

## Supplementary Information

### Water adsorption in porous organic crystals of adamantane-bearing macrocycles

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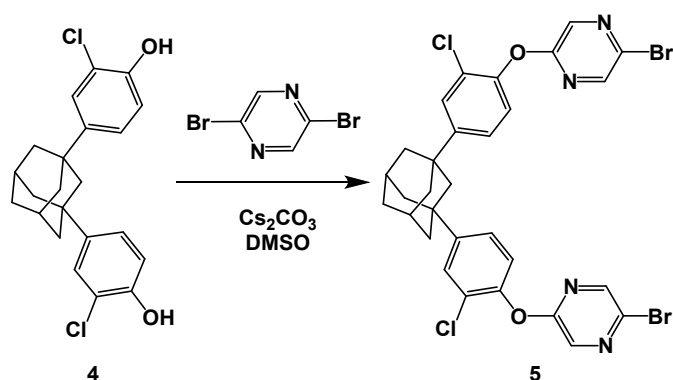
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## General Information

Commercially available reagents and solvents were employed without purification. 1,3-Bis(3-chloro-4-hydroxyphenyl)adamantane (**4**) was synthesized according to the previous literature.<sup>1</sup> Melting points were determined by using an ATM-01 apparatus. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV400 spectrometer at room temperature. Chemical shifts were reported by using tetramethylsilane as the reference standard in CDCl<sub>3</sub>. X-ray crystallographic data were collected using a Bruker D8 VENTURE diffractometer with CuK $\alpha$  radiation. Gel permeation chromatography was performed using recycling preparative HPLC (LC-9204, Japan Analytical Industry Co., Ltd.) and a JAIGEL H series column (Japan Analytical Industry Co., Ltd.). HRMS measurements of **1** and **5** were carried out using Exactive (Thermo Fisher Scientific), which consists of an Orbitrap analyzer and an atmospheric pressure chemical ionization (APCI) source. The Mercury software program was utilized to calculate the void volumes of crystalline materials.

## Synthesis of 5



A mixture of 1,3-bis(3-chloro-4-hydroxyphenyl)adamantane (**4**) (1.56 g, 4.00 mmol), 2,5-dibromopyrazine (2.85 g, 12.0 mmol), and cesium carbonate (3.91 g, 12.0 mmol) in dry dimethyl sulfoxide (50.0 mL) was stirred for 3 h at room temperature, and then for 12 h at 120 °C under an argon atmosphere. The reaction mixture was evaporated under reduced pressure. The resulting residue was suspended in chloroform and washed with H<sub>2</sub>O, brine, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica gel column chromatography (eluent: chloroform/hexane = 1:1, v/v) and gel permeation chromatography (eluent: CHCl<sub>3</sub>) gave the title compound (**5**) as a white solid (2.52 g, 3.58 mmol) in 90% yield. m.p. 173–174 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (sd, *J* = 1.2 Hz, 2H), 8.15 (sd, *J* = 1.2 Hz, 2H), 7.48 (sd, *J* = 2.4 Hz, 2H), 7.35 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 2.37 (br s, 2H), 2.02–1.97 (m, 10H), 1.80 (br s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.9, 149.6, 146.5, 134.4, 135.0, 132.3, 127.6, 126.7, 124.8, 123.1, 48.9, 42.0, 37.3, 35.5, 29.3. HRMS (APCI, *m/z*) Calcd for C<sub>30</sub>H<sub>25</sub>Br<sub>2</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub> [M + H]<sup>+</sup> 700.9716, found 700.9709.

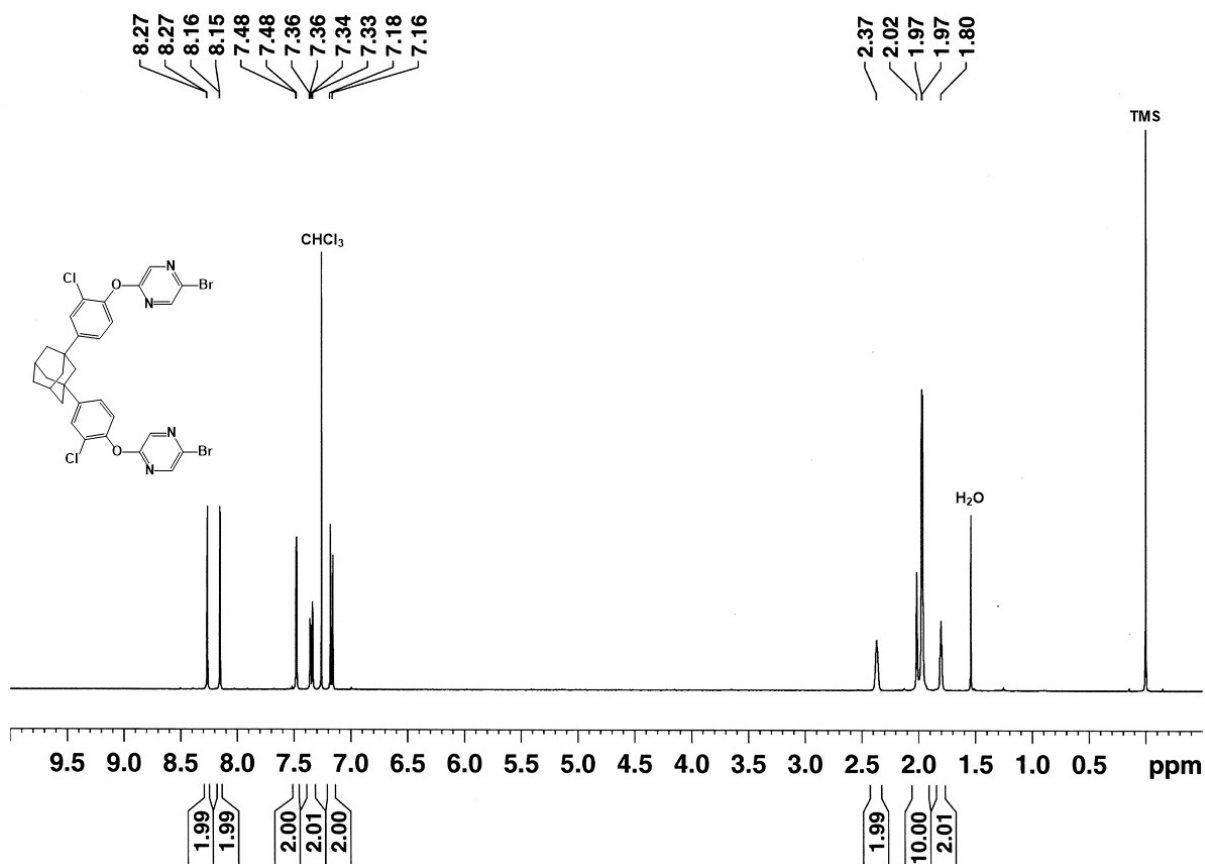


Fig. S1 <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 5.

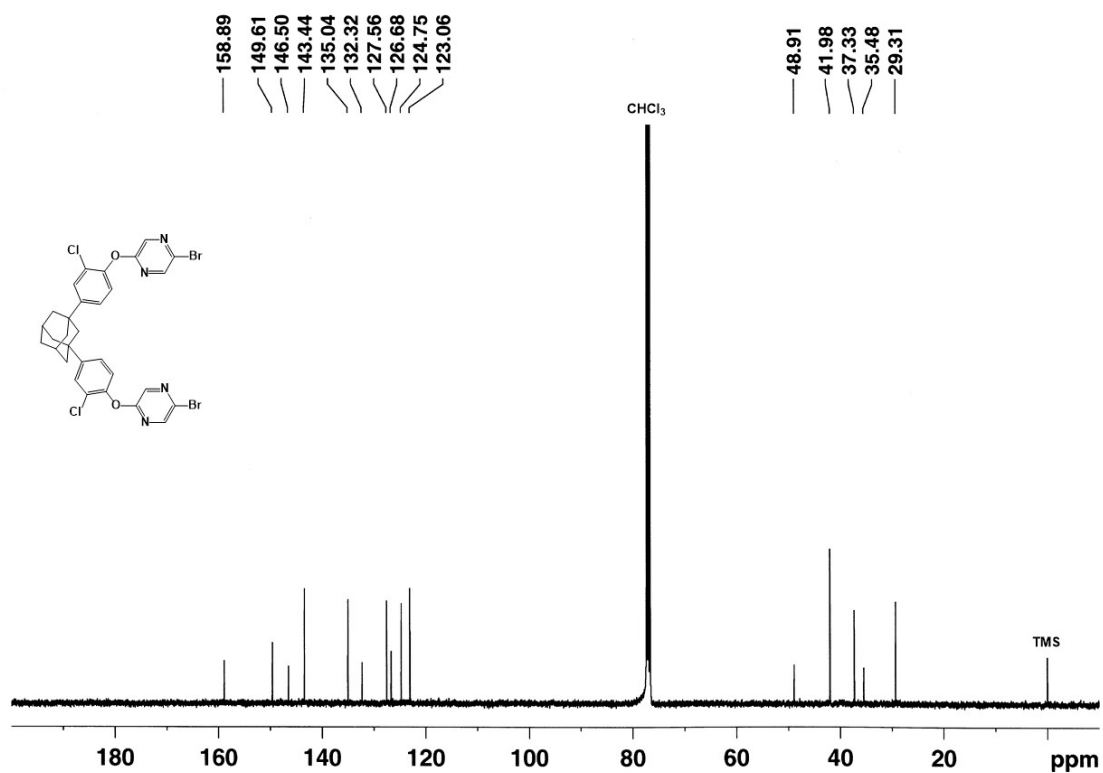
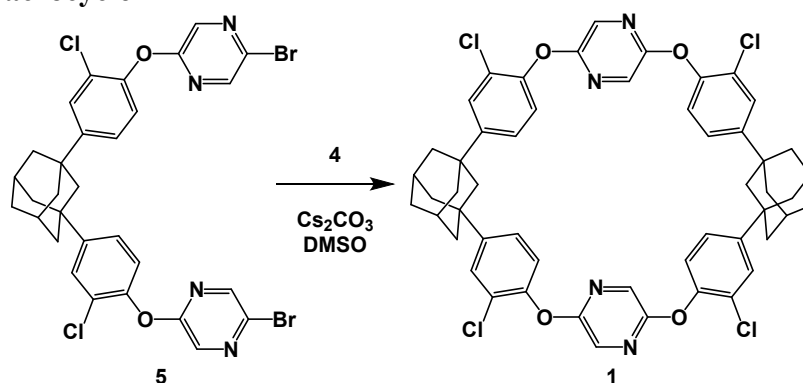


Fig. S2 <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 5.

## Synthesis of macrocycle **1**



A mixture of **4** (38.9 mg, 0.10 mmol), **5** (70.3 mg, 0.10 mmol), and cesium carbonate (97.7 mg, 0.30 mmol) in dry dimethyl sulfoxide (10.0 mL) was stirred for 3 h at room temperature, and then for 16 h at 120 °C under an argon atmosphere. The reaction mixture was evaporated under reduced pressure. The residue was suspended in chloroform and washed with  $\text{H}_2\text{O}$ , brine, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica gel column chromatography (eluent: chloroform/hexane = 2:1, v/v) and gel permeation chromatography (eluent:  $\text{CHCl}_3$ ) afforded the title compound (**1**) as a white solid (33.0 mg, 0.035 mmol) in 35% yield. m.p. > 300 °C (decomposed).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (s, 4H), 7.40 (sd,  $J = 2.0$  Hz, 4H), 7.26–7.24 (m, partly overlapped with  $\text{CHCl}_3$  peak, 4H), 7.10 (d,  $J = 8.8$  Hz, 4H), 2.38 (br s, 4H), 2.07 (d,  $J = 12.4$  Hz, 8H), 1.86 (d,  $J = 11.2$  Hz, 8H), 1.74 (br s, 4H), 1.71 (br s, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.0, 149.1, 147.4, 129.1, 127.4, 126.6, 124.7, 122.9, 51.9, 41.2, 37.2, 35.4, 29.2. HRMS (APCI,  $m/z$ ) Calcd. for  $\text{C}_{52}\text{H}_{45}\text{Cl}_4\text{N}_4\text{O}_4$   $[\text{M} + \text{H}]^+$  929.2189, found 929.2197.

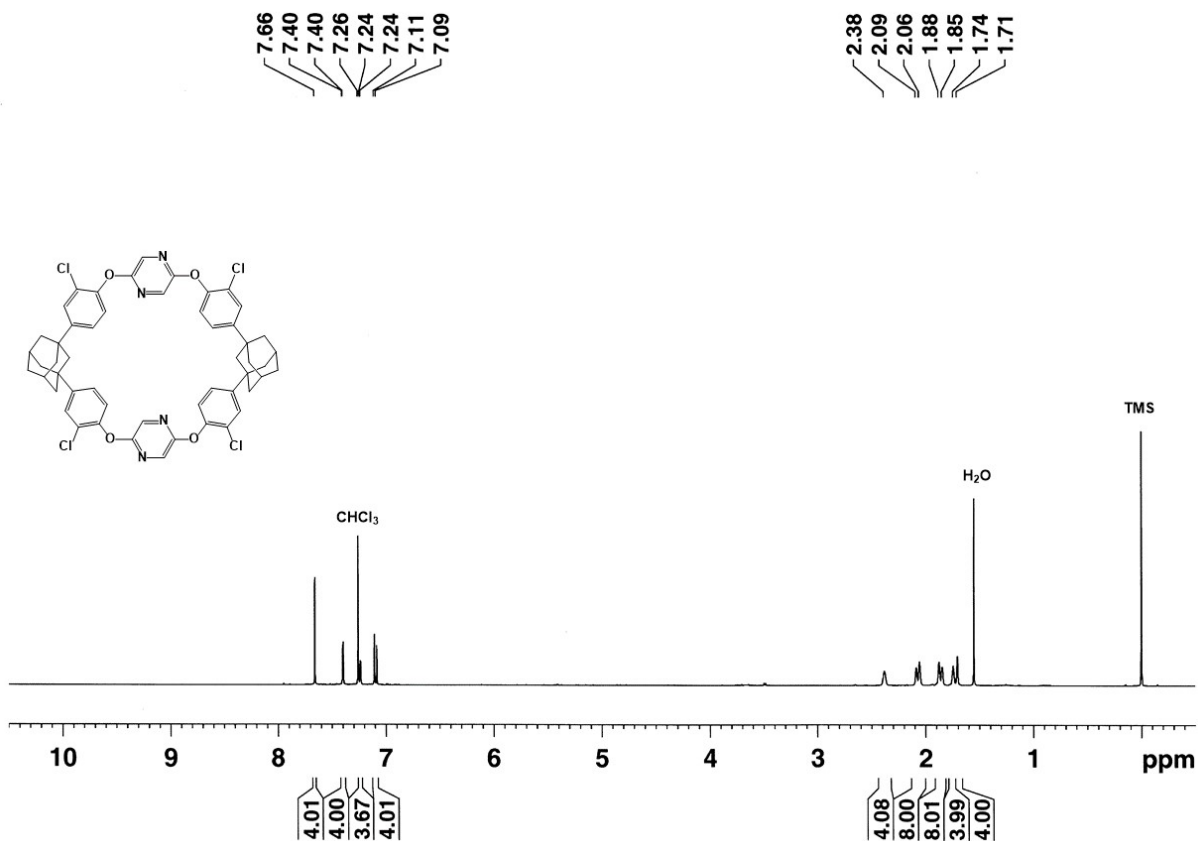


Fig. S3 <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 1.

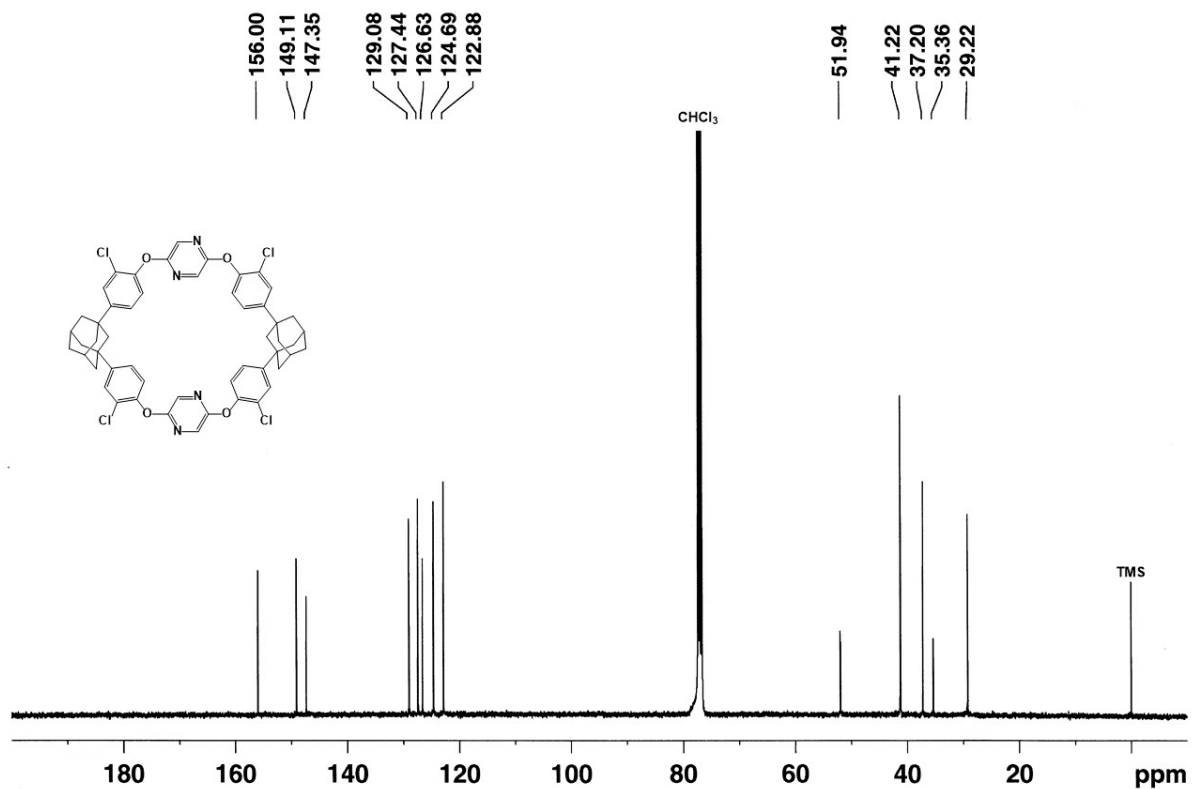
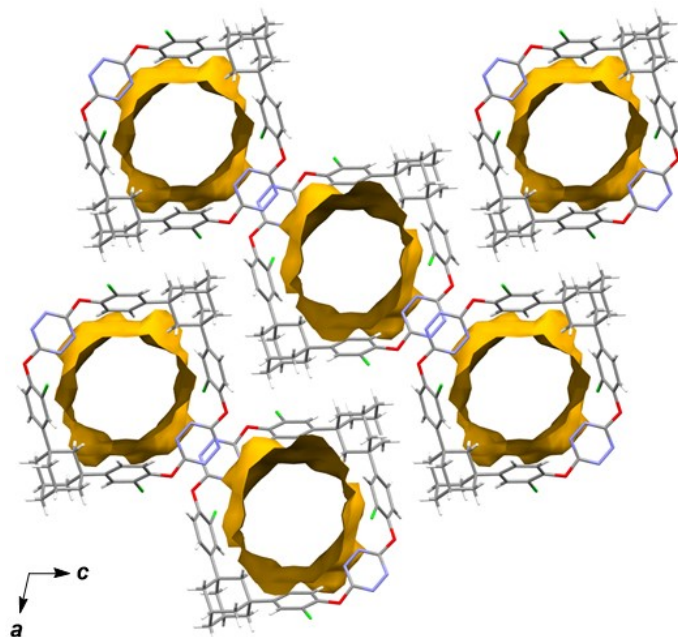


Fig. S4 <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>) of 1.



**Fig. S5** Calculated voids of crystal **2b** with a top view.

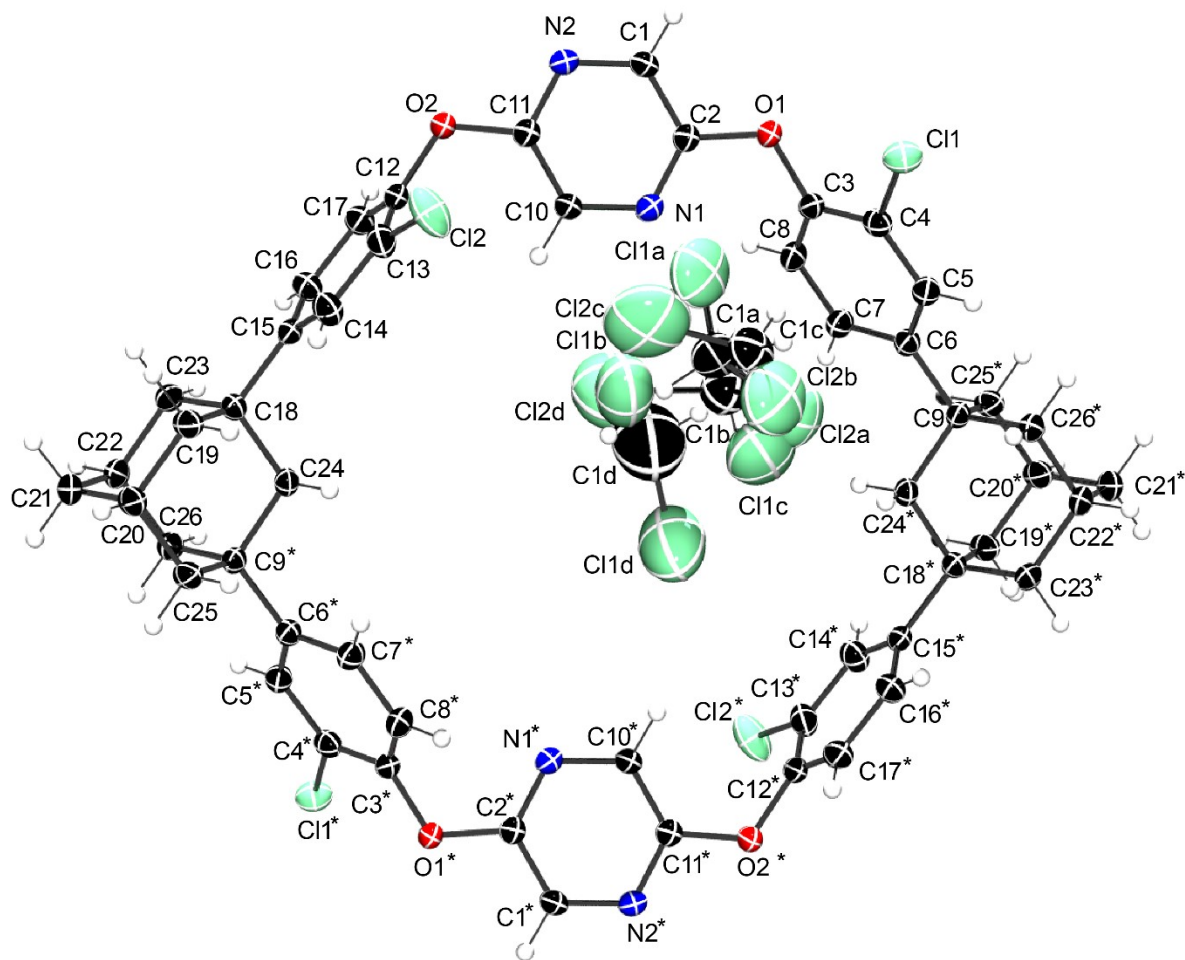
### Single crystal X-ray diffraction experiment for crystal 1a

The colorless prismatic crystal ( $0.200 \times 0.200 \times 0.180 \text{ mm}^3$ ), obtained from dichloromethane, 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>2</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>3</sup> and SHELXL-2018/3<sup>4</sup>.

$\text{C}_{54.31}\text{H}_{48.62}\text{Cl}_{8.62}\text{N}_4\text{O}_4$ ,  $M_r = 1126.80$ ; monoclinic, space group  $P2_1/n$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.422 \text{ g}\cdot\text{cm}^{-3}$ ,  $a = 16.3935(11)$ ,  $b = 7.0220(5)$ ,  $c = 23.5881(15) \text{ \AA}$ ,  $\beta = 104.313(2)^\circ$ ,  $V = 2631.1(3) \text{ \AA}^3$ , 34786 observed and 5275 [ $I > 2\sigma(I)$ ], 5374 [all data] independent reflections, 401 parameters, 82 restraints, final  $R_1 = 0.0634$ ,  $wR_2 = 0.1940$ ,  $S = 1.067$  [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0639$ ,  $wR_2 = 0.1944$ ,  $S = 1.138$  [all data]. CCDC 2190223.

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 dichloromethane molecules were refined with free variables PART –n applying with SADI, SAME, SIMU and, ISOR. Each site occupancy factor was as follows; C1a, C11a, C12a: 41.9%, C1b, C11b, C12b: 17.2%, C1c, C11c, C12c: 20.2%, C1d, C11d, C12d: 36.1%. These guest molecules overlap and are disordered.





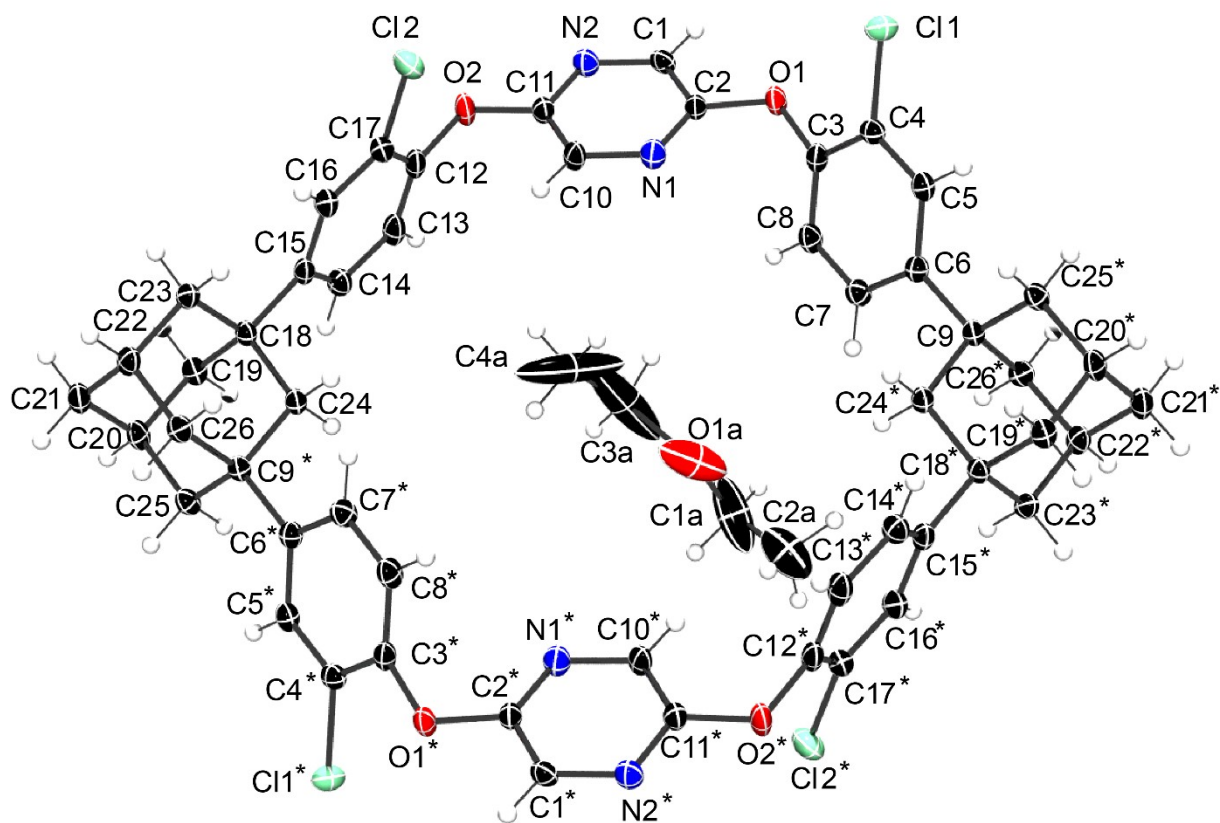
**Fig. S6** Ortep drawing of **1** and dichloromethane in crystal **1a** (50% probability).

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

Crystals **1a** (1.0 mg) were soaked in diethyl ether (1.0 mL) at room temperature. After 12 h, the solvent was removed. This process was repeated twice. The resulting colorless prismatic crystal ( $0.150 \times 0.120 \times 0.120$  mm<sup>3</sup>) 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 $\alpha$ :  $\lambda = 1.54178$  Å). Absorption correction was performed by an empirical method implemented in SADABS.<sup>2</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>3</sup> and SHELXL-2018/3<sup>4</sup>.

C<sub>56</sub>H<sub>54</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>5</sub>,  $M_r = 1004.83$ ; monoclinic, space group  $P2_1/n$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.273$  g·cm<sup>-3</sup>,  $a = 16.326(2)$ ,  $b = 7.0749(9)$ ,  $c = 23.550(3)$  Å,  $\beta = 105.465(3)^\circ$ ,  $V = 2621.7(6)$  Å<sup>3</sup>, 34591 observed and 5224 [ $I > 2\sigma(I)$ ], 5295 [all data] independent reflections, 336 parameters, final  $R_1 = 0.0640$ ,  $wR_2 = 0.2289$ ,  $S = 1.267$  [ $I > 2\sigma(I)$ ], final  $R_1 = 0.0716$ ,  $wR_2 = 0.2478$ ,  $S = 1.267$  [all data]. CCDC 2190224.

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  $U_{\text{iso}}$  values constrained to 1.2  $U_{\text{eq}}$  of their parent atoms. The diethyl ether (C1a, C2a, C3a, C4a, and O1a) was located very close to the symmetry center and refined with PART –n. The occupancy factor was 50%.



**Fig. S7** Ortep drawing of **1** and diethyl ether in crystal **1b** (50% probability).

### Single crystal X-ray diffraction experiment for crystal **1c**

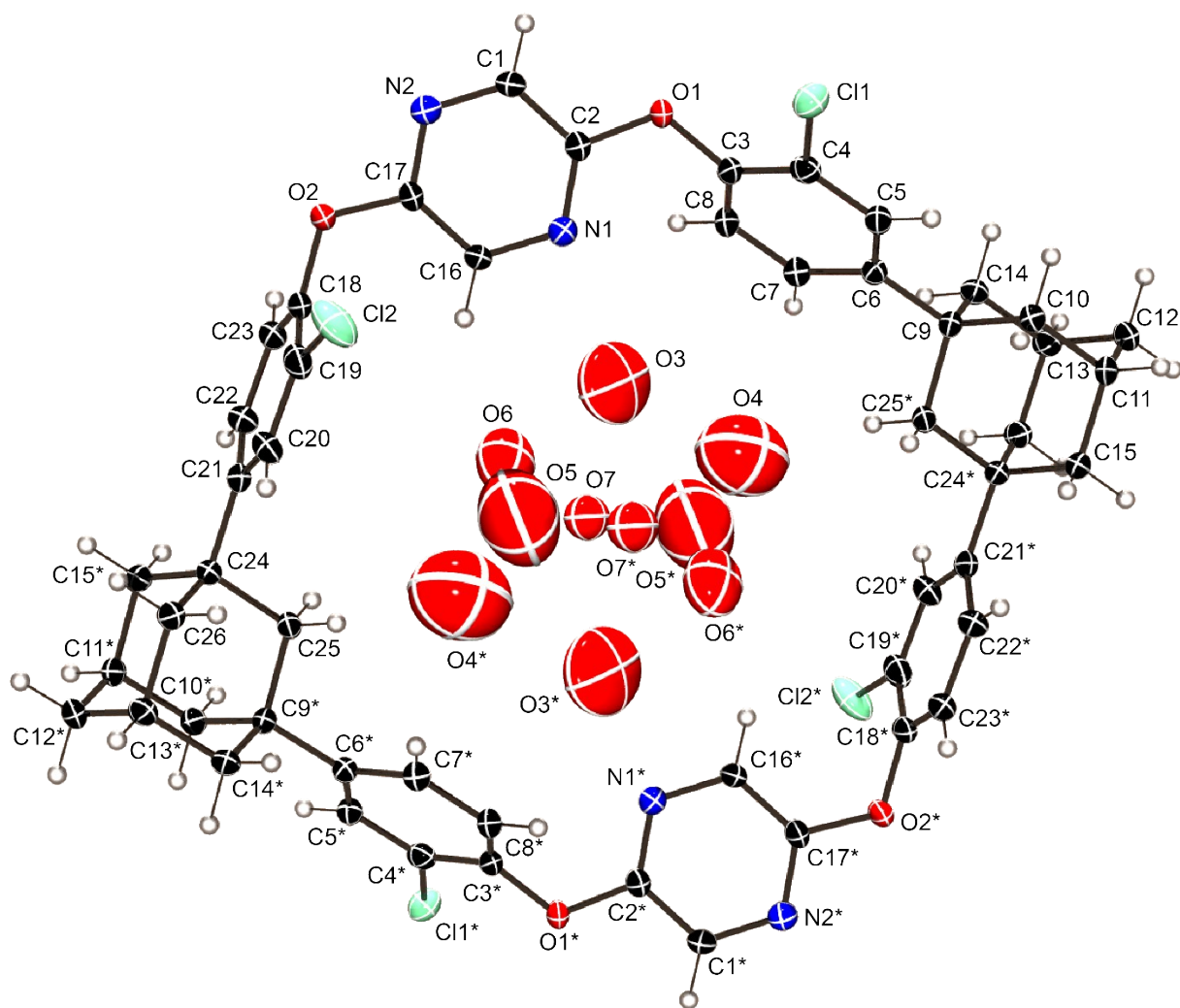
Crystal **1b** was treated under vacuum for 3 days at 100 °C to afford crystal **1c**. The colorless prismatic crystal ( $0.110 \times 0.100 \times 0.080$  mm<sup>3</sup>), was immersed in Paraton-N oil and placed in the N<sub>2</sub> cold stream at 100 K. The diffraction experiment was performed in a Bruker D8VENTURE system (PHOTON-100 CMOS detector, CuK $\alpha$  :  $\lambda = 1.54178$  Å). Absorption correction was performed by an empirical method implemented in SADABS.<sup>2</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>3</sup> and SHELXL-2018/3<sup>4</sup>.

C<sub>52</sub>H<sub>44</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>7.64</sub>, *Mr* = 988.89; monoclinic, space group *P*2<sub>1</sub>/*n*, *Z* = 2, *D*<sub>calc</sub> = 1.257 g·cm<sup>-3</sup>, *a* = 16.4154(14), *b* = 7.0285(6), *c* = 23.505(2) Å,  $\beta$  = 105.531(4)°, *V* = 2612.9(4) Å<sup>3</sup>, 33966 observed and 4404 [*I* > 2 $\sigma$ (*I*)], 5433 [all data] independent reflections, 339 parameters, 30 restraints, final *R*<sub>1</sub> = 0.0512, *wR*<sub>2</sub> = 0.1498, *S* = 1.050 [*I* > 2 $\sigma$ (*I*)], final *R*<sub>1</sub> = 0.0633, *wR*<sub>2</sub> = 0.1586, *S* = 1.064 [all data]. CCDC 2190225.

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*<sub>iso</sub> values constrained to 1.2 *U*<sub>eq</sub> of their parent atoms.

The disordered water molecules (O3, O4, O5, O6 and O7) were refined with PART *n* (–*n* for O7) and ISOR. Each occupancy ratio was 61%/60%/36%/16%/8% for O3/O4/O5/O6/O7, respectively. This suggests a total of 7.2 water molecules were included in a unit cell. The hydrogen atoms of these disordered water molecules were not found in the Fourier map.

Solvent mask<sup>5,6</sup> was performed to verify the number of electrons and the volume in the voids. A solvent mask was calculated and 162 electrons were found in a volume of 674 Å<sup>3</sup> in one void per unit cell. This is consistent with the presence of 8 water molecules per formula unit which account for 160 electrons per unit cell. CCDC 2190226.



**Fig. S8** Ortep drawing of **1** and water in crystal **1c** (50% probability).

## Single crystal X-ray diffraction experiment for crystal 2b

Empty crystal **2a** was prepared according to the published report.<sup>7</sup> Crystal **2a** was soaked in water at room temperature for 1 day. The pink prismatic crystal ( $0.100 \times 0.080 \times 0.080$  mm<sup>3</sup>) was immersed in Paraton-N oil and placed in the N<sub>2</sub> cold stream at 100 K. The diffraction experiment was performed in a Bruker D8VENTURE system (PHOTON-100 CMOS detector, CuK $\alpha$  :  $\lambda = 1.54178$  Å). Absorption correction was performed by an empirical method implemented in SADABS.<sup>2</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>3</sup> and SHELXL-2018/3<sup>4</sup>.

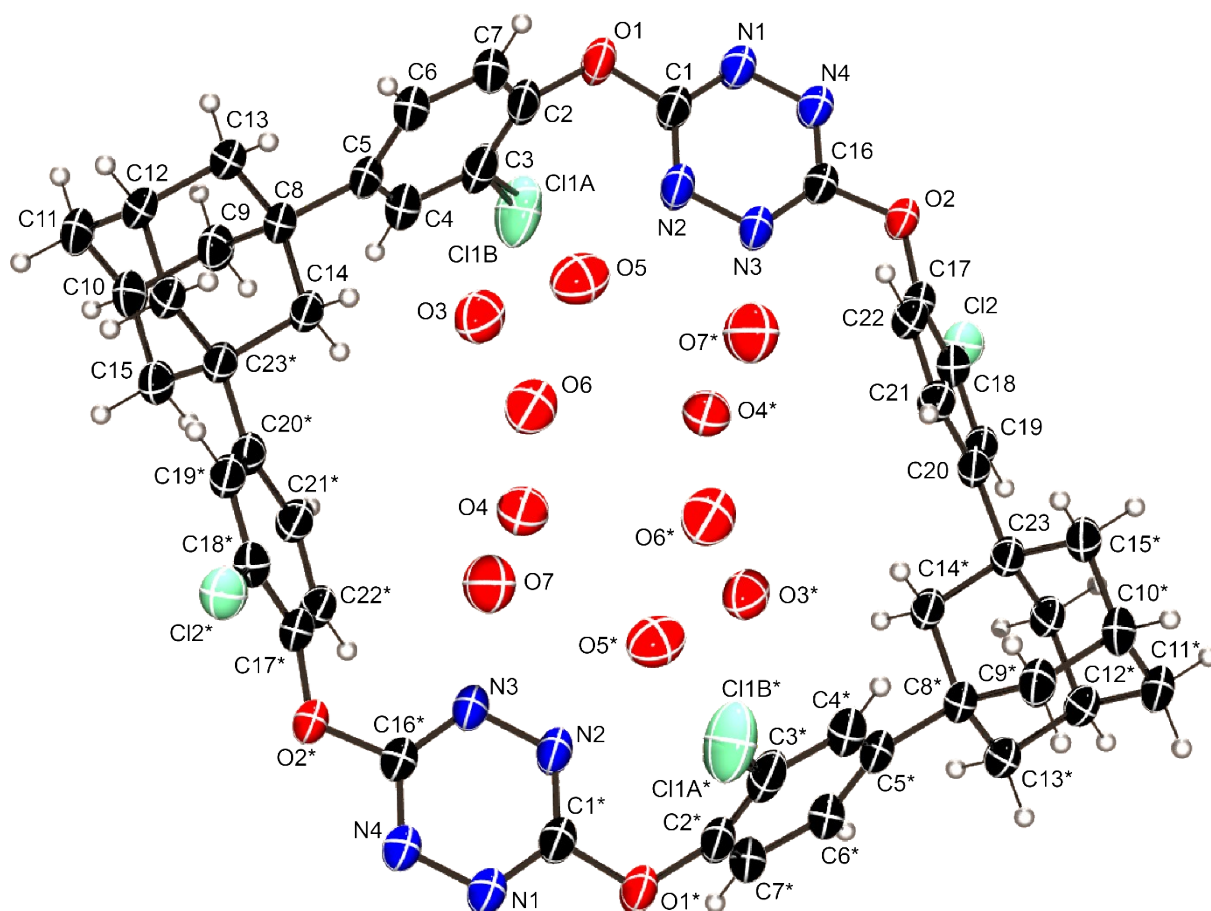
C<sub>48</sub>H<sub>40</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>10</sub>,  $M_r = 1030.71$ ; monoclinic, space group  $P2_1/n$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.317$  g·cm<sup>-3</sup>,  $a = 16.080(6)$ ,  $b = 6.799(5)$ ,  $c = 24.380(11)$  Å,  $\beta = 102.86(3)^\circ$ ,  $V = 2599(2)$  Å<sup>3</sup>, 36296 observed and 4873 [ $I > 2\sigma(I)$ ], 5466 [all data] independent reflections, 349 parameters, final  $R_1 = 0.0545$ ,  $wR_2 = 0.1445$ ,  $S = 1.120$  [ $I > 2\sigma(I)$ ], final  $R_1 = 0.0605$ ,  $wR_2 = 0.1476$ ,  $S = 1.120$  [all data]. CCDC 2190227.

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  $U_{\text{iso}}$  values constrained to 1.2  $U_{\text{eq}}$  of their parent atoms.

A pair of disordered chlorine atom (Cl1A/Cl1B) was refined with PART n and each occupancy ratio was ca. 43/57.

The disordered water molecules (O3, O4, O5, O6 and O7) were refined with PART n. Each occupancy ratio was 59%/58%/62%/61%/60% for O3/O4/O5/O6/O7, respectively. This suggests a total of 12 water molecules were included in a unit cell. The hydrogen atoms of these disordered water molecules were not found in the Fourier map.

Solvent mask<sup>5,6</sup> was performed to verify the number of electrons and the volume in the voids. A solvent mask was calculated and 214 electrons were found in a volume of 678 Å<sup>3</sup> in one void per unit cell. This is consistent with the presence of 10 water molecules per formula unit which account for 200 electrons per unit cell. CCDC 2190228.



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

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

Empty crystal **3a** was prepared according to the published report.<sup>8</sup> Crystal **3a** was soaked in water at room temperature for 1 day. The low diffracting pink prismatic crystal ( $0.100 \times 0.080 \times 0.050$  mm<sup>3</sup>) was immersed in Paraton-N oil and placed in the N<sub>2</sub> cold stream at 100 K. The diffraction experiment was performed in a Bruker D8VENTURE system (PHOTON-100 CMOS detector, CuK $\alpha$  :  $\lambda = 1.54178$  Å). Absorption correction was performed by an empirical method implemented in SADABS.<sup>2</sup> Structure solution and refinement were performed by using SHELXT-2014/5<sup>3</sup> and SHELXL-2018/3<sup>4</sup>.

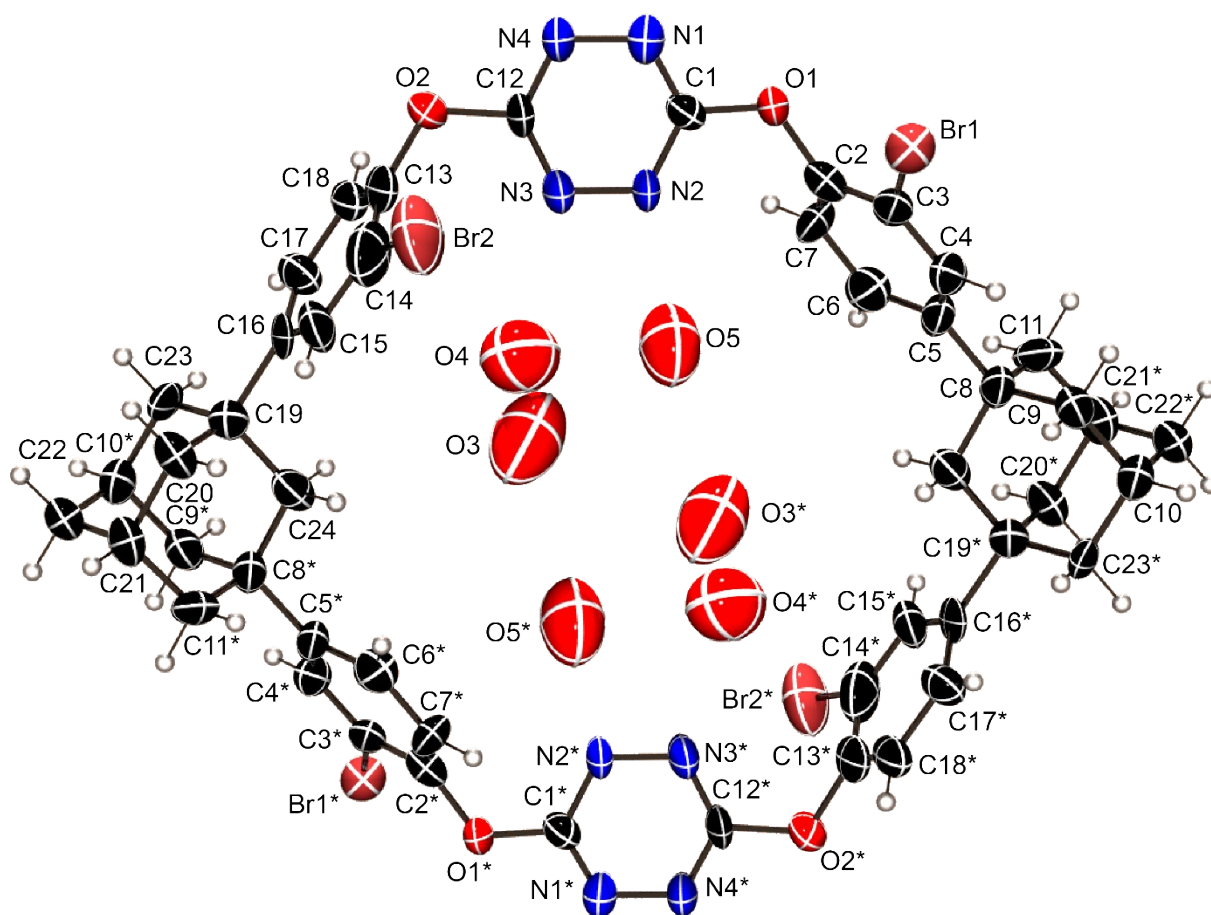
C<sub>48</sub>H<sub>40</sub>Br<sub>4</sub>N<sub>8</sub>O<sub>7.58</sub>, *Mr* = 1169.85; monoclinic, space group *P*2<sub>1</sub>/*n*, *Z* = 2, *D*<sub>calc</sub> = 1.468 g·cm<sup>-3</sup>, *a* = 16.0547(9), *b* = 7.0993(5), *c* = 23.8784(15) Å,  $\beta$  = 103.423(3)°, *V* = 2647.2(3) Å<sup>3</sup>, 18549 observed and 2294 [*I* > 2 $\sigma$ (*I*)], 4328 [all data] independent reflections, 319 parameters, 12 restraints, final *R*<sub>1</sub> = 0.1250, *wR*<sub>2</sub> = 0.3357, *S* = 1.145 [*I* > 2 $\sigma$ (*I*)], final *R*<sub>1</sub> = 0.1861, *wR*<sub>2</sub> = 0.3648, *S* = 1.146 [all data]. CCDC 2190229.

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*<sub>iso</sub> values constrained to 1.2 *U*<sub>eq</sub> of their parent atoms.

The disordered water molecules (O3, O4, O5) were refined with PART *n* and ISOR. Each occupancy ratio was 67%/61%/52% for O3/O4/O5/, respectively. This suggests a total of 7.2 water molecules were included in a unit cell. The hydrogen atoms of these disordered water molecules were not found in the Fourier map.

Solvent mask<sup>5,6</sup> was performed to verify the number of electrons and the volume in the voids. A solvent mask was calculated and 152 electrons were found in a volume of 692 Å<sup>3</sup> in one void per unit cell. This is consistent with the presence of 8 water molecules per formula unit which account for 160 electrons per unit cell. CCDC 2190230.





**Fig. S10** Ortep drawing of **3** and water in crystal **3b** (50% probability).

## References

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- (8) T. Hyodo, M. Tominaga and K. Yamaguchi, *CrystEngComm*, 2021, **23**, 1539–1543.