Molecular Solar Thermal Power Generation

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Introduction

With an increasing global population, total worldwide energy use from all sectors is expected to reach 21 TWy by 2040, corresponding to an increase of 130% compared to 2019.¹ Electricity, alone, is an essential commodity in modern society, and around 3 TW is currently used each year. To complicate matters, about 85% of this current power is derived from fossil fuels.² Therefore, the development of cleaner technologies for generating electricity is becoming increasingly important to offset negative environmental impacts. Solar energy is the most abundant energy resource on Earth, and committing to maximize the utilization of solar power can potentially meet this intensive demand while reducing detrimental effects to the environment.³ In fact, the total solar power that reaches Earth during a year is estimated to be 2.3×10^4 TWy, which equates to only seven hours of sunlight needed to address current annual global energy requirements.^{4,5}

Photovoltaics (**PV**) can directly transform solar energy into electrical power.⁶⁻¹¹ At the end of 2018, the annual global solar **PV** power capacity reached around 508 GW.¹² Natural variations in solar intensity with time and geographical location currently limit the utilization of **PV**; obviously, solar cells do not produce power during the night. Solar thermal power plants with phase change molten salts can generate power for several hours after sunset; however, these plants require solar concentrators of very large dimensions.^{13,14} Hence, it is of our interest to explore alternatives and compact technologies that can derive and store energy from the sun and later provide an energy source for electrical power generation.

To achieve solar energy storage, we have set out to use a class of materials that can capture sunlight via reversible photochemical reactions, and later release the stored energy on-demand; these materials are operating in a closed cycle. Such materials incorporate the use of photochromic chemical compounds, and so form the basis of molecular solar thermal energy

storage systems (**MOST**).¹⁵⁻¹⁸ Upon exposure to sunlight, a suitable **MOST** material can photoisomerize to a high-energy metastable photoisomer, which preferably, can be stored in this form for extended periods of time. Depending on the photoswitch used, the back conversion reaction releasing heat energy can be triggered through different processes, including thermal,^{19,20} catalytic,^{21,22} electrocatalytic,^{23,24} or photoinduced back conversion.²⁵⁻²⁷ Such heat produced can be delivered locally and on-demand, as opposed to almost any other known thermal storage technology.

While **MOST** in closed cycle devices can be used for efficient storage and release of energy in the form of heat, additional engineering is necessary to address the electrical power generation from this heat production. Thermoelectric generator (**TEG**) devices can create electrical power from heat sources, and it has been used in various applications.²⁸ Recently, new technological advances that enable power production from smaller temperature gradients using innovative micromechanical design are emerging.²⁹⁻³⁴

In this work, **MOST** systems are, for the first time, combined with an integrated microelectromechanical thermoelectric generation device (**MEMS-TEG**)³⁵⁻³⁷ to demonstrate the cascading energy flow from solar harvesting and storage to heat energy release which is finally used to generate power (see Figure. 1). Two photoswitches with suitable properties, a norbornadiene derivative (**NBD**) investigated as a solution and a phase interconvertible arylazopyrazole derivative (**AZO**) measured as a neat film, were selected for their potential to produce electricity. We characterized and coupled each of these photoswitches individually with an ultrathin highly sensitive **MEMS-TEG** chip (20 x 20 mm), demonstrating that **MOST** stored chemical energy could successfully generate electrical power, thus affirming that solar energy for electrical power generation can be independent of time and geographical restrictions.

Figure 1. Schematic illustration of MOST to power generation concept. Solar energy can be collected by a **MOST** material. The stored energy can be released on-demand as latent heat, which is then converted to applicable power through a **MEMS-TEG** chip.

Results and discussion

Solar energy storage properties

MOST systems have been demonstrated formerly to function both in liquid and film forms, which can be tailored towards different applications.^{21,38-45} Liquid form **MOST** provides the opportunity to transport stored energy, e.g., that energy storage and release could, in principle, be in two different locations. On the other hand, a **MOST** based film provides opportunities in terms of possible applications in smart windows and other device integrations.^{43,46} Herein, we selected and tested two systems, **NBD** in liquid form (toluene solution), and neat **AZO** in thin films that features suitable energy capture and storage functionality. The molecular structures of both photoswitch couples are shown in Figure. 2a. The photoconversion of **NBD** proceeds via a $[2+2\pi]$ cycloaddition reaction to its corresponding photoisomer **QC**. Thus, the energy storage density $\Delta H_{\text{storage}}$ was experimentally determined to be $93 \text{ kJ}\cdot\text{mol}^{-1}$ ($367 \text{ kJ}\cdot\text{kg}^{-1}$). Meanwhile, **QC** possesses a thermal back conversion half-life of one month at room temperature, demonstrating the possibility for long-term storage of **QC** in toluene. Spectroscopically, **NBD** exhibits an absorption feature around 340 nm with a maximum absorptivity of $\epsilon_{\text{max}@340 \text{ nm}} = 1.4 \times 10^4 \text{ M}^{-1}\cdot\text{cm}^{-1}$. In contrast, the absorption profile of **QC** is virtually negligible above 300 nm, consequently leaving a large transparent optical window

between both forms (Figure. 2b). This significant spectral difference enables near quantitative photoconversion, even in concentrated solutions. In addition, the photoisomerization quantum yield was measured in toluene to be 68%. With all the above suitable **MOST** properties considered, the solar energy storage efficiency of the system could reach upwards of 0.70%.³⁸ (see, Supplementary S2 for calculations)

Figure 2. a) Molecular structures of **NBD-QC** couple (top) and *trans/cis*-**AZO** photoswitch couple (bottom). A thermal (Δ) or catalytic route (cat.) can facilitate the back-conversion of **QC** $\rightarrow$ **NBD**. The back-conversion of *cis* $\rightarrow$ *trans*-**AZO** can be achieved by a thermal or light-induced activation; b) Absorption profile of **NBD** before and after irradiation with 340 nm light (in toluene); c) Absorption profile of **AZO** photoswitch before and after irradiation with 365 nm light (in acetonitrile).

To take advantage of not just the exothermic process from photoisomerization reaction, but also from an additional phase change process (liquid $\rightarrow$ crystal), **AZO** photoswitch was investigated in its neat form. Previously, phase change materials (**PCM**) and **TEG** devices have been investigated for refrigeration applications.⁴⁷ However, **PCM** can only release the stored

latent heat, and the heat release is greatly dependent on the threshold temperature for the reverse phase change to occur. Currently, azo-based compounds have been chemically designed with **PCM** properties to improve the energy storage density.^{46,48-51} In case of *cis*-**AZO**, the stored energy can be easily released by irradiation with a 532 nm light source even with a low absorptivity.⁵² As shown in Figure. 2c, the absorption maximum of the trans-isomer is located at 344 nm with an absorptivity of $\epsilon_{\text{max}@340\text{ nm}} = 2.9 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$, which is twice the extinction coefficient as the maxima determined for **NBD**, in addition to an $\lambda_{\text{onset}} = 484 \text{ nm}$. Unfortunately, **AZO** has a quantum yield of only 41%; however, such value is still considered high for azo-based photoswitches. The photoisomerization energy density ΔH_{isom} was measured as 52 $\text{kJ} \cdot \text{mol}^{-1}$ (168 $\text{kJ} \cdot \text{kg}^{-1}$). In addition to heat release from the chemical reaction, the crystal-to-liquid transition ($\Delta H_{\text{phase_change}}$) can provide an additional 50 $\text{kJ} \cdot \text{mol}^{-1}$ (161 $\text{kJ} \cdot \text{kg}^{-1}$) of thermal energy. As a result, the solar energy storage efficiency for **AZO** was previously estimated to be 1.2%, much higher than previously measured azobenzene photoswitches.⁴⁰ Moreover, *cis*-**AZO** is remarkably stable at room temperature, with a thermal half-life of three months at 25 °C. Thus, the advantage of using such a photoswitch would be from a neat film to take advantage of energy storage from two different sources of energy notably thermal ambient energy and light.^{46,52}

Photoconversion in device under various exposure times and complete interconversion through multiple cycles are important tests for the viability of any given photoswitch in a **MOST** system. These experimental factors have previously been reported for **AZO**.^{46,52} Therefore, additional experiments were necessary for **NBD** to determine the compatibility of this photoswitch for the sake of this study. A custom made 400 mm² microfluidic reactor was used for this photoconversion experiment. (See supplementary S3 for details) A solution of 0.1 M **NBD** (25 $\text{g} \cdot \text{L}^{-1}$) in toluene-*d*₈ was pumped through the microfluidic reactor with residence times that varied from 34 s to 343 s. The degree of photoconversion could be conveniently monitored

immediately afterwards by ^1H NMR spectroscopy. For an ideal **MOST** system, where the absorption of the photoisomer, in this case, **QC**, does not compete with the absorption of the parent **NBD**, the energy storage efficiency, η_{MOST} , should remain approximately unchanged prior to full conversion.^{40,45,53} Here, We observed a decrease in solar energy storage efficiency from $\approx 0.5\%$ at short residence times to 0.25% at full conversion. While not ideal, it is normal to observe a lowering of efficiency progressively during the conversion process. To date, in this context, this is the best system compared to our previous flow conversion results (see Figure 3a).²¹ (See supplementary S4 for details)

Typically, for cyclability testing, solution based photoswitches are irradiated at time intervals at elevated temperatures.^{21,45} However, this method seemed impractical as **QC**, exhibits a long half-life ($t_{1/2} \approx 29$ days) in toluene. By taking this into consideration, an alternate protocol was employed which hastened the time frame for each successive cycle. Previously, It has been found that cobalt (II) phthalocyanine physisorbed on activated carbon (**CoPc@C**), can rapidly facilitate the back-reaction of a very similar quadricyclane structure.²¹ This new setup involved converting and back-converting continuously a **NBD** solution (0.5 mM in toluene) through the microfluidic reactor and the copper catalytic reactor in a closed cycle. Much to our delight, after 54 charge and discharge cycles on **NBD**, no obvious drop in performance was observed. (See figure 3b and 3c, supplementary S5 for details) It should be noted that, with such a setup, the total experimental time could be drastically reduced to only 61 hours.

Figure 3. a) Conversion percentage (in blue) and calculated energy storage efficiency (in red) of 0.1 M **NBD** in toluene as a function of residence time in the device. The solar simulator was calibrated to AM 1.5 solar irradiance; b) Normalized absorbance before irradiation with 340 nm LED light and after catalytic reactor. It has been observed that after 54 cycles, no degradation was observed; Blue dots show the normalized absorbance at 340 nm, red dots show the normalized absorbance after irradiation. c) Cycling test setup for **NBD**. Box 1 and 2 represent the flow UV-Vis spectrometer before and after a catalytic reaction centre. Box 3 refers to the microfluidic chip. 3 mg of **CoPc@C** was loaded in the plastic reaction centre. Around 4 mL of 0.5 mM **NBD** in toluene was prepared and passed through the whole setup with a speed of $50 \mu\text{L} \cdot \text{min}^{-1}$. The conversion process has proceeded with irradiation from a 340 nm LED lamp.

Stored energy release for **NBD** and **AZO**

Once solar energy is stored as **QC** and *cis*-**AZO**, one should be able to release the chemical energy from these metastable compounds as heat. However, it was prudent to perform simulations to determine theoretically how much energy could actually be extracted from these charged materials. To achieve this, a simulation of potential temperature increases based on molecular parameters was performed. In the case of **NBD**, the maximum temperature gradient had a dependence on the saturation point of **QC** in toluene. According to these calculations, the maximum temperature gradient under adiabatic conditions from the charged **QC** solution was estimated to be 40° C, based on saturated concentration of **NBD** in toluene. (0.78 M, see supplementary S6 for details)

We designed a fixed bed catalytic heat release device consisting of a copper tube flanked on two sides with copper plates to maximize heat transfer for later coupling with the **MEMS-TEG** device. (See supplementary S7 for details) By taking advantage of the mobile nature of the **QC**

solution, a heterogenous **CoPc@C** catalyst²¹ was loaded inside the copper tube, and a thermally conductive pad was used to provide a homogeneous thermal distribution through the tube to all areas of the device. A saturated **NBD** solution was initially photoconverted to **QC**, and then pumped through the copper reactor with a flow speed of 5 mL·h⁻¹. This speed leads to complete back-conversion from **QC** to **NBD** and a maximum surface temperature of 37°C (≈13°C temperature gradient), determined by a thermal camera focusing on the top of the device.

Concerning *trans/cis*-**AZO** photoswitch couple, the charged *cis* isomer releases 168 kJ·kg⁻¹ equating to simulated heat increase of 84°C. From here, an additional 161 kJ·kg⁻¹ can be extracted at the crystallisation point of the *trans*-**AZO** (melting point 83 °C) from the phase change event. Thus, *cis*-**AZO** theoretically shows a larger potential thermal gradient than the **QC** solution. In this case, the experimental measurement for the heat release involved the placement of a droplet of liquid *cis*-**AZO** (≈ 8 mg) under ambient conditions onto a glass substrate (1 cm x 0.7 cm). A 532 nm laser was used to irradiate the sample and trigger the heat release in conjunction with a thermal camera. Consequently, a full back-conversion was triggered, affording a maximum surface temperature of 52°C, corresponding to a 17°C temperature gradient after the heat contribution from the laser had been accounted for. The large temperature gradient difference between theoretical and experimental values is likely because of the strong heat dissipation from this thin film under ambient conditions (Figure 4b, see supplementary S8 for details)

Accordingly, both solution-based **NBD** and neat **AZO** photoswitches can successfully generate heat, we now turned our attention towards utilising this heat energy and converting it to electrical power by coupling these two **MOST** formats with a **MEMS-TEG** device.

Figure 4. a) Recorded temperature increment of **QC** heat release over time; Inserted picture shows the thermal image from the heat releasing copper device. The area indicated by the dashed line represents the device position. A maximum absolute temperature of up to 37 °C was recorded (temperature gradient of 13 °C); b) Recorded temperature increment of **AZO** system over time; Inserted picture: thermal image from the heat releasing *cis*-**AZO** sample. The dashed line represents the position of the compound. A maximum absolute temperature increase of 52 °C was recorded (temperature gradient of 17 °C after the heat generated from the laser is subtracted.);

Power generation from NBD and AZO

For the coupled power generation, we used one of the most efficient heat to power converters available, an ultrathin 800 nm N-type Bi₂Te₃/(Au), P-type Sb₂Te₃ multi-layered chip. The unit structure is designed in □ shape, with a resistance of 0.3 Ω and a single P/N surface area of 200 μm x 200 μm. (see Figure 5a and see supplementary S9 for details). In total, 572 units were connected in series, where the height of each thermoelectric column does not exceed 1 μm, and the thickness of the gold electrode is about 300 nm. Most importantly, the thickness of the working part of the chip does not exceed 2 μm. Thus, its ultrathin structure can respond effectively to temperature variations as little as 1×10^{-4} K.³⁵

Figure 5. a) Schematic concept of **MOST** to power generation. The heat from the discharging **MOST** material can create heat flow to drive a **MEMS-TEG** chip for power generation; b) **NBD** solar energy storage for power generation experimental setup. The copper catalytic reactor was placed on top of the **MEMS-TEG** chip with a thermally conductive pad in between. The whole device was later fixed on top of an aluminum brick with and fully covered with a thermal insulation polymer to diminish the heat dissipation into the surrounding environment; The inset picture shows the actual device photo. The scale bar corresponds to 1 cm; c) Heat release monitoring by thermocouple and voltage generated from **MEMS-TEG** chip over time. A maximum voltage up to 0.18 mV was successfully observed; d) Schematic experimental setup of **AZO** solar energy for power generation. *cis*-**AZO** sample was drop cast on the surface of the thermally conductive pad, then positioned on the top of the **MEMS-TEG** chip. A PET

film set on top of the **AZO** sample ensured a homogeneous distribution of the **MOST** material. The back-conversion is triggered by a laser source of 532 nm ($110 \text{ mW}\cdot\text{cm}^{-2}$, the beam diameter of 1.3 cm. The laser source was able to illuminate all areas of **AZO** sample continuously); The inset picture shows the actual device photo. Scale bar corresponds to 1 cm; e) Net voltage generated from **MEMS-TEG** chip over time. A maximum voltage up to 0.13 mV was successfully observed.

Based on the physical properties of **NBD** and **AZO**, two heat-to-power generation device concepts were put forth. For the **NBD** system, a saturated solution of **QC** in toluene was prepared in Gothenburg, Sweden, using a photochemical flow reactor (See supplementary S10 for details) and shipped to Shanghai, China. For this experiment, 5 mg of **CoPc@C** was loaded inside the catalytic reactor (inside the central copper tube), where a thermally conductive pad was used to fill the gap between copper plates in the device (see Figure 5b). The reactor was placed above the **MEMS-TEG** chip, and the whole setup was then placed on top of an aluminum brick heat sink, which ensured a stable ambient temperature and served as the cold side of the device. Importantly, a thermally insulated plastic foam was used to cover the hot side of the system to ensure that the heat generated is reflected instead of losing to the environment. As a result, with less than 1 mL of a 0.78 M solution and a flow speed of $5 \text{ mL}\cdot\text{h}^{-1}$, a measured bias voltage of up to 0.18 mV was recorded. According to **MEMS-TEG** chip characterization, this voltage can generate an output power of $\approx 0.05 \text{ nW}^{35}$ (surface output power of $1.2 \text{ mW}\cdot\text{m}^{-2}$). As the operating time of the experiment is around 800 s, the average heat to electric power conversion efficiency was calculated to be $0.56 \times 10^{-7} \%$ (see Figure 5c).

In the case of **AZO**, a smaller amount of material was employed. In this instance, 7 mg of *cis*-**AZO**, generated from a 365 nm LED light source, was loaded onto the thermally conductive pad. A PET film was gently pressed on top of the material to allow the material to fully cover the surface of the **MEMS-TEG** chip evenly. Laser irradiation at 532 nm triggered the back

conversion (see Figure 5d), leading to a bias output voltage up to 0.13 mV. Such value corresponds to a maximum output power of 0.02 nW (surface power density of $0.6 \text{ mW} \cdot \text{m}^{-2}$). With a heat release time of around 200 s, the average heat to electric power conversion efficiency in this case is calculated to be $1.7 \times 10^{-7} \%$. (See supplementary S11 for details) Interestingly, various peaks were observed when the voltage approached the maximum. This was likely due to the complex heat release behaviour that involved both photo-isomerization and phase transitions. (see Figure 5e) It can also be observed from the figures that less power is generated from **AZO** than from **NBD**, although the former reached a higher surface temperature. Not surprisingly, this is because the amount of heat that is released from these two systems is markedly different, as 1 mL of 0.78 M **QC** could ideally produce 72.5 J, while 7 mg coated **AZO** was only capable of producing 2.3 J of energy.

Hence, to the best of our knowledge, both results show for the first time, a proof-of-principle of solution based **MOST** and **PCM-MOST** systems that have been used to generate electric power. Future developments should focus on red shifting the absorption band (capturing more sun light) and increasing the temperature gradient produced in the back reaction (improving energy density). In addition, as the proof-of-concept, the thermoelectric conversion efficiencies for both demonstrations need to be further improved with mechanical design. A future device construction should include a better thermal management system to avoid heat dissipation from **MOST** to the surrounding environment, thereby increasing the amount of heat energy converted to electrical output power. For instance, in an ideal case, the thermoelectric efficiency is estimated to be up to 10% (See Supplementary S12 for details). If we produce a highly soluble photoswitch of ca. 1.5 M, accompanied by a heat release of 100 kJ mol^{-1} with a $5 \text{ mL} \cdot \text{h}^{-1}$ flow speed, and assuming that an absolute temperature of $100 \text{ }^{\circ}\text{C}$ could be achieved, which is close to what has recently been demonstrated.²¹ The system should be able to produce

an output power of 40 mW ($500 \text{ kW} \cdot \text{m}^{-2}$), enough to power a low power supplied internet of things (IoT) device.⁵⁴

Conclusions

In this work, we have explored the use of two molecular photoswitches in a different physical form (liquid-based **NBD** and neat **AZO** film), for the purpose coupling **MOST** with thermoelectric device. The liquid-based **NBD** exhibits a solar energy storage efficiency of $\approx 0.5\%$ with only 0.5 mM in toluene, more competitive with photosynthesis (0.1%-0.3%).⁵⁵ In addition, the compound was tested through 54 charge and discharge cycles in a continuously operating energy storage and catalysed release cycle, showing no sign of degradation. Alternatively, The **PCM-MOST** hybrid neat **AZO** film captures and releases energy in photochemical solid-liquid transitions, which allows the **MOST** to harness energy both from sunlight and from the ambient environment, meaning that upgraded heat can be produced on-demand.

To demonstrate **MOST** to power generation, an ultrathin, highly sensitive **MEMS-TEG** device was used to capture the heat released arising from either scenario. For the first time, electricity was produced in this setup, with output power up to 0.05 nW (output power per unit surface up to $1.2 \text{ mW} \cdot \text{m}^{-2}$). We note that this is a very compact and local solar energy storage system that operates through an entirely different mechanism than traditional photovoltaic – battery storage combinations. Furthermore, these types of system have the possibility of being charged and discharged across different geographic locations (Sweden to China in this work), ultimately showing the potential of storing and using solar energy for power generation. While the efficiencies of the systems need to be improved, we envision such systems used in future local power generation applications.

Author contributions

Z. W. performed all the material characterizations, conversion tests, cycling tests, heat release experiments, and power generation demonstrations. E.M. and Z.Y.Z. performed the heat release experiments and power generation experiments. Y. L., X. F. and F. W. performed MEMS-TEG chip fabrication. Z. Wu. carried out the thermoelectric efficiency simulation. J.O.H performed the sample preparation with an automated flow system. M.J. and Z.Y.Z synthesized the used compounds. Z. W., Z. H., T.L., and K.M.P. designed the experiments. All authors contributed to writing the manuscript.

Conflicts of interest

There are no conflicts to declare.

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