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Dielectric and Sorption Responses of Hydrogen-Bonding Network of Amorphous C₆₀(OH)₁₂ and C₆₀(OH)₃₆

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Abstract: Hydrophilic fullerene derivatives of $C_{60}(OH)_{12}$ (**1**) and $C_{60}(OH)_{36}$ (**2**) bearing different numbers of $-OH$ groups formed amorphous solids of $\mathbf{1} \cdot x(H_2O)$ ($x = 5-10$) and $\mathbf{2} \cdot x(H_2O)$ ($x = 15-22$), respectively, according to the humidity. The thermally activated dynamic molecular motion of polar H_2O was confirmed in the DSC and dielectric spectra. Three-dimensional $O-H \cdots O$ hydrogen-bonding networks in amorphous **1** and **2** produced extrinsic adsorption-desorption pores with a hydrophilic environment posed by $-OH$ groups, where N_2 , CO_2 , H_2 , and CH_4 gases vapors and polar H_2O , $MeOH$, and $EtOH$ molecules reversibly adsorbed into the networks. Molecular motion of polar H_2O was directly observed in dielectric enhancement and protonic conductivity in three-dimensional $O-H \cdots O$ hydrogen-bonding networks. The Brunauer-Emmett-Teller (BET) specific surface areas of amorphous **1** and **2** were 315 and $351 \text{ m}^2 \text{ g}^{-1}$, respectively, from the CO_2 sorption isotherms. Reversible vapor sorption behaviors with structural changes of amorphous **1** and **2** were also confirmed for the polar H_2O , $MeOH$, and $EtOH$.

1. Introduction

Porous materials, such as zeolites and carbons, have attracted much attention toward utilizing their high performance and selective storage, separation, and purification for global warming gases, clean energy, high energy, etc.¹⁻⁴ Inorganic porous materials have uniform intrinsic nanopores and/or mesopores to selectively capture the target gases. Recently, chemically designable and structurally diverse metal-organic frameworks (MOFs), porous coordination polymers, and covalent organic frameworks (COFs) have been applied to design pores and provide additional functionalities.⁵⁻⁹ Although the structural diversity of organic ligands and monomer molecules drastically enhanced the number of such porous materials, one of the disadvantages of these materials is their low solubility in common organic solvents and low processability to fabricate thin films. To solve this, a new fabrication technique for MOF/COF thin films has been developed using the layer-by-layer technique.¹⁰⁻¹⁴ In contrast, much attention has focused toward low-molecular-weight (LMW) organic sorption materials because of their high processability for thin-film devices using wet-fabrication techniques, such as drop-casting and spin-coating methods, because LMW organic compounds have a high solubility in common organic solvents.¹⁵⁻¹⁷ Recently, the liquid-liquid interface has been utilized for thin film fabrication, resulting in gas-transport free-standing thin films composed of a supramolecular organic framework (SOF) using the porous organic cage molecule on the porous alumina substrate.¹⁸⁻²³ The molecular assembly structures of SOF were constructed based on weak intermolecular hydrogen-bonding and van der Waals interactions.

Although LMW organic compounds usually form the closest packing structures in solids with the absence of pores, two kinds of approaches to obtain the intrinsic and extrinsic pores within the crystalline materials have been used to design a reversible adsorption-desorption crystalline environment.¹⁵⁻¹⁷ The former intrinsic pores of LMW organic compounds have been reported in calix[4]arene,¹⁸⁻²³ [4+6]cycloimine cages,²⁴⁻²⁹ cucurbit[6]uril,³⁰⁻³¹ etc.,³²⁻³⁹ whose intrinsic nanopores can be utilized as adsorption-desorption environments for gaseous CO₂, N₂, H₂, and CH₄. In contrast, the extrinsic pores of LMW organic compounds of tris(*o*-phenylenedioxy)cyclotriphosphazene,⁴⁰⁻⁴¹ 3,3',4,4'-

tetra(trimethylsilylethynyl)biphenyl,⁴² triptycenetrisbenzimidazolone,⁴³ and others,⁴⁴⁻⁵¹ can be reversibly formed by removing the crystallization solvents. Recent Brunauer-Emmett-Teller (BET) specific surface areas of LMW organic compounds exceeded 3000 m² g⁻¹ for a triptycenetrisbenzimidazolone derivative,⁴³ where the chemical designs of weak intermolecular hydrogen-bonding and van der Waals interactions play essential roles in achieving structurally flexible packing structures. Structural reconstruction of the molecular arrangements of LMW organic compounds can form reversible molecular and gas sorption environments within the crystals.

Single crystalline LMW organic compounds, including crystallization solvents, are candidates to form extrinsic molecular and gas sorption pores within the crystals. In the crystalline porous materials, the long-range periodicity of the crystal lattice should be maintained after the removal of solvent molecules, where the molecules and gases can diffuse into the pores of the crystal lattice. The softness and robustness of the crystal lattice are important considerations to obtain LMW organic sorption materials. Recent examinations of intrinsic-cage-type molecules have focused on compounds with large BET specific surface areas, specific chiral recognition pores,⁵² and possible thin film fabrication.⁵³ Development of new types of materials should be considered to expand the variation of LMW organic sorption materials because the molecular design strategy for LMW organic sorption materials is not sufficiently established.

The molecular assembly states of LMW organic sorption materials are another important consideration that affects the deterioration properties of vapor and gas-phase adsorption-desorption cycles. The sorption cycle of amorphous organic materials is much robust than those of single crystalline ones. Such amorphous materials have been widely applied in the fields of device fabrication, e.g., for ferroelectric relaxers,⁵⁴ organic transitions,⁵⁵ and organic electro luminescence.⁵⁶⁻⁵⁷ In the field of LMW organic sorption materials, the CO₂ adsorption property has been reported for the intrinsic pores of amorphous cucurbit[7]uril derivatives and noria.⁵⁸⁻⁵⁹ The formation of extrinsic pores has not been reported for amorphous LMW organic sorption materials.

Scheme 1. Molecular structures of a) $C_{60}(OH)_x$ (**1**: $x = 12$ and **2**: $x = 36$) and b) a possible isomer of $C_{60}(OH)_{36}$.

Polyhydroxylated hydrophilic fullerene derivatives of $C_{60}(OH)_x$ ($x = 12-44$) are easily soluble in water, depending on the average number of hydroxyl groups as a mixture of many isomers, whereby the number of $-OH$ groups (x) on the C_{60} surface modify the hydrophilicity and the magnitude of the intermolecular $O-H\cdots O$ hydrogen-bonding interactions.⁶⁰⁻⁶³ Although the water soluble uniform nanosphere with an average diameter of approximately 1 nm has been utilized for chemical mechanical polishing of slurries⁶²⁻⁶³ and antioxidants because of the free radical scavenging activity,⁶⁴⁻⁶⁸ molecular assembly structures and physical properties of solid state $C_{60}(OH)_x$ have not been sufficiently examined. The high affinity for the water and hydrogen-bonding interactions of $C_{60}(OH)_x$ have the potential to show interesting physical responses coupled with hydrogen-bonding interactions. Herein, two kinds of $C_{60}(OH)_x$ derivatives, i.e., $C_{60}(OH)_{12}$ (**1**) and $C_{60}(OH)_{36}$ (**2**), with different hydrophilicities and hydrogen-bonding abilities were examined in terms of molecular assemblies, proton dynamics, dielectric responses, vapor and gas adsorption-desorption behaviors for H_2O , $MeOH$, $EtOH$, N_2 , CO_2 , H_2 , and CH_4 as a new candidate for LMW organic sorption materials with extrinsic hydrogen-bonding network pores (Scheme 1). Although small molecules, such as H_2 , N_2 , and H_2O , can be captured in the internal space of the spherical C_{60} π -plane, these molecules cannot pass through the outside π -plane of C_{60} under ambient conditions.⁶⁹⁻⁷¹ In contrast, the superconducting transition temperature of 33 K has been reported for a 3:1 salt of $Cs^+ : C_{60}$,

whose crystal structure is that of the closest-packing structure, i.e., the face-centered cubic lattice.⁷²⁻⁷³ The occupation volumes of three molar Cs⁺ ions and C₆₀ are approximately 59 and 540 Å³, respectively, because the ionic and van der Waals radii of Cs⁺ and C₆₀ are 1.67 and 5.05 Å, respectively. Therefore, the closest-packing structure of C₆₀ has a relatively large external pore size (>10% of the volume of C₆₀), which can be utilized for the molecular adsorption-desorption environment.

2. Experimental Section

2.1. Physical measurements. Infrared (IR, 400–4000 cm⁻¹) spectra were measured on a KBr pellet using a Thermo Fisher Scientific Nicolet 6700 spectrophotometer with a resolution of 4 cm⁻¹. The in situ IR measurements under CO₂ were performed using an Oxford cryostat MicrostatN with a neat sample under the control of CO₂ pressure at 195 K. Thermogravimetric (TG) differential thermal analysis and differential scanning calorimetry (DSC) were conducted using a Rigaku Thermo plus TG8120 thermal analysis station and Mettler DSC1-T with an Al₂O₃ reference and a heating and cooling rate of 5 K min⁻¹ under nitrogen. The temperature-dependent dielectric constants were measured using the two-probe AC impedance method from 1 kHz to 1 MHz (Hewlett-Packard, HP4194A) and the temperature controller of a Linkam LTS-E350 system. The electrical contacts were prepared using gold paste (Tokuriki 8560) to attach the 25-μm ϕ gold wires to the 3-mm ϕ compressed pellet. Temperature-dependent powder X-ray diffraction (PXRD) was performed using a Rigaku SmartLab diffractometer with Cu Kα (λ = 1.54187 Å) radiation.

2.2. Preparation of 1 and 2. Polyhydroxylated fullerene C₆₀(OH)₁₂ (**1**) was used as purchased from Frontier Carbon Corporation as nanom spectra D100. The supplier claims an average number of hydroxyl of ~10 by preparation with a modified synthetic method to give C₆₀(OH)₁₂.⁶²⁻⁶³ Polyhydroxylated

fullerene C₆₀(OH)₃₆ (**2**) was prepared by a previously reported method using hydrogen peroxide and nanom spectra D100 as starting materials.⁶⁶⁻⁷⁰

2.3. Sorption measurements. The adsorption/desorption isotherms for H₂O at 298 K, MeOH at 288 K, and EtOH at 298 K were measured with a BELSORP-aqua automatic volumetric adsorption apparatus (BEL Japan, Inc.). The N₂, CO₂, H₂, and CH₄ adsorption/desorption isotherms were measured with BELSORP-max and BELSORP-mini automatic volumetric adsorption apparatuses (BEL Japan, Inc.) at 77, 195 (and 298 K), 77, and 173 K, respectively. The high-pressure CO₂ adsorption and desorption isotherms were measured using a BELSORP-HP volumetric adsorption instrument (BEL Japan, Inc.). Before the measurements, **1**•x(H₂O) and **2**•x(H₂O) were heated at 373-380 K under a reduced pressure (<10⁻² Pa) to remove the H₂O molecules.

3. Results and Discussion

3.1. Thermal property and molecular-assembly. The hydroxyl-functionalized hydrophilic surfaces of **1** and **2** can effectively form the intermolecular hydrogen-bonding network. As-grown amorphous **1** and **2** were obtained as the hydrated species of **1**•x(H₂O) and **2**•x(H₂O), where x depends on the humidity. TG analyses show a gradual dehydration process from room temperature accompanying the gradual weight-loss. The weight-loss percentages of **1**•x(H₂O) and **2**•x(H₂O) at 400 K are approximately 10.6 and 16.2%, respectively (Figure S1), which correspond to calculated weights of 10.5% for **1**•6(H₂O) and of 16.8% for **2**•15(H₂O), respectively. Therefore, the typical formulas of amorphous **1** and **2** at approximately 40% relative humidity are **1**•6(H₂O) and **2**•15(H₂O), respectively. After the dehydration, next weight loss corresponding to the thermal decomposition starts at ca. 460 K for **1**, while **2** starts to decompose just after the dehydration, that is, at ca. 400 K, suggesting that the hydrogen-bonding network in **1** is more thermally stable.

Figure 1. Phase transition and molecular assembly structures of solid-state **1** and **2**. a) DSC diagrams of **1**•6(H₂O) and **2**•15(H₂O). b) PXRD patterns of **1**•15(H₂O) (black pattern), **2**•22(H₂O) (blue pattern), **2** (gray pattern), **2**•14(MeOH) (green pattern), and **2**•9(EtOH) (red pattern) at 298 K.

Figure 1a shows DSC diagrams of **1**•6(H₂O) and **2**•15(H₂O) from 120 to 300 K. Although the first-order phase transition from liquid to solid water is not observed around 273 K in the cooling process, the baseline anomaly around 170 K is associated with the thermally activated solid-glass transition of thermally fluctuated polar H₂O molecules. Figure 1b summarizes the PXRD patterns of **1**•15(H₂O), **2**•22(H₂O), **2** at 298 K, indicating the low crystallinity and amorphous state for all molecular assemblies. The broad diffraction peaks at $2\theta = 9.40^\circ$ and 18.7° for **1**•15(H₂O) are assigned to the short-range order

of $d \approx 0.94$ and $d \approx 0.47$ nm, respectively, whereas those at $2\theta = 7.88^\circ$ and 16.3° for **2**•22(H₂O)₂₂ correspond to $d \approx 1.12$ and $d \approx 0.54$ nm, respectively. Amorphous-like molecular assembly structures of **1**•6(H₂O) and **2**•15(H₂O) are consistent with the glass transition behavior of H₂O around 170 K in the DSC diagrams. The short-range periodicities of $d \approx 0.94$ and $d \approx 1.12$ nm are almost consistent with the average diameters of C₆₀(OH)₁₂ and C₆₀(OH)₃₆, respectively, whereby decreasing the number of –OH groups from $x = 36$ to $x = 12$ reduces the average diameter. The removal of H₂O from (**2**)•15(H₂O) slightly changes the PXRD pattern with a broad diffraction peak around $2\theta = 7.96^\circ$ with $d \approx 1.1$ nm, which is the same as that for **2**•22(H₂O).

3.2. H₂O dynamics in solids. Changes in the DSC baselines of **1**•6(H₂O) and **2**•15(H₂O) around 170 K are associated with the glass transition of thermally activated H₂O molecules within the pores of O–H•••O hydrogen-bonding networks of amorphous **1** and **2**. The dielectric spectra are sensitive to the molecular motion of polar structural units in the measuring frequency range from 1 kHz to 1 MHz.⁷⁵ When the frequency of the molecular motion is close to that of the measuring frequency, a Debye-type dielectric relaxation is observed in the dielectric measurements. Figure 2 summarizes the real part (ϵ_1) and imaginary part (ϵ_2) of the dielectric constants of **1**•6(H₂O) and **2**•15(H₂O), together with dehydrated **1** and **2** on the compressed pellets. Both of the ϵ_1 and ϵ_2 values are largely enhanced by increasing the temperature and decreasing the frequency above ~200 K. The values of $\epsilon_1 = 460$ and $\epsilon_2 = 340$ for **1**•6(H₂O) at 280 K are approximately one hundred times larger than that at 150 K and 1 kHz, suggesting that the molecular motion of the polar structural unit is thermally activated by increasing the temperature above 200 K. The baseline anomaly in the DSC measurements were observed around 170 K, where the molecular motion of H₂O molecules was just thermally activated by increasing in the temperature. On the contrary, the collective motion of the polar hydrogen-bonding network was observed in the frequency-dependent dielectric enhancements. Such dynamic molecular motions have been observed in the huge dielectric responses in organic–inorganic perovskite crystals.^{76, 77} The thermally activated molecular motion of the polar H₂O molecules mainly contributes to the dielectric enhancements in the measuring

frequency range because the magnitude of $\varepsilon_1 = 480$ for **1**•6(H₂O) is six times larger than that of $\varepsilon_1 = 85$ for dehydrated **1** at 280 K. The large value of $\varepsilon_2 \approx 300$ strongly supports the highly protonic conductive behavior of **1**•6(H₂O) around 280 K.

Figure 2. Temperature- and frequency-dependent real (ε_1) and imaginary (ε_2) parts of the dielectric constants for a, b) **1**•6(H₂O) (solid lines) and dehydrated **1** (dashed lines), and c, d) **2**•15(H₂O) (solid lines) and dehydrated **2** (dashed lines) during cooling from 285 K.

Similar dielectric enhancements are clearly observed for **2**•16(H₂O). The ε_1 and ε_2 values of **2**•(H₂O)₁₆ at 280 K are approximately two hundred times larger than those at 150 K with a frequency, $f = 1$ kHz, and the dielectric constants and dielectric enhancements of **2**•16(H₂O) are much larger than those of **1**•6(H₂O)

because of the larger amount of –OH groups and H₂O molecules. A Debye-type dielectric relaxation was observed in the dielectric measurements of **2**•16(H₂O). The frequency-dependent conductance (*G*) and susceptance (*B*) spectra and its Cole-Cole plots indicated a typical semicircular trace at 300 K (Figure S7). A relation time (τ) of the dipole motion of hydrogen-bonding H₂O molecules was estimated as 2.58×10^{-4} sec at 300 K. Relatively high proton conductivity of hydrated **2**•16(H₂O) was observed at 2.8×10^{-4} Scm⁻¹ at 300 K due to the existence of hydrogen-bonding network and acidic –OH group to generate the protonic carrier. The complete H₂O removal from **2**•16(H₂O) decreases the ϵ_1 value from 1050 to 210 at 1 kHz, which is consistent with the dielectric anomaly for the thermally activated molecular motion of polar H₂O in amorphous state **1** and **2**. A broad anomaly for the ϵ_2 value is observed in **2**•16(H₂O) around 255 K because of the motional freedom of H₂O and a relatively large ϵ_2 value of 500 at 280 K, indicating the proton conducting property of **2**•16(H₂O). The dielectric spectra of **1**•6(H₂O) and **2**•15(H₂O) are consistent with the glass transition of polar H₂O molecules around 170~220 K within the hydrogen-bonding networks of amorphous **1** and **2**. Much larger ϵ_1 and ϵ_2 values of **2**•*x*(H₂O) than those of **1**•*x*(H₂O) corresponded to larger magnitude of motional freedom of hydrogen-bonding networks of **2**. The H₂O dependent dielectric responses of crystals **2**•*x*(H₂O) were evaluated in vacuum and fully saturated H₂O condition, respectively, using the compressed pellets (Figure S10). The dehydrated **2** indicated simple dielectric enhancements at low frequency and high temperature condition due to the thermally activated fluctuation of the hydrogen-bonding C₆₀(OH)₃₆ network by increasing in the temperature up to 300 K. On the contrary, the hydrated **2**•16(H₂O) under the saturated H₂O condition indicated huge dielectric enhancements and also discontinuous ϵ_1 - and ϵ_2 -changes around solid–liquid phase transition temperature of bulk H₂O around 273 K. Therefore, sufficient amount of H₂O molecules in hydrogen-bonding C₆₀(OH)₃₆ hydrogen-bonding network formed the bulk environment of H₂O hydrogen-bonding network.⁷⁸ However, the H₂O adsorption-desorption isotherm at 298K clearly indicated the unstable liquid state H₂O sorption state in the hydrogen-bonding C₆₀(OH)₃₆ network. Under

the saturated H₂O condition, the H₂O molecules could be stably existed in the hydrogen-bonding C₆₀(OH)₃₆ network accompanying with dielectric anomaly around 273 K.

3.3. Gas and vapor sorption properties. To elucidate a porosity, gas and vapor adsorption/desorption isotherms were measured. Table 1 summarizes the adsorption-desorption parameters of amorphous **1** and **2**. Figure 3a shows the N₂ adsorption-desorption isotherms of amorphous **1** and **2** at 77 K. The N₂ adsorption amounts for **1** and **2** are about 2 and 28 mol mol⁻¹, respectively, at $P/P_0 \sim 1$. The abrupt adsorption increase for amorphous **2** from $n_{\text{ads}} \approx 12$ to ~ 28 at $P/P_0 \approx 0.92$ may be N₂ adsorption at the macropores of the powdered sample. Therefore, approximately twelve N₂ molecules are adsorbed into the nanopores of amorphous **2**, providing **2**•(N₂)₁₂. **1** has the type-I isotherm typical for nanoporous materials, while the isotherms of **2** shows gradual uptake with a hysteresis. On the other hand, the CO₂ adsorption-desorption isotherms at 195 K are the type-I with almost no hysteresis. The I-type CO₂ sorption isotherm suggests the existence of nanopores in amorphous **1** and **2**. The presence of nanopores in amorphous **1** and **2** was also confirmed from the H₂ adsorption measurements, in which both compounds reversibly adsorb H₂ at 77 K, resulting in the chemical formulas of **1**•2.5(H₂) and **2**•4(H₂), as shown in Figure 3c). The BET specific surface area calculated from the CO₂ adsorption data are 312 and 333 m² g⁻¹ for amorphous **1** and **2**, respectively. Two kinds of amorphous-like LMW organic sorption materials were reported by Atwood et al.⁵⁸ The first compound of noria has an intrinsic cage within the molecule, which showed a high CO₂ selectivity for gas adsorption with a BET specific surface area of 40 m² g⁻¹ from the N₂ adsorption-desorption isotherm at 77 K. The second amorphous compound was reported in the intrinsic cage-type cucurbit[7]uril molecule,⁵⁸ indicating higher CO₂ adsorption behavior than those for N₂ and CH₄. The BET specific surface area of the latter compound is much smaller than those of **1** and **2**. The three-dimensional extrinsic pores of the hydrogen-bonding networks for amorphous **1** and **2** are useful for repeated adsorption-desorption cycles. From the liquid density of N₂ ($d = 0.808$ g cm⁻³) and the solid density of CO₂ ($d = 1.56$ g cm⁻³), the occupied volumes of N₂ ($n_{\text{max}} = 5.35$) and CO₂ ($n_{\text{max}} = 12.0$) for amorphous **2** are approximately 0.368 and 0.115 cm³ g⁻¹, respectively. On the contrary, the occupied volumes of the N₂ ($n_{\text{max}} = 2.34$) and CO₂ ($n_{\text{max}} = 3.17$) for amorphous **1** are approximately

0.089 and 0.098 cm³ g⁻¹, respectively. **2** has similar occupied volumes for both gases, while the occupied volume of **2** for N₂ was larger than that for CO₂, which may be due to the structural expansion of hydrogen-bonding framework. The CH₄ adsorption/desorption isotherms also showed similar trend to N₂: only **2** has large hysteresis as shown in Figure 3d). It is worth noting that more hydrophobic N₂ and CH₄ than CO₂ induced the structural changes. All gas sorption results imply that the balance of hydrophobicity/hydrophilicity in the hydrogen-bonding networks and gas molecules determines the sorption behaviors.

Figure 3. Gas adsorption-desorption properties of **1** and **2**. a) N₂ adsorption-desorption isotherm at 77 K. b) CO₂ adsorption-desorption isotherm at 195 and 298 K. c) H₂ adsorption-desorption isotherm at 77 K. d) CH₄ adsorption-desorption isotherm at 173 K.

It is expected that the surface-modified -OH groups on C₆₀(OH)_x play an important role not only for the formation of hydrogen-bonding network pores but also for the adsorption sites for gas molecules. To evaluate the strength of the interaction between the hydrogen-bonding networks and CO₂ molecules, the enthalpy of CO₂ adsorption (Q_{st}) was calculated. First, the dual-site Langmuir–Freundlich equation (eq. 1) was employed to model the CO₂ adsorption isotherms at 278, 288, and 298 K for amorphous **1** and **2** (Figure S8).⁷⁹

$$q = \frac{q_{sat,A} b_A P^{\alpha_A}}{1 + b_A P^{\alpha_A}} + \frac{q_{sat,B} b_B P^{\alpha_B}}{1 + b_B P^{\alpha_B}} \quad (1)$$

here, q is the amount of adsorbed CO₂ (mmol g⁻¹), p is the pressure (bar), q_{sat} is the saturation capacity (mmol g⁻¹), b is the Langmuir–Freundlich parameter (bar^{- α}), and α is the Langmuir–Freundlich exponent (dimensionless) for adsorption sites A and B. The Clausius–Clapeyron equation (eq. 2) was then used to calculate Q_{st} by determining the slope of the best-fit line for $\ln p$ versus $1/T$ at each loading.

$$(\ln p)_q = \left(\frac{Q_{st}}{R} \right) \left(\frac{1}{T} \right) + C \quad (2)$$

The magnitudes of Q_{st} for CO₂ adsorption of amorphous **1** and **2** are -46 and -42 kJ mol⁻¹ at zero coverage, respectively (Figure 4a). There is no significant difference for the Q_{st} values of amorphous **1** and **2** with different numbers of -OH groups, and increasing q values gradually decrease the absolute value of Q_{st} . Since the Q_{st} values of amorphous **1** and **2** are comparable to that of zeolite ($Q_{st} = -49.1$ and -50.0 for NaX and Na-ZSM-5, respectively),⁸⁰ the hydrogen-bonding network structure of the -OH groups should act as hydrophilic gas adsorption sites. Temperature-dependent in situ vibrational spectra of amorphous **2** were measured (Figure 4b) to evaluate the intermolecular interaction at the -OH hydrogen-bonding network sites.

Figure 4. CO₂ adsorption of **2**. a) Enthalpy of CO₂ adsorption (Q_{st}) as a function of loading. b) Temperature-dependent in situ vibration spectra of the antisymmetric C=O stretching band ($\nu^a_{CO_2}$) under a CO₂ environment.

At 195 K, the antisymmetric C=O stretching mode of CO₂ ($\nu^a_{CO_2}$) is observed at 2338 cm⁻¹, and its intensity gradually decreases as the temperature increases. The $\nu^a_{CO_2}$ band for gas-phase CO₂ molecules is observed at 2349 cm⁻¹. Therefore, the $\nu^a_{CO_2}$ band of amorphous **2** is red-shifted by approximately 10 cm⁻¹ under a CO₂ environment. The physical CO₂ adsorption in various host materials appears as the $\nu^a_{CO_2}$ band from 2328 to 2368 cm⁻¹;⁸¹ thus, the CO₂ molecules in amorphous **2** are physically adsorbed into the pores of the O-H...O hydrogen-bonding network. Adsorption of CO₂ molecules at Lewis acidic and Lewis basic sites result in a blue-shift and red-shift of the $\nu^a_{CO_2}$ bands, respectively.⁸²⁻⁸⁴ The red-shifted $\nu^a_{CO_2}$ band under a CO₂ environment of amorphous **2** indicates the interaction between the carbon atom of CO₂ and the oxygen atom of the -OH sites. Increasing the temperature gradually released CO₂ gas from the hydrogen-bonding network pores of amorphous **2**, decreasing the intensity of the $\nu^a_{CO_2}$ band.

Table 1. Sorption properties of 1 and 2.

		1				2			
Adsorbate	T	P/P_0	P	$n_{\max}$	$n_{\max}$	P/P_0	P_0	$n_{\max}$	$n_{\max}$
	K		kPa	mol mol ⁻¹	cm ³ (STP) g ⁻¹		kPa	mol mol ⁻¹	cm ³ (STP) g ⁻¹
H ₂ O	298	0.95	–	8.87	212	0.95	–	21.8	370
MeOH	288	0.98	–	7.36	178	0.96	–	13.8	235
EtOH	298	0.97	–	5.07	123	0.96	–	9.23	157
N ₂	77	0.99	–	2.34	57.4	0.99	–	12.0 (27.5) ^a	238 (469) ^a
CO ₂	195	0.98	–	3.17	77.9	0.99	–	5.35	91.1
CO ₂	298	–	118	1.24	30.1	–	120	2.30	38.6
H ₂	77	–	101	2.62	64.5	–	100	3.67	61.7
CH ₄	173	–	96.6	1.16	28.5	–	95.4	2.90	48.6

^a $n_{\max}$ in parentheses includes the adsorption for the macropores of the powdered sample.

Table 1 summarizes the adsorption-desorption parameters of amorphous **1** and **2** for H₂O ($T = 298$ K), MeOH ($T = 288$ K), and EtOH ($T = 298$ K). Before the adsorption measurements, the solids were kept at 373 K under vacuum (10^{-2} Pa) for 18 h to completely remove H₂O molecules. The adsorption-desorption isotherms of amorphous **1** and **2** for H₂O indicate reversible adsorption-desorption behavior (Figure 5 and Figure S2), where the maximum adsorption amounts ($n_{\max}$) of **1** and **2** are 10 and 22, respectively, at $P/P_0 \approx 0.95$. Similarly, reversible adsorption-desorption behaviors for MeOH ($T = 288$ K) and EtOH ($T = 298$ K) are observed in amorphous **1** and **2**. The $n_{\max}$ values of amorphous **1** and **2** for MeOH are approximately 7 and 14, respectively, whereas those for EtOH are 5 and 9, respectively (Figure S2). The magnitude of $n_{\max}$ for amorphous **2** is approximately twice that of **1** because **2** has more -OH groups per one fullerene unit. From the liquid densities of H₂O ($d_{293\text{K}} = 0.998$ g cm⁻³), MeOH ($d_{293\text{K}} = 0.793$ g cm⁻³), and EtOH ($d_{293\text{K}} = 0.789$ g cm⁻³), the occupied volumes of the guest H₂O ($n = 21.8$), MeOH ($n = 13.8$),

and EtOH ($n = 9.23$) molecules for amorphous **2** are approximately 0.298, 0.423, and 0.409 $\text{cm}^3 \text{g}^{-1}$, respectively. On the contrary, the occupied volumes of the guest H_2O ($n = 8.87$), MeOH ($n = 7.36$), and EtOH ($n = 5.07$) molecules for amorphous **1** are approximately 0.171, 0.321, and 0.320 $\text{cm}^3 \text{g}^{-1}$, respectively. These values are considerably larger than those calculated from the CO_2 adsorption data. In addition, all vapor adsorption/desorption isotherms showed hysteresis. These results suggest that the molecules with hydroxyl groups induce the structural changes. Hydrophilic pores decorated by OH groups contribute to high adsorption amounts for polar H_2O , CH_3OH , and $\text{C}_2\text{H}_5\text{OH}$ molecules. The similar occupied volumes of **1** and **2** for MeOH and EtOH suggested the similar porosity for the adsorption states. However, the occupied volumes of **1** and **2** for H_2O are considerably smaller than those for MeOH and EtOH, indicating a different porosity and adsorption environment around $-\text{OH}$ groups. The guest polar molecules, such as H_2O , MeOH, and EtOH can be captured in the intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding networks between the surface-modified $-\text{OH}$ groups on C_{60} , where the interaction mode of H_2O is different from those of MeOH and EtOH.

Figure 5. Adsorption-desorption isotherms of **2** for H_2O at 298 K (red), MeOH at 288 K (blue), and EtOH at 298 K (black).

4. Conclusion

Two kinds of –OH-modified C₆₀ derivatives of C₆₀(OH)₁₂ (**1**) and C₆₀(OH)₃₆ (**2**) showed reversible vapor (H₂O, MeOH, and EtOH) and gas (N₂, CO₂, H₂, and CH₄) adsorption-desorption behaviors at the O-H•••O hydrogen-bonding network pores of the amorphous molecular assemblies. The maximum H₂O adsorption amounts were (**1**)•15(H₂O) and (**2**)•22(H₂O), respectively, at $P/P_0 \sim 0.95$ with $T = 298$ K. The surface-modified –OH groups formed hydrogen-bonding hydrophilic network pores to adsorb polar H₂O molecules, which thermally activated dynamics was confirmed in the dielectric enhancement in the low frequency and protonic conductivity. The larger hydrophilic surface of **2** than that of **1** provided relatively high adsorption abilities for the polar molecules. Three-dimensional O-H•••O hydrogen-bonding network pores of surface-modified –OH groups of **1** and **2** formed the hydrophilic extrinsic Lewis acidic network pores, where the reversible adsorption-desorption behaviors were observed for N₂, CO₂, H₂, and CH₄ gases. The BET specific surface areas of amorphous **1** and **2** were 312 and 335 m² g⁻¹, respectively, from the CO₂ adsorption isotherms at 195 K. Hydroxyl-functionalized C₆₀ derivatives can form the extrinsic hydrogen-bonding network pores to control the dielectric constants, which became the first gas sorption LMW amorphous organic materials with extrinsic O-H•••O network pores.

ASSOCIATED CONTENT

Supporting Information. TG charts, adsorption-desorption isotherm of **1** for H₂O at 298 K, CH₃OH at 288 K, C₂H₅OH at 298 K, temperature dependent PXRD patterns of **1**•6(H₂O) and **2**•15(H₂O), proton conducting property of **2**•16(H₂O), high pressure CO₂ adsorption-desorption isotherm of **2** at 278, 288, and 298 K, H₂O dependent dielectric responses of crystals **2**•*n*(H₂O), and IR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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