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Chiral inclusion crystallization of tetra(*p*-bromophenyl)ethylene by exposure to the vapor of achiral guest molecules: a novel racemic-to-chiral transformation through gas–solid reaction

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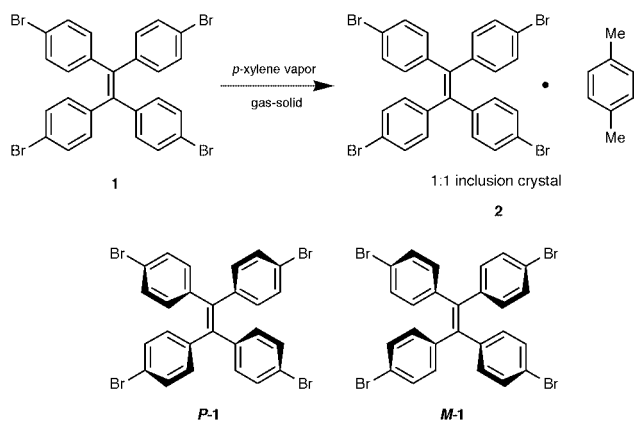
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Racemic crystalline tetra(*p*-bromophenyl)ethylene was converted into chiral inclusion crystals in the solid state by contact with gaseous achiral guest compounds.

Chiral crystallization of achiral molecules in the absence of any external chiral source is of special interest not only for “so-called” absolute asymmetric synthesis¹ but also for its relationship to the prebiotic origin of chirality.² Such chiral crystals have been obtained previously during crystallization of achiral substrates from their solutions. We have now found that chiral inclusion crystals can be obtained by treatment of a racemic host compound with the vapor of achiral guest compounds. This is the first example of the formation of chiral inclusion crystals from achiral components through gas–solid inclusion complexation.



Recently, we have found that tetra(*p*-bromophenyl)ethylene **1**³ forms chiral inclusion compounds with various kinds of achiral guest molecules. For example, recrystallization of **1** from *p*-xylene gave 1:1 inclusion crystals (**2**). The chiral arrangement of **1** molecules in **2** was easily detected by measurement of CD spectra of its Nujol mull. Hence, one single crystal of **2** showed a positive Cotton effect while another showed a negative Cotton effect (Fig. 1). The host compound **1** also formed chiral inclusion crystals with acetone (1:1), dioxane (1:1) and benzene (1:1), whereas it formed racemic inclusion crystals with cyclohexanone (1:1), THF (1:2), β -picoline (1:1) and toluene (1:1), by recrystallization (Table 1).

Very interestingly, however, when exposed to *p*-xylene vapor at room temperature for 24 h, a single crystal of pure **1** prepared by recrystallization from *m*-xylene was gradually changed into the chiral polycrystalline 1:1 inclusion complex (**2**) of **1** with *p*-xylene. The inclusion complex (**2**) thus obtained showed the same CD spectrum as that obtained by the recrystallization

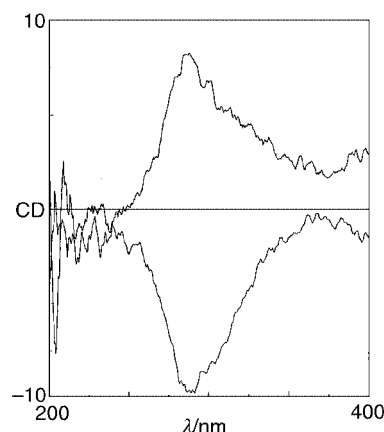


Fig. 1 CD spectra of the enantiomeric 1:1 inclusion crystals of **1** with *p*-xylene in Nujol mulls.

Table 1 Inclusion complexation of **1** with some guest compounds

Guest	Inclusion complex				<i>t</i> /h
	By recrystallization		By gas–solid reaction		
	host: guest	host: guest	host: guest	host: guest	
Acetone	chiral	1:2	—	— ^a	168
Cyclohexanone	<i>rac</i>	1:1	—	— ^a	168
THF	<i>rac</i>	1:2	chiral	1:2	2
1,4-Dioxane	chiral	1:1	chiral	1:1	24
Benzene	chiral	1:1	chiral	1:1	24
Toluene	<i>rac</i>	1:1	—	— ^a	168
<i>p</i> -Xylene	chiral	1:1	chiral	1:1	24
β -Picoline	<i>rac</i>	1:1	chiral	1:1	168

^a No complexation occurred.

method, and its X-ray powder pattern was similar to that obtained by recrystallization (Fig. 2) Gas-solid reaction of **1** with THF, dioxane, benzene and β -picoline also produced their inclusion complexes with the same host–guest ratios as those obtained by recrystallization (Table 1). It is also remarkable that the inclusion crystals of **1** with THF and β -picoline obtained by gas–solid reaction were chiral, whereas those obtained by recrystallization were racemic. Gas–solid inclusion complexation did not occur, however, in the cases of acetone, cyclohexanone and toluene (Table 1). The chiral crystalline lattice formed by chiral arrangement of **1** molecules is very stable and still exists after removal of the guest molecules *via* heating compound **2** under reduced pressure. The chiral crystalline powder left after removal of the guest from **2** showed a very similar X-ray powder diffraction pattern to that of **2**. By

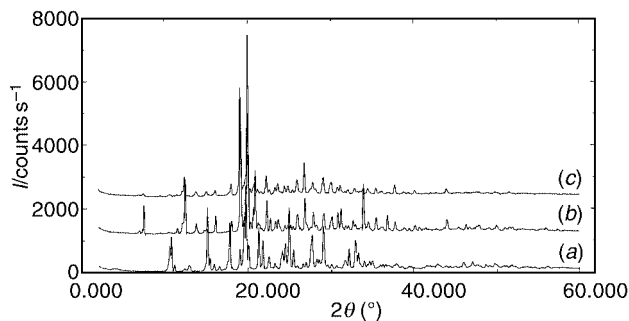


Fig. 2 The X-ray powder patterns of (a) *rac*-crystals of pure **1**, (b) chiral crystals of **2** prepared by recrystallization and (c) chiral crystals of **2** prepared by gas–solid reaction.

exposure to xylene vapor, this chiral crystalline powder was easily converted to the 1:1 inclusion crystals **2** with the same chirality.

X-Ray analysis of the *rac*-crystal of **1** showed that two halves of crystallographically independent molecules of *P*-**1** and *M*-**1** exist in the asymmetric unit (space group: *Pccn*). (Fig. 3)[†] Molecular layers of *P*-**1** and *M*-**1** are arranged perpendicular to the *a*-axis and within these layers the molecules are connected by Br...Br contacts along the *c*-direction. The *P*-**1** molecule has a right-handed and the *M*-**1** molecule has a left-handed propeller structure, respectively (Fig. 4).

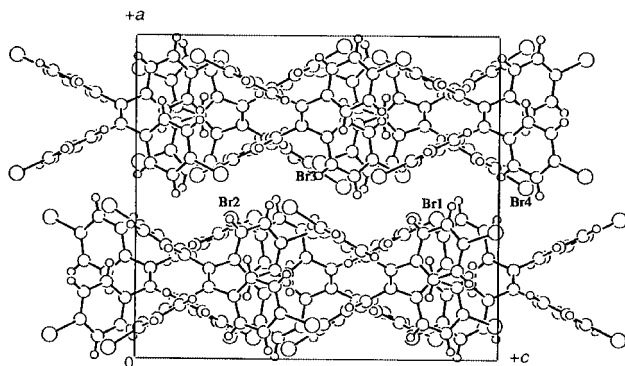


Fig. 3 Crystal structure of **1** viewed along the *b*-axis.

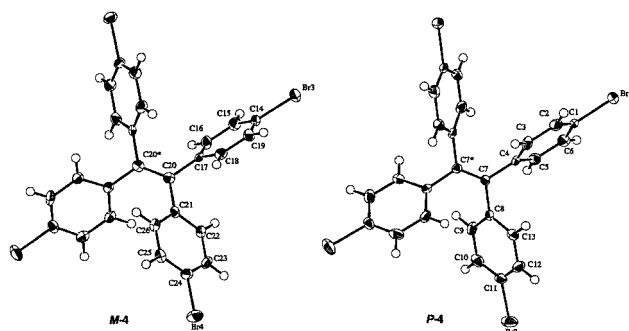


Fig. 4 Molecular structure of *P*-**1** (right molecule) and *M*-**1** (left molecule) in the crystal of **1**. Thermal ellipsoids are drawn at the 50% probability level.

The molecules in **2** occupied the chiral space group $P2_12_12_1$.[‡] The *p*-xylene molecules are included in chiral cavities formed by the bromophenyl rings (Fig. 5) In **2**, molecular layers are arranged perpendicular to the *a*-axis, and within these layers the

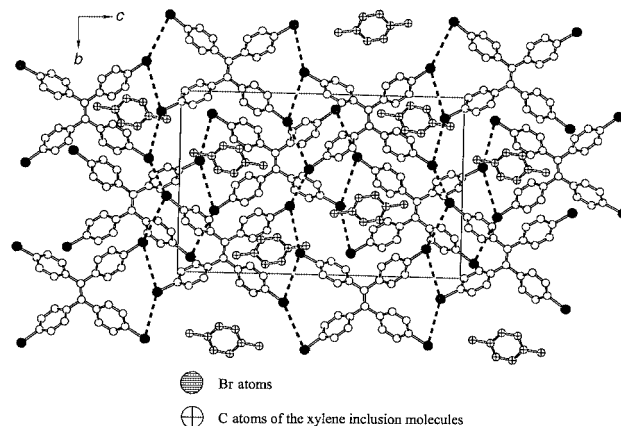


Fig. 5 Crystal structure of **2** viewed along the *a*-axis.

molecules are connected by Br...Br contacts along the *b* direction. It has been found that halogen...halogen contacts act as attractive interactions and the inclusion complex is stabilized by the Br...Br interactions between host molecules.⁴ This is the first example of the construction of a chiral inclusion crystalline lattice by a Br...Br interaction network among achiral host molecules.

In conclusion, we have found a unique example of racemic-to-chiral transformation by exposing racemic crystalline material to the vapor of an achiral guest compound. This provides not only a new strategy for construction of chiral crystals but also a new model for studying the mechanism of generation of chirality in crystals.

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Note and references

[†] *Crystal data for 1*: $C_{26}H_{16}Br_4$, $M = 648.03$, colorless prisms $0.35 \times 0.15 \times 0.15$ mm, orthorhombic, *Pccn*, $a = 16.173(2)$, $b = 16.512(1)$, $c = 18.024(2)$ Å, $V = 4813(1)$ Å³, $Z = 8$, $D_c = 1.788$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 67.19$ cm⁻¹, $F(000) = 2496$, $T = 133$ K, final $R = 0.033$, $R_w = 0.032$ for 272 variables and 3159 reflections with $I > 2\sigma(I)$. The structures were solved by direct methods (SIR97) (ref. 5) and refined by full-matrix least-squares on F^2 .

[‡] *Crystal data for 2*: $C_{26}H_{16}Br_4 \cdot C_8H_{10}$, $M = 754.2$, colorless prisms $0.44 \times 0.2 \times 0.2$ mm, orthorhombic, space group $P2_12_12_1$, $a = 8.762(1)$, $b = 14.942(2)$, $c = 23.472(4)$ Å, $V = 3073.0(8)$ Å³, $Z = 4$, $D_c = 1.63$ g cm⁻³, $T = 218$ K, $\mu(\text{Mo-K}\alpha) = 5.26$ mm⁻¹, $F(000) = 1480$, final $R = 0.047$, $R_w = 0.096$ for 345 variables, 4119 reflections and 2148 observed reflections with $I > 2\sigma(I)$. The structures were solved by direct methods (SHELXS-97) (ref. 6) and refined by full-matrix least-squares on F^2 . CCDC 182/1539. See <http://www.rsc.org./suppdata/cc/a9/a909782a/> for crystallographic files in .cif format.

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