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# Highly efficient organic solar energy-absorbing material based on phthalocyanine derivative for integrated water evaporation and thermoelectric power generation application

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## Experimental Section

## Experimental section

Materials and methods: $^{1}H$ NMR spectra were measured on the AVANCEIIIHD 500 MHz spectrometer (USA) with tetramthylsilane as the internal standard. $^{13}C$ NMR spectra were measured on the AVANCEIIIHD 125 MHz spectrometer (USA) with tetramthylsilane as the internal standard. MALDI-TOF mass spectra were recorded on the Kratos AXIMA-CFR KompactMALDI mass spectrometer with anthracene-1,8,9-triol as the matrix. The optical characteristics of 4OCSPC and 4OCSPC/F127 were investigated by UV−vis absorption spectra (Hitachi U-4100 ultraviolet/visible/near infrared spectrophotometer). All reagents and solvents, unless otherwise specified, were obtained from Aldrich (USA) and Acros (Belgium), and were used as received. All reactions were carried out using Schlenk techniques under a nitrogen atmosphere. 4OCSPC was synthesized as plotted in Scheme 1, where Cl-4OCPN was prepared according to the method reported.[1] Details of synthesis and characterization are presented as follows.

**Steady-state spectral measurements.** The UV-vis-NIR absorption spectrum of 4OCSPC in solvent, solid and PU+4OCSPC was recorded by Hitachi U-4100 ultraviolet/visible/near infrared spectrophotometer. The fluorescence spectrum and fluorescence quantum efficiency are tested on the QM8000 steady-state transient fluorescence spectrometer.

**Water evaporation performance test.** The PU+4OCSPC foam was put on a quartz beaker filled with water. The sunlight, generated by a solar simulator with an optical filter for the standard AM 1.5 G spectrum (CEL-S500), irradiated at the sample under specific optical concentrations. The weight loss of water was measurement by an analytical balance and the temperature over the process was recorded by an IR thermal camera.

**Desalination of seawater.** Collected real seawater samples from the Yellow Sea in China for desalination. Inductively coupled plasma spectrometer (ICP-OES, Avio™ 200) was used to determine the concentration of four main ions ($Na^{+}$, $Mg^{2+}$, $Ca^{2+}$, $K^{+}$) that originally existed in seawater before and after desalination.

**Thermoelectric power generation experiment.** The back of the photothermal material coated with 20 mg 4OCSPC is closely fitted with the circulating water tank to form a temperature difference and generate voltage. The open circuit voltage (Voc) of the thermoelectric is measured and recorded with a Keithley 6514 digital multimeter/electrometer. The subsequent power generation was carried out under 1, 2 and 5 Sun respectively, and the surface temperature was collected and recorded by infrared thermal imager. The thermoelectric sheet is commercial and the model is TEC1-12706. The length is 40 mm, the width is 40 mm, and the height is 3.6 mm.

**Thermal conductivity measurement.** The thermal conductivity of pure PU and PU+4OCSPC foams were measured by a thermostat coefficient meter (C-THERM TCi).

**Thermodynamic performance test.** Thermogravimetric analysis was tested in air with Pyris 1 analyzer at a scanning rate of 10 K $min^{-1}$.

**Supplementary Note 1**

**Calculation of the photothermal conversion efficiency.**

Solar-to-thermal conversion was measured by placing an aqueous solution of sample (50 μg $mL^{-1}$, 1 mL) in a beaker with an insulating layer and illuminating the solution with simulated solar light. The temperature of the solution was recorded using a thermal imaging camera upon simulated solar light irradiation for 30 min and energy conversion efficiency (η) was calculated as the following formula**[S1]**:

$$\eta = \frac{Q}{E} = \frac{Q_1 - Q_2}{E}$$

Where $Q$ refers to the thermal energy generated (i.e., $Q = Q_1 - Q_2$), $Q_1$ is the thermal energy generated of 4OCSPC and $Q_2$ is the thermal energy generated of pure water. $E$ refers to the total energy of the incident light. $Q$ is determined by the heat capacity ($C$), density ($\rho$), volume ($V$) and $\Delta T$ over the period of irradiation of the solution; $E$ is determined by the power ($P$) of the incident light, the irradiation area ($S$) and irradiation

time (*t*). Therefore, the specific formula is as follows:

$$Q_1 = Cm\Delta T_1 = C\rho V\Delta T_1$$

$$Q_2 = Cm\Delta T_2 = C\rho V\Delta T_2$$

$$E = PSt$$

In this paper, Since samples are present in very low amounts in the solution, values of $C$ (4.2 J $g^{-1}$ $^oC^{-1}$) and $\rho$ (1 g $cm^{-3}$) for water were used in the calculations.

For example, the surface temperature of 4OCSPC/F127 micelles was 41.7 °C during the irradiation process, and the initial temperature is 19.6 ℃, therefore ΔT is 22.1 °C. As the above fomulas,

$$Q_1 = C\rho V\Delta T_1 = 4.2 \times 1 \times 1 \times 22.1 = 92.82\ J$$

$$Q_2 = C\rho V\Delta T_2 = 4.2 \times 1 \times 1 \times 10.7 = 44.94\ J$$

$$E = PSt = 0.1 \times 1.5386 \times 1800 = 276.948\ W \cdot s$$

$$\eta = \frac{Q_1 - Q_2}{E} = \frac{92.82 - 44.94}{276.948} = 17.3\%$$

As a result, 4OCSPC energy conversion efficiency $\eta = Q_1\text{-}Q_2/E$ = 17.3% when the temperature difference is 22.1 ℃ is calculated.

**Supplementary Note 2**

**Calculation of the efficiency for solar to vapor generation.**

The conversion efficiency η of solar energy in photothermal assisted water evaporation was calculated as the following formula[S2].

$\eta = \dot{m}hLV/C_{opt}P_0$

$\dot{m} = 1.262$ kg/m$^2$ h

$P_0 = 1$ kW/m$^2$

$C_{opt} = 1$

As a result, evaporation efficiency $\eta = \dot{m}hLV/C_{opt}P_0$ = 86.6% when the latent heat of water vaporization at 36.5 °C is used in calculation. By the way, in this system, the

solar evaporation was applied at temperatures above the environmental temperature, thus it would be unnecessary to deduct the so-called dark evaporation.

**Supplementary Note 3**

**Calculation of Conduction loss $\eta_{cond}$[S2].**

The conductive heat flux from PU+4OCSPC to water is calculated as follows:

$$P_{\mathrm{cond}} = \frac{Cm\Delta T}{At} = \frac{4.18\times5\times1.9}{0.000314\times1800} = 70 \quad W/\mathrm{m}^2$$

$$\eta_{\mathrm{cond}} = \frac{P_{cond}}{p_{in}} = \frac{70}{1000} = 7\%$$

Where C is the specific heat capacity of liquid water (4.18 J/g ℃), t is the irradiation time (1800 s), m is the water weights (~ 5 g) and ΔT is increased temperature of the bulk water within 30 min, A is the projected area (0.000314 $m^2$).

**Calculation of Radiation loss $\eta_{rad}$:**

The radiation flux is based on Stefan-Boltzmann law, which is calculated as follows:

$$P_{rad} = \varepsilon\sigma(T_2^{\,4} - T_1^{\,4}) = 0.53\times5.67\times10^{-8}\times(301.35^4 - 299.35^4) = 7 \quad W/\mathrm{m}^2$$

$$\eta_{rad} = \frac{P_{rad}}{P_{in}} = \frac{7}{1000} = 0.7\%$$

where ε (0.53) is the emissivity, σ is the Stefan–Boltzmann constant 5.67 × $10^{-8}$ W ($m^2$ $K^4$)$^{-1}$, $T_2$ (301.35 K) is the temperature at the surface of PU+4OCSPC steam generator, $T_1$ (299.35 K) is the temperature of the adjacent environment of steam generator. The emissivity of PU+4OCSPC is 0.53, which is calculated using an absorption spectrum and plank formula.

**Calculation of Convection loss $\eta_{conv}$:**

The convection heat loss is calculated based on Newton's law of cooling.

$$P_{conv} = h(T_2 - T_1) = 5\times(301.35 - 299.35) = 10 \quad W/\mathrm{m}^2$$

$$\eta_{conv} = \frac{P_{conv}}{P_{in}} = \frac{10}{1000} = 1\%$$

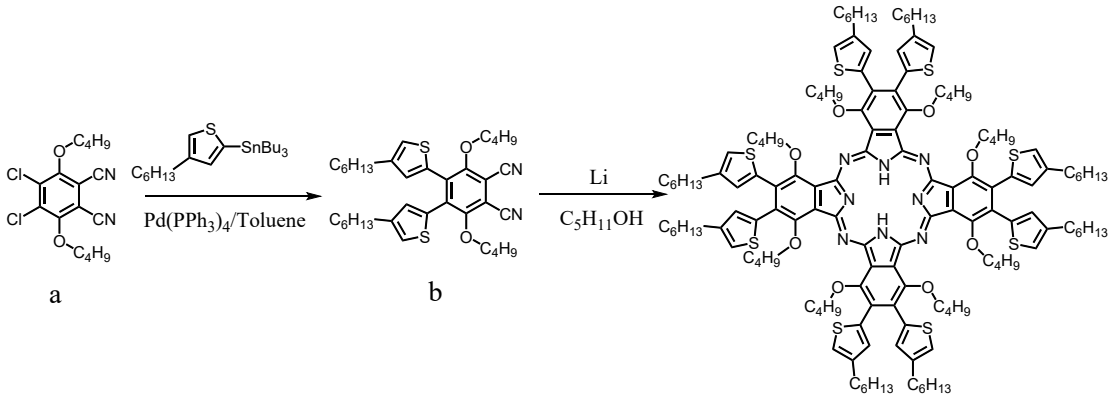
Where h is the heat transfer coefficient is approximately 5 W /$m^2$ K according to the previously reports. $T_2$ (301.35 K) is the temperature at the surface of PU+4OCSPC, $T_1$

(299.35 K) is the temperature of the adjacent environment of steam generator.

**Synthesis of 4OCSPC:**

Cl-4OCPN (3.40 g, 10.0 mmol) and tributyl (4-hexylthiophen-2-yl) stannane (7.64 g, 16.6 mmol) and tetrakis (triphenylphosphine) palladium (0) (1.14 g, 1.0 mmol) were dissolved in degassed 100 mL toluene, and the mixture was stirred at 80$^{o}$C for 8 h. The reaction mixture was allowed to cool to room temperature, solvent was removed by vacuum evaporation and the crude product was purified by column chromatography using silica gel with dichloromethane and petroleum ether as the eluents to obtain 4OCSPN (4.35 g, Yield: 72.0%). Then 4OCSPN (3.02 g, 5.0 mmol) was dissolved in 15 mL dry n-pentanol and the mixture was heated at 100$^{o}$C for 5 min. Under nitrogen atmosphere, lithium (0.11 g, 15.0 mmol) was added, and then the mixture was refluxed for 2 h. After cooling to room temperature, solvent was removed by vacuum evaporation and the crude product was purified by column chromatography using silica gel with dichloromethane and petroleum ether as the eluents to obtain the dark green powder. Yield: 293 mg (10%). $^{1}$H NMR (500 MHz, $CDCl_3$, δ): 7.07 (s, 8 H), 7.02 (s, 8 H), 4.74 (m, 16 H), 1.85 (m, 16 H), 1.64 (m, 16 H), 1.36 – 1.29 (m, 80 H), 0.94 (m, 24 H), 0.88 (m, 24 H). MS (MALDI-TOF): m/z: 2460.3 $[M + K]^{+}$.

**Synthesis of the polymeric 4OCSPC/F127 micelles.** A mixture of 2.0 mg of 4OCSPC and 40.0 mg F127 was completely dissolved in 1.0 mL of THF for 1 h. And they were slowly drop into 5.0 mL deionized water under vigorous stirring at room temperature. After the mixture is stirred for 30 min, then, in order to remove THF, the dispersion was dialyzed against deionized-water by 3.5 KDa dialysis membranes for 72 h.




**Scheme 1.** The synthetic route of 4OCSPC.

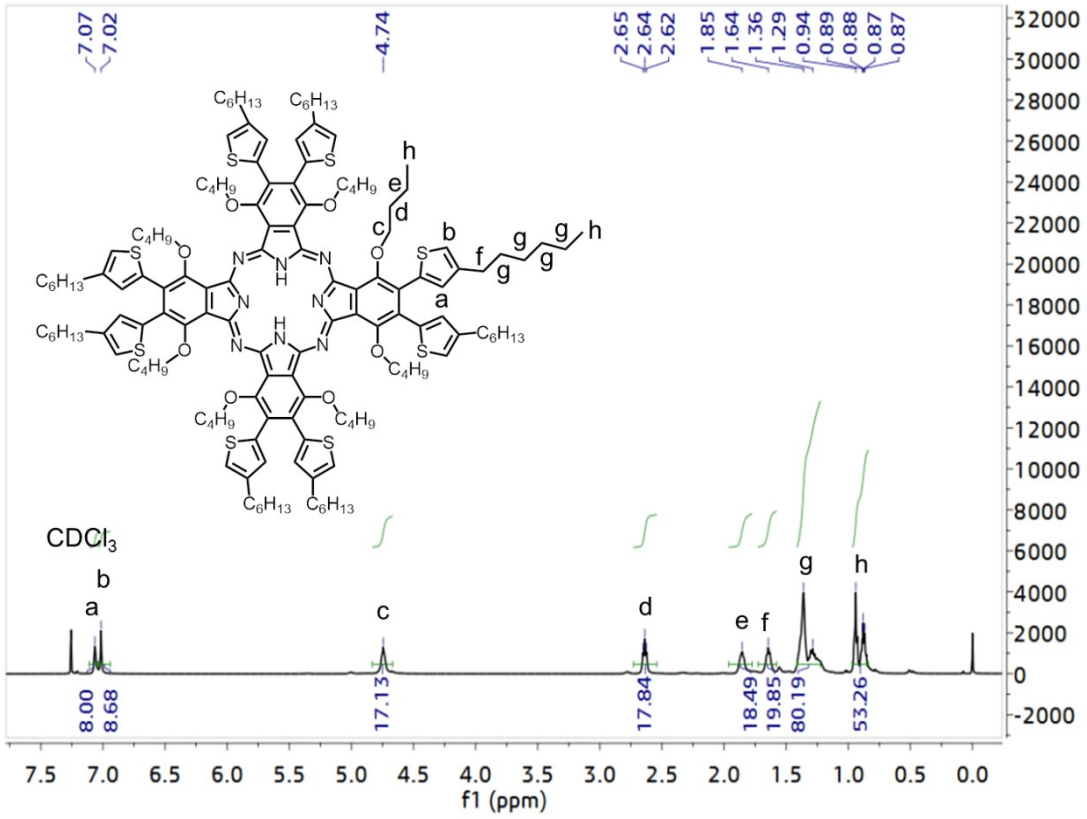



**Figure S1.** $^{1}$H NMR spectrum of 4OCSPC in $CDCl_3$.

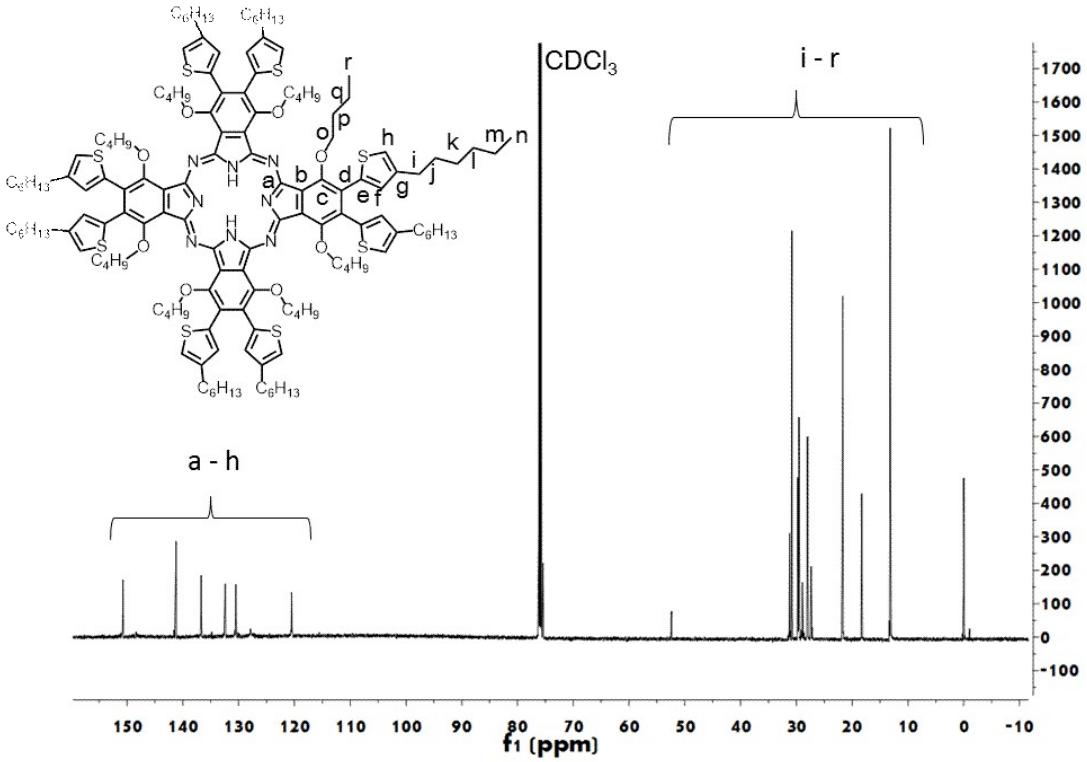



**Figure S2.** $^{13}C$ NMR spectrum of 4OCSPC in $CDCl_3$.

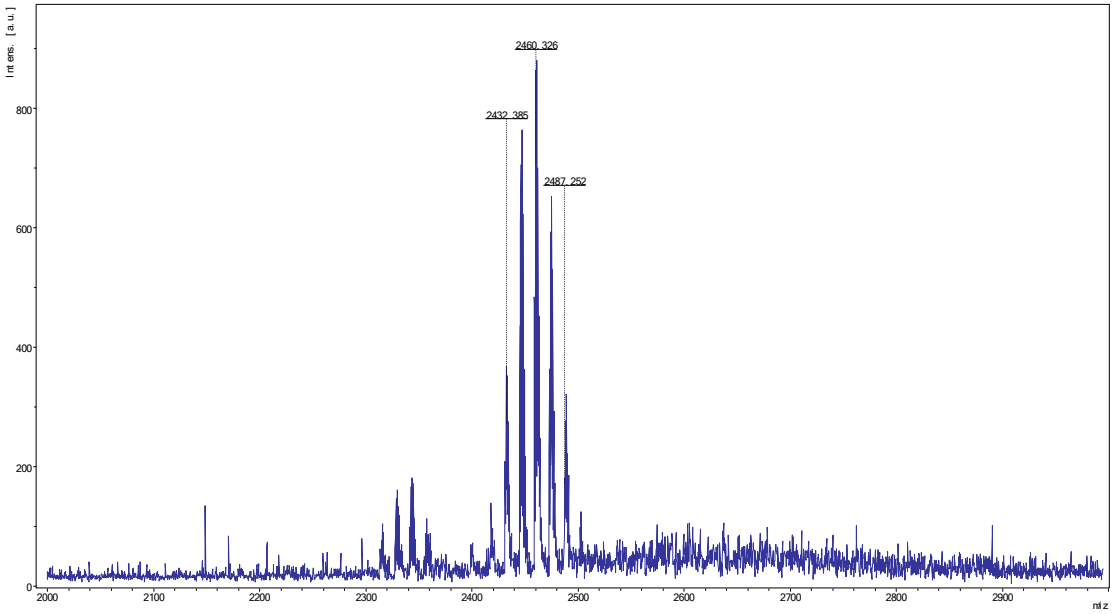



**Figure S3.** MADLI-TOF mass spectrum of 4OCSPC.

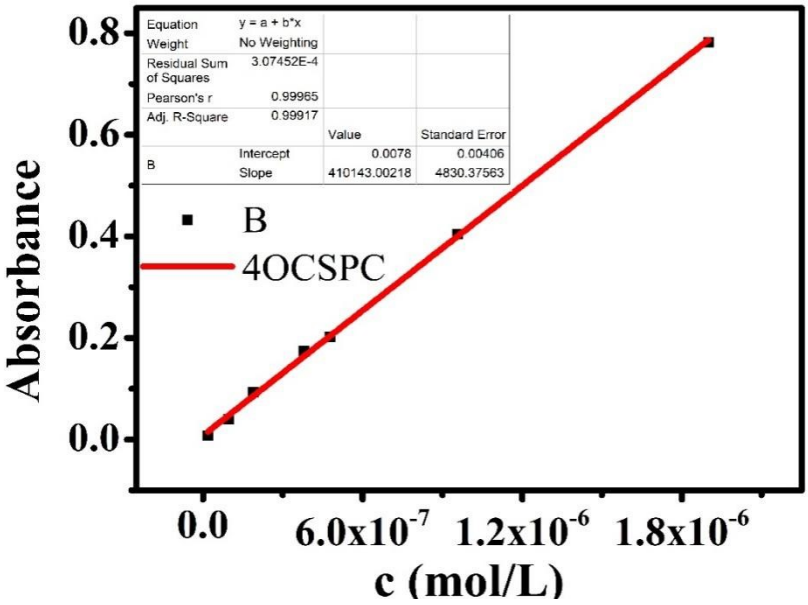



**Figure S4.** The absorption versus concentration curve of 4OCSPC in THF.

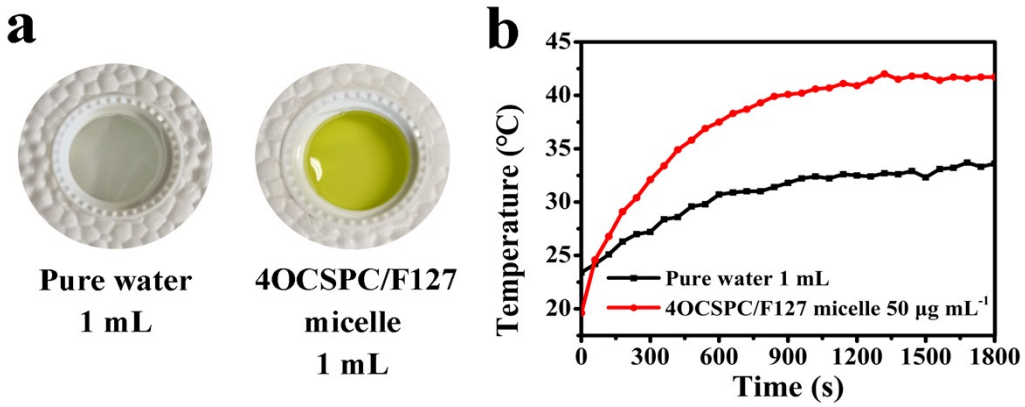



**Figure S5.** (a) Digital photographs of 1 mL pure water and 1 mL 50 μg $mL^{-1}$ 4OCSPC/F127 micelles in containers; (b) The temperature changes of 1 mL pure water and 1 mL 50 μg $mL^{-1}$ 4OCSPC/F127 micelles under simulated sunlight (100 mW $cm^{-2}$).

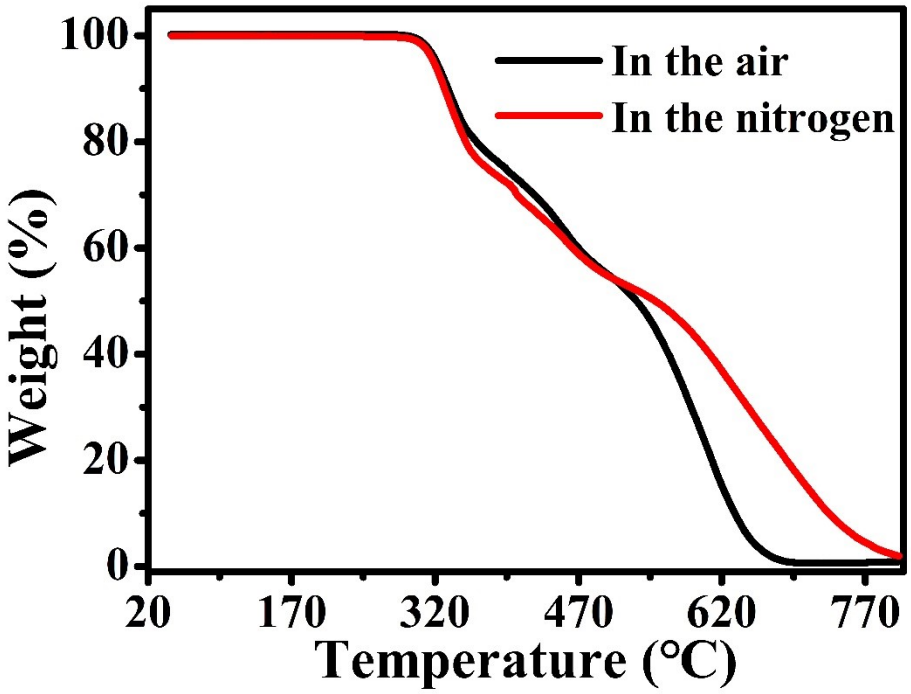



**Figure S6.** 4OCSPC thermogravimetric of air atmosphere and nitrogen atmosphere.

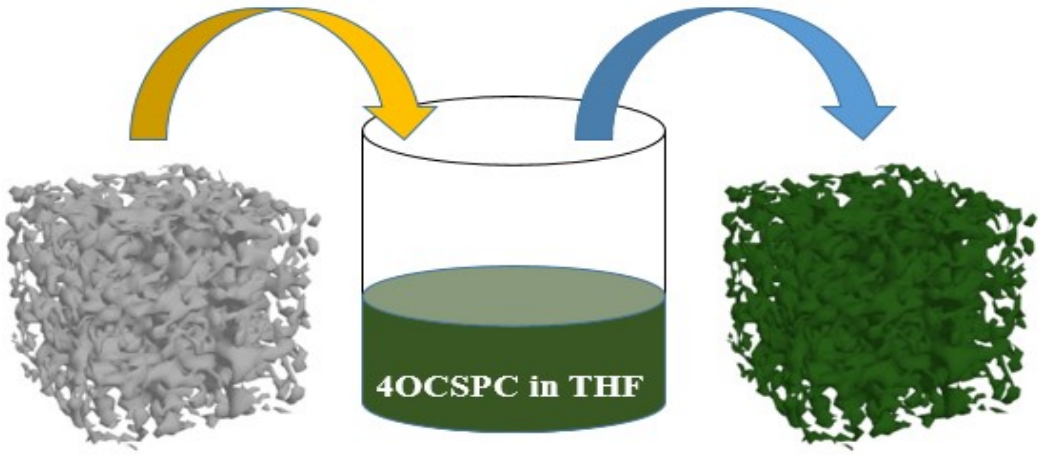



**Figure S7.** 4OCSPC thermogravimetric of air atmosphere and nitrogen atmosphere.

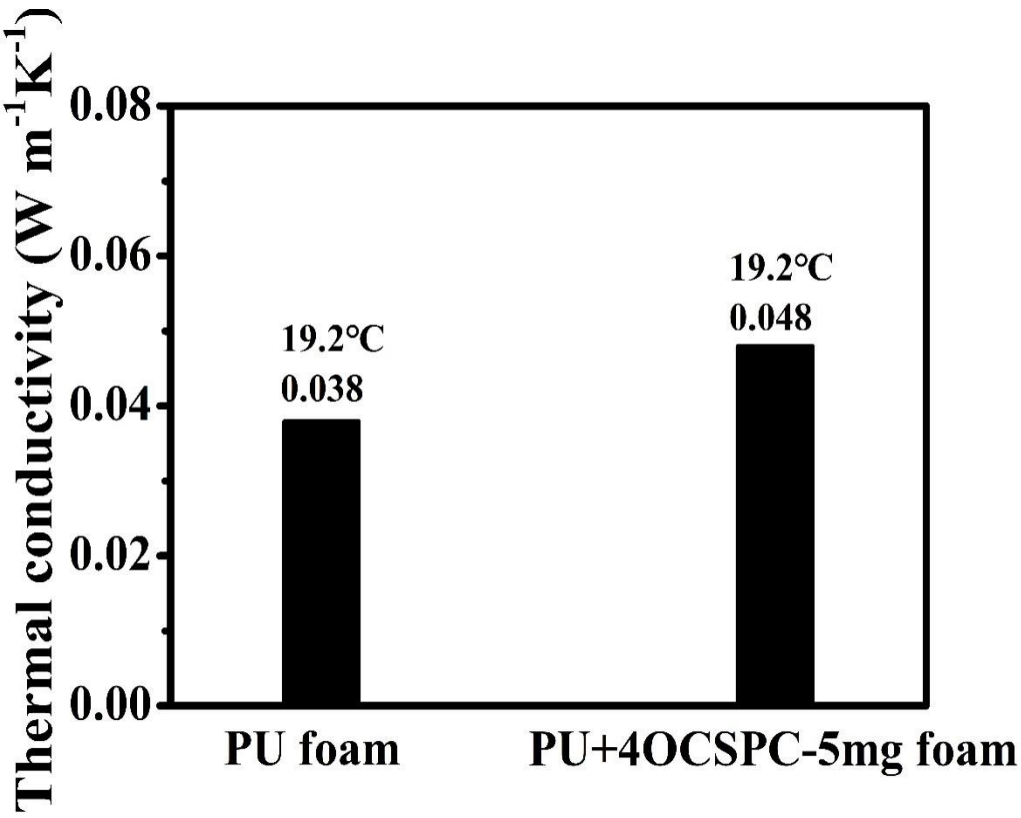



**Figure S8.** Thermal conductivities of PU and PU+4OCSPC-5 mg foams at 19.2 °C.

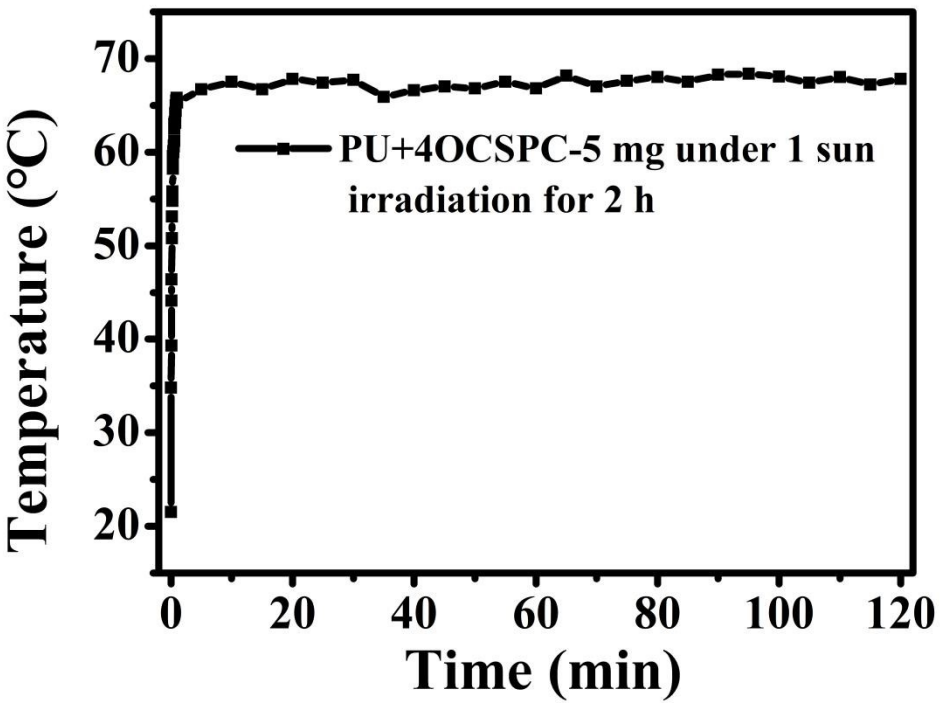



**Figure S9.** The temperature changes of 4 mg 4OCSPC powder under 808 nm laser irradiation (0.8 W $cm^{-2}$) for 2 h.

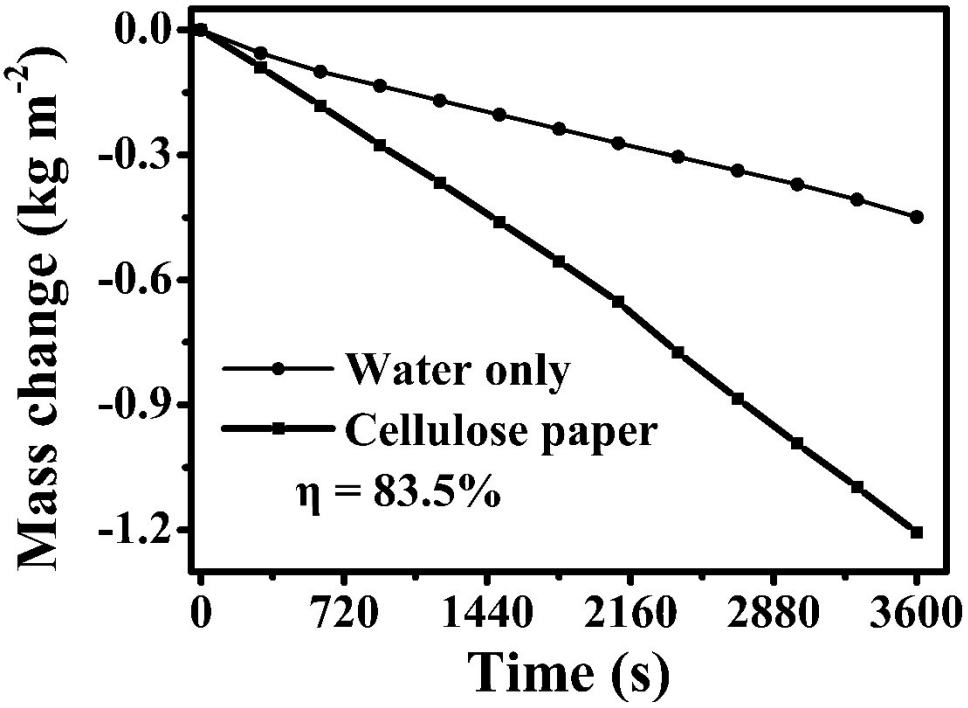



**Figure S10.** Water evaporation curves without (water only) and with cellolose paper-4OCSPC under simulated sunlight with an intensity of 1 kW $m^{-2}$ (1 sun). The amount of 4OCSPC used in preparing cellolose paper-4OCSPC is 5 mg. Room temperature is about 20 °C.

**Supplementary Movies**

**Movie S1**. Photothermal performance of 4OCSPC at mimic solar light of 100 mW $cm^{-2}$.

**Movie S2**. Visible water vapor above the 4OCSPC foam floating on the water surface.

**Movie S3**. Thermoelectric device used to drive small fan.

S1. X. Zhao, C. Huang, D. Xiao, P. Wang, X. Luo, W. Liu, S. Liu, J. Li, S. Li and Z. Chen, *ACS Appl. Mater. Interfaces*, 2021, **13**, 7600-7607.

S2. G. Chen, J. Sun, Q. Peng, Q. Sun, G. Wang, Y. Cai, X. Gu, Z. Shuai and B. Z. Tang, *Adv Mater*, 2020, **32**, e1908537.