Poster

Extended motives of two-electron multicentre bonds (*pancake bonds*): from discrete dimers to 2D networks

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Two-electron multicentre bonds (2e/mc or *pancake bonds*) are strong intermolecular interactions which occur between planar organic radicals [1−3]. They involve the pairing of spins of contiguous radicals due to the extension of the highest occupied molecular orbital (HOMO) between both radicals; this implies a significant covalent contribution to the total interaction, which often exceeds −15 kcal mol^{-1} [1]. Thus, 2e/mc bonds are some of the strongest intermolecular interactions, comparable to the strong hydrogen and halogen bonds, which are also partially covalent. However, in pancake bonds, the electron pair is not localised, but distributed between two radicals, involving multiple centres [1−3]. Bulk properties of radical-based materials are defined by the degree of pancake bonding [2,3], so it is interesting not only from the fundamental aspects of nature of chemical bonding and intermolecular interactions, but also from an applicative point of view. Fine-tuning of this interaction may lead to the design of novel organic magnets and (semi)conductors.

Discrete (0D) pancake-bonded dimers or trimers are the most studied, and typically result in diamagnetic or antiferromagnetic properties of bulk samples [2,3]. These oligomers often stack by weaker (non-bonding) interactions. Extended 1D motives are characterised by (nearly) equidistant radicals with an interplanar separation shorter than 3.2 Å. The close contacts allow electron jumps between the rings and long-range magnetic ordering; therefore, the bulk materials are mostly semiconductive and antiferromagnetic [2,3]. However, these crystals are conductive only in the direction of stacking.

Pancake bonding extending in 2D arrays was recently observed in salts of 7,7,8,8-tetracyanoquinodimethane radical anion (TCNQ) [4]. It involves spin interactions and electron transport in two directions (as evidenced by EPR spectroscopy) and conductivity up to 10^{-2} S cm^{-1} has been reported [4]. Therefore, such 2D pancake-bonded systems may be more interesting than 1D stacks, however, there are only a handful of incentive studies. It is known that TCNQ readily reacts with electron donors forming salts of various stoichiometries; its formal charge is often partial, −1/2 or −2/3. There are also many unknowns that may influence the stacking of radicals: aromaticity and steric influence of the cation, competition with other strong intermolecular interactions (hydrogen and halogen bonding), formation of mixed stacks with electron donors or cations, etc. However, almost all organic TCNQ salts comprise aromatic rings, and are mostly planar.

Here we present detailed quantum crystallographic studies of a series of 2e/mc-bonded radical systems, ranging from discrete dimers to 2D arrays. The simplest examples are dimers of tetracyanoethylene radical anion (TCNE) and *N*,*N*,*N*',*N*'-tetramethyl-*p*-phenylenediamine radical cation (TMPD) [5], which involve a single electron pair. In trimers and tetramers of TCNQ radical anions
[4] the electron pair is distributed over three or four radicals, respectively. Examples of stacks of equidistant radicals are *N*-methylpydirinium salt of tetrachloroquinone radical anions (Cl_4Q) [6] and charge-transfer compounds with partially charged TMPD radical cation [7]. 2D arrays comprise TCNQ radical anions with a partial charge of −1/2 [4].

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This work was financed by the Croatian Science Foundation, grant IP-2019-04-4674. Additionally, funding by the German-Croatian (DAAD-MZOS), the Slovenian-Croatian (grant BI-HR/23-24-007) bilateral collaborations, and the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Programme (grant 950625) is gratefully acknowledged.