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Chiral Macrocycles

A Chiral Hemiporphyrazine Derivative: Synthesis and Chiroptical Properties

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Abstract: The synthesis of an optically active hemiporphyrazine with chiral binaphthyl substituents (**1**) is reported, providing the first example of the incorporation of an intrinsically chiral moiety into the macrocyclic core of a hemiporphyrazine analogue. A negative circular dichroism (CD) signal is observed in the 325–450 nm region of the CD spectrum of (*S,S*)-**1**, while mainly positive bands are observed in the 220–325 nm region. Mirror symmetry is observed across the entire wavelength range of the CD spectra of (*R,R*)-**1** and (*S,S*)-**1**. An irreversible one-electron oxidation wave with an onset potential at 1.07 V is observed by cyclic voltammetry, along with a reversible one-electron reduction wave at −0.85 V. Density functional calculations reproduce the experimentally observed data and trends, and provide further insight into the nature of the electronic transitions.

Phthalocyanines (Pcs) have been the focus of intense research interest because of the optical and redox properties that are associated with their stable heteroaromatic π system.[1] Their better-known low-symmetry analogues include the hemiporphyrazines (Hps),[2] which are four-unit macrocycles linked by aza nitrogen atoms. The macrocycles comprise two oppositely arranged pyrrole units (A) and another aromatic or heteroaromatic moiety (B) arranged in an ABAB manner. Hps are synthesized through a cross-condensation reaction of an aromatic diamine and a diiminoisoindoline.[2,3] Phthalocyanines (Pcs) and hemiporphyrazines (Hps) have been widely studied for use in applications such as photovoltaics, electrochromism, optical discs, laser dyes, liquid crystals, electrocatalysis, chemical sensors, and photodynamic cancer therapy.[4] Recently, there has been an increasing focus on chiral macrocycles.[5] Optical activity is omnipresent in living organisms and has been studied extensively in organic, organometallic, and theoretical chemistry.[6] Previously, chiral Pcs and Hps have been prepared by introducing optically active substituents on the periphery of the macrocycle or as axial ligands on a central coordinated metal, or through the introduction of intrinsic geometrical asymmetry by fused-ring expansion.[5a–c] To the best of our knowledge, there is no previous example of a chiral Pc or Hp analogue that has been formed by incorporating an intrinsically chiral moiety, such as 1,1′-binaphthyl, into the core of the macrocycle to replace pyrrole rings of the parent Pc structure.

1,1′-Binaphthyls represent an important class of chiral substituents due to the non-coplanar arrangement of the two naphthalene rings, which ensures a dissymmetric environment suitable for obtaining a high degree of stereoselectivity.[7] A wide range of diamines have previously been used to prepare Hps.[8,9] If enantiopure 1,1′-binaphthyl-2,2′-diamine reacts with diiminoisoindoline, an optically active Hp can be synthesized. To the best of our knowledge, this is the first example of an optically active Hp analogue being prepared through core modification of the macrocycle through the introduction of an intrinsically chiral ring system into the inner perimeter of the macrocycle.

A condensation reaction of enantiopure 1,1′-binaphthyl-2,2′-diamine and 1,3-diiminoisoindoline was carried out in *n*-butanol at 150 °C for 12 h to yield the (*R,R*)-**1** and (*S,S*)-**1** target compounds (Scheme 1). These compounds were characterized by ^{1}H, ^{1}H-^{1}H and ^{13}C-^{1}H COSY NMR spectroscopy, and by high-resolution MALDI mass spectrometry. The HR-MS spectra of (*R,R*)-**1** and (*S,S*)-**1** contained intense signals for the molecular ion peak at $m/z = 791.2911$ for (*R,R*)-**1** and 791.2930 for (*S,S*)-**1** (calcd for $C_{56}H_{35}N_6$, 791.2918 $[M^{+}+H]$), and the isotopic patterns were in accordance with simulations.

The structure of (*S,S*)-**1** was further confirmed by single crystal X-ray analysis. Crystals of (*S,S*)-**1** for single crystal X-ray analysis were obtained through slow diffusion of CH_3Cl into DMSO solutions. Since (*S,S*)-**1** is optically pure, only one enantiomer is observed in the unit cell. The two naphthyl moieties lie around a pseudo-C_2 axis and are inflexible with an angle $\theta = 85.2°$. The

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