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学位論文の概要及び要旨

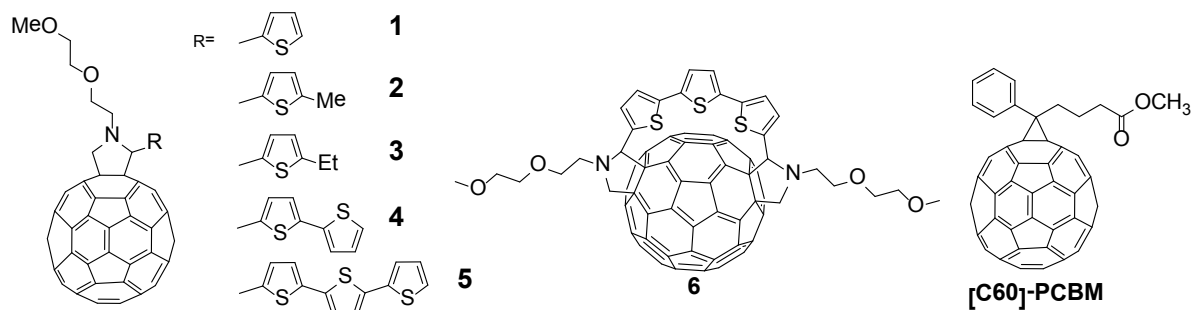
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題 目 Functional fulleropyrrolidine derivatives as acceptors
for organic photovoltaics

学位論文の概要及び要旨

The photovoltaic technology is now recognized as one of the most important ways to prevent the exhaustion of fossil fuels and global warming. The organic photovoltaics (OPV) have several advantages such as flexibility, light weight, transparency, and low cost. It is well known that the fullerene generally has a poor solubility in conventional organic solvents and this makes it difficult to prepare fullerene-based electric devices using economical techniques such as the spin-coating procedure. Therefore, the development of stable fullerene derivatives that show a high power conversion efficiency (PCE) with a sufficient affinity toward organic solvents is desired. OPV based on p-type materials blended with [6,6]-phenyl-C60-butyric acid methyl ester ([C60]-PCBM) or [6,6]-phenyl-C70-butyric acid methyl ester ([C70]-PCBM) has been used as the leading candidates in OPV in the past years. However, it has been required to design new fullerene derivatives with higher PCE that are compatible with the rapidly developed donor polymers for application in OPV.

We were fascinated by the fulleropyrrolidines from the standpoint of their stable nature under atmospheric conditions and ease of producing various types of analogues. We focused on thiophene-substituted fulleropyrrolidine derivatives and investigated the influence of the substituent groups on the photovoltaic devices performance using poly(3-hexyl thiophene) (P3HT) as the model donor polymer. Fulleropyrrolidine derivatives (**1-6**) were prepared by the reaction of N-methoxyethoxyethyl glycine and C60 fullerene in the presence of an corresponding aldehyde in chlorobenzene at 130°C for 3 h. Purification of the desired compounds was accomplished by silica-gel flash column chromatography or silica-gel thin layer chromatography; the desired mono adducts were thus obtained in acceptable yields. The photovoltaic devices were fabricated according to following process: the mixed solution of fulleropyrrolidine and P3HT in chlorobenzene was cast onto ITO or PEDOT:PSS coated ITO substrate. After drying the solvent, LiF and aluminum were deposited under ultra vacuum condition.

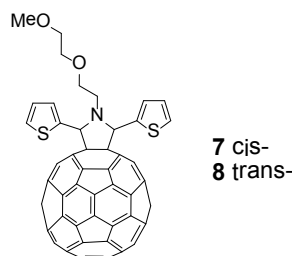


The power conversion efficiency (PCE) values were measured using a solar simulator. The PCE of the devices without PEDOT:PSS using derivatives **1-4** as acceptor molecules was higher than that of [C60]-PCBM. The Voc of these thiophene-substituted fulleropyrrolidine devices was higher than that of [C60]-PCBM, which was assumed to be due to their electron-donating property of thiophene. The bridged type fulleropyrrolidine **6** showed higher Voc than that of [C60]-PCBM, however, poor PCE was obtained due to its low Jsc and FF.

In order to seek the reason for high Voc, the cyclic voltammograms (CV) of the fullerene derivatives **5** has been carried out. The LUMO energy levels of [C60]-PCBM and **5** determined by CV are -3.71 and -3.65 eV, respectively. The LUMO level of **5** is raised by 0.06 eV in comparison with that of [C60]-PCBM. The higher LUMO level of **5** is desirable for its application as acceptor in the active layer to obtain Voc.

We also studied the effect of PEDOT:PSS layer, since it was anticipated that fulleropyrrolidine derivatives might be protonated in the presence of a Brønsted acid such as PSS. We prepared three types of solar cells using ITO electrodes: those that lacked PEDOT:PSS, those having PEDOT:PSS, and those having neutral PEDOT, and evaluated their efficiency using bithiophene substituted fulleropyrrolidine **4** as acceptor partner with P3HT. Using acidic PSS in the electrode with isomer **4** caused a significant drop of PCE, mainly due to reduced Jsc. A slight improvement of PCE was obtained when the cell was prepared by neutral PEDOT, but PCE was still lower than the devices made using an ITO electrode without PEDOT:PSS. To reveal this behavior, the study of UV-visible spectra of fulleropyrrolidine **4** with and without acids (trifluoroacetic acid (TFA) or p-toluenesulfonic acid (p-TsOH)) were conducted. The spectra of **4** with TFA and **4** with p-TsOH were both blue shifted, it is likely that protonation of the fulleropyrrolidine indeed formed to be a quarternary ammonium salt when PEDOT:PSS was used as hole transport layer and prevent from hole transport between active layer and PEDOT:PSS or between PEDOT:PSS and ITO.

In order to prevent from forming quarternary ammonium salt, one of the most effective approach is enhancement steric hindrance nearby N atom on fulleropyrrolidine. Then we designed 2,5-bis-substituted fulleropyrrolidines, and syntheses and device performance were carried out. The bis-thienyl fulleropyrrolidine was synthesized by corresponding glycine derivative and phenyl aldehyde, however, obtained product was mixture of cis- and trans- isomers. We separated these isomers using silica gel chromatography and device performances were separately carried out with and without PEDOT:PSS layer. The device without PEDOT:PSS of **7** and **8** showed the PCE of 1.91% and 2.24%, respectively. On the other hand, the device with PEDOT:PSS of **7** and **8** showed 2.04% and 2.48%, respectively. The device using 2,5-bis-thienyl fulleropyrrolidines with PEDOT:PSS layer showed higher PCEs than that of without PEDOT:PSS layer. We suppose that the result might be caused by the high steric hindrance around N atom on fulleropyrrolidine.



In summary, we have carried out the rational design of thiophene-substituted fulleropyrrolidine derivatives (**1-5**) as the acceptor partner with poly-3-hexylthiophene and established that these fulleropyrrolidines worked as good acceptor partners with P3HT. A high power conversion efficiency was obtained, superior to that of the P3HT-based devices including [C60]-PCBM under the same experimental conditions. It was also found that using an electrode that lacked PEDOT:PSS was essential to obtain good PCE for fulleropyrrolidine based solar cells. The reason for the low PCE when PEDOT:PSS was used is assumed to be due to quarternization of the fulleropyrrolidine. Enhance the steric hindrance of the N atom dramatically reduced the adverse effect from PEDOT:PSS.