Bond Polarization

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# Water Entrapped inside Fullerene Cages: A Potential Probe for Evaluation of Bond Polarization

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***Abstract:*** *The concept of the bond polarization is a useful tool to understand chemical reactions and fundamental properties of compounds. However, experimental considerations are limited owing to its difficulty of reliable description. We demonstrated that geometrically isolated $H_2O$ inside the cage of fullerene $C_{60}$ is a possible probe to evaluate the polarization degree of covalent bonds $C(C_{60})$–$X$ ($X$ = heteroatom) on the $C_{60}$ cage. The $^1H$ NMR relaxation times of entrapped $H_2O$ have been systematically measured at variable temperatures for $H_2O@C_{60}X$ ($X = CR_2$, NR, O, and $O_2$). The results followed in the order of electronegativities of C (2.55), N (3.04), and O (3.44), indicating that entrapped $H_2O$ can sensitively respond to the degree of the bond polarization.*

Chemical reactions and their mechanisms are usually considered in terms of polarity of reagents and solvents as well as electro- or nucleophilicity of substrates.[1,2] Today, we can roughly understand such kind of properties (that is, electronic structure of a molecule) according to a conception of the bond polarization which is recognized as an axis of classical organic chemistry. The bond polarization has been so far understood from the view point of electronegativity (see below). In 1811, the concept was first introduced by Berzelius,[3] and a chemical scale of electronegativity $\chi$ was proposed on the basis of the bond valence theory by Pauling in 1932 (original definition of electronegativity: the power of an atom in a molecule to attract electrons to itself).[4] Soon after, Ingold built a conceptual scale of electrophilicity $\omega$ to describe electro- or nucleophile based on the valence electron theory in 1934.[5] These two parameters are closely related to each other by a simple equation: $\omega = \chi^2/(2\eta)$, where $\eta$ is the hardness of the system.[2]

Unfortunately, the electronegativity is not physically observable and cannot be determined experimentally. Thus, the correlation with other physicochemical parameters has been investigated over the years.[4,6,7] The evaluation of the bond polarization in the gas phase mainly depends on theoretical calculations using the density functional theory (DFT),[8] conceptual density functional theory (CDFT),[9] or bond polarization theory (BPT).[10] In solid and liquid phases, bond lengths, NMR chemical shifts, IR absorbance, and binding energies (X-ray photoelectron spectroscopy, XPS) have been used as convenient parameters even in cases where the influences from the packing force, molecular interactions, surrounding electronic structures, and steric effects are not negligible.[11]

Herein, we propose a reliable experimental method to evaluate the polarization degree of covalent bonds, $C(C_{60})$–X (X = heteroatom), which were introduced on the cage of $H_2O@C_{60}$. We expected that the polarization of the $C(C_{60})$–X bonds on the $C_{60}$ cage would influence the electrostatic environment inside the cage, which leads to restriction of the rotational motion of entrapped $H_2O$; this would be a detectable changes in $^1H$ relaxation times as an observable (Figure 1). Recently, we reported macroscopic-scale syntheses of endohedral aza[60]fullerenes $H_2@RC_{59}N$ and $H_2O@RC_{59}N$ ($R$ = 2-oxopropyl or azafullerenyl) and revealed the existence of the remarkable positive potential on the back side of the nitrogen atom according to an NMR study of entrapped $H_2$ and $H_2O$.[12] By applying the method, we investigated the nuclear magnetic relaxation of $H_2O@C_{60}X$ as a potential probe to evaluate the polarization degree of the $C(C_{60})$–X bonds.

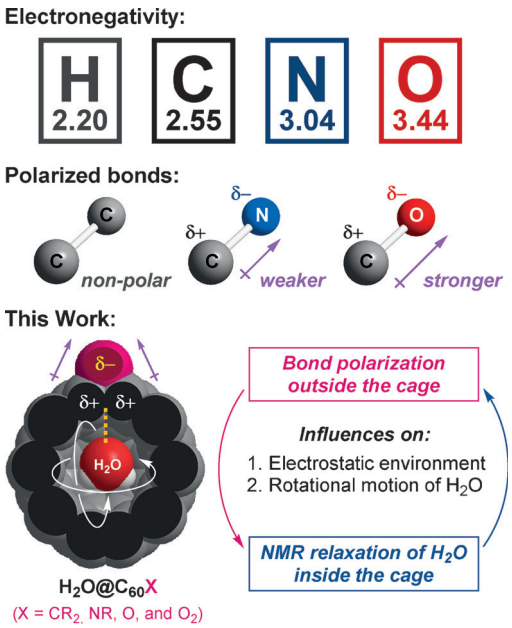


***Figure 1.*** Selected electronegativities in the Pauling's scale and the concept of an experimental method to evaluate the polarization degree of covalent bonds.

For this purpose, we made a choice of model compounds bearing the $C(C_{60})$–X bonds on the $C_{60}$ cage (that is, $C_{60}CR_2$,

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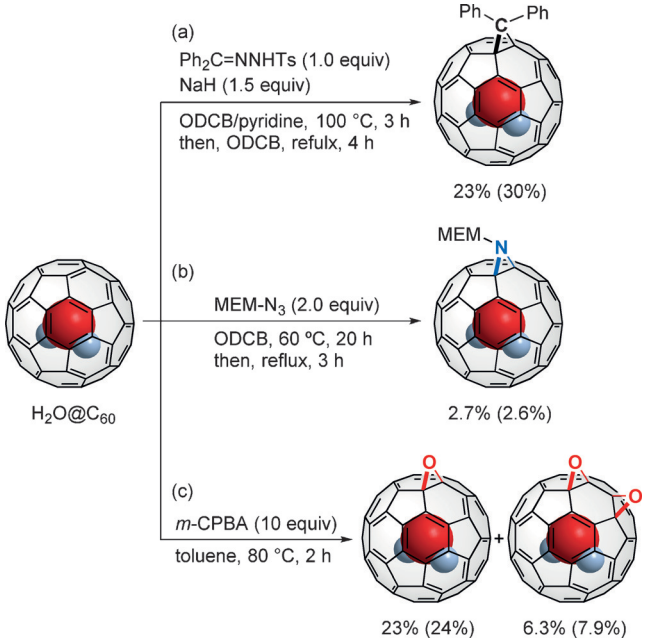
$C_{60}NR$, and $C_{60}O_n$). Note that entrapped $H_2O$ inside the $C_{60}X$ cage is geometrically isolated from outside environment. We synthesized $C_{60}CR_2$,[13] $C_{60}NR$,[14] $C_{60}O$,[15] and $C_{60}O_2$[15] from empty $C_{60}$ according to reported methods. Endohedral derivatives $H_2O@C_{60}X$ were also synthesized in a similar manner using $H_2O@C_{60}$ (100% encapsulation), which was prepared in six steps from $C_{60}$[16] using the molecular surgery method.[17] The [6,6]isomer of $H_2O@C_{60}CR_2$ (R = phenyl) was synthesized from $H_2O@C_{60}$ in 23% yield by 1,3-dipolar cycloaddition of diphenyldiazomethane generated in situ and subsequent thermal isomerization (Scheme 1a). Aziridi-

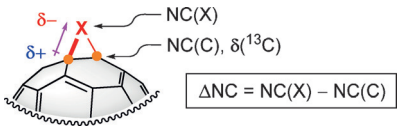



***Scheme 1.*** Synthesis of $H_2O@C_{60}X$ and $C_{60}X$ ($CR_2$, NR, O, and $O_2$). The yields in parentheses are results of empty $C_{60}$ used as a starting material.

nofullerene $H_2O@C_{60}NR$ ($R$ = 2-methoxyethoxymethyl (abbreviated as MEM)) was obtained in 2.7% yield by 1,3-dipolar cycloaddition of MEM-$N_3$ to $H_2O@C_{60}$ (Scheme 1b). Oxidation of $H_2O@C_{60}$ by an excessive amount of *m*-chloroperoxybenzoic acid (*m*-CPBA) gave fullerene epoxides $H_2O@C_{60}O$ and $H_2O@C_{60}O_2$ in 23 and 6.3% yields, respectively (Scheme 1c).

The NMR chemical shifts are generally governed by both electronic density (electronic effects) and magnetic current density (shielding effects).[11l–m] The $^{13}C$ chemical shifts $\delta(^{13}C)$ of the $C(C_{60})$–X bonds for empty $C_{60}CR_2$, $C_{60}NR$, and $C_{60}O$ were summarized in Table 1 as well as natural charges (NC) calculated using natural population analysis (NPA)[18] at the M06-2X/6-31G(d,p) level of theory.[19] The NC values allow us to know the electron distribution of the atomic charge based on occupancies of orthonormal natural atomic orbitals (NAO) of constituent atoms. We defined the ΔNC values which were obtained by subtracting the NC(C) values from the NC(X) values. The ΔNC values suggest the stronger polarization of the $C(C_{60})$–O bond (ΔNC = −0.738) relative

***Table 1:*** Natural charges (NC) calculated using the NPA method at the M06-2X/6-31G(d,p) level of theory and $^{13}C$ NMR chemical shifts $\delta(^{13}C)$ of the $C(C_{60})$-X bonds.




| Compound | NC(X) | NC(C) | ΔNC | δ [ppm] |
|---|---|---|---|---|
| $C_{60}CR_2$ (R = Ph) | −0.034 | −0.026 | −0.008 | 78.64[a] |
| $C_{60}NR$ (R = MEM) | −0.442 | +0.133 | −0.574 | 83.35[a] |
| $C_{60}O$ | −0.476 | +0.262 | −0.738 | 89.77[b] |

[a] Measured in ODCB-$d_4$. [b] Measured in $CS_2$/$CDCl_3$ (1:1).

to the $C(C_{60})$–N bond (ΔNC = −0.574), whereas the $C(C_{60})$–C bond has a negligible effect of polarization (ΔNC = −0.008). There exists a linear correlation between the ΔNC values and $\delta(^{13}C)$, implying the existence of the polarization of the $C(C_{60})$–X bonds, which was also supported by the temperature dependence of $^1H$ chemical shifts of entrapped $H_2O$ (Supporting Information, Figures S25, S26 and Table S1).

To obtain further insights into the degree of bond polarization and its effect on the electrostatic environment surrounding $sp^3$-C atoms of the $C(C_{60})$–X bonds, electrostatic potentials were calculated for $C_{60}CPh_2$, $C_{60}$N-MEM, $C_{60}O$, and $C_{60}O_2$ at the MP2/6-31G(d,p)//M06-2X/6-31G(d,p) level of theory (Figure 2). The partial positive charge is suggested to be located inside the $C_{60}$ cage. The differences were indicated by the more intense positive potential charge (blue spot) on the back side of the $C(C_{60})$–X bonds attached outside the cage, in ascending order of electronegativities of C, N, and

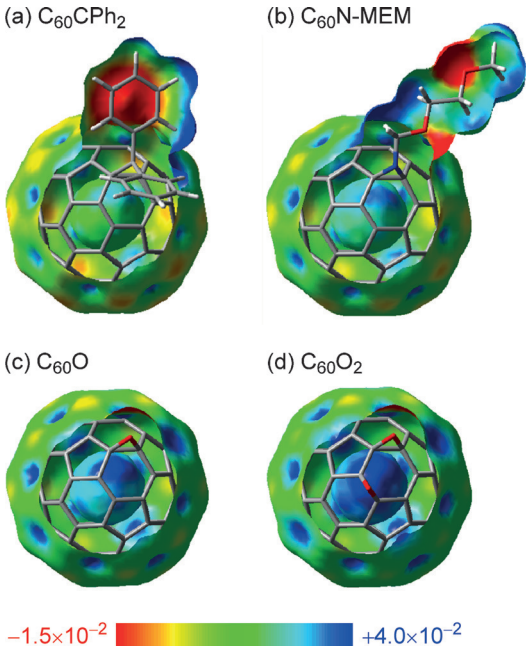



***Figure 2.*** Electrostatic potentials calculated at the MP2/6-31G(d,p)//M06-2X/6-31G(d,p) level of theory: a) $C_{60}CPh_2$, b) $C_{60}$N-MEM, c) $C_{60}O$, and d) $C_{60}O_2$.

O. We expected that this electrostatic influence on inner potentials is magnetically detectable by using entrapped $H_2O$ as a probe.

The 10 mM solutions of $H_2O@C_{60}X$ in ODCB-$d_4$ were prepared for measurements of relaxation times. Only for $H_2O@C_{60}CR_2$, a saturated solution (1.1 mM) was used due to its poor solubility in ODCB-$d_4$. Any oxygen present in the ODCB-$d_4$ solution was thoroughly removed by bubbling with argon gas and then pumping. To avoid the contamination of oxygen, the dry argon gas was introduced over the sample solution in the NMR tube (internal diameter, 5 mm). All measurements were conducted at a field strength of 500 MHz over temperatures between 260 and 360 K in each interval of 20 K. The temperature of the sample solution was kept constant within an error value of 0.1 K. The inversion recovery method and the CPMG method were applied to measure spin–lattice relaxation time $T_1$ and spin–spin relaxation time $T_2$, respectively. Prior to the measurements of relaxation times $T_1$ and $T_2$, the widths of 90° pulse were determined at each temperature (10.1–10.4 μs for $H_2O@C_{60}CR_2$, 9.85–10.1 μs for $H_2O@C_{60}NR$, 9.90–10.3 μs for $H_2O@C_{60}O$, and 9.88–10.2 μs for $H_2O@C_{60}O_2$). The relaxation times were obtained from the average of at least two measurements with measuring error less than 3%. The relaxation times for the reference compounds, $H_2O@C_{60}$ and $H_2O@C_{59}N$ dimers, were picked up from our recent results.[12b]

As shown in Figure 3 (Supporting Information, Figures S27, S28 and Table S3), spin–lattice relaxation times $T_1$ for $H_2O@C_{60}CR_2$, $H_2O@C_{60}NR$, and $H_2O@C_{60}O$ lied between the values of $H_2O@C_{60}$ and $H_2O@C_{59}N$ dimers. In accordance with the degree of the bond polarization, the relaxation times $T_1$ became longer in the order of $H_2O@C_{60}CR_2$, $H_2O@C_{60}NR$, and $H_2O@C_{60}O$ (Figure 3a). In particular for $H_2O@C_{60}O_2$ containing four $C(C_{60})$–O bonds, the relaxation times $T_1$ exceed the values for $H_2O@C_{59}N$ dimers.

For common small molecules in solution, the spin–spin relaxation time $T_2$ is known to coincide with the value of $T_1$.[20] Whereas $H_2O@C_{60}$ followed the typical trend, the difference between $T_1$ and $T_2$ values for $H_2O@C_{59}N$ dimers became larger with decreasing temperature (Supporting Information, Figure S28). As mentioned previously,[12b] the attractive electrostatic interaction between entrapped $H_2O$ and the nitrogen atom on the $C_{59}N$ cage should restrict the rotational motion of entrapped $H_2O$ and reduce the contribution of the spin-rotation mechanism for $T_2$ relaxation, resulting in the larger gap between $T_1$ and $T_2$ values at lower temperatures. This gap should be affected by dynamic behavior of entrapped $H_2O$ and become larger in order by $C_{60}CR_2$, $C_{60}NR$, $C_{60}O$, and $C_{60}O_2$ (Figure 3c–f). We also found a positive correlation between $|\Delta NC|$ values and the $T_1$ values at 300 K for $H_2O@C_{60}CR_2$, $H_2O@C_{60}NR$, and $H_2O@C_{60}O$ (Figure 3b), suggesting that entrapped $H_2O$ is a possible probe on the degree of the bond polarization.

The theoretical calculations at the M06-2X/6-31G(d,p) level of theory provided two types of conformers of $H_2O@C_{60}X$ having different orientations of entrapped $H_2O$ (Table 2; Supporting Information, Figure S33). The most stable conformer **I** has a structure where the oxygen atom of entrapped $H_2O$ is attracted by the positive potential and

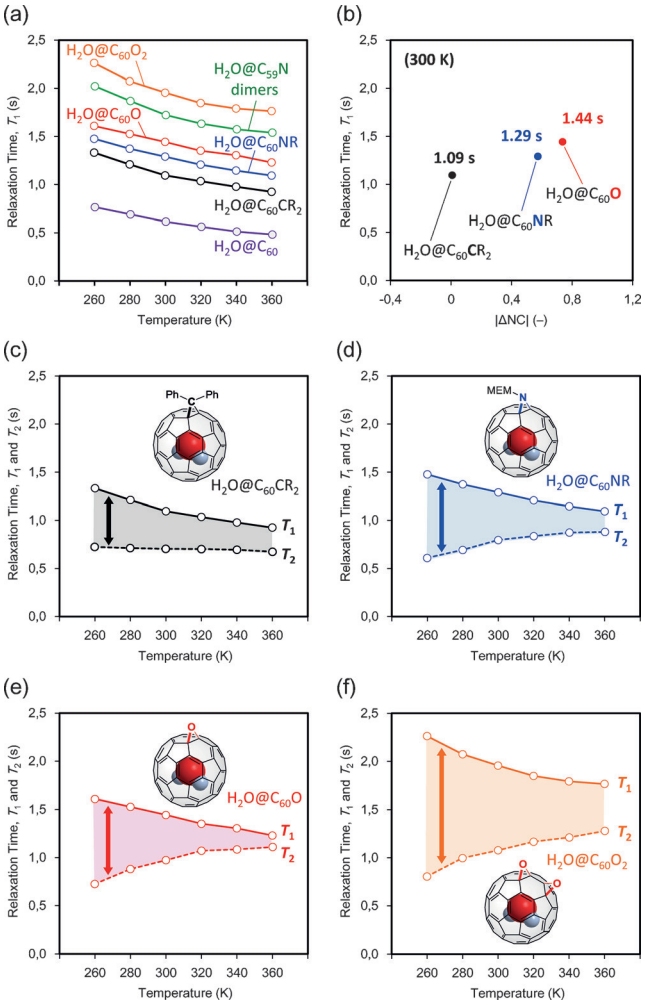
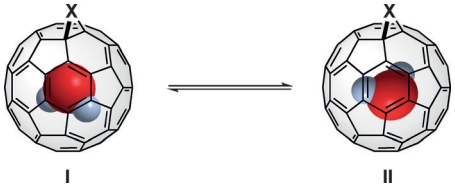



***Figure 3.*** Temperature dependence of relaxation times $T_1$ and $T_2$ of entrapped $H_2O$ (500 MHz, ODCB-$d_4$, 260–360 K), a) graphical overview of $T_1$, b) $T_1$ (300 K) plotted against $|\Delta NC|$ values, c) $H_2O@C_{60}CR_2$, d) $H_2O@C_{60}NR$, e) $H_2O@C_{60}O$, and f) $H_2O@C_{60}O_2$. The data for $H_2O@C_{60}$ and $H_2O@C_{59}N$ dimers were referenced from our recent report.[12b]

***Table 2:*** Computational results of energy differences between two types of conformations, calculated at the M06-2X/6-31G(d,p) level of theory (298 K).




I II

| Compound | $\Delta E$[a] | $\Delta H$[a] | $\Delta G$[a] | I:II[b] |
|---|---|---|---|---|
| $H_2O@C_{60}CH_2$ | −0.14 | +0.02 | −0.08 | 54:46 |
| $H_2O@C_{60}NH$ | −0.67 | −0.75 | −2.84 | 99:1 |
| $H_2O@C_{60}O$ | −0.59 | −0.82 | −2.11 | 97:3 |
| $H_2O@C_{60}O_2$ | −1.21 | −1.42 | −2.08 | 97:3 |

[a] Units in kcal mol$^{-1}$ (at 298 K), $\Delta E = E(\mathbf{I}) - E(\mathbf{II})$, $\Delta H = H(\mathbf{I}) - H(\mathbf{II})$, $\Delta G = G(\mathbf{I}) - G(\mathbf{II})$. [b] Calculated using the values of $\Delta G$.

faces on the back side of the $C(C_{60})$–X bonds. The entrapped $H_2O$ in metastable conformer **II** adopts an opposite orienta-

tion. From the difference in the Gibbs free energies, we calculated the ratio of conformers **I** and **II** under the thermal equilibrium at 298 K. The results exhibited that contribution of conformer **I** except for $H_2O@C_{60}CH_2$ is significantly dominant and should restrict the rotational motion of entrapped $H_2O$ via electrostatic interaction, which causes larger $T_1$ values and $T_1$–$T_2$ gap (Figure 3). As clearly depicted in Figure 3b, this method is quite satisfactory to evaluate the degree of the bond polarization and the electrostatic environment near polarized bonds.

In summary, we experimentally demonstrated that the geometrically isolated $H_2O$ molecule inside the $C_{60}$ cage works as a good indicator to describe the polarization degree of the $C(C_{60})$–X bonds on the $C_{60}$ cage. The existence of the polarization of the $C(C_{60})$–X bonds was confirmed by the $^{13}C$ chemical shifts of $sp^3$-$C(C_{60})$ atoms and temperature dependence of $^1H$ chemical shifts of entrapped $H_2O$. The $^1H$ NMR relaxation times $T_1$ and $T_2$ of $H_2O@C_{60}X$ (X = $CR_2$, NR, O, and $O_2$) were found to be followed in order by the polarization degree: $C(C_{60})$–C < $C(C_{60})$–N < $C(C_{60})$–O, giving a positive correlation between the $T_1$ values and $|\Delta NC|$ values.[21]

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[21] CCDC 1494947 and 1494948 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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