Electronic Supplementary Information (ESI)

Orientational isomerisation of guest molecules in equilibrium in a tubular host crystal formed *via* halogen and hydrogen bonding

Yutaro Yamashita,[a] Shohei Tashiro*[a] and Mitsuhiko Shionoya*[a]

[a] Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Table of contents

S1. Materials and methods 2

S2. Synthesis and crystallisation 2

S3. VT-SCXRD analysis 12

$(BBMP{\cdot}HBr)_2{\supset}CH_2Cl_2$ 12

$BBMP{\cdot}HBr{\supset}CD_2Cl_2$ 17

$BBMP{\cdot}HBr{\supset}CH_2Br_2$ 20

S4. References 21

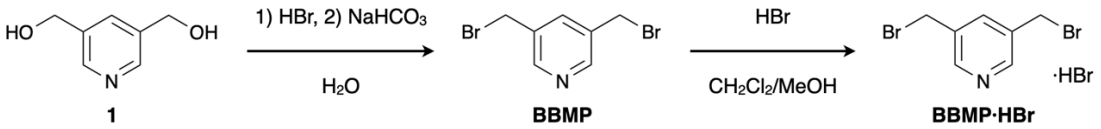
S1. Materials and methods

Solvents and reagents were purchased from TCI Co., Ltd., Kanto chemical Co., Inc. and FUJIFILM Wako Pure Chemical Corporation. All the chemicals were used without further purification. Compound **1** was synthesised in a reported procedure and the ^{1}H NMR signals were consistent with the data.[1] BBMP·HBr was synthesised in a modified procedure from the reported ones.[2,3]

Powder X-ray diffraction (PXRD) was recorded on a Rigaku Miniflex 600 diffractometer using CuKα radiation. Single-crystal X-ray diffraction (SCXRD) analyses were carried out using a Rigaku XtaLAB P200 diffractometer equipped with a low-temperature N_2 gas spray cooler, and the obtained data were processed using the CrysAlisPro platform and analysed using the Olex-2 crystallographic software package except for refinement[4] using SHELXL.[5] ORTEP diagrams, unit cell structures and overlays of SCXRD structures were displayed using a Mercury software. Packing structures were visualised by a PyMOL software. Electron density maps were made with a ShelXle program.[6] The nuclear magnetic resonance (NMR) spectra were measured using a Bruker AVANCE 500 spectrometer. ^{1}H NMR spectra were calibrated as TMS = 0 ppm.

S2. Synthesis and crystallisation

Synthesis of 3,5-bis(bromomethyl)pyridine hydrobromide (BBMP·HBr)[2,3]



Pyridine-3,5-diyldimethanol[1] (**1**, 152.6 mg, 1.097 mmol) was heated at reflux in 48% hydrobromic acid (5 mL) for 6 h. To the brown solution was added 20 mL of water, and it was basified with a saturated aqueous solution of $NaHCO_3$ (50 mL). The solution was extracted with CH_2Cl_2 (40 mL × 3) and the combined organic layer was dried over Na_2SO_4. The obtained solid after evaporation was suspended in CH_2Cl_2 (100 mL) and then filtered to give a colourless solution. HBr-CH_3OH reagent (5–10%, 5 mL) was added to the solution to make the HBr salt of BBMP. The beige solid was obtained by evaporation (288.9 mg). A part of the solid (247.9 mg) was recrystallised by the vapor diffusion of diethyl ether into $CHCl_3$ to afford colourless needle crystals (**II**, 168.9 mg, 0.6375 mmol, 52%).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 4.59 (s, 4H), 8.45 (br, 1H), 8.78 (br, 2H).

Elemental analysis: calcd for BBMP·HBr = $C_7H_8Br_3N$: C 24.31%, H 2.34%, N 4.05%; found C 24.64%, H 2.44%, N 4.20%.

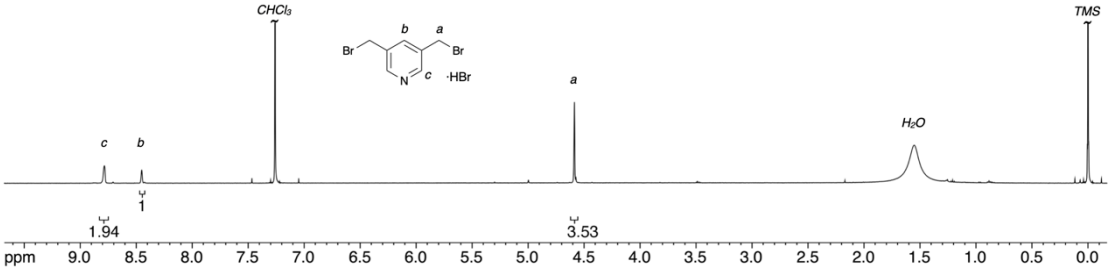


Fig. S1 ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 300 K) of BBMP·HBr.

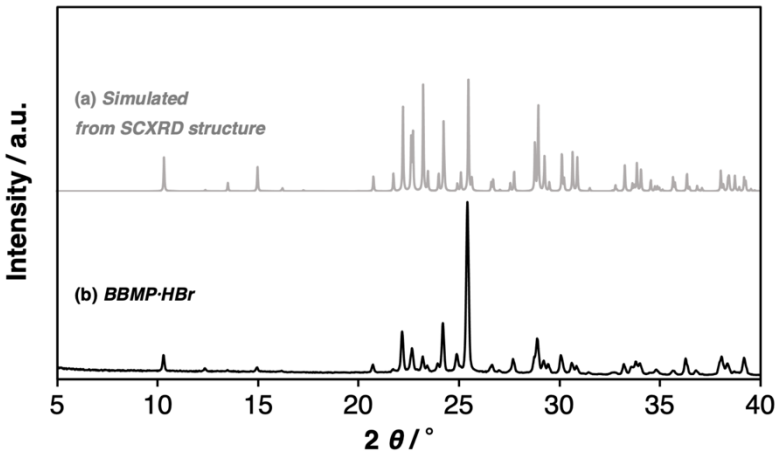


Fig. S2 PXRD patterns (RT) of BBMP·HBr (a) simulated from the SCXRD structure (CCDC 2125695) and (b) observed.

Crystals of $(BBMP{\cdot}HBr)_2{\supset}CH_2Cl_2$

BBMP·HBr (12.2 mg, 35.3 μmol) was dissolved in CH_2Cl_2 (4 mL) under heating to the boiling point, filtered and left at room temperature. Addition of the seed crystals produced in another batch resulted in the appearance of thin colourless platelets, which were collected by filtration and dried briefly in air to afford $(BBMP{\cdot}HBr)_2{\supset}CH_2Cl_2$ (5.76 mg, 14.8 μmol, 42%). In the absence of seed crystals, only a small amount was formed, and the selectivity of the structure **I** vs. **II** was not high. NMR and PXRD measurements were conducted immediately after filtration to avoid evaporation of the clathrated CH_2Cl_2. Crystals of $(BBMP{\cdot}HBr)_2{\supset}CD_2Cl_2$ were synthesised in the same procedure as $(BBMP{\cdot}HBr)_2{\supset}CH_2Cl_2$.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 4.60 (s, 4H), 5.30 (s, CH_2Cl_2, 1H), 8.47 (s, 1H), 8.81 (d, J = 2 Hz, 2H).

Elemental analysis: calcd for BBMP·0.94HBr = $C_7H_{7.94}Br_{2.94}N$: C 24.65%, H 2.35%, N 4.11%; found C 24.91%, H 2.53%, N 4.24%.

The composition of BBMP·0.94HBr calculated from the elemental analysis was different from the expected BBMP·HBr·0.5(CH_2Cl_2). This may be due to the release of CH_2Cl_2 and HBr from the dried crystals with time (one day) or during the analytical procedure.

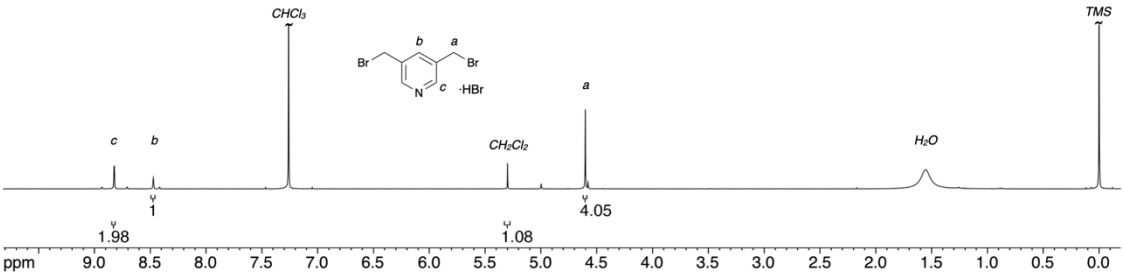


Fig. S3 ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 300 K) of $(BBMP{\cdot}HBr)_2{\supset}CH_2Cl_2$.

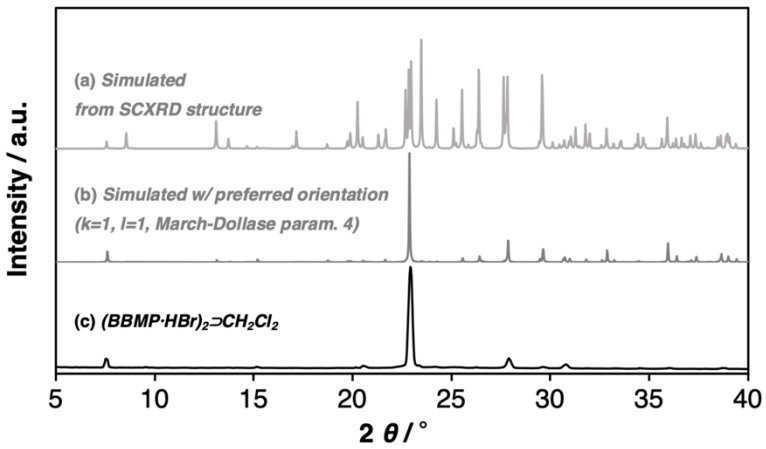


Fig. S4 PXRD patterns (RT) of $(BBMP{\cdot}HBr)_2{\supset}CH_2Cl_2$ (a) simulated from the SCXRD structure (CCDC 2124417), (b) (a) with a preferred orientation (k = 1, l = 1, March-Dollase parameter 4) and (c) observed.

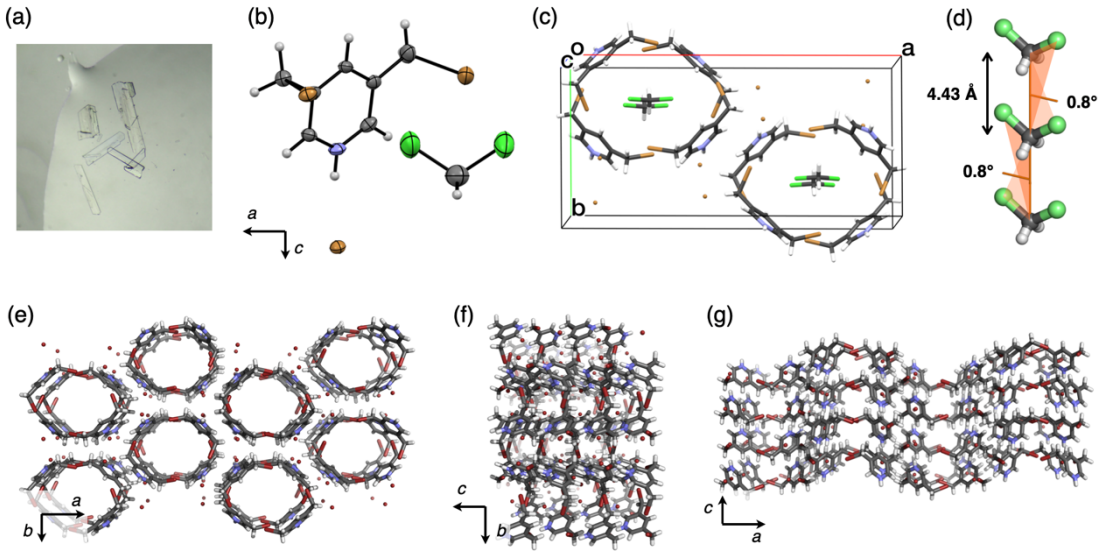


Fig. S5 (a) Photograph of the $(BBMP{\cdot}HBr)_2{\supset}CH_2Cl_2$ crystals. (b–g) Crystal structure of $(BBMP{\cdot}HBr)_2{\supset}CH_2Cl_2$ (**I**, 148 K). (b) ORTEP diagram (50% probability). (c) Unit cell structure. (d) One-dimensional array of the clathrated CH_2Cl_2 molecules along the c-axis. The intermolecular separation and the dihedral angles of the C–Cl bonds between the adjacent CH_2Cl_2 molecules are shown. Packing structure viewed along the (e) c-, (f) a- and (g) b-axes. For (e–g), the solvent molecule CH_2Cl_2 was omitted for clarity. CCDC 2124428.

Crystals of (BBMP·HBr)$_2$⊃CH_2Br_2

BBMP·HBr (9.20 mg, 26.6 μmol) dissolved in CH_2Br_2 (< 1 mL) under heating to 50 °C was filtered and left at room temperature. Addition of the seed crystals produced in another batch resulted in the appearance of thin colourless platelets, which were collected by filtration and dried briefly in air to afford (BBMP·HBr)$_2$⊃CH_2Br_2 (4.21 mg, 9.73 μmol, 37%). In the absence of seed crystals, only a small amount was formed and the selectivity of the structure **I** vs. **II** was not high. NMR and PXRD measurements were conducted immediately after filtration to avoid evaporation of clathrated CH_2Br_2. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 4.58 (s, 4H), 4.93 (s, CH_2Br_2, 1H), 8.46 (s, 1H), 8.77 (d, J = 2 Hz, 2H).

Elemental analysis: calcd for BBMP·HBr·0.42CH_2Br_2 = $C_{7.4}H_{8.8}Br_{3.8}N$: C 21.27%, H 2.13%, N 3.34%; found C 21.22%, H 2.19%, N 3.43%.

The composition of BBMP·HBr·0.42(CH_2Br_2) calculated from elemental analysis was different from the expected BBMP·HBr·0.5(CH_2Br_2). This may be due to the release of CH_2Br_2 from dried crystals with time (2 days) or during the analytical procedure.

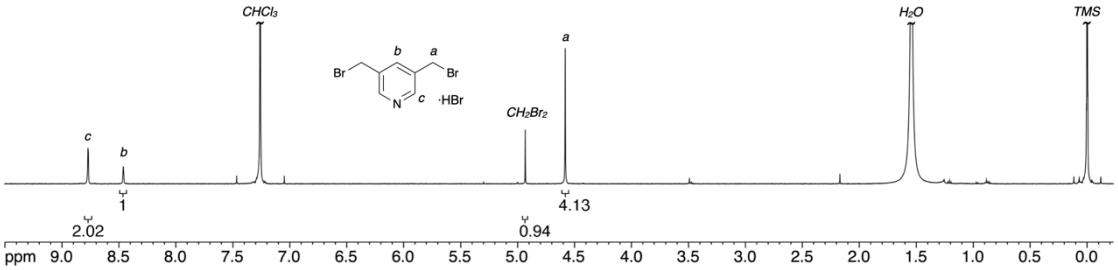


Fig. S6 ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 300 K) of (BBMP·HBr)$_2$⊃CH_2Br_2.

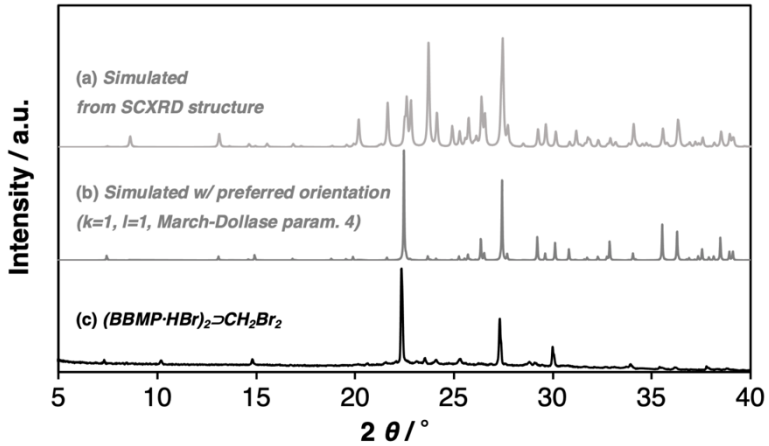


Fig. S7 PXRD patterns (RT) of (BBMP·HBr)$_2$⊃CH_2Br_2 (a) simulated from the SCXRD structure (CCDC 2124429), (b) (a) with a preferred orientation (k = 1, l = 1, March-Dollase parameter 4) and

(c) observed.

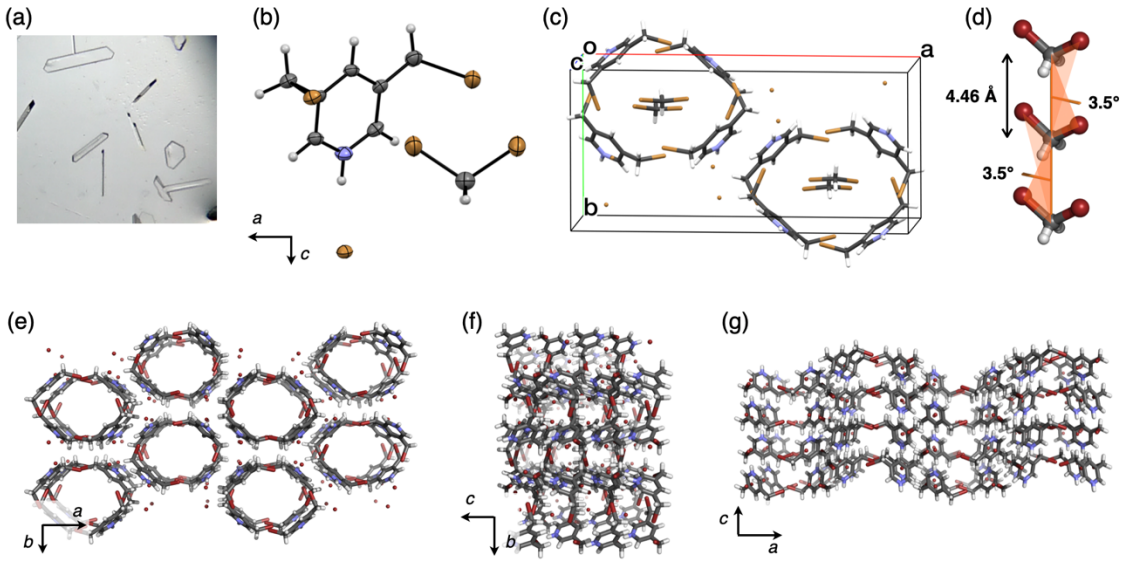


Fig. S8 Photograph of the $(BBMP{\cdot}HBr)_2{\supset}CH_2Br_2$ crystals. (b–g) Crystal structure of $(BBMP{\cdot}HBr)_2{\supset}CH_2Br_2$ (**I**, 148 K). (b) ORTEP diagram (50% probability). (c) Unit cell structure. (d) One-dimensional array of the clathrated CH_2Br_2 molecules along the *c*-axis. The intermolecular separation and the dihedral angles of the C–Br bonds between the adjacent CH_2Br_2 molecules are shown. Packing structure viewed along the (e) *c*-, (f) *a*- and (g) *b*-axes. For (e–g), the solvent molecule CH_2Br_2 was omitted for clarity. CCDC 2124430.

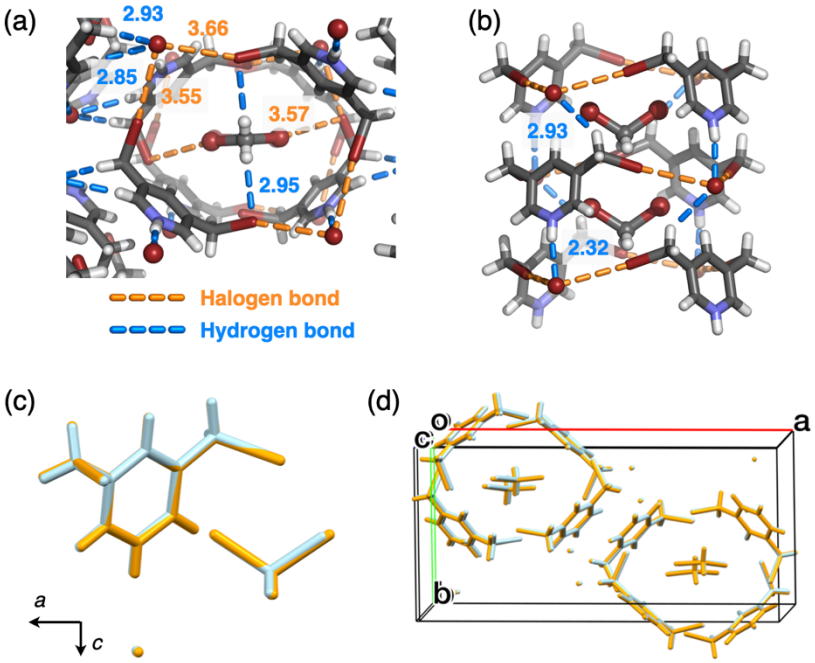


Fig. S9 Non-covalent bonds seen in the crystal structure of $(BBMP{\cdot}HBr)_2{\supset}CH_2Cl_2$ viewed from (a) top and (b) side of the tube. The orange and blue dashed lines indicate halogen and hydrogen bonds, respectively. (c,d) Overlayed crystal structures of $(BBMP{\cdot}HBr)_2{\supset}CH_2Cl_2$ (cyan) and $(BBMP{\cdot}HBr)_2{\supset}CH_2Br_2$ (orange) at 148 K. (c) Stick model of the molecules. (d) Unit cell structures.

Non-tube crystals of BBMP·HBr

When BBMP·HBr was crystallised in solvents other than CH_2Cl_2 and CH_2Br_2, crystals with a non-tubular structure without solvent molecules were obtained. Crystal **II** was readily obtained as blocky to plate-like crystals by cooling the $CHCl_3$ solution of BBMP·HBr or by evaporating the CH_3CN solution. It was also obtained by rapid quenching or evaporating the CH_2Cl_2 or CH_2Br_2 solution. Crystal **III** was obtained only as a minor product of the mixture with crystal **II** by diffusion of diethyl ether into a $(CHCl_2)_2$ solution of BBMP·HBr. The crystals subjected to SCXRD was solved as twins.

Table S1. Structural parameters for the crystals of BBMP·HBr (**II** and **III**) obtained from the $CHCl_3$, CH_3CN and $(CHCl_2)_2$.

Solvent	$CHCl_3$	CH_3CN	CH_2Cl_2	$(CHCl_2)_2/Et_2O$
CCDC No.	2124416	2124411	2125695	2124418
Structure	**II**	**II**	**II**	**III**
Temperature / K	93	93	293	93
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pbca*	*Pbca*	*Pbca*	$P2_1/n$
a / Å	8.1294(2)	8.12360(10)	8.16082(19)	14.72130(10)
b / Å	14.0393(3)	14.0468(2)	14.2650(3)	8.57480(10)
c / Å	16.9502(3)	16.9496(3)	17.0946(4)	23.2614(3)
β / °	—	—	—	94.0110(10)
V / Å^3	1934.54(7)	1934.13(5)	1990.05(8)	2929.15(5)
R_{int}	0.0240	0.0327	0.0493	— (Twin)
R_1 ($I > 2\sigma(I)$)	0.0275	0.0345	0.0568	0.0447
wR_2 (All data)	0.0728	0.0980	0.1694	0.1470
GOF	1.115	1.107	1.100	1.109

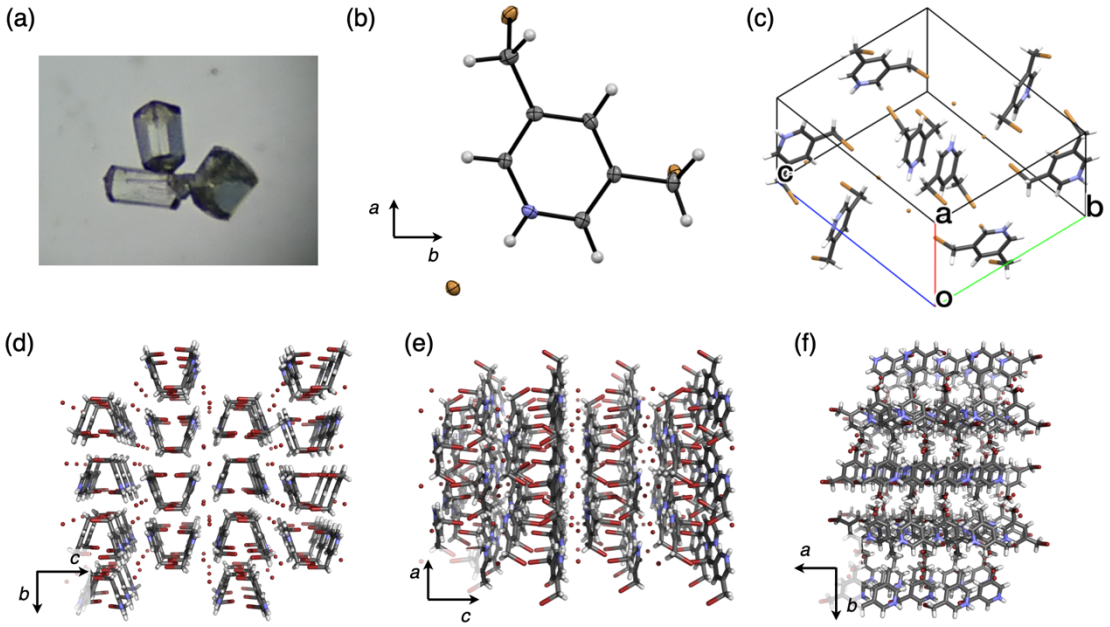


Fig. S10 (a) Photograph of the BBMP·HBr crystals (**II**). (b–f) Crystal structure of BBMP·HBr (**II**, 93 K) obtained from the $CHCl_3$ solution. (b) ORTEP diagram (50% probability). (c) Unit cell structure. Packing structure seen along the (d) *a*-, (e) *b*- and (f) *c*-axes. CCDC 2124416.

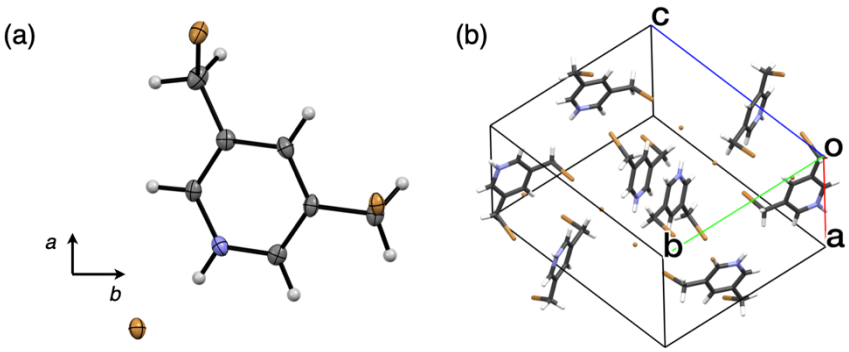


Fig. S11 Crystal structure of BBMP·HBr (**II**, 93 K) obtained from CH_3CN. (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124411.

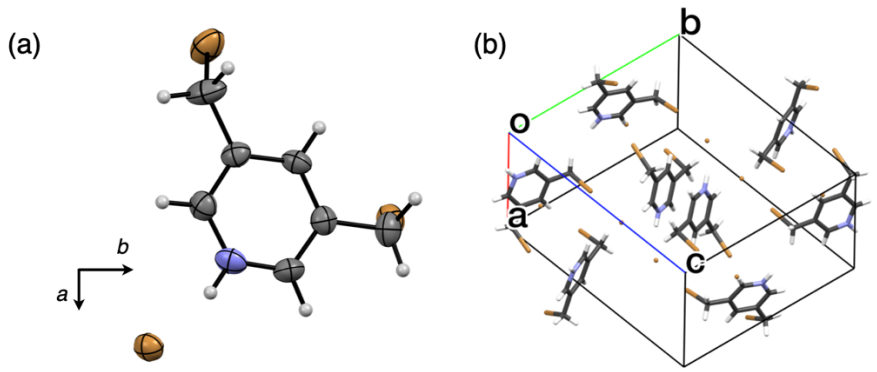


Fig. S12 Crystal structure of BBMP·HBr (**II**, 293 K) obtained from CH_2Cl_2. (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2125695.

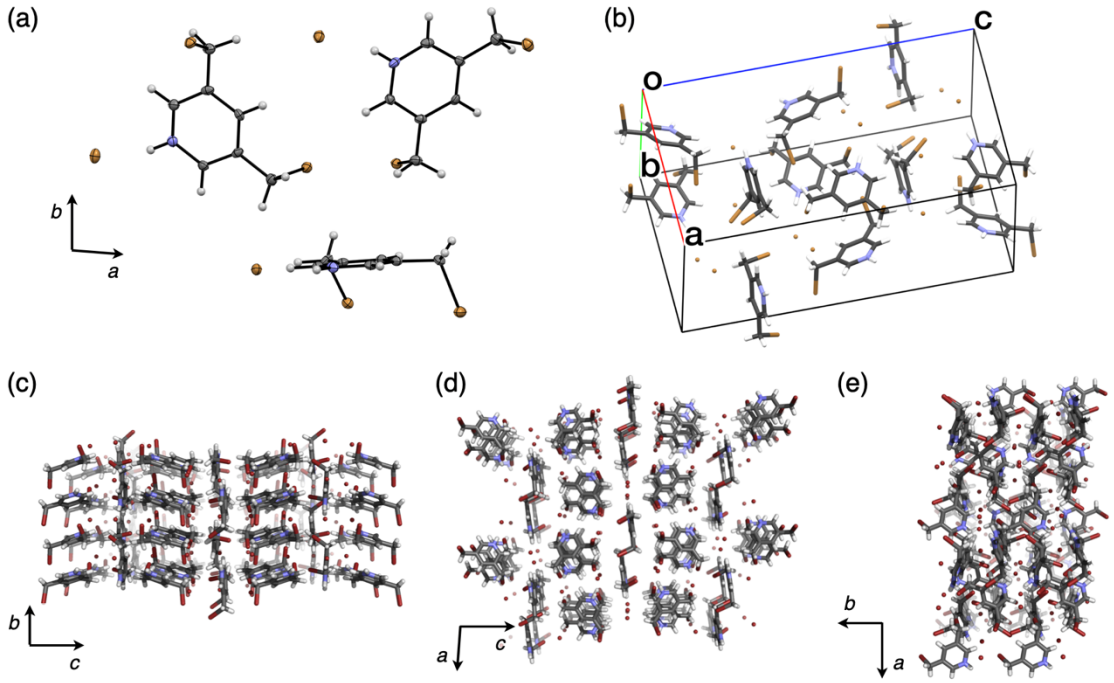


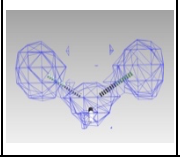
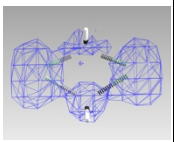
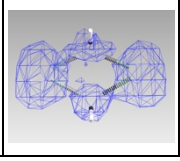
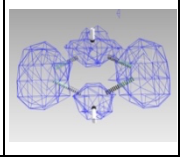
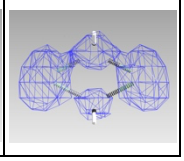
Fig. S13 Crystal structure of BBMP·HBr (**III**, 93 K) obtained from $(CHCl_2)_2$. (a) ORTEP diagram (50% probability). (b) Unit cell structure. Packing structure seen along the (c) *a*-, (d) *b*- and (e) *c*-axes. CCDC 2124418.

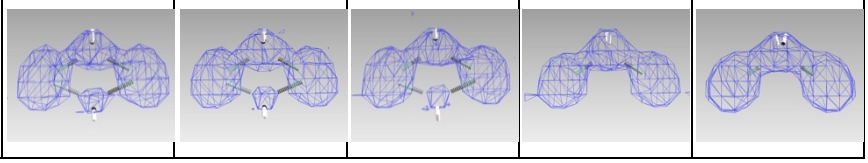
S3. VT-SCXRD analysis

(BBMP·HBr)$_2$⊃CH$_2$Cl$_2$

A colourless plate crystal of (BBMP·HBr)$_2$⊃CH$_2$Cl$_2$ (0.2 × 0.1 × 0.03 mm^3) was mounted on a 150-μm micro mount and irradiated with X-ray while cold N_2 gas was flowing at a constant temperature. After each measurement, the temperature was changed and held at that temperature for 5 to 10 min before the next measurement.

Table S2. Structural parameters for the (BBMP·HBr)$_2$⊃CH$_2$Cl$_2$ crystal observed at each temperature. For all structures, the space group was orthorhombic with *Pccn*.

Temperature / K	148	168	173	178	183
CCDC No.	2124428	2124419	2124420	2124421	2124431
a / Å	23.3045(2)	23.3008(2)	23.3010(2)	23.3004(2)	23.3030(2)
b / Å	11.34090(10)	11.37200(10)	11.37880(10)	11.38610(10)	11.39340(10)
c / Å	8.86430(10)	8.87240(10)	8.87430(10)	8.87680(10)	8.87830(10)
V / Å^3	2342.78(4)	2350.98(4)	2352.91(4)	2355.02(4)	2357.19(4)
R_{int}	0.0280	0.0268	0.0331	0.0290	0.0358
R_1 ($I > 2\sigma(I)$)	0.0346	0.0356	0.0397	0.0377	0.0446
wR_2 (All data)	0.0993	0.0992	0.1090	0.1052	0.1272
GOF	1.053	1.077	1.086	1.062	1.117
Occ. of *V*-CH$_2$Cl$_2$/ %	100	70	65	58	50
Occ. of *Λ*-CH$_2$Cl$_2$ / %	0	30	35	42	50
Electron density map of a CH$_2$Cl$_2$ molecule (> 1.50 e/Å^3)					

Temperature / K	188	193	198	223	293
CCDC No.	2124413	2124412	2124415	2124414	2124417
a / Å	23.3000(2)	23.2933(3)	23.3007(2)	23.3051(2)	23.3401(4)
b / Å	11.40130(10)	11.40910(10)	11.41420(10)	11.43370(10)	11.5126(2)
c / Å	8.88100(10)	8.88390(10)	8.88690(10)	8.89090(10)	8.92070(10)
V / Å^3	2359.24(4)	2360.95(5)	2363.55(4)	2369.10(4)	2397.04(6)
R_{int}	0.0369	0.0246	0.0347	0.0367	0.0217
R_1 ($I > 2\sigma(I)$)	0.0542	0.0375	0.0431	0.0424	0.0393
wR_2 (All data)	0.1577	0.1058	0.1237	0.1192	0.1085
GOF	1.101	1.064	1.061	1.072	1.075
Occ. of *V*-CH_2Cl_2/ %	44	35	35	0	0
Occ. of *Λ*-CH_2Cl_2/ %	56	65	65	100	100
Electron density map of a CH_2Cl_2 molecule (> 1.50 e/Å^3)					

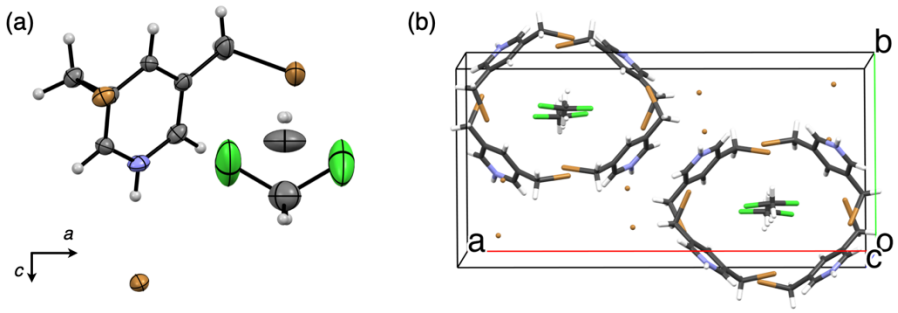


Fig. S14 Crystal structure of (BBMP·HBr)$_2$⊃CH_2Cl_2 (168 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124419.

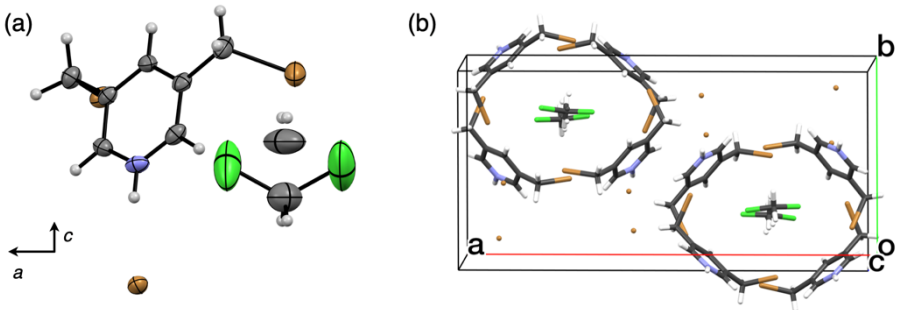


Fig. S15 Crystal structure of (BBMP·HBr)$_2$⊃CH_2Cl_2 (173 K). (a) ORTEP diagram (50% probability).

(b) Unit cell structure. CCDC 2124420.

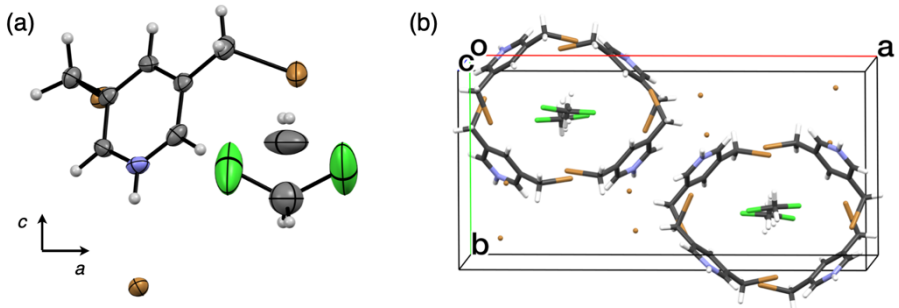


Fig. S16 Crystal structure of $(BBMP \cdot HBr)_2 \supset CH_2Cl_2$ (178 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124421.

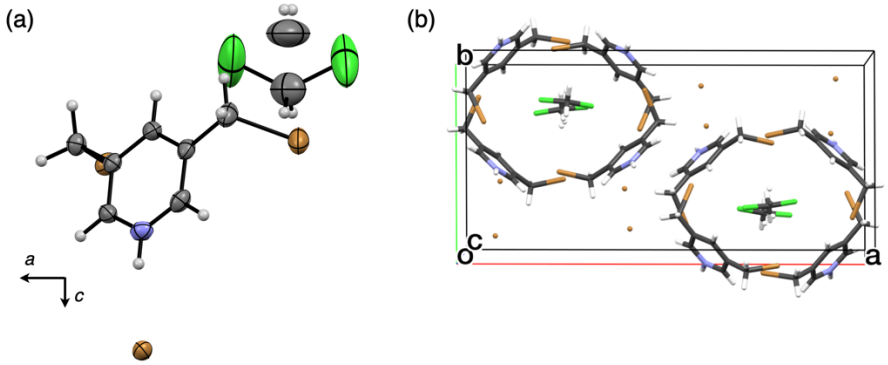


Fig. S17 Crystal structure of $(BBMP \cdot HBr)_2 \supset CH_2Cl_2$ (183 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124431.

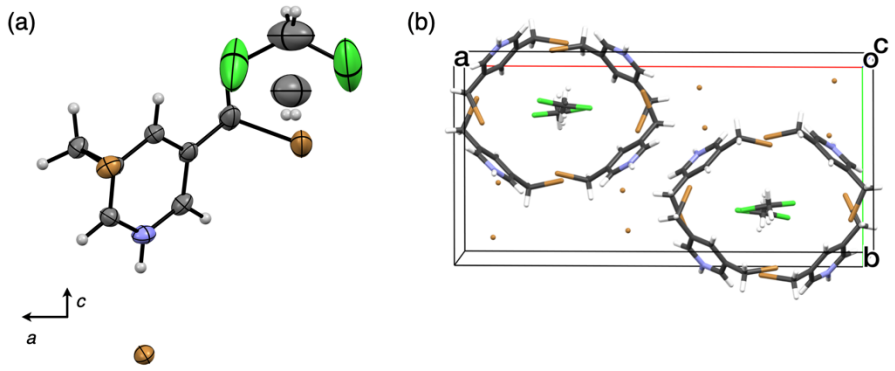


Fig. S18 Crystal structure of $(BBMP \cdot HBr)_2 \supset CH_2Cl_2$ (188 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124413.

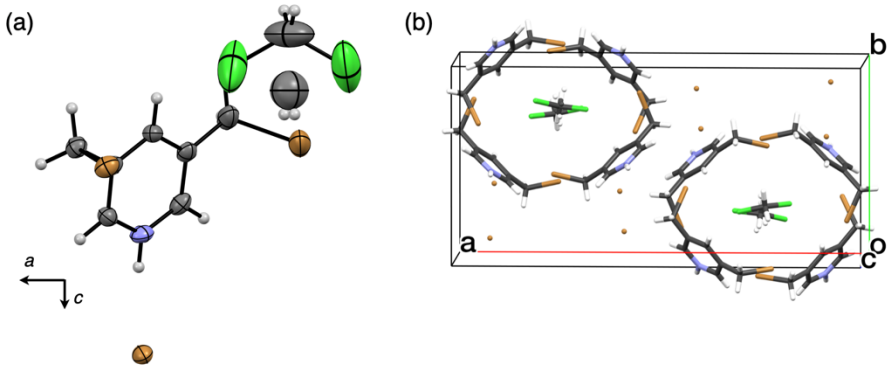


Fig. S19 Crystal structure of $(BBMP \cdot HBr)_2 \supset CH_2Cl_2$ (193 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124412.

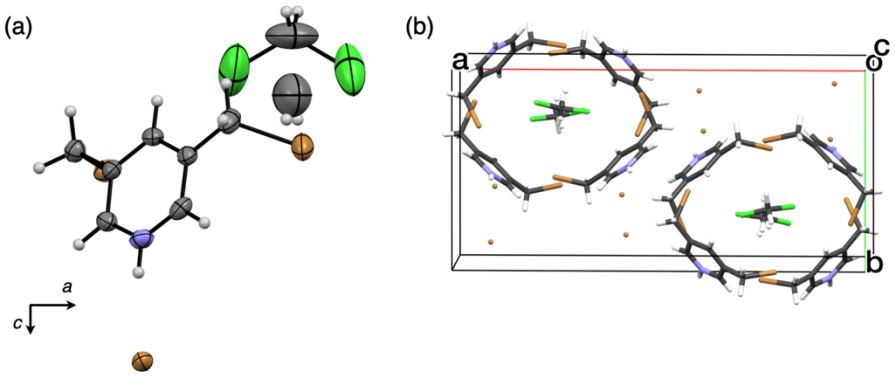


Fig. S20 Crystal structure of $(BBMP \cdot HBr)_2 \supset CH_2Cl_2$ (198 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124415.

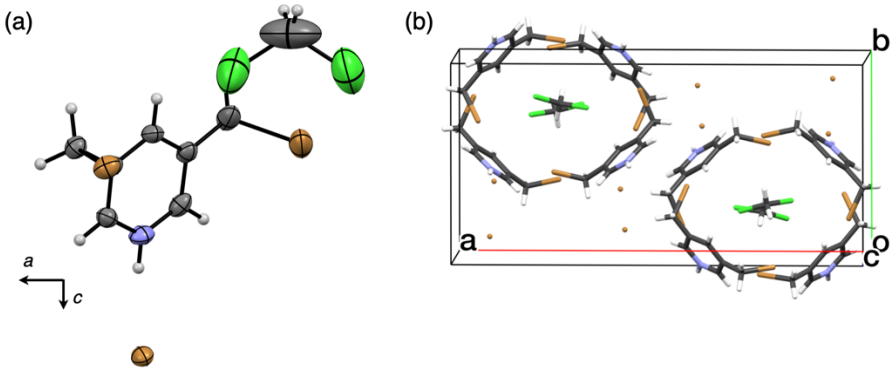


Fig. S21 Crystal structure of $(BBMP \cdot HBr)_2 \supset CH_2Cl_2$ (223 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124414.

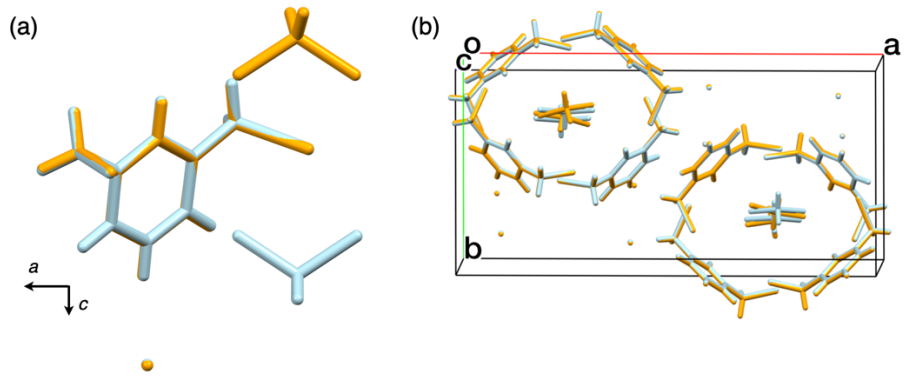


Fig. S22 Overlayed crystal structures of (BBMP·HBr)$_2$⊃CH_2Cl_2 at 148 K (cyan) and 223 K (orange). (a) Stick model of the molecules. (b) Unit cell structures.

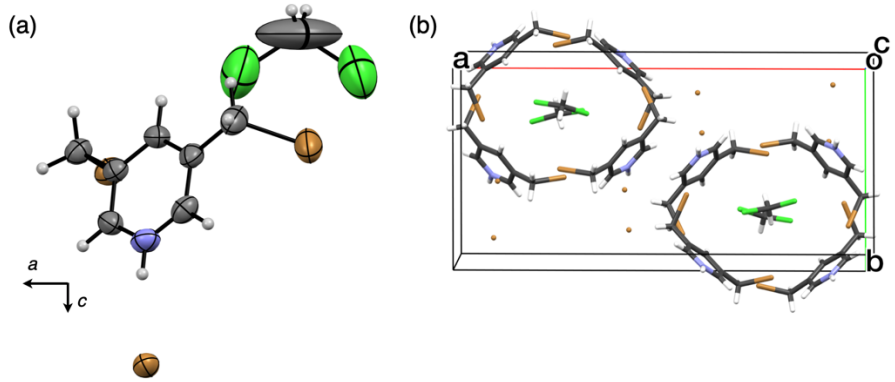
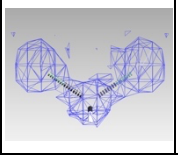
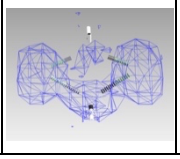
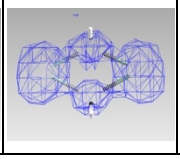
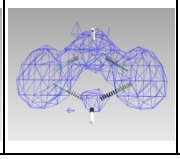
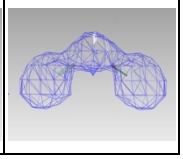


Fig. S23 Crystal structure of (BBMP·HBr)$_2$⊃CH_2Cl_2 (293 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124417.

BBMP·HBr⊃CD_2Cl_2

A colourless plate crystal of (BBMP·HBr)$_2$⊃CD_2Cl_2 (0.35 × 0.18 × 0.05 mm^3) was mounted on a 150-μm micro mount and irradiated with X-ray while cold N_2 gas was flowing at a constant temperature. After each measurement, the temperature was changed and held at that temperature for 5 to 10 min before the next measurement.

Table S3. Structural parameters for the (BBMP·HBr)$_2$⊃CD_2Cl_2 crystal observed at each temperature. For the structures, the space group was orthorhombic with *Pccn*.

Temperature / K	148	193	198	203	223
CCDC No.	2124427	2124425	2124426	2124423	2124424
a / Å	23.3143(5)	23.3229(4)	23.3143(4)	23.3149(5)	23.3005(4)
b / Å	11.3349(3)	11.38030(19)	11.3889(2)	11.3966(3)	11.4213(2)
c / Å	8.8651(2)	8.87309(14)	8.8730(2)	8.87109(18)	8.8820(2)
V / Å^3	2342.74(10)	2355.11(7)	2356.00(8)	2357.14(9)	2363.70(8)
R_{int}	0.0567	0.0527	0.0575	0.0769	0.0726
R_1 ($I > 2\sigma(I)$)	0.0552	0.0560	0.0610	0.0928	0.0811
wR_2 (All data)	0.1598	0.1576	0.1826	0.2658	0.2321
GOF	1.095	1.070	1.066	1.160	1.060
Occ. of *V*-CD_2Cl_2 / %	100	77	55	26	0
Occ. of *A*-CD_2Cl_2 / %	0	23	45	74	100
Electron density map of a CD_2Cl_2 molecule (> 1.50 e/Å^3)					

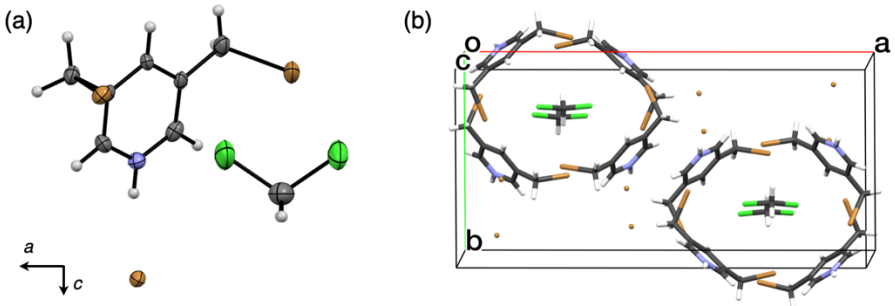


Fig. S24 Crystal structure of (BBMP·HBr)$_2$⊃CD_2Cl_2 (148 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124427.

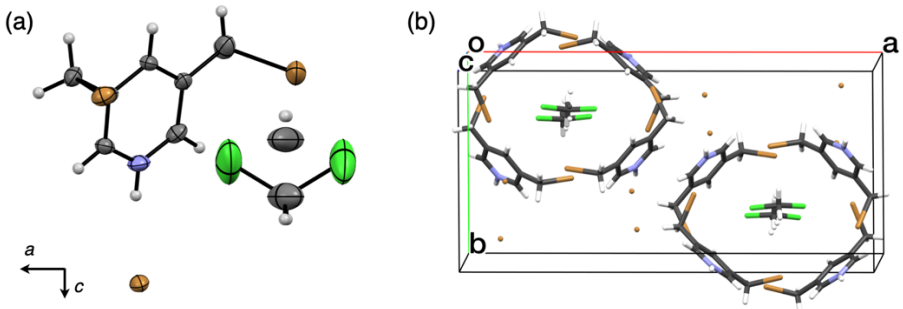


Fig. S25 Crystal structure of $(BBMP{\cdot}HBr)_2{\supset}CD_2Cl_2$ (193 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124425.

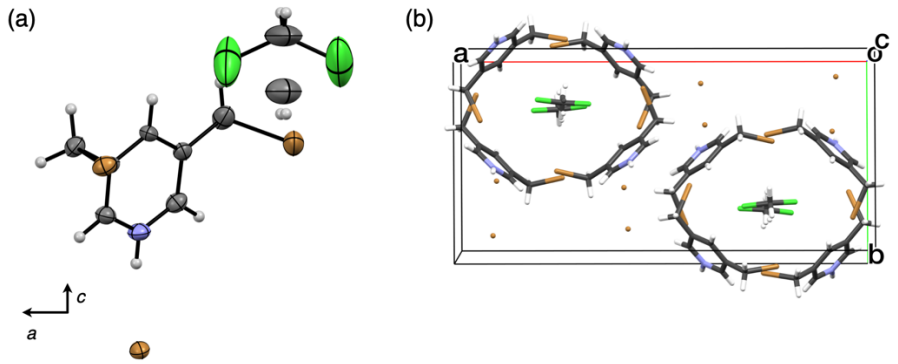


Fig. S26 Crystal structure of $(BBMP{\cdot}HBr)_2{\supset}CD_2Cl_2$ (198 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124426.

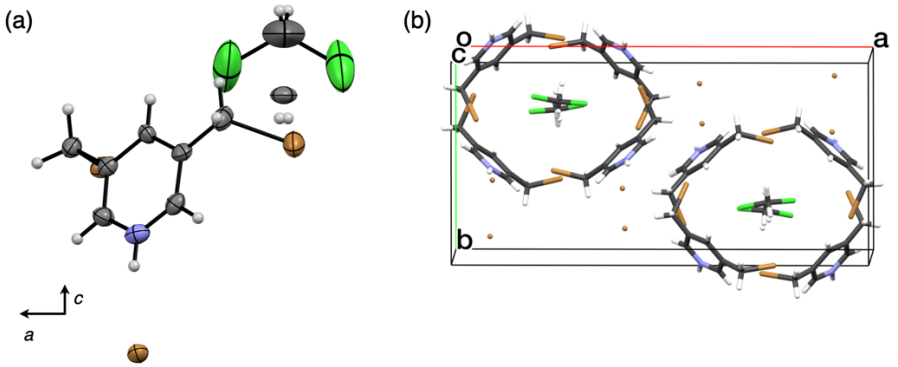


Fig. S27 Crystal structure of $(BBMP{\cdot}HBr)_2{\supset}CD_2Cl_2$ (203 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124423.

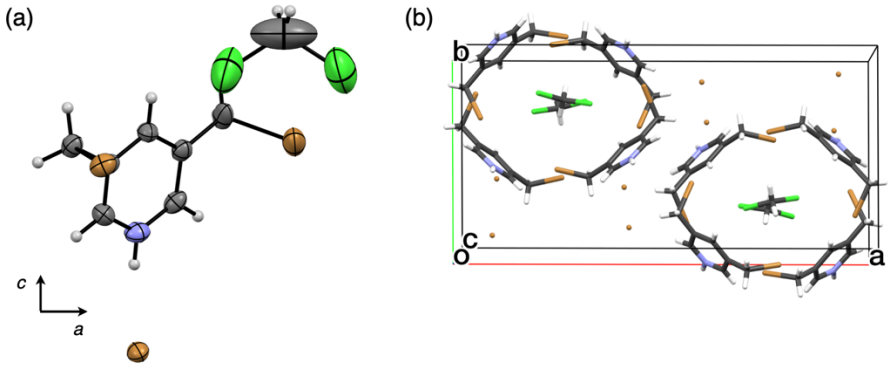
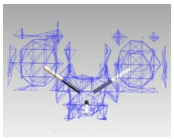
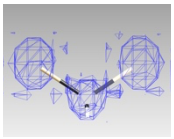
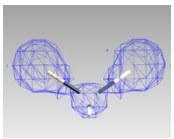


Fig. S28 Crystal structure of $(BBMP \cdot HBr)_2 \supset CD_2Cl_2$ (223 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124424.

BBMP·HBr⊃$\underline{CH_2Br_2}$

A colourless plate crystal of $(BBMP{\cdot}HBr)_2{\supset}CH_2Br_2$ (0.3 × 0.05 × 0.02 mm^3) was mounted on a 150-μm micro mount and irradiated with X-ray while cold N_2 gas was flowing at a aonstant temperature. After each measurement, the temperature was changed and held at that temperature for 10 min before the next measurement.

Table S4. Structural parameters for the $(BBMP{\cdot}HBr)_2{\supset}CH_2Br_2$ crystal observed at each temperature. For the structures, the space group was orthorhombic with *Pccn*.

Temperature / K	148	223	293
CCDC No.	2124430	2124422	2124429
a / Å	23.5252(4)	23.6012(4)	23.7150(8)
b / Å	11.2799(2)	11.3363(2)	11.4034(4)
c / Å	8.9163(2)	8.94002(15)	8.9608(4)
V / $Å^3$	2366.05(8)	2391.89(7)	2423.28(16)
R_{int}	0.0672	0.0418	0.0645
R_1 ($I > 2\sigma(I)$)	0.0458	0.0338	0.0576
wR_2 (All data)	0.1173	0.0953	0.2082
GOF	1.034	1.082	1.131
Occ. of *V*-CH_2Br_2 / %	100	100	100
Occ. of *A*-CH_2Br_2 / %	0	0	0
Electron density map of a CH_2Br_2 molecule (> 1.50 e/$Å^3$)			

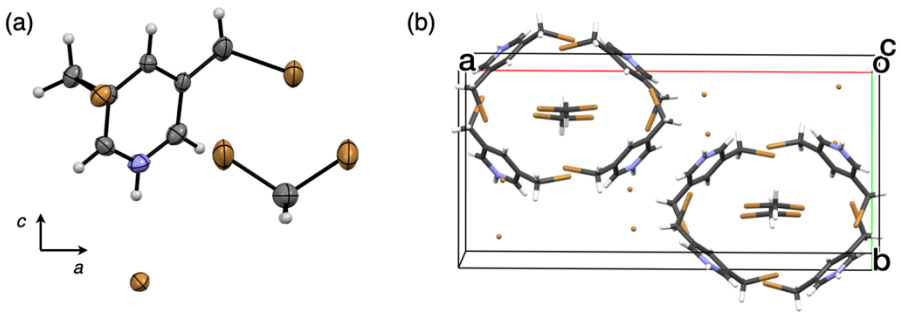


Fig. S29 Crystal structure of $(BBMP{\cdot}HBr)_2{\supset}CH_2Br_2$ (223 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124422.

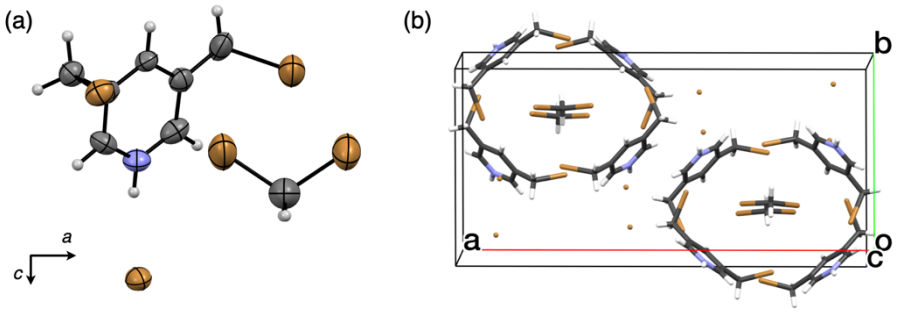


Fig. S30 Crystal structure of $(BBMP \cdot HBr)_2 \supset CH_2Br_2$ (293 K). (a) ORTEP diagram (50% probability). (b) Unit cell structure. CCDC 2124429.

S4. References

1 A.-M. Fuller, D. A. Leigh, P. J. Lusby, I. D. H. Oswald, S. Parsons and D. B. Walker, *Angew. Chem. Int. Ed.*, 2004, **43**, 3914–3918.

2 F. Xue, J. Fang, S. L. Delker, H. Li, P. Martásek, L. J. Roman, T. L. Poulos and R. B. Silverman, *J. Med. Chem.*, 2011, **54**, 2039–2048.

3 S. Monmoton, H. Lefebvre, F. Costa-Torro and A. Fradet, *Macromol. Chem. Phys.*, 2008, **209**, 2382–2389.

4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. a. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

5 G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112–122.

6 C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281–1284.