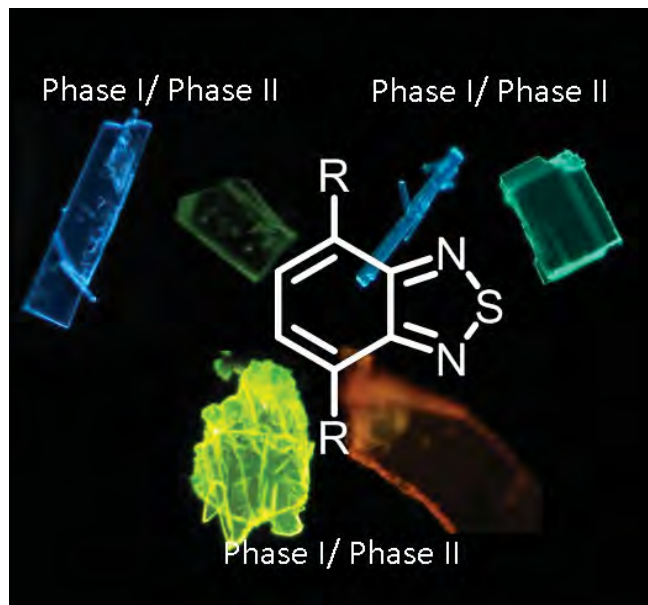


**MS31-P09****Understanding supramolecular role in mechanochromic luminescent polymorphs**Marcelo Echeverri<sup>1</sup>, Berta Gomez-Lor<sup>1</sup><sup>1</sup>. Instituto de Ciencia de Materiales de Madrid, Madrid, Spainemail: [m.echeverri@csic.es](mailto:m.echeverri@csic.es)

Mechanochromic materials (i.e. solids possessing light emitting properties that vary upon mechanical grinding or pressing), arouse much interest in recording or sensing applications that involve luminescent detection. However, only in a few of them an adequate understanding about the origin of the color change has been achieved. Light-emitting single crystalline compounds are especially interesting for allowing correlating the changes in the solid-state luminescent properties with variations in the molecular or supramolecular structure.<sup>1</sup>

In the quest for efficient light emitting compounds, benzothiadiazole (BTD) is one of the preferred moieties. This electron deficient heterocycle presents high fluorescence quantum efficiencies and has a strong propensity to adopt quinoid conformations, thus facilitating charge transfer between attached substituents and enabling the tuning of its emission properties.<sup>2</sup> Herein we present a new BTD-derivatives series, which each one crystallizes in two different polymorphs. These compounds change their light emitting properties due to slight changes of their crystallographic packing, offering an excellent opportunity to establish optimal supramolecular arrangement for photonic applications.



## References:

- (1) S. Varughese, *J. Mater. Chem. C*, 2014, 2, 3499-3516  
 (2) N. J. Findlay, B. Breig, C. Forbes, A. R. Inigo, A. L. Kanibolotsky and P. J. Skabara, *J. Mater. Chem. C*, 2016, 4, 3774-3780

**Keywords:** mechanochromic, luminescent, supramolecular

**MS31-P10****Supramolecular synthons: structural features in various crystalline environment**Olga Lodochnikova<sup>1</sup><sup>1</sup>. Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Kazan, Russiaemail: [lod\\_olga@mail.ru](mailto:lod_olga@mail.ru)

The key concepts of crystalline engineering are intermolecular interactions and the supramolecular synthons which are formed by such interactions. The so-called “Synthon approach” greatly helps to simplify the understanding and description of crystal structures.

In this work, the structural features of a number of known and new supramolecular synthons in a different crystalline environment are studied. By the structural features we mean the geometric parameters of strong “synthon-forming” non-covalent interactions, the conformation of the synthon and the possibility of its additional stabilization through secondary intermolecular interactions, which may turn out to be different in different crystalline forms. Thus, the influence of the crystal environment on the structure and stability of the synthons that are classic for supramolecular chemistry: carboxyl, amide, thioamide, sulfonamide, and some others, in different polymorphic forms and in “racemate-conglomerate” pairs has been studied. To obtain data on the behavior of synthons in different environments, key series of compounds has been studied for polymorphism and for a tendency to spontaneous resolution of enantiomers.

An extremely rare type of polymorphism “conglomerate 1-conglomerate 2” has been discovered [1]. In both polymorphs, the main formative motif is a homochiral chain (helix) based on the same supramolecular  $\alpha$ -hydroxyamide open-chain synthon that takes different symmetry depending on the crystal system.

For the classical carboxylic acid synthon, the ability to form a stable interaction of the “Lp...synton” type is found, which can cause a significant amplification of synthon-forming hydrogen bonds.

For the known thioamide synthon, the effect of a “chiral-dependent conformational memory” is found - a pairs of thiourea molecules “memorize” their mutual arrangement both in the hetero- and homochiral H-bound dimers and reproduce it in the structure of metal complexes corresponding to them by stereochemistry.

The possibility of transferring an amide open-chain supramolecular synthon, which is symmetrical relatively to the glide plane in the crystals of isonyazide derivatives, from the racemic medium into the homochiral one has been discovered [2]. It was achieved by inclusion of a second independent molecule into a cell.

A new tetrameric cyclic sulfinamide synthon has been found, the formation of which is accompanied by the formation of an H-bound tetramer with a sophisticated stereochemical construction.

A new cyclic centrosymmetric  $\beta$ -hydroxysulfoxide synthon, capable of self-assembly in both the racemic and homochiral medium, has two stable conformations realized in the room temperature and low-temperature phases [3].

This work was financially supported by the Russian Science Foundation (grant No 17-13-01209).

References:

- [1] Lodochnikova, O.A., Zaripova, A.R., Fayzullin, R.R. et al (2018). CrystEngComm, DOI: 10.1039/C8CE00369.  
 [2] Lodochnikova, O.A., Dobrynin, A.B., Andreeva, O.V. et al (2014). CrystEngComm, 16, 6234-6243.  
 [3] Lodochnikova, O.A., Startseva, V.A., Nikitina, L.E. et al (2014). CrystEngComm, 16, 4314-4321.

**Keywords:** supramolecular synthon, polymorphism, intermolecular interactions

## MS31-P11

### Combining crystal structure prediction and structural comparison with experimental screening: a potential route to more polymorphs, including a 2-for-the-price-of-1 special

Riccardo Montis<sup>1</sup>, Michael Hursthouse<sup>2</sup>, John Kendrick<sup>3</sup>

1. School of Chemical Engineering and Analytical Science - The University of Manchester, Manchester, United Kingdom
2. Chemistry - University of Southampton, Southampton, United Kingdom
3. Department of Chemistry and Forensic Science - University of Bradford, Bradford, United Kingdom

**email:** riccardo.montis@manchester.ac.uk

Although our current knowledge on polymorphism has been advancing significantly in recent years, this fascinating topic still represents a challenging aspect of structural crystallography and solid-state chemistry. Despite the major enhancements in experimental and computational methods, the highly successful computational studies invariably predict far more feasible structures than are experimentally found, even when further extensive experimental screenings are made. Possible reasons for this discrepancy have been previously suggested but still questions such as *Why don't we find more polymorphs?* remain open.<sup>1</sup>

In this work we explore the idea that detailed comparative analyses of predicted and experimental polymorphs may represent a further useful tool for polymorph screening. The identification of structural similarities and differences might help in discriminating which structure, within the crystal energy landscape, would seem likely to be experimentally isolated.<sup>2</sup> This information might be also used to identify whether pairs or groups of structures are so closely related that they may convert one into the other, during the nucleation/crystal growth stages or by proper solid-solid phase transitions, preventing the observation of some potential metastable forms. To follow these objectives, we compared experimental and predicted structures from the previous results of a CSP study by Asmadi et al.<sup>3</sup> on a group of three rigid, planar small molecules of known crystal structures, 2-methyl-, 3-methyl- and 2,3-dimethyl-benzo[b]thiophene 1,1-dioxide.

The results of the crystal structure comparison of the ten lowest energy predictions from the CSP calculations for each derivative with the known, unique experimental crystal structures are discussed. A short experimental screening leading to the discovery of three new polymorphs is also presented.

References:

1. Price, S. L. (2013). Acta Cryst. B69, 313–328
2. Price, S. L. et al (2016) Chem. Commun. 52, 7065-7077
3. Asmadi, A. et al. (2010). Chem. Eur. J. 16, 12701–12709

**Keywords:** Polymorphism,