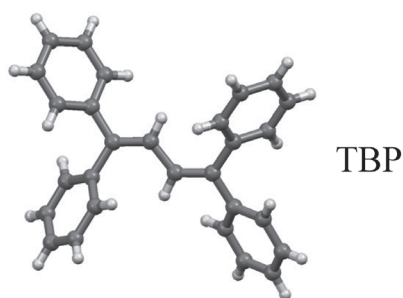


MS24-02 **Trekking on hills and valleys in the polymorph landscape of TPB** Alessia Bacchi,^a Domenico Crocco,^a Alberto Girlando,^{a,b} *Dipartimento di Chimica, University of Parma, Italy*
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TPB (1,1,4,4-tetraphenyl-1,3-butadiene) is a luminescent molecule that displays luminescence also in the crystalline state, if favorably packed by aligning the transition dipoles in the correct orientation. TPB is currently known in three polymorphs α , β , γ , [1], and TPB molecular structure approximately displays C_2 point symmetry in the α form, and C_i point symmetry in β and γ . Among these the β form has proved to be best suited to photoluminescence; unfortunately its crystallization is not reproducible. The γ form, structurally very similar to the β polymorph, is also rarely obtained. It is therefore advisable to develop new crystal forms of TPB (polymorphs, co-crystals, solvates) by using the tools of crystal engineering in order to optimize photoluminescence for the design of light emitting or photovoltaic devices.

We have explored the polymorph landscape of TPB by several techniques, such as crystallization solvent screening, gel crystallization, temperature controlled precipitation, melt quenching, recrystallization by seeding from the melt, sublimation, affording mostly the commercial α phase and sometimes the less stable γ phase, or a cyclohexane solvate with interesting solid/vapour host-guest exchange properties that will be illustrated. Most importantly, by critical inspection of DSC traces we have discovered that immediately after melting, the commercial α phase recrystallizes in a new polymorph δ , previously unknown, with $Z'=1.5$ and comprising both previously known conformers of TPB. By contrast, the pure recrystallized α phase does not transform into the δ phase. This points to the presence of δ polymorph impurities in the commercial product, that seed the crystallization of the δ phase from the melted α . Calculations show that the δ phase could be the thermodynamically stable form of TPB, even if the energy differences of the four phases are of the order of few kJ/mol and result from a delicate balance between conformational and packing energy. The melting points of all these polymorphs are clustered in the range 198-204°C. The structural basis of this intriguing polymorph landscape are discussed. Unexpected behaviour of seeding experiments on the melt will be also discussed and rationalized by means of structural analysis and of PXRD, DSC, Raman, SS-NMR experiments.



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Keywords: polymorphism; crystal engineering; luminescence; guest exchange

MS24-03 **Chiral Discrimination in the Solid State by using the Dutch Resolution Method.** Nikolettta B. Báthori and Luigi R. Nassimbeni, *Department of Chemistry, Cape Peninsula University of Technology, Cape Town, South Africa*
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The worldwide sales of the single enantiomer drug market was about \$300 billion in 2010. An estimated 30-50% of these drugs have been obtained by classical resolution methods. [1] The main reason why chiral discrimination is one of the hot topics of chemistry is that after years of extensive research we still do not fully understand the mechanism of chiral discrimination and cannot design the 'perfect' resolving agent.

A series of inclusion compounds were studied to map the correlation between structure and enantiomeric resolution in the solid state in order to understand the mechanism of the molecular recognition that drives the differentiation of the resolving agent for one particular enantiomer. [2] The known technique was employed to measure the selectivity profile of a given host compound (H) towards a pair of guests A and B, whereby the host, H is dissolved in a series of solutions where the mole fraction X_A varies in steps from 0 to 1. A series of competition experiments were set up where the resolving agent was exposed to mixtures of enantiomers (R and S, mole fractions in the solution are X_R and X_S respectively), and the mole fraction of the starting mixture were varied systematically. The ensuing solutions were allowed to crystallise and the mole fraction of the entrapped enantiomer (Z_R and Z_S) were measured by analysing the crystal structure. The selectivity coefficient at each point is then defined as

$$K_{R:S} = (K_{S:R})^{-1} = Z_R/Z_S * X_S/X_R, \text{ where } (X_R + X_S = 1)$$

and is a measure of the discrimination of the host for a given guest. Correlation has been found between selectivity, the torsional flexibility of the host, and the concomitant remaining volume in the crystal structure that accommodates the guest. This mechanism was confirmed by repeating the competition experiments with a structurally similar chiral host. The so-called 'Dutch Resolution method' was employed in the resolution of the same racemic modification. The procedure uses a combination of two (occasionally three) generally homochiral resolving agents, whose structures are closely related and it was found to greatly improve the enantiomeric excess of the targeted racemate. [3] Again, correlation has been found between selectivity, the torsional flexibility of the host and the available space for the guest. No significant improvement in the overall enantiomeric excess of a single enantiomer was achieved by mixing the pairs of host compounds because the crystal structures all display a constant packing arrangement for the host molecules and the concomitant sites where the guests are located and the rigidity of the packing, controlled by the host...host interactions, did not allow any significant change in the chiral discrimination.

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