned magnetic properties by crystal engineering: we varied size of substituents on the quinoid ring and aromatic organic cations. A combination of crystallographic, magnetic (EPR, SQUID), electrical (impedance spectroscopy) and thermal (TG/DTA, DSC) methods was used to obtain data on stability and magnetic properties of the crystalline compounds. To gain further insight into spin coupling/decoupling, impedance spectroscopy was used to measure band gap between radicals (or dimers of radicals); measurement was done on single crystals with electrical contacts applied in the direction of stacking.

A pair of analogous salts, N-MePy∙CA and N-MePy∙BA is especially interesting, and be described in detail. In triclinic polymorphh of CA salt closely bound radical dimers occur, similar to previously known alkali salts of semiquinones [1,2], and the crystals are diamagnetic due to spin pairing. In its triclinic polymorph and isostructural BA salt radicals are equdistant leading to different spin ordering, similar to high-temperature polymorph of K∙CA∙MeCOEt [3]. All crystals were found to be good semiconductors and stable in air at room temperature.

[1] K. Molčanov, B. Kojić-Prodić, D. Babić, D. Žilić, B. Rakvin, *CrystEngComm*, **13** (2011), 5170-5178; [2] K. Molčanov, D. Babić, B. Kojić-Prodić, J. Stare, N. Maltar-Strmečki, L. Androš, *Acta Crystallogr. B*, **70** (2014), 181-190; [3] K. Molčanov, B. Kojić-Prodić, D. Babić, D. Pajić, N. Novosel, K. Zadro, *CrystEngComm*, **14** (2012), 7958-7964.