Chiral inclusion crystallization of achiral tetrakis(*p*-halophenyl)-ethylenes with achiral guest compounds

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The title host compounds form chiral inclusion complex crystals with various kinds of achiral guest compounds in which the achiral host molecules are arranged in a chiral form through halogen–halogen interactions between host molecules.

Introduction

Chiral crystallization of achiral molecules in the absence of any external chiral source is of special interest not only for "so-called" absolute asymmetric synthesis[1] but also for the development of new chiral materials for applications such as nonlinear optics. This type of chiral crystallization is also interesting in relation to the prebiotic origin of chirality.[2]

We have found that achiral tetrakis(*p*-bromophenyl)ethylene (**2**)[3] forms chiral inclusion compounds with various kinds of achiral guests, although tetraphenylethylene (**1**)[4] did not show any inclusion ability. Similarly, chloro- (**3**),[5] fluoro- (**4**),[6] iodo-derivatives (**5**), and tetrakis(*p*-methoxyphenyl)ethylene (**6**)[5] also formed chiral inclusion crystals with some achiral guest compounds. However, tetrakis(*p*-hydroxyphenyl)ethylene (**7**)[7] formed achiral inclusion crystals. This chiral crystalline lattice of the inclusion compounds is formed by twisting of the *p*-bromophenyl rings in one direction as depicted in Chart 1. It
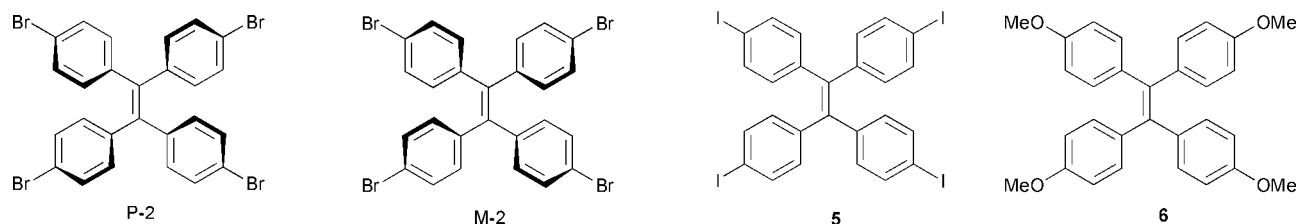

Chart 1 Propeller-shaped chiral conformations of **2**.

was also found that the chiral crystalline lattice is stable and is maintained even after removal of the guest compound. X-Ray analysis[8] showed that molecular aggregation of **2** occurs by intermolecular Br · · · Br, Br · · · π, and π · · · π contacts and that the guest molecules are accommodated in the chiral crystalline lattice only by van der Waals contact with the host. This is the first example of the formation of chiral inclusion crystals of achiral host molecules (**2–6**) with achiral guest molecules, although some tetraphenylethylene derivatives are known to exist in chiral conformers.[9]

Results and discussion

Inclusion complexes of **2–7** were prepared by recrystallization of **2–7** from the various guest compounds shown in Table 1.
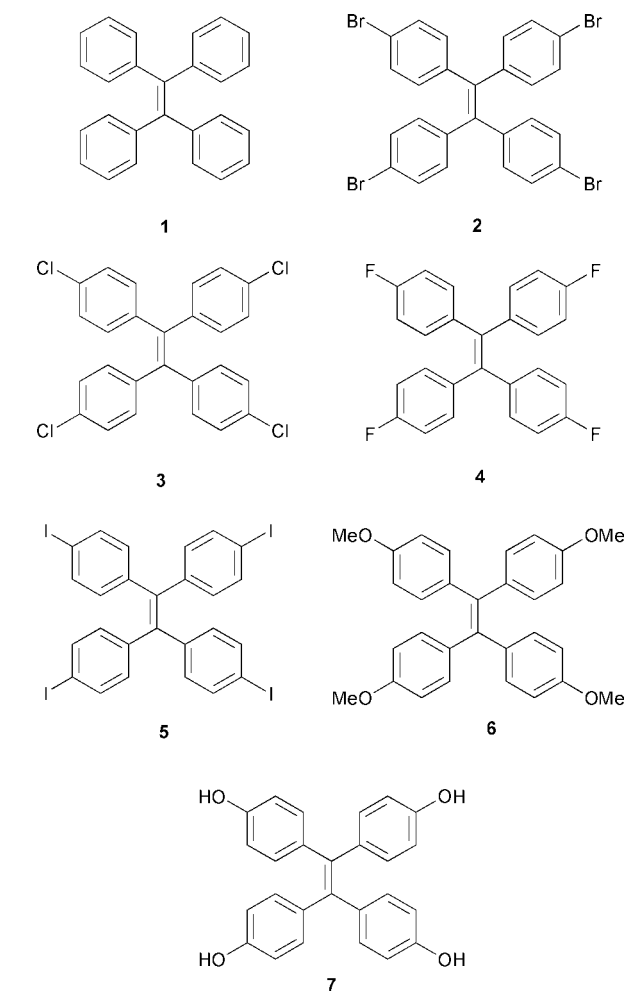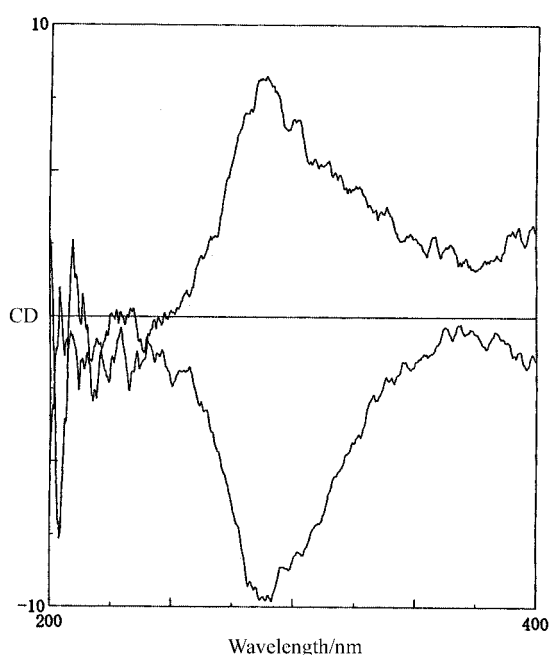
The inclusion ability of the host compound increases in the order **4** > **7** > **2** > **5** > **3** ≫ **6**. Very interestingly, however, the host compounds (**2–6**) formed chiral inclusion crystals with achiral guest molecules, although compounds **2–4** and **6** on their own formed achiral crystals. Contrary to this, **7** formed achiral inclusion crystals. For example, recrystallization of **2** from

Table 1 Host:guest molar ratio of inclusion complexes of tetraphenylethylene derivatives (2–7)[a]
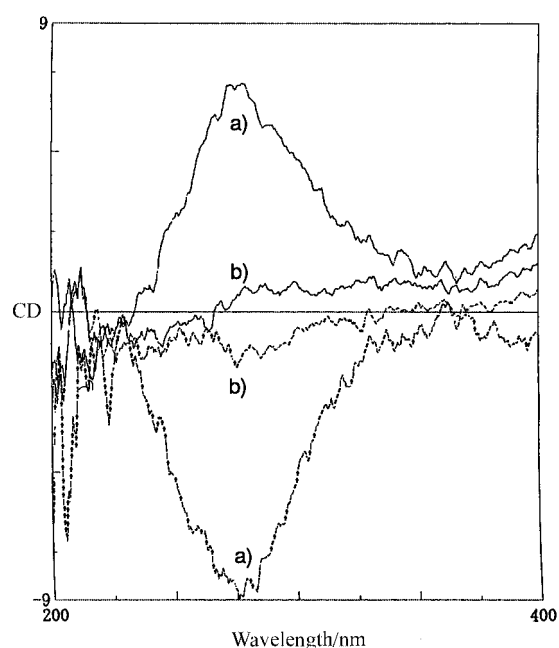
Guest	2	3	4	5	6	7
MeOH	—[b]	—	—	—	—	2:3
Acetone	1:2[c] (8)	—	2:1	—	—	1:2
Cyclohexanone	1:1	—	1:1	1:2[c]	—	1:4
Ethyl acetate	—	—	—	—	—	1:1:H$_2$O (13)
THF	1:2[c] (9)	1:2[c]	1:1	1:2[c]	—	1:4
Dioxane	1:1[c]	1:1[c]	2:1	1:2	1:2[c]	1:4
DMF	—	1:1[c]	1:1	1:2	—	1:2
Benzene	1:1[c]	1:1[c]	2:1	1:1[c]	1:1	—
Toluene	1:1	—	2:1	—	—	—
o-Xylene	—	—	1:1	—	—	—
m-Xylene	—	—	—	—	—	—
p-Xylene	1:1[c] (10)	1:1[c] (11)	2:3 (12)	—	—	—
1-Methylnaphthalene	1:2	—	1:1[c]	1:1	—	—
2-Methylnaphthalene	—	—	2:3[c]	1:1	—	—
α-Picoline	—	—	1:1	—	—	1:4
β-Picoline	1:1	1:1[c]	1:1	1:1[c]	—	1:2
γ-Picoline	—	—	1:1	—	—	1:4

[a] The host:guest ratio was determined by TG and NMR. [b] No inclusion occurred. [c] Chiral crystal.

Fig. 1 CD spectrum of a 1:1 inclusion complex (10) of chiral 2 with p-xylene.

Fig. 2 a) CD spectrum of chiral 2 remaining after evaporation of p-xylene from 10 by heating at 100 °C under 2 mmHg for 30 min in the solid state and b) achiral 2 obtained by heating of the chiral 2 at 240 °C for 5 min.

p-xylene gave a chiral inclusion crystal 10 of 2 with p-xylene in a 1:1 ratio as colorless prisms.[8] The chiral arrangement of 2 molecules in the inclusion crystals were easily detected by measurement of CD spectra in Nujol mull. For example, one piece of crystal of 10 showed a (+)-Cotton effect and the other piece of crystal showed a (−)-Cotton effect (Fig. 1).

Of the the various kinds of guests listed in Table 1, acetone, dioxane, THF and benzene formed the chiral inclusion crystals with 2, although cyclohexanone, toluene, 1-methylnaphthalene and β-picoline formed racemic inclusion crystals. However, o- and m-xylenes, 2-methylnaphthalene, and α- and γ-picolines do not form inclusion complexes with 2. By using this selective inclusion complexation, isomers of xylenes, methylnaphthalenes and picolines can be separated. For example, when a neat solution of 2 (1.0 g, 1.55 mmol) and a 1:1 mixture of m- and p-xylene (2.0 g, 18.9 mmol) was kept at room temperature for 12 h, a 1:1 inclusion crystal of 2 and p-xylene was obtained as colorless prisms (0.84 g, 72% yield) which upon heating in vacuo gave p-xylene of 92% purity in 59% yield. Similar complexation of 2 with a 1:1 mixture of 1- and 2-methylnaphthalene gave a 1:2 inclusion crystal of 2 with 1-methylnaphthalene as colorless prisms, which upon heating

in vacuo gave 1-methylnaphthalene of 77% purity. β-Picoline was also separated from the mixture with γ-picoline by complexation with 2 in 91% purity.

Tetrakis(p-chlorophenyl)ethylene (3), tetrakis(p-fluorophenyl)ethylene (4), tetrakis(p-iodophenyl)ethylene (5), and tetrakis-(p-methoxyphenyl)ethylene (6) also formed chiral inclusion crystals with some guest compounds, although tetrakis(p-hydroxyphenyl)ethylene (7) formed only racemic inclusion crystals (Table 1).
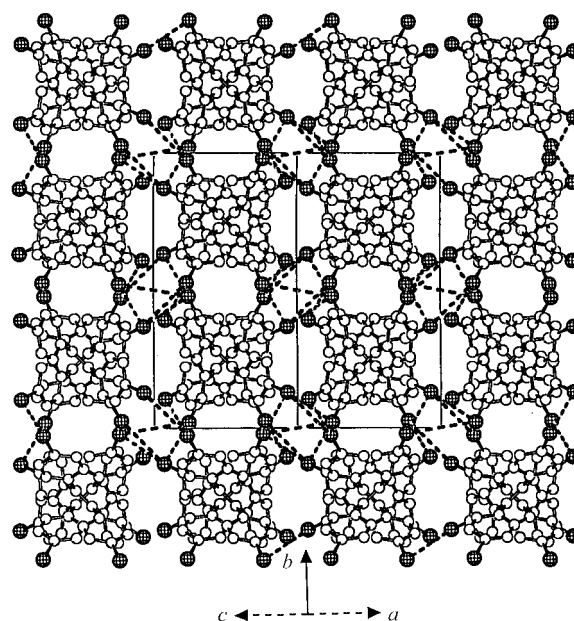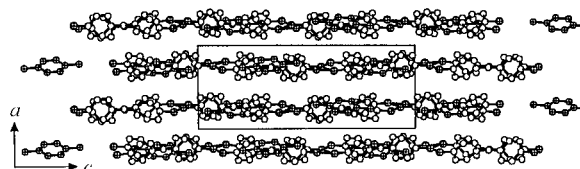
The chiral crystalline lattice formed by chiral arrangement of these host molecules is very stable and still exists after removal of the guest molecule by heating of the inclusion crystals under reduced pressure. For example, the chiral crystalline powder left after removal of p-xylene from 10 by heating at 100 °C under 2 mmHg for 30 min in the solid state showed very similar CD spectra in the solid state (Fig. 2). The chiral crystalline powder of 2 left after removal of the guest from 10 was stable and the racemic crystalline powder of 2 was obtained by heating of chiral 2 at 240 °C for 5 min in the solid state (Fig. 2).

Table 2 Relevant intermolecular contacts

Compound	Short contacts/Å	Symmetry operation	Short contacts/Å	Symmetry operation
3	Cl1A $\cdots$ Cl2′ 3.458	$1 - x, 1 - y, -z$	Cl1A $\cdots$ Cl2A′ 3.563	$1 - x, 1 - y, -z$
5	I1 $\cdots$ I2′ 3.947	$2 - x, 1 - y, -z$	I2 $\cdots$ I4′ 3.965	$0.5 - x, 0.5 + y, -0.5 - z$
	I2 $\cdots$ I3′ 3.977	$1.5 - x, -0.5 + y, 0.5 + z$		
10	Br3 $\cdots$ Br4′ 3.521	$1.5 - x, -0.5 + y, 0.5 + z$	Br2 $\cdots$ Br4′ 4.03	$1.5 - x, 1 - y, 0.5 + z$
11	Cl3 $\cdots$ Cl4′ 3.405	$0.5 - x, 1 - y, -0.5 - z$	Cl4 $\cdots$ Cl3′ 3.405	$0.5 - x, 1 - y, 0.5 + z$
8	Br1 $\cdots$ Br3′ 3.81	$1 - x, -0.5 + y, 0.5 - z$	Br3 $\cdots$ Br4′ 3.88	$0.5 + x, 0.5 - y, -z$
9	Br2 $\cdots$ Br4′ 3.75	$1 - x, -0.5 + y, 0.5 - z$	Br1 $\cdots$ Br2′ 3.89	$0.5 + x, 0.5 - y, -z$
12	F3 $\cdots$ F3′ 2.834	$1 - x, -y, -z$	F2 $\cdots$ F4′ 3.421	$2 - x, 2 - y, 1 - z$
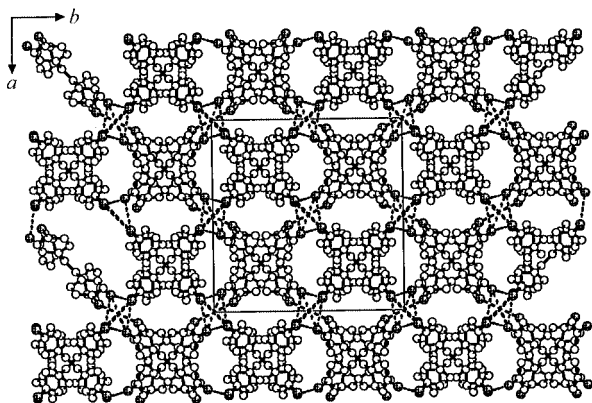
Fig. 3 Packing arrangement of **3** in the projection along the *c*-axis. Hydrogen atoms are omitted for clarity.
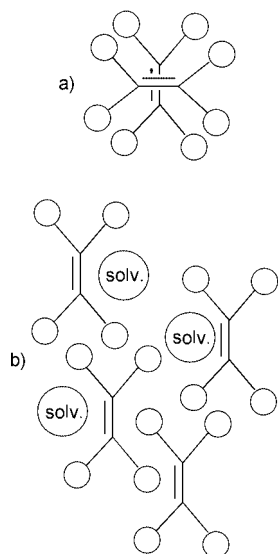
Chart 2 Schematic packing arrangements of the tetraphenylethylene units: a) crossed double bonds corresponding to **2**, **3** and **5**; b) space-filling dense packing corresponding to **10** and **11**.

Fig. 4 Packing arrangement of **5** in the projection of (101).

Fig. 5 Packing arrangement of **11** along the *b*-axis. The crystal structure of **10** is isomorphic and looks almost identical to **11**.

The halogenated tetraphenylethenes **2**[8] and **3** without any guest inclusion form the same stacking arrangements as shown in Fig. 3. The packing arrangement is determined by short X $\cdots$ X contacts[10] between the terminal halogen atoms (Table 2) and by steric constraints. Compounds **2**[8] and **3** have isomorphic crystal structures (*Pccn*; see Table 5). The molecules lie on a crystallographic two-fold rotation axis perpendicular to the double bond axis. Two neighboring molecules are arranged with crossed double bonds as shown in Fig. 3 and in Chart 2. These two molecules are related by a glide plane and are therefore enantiomers. From Chart 2 it can be recognized that by crossing of the double bond axes an optimal space-filling packing arrangement of the large phenyl groups can be obtained. Therefore the crystal consists of stacks of crossed molecules which are connected in the crystal by X $\cdots$ X contacts between the terminal halogen atoms. The iodo deriv-

ative **5** crystallizes in a different space group (*P*2₁/*n*; see Table 5), but the packing arrangement shows only minor deviations from the packing arrangements of **2** and **3** discussed above, as can be seen from Fig. 4.

By inclusion of guest molecules this packing mode is changed to a layer-like arrangement. The isomorphic 1 : 1 inclusion crystals of **2** (**10**)[8] and **3** (**11**) with *p*-xylene have the same crystal symmetry (*P*2₁2₁2₁) and similar lattice parameters (see Table 5). In the xylene inclusion crystals **10** and **11** (Fig. 5) molecular layers are arranged perpendicular to the *a*-axis in such a way that space-filling dense packing can be obtained as shown in Chart 2 and Figs. 5 and 6. This packing of the inclusion crystals **10** and **11** is different from the crystals of the pure compounds **2** and **3**. In the course of the change between both packing systems large shifts of the molecules are necessary and flipping of the phenyl rings has to take place since there is a transformation from a racemic (*Pccn*) to a chiral (*P*2₁2₁2₁) space group.

Within the layers the molecules are connected by Br $\cdots$ Br or Cl $\cdots$ Cl contacts respectively along the *b* direction (Fig. 6). There are several short X $\cdots$ X contacts (Table 2); some of them are even below the sum of the van der Waals radii (Br $\cdots$ Br 3.70, Cl $\cdots$ Cl 3.50 Å).[11] Halogen $\cdots$ halogen contacts are known to be attractive and to control the crystal packing.[10]
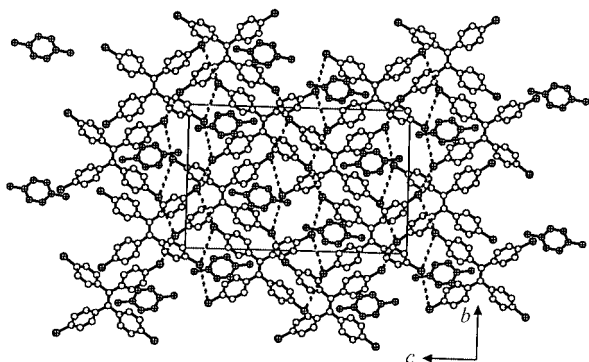
Fig. 6 Packing arrangement of **11** along the *a*-axis. The crystal structure of **10** is isomorphic and looks almost identical to **11**.
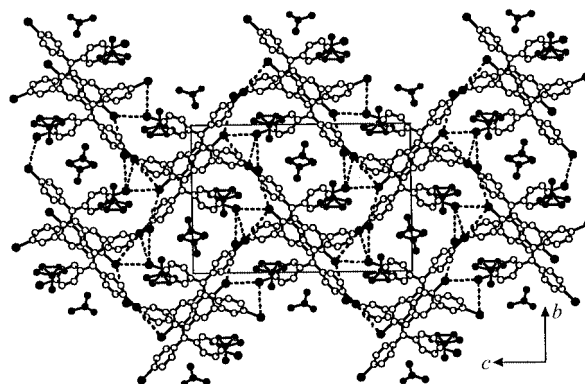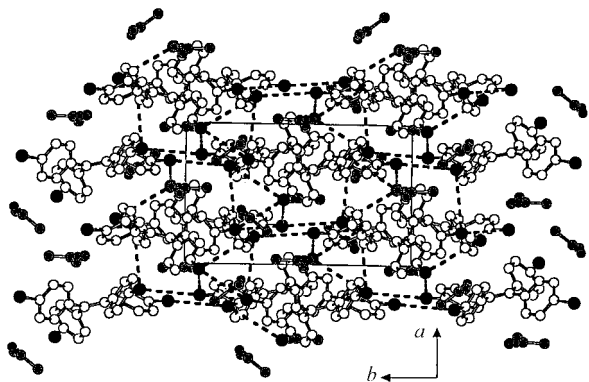

Fig. 7 Packing arrangement of **8** along the *c*-axis. The crystal structure of **9** is isomorphic and looks almost identical to **8**.

Fig. 8 Packing arrangement of **8** along the *b*-axis. The crystal structure of **9** is isomorphic and looks almost identical to **8**.
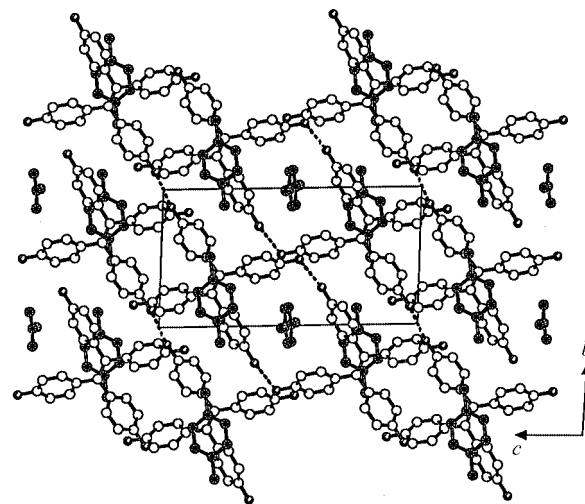
Also in the acetone and THF inclusion crystals (**8** and **9**), which are isomorphic (see Table 5), analogous layers are formed, but now there are short Br···Br contacts between the layers along the *a*-axis (Fig. 7, Table 2). These interlayer contacts are possible because the host molecules are tilted, allowing short Br···Br contacts on one side of the molecule (Fig. 8).

As shown in Fig. 6 the xylene is included in the cavities formed by halophenyl rings in the 1,2-position. In compound **8** one of the two independent acetone molecules is included in channels along the *a*-axis (Fig. 9). The second one lies between the layers. The packing arrangement of **9** is analogous.

The fluoro derivative **4** includes 1.5 *p*-xylene per host molecule (**12**). The molecules of **4** form a framework with two channels along the *a*-axis (Fig. 10) and along the *b*-axis (Fig. 11), which are occupied by the *p*-xylene guest molecules. Since we found only one F···F contact (2.834 Å) below the van der Waals distance (2.94 Å) the crystal framework is held together by van der Waals interactions and polar forces. F···H–C hydrogen bonds were not found.[12]

The phenolic derivative **7** forms 1:1:1 inclusion crystals with ethyl acetate and water (**13**). The three compounds are linked together by hydrogen bonds (Table 3). A sandwich-like crystal structure is found for **13** with a sequence of hydrophobic tetra-

Fig. 9 Packing arrangement of **8** along the *a*-axis. The crystal structure of **9** is isomorphic and looks almost identical to **8**.

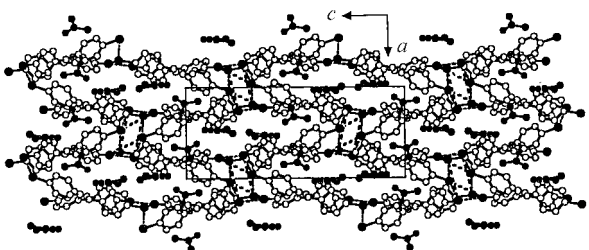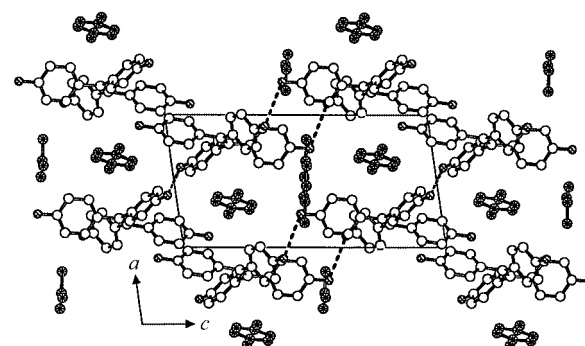**Fig. 10** Packing arrangement of **12** along the *a*-axis.

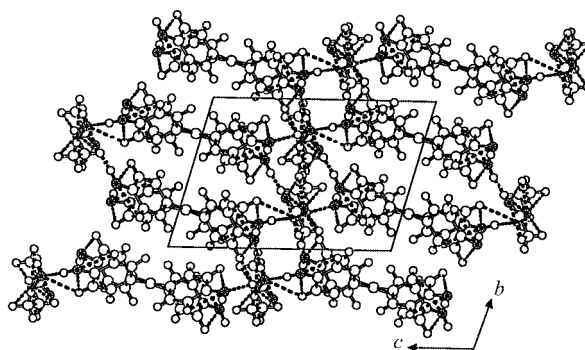**Fig. 11** Packing arrangement of **12** along the *b*-axis.

Fig. 12 Packing arrangement of **13** along the *a*-axis.

phenylethylene groups and a hydrophilic hydrogen bond framework of the OH groups, ethyl acetate and water parallel to *cb* (Fig. 12).

Table 3 Hydrogen bonds in **13**: O1–4 belongs to **7**, O50 and O51 to ethyl acetate and O60 to water

O···H distance/Å	O···O distance/Å	O–H···O angle/°	Symmetry operation
O3···H1′ 1.790	O3···O1′ 2.716	O3···H1′–O1′ 168.0	$x − 1, y, z$
O60···H2 1.681	O60···O2 2.652	O60···H2–O2 175.3	
O50···H3′ 1.834	O50···O3′ 2.721	O50···H3′–O3′ 167.7	$−x + 3, −y + 1, −z + 2$
O2···H4A′ 1.832	O2···O4′ 2.714	O2···H4A′–O4′ 164.6	$x + 1, y, z$
O1···H60A′ 1.911	O1···O60′ 2.806	O1···H60A′–O60′ 170.5	$x, y, z − 1$
O4···H60B′ 1.977	O4···O60′ 2.900	O4···H60B′–O60′ 171.5	$−x + 2, −y, −z + 1$
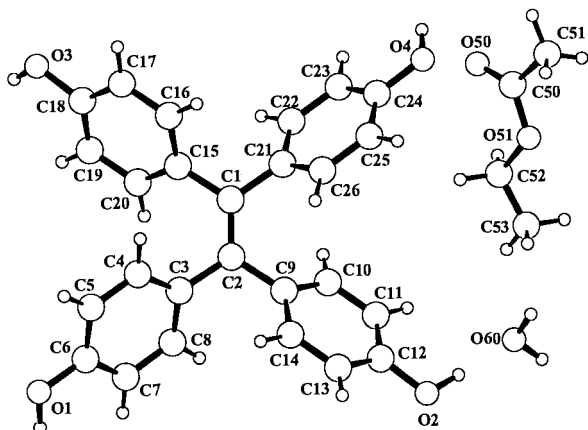
Fig. 13 Propeller-shaped, chiral conformation of **13**, as an example.

The phenyl rings of the tetraarylethylenes in the crystal structures described are arranged in a chiral propeller-shaped conformation (Chart 1, Fig. 13). The range of the twist angles are in the order of 52° and are given in Table 4. In the single crystals of **8**, **9**, **10** and **11** only one enantiomer is found. Compounds **2**, **3**, **5**, **12** and **13** crystallize as racemates.

Conclusion

We have found a unique example of the construction of a chiral inclusion crystalline lattice by a halogen–halogen interaction network among achiral host molecules. The bromo, chloro and iodo derivatives of tetrakis(p-halophenyl)ethylenes **2**, **3** and **5** show a racemic packing arrangement with stacks of crossed molecules. In the corresponding inclusion compounds with p-xylene, acetone and tetrahydrofuran layer-like structures with chiral packing arrangements are adopted. X···X contacts have important contributions to attractive interactions between the molecules in the crystal packing. The fluoro derivative **4** forms a channel-like packing with p-xylene. Hydrogen bonds have the major packing determining effects in the inclusion crystals of the phenol derivative **7**. It has been found that triorthothymotide† (TOT) forms chiral inclusion crystals with various kinds of guest molecules via van der Waals interaction, and chiral recognition between the host and guest molecules occurs, although TOT itself crystallizes in the achiral space group in the absence of guest molecules.[10a] Recently, we also found that achiral 2,3,6,7,10,11-hexahydroxytriphenylene forms chiral inclusion crystals with various kinds of guest compounds via hydrogen bonding, and the racemic guest was resolved by complexation.[13] Chiral inclusion complexation via halogen–halogen interaction in the present study provides a new strategy for designing the lattice inclusion systems.

Experimental

Instrumentation and synthesis

Melting points were recorded on a Yanaco MP-3 melting

† IUPAC name: 1,7,13-trimethyl-4,10,16-tris(1-methylethyl)-6H,12H,18H-tribenzo[b,f,j][1,5,9]trioxacyclododecine-6,12,18-trione.

Table 4 Range of the twist angles of the phenyl rings to the olefin planes

Compound	Range of twist angles/°
3	46.7–56.5
5	50.7–58.7
10	50.2–53.6
11	48.9–55.7
8	46.3–57.0
9	46.6–59.7
12	53.2–57.2
13	45.3–49.5

apparatus and are not corrected. CD spectra were recorded on a JASCO J-720 spectrophotometer in Nujol mulls. ^{1}H NMR spectra were recorded on a JEOL Lambda-300 spectrometer for solutions in CDCl₃ with tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed by a Perkin-Elmer 2400 elemental analyzer. Host compounds **2**,[3] **3**,[5] **4**,[6] **6**,[5] and **7**[7] were prepared by literature procedures. The host–guest inclusion compounds were prepared by recrystallization of host compound from the neat guest solution and the host–guest ratios were determined by thermogravimetric analysis (TG) and NMR. The chirality of the inclusion crystals was determined by CD spectra in Nujol mulls. The data are summarized in Table 1. GC analyses were performed using a GL-Sciences GC-380 system.

Preparation of tetra(p-iodophenyl)ethylene (5). A suspension of tetraphenylethylene (**1**, 8.3 g, 25 mmol), iodine (12.7 g, 50.0 mmol) and bis(trifluoroacetoxy)iodobenzene (26.2 g, 60 mmol) in CHCl₃ (30 ml) was stirred at room temperature. After the iodine color had disappeared, the reaction mixture was filtered, washed with a little hexane, dried and recrystallized from toluene to give **7** as colorless prisms (20.9 g, 76% yield). Mp: 284–287 °C; UV(CHCl₃) λ/nm (ε/dm³ mol⁻¹ cm⁻¹) 270 (162000), 320 (23800); ^{1}HNMR(CDCl₃): δ 7.46 (8H, d, $J = 8.4$ Hz, Ar), 6.70 (8H, d, $J = 8.4$ Hz, Ar); Anal: Found: C, 37.66; H, 2.08%. Calcd. for $C_{26}H_{16}I_4$: C, 37.35; H, 1.93%.

Separation of m- and p-xylene by inclusion crystallization with 2. When a neat solution of **2** (1.0 g, 1.55 mmol) and a 1:1 mixture of m- and p-xylene (2.0 g, 18.9 mmol) was kept at room temperature for 12 h, a 1:1 inclusion crystal of **2** and p-xylene was obtained as colorless prisms (0.84 g, 72% yield), which upon heating in vacuo gave p-xylene of 92% purity in 59% yield. The purity was determined by GC.

Separation of 1- and 2-methylnaphthalene by inclusion crystallization with 2. When a neat solution of **2** (1.0 g, 1.55 mmol) and a 1:1 mixture of 1- and 2-methylnaphthalene (0.88 g, 6.22 mmol) was kept at room temperature for 12 h, a 1:2 inclusion crystal of **2** and 1-methylnaphthalene was obtained as colorless prisms (0.66 g, 54% yield), which upon heating in vacuo gave 1-methylnaphthalene of 77% purity in 60% yield. The purity was determined by GC.

Separation of β- and γ-picoline by inclusion crystallization with 2. When a neat solution of **2** (1.0 g, 1.55 mmol) and a 1:1

Table 5 Crystallographic data

Compound	3	5	11	8	9	12	13
Empirical formula	$C_{26}H_{16}Cl_4$	$C_{26}H_{16}I_4$	$C_{26}H_{16}Cl_4\cdot$ C_8H_{10}	$C_{26}H_{16}Br_4\cdot$ $2C_3H_6O$	$C_{26}H_{16}Br_4\cdot$ $2C_4H_8O$	$C_{26}H_{16}F_4\cdot$ $1.5C_8H_{10}$	$C_{26}H_{20}O_4\cdot$ $C_4H_8O_2\cdot H_2O$
Molecular mass/g mol^{-1}	470.19	835.99	576.35	764.2	792.24	563.63	502.54
Space group	$Pccn$	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
$a/\text{Å}$	15.9523(4)	9.648(1)	8.635(2)	9.203(1)	9.3337(2)	9.175(5)	10.343(4)
$b/\text{Å}$	15.9655(4)	16.605(7)	14.707(4)	14.969(2)	15.1835(3)	9.522(2)	10.887(5)
$c/\text{Å}$	17.8820(3)	15.810(6)	22.89(1)	22.418(3)	21.9443(5)	17.790(4)	13.918(6)
$\alpha/°$	90	90	90	90	90	91.15(2)	103.65(4)
$\beta/°$	90	97.61(2)	90	90	90	97.65(3)	91.19(3)
$\gamma/°$	90	90	90	90	90	104.15(2)	117.64(3)
$V/\text{Å}^3$	4546.6(2)	2511(1)	2907(1)	3088.3(7)	3109.9(1)	1491.5(9)	1334(1)
Z	8	4	4	4	4	2	2
Temperature/K	113	173	173	173	208	173	223
μ/mm^{-1}	0.53	4.98	0.43	5.24	5.21	0.09	0.09
Refl. collected	77955	6370	3951	4150	7236	7597	6848
Refl. unique	7077	6027	3951	4150	7236	7170	6419
Refl. observed [$I > 2\sigma(I)$]	3607	4936	2636	2285	5278	4562	4232
Variables	335	271	425	366	361	470	451
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001	< 0.01	0.001	0.01	< 0.001
R	0.046	0.038	0.034	0.045	0.052	0.041	0.059
R_w	0.089	0.097	0.071	0.090	0.082	0.104	0.164
S(Gof)	0.95	1.06	1.04	1.0	1.04	1.01	1.06
$(\Delta\rho)_{max}/\text{e Å}^{-3}$	0.47	1.68	0.22	0.56	1.25	0.23	0.31
$(\Delta\rho)_{min}/\text{e Å}^{-3}$	-0.35	-0.19	-0.29	-0.61	-0.72	-0.22	-0.30

mixture of γ- and β-picoline (2.0 g, 21.6 mmol) was kept at room temperature for 12 h, a 2:3 inclusion crystal of **2** and β-picoline was obtained as colorless prisms (0.72 g, 60% yield), which upon heating *in vacuo* gave β-picoline of 91% purity in 59% yield. The purity was determined by GC.

X-Ray analyses. Table 5 contains the crystallographic data and details of the refinement procedure. The reflections were collected with a NONIUS KAPPA-CCD diffractometer (compound **3**) and a NONIUS CAD4 diffractometer (all other crystals) with graphite monochromatized Mo-Kα radiation. Numerical and semi-empirical absorption corrections were applied. The structures were solved by direct methods (SHELXS-97,[14] SIR92[15]). All THF guest molecules in **9** were disordered at two positions (50:50). The ethyl acetate molecule in **13** shows disorder effects at two atoms (O51 with 2 positions 75:25 and C53 with 3 positions 40:35:25). Therein the 25% positions were refined only isotropically. In general the hydrogen atoms were refined isotropically with the exception of most of the guest molecules and the host compounds in **5**, **8** and **9**, where the parameters of the hydrogens were fixed.‡ Refinement was carried out with SHELXL-97.[16]

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‡ CCDC reference number 188/262. See http://www.rsc.org/suppdata/ p2/b0/b003473h/ for crystallographic files in .cif format.

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