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Induction of chirality in 4,4'-azopyridine by halogen-bonding interaction with optically active ditopic donors†

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Optically active ditopic halogen bond donors bearing two 4-iodotetrafluorophenyl groups were obtained by reaction of chiral diols with iodopentafluorobenzene. Co-crystallization of these donors with *anti*-4,4'-azopyridine afforded binary complexes containing infinite chains of the alternating component molecules connected by halogen bonds. The solid state CD measurements confirmed that complexation induces optical activity of the azo chromophore due to the twisting of the aryl-N= system or external chiral perturbation exerted by host molecules.

Introduction

The controlled arrangement of molecules in a predictable fashion to generate supramolecular assemblies that can exhibit properties not presented by isolated components has long been an area of interest in materials chemistry.¹ Many multi-component supramolecular structures have been designed and obtained using non-covalent interactions such as hydrogen and halogen bonds or π - π interactions.^{2–4} In particular, halogen bonding has attracted intense interest in recent years as a useful tool in the field of crystal engineering.⁴ It has been presented as an attractive interaction between the electrophilic region of a halogen atom (σ -hole) and the nucleophilic region of another molecule.⁵ Due to the strength and directionality of halogen bonding interactions they could be used as an alternative to hydrogen bonding.⁴ Thus many new examples of halogen bond donors have been developed as substrates in the preparation of ordered solids with a designed architecture. Among a variety of structures, chiral components able to engage in halogen bonds are extremely rare.⁶ Crystalline materials with a chiral framework are of interest because of their potential application in the field of optical resolution,⁷ asymmetric syntheses,⁸ photochirogenesis,⁹ nonlinear optics¹⁰ or chiral molecular conductors.¹¹ Furthermore, chiral solid phases exhibit intriguing spectroscopic properties. A phenomenon

of induced optical activity arises when an achiral guest molecule is complexed by a chiral host. Optical activity can be induced upon dissolution of an achiral solute in a chiral solvent, by inclusion complexation of the achiral guest in the cavity of a chiral host or by chirality transfer between chiral and achiral components in supramolecular polymers.¹² The guest becomes optically active due to a dissymmetry created by a chiral environment or upon assuming a chiral conformation. An asymmetric perturbation of the chromophore leads to induced circular dichroism (ICD), whose magnitude depends on the mutual arrangement of the host and guest molecules.¹³

On account of this, we wish to report a new possibility of inducing optical activity in the azo chromophore by using halogen bonded assemblies of *anti*-4,4'-azopyridine (**apy**) with chiral ditopic halogen bond donors **1–3** (Scheme 1). The induced optical activity of the azo chromophore was detected by using solid state CD measurements.

Azo-dyes, particularly those related to azobenzene, undergo photoinduced *syn-anti* isomerization that is responsible for their potential application in optical switches and sensors, reversible data storage,¹⁴ photoresponsible supramolecular systems,¹⁵ or liquid crystalline polymers.¹⁶ Photochromic properties of crystalline azobenzenes are inspiring for interest in structural investigations of azobenzene solids. In this context, we have recently demonstrated induced optical activity of the azobenzene chromophore by inclusion complexation using chiral hosts as well as using a hydrogen-bonded assembly with optically active dicarboxylic acids.¹⁷

Results and discussion

Ditopic halogen bond donors **1–3** were obtained by the reaction of chiral diols with iodopentafluorobenzene in DMF solution

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