Solar Harvesting: a Unique Opportunity for Organic Thermoelectrics?

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Thermoelectrics have emerged as a strategy for solar-to-electricity conversion, as they can complement photovoltaic devices as IR harvesters or operate as stand-alone systems often under strong light and heat concentration. Inspired by the recent success of inorganic-based solar thermoelectric generators (STEGs), in this manuscript, the potential of benchmark organic thermoelectric materials for solar harvesting is evaluated. It is shown that the inherent properties of organic semiconductors allow the possibility of fabricating organic STEGs (SOTEGs) of extraordinary simplicity. The broadband light absorption exhibited by most organic thermoelectrics combined with their low thermal conductivities results in a significant temperature rise upon illumination as seen by IR thermography. Under 2 sun illumination, a temperature difference of 50 K establishes between the illuminated and the non-illuminated sides of a poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) film, and ≈40 K for a carbon nanotube/cellulose composite. Moreover, when using light as a heat source, the Seebeck coefficient remains unaffected, while a small photoconductivity effect is observed in PEDOT:PSS and carbon nanotubes. Then, the effect of several geometrical factors on the power output of a solar organic thermoelectric generator is investigated, enabling us to propose simple SOTEG geometries that capitalize on the planar geometry typical of solution-processable materials. Finally, a proof-of-concept SOTEG is demonstrated, generating 180 nW under 2 suns.

1. Introduction

The ever-increasing demand for energy and the need to mitigate the effects of climate change have motivated researchers to develop energy conversion technologies capable of harvesting energy from renewable sources.[1] The amount of incident sunlight that reaches the Earth’s surface could readily meet our current and future energetic needs, if suitably harvested.[2] Currently, photovoltaics have become the preeminent solar technology, converting UV and visible light directly into electricity.[3–5] While low bandgap semiconductors are a very active area of research, harnessing the IR fraction of the Sun’s radiation, specifically near-infrared radiation (NIR), remains a distant goal for photovoltaics, particularly when using organic materials.[6] It is important to note that thermalization losses in the semiconductor and undesirable heating from parasitic IR absorptions are unavoidable in single heterojunction devices which result in heating of the solar cell. In most cases, the solar cell performance depends on the cell temperature, so some degree of thermal management is required in real-world applications.

Thermoelectric generators, on the other hand, may be well suited to exploit the solar IR spectrum, including the NIR and mid-infrared (MIR) regions. Similar to photovoltaics, they are solid-state devices, but instead of the photoelectric effect, they convert thermal energy into electricity by means of the Seebeck effect. Over the past decade, thermoelectrics (TEs) have emerged as a promising waste-heat recovery technology, motivated by the fact that ≈60% of energy produced is dissipated as waste heat.[7] In addition to upcycling waste heat, TEs can also be used as solar harvesters. In recent years, solar thermoelectric generators (STEGs) have garnered some attention, as a complement to photovoltaics in hybrid devices or as individual devices.[8–12] The latter could potentially generate electricity during the day and at night and have a more constant output compared to PV since heat lasts longer upon shadowing. The efficiency of STEGs is, however, limited compared to PV systems. Kraemer et al. demonstrated a high-performing proof-of-concept device based on inorganic semiconductors that relied on optical and thermal concentration to drive a unicouple TE generator with a maximum reported efficiency of 7.4%.[13] While the results of such a device are promising, the complex geometry and need for vacuum conditions may limit the practicality of inorganic STEGs.

Typically, there are three components in a STEG: a solar absorber, a TE generator, and a heat management system.[8] The solar absorber uses optical and thermal concentration to transform incident solar radiation into heat. The TE generator converts heat into a voltage difference, and the heat management system removes rejected heat from the TE generator.

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In order to perform efficiently, STEGs must operate at high temperature differences, which requires operating under vacuum and using radiation shields and active cooling. These components complicate the device geometry and lead to coupling losses. However, the total cost of the device is dominated by material costs, so integrating these components can reduce the amount of raw material, thus reducing the overall price of the device.\[14,15\]

The use of comparatively cheap organic semiconductors could allow for a different setup overcoming some of the shortcomings of inorganic materials. For one, STEGs based on organic semiconductors (SOTEGs) do not require a solar absorber since, as we show below, typical organic TE materials already have strong absorption in the solar spectrum. Furthermore, their optical properties can be tuned via doping, shifting their absorption bands toward a specific range of the solar spectrum. The energy that arrives at the Earth's surface is diffuse, and the heat is too low grade for most inorganic solar-thermal applications. Because of their low cost, low toxicity, high abundance, and solution processability, organic TEs can be printed onto large surfaces to capture the otherwise wasted, low-grade heat in a simple device without vacuum, radiation shields, or active cooling. SOTEGs open up an exciting opportunity since they can be integrated with photovoltaics to capture the unused fraction of the AM 1.5 solar spectrum, specifically the NIR–MIR region.

Mainly two classes of organic materials are investigated for TE applications, namely conjugated polymers and semiconducting carbon nanotubes (CNTs).\[16–19\] Conjugated polymers have inherently low thermal conductivities but also low electrical conductivities. Although many polymers are not sufficiently conductive for TE applications, their conductivities can be enhanced through doping using solution- or vapor-based processes.\[20,21\] On the other hand, semiconducting CNTs have high electrical conductivities and potentially high Seebeck coefficients but also high thermal conductivities. An effective approach to optimizing TE performance in CNTs is to combine them with polymers. In this manner, the polymer–CNT composites exhibit good electrical conductivity and low thermal conductivity.\[29\]

To our knowledge, there has not been any report investigating the potential and feasibility of SOTEGs. Herein, we investigate the ability of commonly used organic TE materials to operate as both solar absorbers and active TE material. In this study, we examine a variety of commonly used organic materials, spanning the four main classes of organic TE materials: conducting polymers, doped semiconducting polymers, carbon nanotubes (CNTs), and CNT–polymer composites. Specifically, we investigate semiconducting polymers like poly(3-hexylthiophene (P3HT), poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT), PBTTT vapor-doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ); conducting polymers like poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate (PEDOT:PSS), dimethyl sulfoxide (DMSO) treated PEDOT:PSS; single-wall carbon nanotubes of the CoMoCAT and eDIPS varieties; and CNT–polymer composites including CoMoCAT:P3HT and eDIPS:cellulose. Additionally, we examine if the insulating polymer polylactic acid (PLA) could serve as an absorber material.

In this work we first evaluate the efficiency limit in SOTEGs, drawing on standard theory and available experimental data. Then, we explore the photothermal conversion capability of benchmark organic TE materials in terms of the temperature rise upon illumination as well as the appearance of nonthermal photoinduced effects. Last, we propose a number of device geometries and determine the power output as a function of geometrical factors such as leg length, the ratio between illuminated and shadowed area, and light concentration.

2. Results and Discussion

2.1. SOTEG Efficiency

The main steps involved in the generation of electrical power from light using a TE material are depicted in Figure 1.
Following work done by Kramer et al., the overall efficiency ($\eta$) of a SOTEG can be given by

$$\eta = \eta_{opt} \cdot \eta_{abs} \cdot \eta_{aux} \cdot \eta_{on} \quad (1)$$

where $\eta_{opt}$ is the optical efficiency, $\eta_{abs}$ is the absorber efficiency, $\eta_{aux}$ is the efficiency of a TE generator, and $\eta_{on}$ is the auxiliary efficiency.\[13\] The optical efficiency is limited by optical losses that result from lenses or mirrors in the case of concentration and from reflection and transmission of incident light (steps 1a and 1b in Figure 1a). The absorber efficiency, in the case of SOTEGs, is defined as the ratio of useful heat gain to the total absorbed solar radiation. Semiconducting materials can absorb photons with energy higher than their bandgap (step 2a). Upon absorption, these photons create hot electron–hole pairs (excitons) which eventually thermalize and give off heat (2c). In addition, these photogenerated excitons can recombine via radiative recombination (2b), emitting a low-energy photon, or via nonradiative recombination, which converts electronic energy into heat. Photons with energy below the bandgap are typically transmitted in thin films unless they are absorbed by free charges in the semiconductor or by other materials in the stack. Unlike in organic photovoltaics, where device efficiency is limited by nonradiative and radiative recombination, nonradiative recombination is desired for SOTEGs.

The TEG efficiency is given by

$$\eta_{teg} = \frac{T_s - T_c}{T_h} \frac{1 + zT - 1}{\sqrt{1 + zT} + \frac{T_s}{T_c}} \quad (2)$$

where $T_h$ is the hot-side temperature, $T_c$ is the cold-side temperature, and $zT$ is the dimensionless figure of merit defined for TE materials as

$$zT = \frac{S' \sigma}{\kappa} \quad (3)$$

where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity and $T$ is the average absolute temperature. Included in the TEG efficiency are parasitic losses that will negatively affect device performance including convection (step 3b), conduction losses through electrical contacts (3a), radiation losses (3c), joule heating (3e) and losses that arise from the presence of traps (3d).

The fundamental limit on maximum efficiency for TE generators, like for all other hot engines, is the Carnot limit, which corresponds to $zT = \infty$. The values for TEG efficiency are well below the Carnot limit, but improving material properties can enhance $zT$ and thus lead to higher TEG efficiencies. Figure 1b shows $\eta_{teg}$ versus irradiance, corresponding to experimental temperature differences measured for organic TE materials (see below) of approximately $\Delta T < 100$ K. Note that these values are not theoretical limits, but experimentally measured for samples in air (no vacuum).\[22\] Currently, the highest $zT$ values reported for organic TEs in literature are slightly below 0.5.\[23\] Incorporating optical concentration into SOTEGs made from a similar material could already lead to efficiencies over 1%. Notwithstanding the promising results on organic TEs, the $zTs$ for organic TEs lag behind the highest reported values for inorganic TEs, which are around 2.6.\[24\] With a $zT$ of 2.6, the efficiency of a SOTEG could be over 5%.

### 2.2. Solar Absorber Characterization

An ideal solar absorber material exhibits broadband light absorption across the AM 1.5 solar spectrum (0.3–3 µm), as well as low reflectivity and low IR emissivity. In addition, an adequate solar absorber for photothermal conversion must be able to efficiently convert incident solar radiation into usable heat energy (e.g., radiative losses should be minimal). Figure 2ab shows the absorption spectra for films of several (semi-) conducting polymers and carbon nanotubes, respectively. The optical properties of thin-film organic semiconductors have been widely reported in literature, and common semiconducting polymers, such as P3HT and PBTTT exhibit strong absorption in the UV–vis region, specifically between 400 and 635 nm, as shown in Figure 2a.\[25\] In contrast, a film of PBTTT vapor-doped with F$_4$TCNQ shows broad absorption across the UV–vis regions and even reaching up to 1000 nm in the NIR region. Patel et al. attributed the broadening of the absorption spectrum to polaron absorption and the new peaks to the F$_4$TCNQ anion radical.\[21\] PEDOT:PSS in comparison absorbs weakly in the UV–vis range but absorbs NIR radiation strongly due to a Drude tail of free carriers.\[26–27\] CNTs, on the other hand, exhibit metallic or semiconducting behavior depending on their chiral vector.\[28\] The commercially available CoMoCAT and eDIPS CNTs are mixtures of both species, and thus the two CNT materials absorb across the whole spectrum as shown in Figure 2b.

In order to absorb a higher fraction of the incident solar radiation, the legs of the TE generator are made of thick layers (<5 µm) (See also discussion below). Additionally, the thicker layers enhance the electrical conductance of the individual legs.

In a first step, the photothermal response of freestanding materials as a function of irradiance was investigated using IR thermography and a solar simulator. As for absorption, the thickness of materials will influence their photothermal response. Yet, while thicker films absorb more solar radiation, there is an optimal thickness that will achieve the highest temperature. Above this thickness, no additional light will be absorbed and the excess material will dilute the generated heat, instead of further raising the temperature. To evaluate the effect of thickness on temperature rise, finite element heat transfer simulations were performed using COMSOL Multiphysics. In the case of PEDOT:PSS, average film temperature increased sharply as thickness increased from 100 nm to 10 µm; after 10 µm, the average film temperature reached a plateau before beginning to drop again (see Figure S1, Supporting Information).

In addition to thickness, the photothermal response depends on the thermal conductivity of the material. In a real device, the electrical contacts and support materials will dissipate heat from the TE legs. Materials with lower thermal conductivity can mitigate these heat losses while also maintaining the temperature difference across the illuminated and non-illuminated ends of the device. Table 1 lists the thermal conductivities of the organic TE materials used in this work.\[37\]

| Material      | Thermal Conductivity (W/mK) |
|---------------|-----------------------------|
| PEDOT:PSS     | 0.3                         |
| CoMoCAT       | 0.5                         |
| eDIPS CNTs    | 1.0                         |

The photothermal response of the materials was investigated using a solar simulator as a radiation source and an IR camera to probe the temperature of the materials in ambient room conditions. The materials were constantly illuminated until reaching a steady-state temperature (Figure S2, Supporting Information).
Information), and the power of the solar simulator was adjusted to change the irradiance. For all materials studied, the temperature of the freestanding films increased with irradiance up to 2 sun after which the temperature of the samples starts leveling off.

Before comparing materials, we note that besides the absorption of each material, the thermal conductivity will also contribute to establishing the maximum temperature achievable for a given system. To directly quantify the effect of thermal conductivity on photothermal response, a 3D printer was used to print small rectangles made of black PLA. These pieces were 3D printed varying the infill density to introduce porosity and thus reduce the thermal conductivity. As expected, the most porous PLA sample achieved a steady-state temperature (Figure S3, Supporting Information) about 35% higher than the dense PLA sample. Note that although PLA is not a TE material, PLA could be incorporated as a structural material in a SOTEG using 3D printing (see below).

Table 1. Thermal conductivities of organic TE materials.

| Material                  | Thermal conductivity [W m⁻¹ K⁻¹] | Measurement direction | Refs. |
|---------------------------|----------------------------------|-----------------------|-------|
| PEDOT:PSS                 | 0.2                              | Out-of-plane          | [29,30]|
|                           | 0.5                              | In-plane              |       |
| 5% DMSO-treated PEDOT:PSS | 0.42 ± 0.07                      | In-plane              | [23]  |
| PEDOT:PSS                 | 1.1                              | In-plane              | [31]  |
|                           | 0.30 ± 0.07                      | Out-of-plane          | [23]  |
| PBTTT                     | 0.39                             | Out-of-plane          | [32]  |
|                           | 0.23                             | In-plane              | [32,33]|
|                           | −0.6−0.8                         |                       |       |
| F₄TCNQ-Doped PBTTT        | −0.2                             | Out-of-plane          | [33]  |
| P3HT                      | 0.189 ± 0.023                    | Out-of-plane          | [34]  |
| PLA                       | 0.111                            | –                     | [35]  |
| CoMoCAT CNTs              | 8.5                              | In-plane              | [36]  |
| eDIPS                     | 2.7                              | In-plane              | [36]  |
| eDIPS:cellulose           | 2.7                              | In-plane              | [36]  |

Figure 2c shows the steady-state temperature of the polymers under illumination in ambient conditions as a function of irradiance. From the polymers investigated, the materials that achieved the highest temperatures were the 3D-printed black PLA and PEDOT:PSS. PEDOT:PSS, with a thickness of 46 μm, heated up to around 75 °C under 2 sun. As previously discussed, PEDOT:PSS exhibits broadband absorption in the NIR, and the thickness of the PEDOT:PSS likely enhanced its ability to absorb incident irradiation also in the visible, thus leading to the increase in temperature. Pristine PBTTT heated up to 60 °C, while pristine P3HT heated...
up to 70 °C under 2 sun. The difference in temperature could be attributed in part to the slight difference in thickness (19 µm for PBTTT and 24 for P3HT) (see Table S1, Supporting Information), since PBTTT and P3HT have similar absorption spectra, strongly absorbing between 400 and 635 nm.[38] F₄CNTQ-doped PBTTT, on the other hand, reached a steady-state temperature of 50 °C under 2 sun, much lower than the other materials, which also could be due to thickness (∼3 µm). Note that only thin films (<5 µm) of organic semiconductors can be effectively doped thus constraining the thickness of the F₄CNTQ-doped PBTTT.

Regarding the samples with carbon nanotubes, the composite eDIPS with cellulose sample heated up the most, as shown in Figure 2d. The composite sample is porous and includes a large proportion of cellulose, which has a low thermal conductivity. As a result, the composite has a low thermal conductivity compared to the other CNT-based materials. As reported by Abol-Fotouh et al., the in-plane thermal conductivities of pure eDIPS and eDIPS:cellulose composites were 27 and 2.7 W m⁻¹ K⁻¹, respectively.[36] Most likely, the lower thermal conductivity reduces the conduction losses to the contacts, thus resulting in an enhancement in temperature. In addition, the results shown in Figure 2c,d provide insight on ideal operating conditions for SOTEGs. Like any heat engine, TEG efficiency will be improved by increasing the temperature difference between the hot and cold sides of the device. Optical concentration could be a means to increase temperature difference, however, at higher temperatures, convection and conduction losses will become more prevalent for nonvacuum operation. As the temperature of the material increases, the temperature difference between the material and the ambient air also increases, thus creating convection currents that reduce temperature. Below 2 sun, the steady-state temperature increased steadily. Above 2 sun, the steady-state temperature started to level off. Prudent SOTEG designs should take this into account in order to minimize complexity and maximize performance.

2.3. Thermoelectric Parameter Characterization

Conventionally, the heat source for TEs is waste heat. By using light as a heat source, secondary light effects might appear. When the energy of an incident photon exceeds the bandgap energy of the TE material, an electron–hole pair can be created. The presence of extra, photogenerated charges could enhance the electrical conductivity of materials by increasing the carrier concentration. An enhancement in electrical conductivity could lead to an enhancement in the TE performance of the material.[19] Traditionally, attempts to achieve higher conductivity by doping methods have shown that the corresponding Seebeck coefficient tends to decrease.[23]

To investigate the effect of light on the electrical conductivity of the materials, the illumination of the solar simulator was cycled on and off. The resistance of the sample was monitored continuously using a two-point method. Figure 3b shows the resistance and temperature response of pristine PEDOT:PSS under illumination. The electrical conductivity rises as soon as the material is illuminated and before its temperature has

![Figure 3. Characterization of TE parameters under 1 sun. a) Schematic of the photo-Seebeck experiment. Temporal resistance and temperature response of b) PEDOT:PSS and c) CoMoCAT CNTs under 1 sun. The yellow and shaded regions indicate the time when the materials were illuminated and in dark, respectively. d) Photo-Seebeck (PS) and “normal” Seebeck (NS) measurement for DMSO-treated PEDOT:PSS. The Seebeck voltage was continuously measured as the materials were heated up (HU) and cooled down (CD). e) Photo-Seebeck and “normal” Seebeck measurement for CoMoCAT CNTs.](https://www.advenergymat.de)
significantly increased. Photoconductivity in PEDOT based systems has been previously reported in the literature.[40] Then, as the temperature of the material increases, the conductivity decreases, as expected for a metallic conductor. Conductivity as a function of temperature was measured separately and indicated that PEDOT:PSS was, indeed, in the metallic state (see Figure S4, Supporting Information). On the other hand, Figure 3c shows the case of CoMoCAT CNTs, where a small photoconductivity effect is observed. Following the Widemann–Franz law, we can deduce that any potential changes in the thermal conductivity upon illumination would be concomitantly small.

To characterize the photo-Seebeck effect, a custom-built setup using a solar simulator was built as shown in Figure 3a. Briefly, using a planar geometry, one end of the sample was illuminated while the other end was covered. As the sample was illuminated, temperature and Seebeck voltage were measured with thermocouples contacted at each end of the sample. When a steady-state temperature was reached, the illumination was turned off, and temperature and the Seebeck voltages were recorded. In a similar fashion, the Seebeck coefficients were measured using a conventional heat source. For DMSO-treated PEDOT:PSS, the Seebeck coefficient was found to be around 5.6 µV K⁻¹, independent of the heat source used, as can be seen in Figure 3d. Similarly, there were no observable photoinduced effects in the Seebeck measurements for CoMoCAT CNTs, which revealed a Seebeck coefficient of around 30 µV K⁻¹, as shown in Figure 3e. The lack of any observable difference on the Seebeck coefficient when heated with light is beneficial to TE performance (cf. decrease in S due to a photoinduced increased charge carrier density). To sum up this section, the major effect of light absorption on the studied organic TE materials is to increase temperature, with no significant side effects observed.

2.4. SOTEG Devices

Organic TE devices are in most cases based on thin-film materials and thus are unable to develop an appreciable temperature difference in the thickness direction. Instead, a temperature gradient is achieved in the lateral direction by heating one side of the film. Figure 4 presents possible device geometries for SOTEGs based on the planar geometry. One feature common to all is that one part is exposed to the Sun while the other part is covered. In Figure 4a, the device could be placed on the edge of a brick, for example. The top surface would be exposed to direct sunlight, while special care would be taken to ensure the lateral side is shaded. The T-shaped device in Figure 4b can potentially be stuck into the soil, where the soil would act as a cool sink. Under direct sunlight, there would be a temperature difference between the top side and the lateral legs stuck into the soil. Alternatively, it could be attached to the underside of a hot surface, such as a solar cell, while the lateral parts act as the fins of a heat sink. In Figure 4c, the top part of the S-shaped device would be exposed to direct sunlight while covering the bottom part of the device, which would cause a temperature difference between the covered end of the leg and the exposed end. In this configuration, however, the electrical contacts could introduce additional losses.

In order to assist in the design of the SOTEG generators, we have experimentally investigated the effect of several geometrical parameters on the output power of a single SOTEG leg. The amount of power that can be extracted will be directly dependent on the illuminated area and the leg length. Using a custom-built setup, the materials were illuminated using a solar simulator and the illuminated area of each sample was varied using a translation stage and a cover. Before beginning the measurement, the internal resistance of the materials was measured, and a variable resistance was connected in series to

Figure 4. Possible device architectures of SOTEGs. a) L-shaped device where the top part is exposed to sunlight. b) T-shaped device where the top part is exposed to sunlight and the bottom part can be stuck into soil, for example. c) S-shaped devices where the top part is exposed to sunlight and positioned to cover the bottom part. d) U-shaped devices where the top part is exposed to sunlight and the bottom part is in contact with the ground.
the sample. A nanovoltmeter measured the voltage drop across the load resistor to the circuit to measure the $I$–$V$ curves and power generated by the materials. The measured voltages for each sample can be found in Figures S5–S8 (Supporting Information). Figure 5b displays the maximum power extracted as a function of the illuminated area for pure eDIPS and for the eDIPS:cellulose composite under 2 suns. The cellulose introduces porosity and a low thermal conductivity component into the CNTs that leads to a lower effective thermal conductivity but also reduces the electrical conductivity.[36] The reduced electrical conductivity is compensated by the lower thermal conductivity (Figures S9 and S10, Supporting Information), so the overall performance of the two CNT materials is similar. To achieve a maximum power of $\approx 4$ nW only 40% of the material needs to be illuminated. Figure 5c shows individual $P$–$V$ curves of eDIPS for different amounts of illuminated area. Maximum power is obtained when the load resistance is matched to the resistance, which deviated slightly $\approx 5.7$ ohms.

The influence of leg length on power is shown in Figure 5d. A sample of pure eDIPS was cut multiple times, and the power extracted was measured. It is worthy to note that the amount of area that needs to be illuminated is expected to vary as the sample is shortened (Figure S11, Supporting Information). As the length of the sample was shortened, the resistance of the sample also decreased. However, the TE voltage across the sample was maintained, thus leading to an increase in the amount of power generated. At very small lengths, the thermovoltage across the sample began to decrease due to thermal equilibration, thus leading to a decrease in the amount of power generated.

2.5. SOTEG Geometries with Concentration

In this section, we propose a series of possible device architectures for SOTEGs with concentrating mirrors (Figure 6). An incorporated mirror can serve two purposes, with one being to cover one end of the generator and the other to concentrate the incident solar radiation onto the other end of the SOTEG. In such configurations, sunlight could readily be concentrated to more than 1 sun on the exposed end of the SOTEG. As previously discussed, a device operating under 2 sun may be ideal because there is a compromise between TEG efficiency and heat losses.

The amount of concentration will depend on the incidence angle of incoming radiation, the length of the legs of the SOTEG, and the angle between the mirror and the exposed part of the SOTEG. Figure 7a shows a schematic for light concentration on to the exposed side of the SOTEG of the type shown in Figure 6b, where $L_1$ is the base length of the exposed part and $L_2$ is the base length of the covered part. The amount of light concentrated on to the exposed part of the leg can be defined as

$$C = \frac{L_1 + L_2}{L_1}$$

The exposed and covered leg lengths can be found using geometry.

$$\tan \beta' = \frac{L_1}{H}$$

$$\tan \alpha' = \frac{L_2}{H}$$

Figure 5. Electrical characterization of the TE materials as a function of the illuminated area and leg length. a) Schematic of the power output experiment where A is the area of the entire leg and B is the illuminated area. b) Power output as a function of the illuminated area for eDIPS CNTs (wine triangles) and eDIPS:cellulose (half-filled wine triangles). c) Power curves for eDIPS CNTs for different amounts of illuminated area. d) Power as a function of the distance between electrodes (leg length).
Combing Equations (4–6), we can arrive at an expression for $C$ in terms of $\alpha'$ and $\beta'$.

$$C = 1 + \frac{\tan \alpha'}{\tan \beta'}$$  \hspace{1cm} (7)

The most trivial case is the concentration factor 2, which is obtained when $\alpha' = \beta'$, i.e., a symmetric V-shaped geometry. Similar geometries have been proposed for organic photovoltaics.[41] The mathematical description of the concentration power for the design shown in Figure 6c can be found in Figure S18 (Supporting Information).

Using an architecture similar to the one shown in Figure 6b, we fabricated a proof-of-concept SOTEG consisting of 6 legs and a concentrating mirror. The p-type material was chosen to be eDIPS, while the n-type material was PEI-doped eDIPS. The measured Seebeck coefficients for the pristine eDIPS and PEI-doped eDIPS were 45 and $-35 \, \mu$V K$^{-1}$, respectively (Figures S14 and S15, Supporting Information). The dimension of the legs was 1.5 cm in length by 0.8 cm in width to accommodate for the findings in the previous sections (see Figure 5b,d). The support material was black PLA printed using a 3D printer. A schematic of the SOTEG and a picture of the actual device can be found in Figure 7b and Figure S17 in Supporting Information, respectively.

Figure 7c shows the power generated from the SOTEG as a function of irradiance. Additional characterization of the generator can be found in the supplementary information. Reassuringly, this simple, yet unoptimized, SOTEG generates around 0.18 $\mu$W of power under 1 sun, which due to the presence of the concentrating/shadowing mirror, becomes effectively 2 suns. The simplicity of design for SOTEG, together with the fact that organic semiconductors are based on abundant low-toxicity materials (cf. many inorganic TE) that are potentially reclaimable, makes this technology attractive to power low-consumption electronics, such as sensors being developed for the Internet of Things and for environmental monitoring.[36] This is particularly so for sensors located in areas where photovoltaics might have difficulties to operate reliably, such as deserts (heat and dust strongly decreases silicon PV efficiency) and forests (where oscillating leaf-shadowing may cause catastrophic PV failure).

3. Perspective

In this section, we will briefly outline a number of additional aspects that should be considered to evaluate the potential of SOTEGs.

The first aspect considers the scalability of the proposed planar geometry. From the leg-length experiments, we can determine that for our geometry, there will not be any benefits above a leg length of about 1 cm. Instead, more legs should be added to increase power output. In this respect, SOTEG power output scales linearly with the device area provided that the area is covered with additional legs. On the other hand, the power output will scale quadratically with temperature. This means...
that for SOTEGs operating at low temperatures (corresponding to small convection losses), power scales quadratically with solar concentration. Our unoptimized generator shows power densities of the order of $0.1 \mu W \text{ cm}^{-2}$, which could be enhanced by two orders of magnitude by using organic thermoelectrics with record $zT$s (up to around $10 \mu W \text{ cm}^{-2}$). Highly optimized STEGs with very high optical/thermal concentration have been reported to reach higher power densities, up to $10 \text{ mW cm}^{-2}$ (see Table S2, Supporting Information). This suggests that, beyond the use of better materials, further optimization in the design of the SOTEG geometry needs to be carried out.

Another important aspect that deserves further study is doping. For SOTEGs, doping plays the dual role of not only determining the thermoelectric properties (via the well-known trade-off between $S$, $\sigma$, and $\kappa$), but also the optical properties. The introduction of dopants may shift the absorption to longer wavelengths due to the formation of polarons. Additionally, it may quench radiative recombination, thereby generating more heat. For example, changing the doping level of PEDOT:PSS, can lead to a slight enhancement in IR absorption due to delocalized charge carriers that contribute to the Drude tail. Doping stability may also be affected by using light as a source of heat. It remains to be investigated how far the optimal doping level of a SOTEG is shifted from that of the regular OTE use case due to these optical effects.

Last but not least, compared to this initial exploration, using an optimized organic thermoelectric material, such as PEDOT:PSS with a reported $zT = 0.42$, could increase the thermoelectric conversion efficiency by about a hundred times, approaching 1% efficiency (see Figure 1) and a power output of $10 \mu W \text{ cm}^{-2}$ for a generator under the same conditions. We expect even higher efficiencies upon optimizing the device geometry further. Table S2 (Supporting Information) summarizes some of the results of STEGs reported in the literature. While our proposed geometry is still not competitive on a power-per-area basis, it may well be worthwhile from a power-per-weight standpoint. Finally, it is yet to be determined if an increase in organic photovoltaic performance could be achieved by coupling it to a SOTEG.

4. Conclusion

In this work, we demonstrate the potential of organic TE materials to harvest the solar radiation in a SOTEG configuration. Organic materials are able to absorb incident solar radiation, so in addition to being used as a TE, they can simultaneously be used as a solar absorber, greatly simplifying the geometry and minimizing coupling losses. Temperatures rising more than 50 K
have been observed for most benchmark organic TE upon illumination with a solar simulator and a concentration factor of 2. On the other hand, we have observed a small enhancement in the electrical conductivity of CoMoCAT CNTs and PEDOT:PSS under illumination with no noticeable impact on the Seebeck coefficient. Generally speaking, CNT-containing samples tend to combine cellulose with organic TE materials. For instance, under 2 suns, 4 nWs of power are generated by a single TE leg made of a eDIPS-cellulose composite. Furthermore, we have presented possible device architectures for SOTEGs that incorporate concentrating mirrors. Finally, we have fabricated a proof-of-concept SOTEG with 6 legs, outputting 180 nW under 2 suns. The here demonstrated strong potential of organics to yield simple and efficient SOTEG designs opens the path towards powering small sensors for the Internet of Things and environmental monitoring in locations where PV is unreliable, and the use of abundant, low-toxicity materials is required.

5. Experimental Section

SG65i CoMoCAT single-wall carbon nanotubes were bought from Sigma-Aldrich. eDIPS CNTs were bought from Meijo Nano Carbon. The CNTs were dispersed in an aqueous solution of sodium dodecylbenzenesulfonate (SDBS). Fifty milliliter SDBS solutions with an initial concentration of 1 mg mL\(^{-1}\) were mixed with 10 mg of CNTs. The dispersions were sonicated at 15 ± 5 °C in a bath sonicator and then centrifuged at 6000 rpm for 6 h. Once dispersed, the dispersion was filtered through porous filter paper (PVDF membranes with a 0.2 µm pore size) to achieve thick buckypaper films. Buckypaper thicker than ~5 µm can easily be removed from the supporting filter paper, giving freestanding samples. The preparation of bacterial cellulose CNT composites is explained in detail in an earlier publication.[36] Briefly, bacterial cellulose fibers are grown in an aqueous medium, in the presence of dispersed CNTs, forming well-intermixed films. After washing and drying, the ~10 µm films resemble buckypapers, yet contain only about 10 wt% CNTs, and correspondingly have lower electrical and thermal conductivities.

An aqueous dispersion of PEDOT:PSS (Heraeus Clevisol AI 4083) was bought from Heraeus. Thick, freestanding films (~5 µm) were prepared by drop-casting the aqueous PEDOT:PSS onto PET substrates and allowing them to dry. Due to the poor adhesion of PEDOT:PSS on PET substrates, freestanding films of PEDOT:PSS can be achieved by carefully peeling the dried PEDOT:PSS films that are thicker than 5 µm from the PET substrates. For the DMF-O treated films, DMF was purchased from Sigma-Aldrich and added directly (5%, v/v) to the polymer dispersion. The DMF/PEDOT:PSS dispersion was then drop-casted in a similar fashion as the regular PEDOT:PSS films.

Poly(3-hexylthiophene-2,5-diyl) (P3HT) and poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT-C14) were purchased from Sigma-Aldrich. P3HT was dissolved in chloroform (CF) at a concentration of 7.5 mg mL\(^{-1}\), and thin films were fabricated by spin-coating on glass substrates. Thick, freestanding films of P3HT were obtained by drop-casting in a similar fashion to the freestanding PEDOT:PSS films. PBTTT-C14 was dissolved in chlorobenzene (CB) at a concentration of 20 mg mL\(^{-1}\). Solutions were stirred at 110 °C for three hours and blade coated using a preheated blade coater at 110 °C. A blade height of 200 µm and a speed of 30 mm s\(^{-1}\) were used. Finally, the polymer films were thermally annealed for 30 min at 180 °C and then cooled slowly to room temperature. The doped PBTTT-C14 samples were prepared in a custom-built doping vessel consisting of a 200 mL modified reactor beaker with a heating cartridge on top to hold and heat the sample. The temperature was measured with two k-type thermocouples attached to the heating cartridge and the bottom of the beaker, respectively. Then, ~5 mg of 2,3,5,6-tetrafluoro-2,5-cyclohexadiene-1,4-diyldenedimalononitrile (FT,T-CNQ) on the bottom of the beaker were preheated to 210 °C. The polymer films were placed on the heating cartridge facing the FT,T-CNQ and heated to 130 °C. The system was then sealed and evacuated to 70 kPa.[37] Film thickness was measured using a digital micrometer (Mitutoyo High-Accuracy Digimatic).

Temperature response as a function of irradiance was measured on freestanding films with a solar simulator and an Optiris PI 450 IR camera. The freestanding films were mechanically supported on an annular metal ring and placed under the solar simulator. The IR camera measured the temperature in the middle of the materials (away from the supported edges) under illumination. The materials were illuminated for 5 min to allow the materials to reach a steady-state temperature.

The average Seebeck coefficient was measured using a custom built setup. For the “normal” Seebeck measurement, opposite sides of the sample were placed on a heater and a heat sink, respectively, and contacted electrically with silver paste. For the photo-Seebeck measurement, a solar simulator was used instead of a heater. The temperature gradient between the two contacts was slowly ramped from 0 to 10 K and back. The temperatures and the Seebeck voltages were measured with type T thermocouples using a Keithley 2400 SourceMeter.

Electrical and temperature response upon illumination were characterized using a two probe method and a T-type thermocouple, respectively. Electrical resistance was measured over time using a Keithley 2400 SourceMeter, while a T-type thermocouple simultaneously recorded temperature.

Film absorbance was measured on spin-coated thin samples, using an FTIR (Bruker Vertex 70) attached to an optical microscope (Hyperion). Polyethyleneimine (PEI) was purchased from Sigma Aldrich and used as received. PEI was dissolved in ethanol in a concentration of 5 mg mL\(^{-1}\) and dry eDIPS buckypaper mats were immersed in the PEI/ethanol solution for 15 min. The mats were then quickly dipped in pure ethanol and annealed at 100 °C for 10 min.

The base material for the SOTEG was 3D printed from PLA. The p-type legs were cut from eDIPS buckypaper mats, ~1.5 cm in length by 0.8 cm in width. The n-type legs were cut from the PEI-doped eDIPS mats, approximately of the same dimensions. The interconnects were made using a combination of silver paste and aluminum foil. One side of the legs was exposed while a mirror was covering the other side of the legs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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