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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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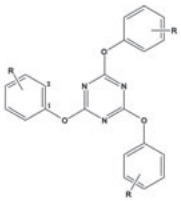
Crystal engineering applies the Piedfort concept in host design many years. The hexahosts idea implies that *sym*-hexasubstituted benzene molecule is mimicked by a self assembled dimer of sym-1,3,5-trisubstituted six-membered aromatic rings. The basic forms of *supramolecular symmetries* in the Piedfort 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.

Keywords: preferential enrichment, chiral separation, crystallization

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Intercalation with steroidal inclusion crystals: Enantioresolution and layer inversion

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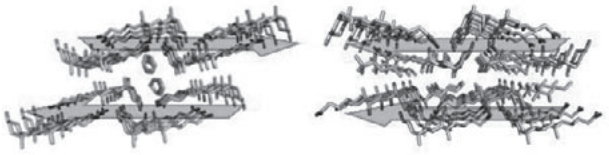
Solid-state dynamic properties contribute to development of gas sorption and storage materials with microporous coordination polymers. Organic crystals function as dynamic materials due to their flexibility and diversity. We study on steroidal bile acid derivatives which serve as host components and form dynamic inclusion crystals for intercalation and enantioresolution of guest molecules. So far, we reported that cholamide has various types of flexible bilayers where secondary aliphatic alcohols are accommodated. Among them, 2,2-dimethyl-3-hexanol induces a rare bilayer structure which is responsible for high enantioselectivity. Here we present intercalation and enantioresolution of 2,2-dimethyl-3-hexanol by using inclusion crystals of cholamide with 1,4-dioxane. It was found that guest exchanges took place with retention of the crystalline state in appearance. The crystal structures were determined before and after the intercalation by means of powder X-ray diffraction, indicating that the intercalation accompanied layer inversion on the lipophilic sides of the bilayers. Moreover, it was found that the resulting crystals include (S)-2,2-dimethyl-3-hexanol in over 95% ee yield.



Guest exchange accompanied by inversion layer

Keywords: inclusion compound, chiral recoginition, intercalation

P06.07.28

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Enantioselective inclusion of methyl phenyl sulfoxides by (*S*)-alkylglycyl-(*S*)-phenylglycine

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As dipeptide host molecules, (*S*)-alkylglycyl-(*S*)-phenylglycines were examined in terms of enantiomeric inclusion for racemic methyl phenyl sulfoxides. Among them, (*S*)-leucyl-(*S*)-phenylglycines (LeuPhg) and (*S*)-isoleucyl-(*S*)-phenylglycines (IlePhg) mainly included *S*-form of methyl phenyl sulfoxides with high enantioselectivity. By single crystal X-ray analyses of these inclusion compounds, it was elucidated that the dipeptide molecules self-assembled to form layer structures and included the sulfoxides between these layers by hydrogen bonding between the proton of $^{+}NH_3$ and the oxygen of the sulfoxide. In the cavity, *C*-terminal phenyl group of the dipeptide interacts with the phenyl group of sulfoxides. In addition to these host-guest interactions, the two homochiral sulfoxides belonging in upper and lower layers make a pair having 2-fold rotation axis or 2-fold screw axis along the channel cavity. In other words, the self-recognition of sulfoxides made a homochial pair to achieve high enantioselectivity.

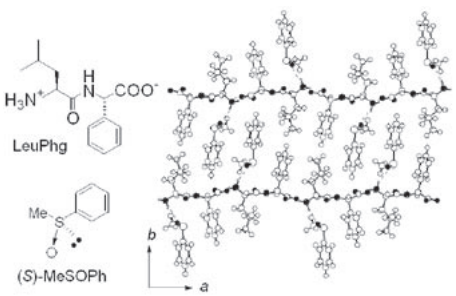

Fig. Inclusion of (S)-methyl phenyl sulfoxide by LeuPhg.

Keywords: inclusion compounds, dipeptides, molecular recognition

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Structure and polymorphism of trans mono-unsaturated triacylglycerols

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Trans fats are in a natural way in small quantities present in animal foods. Moreover, unsaturated plant fats are often partially hydrogenated to raise melting temperatures for preparation of foods, and then, as a minor side reaction, a small part of the cis-bonds will change into trans-configuration. Like saturated fats, fats with trans fatty acid residues will have negative effects for human health (1). The presence of the elaidoyl chain, one of the major trans fatty-acid chains, is suspected of increasing health risks because it resembles the stearoyl chain. When incorporated in biological membranes elaidoyl chains will be influencing the physical-chemical properties of the membranes. Thus insight in the influence of the differences between the fatty-acid composition of trans and saturated triacylglycerols (TAGs) on the conformation and packing, on polymorphic stability, and on phase-transition behavior, will be useful. By combining X-ray powder diffraction (XRPD) techniques a better understanding of trans mono-unsaturated TAGs and their related saturated ones can be obtained. Synchrotron and advanced laboratory time- and temperature-resolved XRPD reveal the stability and phase-transition behavior of the important polymorphs like the β and β'. These results can be related to the underlying crystal structure packing that can be obtained from XRPD data using direct-space search techniques. Our recent results will be discussed including novel meta-stable β' polymorphs and the structure of one them, methyl-end plane packing analysis in relation to observed melting points for various subgroups of TAGs, and the difference in β' to β phase-transition behaviour of symmetric versus asymmetric TAGs.
(1) The EFSA Journal, 2004, 81, 1-49

Keywords: trans mono-unsaturated triacylglycerols, time-temperature-resolved diffraction, powder structures

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Polymorphism and structure solution from powder data of *N,N'*-1,4-phenylene-bis(3-oxobutanamide)

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N,N'-1,4-Phenylene-bis(3-oxobutanamide) (**1**) is an industrial intermediate which is used as a coupling component in the synthesis