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Ionic conductivity of $[Li^+@C_{60}](PF_6^-)$ in organic solvents and its electrochemical reduction to $Li^+@C_{60}^{\bullet -}$

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Hiroshi Ueno,[a] Ken Kokubo,*[a] Yuji Nakamura,[a] Kei Ohkubo,[b] Naohiko Ikuma,[a] Hiroshi Moriyama,[c] Shunichi Fukuzumi[bd] and Takumi Oshima[a]

The ionic conductivity of $[Li^+@C_{60}](PF_6^-)$ was measured in *o*-dichlorobenzene, and found to be higher than that of $TBA^+PF_6^-$. Electrochemical reduction of $[Li^+@C_{60}](PF_6^-)$ without any supporting electrolyte gave the monovalent radical anion $Li^+@C_{60}^{\bullet -}$, as confirmed by the characteristic ESR signal and NIR absorption band.

Lithium-cation-encapsulated [60]fullerene $Li^+@C_{60}$, which was first isolated as the $[Li^+@C_{60}](SbCl_6^-)$ salt, is the only known endohedral metallo[60]fullerene with 100% encapsulation ratio, and its structure has been established by single crystal X-ray analysis.[1–3] It has attracted growing attention because of its unique properties such as stronger electron acceptability than pristine C_{60} and high reactivities in photoinduced electron transfer and regioselective multihydroxylation.[4–8] The most remarkable property of the $[Li^+@C_{60}]$ salt is its high ionicity resulting from the encapsulated lithium cation. Although this ionic nature of $[Li^+@C_{60}](PF_6^-)$ is stated to be responsible for its rock-salt-type crystal structure,[2] no other details of the effects of ionicity have been reported so far.

The fullerene radical anion has been recognised as an intriguing material because of its unique electronic properties such as (super)conductivity and ferromagnetism.[9–12] In addition, the radial anion can serve as an important reaction intermediate for various unique chemical modifications of the fullerene cage.[13] Although many methods for the preparation of empty C_{60} radical anion salts have been reported,[14] studies on endohedral fullerene radical anions are relatively stagnant.

We herein report the high ionic conductivity of $[Li^+@C_{60}](PF_6^-)$ in organic solvents, which has enabled a facile electrochemical synthesis of the radical anion ($Li^+@C_{60}^{\bullet -}$) without any supporting electrolyte.

The ionic conductivity measurements were performed in *o*-dichlorobenzene (*o*-DCB) and benzonitrile (PhCN) since $[Li^+@C_{60}](PF_6^-)$ showed sufficient solubility and electrochemical stability in these solvents.† The molar conductivity Λ is defined in eqn (1), where κ is the measured conductivity at each concentration (c). The Λ values for various concentrations

$$\Lambda = \kappa/c \quad (1)$$

of $[Li^+@C_{60}](PF_6^-)$ are shown in Fig. 1 and listed in Table 1, together with those of tetra-*n*-butylammonium hexafluorophosphate ($TBA^+PF_6^-$), which is commonly used as a supporting electrolyte in organic solvents. The exponential change in Λ with $c^{1/2}$ indicated that $[Li^+@C_{60}](PF_6^-)$ itself acted as a supporting electrolyte. As pristine C_{60} showed no ionic conductivity under the same conditions, the observed conductivity was regarded as a unique feature of the ion-encapsulated fullerene. The observed

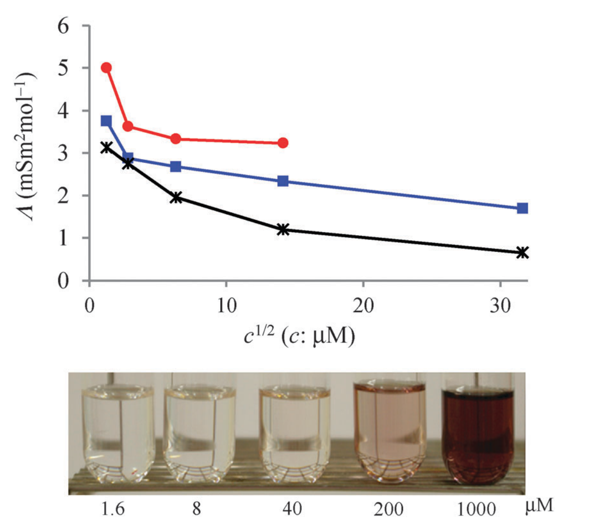

Fig. 1 Molar conductivity of $[Li^+@C_{60}](PF_6^-)$ measured in PhCN (red circles) and *o*-DCB (blue squares) solutions containing various concentrations of $[Li^+@C_{60}](PF_6^-)$ at 298 K. The black line is the result of $TBA^+PF_6^-$ measured as a reference (asterisks). The picture shows the various concentrations of $[Li^+@C_{60}](PF_6^-)$ in *o*-DCB solutions.

[a] Division of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan. E-mail: kokubo@chem.eng.osaka-u.ac.jp; Fax: +81-6-6879-4593; Tel: +81-6-6879-4592

[b] Department of Material and Life Science, Graduate School of Engineering, Osaka University, and ALCA, Japan Science and Technology (JST), Suita, Osaka 565-0871, Japan

[c] Department of Chemistry, Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan

[d] Department of Bioinspired Science, Ewha Womans University, Seoul, 120-750, Korea

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Table 1 Ionic conductivities of $[Li^+@C_{60}](PF_6^-)$ and $TBA^+PF_6^-$ measured in *o*-DCB at 298.0 K

c/μM	κ/mS m^{-1}	Λ/mS m^{-2} mol^{-1}
$[Li^+@C_{60}](PF_6^-)$		
1.6	0.006 (0.008)[a]	3.75 (5.00)[a]
8	0.023 (0.029)[a]	2.88 (3.63)[a]
40	0.107 (0.133)[a]	2.68 (3.33)[a]
200	0.466 (0.646)[a]	2.33 (3.23)[a]
1000	1.688 (—[b])[a]	1.69 (—[b])[a]
$TBA^+PF_6^-$		
1.6	0.005	3.13
8	0.022	2.75
40	0.078	1.95
200	0.238	1.19
1000	0.649	0.50
Pristine C_{60}		
Any	0.000	0.00

[a] Values in parentheses are measured in PhCN. [b] Not determined due to the solubility limitation.

ionic conductivity of $[Li^+@C_{60}](PF_6^-)$ was higher than that of $TBA^+PF_6^-$, indicating the weak interaction between the counter anion PF_6^- and encapsulated Li^+ even in such less polar solvents.

To discuss the ionizability of $[Li^+@C_{60}](PF_6^-)$, the electrostatic potential of the $[Li^+@C_{60}]$ cation and the distance between the cation and the PF_6^- anion at the most stable position were calculated by the density functional theory (DFT) at the B3LYP/6-31G* level. The result showed that the positive charge of the $[Li^+@C_{60}]$ cation was not only located on the encapsulated Li^+ but also strongly delocalised on the carbon atoms of the C_{60} cage. Because of the thermal motion of the encapsulated Li^+ in the C_{60} cage, the charge delocalization might be more dynamically significant.[2] Furthermore, the Li–P distance of $[Li^+@C_{60}](PF_6^-)$ was calculated to be 5.65 Å, which was much longer than that in $LiPF_6$ (2.63 Å). This difference implied that the positional relationship observed between Li^+ and PF_6^- in $[Li^+@C_{60}](PF_6^-)$ is unusual in common ion pairs, indicating that the electrostatic attractive force between the $[Li^+@C_{60}]$ cation and PF_6^- is weak due to the delocalised positive charge on the C_{60} cage and the distance limitation by this cage. This result is consistent with the previous report that the encapsulated Li^+ is in thermal motion at around room temperature even if the $[Li^+@C_{60}]$ cation forms an ion pair with PF_6^-.[2]

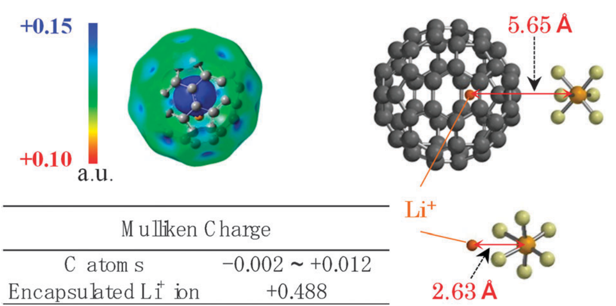

Fig. 2 Electrostatic potential of the $[Li^+@C_{60}]$ cation and the distance between encapsulated Li^+ and outer PF_6^- obtained by the theoretical calculation (B3LYP/6-31G* method), the distances between Li^+ and P for $Li^+@C_{60}$ and $LiPF_6$, and the Mulliken charges on C and Li^+ atoms of the $[Li^+@C_{60}]$ cation.

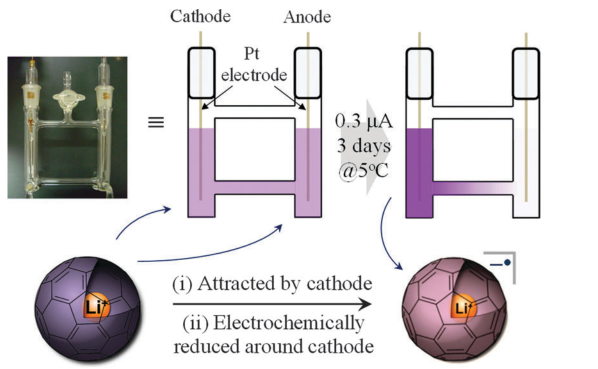

Fig. 3 Pattern diagram of the electrochemical synthesis of $Li^+@C_{60}^{\bullet-}$.

Moreover, the solvation effect is also important for the ion pair formation.[15] Because C_{60} is a π-conjugated molecule, there must be strong π–π interaction between the cage and the aromatic solvent molecules, and the solvation can stabilize the ionized $[Li^+@C_{60}]$ cation.[16] Thus, $[Li^+@C_{60}](PF_6^-)$ tends to ionize, showing ionic conductivity, to be used as a unique electrolyte which, despite its high ionicity, can be used in low-polarity aromatic solvents. Incidentally, the higher value of Λ in PhCN than that in *o*-DCB was explained by the difference in the relative permittivity (ε_r) between PhCN (ε_r = 25.2) and *o*-DCB (9.93).[17]

Based on the above results, we attempted at synthesis of the Li^+-encapsulated fullerene radical anion electrochemically without using any supporting electrolyte. All the synthetic process was carried out under N_2 atmosphere. The synthetic scheme is shown in Fig. 3. An *o*-DCB solution of $[Li^+@C_{60}](PF_6^-)$ (0.25 mg mL^{-1}, 0.29 μM) was set in an H-type cell, cooled to 278 K, and electrolyzed using a Pt electrode at a constant current (0.3 μA) for 3–4 days. The homogeneous purple solution gradually became gradated because of ion conduction by the $[Li^+@C_{60}]$ cation and PF_6^-. The cation was electrochemically reduced at the cathode, and a monovalent radical anion of Li^+-encapsulated fullerene $Li^+@C_{60}^{\bullet-}$ was selectively formed.

The generated $Li^+@C_{60}^{\bullet-}$ was characterised by UV-vis-NIR and ESR spectroscopy. ^{7}Li and ^{13}C NMR, dynamic light scattering (DLS), and ζ potential distribution measurements did not furnish meaningful signals/results, probably because of the low concentration of the target species, in addition to paramagnetic relaxation. The UV-vis-NIR spectra of the solution collected from the cathode side after 3 days are shown in Fig. 4, along with the spectrum of the starting $[Li^+@C_{60}](PF_6^-)$ solution. The absorption maximum observed at 1035 nm was clearly assignable to the monovalent radical anion of the Li^+-encapsulated C_{60}.[7,8] The generation of $Li^+@C_{60}^{\bullet-}$ was also confirmed by the ESR spectrum (Fig. 5). The observed g value (2.00058) clearly indicated that the monovalent radical anion was exclusively produced through one-electron reduction. At 77 K, the thermal motion of the encapsulated Li^+ may stop, and thus, the spectrum showed a sharp signal. The calculated spin density of $Li^+@C_{60}^{\bullet-}$ for the optimised structure indicated that the delocalised spin density is somewhat close to the encapsulated Li^+. However, because of the small hyperfine coupling constant of the Li species, the interaction between the encapsulated Li^+ and

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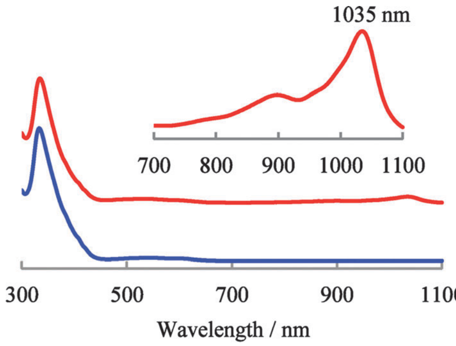

Fig. 4 UV-vis-NIR absorption spectra of the product solution by electrochemical reduction of $[Li^+@C_{60}](PF_6^-)$ (red line) and starting $[Li^+@C_{60}](PF_6^-)$ solution (blue line) in *o*-DCB. The inset shows the expanded view of the NIR region of the spectrum of the product.

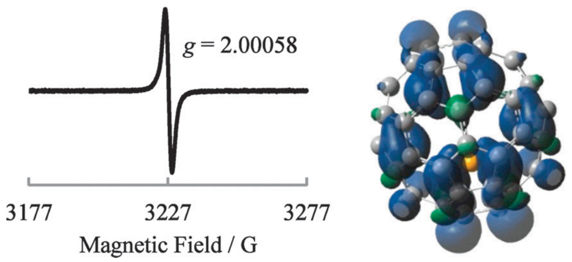

Fig. 5 ESR spectrum of the product measured at 77 K (left) and calculated spin density (B3LYP/6-31G* method) of $Li^+@C_{60}^{\bullet-}$ in the optimised structure (right).

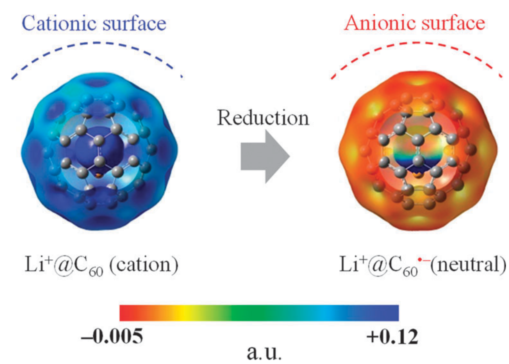

Fig. 6 Calculated electrostatic potential (B3LYP/6-31G* method) of $Li^+@C_{60}$ (left) and $Li^+@C_{60}^{\bullet-}$ (right). The left figure is different from Fig. 2 only in the potential range. $Li^+@C_{60}^{\bullet-}$ had a slightly negative potential on the C_{60} cage (∼0.022). In order to simplify the map, the range was set in +0.002 to +0.12.

the spin centre could not be evidenced from the spectrum. Although the ζ potentials of the starting $[Li^+@C_{60}](PF_6^-)$ and the resulting $Li^+@C_{60}^{\bullet-}$ could not be compared because of the above reasons, the two species could be clearly distinguished from each other on the basis of the calculated electrostatic potential (Fig. 6). This result indicated that the chemical reactivities of the two types of Li^+-encapsulated fullerenes, the external-counter-anion-type $[Li^+@C_{60}](PF_6^-)$ and the cation-encapsulated-anion-type $Li^+@C_{60}^{\bullet-}$, are much different, and hence, $Li^+@C_{60}^{\bullet-}$ is a potential nucleophilic reactant for unique chemical transformations.

In conclusion, the ionic conductivity of Li^+-encapsulated [60]fullerene $[Li^+@C_{60}](PF_6^-)$ was measured in two organic solvents, *o*-DCB and PhCN. $[Li^+@C_{60}](PF_6^-)$ showed higher ionic conductivity than $TBA^+PF_6^-$, indicating the possibility of electrochemical applications even in the absence of any supporting electrolyte. Furthermore, the Li^+-encapsulated [60]fullerene monovalent radical anion $Li^+@C_{60}^{\bullet-}$ was synthesised selectively by a very facile electrochemical method. Further studies on the use of anion-exchanged $[Li^+@C_{60}]$, application of $[Li^+@C_{60}](PF_6^-)$ as a unique electrolyte, and derivatisation *via* the anion species are now in progress, in addition to the synthesis and characterization of multivalent anions.

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† General procedure: $[Li^+@C_{60}](PF_6^-)$ was obtained from Idea International Corporation and purified by recrystallization from chlorobenzene/acetonitrile. All other reagents were commercially available and used without further purification. Ionic conductivity measurement was performed using a HORIBA ES-51 under N_2 atmosphere. UV-vis-NIR spectra were recorded on a Shimadzu UV-1800 spectrometer. The ESR spectrum was measured on a JEOL JES-FA100. A YAZAWA CS-12Z constant current regulator was used for electrochemical synthesis of $Li^+@C_{60}^{\bullet-}$.

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