

## Supplementary Information

### Structure analysis of inclusion crystals of diimide-based macrocycles with halocarbons

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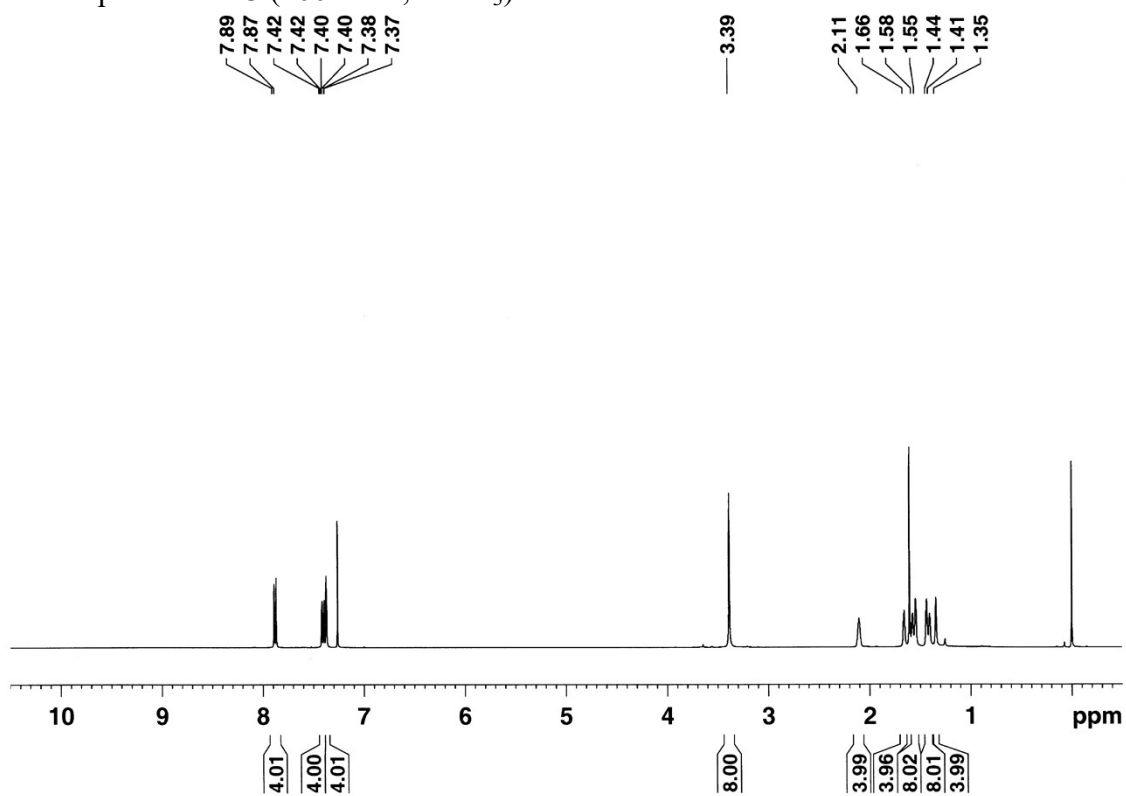
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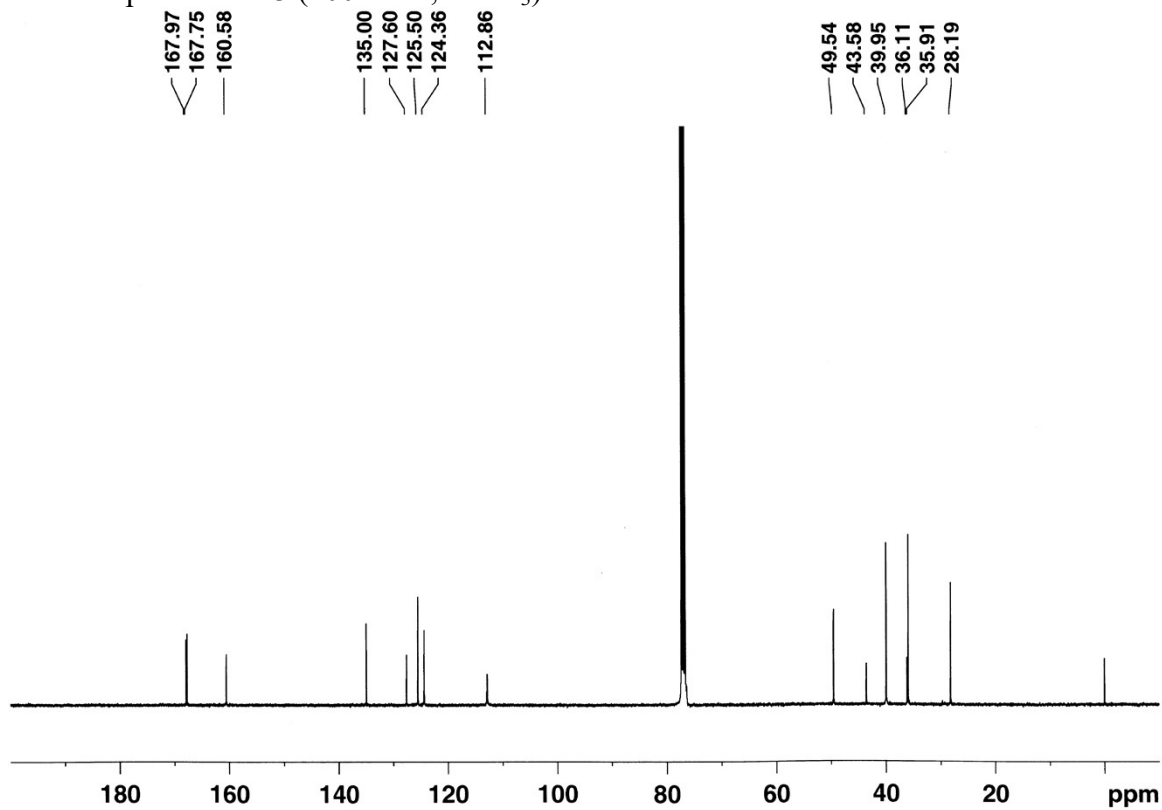
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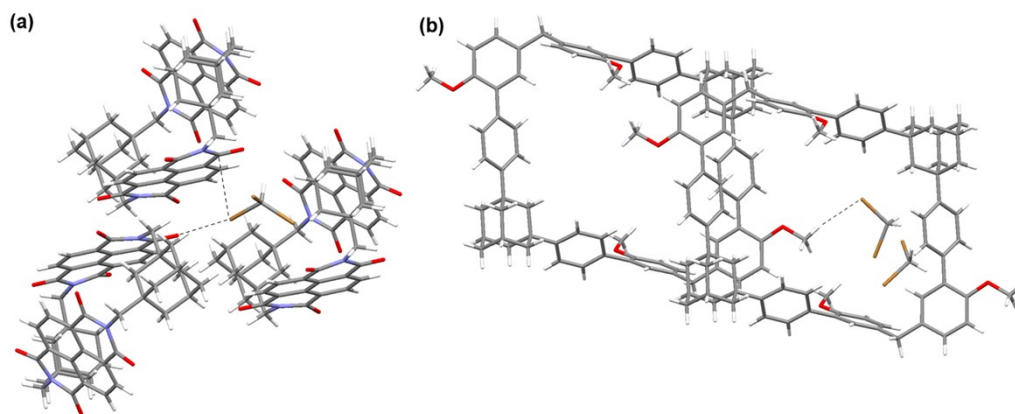
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$^1\text{H}$  NMR spectrum of **3** (400 MHz,  $\text{CDCl}_3$ )

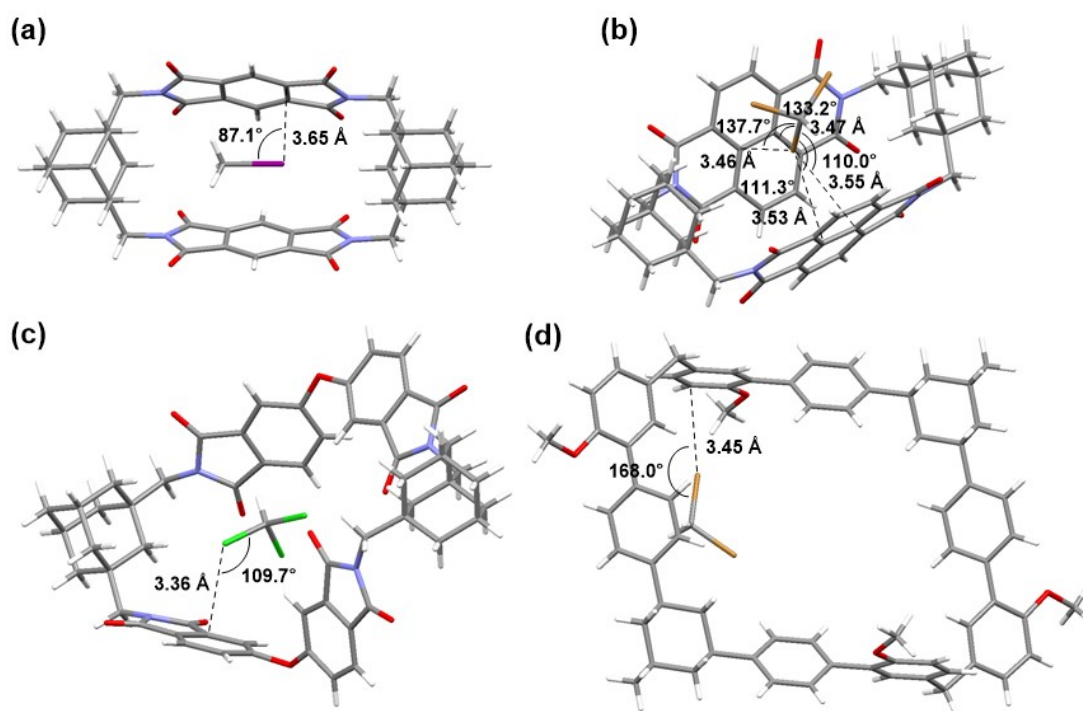


$^{13}\text{C}$  NMR spectrum of **3** (100 MHz,  $\text{CDCl}_3$ )





**Fig. S1** Other halogen-related interactions between halogen atoms and adjacent macrocycles in crystals **2a** (a) and **4a** (b). Disordered atoms and other guests are omitted for clarity. Halogen-related interactions are denoted by dotted lines.



**Fig. S2** Molecular structures of macrocycles and captured guests in crystals (a) **1a**, (b) **2a**, (c) **3a**, and (d) **4a**. Disordered atoms and other guests are omitted for clarity. C–X··· $\pi$  contacts (the closest carbon atoms of aromatic diimides or methoxybiphenyl units) are denoted by dotted lines.

### Single crystal X-ray diffraction experiment for crystal 1a

The colorless prismatic crystal ( $0.200 \times 0.150 \times 0.100 \text{ mm}^3$ ), obtained from vapor diffusion of hexane into a mixture of iodomethane and acetone containing **1**, was immersed in Paratone-N oil and placed in the  $\text{N}_2$  cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE,  $\text{CuK}\alpha$ :  $\lambda = 1.54178 \text{ \AA}$ ). Absorption correction was performed by an empirical method implemented in SADABS.<sup>1</sup> Structure solution and refinement were performed by using SHELXT-2018/2<sup>2</sup> and SHELXL-2018/3<sup>3</sup>.

$\text{C}_{45}\text{H}_{43}\text{IN}_4\text{O}_8$ ,  $M_r = 894.73$ ; monoclinic, space group  $P2_1/c$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.295 \text{ g}\cdot\text{cm}^{-3}$ ,  $a = 18.087(3)$ ,  $b = 16.027(3)$ ,  $c = 16.477(3) \text{ \AA}$ ,  $\beta = 106.124(4)^\circ$ ,  $V = 4588.6(13) \text{ \AA}^3$ , 67015 observed and 9518 independent [ $I > 2\sigma(I)$ ] reflections, 527 parameters, final  $R_1 = 0.0448$ ,  $wR_2 = 0.1505$ ,  $S = 1.095$  [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0489$ ,  $wR_2 = 0.1586$ ,  $S = 1.095$  [all data]. (CCDC 2133051, refined with SQUEEZE).

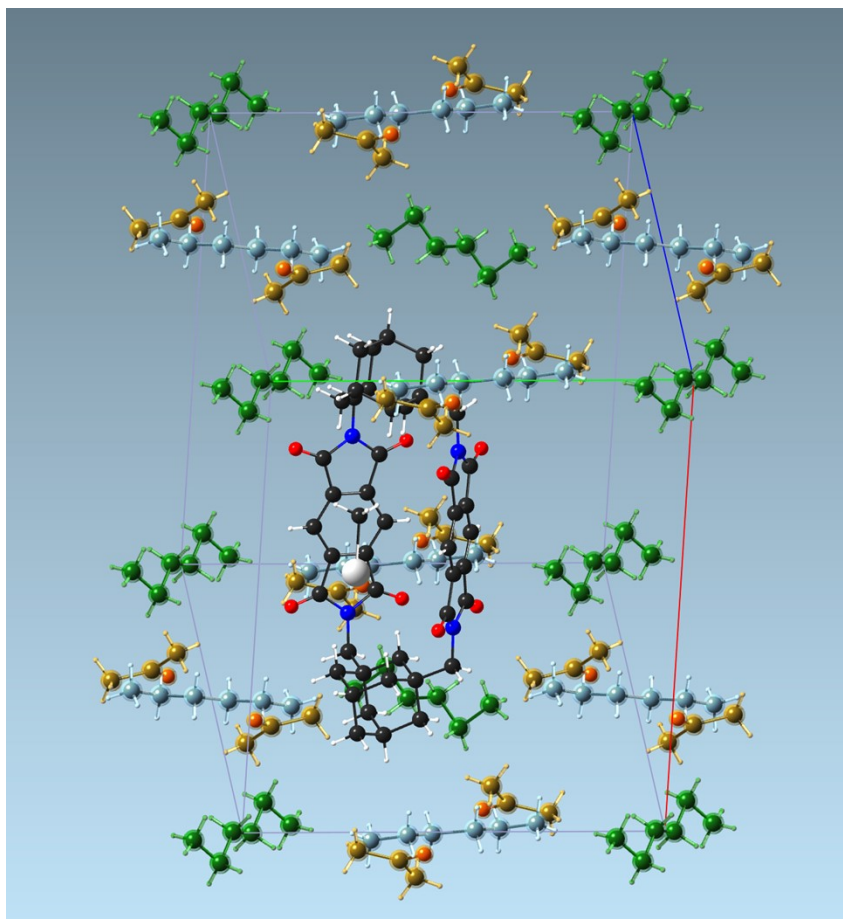
All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23, and 43) with  $U_{\text{iso}}$  values constrained to 1.2/1.5  $U_{\text{eq}}$  of their parent atoms.

The purpose of this refinement is to examine the interactions between the macrocycle host and the iodomethane guest. This crystal structure contains overlapped and highly disordered solvent molecules across the unit cells.

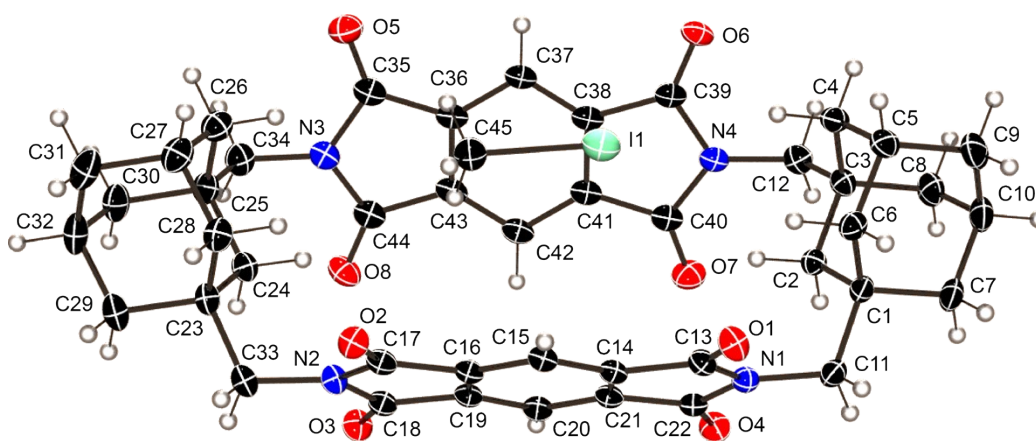
To meet the purpose, at first, the solvent molecules were isotropically refined with DFIX, DANG, EADP, EQIV, FLAT, SADI, SAME and PART, then the structure was converged (Fig. S3, green, light blue and brown molecules) (CCDC 2133052, refined without SQUEEZE). The structure contained 1.6 *n*-hexane molecules and 0.6 acetone molecules can be presented in asymmetric unit. This means 100(400) electrons of solvent molecules contain in one complete unit (in the unit cell,  $Z = 4$ ).

We performed PLATON/SQUEEZE<sup>4</sup> on this structure, excluding solvent molecules. The void volume obtained was  $944 \text{ \AA}^3$  and the unit cell contained 435 electrons.

Finally, PLATON/SQUEEZE data was refined to give the final structure. We believe the final structure meets the purpose of this refinement (Fig. S4).



**Fig. S3** Overlapped and disordered solvent molecules in the unit cell (green and light blue: *n*-hexane, brown: acetone).



**Fig. S4** ORTEP drawing of **1** and iodomethane in crystal **1a** (50% probability).

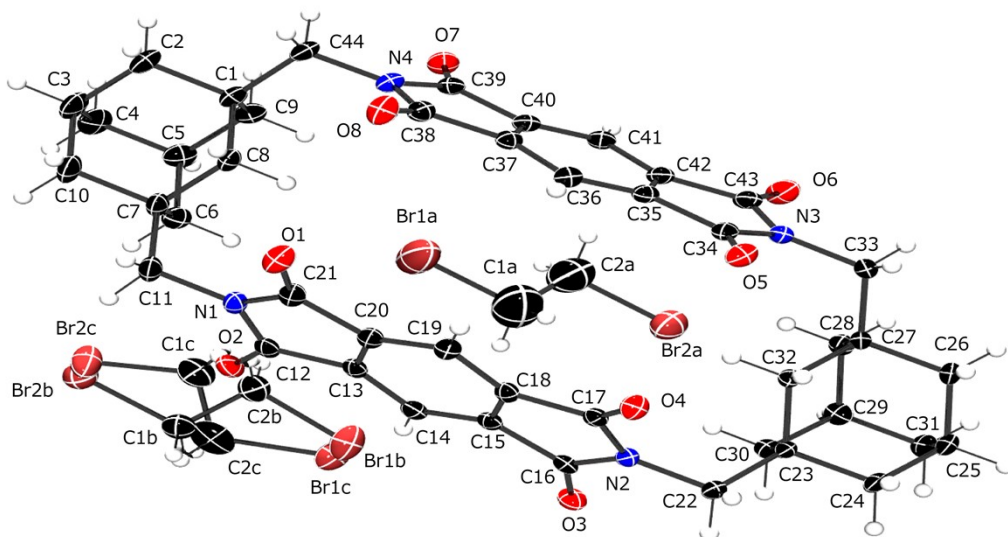
### Single crystal X-ray diffraction experiment for crystal 1b

The colorless prismatic crystal ( $0.120 \times 0.100 \times 0.050 \text{ mm}^3$ ), obtained from vapor diffusion of hexane into a 1,2-dibromoethane solution of **1**, was immersed in Paraton-N oil and placed in the  $\text{N}_2$  cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE,  $\text{CuK}\alpha$ :  $\lambda = 1.54178 \text{ \AA}$ ). Absorption correction was performed by an empirical method implemented in SADABS.<sup>1</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>2</sup> and SHELXL-2018/3<sup>3</sup>.

$\text{C}_{48}\text{H}_{48}\text{Br}_4\text{N}_4\text{O}_8$ ,  $M_r = 1128.54$ ; monoclinic, space group  $P2_1/c$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.616 \text{ g}\cdot\text{cm}^{-3}$ ,  $a = 14.5014(16)$ ,  $b = 13.1843(15)$ ,  $c = 24.596(3) \text{ \AA}$ ,  $\beta = 99.374(4)^\circ$ ,  $V = 4639.8(9) \text{ \AA}^3$ , 62659 observed and 8711 independent [ $I > 2\sigma(I)$ ] reflections, 614 parameters, final  $R_1 = 0.0465$ ,  $wR_2 = 0.1389$ ,  $S = 1.069$  [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0505$ ,  $wR_2 = 0.1421$ ,  $S = 1.069$  [all data]. CCDC 2133054.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 23, and 43) with  $U_{\text{iso}}$  values constrained to  $1.2 U_{\text{eq}}$  of their parent atoms.

The crystal contained two 1,2-dibromoethane molecules in three positions in the unit cell. One 1,2-dibromoethane molecule (Br1a, Br2a, C1a, C2a) encapsulated in the host molecule is normally refined with the occupancy of 100%. Two disordered 1,2-dibromoethane molecules (Br1b, Br2b, C1b, C2b and Br1c, Br2c, C1c, C2c) filled in the void space are refined with the occupancy of 75.3 and 24.7% (combination with PART -n), respectively.



**Fig. S5** ORTEP drawing of **1** and 1,2-dibromoethane in crystal **1b** (50% probability).

## Single crystal X-ray diffraction experiment for crystal **2a**

The colorless prismatic crystal ( $0.120 \times 0.120 \times 0.100 \text{ mm}^3$ ), obtained from vapor diffusion of hexane into a bromoform solution of **2**, was immersed in Paraton-N oil and placed in the  $\text{N}_2$  cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE,  $\text{CuK}\alpha$ :  $\lambda = 1.54178 \text{ \AA}$ ). Absorption correction was performed by an empirical method implemented in SCALE3 ABSPACK. Structure solution and refinement were performed by using SHELXT-2018/2<sup>2</sup> and SHELXL-2018/3<sup>3</sup>.

$\text{C}_{55}\text{H}_{47}\text{Br}_9\text{N}_4\text{O}_8$ ,  $M_r = 1611.15$ ; triclinic, space group  $P-1$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.953 \text{ g}\cdot\text{cm}^{-3}$ ,  $a = 9.8012(3)$ ,  $b = 15.8268(4)$ ,  $c = 18.8202(4) \text{ \AA}$ ,  $\alpha = 87.366(2)$ ,  $\beta = 80.576(2)$ ,  $\gamma = 72.004(2)^\circ$ ,  $V = 2739.09(13) \text{ \AA}^3$ , 32381 observed and 10016 independent [ $I > 2\sigma(I)$ ] reflections, 759 parameters, 24 restraints, final  $R_1 = 0.0859$ ,  $wR_2 = 0.2184$ ,  $S = 1.051$  [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0899$ ,  $wR_2 = 0.2232$ ,  $S = 1.051$  [all data]. CCDC 2133053.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 23, and 43) with  $U_{\text{iso}}$  values constrained to  $1.2 U_{\text{eq}}$  of their parent atoms. The disordered bromoform molecules were refined with PART, SAME and ISOR. A total of three bromoform molecules was included in the asymmetric unit.

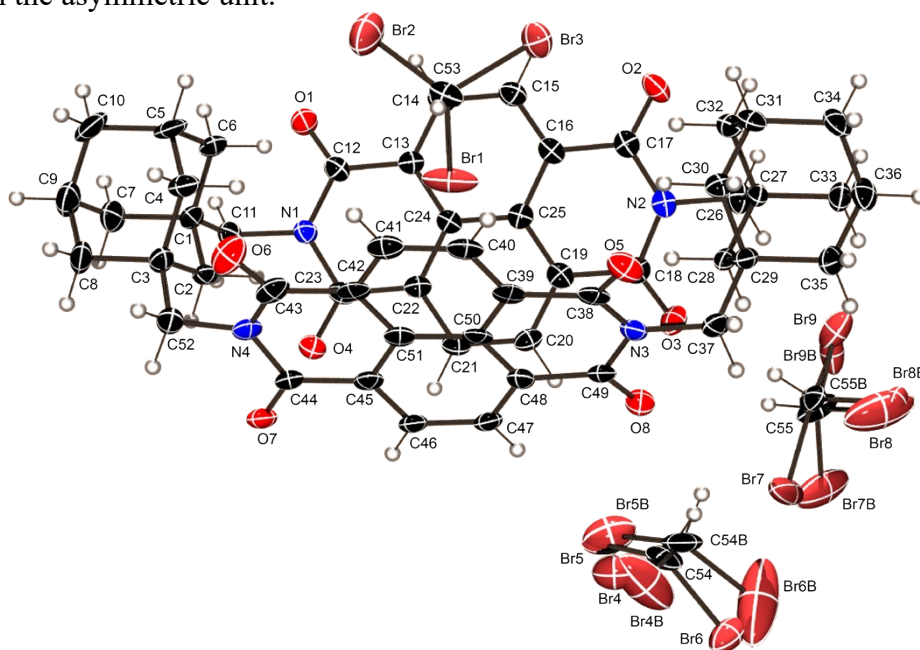


Fig. S6 ORTEP drawing of **2** and bromoform in crystal **2a** (50% probability).



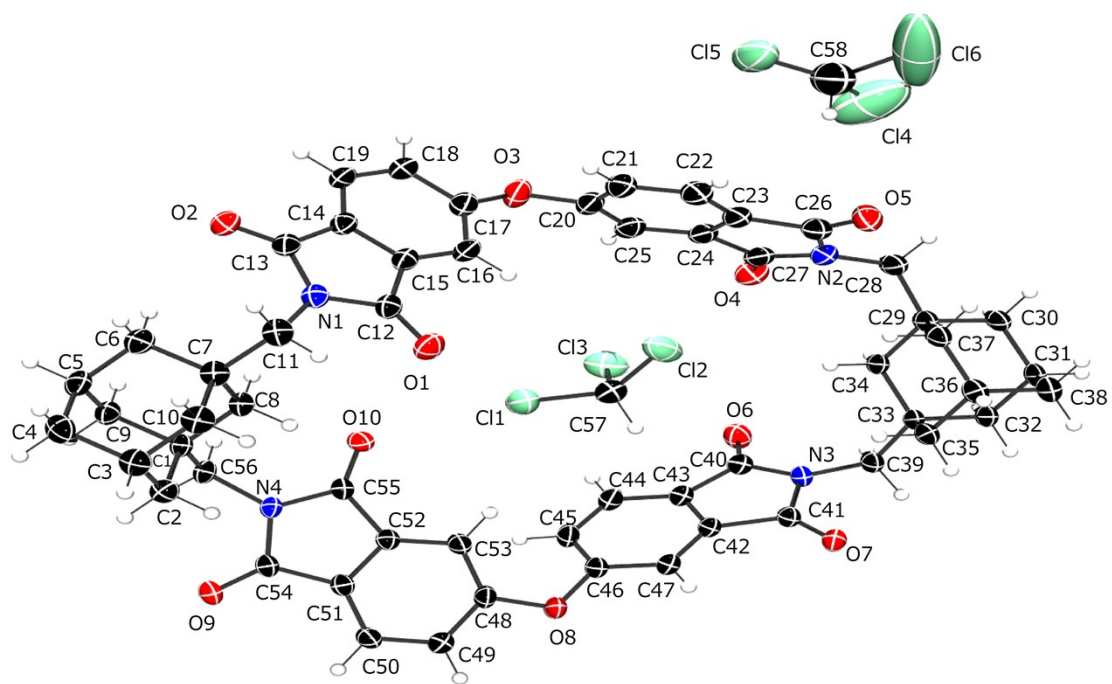
### Single crystal X-ray diffraction experiment for crystal 3a

The colorless prismatic crystal ( $0.080 \times 0.060 \times 0.020 \text{ mm}^3$ ), obtained from vapor diffusion of hexane into a chloroform solution of **3**, was immersed in Paraton-N oil and placed in the N<sub>2</sub> cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK $\alpha$ :  $\lambda = 1.54178 \text{ \AA}$ ). Absorption correction was performed by an empirical method implemented in SADABS.<sup>1</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>2</sup> and SHELXL-2018/3<sup>3</sup>.

C<sub>57.5</sub>H<sub>49.5</sub>Cl<sub>4.5</sub>N<sub>4</sub>O<sub>10</sub>,  $M_r = 1116.03$ ; monoclinic, space group  $P2_1/n$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.429 \text{ g}\cdot\text{cm}^{-3}$ ,  $a = 24.0138(10)$ ,  $b = 7.9580(3)$ ,  $c = 27.4313(12) \text{ \AA}$ ,  $\beta = 98.369(2)^\circ$ ,  $V = 5186.3(4) \text{ \AA}^3$ , 60354 observed and 7759 independent [ $I > 2\sigma(I)$ ] reflections, 703 parameters, final  $R_1 = 0.0640$ ,  $wR_2 = 0.1633$ ,  $S = 1.035$  [ $I > 2\sigma(I)$ ] and  $R_1 = 0.1018$ ,  $wR_2 = 0.1796$ ,  $S = 1.035$  [all data]. CCDC 2133056.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 23, and 43) with  $U_{\text{iso}}$  values constrained to 1.2  $U_{\text{eq}}$  of their parent atoms.

A total of 1.5 chloroform molecule was contained in the asymmetric cell. One chloroform molecule (C57, C11, C12, C13) encapsulated in the host molecule is normally refined with the occupancy of 100%. The other chloroform molecule (C58, C14, C15, C16) lied near a symmetric center was firstly refined with the free variable and finally fixed with the site occupancy of 50% (combination with PART -n).



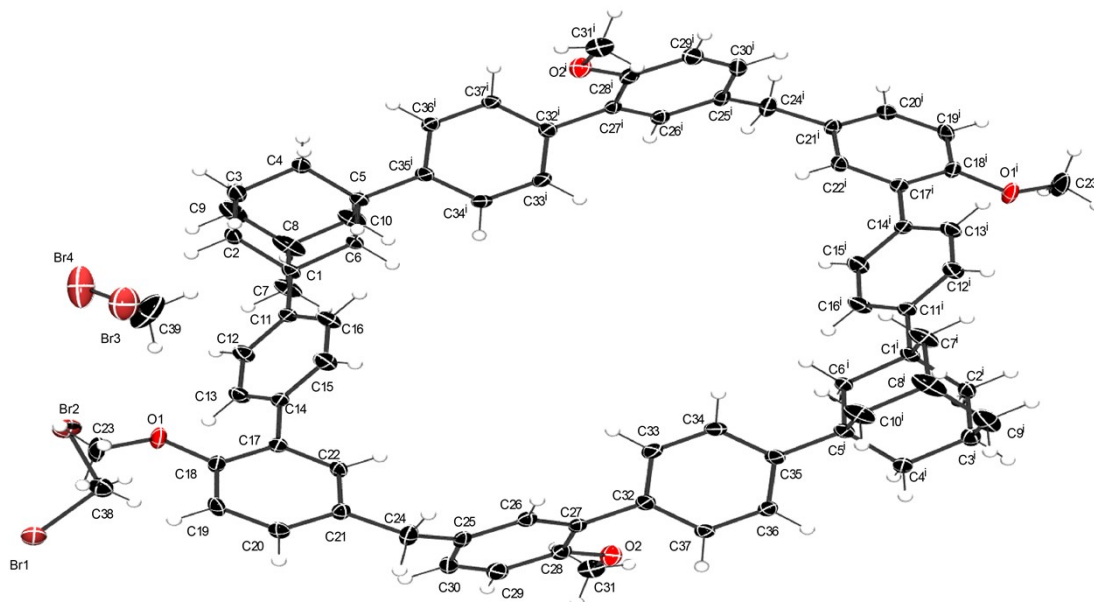
**Fig. S7** ORTEP drawing of **3** and chloroform in crystal **3a** (50% probability).

## Single crystal X-ray diffraction experiment for crystal **4a**

The colorless prismatic crystal ( $0.110 \times 0.100 \times 0.100 \text{ mm}^3$ ), obtained from vapor diffusion of *n*-hexane into a dibromomethane solution of **4**, was immersed in Paraton-N oil and placed in the  $\text{N}_2$  cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE,  $\text{CuK}\alpha$ :  $\lambda = 1.54178 \text{ \AA}$ ). Absorption correction was performed by an empirical method implemented in SADABS.<sup>1</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>2</sup> and SHELXL-2018/3<sup>3</sup>.

$\text{C}_{78}\text{H}_{80}\text{Br}_8\text{O}_4$ ,  $M_r = 1720.70$ ; triclinic, space group  $P-1$ ,  $Z = 1$ ,  $D_{\text{calc}} = 1.641 \text{ g}\cdot\text{cm}^{-3}$ ,  $a = 10.3961(12)$ ,  $b = 11.9472(13)$ ,  $c = 14.8227(16) \text{ \AA}$ ,  $\alpha = 101.231(3)$ ,  $\beta = 104.003(3)$ ,  $\gamma = 93.302(3)^\circ$ ,  $V = 1741.5(3) \text{ \AA}^3$ , 23618 observed and 6695 independent [ $I > 2\sigma(I)$ ] reflections, 408 parameters, final  $R_1 = 0.0474$ ,  $wR_2 = 0.1210$ ,  $S = 1.111$  [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0488$ ,  $wR_2 = 0.1220$ ,  $S = 1.111$  [all data]. CCDC 2133055.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23, and 43) with  $U_{\text{iso}}$  values constrained to 1.2/1.5  $U_{\text{eq}}$  of their parent atoms.



**Fig. S8** ORTEP drawing of **4** and dibromomethane in crystal **4a** (50% probability).

## References

- (1) G. M. Sheldrick, *SADABS*. University of Göttingen, Germany, 1996.
- (2) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3–8.
- (3) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.
- (4) A. L. Spek, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 9–18.