Structure of [60]fullerene with a mobile lithium cation inside

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The structure of crystalline [60]fullerene with a lithium cation inside (Li+@C60) was determined by synchrotron radiation X-ray diffraction measurements to understand the electrostatic and thermal properties of the encapsulated Li+ cation. Although the C60 cages show severe orientation disorder in [Li+@C60](TFPB−)·C4H10O and [Li+@C60](TFSI−)·CH2Cl2, the Li+ cations are rather ordered at specific positions by electrostatic interactions with coordinated anions outside the C60 cage. The Li+@C60 molecules in [Li+-Li+]·(ClO4−)2 with a rock-salt-type cubic structure are fully disordered with almost uniform spherical shell charge densities even at 100 K by octahedral coordination of ClO4− tetrahedra and show no orientation ordering, unlike [Li+@C60](PF6−) and pristine C60. Single-bonded (Li+@C60)2 dimers in [Li+@C60]·(NiOEP)·CH2Cl2 are thermally stable even at 400 K and form Li+-C bonds which are shorter than Li+-C bonds in [Li+@C60](PF6−) and suppress the rotational motion of the Li+ cations.

1. Introduction

Hollow spherical carbon molecules called fullerenes or buckyballs with a molecular formula of C2n (n ≥ 30) can contain various atoms and molecules [1,2]. Endohedral fullerenes containing...
atoms and molecules with magnetic and electric moments have the potential to be used for molecular devices such as quantum bits [3,4], magnetic resonance imaging agents [5,6] and molecular switches [7,8]. Fullerene C_{60} with a soccer-ball shape of 1 nm diameter is the most abundant fullerene in soot obtained by arc discharge of graphite electrodes and is valuable in applications such as solar cells [9,10]. Endohedral C_{60} with a lithium cation inside (Li^+@C_{60}) is efficiently obtained by lithium plasma bombardment with C_{60} vapour onto a target plate and is commercially available from Idea International Co., Ltd. [11–13]. It has been reported that Li^+@C_{60} shows outstanding electron-accepting properties for applications such as photoelectrochemical solar cells [14–16] and non-volatile organic transistor-based memories [17].

Li^+@C_{60} forms crystalline salts with anions such as SbCl$_6^-$ and PF$_6^-$ [11,18]. The PF$_6^-$ salt, [Li^+@C$_{60}$](PF$_6^-$), has a rock-salt-type cubic structure and shows a fast response to an alternating electric field by free rotational motion of the Li$^+$ cation on a shell with a radius of 1.5 Å inside the C$_{60}$ cage [18–20]. The free rotational motion of the Li$^+$ cation is suppressed so that it is localized at two off-centre equivalent positions on the threefold inversion axis of the cubic crystal below 100 K. The simultaneous occupation of the two positions at low temperature is attributed to a quantum tunnelling of the Li$^+$ cation between the two positions with an interval of 2.7 Å. The tunnelling motion is also hindered below $T_C=24$ K with an abrupt decrease in the dielectric permittivity by antiferroelectric interactions among local electric dipole moments formed between the Li$^+$ cations inside and the PF$_6^-$ anions outside the C$_{60}$ cages. The tunnelling motion and intermolecular interaction of the Li$^+$ cation suggest that Li$^+@C_{60}$ has the potential to be used as a quantum bit in quantum computers using electric dipole moments.

The position and motion of a Li$^+$ cation inside C$_{60}$ are significantly affected by the coordinated anions and molecules outside the C$_{60}$. For instance, the Li$^+$ cation in the SbCl$_6^-$ salt is localized at two adjoining off-centre positions at 370 K by asymmetric coordination of SbCl$_6^-$ anions around an Li$^+@C_{60}$ molecule [11]. Such anion exchange effects should be investigated in more depth to understand the electrostatic responses of the encapsulated Li$^+$ cations. Crystals of [Li$^+@C_{60}$](PF$_6^-$), [Li$^+@C_{60}$](SbCl$_6^-$) and [Li$^+@C_{60}$](TFPB$^-$) (TFPB, tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) were previously obtained and structurally characterized [11,18,21]. Further structural study of [Li$^+@C_{60}$](TFPB$^-$) is required, because the position and motion of the Li$^+$ cation have not been revealed in the previous structural analysis [21]. The anions of the previously obtained crystals are all non-polar. Li$^+@C_{60}$ crystals combined with polar anions such as TFSI$^-$ (TFSI, bis(trifluoromethylsulfonylimide) should also be obtained and structurally characterized. PF$_6^-$ and SbCl$_6^-$ are small octahedral anions, whereas TFPB$^-$ is a large tetrahedral anion. It is worthwhile obtaining and investigating Li$^+@C_{60}$ crystals combined with small tetrahedral anions such as ClO$_4^-$.

A crystal of dimerized Li$^+@C_{60}$ without anions was also obtained by electrochemical reduction [22]. The crystal is different from other dimerized endohedral metallofullerenes crystals that consist of negatively charged endohedral metallofullerenes and positively charged donor molecules [23,24]. The Li$^+$ cation in the dimerized Li$^+@C_{60}$ is localized near the carbon atom that is nearest to the carbon atom forming an inter-fullerene single C–C bond at 100 K. Temperature dependence of the position and motion of the localized Li$^+$ cation in the dimerized Li$^+@C_{60}$ would provide us with essential information about the thermal stability of the (Li$^+@C_{60}$)$_2$ dimer and the Li$^+-$C bond.

To understand the electrostatic and thermal properties of the mobile Li$^+$ cation inside C$_{60}$, we investigated the effects of the coordination structure and temperature on the position and motion of the encapsulated Li$^+$ cations in Li$^+@C_{60}$ crystals by synchrotron radiation (SR) X-ray structure analysis in this study.

2. Material and methods

We performed the X-ray crystal structure analyses of [Li$^+@C_{60}$](TFPB$^-$), [Li$^+@C_{60}$](TFSI$^-$), [Li$^+@C_{60}$](ClO$_4^-$) and [Li$^+@C_{60}$]$^-$ (NiOEP) (OEP, octaethylpolyphyrine). The TFPB$^-$, TFSI$^-$ and ClO$_4^-$ salts were obtained by anion exchange of [Li$^+@C_{60}$](PF$_6^-$) [21]. Single crystals of the TFPB$^-$ and TFSI$^-$ salts and powder crystals of the ClO$_4^-$ salt were obtained by vapour diffusion from solutions. The crystal structure of [Li$^+@C_{60}$](TFPB$^-$) without solvent molecules at 123 K has already been reported [21]. A single crystal of [Li$^+@C_{60}$](TFPB$^-$) containing diethyl ether solvent molecules was obtained in this study. Single crystals of [Li$^+@C_{60}$]$^-$ (NiOEP) were obtained by electrochemical reduction in [Li$^+@C_{60}$](TFSI$^-$) solution in the presence of NiOEP [22]. The crystal structure of [Li$^+@C_{60}$]$^-$ (NiOEP) containing dichloromethane solvent molecules at 100 and 250 K has already been reported [22]. We report the crystal structure of [Li$^+@C_{60}$]$^-$ (NiOEP) at 400 K and discuss the temperature dependence of the crystal structure in this study. The SR X-ray diffraction (XRD) measurements were performed
Table 1. Experimental conditions and crystallographic data. The reliable factors based on absolute structure factors (R) and the weighted reliable factors based on squared structure factors (Rwp) are given for the single-crystal structure refinements of [Li\textsuperscript{+}][C\textsubscript{60}]([TFTBP\textsuperscript{−}], [Li\textsuperscript{+}][C\textsubscript{60}][TFSI\textsuperscript{−}], [Li\textsuperscript{+}][C\textsubscript{60}][ClO\textsubscript{4}\textsuperscript{−}], [Li\textsuperscript{+}][C\textsubscript{60}][NiOEP]). The weighted profile reliable factor (Rwp) and the reliable factor based on Bragg intensities (R) are given for the Rietveld refinement of [Li\textsuperscript{+}][C\textsubscript{60}](ClO\textsubscript{4}\textsuperscript{−}).

|                  | [Li\textsuperscript{+}][C\textsubscript{60}][TFTBP\textsuperscript{−}] | [Li\textsuperscript{+}][C\textsubscript{60}][TFSI\textsuperscript{−}] | [Li\textsuperscript{+}][C\textsubscript{60}][ClO\textsubscript{4}\textsuperscript{−}] | [Li\textsuperscript{+}][C\textsubscript{60}][NiOEP] |
|------------------|---------------------------------------------------------------------|---------------------------------------------------------------------|---------------------------------------------------------------------|--------------------------------------------------|
| formula          | LiC\textsubscript{60}·C\textsubscript{2}H\textsubscript{4}BF\textsubscript{2}·C\textsubscript{4}H\textsubscript{10}OCl | LiC\textsubscript{60}·C\textsubscript{2}F\textsubscript{2}NO\textsubscript{4}·S\textsubscript{2}·C\textsubscript{3}H\textsubscript{7}Cl | LiC\textsubscript{60}·O\textsubscript{4}·Cl | LiC\textsubscript{60}·NiC\textsubscript{3}H\textsubscript{12}BF\textsubscript{2}·CH\textsubscript{2}Cl\textsubscript{2} |
| formula weight   | 1664.88                                                             | 1092.62                                                             | 827.03                                                             | 1403.93                                          |
| crystal size (mm)| 0.25 × 0.12 × 0.11                                                   | 0.30 × 0.08 × 0.04                                                  | powder                                                             | 0.25 × 0.3 × 0.03                                |
| temperature (K)  | 260                                                                 | 150                                                                | 30–450                                                            | 400                                              |
| X-ray wavelength (Å) | 0.41324                                                                | 0.70220                                                            | 0.64898                                                            | 0.41400                                          |
| crystal system   | monoclinic                                                          | orthorhombic                                                        | cubic                                                             | monoclinic                                       |
| space group      | P2\textsubscript{1}/c                                               | Pnma                                                               | Fm\textsubscript{3}m                                                | C2/m                                            |
| unit cell parameters | a = 17.1122(9) Å, b = 20.3829(12) Å, c = 19.8912(18) Å             | a = 18.963(5) Å, b = 13.892(3) Å, c = 13.964(3) Å                   | a = 14.133(1) Å, b = 2822.9(6) Å, c = 17.076(15) Å           | a = 26.679(13) Å, b = 14.969(6) Å, c = 17.06(15) Å |
|                  | V = 3678.5(15) Å, β = 105.157(5)°                                    | V = 6696.6(8) Å, β = 105.157(5)°                                   | V = 3678.5(15) Å, β = 105.157(5)°                           | V = 6696.6(8) Å, β = 105.157(5)°                |
|                  | Z = 4                                                                | 4                                                                  | 4                                                                 | 4                                                |
| no. of independent reflections | 13 115 (d > 0.80 Å)                                                   | 3684 (d > 0.78 Å)                                                  | 162 (d > 0.85 Å)                                                | 8779 (d > 0.70 Å)                                |
| no. of parameters | 1459                                                                | 433                                                                | 55                                                                | 657                                             |
| reliable factors | R = 0.125 (|F| > 4σ), Rwp = 0.036 (100 K)                              | R = 0.098 (|F| > 4σ), Rwp = 0.036 (100 K)                           | R = 0.067 (|F| > 4σ), Rwp = 0.200 (|F| > 4σ)                  | R = 0.067 (|F| > 4σ)                              |
|                  | Rw = 0.363 (|F| > 4σ), Rw = 0.312 (|F| > 4σ)                          | Rw = 0.124 (100 K)                                                  | Rw = 0.124 (100 K)                                             | Rw = 0.200 (|F| > 4σ)                           |

at beamline BL02B1 of the SPring-8 large SR facility [25]. The crystal structures were determined by using SIR [26], SHELX [27] and SP [28]. The experimental conditions and crystallographic data are summarized in Table 1 and crystallographic information files (CIFs) as the electronic supplementary material. The CIF deposition numbers at the Cambridge Crystallographic Data Centre (CCDC) are 1826722 for [Li\textsuperscript{+}][C\textsubscript{60}][TFTBP\textsuperscript{−}], 1826723 for [Li\textsuperscript{+}][C\textsubscript{60}][TFSI\textsuperscript{−}] and 1826724 for [Li\textsuperscript{+}][C\textsubscript{60}][NiOEP].

3. Results and discussion

3.1. [Li\textsuperscript{+}][C\textsubscript{60}][TFTBP\textsuperscript{−}]·C\textsubscript{4}H\textsubscript{10}O

Figure 1 shows the crystal structure of [Li\textsuperscript{+}][C\textsubscript{60}][TFTBP\textsuperscript{−}] containing diethyl ether (C\textsubscript{4}H\textsubscript{10}O) solvent molecules at 260 K. The crystal shows a structural phase transition with a non-merohedral twinning around 250 K. The crystal structure above the phase transition temperature was determined in this study. The monoclinic lattice constants (a = 17.11 Å, b = 20.38 Å, c = 19.89 Å, β = 105.16°) and molecular arrangement are rather different from those of a solvent-free crystal (a = 13.40 Å, b = 26.03 Å, c = 17.03 Å, β = 90.52°) reported in [21]. The volume of the unit cell containing four [Li\textsuperscript{+}][C\textsubscript{60}][TFTBP\textsuperscript{−}] ion pairs for the solvent-containing crystal (6697 Å\textsuperscript{3}) is larger than that for the solvent-free crystal (5939 Å\textsuperscript{3}). As a result, the coordination structures around the Li\textsuperscript{+} are different between the solvent-free and solvent-containing crystals. The C\textsubscript{60} centres are in the general positions of monoclinic structures in both crystals. The Li\textsuperscript{+} molecule in the solvent-free crystal is coordinated by six TFPB anions with an octahedral arrangement. The distance from the C\textsubscript{60} centre to the nearest central boron atom of TFTBP\textsuperscript{−} is 8.1 Å. The distance from the C\textsubscript{60} centre to the nearest C\textsubscript{60} centre is 11.4 Å. The crystal structure of the solvent-containing [Li\textsuperscript{+}][C\textsubscript{60}][TFTBP\textsuperscript{−}] consists of one-dimensional Li\textsuperscript{+} arrays and TFTBP\textsuperscript{−} arrays along the
Figure 1. Crystal structure of \([\text{Li}^+@\text{C}_{60}]\)(\text{TFPB}^-)\cdot\text{C}_4\text{H}_{10}\text{O}\) at 260 K. (a) Structure with thermal ellipsoids at the 50% probability level viewed along the c-axis. Hydrogen atoms are drawn as small spheres. Disordered structures are omitted. (b) Molecular arrangement viewed along the c-axis. (c) Molecular arrangement viewed along the b-axis. (d) Disordered structure of the C\(_{60}\) cage with the electron charge-density surface at 1.5 e/Å\(^3\) obtained by the maximum entropy method. A pentagon of the major orientation and four hexagons of the minor orientations are overlapping in the structure. (e) Structure of Li\(^+\)@C\(_{60}\) with thermal ellipsoids at the 50% probability level viewed perpendicular to a hexagon near the violet encapsulated Li\(^+\) cation.

c-axis, as shown in figure 1b,c. The distance from the C\(_{60}\) centres to the nearest central boron atom of TFPB\(^-\) is 8.7 Å. The distance from the C\(_{60}\) centre to the nearest two C\(_{60}\) centres along the c-axis is 10.0 Å. Therefore, Li\(^+\)@C\(_{60}\) to TFPB\(^-\) distances are increased and Li\(^+\)@C\(_{60}\) to Li\(^+\)@C\(_{60}\) distances are decreased by intercalation of C\(_4\)H\(_{10}\)O solvent molecules.

The differences in coordination structure around Li\(^+\)@C\(_{60}\) between the solvent-free and solvent-containing crystals affect the rotational motion of the C\(_{60}\) cages. Fullerene molecules often show rotational motion and orientation disorder in crystals. For instance, C\(_{60}\) cages in [Li\(^+\)@C\(_{60}\)](PF\(_6^-\)) and pristine C\(_{60}\) crystals show free rotational motion at high temperature [18,29]. The free rotational motions are stopped at low temperature by phase transitions at 370 K in [Li\(^+\)@C\(_{60}\)](PF\(_6^-\)) and 260 K in pristine C\(_{60}\). Although the C\(_{60}\) orientation is perfectly ordered in the low temperature [Li\(^+\)@C\(_{60}\)](PF\(_6^-\)) [18],...
orientation disorder with two molecular orientations remains in the low-temperature pristine C\textsubscript{60} [30,31]. This suggests that rotational motion of the C\textsubscript{60} cages is hindered by electrostatic interactions between the cationic Li\textsuperscript{+}@C\textsubscript{60} and coordinated anions. C\textsubscript{60} cages in the reported crystal structure of the solvent-free [Li\textsuperscript{+}@C\textsubscript{60}](TFPB\textsuperscript{−}) show no orientation disorder [21]. The electrostatic interactions between Li\textsuperscript{+}@C\textsubscript{60} and TFPB\textsuperscript{−} should be weakened by the increase in Li\textsuperscript{+}@C\textsubscript{60} to TFPB\textsuperscript{−} distances by intercalation of C\textsubscript{4}H\textsubscript{10}O solvent molecules. As a result, C\textsubscript{60} cages in the solvent-containing [Li\textsuperscript{+}@C\textsubscript{60}](TFPB\textsuperscript{−}) crystal show a severe orientation disorder with five molecular orientations, as shown in figure 1d. The site occupancies for the five C\textsubscript{60} orientations are 0.372(5), 0.253(4), 0.155(4), 0.132(3) and 0.124(4).

A weak electron charge-density peak for an Li\textsuperscript{+} cation was observed inside the disordered C\textsubscript{60} cage of the solvent-containing [Li\textsuperscript{+}@C\textsubscript{60}](TFPB\textsuperscript{−}) at 260 K. The Li\textsuperscript{+} position at (x, y, z) = (0.235, 0.758, 0.151) is close to the gravity centre at (0.228, 0.741, 0.147) for the central boron atoms of the six TFPB\textsuperscript{−} anions adjacent to the Li\textsuperscript{+}@C\textsubscript{60} with an interval of 0.13 Å, and hence, the Li\textsuperscript{+} position is electrostatically consistent with the anion arrangement. The Li\textsuperscript{+} position is beneath the centre of a hexagon of the C\textsubscript{60} with the major orientation, as shown in figure 1e. The average Li\textsuperscript{+}–C distance is 2.35(10) Å, which agrees with the value for [Li\textsuperscript{+}@C\textsubscript{60}](PF\textsubscript{6}\textsuperscript{−}) at low temperature [18,19]. Assuming that the site occupancy for the Li\textsuperscript{+} position is the same as that of the major C\textsubscript{60} orientation (0.372(5)), the isotropic atomic displacement parameter of the Li\textsuperscript{+} is refined to 0.24(3) Å\textsuperscript{2}, and the remaining fraction of the Li\textsuperscript{+} cation would occupy other positions inside the C\textsubscript{60} by a positional disorder. The Li\textsuperscript{+} position in the solvent-free [Li\textsuperscript{+}@C\textsubscript{60}](TFPB\textsuperscript{−}) has not been determined even at 123 K [21]. The Li\textsuperscript{+} cation of cubic [Li@C\textsubscript{60}](PF\textsubscript{6}\textsuperscript{−}) is freely rotating on a shell with a radius of 1.5 Å inside the C\textsubscript{60} cage above 100 K [18–20]. Therefore, the Li\textsuperscript{+} cation is partially ordered in the solvent-containing [Li\textsuperscript{+}@C\textsubscript{60}](TFPB\textsuperscript{−}) by the asymmetric coordination of TFPB\textsuperscript{−} anions and C\textsubscript{4}H\textsubscript{10}O molecules, as shown in figure 1b,c.

3.2. [Li\textsuperscript{+}@C\textsubscript{60}](TFSI\textsuperscript{−})·CH\textsubscript{2}Cl\textsubscript{2}

Figure 2 shows the crystal structure of [Li\textsuperscript{+}@C\textsubscript{60}](TFSI\textsuperscript{−}) containing dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) solvent molecules at 150 K. The crystal shows a structural phase transition with a non-merohedral twinning around 130 K. The crystal structure above the phase transition temperature was determined in this study. The TFSI\textsuperscript{−} anion and CH\textsubscript{2}Cl\textsubscript{2} molecule are polar molecules, while the TFPB\textsuperscript{−}, ClO\textsubscript{4}\textsuperscript{−}, SbCl\textsubscript{6}\textsuperscript{−} and PF\textsubscript{6}\textsuperscript{−} anions are non-polar molecules. Permanent electric dipole moments of such polar molecules should electrostatically interact with the Li\textsuperscript{+} cations inside the C\textsubscript{60} cages in crystals. However, the electric dipole moments of TFSI\textsuperscript{−} and CH\textsubscript{2}Cl\textsubscript{2} are cancelled by the antiferroelectric arrangements in the crystal structure with a non-polar space group of Pnma. If an Li\textsuperscript{+}@C\textsubscript{60} crystal containing polar anions with a polar space group was obtained, the crystal could have a macroscopic electric dipole moment and exhibit ferroelectricity due to a switching of the polar anions and motion of the Li\textsuperscript{+} cations. Ferroelectric crystals of C\textsubscript{60} encapsulating a polar molecule have been predicted theoretically [32]. Actually, a cubic crystal of C\textsubscript{60} with a polar water molecule inside (H\textsubscript{2}O@C\textsubscript{60}) shows an increase in the dielectric permittivity according to the Curie–Weiss law at low temperature, although no ferroelectric phase transition is observed down to 8 K [33].

The molecular arrangement of Li\textsuperscript{+}@C\textsubscript{60} molecules in the bc-plane shown in figure 2b is similar to that of [Li\textsuperscript{+}@C\textsubscript{60}](TFPB\textsuperscript{−})·C\textsubscript{4}H\textsubscript{10}O in the ab-plane shown in figure 1b and the face-centred molecular arrangement in [Li\textsuperscript{+}@C\textsubscript{60}](PF\textsubscript{6}\textsuperscript{−}). The lattice constants for b = 13.89 Å and c = 13.96 Å for [Li\textsuperscript{+}@C\textsubscript{60}](TFSI\textsuperscript{−})·CH\textsubscript{2}Cl\textsubscript{2} at 150 K are much smaller than a = 17.11 Å and b = 20.38 Å for [Li\textsuperscript{+}@C\textsubscript{60}](TFPB\textsuperscript{−})·C\textsubscript{4}H\textsubscript{10}O at 260 K, and comparable to the cubic lattice constant of a = 14.30 Å for [Li\textsuperscript{+}@C\textsubscript{60}](PF\textsubscript{6}\textsuperscript{−}) at 150 K. The monolayer lattice in the bc-plane of [Li\textsuperscript{+}@C\textsubscript{60}](TFSI\textsuperscript{−})·CH\textsubscript{2}Cl\textsubscript{2} is stacked along the a-axis with a shift to the c-axis. If the shift is 0, the Li\textsuperscript{+}@C\textsubscript{60} arrangement becomes similar to that in [Li\textsuperscript{+}@C\textsubscript{60}](TFPB\textsuperscript{−})·C\textsubscript{4}H\textsubscript{10}O, as shown in figure 1b,c. If the shift is c/2, the Li\textsuperscript{+}@C\textsubscript{60} arrangement becomes similar to the face-centred molecular arrangement in [Li\textsuperscript{+}@C\textsubscript{60}](PF\textsubscript{6}\textsuperscript{−}). Therefore, the molecular arrangements of [Li\textsuperscript{+}@C\textsubscript{60}](TFPB\textsuperscript{−})·C\textsubscript{4}H\textsubscript{10}O (figure 1b,c) and [Li\textsuperscript{+}@C\textsubscript{60}](TFSI\textsuperscript{−})·CH\textsubscript{2}Cl\textsubscript{2} (figure 2b,c) can be classified into deformed rock-salt-type structures.

C\textsubscript{60} cages in [Li\textsuperscript{+}@C\textsubscript{60}](TFSI\textsuperscript{−})·CH\textsubscript{2}Cl\textsubscript{2} also show a severe orientation disorder, as shown in figure 2d. The C\textsubscript{60} cage was modelled by an overlap of three partially occupied C\textsubscript{60} cages with different orientations. The site occupancies for the three C\textsubscript{60} orientations are 0.413(3), 0.413(3) and 0.174(5). The two major orientations are equivalent to the crystallographic mirror symmetry. The number of overlapping orientations is less than that in [Li\textsuperscript{+}@C\textsubscript{60}](TFPB\textsuperscript{−})·C\textsubscript{4}H\textsubscript{10}O (figure 1d). The orientation disorder of C\textsubscript{60} is strongly affected by the exchange of anion and solvent molecules and is suppressed at low temperature. Anion exchange from larger TFPB\textsuperscript{−} to smaller TFSI\textsuperscript{−} should increase the van der Waals inter-fullerene interactions and electrostatic Li\textsuperscript{+}–anion interactions. The measurement temperature of
Figure 2. Crystal structure of [Li\(^+\)@C\(_{60}\)](TFSI\(^-\))·CH\(_2\)Cl\(_2\) at the 150 K. (a) Structure with thermal ellipsoids at the 50% probability level viewed along the b-axis. Hydrogen atoms are drawn as small spheres. Disordered structures are omitted. (b) Molecular arrangement viewed along the a-axis. (c) Molecular arrangement viewed along the c-axis. (d) Disordered structure of the C\(_{60}\) cage with the electron charge-density surface at 1.7 e/Å\(^3\) obtained by the maximum entropy method. Two hexagons of the major orientations and a pentagon of the minor orientation are overlapping in the structure. (e) Structure of Li\(^+\)@C\(_{60}\) with thermal ellipsoids at the 50% probability level viewed perpendicular to a hexagon near the violet encapsulated Li\(^+\) cation.

[Li\(^+\)@C\(_{60}\)](TFSI\(^-\))·CH\(_2\)Cl\(_2\) (150 K) is also lower than that of [Li\(^+\)@C\(_{60}\)](TFPB\(^-\))·C\(_4\)H\(_{10}\)O (260 K). These are reasons for the suppression of C\(_{60}\) orientation disorder in [Li\(^+\)@C\(_{60}\)](TFSI\(^-\))·CH\(_2\)Cl\(_2\). On the other hand, C\(_{60}\) cages in the solvent-free [Li\(^+\)@C\(_{60}\)](TFPB\(^-\)) show no orientation disorder [21]. It is expected that C\(_{60}\) orientations are also ordered in solvent-free [Li\(^+\)@C\(_{60}\)](TFSI\(^-\)).

The Li\(^+\) cation in [Li\(^+\)@C\(_{60}\)](TFSI\(^-\))·CH\(_2\)Cl\(_2\) also locates beneath the centre of a hexagon of the C\(_{60}\) with the major orientation, as shown in figure 1e. The average Li\(^+\)–C distance of 2.42(7) Å is consistent with that in [Li\(^+\)@C\(_{60}\)](TFPB\(^-\))·C\(_4\)H\(_{10}\)O. The Li\(^+\) position at (0.803, 0.750, 0.040) is close to the gravity centre at (0.763, 0.750, 0.083) for central nitrogen atoms of the six TFSI\(^-\) anions adjacent to the Li\(^+\)@C\(_{60}\) with an interval of 0.98 Å, and, hence, the Li\(^+\) position is electrostatically consistent with the anion arrangement. The flat thermal ellipsoid for the Li\(^+\) cation with a site occupancy of 1.0 suggests a large librational motion of the Li\(^+\) cation. The free rotational motion and positional disorder of the Li\(^+\) cation in [Li\(^+\)@C\(_{60}\)](PF\(_6\)^-) and solvent-free and solvent-containing [Li\(^+\)@C\(_{60}\)](TFPB\(^-\)) will be suppressed by anion exchange from non-polar PF\(_6\)^- and TFPB\(^-\) anions to polar TFSI\(^-\) anions.
3.3. [Li+@C60](ClO4−)

Figure 3a,b shows the powder XRD pattern of [Li+@C60](ClO4−) at 100 K (X-ray wavelength: 0.649 Å) with a fitting result by the Rietveld refinement. A face-centred-cubic (fcc) structure model similar to the crystal structure of [Li+@C60](PF6−) above 370 K was used in the refinement. [Li+@C60](PF6−) and pristine C60 undergo a phase transition from the fcc structure (space group: Fm3m) to the low-temperature simple-cubic structure (space group: Pa3) at 370 K and 260 K, respectively [18,29]. Surprisingly, [Li+@C60](ClO4−) has an fcc structure even at 100 K. The cubic lattice constant of [Li+@C60](ClO4−) is 𝑎 = 14.13 Å at 100 K, which is smaller than that of [Li+@C60](PF6−) at 100 K (𝑎 = 14.28 Å) and larger than that of pristine C60 at 100 K (𝑎 = 14.06 Å) [18,31]. This relationship is consistent with the fact that a ClO4− anion is smaller than a PF6− anion.

Figure 3c shows the crystal structure model used in the powder pattern fitting. The space group is Fm3m. The uniform spherical C60 shell with a radius of 3.55 Å centred at 0, 0, 0 and the disordered ClO4− anion centred at 1/2, 1/2, 1/2 form a rock-salt-type cubic structure. The disordered ClO4− anion was modelled by a Cl atom at 1/2, 1/2, 1/2 and partially occupied O atoms at 1/2 ± 0.059, 1/2 ± 0.059, 1/2 ± 0.059 with a site occupancy of 1/2. The disordered structure is given by orthogonal overlap of two ClO4− tetrahedra with a Cl–O distance of 1.44 Å. The powder pattern was fitted by using the simple structure model with acceptable reliable factors (Rwp = 0.036, Rl = 0.124). However, the reliable Li+ position could not be determined due to the multi-site occupation or free rotational motion. The remaining deviations between the observed and calculated intensities in figure 3a,b are mainly due to non-uniformity of the electron charge densities on the C60 shell.
Figure 3d shows the temperature dependence of the cubic lattice constant of \([\text{Li}^+@\text{C}_{60}](\text{ClO}_4^-)\) from 30 to 450 K. No phase transition was observed in the temperature range. A ternary alkali-doped fulleride \(\text{Li}_2\text{CsC}_{60}\) also shows no phase transition and has an fcc structure from 50 to 300 K [34]. Disordered occupation of small \(\text{Li}^+\) and large \(\text{Cs}^+\) cations at tetrahedral voids at \(1/4, 1/4, 1/4\) and octahedral voids at \(1/2, 1/2, 1/2\) would hinder the orientation ordering of \(\text{C}_{60}\) at low temperature in \(\text{Li}_2\text{CsC}_{60}\). By contrast, tetrahedral \(\text{ClO}_4^-\) anions occupy the octahedral voids in \([\text{Li}^+@\text{C}_{60}](\text{ClO}_4^-)\), as shown in figure 3c. The mismatch between the molecular symmetry and the site symmetry would hinder the orientation ordering of \(\text{ClO}_4^-\) and \(\text{C}_{60}\) at low temperature in \([\text{Li}^+@\text{C}_{60}](\text{ClO}_4^-)\). \([\text{Li}^+@\text{C}_{60}](\text{PF}_6^-)\), in which octahedral \(\text{PF}_6^-\) anions occupy the octahedral voids, shows perfect orientation ordering of \(\text{C}_{60}\) below 370 K [18].

3.4. \([\text{Li}^+@\text{C}_{60}^-]\)(\text{NiOEP})\cdot\text{CH}_2\text{Cl}_2

Figure 4 shows the temperature dependence of the molecular structure of the single-bonded \((\text{Li}^+@\text{C}_{60}^-)_2\) dimer in \([\text{Li}^+@\text{C}_{60}^-]\)(\text{NiOEP})\cdot\text{CH}_2\text{Cl}_2\). The \((\text{Li}^+@\text{C}_{60}^-)_2\) dimer has a disordered structure by a ratchet-type rotation along the inter-fullerene single \(\text{C}–\text{C}\) bond with a rotation angle of about 39° above the phase transition temperature around 250 K [22]. The disordered structures at 250 and 400 K are omitted in the figure. \((\text{C}_{60}^-)_2\) dimers in complex crystals of \(\text{C}_{60}\) with donor and solvent molecules dissociate above 160–220 K [35,36]. By contrast, the \((\text{Li}^+@\text{C}_{60}^-)_2\) dimers in \([\text{Li}^+@\text{C}_{60}^-]\)(\text{NiOEP})\cdot\text{CH}_2\text{Cl}_2\) are thermally stable even at 400 K, as shown in figure 4c. It is suggested that the inter-fullerene single \(\text{C}–\text{C}\) bond is stabilized by the encapsulation of \(\text{Li}^+\) cations. Low stability of \((\text{C}_{60}^-)_2\) dimers is due to the strong repulsion of two negative charges within the dimer. The \(\text{Li}^+\) cation inside the cage which compensates this negative charge contributes essential stabilization of \((\text{Li}^+@\text{C}_{60}^-)_2\) dimers.

The encapsulated \(\text{Li}^+\) cation is localized with a site occupancy of 1.0 near the carbon atom (C2) nearest to the carbon atom (C1) forming the inter-fullerene single \(\text{C}–\text{C}\) bond (figure 4a). The \(\text{Li}^+–\text{C2}\) distance is 2.21(1), 2.31(2) and 2.36(6) Å at 100, 250 and 400 K, respectively. The value at 100 K is obviously shorter than the \(\text{Li}^+–\text{C}\) distance of 2.37(1) Å in \([\text{Li}^+@\text{C}_{60}^-]([\text{PF}_6^-])\) at 40 K [19]. It is also noted that the \(\text{Li}^+\) cation in the \((\text{Li}^+@\text{C}_{60}^-)_2\) dimer locates near the centre of a pentagon involving C2, as shown in figure 4d,e,
while the Li\(^+\) cation in \([\text{Li}^+@\text{C}_{60}]^-(\text{PF}_6^-)\) locates near the centre of the hexagons \([18,19]\). The formation of the shorter Li\(^+\)--C bond contributes to stabilization of the \((\text{Li}^+@\text{C}_{60})^-\)_2 dimer. The inter-fullerene C1--C1 distance shows almost no temperature dependence, which are 1.59(1), 1.59(1) and 1.60(1) Å at 100, 250 and 400 K, respectively.

The thermal ellipsoid of the Li\(^+\) cation is unusually large perpendicular to the radial direction from the C\(_{60}\) centre at 400 K (\textit{figure} 4c,f). The equivalent atomic displacement parameters of the Li\(^+\) cation and C2 atom are 0.8(1) and 0.077(2) Å\(^2\), respectively. The thermally induced large librational motion of the Li\(^+\) cation in the \((\text{Li}^+@\text{C}_{60})^-\)_2 dimer is basically consistent with the free rotational motion of the Li\(^+\) cation in \([\text{Li}^+@\text{C}_{60}]^-(\text{PF}_6^-)\) above 100 K. The Li\(^+\) cation bonded to the C2 atom cannot rotate freely in the \((\text{Li}^+@\text{C}_{60})^-\)_2 dimer even at 400 K.

4. Conclusion

We determined structures of cationic \((\text{Li}^+@\text{C}_{60})^-\)_2 monomers and neutral \((\text{Li}^+@\text{C}_{60})^–\)_2 dimers in crystals by SR XRD measurements to understand the electrostatic and thermal properties of the encapsulated Li\(^+\) cation. \([\text{Li}^+@\text{C}_{60}](\text{TFPB}–)_2\text{C}_8\text{H}_{12} \text{O} \text{ and} \ [\text{Li}^+@\text{C}_{60}](\text{TFSI}–)_2\text{CH}_2\text{Cl}_2\) involve severe orientation disorder of the C\(_{60}\) cage at low temperature. However, the Li\(^+\) cations are rather ordered at specific positions by electrostatic interactions from non-polar TFPB\(^–\) or polar TFSI\(^–\) anions, which asymmetrically coordinate to the C\(_{60}\) cage. \([\text{Li}^+@\text{C}_{60}](\text{ClO}_4^-)\) has a rock-salt-type cubic structure similar to the structure of \([\text{Li}^+@\text{C}_{60}]^-(\text{PF}_6^-)\). The \((\text{Li}^+@\text{C}_{60})^-\) molecules in \([\text{Li}^+@\text{C}_{60}](\text{ClO}_4^-)\) are fully disordered with almost uniform spherical shell charge densities by octahedral coordination of ClO\(_4\)\(^–\) tetrahedra even at 100 K, and show no orientation ordering or structural phase transition unlike \([\text{Li}^+@\text{C}_{60}]^-(\text{PF}_6^-)\) and pristine C\(_{60}\). Single-bonded \((\text{Li}^+@\text{C}_{60})^-\)_2 dimers in \([\text{Li}^+@\text{C}_{60}](\text{NiOEP})\)-CH\(_2\)Cl\(_2\) are stable even at 400 K, while \((\text{C}_{60})^-\)_2 dimers in a complex of C\(_{60}\) dissociate. The formation of Li\(^+\)--C bonds, which are shorter and thermally more stable than Li\(^–\)--C bonds in \([\text{Li}^+@\text{C}_{60}]^-(\text{PF}_6^-)\), stabilizes the inter-fullerene single C--C bond and suppresses the free rotational motion of the Li\(^+\) cation. The variety of structures of \((\text{Li}^+@\text{C}_{60})^-\) revealed in this study proves the controllability of the position and motion of the encapsulated Li\(^+\) cation from outside the C\(_{60}\) cage, which would be valuable in future applications of \((\text{Li}^+@\text{C}_{60})^-\) as molecular devices.

This study shows that the spherical Li\(^+\)\@C\(_{60}\) cation forms various ionic crystals with common inorganic and organic anions, and the neutral \((\text{Li}^+@\text{C}_{60})^-\) consisting of a positive Li\(^+\) core and a negative C\(_{60}\) cage forms thermally stable molecular crystals of covalently bonded \((\text{Li}^+@\text{C}_{60})^-\)_2 dimers. The results are essential and important to support the strong supratomic character of \((\text{Li}^+@\text{C}_{60})^-\).

Data accessibility. The CIFs are available as the electronic supplementary material and from the Cambridge Crystallographic Data Centre (CCDC) (www.ccdc.cam.ac.uk/structures) with deposition numbers 1826722, 1826723 and 1826724.

Authors’ contributions. S.A. carried out the SR XRD experiments and crystal structure analyses, and wrote the manuscript. K.M. carried out the crystallographic data collection and crystal structure analysis. H.U. and H.O. carried out the anion exchange and organic dissolution. Y.M. and K.K. supervised and conducted the sample preparations and electrical measurements. All authors gave final approval for publication.

Competing interests. We declare we have no competing interests.

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