Computational analysis of charge-transfer crystalline complexes

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Molecular complexes built of two or more organic molecules (cocrystals, organic salts) provide additional opportunities to tune their properties for several areas of application such as pharmaceutical, agricultural and electronic. This work is devoted to search for new materials with improved performance, and deeper understanding the properties of binary charge transfer (CT) organic crystals, where one molecular component acts as an electron donor (D) and the other as an acceptor (A). Data on molecular structures of series of donor and acceptor molecules as well as their complexes have been obtained from Cambridge Structural Database and from our X- ray diffraction studies for compounds which were not presented in the Database. To evaluate which D and A pairs will be more favorable to produce CT complexes, energies of HOMO and LUMO orbitals were calculated using Gaussian 16 software at B3LYP/6-311+G(d,p) level of theory. The series of potential donors (tetrathiafulvalene derivatives, dithieno[3,2-b:2',3'-d]thiophene and others) and acceptors (pyromellitic dianhydride (PMDA), tetracyanoquinodimethane (TCNQ), F_4TCNQ[1], tetracyanonaphthoquinodimethane (TNAP), F_6TNAP[2] and others) were evaluated. Based on computational data several binary complexes were obtained using co-crystallization from solution and their structures were characterized via X-ray diffraction.

[1] Peng Hu, Henan Li, Yongxin Li, Hui Jiang and Christian Kloc, CrystEngComm, 2017, 19, 618

[2] Peng Hu, Shancheng Wang, Apoorva Chaturvedi, Fengxia Wei, Xiaoting Zhu, Xiaotao Zhang, Rongjin Li, Yongxin Li, Hui Jiang, Yi Long and Christian Kloc. Cryst. Growth Des. 2018, 18, 1776-1785