

Supplementary Information

Co-inclusion of cyclic ethers and chloroform by a macrocycle with benzophenone-3,3',4,4'-tetracarboxylic diimide units

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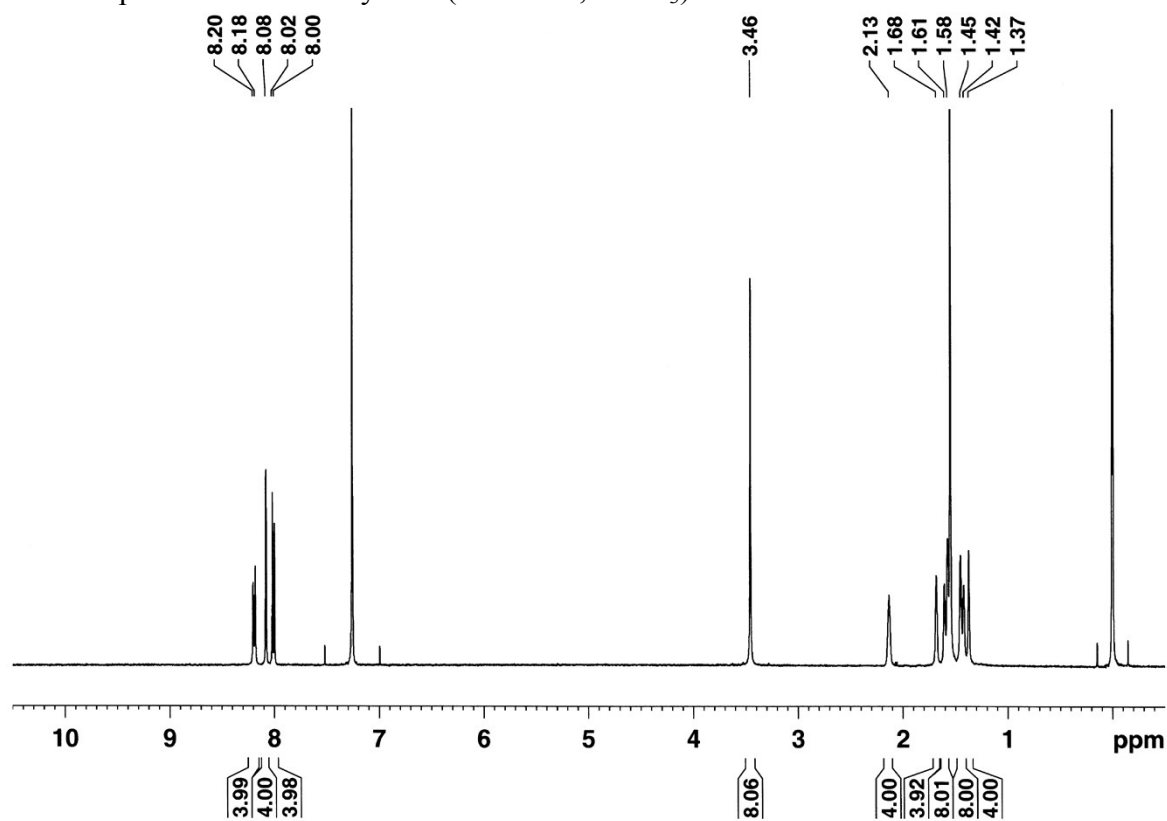
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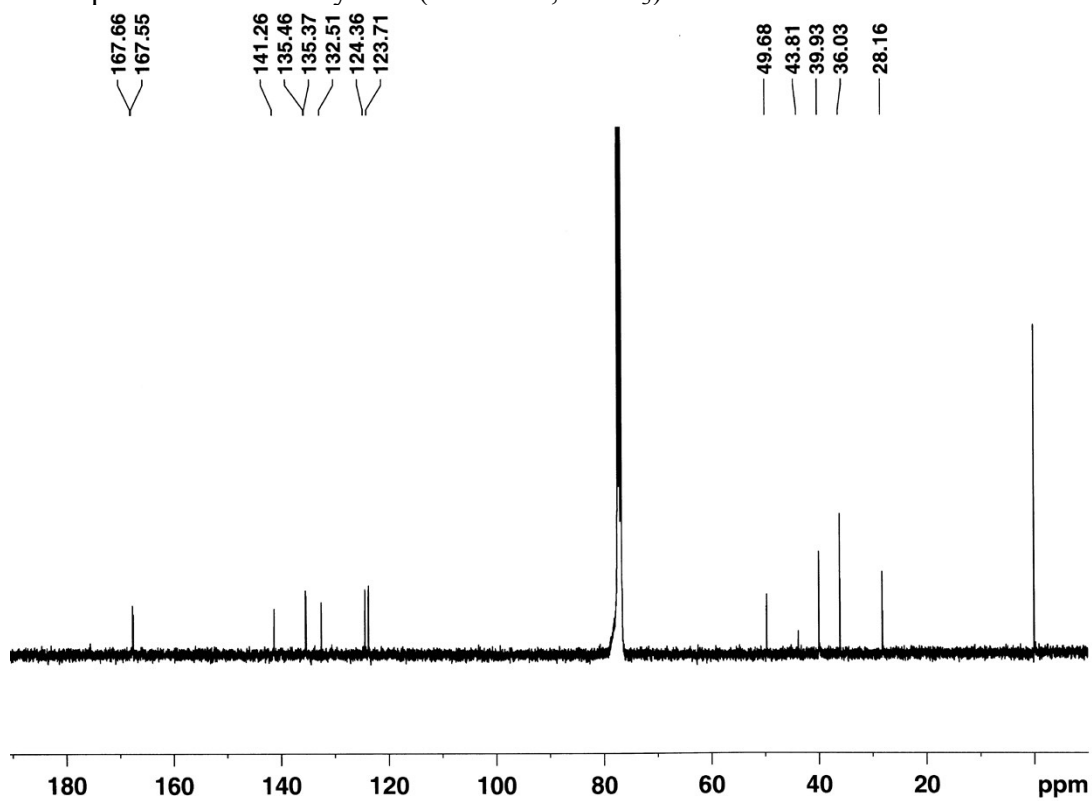
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^1H NMR spectrum of macrocycle **1** (400 MHz, CDCl_3)



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



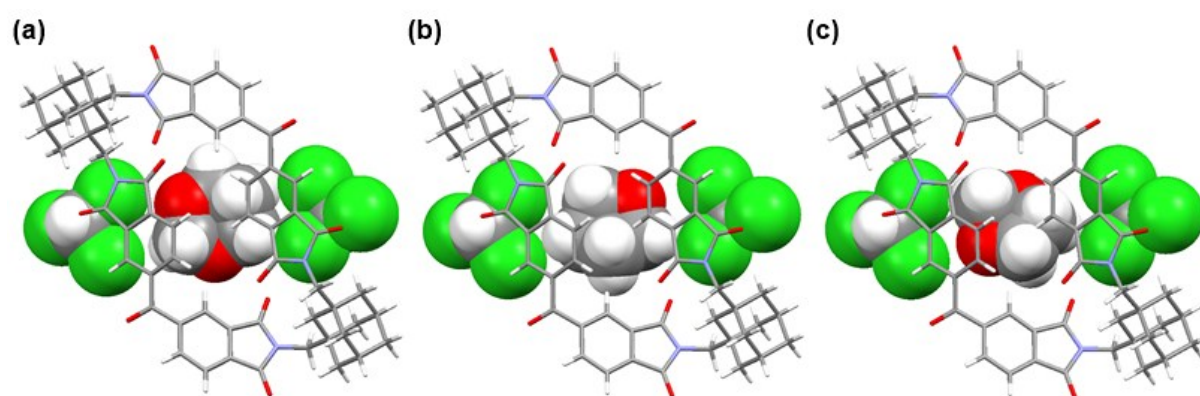


Fig. S1 Top views of the complexes in (a) crystal **1b**, (b) crystal **1c**, and (c) crystal **1d**. Disordered atoms are omitted for clarity.

Single crystal X-ray diffraction experiment for crystal 1a

The colorless prismatic crystal ($0.100 \times 0.080 \times 0.050$ mm³), obtained from 1,4-dioxane/chloroform, was immersed in Paraton-N oil and placed in the N₂ cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK α : $\lambda = 1.54178$ Å). 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.

C₆₄H₅₈Cl₆N₄O₁₂, $M_r = 1287.84$; triclinic, space group $P-1$, $Z = 1$, $D_{\text{calc}} = 1.522$ g·cm⁻³, $a = 7.6112(5)$, $b = 11.9128(7)$, $c = 16.0046(10)$ Å, $\alpha = 81.915(3)$, $\beta = 81.796(3)$, $\gamma = 80.150(3)^\circ$, $V = 1405.04(15)$ Å³, 17785 measured and 4718 independent [$I > 2\sigma(I)$] reflections, 388 parameters, final $R_1 = 0.0560$, $wR_2 = 0.1485$, $S = 1.047$ [$I > 2\sigma(I)$]. CCDC 1982945

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 23, and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms. The 1,4-dioxane (O1a, C1a and C2a), guest molecule as well as the cage molecule lied on the crystallographic symmetry positions were firstly refined with the free variable and finally fixed with the site occupancy factor of 100%. A chloroform (C30, C11, C12 and C13) was refined with free variable and the occupancy rate was 100%.

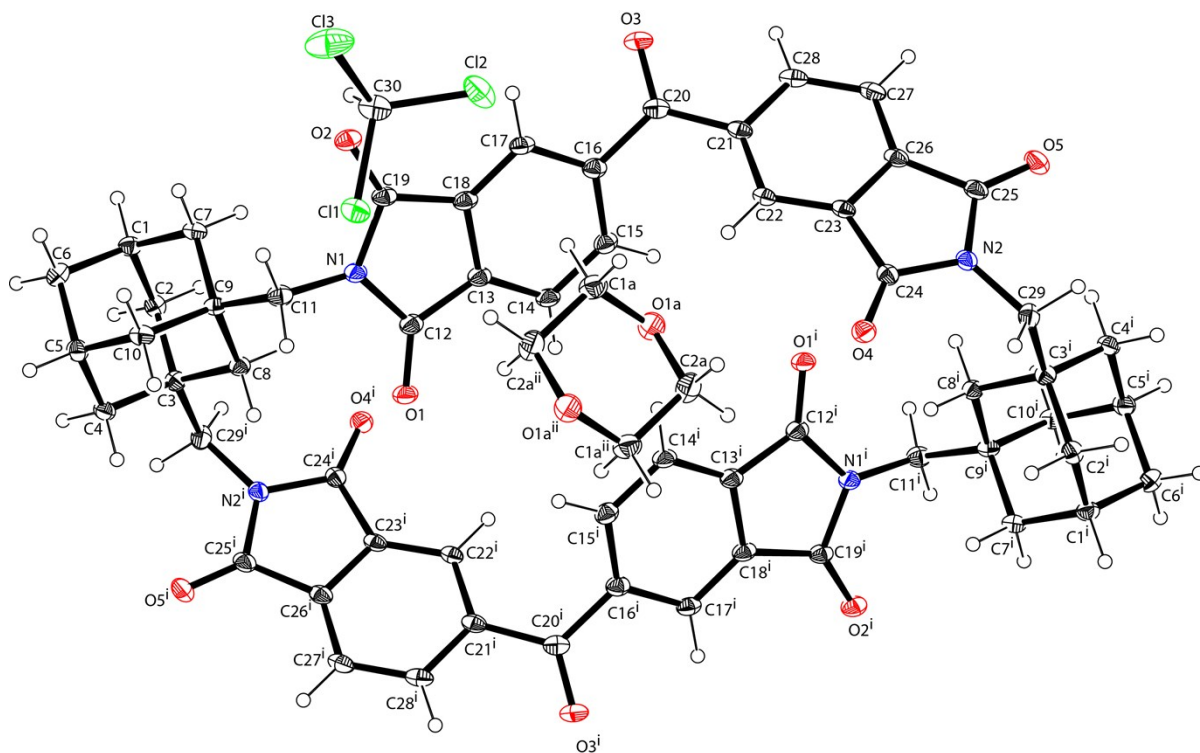


Fig. S2 Ortep drawing of complexes in crystal **1a** (30% probability).

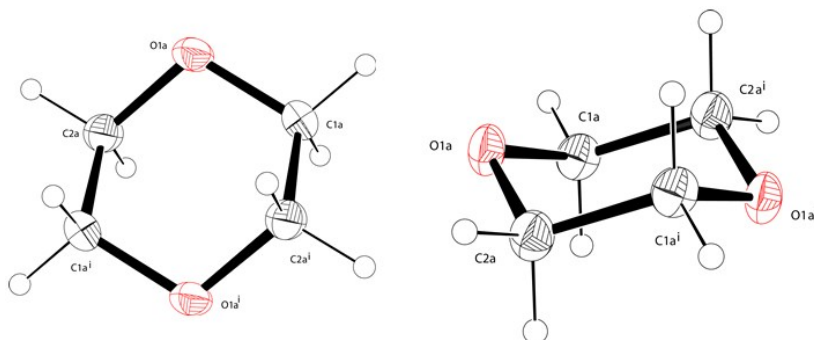


Fig. S3 Ortep drawing of guest molecule (**a**); top and side views (30% probability).

Single crystal X-ray diffraction experiment for crystal 1b

The colorless prismatic crystal ($0.120 \times 0.050 \times 0.050$ mm³), obtained from 1,3-dioxane/chloroform, was immersed in Paraton-N oil and placed in the N₂ cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK α : $\lambda = 1.54178$ Å). 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.

C₆₄H_{58.01}Cl_{5.97}N₄O₁₂, $M_r = 1286.79$; triclinic, space group $P-1$, $Z = 1$, $D_{\text{calc}} = 1.502$ g·cm⁻³, $a = 7.6781(5)$, $b = 12.0451(8)$, $c = 15.9522(11)$ Å, $\alpha = 81.688(3)$, $\beta = 81.540(3)$, $\gamma = 79.019(3)^\circ$, $V = 1422.19(17)$ Å³, 17776 measured and 4227 independent [$I > 2\sigma(I)$] reflections, 446 parameters, 15 restraints, final $R_1 = 0.0868$, $wR_2 = 0.2291$, $S = 1.027$ [$I > 2\sigma(I)$]. CCDC 1982946

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 23, and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms. A couple of disordered and overlapped chloroform molecules (C30, Cl1a, Cl2a, Cl3a, occupancy; 66.3% and C30, Cl1b, Cl2b, Cl3b, occupancy; 33.1%) were refined with PART n. The 1,3-dioxane molecule (C1a, C2a, C3a, C4a, O1a, and O2a) which is riding on the crystallographic symmetry center was firstly refined with the free variable and finally refined with PART -n fixing the site occupancy factor to be 50%. These atoms were refined by PART applying with DANG, DELU and SUMP.

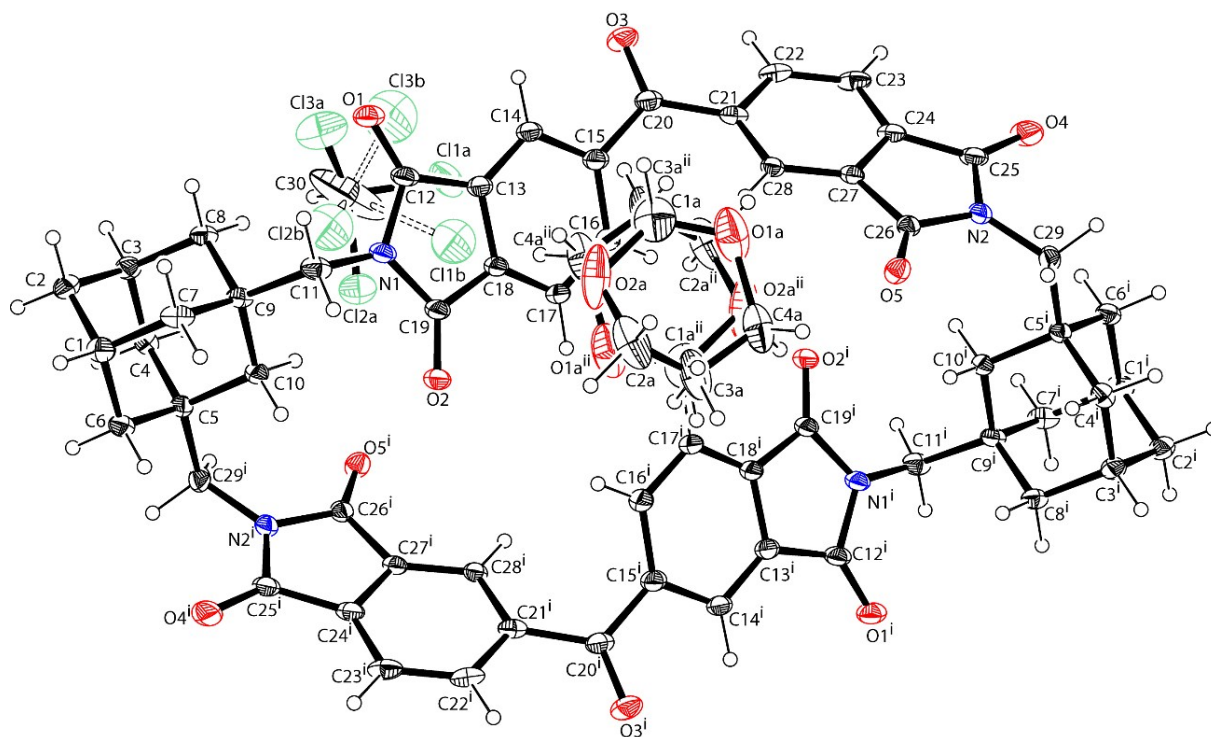


Fig. S4 Ortep drawing of complexes in crystal **1b** (30% probability).

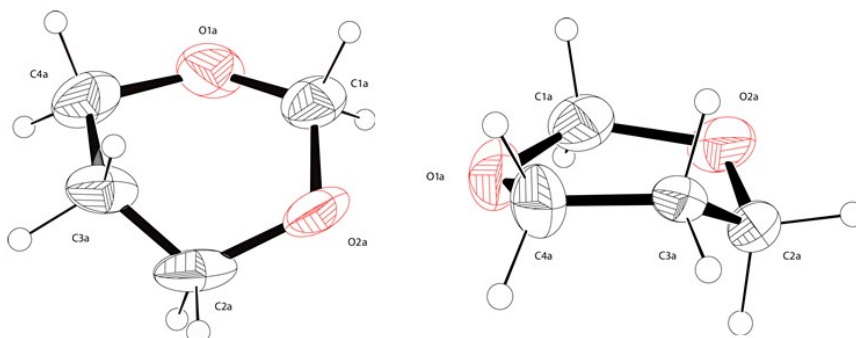


Fig. S5 Ortep drawing of guest molecule (**b**); top and side views (30% probability).

Single crystal X-ray diffraction experiment for crystal 1c

The colorless prismatic crystal ($0.100 \times 0.100 \times 0.100$ mm³), obtained from tetrahydrofuran/chloroform, was immersed in Paraton-N oil and placed in the N₂ cold stream at 100 K. Data were collected using diffractometer with CMOS detector (Bruker D8 VENTURE, CuK α : $\lambda = 1.54178$ Å). 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.

C₆₄H₅₈Cl₆N₄O₁₁, $M_r = 1271.84$; triclinic, space group *P*-1, $Z = 1$, $D_{\text{calc}} = 1.501$ g·cm⁻³, $a = 7.6225(8)$, $b = 12.0460(13)$, $c = 15.9044(17)$ Å, $\alpha = 81.746(5)$, $\beta = 80.373(5)$, $\gamma = 79.855(5)^\circ$, $V = 1407.4(3)$ Å³, 16465 measured and 4707 independent [$I > 2\sigma(I)$] reflections, 383 parameters, 53 restraints, final $R_1 = 0.0861$, $wR_2 = 0.2402$, $S = 1.077$ [$I > 2\sigma(I)$]. CCDC 1982947

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 23, and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms. A chloroform (C30, C11, C12 and C13) was refined with free variable and the occupancy rate was 100%. The tetrahydrofuran molecule (C1a, C2a, C3a, C4a, and O1a) which is riding on the crystallographic symmetry center was firstly refined with the free variable and finally refined with PART -n fixing the site occupancy factor to be 50%. These atoms were refined by PART applying with DFIX, DAHG, RIGU, SIMU, SUMP, and EADP.

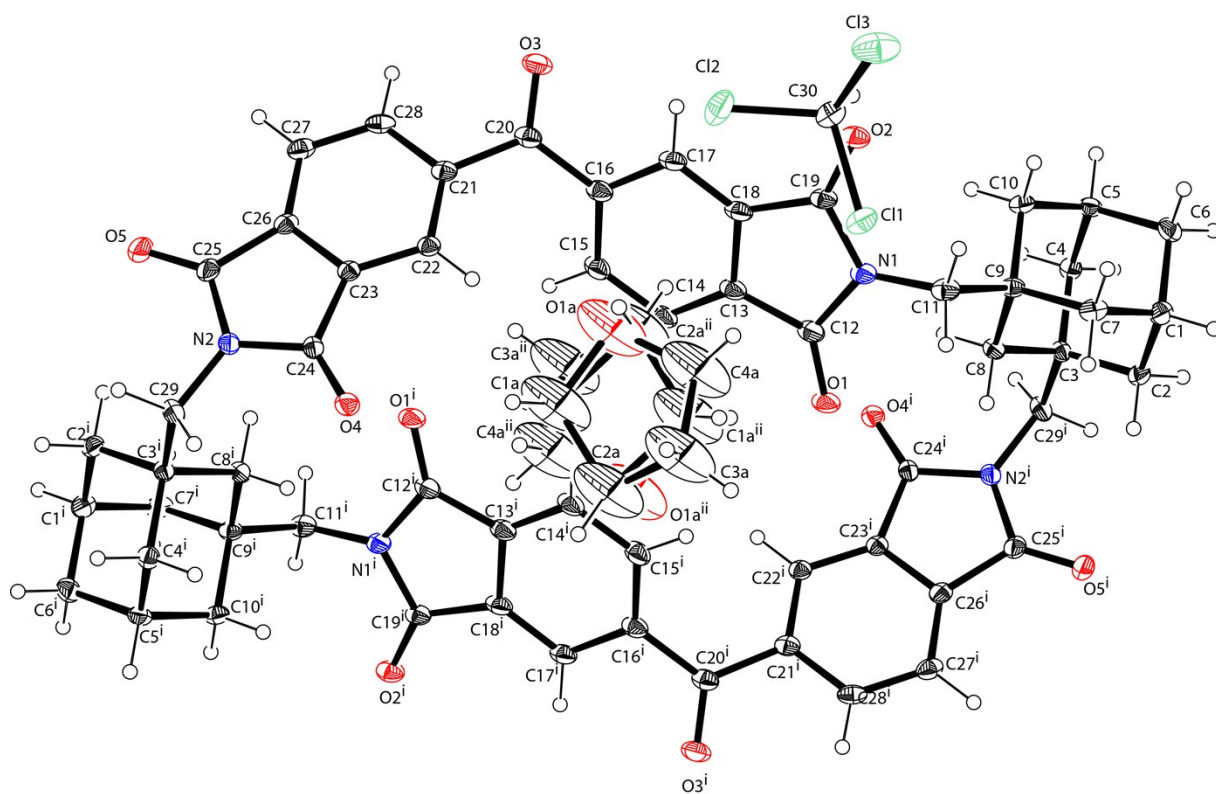


Fig. S6 Ortep drawing of complexes in crystal **1c** (30% probability).

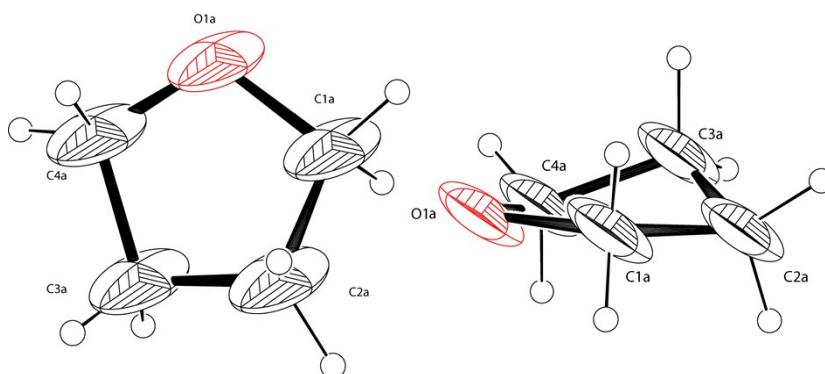


Fig. S7 Ortep drawing of guest molecule (**c**); top and side views (30% probability).

Single crystal X-ray diffraction experiment for crystal 1d

The colorless prismatic crystal ($0.050 \times 0.050 \times 0.050 \text{ mm}^3$), obtained from 1,3-dioxolane/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.

$\text{C}_{63}\text{H}_{56}\text{Cl}_6\text{N}_4\text{O}_{12}$, $M_r = 1273.81$; triclinic, space group $P-1$, $Z = 1$, $D_{\text{calc}} = 1.503 \text{ g}\cdot\text{cm}^{-3}$, $a = 7.6120(5)$, $b = 12.0404(7)$, $c = 15.8636(10) \text{ \AA}$, $\alpha = 81.859(2)$, $\beta = 81.279(2)$, $\gamma = 80.545(2)^\circ$, $V = 1407.40(15) \text{ \AA}^3$, 17946 measured and 4545 independent [$I > 2\sigma(I)$] reflections, 407 parameters, 34 restraints, final $R_1 = 0.0621$, $wR_2 = 0.1683$, $S = 1.066$ [$I > 2\sigma(I)$]. CCDC 1982948

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 23, and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms. A chloroform (C30, C11, C12 and C13) was refined with free variable and the occupancy rate was 100%. The 1,3-dioxolane molecule (C1a, C2a, C3a, O1a, and O2a) which is riding on the crystallographic symmetry center was firstly refined with the free variable and finally refined with PART -n fixing the site occupancy factor to be 50%. These atoms were refined by PART applying with DFIX, RIGU, and SUMP.

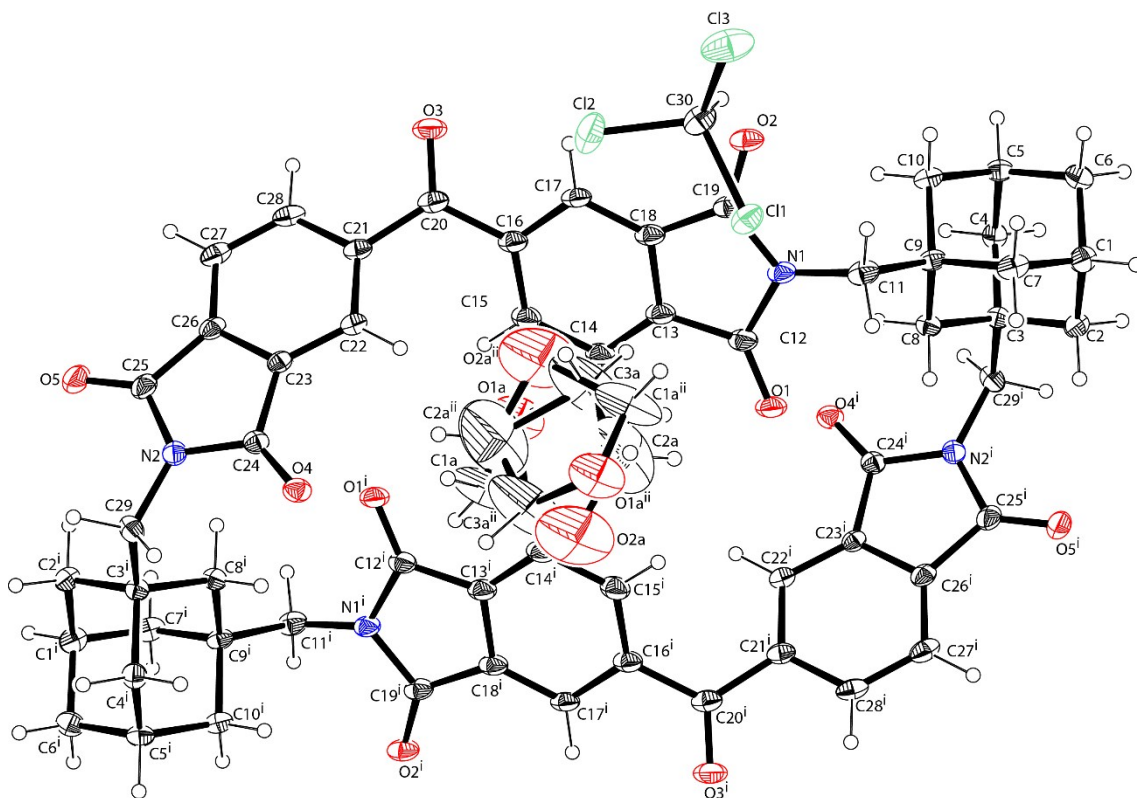


Fig. S8 Ortep drawing of complexes in crystal **1d** (30% probability).

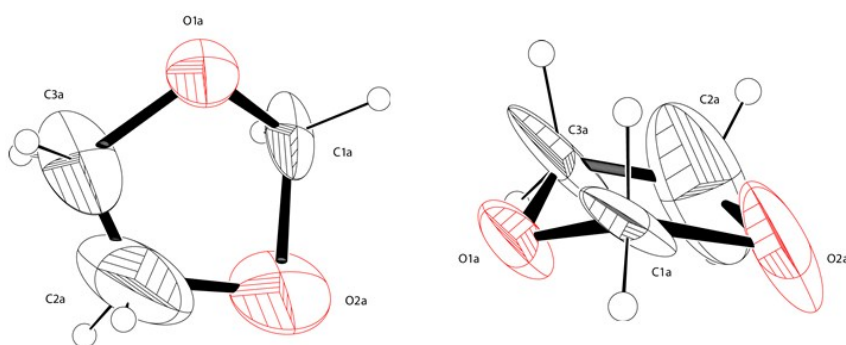


Fig. S9 Ortep drawing of guest molecule (**d**); top and side views (30% probability).

References

- (1) G. M. Sheldrick, *SADABS*. University of Göttingen, Germany, 1996.
- (2) G. M. Sheldrick, *Acta. Cryst.*, 2015, **A71**, 3–8.
- (3) G. M. Sheldrick, *Acta. Cryst.*, 2015, **C71**, 3–8.