

# Supplementary Information

## Halogen bond effect on bundling of hydrogen bonded 2-fold helical columns

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### Table of Contents

#### Experimental procedure

General Methods

Crystallographic study

#### Crystallographic data

**Figure S1.** Supramolecular chirality and crystal structures.

**Figure S2.** Molecular packings of **1·2-Br** for *ab initio* calculation.

**Table S1.** Calculated energies of **1·2-Br** from *ab initio* calculation

**Figure S3.** Molecular packings of **1·2-I** for *ab initio* calculation.

**Table S2.** Calculated energies of **1·2-I** from *ab initio* calculation

**Figure S4.** Experimental IR spectra of the crystals of **1·2-H**, **1·2-F**, **1·2-Cl**, **1·2-Br** and **1·2-I**.

**Table S3.** Crystallographic parameters of **1·2-H**, **1·2-F** and **1·2-Cl**.

**Table S4.** Crystallographic parameters of **1·2-Br** and **1·2-I**.

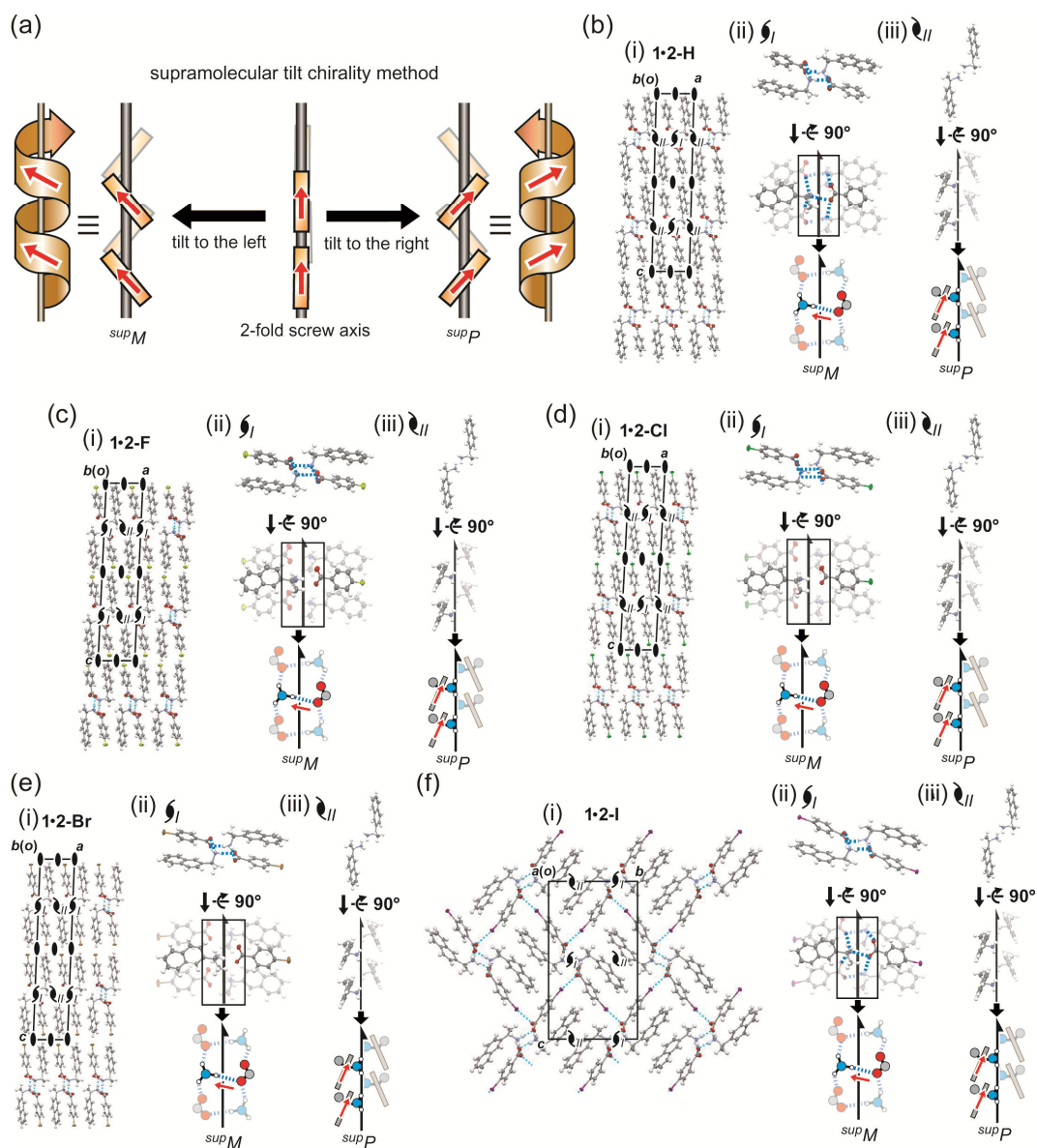
#### References

## General Methods

Reagents, (*R*)-(+)-1-(1-naphthyl)ethylamine (**1**), benzoic acid (**2-H**), 4-fluorobenzoic acid (**2-F**), 4-chlorobenzoic acid (**2-Cl**), 4-bromobenzoic acid (**2-Br**) and 4-iodobenzoic acid (**2-I**) were purchased from Tokyo Chemical Industry. The corresponding amine and acids were mixed in methanol and followed by evaporation in vacuo, yielding powdered salts. The salts were then recrystallized from ethanol at ordinary temperatures and pressures to give single crystals which were suitable for X-ray analysis. FT-IR spectra of the crystals in a KBr pellet were recorded using JASCO FT/IR-4200 spectrometer.

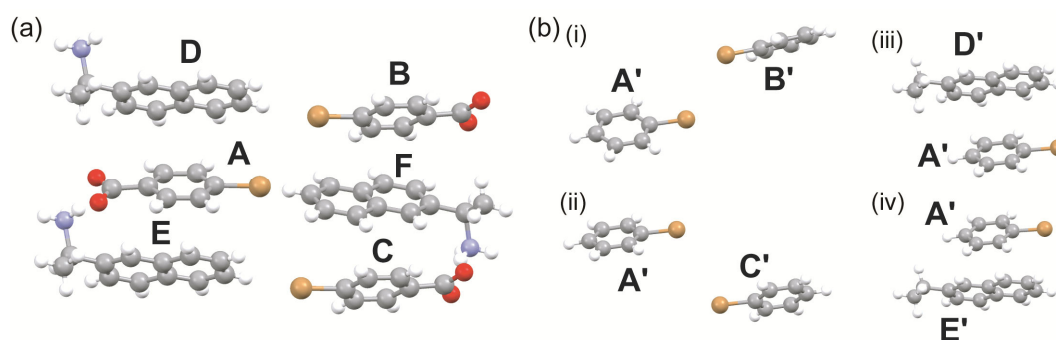
## Crystallographic study

Data collection: Single-crystal X-ray diffraction data were collected on a Rigaku RAXIS-RAPID imaging-plate diffractometer with graphite-monochromated CuK $\alpha$  radiation ( $\lambda = 1.54187 \text{ \AA}$ ). Lattice parameters were obtained by least-squares analysis from reflections for three oscillation images. Structure solution was achieved by direct methods, SIR2004 and SHELXS97.<sup>[S1],[S2]</sup> The structures were refined by a full-matrix least-squares procedure with all the observed reflections based on  $F^2$ . All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. All calculations were performed using CrystalStructure crystallographic software package<sup>[S3]</sup> except for refinement, which was performed using SHELXL-97. Absolute configuration of the crystals was defined according to the chiral amine with (*R*)-configuration. Crystallographic data for this paper has been deposited at the Cambridge Crystallographic Data Centre under deposition number CCDC: **1·2-H** (884890), **1·2-F** (884893), **1·2-Cl** (884892), **1·2-Br** (884891), **1·2-I** (884894).



**Figure S1.** Supramolecular chirality and crystal structures. (a) Supramolecular tilt chirality method. Crystal structures of (b) **1·2-H**, (c) **1·2-F**, (d) **1·2-Cl**, (e) **1·2-Br** and (f) **1·2-I**. (i) Packing diagrams, 2-fold helices by (ii) caH-Bs and (iii) naphthalene rings are drawn with thermal ellipsoid with 50% probability.

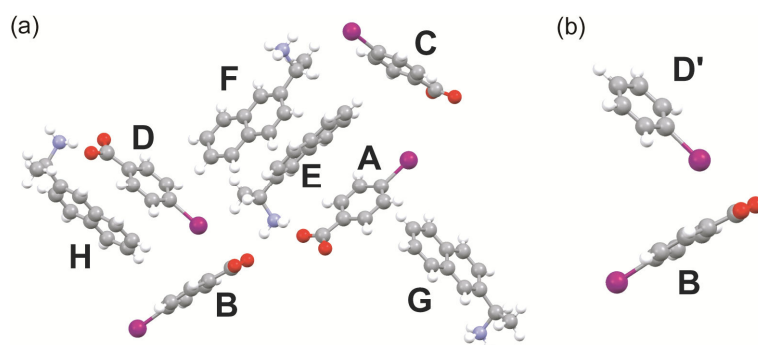
As schematically drawn in Fig. S1(a), handedness of 2-fold helical assemblies can be distinguished according to tilt of molecules in front of the 2-fold screw axis. That is, the assembly with the front orange blocks tilting to the right is right-handed, denoted as  $supP$ , and with the front orange blocks tilting to the left is left-handed, denoted as  $supM$ . Therefore, the 2-fold helical assemblies composed of hydrogen bonds and naphthalene rings in the crystals are defined as  $supM$  and  $supP$ , respectively.



**Figure S2.** Molecular packings of **1·2-Br** for *ab initio* calculation. (a) Three acids (**A**, **B** and **C**) and three amines (**D**, **E** and **F**) which were extracted from the crystal structure of **1·2-Br**. (b) Four pairs of molecules: **A'-B'** (i), **A'-C'** (ii), **A'-D'** (iii) and **A'-E'** (iv). The anionic carboxylate groups of **A**, **B**, **C** and the cationic ammonium groups of **D**, **E** were replaced by hydrogen atoms, of which positions were optimized (PW91/6-311G\*\*), resulting in molecules **A'**, **B'**, **C'**, **D'** and **E'**, respectively, to eliminate repulsion forces between the two anions (**A-B**, **A-C**) or attractive forces between a cation and an anion (**A-D**, **A-E**).

**Table S1.** Calculated energies from *ab initio* calculation (MP2/6-311G\*\* and HF/6-311G\*\*)

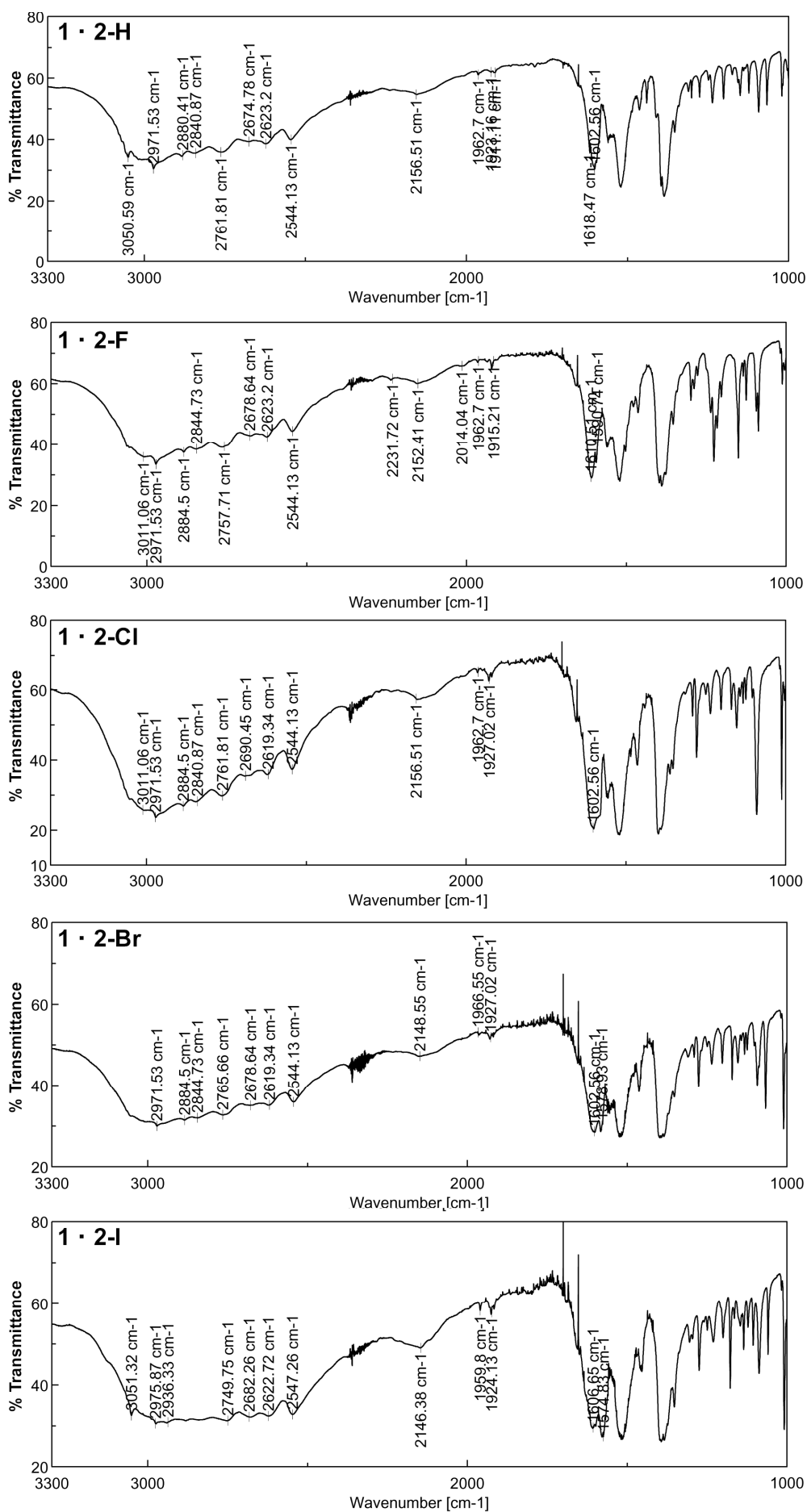
Entries	Interaction energies (HF/6-311G**) (kcal·mol <sup>-1</sup> )	Interaction energies (MP2/6-311G**) (kcal·mol <sup>-1</sup> )
<b>A-B</b>	25.5	26.1
<b>A-C</b>	25.7	25.7
<b>A-D</b>	-53.4	-58.8
<b>A-E</b>	-100.7	-93.0
<b>A'-B'</b>	0.1	1.3
<b>A'-C'</b>	-0.1	0.5
<b>A'-D'</b>	-4.3	0.1
<b>A'-E'</b>	-3.5	2.5



**Figure S3.** Molecular packings of **1·2-I** for *ab initio* calculation. (a) Four acids (**A**, **B**, **C** and **D**) and four amines (**E**, **F**, **G** and **H**) which were extracted from the crystal structure of **1·2-I**. (b) A pair of halogen bonded molecules, **B-D'**. The anionic carboxylate group of molecule **D** was replaced by a hydrogen atom, resulting in a molecule **D'** to eliminate repulsion of **B-D** owing to their negative charges.

**Table S2.** Calculated energies from *ab initio* calculation (MP2/6-311G<sup>\*\*</sup>)

Entries	Interaction energy (kcal·mol <sup>-1</sup> )
<b>A-E</b>	-91.0
<b>B-D</b>	34.0
<b>B-E</b>	-100.7
<b>E-F</b>	29.8
<b>B-D'</b>	-5.0



**Figure S4.** Experimental IR spectra of the crystals of **1·2-H**, **1·2-F**, **1·2-Cl**, **1·2-Br** and **1·2-I**.

**Table S3.** Crystallographic parameters of **1·2-H**, **1·2-F** and **1·2-Cl**.

	<b>1·2-H</b>	<b>1·2-F</b>	<b>1·2-Cl</b>
Formula	C <sub>19</sub> H <sub>19</sub> NO <sub>2</sub>	C <sub>19</sub> H <sub>18</sub> FNO <sub>2</sub>	C <sub>19</sub> H <sub>18</sub> ClNO <sub>2</sub>
Mw	293.36	311.36	327.81
Crystal shape	platelet	chunk	block
Crystal color	colorless	colorless	colorless
Crystal size [mm]	0.50 × 0.15 × 0.05	0.30 × 0.10 × 0.10	0.70 × 0.40 × 0.40
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2 (#5)	C2 (#5)	C2 (#5)
<i>a</i> (Å)	34.7123(6)	35.5961(9)	37.4749(7)
<i>b</i> (Å)	6.19971(11)	6.21689(18)	6.19581(11)
<i>c</i> (Å)	7.24791(13)	7.1819(2)	7.19661(13)
$\alpha$ (°)	90	90	90
$\beta$ (°)	91.5454(7)	92.5391(14)	92.8197(8)
$\gamma$ (°)	90	90	90
<i>V</i> (Å <sup>3</sup> )	1559.23(5)	1587.77(8)	1668.94(5)
<i>Z</i>	4	4	4
<i>D<sub>c</sub></i> (g/cm <sup>3</sup> )	1.250	1.302	1.305
<i>2</i> $\theta$ <sub>max</sub>	136.4	136.4	136.4
<i>T</i> (K)	213.1	213.1	213.1
collected reflections	13350	8554	8785
unique reflections	2830	2845	2916
<i>R</i> 1 ( <i>I</i> > 2.0 $\sigma$ ( <i>I</i> ))	0.0395	0.0619	0.0420
<i>wR</i> 2 (all data)	0.1172	0.1914	0.1111
<i>F</i> <sub>000</sub>	624.00	656.00	688.00
GOF	1.116	1.109	1.061
Flack parameter	-0.3(3)	-0.1(4)	0.019(18)
CCDC	884890	884893	884892

**Table S4.** Crystallographic parameters of **1·2-Br** and **1·2-I**.

	<b>1·2-Br</b>	<b>1·2-I</b>
Formula	C <sub>19</sub> H <sub>18</sub> BrNO <sub>2</sub>	C <sub>19</sub> H <sub>18</sub> INO <sub>2</sub>
Mw	372.26	419.26
Crystal shape	chunk	block
Crystal color	colorless	colorless
Crystal size [mm]	0.30 × 0.20 × 0.20	0.60 × 0.10 × 0.10
Crystal system	monoclinic	orthorhombic
Space group	<i>C</i> 2 (#5)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (#19)
<i>a</i> (Å)	38.2177(7)	5.96084(15)
<i>b</i> (Å)	6.19540(11)	12.8706(2)
<i>c</i> (Å)	7.19732(13)	22.8019(4)
$\alpha$ (°)	90	90
$\beta$ (°)	92.0811(7)	90
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	1703.01(5)	1749.35(6)
<i>Z</i>	4	4
<i>D</i> <sub>c</sub> (g/cm <sup>3</sup> )	1.452	1.460
$2\theta_{max}$	136.5	136.5
<i>T</i> (K)	213.1	213.1
collected reflections	9154	18299
unique reflections	3025	3189
<i>R</i> 1 ( <i>I</i> > 2.0σ( <i>I</i> ))	0.0387	0.0625
<i>wR</i> 2 (all data)	0.1096	0.1574
<i>F</i> <sub>000</sub>	760.00	832.00
GOF	1.207	1.046
Flack parameter	-0.02(2)	-0.028(14)
CCDC	884891	884894

## References

- S1 SIR-2004. Altomare, A.; Burla, M.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* 1999, 32, 115-119.
- S2 SHELXL-97. Sheldrick, G. M.; *Acta Crystallogr., Sect. A* 2008, 64, 112-122.
- S3 CrystalStructure ver 3.8. Crystal Structure Analysis Package; Rigaku and Rigaku Americas: The Woodlands, TX, 2000–2010.