Supporting Information

For

Superphane: a new lantern-like receptor for encapsulation of a water dimer

Aimin Li, Shenglun Xiong, Wei Zhou, Huijuan Zhai, Yuanchu Liu, and Qing He*

State Key Laboratory of Chemo/Biosensing and Chemometrics, Advanced Catalytic Engineer Research Center of the Ministry of Education, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China

* Correspondence: Qing He (heqing85@hnu.edu.cn)

Contents

1. General information

All solvents and chemicals used were purchased from Sigma–Aldrich, TCI, Energy–Chemical, or Acros and used without further purification. TLC analyses were carried out using Sorbent Technologies silica gel (200 mesh) sheets. Flash column chromatography was performed on silica gel (300–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 spectrometers and the spectroscopic solvents were purchased from Cambridge Isotope Laboratories or Sigma–Aldrich. Tetramethylsilane (TMS) was used as an internal reference. The chemical shifts are expressed in δ (ppm). High–resolution mass spectra (HRMS) were recorded on a Bruker Apex–Q IV FTMS mass spectrometer using ESI (electrospray ionization) employing a mixture of $CHCl_3/CH_3OH$ (9:1, v/v) as the solvent. X–ray crystallographic analyses were carried out on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focused Cu Kα radiation source (λ = 1.5418 Å) with collimating mirror monochromators. All theoretical calculations were carried out with the Gaussian 09 suite[1] of programs using the X3LYP density functional.[2] Structural optimization was performed using a 6–31G* basis set while single–point energy was calculated with a 6–31+g* basis set. Complexation energies were corrected for basis set superposition error (BSSE) using the counterpoise correction method.[3, 4]

2. Synthesis and characterizations

Compounds **3** and **4** were prepared according to literature procedures.[5–7]

Synthesis of 5

Hexakis–(aminomethyl)–benzene **3** (126.7 mg, 0.5 mmol) and commercially available *m*-phthalaldehyde (214.4 mg, 1.6 mmol) were dissolved in DMSO (200 mL) under an N_2 atmosphere. The mixture was stirred at 80 ℃ for 4 h. After cooled to room temperature, the precipitates were filtered off. The filtrate was diluted with chloroform (200 mL) and washed with water (3 × 200 mL). The organic phase was separated and dried over anhydrous Na_2SO_4, filtered off and concentrated in vacuo. The crude sample was washed with acetonitrile (20 ml) to give a yellowish solid **5** (87 mg, 32 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 12H), 7.37 (s, 6H), 7.33 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz), 6.92 (t, J = 8.0 Hz, 12H), 5.10 (s, 24H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 162.9, 139.4, 136.0, 129.1, 129.1, 128.1, 57.4. HRMS (ESI) m/z 1093.5137 $[M + H]^+$ calcd for $C_{72}H_{60}N_{12}$, found 1093.5192. This compound was further characterized via a single crystal X–ray diffraction analysis.

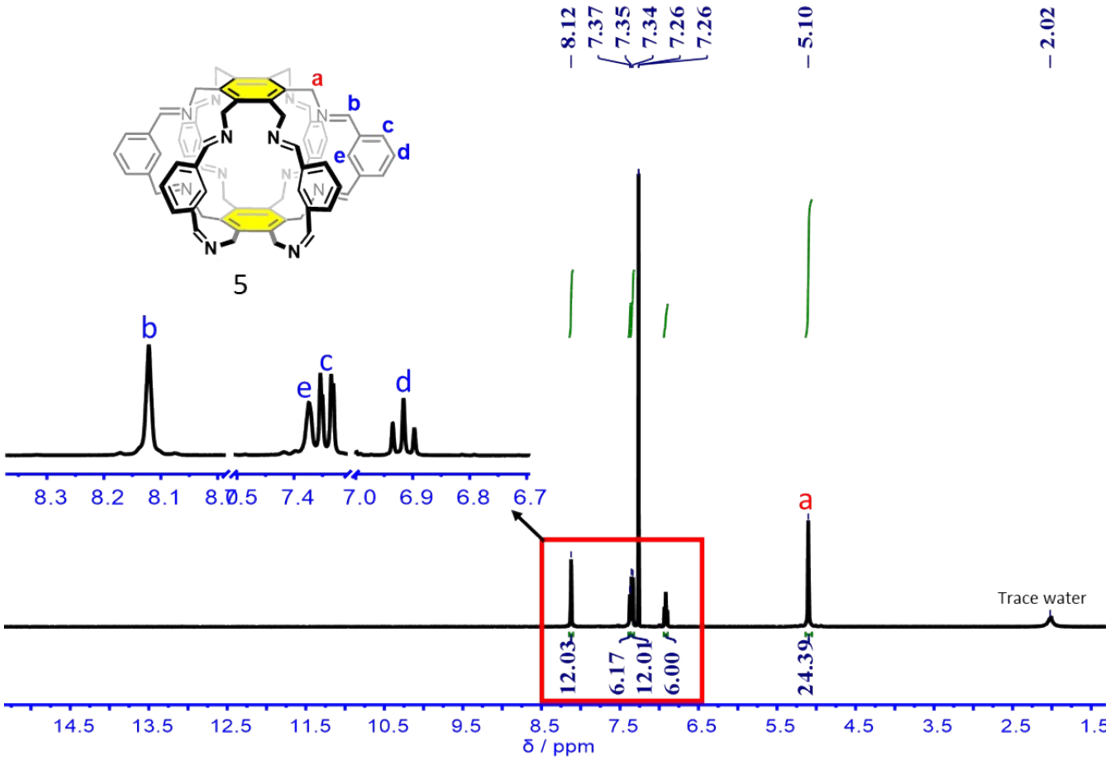


Figure S1. The ^{1}H NMR spectrum of **5** carried out in $CDCl_3$ at 298 K.

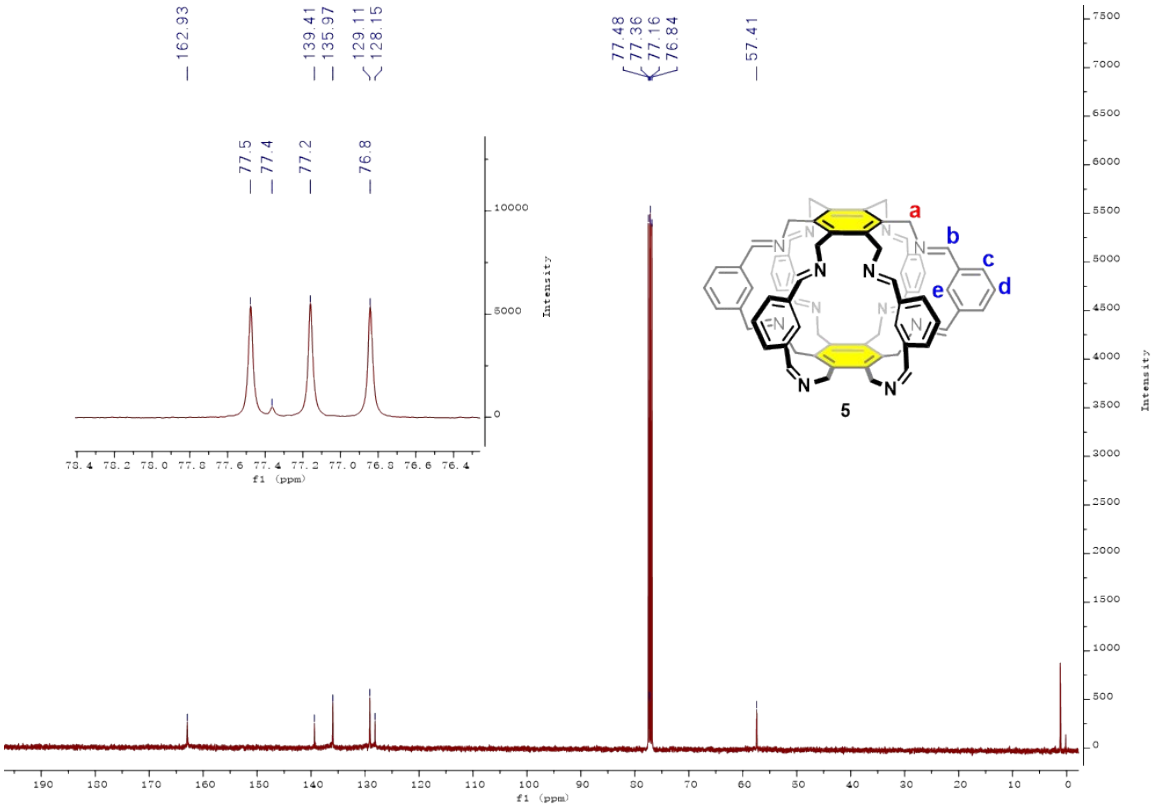


Figure S2. The ^{13}C NMR spectrum of **5** carried out in $CDCl_3$ at 298 K.

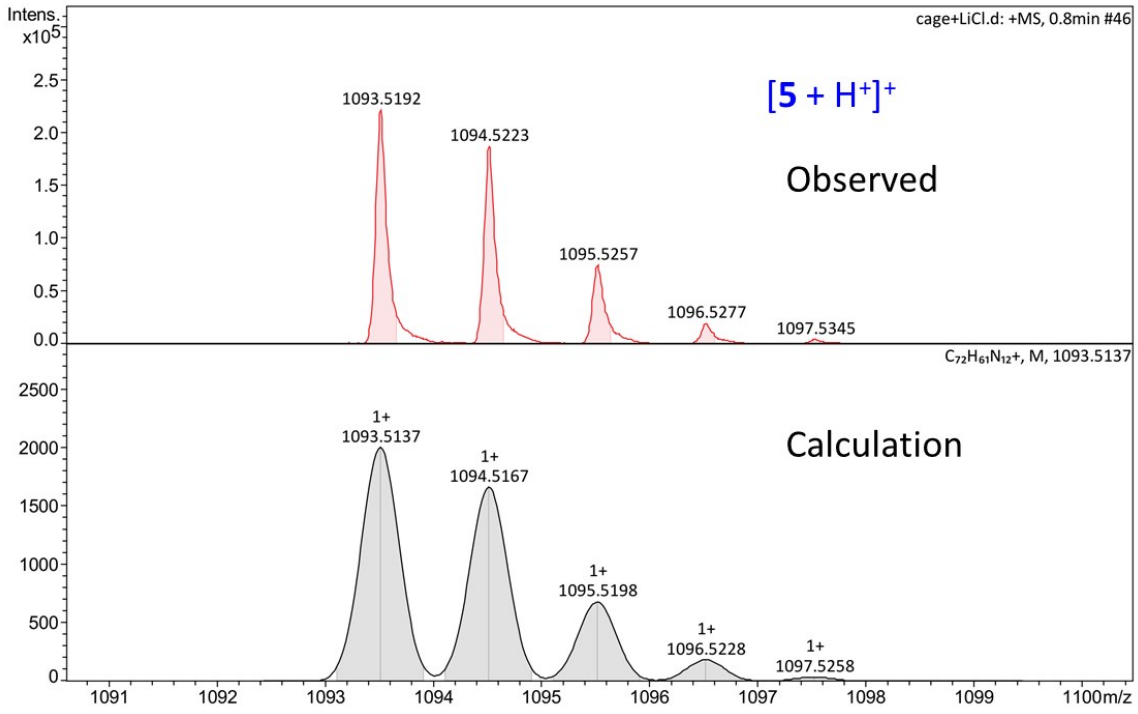


Figure S3. High–resolution spectrum of superphane **5** ([**5**+H$^+$]$^+$).

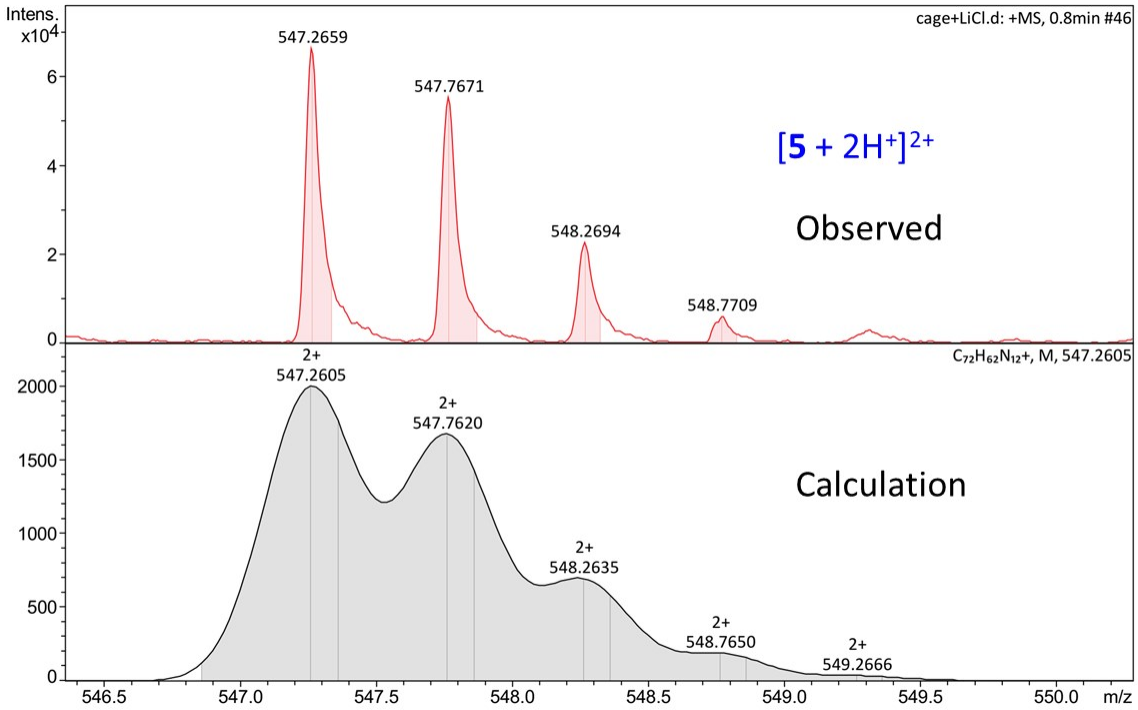


Figure S4. High–resolution spectrum of superphane **5** ([**5**+2H$^+$]$^{2+}$).

3. Theoretical calculations and crystal structures

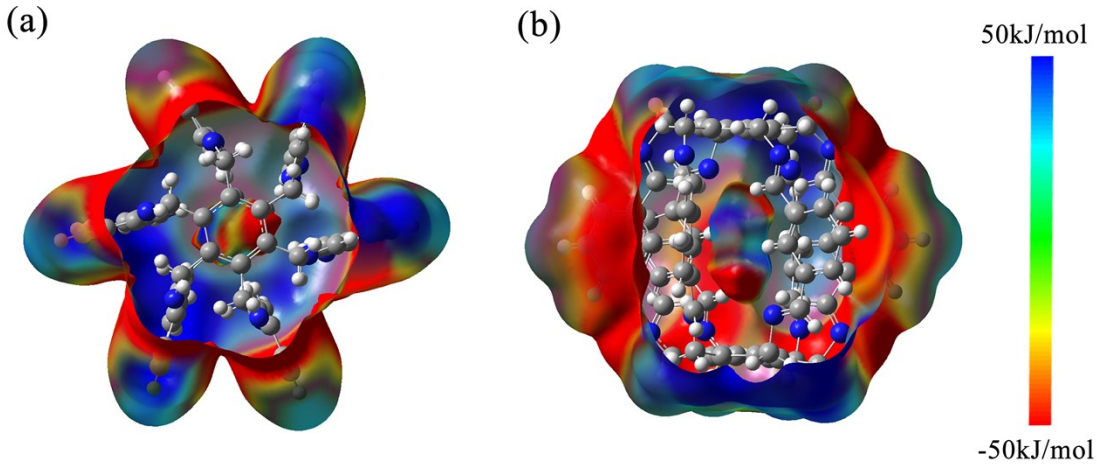


Figure S5. (a) Top view and (b) front view of molecular structure and electrostatic potential surfaces (EPS) (at X3LYP/6–31g* level) of **5**. For all surfaces shown in this work, the potential energy values range from −50 kJ mol^{-1} (red) to 50 kJ mol^{-1} (blue).

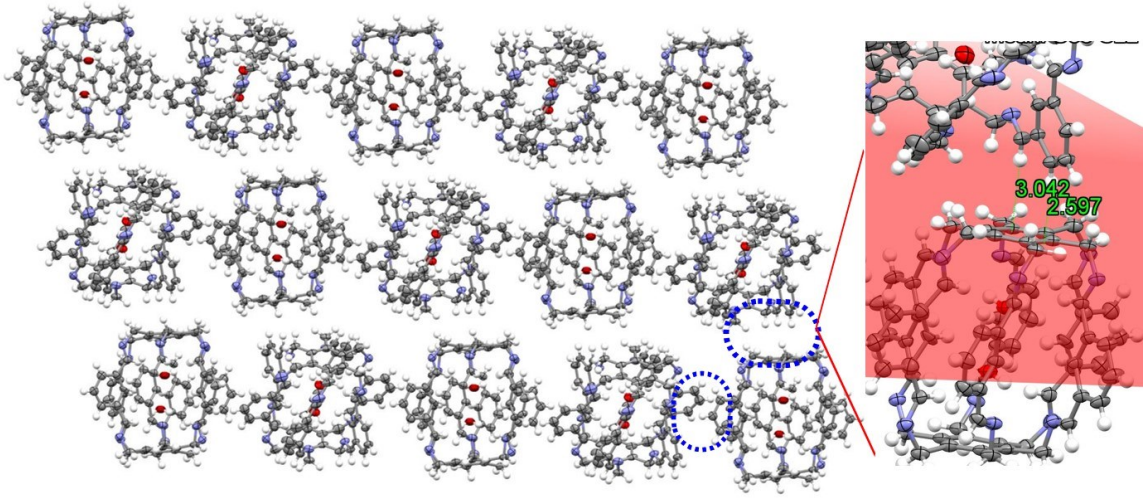


Figure S6. The coordination network in the $(H_2O)_2$⊂**5** complex. Insert: multiple edge–to–face π···π interactions between each hexasubstituted benzene ring and its adjacent disubstituted benzyl groups on the periphery of **5**.

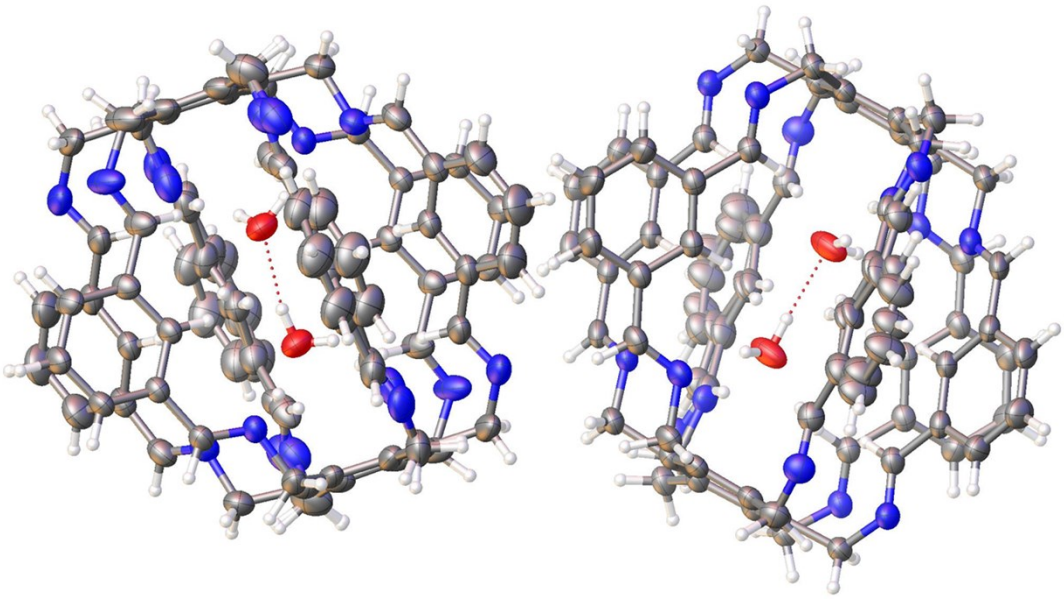


Figure S7. The crystal structure of the $(H_2O)_2\subset$**5** complex shown in ellipsoid model. Two $(H_2O)_2\subset$**5** complexes are found in each asymmetric unit. It reveals that the water dimer nestled within **5** was found to be the linear non-planar water dimer isomer. The single crystals for this structure ware obtained by slow evaporation of a solution of **5** in a mixture of $CHCl_3/CH_3CN$.

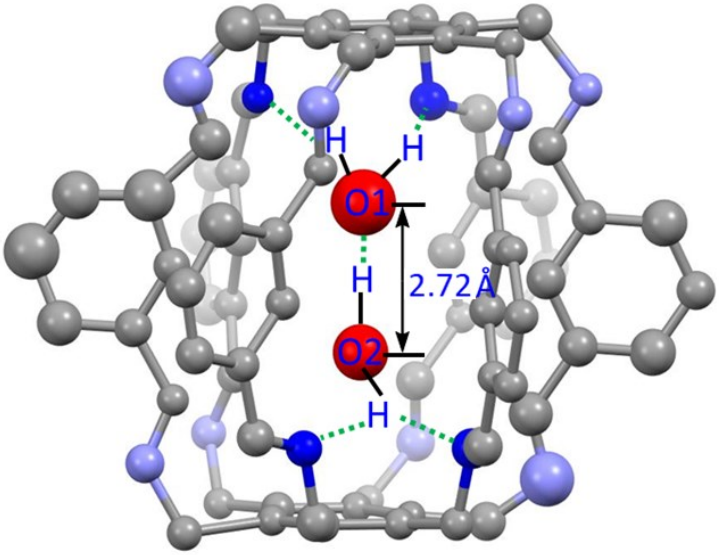


Figure S8. The crystal structure of the $(H_2O)_2\subset$**5** complex shown in ellipsoid model with hydrogen omitted for clarity. According to the orientations of imino groups, the water dimer nestled within **5** was assumed to be the linear non-planar water dimer isomer. The assumed hydrogen orientations of the bound water dimer and the hydrogen bonding network was indicated. The N atoms of the imino groups with lone pairs pointed inside the cavity are shown in dark blue while other N atoms are presented in light blue.

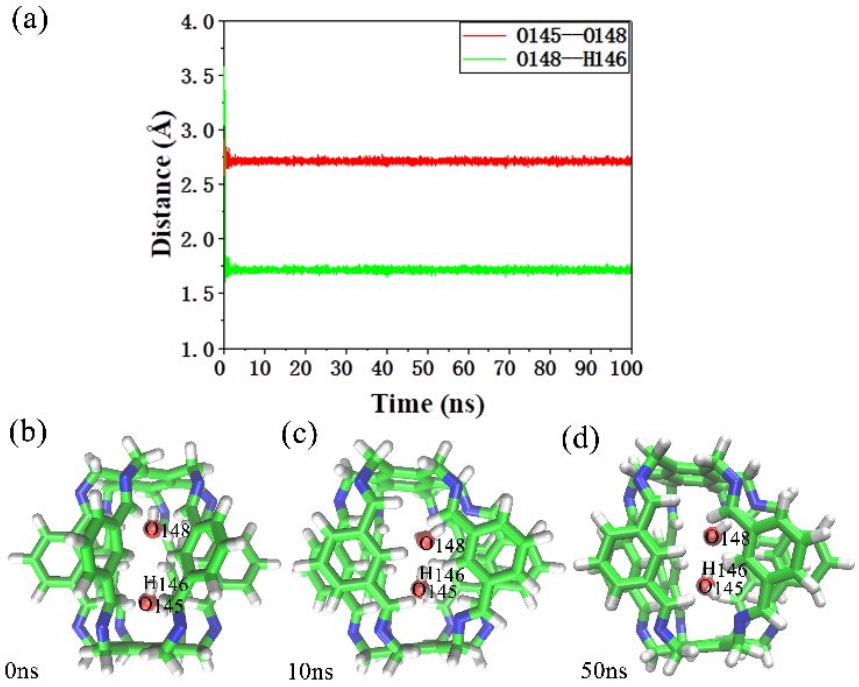


Figure S9. Molecular dynamics run on the complex **5** • $2H_2O$ in the gas phase using periodic boundary conditions at 300 K. (a) Traces of selected distances versus time; the key elements, e.g. O145, O148, and H146, are labeled in the molecular models. In this case, a hydrogen bond is formed between the two water molecules and remains stable.

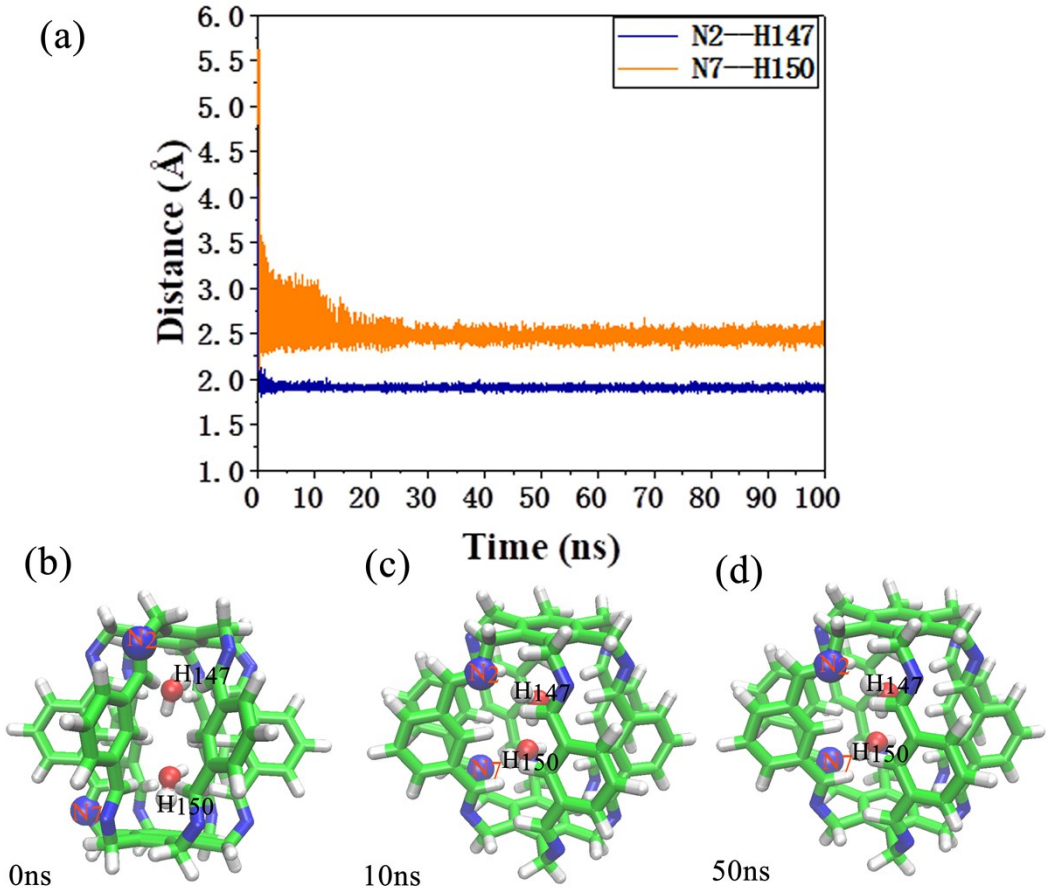


Figure S10. Molecular dynamics run on the complex **5** • $2H_2O$ in the gas phase using periodic boundary conditions at 300 K. (a) Traces of selected distances versus time; the key elements, e.g. N2, N7, H147 and H150, are labeled in the molecular models. In this case, the water dimer is stable enough to stay in the cavities of cage on the simulation time scale. The hydrogens of water dimer form hydrogen bonds with the nitrogen of **5**, and such hydrogen network can be maintained on the simulation time scale.

All molecular dynamics simulations were carried out using the GROMACS molecular dynamics software with OPLS-AA force field.[13] Multiwfn was used to construct RESP charges.[14] The starting coordinates of cage and water dimer used for the associated simulations were obtained from the DFT-optimized **5**·$2H_2O$ complex. The coordinates and topology were converted to GROMACS format using acpype.py program.[15] In each simulation, the system was simulated for 100 ns at constant temperature (300K) using the Berendsen thermostat with a coupling constant of 0.1ps.[16] The time step of each simulation was taken as 2fs. The system was placed in a box of $3.0\times3.0\times3.0$ nm^3 and then simulated for 100 ns at constant temperature (300 K) using the Berendsen thermostat with a coupling constant of 0.1 ps.[16] The time step of each simulation was 2 fs. Output topology structure every 5000 steps.

4. MALDI-TOF and NMR results

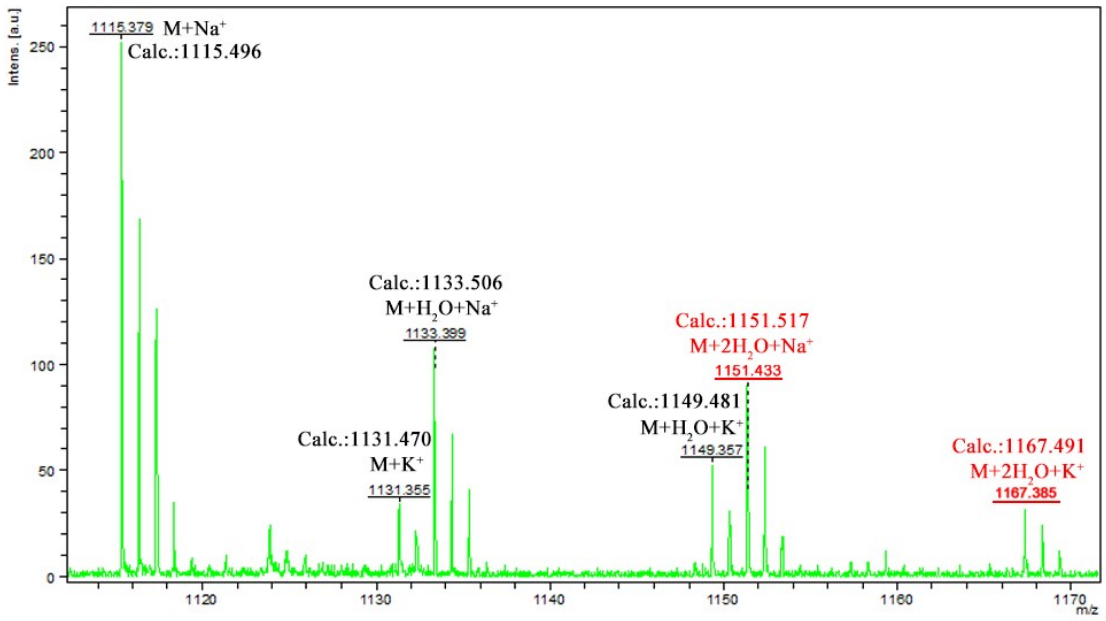


Figure S11. MALDI–TOF mass spectrum of superphane **5**.

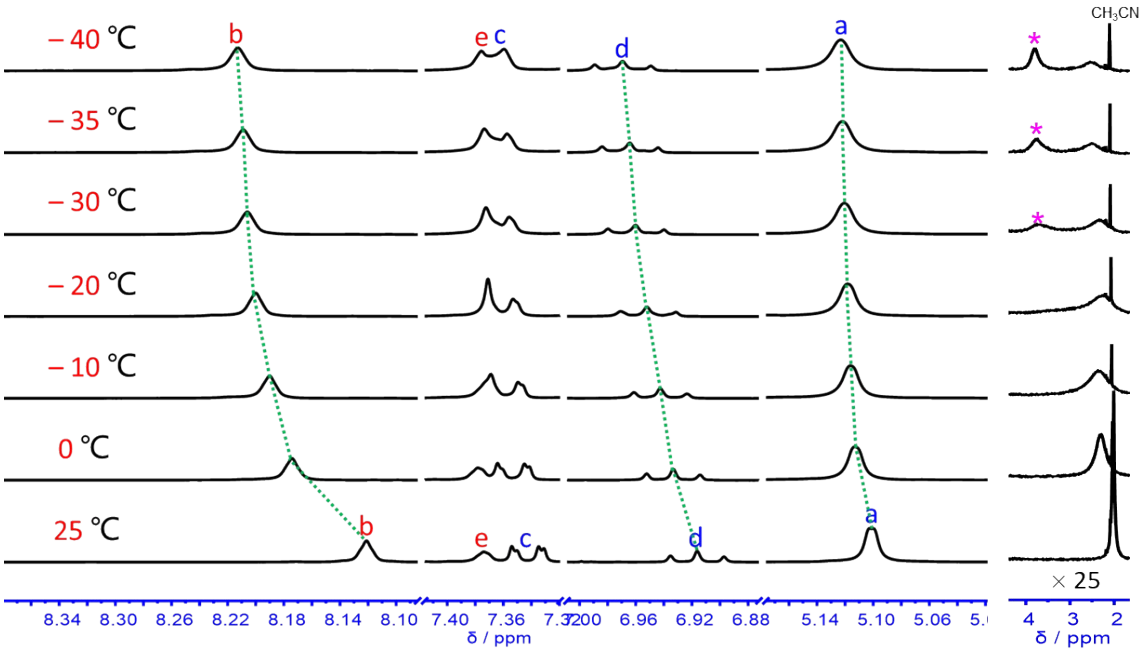


Figure S12. Selected regions of the ^{1}H NMR spectra of solutions of **5** (2.5 mM) recorded in $CDCl_3$ at the temperatures ranging from 25 ℃ to -40 ℃. New peaks corresponding to the bound water molecules are marked with an asterisk in the selected region on the right (scaled by 25).

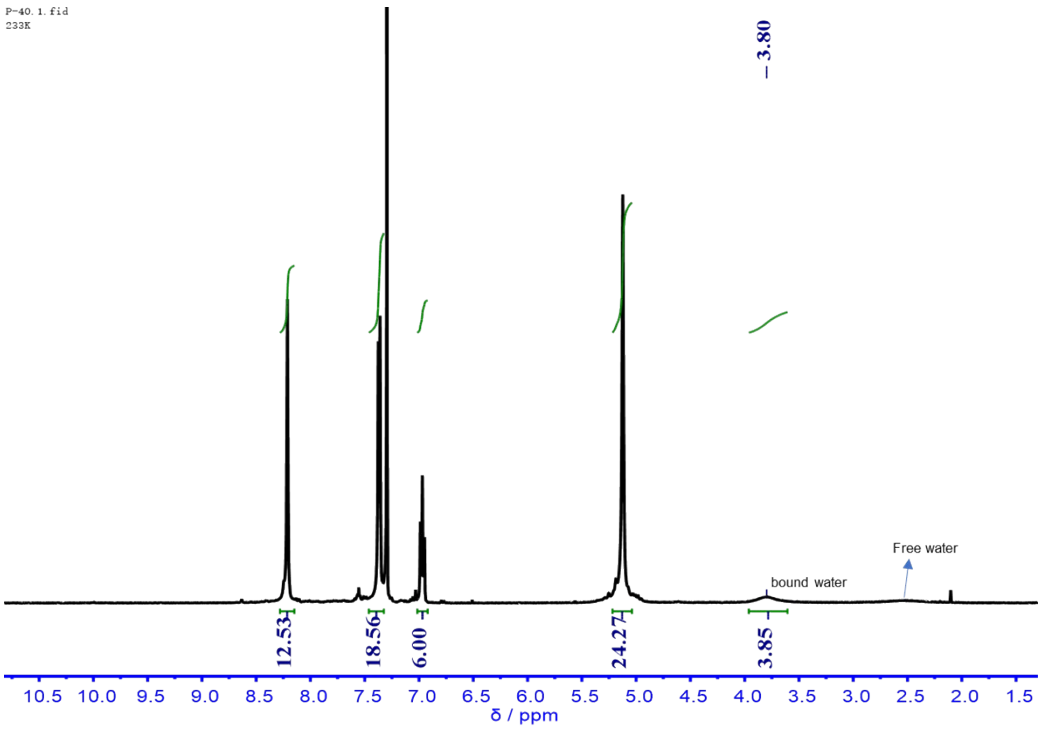


Figure S13. The ^{1}H NMR spectrum carried out in $CDCl_3$ at 233 K. Integration of peaks of interest gave a **5**-H_2O stoichiometry of 1:2.

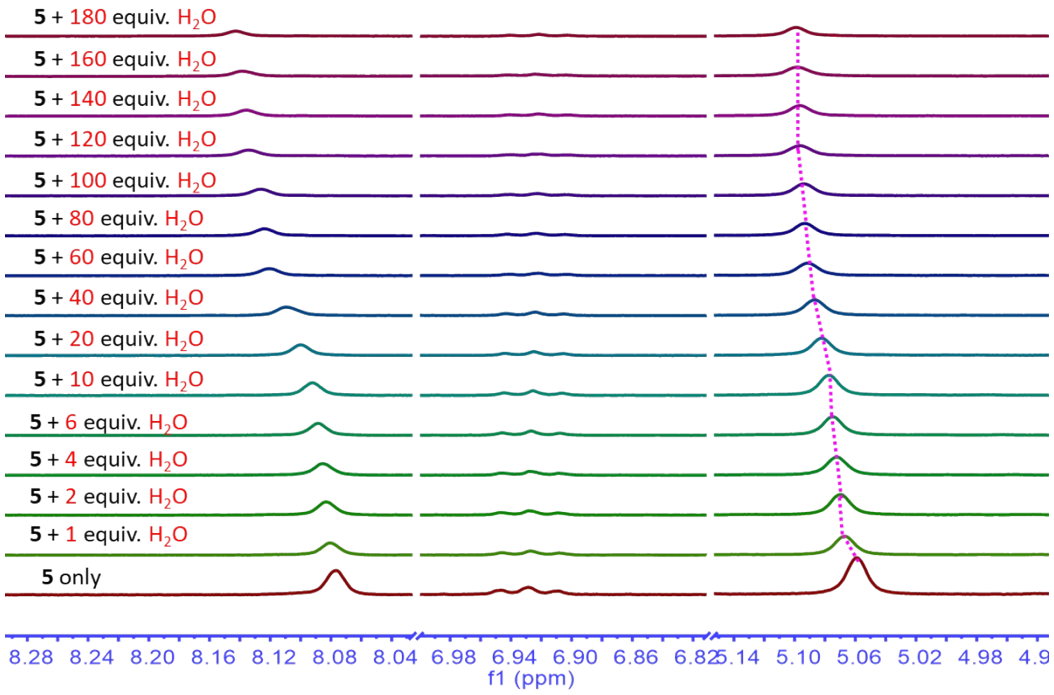


Figure S14. Selected regions of ^{1}H NMR spectra ($CDCl_3$/DMSO-d_6, 9/1 v/v, 298 K) acquired during the titration of **5** with increasing quantities of water: 0, 1, 2, 4, 6, 10, 20, 40, 60, 80, 100, 120, 140, 160, and 180 equiv.

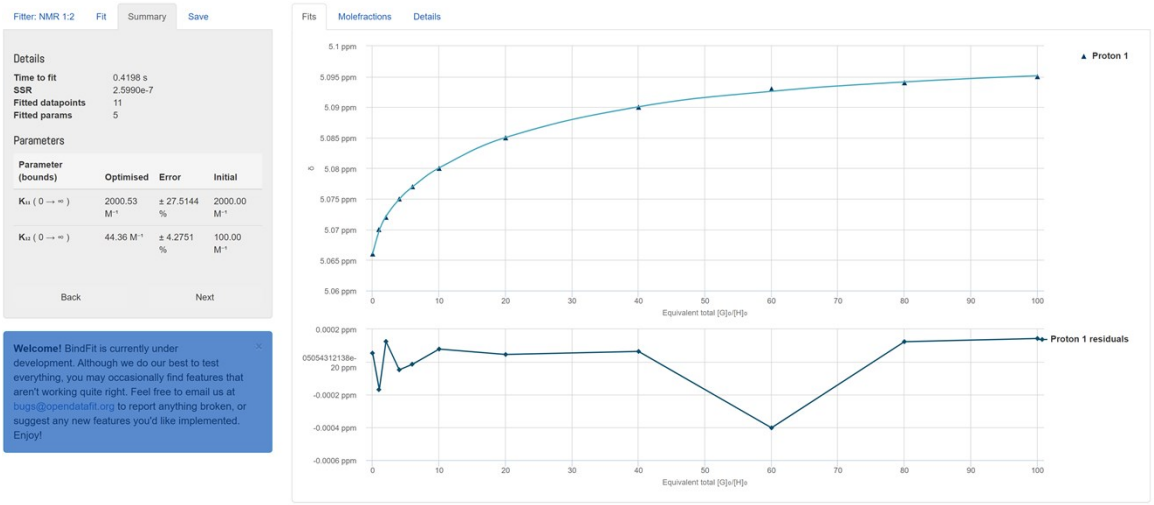


Figure S15. Nonlinear least-square analysis of the ^{1}H NMR binding data corresponding to the formation of $(H_2O)_2\subset$**5** complex. The data were fitted to a 1:2 binding model to give K_{11} = (2.0 ± 0.5) × 10^3 and K_{12} = 44.4 ± 1.8 M^{-1}, respectively. The residual distribution is shown below the binding isotherm. All solid lines were obtained from non-linear curve-fitting to a 1:2 binding model using the www.supramolecular.org web applet.

5. X–ray experimental

X–ray experimental for $(H_2O)_2\subset$**5**

Single crystals of superphane **5** were obtained as colorless blocks by slow evaporation of a solution of **5** in a mixture of $CHCl_3/CH_3CN$. A suitable crystal was selected and the data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus CuKα radiation source (λ = 1.5418 Å) with collimating mirror monochromators. The crystal was kept at 100 K during data collection. Using Olex2,[12] the structure was solved with the ShelXT[13] structure solution program using Direct Methods and refined with the ShelXL[14] refinement package using Least Squares minimization. Three water molecules inside the cavity are located and refined. The Olex2 implementation of SQUEEZE[15] was used to treat the rest of the solvent region. A solvent mask was calculated and 129 electrons were found in a volume of 440 $Å^3$ in 1 void per unit cell. This is consistent with the presence of 6[CH_3CN] per asymmetric unit which account for 132 electrons per unit cell. Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are in the CIF file. CCDC deposition number: 2072390.

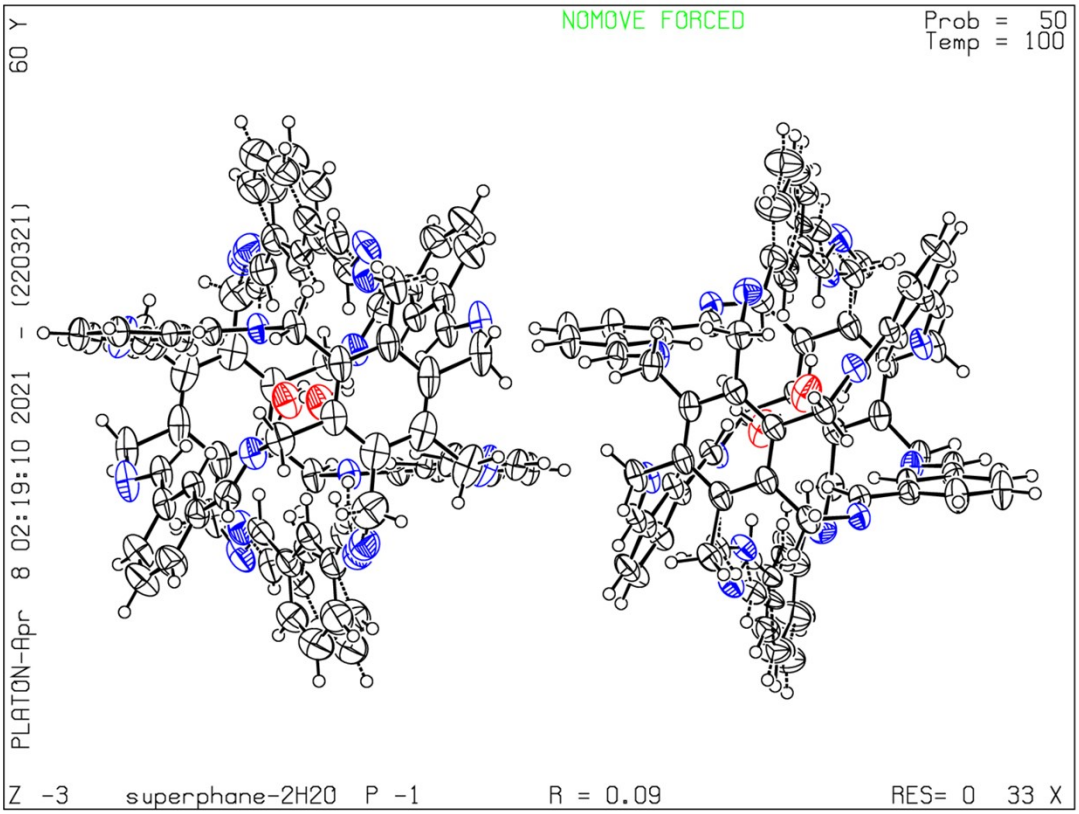


Figure S16. View of superphane $(H_2O)_2\subset$**5**. Displacement ellipsoids are scaled to the 50% probability level.

Table 1 Crystal data and structure refinement for superphane-2H2O-re-worked.

Identification code	superphane-$2H_2O$-re-worked
Empirical formula	$C_{72}H_{64}N_{12}O_2$
Formula weight	1129.35
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.8370(3)
b/Å	13.5455(2)
c/Å	19.9735(3)
α/°	77.7928(13)
β/°	73.9712(16)
γ/°	70.0209(17)
Volume/Å^3	3110.68(10)
Z	2
ρ_{calc}g/cm^3	1.206
μ/mm^{-1}	0.591
F(000)	1192.0
Crystal size/mm^3	0.124 × 0.098 × 0.056
Radiation	CuKα (λ = 1.54184 Å)
2Θ range for data collection/°	4.642 to 159.924
Index ranges	$-16 \leq h \leq 16$, $-17 \leq k \leq 16$, $-25 \leq l \leq 25$
Reflections collected	77364
Independent reflections	13186 [R_{int} = 0.0726, R_{sigma} = 0.0462]
Data/restraints/parameters	13186/1691/903
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0888, wR_2 = 0.2194
Final R indexes [all data]	R_1 = 0.1080, wR_2 = 0.2336
Largest diff. peak/hole / e Å^{-3}	0.45/-0.40

6. REFERENCES

(1). Gaussian 09, R. E., Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams–Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

(2) Xu, X., Goddard, W. A. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 2673–2677.

(3) Boys, S. F., Bernardi, F. *Mol. Phys.* **1970**, *19*, 553–566.

(4) van Duijneveldt, F. B., van Duijneveldt–van de Rijdt, J. G. C. M., van Lenthe, J. H. *Chem. Rev.* **1994**, *94*, 1873–1885.

(5) Zavada, J., Pankova, M., Holy, P., Tichy, M. *Synthesis–Stuttgart* **1994**, 1132–1132.

(6) Gavette, J. V., Sargent, A. L. Allen, W. E. *J. Org. Chem.* **2008**, *73*, 3582–3584.

(7) Fossey, J. S., Richards, C. J. *Organometallics* **2002**, *21*, 5259–5264.

(8) Lindahl, E., Hess, B., van der Spoel, D. *J. Mol. Mod.* **2001**, *7*, 306.

(9) Lu, T.; Chen, F. *J. Comput. Chem.* **2012**, *33*, 580.

(10) Sorin, E. J., Pande, V. S. *Biophys. J.* **2005**, *88*, 2472.

(11) Berendsen, H. J. C., Postma, J. P. M., Van Gunsteren, W. F., DiNola, A., Kaak, J. R. *J. Chem. Phys.* **1984**, *81*, 3684.

(12) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339–341.

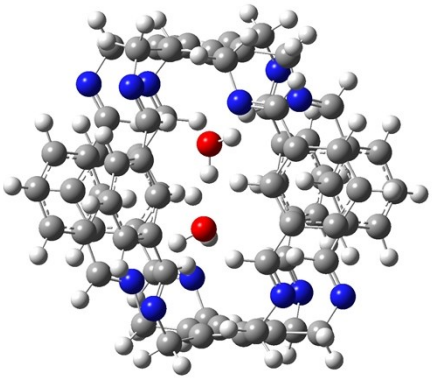
(13) Sheldrick, G. M. *Acta Cryst.* **2015**, A71, 3.

(14) Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3.

(15) Spek, A. L. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 9–18.

7. Energies and geometrical coordinates of the optimized models in the gas phase

Structure: **$(H_2O)_2 \subset 5$**



Charge, Spin Multiplicity: 0, 1

Counterpoise corrected energy =	-3588.122854680288
BSSE energy =	0.023281666622
sum of fragments =	-3588.075615124726
complexation energy =	-44.25 kcal/mole (raw)
complexation energy =	-29.64 kcal/mole (corrected)

Cartesian coordinates

Symbol	X	Y	Z
N	-1.46666600	4.70959300	-1.64293400
N	-0.55886100	3.62488500	1.63562200
N	-1.88067700	1.45535800	3.43486800
N	-4.48317100	-0.74933200	2.53902200
N	-5.21097500	-0.76695200	-0.80556000
N	-3.80467300	1.42389900	-2.95071700
N	1.90190700	-1.44797200	-3.42509600
N	4.49215700	0.76646000	-2.51322400
N	5.23824800	0.75590100	0.82320200
N	3.77976000	-1.43376800	2.95495800
N	1.45651600	-4.66905500	1.63501400
N	0.57624300	-3.65791600	-1.59022800
C	-3.24037100	3.56109600	-0.16306400
C	-2.94969800	3.34072400	1.19404400
C	-3.57291700	2.28878100	1.88795100
C	-4.48989900	1.45871300	1.22515700
C	-4.69829200	1.61251200	-0.15664900
C	-4.04778300	2.64155300	-0.85285000

C	-4.15181000	2.72024400	-2.37591600
H	-5.17511900	2.96324700	-2.68595400
H	-3.48927100	3.50020300	-2.76317400
C	-2.59693200	1.22337300	-3.27840000
H	-1.81772500	1.99481400	-3.20009000
C	-2.15495200	-0.10491300	-3.74650900
C	-3.09438700	-1.08988600	-4.08448500
H	-4.14945600	-0.84701300	-4.00627600
C	-2.67073900	-2.34481600	-4.49676800
H	-3.39848800	-3.10617100	-4.75776400
C	-1.30808800	-2.63114600	-4.55796200
H	-0.96969600	-3.61885100	-4.86233800
C	-0.36738500	-1.66604100	-4.19465700
C	-0.79461200	-0.39359200	-3.80250300
H	-0.05855600	0.36307100	-3.53564500
C	1.05064500	-2.05162600	-4.14672500
H	1.32102100	-2.95241400	-4.72100400
C	3.24880100	-2.00214000	-3.34217600
H	3.93056100	-1.25866300	-3.75741900
H	3.34784200	-2.91222200	-3.95396400
C	5.24581800	-0.36582700	-1.98109200
H	6.03394600	0.07372900	-1.36470000
H	5.76171700	-0.82841000	-2.83157800
C	3.31910900	0.98673700	-2.08220900
H	2.83066400	0.33600100	-1.34513600
C	2.52193000	2.15176300	-2.51298000
C	3.01758000	3.10155900	-3.41150900
H	4.00818800	2.95201300	-3.82968000
C	2.25096200	4.21555000	-3.74149500
H	2.64065300	4.94926900	-4.44077100
C	0.99456000	4.40367200	-3.17036000
H	0.39348800	5.27849700	-3.39891700
C	0.48975500	3.45929500	-2.27313000
C	1.25332700	2.33220400	-1.96194300
H	0.85948900	1.61187700	-1.24550600
C	-0.80538200	3.62449400	-1.58367700
H	-1.13304400	2.75318900	-0.99996200
C	-2.71630500	4.79355000	-0.89314500
H	-3.48154600	5.14562100	-1.59399600
H	-2.59914400	5.62475400	-0.19093400
C	-1.88920300	4.18134200	1.88360700

H	-1.94324800	5.23252700	1.57217800
H	-2.05392100	4.17627700	2.96353900
C	0.32375100	4.42566900	1.19637900
H	0.08445200	5.48138600	0.98881900
C	1.70990400	4.03388700	0.88746000
C	2.53042000	4.97381300	0.26103500
H	2.13099300	5.95884500	0.03121600
C	3.83706700	4.64791900	-0.09648500
H	4.46024400	5.37918800	-0.60128300
C	4.32846200	3.37938400	0.17193600
H	5.33171700	3.08639300	-0.12089700
C	3.51277400	2.42184500	0.79085000
C	2.20608000	2.75004100	1.14618300
H	1.55563900	2.00862700	1.60922100
C	4.00512800	1.03586300	0.95349300
H	3.23047100	0.27610500	1.12466500
C	5.64157700	-0.65078700	0.88883500
H	5.76007200	-0.91937100	1.93903400
H	6.63473900	-0.71998600	0.43172000
C	4.13339600	-2.72974100	2.38845200
H	5.15557700	-2.96986600	2.70509400
H	3.47147000	-3.51446800	2.76797000
C	2.59803600	-1.25778100	3.38185200
H	1.84024300	-2.05538700	3.39371800
C	2.15887600	0.07753900	3.83520500
C	3.10664900	1.05635200	4.16862100
H	4.15997700	0.79969600	4.11492300
C	2.69244000	2.32440000	4.54829700
H	3.42559700	3.08128600	4.80746900
C	1.33266700	2.62975200	4.57759000
H	1.00268700	3.62868200	4.85291800
C	0.38426000	1.67171700	4.21788600
C	0.80033500	0.38511300	3.86224900
H	0.05201700	-0.35651900	3.58839900
C	-1.03062700	2.07374200	4.14111900
H	-1.28803100	2.99812200	4.68520400
C	-3.22178900	2.02176800	3.34722900
H	-3.31590900	2.94041300	3.94842300
H	-3.90887000	1.28898700	3.77294100
C	-5.23633900	0.38412500	2.00986000
H	-5.74433200	0.85206800	2.86275000

H	-6.03242900	-0.05395600	1.40262300
C	-3.28981200	-0.92647900	2.14183300
H	-2.77549600	-0.25386700	1.44473800
C	-2.49718500	-2.09571300	2.56820700
C	-2.99339200	-3.06224400	3.44659000
H	-3.98505800	-2.91952900	3.86476500
C	-2.22704500	-4.18278900	3.75696300
H	-2.61517500	-4.92910200	4.44366400
C	-0.97401500	-4.36122800	3.17860100
H	-0.37411000	-5.24172300	3.38672400
C	-0.47088800	-3.39846500	2.29804800
C	-1.22887900	-2.26265900	2.01339100
H	-0.85047200	-1.51008800	1.32083000
C	0.81522600	-3.57272200	1.60154300
H	1.16215300	-2.69862200	1.02889800
C	2.69965200	-4.78383300	0.88353200
H	2.55938100	-5.61003100	0.18011300
H	3.45790000	-5.15565100	1.58170500
C	1.90759600	-4.18445100	-1.89194000
H	1.98498100	-5.24363700	-1.61605500
H	2.04506300	-4.14256100	-2.97456000
C	-0.33011800	-4.46951400	-1.21989500
H	-0.11609400	-5.54404100	-1.10743400
C	-1.70127200	-4.05806800	-0.87655900
C	-2.52784100	-5.00111400	-0.26104500
H	-2.14343600	-5.99903900	-0.06362200
C	-3.82148100	-4.66040800	0.12632600
H	-4.44877300	-5.39202100	0.62538000
C	-4.29732800	-3.37879700	-0.10998000
H	-5.29295700	-3.07805700	0.20074700
C	-3.47958800	-2.41915700	-0.72231900
C	-2.18139100	-2.75863600	-1.09859700
H	-1.53400400	-2.00728300	-1.54936400
C	-3.96728000	-1.02615700	-0.86935100
H	-3.18933300	-0.25691900	-0.96262600
C	-5.62950700	0.63645400	-0.86151700
H	-6.62215100	0.69055600	-0.40130200
H	-5.75987200	0.90070800	-1.91176300
C	2.96773100	-3.34083500	-1.19970600
C	3.59216200	-2.28176800	-1.88281000
C	4.49860600	-1.44930500	-1.20729200

C	4.70260900	-1.61327000	0.17530800
C	4.04605200	-2.64468400	0.86300900
C	3.24571100	-3.56082600	0.15949500
O	-1.25681700	0.80299300	0.07500600
H	-0.50757600	0.21642900	-0.16384000
H	-0.99904300	1.28410800	0.88268700
O	0.76552000	-0.89654800	-0.82444200
H	0.55989300	-1.84885900	-0.95470500
H	1.14047200	-0.68238800	-1.70243600