Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Orientation of carbonyl groups in inclusion crystals formed from ketones with aromatic diimide-based macrocycles

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General procedure of single crystal X-ray diffraction experiment

A single crystal was immersed in Paratone-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-2018/3[3].

Single crystal X-ray diffraction experiment for crystal 1a

The colorless prismatic crystal (0.100 × 0.100 × 0.010 mm^3) was obtained from slow evaporation of an acetone solution of **1**.

$C_{47}H_{46}N_4O_9$, *M*r = 810.88; monoclinic, space group $P2_1/c$, $Z = 4$, $D_{calc} = 1.309$ g·cm^{-3}, a = 17.323(2), b = 12.9780(15), c = 18.983(2) Å, β = 105.428(6)°, V = 4114.0(8) $Å^3$, 60074 observed and 7188 [$I > 2\sigma(I)$], 8586 [all data] independent reflections, 543 parameters, final R_1 = 0.0395, wR_2 = 0.0977, S = 1.035 [$I > 2\sigma(I)$] and R_1 = 0.0496, wR_2 = 0.1034, S = 1.035 [all data]. CCDC 2224836.

All non-hydrogen atoms were refined anisotropically. The 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.

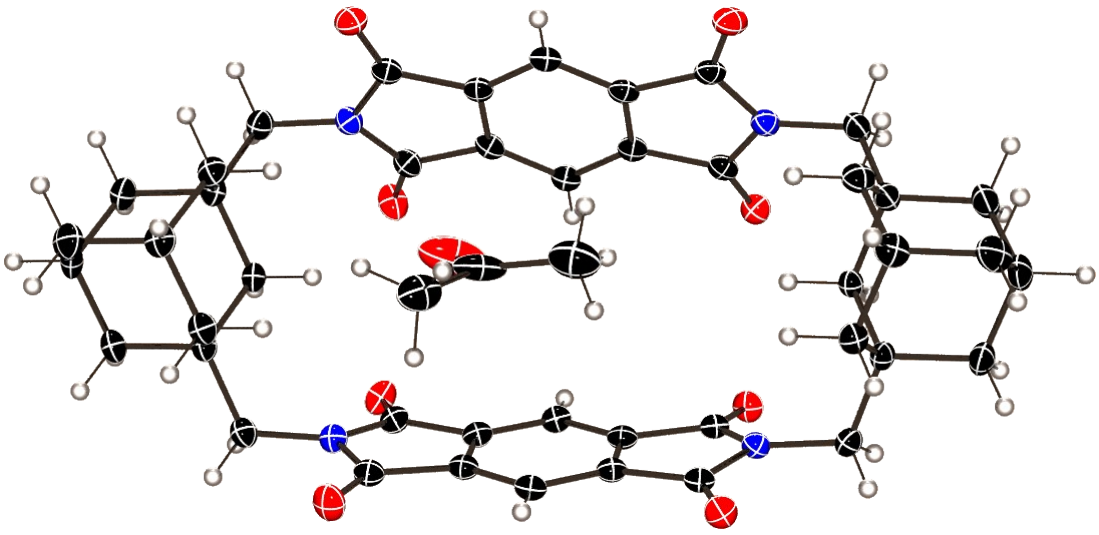

Fig. S1 Ortep drawing of crystal **1a** (50% probability).

Single crystal X-ray diffraction experiment for crystal 1b

The low diffracting colorless prismatic crystal (0.100 × 0.050 × 0.050 mm^3) was obtained from slow evaporation of a dichloromethane solution of **1** and cyclopentanone.

$C_{74}H_{88}N_4O_{14}$, *M*r = 1257.48; monoclinic, space group $P2_1/n$, $Z = 8$, $D_{calc} = 1.308$ g·cm^{-3}, $a = 28.327(3)$, $b = 14.6276(17)$, $c = 30.858(4)$ Å, $\beta = 93.076(7)°$, $V = 12768(3)$ $Å^3$, 155269 observed and 19953 [$I > 2\sigma(I)$], 22651 [all data] independent reflections, 1822 parameters, 170 restraints, final $R_1 = 0.0728$, $wR_2 = 0.1650$, $S = 1.198$ [$I > 2\sigma(I)$] and $R_1 = 0.0813$, $wR_2 = 0.1688$, $S = 1.201$ [all data]. CCDC 2224837.

All non-hydrogen atoms were refined anisotropically. The 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 U_{eq} of their parent atoms.

The disordered cyclopentanone molecules were refined with PART n, SAME, SIMU. Each occupancy was as follows. C134-C138, O26: 86% (as free variable 21), C139-C143, O27: 14% (as free variable −21), C144-C148, O28: 81.5% (as free variable 31), C149-C153, O29: 18.5% (as free variable −31), C154-C158, O30: 52.1% (as free variable 41), C159-C163, O31: 47.9% (as free variable −41). (Fig. S3)

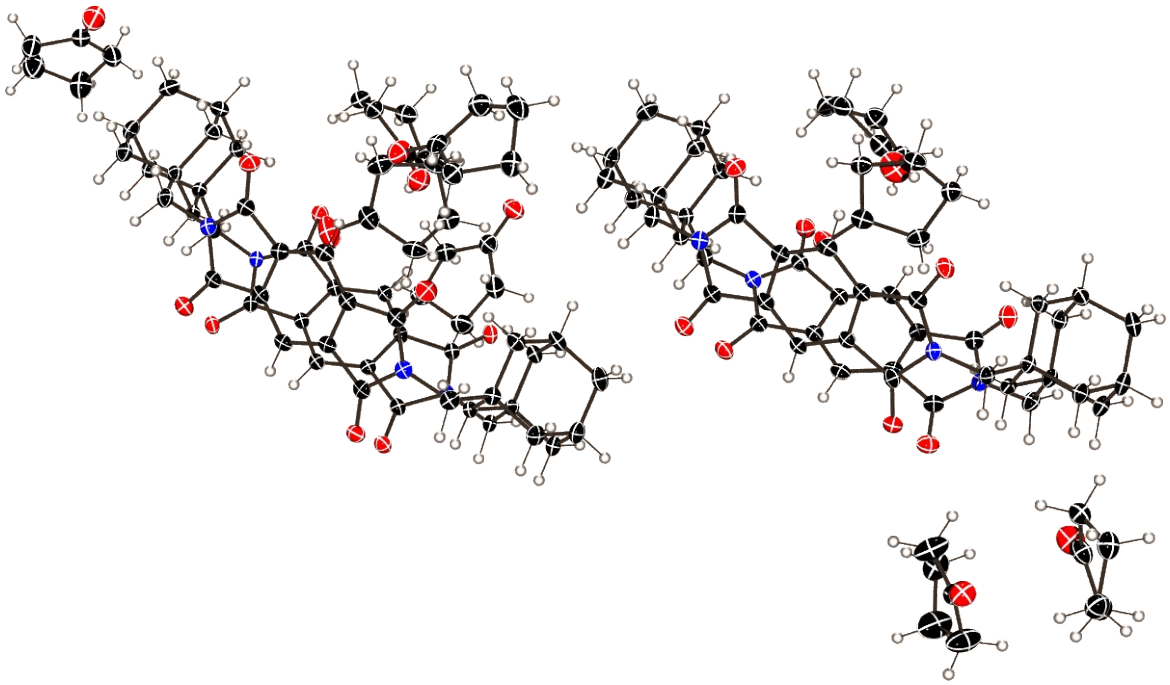

Fig. S2 Ortep drawing of crystal **1b** (50% probability). Disordered cyclopentanones are

omitted.

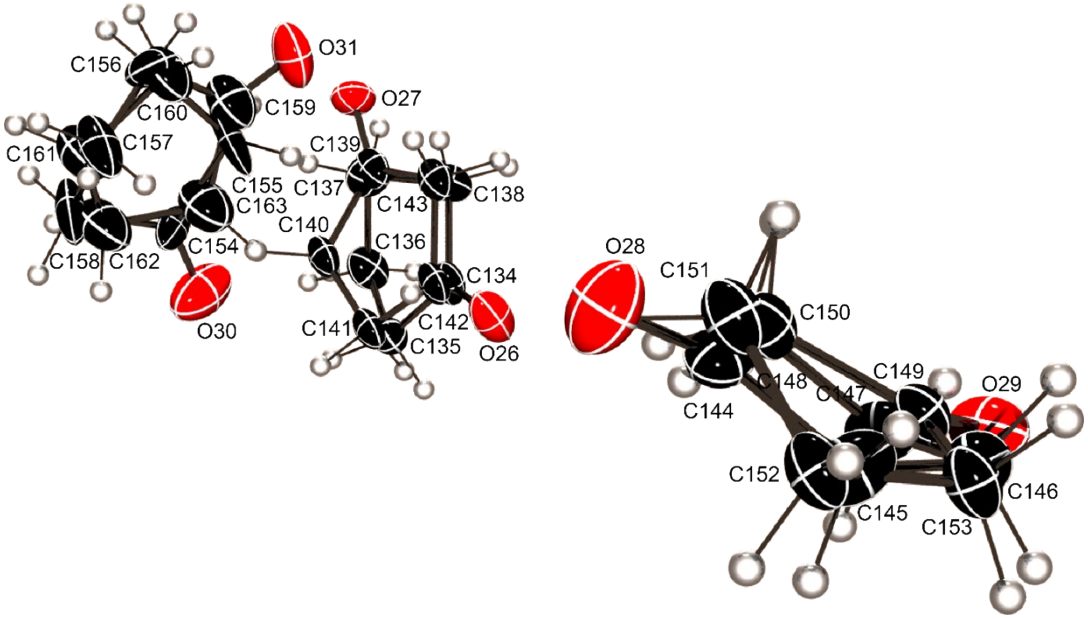

Fig. S3 Ortep drawing of disordered cyclopentanones (50% probability).

Single crystal X-ray diffraction experiment for crystal 1c

The low diffracting colorless prismatic crystal (0.150 × 0.100 × 0.100 mm^3) was obtained from slow evaporation of a dichloromethane solution of **1** and 3-oxetanone.

$C_{51.30}H_{50.40}Cl_2N_4O_{12.20}$, *Mr* = 989.05; orthorhombic, space group *Cmcm*, *Z* = 4, D_{calc} = 1.342 $g \cdot cm^{-3}$, *a* = 25.162(4), *b* = 13.623(2), *c* = 14.286(2) Å, *V* = 4896.9(12) $Å^3$, 32220 observed and 2290 [$I > 2\sigma(I)$], 2392 [all data] independent reflections, 226 parameters, 22 restraints, final R_1 = 0.1359, wR_2 = 0.4382, *S* = 2.492 [$I > 2\sigma(I)$] and R_1 = 0.1376, wR_2 = 0.4501, *S* = 2.499 [all data]. CCDC 2224838.

All non-hydrogen atoms were refined anisotropically. The 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 U_{eq} of their parent atoms.

Two highly disordered 3-oxetanone molecules locating on the special positions were partly refined with EADP. Each occupancy was as follows. C15, C16, O3 and O4: 71% (as free variable 21.0 or 20.5), C17, C18, O5 and O6: 34% (as free variable 31.0 or 30.5).

The highly disordered dichloromethane molecules locating on the special position were refined with SIMU, SAME and SUMP combined with PART −n. Each occupancy was as follows. C19, Cl1 and Cl2: 14%, C20, Cl3 and Cl4: 11%.

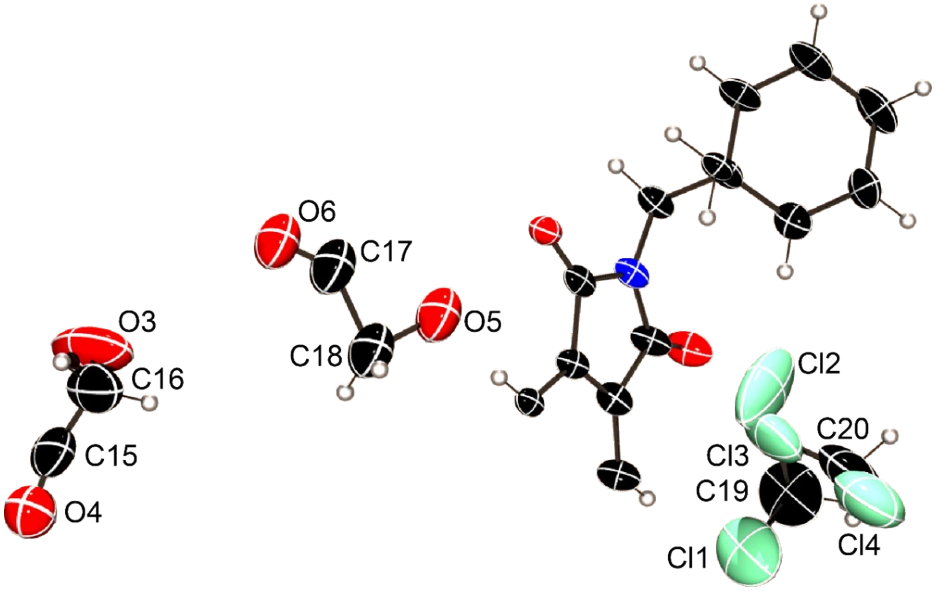

Fig. S4 Ortep drawing of crystal **1c** (asymmetric unit, 50% probability).

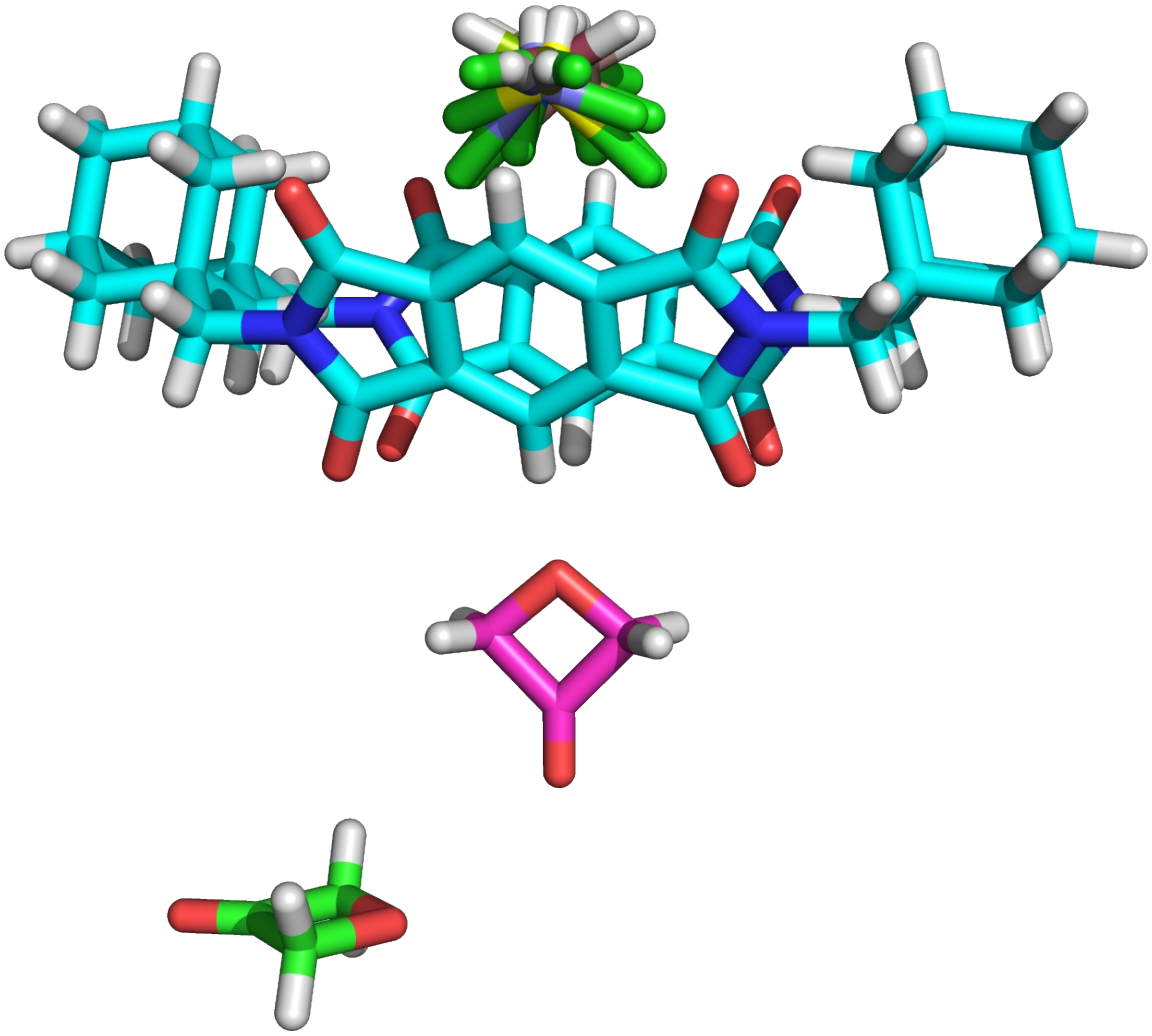

Fig. S5 One complete unit of crystal **1c**.

Single crystal X-ray diffraction experiment for crystal 2a

The low diffracting colorless prismatic crystal (0.120 × 0.100 × 0.100 mm^3) was obtained from slow evaporation of a dichloromethane solution of **2** and cyclopentanone.

$C_{77}H_{84}N_4O_{13}$, Mr = 1273.48; triclinic, space group P-1, Z = 2, D_{calc} = 1.327 $g \cdot cm^{-3}$, a = 14.9566(14), b = 14.9948(14), c = 16.2793(15) Å, α = 64.136(3), β = 79.706(3), γ = 76.944(3)°, V = 3186.9(5) $Å^3$, 44766 observed and 11343 [$I > 2\sigma(I)$], 12318 [all data] independent reflections, 1175 parameters, 151 restraints, final R_1 = 0.0472, wR_2 = 0.1182, S = 1.022 [$I > 2\sigma(I)$] and R_1 = 0.0504, wR_2 = 0.1209, S = 1.026 [all data]. CCDC 2224839.

All non-hydrogen atoms were refined anisotropically. The 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 U_{eq} of their parent atoms.

Overlapped disordered cyclopentanone molecules were fully or partly refined with PART n and SIMU. Each occupancy was as follows. C53-C57, O9: 65% (as free variable 21), C58-C62, O10: 35% (as free variable −21), C63-C67, O11: 76% (as free variable 31), C68-C72, O12: 24% (as free variable −31), C73-C77, O13: 52% (as free variable 41), C78-C82, O14: 48% (as free variable −41), C83-C87, O15: 53% (as free variable 51), C88-C92, O16: 47% (as free variable −51). (Fig. S7)

The cyclopentanone molecules locating on special positions were fully or partly refined with PART −n, SAME and SIMU. Each occupancy was firstly refined with each free variable and finally fixed as follows, C93-C97, O17: 50%, C98-C102, O18: 25%, C103-C107, O19: 25%. (Fig. S8)

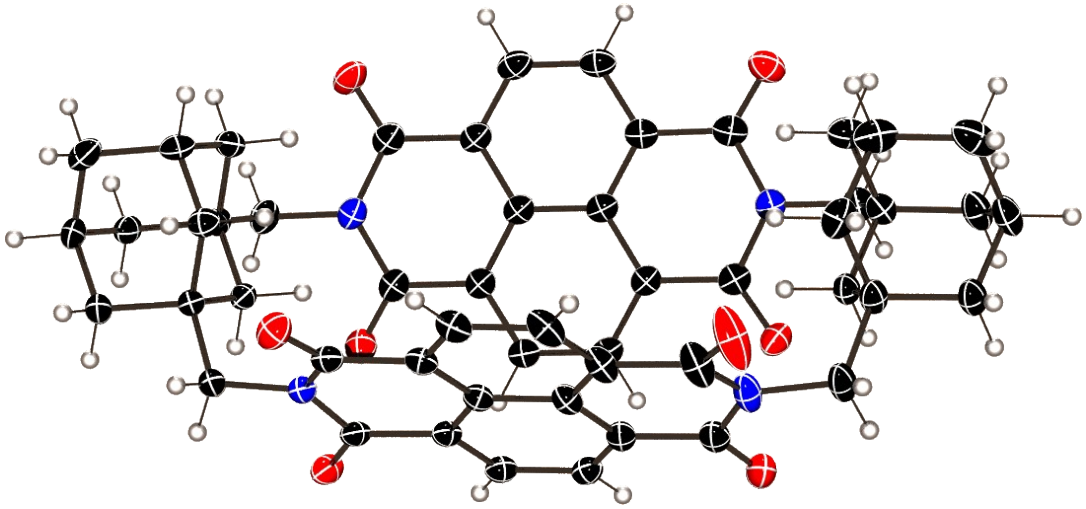

Fig. S6 Ortep drawing of **2** (50% probability).

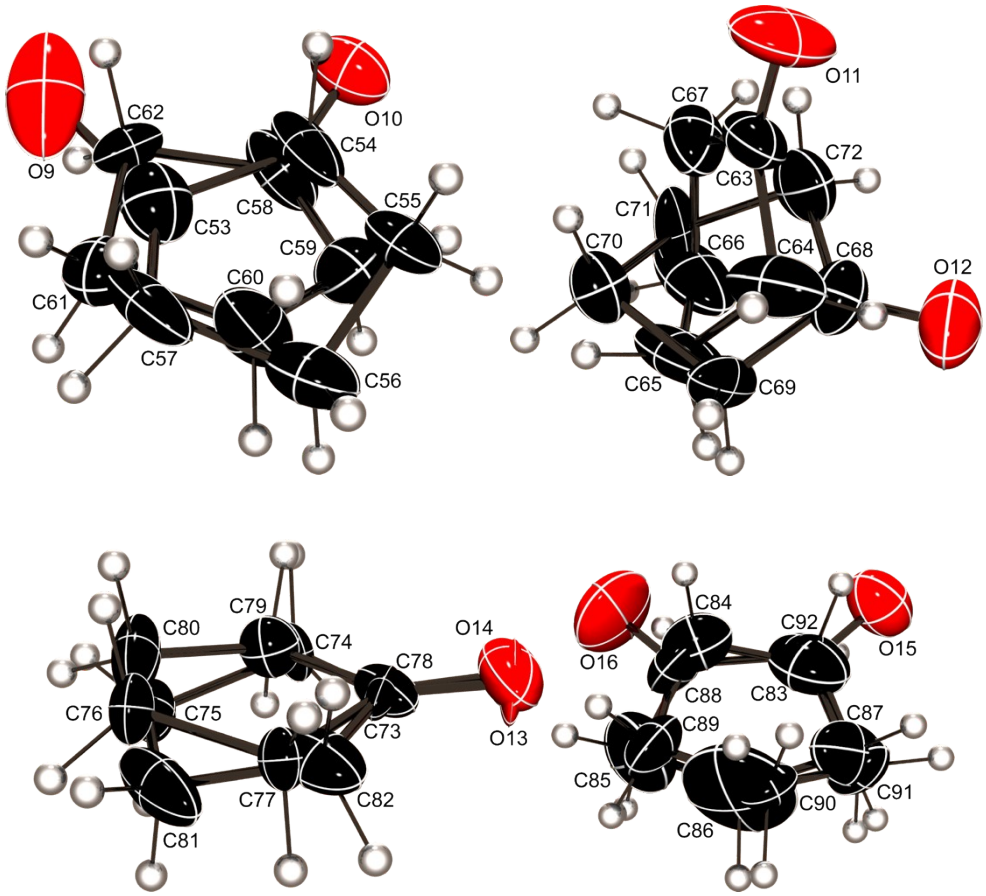

Fig. S7 Ortep drawing of overlapped disordered cyclopentanone molecules (50% probability).

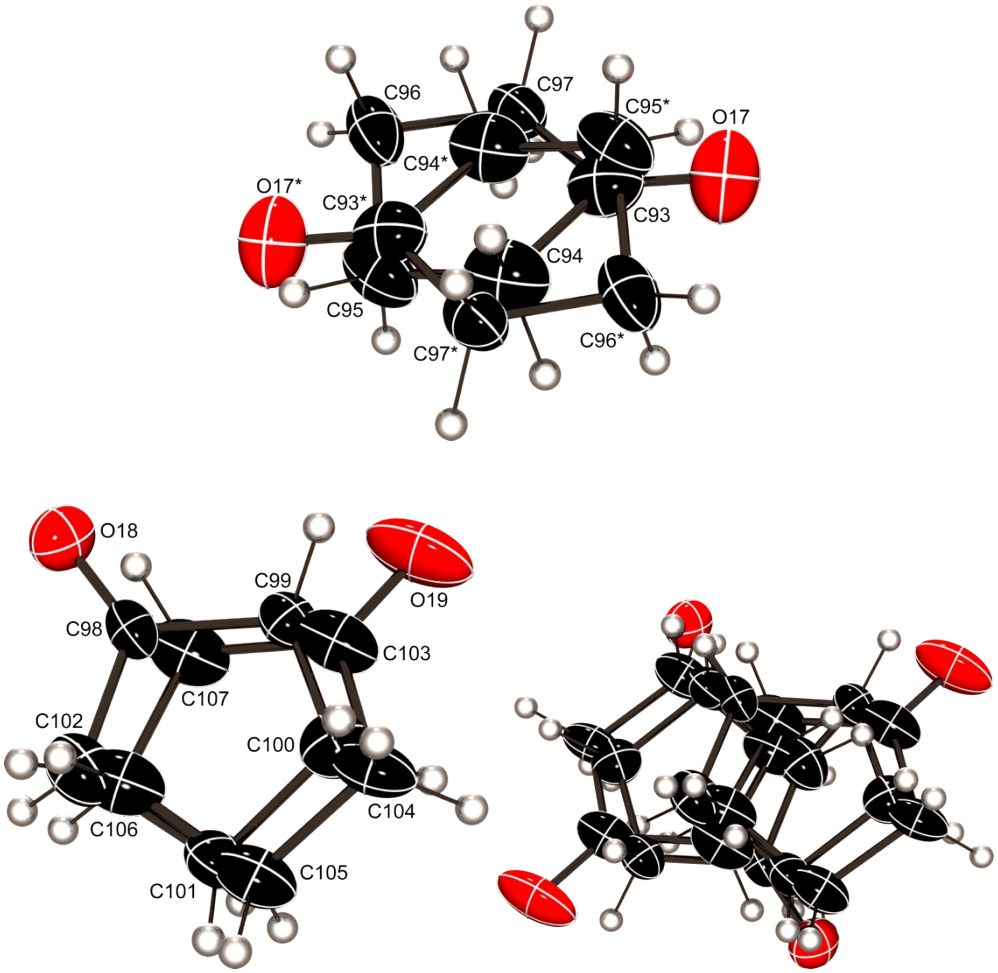

Fig. S8 Ortep drawing of cyclopentanone molecules locating on special positions (50% probability). Bottom left: asymmetric unit, bottom right: one complete unit.

Single crystal X-ray diffraction experiment for crystal 2b

The colorless prismatic crystal (0.100 × 0.080 × 0.080 mm^3) was obtained from slow evaporation of a dichloromethane solution of **2** and 2-cyclohexen-1-one.

$C_{54}H_{48}Cl_4N_4O_8$, *M*r = 1022.76; monoclinic, space group $P2_1/c$, $Z = 4$, $D_{calc} = 1.458$ g·cm^{-3}, a = 15.5518(11), b = 18.9095(14), c = 16.7038(12) Å, β = 108.490(2)°, V = 4658.6(6) $Å^3$, 68492 observed and 9465 [$I > 2\sigma(I)$], 9886 [all data] independent reflections, 631 parameters, final R_1 = 0.0344, wR_2 = 0.0936, S = 1.031 [$I > 2\sigma(I)$] and R_1 = 0.0355, wR_2 = 0.0945, S = 1.031 [all data]. CCDC 2224840.

All non-hydrogen atoms were refined anisotropically. The 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 U_{eq} of their parent atoms.

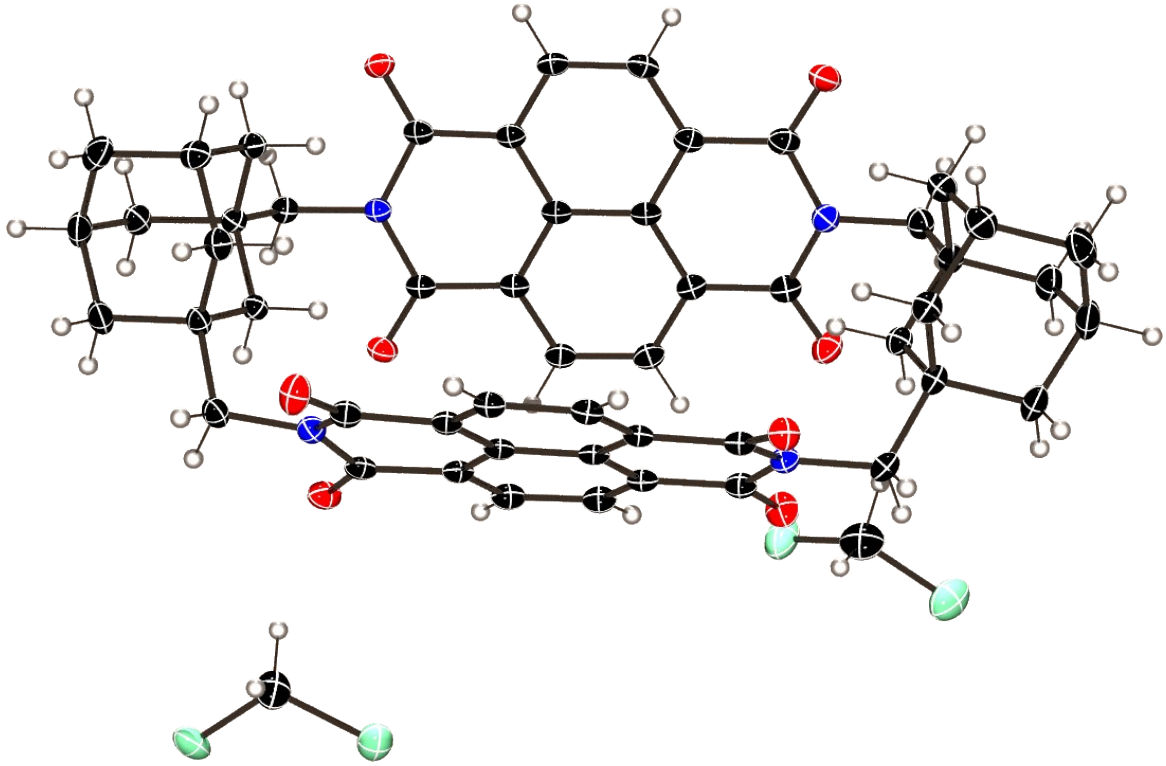

Fig. S9 Ortep drawing of crystal **2b** (50% probability).

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.