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Asymmetric Autocatalysis Initiated by Finite Single-Wall Carbon Nanotube Molecules with Helical Chirality

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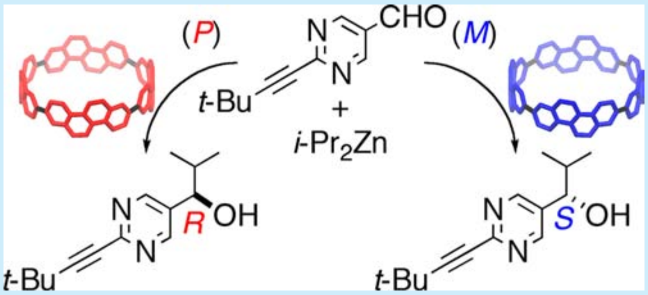
S *Supporting Information*

ABSTRACT: An asymmetric autocatalysis reaction was initiated by a finite single-wall carbon nanotube molecule with helical chirality. The asymmetric induction was initiated by the chiral environment arising from the planar chirality of the tubular polyaromatic hydrocarbons.



Noncovalent supramolecular chemistry of carbon nanotubes (CNTs) is attracting much interest due to their utilization in a diversity of subjects. Surfaces of CNT function as unique adsorbents for various entities, which also allow liberation and manipulation of CNTs.[1] On the other hand, the effect of sp^2-carbon networks over the adsorbed entities is much less explored, partly due to the lack of access to discrete CNT molecules. Understanding the chemical outcome at the molecular level was not readily possible with a mixture of CNTs comprising various structures.[2,3] Recently, we introduced discrete and finite single-wall CNT (SWNT) molecules with persistent belt shapes through bottom-up chemical synthesis and found that the noncovalent supramolecular method is also effective for the isolation of finite congeners.[4−6] Specifically, noncovalent $\alpha-\pi$ interactions of the steroidal stationary phase on silica gel allowed the separation of (12,8)-, (11,9)-, and (10,10)-diastereomers and, moreover, (*P*)- and (*M*)-helical enantiomers.[4] Although the $\alpha-\pi$ interactions with steroids have also been utilized for the separation of infinite helical SWNTs,[7] the $\alpha-\pi$ interactions with the finite SWNT molecules further permitted the stereoselective synthesis of helical congeners.[4] Observing the intriguing effect of the adsorbed entities on the finite SWNT surface, we conjecture that the unique chirality inherent to the sp^2-carbon arrangements at the surface may also exert an asymmetric influence over the outer chemical space. We herein report the first example of finite SWNT molecules as a chiral initiator in asymmetric catalysis.

The finite SWNT molecules in our study are (*P*)- and (*M*)-(12,8)-[4]cyclo-2,8-chrysenylene ([4]$CC_{2,8}$).[4] The molecule is a pure hydrocarbon with a chemical composition of $C_{120}H_{136}$, and in the absence of any stereogenic centers, the chirality of the molecule arises from the helical sp^2-carbon arrangement in the tubular structure.[8,9] The reaction that we examined was an asymmetric autocatalyis reaction (Soai Reaction).[10−13] The reaction of diisopropylzinc with 2-*tert*-butylethynylpyrimidine-5-carbaldehyde **1** was thus carried out in the presence of 25 mol % of (12,8)-[4]$CC_{2,8}$ in the first stage, and the subsequent asymmertic autocatalysis reaction was carried out through addition of **1** and diisopropylzinc to give alkanol **2** (Table 1).[14,15] The asymmetric initiators with (*P*)- and (*M*)-helicity led to the product with opposite chiralty to afford (*R*)- and (*S*)-**2**, respectively. The enantioselectivity of the first round of reaction was improved to >99.5% *ee* after the additional two rounds of autocatalysis reaction (entries 2 and 4). The results clearly show that the helical chirality of the finite SWNT molecules acts as an asymmetric initiator for the reaction.

The tubular structure with a wide bore suggests an interesting mechanistic insight. The tubular structure gives rise to an interesting chiral topology of sp^2-carbon networks in the helical congeners, and the chirality can concurrently be categorized in the planar chirality.[16] This unique chirality may be understood in the following manner: an SWNT is made from a graphene sheet, and the helical chirality does not exist in the flat graphene form. When the flat graphene sheet is rolled up to a tubular shape, there arises the helical chirality (Figure 1).[8] The sense of chirality is determined by the roll-up direction of the graphene sheet, which also leads to the emergence of the planar chirality. When viewed from the inside of the tube, the

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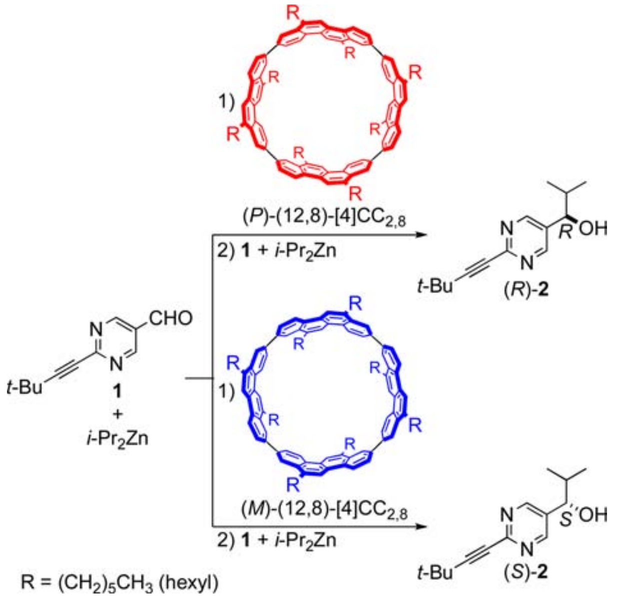
Table 1. Asymmetric Autocatalysis Reaction with Hexyl-Substituted (12,8)-[4]$CC_{2,8}$[a]



entry	(12,8)-[4]$CC_{2,8}$	product **2** yield (%)	 *ee* (%)	 configuration
1	*P*	69	87	*R*
2	*P*	86	91 (>99.5)[b]	*R*
3	*M*	89	89	*S*
4	*M*	83	91 (>99.5)[b]	*S*

[a] Reactions were performed in toluene at 0 °C using **1**/*i*-Pr_2Zn/(12,8)-[4]$CC_{2,8}$ = 1:4:0.25 in the first stage, and additional portions of **1** (4 and 16 equiv) and *i*-Pr_2Zn (10 and 32 equiv) were added in the second stage. [b] After two additional rounds of asymmetric autocatalysis reaction.

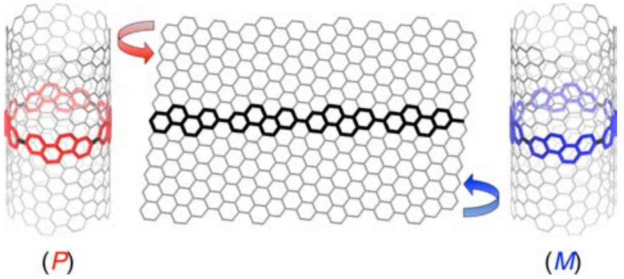


Figure 1. (12,8)-SWNT and its base graphene unit. Chrysenylene units for (12,8)-[4]$CC_{2,8}$ are colored in red for the (*P*)-isomer and in blue for the (*M*)-isomer. The arrows show the roll-up directions.

chiral sense of the carbon arrangement is opposite from that viewed from the outside. Two sides of the helical tube, outer and inner, are therefore different in two points: One is the convex/concave shape, and the other is the chirality sense. The observation of asymmetric autocatalysis with (*P*)/(*M*)-(12,8)-[4]$CC_{2,8}$ shows that the asymmetric induction originates from chiral initiation on one side, which indicated the difference in the effectiveness of the asymmetric induction between these two faces. Further mechanistic investigations are currently being carried out in our laboratories.

In summary, we have demonstrated the use of a finite SWNT molecule as an asymmetric inducer of asymmetric autocatalysis. The results show the asymmetric influence of helical SWNT molecules over the other substances and may encourage various explorative applications of chiral SWNTs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimantal details and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) A typical procedure: To a mixture of **1** (4.7 mg, 0.025 mmol) and (*P*)-(12,8)-[4]$CC_{2,8}$ (9.9 mg, 6.25 μmol) was added *i*-Pr_2Zn in toluene (1.0 M; 0.10 mL, 0.10 mmol) at 0 °C over 2 h, and the mixture was stirred for 12 h at 0 °C. The mixture was diluted with toluene (0.40 mL), and *i*-Pr_2Zn in toluene (1.0 M; 0.25 mL, 0.25 mmol) was added, which was followed by the slow addition of **1** (18.8 mg, 0.10 mmol) in toluene (0.50 mL) over 1 h. After 2 h, a second set of reagents and substrates [toluene: 3.6 mL, 1.0-M *i*-Pr_2Zn in toluene: 0.80 mL (0.80 mmol), **1**: 75.3 mg (0.40 mmol) and toluene: 3.0 mL] was introduced in the same manner. The asymmetric inducer is present at *ca.* 1 mol% of aldehyde in this stage. After aqueous quenching of the reaction with sat. aq. NH_4Cl and 30% aq. NH_3, the mixture was extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, and the volatiles were removed under reduced pressure. The products were purified by silica gel column chromatography (eluent: hexane/EtOAc = 2/1) to give (*R*)-**2** (107 mg) in 86% yield with 91% *ee*. The *ee* value was determined by HPLC analysis with a retention time of 10.9 min for (*S*)-**2** and 15.5 min for (*R*)-**2** (Daicel Chiralpak IB, 4.6 mm × 250 mm; rt; eluent: 5% *i*-PrOH/hexane, 1.0 mL/min).

(15) The rotation of the chrysenylene unit is negligible under the reaction conditions, as the half-life of (*P*)-(12,8)-[4]$CC_{2,8}$ in toluene at 0 °C is estimated as 24.6 years. See: Hitosugi, S.; Nakanishi, W.; Isobe, H. *Chem.—Asian J.* **2012**, *7*, 1550−1552.

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