

SPANPS – The radiant polymorphs

Lennard Krause¹, Ann-Christin Pöppler², Steven P. Brown³, Regine Herbst-Irmer⁴, Dietmar Stalke⁴

¹Department Of Chemistry, Aarhus University, Aarhus, Denmark, ²Institute of Organic Chemistry, University of Würzburg, Würzburg, Germany, ³Department of Physics, University of Warwick, Coventry, United Kingdom, ⁴Institute For Inorganic Chemistry, University Of Göttingen, Göttingen, Germany
E-mail: lkrause@gwdg.de

In 2003, Fei et al. [1] published an article on the fluorescence properties of trans-9,10-bis(diphenylthiophosphoryl)-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 (excited 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).

[1] Fei, Z. et al. (2003). *Angew. Chem. Int. Ed.* 42, 783 – 787.

[2] Turner, M. J. et al. (2014) *J. Phys. Chem. Lett.* 5, 4249 – 4255.

[3] Pickard, C. J. & Mauri, F. (2001) *Phys. Rev. B*, 63, 245101.

Keywords: [Co-crystals](#), [Polymorphism](#), [Solid-State Fluorescence](#)