

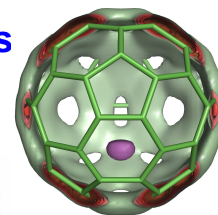
**New Products**  
**Launch June 1, 2014**

$[\text{Li}^+\text{@C}_{60}]$  is constantly being improved.

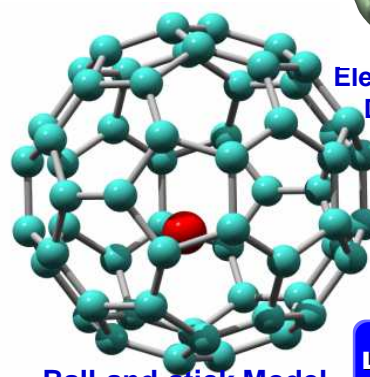
In order to respond to the user's request, we will launch **two new products** in Jun 2014.

1. Our new product,  $[\text{Li}^+\text{@C}_{60}]\text{NTf}_2^-$  salt, achieved the increase of the chemical stability, and high solubility in various solvents, compared with  $\text{PF}_6^-$  salt.
2. We offer  $[\text{Li}^+\text{@C}_{60}]\text{PF}_6^-$  single crystals having high purity, it can directly be used to the research field of material science.
3. Quality assurance is achieved by NMR spectroscopy.

A lithium cation is encapsulated in the cage



Electron Density Distribution Image



Ball-and-stick Model

LiC Fullerene

## 1. $[\text{Li}^+\text{@C}_{60}]\text{NTf}_2^-$ salt powder

Code No. 001E01

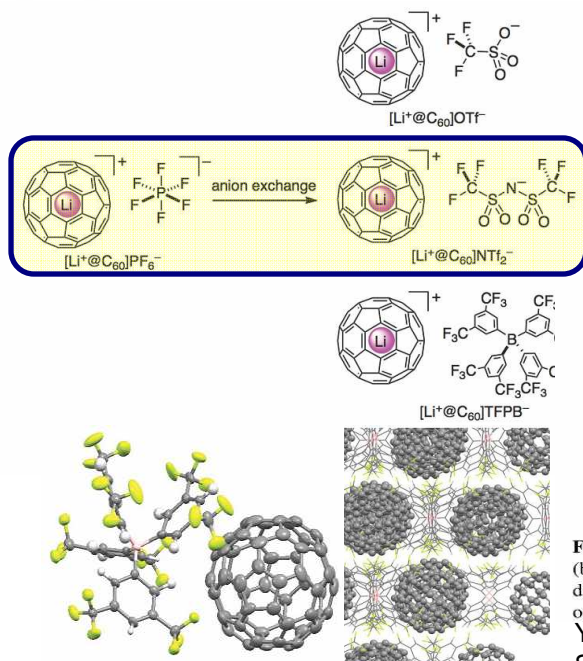


Table 1

Solubilities<sup>a</sup> of  $\text{Li}^+\text{@C}_{60}$  salts in chlorobenzene and dichloromethane

	$[\text{Li}^+\text{@C}_{60}]\text{PF}_6^-$	$[\text{Li}^+\text{@C}_{60}]\text{OTf}^-$	$[\text{Li}^+\text{@C}_{60}]\text{NTf}_2^-$	$[\text{Li}^+\text{@C}_{60}]\text{TFPB}^-$
chlorobenzene	0.16 (0.14)	1.6 (1.4)	5.1 (5.2)	2.8 (4.4)
dichloromethane	1.3 (1.1)	2.3 (2.0)	15 (15)	14 (22)

<sup>a</sup> Values expressed as molar concentration (mM) with weight per unit volume (mg/mL) shown in parentheses.

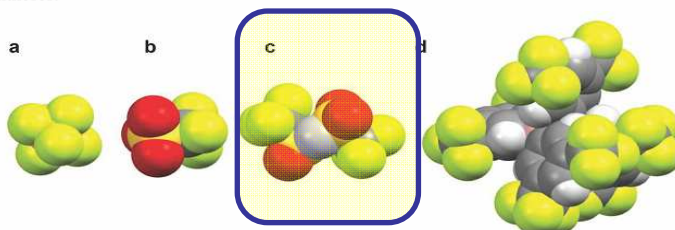


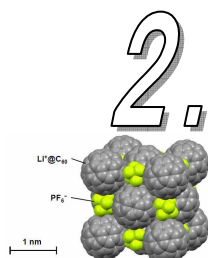
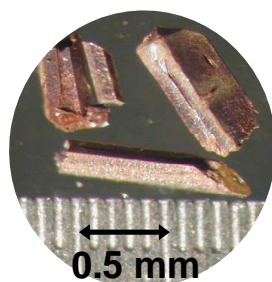
Figure 3. Space-filling model of counteranions. (a)  $\text{PF}_6^-$  in the crystal of  $[\text{Li}^+\text{@C}_{60}]\text{PF}_6^-$  (8). (b)  $\text{OTf}^-$  in the crystal of the tetrabutylammonium salt (12). (c)  $\text{NTf}_2^-$  in the crystal of the *N,N*-dimethylpyrrolidinium salt (13). (d)  $\text{TFPB}^-$  in the crystal of  $[\text{Li}^+\text{@C}_{60}]\text{TFPB}^-$  (color figure available online).

Y. Matsuo et. al., Anion Exchange of  $\text{Li}^+\text{@C}_{60}$  Salt for Improved Solubility, *Fullerenes, Nanotubes and Carbon Nanostructures*, 2014, **22** (1-3), 262-268

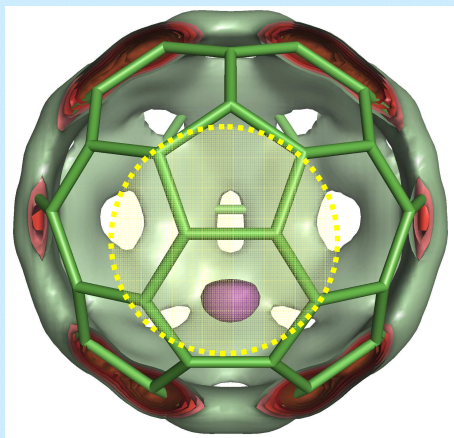
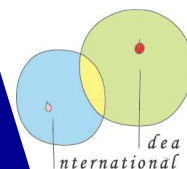
## 2. $[\text{Li}^+\text{@C}_{60}]\text{PF}_6^-$ Single Crystals

Code No.001F01

S. Aoyagi et. al., Rock-Salt-Type Crystal of Thermally Contracted  $\text{C}_{60}$  with Encapsulated Lithium Cation, *Angewandte Chemie International Edition.*, 2012, **51** (14), 3377-3381



# What's happened in C<sub>60</sub> through encapsulation of Li<sup>+</sup>-cation inside?



Distribution image of  
Electron density = 0.25e/A<sup>3</sup>

**Inside the dashed line,  
it's full vacuum space there are  
nothing except a Li<sup>+</sup>-ion flying  
around at high speed**

**C<sub>60</sub> with ideal spherical  
symmetry is rotating at high  
speed at room temperature**

1. Site-selective hydroxylation was caused by lower HOMO level of Li<sup>+</sup>@C<sub>60</sub> than that of empty C<sub>60</sub>! >>>> **single major isomer with two minor isomers (Li<sup>+</sup>@C<sub>60</sub>O<sup>-</sup>(OH)<sub>7</sub>)**

2. The DA reaction was ca. **2400 times accelerate** as compared with that of empty C<sub>60</sub>! >>>>**intramolecular catalyst**

3. The encapsulated Li<sup>+</sup> **strengthens the π back-bonding from the transition-metal center to the fullerene cage** and is attacked toward the two negatively charged carbon atoms bound to the transition metal in the solid state.

4. [Li<sup>+</sup>@C<sub>60</sub>] salts were showed enough ionic conductivity for electrochemical application! >>>>**Li<sup>+</sup>@C<sub>60</sub><sup>-</sup> (Supraatom type) was synthesized selectively by facile electrochemical method.**

5. long-lived photoinduced charge separation, enhance photoinduced electron-transfer! >>>>**enhanced photoelectrochemical performance of composite photovoltaic cells (up to 77% IPCE)**

6. Reduction of Li<sup>+</sup>-Anion coulomb interaction>> **Solvation free >>>high performance Supercapacitor, >>>molcular switching, >>>> Ultra Super Energy Strage device**

..... In progress

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S. Aoyagi et. al., Rock-Salt-Type Crystal of Thermally Contracted C<sub>60</sub> with Encapsulated Lithium Cation, *Angewandte Chemie International Edition*, 2012, **51** (14), 3377-3381  
<http://onlinelibrary.wiley.com/doi/10.1002/ange.201108551/abstract>

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<http://pubs.rsc.org/en/Content/ArticleLanding/2012/RA/c2ra21244g>

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[http://www.tandfonline.com/doi/abs/10.1080/1536383X.2013.812639#U2iPG61\\_vrY](http://www.tandfonline.com/doi/abs/10.1080/1536383X.2013.812639#U2iPG61_vrY)

E. Kwon, Solid-State Nuclear Magnetic Resonance Properties of Lithium-Cation Endohedral Metallofullerene, *94th Annual Meeting of The Chemical Society of Japan*, 2014.

**2)** K. Ohkubo et al, Strong supramolecular binding of Li<sup>+</sup>@C<sub>60</sub> with sulfonated meso-tetraphenylporphyrins and long-lived photoinduced charge separation, *Chem. Commun.*, 2012, **48** (36), 4314-4316.  
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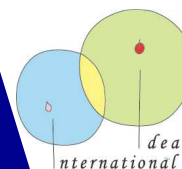
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<http://pubs.acs.org/doi/abs/10.1021/ja404830y>

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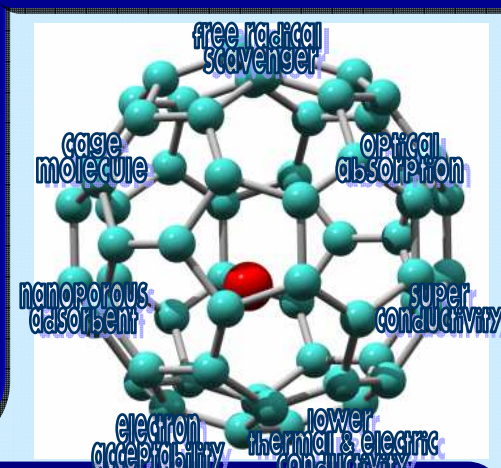
# What's happened in C<sub>60</sub> through encapsulation of Li<sup>+</sup>-cation inside?



## Structure and physical property<sup>1)</sup>

X-ray structure

NMR analysis



### Photoinduced electron transfer<sup>2)</sup>

n-type semiconductor  
molecular switch  
ferroelectric sheet  
artificial photosynthesis  
unique electrolyte

### Photovoltaic property<sup>3)</sup>

organic photovoltaic  
organic solar cell  
charge-storage device  
solar energy conversion

### Another electric property<sup>4)</sup>

ionic conductivity    superconductivity  
molecular memory  
high performance super capacitor

### Biomedical & Pharmaceutical<sup>4)</sup>

anti-influenza activity  
anti-microbial activity

K. Kokubo et. al., Synthesis of a new class of fullerene derivative Li<sup>+</sup>@C<sub>60</sub>O<sup>-</sup>(OH)<sub>7</sub> as a "cation-encapsulated anion nanoparticle", *Nanoscale*, 2013, **5**, 2317-2321.

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Y. Kawashima et al, Photoinduced Electron Transfer in Supramolecular Complex of Zinc Chlorin Carboxylate Anion with Li<sup>+</sup>@C<sub>60</sub> Affording the Long-Lived Charge-Separated State, *J. Phys. Chem. C*, 2013, **117**, 21166–21177.

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E. Kwon et. al., Supercapacitor using Lithium-Ion Endohedral Metallofullerene, *46th Fullerenes- Nanotubes- graphen General Symposium*, 2014

**3)** Y. Matsuo et. al., Covalently Chemical Modification of Lithium Ion-Encapsulated Fullerene: Synthesis and Characterization of [Li<sup>+</sup>@PCBM]PF<sub>6</sub><sup>-</sup>, *Org. Lett.*, 2012, **14** (14), 3784–3787.

<http://pubs.acs.org/doi/abs/10.1021/ol301671n>

K. Ohkubo et. al., Ion-Controlled On-Off Switch of Electron Transfer from Tetrathiafulvalene Calix[4]pyrroles to Li<sup>+</sup>@C<sub>60</sub>, *J. Am. Chem. Soc.*, 2011, **133** (40), 15938-15941.

<http://pubs.acs.org/doi/abs/10.1021/ja207588c>

K. Ohkubo et. al., Enhanced Photoinduced Electron-Transfer Reduction of Li<sup>+</sup>@C<sub>60</sub> in Comparison with C<sub>60</sub>, *J. Phys. Chem. A*, 2012, **116** (36), 8942-8948.

<http://pubs.acs.org/doi/abs/10.1021/jp3059036>

K. Ohkubo et. al., Enhanced photoelectrochemical performance of composite photovoltaic cells of Li<sup>+</sup>@C<sub>60</sub>-sulphonated porphyrin supramolecular nanoclusters, *Chem. Commun.*, 2013, **49**, 4474-4476.

<http://pubs.rsc.org/en/Content/ArticleLanding/2013/CC/C3CC41187G>

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T. Watanabe et. al., Iridium and Platinum Complexes of Li<sup>+</sup>@C<sub>60</sub>, *Organometallics*, 2014, **33** (3), 608-611.

<http://pubs.acs.org/doi/abs/10.1021/om4008899>

Y. Matsuo et. al., Efficient Diels–Alder Addition of Cyclopentadiene to Lithium Ion Encapsulated [60]Fullerene, *Org. Lett.*, 2013, **15** (17), 4466–4469. <http://pubs.acs.org/doi/abs/10.1021/ol4020046>

**4) In Progress**





	Maker Code	Product	purity <sup>*1)</sup>	Unit	Price yen
<b>New</b>	001E01	[Li <sup>+</sup> @C <sub>60</sub> ]INTf <sub>2</sub> <sup>-</sup> Salt, powder	>98%	10mg	
				20mg	
				30mg	
				40mg	
				50mg	
<b>New</b>		[Li <sup>+</sup> @C <sub>60</sub> ]OTf Salt, powder		Built-to-order manufacturing	
<b>New</b>		[Li <sup>+</sup> @C <sub>60</sub> ]TFPB <sup>-</sup> Salt, powder			
<b>New</b>	001F01	[Li <sup>+</sup> @C <sub>60</sub> ]PF <sub>6</sub> <sup>-</sup> Salt, single crystals <sup>*2)</sup>		10mg	¥350,000
	001D04	[Li <sup>+</sup> @C <sub>60</sub> ]PF <sub>6</sub> <sup>-</sup> Salt, powder	>98%	10mg	¥210,000
				20mg	¥390,000
				30mg	¥570,000
				40mg	¥747,000
				50mg	¥930,000
	001B01	[Li <sup>+</sup> @C <sub>60</sub> ]/C <sub>60</sub> (Cluster) , powder		500mg	¥250,000
				1g	¥500,000
	TS001	[Li <sup>+</sup> @C <sub>60</sub> ]/C <sub>60</sub> /Li(Cluster) , powder		500mg	¥200,000
				1g	¥400,000

\*1) Quality assurance is achieved by NMR spectroscopy.

\*2) Rod-shaped crystals of the long side about 1mm

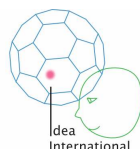
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