Poster Presentation

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Affirmative polymorph generation of annulenes by using CH/O interactions

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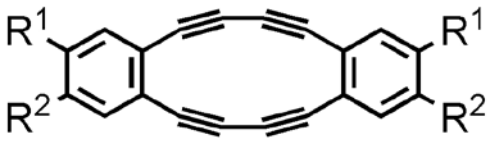
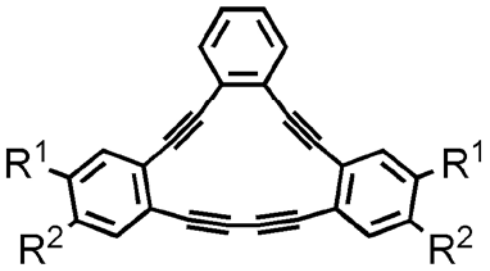
CH/O interaction is recognized as a weak hydrogen bond with less directionality, compared with a strong hydrogen bond such as that between carboxylic acids. Therefore, the interaction does not seem to be suitable for precise design of crystal structures. In connection with this, however, we emphasized that the CH/O interaction, particularly that provided by methyl ester group, can utilize for affirmative generation of polymorphs of cyclic pi conjugated molecules. Since functionality of solid state materials based on pi conjugated molecules is crucially affected by their molecular arrangements, polymorphs are exactly appropriate systems to reveal the superstructure-dependent properties of such the materials, and therefore, affirmative preparation of polymorphs of pi conjugated molecules is challenging. Herein, we describe formation, crystallographic characterization, and superstructure-dependent properties of polymorphs of methyl ester functionalized dehydrobenzoannulenes (DBAs), a family of cyclic conjugated molecules consisted of benzene rings and acetylene units. We synthesized five DBA derivatives 1-5 with two types of annulene cores (octadehydrodibenzo[12]annulene and octadehydrotribenzo[14]annulene cores) and different number and position of methyl ester groups (Scheme1). These derivatives exhibit two to five polymorphic crystals with physical properties strongly depending with their supramolecular structures.[1-3] We believe that the present polymorph generation is exactly provided by rotationally flexible conformations of the ester groups and versatile ways of directionally tolerant CH/O interactions of the ester groups.

[1] *I. Hisaki et al, Cryst. Growth Des. 2009, 9, 414.,* ***[2]*** *I. Hisaki et al, Cryst. Growth Des. 2011, 11, 5488.,* ***[3]*** *I. Hisaki et al, Chem. Asian J. 2013, 8, 1372.*



1 : R^1 = COOMe, R^2 = H
2 : R^1 = R^2 = COOMe



3 : R^1 = H, R^2 = COOMe
4 : R^1 = COOMe, R^2 = H
5 : R^1 = R^2 = COOMe

Keywords: polymorph, pi conjugated system, CH/O interaction