Electronic Supplementary Information

Highly-efficient solar steam generation of supported metal-organic

framework membranes by a photo-induced electron transfer process

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Experimental Section

Materials and characterization methods

All chemical reagents were used as received. Nafion solution (5 *wt*% in mixture of water and 2-propanol), tetra-*n*-butylammonium hexafluorophosphate and polyvinylpyrrolidone (PVP, M_w: 5500) were purchased from Sigma Aldrich, and other chemicals and solvents, including cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), cobalt chloride ($CoCl_2 \cdot 6H_2O$), methyl *p*-formylbenzoate, propionic acid, pyrrole, methanol, ethanol, ethyl acetate, tetrahydrofuran (THF), ethyl acetate, N,N-dimethylformamide (DMF), 4,4'-bipyridine, potassium hydroxide (KOH), and hydrochloric acid (HCl), were purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Microstructural and morphological characterization was performed on a Tecnai F30 operated at 300 kV, HITACHI UHR FE-SEM SU8220, and Park Systems XE-70 with non-contact mode to achieve transmission electron microscopy (TEM), Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images, respectively. X-ray diffraction (XRD) was conducted with a Rigaku D/Max 2400 automatic powder X-ray diffractometer with Cu-*K*α radiation (λ = 1.5418 Å). The content of metal elements was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Optima 2000DV. Cyclic voltammetry (CV) were measured on a CHI660C electrochemical workstation with a three-electrode cell using DMF solution of tetra-*n*-butylammonium hexafluorophosphate as electrolyte. Nuclear magnetic resonance (NMR) data were collected on a Bruker advance III 500. UV-Vis absorption spectroscopy was performed on TU-1900 spectrophotometer, and broadband absorption spectroscopy was conducted on U-4100 spectrophotometer. Fourier-transform infrared (FTIR) spectroscopy were performed on FTIR EQUINOX 55 spectrometer. Steady state and time-resolved PL spectra were collected on FLS 920 fluorescence spectrometer under excitation wavelength of 405 nm.

Materials synthesis

Preparation of 5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrin. In a typical synthetic procedure, methyl *p*-formylbenzoate (6.9 g, 0.042 mol) was added in a 250-mL round-bottom flask containing propionic acid (100 mL). Pyrrole (3 mL, 0.043 mol) was added dropwise to the solution. The resultant mixture was refluxed for 12 h at 140 °C. Afterwards, the flask was cooled down to room temperature, and then the purple precipitate was collected by suction filtration before washing with methanol, ethyl acetate, and THF in sequence. The final product was dried in vacuum at 80 °C for 12 h before being subjected to characterization. 1H NMR (500 MHz, DMSO) δ 8.87 (s, 8H) δ 8.39 (d, 8H), and δ 8.35 (d, 8H).

Preparation of 5,10,15,20-tetrakis (4-carboxyphenyl) porphyrine (TCPP). The as-synthesized ester (1.95 g) was dispersed into a round-bottom flask containing a mixture solvent of THF and methanol (120 mL, V:V = 1:1) with stirring. An aqueous solution of KOH (6.28 g, in 60 mL of water) was introduced to the aforementioned

flask. The resultant mixture was refluxed for 12 h at 60 °C before cooling down to room temperature. Methanol and THF were evaporated from the mixutre, and then additional water was added until the solid was completely dissolved. Afterwards, the aqueous solution was acidified with HCl (1 M) until no precipitate was further produced. The final purple product was collected by suction filtration, wash with water and dried in vacuum at 80 °C for 12 h before being subjected to characterization.

Preparation of porphyrin paddle-wheel frameworks-3 (PPF-3). $Co(NO_3)_2 \cdot 6H_2O$ (4.4 mg, 0.015 mmol), 4,4'-bipyridine (1.56 mg, 0.01 mmol), and PVP (10 mg) were dissolved into a mixture solvent of DMF and ethanol (6 mL, V:V = 3:1) in a vial. A solution of TCPP (4.0 mg, 0.005 mmol) in DMF and ethanol (2 mL, V:V = 3:1) was added dropwise to the vial. After sonication for 25 min, the resultant mixture was thermal treatment for 24 h at 100 °C. The final brick-red product was washed with ethanol, collected by centrifugation at 8000 g, and dried in vacuum at 80 °C for 12 h.

Solar steam generation experiments

Preparation of the supported PPF-3 membranes. Typically, different amount of PPF-3 was dispersed into ethanol (20 mL) and sonicated for 30 min. The solution was poured onto polyvinylidene fluoride (PVDF) filter to prepare a well-dispersed membranes by filtration. To prevent exfoliation of PPF-3 from PVDF, Nafion solution (10 μL) was added to the ethanolic solution of PPF-3.

Solar-driven water evaporation. In a 50-mL beaker containing 50 mL of water, the supported PPF-3 membranes was floated at the air-water interface. The beaker was located at a Xe lamp (CHF-XM500, 500 W), and the variation of water weight upon illumination was measured at desirable time interval by placing the beaker on an electronic precision balance with resolution of 0.1 mg (Mettler Toledo, ML204) connected with a computer. By changing the distance between the Xe lamp and the membrane, the intensity of light illuminating on the membranes was adjusted to 1 and 2 kW m^{-2}, which was monitored by a power meter (PL-MW2000). An IR camera (Ti400, Fluke, USA) was used to record the temperature distribution of the photothermal system.

Note that water evaporation without illumination was studied, and solar generation efficiency was calibrated by subtraction of the background evaporation.
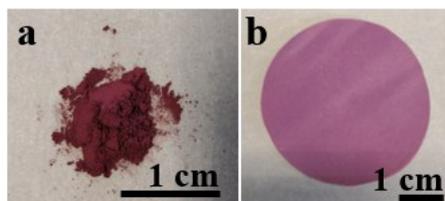
Fig. S1 Optical photos of (a) PPF-3 powder and (b) PPF-3 membrane supported on the PVDF filter.
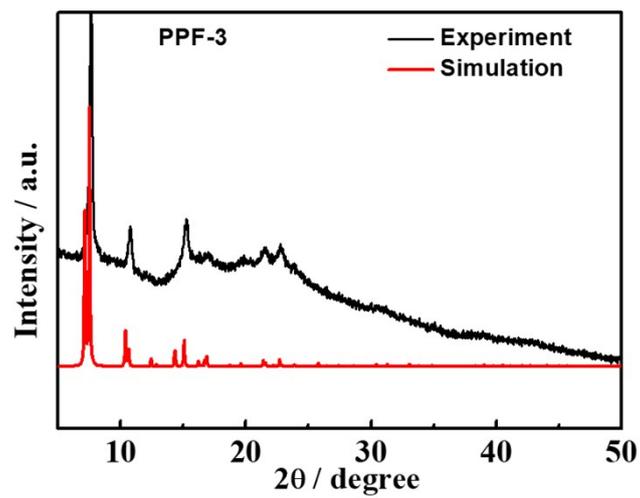
Fig. S2 XRD patterns of PPF-3.
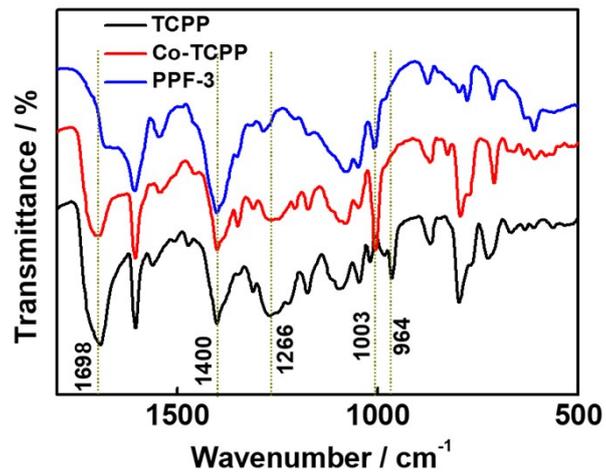
Fig. S3 FTIR spectra of PPF-3, Co-TCPP and TCPP.
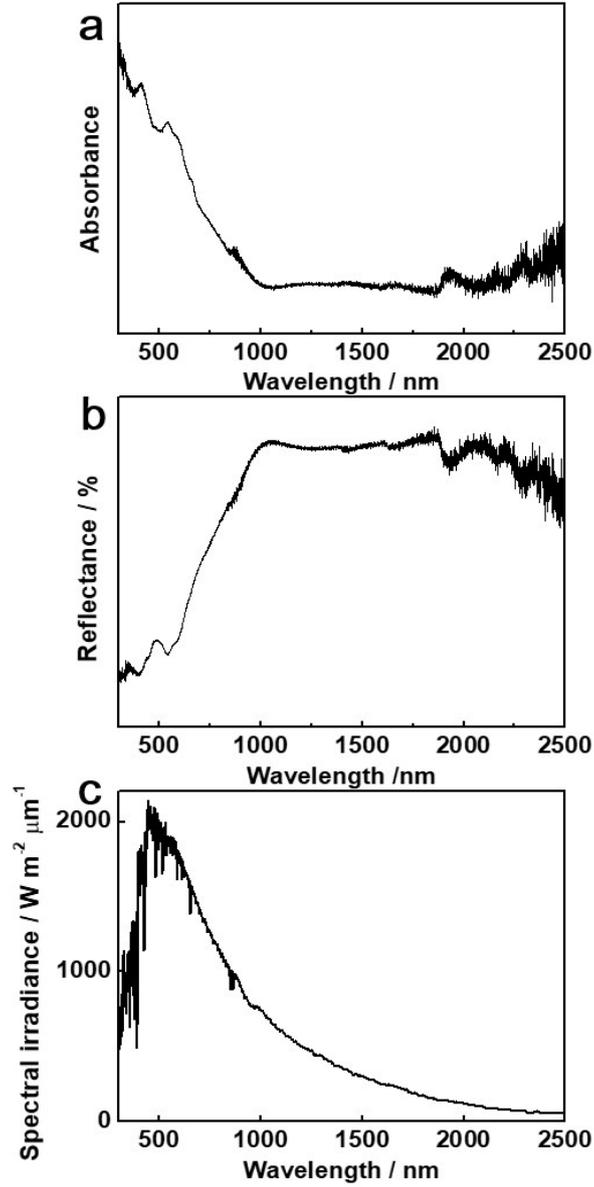
Fig. S4 (a) Broadband absorption and (b) reflection spectra of PPF-3, and (c) full solar spectrum ranging from 300 to 2500 nm.

The absorption ratio of solar light was dependent on absorption spectrum, and reflection spectrum of PPF-3, and was calculated by the equation of

$$\alpha = \frac{P_{abs}}{P_{abs} + P_{ref}} \times 100\%$$

, wherein

$$P = \int_{300}^{2500} I(\lambda)C(\lambda)d\lambda$$

(*Solar Energy* **2018**, 17-24).
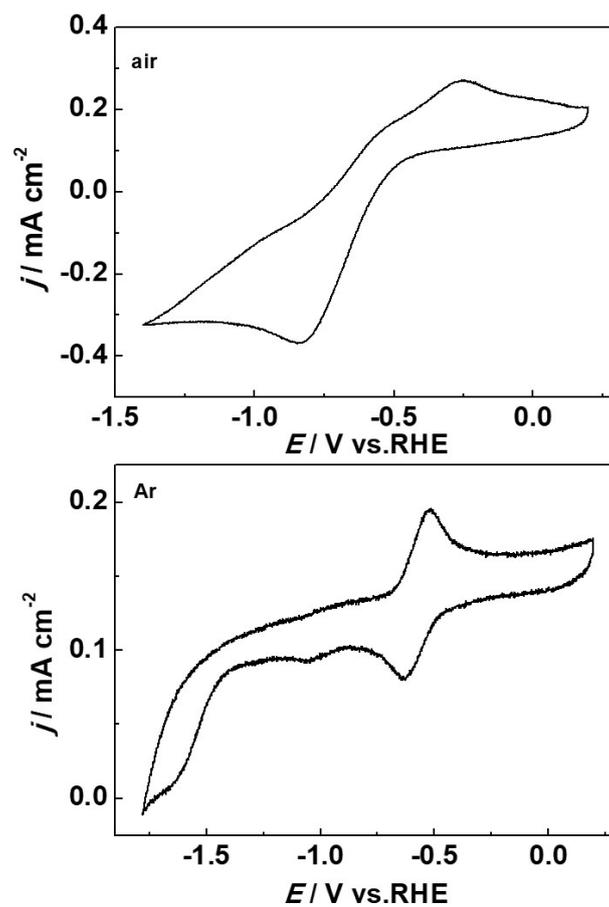
Fig. S5 Cyclic voltammetry curves of Co-TCPP in different gas atmospheres with a conventional three-electrode cell, wherein Ag/AgCl (3.5 M KCl) and polished Pt wire were used as the reference electrode and the counter electrode, respectively.
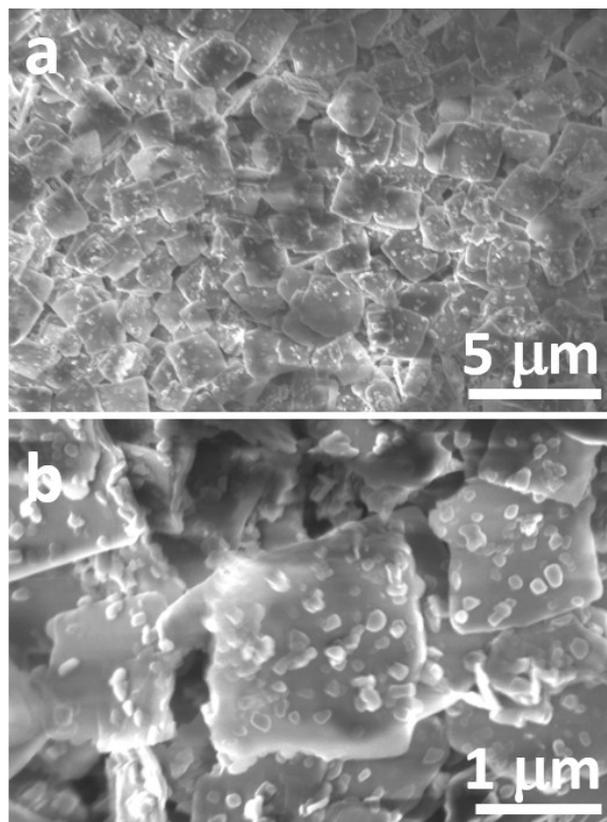
Fig. S6 (a) and (b) SEM images of the PVDF-supported PPF-3 membrane with different magnification.
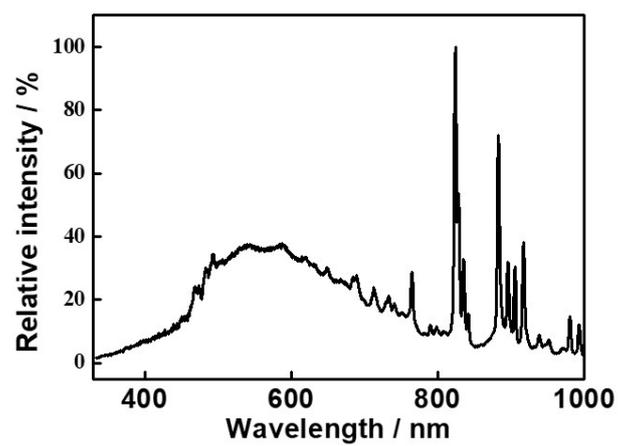
Fig. S7 The spectrum of the used Xe lamp.
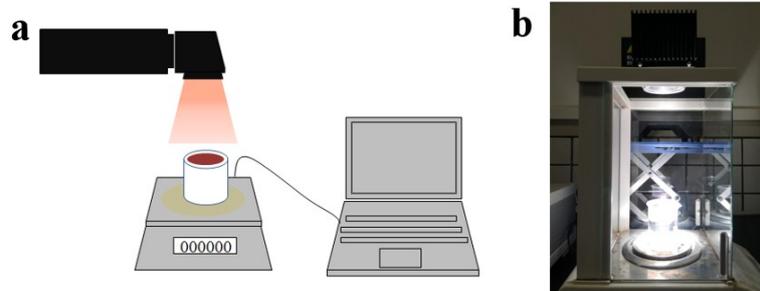
Fig. S8 (a) a schematic and (b) an optical photo of setup for solar energy driven water evaporation experiments.
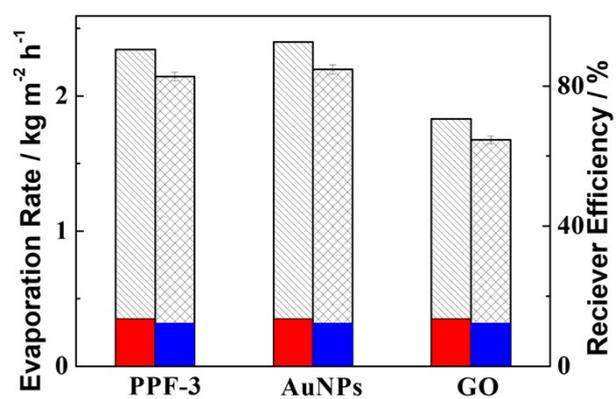
Fig. S9 Evaporation rate and solar thermal receiver efficiency of the supported membranes of PPF-3, AuNPs and GO upon illumination at 2 kW m^{-2} for 90 min. The mass of these photothermal materials is 5 mg. Red bars and blue bars is corresponding to evaporation rate and receiver efficiency of PVDF filter, respectively.
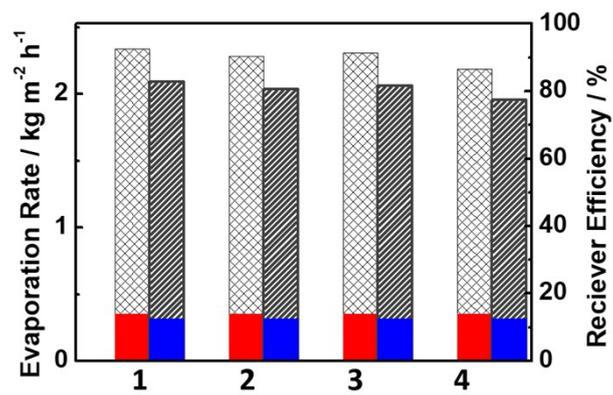
Fig. S10 Stability of solar steam generation performance of PPF-3 for successive four runs. Red bars and blue bars is corresponding to evaporation rate and receiver efficiency of PVDF filter, respectively.
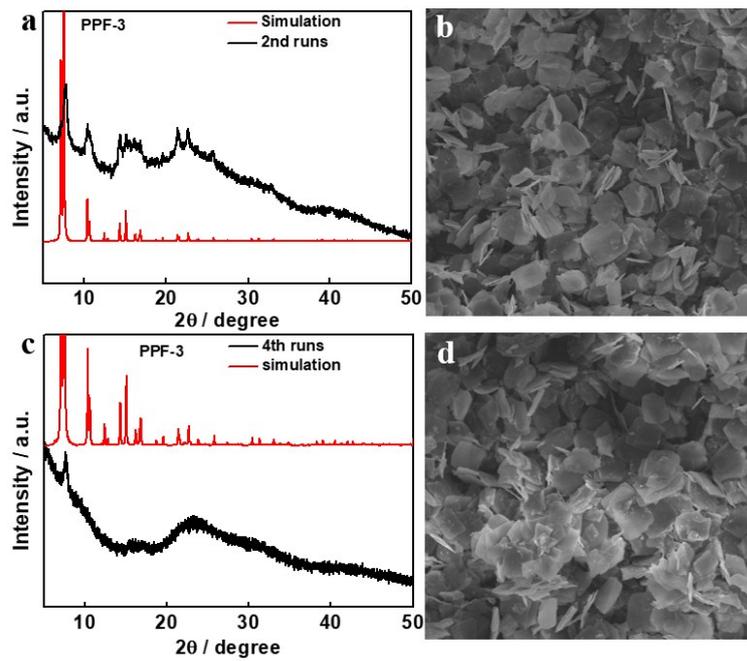
Fig. S11 (a, c) XRD patterns and (b, d) SEM images of the supported PPF-3 membrane via successive cyclic measurements for solar steam generation.
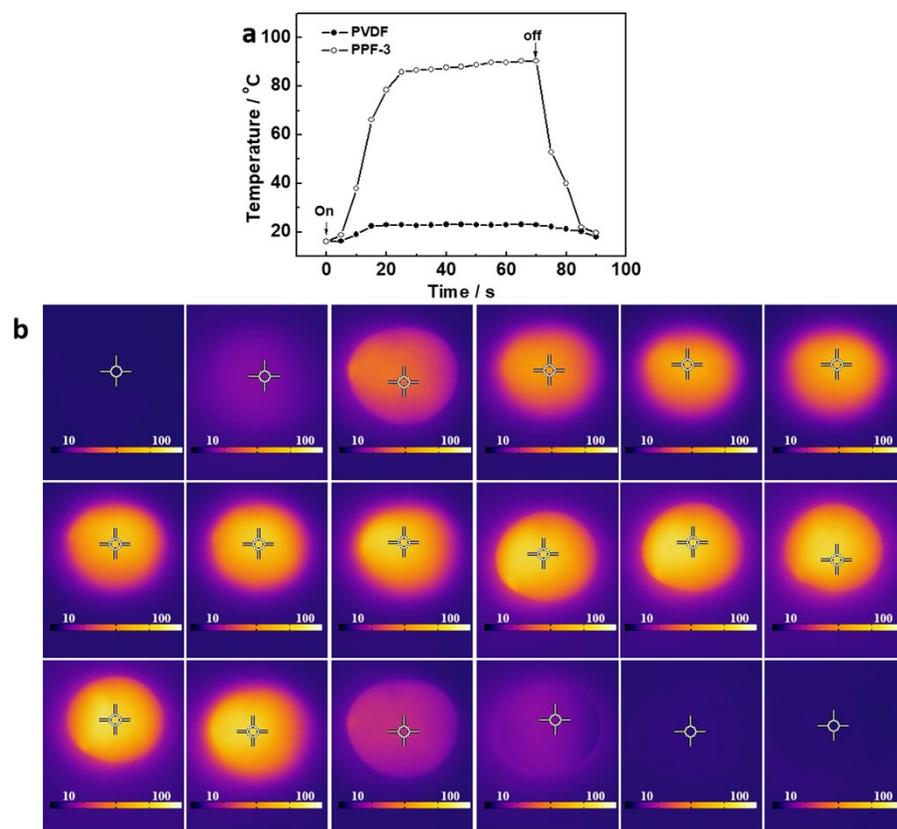
Fig. S12 (a) Temperature curves of the supported PPF-3 membrane and the PVDF filter in response to illumination from a Xe lamp at 2 kW m⁻², and (b) IR thermal images of the supported PPF-3 membrane.
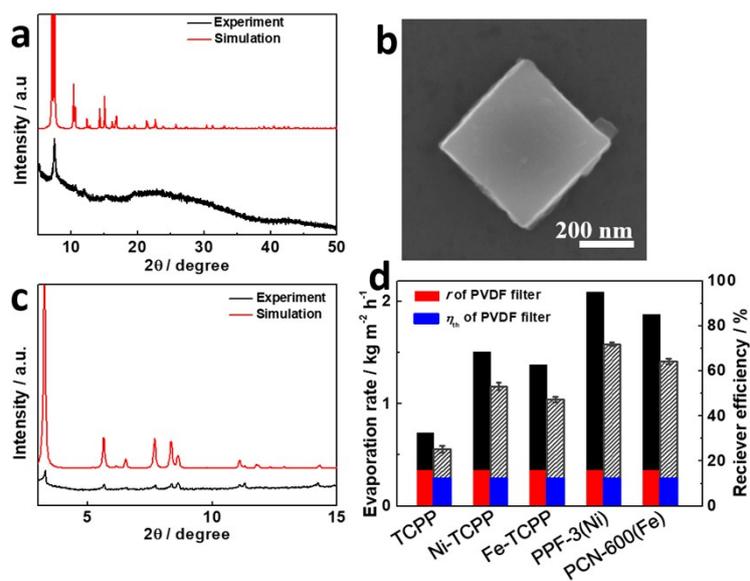
Fig. S13 (a) XRD pattern and (b) SEM image of PPF-3(Ni), (c) XRD pattern of PCN-600(Fe), and (d) solar steam generation performance of different photothermal materials upon illumination of a Xe lamp at 2 kW m^{-2} for 90 min.

Calculation of solar thermal receiver efficiency

The solar thermal receiver efficiency is estimated by the equation of $\eta_{th} = \dot{m}(h_s + h_{LV})/I$, wherein $\dot{m}$ is the mass flux, h_s is the sensible heating, h_{LV} is enthalpy of liquid–vapor phase change of water, and I is the power density (2 kW m^{-2}) of incident light.

As   for   PPF-3,

$$\eta_{th} = \frac{\dot{m}(h_s + h_{LV})}{I} \times 100\% = \frac{1.99 kg\ m^{-2}\ h^{-1} \times (83.6 kJ\ kg^{-1} + 2457 kJ\ kg^{-1})}{7200 kJ\ m^{-2}\ h^{-1}} \times 100\% = 70.3\%$$

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