

Organic Thermoelectric Device Utilizing Charge Transfer Interface as the Charge Generation by Harvesting Thermal Energy



Open Access This file is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. In the cases where the authors are anonymous, such as is the case for the reports of anonymous peer reviewers, author attribution should be to 'Anonymous Referee' followed by a clear attribution to the source work. The images or other third party material in this file are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

An interesting novel idea with impressive results are presented. But the authors may consider to modify the article title to indicate that the thermoelectric effect arises from the charge transfer interface sensitive to the temperature. This can make the readers easier to understand a new thermoelectric effect quite different from the Seebeck effect.

Reviewer #2 (Remarks to the Author):

In this manuscript, the authors introduce a novel thermoelectric device concept that operates without the need for a temperature gradient, utilizing an organic charge transfer (CT) interface alongside carrier transport layers. They elucidate a mechanism that facilitates charge separation through thermal excitation with energies in the range of several tens of millielectronvolts. By leveraging donors and acceptors to promote charge generation, they achieved an initial modest maximum power output (P_{max}) of approximately 0.23 nW/cm² following systematic device optimizations. Subsequent refinement of layer thicknesses led to a notable enhancement in P_{max} to around 100 nW/cm². Furthermore, the authors conducted a thorough investigation into the operational principles of the device, delving into temperature dependencies and surface potential characteristics. While the study presents an intriguing new concept, there are certain aspects that warrant further scrutiny.

1. The proposed device architecture hinges on the effective separation of charges from charge-bound CT excitons through the utilization of minimal thermal energy, followed by the diffusion and extraction of the resulting electrons and holes to the respective electrodes. To bolster their claims, the authors are encouraged to employ more precise characterization techniques to scrutinize the band bending at the interface, possibly utilizing ultraviolet photoelectron spectroscopy (UPS) for enhanced insight into energy alignment.

2. The discrepancies observed in current density, notably in Figure S1 where values peak at around 60 mA/cm² compared to Figure 2a, raise questions regarding the underlying causes of such elevated leakage currents. A detailed analysis of the factors contributing to this disparity would be beneficial for a comprehensive understanding of device performance.

3. It would be advantageous for the authors to include IV curves under AM1.5 illumination conditions to provide a more thorough assessment of energy alignment and to validate the efficacy of the device under standard operating conditions.

4. To mitigate potential confounding factors such as light-induced photocurrent, a comprehensive description of the measurement setup employed during experimentation needs to be provided.

Reviewer #3 (Remarks to the Author):

In the manuscript, the authors utilize the ITO/CuPc/F16CuPc/C60/BCP/Al structure to achieve an organic CT interface with a carrier transport layer, and successfully constructs a new type of thermoelectric device, improving the thermoelectric properties of devices. Though the mechanism maybe novel, some critical issues need to address:

Some major issues:

1. The basic thermoelectric parameters need to provide such as power factor, Seebeck coefficient to compare with other organic thermoelectric materials or devices.
2. Considering the thermoelectric property shown in Figure 2, what is the input thermal energy during the test? And what is the detail temperature difference, even it is in the range of millielectronvolts, it is necessary to show such value.
3. The interface energy level alignment can be further confirmed through UPS measurements. In addition, the interface of CuPc/F16CuPc should be a high conductivity state due to the accumulation of hole and electrons, as suggested from several previous publication. As a result, the IV curve shown in Figure 1 of CuPc/F16CuPc demonstrate comparable current in forward and reverse bias.

Some minor issues

1. The LUMO of F16CuPc mentioned in the manuscripts is -4.8 eV, but in Figure 1c, the LUMO of the schematic energy diagram for the ITO/CuPc/F16CuPc/Al device (③ forward and ④ reverse bias) is -4.2 eV. Please explain. Meanwhile, Fig. 1c lacks the serial number (c).
2. “In the CuPc/PTCBI device case, the current density when a reverse bias was applied was approximately two orders of magnitude lower than that when a forward bias was applied at ± 2.0 V.” Here, ± 2 V should be +2 V?

3. “Such pinhole issues, which are parasitic in organic thin-film devices, have been widely recognized in OLEDs.” Include a little more previous works.

4. “Finally, as shown in Fig. 6, the best thermoelectric performance of $V_{oc} = 384 \text{ mV}$, $J_{SC} = 1.1 \mu\text{A}/\text{cm}^2$, and $P_{max} = 94 \text{ nW}/\text{cm}^2$ was obtained for the CuPc (180 nm)/F16CuPc (320 nm)/C60 (20 nm)/BCP (20 nm) device, with results that were more than ~ 100 times better than those of the initial device.” Here, Fig. 6 should be Fig. 7?

5. Authors need to carefully modify the Syntax, formatting and drawing error. For example, “-50nm”, “ $\pm 2\text{V}$ ” and so on should have a space between the number and the unit.

Reply letter

Reviewer #1 (Remarks to the Author):

An interesting novel idea with impressive results are presented. But the authors may consider to modify the article title to indicate that the thermoelectric effect arises from the charge transfer interface sensitive to the temperature. This can make the readers easier to understand a new thermoelectric effect quite different from the Seebeck effect.

Reply: We sincerely thank reviewer #1 for his/her very positive evaluation of our result and for suggesting the modification of the title. We modified the original title as below.

(Original) Organic Thermoelectric Device Utilizing Charge Transfer Interface

(Revised title) Organic Thermoelectric Device Utilizing Charge Transfer Interface as the Charge Generation by Harvesting Thermal Energy

Reviewer #2 (Remarks to the Author):

In this manuscript, the authors introduce a novel thermoelectric device concept that operates without the need for a temperature gradient, utilizing an organic charge transfer (CT) interface alongside carrier transport layers. They elucidate a mechanism that facilitates charge separation through thermal excitation with energies in the range of several tens of millielectronvolts. By leveraging donors and acceptors to promote charge generation, they achieved an initial modest maximum power output ($P_{\max}$) of approximately 0.23 nW/cm² following systematic device optimizations. Subsequent refinement of layer thicknesses led to a notable enhancement in $P_{\max}$ to around 100 nW/cm². Furthermore, the authors conducted a thorough investigation into the operational principles of the device, delving into temperature dependencies and surface potential characteristics. While the study presents an intriguing new concept, there are certain aspects that warrant further scrutiny.

Reply: We sincerely thank reviewer #2 for his/her evaluation of our result and the successive insightful comments.

1. The proposed device architecture hinges on the effective separation of charges from charge-bound CT excitons through the utilization of minimal thermal energy, followed by the diffusion and extraction of the resulting electrons and holes to the respective electrodes. To bolster their claims, the authors are encouraged to employ more precise characterization techniques to scrutinize the band bending at the interface, possibly utilizing ultraviolet photoelectron spectroscopy (UPS) for enhanced insight into energy alignment.

Reply: We also understand the importance of UPS measurements for the precise energy states analysis at the organic layer interfaces. However, at present, our laboratory cannot make measurements with

UPS. In particular, to conduct accurate measurements, we need advanced equipment that integrates UPS measurements with the vacuum deposition system, which currently makes it impossible to carry out the experiment. We believe that the basic analysis with the Kelvin probe is sufficient as the first rapid report. In the future, in addition to the Kelvin probe measurement, we would like to proceed with UPS measurements with other research institutes and obtain a comprehensive picture of our new device operation. At present, we are doing the best we can in our laboratory. We would be happy if you understood it and could accept our present report without UPS data.

2. The discrepancies observed in current density, notably in Figure S1 where values peak at around 60 mA/cm² compared to Figure 2a, raise questions regarding the underlying causes of such elevated leakage currents. A detailed analysis of the factors contributing to this disparity would be beneficial for a comprehensive understanding of device performance.

Reply: We thank the reviewer #2 for raising this important point. We have fabricated more than 10 devices in a single device configuration in this study. During this experiment, unstable characteristics were occasionally observed in the CuPc/F₁₆CuPc bilayer stacked devices. We think this is due to pinhole problems associated with the film inhomogeneity, as both CuPc and F₁₆CuPc show crystalline textures in their thin films. This is why Figs. 2(a) and S1 show variations in the *J-V* characteristics. To escape this issue, we found the formation of additional layers of C₆₀/BCP significantly stabilized the device performance. The point the referee raised is important from a materials process-engineering point of view, and the explanation was added to the caption of Fig. S1.

(Added text in **Fig. S1**): CuPc/F₁₆CuPc bilayer devices provided unstable *J-V* characteristics occasionally since these molecules formed polycrystalline textures in their thin films formed by vacuum evaporation. Therefore, there is a discrepancy between the *J-V* characteristics of **Figs. 1(c)** and **S1**. However, such instability has been significantly overcome by forming a C₆₀/BCP layer on top of the CuPc/F₁₆CuPc layers, resulting in highly reproducible *J-V* and thermoelectric properties.

3. It would be advantageous for the authors to include IV curves under AM1.5 illumination conditions to provide a more thorough assessment of energy alignment and to validate the efficacy of the device under standard operating conditions.

Reply: Based on this comment, we conducted a photo-irradiation experiment under AM1.5 using ITO (100 nm)/CuPc (110 nm)/F₁₆CuPc (45 nm)/C₆₀ (40 nm)/BCP (20 nm)/Al (100 nm). The result is shown in Fig. R1 below. The V_{OC} did not change largely (V_{OC}=437 mV under dark and V_{OC}=400 mV under light irradiation), while the J_{SC} showed a large increase (J_{SC}=1.2 mA/cm² under dark and J_{SC}=3.4 mA/cm² under light irradiation). The nearly similar V_{OC} indicates that the origin of electromotive force in this device is located certainly at the CuPc/F₁₆CuPc interface. However, while a J_{SC} of the order of mA/cm² can be obtained in normal organic solar cells using CuPcs, the J_{SC} in this device increases

only about three times the dark current, suggesting that the excitons generated by light absorption in the visible region do not contribute significantly to the power generation, that is, they do not contribute to the CT formation at the interface and may be nonradiatively deactivated. The excitons generated by optical absorption in the visible light region do not contribute significantly to power generation. Thus, since we need very careful consideration of various parameters, we would like to conduct detailed experiments on the dependence on film thickness and investigate various device structures in our successive study.

(Added text on page 6 with **Fig. S2b**): Further, to confirm the origin of the electromotive force, we conducted a photo-irradiation experiment under AM1.5 using ITO (100 nm)/CuPc (110 nm)/F₁₆CuPc (45 nm)/C₆₀ (40 nm)/BCP (20 nm)/Al (100 nm) as shown in Fig. S2b. The V_{OC} did not change largely, i.e., V_{OC}=0.44 V under dark and V_{OC}=0.40 V under light irradiation. The nearly similar V_{OC} indicates that the origin of electromotive force in this device is located at the CuPc/F₁₆CuPc interface.

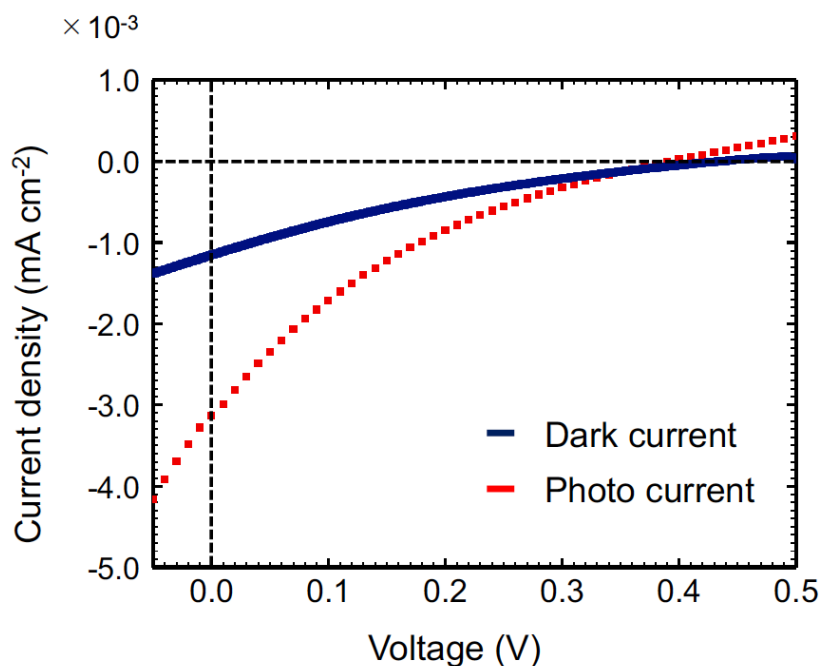


Fig. R1. *J-V* characteristics of ITO (100 nm)/CuPc (110 nm)/F₁₆CuPc (45 nm)/C₆₀ (40 nm)/BCP (20 nm)/Al (100 nm) device under dark and light irradiation condition (AM1.5).

4. To mitigate potential confounding factors such as light-induced photocurrent, a comprehensive description of the measurement setup employed during experimentation needs to be provided.

Reply: The description of the conditions of the measurement is insufficient and the description has been added in the current-voltage characteristic measurement section. The measurement condition for

temperature dependence was already described in the section “Temperature dependence of current-density-voltage measurement.”

(Added text in **Experimental Section**): The fabricated device, which was sealed in a glove box, was set in a measurement holder installed in a measurement box covered in all directions by a steel plate and electromagnetically shielded, and thus, all measurements were carried out in completely dark room conditions.

Reviewer #3 (Remarks to the Author):

In the manuscript, the authors utilize the ITO/CuPc/F16CuPc/C60/BCP/Al structure to achieve an organic CT interface with a carrier transport layer, and successfully constructs a new type of thermoelectric device, improving the thermoelectric properties of devices. Though the mechanism maybe novel, some critical issues need to address:

Reply: We sincerely thank reviewer #3 for his/her valuable comments. We revised our manuscript as much as we could at this stage.

Some major issues:

1. The basic thermoelectric parameters need to provide such as power factor, Seebeck coefficient to compare with other organic thermoelectric materials or devices.

Reply: In conventional thermoelectric power generation, the thermal gradient causes the diffusion of charge carriers, which generates an electromotive force, but the proposed device considers an operating mechanism like that of an organic p-n solar cell. Therefore, it is essentially impossible to calculate the power factor and Seebeck coefficient.

2. Considering the thermoelectric property shown in Figure 2, what is the input thermal energy during the test? And what is the detail temperature difference, even it is in the range of millielectronvolts, it is necessary to show such value.

Reply: At this moment, we think that the thermal energy can be supplied to the devices from the surrounding air which possesses thermal energy such as 25 meV at room temperature. The air surrounding the devices can be considered as an infinite heat bath, and the analogized conditions of steady light irradiation in a solar cell, i.e., “photon absorption,” are considered to be formed by “phonon absorption.” Our previously reported thermally activated delayed fluorescence (TADF) also overcomes about 200 meV of an S_1 - T_1 gap by absorbing ambient heat (phonon), and the separation of CT excitons by ambient heat (phonon) is considered to be fully feasible.

3. The interface energy level alignment can be further confirmed through UPS measurements. In addition, the interface of CuPc/F16CuPc should be a high conductivity state due to the accumulation

of hole and electrons, as suggested from several previous publication. As a result, the IV curve shown in Figure 1 of CuPc/F16CuPc demonstrate comparable current in forward and reverse bias.

Reply: We also understand the importance of UPS measurements for the precise energy states analysis at the organic layer interfaces. However, at present, our laboratory cannot make measurements with UPS. In particular, to conduct accurate measurements, we need advanced equipment that integrates UPS measurements with the vacuum deposition system, which currently makes it impossible to carry out the experiment. We believe that the basic analysis with the Kelvin probe is sufficient as the first rapid report. In the future, in addition to the Kelvin probe measurement, we would like to proceed with UPS measurements with other research institutes and obtain a comprehensive picture of our new device operation. At present, we are doing the best we can in our laboratory. We would be happy if you understood it and could accept our present report without UPS data.

In fact, the current densities between the forward and reverse bias is appreciably different. At ± 2 V, almost 10 times difference was observed. At the forward bias of the ITO/CuPc/F16CuPc/Al device, the amount of current is controlled (limited) by the carrier injection or transport through the organic layers, while at the reverse bias, the amount of current can be controlled to charge separation, at the CuPc/F16CuPc interface. Very interestingly, nearly one order of magnitude higher current in the reverse bias clearly proves that the current originated from the carrier generation and separation at the CuPc/F16CuPc interface provides higher current than the current originating from the carrier injection and transport in the forward bias.

Some minor issues

1. The LUMO of F16CuPc mentioned in the manuscripts is -4.8 eV, but in Figure 1c, the LUMO of the schematic energy diagram for the ITO/CuPc/F16CuPc/Al device (③ forward and ④ reverse bias) is -4.2 eV. Please explain. Meanwhile, Fig. 1c lacks the serial number (c).

Reply: We apologize for the wrong value of the LUMO of F16CuPC in Fig. 1c. The correct value is -4.8 eV. We corrected Fig. 1c and corrected the serial numbers, which appeared wrong due to the Japanese fonts.

2. “In the CuPc/PTCBI device case, the current density when a reverse bias was applied was approximately two orders of magnitude lower than that when a forward bias was applied at ± 2.0 V.” Here, ± 2 V should be +2 V?

Reply: We are sorry for the wrong sign. We corrected it as +2 V.

3. “Such pinhole issues, which are parasitic in organic thin-film devices, have been widely recognized in OLEDs.” Include a little more previous works.

Reply: The removal of pinholes by introducing trace oxygen is, in practice, a very important know-how for organic device processes. Academically, no literature analyzes the details of this process. Therefore, it is impossible to include the literature, but the case is described in some patents. Unfortunately, it is in Japanese, but we would like to include it because it is a very useful document.

Japanese Unexamined Patent Application Publication No. Hei11-40346

Japanese Unexamined Patent Application Publication No. 2001-313170A

Japanese Unexamined Patent Application Publication No. 2003-282249A

Ref. 23 was added. [23] Japanese unexamined patent application publication No. Hei11-40346, No. 2001-313170A, and No. 2003-282249A

4. “Finally, as shown in Fig. 6, the best thermoelectric performance of $V_{oc} = 384 \text{ mV}$, $J_{sc} = 1.1 \mu\text{A}/\text{cm}^2$, and $P_{max} = 94 \text{ nW}/\text{cm}^2$ was obtained for the CuPc (180 nm)/F₁₆CuPc (320 nm)/C₆₀ (20 nm)/BCP (20 nm) device, with results that were more than ~100 times better than those of the initial device.” Here, Fig. 6 should be Fig. 7?

Reply: We are sorry for this mistake. We corrected it to Fig. 7.

5. Authors need to carefully modify the Syntax, formatting and drawing error. For example, “-50nm”, “±2V” and so on should have a space between the number and the unit.

Reply: We are sorry for the errors. We checked the manuscript again and made the necessary corrections.

Additional correction:

We added reference #39 about the mid-gap formation in a BCP layer with the necessary description.

[39] H. Yoshida, J. Phys. Chem. **119**, 24459 (2015).

REVIEWERS' COMMENTS

Reviewer #2 (Remarks to the Author):

The authors addressed my comments well. I recommend to accept the manuscript in its present form.

Reviewer #3 (Remarks to the Author):

The revised version provides better clarification and the authors have address most of my concerns,it maybe suitable to accepte currently.