

Supplementary Information

Solvent-dependent alignments and halogen-related interactions in inclusion crystals of adamantane-based macrocycle with pyridazine moieties

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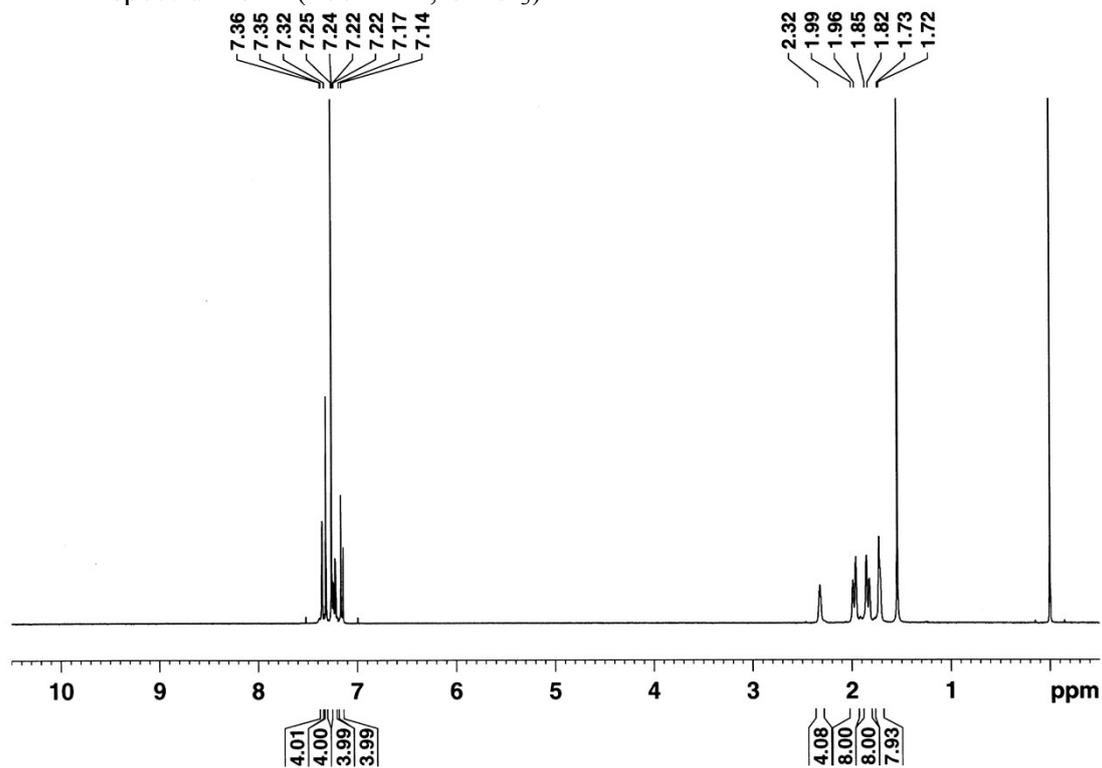
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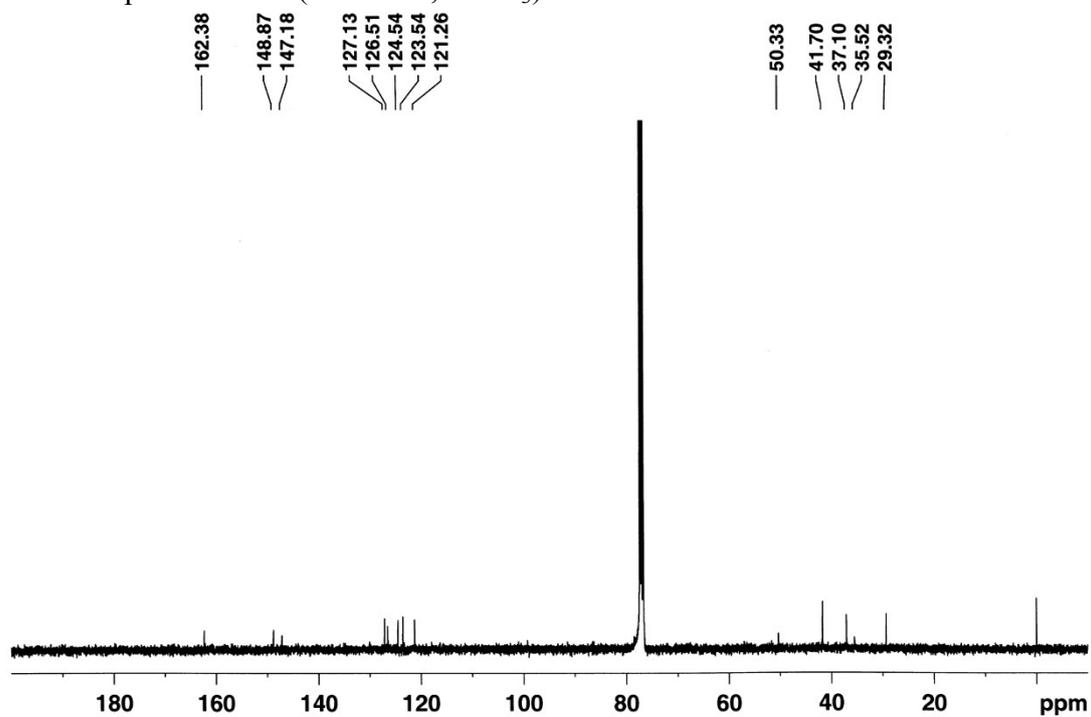
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^1H NMR spectrum of **1** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **1** (100 MHz, CDCl_3)



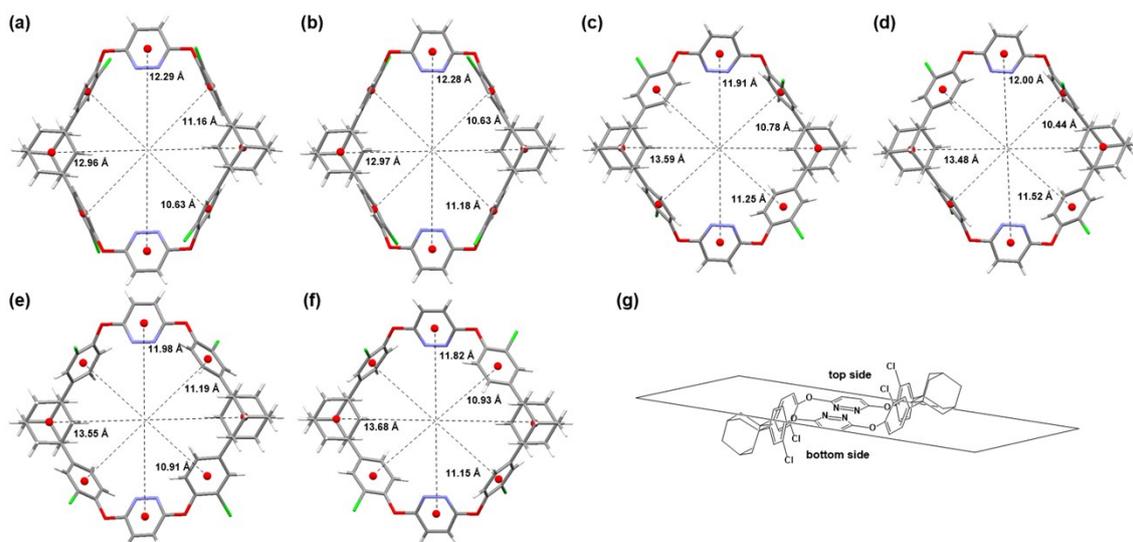


Fig. S1 The centroid-centroid distances between each aromatic and aliphatic moieties in crystals (a) **1a**, (b) **1b**, (c) **1c**, (d) **1d**, (e) **1e**, and (f) **1f**. Solvents and disordered atoms are omitted for clarity. (g) Schematic representation of position of chlorine atoms in **1**.

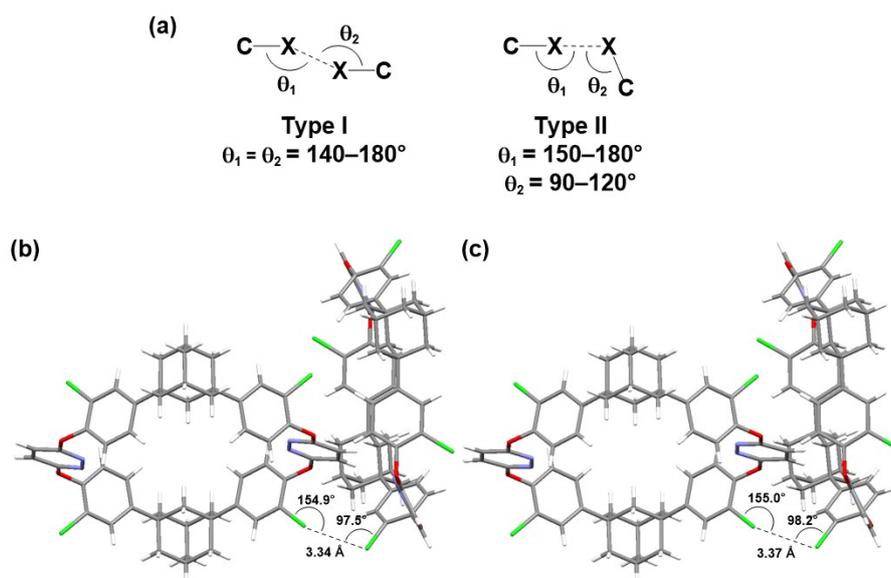


Fig. S2 (a) Halogen...halogen interactions. The angles and the distances of the intermolecular halogen...halogen interactions in crystals (b) **1a** and (c) **1b**. Halogen...halogen interactions are shown in the dotted lines. Cyclic ethers are omitted for clarity.

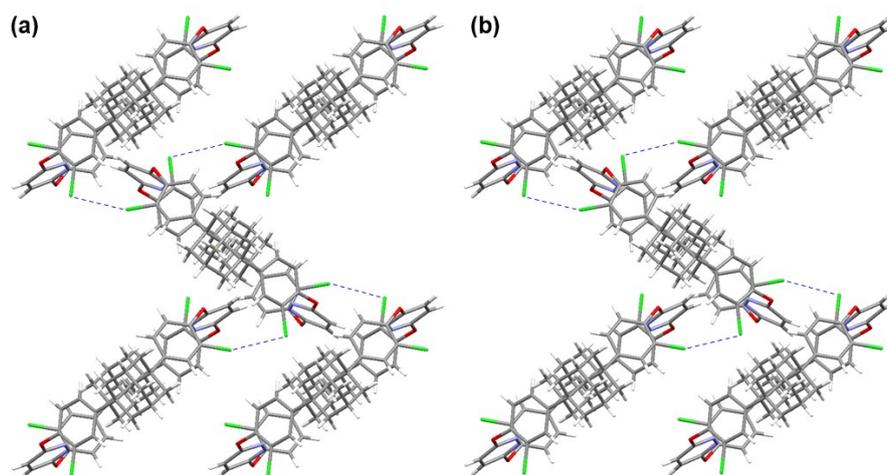


Fig. S3 Halogen \cdots halogen interactions between the chlorine atoms of **1** in network structures of crystals (a) **1a** and (b) **1b**. Halogen \cdots halogen interactions are shown in the blue dotted lines. Cyclic ethers are omitted for clarity.

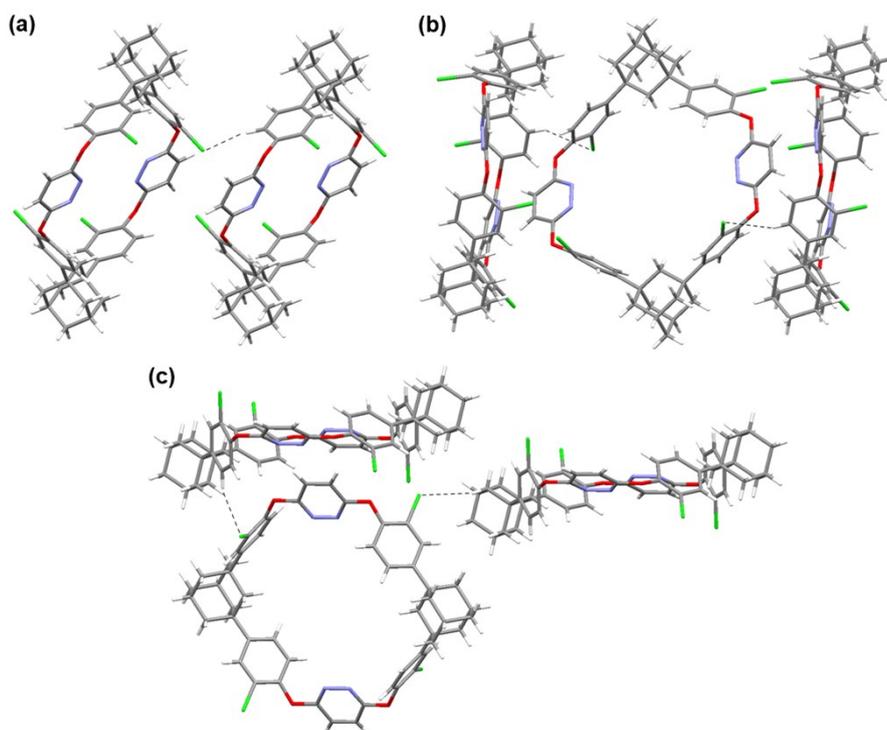


Fig. S4 CH \cdots Cl interactions in crystals (a) **1d**, (b) **1e**, and (c) **1f**. CH \cdots Cl interactions are shown in the dotted lines. Guest molecules and disordered atoms are omitted for clarity.

Single crystal X-ray diffraction experiment for crystal 1a

The colorless prismatic crystal ($0.200 \times 0.100 \times 0.100 \text{ mm}^3$), obtained from bicyclohexyl/1,4-dioxane, was immersed in Paraton-N oil and placed in the 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.¹ Structure solution and refinement were performed by using SHELXT-2014/5² and SHELXL-2018/3³.

$\text{C}_{64}\text{H}_{68}\text{Cl}_4\text{N}_4\text{O}_{10}$, $M_r = 1195.02$; monoclinic, space group $P2_1/c$, $Z = 2$, $D_{\text{calc}} = 1.404 \text{ g}\cdot\text{cm}^{-3}$, $a = 17.217(3)$, $b = 11.2747(18)$, $c = 16.415(3) \text{ \AA}$, $\beta = 117.459(3)^\circ$, $V = 2827.4(8) \text{ \AA}^3$, 35202 measured and 5851 independent [$I > 2\sigma(I)$] reflections, 370 parameters, final $R_1 = 0.0312$, $wR_2 = 0.0892$, $S = 1.150$ [$I > 2\sigma(I)$]. CCDC 2025175

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically placed on the calculated positions using a riding model (AFIX 13, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. Two 1,4-dioxane molecules found were refined as follows. The 1,4-dioxane molecule (C27-C30, and O3-O4) was normally refined. Another 1,4-dioxane molecule (C31-C32, and O5) lied on a symmetric center was firstly refined with the free variable and finally fixed with the site occupancy factor of 1.0.

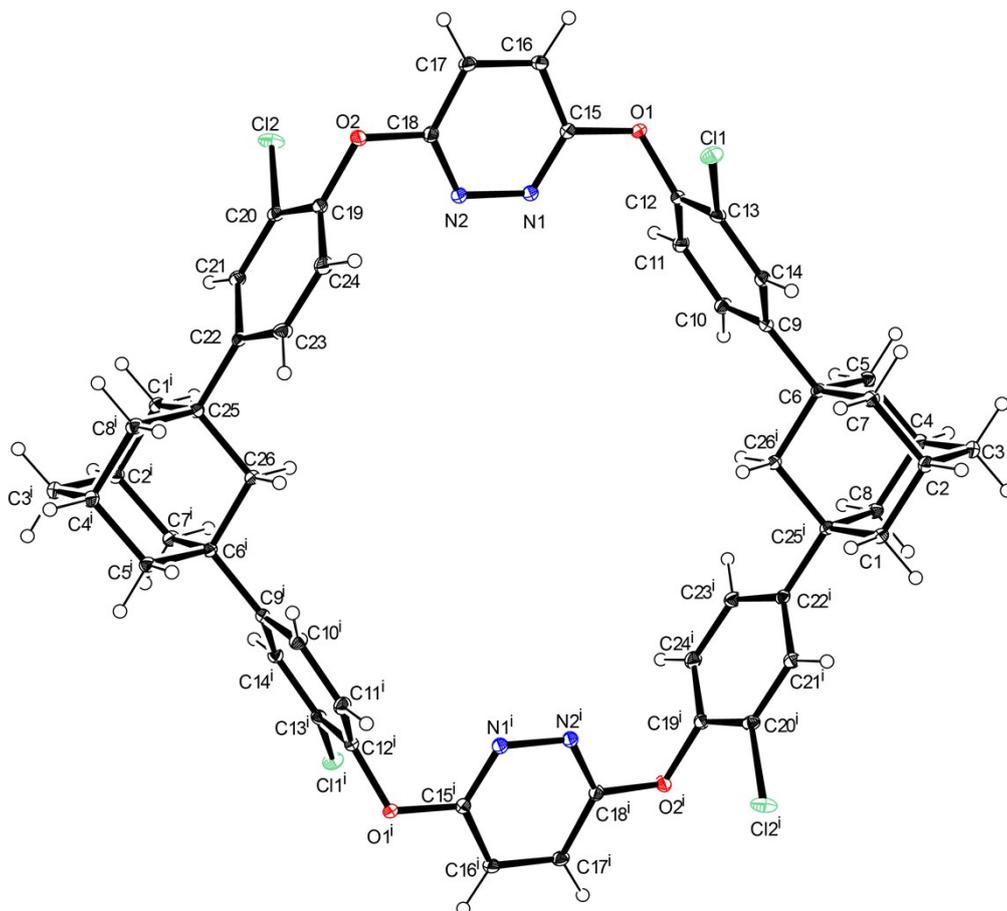


Fig. S5 Ortep drawing of macrocycle in crystal **1a** (30% probability).

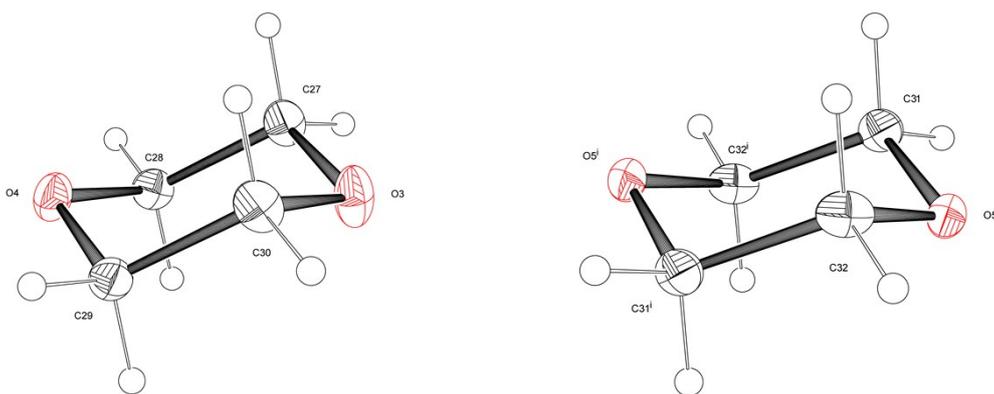


Fig. S6 Ortep drawing of 1,4-dioxane in crystal **1a** (30% probability).

Single crystal X-ray diffraction experiment for crystal 1b

The colorless prismatic crystal ($0.120 \times 0.100 \times 0.100 \text{ mm}^3$), obtained from cyclohexane/tetrahydrofuran, was immersed in Paraton-N oil and placed in the 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.¹ Structure solution and refinement were performed by using SHELXT-2014/5² and SHELXL-2018/3³.

$\text{C}_{64}\text{H}_{68}\text{Cl}_4\text{N}_4\text{O}_7$, $M_r = 1147.02$; monoclinic, space group $P2_1/c$, $Z = 2$, $D_{\text{calc}} = 1.364 \text{ g}\cdot\text{cm}^{-3}$, $a = 17.1722(16)$, $b = 11.3008(10)$, $c = 16.1727(15) \text{ \AA}$, $\beta = 117.160(2)^\circ$, $V = 2792.4(4) \text{ \AA}^3$, 36622 measured and 5721 independent [$I > 2\sigma(I)$] reflections, 380 parameters, 9 restraints, final $R_1 = 0.0463$, $wR_2 = 0.1454$, $S = 1.154$ [$I > 2\sigma(I)$]. CCDC 2025176

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_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. Two tetrahydrofuran molecules found were refined as follows. The tetrahydrofuran molecule (C27-C30, and O3) was normally refined. The overlapped and disordered tetrahydrofuran (C31-C34, and O4) in which the centroid of this molecule is riding on a symmetric center were refined with PART n, and occupancy ratio was 0.5:0.5. DELU, DFIX and SIMU was applied to C31-C32.

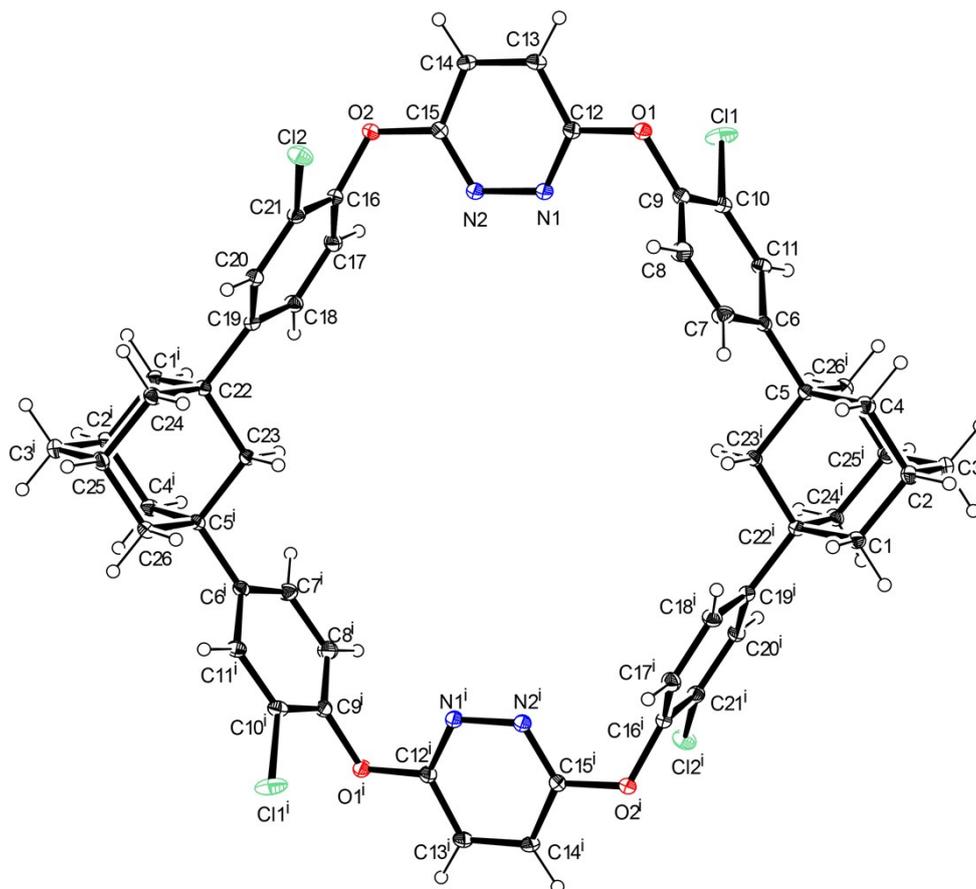


Fig. S7 Ortep drawing of macrocycle in crystal **1b** (30% probability).

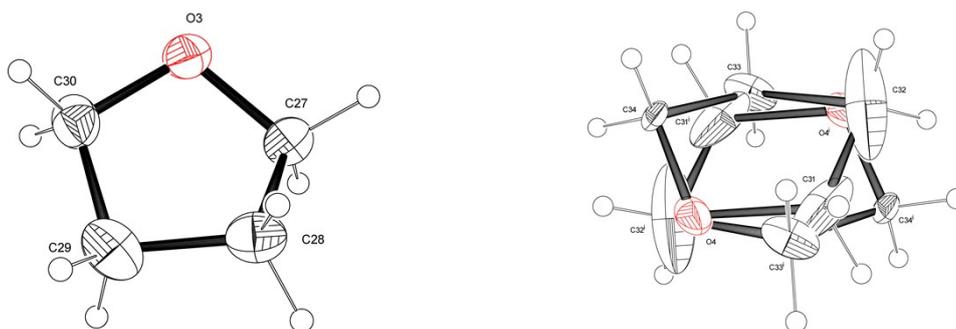


Fig. S8 Ortep drawing of tetrahydrofuran in crystal **1b** (30% probability).

Single crystal X-ray diffraction experiment for crystal 1c

The colorless prismatic crystal ($0.120 \times 0.100 \times 0.100 \text{ mm}^3$), obtained from *p*-xylene/tetrahydrofuran, was immersed in Paraton-N oil and placed in the 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.¹ Structure solution and refinement were performed by using SHELXT-2014/5² and SHELXL-2018/3³.

$\text{C}_{60}\text{H}_{54}\text{Cl}_4\text{N}_4\text{O}_4$, $M_r = 1036.87$; monoclinic, space group $P2_1/c$, $Z = 2$, $D_{\text{calc}} = 1.382 \text{ g}\cdot\text{cm}^{-3}$, $a = 16.5240(14)$, $b = 13.9309(12)$, $c = 11.3445(9) \text{ \AA}$, $\beta = 107.390(3)^\circ$, $V = 2492.1(4) \text{ \AA}^3$, 28692 measured and 4926 independent [$I > 2\sigma(I)$] reflections, 336 parameters, final $R_1 = 0.0643$, $wR_2 = 0.1706$, $S = 1.070$ [$I > 2\sigma(I)$]. CCDC 2025177

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_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. One chlorine atom is disordered to two positions (Cl1 and Cl3). The occupancies of the disordered atoms are refined (0.73 and 0.27). The *p*-xylene molecule lied on a symmetric center was firstly refined with the free variable and finally fixed with the site occupancy factor of 1.0.

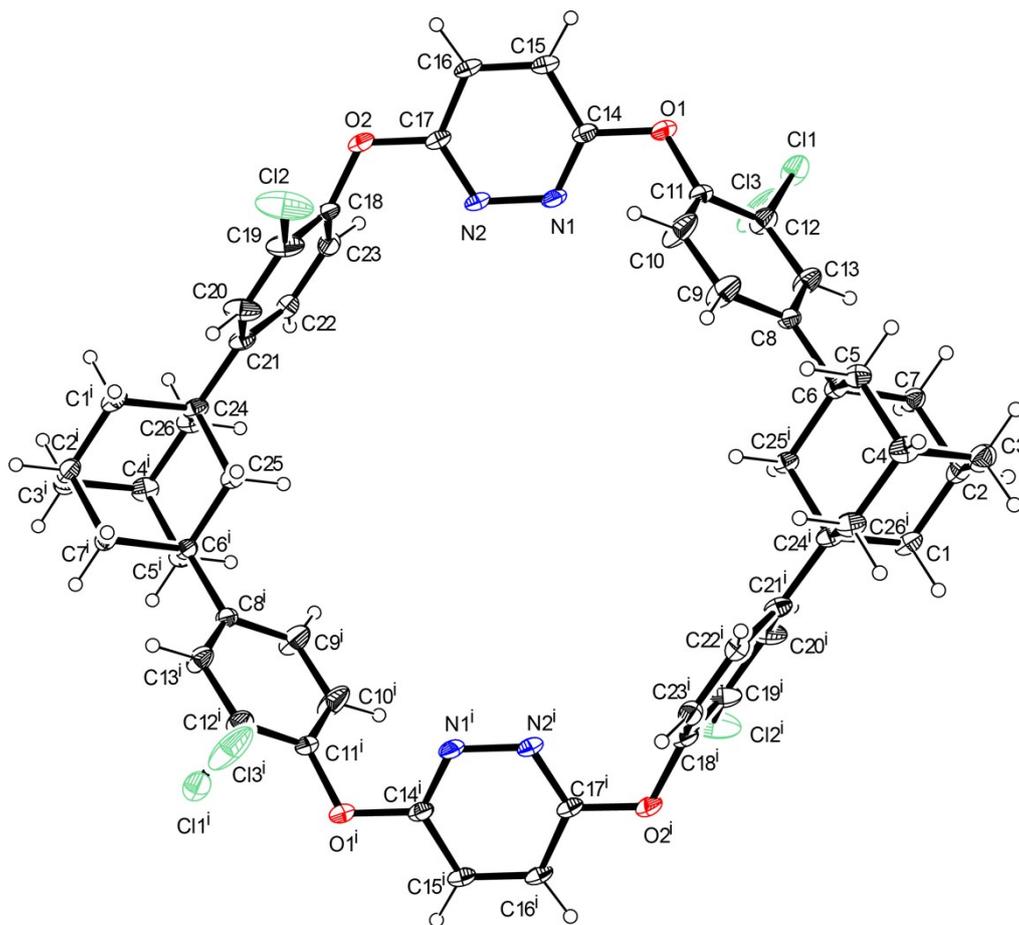


Fig. S9 Ortep drawing of macrocycle in crystal **1c** (30% probability).

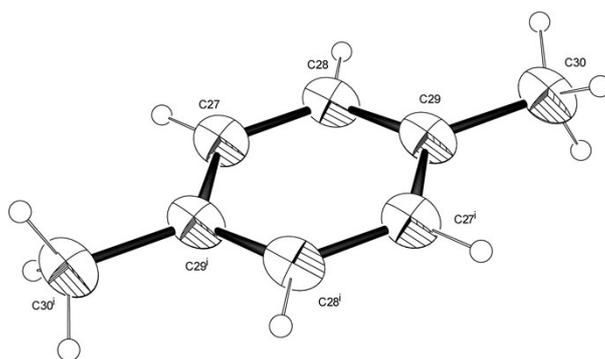


Fig. S10 Ortep drawing of *p*-xylene of crystal **1c** (30% probability).

Single crystal X-ray diffraction experiment for crystal 1d

The colorless prismatic crystal ($0.200 \times 0.100 \times 0.100 \text{ mm}^3$), obtained from toluene/tetrahydrofuran, was immersed in Paraton-N oil and placed in the 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.¹ Structure solution and refinement were performed by using SHELXT-2014/5² and SHELXL-2018/3³.

$\text{C}_{59}\text{H}_{52}\text{Cl}_4\text{N}_4\text{O}_4$, $M_r = 1022.84$; orthorhombic, space group $Pbca$, $Z = 4$, $D_{\text{calc}} = 1.391 \text{ g}\cdot\text{cm}^{-3}$, $a = 13.6415(17)$, $b = 11.1851(14)$, $c = 32.017(4) \text{ \AA}$, $V = 4885.2(10) \text{ \AA}^3$, 62640 measured and 5118 independent [$I > 2\sigma(I)$] reflections, 365 parameters, 1 restraints, final $R_1 = 0.0631$, $wR_2 = 0.1729$, $S = 1.288$ [$I > 2\sigma(I)$]. CCDC 2025178

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_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. One chlorine atom is disordered to two positions (Cl1a and Cl1b). The occupancies of the disordered atoms are refined (0.53 and 0.47). The toluene molecule lied on a symmetric center was firstly refined with free variable and finally fixed with the occupancy of 0.5 (combination with PART -n).

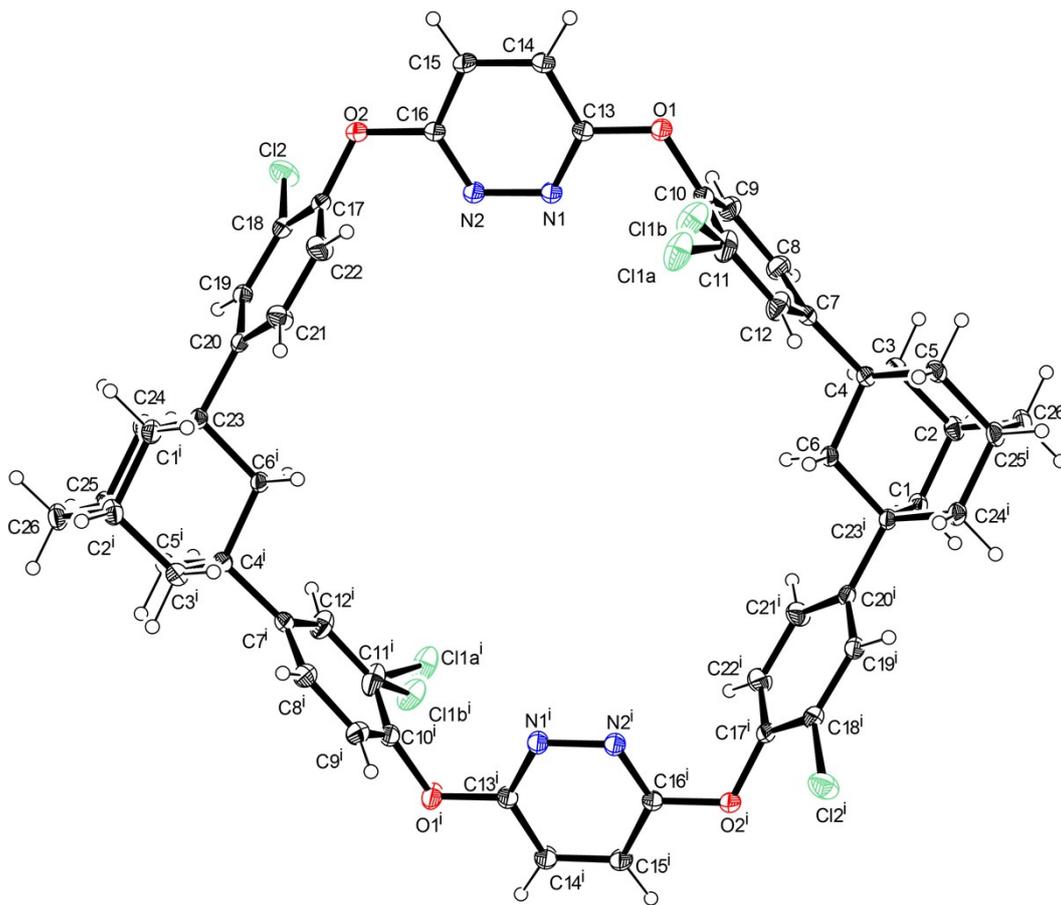


Fig. S11 Ortep drawing of macrocycle in crystal **1d** (30% probability).

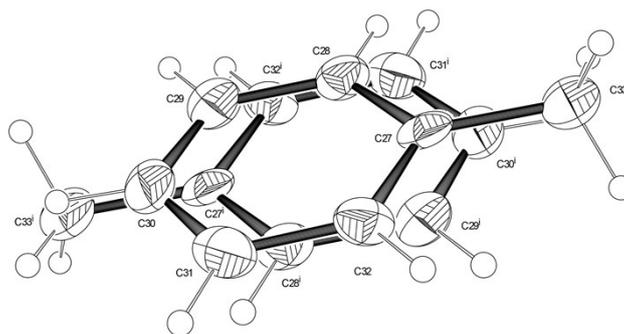


Fig. S12 Ortep drawing of toluene in crystal **1d** (30% probability).

Single crystal X-ray diffraction experiment for crystal 1e

The colorless prismatic crystal ($0.100 \times 0.050 \times 0.050 \text{ mm}^3$), obtained from acetone/chloroform, was immersed in Paraton-N oil and placed in the 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.¹ Structure solution and refinement were performed by using SHELXT-2014/5² and SHELXL-2018/3³.

$\text{C}_{54}\text{H}_{46}\text{Cl}_{10}\text{N}_4\text{O}_4$, $M_r = 1169.45$; orthorhombic, space group $P2_12_12_1$, $Z = 4$, $D_{\text{calc}} = 1.518 \text{ g}\cdot\text{cm}^{-3}$, $a = 11.8817(5)$, $b = 13.9512(6)$, $c = 30.8666(13) \text{ \AA}$, $V = 5116.6(4) \text{ \AA}^3$, 60546 measured and 7493 independent [$I > 2\sigma(I)$] reflections, 659 parameters, final $R_1 = 0.0584$, $wR_2 = 0.1336$, $S = 1.030$ [$I > 2\sigma(I)$]. CCDC 2025179

All non-hydrogen atoms including two chloroform molecules were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. One chlorine atom in the host molecule is disordered to two positions (Cl1a and Cl1b). The occupancies of the disordered atoms are refined (0.57 and 0.43).

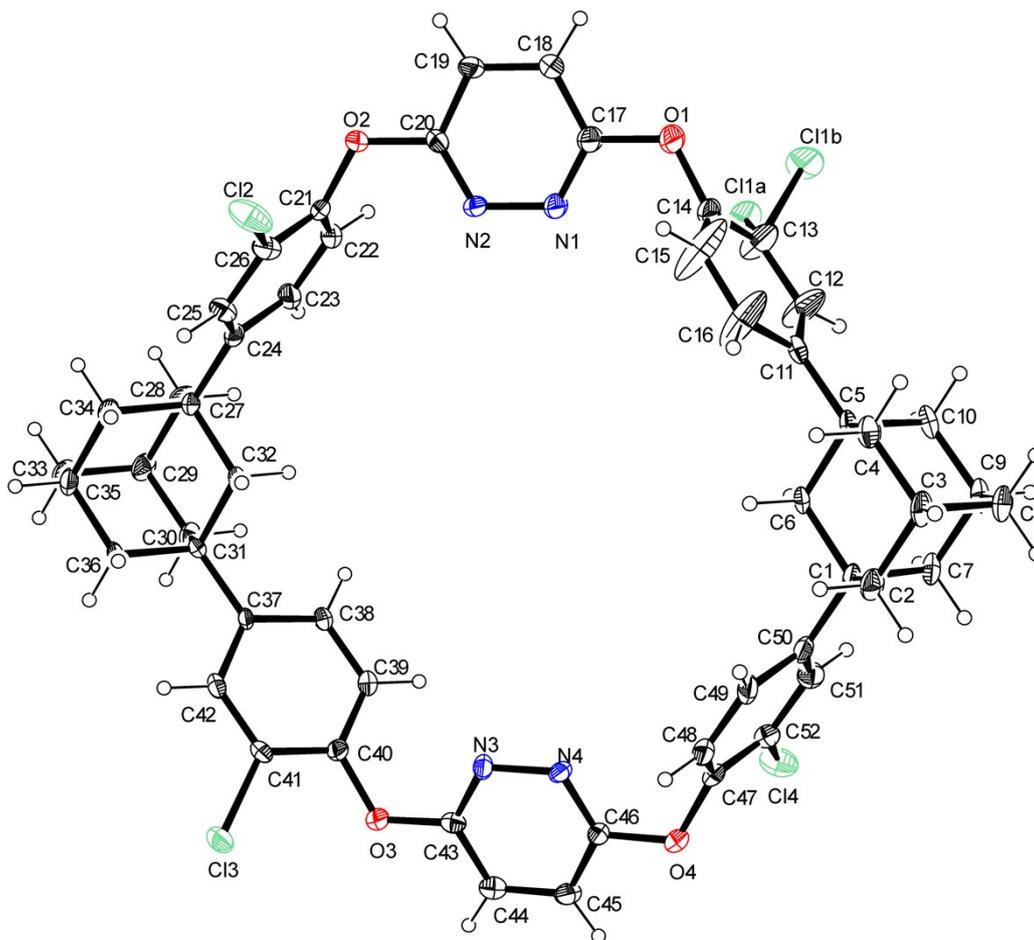


Fig. S13 Ortep drawing of macrocycle in crystal **1e** (30% probability).

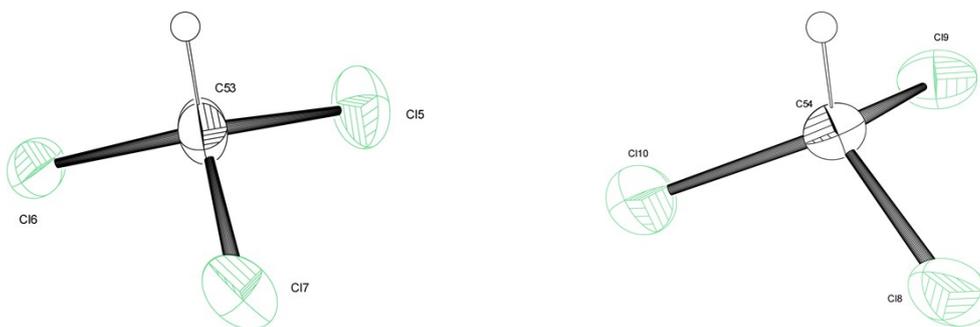


Fig. S14 Ortep drawing of chloroform in crystal **1e** (30% probability).

Single crystal X-ray diffraction experiment for crystal 1f

The colorless prismatic crystal ($0.300 \times 0.200 \times 0.100 \text{ mm}^3$), obtained from hexane/dichloromethane was immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. The diffraction experiment was performed in a Bruker APEX II system (APEX II CCD detector, $\text{MoK}\alpha$: $\lambda = 0.71073 \text{ \AA}$) Absorption correction was performed by an empirical method implemented in SADABS.¹ Structure solution and refinement were performed by using SHELXT-2014/5² and SHELXL-2018/3³.

$\text{C}_{54}\text{H}_{48}\text{Cl}_8\text{N}_4\text{O}_4$, $M_r = 1100.56$; monoclinic, space group $P2_1/c$, $Z = 2$, $D_{\text{calc}} = 1.461 \text{ g}\cdot\text{cm}^{-3}$, $a = 16.397(4)$, $b = 13.840(3)$, $c = 11.647(3) \text{ \AA}$, $\beta = 108.793(3)^\circ$, $V = 2502.1(10) \text{ \AA}^3$, 22485 measured and 3020 independent [$I > 2\sigma(I)$] reflections, 344 parameters, final $R_1 = 0.0552$, $wR_2 = 0.1480$, $S = 1.037$ [$I > 2\sigma(I)$]. CCDC 2025180

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_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. Disordered and overlapped two dichloromethane molecules, C27, Cl3, Cl4 and C28, Cl5, Cl6, were refined by PART with occupancies of 0.72 and 0.28, respectively.

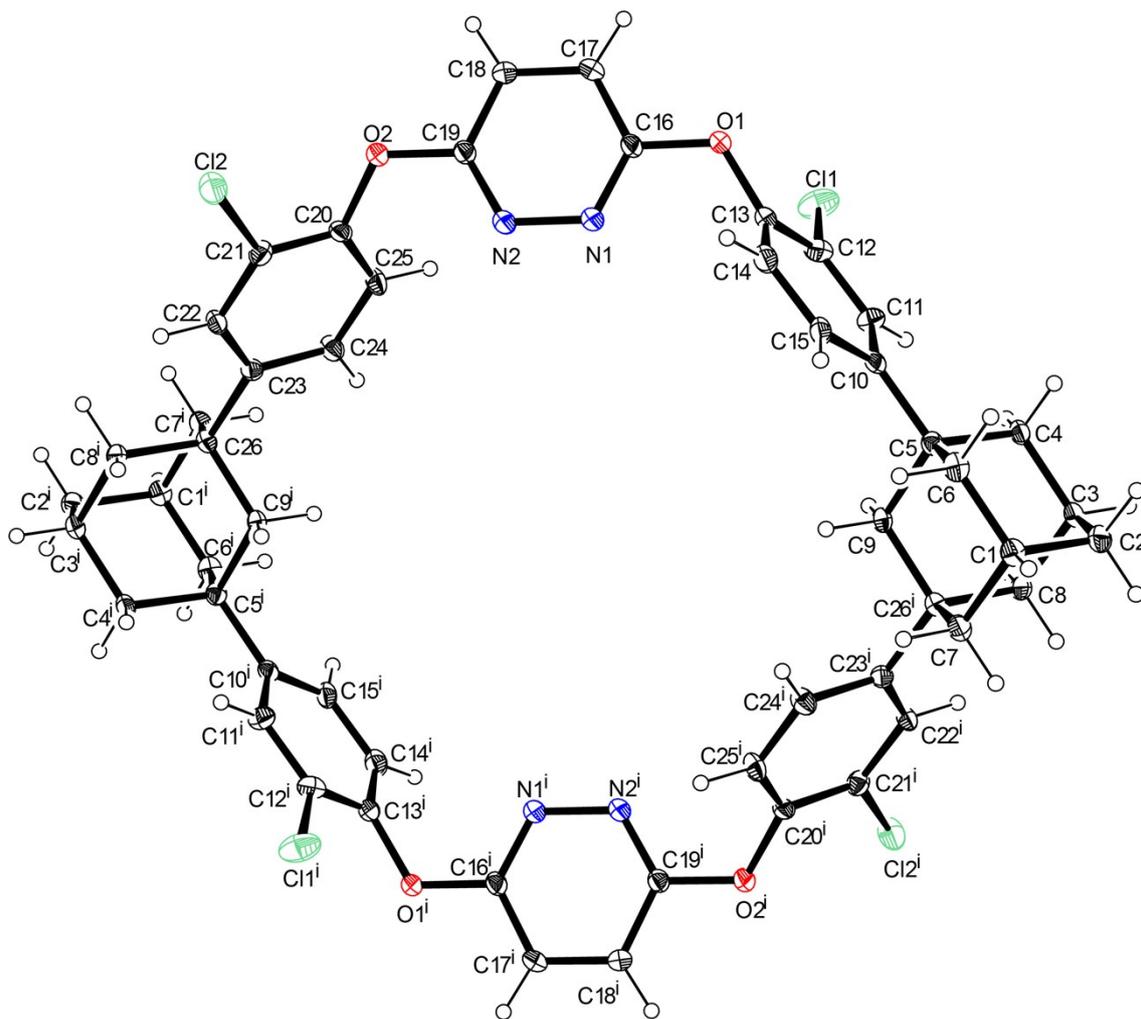


Fig. S15 Ortep drawing of macrocycle in crystal **1f** (30% probability).

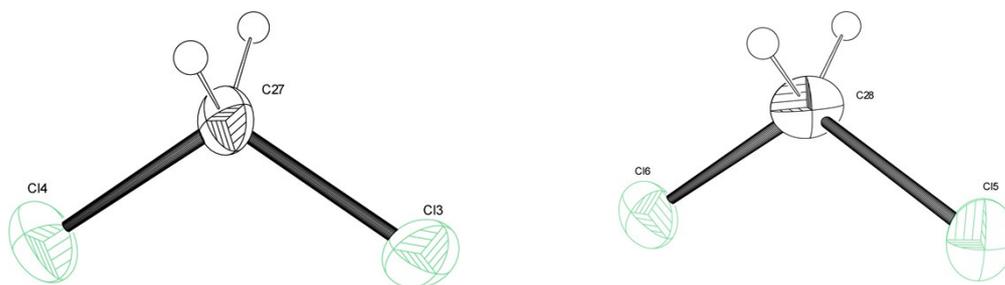


Fig. S16 Ortep drawing of dichloromethane in crystal **1f** (30% probability).

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.