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Helicity Discrimination in Diaryl Dichalcogenides Generated by Inclusion Complexation with Chiral Hosts

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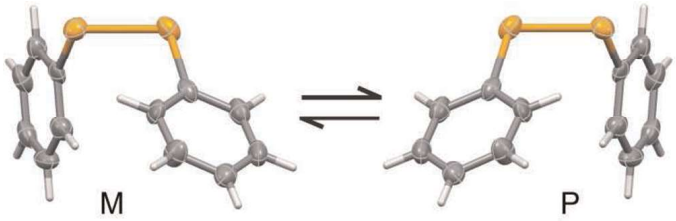
ABSTRACT



Inclusion complexation of diaryl dichalcogenides with either cholic acid or chiral diols results in their helicity discrimination and an induction of optical activity that can be detected by solid-state CD measurements.

Some molecules lacking stereogenic centers can adopt chiral conformations caused by internal rotation. They occasionally form optically active crystals with the component molecules frozen in a chiral conformation yielding conglomerates as a mixture of homochiral crystals.[1] Notable examples are diphenyl dichalcogenides **1**–**3** which crystallize in the Sohnke space group $P2_12_12_1$.[2] Due to a gauche effect caused by the interaction of adjacent electron lone pairs, they assume a skewed conformation with the torsional angle around the chalcogen–chalcogen bond being close to 90°.[3] Thus, dichalcogenides exist in chiral *P*- and *M*-helical forms. A low energy barrier to internal rotation (ranging from to 8.6 to 5.3 kcal/mol) going from diphenyl disulfide to ditelluride causes their rapid racemization in solution.[4] However, their optical activity should be detected in the solid state. Unfortunately, our attempts to measure their circular dichroism (CD) in KBr disks resulted only in very poor quality and noisy spectra. Similar noisy CD curves exhibiting extremely weak Cotton effects (CEs) have been reported by Kamigata and coworkers.[4] The spectra presented by these authors show monosignate CD in the region of two low energy n–σ^* electronic transitions. According to the theoretical predictions confirmed by several experimental results, typical CD curves of optically active dichalcogenides should consist of two oppositely signed CEs in the long-wavelength part of the spectra.[5,6]

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