

Charge transfer co-crystals based on donor-acceptor interactions for near-infrared photothermal conversion

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Supporting Information

Table of contents

1. Supporting Methods

1.1	General materials and methods.....	S1
1.2	Crystal growth and characterization.....	S1
1.3	Theoretical calculations.....	S1
1.4	Photothermal conversion properties measurement.....	S2
1.5	Water evaporation performance under one sun.....	S2

2. Supporting Figures and Calculations

2.1	The single-crystal data of co-crystal.....	S3
2.2	Other characterization of co-crystal.....	S4
	Figure S1: DSC spectrum of TTF crystal, co-crystal and Tri-PMDI crystal.....	S4
	Figure S2: PT cycling test of co-crystal (808 nm, 0.7 W/cm ²).....	S4
	Figure S3: Temperature time course of co-crystal-PTFE membrane and PTFE membrane in air under the sun illumination. Both batches were irradiated for 60 min to achieve water steam generation equilibrium.....	S4
2.3	Calculation of the photothermal conversion efficiency.....	S5
	Figure S4: The cooling curve of co-crystal samples after the irradiation of 808 nm laser (0.7 W/cm ²) (a) and its corresponding time-lnθ linear curve (b).....	S5
2.4	Calculation of the water evaporation efficiency under one sun.....	S6
	Table S1: Light to water evaporation efficiency of the control experiments.....	S7

1. Supporting Methods

1.1 General materials and methods

Tetrathiafulvalene (TTF, C₆H₄S₄, 98%) 1,2,4,5-Benzenetetracarboxylic anhydride (C₁₀H₂O₆, 98%), (1R, 2R)-(-)-1,2-Diaminocyclohexane (C₆H₁₄N₂, 98%), 1-Methyl-2-pyrrolidinone (NMP, C₅H₉NO, 99%) and acetic acid (AcOH, C₂H₄O₂, 99.5%) were all purchased from Tansoole and used as received. Deionized water is prepared using Milli-Q water.

1.2 Crystal growth and characterization

In a typical experiment, 80 mg solution of Tri-PMDI and 60 mg TTF in 2 mL NMP was added 450 μ L H₂O. The crystal structure was performed in an X-ray diffractometer (XRD, X-Pert, PANalytic, Netherlands) with Cu K α radiation (40 kV, 30 mA). The absorption spectra were analyzed with a U-3900 (Hitachi, Japan). DSC measurements were performed on a TA differential scanning calorimeter DSC 25 that was calibrated using high purity indium. Electron spin resonance (ESR) spectrum was collected on Bruker E500-10/12 instrument with microwave frequency of 9.5 GHz.

1.3 Theoretical calculations

The intermolecular potentials were calculated using UNI force field by Mercury software (copyright CCDC). Moreover, the calculations of the energy levels were using density functional theory (DFT) by Gaussian 09 package. The structure of the D-A molecular pair was directly imported from the crystal document and the molecular orbitals were obtained at the B3LYP/6-311G(d,p) level. Calculations of excitation energy for the vertical excitation from the ground state were carried out using TDDFT

(Time-dependent density functional theory). TDDFT calculations, carried out at the B3LYP structures, were done using the same basis sets as those used in the ground-state DFT calculations. The hybrid functional of Perdew, Burke, and Erzerhof, known as PBE0 (PBE1PBE in Gaussian), were used for the TDDFT. At the obtained geometries, corresponding excited-state structures up to 10 lowest excited states were calculated. The electron excitation analysis was carried out by Multiwfn.

1.4 Photothermal conversion properties measurement

Co-crystal powders were put in a cuvette and covered its bottom. The 808 nm laser beam (Hi-Tech Optoelectronics Co., Ltd, Beijing, China) irradiated at a power density of 0.7 W/cm². And the temperature was measured with an IR thermal camera (FLUKE TiS20 Thermal Imaging Camera). The calculation of PT conversion efficiency was determined according to previous methods.

1.5 Water evaporation performance under one sun

For photothermal water evaporation performance testing, co-crystal powders (40mg) are put on polytetrafluoroethylene microfiltration membrane ($\Phi=25$ mm) tightly. DI water was placed in a cylindrical polypropylene (PP) container with a mouth diameter of 2.5 cm, and the microfiltration membrane with the cocrystal powders was put and self-floated on the top of water. The sun solar light irradiation (2500 W/m²) was illuminated from the top and onto the surface of the co-crystal powders vertically. the temperature of the co-crystal powders was recorded by IR camera and the mass of the water evaporated was real time monitored by a digital balance.

2. Supporting Figures and Calculations

2.1 The single-crystal data of co-crystal.

Temperature 169.99 K

Crystal system Triclinic

Space group P 1

Unit cell dimensions

a=14.26 Å $\alpha=70.97^\circ$

b=18.38 Å $\beta=78.34^\circ$

c=25.43 Å $\gamma=79.57^\circ$

Volume 6122.15

Density (calculated) 1.752 mg/m³

Index ranges -17<=h<=17 -22<=k<=23 -31<=l<=31

Independent reflections 2367 [R(int) = 0.0303]

Goodness-of-fit on F² 1.161

Final R indices [$I > 2\sigma(I)$] R1 = 0.0420, wR2 = 0.0878

R indices (all data) R1 = 0.0466, wR2 = 0.0902

Extinction coefficient n/a

2.2 Other characterization of co-crystal

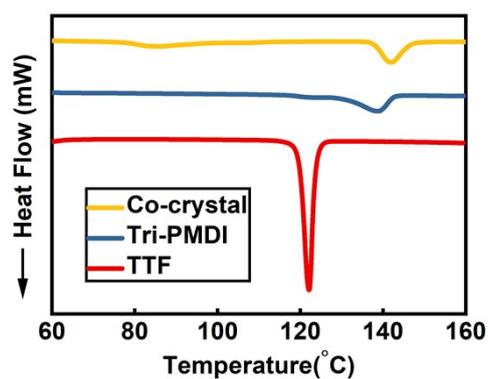


Figure S1. DSC spectrum of TTF crystal, co-crystal and Tri-PMDI crystal.

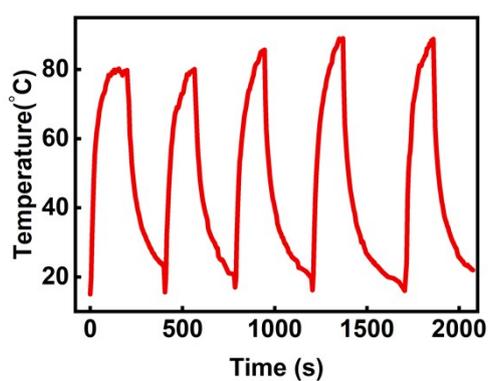


Figure S2. PT cycling test of co-crystal (808 nm, 0.7 W/cm²).

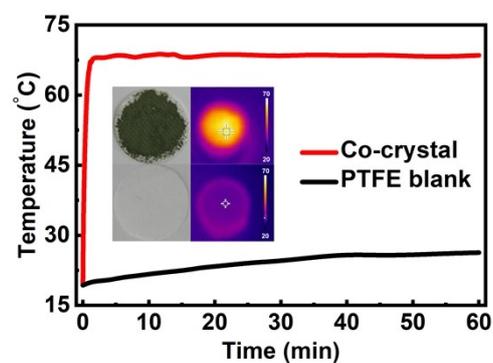


Figure S3. Temperature time course of co-crystal-PTFE membrane and PTFE membrane in air under the sun illumination, insert figure is IR photo of co-crystal-PTFE membrane and PTFE, respectively. Both batches were irradiated for 60 min to achieve water steam generation equilibrium

2.3 Calculation of the photothermal conversion efficiency

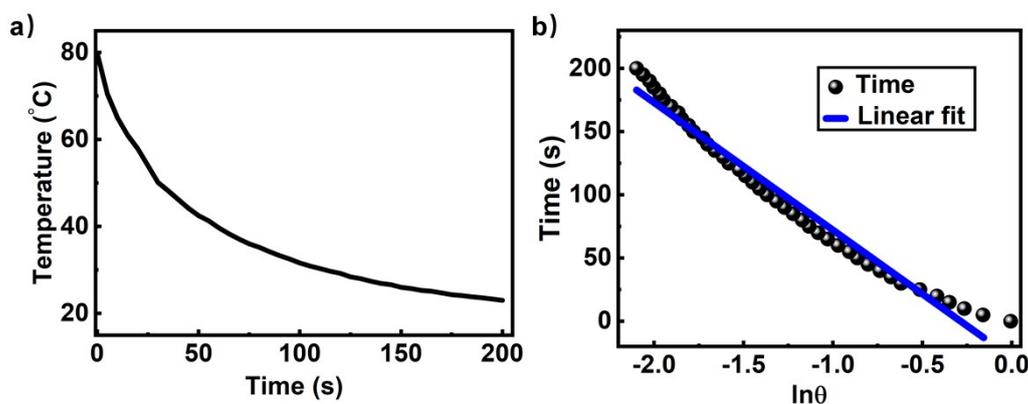


Figure S4. The cooling curve of co-crystal samples after the irradiation of 808 nm laser (0.7 W/cm²) (a) and its corresponding time-Inθ linear curve (b).

The photothermal conversion efficiency of co-crystal was determined according to previous method.^{S1} Details are as follows:

Based on the total energy balance for this system:

$$\sum_i m_i C_{p,i} \frac{dT}{dt} = Q_s - Q_{loss}$$

Where m_i (0.43 g) and $C_{p,i}$ (0.281 J/(g.°C)) are the mass and heat capacity of system components (cocystal samples and substrate), respectively. Q_s is the photothermal heat energy input by irradiating NIR laser to co-crystal samples, and Q_{loss} is thermal energy lost to the surroundings. When the temperature is maximum, the system is in balance.

$$Q_s = Q_{loss} = hS\Delta T_{max}$$

Where h is heat transfer coefficient, S is the surface area of the container, T_{max} is the maximum temperature change.

The photothermal conversion efficiency η is calculated from the following equation:

$$\eta = \frac{hS\Delta T_{max}}{I(1 - 10^{-A_{808}})}$$

Where I is the laser power (0.7 W/cm²) and A_{808} is the absorbance of the samples at the wavelength of 808 nm (0.585).

In order to get the hS , a dimensionless driving force temperature, θ is introduced as follows:

$$\theta = \frac{T - T_{surr}}{T_{max} - T_{surr}}$$

Where T is the temperature of cocrystal, T_{max} is the maximum system temperature (80 °C), and T_{surr} is the initial temperature (15 °C).

And a sample syste T_m time constant τ_s

$$\tau_s = \frac{\sum_i m_i C_{p,i}}{hS}$$

$$\text{Thus } \frac{d\theta}{dt} = \frac{1}{\tau_s} \frac{Q_s}{hS\Delta T_{max}} - \frac{\theta}{\tau_s}$$

When the laser is off, $Q_s = 0$, therefore $\frac{d\theta}{dt} = -\frac{\theta}{\tau_s}$, and $t = -\tau_s \ln\theta$

So hS could be calculated from the slope of cooling time vs $\ln\theta$. Therefore, τ_s is 100.92 s (Figure S2b). And the photothermal conversion efficiency η is 15.0%.

2.4 Calculation of the water evaporation efficiency under one sun.

The water evaporation rate was calculated by the following equation:

$$v = \frac{dm}{S \times dt}$$

Where m is the mass of evaporated water, S is the illuminated area, t is time, and v is evaporation rate.

In the end, Light to water evaporation efficiency (EF) was calculated based on following equation:

$$Q_e = \frac{dm \times H_e}{dt} = v \times H_e$$

$$EF = \frac{Q_e}{Q_s}$$

Where Q_e is energy consumed for water evaporation, Q_s is the incident simulated solar light power (2500 W/m²), m is the mass of evaporated water recorded by the balance, and H_e is the enthalpy of vaporization of water (2266 KJ/kg).

Table S1 Light to water Evaporation efficiency of the control experiments.

	Evaporated mass (kg/m ² 60 min)	Evaporation efficiency
The PTFE membrane	0.72	18.3%
The co-crystal-PTFE membrane	1.77	46.2%

References

- S1. Y. Wang, W. Zhu, W. Du, X. Liu, X. Zhang, H. Dong and W. Hu, *Angew. Chem., Int. Ed.*, 2018, **130**, 4027-4031.