In 2003, Fei et al. [1] published an article on the fluorescence properties of trans-9,10-bis(diphenylthiophosphoryle)-anthracene, short: trans-SPAnPS@toluene. Solid-state fluorescence was found whose origin seemed to be exclusively related to the intercalation or co-crystallisation of toluene. In solution, the compound was non-emissive. Moreover, the loss of toluene from the crystal framework upon vacuum drying was directly indicated by the vanishing of the fluorescence. The re-exposure to toluene readily restored the emission and on this basis an exciplex (exited complex) formation was suggested.

A detailed charge density investigation is presented that was performed on the trans-SPAnPS@toluene (P21/n) co-crystal in order to further investigate the role of the intermolecular host/guest interactions [2]. Additionally, a variety of orthogonal strategies are combined in order to shed light on the complex mechanisms that take place in the solid form of trans-SPAnPS@toluene. The investigation included single crystal as well as powder X-ray diffraction, neutron diffraction, solid-state NMR and computational chemistry using different levels of theory. Hereby, new and complementary aspects were added to the discussion and, until now, more than 20 polymorphs and co-crystals were discovered.

The solid-state NMR chemical shifts supported by the GIPAW DFT method [3] and topological features from the experimental charge density were used to draw a more complete picture of the forces acting in the solid-state forms of SPAnPS.

Finally, a rationale for the solid-state fluorescence behaviour of the investigated SPAnPS compounds is herein suggested.

Acknowledgement:
The neutron data collection at the Chemical and Engineering Materials Division, BL-12 TOPAZ, Oak Ridge National Laboratory is gratefully acknowledged. This work was supported by a Feodor Lynen Research Fellowship of the Alexander von Humboldt Foundation and a Newton International Fellowship of the Royal Society (A.-C. P).


Keywords: Co-crystals, Polymorphism, Solid-State Fluorescence