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**Synthesis of Neutral Li-Endohedral PCBM: An n-Dopant for Fullerene Derivatives**

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## COMMUNICATION

## Synthesis of Neutral Li-Endohedral PCBM: An n-Dopant for Fullerene Derivatives

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**Li@PCBM, the first neutral Li@C<sub>60</sub> derivative, was synthesized. The Li@PCBM exists in a monomer-dimer equilibrium in solution but as a monomer in the PCBM matrix. The fully dispersed Li@PCBM n-doped the surrounding empty PCBM, raising the Fermi level by 0.13 eV compared with the undoped PCBM film. The hybrid films were utilized as ETL for PSCs, promoted efficiency of the device.**

Significant progress has been achieved in organic photovoltaic devices, leading to dramatic improvements in performance, including both efficiency and durability. In addition to the structural design and synthesis of organic semiconductors, doping—the addition of a small amount of charge carrier—is a fascinating and therefore widely studied technology for improving their performance.<sup>1</sup> Recent pioneering studies on dopants and doping processes have demonstrated effective improvement of conductivity, carrier mobility, and Fermi level tunability, which have strongly contributed to the development of organic electronics.<sup>2</sup> However, doping has several intrinsic risks, such as the disruption of molecular order and migration of the dopant, both of which are the major drawbacks in doped organic semiconductor electronics.<sup>3</sup> In our previous study, a new doping concept, which we called supraatomic doping (Fig. 1), was

developed using Li@C<sub>60</sub> (=Li<sup>+</sup>@C<sub>60</sub><sup>•-</sup>) as a dopant for an empty C<sub>60</sub> semiconductor.<sup>4</sup> This strategy relies on the dopant having both a structure highly similar to that of the semiconductor molecule and a different number of electrons, which allows the dopants to be hybridized with the semiconductor molecules without seriously decreasing crystallinity. Although this strategy is expected to be a breakthrough in organic electronics, the design and synthesis of dopants satisfying the structural and electronic requirements seen in the Li@C<sub>60</sub>-C<sub>60</sub> pair are still limited.

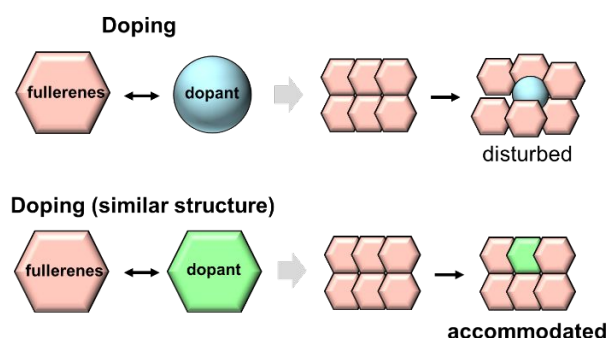


Fig. 1. Concept of this work.

Chemical functionalization of fullerenes is an attractive strategy for endowing them with various characteristic functions, and plays a significant role in fullerene-based materials science.<sup>5</sup> Numerous kinds of (endohedral metallo)fullerene derivatives have been synthesized, leading to the broad and interdisciplinary expansion of the materials. Within the entire family of fullerenes, Li@C<sub>60</sub>, structurally well-defined C<sub>60</sub>-based metal-encapsulating fullerene, is attracting a great deal of interest owing to its unique characteristic properties as well as its bulk availability.<sup>6</sup> However, no derivatives of Li@C<sub>60</sub> have been reported.

Continuing our study of endohedral fullerene materials and organic device engineering based on our supraatomic doping strategy, we focused here on phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) as the first Li@C<sub>60</sub> derivative target because it is the most studied and widely used fullerene derivative in organic electronics.<sup>7</sup> Although the generation of Li@PCBM has been

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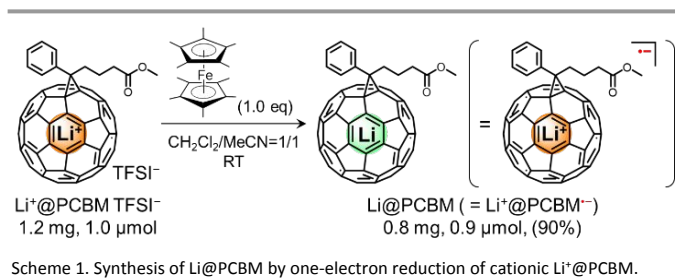
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Electronic Supplementary Information (ESI) available: [UV-vis-NIR absorption spectrum, calculated spin density, VT-ESR spectra, particle size distribution, list of Fermi level, and computational results]. See DOI: 10.1039/x0xx00000x

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confirmed in the solution phase, the material has not yet been isolated.<sup>8</sup> In this work, highly dispersible Li@PCBM, the first neutral Li@C<sub>60</sub> derivative, was synthesized by applying the previously developed selective chemical reduction method to cationic Li<sup>+</sup>@PCBM salt. The electron-donating behaviour of Li@PCBM to empty PCBM and the paramagnetic character of Li@PCBM in a PCBM matrix were observed. The results indicate that Li@PCBM can be utilized as an effective supraatomic n-dopant for an empty PCBM semiconductor.

Li@PCBM was synthesized by one-electron reduction of previously reported Li<sup>+</sup>@PCBM (Scheme 1).<sup>9</sup> Among the Li<sup>+</sup>@PCBM salts, the TFSI<sup>-</sup> (bis(trifluoromethanesulfonyl)imide) salt was selected as the starting material because of its convenience in synthesis and purification. A mixture of dichloromethane (DCM)/acetonitrile (MeCN) (1/1, v/v) was chosen as the solvent for the reduction, and decamethylferrocene (Fc\*) was used as the reducing agent. This solvent mixture can dissolve both the starting material Li<sup>+</sup>@PCBM and the reducing agent, but is a poor solvent for the target Li@PCBM. Thus, the product can be easily isolated and purified by a simple washing process. In addition, cyclic voltammetry measurements showed a reversible redox wave for the one-electron reduction of Li<sup>+</sup>@PCBM, which clearly indicated that Li@PCBM was sufficiently stable in this reaction system (Fig. S1a). Further reduction of Li@PCBM in the solvent should be avoided due to the instability of the divalent anion of the PCBM cage. The oxidation potential of Fc\* was suitable for the desired one-electron reduction of Li<sup>+</sup>@PCBM, and hence, Li@PCBM can be selectively generated in excellent yield without excessive reduction to the unstable divalent PCBM anion (Fig. S1b). By simply adding 1 equiv Fc\* to a solution of Li<sup>+</sup>@PCBM TFSI<sup>-</sup> salt, the target Li@PCBM was immediately obtained as a black solid.



The generation of Li@PCBM was confirmed by UV-vis-NIR absorption and electron spin resonance (ESR) spectroscopy. First, the solubility of the product was examined to characterize its behaviour in solution. Whereas pristine Li@C<sub>60</sub> can be dissolved in only a very limited number of organic solvents, such as ortho-dichlorobenzene and carbon disulfide, the product was highly soluble in common organic solvents, such as chlorobenzene and DCM. Here, the product was characterized in DCM. The UV-vis absorption spectrum of the product showed characteristic absorption bands at 993, 888, and 798 nm, which provided clear evidence for the generation of the PCBM monovalent radical anion (Fig. S2).<sup>10</sup> The ESR spectra of Li@PCBM solution measured at 263 K showed a signal at  $g = 2.00057$ , clearly indicating that the PCBM monovalent radical anion was

exclusively generated by selective one-electron reduction of Li<sup>+</sup>@PCBM (Fig. 2a and 2b, black line). From theoretical calculations, the spin density of Li@PCBM was somewhat close to that of the encapsulated Li<sup>+</sup>, but no interaction between the encapsulated Li<sup>+</sup> and the spin centre was observed in our experimentally obtained spectra, probably due to the small hyperfine coupling constant of Li<sup>+</sup> (Fig. S3). The ESR signal decreased with decreasing temperature, and disappeared below 173 K (Fig. 2a, red line). This was due to the dimerization of Li@PCBM via coupling of the spin centres of Li@PCBM, which has been also reported for several open-shell fullerene derivatives and endohedral metallofullerenes.<sup>11</sup> We also measured <sup>1</sup>H and <sup>7</sup>Li NMR spectra at room temperature (RT) and 193 K to explore the structural details of Li@PCBM at each temperature. While no NMR signal was observed at RT due to the paramagnetic relaxation, <sup>1</sup>H NMR spectrum exhibited signals derived from the addend with appropriate integration ratio at 193 K (Fig. S4). It should be noted that the Li@PCBM dimer should be racemic mixture (or isomers) as observed in other singly bonded fullerene dimer derivatives,<sup>12</sup> and therefore exhibited the complicated <sup>1</sup>H and <sup>7</sup>Li NMR signals. When the temperature was increased, the ESR signal appeared

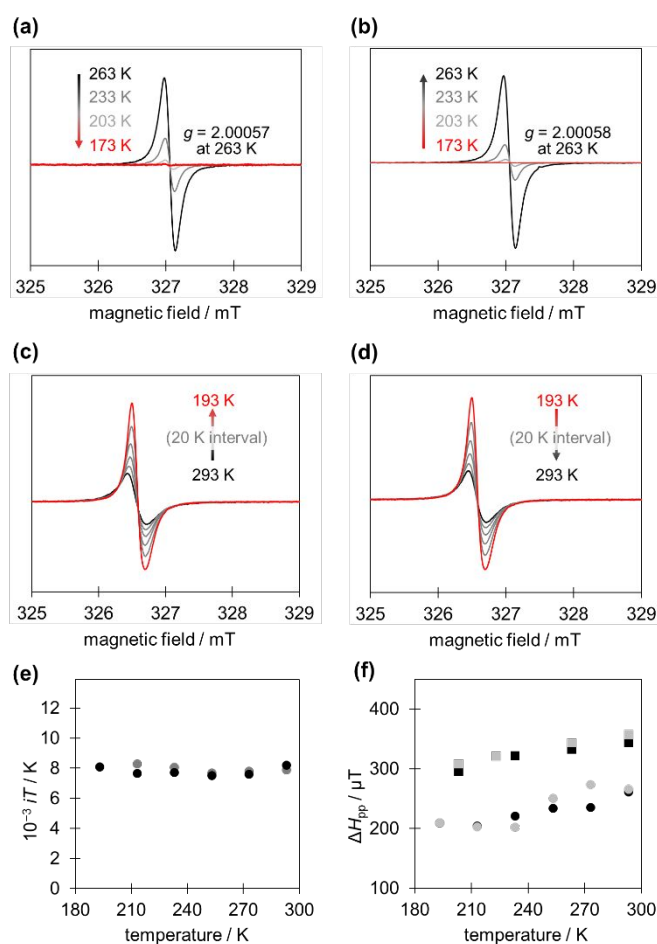


Fig. 2. (a-d) VT-ESR spectra: Measured in CD<sub>2</sub>Cl<sub>2</sub> during (a) cooling and (b) heating. 1% Li@PCBM:PCBM mixed solid during (c) cooling and (d) heating. (e)  $T$ - $I$  plots from VT-ESR spectra of a 1% Li@PCBM:PCBM mixed solid during heating (black) and cooling (gray). (f) ESR signal width ( $\Delta H_{pp}$ ) of Li@PCBM solid (square) and 1% Li@PCBM:PCBM mixed solid (circle) samples during heating (black) and cooling (gray).

again with the disappearance of NMR signals upon disassociation of the Li@PCBM dimer (Fig. 2b). These results revealed the equilibrium between Li@PCBM and (Li@PCBM)<sub>2</sub> in solution.

Interestingly, when 1 wt % Li@PCBM was diluted with non-magnetic empty PCBM, the mixed solid exhibited ESR signals at all measurement temperatures with constant intensity  $\times$  temperature ( $iT$ ) values, showing the stable paramagnetic characteristics of Li@PCBM in the PCBM matrix (Fig. 2c–2e). This result revealed that, in the solid phase, dimerization of Li@PCBM was strongly prevented by the surrounding empty PCBM. It should be noted that the powder solid of Li@PCBM also showed an ESR signal even at 173 K (Fig. S5). We ascribed this to the presence of some open-shell Li@PCBM monomer in the disordered solid-state, as seen in our previous study on Li@C<sub>60</sub> solid.<sup>6b</sup> Unfortunately, the monomer/dimer ratio in the Li@PCBM solid sample could not be determined because of an insufficient amount of the sample. However, the peak-to-peak width ( $\Delta H_{pp}$ ) of the Li@PCBM solid was clearly wider than that of the Li@PCBM/PCBM mixed solid, which is clear evidence of the segregation of Li@PCBM in the PCBM matrix (Fig. 2f).

Neutral Li@PCBM prepared by reduction of cationic Li<sup>+</sup>@PCBM has an external structure very similar to that of empty PCBM with an anionic molecular surface and an extra electron on the cage (Fig. 3). These structural and electronic features enable Li@PCBM to be utilized as an n-type dopant for a PCBM semiconductor, in the same manner as the previously developed supraatomic doping using the Li@C<sub>60</sub>:C<sub>60</sub> pair. The

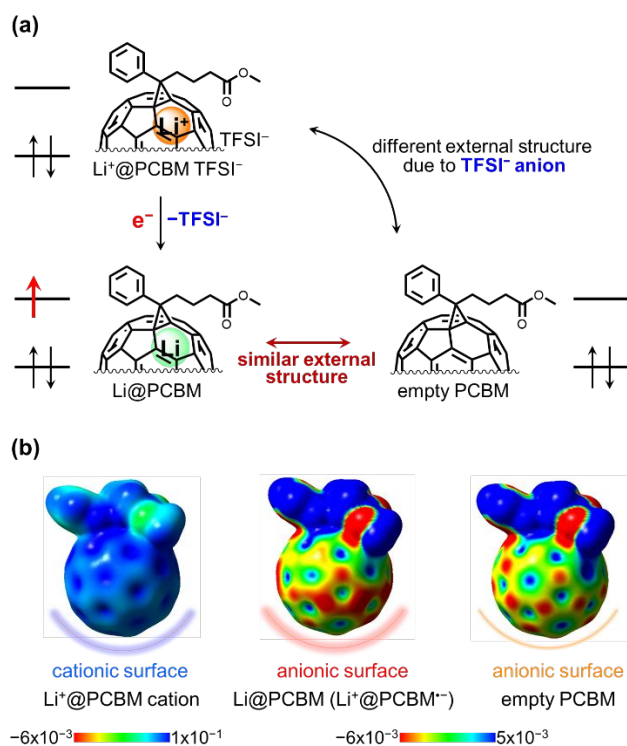


Fig. 3. (a) Illustration of structural similarity between Li@PCBM and empty PCBM. (b) Calculated electrostatic potential of Li<sup>+</sup>@PCBM cation, Li@PCBM, and empty PCBM at the M06-2x/6-31G(d) level. To simplify the map, the described potential ranges were set to  $-6 \times 10^{-3}$  to  $+1 \times 10^1$  for Li<sup>+</sup>@PCBM, and  $-6 \times 10^{-3}$  to  $+5 \times 10^{-3}$  for Li@PCBM and empty PCBM.

Li@PCBM:PCBM thin films were fabricated with dopant ratios of 0–5.0 wt % by spin-coating and their Fermi levels were measured using a Kelvin probe (Table S1). Doping with Li@PCBM raised the Fermi level of PCBM film by about 0.13 eV, which indicated that Li@PCBM acted as an n-type dopant for empty PCBM. Increasing the dopant concentration did not affect the Fermi level of the films, suggesting that the controllability of the Fermi level by doping reaches a limit at a low dopant concentration. Notably, the quality of the films was quite uniform even in the high dopant concentration range, whereas the addition of the previously reported Li@C<sub>60</sub> dopant of more than 2 wt % induced uneven Fermi level distributions in Li@C<sub>60</sub>:C<sub>60</sub> films due to the poor dispersibility of Li@C<sub>60</sub> and Li@C<sub>60</sub>-induced aggregation of empty C<sub>60</sub>.<sup>4</sup> Dynamic light scattering measurements revealed that Li@PCBM can be dispersed as single molecules in chlorobenzene in contrast to the poor solubility of Li@C<sub>60</sub> (Fig. S5a). Moreover, the addition of Li@PCBM did not induce aggregation of empty PCBM (Fig. S5b), which allowed Li@PCBM to homogeneously hybridize with empty PCBM via a facile solution process.

Considering that empty PCBM has been widely used as an electron transport material for perovskite solar cells (PSCs), inverted PSCs with a typical methylammonium lead iodide absorber were fabricated using Li@PCBM:PCBM as an electron transport layer (Fig. 4). The 1% Li@PCBM:PCBM device showed a better power conversion efficiency of 9.6% compared with a PCBM control device (5.7%), with improvements in all photovoltaic parameters ( $J_{sc}$ ,  $V_{oc}$  and FF). These results demonstrated the effectiveness of this novel doping concept, which may be a key to designing new organic semiconducting materials for both present and future device technologies.

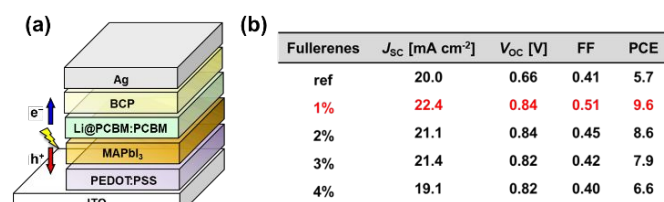


Fig. 4. (a) Schematic of the inverted PSC. BCP: bathocuproine. (b) List of photovoltaic parameters of the PSCs with 1.0% Li@PCBM-doped PCBM or PCBM as the electron transport layer.

In summary, we have successfully synthesized and isolated lithium-encapsulating PCBM (Li@PCBM), the first neutral Li@C<sub>60</sub> derivative. Despite the poor solubility of pristine Li@C<sub>60</sub>, Li@PCBM can be dissolved in common organic solvents such as chlorobenzene and DCM. VT-ESR measurements revealed the monomer-dimer equilibrium of Li@PCBM via coupling of the spin centre in solution. When Li@PCBM was dispersed in a PCBM matrix, dimerization of Li@PCBM was strongly prevented, and thus the hybrid material showed stable paramagnetic characteristics. The electron-donating behaviour of Li@PCBM to PCBM was confirmed by Fermi level measurements for a Li@PCBM-doped PCBM hybrid thin film, which clearly indicated that Li@PCBM can act as an effective n-type dopant for PCBM.

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### Conflicts of interest

There are no conflicts to declare.

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