Supplementary Information (SI) for CrystEngComm.

Supplementary Information

Co-crystals built from macrocycles with pyromellitic diimides and naphthalene derivatives: transformation of a binary co-crystal solvate to a solvate through solvent exchange

Masahide Tominaga,* Ryusei Kamada, Tadashi Hyodo and Kentaro Yamaguchi*

Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, Takamatsu, Kagawa 760-8542, Japan

E-mail: tominagam@kph.bunri-u.ac.jp and kyamaguchi@kph.bunri-u.ac.jp

Table of Contents

Single crystal X-ray diffraction experiment for crystal 1a

The yellowish-brown prismatic crystal (0.120 × 0.050 × 0.050 mm^3), obtained from slow evaporation of a mixture of chloroform and acetone containing **1** and **2**, was immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. Data were collected using diffractometer with a CMOS detector (Brukerd D8 VENTURE, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2019/2[3].

$C_{57.8}H_{52.8}Br_2Cl_{2.39}N_4O_{11}$, $Mr = 1223.90$; triclinic, space group P-1, $Z = 2$, $D_{\mathrm{calc}} = 1.555$ g·cm^{-3}, a = 9.7752(10), b = 11.4458(12), c = 24.731(3) Å, α = 94.352(3), β = 93.154(3), γ = 108.044(3)°, V = 2614.4(5) Å^3, 36841 observed and 10049 [$I > 2\sigma(I)$], 10481 [all] independent reflections, 782 parameters, 48 restraints, final $R_1 = 0.0343$, $wR_2 = 0.0885$, S = 1.025 [$I > 2\sigma(I)$] and $R_1 = 0.0357$, $wR_2 = 0.0907$, $S = 1.052$ [all data]. CCDC 2389266.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 147, 23, and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. The two disordered chloroform molecules (C58, Cl1-Cl3 and C59, Cl4-Cl6) overlapped in almost identical positions. In addition, the disordered another chloroform molecule (C60, Cl7-Cl9) was also overlapped in the same position. They were refined with PART −n. Each occupancy was as follows. C58, Cl1-Cl3: 50%, C59, Cl4-Cl6: 15%, C60, Cl7-Cl9: 15%.

The ratio of **1**:**2**:$CHCl_3$:acetone included in the crystal was 1:1:0.8:1.

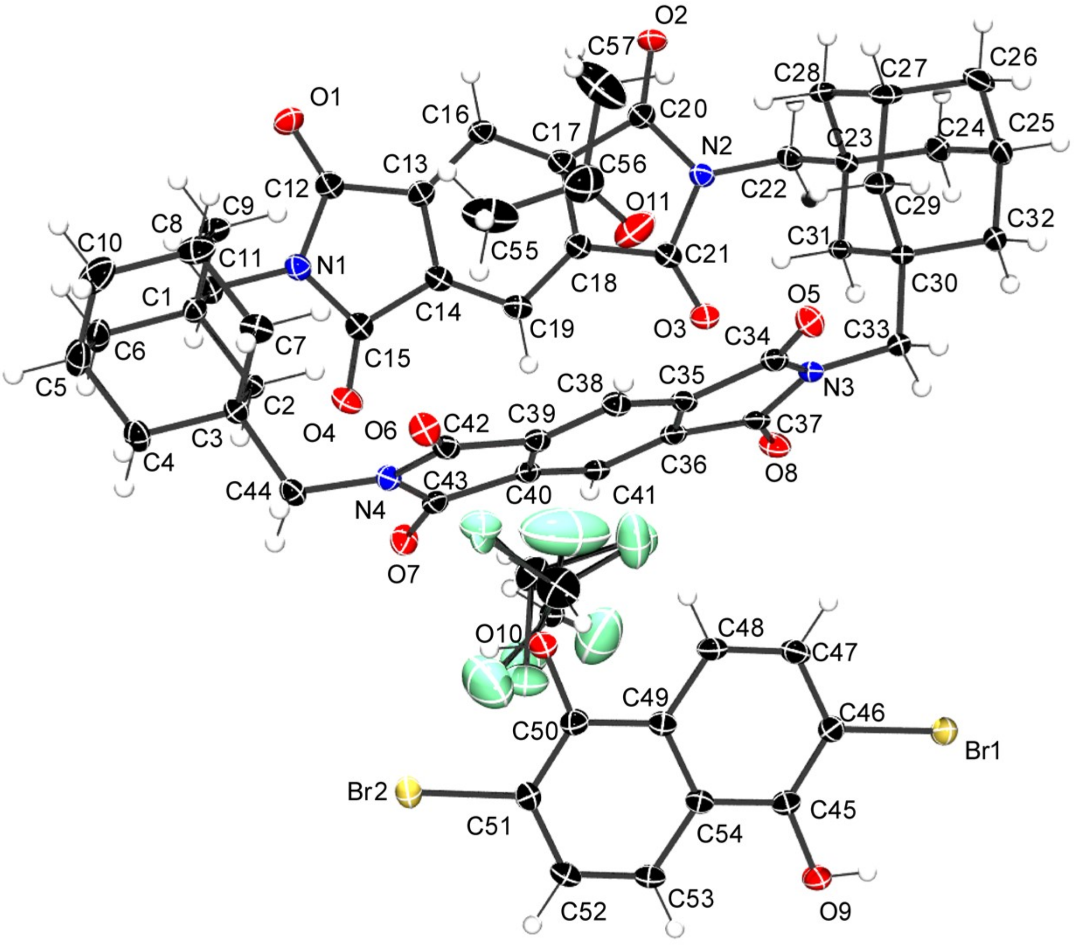

Fig. S1 ORTEP drawing of **1**, **2**, chloroform, and acetone in an asymmetric unit in crystal **1a** (50% probability).

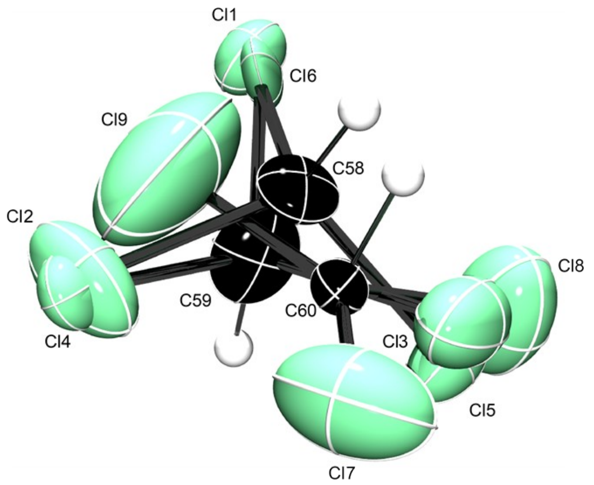

Fig. S2 ORTEP drawing of disordered chloroform molecules in crystal **1a** (50% probability).

Single crystal X-ray diffraction experiment for crystal 1b

The yellowish-brown prismatic crystal (0.120 × 0.120 × 0.080 mm^3), obtained from slow evaporation of an acetone solution of **1** and **2**, 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, CuKα: $\lambda = 1.54178$ Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2019/2[3].

$C_{60}H_{58}Br_2N_4O_{12}$, Mr = 1186.92; triclinic, space group P-1, $Z = 2$, $D_{\text{calc}} = 1.522$ g·cm^{-3}, $a = 9.7166(6)$, $b = 11.3692(7)$, $c = 24.7966(16)$ Å, $\alpha = 94.639(2)$, $\beta = 92.734(2)$, $\gamma = 107.934(2)$°, $V = 2590.0(3)$ Å^3, 38075 observed and 10351 [$I > 2\sigma(I)$], 10549 [all] independent reflections, 709 parameters, final $R_1 = 0.0256$, $wR_2 = 0.0680$, $S = 1.065$ [$I > 2\sigma(I)$] and $R_1 = 0.0261$, $wR_2 = 0.0683$, $S = 1.065$ [all data]. CCDC 2389267.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 147, 23, and 43) with U_{iso} values constrained to 1.2 U_{eq} of their parent atoms.

The ratio of **1**:**2**: acetone included in the crystal was 1:1:2.

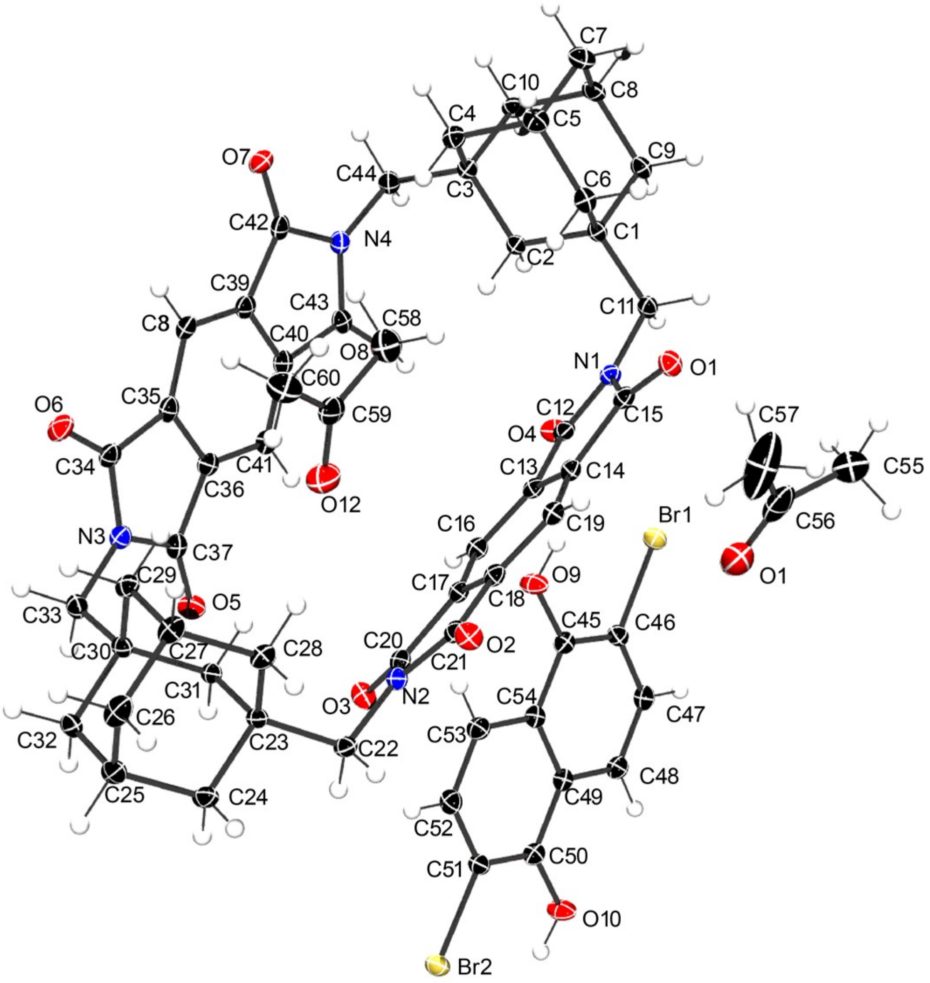

Fig. S3 ORTEP drawing of **1**, **2**, and acetone in an asymmetric unit in crystal **1b** (50% probability).

Single crystal X-ray diffraction experiment for crystal 1c

The yellowish-brown plate crystal (0.120 × 0.120 × 0.080 mm^3), obtained from slow evaporation of a chloroform solution of **1** and **2**, 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, CuKα: $\lambda = 1.54178$ Å). Absorption correction was performed by an empirical method implemented in SCALE3 ABSPACK. Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2019/2[3].

$C_{59}H_{51}Br_2Cl_5N_4O_{10}$, $M\mathrm{r} = 1667.60$; monoclinic, space group $P2_1/m$, $Z = 2$, $D_{\mathrm{calc}} = 1.635$ g·cm^{-3}, $a = 9.6670(8)$, $b = 22.9197(19)$, $c = 15.4712(13)$ Å, $\beta = 98.877(3)°$, $V = 3386.8(5)$ Å^3, 44054 observed and 6548 [$I > 2\sigma(I)$], 7202 [all] independent reflections, 498 parameters, 7 restraints, final $R_1 = 0.0573$, $wR_2 = 0.1451$, $S = 1.056$ [$I > 2\sigma(I)$] and $R_1 = 0.0622$, $wR_2 = 0.1494$, $S = 1.056$ [all data]. CCDC 2389268.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 147, 23, and 43) with U_{iso} values constrained to 1.2 U_{eq} of their parent atoms. The crystals contained 2.5 chloroform molecules in five positions in an asymmetric unit. One-half chloroform molecule (C32, Cl1, Cl2, Cl1b) encapsulated in the host molecule located on the symmetry axis was refined to 50% occupancy. Two pairs of disordered chloroform molecules (C33, Cl3, Cl4, Cl5; C34, Cl6, Cl7, Cl8 and C35, Cl9, Cl10, Cl11; C36, Cl12, Cl13, Cl14) filled in the void are refined with 61.9; 38.1% and 51.7; 48.3% occupancy (with PART -n), respectively.

The ratio of **1**:**2**:$CHCl_3$ included in the crystal was 1:1:5.

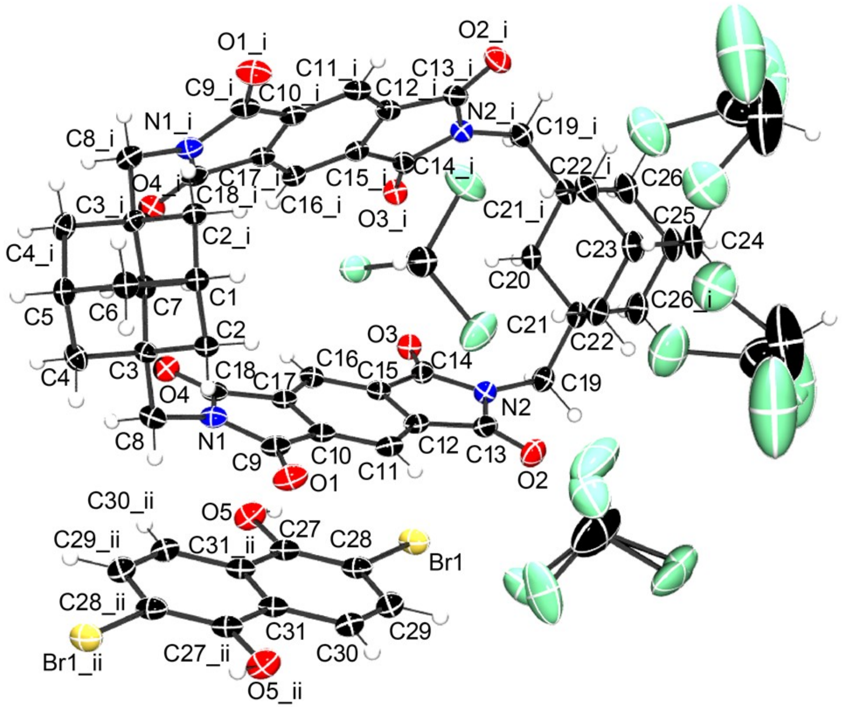

Fig. S4 ORTEP drawing of complete structure **1**, **2**, and chloroform in crystal **1c** (50% probability).

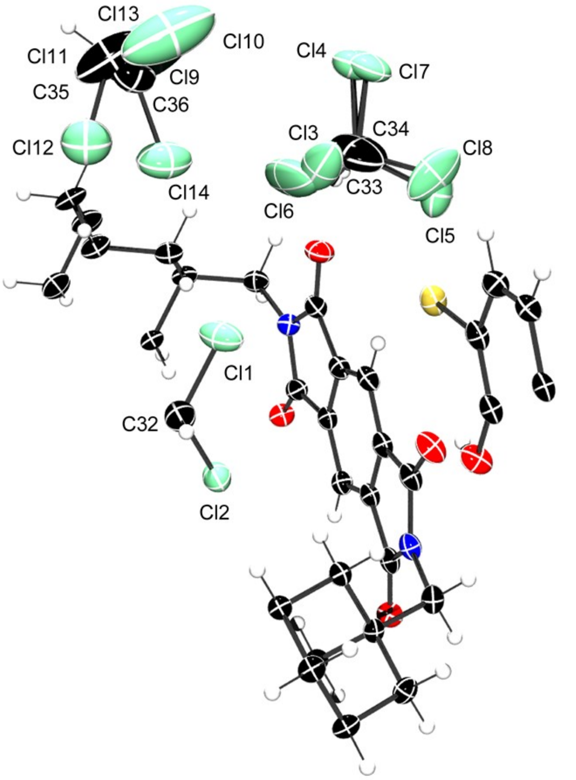

Fig. S5 ORTEP drawing of **1**, **2**, and chloroform in an asymmetric unit in crystal **1c** (50% probability).

Single crystal X-ray diffraction experiment for crystal 1d

The reddish-brown plate crystal (0.200 × 0.200 × 0.020 mm^3), obtained from slow evaporation of a mixture of chloroform and acetone containing **1** and **3**, 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, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2019/2[3].

$C_{58}H_{52}Cl_{12}N_4O_{10}$, $M\mathrm{r}$ = 1390.43; monoclinic, space group $P2_1/c$, Z = 4, D_{calc} = 1.548 g·cm^{-3}, a = 9.3975(6), b = 23.0975(14), c = 27.7307(17) Å, β = 97.683(3)°, V = 5965.2(6) Å^3, 76857 observed and 9908 [$I > 2\sigma(I)$], 12549 [all] independent reflections, 796 parameters, 6 restraints, final R_1 = 0.0909, wR_2 = 0.2720, S = 1.037 [$I > 2\sigma(I)$] and R_1 = 0.1061, wR_2 = 0.2905, S = 1.037 [all data]. CCDC 2389269.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 147, 23, and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. The crystals contained four chloroform molecules in five positions in an asymmetric unit. Three chloroform molecules (C55, Cl1-Cl3 and C56, Cl4-Cl6 and C57, Cl7-Cl9) in the void were refined normally. Two disordered chloroform molecules (C60, Cl10-Cl12 and C61, Cl13-Cl15) in the void were refined with 58.1 and 41.9% occupancy (with PART -n), respectively.

The ratio of **1**:**3**:$CHCl_3$ included in the crystal was 1:1:4.

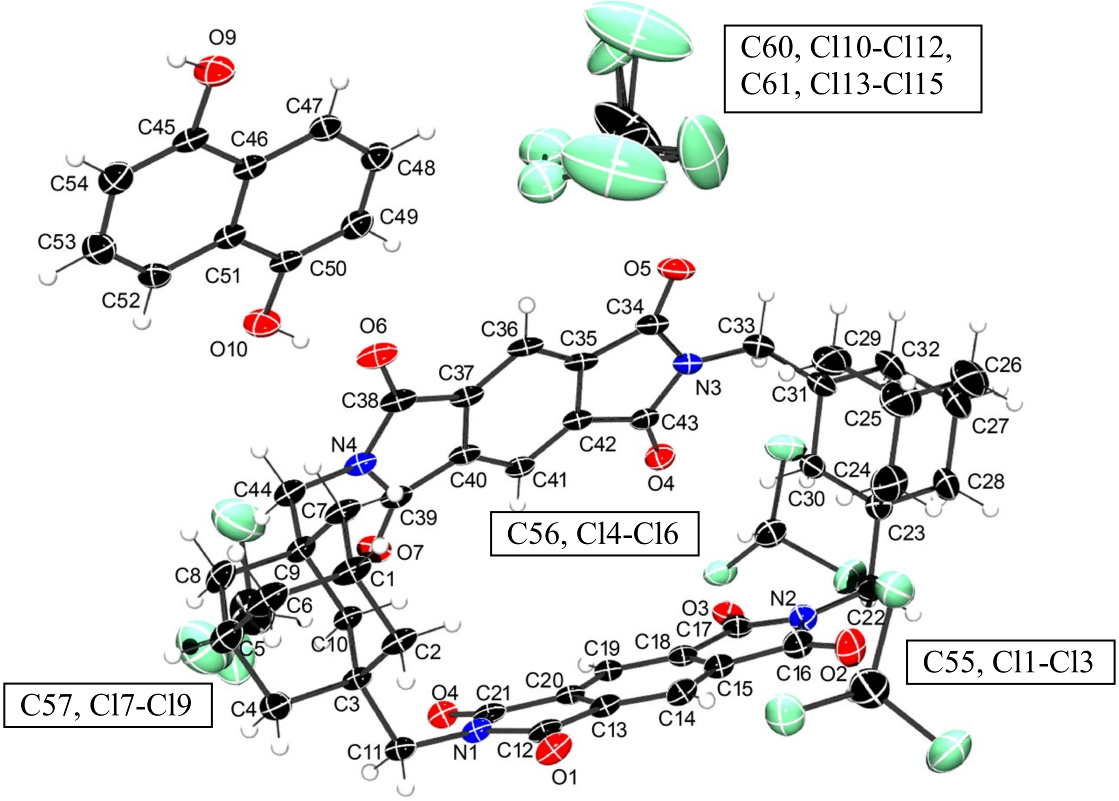

Fig. S6 ORTEP drawing of **1**, **3**, and chloroform in an asymmetric unit in crystal **1d** (50% probability).

Single crystal X-ray diffraction experiment for crystal 1e

The colorless prismatic crystal (0.200 × 0.150 × 0.080 mm^3), obtained from slow evaporation of a mixture of chloroform and acetone containing **1** and **4**, 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, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2019/2[3].

$C_{103.50}H_{93.75}Br_2Cl_{9.75}N_8O_{16.75}$, Mr = 2223.03; triclinic, space group P-1, $Z = 1$, $D_{\mathrm{calc}} = 1.485$ g·cm^{-3}, $a = 9.590(2)$, $b = 15.202(4)$, $c = 18.069(3)$ Å, $\alpha = 107.935(14)$, $\beta = 95.420(14)$, $\gamma = 92.865(17)$°, $V = 2486.5(10)$ Å^3, 35907 observed and 9339 [$I > 2\sigma(I)$], 10087 [all] independent reflections, 708 parameters, 19 restraints, final $R_1 = 0.0529$, $wR_2 = 0.1358$, $S = 1.117$ [$I > 2\sigma(I)$] and $R_1 = 0.0563$, $wR_2 = 0.1394$, $S = 1.130$ [all data]. CCDC 2389270.

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. The disordered and overlapped chloroform (C50, Cl1-Cl3) and acetone (C54-C56, O9) molecules were located in almost identical positions. They were refined with PART −n. The occupancies of C50, Cl1-Cl3: 62.5% and C54-C56, O9: 37.5% have been refined. In addition, other disordered chloroform molecules C51, Cl4-Cl6, and C52, Cl7-Cl9 in the void were normally refined with 51.8% and 48.2% occupancy (with PART -n), respectively.

The ratio of **1**:**4**:$CHCl_3$:acetone included in the crystal was 1:1:3:1.

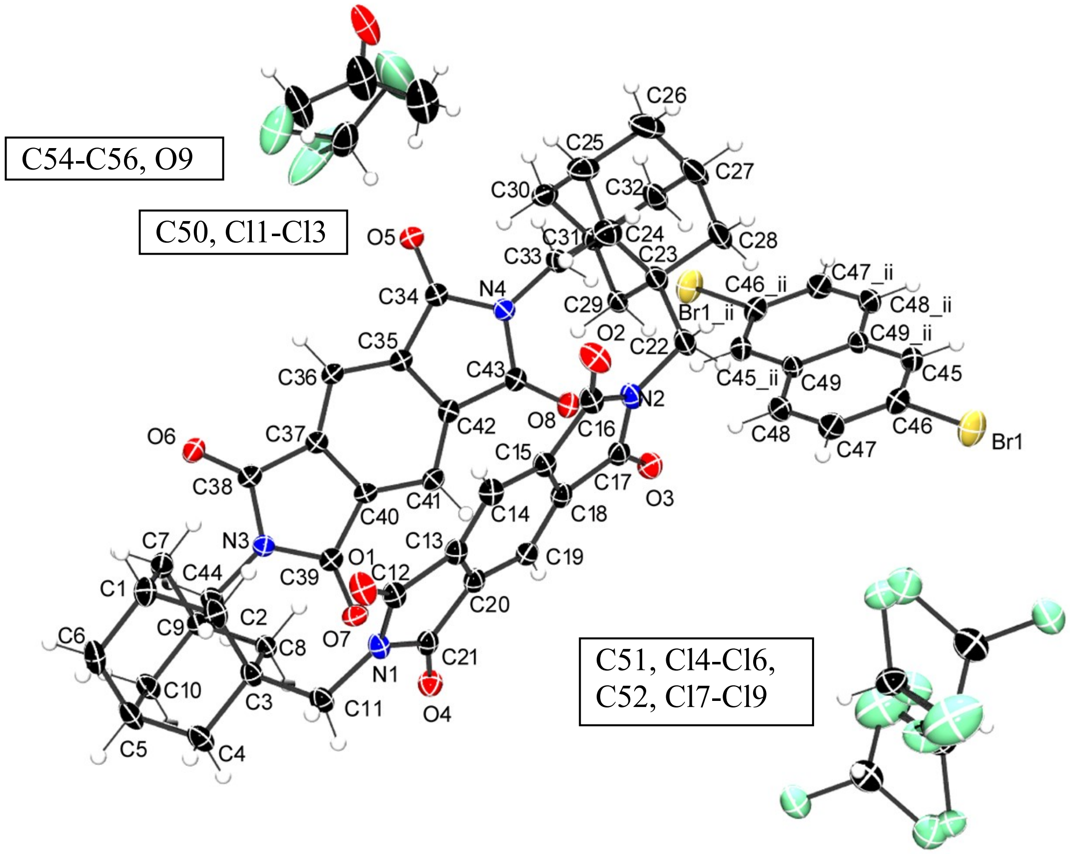

Fig. S7 ORTEP drawing of **1**, **4**, chloroform, and acetone in crystal **1e** (50% probability).

Single crystal X-ray diffraction experiment for crystal 1f

The colorless prismatic crystal (0.080 × 0.080 × 0.060 mm^3), obtained from crystal of **1d** soaked with diethyl ether at room temperature for 3 d, 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, CuKα: λ = 1.54178 Å). Absorption correction was performed by an empirical method implemented in SADABS.[1] Structure solution and refinement were performed by using SHELXT-2018/2[2] and SHELXL-2019/2[3].

$C_{48}H_{50}N_4O_9$, Mr = 826.92; triclinic, space group P-1, $Z = 4$, D_{calc} = 1.319 g·cm^{-3}, a = 16.4443(5), b = 16.6197(5), c = 17.6078(6) Å, α = 113.668(2), β = 105.994(2), γ = 92.943(2)°, V = 4164.5(2) Å^3, 45481 observed and 9797 [$I > 2\sigma(I)$], 15905 [all] independent reflections, 1104 parameters, final R_1 = 0.0918, wR_2 = 0.2143, S = 1.053 [$I > 2\sigma(I)$] and R_1 = 0.1505, wR_2 = 0.2668, S = 1.053 [all data]. CCDC 2444562.

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. The ratio of **1**:**Et_2O** included in the crystal was 1:1.

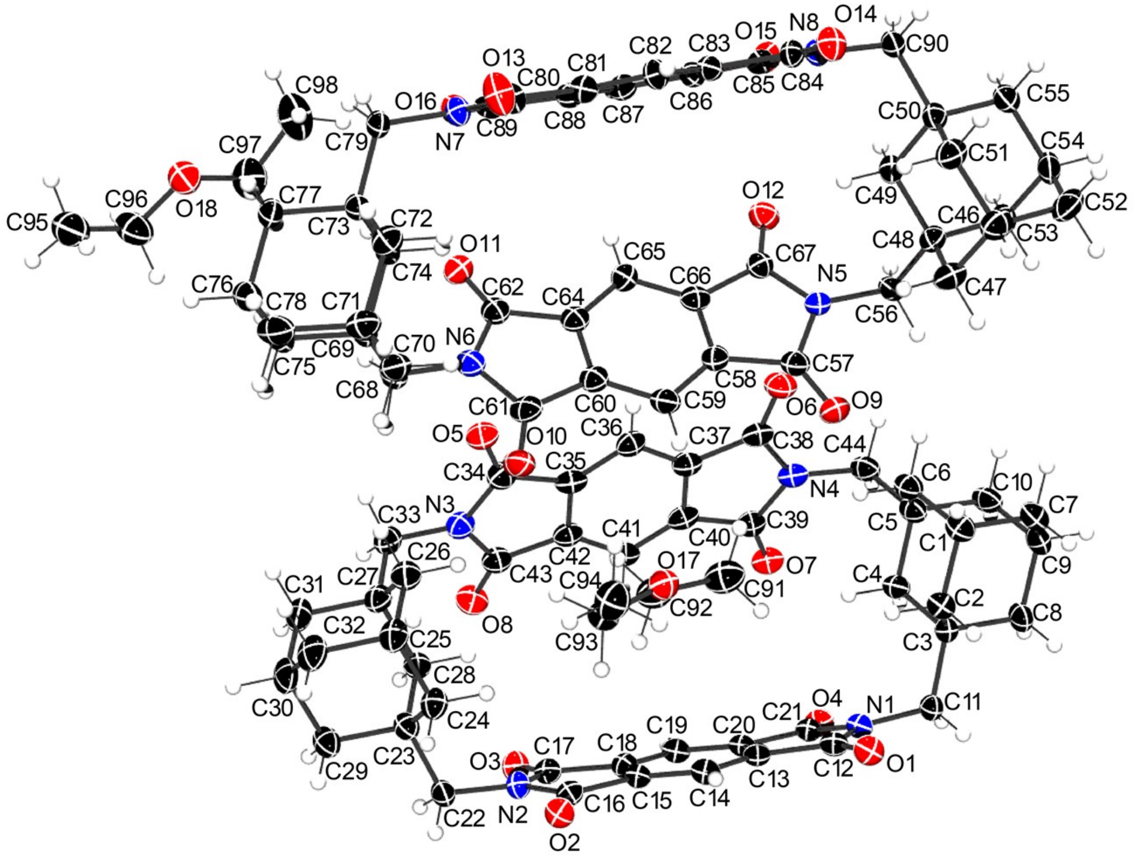

Fig. S8 ORTEP drawing of **1** and diethyl ether in crystal **1f** (50% probability).

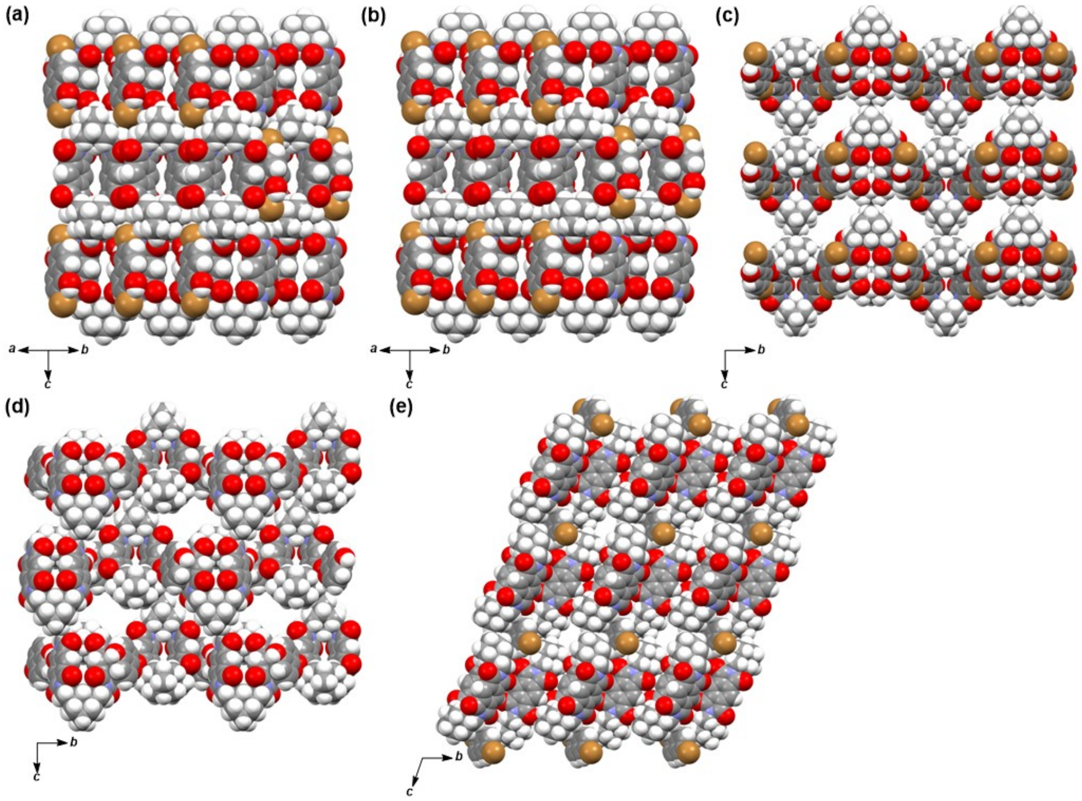

Fig. S9 Packing diagrams of **1** and naphthalene derivatives in crystals (a) **1a**, (b) **1b**, (c) **1c**, (d) **1d**, and (e) **1e**.

The stoichiometric ratio of 1 and diethyl ether in crystal 1f by ^{1}H NMR experiments

Crystal **1d** was immersed into diethyl ether at room temperature for 3 d. The resulting crystals **1f** were collected, and dried under air for 0.5 h on a filter paper. The crystals were dissolved in $CDCl_3$ followed by ^{1}H NMR analysis (Fig. S10). The composition of crystals was evaluated from the integral ratios of the signal of the aromatic proton at δ 8.22 ppm of **1** and the corresponding protons of diethyl ether. The molar ratio of **1** and diethyl ether was approximately 1:1.

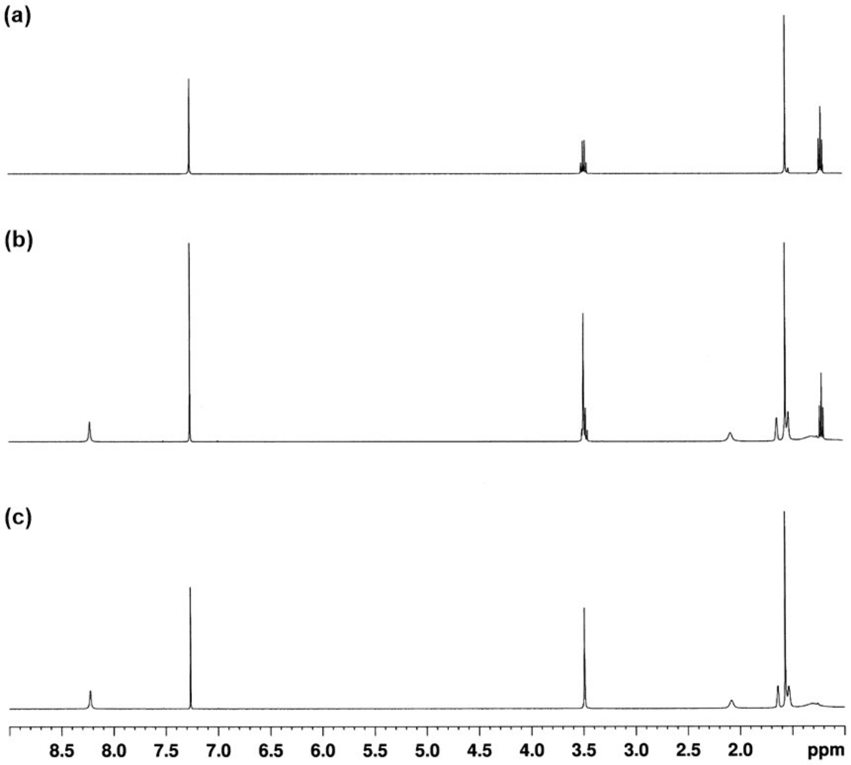

Fig. S10 ^{1}H NMR spectra (400 MHz, $CDCl_3$); (a) diethyl ether, (b) crystal **1f**, and (c) macrocycle **1**.

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.