

Inherently Chiral Ionic Liquids with Axial, Helical and Central Stereogenicity for Highly Efficient Enantioselective Sensors

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Abstract:

We recently defined as "inherently chiral" functional materials the compounds in which the stereogenic scaffold responsible for chirality and the molecular group responsible for their specific properties coincide.^[1] This structural combination results in outstanding enantioselection properties, much higher than those exhibited by the compounds in which stereogenic unit and functional group are independent molecular portions. We first tested the validity of this concept in the design of macrocyclic fully conjugated poly-thiophenes in which chirality results from a tailored distortion of regio-regular oligo-thiophene sequences. They were employed as highly stereoselective electrode surfaces.^[2]

We decided to apply the inherent chirality concept to Chiral Ionic Liquids (CILs), experimenting first the effects produced by a stereogenic axis and then extending the research to completely new Inherently Chiral Ionic Liquids (ICILs) based on helices and classical stereocenters. In our project the ICILs based on a stereogenic axis are characterized by suitably substituted 3,3'-bipyridinium (1) or 1,1'-bibenzimidazolium (2) atropisomeric scaffolds.^[1] Considering that pyridinium and imidazolium groups are classical IL functionalities, and that a pair of them are involved in the hindered rotation around the interannular bond, responsible for chirality, it is evident that the attribute of ICILs to these compounds is correct. Aza- and di-aza-hexahelicenium cations (3) also fulfill the requirements to be defined as ICILs, since the pyridinium unit is essential part of the helical scaffold. As for ICILs based on stereogenic centers, we have planned the alkylation of configurationally stable phosphanes (4) as the key step to easily obtain them. Synthesis and

characterization of all new ICILs and electrochemical enantio-differentiation experiments of the antipodes of several chiral probes are discussed in comparison with the behaviour of classical CILs.

Keywords: Ionic liquids, Chiral additives, Inherent chirality, Chiral electrochemistry and electroanalysis, aza-hexahelicenium cation, phosphonium cation

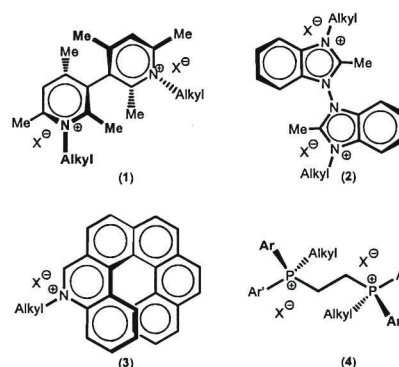


Figure 1: Prototypes of Inherently Chiral organic salts characterized by 3,3'-bipyridine (1), 1,1'-bibenzimidazole (2), 5-aza-hexahelicene (3) and phosphane (4) scaffolds.

References:

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