Co-Crystals of Dithieno[3,2-*a*:2',3'-*c*]phenazine Derivatives and Trimeric Perfluoro-*ortho*-Phenylene Mercury

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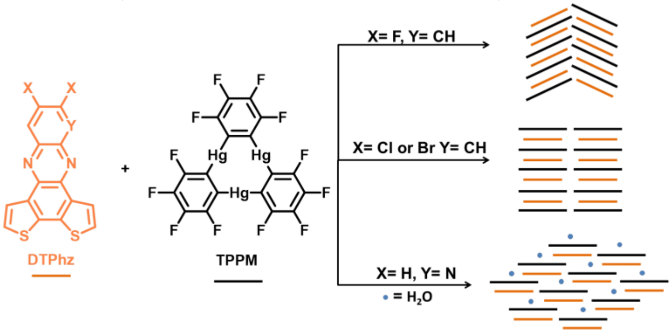

Dithienophenazine and tetrathienophenazine are planar molecules that had been studied as building blocks in organic semiconductors with a potential application in organic field-effect transistors and organic photovoltaics.[1-2] In this work a series of unsubstituted dithieno[3,2-*a*:2',3'-*c*]phenazine (DTPhz), 9,10-dihalo-DTPhz derivatives and closely related pyrido[2,3-*b*]dithieno[3,2-*f*:2',3'-*h*]quinoxaline (8N-DTPhz) were synthesized and investigated as donors (D) in co-crystals with trimeric perfluoro-*ortho*-phenylene mercury (TPPM), a known acceptor (A) that can form co-crystals with a variety of donor molecules.[3] No co-crystals were obtained when unsubstituted DTPhz was used in co-crystal growth with TPPM. Introduction of halogen atoms at positions 9 and 10 of the DTPhz core aided formation of co-crystals, and 1:1 D-A mixed co-crystals (F–DTPhz)•TPPM, (Cl–DTPhz)•TPPM and (Br–DTPhz)•TPPM were isolated. Donor 8N–DTPhz also produced co-crystals in a form of a hydrate (8N–DTPhz)•TPPM•H_2O. All these four co-crystals have short Hg···C, Hg···S and Hg···N contacts. Co-crystal (F–DTPhz)•TPPM crystallizes in the non-centrosymmetric space group $P2_12_12_1$ and has herringbone packing of the mixed D-A stacks. Mixed D-A stacks were also observed in co-crystals (Cl–DTPhz)•TPPM and (Br–DTPhz)•TPPM, which are isomorphic structures with the centrosymmetric *P-1* space group. Crystal packing of (Cl–DTPhz)•TPPM and (Br–DTPhz)•TPPM has parallel layers instead of the herringbone motif observed in (F–DTPhz)•TPPM. In hydrate (8N–DTPhz)•TPPM•H_2O molecules form parallel layers with no D-A stacks, although 8N-DTPhz still interacts with one side of the TPPM molecule. This structure has the space group *P-1*. This work is an example of how small changes in substituents give a variety of packing motifs and interactions in D-A co-crystals.

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