

Electronic Supplementary Information (ESI) for:

Cubic Dipole Lattice of Water Molecules Trapped inside Carbon Cages

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Experimental details

The H₂O@C₆₀ molecule was synthesized by the molecular surgical approach.^{S1} The black single crystals with a size of 0.2 mm were obtained by a slow evaporation of the *o*-xylene solution at 140°C. The synchrotron-radiation X-ray diffraction measurement was performed by using the large cylindrical image-plate camera at SPring-8 BL02B1 (Hyogo, Japan) from 300 to 20 K.^{S2} The crystal structure analysis was performed by using *SHELX*.^{S3} The electron charge density distribution was obtained by the maximum entropy method (MEM) using *ENIGMA*.^{S4} The temperature dependence of the dielectric permittivity was measured for the single crystal from 299 to 8 K with frequencies under 1.0 MHz by using an AC impedance analyzer (HP 4194A) and cryogenic refrigerating system (Daikin PS24SS). The electrical contacts were prepared by using gold paste (Tokuriki 8560) to attach ϕ 10 μ m gold wires to the single crystal. The temperature dependences of the lattice constant and dielectric permittivity of empty C₆₀ were also measured for the single crystals with a size of 0.2 mm by the same method for the reference.

Temperature dependence of the crystal structure

The crystal structure and phase transition of the H₂O@C₆₀ crystal are similar to that of empty C₆₀ crystal except that water molecules are trapped inside the carbon cages. The temperature dependence of the lattice constant of H₂O@C₆₀ is shown in Fig. S1a. The crystal undergoes a first order phase transition at 257(1) K. The H₂O@C₆₀ molecules are freely rotating in the high-temperature fcc phase with the space group $Fm\bar{3}m$. The carbon-cage orientation is ordered in the low-temperature sc phase with the space group $Pa\bar{3}$. The low-temperature phase is twinned along the {110} plane by the breaking of the mirror symmetry.^{S5}

The carbon-cage orientation can be represented by an angle ϕ which is an anticlockwise rotation about [111] direction of an ideal molecular configuration with $Fm\bar{3}$ symmetry.^{S6,S7} The carbon cage of $H_2O@C_{60}$ has two orientations with the occupancies of 0.8 and 0.2 at $\phi = 99.9$ and 41.9° , respectively, at 20 K. The results of crystal structure analysis at 20 K are summarized in Table S1-S4 and the CIF file (CCDC 930396).^{S8} The crystal structures above 20 K were also refined by using the structure model. The temperature dependence of the occupancy of the major orientation at $\phi = 99.9^\circ$ is shown in Fig. S1b. The occupancy is increased from 0.6 at 250 K by lowering the temperature, and frozen at 0.8 below around 90 K by a glass-like transition.^{S7}

The two components of the mean-square thermal displacement of a carbon atom, $U_C(1)$ and $U_C(2)$, which are parallel and perpendicular component to the librational motion of the carbon cage, are plotted in Fig. S1c. The $U_C(1)$ and $U_C(2)$ are comparable at 20 K while the former is three-times larger than the later at 250 K. The isotropic mean-square thermal displacement of the oxygen atom of the water molecule, U_O is also plotted in the figure. The U_O is four-times larger than $U_C(2)$ at 20 K.

Conformation of the water molecule

The encapsulated water molecule is observed as an isolated charge density peak at the cage centre. The charge density peak is modeled by an oxygen atom at the cage centre, and off-centred two hydrogen atoms that rotates around the cage centre. To visualize the hydrogen atoms, model MEM charge densities calculated based on the refined structure model without hydrogen atoms are subtracted from the experimental ones. The difference-MEM charge density distribution around the oxygen atom is shown in Fig. S2a. Positive difference densities are found $\sim 0.7 \text{ \AA}$ away from the

oxygen atom. The excess charges are regarded as the O-H bonding electrons because the distance ($\sim 0.7 \text{ \AA}$) is shorter than a common O-H bond length of a water molecule (0.96 \AA). Such bonding electrons are also found between carbon atoms of the carbon cage. Figure S2b shows the charge density map through a hexagon of the carbon cage on the (111) plane. The charge density at the C-C saddle point ($\sim 1.8 e\text{\AA}^{-3}$) is slightly higher than that of diamond ($\sim 1.6 e\text{\AA}^{-3}$).^{S9} The C-C bonding electrons are also seen in the difference charge density map as shown in Fig. S2c.

The delocalized O-H bonding-electron distribution can be modeled by a disordered water molecule. The delocalized but non-uniform shell-like charge distribution demonstrates a hindered rotation of the water molecule. Probable conformations of the water molecule are suggested from the O-H bonding-electron distribution. An ideal water molecule with a common O-H bond length (0.96 \AA) and H-O-H angle (104.5°) was fitted to the difference charge density distribution and then refined by the least-square refinement as shown in Fig. S2a. Six equivalent water molecules with the occupancy of $1/6$ given by the $\bar{3}$ site symmetry are depicted in the figure.

The refined molecular structure of $\text{H}_2\text{O}@C_{60}$ at 20 K is shown in Fig. S3. Only the major carbon cage and independent water molecule are depicted in the figure. The C-C bond lengths and radial distances from the cage centre for the ten independent major carbon atoms at 20 K are summarized in Table S3 and S4, respectively. The radial distances for C(3) and C(8) near the threefold inversion axis are longer than that for C(4), C(9), and C(10) far away from the axis. Thus the carbon cage is slightly elongated along the threefold inversion axis. The shortest interatomic distance between the hydrogen and carbon atom is 2.60 \AA .

Table S1 Crystallographic data for H₂O@C₆₀.

formula	H ₂ OC ₆₀
formula weight	738.62
color of crystal	black
temperature	20 K
X-ray wavelength	0.49917 Å
crystal system	cubic
space group	<i>Pa</i> $\bar{3}$
unit cell parameters	14.0669(1) Å
<i>Z</i>	4
No. of independent reflections	7591 ($d > 0.33$ Å, $ F > 2\sigma$)
$\Sigma\sigma_I/\Sigma I$	0.0728
No. of parameters	127
<i>R</i> 1	0.0360 ($ F > 2\sigma$)
GOF	0.680 ($ F > 2\sigma$)

Table S2 Refined structure parameters for H₂O@C₆₀ at 20 K.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	<i>U</i> _{iso} (Å ²)
O(1)	0	0	0	1.0	0.01827(6)
H(1)	0.0606	0.0305	0.0063	1/6	0.022
H(2)	-0.0402	0.0472	-0.0281	1/6	0.022
C(1)	0.22887(1)	-0.03325(1)	0.10186(1)	0.7925(4)	0.00708(2)
C(2)	0.24637(1)	-0.05503(1)	0.00674(1)	0.7925(4)	0.00720(2)
C(3)	0.20744(6)	0.06409(5)	0.12963(7)	0.7925(4)	0.00686(3)
C(4)	0.20633(1)	-0.14076(1)	-0.03496(1)	0.7925(4)	0.00714(2)
C(5)	0.17058(1)	-0.09654(1)	0.15947(1)	0.7925(4)	0.00716(2)
C(6)	0.22270(2)	0.11306(1)	-0.03829(2)	0.7925(4)	0.00708(2)
C(7)	0.24326(1)	0.01958(1)	-0.06476(1)	0.7925(4)	0.00714(2)
C(8)	0.20430(4)	0.13626(7)	0.06066(4)	0.7925(4)	0.00709(4)
C(9)	0.15044(1)	-0.20125(1)	0.02011(1)	0.7925(4)	0.00711(2)
C(10)	0.13223(1)	-0.17871(1)	0.11940(1)	0.7925(4)	0.00715(2)
C(11)	0.10142(6)	-0.03329(7)	0.22859(8)	0.2075(4)	0.00809(4)
C(12)	0.13162(4)	-0.11540(4)	0.18201(4)	0.2075(4)	0.00809(4)
C(13)	0.1369(3)	0.05958(17)	0.1999(2)	0.2075(4)	0.00809(4)
C(14)	0.06273(4)	-0.18797(5)	0.15620(5)	0.2075(4)	0.00809(4)
C(15)	0.00136(4)	-0.02019(4)	0.25203(4)	0.2075(4)	0.00809(4)
C(16)	0.23875(5)	-0.02113(4)	0.07921(5)	0.2075(4)	0.00809(4)
C(17)	0.20150(4)	-0.10914(4)	0.10610(4)	0.2075(4)	0.00809(4)
C(18)	0.2058(3)	0.0639(2)	0.1276(3)	0.2075(4)	0.00809(4)
C(19)	-0.03316(4)	-0.17546(4)	0.17795(5)	0.2075(4)	0.00809(4)
C(20)	-0.06461(4)	-0.08979(4)	0.22678(4)	0.2075(4)	0.00809(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.00575(4)	0.00800(4)	0.00749(4)	-0.00010(3)	-0.00103(3)	0.00038(3)
C(2)	0.00544(4)	0.00803(4)	0.00814(4)	-0.00020(3)	-0.00026(3)	0.00055(3)
C(3)	0.00576(6)	0.00774(4)	0.00710(7)	-0.00024(4)	-0.00146(5)	-0.00053(3)
C(4)	0.00620(4)	0.00705(4)	0.00816(5)	-0.00019(3)	0.00018(3)	0.00129(3)
C(5)	0.00696(4)	0.00746(4)	0.00706(4)	0.00051(3)	-0.00109(3)	0.00066(3)
C(6)	0.00583(5)	0.00700(5)	0.00841(5)	0.00024(4)	0.00062(3)	-0.00142(4)
C(7)	0.00562(4)	0.00803(4)	0.00778(4)	0.00001(3)	0.00070(3)	-0.00025(3)
C(8)	0.00548(8)	0.00773(5)	0.00807(5)	-0.00072(4)	-0.00055(5)	-0.00182(7)
C(9)	0.00690(4)	0.00638(4)	0.00806(4)	0.00001(3)	-0.00019(3)	0.00140(3)
C(10)	0.00739(4)	0.00655(4)	0.00750(4)	0.00074(3)	-0.00072(3)	0.00095(3)

Table S3 C-C bond lengths (Å) for the major carbon cage of H₂O@C₆₀ at 20 K. Shorter five bonds are fusing two hexagons. Longer ten bonds are fusing a hexagon and pentagon.

bond	bond length (Å)
C(1)-C(2)	1.3946(2)
C(3)-C(8)	1.405(1)
C(4)-C(9)	1.3937(2)
C(5)-C(10)	1.3945(2)
C(6)-C(7)	1.3969(2)
C(1)-C(5)	1.4566(2)
C(1)-C(3)	1.4555(5)
C(2)-C(4)	1.4546(2)
C(2)-C(7)	1.4543(2)
C(3)-C(8)	1.4520(5)
C(4)-C(10)	1.4537(2)
C(5)-C(6)	1.4552(2)
C(6)-C(8)	1.4529(4)
C(7)-C(9)	1.4538(2)
C(9)-C(10)	1.4550(2)

Table S4 Radial distances (Å) of the carbon atoms from the cage centre for the major carbon cage

of H₂O@C₆₀ at 20 K.

atom	radial distance (Å)
C(1)	3.5549(2)
C(2)	3.5524(2)
C(3)	3.557(1)
C(4)	3.5478(2)
C(5)	3.5544(3)
C(6)	3.5544(4)
C(7)	3.5518(2)
C(8)	3.558(1)
C(9)	3.5458(2)
C(10)	3.5497(3)

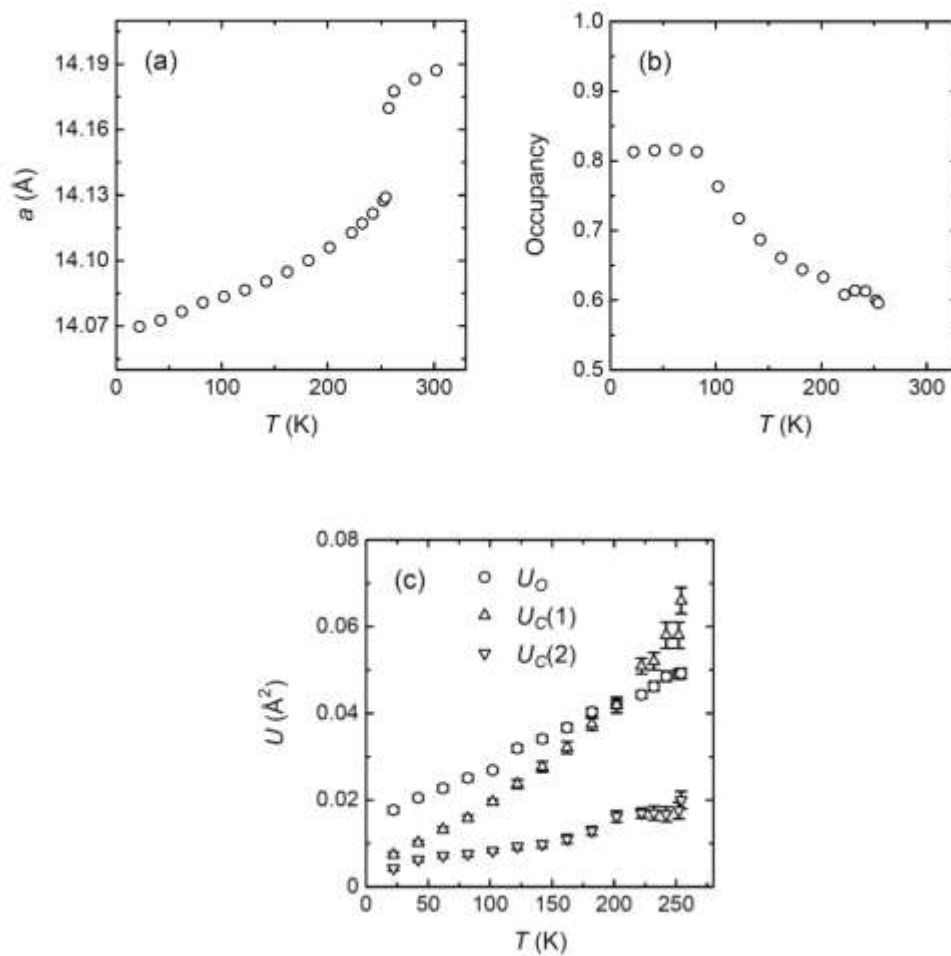


Fig. S1 Temperature dependence of the (a) lattice constant, (b) occupancy of the major carbon cage at $\phi = 99.9$, and (c) refined mean-square thermal displacements of the oxygen atom of the water molecule (U_O) and a carbon atom of the major carbon cage (U_C) of H₂O@C₆₀. The $U_{C(1)}$ and $U_{C(2)}$ are parallel and perpendicular component to the librational motion of the carbon cage, respectively.

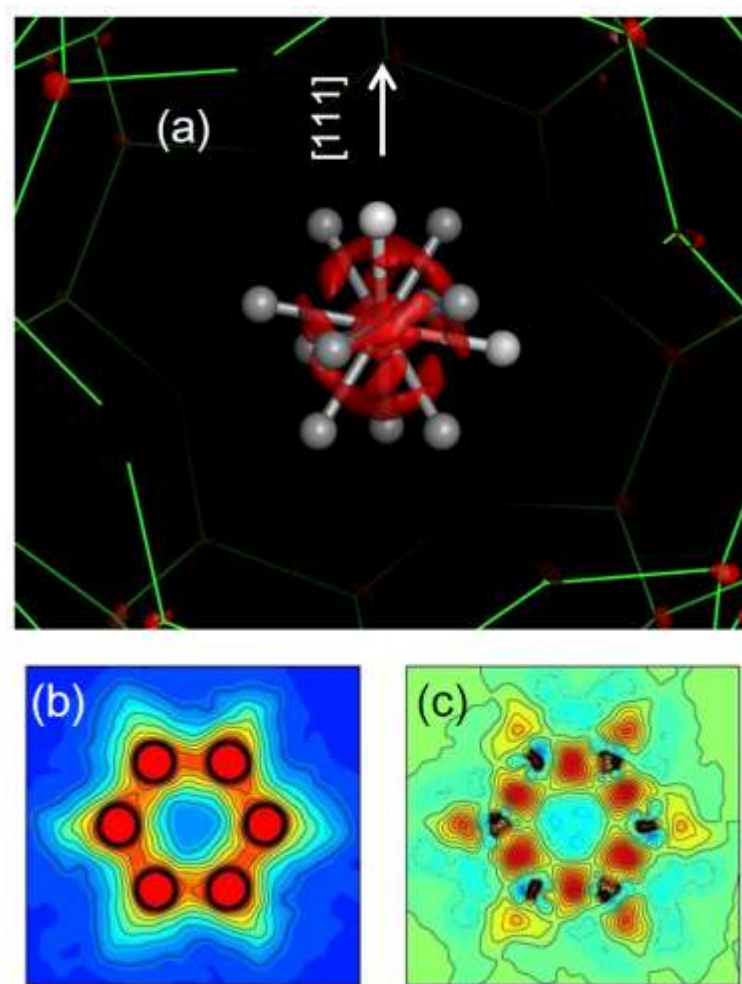


Fig. S2 (a) Equidensity surface of the difference charge densities for the water molecule at $0.4 e\text{\AA}^{-3}$ with the fitted water molecule. Six equivalent water molecules with the occupancy of $1/6$ are overlapped. Independent two hydrogen atoms and others are shown as white and gray, respectively. (b) Charge-density map on the (111) plane through a hexagon of C(3) and C(8). The contour lines are drawn from 0 to $4.0 e\text{\AA}^{-3}$ at intervals of $0.25 e\text{\AA}^{-3}$. (c) Difference charge-density map for panel (b) with the contour lines from -0.5 to $0.5 e\text{\AA}^{-3}$ at intervals of $0.05 e\text{\AA}^{-3}$.

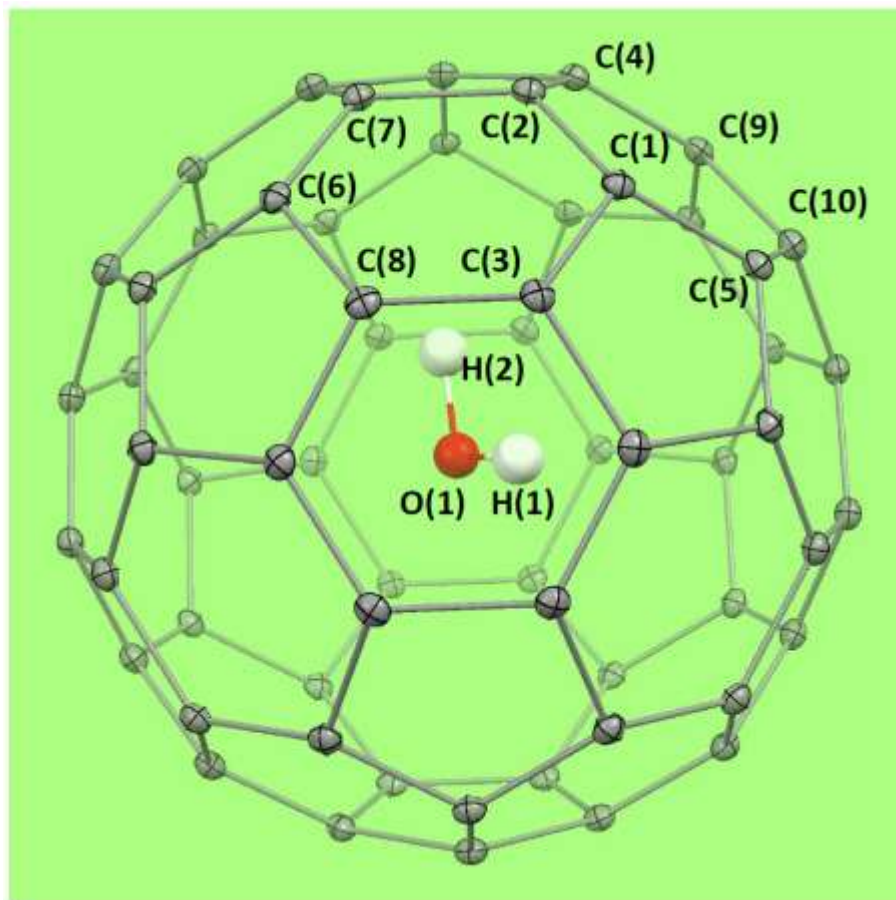


Fig. S3 Refined molecular structure of H₂O@C₆₀ at 20 K viewed from the threefold inversion axis. Only the major carbon cage and independent water molecule are depicted in the figure. The thermal ellipsoids are drawn at 50% probability level.

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