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Control of polymorphic transition inducing preferential enrichment

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Preferential Enrichment is an unusually symmetry-breaking enantiomeric resolution phenomenon that is ascribed to an event of a complexity system [1]. We have shown that Preferential Enrichment is initiated by the solvent-assisted solid-to-solid transformation of a metastable polymorphic form into a thermodynamically stable one occurring during crystallization from the supersaturated EtOH solution of a certain kind of racemic mixed crystals (i.e., solid solutions or pseudoracemates) composed of the two enantiomers, followed by partial crystal-disintegration inside the crystal lattice to release the excess enantiomer existing in the initially-formed crystal into solution [1,2]. Accordingly, Preferential Enrichment is strongly affected by the surrounding conditions, such as additives (seed crystals), solvent, concentration, and temperature, as well as the molecular structure. Here we report (i) the modes of polymorphic transition relevant to the occurrence of Preferential Enrichment and (ii) two complimentary strategies for the induction of Preferential Enrichment by controlling the mode polymorphic transition; one is the slight modification of the molecular structure so as to prevent the undesired polymorphic transition, and the other is the use of the appropriate seed crystals to induce the desired “epitaxial transition” [1,3].

[1] Top. Curr. Chem. 2007, 269, 53-82.
[2] (a) J. Am. Chem. Soc. 2002, 124, 13139-13153. (b) Cryst. Growth Des. 2003, 3, 973-979. (c) Enantiomeric Separation: Fundamentals and Practical Methods; Toda, F. Ed, Kluwer Academic Publishers, Dortrecht, 2004, pp. 135-163.
[3] (a) Chem. Eur. J. 2006, 12, 3515-3527. (b) Cryst. Growth Des., 2007, 7, 1643-1652. (c) Cryst. Growth Des., 2008, 8, 540-548.

Keywords: polymorphic transition, chirality, enantiomeric resolution

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Supramolecular symmetries in the Piedfort units

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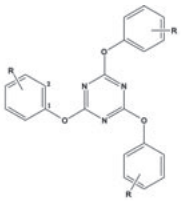
Crystal engineering applies the Piedfort concept in host design many years. The hexahosts idea implies that *sym*-hexasubstituted benzene molecule is mimicked by a self assembled dimer of sym-1,3,5-trisubstituted six-membered aromatic rings. The basic forms of *supramolecular symmetries* in the Piedfort Units (PUs) observed in the crystal structures of 2,4,6-triaryloxy-1,3,5-triazines are revisited. The semirigid molecules in their column are stacked around a C_3 axis which may associate with three parallel glide planes ($C_{3(g)}$), centres of inversion (C_{3i}), or three perpendicular 2-fold axes (D_3). The extended canonical classification is given, descriptors and graphical presentation are improved. The parity of the synclinal and anticlinal phenyl-triazine angles assumes pseudochirality. In the case when C_3 symmetric ‘enantiomorphic’ molecules are arranged by three glide planes, the formed diad ($C_{3(g)}$-PU) is a unique form of supramolecular symmetry since a molecule itself cannot exhibit glide plane. The molecular columns are formed from heterochiral $C_{3(g)}$-PUs in *R*3*c* and C_{3i}-PUs in *R*-3. The occurrence of homochiral D_3-PUs in *P*-3*c*1 is inseparable from the presence of C_{3i}-PUs. (OTKA T049712)



n-RPOT: $n = 2, 3, 4$, R = halogen atoms or alkyl groups

Keywords: supramolecular structures, supramolecular symmetries, Piedfort unit

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Application of preferential enrichment to amino acids

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In 1996 we reported the first instance in which enantiomeric resolution by simple recrystallization of a racemic crystal from organic solvents was feasible; this unusual symmetry-breaking enantiomeric resolution phenomenon that is ascribed to an event of a complexity system was referred to as preferential enrichment [1]. Preferential enrichment is initiated by the solvent-assisted solid-to-solid transformation of a metastable polymorphic form into a thermodynamically stable form occurring during crystallization from the supersaturated solution of certain kinds of racemic mixed crystals (i.e., solid solutions or pseudoracemates) composed of two enantiomers. This process is followed by partial crystal-disintegration inside the crystal lattice to release the excess enantiomer existing in the initially-formed crystal into solution [1,2]. Recently we have investigated whether preferential enrichment is applicable to amino acids which are classified into a racmic compound crystal. Here we report that the amino acid leucine shows a quite similar phenomenon to that of preferential enrichment whenever slightly D- or L-enriched leucine of 5 % ee is recrystallized from the mixed solvent of water and ethanol. The polymorphic transition behavior during crystallization has been followed by the in situ ATR-FTIR (ReactIR) measurement of the crystallization mixture and DSC analysis of the deposited crystals.

[1] R. Tamura, H. Takahashi, D. Fujimoto, T. Ushio, Top. Curr. Chem. 2007, 269, 53-82.
[2] R. Tamura, T. Ushio, A Dynamic Enantiomeric Resolution Phenomenon Caused by Polymorphic Transition During Crystallization. In Enantiomer Separation: Fundamentals and Practical Methods; Toda, F., Ed.; Kluwer Academic Publishers: Dordrecht, 2004, pp. 135-163.

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Intercalation with steroidal inclusion crystals: Enantioresolution and layer inversion

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