Preparation, X-ray structure and chiroptical response of 5,6-dihydrophenanthroline-5,6-diols
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The hydrogen bond is one of the strongest intermolecular interactions, thus playing an important role in many areas of natural science. In the field of supramolecular chemistry, hydrogen bond is frequently used as a tool to build a large structure by sequential connection of the small units. Reversible formation/destruction depending on the external conditions is the characteristic feature of the supramolecular architecture.

We have been interested in constructing the one-dimensional rod-like supramolecular structure that could be used for molecular electronics such as “molecular wire”. Here we design the title molecules 1 having both of the hydrogen-bond donors and accepters, so that they can form rod-like supramolecular structure by connected to each other through a pair of hydrogen bond. We also expect that they will exhibit a drastic change in chiroptical property due to the unique asymmetric elements shown below, if they reversibly form the “supramolecular rod” in solution.

Dihydrophenanthrolinediols 1 have contiguous two asymmetric centers and helicity. Two hydroxyl groups on the asymmetric carbons prefer to occupy the equatorial position, which is favored for intra/intermolecular hydrogen bond. In addition, the ring flipping of the fused bipyridine induces change in the sign of the helicity. Thus, the conformational preference of the hydroxyl groups can control the helicity of 1 (Scheme 1), and the exciton coupling of chromophores may induce large change of chiroptical property.

Diols 1 were prepared by the reaction of the corresponding Grignard reagent and 1,10-phenanthroline-5,6-dione, which in turn was prepared from 1,10-phenanthroline by the known procedure. Delightfully, the diols were proven to build the supramolecular-rod structure in crystals (Figure 1).

Optical resolution could be conducted by using the chiral-HPLC. Their absolute configuration was determined by transforming 1b to 2b, which was analyzed by anomalous dispersion of X-ray. We found that the CD spectrum of 1 showed very interesting dependence on solvent polarity. The intensity of CD spectrum measured in CH₂Cl₂ gradually decreased by adding MeOH (Fig. 2), which would be best accounted for by the change of intra/intermolecular hydrogen bond.
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