# Study on Crystal Engineering and Application Based on Trifluorolactates

(トリフルオロ乳酸エステルを用いた結晶工学及びその物性に関する研究)

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#### **1. General Introduction**

#### 1.1 Nanotechnology

Nanotechnology is defined as following: the technology which controls structure and function in atomic or molecular sized scale [1]. Molecular nanotechnology is different from conventional manufacturing. Several existing production processes are compared in Table 1.1 [2].

characteristic	Solution-phase chemistry (nanotechnology)	Mechanosynthetic chemistry (conventional manufacturing)
Reagent transport	Diffusion	Mechanical conveyance
Reaction site selectivity	Structural influences	Direct positional control
Reaction environment	Solution	Mechanism in vasuum
Control of reaction environment	Relatively little	Relatively great
Intermolecular reactions	Ubiquitous opportunities	Strictly controlled opportunities
Unwanted reactions	Inter- and intramolecular	Chiefly intramolecular
Sensitivity to energy differences	10 <sup>-20</sup> J is large	10 <sup>-20</sup> J is (often) sma <b>ll</b>
Typical product size	10 to 100 atoms	>10 <sup>10</sup> atoms

**Table 1.1**. Contrast between nanotechnology and microfabrication.

Conventional manufacturing relies on technologies (photolithographic pattern definition, etching, deposition and diffusion) essentially unrelated to those of molecular manufacturing. These technologies are moving in opposite directions: microfabrication attempts to make bulk-material structures smaller despite fabrication irregularities; nanotechnology attempts to make molecular structures larger without losing the atomic precision characteristic of stereo specific chemical synthesis. Making structures consisting of a few dozen precisely arranged atoms seems unachievable using microfabrication. Nanotechnology product would cause unique properties. For example, Kelly et al. prepared prototype of Brownian motor by fabricating triptycene [3]. Scheme 1.1 shows uni-directional rotation of triptycene by sequential chemical reaction. The sequential reactions convert chemical energy into uni-directional rotation of triptycene. The uni-directional rotation of triptycene would be prototype molecular weight device convert energy into work.



Scheme 1.1. Rotation powered by sequent chemical reactions.

Prototype of Brownian motor described above also shows importance of shape-control in atomic scale. Crystal consists of repeated accurate molecular arrangement. Thus, crystal engineering process enables molecular manufacturing in molecular scale. In this thesis, crystal engineering study and characteristic study are described.

#### **1.2 Crystal engineering**

Crystallographic studies have been revealed various crystal structures along with development of single crystal X-ray diffraction analysis, for example, simple NaCl structure, complex organic molecules and bioorganic molecules. Until now, crystallographic studies have revealed not only crystal structures but also crystallization motif. Similar patterns such as hydrogen bonding exist in crystal structures (Figure 1.1, [4]). On the other hand, Maddox described that "One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition" [5]. In fact, predicting crystal structure from molecular shape is tough work. This is because there are a large number of candidate structures in crystallization process of even simple molecules [6].



Figure 1.1. Representative supramolecular motifs.

In chapter 2, crystal structures of trifluorolactates are described. Trifluorolactates aligned molecules along with 1D hydrogen-bonding chain in their crystals [7]. Therefore, crystallization rule of trifluorolactates was so simplified that systematic understanding of the crystal structure became possible.

#### 1.3 Properties of nano-sized material

Until now, large numbers of characteristic study on nano-sized materials have been reported [8]. Here, a few examples are cited.

#### Adsorption materials

Microporous materials ( $\omega < 2$  nm) are widely used as adsorption material. Micropores ( $\omega < 2$  nm) would be functioned as strong adsorption site by accumulating tunnel wall potentials (Figure 1.2, [9]). Microporous materials would adsorb various gases such as hydrogen gas [10]. At the present, large numbers of gas adsorption materials have been developed. In particular, hydrogen gas storage material has been required for realization of hydrogen economy.



Figure 1.2. Potential energy in slit-shaped micropores.

#### Active transportation

Fluctuation promoted by chemical reaction of asymmetric structure such as ion pump causes effective uni-directional transportation (Figure 1.3, [11]). In the case of ion pump, fluctuation of asymmetric structure is promoted by the energy of ATP hydrolysis. Fluctuation of asymmetric structure enables rectification from random move. As shown in table 1.1, small energy would enable to affect nanometer-sized materials. Therefore, nanometer-sized asymmetric structures are expected to be effective molecular rectification device.



**Figure 1.3**. A chemically driven molecular rectification device. Charge fluctuations caused by chemical reaction would drive net motion even when the reaction is at equilibrium.

These cited examples showed that nanometer-sized materials would show various properties based on their structures. Therefore, crystal structure control would be an important item for property control. In chapter 3, 4 and Appendix, studies on characterization of trifluorolactate crystals are described.

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#### 2. The 2D Crystal Engineering

#### 2.1 Introduction

A supramolecule consists of assembled molecules. And supramolecules show various functions caused by molecular assembly, for example, molecular machines [1], drug delivery systems [2] and self-healing materials [3]. Crystal consists from repeated molecular arrangement can be regarded as a kind of supramolecule. Crystals are expected to have characteristic properties based on the repeated structure [4]. Thus, controlling crystal structure by molecular design would be a key technology for supramolecular chemistry.

Crystal structure is constructed by various intermolecular interactions. Crystals constructed by relatively strong interactions such as metal organic frameworks would be able to modify their structures by molecular design [5]. However, their crystal component would be limited to simple structures. Besides, complex organic molecules construct crystal structures by relatively weak interaction such as dispersion attraction and/or  $\pi$ - $\pi$  attraction. These relatively weak interactions would generate various candidates for their crystal structures. Thus, prediction of crystal structures from single molecular structure is difficult even in the case of simple molecule [6]. These difficulties of prediction of crystal structure from the structure of molecule are caused by 3D anisotropic interactions of organic molecules in crystallization process.

As described above, 3D crystal engineering is hard to predict the crystal structure because of large number of candidate for the structure. On the other hand, crystal engineering would be regarded as 2D tiling by packing of 1D aligned supramolecular structure. The 2D crystal engineering would be able to predict crystal structure by molecular design because 2D tiling would be less number of crystallization patterns than 3D crystal engineering. In order to study 2D crystal engineering, 1D supramolecular motif would be needed.

Katagiri et al. have reported crystal structures of trifluorolactates. The trifluorolactate aligned molecule into 1D ribbon type supramolecular structure along with the hydrogen-bonding chain [7]. Thus, trifluorolactates would realize 2D crystal engineering. Until now, we have reported highly symmetric conformation of trifluorolactates [8]. Here I show 2D crystal engineering of trifluorolactates including asymmetric conformation.

#### 2.1.1 Hydrogen-bonding system

The distance parameters and structures for the intermolecular hydrogen bonds were summarized in Table 2.1 and Figure 2.1 respectively. The distance parameters were similar to each other. Type I showed typical homochiral hydrogen-bonding chain of trifluorolactates. Type I hydrogen-bonding chain could be seen the most frequently regardless of molecular structure. Type II was observed in ribbon type supramolecular structure. In Type II, one of two trifluorolactates of the molecule formed Type I hydrogen-bonding chain, and two other trifluorolactate made hydrogen-bondings toward neighboring Type I hydrogen-bonding chain. Thus, Type II could regard to be consisted of type I and additional hydrogen-bondings. Type III was polymorph of meso double-headed trifluorolactates. Most meso double-headed trifluorolactates formed homochiral hydrogen-bonding chain (Type I hydrogen bonding chain). While in case of Type III, (S)-trifluorolactate moiety interacted with (R)-trifluorolactate to form a heterochiral hydrogen-bonding chain. The hydrogen-bonding distances of Type III were similar to that of Type I homochiral hydrogen-bonding. A necessary difference between the two hydrogen-bonding chains was the orientation of the CF<sub>3</sub> groups: the homochiral (Type I) and heterochiral (Type III) hydrogen-bonding chains have antiparallel and parallel orientation of the CF<sub>3</sub> groups, respectively. Type IV was observed in compound **7**. Although the structure of the Type IV was similar to that of the Type III, Type IV was consisted of homochiral hydrogen-bonding chain. In case of Type V, although one of two trifluorolactate moieties of the molecule formed a 1D chain, another moiety had long HO…OH distance (5.3 Å) so as to form only a one-by-one HO…O=C hydrogen bond [9].

type	inter HOOH	inter HOO=C	iner CHO=C	intra HOO=C	ex inter	ex inter
· · · · · · · · · · · · · · · · · · ·	2.00 + 0.12	2.02 + 0.15	2.50 . 0.20	0.65 + 0.04		
type I aromatic $(n = 19)$	$2.89 \pm 0.12$	$2.93 \pm 0.15$	$2.50 \pm 0.38$	$2.65 \pm 0.04$		
trpe I ( $S$ , $S$ ) alkyl (n = 6)	$2.84 \pm 0.05$	$2.90 \pm 0.08$	$2.34 \pm 0.10$	$2.65 \pm 0.01$		
type I ( $R$ , $S$ ) alkyl ( $n = 6$ )	$2.82 \pm 0.06$	$2.94 \pm 0.12$	$2.32 \pm 0.05$	$2.64 \pm 0.02$		
type II (ribbon) $(n = 5)$	2.92±0.10	2.86±0.10	2.40±0.12	$2.68 \pm 0.05$	$3.04 \pm 0.26$	$3.70 \pm 0.4$
type III	2.83	2.94	2.31	2.62		
$(R, S \operatorname{CF}_3 \text{ parallel})$	2.94	2.93	2.32	2.63		
tune IV (7)	2.79	2.95	2.28	2.69		
type IV (7)	2.82	2.95	2.26	2.8		
type V ( $S S d-4$ )	5 29	2 99		2 66		

Table 2.1. Hydrogen bonding distances (Å).



Figure 2.1. Hydrogen-bonding chains of trifluorolactate.

#### 2.1.2 Hierarchic structure of trifluorolactates

Previous reported trifluorolactates containing polymethylene moiety constructed hierarchic crystal structures. At first, molecules constructed sheet type supramolecular structure by hydrogen-bonding chain. Then, supramolecular structure constructed crystal structure by sheet packing (stacking). Hierarchic crystal structures of trifluorolactates would be regarded as 2D crystal engineering based on 1D hydrogen-bonding chain. 1D hydrogen-bonding chain aligned molecules into supramolecular structure. Contribution of the supramolecular structure made the crystallization process of 3D space to simple tiling of 2D plane. Possibilities of tile packing pattern in 2D plane would be simpler than that of molecular packing pattern in 3D space. In other words, 2D crystal engineering would be easier to predict than that of 3D.



Figure 2.2. Hierarchic crystal structure of trifluorolactate.

#### 2.1.3 Symmetry in double-headed trifluorolactate crystal

Chirality and symmetry critically affected crystal structures of trifluorolactate. As described above, trifluorolactates would recognize chirality in crystallization process [10]. In most meso double-headed trifluorolactate, (S)-trifluorolactate interacted with (S)-trifluorolactate and (R)-trifluorolactate interacted with (R)-trifluorolactate to form Type I homochiral hydrogen-bonding chain (Figure 2.3).



Figure 2.3. Homochiral hydrogen-bonding chain of meso double-headed trifluorolactate.

Single molecular conformations were found also important factor of crystal structure (Figure 2.4). Double-headed trifluorolactates containing polymethylene moieties were highly symmetric single molecular conformation in their crystals [8]. They alternated cisoid-transoid conformation according to even-odd polymethylene in order to keep symmetric conformation. Homochiral double-headed trifluorolactates needed to superpose (S)-trifluorolactates by symmetric operation. Thus homochiral double-headed trifluorolactates was C<sub>2</sub> symmetric conformation. While meso double-headed trifluorolactates had mirror or inversion center in each molecule in order to superpose (S)- and (R)-trifluorolactate by mirror symmetric operation. Therefore symmetry would be also the key factor for crystal structures of double-headed trifluorolactates with aromatic moieties.



Figure 2.4. Single molecular conformations and their symmetry.

# 2.2. Preparation of crystals of homochiral trifluorolactates containing aromatic moiety 2.2.1 Synthesis of (S,S) double-headed trifluorolactates.

Double-headed trifluorolactates were synthesized from optically pure (S)-trifluorolactic acid (Scheme 2.1) with retention of configuration. Esterification of (S)-trifluorolactic acid with diols gave (S,S)-double headed trifluorolactates (2-4) (Scheme 2.3, 2.4). On the other hand, benzylic diesters (1) were synthesized by alkylation of (S)-trifluorolactic acid with corresponding benzylic dihalides. Double-headed trifluorolactates with naphthalene or biphenyl moiety (6-11) were also synthesized by alkylation of (S)-trifluorolactic acid with corresponding halides (Scheme 2.2, 2.5), because benzylic diols were polymerized under acidic conditions.

Double-headed trifluorolactates (1-11) were soluble in polar solvents such as diethyl ether or THF, and slightly soluble in non-polar solvents such as hexane or octane. Crystallization of (1-11) was performed by slow evaporation (around 1 week for evaporation of 3 ml) of solvents and solvent conditions were summarized in Table 2.2. Solvent combinations except in Table 2.2 were also examined (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, methanol, 1,4-dioxane, ethyl acetate as polar solvents, benzene toluene, *iso*-octane as non-polar solvents). At this moment, solvent conditions were limited to table 2.2 in order to obtain enough size crystal for X-ray diffraction measurements. And sometimes, preparation of single crystal was hard to reproduce even in Table 2.2 conditions. Thus crystallization process is capable of improvement. These single crystals were submitted to single-crystal X-ray diffraction analysis.



Scheme 2.1. Preparation of optically pure trifluorolactic acid..



Scheme 2.2. Double-headed trifluorolactates with aromatic moiety from benzylic dihalides 1, 5-10.



Scheme 2.3. Preparation of diols with aromatic moiety S-3, S-5 and S-6.



Scheme 2.4. Double-headed trifluorolactates with aromatic moiety from diols 2-4.



Scheme 2.5. Preparation of tetra-headed trifluorolactate 11.

entry	solvent	solvents in crystal <sup>a</sup>	supramolecular type <sup>b</sup>
1a, 1a'	diethyl ether / hexane	O, -	ribbon, ribbon
1b, 1b', 1b''	diethylether	-, -, -	sheet, sheet, sheet
1c, 1c'	diethyl ether / hexane	-,-	tube, sheet
2a	diethyl ether / o-xylene	0	sheet
2b, 2b'	diethylether	-,-	sheet, sheet
2c	diethyl ether / n-octane	0	sheet
<b>3</b> a	diethyl ether / p-xylene	0	sheet
<b>3</b> b	diethyl ether / o-xylene	-	sheet
3c	diethyl ether / hexane	-	sheet
<b>4a</b>	ethanol / n-octane	-	sheet
<b>4</b> b	diethyl ether / n-octane	-	tube
<b>4</b> c	diethyl ether / n-octane	0	ribbon
5	diethyl ether / hexane	-	sheet
6	diethyl ether / hexane	-	sheet
7	diethyl ether / hexane	-	sheet
8	diethyl ether / hexane	0	tube
9	diethyl ether / hexane	-	sheet
10	THF / <i>n</i> -octane	0	ribbon
11	ethanol / toluene	-	small tube and large tube

**Table2.2.** Crystallization conditions.(a) Including solvents were confirmed by <sup>1</sup>H NMR.(b)Polymorphs were observed in **1a**, **1b**, **1c**, and **2b**. Detail of the polymorph is described in section 2.6.

# 2.2.2 Crystal structure of trifluorolactates







**Figure 2.5**. Crystal structures of double-headed trifluorolactate 1-11 viewed along with their hydrogen-bonding chain. Carbon, oxygen, fluorine, and hydrogen atoms are shown in grey, red, green and light blue, respectively.

Crystal structures of compounds 1-11 were summarized in Figure 2.5. In several cases (1a, 2a, 2b, 3a, 3c, 4c, 8 and 10) 1D tunnel microporous structures were observed by single-crystal X-ray diffraction analysis (Figure 2.6). Proton NMR analysis of the crystals 1a, 2a, 3a, 4c, 8 and 10 suggested the inclusion of crystallization solvents in their tunnel. Release of guest solvents in 1a under an ambient temperature collapsed its crystallinity. While, guest solvents in 2a, 3a, 4c, 8 and 10 were stable at ambient temperature. These crystals kept their crystallinity for over one month.



**Figure 2.6**. Space-filling representation of tunnel microporous structures viewed along their hydrogen bonding chain. Carbon, oxygen, fluorine, and hydrogen atoms are shown in grey, red, green and white, respectively.

Double-headed trifluorolactates with aromatic moiety were also arranged by hydrogen-bonding chain. Therefore, crystal structures of (S,S) homochiral compounds **1-11** expected to be constructed by C<sub>2</sub> symmetry in the same way to double-headed trifluorolactates with polymethylene moiety. In fact, molecular conformations were asymmetric except for **3c** and **9**, although the single molecular conformations of double-headed trifluorolactates with polymethylene moieties (without aromatic moieties) were highly symmetric. The crystal structures of the double-headed trifluorolactates without aromatic moieties had been explained by single molecular conformations with symmetry as illustrated in Figure 2.4. Therefore, double-headed trifluorolactates with aromatic moiety would need additional criteria to explain their crystal structure.

#### 2.3 Crystal structures containing ribbons or tubes

Ribbon and tubular supramolecular structures were explained by C<sub>2</sub> symmetry on projected tiling plane. They were constructed by molecular pair as C<sub>2</sub> symmetric unit. Detail of supramolecular structure and asymmetry are described in below.





**Figure 2.7**. Ribbon packing viewed along their hydrogen-bonding chain. Carbon, oxygen, fluorine, and hydrogen atoms are shown in grey, red, green and light blue, respectively.

Ribbon structures were summarized in Figure 2.7. Ribbon type supramolecular structures were constructed by Type II hydrogen-bonding chain. One of two trifluorolactate of the molecule formed Type I hydrogen-bonding chain, another trifluorolactate formed hydrogen-bonding toward neighboring Type I hydrogen-bonding chain. (Figure 2.1b, 2.8d). Thus, ribbon type supramolecular structure was regarded to be constructed from one line of hydrogen bonding chain. Projection of ribbon to the tiling plane have C<sub>2</sub> rotational axis in center of the hydrogen-bonding chain (Figure 2.8c). Single molecular conformation was asymmetric conformation. Thus, each molecule would construct molecular pairs in order to be C<sub>2</sub> symmetric supramolecular unit.



**Figure 2.8**. Explanation of ribbon structure based on  $C_2$  symmetry. (a) Asymmetric single molecular conformation. (b)  $C_2$  symmetric molecular pair. (c) Successive supramolecular ribbon. (d) Schematic illustration of (c).

#### 2.3.2. Tubes

Tubular structures were summarized in Figure 2.9. Each tube was unique

supramolecular structure. Detail of structures and thermal properties are described below.



**Figure 2.9**. Tubular structure packing viewed along their hydrogen bonding chain. Carbon, oxygen, fluorine, and hydrogen atoms are shown in grey, red, green and light blue, respectively.

Figure 2.10 showed typical tubular structure (1c). Each molecule was aligned by two lines of Type I hydrogen-bonding chains (Figure 2.10a). In case of 1c tube, tubular tunnel was closed (Figure 2.10b). The two lines of hydrogen-bonding chains oriented toward the same direction (Figure 2.10c). Each molecule connected to neighboring two molecules along with the two lines of hydrogen-bonding chains (Figure 2.10d).



**Figure 2.10**. Tubular structure of **1c**. (a) Top view, (b) CPK model of (a), (c) side view, (d) illustration of simple stacked tube.

Figure 2.11 showed complex tubular structure **4b**. Each molecule was aligned by two lines of Type I hydrogen-bonding chains (Figure 2.11a), and tubular tunnel was closed (Figure 2.11b) in the same way to **1c** tube. Complex tubular structure of **4b** was caused by the half-spiral shaped conformation in its crystal. One methylene chain extended horizontally from the benzene ring with all anti-conformations in its C-C bonds. Meanwhile, another methylene chain extended vertically with two gauche-conformations in its chain. Thus, every molecule was connected to four neighboring molecules by the two lines of hydrogen-bonding chains, with two neighboring molecules on one side and two molecules on the other side (Figure 2.11c, 2.11d). A pair of molecules in a full spiral coil, in the interpenetrated by the other full spiral coil, successive fashion. In other words, the tubes in the **4b** crystal would not be constructed by a simple stacking or piling up of the molecules (Figure 2.11d, 2.15); instead, they would by woren.



**Figure 2.11**. Tubular structure of **4b**. (a) Top view, (b) CPK model of (a), (c) side view, (d) illustration of simple stacked tube.

Figure 2.12 showed microporous tubular structure of compound 8. Supramolecular structure of 8 resembled 1c in point of simple stacked tube. Each molecule was aligned by two line of hydrogen-bonding chains. And two lines of hydrogen-bonding chains aligned toward the same direction (Figure 2.12c). Each molecule connected to neighboring two molecules along with the two lines of hydrogen-bonding chains (Figure 2.12d). As shown in Figure 2.12b, there was microporous tunnel in the tube. Tunnel diameter was  $4.1 \text{ Å} \times 3.1 \text{ Å}$ . Proton NMR analysis of the crystal of compound **8** suggested the inclusion of crystallization solvents (diethyl ether and hexane) in the tunnel. Behaviors of crystallization solvents in the tunnel are described in chapter 3.



**Figure 2.12**. Tubular structure of **8**. (a) Top view, (b) CPK model of (a), (c) side view, (d) illustration of simple stacked tube.

Here, the torsion angle of biphenyl moiety of the 8 crystal was 1.07°. The biphenyl moiety was almost coplanar. In general, coplanar biphenyl conformation is unstable (Figure 2.13). Coplanar biphenyl conformation is less stable than the most stable conformation by 2.5 kcal/mol. The torsion energy of coplanar conformation was estimated to be larger than the stabilization energy of parallel offset stacking of benzene ring [11]. While, herringbone CH- $\pi$  interaction of the anisotropic rings was also observed in the tube packing. Sum of the stabilizing energy by herringbone type stacking would be larger than torsion energy by coplanar biphenyl conformation. Observation of coplanar biphenyl in crystal suggested that infinite length tubular supramolecular structure would be constructed by harmonic (or concerted) interaction to other tube.



**Figure 2.13.** Coplanar biphenyl of **8** in the crystal. (a) Single molecular conformation, (b) herringbone CH- $\pi$  interaction, (c) torsion angle and potential energy difference from the most stable conformation.

Thermal property was characterized by low angle XRD analysis under a heating condition. Figure 2.14a showed low angle XRD pattern of **4b** tube and Figure 2.14b showed low angle XRD pattern of 8 tube respectively. Both result showed a sole broad halo at  $2\theta = 19^{\circ}$  at a temperature above the melting point of the crystal. According to Bragg equation, broad halo at  $2\theta = 19^{\circ}$  corresponds d = 5 Å pitch structure in the melt. The pitch size was almost the same to the one size of the single crystal lattice which is parallel to the tube. Thus, the halo would be caused by the repeated molecular assembly structure along the tube. That is, the tubular molecular assembly structure survived, even in their melt. Furthermore, half peak width of the 4b halo  $(2\theta_{1/2} = 7.2^{\circ})$  was sharper than that of **8** halo  $(2\theta_{1/2} = 8.5^{\circ})$ . The half peak width of the halo difference could be explained by following two interpretations. (1) Relatively sharp halo of 4b suggested stronger tubular structure. An elimination of one half-spiral molecule does not lead to a scission of the woven tube (Figure 2.15). (2) Relatively broad halo of 8 consisted with unstable coplanar biphenyl conformation. The unstable energy of coplanar conformation is larger than stable energy of parallel offset stacking of benzene ring [11]. Single tube without herringbone  $CH-\pi$  packing in the melt would be unstable. Thus, low angle XRD pattern would be broad.



**Figure 2.14**. Low angle XRD patterns. (a) Double helices tubular structure of **4b**, (b) Simple stacked microporous tube of **8**.



**Figure 2.15**. Illustrated woven structure of **4b**. Removal of one molecule from the tube does not result in a complete scission of the tubular structure.

These tubes were also explained by  $C_2$  symmetry on projected tiling plane in the same way to ribbons (Figure 2.16). Tubular supramolecular structures were constructed by two lines of hydrogen bonding chains. And, the two lines of hydrogen-bonding chain aligned toward the same direction. Thus, the projection of tubes to the tiling plane had  $C_2$  rotational axis. Here, the  $C_2$  rotational axis on projected tiling plane located at the center of the tube. Single molecular conformation of tubular structure was asymmetric. Therefore, each molecule would construct tubular pairs in order to be C<sub>2</sub> symmetric unit.



**Figure 2.16**. Explanation of tubular structure based on projected  $C_2$  symmetry. (a) Asymmetric single molecular conformation. (b)  $C_2$  symmetric molecular pair. (c) Re-inset Figure 2.10c to show hydrogen-bonding chains looked toward the same direction.

These supramolecular structures implied that crystal structures of homochiral (S,S) double-headed trifluorolactates tend to construct  $C_2$  symmetric supramolecular unit on projected tiling plane. In particular, ribbon type supramolecular structures constructed incomplete hydrogen-bonding chain (bluish part in Figure 2.8d) in order to be  $C_2$  symmetric on projected tiling plane. These results implied that maintaining  $C_2$  symmetry on projected tiling plane in crystallization process, sometimes, would be prior to construct hydrogen-bonding chain in the case of (S,S)-double-headed trifluorolactates.

#### 2.3.3 Packing patterns of ribbons and tubes

Supramolecule to crystal structure step also would be explained based on C<sub>2</sub> symmetry in the same way to single molecule to supramolecule step. The directional hydrogen-bonding chains of trifluorolactates would enable to distinguish direction of supramolecular structure. Thus, packing patterns of supramolecular structures would be classified into four patterns; parallel move, up-down rotation, back-forth rotation and both up-down and back-forth rotation (Figure 2.17). Parallel move would pack supramolecules by parallel movement without any rotational operations. Up-down rotation would pack supramolecules by alternate rotation along with hydrogen-bonding chain. Back-forth rotation would pack supramolecules by alternate rotation perpendicular to the hydrogen-bonding chain. Up-down and back-forth rotation would pack supramolecules by the both of rotational operations.



Figure 2.17. Packing patterns of supramolecular structures.

Ribbon and tube packings were summarized in table 2.3 and 2.4 respectively (detail of **TFLA-2,3-naph** and **TFLA-py** are described in chapter 4 and Appendix respectively). Ribbons and tubes constructed  $C_2$  symmetric supramolecular structures on projected tiling plane regardless of single molecular symmetry. Ribbons and tubes were constructed by one or two lines of hydrogen-bonding chain with  $C_2$  symmetric molecular pair on projected tiling plane. Thus, up-down rotational operation to the ribbon or tube would generate original structure. Up-down rotation would not be able to distinguish from parallel move. Therefore, ribbon or tube would be packed by parallel move or back-forth rotation. In addition to the geometric rule, (S,S)homochiral trifluorolactate would be difficult to construct tubular supramolecular structures by alternate-directional hydrogen-bonding chain. The tube constructed by alternate-directional hydrogen-bonding chain cannot made C<sub>2</sub> symmetric supramolecular structure projection on tiling plane and repulsion of CF<sub>3</sub> would prevent the inside-oriented conformation (Figure 2.18b).

<b>Table 2.3</b> . Pa	acking pa	atterns of	ribbon	structure.
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ribbon		
	TFLA-cyc-hex	4c
Parallel move	<b>1a</b>	2,3-naph
	1a'	TFLA-py
Up-down rotation		
	TFLA- <sup><i>t</i></sup> Bu	TFLA-Et
Back-forth rotation	TFLA-Me	TFLA-PhEt
	TFLA- <sup>i</sup> Pr	
up-down and back-forth		
rotation		



 Table 2.4. Packing patterns of tubular structure.

tube	Parallel H-bond	Alternate H-bond
Parallel move	1c 8	
Up-down rotation		
Back-forth rotation	4b	
Up-down and back-forth		
rotation		



Figure 2.18. Supramolecular tube. (a) Constructed by parallel hydrogen bonding chain, (b) alternate hydrogen bonding chain.
In case of trifluorolactates containing aromatic moiety, packing pattern was affected by  $CH \cdots \pi$  interaction (Figure 2.19, 2.20). Herringbone stack was observed in parallel move packing. On the other hand, herringbone stack was not observed in back-forth rotational packing (Figure 2.20, **4b**). These packing patterns suggested that originally C<sub>2</sub> symmetric ribbon or tubular structure on projected tiling plane would be affected by even weak interaction such as  $CH \cdots \pi$  interaction.



Figure 2.19. Ribbon structure packing.



Figure 2.20. Tubular structure packing.

Hierarchic crystallization process of ribbon type or tubular supramolecular structure was summarized in Scheme 2.6. At first, C<sub>2</sub> symmetric dimer unit on projected tiling plane was formed. Next, supramolecular structure was formed by hydrogen-bonding chains. Then, supramolecular structures constructed crystal structure. And packing patterns also suggested importance of weak interaction such as  $CH - \pi$  interaction in crystallization process.



Scheme 2.6. 2D crystal engineering by ribbon type or tubular supramolecular structure.

# 2.4 Crystal structures containing sheets

# 2.4.1 Two types of sheets

Sheet type supramolecular structures were shown in Figure 2.21 and 2.22. Every molecule in sheet was aligned by two lines of hydrogen-bonding chains. There were two kinds of sheet type supramolecular structures. In type A sheet, two lines of Type I hydrogen-bonding chains surrounding one molecule oriented toward the same direction (Figure 2.23a). On the other hand, two lines of Type I hydrogen-bonding chains of type B sheet oriented toward the opposite direction each other (Figure 2.23c).



**Figure 2.21**. Type A sheet packing viewed along their hydrogen bonding chain. Carbon, oxygen, fluorine, and hydrogen atoms are shown in grey, red, green and light blue, respectively.



**Figure 2.22**. Type B sheet packing viewed along their hydrogen bonding chain. Carbon, oxygen, fluorine, and hydrogen atoms are shown in grey, red, green and light blue, respectively.



**Figure 2.23**. Two types of sheet structure. (a) and (b) shows type A sheet, (c) and (d) shows type B sheet.

#### 2.4.2 Sheets by Type IV hydrogen-bonding chain

Exceptional sheet type supramolecular structure was also confirmed. Figure 2.24 showed sheet structures by irregular Type IV hydrogen-bonding chain. In general,  $CF_3$  groups in hydrogen-bonding chain locate opposite side each other in order to avoid electrostatic repulsion. In case of (7),  $CF_3$  groups located the same side along the hydrogen-bonding chain. The crystal structure would not be explained based on the above described  $C_2$  symmetry on projected tiling plane. At the present, reason for irregular hydrogen-bonding chain is unclear. However the irregular hydrogen-bonding chain is unclear.



**Figure 2.24**. Sheet structure **7** by type IV hydrogen bonding chain. (a) Viewed along hydrogen bonding chain. (b) Re-insert Figure 2.1e.

#### 2.4.3 Packing patterns of sheets

Sheet type supramolecular structures were distinguished into two kinds of sheets by combination of directional hydrogen-bonding chain. Table 2.5 summarized patterns of sheet packings. Type A sheet consisted of uni-directional hydrogen-bonding chains. Type A sheet would be able to distinguish back and forth of the supramolecular structure. On the other hand, Type B sheets contained alternate directional hydrogen-bonding chains. Thus, the Type B sheets would not be able to distinguish back and forth. That is, the back-forth rotation cannot exist in type B sheets.

**Table 2.5**. Packing patterns of sheet structure. Parallel H-bond corresponds to type A sheet and alternate H-bond corresponds to type B sheet.

shaat	Type A		Type B	
Sileet	(Parallel H- bond)		(Alternate H-bond)	
	9	( <i>S</i> , <i>S</i> ) <b>d-7</b>	2a	( <i>S</i> , <i>S</i> ) <b>d-8</b>
Parallel move	( <i>S</i> , <i>S</i> ) <b>d-4</b>	( <i>S</i> , <i>S</i> ) <b>d-9</b>	3c	( <i>S</i> , <i>S</i> ) <b>d-10</b>
	( <i>S</i> , <i>S</i> ) <b>d-5</b>		( <i>S</i> , <i>S</i> ) <b>d-6</b>	
	2b	4a	1b	2c
Up-down rotation	<b>3</b> a		1c'	5
	3b		2b'	6
Back-forth rotation	1b'	1b"		
Up-down and back-forth		_		
rotation				



(S,S)-Double-headed trifluorolactates without aromatic moiety were all "parallel move" type stacks of supramolecular structures. And those in parallel move cases in Table 2.5, supramolecular structures had no herringbone stacking of the aromatic rings (Figure 2.25).



Figure 2.25. Sheet packing by parallel move.

Up-down rotation packing was observed in containing aromatic moiety compounds. Conformational asymmetric sheet constructed C<sub>2</sub> symmetric sheet pair. Then, the C<sub>2</sub> symmetric sheet pair constructed crystal structure. In most of up-down rotation packing, herringbone stacking was observed (Figure 2.26). Therefore,  $CH \cdots \pi$ interaction would cause C<sub>2</sub> symmetric sheet pair by herringbone stacking.





Figure 2.26. Sheet packing by up-down rotation.

Back-forth rotation packing was observed in **1b'** and **1b"**. In this case, crystal structures were constructed by conformational asymmetric sheet. C<sub>2</sub> symmetry was not existed between sheet structures at all. And herringbone stacking was not observed (Figure 2.27).



Figure 2.27. Supramolecular sheet packing by back-forth rotation.

Scheme 2.7 summarized hierarchic crystallization process of sheet type supramolecular structure. Above described sheet packing suggested that crystal structure was constructed by sheet type  $C_2$  symmetric supramolecular unit. In general, crystal structure is constructed by repeated molecular arrangement with minimum void or gap. Highly symmetric supramolecular sheet would enable effective packing. In particular,  $CH \cdots \pi$  interaction would contribute to  $C_2$  symmetric sheet pair by combination of conformational asymmetric sheet.



Scheme 2.7. 2D crystal engineering by sheet structures.

# 2.5 Crystal structures of multi-headed trifluorolactates

As shown in previous section, crystal structure as well as supramolecular structures of double-headed trifluorolactates could be explained by the  $C_2$  symmetry on projected to the tiling plane. Next, crystal structures of more complex compounds such as multi-headed trifluorolactates was investigated in order to verify 2D crystal engineering process based on  $C_2$  symmetry on projected tiling plane.

## 2.5.1. Triple-headed trifluorolactate

Figure 2.28 showed crystal structure of triple-headed trifluorolactate 10 and its packing. Tunnel micropores (5 Å  $\times$  7 Å) were observed by single-crystal X-ray diffraction (Figure 2.28c). Proton NMR analysis of the crystals suggested the inclusion of crystallization solvents (THF-hexane) in their tunnel. Supramolecular structure of 10 was categorized into ribbon structure. Two trifluorolactates formed Type II hydrogen-bonding chain. Thus, one trifluorolactate formed hydrogen bonding chain, one trifluorolactate looked toward neighboring hydrogen bonding chain, and remained trifluorolactate formed no hydrogen bonding (Figure 2.28b). Except for 10, trifluorolactates formed some hydrogen bonding in their crystals. Trifluorolactate 10 which formed no hydrogen bonding suggested that maintaining C<sub>2</sub> symmetric unit on projected tiling plane priors to forming hydrogen bonding.



Figure 2.28. Crystal structure of triple-headed trifluorolactate 10. (a) Single molecular conformation, (b) packing pattern, (c) CPK model.

#### 2.5.2 Tetra-headed trifluorolactate (Co-work with Mr. Daisuke Mori)

Figure 2.29 showed crystal structure of tetra-headed trifluorolactate **11** and its packing pattern of biphenyl moieties. Single molecular structure showed that three trifluorolactates toward the same direction and another trifluorolactate toward the opposite direction. Each molecule was aligned by four lines of Type I hydrogen-bonding chains. Packing structure of **11** was complex block like one. In this case, supramolecular structure corresponded to crystal structure. Each biphenyl moiety was separated by trifluorolactate moiety. Thus, herringbone stack was not observed (Figure 2.29b). Packing structure was consisted of small tubular structures by two molecules and large tubular structures by six molecules. Each large tubular structure was constructed by two small tubular structures with alternate hydrogen-bonding chain (Figure 2.30b). Crystal structure of **11** would be explained by C<sub>2</sub> symmetry on projected tiling plane because the crystal structure was consisted of tubular supramolecular structure.



**Figure 2.29**. Crystal structure of tetra-headed trifluorolactate **11**. (a) Re-inset Figure 2.5, (b) packing pattern of biphenyl moieties.

Figure 2.30 showed plausible crystallization process. At first, small tubular

supramolecular structure was constructed by two lines of hydrogen-bonding chains (Figure 2.30a). Relation of each small tube was parallel move. Next, large tubular supramolecular structure was constructed by additional four lines of alternate directional hydrogen-bonding chains (Figure 2.30b). The large tube itself had C<sub>2</sub> symmetric axis on projected tiling plane in center of the large tube. While alternate directional hydrogen-bonding chains invert neighboring large tubes (Figure 2.30c). Relation of each large tube was back-forth rotational packing. Therefore whole structure of **11** was consisted of small tubular supramolecular structure and large tubular supramolecular structure by back-forth rotational packing (Figure 2.30d).



**Figure 2.30**. Plausible crystallization process of tetra-headed trifluorolactate **11**. (a) Small tube painted by blue, (b) large tube painted by pale blue, (c) back-forth rotated tube painted by reddish color, (d) painted whole structure.

Crystal structure of tetra-headed trifluorolactate **11** could be explained by C<sub>2</sub> symmetry on projected tiling plane. Crystal structure based on C<sub>2</sub> symmetry on projected tiling plane also suggested crystallization process from single molecule to crystal structure.

#### 2.6 Polymorph structure of trifluorolactate

Polymorphs were observed in some compounds (1a, 1b, 1c and 2b, Figure 2.31, 2.32). There were two types of polymorphs. These polymorphs had different origins each other (Table 2.6). In case of other compounds, polymorph has not yet been formed. Table 2.6. Two kinds of polymorph.

polymorph type	type $\alpha$	type $\beta$
supramolecular structure	different	same
reversible change	no	yes

#### 2.6.1 Type $\alpha$ polymorph

In case of type α polymorph, except for **1a**, each compound was aligned by different orientation of hydrogen-bonding chains (toward the same direction or opposite direction). Crystals of **1a** constructed ribbon type supramolecular structure by Type II hydrogen-bonding chain regardless of crystallization temperature. Actually, single molecular conformation (cisoid and transoid of two trifluoromethyl group) was obviously different. Crystallized at 283 K, **1b** constructed type II sheet, and crystallized at 308 K, **1b'** constructed type I sheet respectively. Orientation of hydrogen-bonding chain was described in section 2.4.1 (Figure 2.23). Crystals of **1c** constructed different types of supramolecular structure also responded to the crystallization temperature. Crystallized at 283 K, **1c** constructed tubular structure, and crystallized at 308 K, **1c'**  constructed type II sheet. Crystals of **2b** constructed sheet type supramolecular structure similarly to **1b**. Crystallized at 283 K, **2b** constructed type I sheet, and crystallized at 308 K, **2b'** constructed type II sheet respectively. These results indicated that there is different type of hydrogen-bonding chains in type  $\alpha$  polymorph. In other words, type  $\alpha$  polymorph caused different types of supramolecular structure by different arrangement of the hydrogen-bonding chains. Except for **1c**, kind of supramolecular structure was the same each other. The same type supramolecular structure indicated that entropy difference between two structures ( $\Delta S^{\circ}$ ) was not critically affected in the course of crystallization process. In fact, lattice volumes per molecule (V/Z) were almost the same value each other (solvent containing **1a** was larger than without solvent **1a'**). At the present, I considered crystallization temperature would affect supramolecular structure kinetically ( $\Delta G^{\sharp} = \Delta H^{\sharp} \cdot T\Delta S^{\sharp}$ ).



**Figure 2.31**. Type  $\alpha$  polymorphs observed in **1a**, **1b**, **1c** and **2b**. Carbon, oxygen, fluorine, and hydrogen atoms are shown in grey, red, green and light blue, respectively.

#### 2.6.2 Type β polymorph

Crystal structure of **1b**' showed another type  $\beta$  polymorph. In single crystal X-ray diffraction analysis of 1b', diffraction spot changed under cryogenic conditions. Therefore, X-ray diffraction was performed at ambient temperature (283 K) and low temperature (150 K). In result, **1b'** crystal changed crystal structure into **1b"** at low temperature. Both of them have supramolecular structure with the same directional arrangements of the hydrogen-bonding chain (type A sheet, Figure 2.32). Figure 2.33 showed relation between temperature and crystal lattice size. Crystal lattice of 1b' was changed into 1b" between 180K and 170 K in cryogenic process. On the other hand, crystal lattice of 1b" was changed into 1b' between 220 K and 230 K in warming process. These results showed that type  $\beta$  polymorph between **1b**' and **1b**'' was caused by sheet sliding under the cryogenic condition. And the sheet sliding was reversible Comparing lattice volume per molecule, 1b" (low process (Figure 2.33, 34). temperature) was smaller than that of 1b' (high temperature). Volume is in proportion to entropy. The volume difference indicated that entropy ( $\Delta S^{\circ}$ ) of **1b**" was smaller than that of **1b**'. The temperature-responding reversible lattice change implied that type  $\beta$ polymorph was thermodynamic process ( $\Delta G^{\circ} = \Delta H^{\circ} \cdot T \Delta S^{\circ}$ ).



Figure 2.32. Hydrogen bonding chains of 1b' crystal in type  $\beta$  polymorph.



Figure 2.33. Relation between temperature and crystal lattice size in type  $\beta$  polymorph.



Figure 2.34. Reversible supramolecular sheet sliding by type  $\beta$  polymorph.

Type  $\alpha$  polymorph was caused by different directional arrangement of hydrogen-bonding chain, which would be constructed at construction of supramolecular step. While, type  $\beta$  polymorph was caused by the different packing pattern of supramolecular to crystal. These polymorphs were consistent with the hierarchic crystal structure of trifluorolactate. Trifluorolactate crystals could have chance to change their structures at both steps.

#### 2.7 Conclusion

Crystal structures of homochiral (S,S) double-headed trifluorolactates showed systematic 2D crystal engineering process based on  $C_2$  symmetry on projected tiling plane. Each molecule constructed supramolecular structure by 1D hydrogen-bonding chain. Then, supramolecular structure constructed crystal structure by dispersion attraction packing. The 1D hydrogen-bonding chain of trifluorolactate enabled 2D crystal engineering. The 2D crystal engineering would potentially make 3D crystallization into simple 2D tiling. In other words, 2D crystal engineering would design crystal structure by molecular design.

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#### **Experimental section**

#### 1. General Methods

- NMR: <sup>1</sup>H (300 MHz) and <sup>19</sup>F NMR (282 MHz) spectra were recorded on a Varian MERCURY 300 instrument. <sup>1</sup>H NMR (300 MHz) spectra were recorded by Varian GEMINI 2000 instrument. <sup>13</sup>C (50 MHz) NMR spectra were recorded by Varian GEMINI 200 instrument. Chemical shifts were determined with non-deuterated residual CHCl<sub>3</sub> (δ 7.26) as an internal standard for <sup>1</sup>H NMR, CDCl<sub>3</sub> (δ 77.0) as an internal standard for <sup>13</sup>C NMR and C<sub>6</sub>F<sub>6</sub> (δ 0.00) as a standard for <sup>19</sup>F NMR.
- IR: IR spectra were recorded on a Hitachi Model 270-40 Infrared Spectrophotometer.MS: GC/MS analyses were carried out on a Shimadzu GCMS-QP5050A.
- **Elemental Analysis**: Elemental analyses were performed on a Perkin Elmer series II CHNS/O Analyzer 2400.
- Single crystal X-ray Diffraction: Single crystal X-ray diffraction was performed on Rigaku R-AXIS IV and Rigaku VariMax + Saturn724 (3b, 4b). X-ray data were collected using a Rigaku IP detector (R-AXIS IV) and Rigaku CCD detector (Saturn 724). Mo-Ka radiation was used. X-ray diffraction analysis was performed by Dr. Kimiko Hasegawa, Dr. Mikio Yamasaki (3b, 4b) and Dr. Hiroyasu Sato (11), Rigaku Corporation.
- **DSC-XRD**: DSC-XRD measurement was performed on Rigaku RINT-TTR III, XRD-DSC with D/teXUltra by Dr Atsushi Ohbuchi (4b) and Dr. Yukiko Namatame (8), Rigaku Corporation.

#### 2. Materials

#### Solvents:

THF : Wako pure Chemicals. THF was distilled from sodium-benzophenone ketyl prior to use.

Toluene : Nacalai Tesque. Toluene was used without further purification.

Diglyme : Wako pure chemicals. Diglyme was distilled from sodium-benzo-

phenone ketyl prior to use.

Diethyl ether : Merck. Diethyl ether was distilled from sodium-benzophenone ketyl prior to use.

*tert*-Butyl methyl ether : Wako pure Chemicals. *tert*-Butyl methyl ether was used without further purification.

*n*-Octane : Nacalai Tesque. *n*-Octane was used without further purification.

*n*-Hexane : Daishin chemicals. *n*-Hexane was distilled from conc. H<sub>2</sub>SO<sub>4</sub> (95%).

2-Propanol : Nacalai Tesque. 2-Propanol was used without further purification.

Chloroform (CHCl<sub>3</sub>) : Nacalai Tesque. CHCl<sub>3</sub> was used without further

purification.

Benzene : Nacalai Tesque. Benzene was used without further purification.

# Reagents

All reagents were purchased from following suppliers and used without further purification.

Boron trifluoride diethyl etherate (BF <sub>3</sub> OEt <sub>2</sub> ) :	Nacalai Tesque.
Sodium borohydride (NaBH4) :	Nacalai Tesque.
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> ) 35% :	Kanto Chemicals.
Sodium hydroxide (NaOH) :	Nacalai Tesque.
Allyl bromide :	TCI.

Magnesium turnings (Mg) :	Nacalai Tesque.	
α,α'-dichloro <i>-m</i> -xylene :	TCI.	
Sulfuric acid (96%) :	Kanto Chemicals.	
Hydrochloric acid (35%) :	Kanto Chemicals.	
Acetic acid (99%):	Nacalai Tesque.	
Nitric acid (60%) :	Kanto Chemicals.	
(S,S)-(-)- $N$ - $N$ -Bis $(3,5$ -di- $tert$ -butylsalicylidene)-1,2-cyclohexanediaminocobalt(II)		
(salen-Co):	Aldrich.	
2-Thionaphthol:	Kanto Chemicals.	
Triethylamine (Et <sub>3</sub> N) :	Nacalai Tesque.	
Sodium hydrogen carbonate (NaHCO <sub>3</sub> ) :	Kanto Chemicals.	
Magnesium sulfate anhydrous (MgSO <sub>4</sub> ) :	Nacalai Tesque.	
(S)-3,3,3-Trifluoropropene oxide (TFPO) :	gift from Japan Energy Co.	

# Others

Silica (Silica gel 60 for column chromatography) :	Merck.
CDCl <sub>3</sub> (for all NMR analysis) :	Acros Organics.

# 3. Synthesis of Double Headed Trifluorolactate

**Optically pure (S)-3,3,3-trifluoropropene oxide** [s-1].



A solution of the salen-Co catalyst (0.381 g, 0.63 mmol, 0.25 mol%) in toluene (5 ml) was treated with 0.3 ml AcOH for 1 h. Then, a residual solid which obtained after evaporation was allowed to react with (S)-3,3,3-trifluoropropene oxide (25.8 ml, 300 mmol with ca. 75% ee). The solution was cooled to 0 °C and treated with H<sub>2</sub>O (0.68 ml, 37.5 mmol, 11 mol%). The reaction mixture was warmed up to room temperature and stirred for more 16 h. Then, (S)-3,3,3-trifluoropropene oxide was isolated by vacuum distillation (30 mmHg) from the reaction mixture into vessel cooled by liq. N<sub>2</sub>. Another optical resolution procedure gave optically pure (>99.5% ee) (S)-3,3,3-Trifluoropropene oxide was determined by chiral HPLC analysis with Daicel Chiralcel<sup>®</sup> OD-H column (eluent: *n*-hexane : 2-propanol (20 : 1), flow rate: 1 ml / min, retention time: t<sub>R</sub>(minor) = 11.9 min, ts(major) = 14.2 min) of its 2-napthylesulfide derivative, which obtained by ring opening reaction with 2-napthalenethiol with 1 eq. Et<sub>3</sub>N in THF.

#### (S)-3,3,3-Trifluorolactic acid [s-2]

$$F_{3}C$$
  $\xrightarrow{O}$   $\xrightarrow{HNO_{3}, Cu (cat)}$   $F_{3}C$   $\xrightarrow{OH}$   $\xrightarrow{OH}$   $OH$ 

In a two-necked round-bottomed flask equipped with a reflux condenser and an addition funnel, metal Cu powder (0.145 g, 2.2 mmol, 0.01 eq.) was dissolved in 60%

nitric acid (d 1.38, 68 ml, 900 mmol, 4.5 eq.) and the solution was stirred. (S)-3,3,3-Trifluoropropene oxide (17.3 ml, 200 mmol, >99.5% ee) was slowly added to the green colored solution at 0 °C. The reaction mixture was slowly warmed up to 80 °C. Soon the first vigorous generation of NO<sub>2</sub> started. The reaction mixture was vigorously stirred at 80 °C for 12 h until stopping of NO<sub>2</sub> generation, then cooled to room temperature. NO<sub>2</sub> was removed to external in fume hood. Saturated Na<sub>2</sub>CO<sub>3</sub> solution was added to the cooled solution to make the solution basic, then the reaction mixture was stirred for at least 2 h to completely decompose any possible nitric ester. Just prior to the work up, one should ascertain that the solution is basic. The solution was again acidified with an appropriate amount of concentrated HCl to make the solution to be pH 2. The acidic solution was repeatedly extracted with ether  $(6 \times 50 \text{ ml})$ , with keeping pH 2. The combined organic phase was dried by anhydrous sodium sulfate, filtered, and concentrated. If the residue was not solid, azeotropic dehydration with benzene was performed using Dean-Stark apparatus. The resulted solid was recrystallized from  $CHCl_3$  solution at -18 °C. (S)-3,3,3-Trifluorolactic acid was isolated in 53% yield as a hydroscopic solid. The filtrate was concentrated, and the residue was distilled under a reduced pressure (110 °C / 20 mmHg), to give (S)-3,3,3-trifluorolactic acid in 31% yield.

**Caution**! The reaction is an exothermic oxidation reaction. Thus, all **safety precautions** should be taken. Do not carry out these reactions on a large scale (<200 mmol scale). Also, precautions against the generation of vigorous amounts of obnoxious fumes (NO<sub>2</sub>), which are generated during the oxidation, should be taken.

# General procedure for the preparation of the double-headed trifluorolactates with benzene moiety (1)



CsF (5.75 g, 37.9 mmol) and corresponding  $\alpha,\alpha$ -dibromoxylene (2.36 g, 8.94 mmol) was dissolved in DMF (9 ml). A solution of (*S*)-trifluorolactic acid (3.91 g, 27.2 mmol) in DMSO (9 ml) was then added slowly. The reaction mixture was stirred for 24 h at ambient temperature. Water was added to the mixture then, extracted with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude products were purified by silica gel column chromatography (hexane : ether = 1: 1) and distilled under reduced pressure (1 mmHg) at 180 °C to give target compounds.

#### benzene-1,2-(S,S)-bis(methyl-3,3,3-trifluorolactate) (1a)

84% yield. Colorless platelet crystal. Mp 94 -95 °C. IR(KBr): 3460, 1750, 1320, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.44 (s, 4H), 5.44 (s, 4H), 4.52 (quint, *J* = 7.5 Hz, 2H), 3.40 (d, *J* = 7.8 Hz, 2OH); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.8 (d, *J* = 4.5 Hz, 6F); <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ167.1, 132.7, 130.5, 130.3, 129.7, 124.9, 119.3, 113.6, 69.9 (q, *J* = 33.0 Hz), 66.3; MS: m/z 246 (30), 147 (6), 120 (100), 104 (16), 91 (63), 77 (26). Anal. Calcd for C<sub>14</sub>H<sub>12</sub>F<sub>6</sub>O<sub>6</sub>: C 43.08, H 3.08, Found: C 43.08, H 3.26.

#### benzene-1,3-(S,S)-bis(methyl-3,3,3-trifluorolactate) (1b)

85% yield. Colorless platelet crystal. Mp 84 - 85 °C. IR(KBr): 3440, 1760, 1220, 1130

cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.41 – 7.36 (m, 4H), 5.34 (s, 4H), 4.53 (quint, *J* = 6.9 Hz, 2H), 3.40 (d, *J* = 7.8 Hz, 2OH); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.8 (d, *J* = 7.1 Hz, 6F); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 167.4, 134.7, 129.3, 128.8, 128.0, 127.8, 124.0, 120.3, 116.5, 69.9 (q, *J* = 33.3 Hz), 68.6; MS: m/z 246 (73), 120 (100), 104 (25), 91 (23), 77 (14). Anal. Calcd for C<sub>18</sub>H<sub>20</sub>F<sub>6</sub>O<sub>6</sub>: C 43.08, H 3.08, Found: C 43.27, H 3.10.

#### benzene-1,4-(S,S)-bis(methyl-3,3,3-trifluorolactate) (1c)

83% yield. Colorless platelet crystal. Mp 91 - 92 °C. IR(KBr): 3410, 1740, 1580, 1380, 1270, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.39 (s, 4H), 5.34 (s, 4H), 4.47 (quint, J= 6.9 Hz, 2H), 3.41 (d, J= 8.1 Hz, 2OH); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.8 (d, J= 7.1 Hz, 6F); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 167.3 (d, J = 2.26 Hz), 134.7, 128.7, 127.8, 124.0, 127.8, 120.3, 116.5, 69.9 (q, J = 33.1 Hz), 68.5; MS: m/z 246 (100), 120 (70), 104 (28), 91 (51), 77 (33); Anal. Calcd for C<sub>18</sub>H<sub>20</sub>F<sub>6</sub>O<sub>6</sub>: C 43.08, H 3.08, Found: C 43.21, H 3.06.

#### naphthalene-1,4(S,S)-bis(methyl-3,3,3-trifluorolactate) (6)

53% yield. Colorless platelet crystal. Mp 156 °C. IR(KBr): 3440, 1740, 1450, 1380, 1320, 1240, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ8.02 (d, J = 7.2 Hz, 3H), 7.76-7.65 (m, 3H), 5.79 (s, 4H), 4.58-4.48 (m, 2H), 3.38 (d, J = 8.0 Hz, 2OH); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.1 (d, J = 7.5 Hz, 6F).

#### naphthalene-2,7(S,S)-bis(methyl-3,3,3-trifluorolactate) (7)

91% yield. Colorless platelet crystal. Mp 103 °C. IR(KBr): 3400, 1750, 1350, 1310, 1280,
1210, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.91-7.85 (m, 4H), 7.49 (d, J = 8.2 Hz, 2H), 5.50 (s,
4H), 4.63-4.48 (m, 2H), 3.42 (d, J = 7.4 Hz, 2OH); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.2 (d, J = 7.8 Hz,

6F); Anal. Calcd for C<sub>18</sub>H<sub>14</sub>F<sub>6</sub>O<sub>6</sub>: C 49.10, H 3.20, Found: C 49.00, H 3.14.

#### biphenyl-2,2'-(*S*,*S*)-bis(methyl-3,3,3-trifluorolactate) (9)

92% yield. Colorless platelet crystal. Mp 125-126 °C. IR(KBr): 3470, 1770, 1410, 1340, 1270, 1210, 1140 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.57-7.39 (m, 6H), 7.28-7.19 (m, 2H), 5.16-4.96 (m, 4H), 4.48-4.36 (m, 2H); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.1 (d, *J* = 7.5 Hz, 6F); MS: m/z 178 (14), 164 (20), 152(9), 99 (3), 89 (15), 76 (6), 51 (6); Anal. Calcd for C<sub>20</sub>H<sub>16</sub>F<sub>6</sub>O<sub>6</sub>: C 51.51, H 3.46, Found: C 51.33, H 3.76.

#### 2,4,6-trimethylbenzene-1,3,5-(S,S,S)-tris(methyl-3,3,3-trifluorolactate) (10)

66% yield. Colorless platelet crystal. Mp 172 °C. IR(KBr): 3460, 1760, 1430, 1350, 1230, 1210, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ5.88 (d, *J* = 7.6 Hz, 2H), 5.48 (d, *J* = 13 Hz, 3H), 5.41 (d, *J* = 13 Hz, 3H), 4.82(q, *J* = 7.2 Hz, 2H), 2.43 (s, 9H); <sup>19</sup>F NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ88.3 (d, *J* = 7.8 Hz, 9F); Anal. Calcd for C<sub>21</sub>H<sub>21</sub>F<sub>9</sub>O<sub>9</sub>: C 42.87, H 3.60, Found: C 42.58, H 3.70.

Preparation and spectra data of 8 [TFLA-bis(4,4')], TFLA-2,3-naph and TFLA-py are described in chapter 3, chapter 4 and Appendix respectively.

#### General procedure for the preparation of the benzenedimethylcyanide (S-1)



KCN (7.16 g, 110 mmol) was dissolved in DMSO (70 ml) at 40 °C. A solution of

corresponding  $\alpha, \alpha$ -dibromoxylene (13.2 g, 50 mmol) in DMSO (70 ml) was then added slowly. The reaction mixture was stirred for 3 h at 40 °C, then poured into ice-water (200 ml) and extracted with Et<sub>2</sub>O. The combined organic layers were washed with brine, dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was used without further purification. In case of purification, the crude obtained was distilled under reduced pressure (5 mmHg) at 120 °C to give colorless solid.

#### 1,2-benzenedimethylcyanide (S-1a)

86% yield. Colorless block crystal. IR(KBr): 2940, 2260, 1498, 1460, 750 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ7.49 – 7.38 (m, 4H), 3.78 (s, 4H); MS: m/z 156 (31), 129 (100), 116 (25), 102 (21), 89 (15).

Referred to authentic data [s-3].

# 1,3-benzenedimethylcyanide (S-1b)

87% yield. Colorless block crystal. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 7.2 - 7.4 (m, 4H), 3.73 (s, 4H); MS: m/z 156 (26), 129 (10), 116 (100), 102 (9), 89 (14), 77 (7). Referred to authentic data [s-3].

#### 1,4-benzenedimethylcyanide (S-1c)

56% yield. Colorless block crystal. IR(KBr): 2920, 2260, 1520, 1430, 1400, 1020, 780 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ7.36 (s, 4H), 3.78 (s, 4H); MS: m/z 156 (19), 129 (2), 116 (100), 102 (4), 89 (13), 77 (6).

Referred to authentic data [s-3].

#### General procedure for the preparation of the diethylisophtalates (S-2)



A solution of corresponding S-1 (7.67 g, 49.2 mmol) in EtOH (12 ml) and concd  $H_2SO_4$  (9.61 g, 98 mmol) was stirred under reflux for 18 h. The reaction mixture was cooled in an ice bath and was diluted with  $H_2O$ . Extraction with EtOAc, washing with saturated NaHCO<sub>3</sub> aq. and brine, dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was used without further purification. In case of purification, the crude obtained was distilled under reduced pressure (5 mmHg) at 150 °C to give colorless solid S-2.

#### 1,2-diethylisophthalate (S-2a)

81% yield. Colorless block crystal. IR(KBr): 2990, 1740, 1460, 1170, 1030, 750 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 87.24 (s, 4H), 4.14 (q, *J* = 7.2 Hz, 4H), 3.59 (s, 4H), 1.25 (t, *J* = 7.2 Hz, 6H); MS: m/z 250 (3), 204 (85), 177 (49), 158 (57), 147 (30), 130 (100), 121 (37), 104 (68), 93 (43), 77 (41).

#### 1,3-diethylisophthalate (s-2b)

54% yield. Colorless block crystal. IR(KBr): 2990, 1720, 1610, 1370, 1160, 1030, 920 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ7.30 - 7.17 (m, 4H), 4.15 (q, *J* = 7.2 Hz, 4H), 3.60 (s, 4H), 1.25 (t, *J* = 7.2 Hz, 6H); MS: m/z 250 (4), 177 (49), 149 (15), 132 (19), 121 (11), 104 (58), 91 (9), 77 (15).

Referred to authentic data [s-4].

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 67.36 - 7.24 (m, 4H), 4.20 (q, 4H), 3.65 (s, 4H), 1.31 (t, 6H).

#### 1,4-diethylisophthalate (S-2c)

59% yield. Colorless block crystal. IR(KBr): 2990, 1730, 1370, 1170, 1030, 920 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ7.25 (s, 4H), 4.15 (q, *J* = 7.2 Hz, 4H), 3.59 (s, 4H), 1.25 (t, *J* = 7.2 Hz, 6H); MS: m/z 250 (25), 177 (100), 149 (9), 131 (2), 104 (69), 91 (36), 78 (10).

Referred to authentic data [s-5].

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 7.24 (s, 4H), 4.14 (q, J = 7 Hz, 4H), 3.58 (s, 4H), 1.24 (t, J = 7 Hz, 6H).

# General procedure for preparation of the benzenediethanol (S-3)



A solution of corresponding S-2 (7.60 g, 30.4 mmol) in THF (70 ml) under Ar atmosphere was added to a solution of LiAlH<sub>4</sub> (1.73 g, 45.6 mmol) in THF (70 ml) under Ar atmosphere and cooled to 0 °C. Then the solution was stirred at 0 °C to 70 °C for 5 h. The mixture was slowly poured into H<sub>2</sub>O-MeOH with efficient stirring to decompose an excess LiAlH<sub>4</sub>. The solution was filtered and concentrated under reduced pressure. The residue was dissolved in THF, filtered again and concentrated under reduced pressure. The residue was distilled under reduced pressure (1 mmHg) at 130 °C to give colorless solid S-3.

#### 1,2-benzenediethanol (S-3a)

80% yield. White powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ7.25 (s, 4H), 3.84 (q, *J* = 6.9 Hz, 4H), 2.78 (t, *J* = 6.9 Hz, 4H); MS: m/z 148 (11), 136 (48), 117 (100), 105 (77), 105 (77), 91 (76), 77 (32).

Referred to authentic data [s-6].

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 87.2 (s, 4H), 3.9 (s, 4H), 3.0 (m, 4H), 2.4 (m, 2H).

#### 1,3-benzenediethanol (S-3b)

69% yield. White powder. IR(KBr): 3410, 2960, 2860, 1490, 1170, 1050, 810 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ7.19(t, J = 6.3 Hz, 1H), 7.09 (s, 1H), 7.07 (d, J = 6.0 Hz, 2H), 4.88 (s, 2OH), 3.73 (t, J = 7.2 Hz, 4H), 2.79 (t, J = 7.2 Hz, 4H); MS: m/z 166 (7), 148 (5), 136 (30), 118 (100), 105 (22), 91 (68), 79 (30).

#### 1,4-benzenediethanol (S-3c)

85% yield. White powder. IR(KBr): 3410, 2940, 1520, 1050, 830 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>Cl): δ7.19 (s, 4H), 3.87 (t, *J* = 6.4 Hz, 4H), 2.85 (t, *J* = 6.4 Hz, 4H); MS: m/z 166 (13), 135 (50), 118 (76), 105 (100), 91 (18), 77 (15).

General procedure for the preparation of the double-headed trifluorolactates (2)



Round-bottomed flask equipped with a Dean-Stark apparatus surmounted by reflux condenser was charged with corresponding diol S-3 (3.81 g, 23 mmol), (S)-trifluorolactic acid (8.26 g, 57.3 mmol), and one drop of  $H_2SO_4$  as a catalyst in toluene (40 mm). The reaction mixture was brought to reflux with the removal of water for 15 h. The resulting mixture was cooled to ambient temperature and water was added to the mixture then, extracted with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude distilled under reduced pressure (1 mmHg) at 150 °C to give target compounds **2**.

#### benzene-1,2-(S,S)-bis(ethyl-3,3,3-trifluorolactate) (2a)

88% yield. White powder. Mp 72 - 74 °C. IR(KBr): 3460, 1750, 1420, 1240, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.24 – 7.19 (m, 4H), 4.57 – 4.46 (m, 6H), 3.35 (d, *J* = 8.0 Hz, 2OH), 3.08 (t, *J* = 7.0 Hz, 4H); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.7 (d, *J* = 7.0 Hz, 6F); <sup>13</sup>C NMR (CDCl3), δ167.4 (d, *J* = 1.86 Hz), 134.7, 130.5, 130.0, 127.5, 124.9, 119.3, 113.7, 69.9 (q, *J* = 33.0 Hz), 67.4, 31.3; MS: m/z 274 (4), 130 (100), 117 (29), 91 (35), 79 (17); Anal. Calcd for C<sub>16</sub>H<sub>16</sub>F<sub>6</sub>O<sub>6</sub>: C 45.93, H 3.83, Found: C 45.98, H 3.76.

#### benzene-1,3-(S,S)-bis(ethyl-3,3,3-trifluorolactate) (2b)

83% yield. Colorless platelet crystal. Mp 108 -109 °C. IR(KBr): 3450, 1760, 1420, 1230, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.27 (t, J= 8.1 Hz, 1H), 7.12 (s, 1H), 7.08 (d, J= 7.8 Hz, 2H), 4.62 - 4.40 (m, 6H), 3.37 (d, J= 3.4 Hz, 2OH), 3.00 (t, J= 6.9 Hz, 4H); <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ85.7 (d, J= 7.1 Hz, 6F); <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ167.2 (d, J= 1.86 Hz), 134.7, 130.5, 128.6, 124.9, 119.3, 113.7, 69.8 (q, J= 33.0 Hz), 66.8, 31.3, 29.9; MS: m/z 274 (4), 130 (100), 117 (17), 91 (24), 79 (9); Anal. Calcd for C<sub>18</sub>H<sub>20</sub>F<sub>6</sub>O<sub>6</sub>: C 45.93, H 3.83, Found: C 46.11, H 3.74.

#### benzene-1,4-(S,S)-bis(ethyl-3,3,3-trifluorolactate) (2c)

86% yield. Colorless platelet crystal. Mp 91 - 93 °C. IR(KBr): 3450, 1750, 1230, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.16 (s, 4H)、 4.60 – 4.39 (m, 6H), 3.39 (d, *J* = 7.5 Hz, 2OH), 2.99 (t, *J* = 6.9 Hz, 4H); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.7 (d, *J* = 7.1 Hz, 6F); <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ167.3, 135.2, 130.6, 129.1, 124.9, 119.3, 113.7, 69.8 (q, *J* = 32.3 Hz), 67.8, 34.4; MS: m/z 130 (100), 117 (32), 91 (29), 79 (9); Anal. Calcd for C<sub>18</sub>H<sub>20</sub>F<sub>6</sub>O<sub>6</sub>: C 45.93, H 3.83, Found: C 46.17, H 3.40

General procedure for the preparation of the diallylbenzene (S-4)



CuCN (2.69 g, 30mmol) was azeotropically dried with toluene under reduced pressure at room temperature. After addition of THF (10 ml), 1.0 M vinylmagnesium bromide solution in THF (60 ml, 60 mmol) was added at -78 °C. The reaction mixture was warmed to 0 °C and cooled to -78 °C. Corresponding  $\alpha, \alpha'$ -dibromoxylene (2.64 g, 10 mmol) in THF was added and the mixture was warmed to 0 °C, stirred for 3 h. The mixture was quenched with NH<sub>4</sub>Cl and extracted with ether. The combined organic layer was washed with brine, dried with MgSO<sub>4</sub> filtrated and concentrated. The residue was used without further purification. In case of purification, the crude product was distilled under reduced pressure (1 mmHg) at 60 °C to give **S-4**.

#### 1,2-diallylbenzene (S-4a)

69% yield. Colorless liquid. IR(neat): 2920, 1640, 1490, 1000, 750 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>Cl):

87.18 (s, 4H), 6.07 - 5.87 (ddt, J = 17.2, 10.2, 6.4 Hz, 2H), 5.05 (dq, J = 22, 1.6 Hz, 2H),
4.96 (dq, J = 9.4, 1.6 Hz, 2H), 3.41 (dt, J = 4.6, 1.6 Hz, 4H); MS: m/z 158 (5), 143 (55), 129 (100), 115 (82), 91 (31), 77 (14).

Referred to authentic data [s-7].

<sup>1</sup>H NMR (CD<sub>3</sub>Cl): δ7.15 (s, 4H), 5.94 (ddt, *J* = 16.9, 10.3, 6.3 Hz, 2H), 5.04 (dq, *J* = 10.2, 1.2 Hz, 2H), 4.98 (dq, *J* = 17.0, 1.3 Hz, 2H), 3.38 (dt, *J* = 6.3, 1.3 Hz, 4H).

# 1,3-diallylbenzene (S-4b)

76% yield. Colorless liquid. IR(neat): 2980, 1650, 1490, 1000, 910 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>Cl):
δ7.23 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.5 Hz, 2H), 7.03 (s, 1H), 6.02 - 5.94 (ddt, J = 17.0, 10.5, 6.5 Hz, 2H), 5.11 (J<sub>1</sub> = 19, 1.0 Hz, 2H), 5.07 (dq, J = 8.5, 1.0 Hz, 2H), 3.38 (d, J = 6.5 Hz, 4H); MS: m/z 158 (7), 129 (22), 117 (100), 91 (19).

# 1,4-diallylbenzene (S-4c)

57% yield. Colorless liquid. IR(neat): 2910, 1640, 1450, 980, 910 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>Cl): δ7.13 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.5 Hz, 2H), 7.03 (s, 1H), 6.07 – 5.87 (ddt, J = 16.8, 10.2, J<sub>3</sub> = 6.6 Hz, 2H), 5.10 (dq, J = 8, 1.4 Hz, 2H), 5.04 (dq, J = 13.4, 1.4 Hz, 2H), 3.37 (dt, J = 6.6, 1.4 Hz, 4H); MS: m/z 158 (57), 143 (21), 129 (36), 117 (100), 91 (21). Referred to authentic data [s-8].

<sup>1</sup>H NMR (CD<sub>3</sub>Cl): δ7.13 (s, 4H), 5.98 (ddt, *J* = 17.8, 10.1, 6.7 Hz, 2H), 5.09 (dd, *J* = 6.7, 1.3 Hz, 2H), 5.08 (dd, *J* = 17.8, 1.3 Hz, 2H), 3.37 (dd, *J* = 6.7, 1.3 Hz, 2H).

#### General procedure for the preparation of the benzenedipropanol (S-5)



BF<sub>3</sub>OEt<sub>2</sub> (1.02 g, 7.19 mmol) was slowly added to a solution of NaBH<sub>4</sub> (0.19 g, 5.03 mmol) and corresponding diallylbenzene **S-4** (1.14 g, 7.19 mmol) in diglyme (70 ml), then stirring under an Ar atmosphere and cooled to 0 °C for 2.5 h. Then the solution was stirred for further 1 h. 3 N NaOH aq. (1.5 ml) and 30% H<sub>2</sub>O<sub>2</sub> aq. (1.5 ml) was added to the mixture, then decomposed with water, and extract with ether. The combined organic layers was washed with brine, dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. The crude obtained was distilled under reduced pressure (1 mmHg / 160 °C) afforded the product **S-5**.

# 1.2-benzenedipropanol (S-5a)

91% yield. Colorless liquid. <sup>1</sup>H NMR (CD<sub>3</sub>Cl): δ7.16 (s, 4H), 3.71 (t, *J* = 7.6 Hz, 4H), 1.86 (quint, *J* = 6.4 Hz, 4H); MS: m/z 194 (3), 176 (10), 143 (19), 131 (53), 117 (59), 105 (100), 91 (55).

# 1.3-benzenedipropanol (S-5b)

82% yield. Colorless liquid. <sup>1</sup>H NMR (CD<sub>3</sub>Cl): δ7.21 (t, J = 5.4 Hz, 1H), 7.05 (s, 1H), 7.06 (d, J = 4.4 Hz, 2H), 3.68 (t, J = 6.6 Hz, 4H), 2.69 (t, J = 7.5 Hz, 4H), 1.89 (quint, J = 6.6 Hz, 4H); MS: m/z 176 (17), 143 (6), 132 (47), 117 (100), 105 (45), 91 (55).

# 1.4-benzenedipropanol (S-5c)

30% yields. <sup>1</sup>H NMR (CD<sub>3</sub>Cl): δ7.12 (s, 4H), 3.57 – 3.52 (m, 6H), 2.64 (t, J = 6.3 Hz, 4H),
1.79 (quint, J = 6.3 Hz, 4H).
Referred to authentic data [s-9].
<sup>1</sup>H NMR (CD<sub>3</sub>Cl): δ7.13 (s, 4H), 3.68 (t, J = 6.4 Hz, 4H), 2.68 (t, J = 7.6 Hz, 4H), 1.88 (m, 4H), 1.27 (br, 2OH).

#### General procedure for the preparation of the double-headed trifluorolactates (3)

Preparation method of the double-headed trifluorolactates **3** is same to **2** from benzenediethanol (**S-3**). The products were purified by silica gel column chromatography (hexane : ether = 1: 1) and distilled under reduced pressure (1 mmHg) at 180 °C to give target compounds

#### benzene-1,2-(S,S)-bis(propyl-3,3,3-trifluorolactate) (3a)

68% yield. Colorless platelet crystal. Mp 75 - 76 °C. IR(KBr): 3440, 1750, 1220, 1130
cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ7.18 - 7.14 (m, 4H), 4.53 - 4.23 (m, 6H), 3.42 (d, J = 7.6 Hz, 2OH), 2.71 (t, J = 6.8 Hz, 4H), 2.02 (quint, J = 6.2 Hz, 4H); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.7 (d, J = 7.1 Hz, 6F); <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ167.4, 138.2, 130.7, 129.3, 126.7, 125.3, 119.4, 113.8, 69.8 (q, J = 33.0 Hz), 67.0, 29.6, 28.5. Anal. Calcd for C<sub>18</sub>H<sub>20</sub>F<sub>6</sub>O<sub>6</sub>: C 48.44, H4.52, Found: C 48.48, H 4.29.

## benzene-1,3-(S,S)-bis(propyl-3,3,3-trifluorolactate) (3b)

75% yield. Colorless platelet crystal. Mp 85 - 86 °C. IR(KBr): 3450, 1760, 1230, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.24 (t, J = 8.2 Hz, 1H),7.03 (s, 1H), 6.98 (d, J = 8.2 Hz, 2H), 4.55 - 4.21 (m, 6H), 3.43 (d, J = 7.8 Hz, 2OH), 2.69 (t, J = 7.4 Hz, 4H), 2.03 (quint, J = 6.4 Hz,
4H); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.7 (d, J = 7.0 Hz, 6F); <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ167.4 (d, J = 1.96 Hz), 140.7, 130.7, 128.6 (d, J = 10.1 Hz), 126.2, 125.0, 119.4, 113.8, 69.8 (q, J = 32.9 Hz), 66.7, 31.6, 29.8; MS: m/z 302 (3), 159 (37), 143 (42), 129 (83), 117 (100), 105 (28), 91 (64), 79 (27). Anal. Calcd for C<sub>18</sub>H<sub>20</sub>F<sub>6</sub>O<sub>6</sub>: C 48.44, H4.52, Found: C 48.56, H 4.34.

# benzene-1,4-(S,S)-bis(propyl-3,3,3-trifluorolactate) (3c)

74% yield. Colorless platelet crystal. Mp 113-114 °C. IR(KBr): 3430, 1740, 1220, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.10 (s, 4H), 4.47 (quint, J = 7.5 Hz, 2H), 4.38 (dt, J = 10.8, 6.3 Hz, 2H), 3.40 (d, J = 7.5 Hz, 2OH), 2.68 (t, J = 7.5 Hz, 4H), 2.02 (quint, J = 1.8, 6.3 Hz, 4H); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.7 (d, J = 6.8 Hz, 6F); <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ167.5 (d, J = 2.32 Hz), 138.4, 128.6, 124.1, 120.4, 69.8 (q, J = 33.0 Hz), 66.8, 31.3, 29.9; MS: m/z 302 (3), 159 (37), 143 (42), 129 (83), 117 (100), 105 (28), 91 (64), 79 (27). Anal. Calcd for C<sub>18</sub>H<sub>20</sub>F<sub>6</sub>O<sub>6</sub>: C 48.44, H4.52, Found: C 48.46, H 4.37.





In a two-necked round-bottomed flask, magnesium (6.74 g, 288 mmol, 7.2 eq.) was added to  $Et_2O$  (40 ml). A solution of allyl bromide (11.6 g, 96 mmol, 2.4 eq.) in  $Et_2O$  (40 ml) was added and allylmagnesium was prepared. The reagent was placed in another flask equipped with a flask condenser by cannulation to remove magnesium residue and a solution of corresponding  $\alpha, \alpha$ '-dichloroxylene (7.0 g, 40 mmol) in  $Et_2O$  was

added. Then the reaction mixture was refluxed for 12 h. Sequent to hydrolysis with water phase was extracted with three portions of  $Et_2O$  (40 ml). The organic fractions were combined and washed with water and a saturated solution of NaHCO<sub>3</sub> until no acidic reaction was detected, dried over MgSO<sub>4</sub>, and filtered. Distillation under reduced pressure (1 mmHg / 60 °C) afforded the product **S-6**.

## 1,2-di(3-butenyl)benzene (S-6a)

86% yield. Colorless liquid. IR(neat): 3080, 2940, 1640, 1450, 1420, 990, 920, 750 cm<sup>-1</sup>;
<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ7.15 (s, 4H), 6.00 – 5.80 (ddt, J = 17, 10, 6.4 Hz, 2H), 5.05 (dq, J = 18, 1.4 Hz, 2H), 5.00 (dq, J = 9.8, 1.2 Hz, 2H), 2.72 (t, J = 7.6 Hz, 4H), 2.35 (dqt, J = 7.2, 1.2 Hz, 4H); MS: m/z 186 (8), 171 (9), 158 (3), 145 (100), 128 (8), 117 (73), 105 (21), 91 (39). Referred to authentic data [s-10].

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ7.20 (s, 4H), 6.04 – 5.88 (m, 2H), 5.18 – 5.04 (m, 4H), 2.82 – 2.75 (m, 4H), 2.45 – 2.36 (m, 4H).

## 1,3-di(3-butenyl)benzene (S-6b)

89% yield. Colorless liquid. IR(neat): 3080, 2930, 1640, 1610, 1450, 1420, 1000, 910 cm<sup>-1</sup>;
<sup>1</sup>H NMR (CDCl<sub>3</sub>): 87.21 (t, J = 7.4 Hz, 1H), 7.04 (s, 1H), 7.01 (d, J = 2.7 Hz, 2H) 5.94 –
5.81 (ddt, J = 16.8, 10.2, 6.6 Hz, 2H), 5.09 – 5.02 (dq, J = 19.2, 1.8 Hz, 2H), 5.01 – 4.96 (dq, J = 10.2, 1.8, 1.2 Hz, 2H), 2.70 (t, J = 8.1, 7.5 Hz, 4H), 2.41-2.32 (m, 4H); MS: m/z 186 (9), 171 (2), 158 (3), 145 (100), 130 (23), 117 (45), 105 (21), 91 (29).Referred to authentic data [s-10].

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 7.49 - 7.27 (m, 4H), 6.22 - 6.06 (m, 2H), 5.36 - 5.24 (m, 4H), 2.99 - 2.93 (m, 4H), 2.69 - 2.63 (m, 4H).

## 1,4-di(3-butenyl)benzene (S-6c)

93% yield. Colorless liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.16 (s, 4H), 5.91 (ddt, J = 6.6, 10.6, 6.6
Hz, 2H), 5.09 (dd, J=17.2, 1.2 Hz, 2H), 5.02 (dd, J= 10.0, 1.2 Hz, 2H), 2.73 (dd, J= 9.6,
8.8 Hz, 4H), 2.41 (dt, J= 7.8, 7.1 Hz, 4H); MS: m/z 186 (5), 145 (100), 128 (16), 117 (24),
104 (78), 91 (30), 78(12).

Referred to authentic data [s-10].

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ7.36 (s, 4H), 6.20 – 5.96 (m, 2H), 5.34 – 5.22 (m, 4H), 2.97 – 2.89 (m, 4H), 2.66 – 2.58 (m, 4H).

## General procedure for the preparation of the benzenedibutanol (S-7)

Preparation method of the benzenedibutanol (S-7) is same to benzenedipropanol (S-5) from diallylbenzene (S-4).

## 1,2-benzenedi-3-butanol (S-7a)

32% yield. Colorless solution. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 7.13 (m, 4H), 3.69 (t, J = 6.3 Hz, 4H), 2.65 (t, J = 7.5 Hz, 4H), 1.67 (quint, J = 3.0 Hz, 8H); MS: m/z 222(5), 186(5), 171(1), 158(23), 145(100), 131(71), 117(27), 105(28).

# 1,3-benzenedi-3-butanol (S-7b)

82% yield. Colorless solution. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ7.19 (t, J = 7 Hz, 1H), 7.01 (s, 1H), 7.00 (d, J = 7 Hz, 2H), 3.66 (t, J = 6.3 Hz, 4H), 2.62 (t, J = 7.2 Hz, 4H), 1.2-1.8 (m, 9H); MS: m/z 222(6), 204(8), 189(11), 172(11), 157(73), 145(100), 131(61), 117(36), 103(47).

## 1,4-benzenedi-3-butanol (S-7c)

10% yield. Colorless solution. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.10 (s, 4H), 3.57 (q, J = 5.4 Hz 4H), 3.43 (t, J = 5.1 Hz, 2OH), 2.57 (t, J = 7.8 Hz, 4H), 1.71 – 1.61 (m, 4H), 1.58 – 1.48 (m, 4H); MS: m/z 222(14), 204(4), 186(7), 176(21), 158(43), 145(100), 131(67), 117(84), 104(36).

Referred to authentic data [s-11].

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.09 (s, 4H), 3.65 (t, J = 6.3 Hz 4H), 2.61 (t, J = 6.8 Hz, 4H), 1.57 – 1.71 (m, 8H), 1.35 (br, 2H).

#### General procedure for the preparation of the double-headed trifluorolactates (4)

Preparation method of the double-headed trifluorolactates **4** is same to **2** from benzenediethanol (**S-3**). The products were purified by silica gel column chromatography (hexane : ether = 1: 1) and distilled under reduced pressure (1 mmHg) at 180 °C to give target compounds.

## benzene-1,2-(S,S)-bis(butyl-3,3,3-trifluorolactate) (4a)

56% yield. Colorless powder. Mp 82 - 84 °C. IR(KBr): 3450, 1760, 1270, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 7.18 - 7.11 (m, 4H), 4.52 - 4.27 (m, 6H), 3.43 (d, *J* = 7.8 Hz, 2OH), 2.64 (t, *J* = 7.8 Hz, 4H), 1.85 - 1.61 (m, 8H); <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$ 85.7 (d, *J* = 6.8 Hz, 6F); <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$ 167.5 (d, *J* = 1.81 Hz), 139.2, 130.6, 129.1, 126.2, 125.0, 119.4, 113.8, 69.8 (q, *J* = 32.9 Hz), 67.4, 32.0, 28.3, 27.0; MS: m/z 186 (16), 158 (33), 145 (100), 131 (42), 117 (34), 105 (37), 91 (42) Anal. Calcd for C<sub>20</sub>H<sub>24</sub>F<sub>6</sub>O<sub>6</sub>: C 50.63, H 5.06, Found: C 50.69, H 4.98.

## benzene-1,3-(S,S)-bis(butyl-3,3,3-trifluorolactate) (4b)

53% yield. Colorless powder. Mp 79 - 80 °C. IR(KBr): 3460, 2940, 1760, 1270, 1180, 1130

cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 7.21 (t, J = 7.5 Hz, 1H), 7.01 (s, 1H), 6.98 (d, J = 6.6 Hz, 2H), 4.52 - 4.25 (m, 6H), 3.45 (d, J = 7.5 Hz, 2OH), 2.62 (t, J = 7.5 Hz, 4H), 1.80 - 1.69 (m, 8H); <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$ 85.7 (d, J = 7.1 Hz, 6F); <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$ 167.5 (d, J = 1.81Hz), 141.7, 130.7, 128.4 (d, J = 1.81 Hz), 125.9, 125.0, 119.4, 113.8, 69.8 (q, J = 32.9 Hz), 67.5, 35.2, 27.9, 27.3; MS: m/z 302 (12), 247 (30), 186 (37), 171 (13), 158 (56), 145 (100), 130 (78), 117 (65), 104 (27), 91 (46), 79 (23). Anal. Calcd for C<sub>18</sub>H<sub>20</sub>F<sub>6</sub>O<sub>6</sub>: C 50.63, H 5.06, Found: C 50.71, H 5.10.

#### benzene-1,4-(S,S)-bis(butyl-3,3,3-trifluorolactate) (4c)

52% yield. Colorless powder. Mp 53 - 55 °C. IR(KBr): 3460, 2940, 1740, 1230, 1180 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.09 (s, 4H), 7.01 (s, 1H), 4.54 – 4.25 (m, 6H), 3.41 (d, *J* = 7.8 Hz, 2OH), 2.62 (t, *J* = 7.2 Hz, 4H), 1.73 – 1.64 (m, 8H); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.7 (d, *J* = 7.1 Hz, 6F); <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ167.4 (d, *J* = 1.81 Hz), 139.1, 130.6, 128.3, 125.0, 119.4, 113.7, 69.8 (q, *J* = 33.0 Hz), 67.5, 34.8, 27.9, 27.3; MS: m/z 302 (13), 289 (20), 247 (3), 186 (27), 171 (4), 158 (43), 145 (61), 130 (46), 117 (65), 104 (33), 91 (36), 79 (15). Anal Calcd for C<sub>18</sub>H<sub>20</sub>F<sub>6</sub>O<sub>6</sub>: C 50.63, H 5.06, Found: C 50.78, H 4.94.

#### Preparation of 5-bromoisophalic acid (S-8)



In a two-necked round-bottomed flask equipped with a reflux condenser, iodine (0.015 g, 0.057 mmol) was dissolved in 60% fuming sulfuric acid (15 ml), 95% sulfuric

acid (9 ml) and the solution was stirred. Isophthalic acid (5.01, 30 mmol) was added little by little under cooled condition and stirred to dissolve. The reaction mixture was warmed up to 55 °C, bromine (5.01 g, 31.3 mmol) was added over 30 min. The reaction mixture was stirred at 55 °C for 24 h. The HBr gas got out from reaction mixture was trapped with dilute NaOH aq. After the reaction, the reaction mixture was added to a solution of ice water (300ml) and 1% sodium sulfite aq. (100 ml) slowly and a white precipitate gave **S-8**.

#### 5-bromoisophalic acid (S-8)

98% yield. White solid. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ12.00 (broad, 2CO<sub>2</sub>H), 8.70 (m, 1H), 8.45 (m, 2H).

#### Preparation of 5-bromodimethylisophthalate (S-9)



A solution of 2,3-naphthalenedicarboxylic acid (2.31g, 9.4 mmol) in MeOH (15 ml) and 95% H<sub>2</sub>SO<sub>4</sub> (0.5ml, cat.) was stirred under reflux for 24 h. Half amount of MeOH was evaporated, and H<sub>2</sub>O (5ml) was added then, extracted with diethyl ether (30 ml  $\times$  2). The combined organic layers was washed with brine, dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure gave **S-9**.

## 5-bromodimethylisophthalate (S-9)

87% yield. White solid. IR(KBr): 1730, 1260 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 88.60 (d, J = 1.5 Hz, 1H), 8.35 (t, J = 0.9 Hz, 2H), 3.96 (s, 6H); MS: m/z 272(37), 243(100), 198(15), 75(40).



Preparation of 3,3',5,5'-biphenyltetracarboxylic acid-3,3'5,5'-tetramethyl ester (S-10)

In a two-necked round-bottomed flask filled with Ar gas, NiBr<sub>2</sub>·(PPh<sub>3</sub>)<sub>2</sub> (0.38 g, 0.5 mmol), zinc powder (0.98 g, 5.0 mmol), and Et<sub>4</sub>NI (0.14 g, 0.52 mmol) were added. Dry THF (5 ml) was added, and the reaction mixture was stirred at room temperature for 30 min. The solution of **S-9** (1.37g, 5.0 mmol) was added and the resulting mixture was stirred at 50 °C for 24 h. After reaction, the hot and black colored mixture was filtrated to remove inorganic, black precipitates with CHCl<sub>3</sub> and yellow solution was obtained. After cooled, the yellow solution was re-filtrated to remove inorganic, green precipitates, then the solution was evaporated under reduced pressure. The residue was recrystallized from CHCl<sub>3</sub>/THF solution in a refrigerator to give **S-10**.

# 3,3',5,5'-biphenyltetracarboxylic acid-3,3'5,5'-tetramethyl ester (S-10)

84% yield. White solid. IR(KBr): 1730, 1250 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ8.72 (t, J = 1.5 Hz, 2H), 8.52 (t, J = 1.5 Hz, 4H), 4.00 (s, 12H).

## Preparation of 3,3',5,5'-biphenyltetramethanol (S-11)



In a two-necked round-bottomed flask equipped with a reflux condenser, to 30

ml THF solution of S-10 (0.96 g, 2.48 mmol), LiAlH<sub>4</sub> solution (0.51 g, 13.5 mmol, 10ml THF) was added at 0 °C. Then, the reaction mixture was refluxed for 6 h. The cooled mixture was evaporated under reduced pressure. Water (50 ml) was added to the residue and the obtained suspension was stirred 12 h at room temperature to dissolve the inorganic salts, while the tetraol remained as white powder. The tetraol was filtered, washed with water, and dried in vacuo to give S-11.

#### 3,3',5,5'-biphenyltetramethanol (S-11)

63% yield. White solid. IR(KBr): 3290 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ7.55 (s, 4H), 7.33 (s, 2H), 4.67 (s, 8H).

# Preparation of 3,3',5,5'-tetrakis(bromomethyl)biphenyl (S-12)



A solution of S-11 (0.41g, 1.5 mmol), triphenylphosphine (1.98 g, 7.54 mmol), tetrabromomethane (2.77 g, 8.34 mmol) in dry THF (30 ml) was stirred at ambient temperature for 24 h. Diethyl ether was added to the mixture then, white solid was precipitated. After filtration of the white solid, remained solution was concentrated under reduced pressure. The residue was purified by silica gel chromatography (diethyl ether) to give S-12.

# 3,3',5,5'-tetrakis(bromomethyl)biphenyl (S-12)

86% yield. White solid. IR(KBr): 1210 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ7.53 (s, 4H), 7.52 (s, 2H),
4.54 (s, 8H).



#### Preparation of biphenyl-3,3'5,5'-(S,S,S,S)-tetrakis(methyl-3,3,3-trifluorolactate) (11)

CsF (0.69g, 4.5 mmol) and S-12 (0.26 g, 0.5 mmol) was dissolved in DMF (5 ml). A solution of (S)-trifluorolactic acid (0.51 g, 3.5 mmol) in DMF (5 ml) was then added slowly. The reaction mixture was stirred for 24 h at ambient temperature. Water was added to the mixture then, extracted with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude products were purified by silica gel column chromatography (hexane : ether = 1: 4) to give target compounds.

## biphenyl-3,3'5,5'-(S,S,S,S)-tetrakis(methyl-3,3,3-trifluorolactate) (11)

59% yield. Colorless powder. Mp 130 - 132 °C. IR(KBr): 3460, 1750, 1210, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>) δ7.73 (s, 4H), 7.52 (s, 2H), 5.92 (d, *J* = 8 Hz, 8H), 4.88 (quint, *J* = 7.6 Hz, 4H); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ88.4 (d, *J* = 6.8 Hz, 6F); <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>), δ167.6, 142.0, 138.0, 128.5, 128.1 124.5 (q, *J* = 280 Hz), 71.5 (q, *J* = 31 Hz), 70.5, 35.2, 27.9, 27.3; Anal. Calcd for C<sub>28</sub>H<sub>22</sub>F<sub>12</sub>O<sub>12</sub>: C 43.18, H 2.83, Found: C 43.20, H 2.65.

## 4. X-ray diffraction images of type β polymorph



Figure S-1. Diffraction images of 1b' crystal.

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## 3. Mechanosorption of Hydrogen Gas

## 3.1 Introduction

#### 3.1.1 Small dispersion attraction of fluorine containing compounds

Physisorption on microporous material is mainly caused by dispersion attraction (surface tension) [1]. Dispersion attraction is understood as following; even non-polar atom such as He has finite momentary dipole moment by fluctuation of electron. Then, the momentary dipole moment induces momentary dipole moment of neighboring atom. These dipole moments cause momentary attractions as dispersion attraction. Large electronic polarizability caused by wide-spread  $\pi$ -system and/or a heavy element would generate large dispersion attraction. Dispersion attraction could work with various gases, even hydrogen gas although the extent should be small [2].

On the other hand, in general, fluorine-containing compounds have small dispersion attraction [3]. Because fluorine strongly withdraws electrons and fluorine suppresses electron fluctuation [4]. Fluorine-containing compounds are used to improve dispersion property by small dispersion attraction [5], thus they have not been applied for adsorption materials.

#### 3.1.2 Mechanosorption by organofluorine tunnel

Katagiri et al. have reported two types hysteresis in adsorption-desorption isotherm curves using 1D organofluorine tunnel crystals [6]. Type A hysteresis was observed in adsorption-desorption isotherm of Ar@**TFLA-d8** and N<sub>2</sub>@**TFLA-d8** (Figure 3.1). A gradual gas adsorption after the initial micropore filling (type I) and a large hysteresis even at the low  $p/p_0$  region in the degassing process suggested a slow movement of the guest gas molecules in the macro-length tunnel.



Figure 3.1. Type A hysteresis in adsorption-desorption isotherm curve.

Katagiri et al. directly observed induce-fitted Ar molecule in the **TFLA-d8** tunnel micropore by single-crystal X-ray diffraction (Figure 3.2, [7]). X-ray diffraction showed that the Ar atom was located at the center of the room surrounded by the four CF<sub>3</sub> group. X-ray diffraction also showed lattice expansion of **TFLA-d8**. These results suggested that type A hysteresis caused by following; guest ( $\phi_{Ar} = 3.6$  Å,  $\phi_{N2} = 3.0$  Å) molecule was stuffed into small tunnel ( $\phi = 2.5$  Å) by micropore filling, then slow movement of guest molecule was explained by the suppressed movement in 1D tunnel micropores by induce-fit of the soft micropores.



Figure 3.2. Ar atom in tunnel micropore of TFLA-d8.

Type B hysteresis was observed in adsorption-desorption isotherm of N<sub>2</sub>@**TFLA-d10** and CO<sub>2</sub>@**TFLA-d10** (Figure 3.3). A gradual gas adsorption after the initial surface adsorption (type II) and incomplete degassing process suggested other irreversible gas sorption mechanism.



Figure 3.3. Type B hysteresis in adsorption desorption isotherm curve.

## 3.1.3 Problem to be solved

Above mentioned adsorption-desorption isotherm suggested that 1D organofluorine tunnel materials caused guest (gas) storage phenomena by their shape rather than physisorption. However, detail of the storage phenomena (type B hysteresis) is unclear because of a little amount of the adsorbed gas. Therefore, following experiments were performed to investigate guest storage phenomena in 1D organofluorine tunnel.

In the case of  $H_2$  storage in **TFLA-d8**, relative size relation would be similar to type B hysteresis (N<sub>2</sub>@**TFLA-d10** CO<sub>2</sub>@**TFLA-d10**). Thus, high pressure gas storage experiments were performed to introduce a larger amount of  $H_2$  gas. In this case, organofluorine tunnel and hydrogen gas would have a little physisorption. Therefore, "pure" shape effect in type B hysteresis could be found.

#### 3.2 Results and discussion

#### 3.2.1 H<sub>2</sub>@TFLA-d8 gas storage under a high pressure

Crystal engineering molecular architectures using trifluorolactates as supramolecular synthons have led to double-headed trifluorolactate crystals having sub-nanometer-sized 1D tunnel [8]. The crystal of double-headed trifluorolactate (**TFLA-d8**) have almost straight 1D nano-tunnel  $\phi = 2.5$  Å in diameter tunnel, as shown in Figure 3.4. The inner walls of the tunnel were lined with CF<sub>3</sub> group spaced at 5.1 Å intervals. Each CF<sub>3</sub> group was placed "face-to-face" with another CF<sub>3</sub> group across the tunnel. Thus, the tunnel had "narrow neck regions" (gated by two CF<sub>3</sub> groups) and "wide cage regions" (surrounded by four CF<sub>3</sub> groups) in every 5.1 Å intervals. This size of the tunnel diameter at gate regions is bigger than short axis size of hydrogen molecule (2.0 Å $\phi$ ) and smaller than the long axis size (2.7 Å $\phi$ ) of it. Here, the electrostatic repulsions between negatively charged CF<sub>3</sub> groups on the opposite walls sustained the vacant tunnel structure without collapse in the packed crystals, although the backbone of the component molecule is soft and flexible polymethylene [8].



**Figure 3.4**. Shape of 1D nano-tunnel in the crystal of **TFLA-d8**: (a) chemical structure of **TFLA-d8**, (b) slice view of the tunnel, (c) side view of the tunnel.

Hydrogen gas introduction-storage-release process of the crystal of TFLA-d8

was studied. The crystal was put into the vessel with a high-pressure hydrogen gas at 293 K. Then the vessel was cooled to 77 K and kept for 2 hours. After the introduction procedure of the hydrogen gas, the hydrogen gas in the vessel was released to 0.1 MPa at 77 K, then pressure and the temperature of the vessel were recorded with gradual rise of the temperature. The results were illustration in Figure 3.5. Reddish curves show gas release in the course of temperature rising, and bluish dots show no re-adsorption of hydrogen, when re-cooled to 77 K.



**Figure 3.5**. Hydrogen-storage by **TFLA-d8**. Typical gas release curve, released gas did not re-adsorbed by decreasing of the temperature (bluish dots).

The crystal stored around 0.2 wt% amount of hydrogen with use of 10 MPa at 293 K of initial hydrogen gas pressure. Estimated from the tunnel rooms and their sizes, half amount of the tunnel rooms would be occupied with hydrogen molecules. The results showed release of the hydrogen gas was started at 160 K, independent from the amount of the gas storage. Interestingly, the amounts of hydrogen-storage were linearly related to the initial pressure for gas introduction (Figure 3.6). That is, the hydrogen gas would not spontaneously get into the tunnel, but would be stuffed by the pressure. Experiments showed that the hydrogen gas was stored for 48 h at 77 K

without release.



**Figure 3.6**. Correlation between initial gas pressure and the amount of stored gas (mean values of 3 times experiments were shown with standard deviations).

Moreover, the crystal was reusable for more than 8 cycles of hydrogen introduction-release processes (Figure 3.7), without remarkable change of the size of the crystal. First cycle of hydrogen introduction-storage-release made the sizes of the single crystals small. The initial sizes of the crystals were a few millimeter long with needle shape and those after the first cycle were ca.  $0.1 \times 0.1 \times 0.1$  mm cubic block. However, single crystal X-ray diffraction indicated that crystal structure of the **TFLA-d8** was kept during hydrogen introduction-release processes. Therefore, increase of the open tunnel micropores of the crystals by shuttering would make hydrogen-storage capacities to be quadruple. Re-cooling of the crystal did not promote an adsorption of the hydrogen, which is completely different from the physisorption of the gas by activated carbon.



Figure 3.7. Repeated use of the crystal up to 9 times.

A plausible mechanism for the present hydrogen-storage and release is illustrated in Figure 3.8. At first, the hydrogen was stuffed into the tunnel micropore with high surrounding pressure of the crystal (Figure 3.8a). Then, some upright hydrogen molecules in the tunnel worked as the ball of "stop valves", even after the surrounding pressure was released to an ordinal pressure (Figure 3.8b). And, this stop valve works to stop the movement of hydrogen molecules in the tunnel, until the tunnel gates start to fluctuate at 160 K. Finally, the stop valve mechanism was no more work by the fluctuation of the gates in the tunnel to release the hydrogen gas from the tunnel micropore, above 160 K (Figure 3.8c to 3.8d). Thus, the microporous crystal of the **TFLA-d8** could be regard as a molecular hydrogen gas cylinder with infinitely successive stop valve. Based on this mechanism, type B hysteresis of N<sub>2</sub>@**TFLA-d10** and CO<sub>2</sub>@**TFLA-d10** could be regard as gas introduction under low initial pressure conditions (Figure 3.3). Adsorption-desorption isotherm curve was recorded under low pressures. Therefore, N<sub>2</sub>@**TFLA-d10** and CO<sub>2</sub>@**TFLA-d10** showed little amount of gas storage.



Figure 3.8. Plausible mechanism of hydrogen gas storage and release.

Similar mechanistic packs of the hydrogen gas by clathrates have been reported [9]. Actually, type A hysteresis, Ar@**TFLA-d8** resembles to that of the clathrates, because it needs destroy of the lattice for release of the gas. Meanwhile, in the present hydrogen storage-release process (type B hysteresis), which uses molecular stop valve mechanism, the crystal did not change its structures, characters and specifications. Therefore, repeating use of the crystal for hydrogen-storage would become possible.

#### Appendix of chapter 3: XRD-DSC studies of TFLA-bis(4,4') crystal

In the course of the 2D crystal engineering (chapter 2), tubular microporous crystal was prepared. The 1D tubular microporous structure (3.1 Å  $\times$  4.1 Å) was observed in **TFLA-bis(4,4')** crystal by single-crystal X-ray diffraction (Figure 3.9). Proton NMR analysis of the crystal suggested the inclusion of crystallization solvents (ether and hexane) in tubular micropores. Crystallization solvents in the tubular crystal could be removed at 80 °C.



Figure 3.9. 1D nano-tube in the crystal of TFLA-bis(4,4')

At first,  $N_2$  gas adsorption-desorption isotherm curve was recorded to characterize porosity of the tubular structure.  $N_2$  gas adsorption-desorption isotherm showed little gas adsorption (Figure 3.10). There could be two explanations; 1) little amount of  $N_2$  gas was adsorbed in highly fluorinated tube under low pressure (in the same way to type B hysteresis of  $N_2@TFLA-d10$  and  $CO_2@TFLA-d10$ ), 2); tubular structure was collapsed by solvent removal. Therefore, crystal structure change should be confirmed in solvent remove process.



Figure 3.10. N<sub>2</sub> gas adsorption-desorption isotherm curve of TFLA-bis(4,4')

Next, XRD-DSC measurements were performed to investigate crystal structure change under heating condition. Figure 3.11 showed XRD-DSC results. X-ray diffraction pattern was definitely changed during 75 - 105 °C. Monitoring solvent by proton NMR showed that the different diffraction pattern was caused by remove of solvent (Figure 3.12).



Figure 3.11. XRD-DSC result of TFLA-bis(4,4'). (a) Different XRD pattern of TFLA-bis(4,4'). (b) DSC result.



Figure 3.12. Solvent release monitored by <sup>1</sup>H NMR.

While, DSC detected no endothermic nor exothermic peak except for melting (mpTFLA-bis(4,4) = 117 - 118 °C) (Figure 3.11b). Thus, DSC result indicated that remove of guest solvents from organofluorine tubular micropore was not that of thermodynamic process. And no exothermic or endothermic peak during remove solvent process suggested that tubular crystal structure was not collapsed by solvent remove (if crystal structure was changed, endothermic or exothermic peak would be detected by DSC). Therefore, little gas adsorption would be explained by 1); little amount of N<sub>2</sub> gas was absorbed on highly fluorinated tubular micropores (in the same way to type B hysteresis of N<sub>2</sub>@TFLA-d10 and CO<sub>2</sub>@TFLA-d10, Figure 3.13). And solvent storage could be explained by above mentioned stop valve mechanism.



Figure 3.13. Plausible mechanism of guest storage and release process of TFLA-bis(4,4').

Crystallization solvent molecules were mechanically suppressed their movements in tubular micropores of **TFLA-bis(4,4')** and worked as balls of stop valves even surrounding pressure was reduced. And, the stop valves worked to stop the movements of solvents until the tubes start to fluctuate at 75 °C. Then, the stop valve mechanisms were no more work by the fluctuation of the tube to release the crystallization solvents from the tubular micropore above 75 °C. In this case, no endothermic or exothermic peak in gas remove process would be consisted to the mechanical guest storage caused by stop valve mechanism (Figure 3.13).

#### 3.3 Conclusion

H<sub>2</sub>@TFLA-d8 gas storages under high pressures and XRD-DSC studies of TFLA-bis(4,4') crystal showed "mechanosorption" phenomena. Mechanosorption would not be thermodynamic process and guest storage was depended on relation of the host-guest shapes and size. Therefore, mechanosorption could be applied to hydrogen gas storage. In nanotechnology field, mechanosorption phenomena suggested that fluorinated compounds having small dispersion attraction effect would be key item to control properties by their shape itself.

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#### **Experimental section**

# 1. Preparation of double-headed trifluorolactates and its tunnel microporous crystal General

**NMR**: <sup>1</sup>H (300 MHz) and <sup>19</sup>F NMR (282 MHz) spectra were recorded on a Varian MERCURY 300 instrument. <sup>1</sup>H NMR (300 MHz) spectra were recorded by Varian GEMINI 2000 instrument. <sup>13</sup>C (50 MHz) NMR spectra were recorded by Varian GEMINI 200 instrument. Chemical shifts were determined with non-deuterated residual CHCl<sub>3</sub> ( $\delta$  7.26) as an internal standard for <sup>1</sup>H NMR, CDCl<sub>3</sub> ( $\delta$  77.0) as an internal standard for <sup>13</sup>C NMR and C<sub>6</sub>F<sub>6</sub> ( $\delta$  0.00) as a standard for <sup>19</sup>F NMR.

**IR**: IR spectra were recorded on a Hitachi Model 270-40 Infrared Spectrophotometer.

MS: GC/MS analyses were carried out on a Shimadzu GCMS-QP5050A.

**Elemental Analysis**: Elemental analyses were performed on a Perkin Elmer series II CHNS/O Analyzer 2400.

Single crystal X-ray Diffraction: Single crystal X-ray diffraction was performed on Rigaku Rigaku R-AXIS IV and Rigaku VariMax + Saturn.

 $N_2$  gas adsorption: Isotherm adsorption-desorption measurement was performed by BELSORPminiII.

**DSC-XRD**: DSC-XRD measurement was performed on Rigaku SmartLab by Dr. Yukiko Namatame, Rigaku Corporation..

#### Materials

Reagents and solvents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Aldrich Chemical., Ltd. and used without further purification (same to chapter 2). Preparation of TFLA-d8 crystals and/or solids

$$CF_{3} \xrightarrow{OH} OH + HO-(CH_{2})_{8}-OH \xrightarrow{H_{2}SO_{4}} CF_{3} \xrightarrow{OH} O-(CH_{2})_{8}-OH \xrightarrow{I} CF_{3} \xrightarrow{I}$$

Preparation method of the double-headed trifluorolactates **TFLA-d8** is same to double-headed trifluorolactate with benzene moiety **2** from benzenediethanol (**S-3**), (chapter 2). The products were purified by distillation under reduced pressure (1 mmHg) at 180 °C to give target compounds.

## octamethylene-(S,S)-bis(3,3,3-trifluoro-2-hydroxypropanoate) (TFLA-d8)

90% yield. Colorless crystal. Mp. 71-72 °C. IR (KBr): 3450, 2950, 1750, 1730, 1220, 1200, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.47 (quintet, J = 7.2 Hz, 2H), 4.36 (dt, J = 10.5 Hz, J = 6.6 Hz, 2H), 4.30 (dt, J = 10.8 Hz, J = 6.6 Hz, 2H), 3.41 (d, J = 7.8 Hz, 2OH), 1.71 (quintet, J = 6.6 Hz, 4H), 1.35 (brs, 8H). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  85.0 (d, J = 6.9 Hz, 6F); <sup>13</sup>C NMR (CDCl<sub>3</sub> <sup>1</sup>H decoupled):  $\delta$  167.5, 122.2 (q, J = 284 Hz), 69.7 (q, J = 33.3 Hz), 67.6, 28.7, 28.1, 25.3. MS: m/z 145 (1), 129 (1), 111 (21), 110 (12), 98 (8), 95 (7), 83 (10), 82 (41), 81 (22), 69 (100), 68 (31), 67 (42), 56 (10), 55 (84), 54 (37), 43 (16), 42 (16), 41 (62); Anal. Calcd. for C<sub>14</sub>H<sub>20</sub>F<sub>6</sub>O<sub>6</sub>: C 42.22, H 5.06, Found: C 42.0, H 5.29. [ $\alpha$ ]<sup>25</sup>D -4.38 (c 1.1, acetone). The ee was determined to be >99% ee by HPLC analysis of the dibenzoate ester (Daicel Chiralcel<sup>®</sup> OD-H, 100:1 hexane: $\dot{r}$ PrOH, 1.0 mL / min, 254 nm,  $t_{SS}$ (major) = 13.3 min,  $t_{RS}$ (minor) = 15.6 min,  $t_{RR}$ (minor) = 19.1 min).

Single crystal of **TFLA-d8** was prepared by slow evaporation of the *n*-hexane/ether solutions. An amorphous solid of **TFLA-d8** was prepared by rapid evaporation of EtOH

solution. Other amorphous solids were prepared by rapid addition of hexane into the concentrated ethereal solution of **TFLA-d8**.

Preparation of TFLA-bis(4,4')



Preparation method of the double-headed trifluorolactates **TFLA-bis(4,4')** is same to double-headed trifluorolactate with benzene moiety **1** from  $\alpha,\alpha$ -dibromoxylene, (chapter 2). The products were purified by silica gel column chromatography (hexane : ether = 1: 1).

#### biphenyl-4,4'-(S,S)-bis(methyl-3,3,3-trifluorolactate) [TFLA-bis(4,4')]

80% yield. Colorless platelet crystal. Mp 116 - 117 °C. IR(KBr): 3470, 1770, 1270, cm<sup>-1</sup>;
<sup>1</sup>H NMR (CDCl<sub>3</sub>) 87.61 (d, J = 8.4 Hz, 4H), 7.45 (d, J = 8.4 Hz, 4H), 5.38 (s, 4H), 4.54 (quint, J = 6.9 Hz, 2H), 3.42 (d, J = 8.1 Hz, 2OH); <sup>19</sup>F NMR (CDCl<sub>3</sub>): 885.4 (d, J = 7.3 Hz, 6F); Anal. Calcd for C<sub>20</sub>H<sub>16</sub>F<sub>6</sub>O<sub>6</sub>: C 51.51, H 3.45, Found: C 51.63, H 3.34.

## X-ray crystallographic analysis of TFLA-d8

Single crystal X-ray diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.071069 nm); crystallographic information files (CIF) number of **TFLA-d8** in CCDC is

CCDC 246922.

# 2. Equipment for hydrogen gas storage measurements

# 2.1 Pressure measurement apparatus

The amount of hydrogen-storage was measured by change of the pressure of the custom-made vessels as illustrated in Figure S-1a, and showed its photo in Figure S-1b and S1-c.



(a)



**Figure S-1**. Apparatus for hydrogen-storage measurements. (a) Schematic illustrates, (b) and (c) shows photo.

Vessels (SUS316) were purchased from Taiatsu Techno Corporation. Inner volume of each vessel is 10.5 ml that contains dead volumes of piping. Keyence type AP-15S gas pressure sensor and type AP-V80 amp unit were used for high pressure measurements, and type AP-13S sensor and type AP-V82 amp unit were used for ordinal pressure measurement. AS-ONE type 1-9930-11 K-type thermocouple was inserted into the sample vessel to measure the temperature of the atmosphere of the sample crystal. The pressure was registered with the temperature via MTT corporation type MS3701-A-K6 thermocouple converter and Keyence type NR-110 data logger with FLEX LOGGER /EX software (ver. 3.00) to PC (Dynabook Satellite 2510, with Windows 98 OS). The data were processed on Microsoft Excel 97.

# 2.2 Process for measurements

Procedure for the hydrogen-storage measurement is summarized in Scheme S-1



Scheme S-1.

At first, hydrogen gas was introduced into the vessel with high pressure (11 MPa), as shown in Scheme S-1a. Then, pressure of hydrogen gas was adjusted by gradual release to 10 MPa (Scheme S-1b). In case of 14, 18 MPa, hydrogen gas was introduced into the vessel at 77 K. Then, the pressure of the hydrogen gas was adjusted by gradual release at 293 K. The vessels were cooled to 77 K and kept for 2 · 9 hours (Scheme S-1c). Pre-treatment of the crystals needs 9 h at 77 K at 10 MPa of hydrogen. The crystals need 2 h cooling to introduce hydrogen gas into the tunnel micropore. After the introduction of the hydrogen gas, the hydrogen gases in the vessels were released to 0.1 MPa at 77 K (Scheme S-1d). Then, close center valve between the vessels to separate the sample vessel from the blank vessel (Scheme S-1e). Then, the differential pressure (between the sample vessel and blank vessel) and the temperature of the sample were recorded with rising of the vessel temperatures. We cryogenized the vessels by a mixture of ethanol and 2-propanol with liquid nitrogen for gradual temperature change.

#### 2.3 Conversion of pressure to the amount of hydrogen

The raw data of pressure measurements were converted to the amount of the gas, with using the gas equation of ideal gas, without any corrections. Similarly, the pressures at 298 K were estimated with using the same equation, without corrections.

## 3. Pre-treatment of the crystal for gas measurements

#### 3.1 Crystal fragmentation at the first cycle of gas storage-release procedure

The crystal of **TFLA-d8** needs pre-treatment before the measurements, which is the first cycle of hydrogen gas introduction-storage-release procedures. Figure S-2a is the crystal before the pre-treatment and Figure S-2b is that after the pretreatment. It is obvious that the pre-treatment made the size of the crystal small; the initial size of the crystals were a few mm long with needle shape and that after the pre-treatment were ca.  $0.1 \ge 0.1 \ge 0.1 \le 0.1 \le$ 



**Figure S-2**. Size and shape of the crystals used for hydrogen-storage measurements. (a) before the pre-treatment, (b) after the pre-treatment, (c) after the 9<sup>th</sup> cycle of hydrogen-storage-release.

# 4. Effect of crystallinity of the sample on the capacity for the hydrogen gas

Effects of the crystallinity of the **TFLA-d8** on the capacity for the hydrogen-storage were summarized in Figure S-3 with the photo of the crystal.

(a)



**Figure S-3**. Effect of the crystallinity of the **TFLA-d8** on the capacity for the hydrogen-storage. (a) Recrystallized from hexane-ether, and the gas storage release curve (b) crushed crystal prepared by a rapid evaporation of **TFLA-d8** dissolved in EtOH, (c) raw solid prepared by addition of hexane to the

solution of **TFLA-d8** in ether.

The result suggested that the crystallinity of the **TFLA-d8** affected the capacities for the hydrogen.

# 5. A 48h hydrogen-storage at 0.1 MPa at 77 K

The Figure S-4 is a pressure change of the vessel with hydrogen-containing crystals at 77 K for 46 hours. No appreciable amount of gas release was seen for this 48 h, until the temperature became 160 K.



Figure S-4. Pressure change of the vessel for 46 h at 77 K, and then rise to 293 K.

#### 4. Directional Molecule Transportation

#### 4.1 Introduction

#### 4.1.1 Sub-nanometer sized Brownian ratchet

Non-equilibrium fluctuations can drive uni-directional transport along an anisotropic structure in an isothermal medium by biasing the effect of thermal noise  $(k_{\rm B}T)$ . Mechanisms based on this principle are called Brownian ratchets [1]. Some experimental demonstrations of micrometer-scale Brownian linear ratchet have been achieved [2]. Applying a voltage difference [3], ATP hydrolysis [1] provides energy to fluctuate anisotropic structure for uni-directional transportation. The construction and utilization of molecular-sized ratchet gears is one of the final targets of nanotechnology [4]. Because sub-nanometer (Angstrom)-sized structure is expected to move the molecules by thermal fluctuation without energy supply.

#### 4.1.2 Brownian ratchet violates the second law of thermodynamics?

According to the second law of thermodynamics, work engine needs some thermal difference. Sub-nanometer sized ratchet would also need some thermal difference for uni-directional transportation. In other words, sub-nanometer sized ratchet gear does not work in isothermal system. Feynman explained relation between asymmetric structure and the second law by ratchet-gear machine model (Figure 4.1, [5]). Ratchet and gear are adiabatically separated, and their movement is connected by shaft. In case of  $T_1 > T_2$ , ball at the ratchet will be worked as ratchet stopper. Then the shaft will rotate counterclockwise (backward ball will be lift up). On the contrary  $T_1 < T_2$ , active fluctuation of ball at the ratchet will push the ratchet rather than stop counterclockwise rotation. Then the shaft will rotate clockwise (front ball will be lift up). In case of  $T_1 = T_2$  (isothermal system), shaft would not move. Rotations caused by ratchet and gear would be canceled.



Figure 4.1. Feynman ratchet.

Figure 4.2a illustrates model of the ratchet-gear machine. Gear rotation corresponds to horizontal fluctuation of ratchet (T<sub>1</sub>). Ball fluctuation of ratchet corresponds to vertical fluctuation of ball (T<sub>2</sub>). The model clearly shows that 2D isothermal system cancels asymmetric move. Therefore, the second law requires thermal difference to move the machine. And above mentioned Brownian ratchets can be explained following; applying voltage difference or ATP hydrolysis corresponds to generate thermal difference (T<sub>1</sub>  $\neq$  T<sub>2</sub>).



Figure 4.2. Model of Feynman ratchet. (a) In 2-D model, the ball could move horizontally and vertically.(b) In 1D model, the ball could be prevented vertical move.

#### 4.1.3 Problem to be solved

How about 1D system? Asymmetric 1D machine has potential to cause active transportation (Figure 4.2b). The ball will be suppressed to move vertically rather than move horizontally in asymmetric 1D tunnel. Therefore, molecule restricted asymmetric 1D tunnel should be thermally anisotropic. Thus, it requires to be investigated such active transportation. Tunnel microporous crystals of trifluorolactates are appropriate model for the study. Small dispersion effect of organofluorine tunnel crystals would move guest by thermal fluctuation and their shape.

#### 4.2 Results and discussion

## 4.2.1 Method

In the course of 2D crystal engineering (chapter 2), **1a** constructed asymmetric 1D tunnel in its crystal. However, tunnel diameter of **1a**  $(3.9 \times 3.9 \text{ Å})$  was too small for guest molecule. Thus, naphthalene ring was introduced into double-headed

trifluorolactate (**TFLA-2,3-naph**) instead of benzene ring in order to expand tunnel diameter. Single-crystal X-ray diffraction showed that tunnel diameter of **TFLA-2,3-naph** was large  $(6.7 \times 3.1 \text{ Å})$  enough to introduce guest molecule. Then, anthracene was introduced into **TFLA-2,3-naph** tunnel by co-crystallization. Anthracene introduction was confirmed by proton NMR and X-ray diffraction (Figure 4.3). Anthracene containing crystal (anth@**TFLA-2,3-naph**) emitted blue-white fluorescence under UV radiation (254 nm) as shown in Figure 4.4a. Guest (anthracene) transportation was monitored by fluorescence in the crystal.



Figure 4.3. Space-filling representation of anth@TFLA-2,3-naph crystal. Carbon, oxygen, fluorine, and hydrogen atoms are shown in grey, red, green, white respectively. Anthracene molecules are shown in light blue.

## 4.2.2. Anthracene movement in 1D asymmetric tunnel

Anthracene transportation was observed when the crystal was kept at room temperature for two days. Homogeneously distributed anthracene was observed throughout the needle crystal soon after the recrystallization (Figure 4.4a). Then, the anthracene molecules were transported toward one side of the needle crystal (Figure 4.4b) within 2 day. The direction of the transport was also observed by X-ray crystallographic analysis to be rightward in Figure 4.5a.


**Figure 4.4.** Movement of anthracene fluorescence in the crystal. (a) Fluorescence soon after the recrystallization. (b) After two days. (c) Crystal structure of the fluorescent part. CCDC No. 837539: a = 13.1176(10) Å, b = 5.17328(11) Å, c = 17.1353(12) Å,  $\beta = 112.756(8)$  °. (d) Crystal structure of the less fluorescent part. CCDC No. 837540: a = 13.308(6) Å, b = 5.176(3) Å, c = 15.272(7) Å,  $\beta = 98.749(10)$  °



**Figure 4.5**. Direction of anthracene movement. Anthracene moved rightward in this figure. (a) Determined by single-crystal X-ray diffraction. Anthracene was depicted based on the electron density clouds in the tunnel. (b) Illustration of guest molecule movements via thermal fluctuation of the microporous crystal.

The direction of anthracene transportation suggested that the inclined ratchets did not work as flap-check valves. Meanwhile, the direction of the movement seems to be consistent with that caused by Brownian ratchet where temperature of the lattice crystal would be higher than that of guest molecule [1]. At a glance, this active transportation seems to violate the second law because anth@**TFLA-2,3-naph** crystal was not supplied energy or thermal difference. The anthracene molecules did not get any kinetic nor potential energy in this process. This active transportation implies just a Maxwell's demon in the asymmetric 1D system.

Figure 4.6 is an image of the Maxwell's demon. A room contains two kinds molecule is separated by door. Each molecule randomly moves by thermal fluctuation. Maxwell's demon can recognize molecule and move the door. The demon can change molecular distribution by the door open/close operation. The demon does not work at all because molecular movement is caused by thermal fluctuation, the demon simply rectify molecule. Actually, Maxwell's demon cannot be exited. The demon would not recognize molecule by thermal fluctuation of the demon itself. However recently, Toyobe et al. realized Maxwell's demon which can convert "information" into energy [6]. In case of anth@**TFLA-2,3-naph**, 1D tunnel would focus 3D random thermal fluctuation into back and forth fluctuation. And asymmetric **TFLA-2,3-naph** tunnel would rectify molecule based on molecular shape. Therefore, the asymmetric tunnel would be worked as Maxwell's demon.



Figure 4.6. Maxwell's demon.

# 4.3. Conclusion

In conclusion, using the crystal engineering process, an asymmetric tunnel crystal acted as a molecular-sized linear ratchet motor was constructed. The crystal changed the distribution of guest molecules from uniform condition to distribute on only one side in a macro-length tunnel. Here, the guest molecules in the tunnel should be stabilized equally by the tunnel wall. The guest molecules simply changed their locations in the tunnel. The movement of the guest molecules was caused by thermal fluctuation of the crystal lattice which should be anisotropic (Figure 4.5b). A molecular-sized device that can recognize the shape of a molecule would be able to use the thermal fluctuation for uni-directional molecular movement.

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#### **Experimental section**

# 1. Preparation of double-headed trifluorolactates and its tunnel microporous crystal General

**NMR**: <sup>1</sup>H (300 MHz) and <sup>19</sup>F NMR (282 MHz) spectra were recorded on a Varian MERCURY 300 instrument. <sup>1</sup>H NMR (300 MHz) spectra were recorded by Varian GEMINI 2000 instrument. <sup>13</sup>C (50 MHz) NMR spectra were recorded by Varian GEMINI 200 instrument. Chemical shifts were determined with non-deuterated residual CHCl<sub>3</sub> ( $\delta$  7.26) as an internal standard for <sup>1</sup>H NMR, CDCl<sub>3</sub> ( $\delta$  77.0) as an internal standard for <sup>13</sup>C NMR and C<sub>6</sub>F<sub>6</sub> ( $\delta$  0.00) as a standard for <sup>19</sup>F NMR.

**IR**: IR spectra were recorded on a Hitachi Model 270-40 Infrared Spectrophotometer.

MS: GC/MS analyses were carried out on a Shimadzu GCMS-QP5050A.

**Elemental Analysis**: Elemental analyses were performed on a Perkin Elmer series II CHNS/O Analyzer 2400.

**Single crystal X-ray Diffraction**: Single crystal X-ray diffraction was performed on Rigaku R-AXIS RAPID II by Dr. Hiroyasu Sato and Dr. Akihito Yamano, Rigaku Corporation.

# Materials

Reagents and solvents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Aldrich Chemical., Ltd. and used without further purification (same to chapter 2).

Procedure for the preparation of the dimethyl 2,3-naphthalenedicarboxylate (S-12)



A solution of 2,3-naphthalenedicarboxylic acid (1.074 g, 5 mmol) in MeOH (9.4 ml) and concd H<sub>2</sub>SO<sub>4</sub> (0.3 ml, cat.) was stirred under reflux for 18 h. The reaction mixture was cooled in an ice bath and was diluted with H<sub>2</sub>O. Extraction with EtOAc, washing with saturated NaHCO<sub>3</sub> aq. and brine, dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure to give yellowish white powder. Synthesis of **S-12** was confirmed by comparing to authentic data [s-1].

# dimethyl 2,3-naphthalenedicarboxylate (S-12)

1.136 g, 93% yield. Yellowish white powder.

IR(KBr): 1740 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 88.26 (s, 2H), 7.93 (dd, *J* = 3.2, 6.2 Hz, 2H), 7.63 (dd, *J*<sub>1</sub> = 3.2, 6.2 Hz, 2H), 3.96 (s, 6H); MS: m/z 244 (32), 213 (100), 183 (7), 127 (32), 114 (8)

Authentic data [s-1]

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 88.28 (s, 2H), 7.95-7.93 (m, 2H), 7.66-7.64 (m, 2H), 3.98 (s, 6H).

Procedure for the preparation of the 2,3-bis(hydroxymethyl)naphthalene (S-13)



A solution of dimethyl 2,3-naphthalenedicarboxylate (0.734 g, 3.0 mmol) in THF (25 ml) under Ar atmosphere was added to a solution of LiAlH<sub>4</sub> (0.263 g, 6.9 mmol, 2.3 eq.) in THF (25 ml) under Ar atmosphere and cooled to 0 °C. Then the solution was stirred at 0 °C to 70 °C for 15 h. Water was added to the mixture then, extracted with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was recrystallized with THF and hexane to give white powder. Synthesis of **S-13** was confirmed by comparing to authentic data [s-2].

#### 2,3-bis(hydroxymethyl)naphthalene (S-13)

0.452 g, 80% yield. White powder. IR(KBr): 3050 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ7.83 (dd, J = 3, 6 Hz, 2H), 7.82 (s, 2H), 7.50 (dd, J = 3, 6 Hz, 2H), 4.91 (s, 4H), 2.2 (br); MS: m/z 188 (27), 170 (90), 169 (73), 141 (100), 128 (34), 115 (47).

Authentic data [s-2]

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 67.89 (s, 2H), 7.93-7.40 (m, 4H), 4.87 (d, *J* = 5.6 Hz, 4H), 4.44 (t, *J* = 5.6 Hz, 2H).

# Procedure for the preparation of the 2,3-bis(bromomethyl)naphthalene (S-14)



A solution of diol (0.509 g, 2.7 mmol), triphenylphosphine (1.745 g, 6.7 mmol), tetrabromomethane (2.70 g, 8.1 mmol) in  $CH_2Cl_2$  (5 ml) was stirred at ambient temperature for 12 h. Diethyl ether was added to the mixture then, white solid was precipitated. After filtration of the white solid, remained solution was concentrated under reduced pressure. The residue was purified by silica gel chromatography (diethyl ether) to give white powder. Synthesis of **S-14** was confirmed by comparing to authentic data [s-2].

# 2,3-bis(bromomethyl)naphthalene (S-14)

0.599 g, 71% yield. White solid. IR(KBr): 1260 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 7.87 (s, 2H), 7.81 (dd, J = 3, 6 Hz, 2H), 7.51 (dd, J = 3, 6 Hz, 2H), 4.89 (s, 4H). MS: m/z 314 (11), 235 (58), 233 (59), 154 (100), 76 (31).

Authentic data [s-2]

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ8.05 (s, 2H), 7.98-7.49 (m, δ7.74, 4H), 5.01 (s, 4H).



CsF (1.0 g, 6.6 mmol) and dibromide (0.828 g, 2.6 mmol) was dissolved in DMF (5 ml). A solution of (*S*)-trifluorolactic acid (1.13 g, 7.9 mmol) in DMF (5 ml) was then added slowly. The reaction mixture was stirred for 24 h at ambient temperature. Water was added to the mixture then, extracted with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and

concentrated under reduced pressure. The crude products were purified by silica gel column chromatography (hexane : ether = 1: 1) and distilled under reduced pressure (1 mmHg) at 180 °C to give white powder.

# naphthalene-2,3(S,S)-bis(methyl-3,3,3-trifluorolactate) (TFLA-2,3-naph)

0.895 g, 77% White powder. Mp 130 - 131 °C. IR(KBr): 3460, 3380, 1770, 1750 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ7.93 (s, 2H), 7.87 (dd, J= 3, 6 Hz, 2H), 7.58 (dd, J= 3, 6 Hz, 2H), 5.58 (s, 4H), 4.54 (quint, J= 8 Hz, 2H), 3.39 (d, J= 8 Hz, 2OH); <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ85.9 (d, J= 7 Hz, 6F). MS: m/z 440 (4), 297 (8), 197 (17), 170 (100), 141 (41). Anal. Calcd for C<sub>18</sub>H<sub>14</sub>F<sub>6</sub>O<sub>6</sub>: C 49.10, H 3.18, Found: C 49.02, H 3.06.

## Crystallization of TFLA-2,3-naph and anthracene (anth@TFLA-2,3-naph)

**TFLA-2,3-naph** (0.1 g, 0.2 mmol) was recrystallized from ether/*n*-hexane (0.2 ml; 0.2 ml) solution with anthracene (0.4 g, 2.2 mmol) for UV fluorescence observation. Crystals containing anthracene were confirmed by <sup>1</sup>H NMR. <sup>1</sup>H NMR indicated that the co-crystal contained 11 mol% amount of anthracene.

# 2. Fluorescence observation apparatus

The fluorescence moving was confirmed by observation of crystals. Fluorescence of crystal was observed by following combination of microscope and UV-lamp (Figure S-1).



Figure S-1. Fluorescence observation apparatus.

Microscope type SZ-3003 (ocular lens: 10×, objective lens: 0.7 – 4.5×, observed by 30×) was purchased from AS-ONE. Crystals were radiated every other day by AS-ONE type SUV-16 UV lamp (254 nm, 22.0 W) to observe fluorescence distribution. Shimadzu Moticam 480N USB camera was attached to the microscope to take photos. Photos were processed on Shimadzu Motic Image Plus 2.2S program ver. 2.21.

# 3. X-ray crystallography of fluorescence part and quenched part

A co-crystal of double-headed trifluorolactate **TFLA-2,3-naph** and anthracene was obtained by slow evaporation of diethyl ether / *n*-hexane solvents at room temperature. Fluorescence and crystallographic change was confirmed. The diffraction measurement was performed on a Rigaku RAXIS RAPID. Detail parameters are summarized in the Table S-1.

Compound	With anthracene	No anthracene
Empirical formula	$C_{21.50}H_{16.5}F_6O_6$	$C_{18}H_{14}F_6O_6$
Formula weight	484.85	440.3
Crystal size (mm <sup>3</sup> )	$5.1 \ge 0.015 \ge 0.015$	5.1 x 0.015 x 0.015
Crystal color	colorless	colorless
Crystal habit	needle	needle
Crystal System	monoclinic	monoclinic
Space group	$P2_1(#4)$	$P2_1(#4)$
a (Å)	13.118(1)	13.308(6)
b (Å)	5.1733(1)	5.176(3)
c (Å)	17.135(2)	15.272(7)
ß	112.756(8)	98.75(1)
Dcalc (g cm <sup>-3</sup> )	1.502	1.406
Volume (Å ³)	1072.3(2)	1039.7(8)
Z value	2	2
$\mu$ (cm <sup>-1</sup> )	12.623	1.382
Temperature (°C)	$25 \pm 1$	$25 \pm 1$
Reflection measured	12752	9888
Unique reflection	3574	2635
R(int)	0.0399	0.1008
$2\theta_{max}$	136.4	55
Reflection/parameter Ratio	12.2	9.65
$\mathrm{R}_{1} \mathrm{for} \left[ \mathrm{I}\!\!>\!\!2\square(\mathrm{I})  ight]$	0.0583	0.1057
${ m R}_1$ for all data	0.0603	0.183
$ m wR_2(F^2)$ for all data	0.1669	0.3487
Max shift error	0	0
Goodness of fit	1.135	1.032
Maximum peak in Final Diff. Map (e 'Å <sup>-3</sup> )	0.32	0.39
Minimum peak in Final Diff. Map (e ·Å <sup>·3</sup> )	-0.38	-0.28

# 4. Confirmation of crystal direction by plane indices

Plane indices were determined by "Shape" software. 3D model was prepared by tracing crystal outline in order to connect plane indices with lattice constant. Then, plane indices were determined based on mounted crystal angle and lattice constant. Mounted crystal angle was confirmed by oscillation photograph. Tunnel direction was determined based on lattice constant and naphthalene location.



Figure S3. Plane indices and tunnel direction. (a) Determining plane indices. (b) Tunnel direction based on plane indices.

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# Appendix: Trifluorolactate Containing Pyrene Moiety for Perfect Crystal Detection (Co-work with Mr. Akira Fukuda)

#### A.1 Introduction

#### A.1.1 Perfect crystal and its detection

Crystal is defined as solid consists of highly repeated periodic structure in 3D space by components such as atoms, molecules, ions, etc. However in fact, crystal consists from small block packing with some discontinuous parts. In other words, crystal has some mosaicity. Moreover, defect points in the crystal are considered to make the crystal more thermodynamically stable than that without defect. While, perfect crystal is an ideal repeated structure with no discontinuous part. Perfect crystal is expected to show phenomenon by its perfectness. However, recognizing method for perfect crystal has not developed yet.

Single-crystal X-ray diffraction analysis determines crystal structure by X-ray diffraction. Output of diffraction is averaged structure, caused by large number of repeated structure. Some discontinuous parts are canceled by the large number of repeated structure or discovered as disordered structure [1]. Therefore, single-crystal X-ray diffraction cannot be an appropriate method for recognizing perfect crystal.

# A.1.2 Recognizing perfect crystal by gas passage test (Kataoka master thesis)

Kataoka performed gas passage test in order to characterize perfectness of crystal [2]. As described in chapter 3 (mechanosorption), tunnel crystal of **TFLA-d8** did not storage hydrogen gas at ambient pressure. This result could be explained as following; highly fluorinated tunnel with small dispersion attraction would not adsorb hydrogen gas in the tunnel and hydrogen gas would move freely in the fluorinated tunnel. Therefore, tunnel crystal of **TFLA-d8** is expected to be worked as gas filter at ambient pressure. Hydrogen gas filter requires penetrated tunnel structure through the crystal. Thus, perfect crystal was required as molecular gas filter. On the contrary, imperfect crystal would not be worked as gas filter. Kataoka sometimes recognized perfectness of crystal by gas passage test.



Figure A.1. Custom-made apparatus for gas passage test.

Gas passage tests were performed by using custom-made apparatus sown in Figure A.1. The apparatus was consists of two rooms separated by **TFLA-d8** crystal. Gas passage was detected by pressure change of right room. The typical hydrogen gas passage result was shown in Figure A.2. Increasing pressure indicated hydrogen molecule ( $\phi$ 2.0 Å) passage through the **TFLA-d8** tunnel ( $\phi$ 2.5 Å). On the other hand, keeping pressure indicated that argon molecule ( $\phi$ 3.6 Å) could not pass the **TFLA-d8** tunnel. Kataoka et al. obtained three pieces of perfect crystals during 300 examples. In conclusion, their method was not efficient because gas passage test required long time (ca. 18 h/sample) and recovering test sample was almost impossible. Thus, recognizing method for crystal perfectness is needed to study material science of perfect crystal.



Figure A.2. Typical result of hydrogen gas passage test.

# A.1.3 Recognize crystal perfectness by fluorescent molecule

Fluorescence of pyrene is caused by emission from eximer. Fluorescence spectra of pyrene are affected by its concentration. In solution [3] or solid state [4], fluorescence spectra of pyrene are changed according to concentration. Fluorescence spectra respond to the concentration indicates degree of aggregation or intermolecular interaction [5]. Pyrene has potential to recognize crystal perfectness by its fluorescence behavior. In this section, preparation of trifluorolactate with pyrene moiety and fluorescence behavior under UV radiation is described.

# A.2 Result and discussion

Double-headed trifluorolactates with pyrene moiety (**TFLA-py**) was synthesized from optically pure (*S*)-trifluorolactic acid with retention of configuration. Esterification of (*S*)-trifluorolactic acid with diol gave (*S*,*S*)-double headed trifluorolactates (**TFLA-py**). Crystallization of **TFLA-py** was performed by slow evaporation from diethyl ether/hexane.



Scheme A.1. Synthesis of trifluorolactate with pyrene moiety TFLA-py.

Single crystal of **TFLA-py** was submitted to single-crystal X-ray diffraction analysis. **TFLA-py** constructed supramolecular ribbon in its crystal along hydrogen-bonding chains. And pyrene moiety of **TFLA-py** constructed sheet structure by  $CH \cdots \pi$  herringbone stacking of supramolecular ribbon (Figure A.3b).



**Figure A.3**. Crystal structure of **TFLA-py**. (a) Supramolecular ribbon viewed along hydrogen-bonding chain, (b) space-filling representation of pyrene sheet viewed along hydrogen bonding chain, (c) painted pyrene sheet.

Then, UV radiation to the crystal was performed. Interestingly, only terminal part of the crystal emitted fluorescence under UV radiation (Figure A.4a).

Furthermore, central part of the crystal also emitted fluorescence under UV radiation by cutting (Figure A.4b, A.4c). Fluorescence at the terminal part of the crystal suggested that discontinuous part of the crystal caused emitting fluorescence.



**Figure A.4**. Fluorescence of **TFLA-py** crystal under UV radiation. (a) Before cutting, (b) cut crystal, (c) enlarged cut part.

Fluorescent behavior of the crystal was changed by heating-cooling process (Figure A.5). Fluorescent behavior was observed under UV radiation during heating and cooling process. Melted crystal emitted fluorescence from entire the crystal. Therefore, crystallinity would be collapsed in melt. While, solidified melt crystal emitted fluorescence from terminal part similar to before the melting. These behaviors suggested that collapsed crystal structure during melt would be self-repaired, some, in re-solidified process.



Figure A.5. Fluorescence of TFLA-py crystal under UV radiation. (a) Before heating, (b) just before melt, (c) melt, (d) solidified melt.

# A.3 Conclusion

**TFLA-py** crystal emitted fluorescence at the terminal or cutting edge of the crystal under UV radiation. Furthermore, fluorescence behavior would have some reversibility in melt-solidified processes. Although detail of fluorescent properties is not revealed, fluorescent behavior of **TFLA-py** would detect discontinuous part of the crystal. Alignment of pyrene along hydrogen bonding chain would be efficient method for perfect crystal recognizing. Besides, reversible fluorescent behavior would be key method for recognize self-repairing such as double-helices structure (as shown in section 2.4.2).

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### **Experimental section**

#### **1. General Methods**

**NMR**: <sup>1</sup>H (300 MHz) and <sup>19</sup>F NMR (282 MHz) spectra were recorded on a Varian MERCURY 300 instrument. <sup>1</sup>H NMR (300 MHz) spectra were recorded by Varian GEMINI 2000 instrument. <sup>13</sup>C (50 MHz) NMR spectra were recorded by Varian GEMINI 200 instrument. Chemical shifts were determined with non-deuterated residual CHCl<sub>3</sub> ( $\delta$  7.26) as an internal standard for <sup>1</sup>H NMR, CDCl<sub>3</sub> ( $\delta$  77.0) as an internal standard for <sup>13</sup>C NMR and C<sub>6</sub>F<sub>6</sub> ( $\delta$  0.00) as a standard for <sup>19</sup>F NMR.

IR: IR spectra were recorded on a Hitachi Model 270-40 Infrared Spectrophotometer.

MS: GC/MS analyses were carried out on a Shimadzu GCMS-QP5050A.

**Elemental Analysis**: Elemental analyses were performed on a Perkin Elmer series II CHNS/O Analyzer 2400.

Single crystal X-ray Diffraction: Single crystal X-ray diffraction data were collected on a Rigaku RAXIS-IV.

#### Materials

Reagents and solvents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Aldrich Chemical., Ltd. and used without further purification (same to chapter 2).

# 2. Preparation of TFLA-py

Procedure for the preparation of the 2-tert-butylpyrene (S-15)



Anhydrous AlCl<sub>3</sub> (14.7 g, 110 mmol, 1.1 eq.) was added in one portion to a stirred solution of pyrene (20.2 g, 100 mmol, 1.0 eq.) and 2-chloro-2-methylpropane (13.2 ml, 120 mmol, 1.2 eq.) in 1,2-dichloroethane (160 ml) at 0 °C. The resulting mixture was stirred for 3 h at room temperature and poured into a large excess of ice/water. The organic layer was extracted with AcOEt, dried over MgSO<sub>4</sub>, filtered and evaporated to dryness. The residue was used without further purification.

### 2-*tert*-butylpyrene (S-15)

GC/MS: m/z 258, 243, 266, 215, 202, 129, 113, 107, 94.

# Procedure for the preparation of the 1,3-Dibromo-7-tert-butylpyrene (S-16)



A solution of Br<sub>2</sub> (10 mL, 200 mmol, 2 eq.) in CH<sub>2</sub>Cl<sub>2</sub> (100 ml) was slowly added to

a degassed solution of (S-15) (25.8 g, 100 mmol, 1.0 eq.) in anhydrous  $CH_2Cl_2$  (150 ml) at -78 °C under Ar atmosphere. The resulting mixture was allowed to slowly warm up to room temperature and stirred 4 h. The solution was concentrated under reduced pressure. The resultant was washed by hexane to give S-16.

#### 1,3-Dibromo-7-*tert*-butylpyrene (S-16)

35.3 g, 84%. Yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 88.45 (s, 1H), 8.35 (d, J = 9.0 Hz, 2H), 8.29 (s, 2H), 8.16 (d, J = 9.0 Hz, 2H), 1.60 (s, 9H).

Authentic data [s-1].

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ8.48 (s, 1H), 8.36 (d, *J* = 9 Hz, 2H), 8.35 (s, 2H), 8.21 (d, *J* = 9Hz, 2H), 1.59 (s, 9H).

# Procedure for the preparation of the 1,3-Diallyl-7-tert-butylpyrene (S-17)



*n*-Butyllithium (12 ml of a 2.5 M solution in hexane, 30 mmol, 1.2 eq.) was slowly added to a solution of (**S-16**) (10.2 g, 25 mmol, 1.0 eq.) in diethyl ether (100 ml)-benzene (25 ml) in ice bath under Ar atmosphere. After stirring of the mixture for 30 min, 3-bromopropene (3.9 g, 32 mmol, 1.3 eq.) was added to the solution and the mixture was stirred. After 1 hour, *n*-butyllithium (12 ml of a 2.5 M solution in hexane, 30 mmol, 1.2 eq.) was added to the solution again. After stirring of the mixture for 30 min, aryl bromide (3.9 g, 32 mmol, 1.3 eq.) was added to the solution and the mixture was stirred for 1 h before being quenched by the addition of saturated aq. NH<sub>4</sub>Cl in an ice bath. The mixture was extracted with diethyl ether (50 ml × 3), and the organic layer was washed with brine, dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (*n*-hexane only) to give **S-17**.

# 1,3-Diallyl-7*-tert*-butylpyrene (S-17)

6.7 g, 76%. White solid. IR (KBr): 2970, 2910, 1600, 1420, 900, 870, 710 cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>): δ8.20 (d, J = 9.6, 2H), 8.18 (s, 2H), 8.03 (d, J = 9.2 Hz, 2H), 7.72 (s, 1H), 3.76 (t, J = 6.0 Hz, 4H), 3.42 (t, J = 8.0 Hz, 4H), 2.12 (tt, J = 6.0 Hz, 8Hz, 4H), 1.58 (s, 9H); GC/MS: m/z 338, 323, 282, 253, 241, 226, 126,120, 57; Anal. Calcd for C<sub>26</sub>H<sub>26</sub>: C 92.29, H7.74. Found: C 92.22, H 7.74.

Procedure for the preparation of the 2-tert-Butyl-5,7-pyrenedipropan-1-ol (S-18)



Preparation method of the **S-18** was same to benzenedipropanol (**S-5**) from diallylbenzene (**S-4**). The crude product was purified by silica gel column chromatography (*n*-hexane : AcOEt= 1:3) to give **S-18**.

## 2-*tert*-Butyl-5,7-pyrenedipropan-1-ol (S-18)

85% yield. White solid. IR (KBr): 3330, 2890, 1450, 1060, 880 cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>)
δ8.23 (d, J = 9.3, 2H), 8.17(s, 1H), 8.02 (d, J = 9.3 Hz, 2H), 7.75 (s, 1H), 3.76 (t, J = 6.0Hz,
4H), 3.42 (t, J = 8 Hz, 4H), 2.12 (tt, J = 6Hz, 8Hz, 4H), 1.58(s, 9H); Anal. Calcd for
C<sub>26</sub>H<sub>30</sub>O<sub>2</sub>: C83.38 H8.07. Found: C 83.38, H 8.04.

Preparation of the 2-*tert*-Butylpyrene-5,7(S,S)-bis(propyl-3,3,3-trifluorolactate) (TFLA-py)



Round-bottomed flask with equipped with a Teflon-coated magnetic stirring bar and a Dean-Stark apparatus surmounted by a reflux condenser was charged with (S)-3,3,3-trifluorolactic acid (6.9 g, 48 mmol, 2.7 eq.), **S-18** (6.7 g,18 mmol, 1.0 eq.) and HfCl<sub>4</sub>.(thf)<sub>2</sub> (0.62 g, 1.3 mmol, 0.07 eq.) as a catalyst in toluene (36 ml). The mixture was brought to reflux under Ar atmosphere with the removal of water. After 15 h, the resulting mixture was cooled to ambient temperature and filtered with very short silica gel column chromatography by diethyl ether. The crude product was purified by silica gel column chromatography (*n*-hexane: diethyl ether=1:1) to give **TFLA-py**.

# 2-tert-Butylpyrene-5,7(S,S)-bis(propyl-3,3,3-trifluorolactate) (TFLA-py)

5.4 g, 48% yield. White solid. IR (KBr) 3540, 3450, 2970, 1740 cm<sup>-1</sup>; <sup>1</sup>H NMR(CDCl<sub>3</sub>) δ8.12 (s, 2H), 8.06 (d, J= 9.2 Hz, 2H), 8.15 (d, J= 9.2 Hz, 2H), 7.17 (s, 1H), 3.41 (tt, J= 7.6 Hz, 4H), 2.26 (quint, J= 8.0 Hz, 4H), 4.40 (dt, J= 6.0Hz, 1.2Hz, 4H), 4.57 (q, J= 6.4 Hz, 2H), 3.48 (d, J= 7.2 Hz), 1.55 (s, 9H); <sup>13</sup>C NMR(CDCl<sub>3</sub>) δ167.6 (d, J= 1.6 Hz), 149.2, 134.1, 130.9, 128.5, 127.5, 127.3, 125.7, 123.5, 122.7, 122.4 (q, J= 284 Hz) 122.3, 77.2, 69.9 (q, J= 33 Hz), 35.2, 31.9, 30.1, 29.2; <sup>19</sup>F NMR(CDCl<sub>3</sub>) δ85.8 (d, J= 7.1 Hz, 6F); Anal. Calcd for C<sub>32</sub>H<sub>32</sub>F<sub>6</sub>O<sub>6</sub>: C61.34 H5.15. Found: C 61.22, H5.19.

#### Reference

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