Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information

Table of content:

I. Materials and Methods

General

A class B/C Solarlux solar simulator was used to irradiate the device; a Sciencetech sun calibrated reference detector was used to measure the solar simulator lamps intensity; T-Type Thermocouples coupled to an Agilent 34972A data acquisition unit were used to measure the temperatures. A fused silica custom made microfluidic chip (Litcon) was used as MOST collector; Maker Bot 3D printer, PTFE tubes and bicomponent epoxy glue (Epotek 301-2) were used to fabricate the hybrid device; two single syringe pumps (Fisher Scientific) were used to control the flow rate in the devices; T-junctions from Scanivalve were used for the insertion of the thermocouples. ^{1}H-NMR spectra were obtained at 400 MHz, using a Varian 400/54 MHz spectrometer; differential scanning calorimetry (DSC) experiments were carried out using a Mettler Toledo DSC 2. UV-vis spectroscopy was carried out using an Agilent Cary 4000 UV-Vis spectrometer. LED light source (Thorlabs - M365F1, 365 nm) was used for the cyclability test. **1** and **2** were synthesized according to previously published procedures[1,2]; Toluene-d_8 was purchased from Sigma Aldrich.

Hybrid device

The solar water heating (SWH) and molecular solar thermal energy storage (MOST) hybrid device was built in the following way. The SWH collector was made combining a 3D printed plastic flow collector (figure S1 b) with a microscope cover slide made of quartz glass (the two parts were glued together using epoxy glue). Two thermocouples inserted through T-pieces were used to monitor the temperature before and after the SWH collector (figure S1, c and d). The MOST collector was a custom-made fused silica microfluidic chip (Figure S1 a) previously used in another device[3] fabricated by us. The chip has a 60 μm deep and 3.5 mm wide winding channel, forming a total irradiated area of 400 mm^2 and an internal volume of 25 μl. Placing the MOST collector on top of the SWH made the hybrid device, as seen in Figure S1e. The flow in the two collectors was regulated using two syringe pumps. Two syringe needles (with the pointy extremity cut) were carefully glued to the inlet and outlet holes. The syringe needles on the silica chip were connected to PTFE tubes, and sealed with epoxy glue. The tubes were connected to a syringe pump and the outlet to a vial or an NMR tube. To calibrate the intensity of the lamp of the solar simulator a diode connected to a data acquisition unit was used. The device was positioned in a way that it received the intensity of a 1.5 AM standard solar spectrum (1000 wm^2).

A triple layer insulating mask composed of cardboard, insulating plastic and aluminium foil was used during the experiments to avoid parasitic heating of thermocouples, syringes, and connection tubes, leaving only the collectors exposed to the light of the solar simulator lamp.

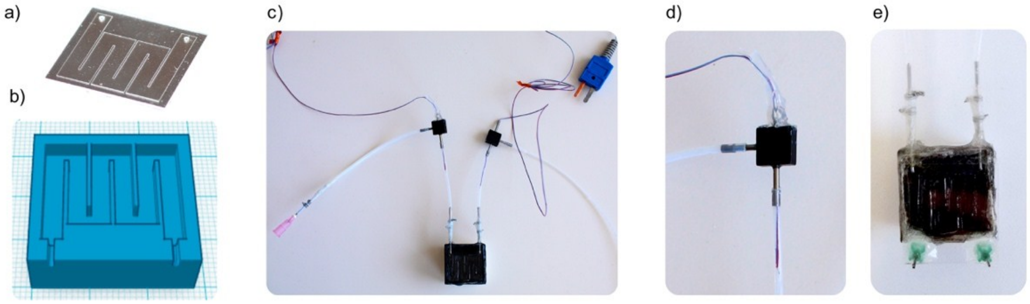

Fig S1: a) Custom made microfluidic chip; b) 3D model of the SWH collector; c) picture of the assembled SWH collector including connection tubes and thermocouples; d) detail of a T-junction with the thermocouple inserted; e) detail of the combined hybrid collector.

Solubility of NBD2

Toluene was chosen as a solvent, because of the high solubility of the compounds in it (112 g/L is the measured solubility of NBD **2** in toluene). A more environmentally friendly solvent as ethanol was also considered, but the solubility of the compounds was much lower in this solvent (8.73 g/L is the measured solubility of NBD **2** in ethanol).

Kinetic properties 1 and 2

The kinetic characterization for the thermal back conversion of QC to NBD for 1 and 2 has been previously published by us.[1,2] Measured rate constant values for an unimolecular reaction at different temperatures are here reported as useful information on the systems:

Table 1: Kinetic constant of back conversion of QC1 to NBD1

T [K]	*k* [s^{-1}]
341	0.044×10^{-3}
336	0.034×10^{-3}
351	0.17×10^{-3}
346	0.10×10^{-3}
363	0.58×10^{-3}
356	0.29×10^{-3}

Table 2 Kinetic constant of back conversion of QC2 to NBD2

T [K]	*k* [s^{-1}]
293	2.1×10^{-5}
298	3.8×10^{-5}
304	7.9×10^{-5}
315	3.0×10^{-4}
326	1.0×10^{-3}
330	1.6×10^{-3}

II. Cyclability test

A solution of **2** in toluene was prepared (~3×10^{-5}M) and degassed by flowing nitrogen through the solution for about 1 hour. A quartz cuvette with four optically clear sides was connected to a magnetic stirrer and a heating block connected to a water heating system, and inserted in a spectrophotometer (Agilent Cary 4000 UV-Vis). The solution was heated to 60°C and the absorption monitored at 400 nm. A LED light source (Thorlabs - M365F1, 365 nm) was used to irradiate the sample orthogonally respect to the spectrophotometer beam. The light sources were switched ON/OFF controlled by a custom made LabVIEW program, providing a cycle with 180 s ON and 1500 s OFF, which correspond to a photoconversion of about 75%, and a thermal back-conversion of about 80% (about 2.5 times the $t_{1/2}$ at the selected temperature). A linear fitting of the maximum absorbance in each cycle shows that the degradation over 127 cycles is within the experimental error (see Figure 4 in main text).

A test without degassing the sample was carried out in the same way as above. In this case about 5.6% of 2 degrades after 24 cycles. This experiment show how the robustness of the MOST system can be significantly improved simply by degassing the solution.

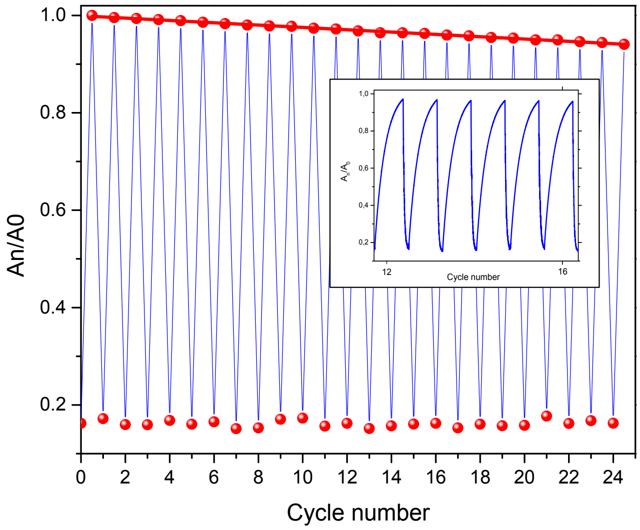

Fig S2: Cyclability test of a solution of 2 in toluene at 60°C. The solution was not degassed, and about 5.6% of the compound degrade after 24 cycles corresponding to 99.8 % yield per conversion cycle.

III. Differential Scanning Calorimetry

Norbornadiene **1** (15 mg) was dissolved in 1 mL of hexane and irradiated for 45 minutes (with cold water bath cooling) using an Osram Powerstar HQI-R 150 W, metal halide lamp to convert to the quadricyclane isomer (conversion confirmed by UV-vis). The solvent was evaporated, and 1.2 mg of quadricyclane oil was placed in a sealed 40 μl aluminium pan and inserted in the DSC at 25°C. The DSC method involved a double cycle of heating (at 5 °C/min from 25 to 250 °C) and cooling (at 5 °C/min from 250 to 25 °C). In the second cycle no exothermic peaks were observed, demonstrating how the quadricyclane completely back-converted in the first cycle.

The DSC characterization of **2** was performed as described in a previous work by us.[2]

In order to distinguish the peaks related to phase transitions of the norbornadienes, norbornadienes **1** and **2** were also analyzed by DSC, using a DSC method involving a cycle of heating at 10 °C/min from 0 to 180 °C (curves 1 in figure S4), and cooling at 40 °C/min from 180 to 0 °C (curves 2 in figure S4); the thermograms are shown in figure S 4.

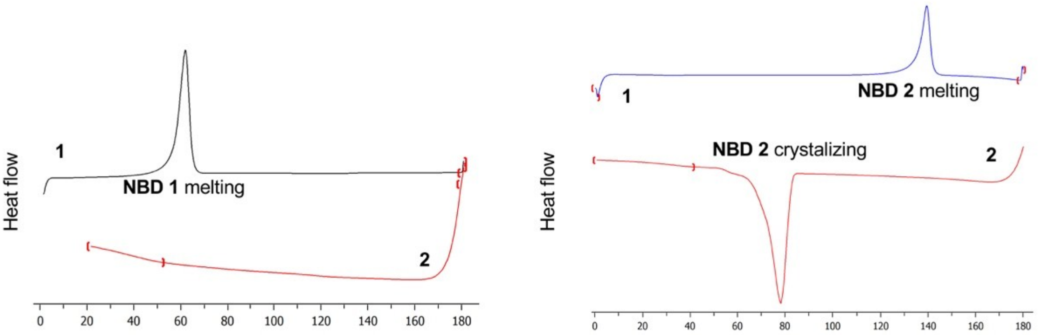

Fig S3: DSC thermograms of NBD 1 (left) and 2 (right). Peaks associated to the melting of the two norbornadienes are observed, and a peak associated to the crystalizing of NBD 2 is also obser

IV. Heat Transfer Model and Simulation of the System

Modelling MOST/thermal hybrid collector

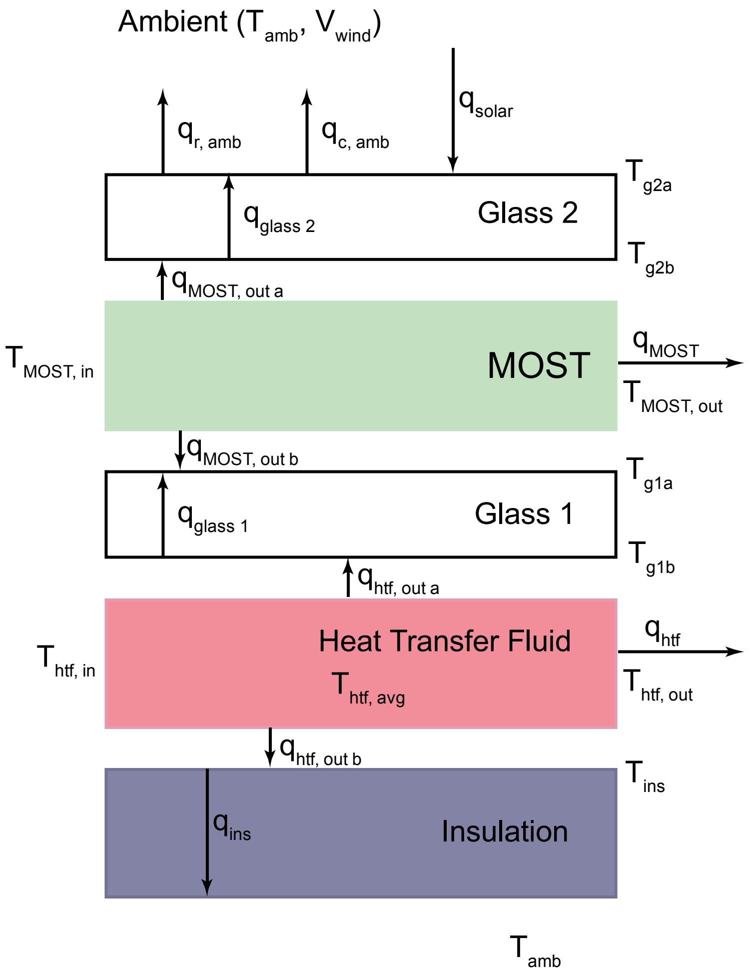

Figure S4. A schematic picture of how the combined MOST/thermal collector is modelled. Heat fluxes are denoted by q and temperatures are denoted by T.

To model a combined MOST/thermal hybrid collector system, heat fluxes between all components were set up in accordance to Figure S3. In the model it is assumed that no other means of energy transfer to/from the closed system or within it takes place. The applied method is an adaptation of the combined PV/thermal collector system as applied in Norwood et al.[4,5] The heat fluxes between the components in Figure S3 is defined in Equation S6-S16, where T denotes the temperature at specific points defined in Figure S3, h is the heat transfer coefficient, K the thermal conductivity, δ the element distance, c_p the specific heat capacity of the heat transfer fluid, $\dot{m}$ the mass flow rate of the heat transfer fluid, ε the emissivity of the top glass, and σ the Stefan-Boltzmann constant.

$$q_{ins} = h_{ins}(T_{ins} - T_{amb}) \tag{S6}$$

$$q_{htf,\,out\,a} = \frac{K_{htf}}{\delta_{htf}}\left(T_{htf,\,ave} - T_{g1b}\right) \tag{S7}$$

$$q_{htf,\,out\,b} = \frac{K_{htf}}{\delta_{htf}}\left(T_{htf,\,ave} - T_{ins}\right) \tag{S8}$$

$$q_{glass\,1} = \frac{-K_{glass}}{\delta_{glass\,1}}\left(T_{g1a} - T_{g1b}\right) \tag{S9}$$

$$q_{htf} = \dot{m}_{htf}c_{p,\,htf}\left(T_{htf,\,out} - T_{htf,\,in}\right) \tag{S10}$$

$$q_{MOST,\,out\,b} = \frac{K_{MOST}}{\delta_{MOST}}\left(\frac{T_{MOST,\,out} - T_{MOST,\,in}}{2} - T_{g1a}\right) \tag{S11}$$

$$q_{MOST} = \dot{m}_{MOST}c_{p,\,MOST}\left(T_{MOST,\,out} - T_{MOST,\,in}\right) \tag{S12}$$

$$q_{MOST,\,out\,a} = \frac{K_{MOST}}{\delta_{MOST}}\left(\frac{T_{MOST,\,out} - T_{MOST,\,in}}{2} - T_{g2b}\right) \tag{S13}$$

$$q_{glass\,2} = \frac{-K_{glass}}{\delta_{glass\,2}}\left(T_{g2a} - T_{g2b}\right) \tag{S14}$$

$$q_{r,\,amb} = \varepsilon_{glass}\sigma\left({T_{g2a}}^{4} - {T_{amb}}^{4}\right) \tag{S15}$$

$$q_{c,\,amb} = h_{wind}\left(T_{g2a} - T_{amb}\right) \tag{S16}$$

At steady state, the net heat transfer to components is zero, which is expressed in the following seven energy balance equations (Equation S17-23):

$$q_{htf,\,out\,b} = q_{ins} \tag{S17}$$

$$q_{htf} + q_{htf,\,out\,b} + q_{htf,\,out\,a} = \tau_{g2}\tau_{g1}\tau_{MOST}\alpha_{htf}CG \tag{S18}$$

$$q_{glass\,1} = q_{htf,\,out\,a} \tag{S19}$$

$$0 = q_{glass\,1} + q_{MOST,\,out\,b} \tag{S20}$$

$$\tau_{g2}\alpha_{MOST}\left(1 - \eta_{MOST}\right)CG = q_{MOST} + q_{MOST,\,out\,a} + q_{MOST,\,out\,b} \tag{S21}$$

$$q_{MOST,\,out\,a} = q_{glass\,2} \tag{S22}$$

$$q_{glass\,2} = q_{r,\,amb} + q_{c,\,amb} \tag{S23}$$

Where τ is the transmittance, α is the amount of absorbed solar energy, *CG* is the solar flux, and η is the amount of energy of the absorbed photons that are stored as chemical energy in the MOST system. It is assumed that the transmittance of the MOST fluid is zero above the bandgap and one below the bandgap of the MOST molecule. An in-house made MATLAB script employing the Newton-Rapson method was used to solve the energy balance equations, using $T_{htf,\,in}$ and $T_{htf,\,out}$ as given and T_{g2a}, T_{g2b}, T_{g1a}, T_{g1b},

T_{ins}, $T_{MOST,\ out}$, $\dot{m}_{htf}$ as unknown parameters. The efficiency of the heat collector system was calculated using the temperature difference over the collector, the mass flow rate and the specific heat capacity of the heat transfer fluid.

Reference List

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