

MS13-2-2 Crystal engineering of charge transfer complexes with TMPD (Wurster's blue) as electron donor and quinones as electron acceptors
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Abstract

Charge transfer complexes are systems of two or more molecules in which portion of charge is transferred between molecular units. Such complexes are stabilized by the electrostatic attraction between electron-rich donors and electron-deficient acceptors.¹ One of the well-known electron donors is N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD).² TMPD or Wurster's blue can form charge-transfer complexes as a radical cation with electronegative quinones or semiquinone radical anions (e.g. tetracyanoquinone and tetrachloroquinone).³ Interest in charge-transfer complexes can be attributed to their conductive properties as well as their stability, interesting intermolecular interactions between components and easy preparation.

Here we report a study on π -stacking and multicentric bonding in charge-transfer complexes with partially charged TMPD radical cation. We have prepared a series of co-crystals of TMPD and different quinones; 2,3-dicyano-5,6-dichloroquinone (1), tetrafluoroquinone (2), tetrachloroquinone (3), tetrabromoquinone (4), 7,7,8,8-tetracyanoquinodimethane (5) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (6). These systems were studied by means of variable-temperature crystallography (80 - 400 K) and X-ray charge density. Complexes of TMPD with 3 and 5 have been observed previously.³

In prepared charge transfer compounds stacking interactions between TMPD and quinone molecules are present. There are three types of stacks observed (Figure 1.). First, in co-crystals with 1, 3, 4 and 5 moieties form equidistant stacks of alternating TMPD and quinones. The second type is pancake-bonded dimers of TMPD and quinone in complex with 2. And in co-crystal with 6 moieties form 2D arrays of alternating TMPD and quinone molecules. For crystals of TMPD with 3 and 4, a polymorphic phase transition at lower temperature was observed when moieties change the type of stacking to the second type mentioned, pancake-bonded dimers.

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References

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Three types of stacking in co-crystals of TMPD

