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Influence of PEI doping on thermoelectric performance of PC70BM

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For the first time, effect of polyethylenimine (PEI) doping on thermoelectric performance of [6,6]-phenyl-C71 butyric acid methyl ester, commonly known as PC70BM, is investigated. This report shows a very good compatibility of these two materials in a thermoelectric system and significant improvement of the thermoelectric power factor of PC70BM as a result of doping with PEI compared to the previous studies on PC70BM reported by the first author. Here, samples were prepared from solutions of PC70BM in three different solvents: chlorobenzene, chloroform, and toluene without and with PEI of 2 different concentrations. As it was expected, addition of electron-rich PEI material increased electrical conductivity of the thermoelectric system and in contrast, decreased the absolute value of negative Seebeck coefficient due to introducing more charge carriers. As a result of doping, enhancement in thermoelectric power factor of PC70BM was observed.

Keywords: electrical conductivity, Seebeck coefficient, power factor, PC70BM, PEI.

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1. Introduction

A thermoelectric material's role is to transform temperature gradient directly into electricity or because thermoelectric conversion is reversible, convert electric energy into thermal energy [1,2].

Traditionally, inorganic materials, such as Bi_2Sb_3, $Bi2Te_3$, and PbTe, have been used for thermoelectric applications [3]. However, high production costs, toxicity, and scarcity of materials are some issues for application of inorganic materials. To overcome these problems, organic thermoelectric materials have attracted considerable attention due to their non-toxicity, facile synthesis, being light-weight and low-cost, mechanical flexibility, abundance of raw materials, solution processability, and low thermal conductivity which is beneficial for a thermoelectric device in order to gain higher efficiency [4–10]. These advantages can promote organic thermoelectric materials and devices and their development and application in green energy field.

To evaluate the efficiency of a thermoelectric system, a dimensionless quantity called thermoelectric figure of merit ZT is applied. Figure of merit is defined as $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity. Thermoelectric materials with high efficiency have a high Seebeck coefficient, high electrical conductivity, low thermal conductivity, and therefore high ZT. To design an effective thermoelectric device, it is necessary to increase electrical conductivity and Seebeck coefficient.

[6,6]-phenyl-C71 butyric acid methyl ester commonly known as PC70BM is a fullerene derivative and an *n*-type organic semiconductor, which is widely used in organic bulk hetero-junction solar cells and organic electronics [11,12]. This material shows high negative Seebeck coefficient in pristine form. Such materials showing negative values of the Seebeck coefficient are rare, but needed to assemble a multi-layer of $p-n$ junctions in thermoelectric modules. Therefore, it is worth working more on PC70BM to improve its thermoelectric efficiency.

The positive *n*-type doping effect of polyethyleneimine (PEI) on PCBM was studied before for the solar-cell system [13]. PEI is a strong *n*-type dopant, that is cheap, easily accessible and easy to process (e. g., it doesn't need special solvent and can be easily dissolved in water and needs no further purification). In our work, for the first time PEI is used as a dopant to improve thermoelectric performance of PC70BM. Our work reveals good compatibility of PC70BM and PEI in a thermoelectric device and positive role of PEI to improve thermoelectric power factor of PC70BM. Two different concentrations of PEI were studied and significant enhancement in thermoelectric power factor of PC70BM was observed.

2. Experimental methods

PC70BM was purchased from 1-Material Company. Chlorobenzene (CB), chloroform (CF), toluene (TO), ethanol, and PEI were all purchased from Sigma-Aldrich

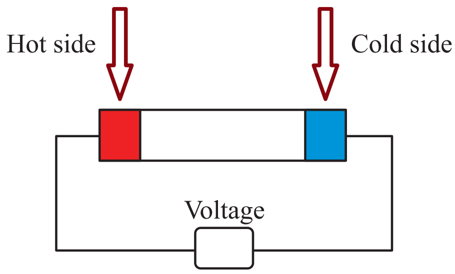

Figure 1. Schematic presentation of thermoelectrics device setup.

and used as received. Three solutions were prepared by dissolving 40 mg of PC70BM in 1 ml of each solvent. For the samples containing PEI, first two other sets of the PC70BM solutions in the solvents were prepared, then PEI was dissolved in ethanol (10 mg in 2 ml) and then, 0.1 and 0.2 ml of that was added to each of the PC70BM solutions stirred for 12 hours. The fabrication process was done under argon atmosphere of glove box. Samples were fabricated by drop-casting the solutions on glass substrates that were cleaned by sonication in acetone, isopropyl alcohol, and deionized water in ultrasonic bath, and treated with UV ozone for 15 min before use. The cast solutions were dried in a glove box. The thickness of the samples was, on average, 3 μm determined by the profilometer. The in-plane electrical conductivity was determined at room temperature by 4-probe method. A temperature gradient (ΔT) was established and maintained along the samples. Since the temperature measurement is a crucial issue in thermoelectric measurements, two K-type thermocouples were used at the ends of the samples to measure the temperature on both ends of each sample. The Seebeck coefficient value was calculated from $S = -\Delta V/\Delta T$ for the samples. Fig. 1 shows a schematic illustration of thermoelectrics device setup.

3. Results and discussion

PC70BM is a fullerene derivative compound showing electron-transporting properties and high negative Seebeck coefficient value in pristine form. Therefore, it offers promising prospects to be used as an n-type component in the thermoelectric $p-n$ junctions in organic thermoelectric devices. However, its low electrical conductivity is a limiting factor for application in practical $p-n$ junctions. Hence, improving its electrical conductivity is essential. Therefore, PEI-doped PC70BM samples were prepared and investigated. Fig. 2 shows the values of the electrical conductivity of the samples. As it was reported and fully explained in [14], the value of the PC70BM electrical conductivity changes with the type of the solvent used to fabricate the samples. It has been demonstrated that applying different solvents affects some of the properties of the materials such as degree of crystallinity and mobility, and as a result, different values of electrical conductivity can be obtained by using different types of solvents [14–16]. The table shows the boiling points of the solvents.

Boiling points of the solvents

Organic solvent	Boiling point, °C
Chlorobenzene (CB)	131
Toluene (TO)	110
Chloroform (CF)	61

CB has the highest boiling point and CF has the highest vapor pressure and the lowest boiling point. Considering the boiling points of the solvents, it is clear that the sample made of a higher boiling point solvent needs a longer time for drying as the solvent evaporates slower. Slow evaporation of the solvent allows for better ordering and self-organization within the molecular packing of the PC70BM in the film. Depending on the type of solvent, the structure of the material and its ability to transport charge carriers is affected and leads to different values of electrical conductivity. However, the lowest electrical conductivity was measured for the film fabricated from TO, although this solvent has a quite high boiling point higher than that of CF. The reason is that TO has the lowest polarity. This leads to weaker interaction force with PC70BM molecules leading to the lowest solubility [14,17]. Hence, the boiling point does not play a dominant role for this solvent. In addition, Fig. 2 shows enhancement of electrical conductivity upon addition of PEI. Obviously, the chemical doping of PC70BM caused by adsorbed dopant molecules is responsible for the observed changes in electrical conductivity. PEI contains nitrogen atoms in its backbone. Therefore, it is supposed to act as electron donor. In fact, PEI has been shown to be an effective n-type dopant as it donates its lone electron pair from the amine groups of its backbone [18–21], which generates additional charge carriers to PC70BM. By increas-

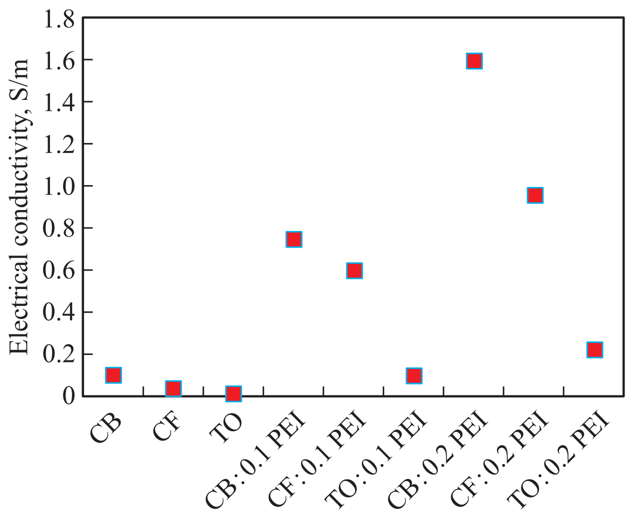

Figure 2. Electrical conductivity of doped and non-doped samples.

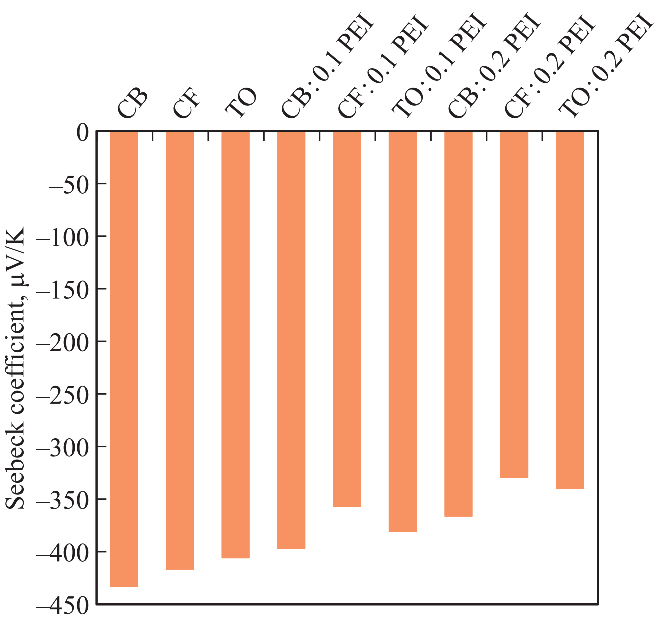

Figure 3. Seebeck coefficient values of doped and non-doped samples.

ing the number of charge carriers after introducing PEI to PC70BM, it is reasonable to observe enhancement in the electrical conductivity. After doping with PEI, the values of electrical conductivity increased by a factor of 7, 15, and 5 for CB, CF, and TO samples, containing 0.1 ml of PEI, and 15, 24, and 11 for CB, CF, and TO samples, containing 0.2 ml of PEI, respectively.

Fig. 3 presents the corresponding Seebeck coefficient values for the investigated PC70BM samples. The negative sign of the Seebeck coefficient indicates that the major charge carriers are electrons in all of the samples, confirming PC70BM as *n*-type semiconductor and effective *n*-type doping by PEI. The highest Seebeck coefficient was obtained from the sample made of CB solvent in pristine form. The diagram shows that the absolute values of the Seebeck coefficient for pristine PC70BM before doping increase with increasing electrical conductivity in a similar way due to increasing in the mobility values, and a simultaneous enhancement of Seebeck coefficient and electrical conductivity was observed for pristine PC70BM [14]. After addition of PEI, the number of charge carriers increased as PEI donates its lone electron pair from the amine groups of its backbone. However, improving the electrical conductivity by increasing the number of charge carriers as a result of chemical doping will generally decrease the absolute value of the Seebeck coefficient, as both parameters are inversely correlated [22,23]. Seebeck coefficient is defined by entropy per charge carriers, thus, it is expected to observe reduction in the absolute value of the Seebeck coefficient of the samples as a result of introducing more charge carriers after addition of PEI while maintaining the negative sign of the Seebeck coefficient confirming the *n*-type nature of the samples before and after effective *n*-type doping by introducing PEI. This is important because advances in *n*-type thermoelectric materials, especially in organics, lag far behind *p*-type materials. Such materials showing negative values of the Seebeck coefficient are rare, but needed to assemble a multi-layer of $p-n$ junctions in thermoelectric modules.

Fig. 4 shows power factor values of the samples calculated from $P = S^2\sigma$. The best value was obtained for the sample fabricated from CB both in pristine and doped forms. After doping with PEI, the values of power factor increased by a factor of 6, 11, and 4.45 for CB, CF, and TO samples containing 0.1 ml of PEI and 10.75, 15, and 7.64 for CB, CF, and TO samples containing 0.2 ml of PEI, respectively. However, it is worth noting that in this report the performance of PEI as a dopant for PC70BM was not optimized and it is expected to gain higher values and more improvements in thermoelectric power factor after optimization and finding the best concentration of PEI or by trying other solvents and doping methods.

Assuming that the thermal conductivity of fullerene derivatives is about $0.05\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ [24], the ZT values of the samples calculated from $ZT = S^2\sigma T/\kappa$ were found to be 0.00012, 0.000042, 0.000020 for CB, CF, and TO samples before doping and 0.00071, 0.00046, 0.0001, 0.0013, 0.00063, 0.00016 for CB, CF, and TO samples with 0.1 and 0.2 ml of PEI, respectively. The values of power factor and ZT for PEI-doped PC70BM are considerably higher compared to the previous reports on PC70BM by the first author [14,25].

It is worth noting that although in the paper published by Jiong Yang et al. [26], very high values of ZT were reported, all materials were inorganic semiconductors or inorganic alloys and compounds, while we are reporting on organic class of semiconductors. In addition, while the values of power factor and ZT for PEI-doped PC70BM are considerably higher compared to the previous studies reported on PC70BM by the first author, the performance of PEI as a dopant for PC70BM was not optimized and

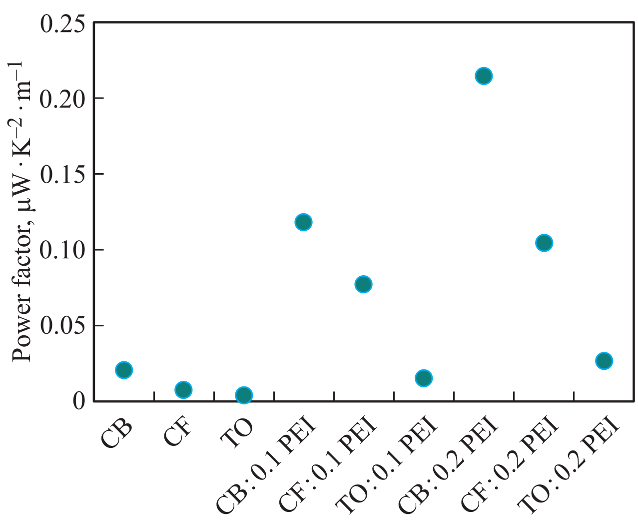

Figure 4. Power factor values of doped and non-doped samples.

additional work and studies are required for optimization. By trying other types of solvents, different concentrations of PEI, or introducing other doping methods, it is expected to gain higher values and more improvements in thermoelectric efficiency for PEI-doped PC70BM.

4. Conclusions

This work was the first effort to demonstrate that polyethyleneimine as an *n*-type dopant has good compatibility with PC70BM in a thermoelectric system and improves its thermoelectric power factor. However, additional work and studies is required to optimize and find the highest value for thermoelectric power factor of PEI-doped PC70BM. Although the values of power factor and ZT for PEI-doped PC70BM are considerably higher compared to the previous studies reported on PC70BM by the first author, by trying other types of solvents, different concentrations of PEI or introducing other methods of doping, it is expected to have higher values of thermoelectric power factor for PEI-doped PC70BM.

Author contributions

Mina Rastegaralam conceived, designed, and performed the experiments, and Miroslav Mahdal interpreted the experimental results, and coordinated scientific work.

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Conflict of interest

The authors declare that they have no conflicts of interest.

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