# A Rational Design of Helix: Absolute Helix Synthesis by Binaphthyl-Salen Fusion

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A rational design of helical molecules is presented. Fusing chiral binaphthyl units and metallosalen complexes resulted in formation of molecules which inevitably adopt certain helical conformations.

Helices are the most interesting dissymmetric shapes found in nature. It was adopted in natural systems in the early stage of evolution, and has been used as the structural motif for biomolecules, such as nucleic acids and peptides. A certain number of synthetic polymers which adopt stable helical conformations have been reported to date.[1] Most of them have been prepared by helix-sense selective polymerization of achiral monomers or enantioselective polymerization of a racemic monomer mixture with chiral initiators.[1d] Another method relies on introduction of chiral units to the side chains or main chains of polymers, taking advantage of polymerization of chiral monomers.[1f,g] We also synthesized chiral polycarbonates having $C_2$-chiral binaphthyl or biphenyl units in the main chain and proved that they adopted stable helical conformations in solution.[2] The helical structures of these polymers, however, were quite difficult to be established even by exhaustive spectroscopic studies. Thus, a rational design of helical polymers, i.e., design of molecule which inevitably takes a certain helical conformation, is strongly desired. This issue is primarily due to the uncertainty of directionality of the junction between the monomer units. We have proposed that connecting twisted chiral units in such a way that the junction has almost no freedom of movement, a priori, should lead to a helical polymer.[3] Katz et al. reported the synthesis of helical ladder polymers having (salophen)Ni(II) units, which is analogous to our method.[4] Our interests have been focused on binaphthyls as twisted chiral sources for helical polymers.[2] We report herein the absolute synthesis of helical polymers from chiral binaphthol derivatives and metallosalen complexes based on our rational design of helices and their application as chiral catalysts.[5]

Our strategy to construct a specific helical structure is as follows. A $3_1$-helical structure is formed if chiral binaphthyl units and metallosalen complexes are consecutively fused together, as illustrated in Figure 1a. In order to ascertain the helicity of poly(binaphthyl metallosalen) complexes thus formed, a 10 mer model of **3**–Zn was subjected to molecular mechanics calculation. The MM2 calculation showed that it inevitably adopted a helical conformation (pseudo $3_1$-helix), as expected from the structure of the monomers (Figure 1b). The MD simulations indicated that no break of the helix occurred at least in tens of picoseconds at 400 K.[6] Careful studies with CPK space-filling models also indicated that the $3_1$-helix was the only one conformation which **3**–Zn could adopt.

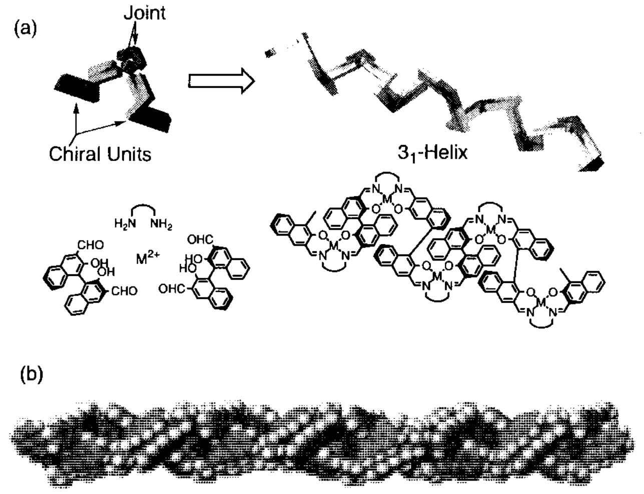
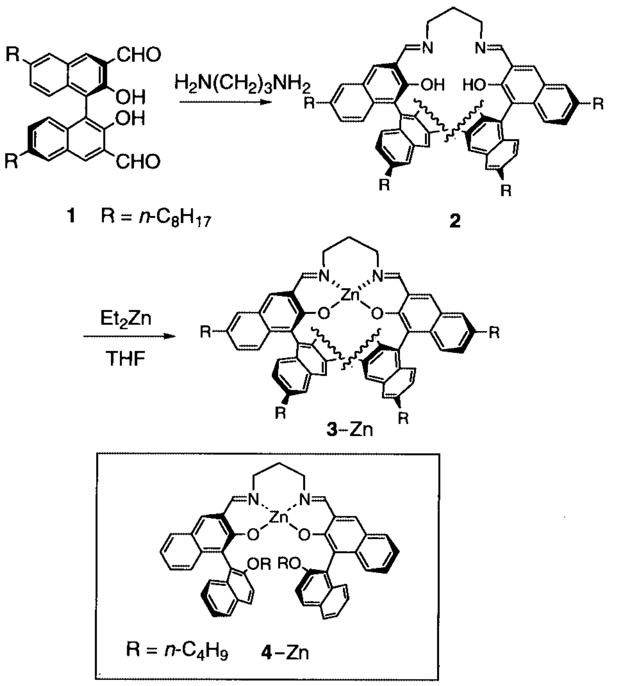


**Figure 1.** (a) Schematic diagram of the formation of helical polymer. (b) MM2-Calculated structure of **3**–Zn.

Poly(binaphthyl salen) zinc complex **3**–Zn was synthesized by a two-step procedure. Polycondensation of (*R*)-3,3'-diformylbinaphthol derivative **1**[7] and 1,3-propanediamine in $CHCl_3$ afforded poly(Schiff base)s **2**,[8] which were combined with either zinc acetate or diethylzinc in $CH_2Cl_2$. Both zinc acetate and diethylzinc gave **3**–Zn which exhibited similar molecular weights and spectra.[9] Incorporation of zinc was con-



**Scheme 1.** Synthesis of **3**–Zn.

firmed by the absence of $\nu_{\mathrm{O-H}}$ in the IR spectrum of **3**–Zn. The lower wave number shift of the $\nu_{\mathrm{C=N}}$ ($\Delta\nu = -10\ \mathrm{cm^{-1}}$) showed coordination of the nitrogens to the central zinc, suggesting the formation of salen complex units.[10] The molecular weight was estimated to be 1800 ($M_n$, PSt standards) by GPC.[11] A polymer unit model **4**–Zn was prepared from the corresponding monoformylbinaphthol derivative.[12]

UV and CD spectroscopic data of **3**–Zn well supported its helical structure. In UV spectroscopy, the absorption band of **3**–Zn (270 nm), which is assigned to the $^1B_b$ transition of naphthalene units, exhibited a remarkable red shift, compared with that of the unit model **4**–Zn (230 nm). This red shift is in agreement with the arrangement of naphthalene rings in close proximity to each other, as shown in Figure 1b. The CD spectrum of **3**–Zn differed from that of **4**–Zn. This difference of Cotton effects supports the helical structure, as demonstrated for optically active poly(binaphthyl carbonate)s.[2c]

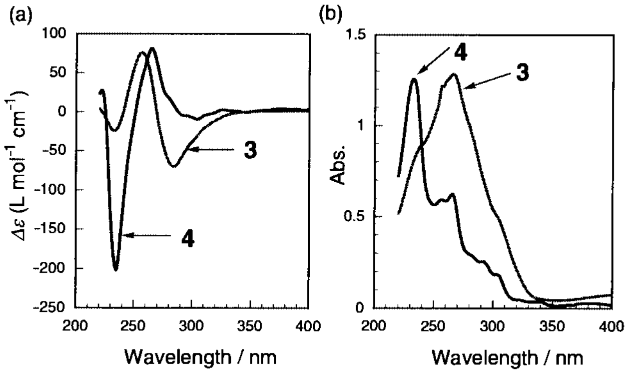
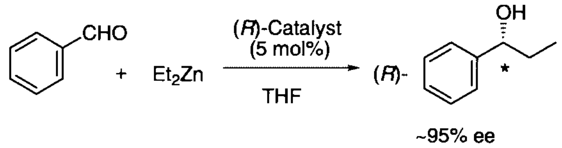


**Figure 2.** (a) CD spectra of **3**–Zn and **4**–Zn in THF (20 $\mu$M, 295 K). (b) UV spectra of of **3**–Zn and **4**–Zn in THF (20 $\mu$M, 295 K).



**Scheme 2.** Asymmetric addition of diethylzinc to benzaldehyde.

In the presence of a catalytic amount of poly(binaphthyl zinc-salen complex) **3**–Zn (5 mol%), diethylzinc was allowed to react with benzaldehyde in THF at r.t. for 24 h to quantitatively afford the corresponding (*R*)-1-phenyl-1-propanol with a high enantioselectivity (77% ee) (Scheme 2).[13] The enantioselectivity increased up to 95% ee at –60 °C. On the other hand, use of the unit model **4**–Zn resulted in a low enantioselectivity (r.t., 24 h, 5% ee (*R*)). Hence, the chiral space provided with the helical poly(binaphthyl-salen) zinc complex was demonstrated to be effective for the asymmetric addition of diethylzinc to benzaldehyde.[14]

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## References and Notes

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5 Pu et al. have recently reported the synthesis of poly(binaphthyl Ni(II)salen) complexes similar to our polymers; see, H.-C. Zhang, W.-S. Huang, and L. Pu, *J. Org. Chem.*, **66**, 481 (2001).

6 The calculations were performed by use of a CAChe (computer-aided chemistry) calculation package developed by Sony-Tektronix corporation.

7 **1** was synthesized from (*R*)-binaphthol in 7 steps (the overall yield was 13%).

8 $M_n$ 8300 ($M_w/M_n$ 1.80, PSt standards). IR (KBr) $\nu$ = 2925 ($\nu_{\mathrm{O-H}}$), 1631 ($\nu_{\mathrm{C=N}}$) $\mathrm{cm^{-1}}$.

9 $M_n$ 1800 ($M_w/M_n$ 1.29, PSt standards); IR (NaCl) $\nu$ = 1621 ($\nu_{\mathrm{C=N}}$) $\mathrm{cm^{-1}}$; UV–vis (THF, 20 $\mu$M): $\lambda_{\max}$ ($\varepsilon$) = 267 (64000), 236 (sh, 42000); CD $\lambda_{\mathrm{ext}}$ (THF, 20 $\mu$M), nm ([$\Delta\varepsilon$]): 284 (–71), 257 (+77), 233 (–24).

10 A. L. Singer and D. A. Atwood, *Inorg. Chim. Acta*, **277**, 157 (1998).

11 The molecular weight based on polystyrene standards might be underestimated presumably due to not only the helical structure but also the metallosalen structure of **3**–Zn.

12 $^1$H NMR (400 MHz, $\mathrm{CDCl_3}$) $\delta$ 8.61 (s, 2H), 8.00–7.80 (m, 10H), 7.50–7.10 (m, 12H), 4.00 (m, 4H), 3.73 (br t, $J$ = 6.5 Hz, 4H), 2.06 (qui, $J$ = 6.5 Hz, 2H), 1.38 (m, 2H), 0.95 (m, 2H), 0.60 (t, $J$ = 7.3 Hz, 3H); IR (NaCl) $\nu$ 1617 ($\nu_{\mathrm{C=N}}$) $\mathrm{cm^{-1}}$.

13 The e.e. values were determined by use of a chiral separation column (Daicel CHIRALCEL OD): 0.46$\phi$ × 25 cm, eluent: *n*-hexane/2-propanol (20:1), flow rate: 1.0 mL $\mathrm{min^{-1}}$, $t_R$: 13.6 and 15.5 min for (*R*)- and (*S*)-1-phenyl-1-propanol, respectively.

14 As shown in Figure 1b, the reaction would occur inside the groove of the helical polymer.