Electronic Supporting Information

Trapping of octameric water cluster by the neutral unclosed cryptand environment

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Contents

1. Crystal data for 1·$(H_2O)_4$ and 1·(H_2O)

Compounds crystallizations: Crystals of hydrates were obtained by diffusion of water vapor into DMSO solution of a mixture of **1** and excess amount of corresponding TBA salt (8-10 eq).

Diffractometer and data collection: Measurements of **1**·$(H_2O)_4$ at 100K were performed on a KM4CCD κ-axis diffractometer with graphite-monochromated MoKα radiation. Data reduction and analysis were carried out with the Oxford Diffraction programs.[1] X-ray data for **1**·$(H_2O)_4$ measured at 293K on a SuperNova Agilent diffractometer using Cu*K*α radiation.[2] The data was processed with CrysAlisPro.[3] Measurements of **1**·H_2O at 100K were performed on a Bruker Kappa CCD diffractometer with graphite monochromated MoKα radiation. Data was processed with Denzo and Scalepak.[4]

Structure refinement: The structure was solved by direct methods and refined using SHELXL.[5]

Crystallographic data (excluding structure factors) for the structures discussed in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

The H-bonds in crystal structure were determined according to IUPAC recommendation.[6]

Tab. S1 Geometrical parameters of H-bonds in **1**·$(H_2O)_4$ of the water clusters.

D–H···A	Length	$d_{D\cdots A}$ @100K	$d_{D\cdots A}$ @293K	$\Delta d_{D\cdots A}$
O2W–H2WA···O1W	C	2.788(2)	2.791(5)	0.003
O3W–H3WA···O2W	F	2.818(2)	2.833(5)	0.015
O3W–H3WB[a]···O2W	D	2.925(3)	2.980(5)	0.055
O4W–H4WA···O3W	G	2.831(2)	2.840(5)	0.009
O1W–H1WA···O5[b]	B	2.697(3)	2.692(5)	-0.005
O1W–H1WB···O7[c]	A	2.738(2)	2.742(5)	0.004
O2W –H2WB···O8[d]	E	2.797(2)	2.821(4)	0.024
O4W–H4WB···O3	I	2.856(2)	2.828(4)	-0.028
N4–H4···O4W	H	3.032(2)	3.060(5)	0.028
N6–H6···O4W	J	3.075(2)	3.101(5)	0.026
Average		2.856	2.869	0.013

Symmetry codes: a = 1-x, 1-y, 2-z; b = -1+x, y,z; c = x, 1+ y, z; d = 1-x, -y, 2-z.

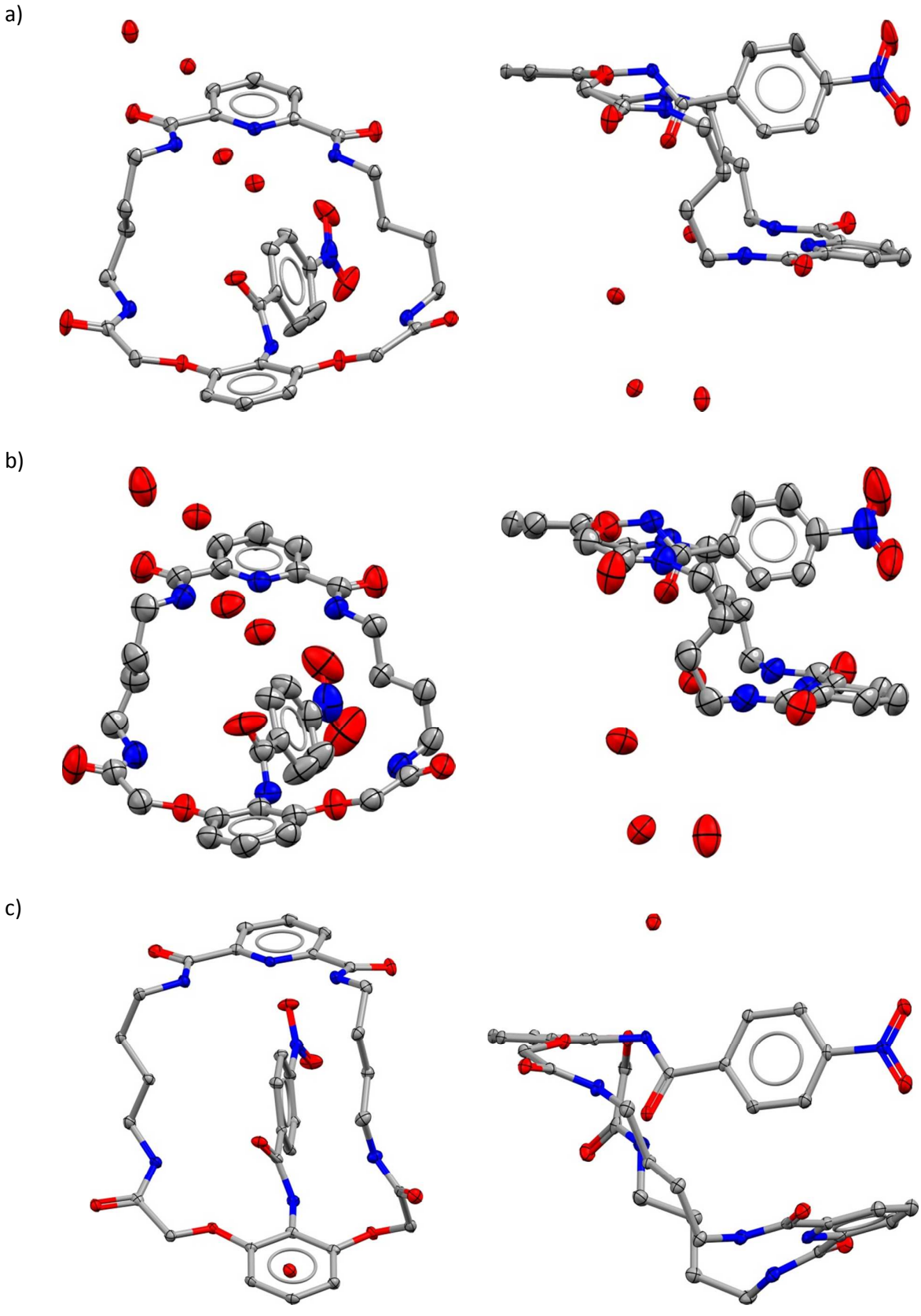


Fig. S1 Front (left) and side view (right) of Oak Ridge thermal ellipsoid plot (ORTEP) diagrams for structures of **1**·$(H_2O)_4$ measured at 100K (a) and 293K (b), and for structure of **1**·(H_2O) with the thermal ellipsoids shown at a 50% probability level.

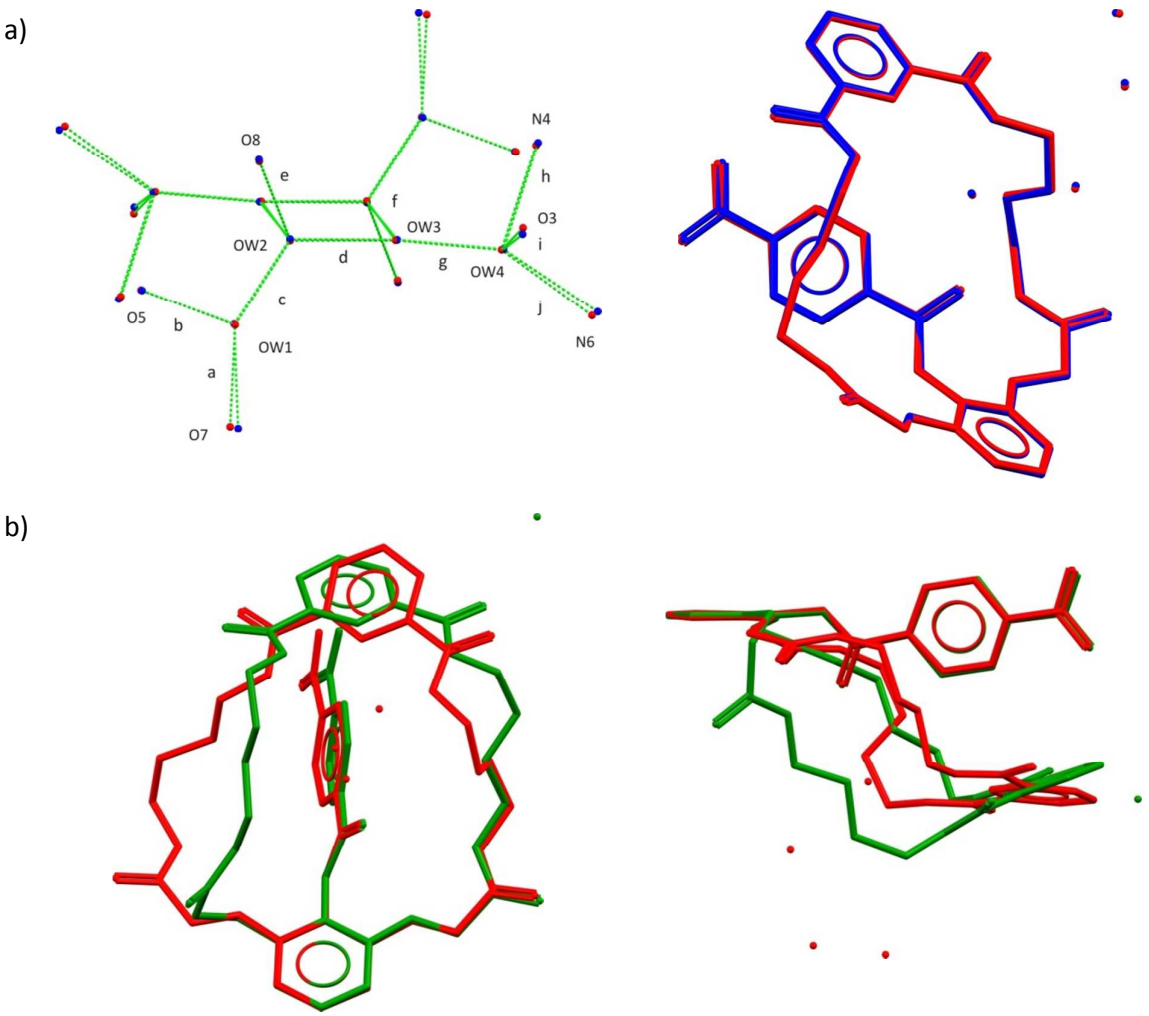


Fig. S2 (a) Superposition of the water clusters (left) and host molecules (right) for structures measured at 100K (red) and 293K (blue), H-bonds are shown in green dotted lines, the overall r.m.s. difference between two crystal structures is 0.092 Å; (b) Superposition of the structures of **1**·$(H_2O)_4$@100K (red) and **1**·(H_2O)@100K (green) through resorcine ring.

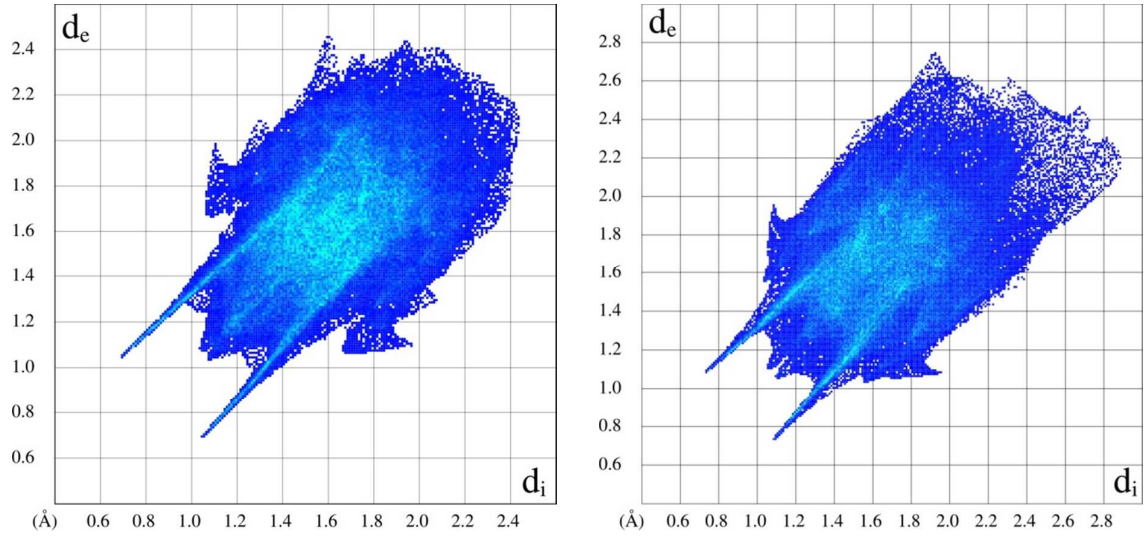


Fig. S3 Hirshfeld fingerprints for the crystals of **1**·$(H_2O)_4$@100K (left) and **1**·(H_2O) (right).

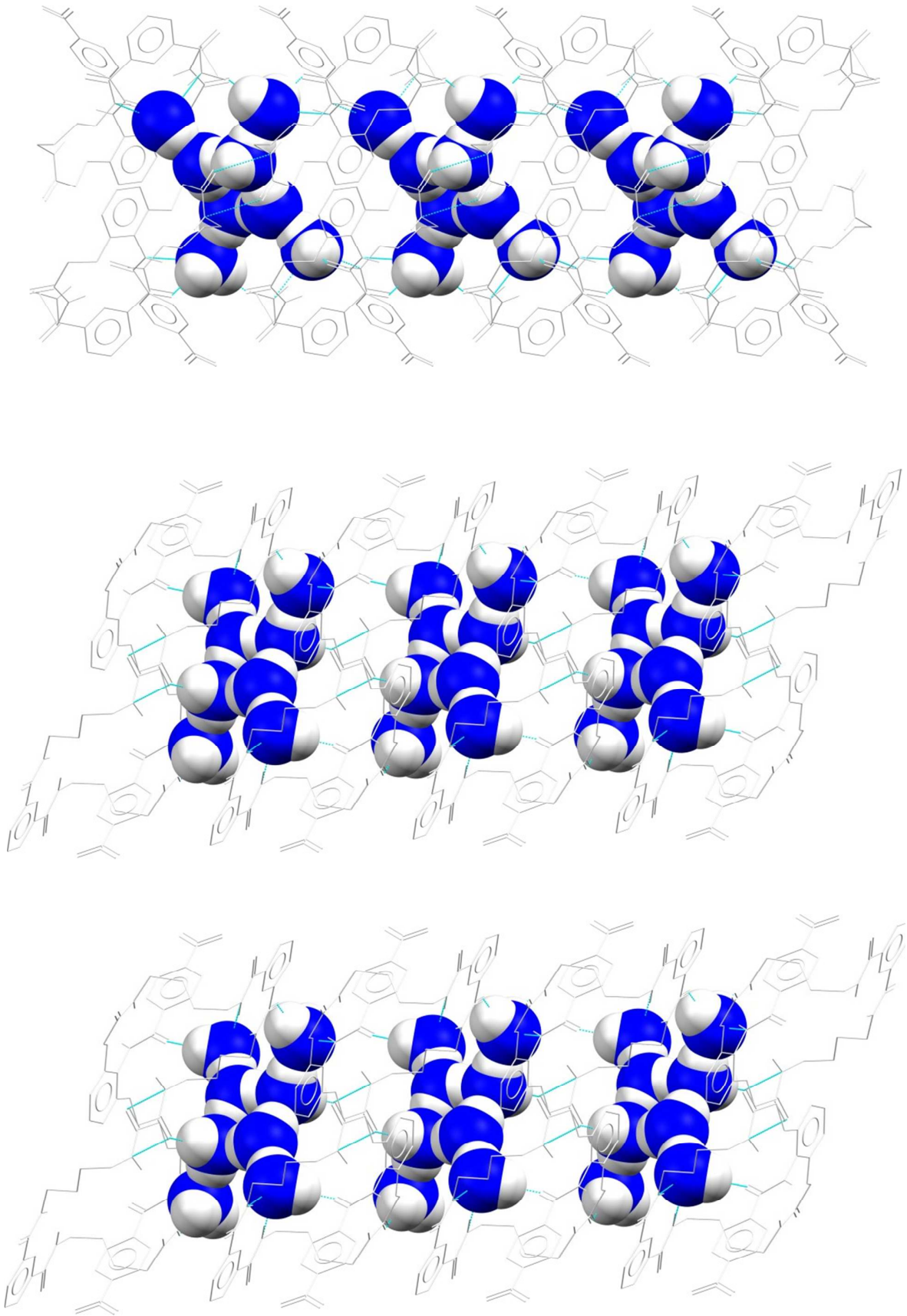
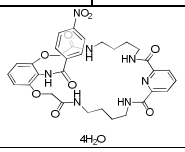
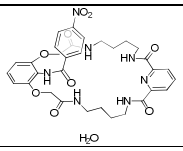


Fig. S4 Packing of the water octamers along *a* axis (top), *b* axis (middle), and *c* axis (bottom) in the crystal lattice, clusters are shown in space-fill representation, receptor **1** in gray, and H-bonds as green dashed lines.

Tab. S2 Crystal data and structure refinement details for **1**·$(H_2O)_4$ and **1**·(H_2O).

Compound	**1**·$(H_2O)_4$ at 100K		**1**·$(H_2O)_4$ at 293K		**1**·(H_2O) at 100K	
Structure	 $4H_2O$				 H_2O	
Empirical formula	$C_{32}H_{43}N_7O_{13}$				$C_{32}H_{37}N_7O_{10}$	
Moiety formula	$C_{32}H_{35}N_7O_9·4H_2O$				$C_{32}H_{35}N_7O_9·H_2O$	
Formula weight	733.73				679.69	
CCDC No.	997178		997179		1009725	
Temperature	100 K		293 K		100 K	
Wavelength	0.71073 Å (MoK_α)		1.54184 Å (CuK_α)		0.71073 Å (MoK_α)	
Crystal system	Triclinic				Monoclinic	
Space group	*P*-1				$P2_1/c$	
Unit cell dimensions	*a*=9.6293(4) Å	α=79.251(3) °	*a* =9.807(1) Å	α=79.07(1) °	*a*=16.5500(5) Å	α=90.00 °
	b=10.5860(4) Å	β=74.914(3) °	*b*=10.691(2) Å	β=74.95(1) °	*b*=9.2150(3) Å	β=121.388(2) °
	c=18.1620(7) Å	γ=80.515(3) °	*c*=18.124(2) Å	γ=80.47(1) °	*c*=25.1110(8) Å	γ=90.00 °
Volume	*V* = 1743.0(1) Å^3		*V* = 1788.1(5) Å^3		*V* = 3269.2(2) Å^3	
Z	2		2		4	
Density Calc.	1.398 g/cm^3		1.363 g/cm^3		1.381 g/cm^3	
Absorption coefficient	0.110 mm^{-1}		0.902 mm^{-1}		0.104 mm^{-1}	
F(000)	776		776		1432	
Crystal	Prismatic, colourless		Prismatic, colourless		Block, colourless	
Crystal size	0.45 × 0.14 × 0.03 mm		0.35 × 0.2 × 0.05 mm		0.40 × 0.30 × 0.15 mm	
θ range for data collection	2.0 – 28.7 °		4.2 – 71.6 °		2.8 – 26.7 °	
Index ranges	−12≤ h ≤12, −13≤ k ≤14, −23≤ l ≤23		−11≤ h ≤10, −12≤ k ≤13, −21≤ l ≤12		−20≤ h ≤20, −11≤ k ≤11, −31≤ l ≤27	
Reflections collected (all / independent)	8213 / 5584 [R_{int} = 0.048]		5630 / 3712 [R_{int} = 0.027]		30859 / 25976 [R_{int} = 0.146]	
Absorption correction	Empirical sorption correction using spherical harmonics				None	
Refinement method	Full-matrix least-squares on F^2					
Data / restraints / parameters	8213/ 0 / 521		5630 / 3 / 479		6804/ 0 / 441	
Goodness-of-fit on F^2	1.04		1.14		1.06	
Final R indices [F^2 > 2σ(F^2)]	R_1 = 0.0459, ωR_2 = 0.1093		R_1 = 0.0649, ωR_2 = 0.1792		R_1 = 0.0784, ωR_2 = 0.1533	
R indices (all data)	R_1 = 0.0782, ωR_2 = 0.1206		R_1 = 0.0993, ωR_2 = 0.2352		R_1 = 0.1276, ωR_2 = 0.1713	
Largest diff. peak and hole	0.40 and -0.59 e Å^{-3}		0.41 and -0.33 e Å^{-3}		0.37 and -0.31 e Å^{-3}	

2. Cambridge Structural Database (CSD) survey

The search in CSD (version 5.35 + update February 2014) was restricted to organic crystal structures with no errors, low degree of similarity, and having at least one water-water contact with an O···O distance less than 3.2 Å. The search for D_{2h} symmetric tetrameric water cluster resulted in 390 structures, of which only 49 structures contain both discrete and polymeric clusters without metal atom or salt. The search for water octamer motif resulted in 77 structures, of which 74 are polymeric and 56 contain metal atom or salt. The three remaining discrete clusters – decameric RERPIN, tetradecameric HEYZAO, and hexadecameric TUWPEH contain a metal atom. In addition, extensive search of literature, for any type of discrete octameric cluster stabilized in neutral environement, resulted in only one example, namely cyclic „ice-like" water octamer trapped by H-bonds from phenolic hydroxyl groups of calix[4]arenes.[7]

3. FT-IR ATR studies

The measurements were done using JACSO FT/IR-6200 Spectrometer at 293K using high resolution Attenuated Total Reflectance (ATR) technique with crystalline ZnSe. Copies of the corresponding spectra are given in Figures S7-S13 and the assignment of the vibrational bands for crystals of **1**·$(H_2O)_4$ is given in Tab. S3. Comparative spectra obtained using KBr were in total agreement with spectra obtained by ATR-FTIR, but were characterized by much less quality (see Fig. S10). To distinguish which peaks arrive from amide groups and water molecules we also measured the spectra of α,ω-diester and α,ω-di-Boc-amine which were used in the synthesis of receptor **1** (Fig. S12 and S13).

Sample preparation for crystals of **1**·$(H_2O)_4$ – crystallization solution was decanted then crystals were carefully washed with distilled water and immediately transferred into the measuring cell. After measurement the crystals were transferred to the clean glass vial for drying (p = 2 mBar, T = 40^{o}C, t = 24h). After that, the resulting white amorphous residue was transferred again to the measuring cell to record a new spectrum. It should be mentioned here that results of the elemental analysis for the extensively dried (p = 2 mBar, T = 100^{o}C, t = 24h) sample of amorphous **1** indicate the 1:1 receptor:water composition. Therefore, due to similar pattern of spectra, i.e. for amorphous **1** and that for dried **1**·$(H_2O)_4$ one can conclude that in both cases the receptor is present in the form of monohydrate. Presumably, the water molecule is so strongly bound in the macrocyclic cavity of **1** that it could not evaporate, even in the very "harsh conditions".

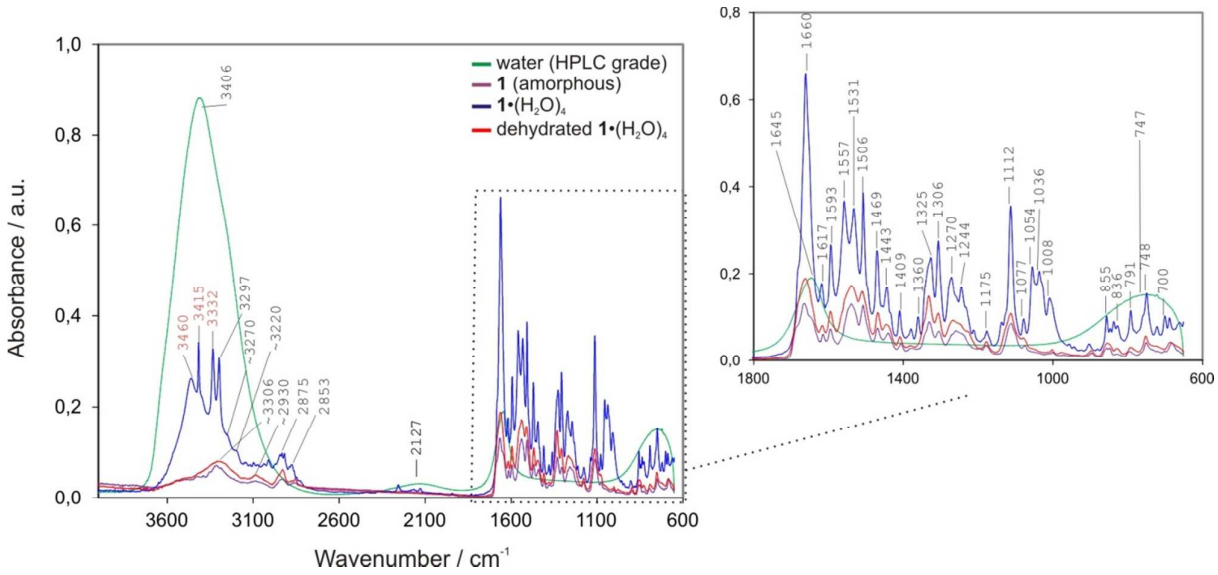


Fig. S5 Superposition of the ATR IR spectra, peaks labeled in red are absent in the spectra of both amorphous **1** and dehydrated crystals of **1**·$(H_2O)_4$ and are attributed to clustered H-bonded water.

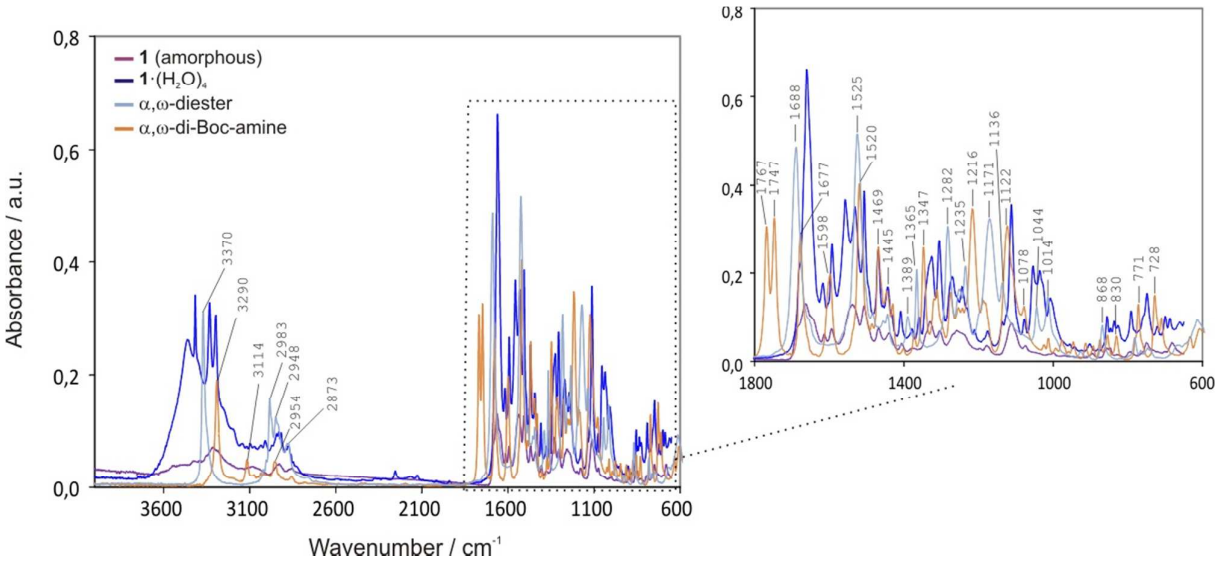


Fig. S6 Superposition of the ATR IR spectra, the α,ω-diester and α,ω-di-Boc-amine are compounds used in the synthesis of host **1**.

Tab. S3 The assignment of the vibrational bands of the FT-IR ATR spectrum of **1**·$(H_2O)_4$.

No	Peak (cm^{-1})	Appearance	Assignment	Ref
1	3460	Medium	Four-coordinated water molecules with eventually one H being a poor H-bond donor	8-10
2	3415	Strong	Water tetramer ring	11
3	3332	Strong	Three-coordinated water (DDA) with adjacent molecules of the same type or clustered H-bonded four-coordinated water molecules or secondary H-bonded amide N-H stretching of 4-carbamoyl-nitrobenzene moieties	12,13
4	3297	Strong	Secondary H-bonded amide N–H stretching of 2,6-dicarbamoyl pyridine moieties	14-16
5	~3270	Medium	Unresolved	-
6	~3220	Medium	Symmetric stretching of "ice-like" four oscillating dipoles of four-coordinated H-bond water molecules	8,17,18
7	3101	Weak	Secondary H-bonded amide - overtone of secondary amide band	14,15
8	3009	Weak	Aromatic C-H stretching	14,15
9	2931	Weak	CH_2 asymmetric C–H stretching	14,15
10	2875	Weak	CH_2 symmetric C–H stretching	14,15
11	2254	Weak	Unresolved	-
12	1660	very strong	Secondary amide C=O stretching	14,15
13	1617	Strong	Pyridine ring C=N stretching	15
14	1593	Strong	Pyridine ring C=C stretching	15
15	1557	Strong	Secondary acyclic amide N-H bending or $ArNO_2$ asymmetric stretching	14,15
16	1531	Strong	Secondary amide C-N stretching or $ArNO_2$ asymmetric stretching	14,15
17	1508	Strong	aromatic NO_2 asymmetric stretching	14,15
18	1469	Strong	CH_2 scissoring	14,15
19	1443	Medium	Aromatic C=C stretching	14,15
20	1409	Medium	C-H deformation stretching of the $–CH_2CO-$ group	14
21	1378	Weak	Unresolved	-
22	1360	Medium	$ArNO_2$ symmetric stretching	14,15
23	1325	Strong	Unresolved	-
24	1306	Strong	CH_2 wagging	
25	1270	Medium	Aromatic in plane C-H bending or C-O stretching of the alkyl-O bond	14,15
26	1244	Weak	Aromatic in plane C-H bending or secondary amide C-N stretching with N-H scissoring	15
27	1175	Weak	Aromatic in plane C-H bending or C-O stretching of the alkyl-O bond	14,15
28	1112	Strong	Aromatic in plane C-H bending	15
29	1077	Weak	Aromatic in plane C-H bending or C-O stretching of the alkyl-O bond	14,15
30	1054	Medium	Aromatic in plane C-H bending	15
31	1036	Medium	Aromatic in plane C-H bending	15
32	1008	Weak	Aromatic in plane C-H bending	15
33	903	Weak	Aromatic out-of-plane C–H bending	15
34	855	Weak	Aromatic out-of-plane C–H bending (1,4 substitution)	14,15
35	836	Weak	Aromatic out-of-plane C–H bending (1,4 substitution)	14,15
36	791	Medium	Aromatic out-of-plane C–H bending (1,2,3 substitution)	14,15
37	748	Strong	Secondary amide N-H wagging	14,15
38	720	Weak	CH_2 rocking	14-16
39	700	Weak	Aromatic out-of-plane C–H bending (1,2,3 substitution)	15
40	688	Weak	Aromatic out-of-plane C–H bending (1,2,3 substitution)	15
41	647	Weak	Unresolved	-

2.1 Copies of the FT-IR ATR spectra

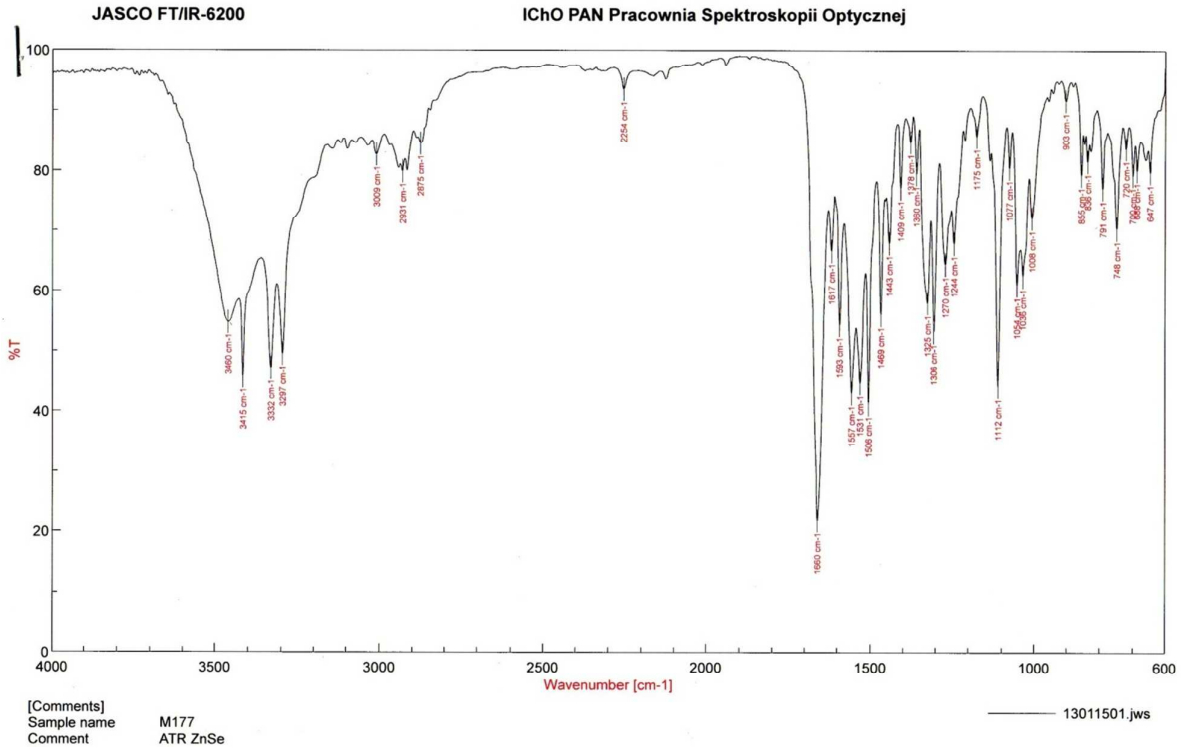


Fig. S7 FT-IR ATR (ZnSe) spectrum of the crystals of **1**·$(H_2O)_4$.

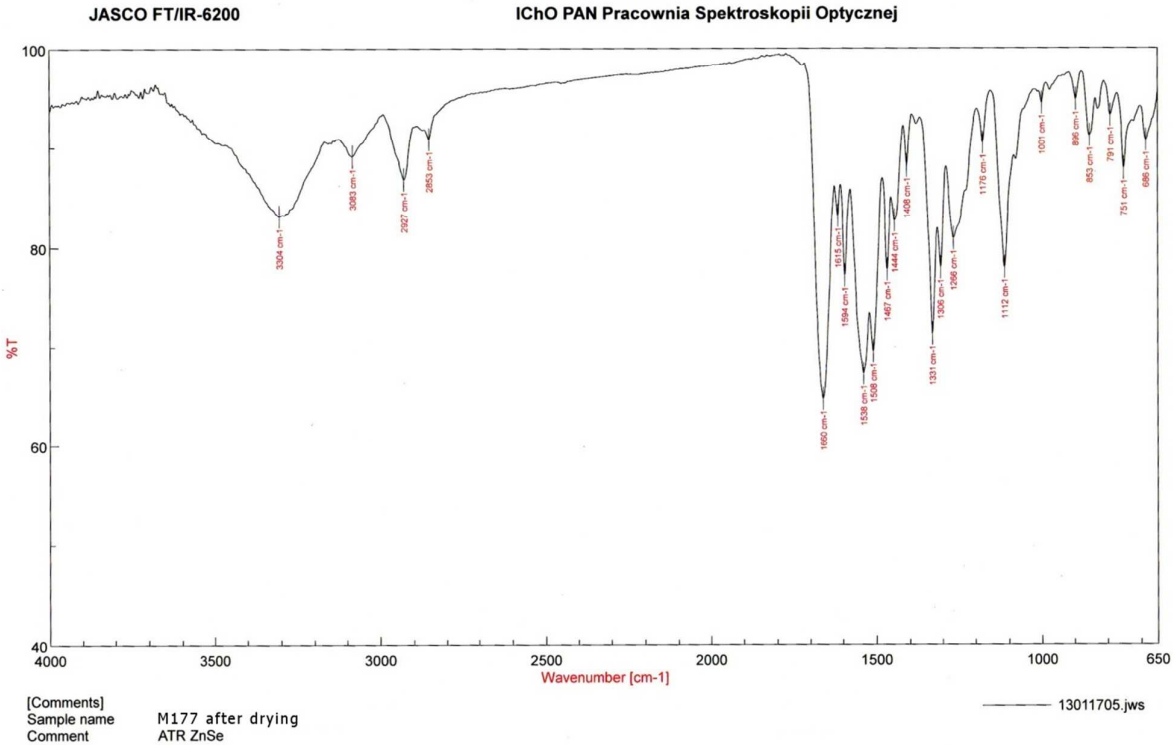


Fig. S8 FT-IR ATR (ZnSe) spectrum of the crystals of **1**·$(H_2O)_4$ after drying.

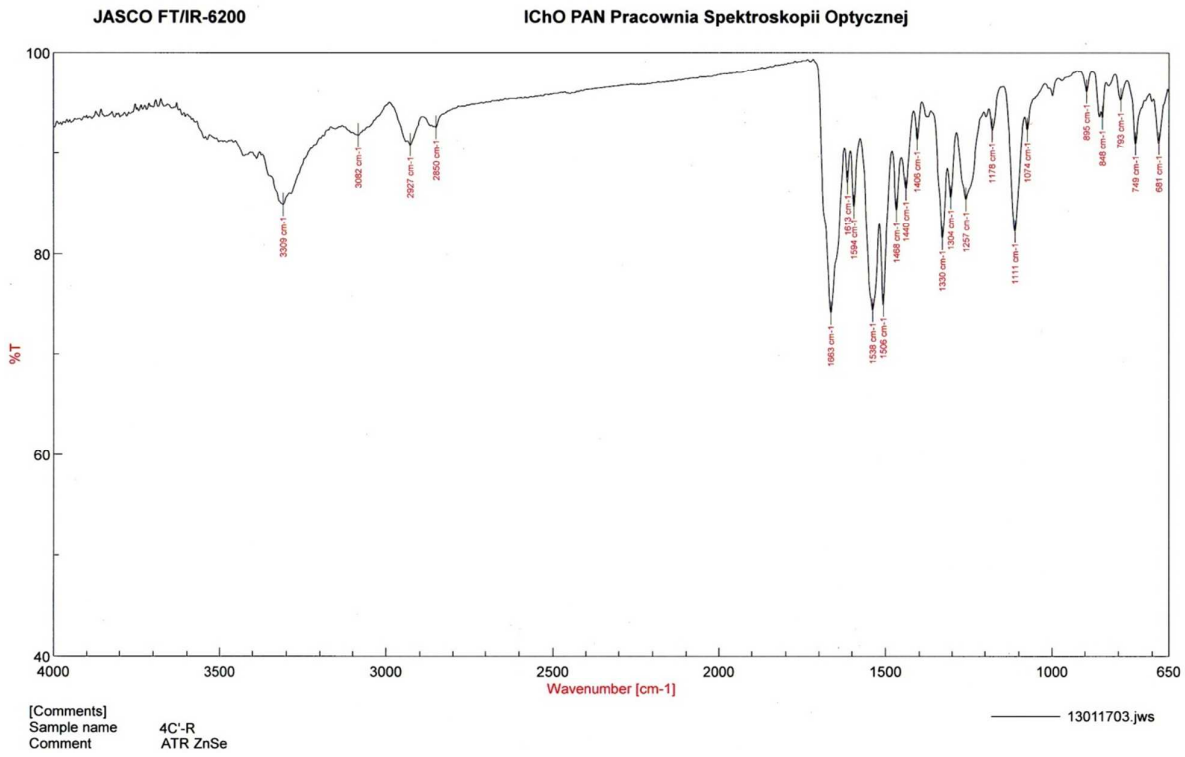


Fig. S9 FT-IR ATR (ZnSe) spectrum of the amorphous **1**·(H_2O).

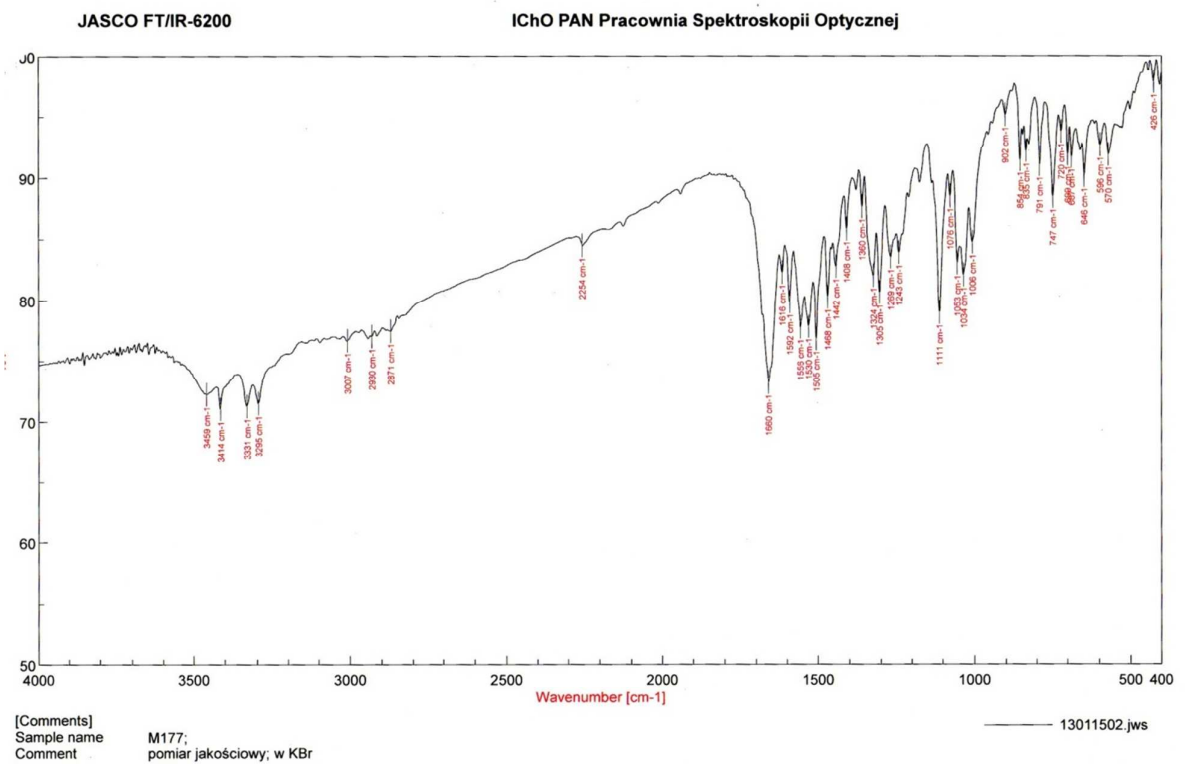


Fig. S10 FT-IR (KBr pellet) spectrum of the crystals of **1**·(H_2O)$_4$.

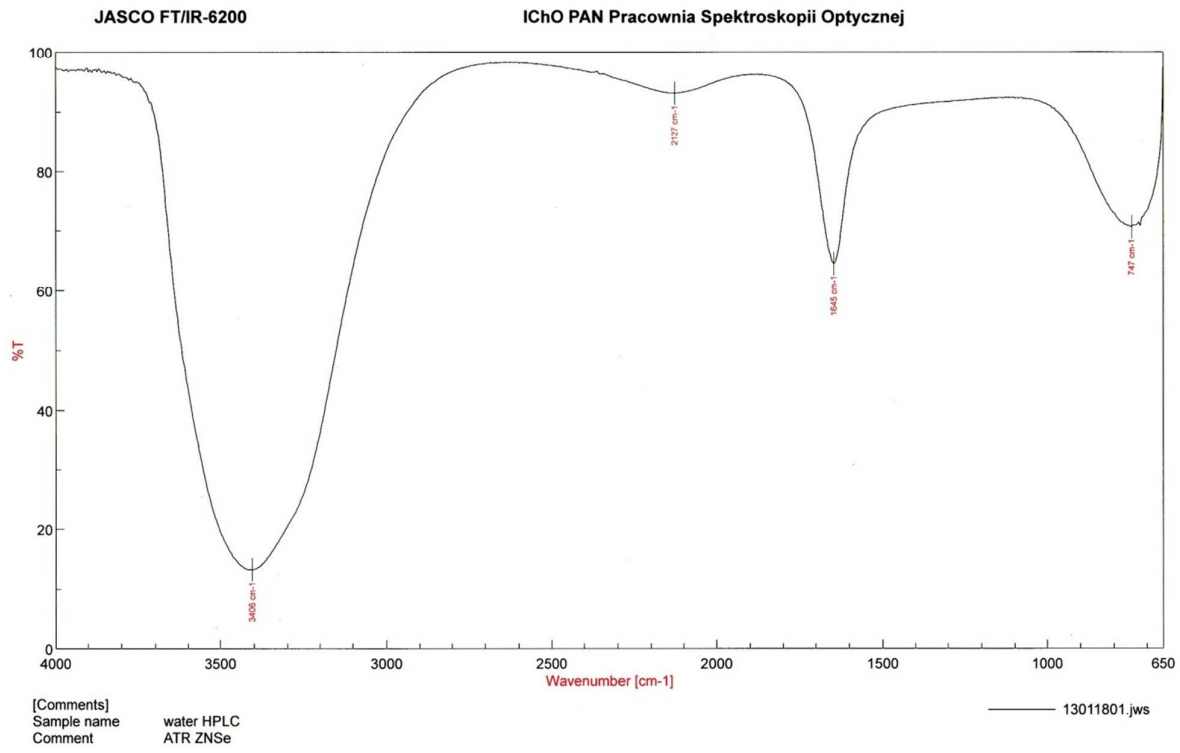


Fig. S11 FT-IR ATR (ZnSe) spectrum of the liquid water (HPLC grade).

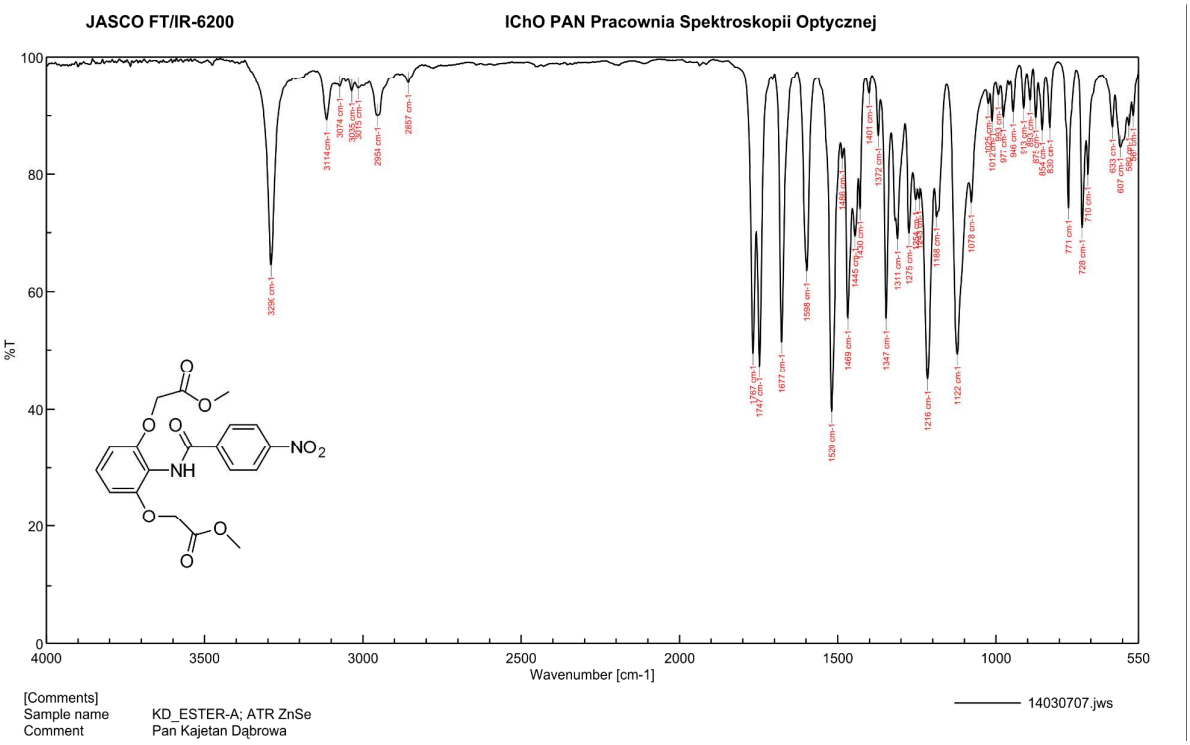


Fig. S12 FT-IR ATR (ZnSe) spectrum of the α,ω-diester used in the synthesis of receptor **1**.

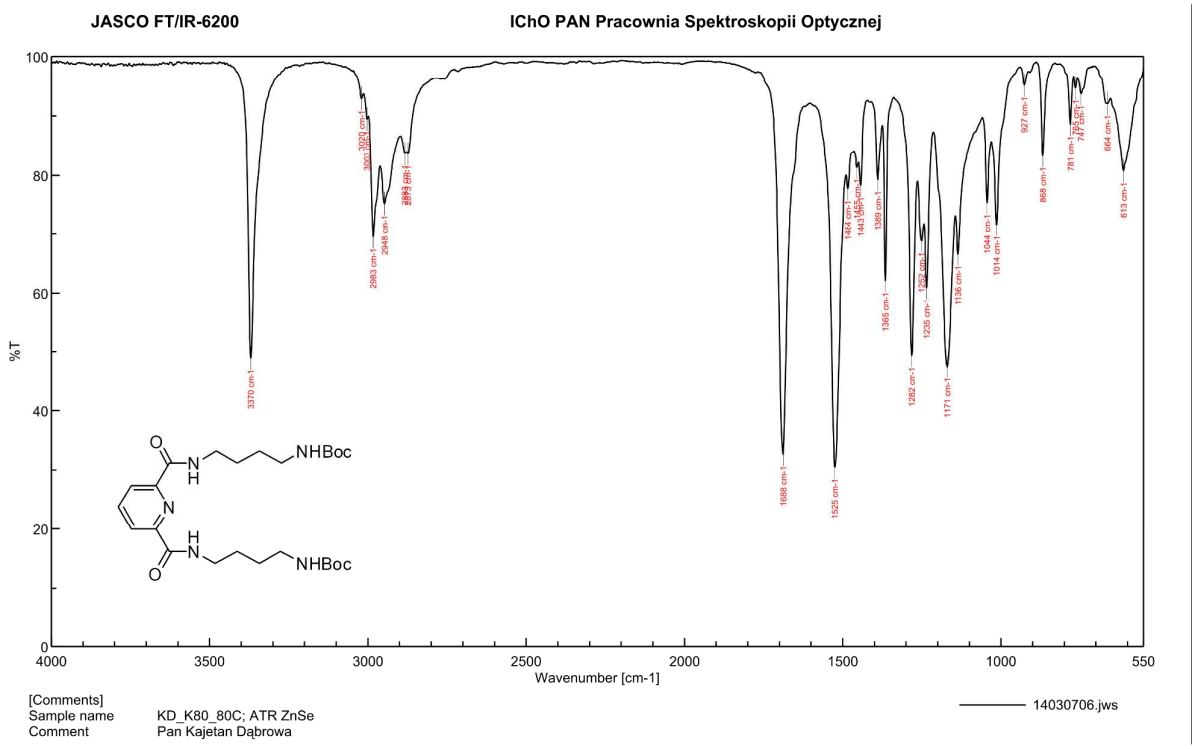
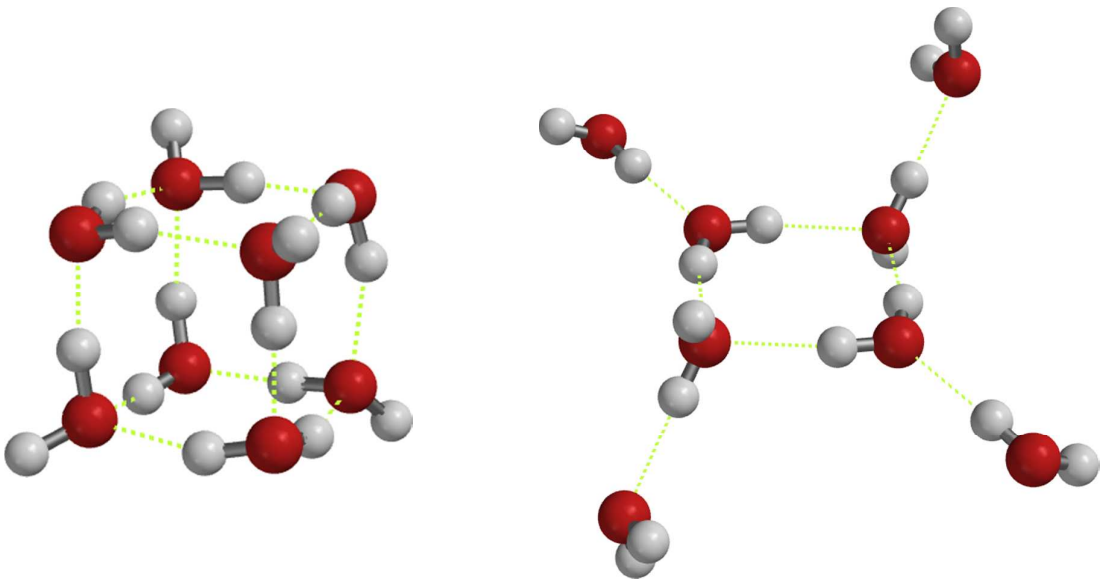


Fig. S13 FT-IR ATR (ZnSe) spectrum of the α,ω -di-Boc-amine used in the synthesis of receptor **1**.

4. DFT Calculations

All calculations were done using Spartan'10 for Windows[19] program. The conformational search for **1** and **1**·(H_2O) was done using semi-empirical model PM6 in gas-phase. Part of the **1**·(H_2O)$_4$ X-ray structure was taken as an initial structure. The search resulted in the list of 128 conformers which were analyzed for removing duplicated and nearly identical rotamers. The remaining conformers were geometry optimized at DFT ωb97x-d[20-22] 6-31G* level of theory. Conformers with lowest energies (~5-6) were further geometry optimized at the DFT ωb97x-d 6-31+G* level of theory. Any structure having imaginary frequencies in IR spectra was no longer considered. Due to complexity of the compounds the calculations of IR spectra were done for the fully optimized structures using parameterized functional EDF2[23,24] and 6-31G* basis set. The resulting structures differs only slightly from the structures obtained at ωb97x-d 6-31+G* level of theory.

Calculated IR spectrum of water cluster with constrained positions of the heavy atoms has several imaginary frequencies and taking into account contacts with the host molecules did not change the situation. On the other hand structure of water octamer with fully-relaxed atomic positions transformed to the more stable isomers (i.e. cubic form) during geometry optimization process.

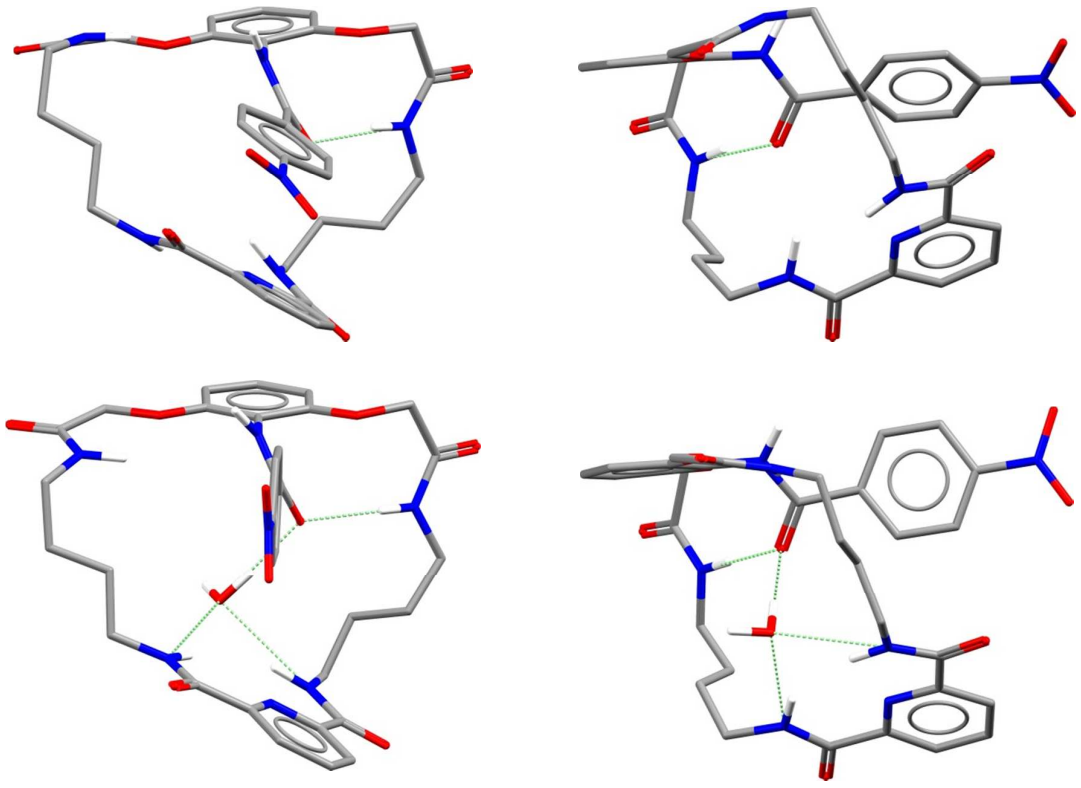


E_{rel} = 0.0 E_{rel} = +35.3 (kcal/mol)

Fig. S14 Structure of the cubic form of water octamer, reported to be the global minimum[25] (left) and water octamer taken from the X-ray structure (right); energies and geometries of both conformers were calculated at DFT ωb97x-d/cc-PVTZ level of theory, in the latter case the hydrogens atoms were geometry optimized prior to the single point energy (SPE) calculation.

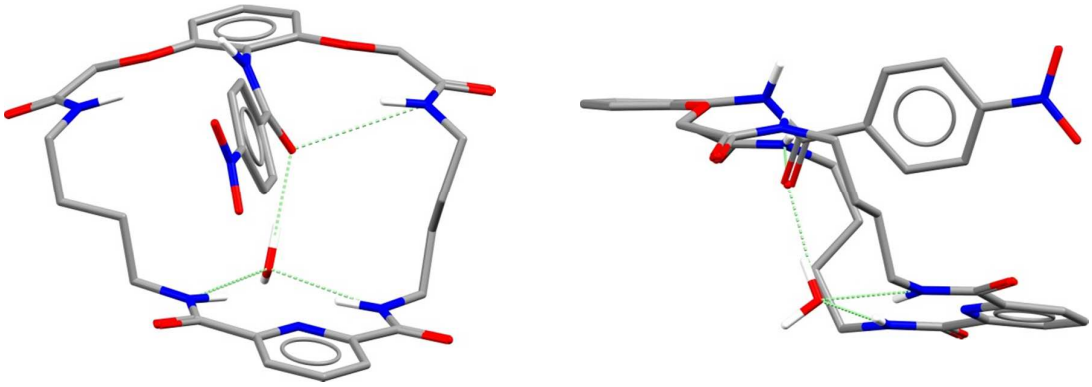
a)

b)



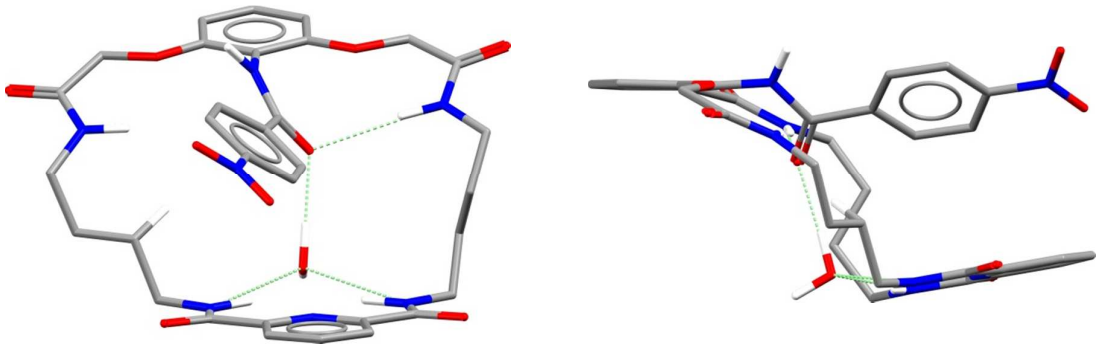
E_{rel} = 0

c)



E_{rel} = + 3.39 (8.79)

d)



E_{rel} = -4.65 (0.20)

Fig. S15 Energy minimized structures of **1** (a), **1**·(H_2O) (b), and **1**·$(H_2O)_{X\text{-}ray}$ with constrained (c) and relaxed positions of heavy atoms (d) calculated at ωb97x-d/6-31+G* and EDF2/6-31G* (in parentheses) level of theory; the energy difference (kcal·mol^{-1}) is relative to the minimum found for **1**·(H_2O) in the conformational analysis search; for the sake of clarity only acidic hydrogen atoms are visible.

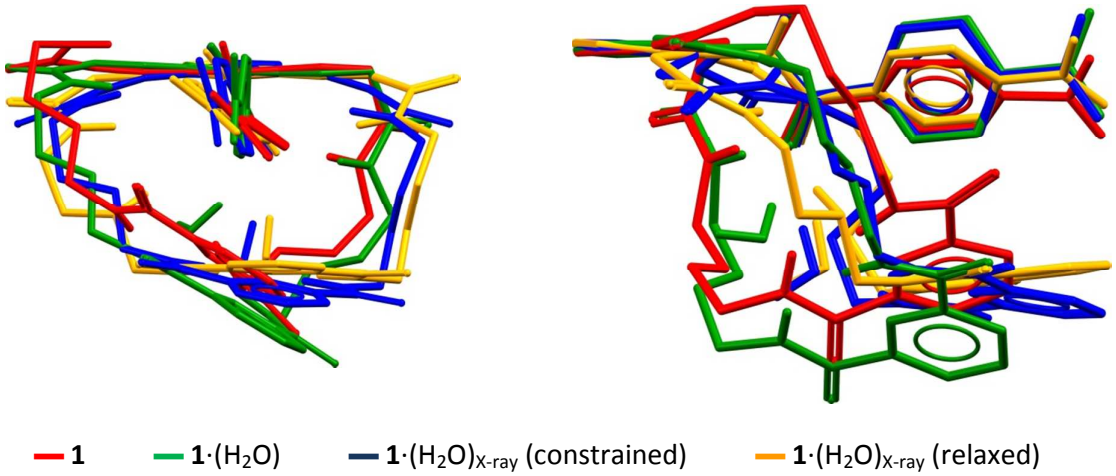


Fig. S16 Superposition of structures from Fig. S15.

Tab. S4 Cartesian coordinates and energies (in Hartree) of the optimized geometries of the monohydrates of host **1** calculated at DFT ωb97x-d/6-31+G* level of theory.

1·(H_2O) (conf. analysis) E = -2376.55374 au				**1**·(H_2O) (X-ray structure with constrains) E = -2376.54834 au				**1**·(H_2O) (X-ray structure without constrains) E = -2376.56115 au			
O	4.177405	-2.246924	4.765651	O	1.138644	-3.467694	-4.943172	O	3.054349	-3.208418	3.558531
O	5.141384	-0.838455	3.418799	O	-0.704982	-2.331868	-5.079733	O	4.261131	-1.519733	2.941568
O	-5.299815	3.439447	2.106951	O	3.322760	5.196039	0.943152	O	-2.272144	6.149964	0.848309
O	1.024972	5.398177	-1.639297	O	-2.407430	4.328324	-3.153594	O	4.480757	3.487680	-0.823529
O	-0.988148	0.531931	0.549093	O	0.777854	0.796581	0.905761	O	-1.214323	0.846790	-0.614794
O	-3.507478	0.338755	2.080805	O	3.443638	1.757041	1.818662	O	-3.207603	2.736492	0.801078
O	4.961798	-0.395571	-0.969016	O	-3.858893	-2.515381	-2.490071	O	3.430729	-3.460884	-0.881134
O	-1.392370	-5.900195	-2.761777	O	-0.286983	-4.993680	4.200847	O	-4.531867	-5.144432	-0.774629
O	-2.425245	-3.260987	-0.634546	O	1.902669	-2.387410	3.275699	O	-4.212315	-1.770568	0.236407
N	4.167418	-1.452853	3.831549	O	-2.064172	1.073829	0.941441	O	0.644842	0.508622	-2.625874
N	-1.741544	-1.500255	1.241844	H	-2.381621	1.387087	1.795834	H	0.169417	0.661627	-3.450153
H	-1.459018	-2.400318	1.604839	H	-1.091161	1.016619	1.017040	H	-0.013608	0.626202	-1.909254
N	-3.330112	2.890740	1.104977	N	0.334018	-2.648705	-4.511533	N	3.208265	-2.134930	2.998519
H	-2.594865	2.195213	1.026446	N	2.394487	-0.727123	1.288310	N	-2.536518	0.108266	1.069473
N	0.289068	3.323624	-2.255466	H	2.808218	-1.598576	0.994014	H	-2.562768	-0.350208	1.969798
H	0.495985	2.326746	-2.244796	N	2.662081	3.322496	-0.126783	N	-1.035716	4.233749	0.976489
N	2.628444	2.233732	-1.469053	H	2.472310	2.336210	-0.004766	H	-1.089221	3.226557	0.901172
N	2.939910	-0.381312	-2.034408	N	-2.200737	3.252459	-1.163424	N	2.686270	2.520459	-1.850124
H	2.112564	0.176011	-2.227954	H	-2.308695	2.374251	-0.661024	H	2.233828	1.642648	-2.098040
N	-0.275199	-4.538596	-1.298038	N	-3.049654	0.939664	-2.314423	N	3.630872	0.065312	-1.232641
H	-0.401177	-3.725519	-0.713656	N	-3.173301	-1.253417	-0.734559	N	2.066651	-2.017798	-1.992063
C	2.882460	-1.217633	3.159825	H	-2.919409	-0.323419	-0.410864	H	1.855073	-1.044514	-2.200746
C	2.846823	-0.390066	2.045230	N	0.376464	-4.111979	2.209952	N	-2.725820	-3.872745	-0.176662
H	3.763939	0.041941	1.665080	H	0.911592	-3.366822	1.790189	H	-2.450182	-2.923263	0.030174
C	1.623537	-0.162044	1.432193	C	0.656976	-1.982732	-3.229769	C	2.031646	-1.531900	2.347472
H	1.556564	0.489070	0.569316	C	-0.174409	-0.992323	-2.772228	C	2.194181	-0.363483	1.618048
C	0.464208	-0.777487	1.912101	H	-1.044137	-0.703609	-3.349643	H	3.172145	0.096418	1.541034
C	0.530545	-1.601239	3.041419	C	0.114407	-0.392967	-1.555172	C	1.084123	0.185293	0.987755
H	-0.371023	-2.037992	3.458569	H	-0.550625	0.373143	-1.171522	H	1.195460	1.073005	0.373501
C	1.744405	-1.823633	3.674339	C	1.223536	-0.792667	-0.821841	C	-0.172598	-0.401259	1.138113
H	1.824343	-2.445644	4.556110	C	2.083525	-1.751463	-1.351643	C	-0.307744	-1.577228	1.884929
C	-0.810832	-0.513773	1.184094	H	3.004364	-2.037365	-0.852881	H	-1.269500	-2.075291	1.976555
C	-3.014601	-1.409789	0.636997	C	1.801168	-2.359382	-2.563273	C	0.800418	-2.160438	2.483135
C	-3.376280	-2.332875	-0.351086	H	2.454798	-3.113827	-2.984122	H	0.723254	-3.085327	3.041674
C	-4.630448	-2.265772	-0.952406	C	1.438533	-0.174345	0.533057	C	-1.341835	0.237389	0.448055
H	-4.924584	-2.980827	-1.709624	C	2.714677	-0.316297	2.613576	C	-3.777509	0.496719	0.500544
C	-5.501247	-1.251874	-0.566225	C	2.495988	-1.217962	3.661291	C	-4.664693	-0.500904	0.080390
H	-6.470909	-1.179248	-1.047235	C	2.880769	-0.916684	4.959996	C	-5.912703	-0.164527	-0.442747
C	-5.169176	-0.332870	0.421324	H	2.718014	-1.618650	5.769514	H	-6.619252	-0.926511	-0.748673
H	-5.868471	0.447333	0.692139	C	3.511920	0.293837	5.190235	C	-6.243778	1.181788	-0.556453
C	-3.927901	-0.433085	1.052725	H	3.843443	0.531395	6.196582	H	-7.214366	1.453882	-0.959419
C	-4.387381	1.308051	2.628111	C	3.729686	1.215148	4.178712	C	-5.371944	2.190205	-0.161279
H	-4.023323	1.482500	3.644012	H	4.225896	2.153906	4.392812	H	-5.672874	3.226176	-0.254499
H	-5.412367	0.937087	2.701051	C	3.298768	0.915453	2.885204	C	-4.127238	1.845655	0.373286
C	-4.392010	2.645900	1.896563	C	3.610653	3.155697	2.094752	C	-3.440000	4.115577	0.571213
C	-3.141324	4.214851	0.531485	H	4.658259	3.384537	2.314324	H	-4.232590	4.492879	1.225769
H	-3.014287	4.938618	1.346006	H	2.988497	3.451980	2.945677	H	-3.724251	4.289357	-0.473590
H	-4.062322	4.499021	0.011477	C	3.178813	3.968716	0.901462	C	-2.179890	4.929182	0.829626
C	-1.948585	4.273216	-0.407957	C	2.147194	3.981737	-1.329919	C	0.262169	4.880483	1.093487
H	-1.750539	5.325330	-0.638659	H	2.638816	3.544694	-2.205430	H	0.596086	4.858792	2.138065
H	-1.054144	3.913369	0.115329	H	2.442208	5.030461	-1.256818	H	0.110888	5.928452	0.821292
C	-2.133821	3.500156	-1.710839	C	0.625603	3.846895	-1.449796	C	1.312241	4.235655	0.192066
H	-3.082804	3.792037	-2.179705	H	0.306927	4.425810	-2.326149	H	2.232985	4.825358	0.268768
H	-2.205702	2.423711	-1.507642	H	0.373582	2.800487	-1.669781	H	1.568764	3.239279	0.575508
C	-1.010897	3.752282	-2.718624	C	-0.144882	4.296731	-0.217068	C	0.879983	4.130902	-1.271997
H	-1.232575	3.231772	-3.657378	H	0.223096	5.271894	0.127399	H	0.463337	5.091801	-1.603707
H	-0.936517	4.820471	-2.937405	H	0.043815	3.587590	0.599963	H	0.077786	3.388669	-1.374751
C	1.191707	4.185015	-1.742378	C	-1.650787	4.410312	-0.462063	C	2.032655	3.763650	-2.210762
C	2.476323	3.545883	-1.284598	H	-2.182463	4.526309	0.488402	H	1.660295	3.669483	-3.236598
C	3.456192	4.343250	-0.695921	H	-1.871010	5.281256	-1.083188	H	2.794576	4.547926	-2.197106
H	3.262717	5.402851	-0.582883	C	-2.500626	3.313192	-2.466781	C	3.856031	2.491697	-1.181087
C	4.637212	3.741167	-0.280942	C	-3.004440	2.032073	-3.091099	C	4.369329	1.108193	-0.854337
H	5.421375	4.329277	0.184983	C	-3.418748	2.037076	-4.415268	C	5.557441	0.975291	-0.135999
C	4.804482	2.375260	-0.476475	H	-3.341348	2.959818	-4.979523	H	6.104982	1.866685	0.148605
H	5.703616	1.844441	-0.188092	C	-3.939171	0.874549	-4.959444	C	5.987044	-0.304438	0.196534
C	3.771342	1.663661	-1.082563	H	-4.284956	0.851322	-5.988189	H	6.900339	-0.449541	0.764735
C	3.951410	0.192401	-1.348133	C	-3.998227	-0.258050	-4.170222	C	5.217010	-1.396737	-0.187621
C	2.980201	-1.755384	-2.475555	H	-4.373890	-1.206587	-4.538060	H	5.485707	-2.415935	0.065370
H	4.014680	-2.091981	-2.377045	C	-3.532245	-0.189072	-2.866406	C	4.044100	-1.158680	-0.899805
H	2.715735	-1.787742	-3.539957	C	-3.535013	-1.419763	-2.001924	C	3.155131	-2.323561	-1.259974
C	2.041301	-2.672384	-1.692984	C	-3.141005	-2.349776	0.218612	C	1.107051	-3.042118	-2.346149
H	1.058218	-2.187281	-1.645977	H	-3.898184	-3.076858	-0.089797	H	1.660463	-3.952161	-2.599465
H	2.407153	-2.760721	-0.661910	H	-3.425149	-1.952534	1.198318	H	0.571951	-2.708899	-3.241174
C	1.922410	-4.050685	-2.337830	C	-1.775356	-3.025649	0.296630	C	0.123987	-3.337637	-1.212119
H	1.502409	-3.948930	-3.346124	H	-1.051880	-2.316188	0.722668	H	-0.496327	-2.444288	-1.052961
H	2.920414	-4.491461	-2.457394	H	-1.439901	-3.263469	-0.721374	H	0.700465	-3.501064	-0.293137
C	1.064354	-5.033760	-1.543185	C	-1.839025	-4.305461	1.133041	C	-0.742073	-4.565023	-1.491302
H	0.953309	-5.974249	-2.085586	H	-2.296322	-4.106967	2.110765	H	-1.318568	-4.431321	-2.416165
H	1.538999	-5.253554	-0.579435	H	-2.482725	-5.033794	0.623709	H	-0.088122	-5.433196	-1.643172
C	-1.366153	-4.980072	-1.960322	C	-0.474298	-4.937767	1.362580	C	-1.705777	-4.893285	-0.350980
C	-2.653017	-4.218555	-1.657490	H	-0.579500	-5.907470	1.855200	H	-2.232497	-5.829944	-0.544226
H	-2.978291	-3.729229	-2.582741	H	0.048657	-5.091361	0.412244	H	-1.150055	-5.006371	0.588582
H	-3.424643	-4.936071	-1.358890	C	0.385691	-4.191962	3.537413	C	-4.033585	-4.077975	-0.446050
H	-0.844786	0.122992	-2.607036	C	1.285359	-3.205172	4.256763	C	-4.924364	-2.843386	-0.357360
O	-0.071283	0.380579	-2.086976	H	0.669424	-2.602867	4.933342	H	-5.227172	-2.587262	-1.379630
H	-0.406746	0.482682	-1.170932	H	2.029562	-3.759507	4.839195	H	-5.814806	-3.095097	0.227783

Tab. S5 Cartesian coordinates and energies (in Hartree) of the optimized geometries of host **1** and monohydrates of host **1** calculated at DFT EDF2/6-31G* level of theory.

1 (conf. analysis) E = -2299.25932 au				**1**·(H_2O) (conf. analysis) E = -2375.65590 au				**1**·(H_2O) (X-ray structure with constrains) E = -2375.64188 au				**1**·(H_2O) (X-ray structure without constrains) E = -2375.65558 au			
O	5.054900	-0.927354	3.383968	O	-4.442575	-1.839980	-5.086128	O	1.138644	-3.467694	-4.943173	O	2.819440	-3.152762	4.116228
O	5.049202	1.208700	2.984581	O	-3.403307	0.016041	-5.535752	O	-0.704982	-2.331868	-5.079734	O	4.198205	-1.727425	3.225173
O	-5.745694	3.244016	1.460283	O	4.916532	-4.314869	0.872329	O	3.322760	5.196040	0.943152	O	-2.006499	6.211019	1.054201
O	0.631288	4.757670	-2.446277	O	4.538596	2.652269	-2.159183	O	-2.407430	4.328325	-3.153594	O	4.847257	3.128098	-0.841008
O	-1.302215	0.848410	0.531603	O	0.705398	-1.025138	-0.084255	O	0.777854	0.796581	0.905761	O	-0.999046	1.141752	-0.277221
O	-3.675600	0.389883	2.099154	O	1.381405	-3.740175	0.865515	O	3.443638	1.757041	1.818663	O	-3.027366	2.846492	0.771394
O	4.772650	-0.471127	-0.226669	O	-2.396154	3.491338	-3.008052	O	-3.858894	-2.515381	-2.490071	O	3.144543	-3.692022	-1.104335
O	-0.932888	-6.258867	-1.826261	O	-4.535981	0.384070	4.715700	O	-0.286983	-4.993681	4.200847	O	-4.932770	-4.994425	-0.549775
O	-2.117825	-3.310576	-0.250230	O	-1.985527	-1.503573	3.137933	O	1.902669	-2.387410	3.275699	O	-4.287690	-1.625671	0.353146
N	4.513454	0.106469	3.017295	N	-3.607682	-0.974414	-4.847501	O	-2.064173	1.073829	0.941441	O	0.638782	0.606222	-2.445579
N	-1.646901	-1.239188	1.369819	N	-0.904427	-2.333373	0.850769	H	-2.381622	1.387088	1.795835	H	0.077066	0.835510	-3.197967
H	-1.245381	-2.004283	1.891103	H	-1.877803	-2.600745	0.798318	H	-1.091162	1.016619	1.017040	H	0.089450	0.786181	-1.651436
N	-3.716543	2.676442	0.593759	N	3.732176	-2.457963	0.294435	N	0.334018	-2.648705	-4.511533	N	3.079311	-2.192558	3.401427
H	-2.924509	2.039644	0.646927	H	2.810927	-2.077887	0.101161	N	2.394488	-0.727123	1.288310	N	-2.505003	0.156931	1.106998
N	0.057276	2.547746	-2.560942	N	3.042364	2.394643	-0.450410	H	2.808218	-1.598577	0.994015	H	-2.621684	-0.495044	1.869421
H	0.349519	1.630128	-2.254226	H	2.055463	2.350189	-0.203949	N	2.662081	3.322497	-0.126783	N	-0.806211	4.312813	0.653102
N	2.486436	1.857054	-1.591931	N	0.999730	2.950479	-2.123035	H	2.472311	2.336210	-0.004766	H	-0.871324	3.318886	0.462221
N	3.313114	-0.679530	-1.971470	N	-1.421858	3.174508	-0.965098	N	-2.200737	3.252460	-1.163424	N	2.968452	2.374284	-1.901778
H	2.607816	-0.165608	-2.483108	H	-0.554487	2.937131	-0.491928	H	-2.308695	2.374252	-0.661024	H	2.398023	1.558722	-2.121865
N	0.095405	-4.620659	-0.604672	N	-3.943627	0.073123	2.525498	N	-3.049655	0.939664	-2.314423	N	3.603789	-0.172436	-1.254311
H	-0.074204	-3.724947	-0.171537	H	-3.228365	-0.340280	1.945874	N	-3.173301	-1.253417	-0.734559	N	1.863874	-2.084027	-2.081786
C	3.111721	0.025615	2.596784	C	-2.784859	-1.144709	-3.642669	H	-2.919409	-0.323419	-0.410864	H	1.707342	-1.085884	-2.212180
C	2.431449	1.196745	2.295215	C	-1.887221	-0.144379	-3.293320	N	0.376464	-4.111980	2.209952	N	-2.987729	-3.807672	-0.336894
H	2.937885	2.147562	2.389722	H	-1.828167	0.758557	-3.887849	H	0.911592	-3.366823	1.790189	H	-2.628577	-2.879122	-0.169199
C	1.121466	1.108453	1.852312	C	-1.103407	-0.327018	-2.163489	C	0.656976	-1.982732	-3.229769	C	1.960157	-1.546344	2.704873
H	0.567072	1.996668	1.575066	H	-0.382852	0.426215	-1.869498	C	-0.174409	-0.992323	-2.772229	C	2.210154	-0.435751	1.912441
C	0.492061	-0.132294	1.726660	C	-1.240615	-1.478746	-1.383860	H	-1.044137	-0.703609	-3.349643	H	3.222093	-0.065950	1.808110
C	1.197079	-1.293751	2.061598	C	-2.149229	-2.472472	-1.764985	C	0.114407	-0.392967	-1.555173	C	1.144399	0.165804	1.260412
H	0.746982	-2.276132	1.955371	H	-2.223464	-3.396742	-1.201242	H	-0.550625	0.373143	-1.171522	H	1.312040	1.022322	0.619469
C	2.512221	-1.221343	2.497555	C	-2.926495	-2.310320	-2.902116	C	1.223536	-0.792667	-0.821841	C	-0.153675	-0.329827	1.404796
H	3.086359	-2.105667	2.740446	H	-3.628394	-3.066608	-3.227960	C	2.083526	-1.751464	-1.351643	C	-0.368567	-1.467935	2.193262
C	-0.895399	-0.125849	1.159863	C	-0.389296	-1.593818	-0.164319	H	3.004364	-2.037365	-0.852881	H	-1.351961	-1.919560	2.279611
C	-2.943042	-1.420663	0.836875	C	-0.225382	-2.572896	2.065770	C	1.801168	-2.359382	-2.563273	C	0.686897	-2.080214	2.850460
C	-3.187503	-2.498356	-0.023323	C	-0.790299	-2.136250	3.269686	H	2.454799	-3.113827	-2.984122	H	0.545527	-2.962315	3.460809
C	-4.450656	-2.687930	-0.577442	C	-0.140559	-2.371302	4.478659	C	1.438533	-0.174345	0.533057	C	-1.246110	0.381591	0.666639
H	-4.648995	-3.517428	-1.243285	H	-0.573411	-2.047701	5.416272	C	2.714677	-0.316297	2.613576	C	-3.706381	0.622832	0.523254
C	-5.455559	-1.774631	-0.276868	C	1.086661	-3.026264	4.459321	C	2.495989	-1.217962	3.661291	C	-4.672468	-0.331642	0.173256
H	-6.435039	-1.901777	-0.725597	H	1.609703	-3.191873	5.395210	C	2.880770	-0.916684	4.959997	C	-5.920269	0.062074	-0.302644
C	-5.242939	-0.709056	0.586835	C	1.660138	-3.480272	3.278181	H	2.718014	-1.618650	5.769515	H	-6.682070	-0.667147	-0.542787
H	-6.045212	-0.013384	0.794233	H	2.619715	-3.980109	3.299337	C	3.511921	0.293837	5.190236	C	-6.178874	1.419033	-0.451424
C	-3.987117	-0.549919	1.176979	C	0.982137	-3.281929	2.073836	H	3.843443	0.531395	6.196583	H	-7.148567	1.734974	-0.821075
C	-4.635717	1.378146	2.436838	C	2.552502	-4.536276	0.775728	C	3.729687	1.215148	4.178713	C	-5.234076	2.381427	-0.125182
H	-4.285429	1.799136	3.382618	H	2.436828	-5.110795	-0.147080	H	4.225897	2.153906	4.392813	H	-5.476829	3.429943	-0.229795
H	-5.625618	0.949214	2.611410	H	2.630305	-5.246406	1.602282	C	3.298769	0.915453	2.885204	C	-3.991250	1.988425	0.378266
C	-4.760722	2.516715	1.426276	C	3.851763	-3.744662	0.674287	C	3.610654	3.155698	2.094752	C	-3.239884	4.240692	0.605074
C	-3.668080	3.809045	-0.316109	C	4.920236	-1.682884	-0.030480	H	4.658259	3.384537	2.314325	H	-3.979562	4.613379	1.320181
H	-3.691449	4.736218	0.269186	H	5.422751	-2.147770	-0.887674	H	2.988498	3.451981	2.945678	H	-3.596170	4.458521	-0.409092
H	-4.579027	3.811649	-0.926478	H	5.619078	-1.756044	0.809558	C	3.178813	3.968716	0.901462	C	-1.945662	5.012863	0.815732
C	-2.428415	3.777735	-1.197332	C	4.596338	-0.231247	-0.341004	C	2.147195	3.981738	-1.329920	C	0.490788	4.952793	0.792176
H	-2.360807	4.737088	-1.721825	H	5.493242	0.232467	-0.765178	H	2.638816	3.544694	-2.205430	H	0.779970	4.986468	1.851091
H	-1.534736	3.717432	-0.565391	H	3.839667	-0.187921	-1.134045	H	2.442209	5.030462	-1.256818	H	0.368451	5.990675	0.470291
C	-2.413826	2.642313	-2.217329	C	4.132590	0.582893	0.863799	C	0.625603	3.846896	-1.449796	C	1.575699	4.254164	-0.013150
H	-3.338465	2.670101	-2.809082	H	4.843698	0.453814	1.690396	H	0.306927	4.425811	-2.326149	H	2.520516	4.780589	0.162818
H	-2.394661	1.673302	-1.705846	H	3.165139	0.210472	1.225086	H	0.373583	2.800487	-1.669781	H	1.730334	3.241410	0.379747
C	-1.235163	2.726394	-3.188649	C	4.020747	2.079038	0.565137	C	-0.144882	4.296732	-0.217068	C	1.302421	4.180688	-1.512925
H	-1.343614	1.968823	-3.972976	H	3.755869	2.620244	1.480706	H	0.223096	5.271894	0.127399	H	1.029572	5.175111	-1.889654
H	-1.211315	3.706405	-3.671674	H	4.981606	2.464084	0.214548	H	0.043815	3.587590	0.599963	H	0.442936	3.527626	-1.707199
C	0.875682	3.573561	-2.240430	C	3.386685	2.641732	-1.731190	C	-1.650787	4.410313	-0.462063	C	2.506855	3.681196	-2.313735
C	2.159714	3.151723	-1.574144	C	2.225154	2.919855	-2.648678	H	-2.182464	4.526310	0.488402	H	2.253436	3.647516	-3.379815
C	2.951176	4.120127	-0.960116	C	2.470679	3.141211	-4.002634	H	-1.871011	5.281257	-1.083188	H	3.351225	4.363450	-2.190904
H	2.633387	5.154560	-1.005227	H	3.493674	3.104293	-4.356305	C	-2.500627	3.313193	-2.466781	C	4.110238	2.211993	-1.199166
C	4.109187	3.713900	-0.308457	C	1.390441	3.399347	-4.836884	C	-3.004440	2.032073	-3.091099	C	4.443311	0.784568	-0.855998
H	4.742809	4.438663	0.192455	H	1.542393	3.572820	-5.897398	C	-3.418749	2.037077	-4.415269	C	5.601884	0.520522	-0.126075
C	4.443970	2.364822	-0.301781	C	0.111572	3.439208	-4.293911	H	-3.341348	2.959819	-4.979523	H	6.232335	1.351713	0.164769
H	5.317575	1.980402	0.210043	H	-0.772920	3.646449	-4.883909	C	-3.939172	0.874549	-4.959445	C	5.892056	-0.798985	0.197634
C	3.608141	1.476320	-0.974209	C	-0.032444	3.214322	-2.926512	H	-4.284957	0.851322	-5.988190	H	6.778846	-1.044123	0.772677
C	3.958474	0.013374	-1.006582	C	-1.403232	3.301160	-2.309295	C	-3.998227	-0.258050	-4.170222	C	5.024661	-1.800932	-0.219449
C	3.426135	-2.112608	-2.122925	C	-2.626007	3.336014	-0.185195	H	-4.373891	-1.206587	-4.538061	H	5.186565	-2.848418	0.002034
H	4.440922	-2.392280	-1.829398	H	-3.367679	3.803911	-0.836458	C	-3.532245	-0.189072	-2.866406	C	3.892549	-1.437951	-0.945981
H	3.304292	-2.355681	-3.184002	H	-2.417069	4.029234	0.639263	C	-3.535014	-1.419763	-2.001924	C	2.935968	-2.512276	-1.382948
C	2.403793	-2.876325	-1.282370	C	-3.163087	2.022738	0.381983	C	-3.141005	-2.349776	0.218612	C	0.856010	-3.024764	-2.512733
H	1.411907	-2.443017	-1.463578	H	-2.326102	1.491417	0.852238	H	-3.898185	-3.076859	-0.089797	H	1.365623	-3.936872	-2.836932
H	2.635999	-2.704976	-0.223836	H	-3.518714	1.396053	-0.446002	H	-3.425149	-1.952534	1.198318	H	0.337820	-2.599467	-3.377902
C	2.367613	-4.369460	-1.590199	C	-4.280803	2.254318	1.395273	C	-1.775356	-3.025649	0.296630	C	-0.142741	-3.373560	-1.407148
H	3.374985	-4.795481	-1.502796	H	-3.893543	2.833507	2.242610	H	-1.051881	-2.316189	0.722668	H	-0.681059	-2.456846	-1.129366
H	2.048119	-4.525216	-2.627778	H	-5.075071	2.859255	0.939442	H	-1.439901	-3.263469	-0.721374	H	0.428516	-3.691704	-0.527873
C	1.441717	-5.153139	-0.658947	C	-4.912300	0.967892	1.924875	C	-1.839025	-4.305462	1.133041	C	-1.115085	-4.477656	-1.809594
H	1.352003	-6.189684	-0.989221	H	-5.650225	1.190486	2.697512	H	-2.296323	-4.106967	2.110765	H	-1.695288	-4.178847	-2.691843
H	1.855266	-5.159651	0.356952	H	-5.423255	0.437548	1.112427	H	-2.482725	-5.033795	0.623709	H	-0.541212	-5.367210	-2.095777
C	-0.962845	-5.207676	-1.206950	C	-3.813028	-0.098086	3.858664	C	-0.474298	-4.937768	1.362580	C	-2.076332	-4.879002	-0.693403
C	-2.281596	-4.454744	-1.072485	C	-2.632454	-0.966852	4.281894	H	-0.579500	-5.907470	1.855200	H	-2.703751	-5.720777	-0.992460
H	-3.023688	-5.140421	-0.648828	H	-1.944174	-0.338647	4.858924	H	0.048657	-5.091362	0.412245	H	-1.505387	-5.191157	0.190914
H	-2.615090	-4.169205	-2.076933	H	-2.999358	-1.764882	4.936054	C	0.385691	-4.191963	3.537414	C	-4.329752	-3.954246	-0.337208
				H	0.660553	1.518818	1.832829	C	1.285359	-3.205172	4.256764	C	-5.127386	-2.675289	-0.109636
				O	0.511756	1.591155	0.880072	H	0.669424	-2.602868	4.933342	H	-5.583760	-2.408901	-1.069121
				H	0.630699	0.679959	0.537038	H	2.029562	-3.759508	4.839195	H	-5.926618	-2.882678	0.608258

Tab. S6 Cartesian coordinates and energies (in Hartree) of the optimized geometries of water octamers at the DFT ωb97x-d/ccPVTZ level of theory.

Cubic form of water octamer (global minimum) E = -611.621114 au				Water octamer taken from the X-ray structure E = -611.564916 au			
H	-0.382848	-2.136076	-0.286070	O	-3.962320	-2.622096	-0.071164
O	-1.347687	-1.942196	-0.327640	H	-3.111733	-2.163652	-0.147435
H	-1.527037	-1.499711	0.533379	H	-4.020210	-2.848813	0.855759
H	2.049153	-2.587749	-0.036895	O	-1.166815	1.481554	-0.781850
O	1.425217	-1.857543	-0.161869	H	-1.206345	1.594483	-1.731736
H	1.470528	-1.301049	0.681770	H	-1.809178	2.112072	-0.410793
H	0.492916	0.289941	-2.106319	O	-1.568098	-1.223841	-0.129556
O	1.447935	0.338139	-1.869697	H	-0.677626	-1.461914	0.152273
H	1.615082	-0.523451	-1.424489	H	-1.512452	-0.286188	-0.353315
H	-1.396883	-0.691646	-1.371657	O	-3.056434	3.201241	0.270743
O	-1.324473	0.153906	-1.923248	H	-3.790892	2.708113	0.639030
H	-1.906905	0.028926	-2.686950	H	-2.753583	3.778783	0.972327
H	1.426847	1.381710	-0.615899	O	1.166815	-1.481554	0.781850
O	1.305783	1.932742	0.224255	H	1.206345	-1.594483	1.731736
H	1.891693	2.698615	0.130905	H	1.809178	-2.112072	0.410793
H	-0.517919	2.107832	0.268122	O	1.568098	1.223841	0.129556
O	-1.472915	1.865879	0.262337	H	0.677626	1.461914	-0.152273
H	-1.588048	1.417866	-0.606188	H	1.512452	0.286188	0.353315
H	-2.043314	-0.149799	2.585919	O	3.962320	2.622096	0.071164
O	-1.407234	-0.229223	1.859708	H	3.111733	2.163652	0.147435
H	-1.505336	0.611329	1.304992	H	4.020210	2.848813	-0.855759
H	1.513856	0.609806	1.499016	O	3.056434	-3.201241	-0.270743
O	1.373379	-0.260849	1.935981	H	3.790892	-2.708113	-0.639030
H	0.408181	-0.263382	2.131749	H	2.753583	-3.778783	-0.972327

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