Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

The cooperation of charge transfer and electron transfer for manipulating photothermal behaviour of donor-acceptor co-crystals

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Table of content

Supplementary Tables

X-ray crystallography

Table S1. Crystal Data and Structural Refinement Parameters of **CTC-1OH** and **CTC-2OH**

Compound name	**CTC-1OH**	**CTC-2OH**
Structural formula	H_2BCbpe·2Hbdc-OH·0.5H_2bdc-OH·4H_2O	BCbpe·H_2bdc-$(OH)_2$·H_2O
Empirical formula	$C_{40}H_{39}N_2O_{18.5}$	$C_{28}H_{24}N_2O_9$
Formula weight	843.73	532.49
Temperature (K)	298	298
Crystal system	triclinic	orthorhombic
Space group	*P*-1	$P2_12_12_1$
a (Å)	8.2694	4.7835
b (Å)	8.7155	43.651
c (Å)	26.765	11.3771
α (°)	87.121	90
β (°)	85.505	90
γ (°)	80.356	90
Volume ($Å^3$)	1894.6	2375.64
Z	2	4
D_{calcd} (g/cm^3)	1.479	1.489
Absorption coefficient (mm^{-1})	0.119	0.113
F (000)	882.0	1112.0
Reflections collected	22553/9057	23001/4156
GOOF on F^2	1.037	1.135
R_1, wR_2 ($I > 2\sigma(I)$)	R_1 = 0.0551, wR_2 = 0.1372	R_1 = 0.1661, wR_2 = 0.4510
R_1, wR_2 (all data)	R_1 = 0.0952, wR_2 = 0.1637	R_1 = 0.1739, wR_2 = 0.4690

Supplementary Figures

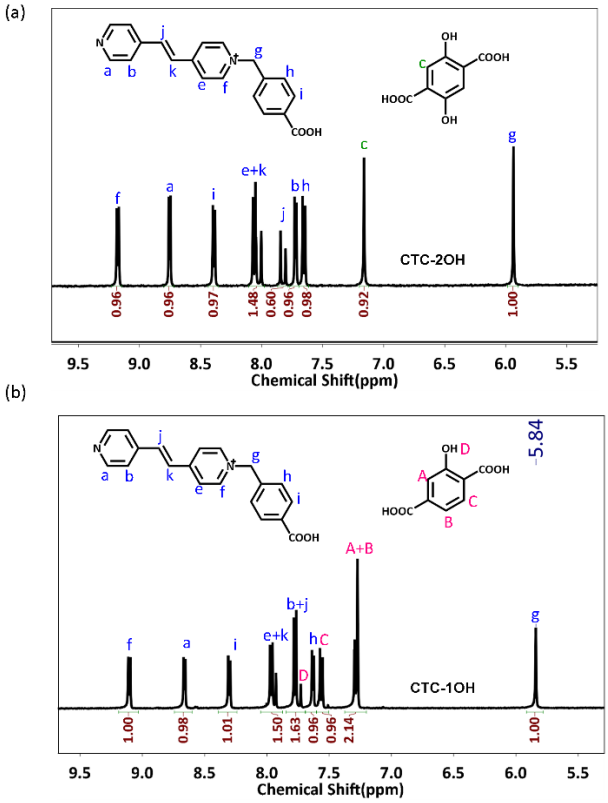

Fig. S1 ^{1}H NMR spectra (400 MHz, d_6-DMSO) of **CTC-2OH** (a) and **CTC-1OH** (b), and the attribution of characteristic peaks.

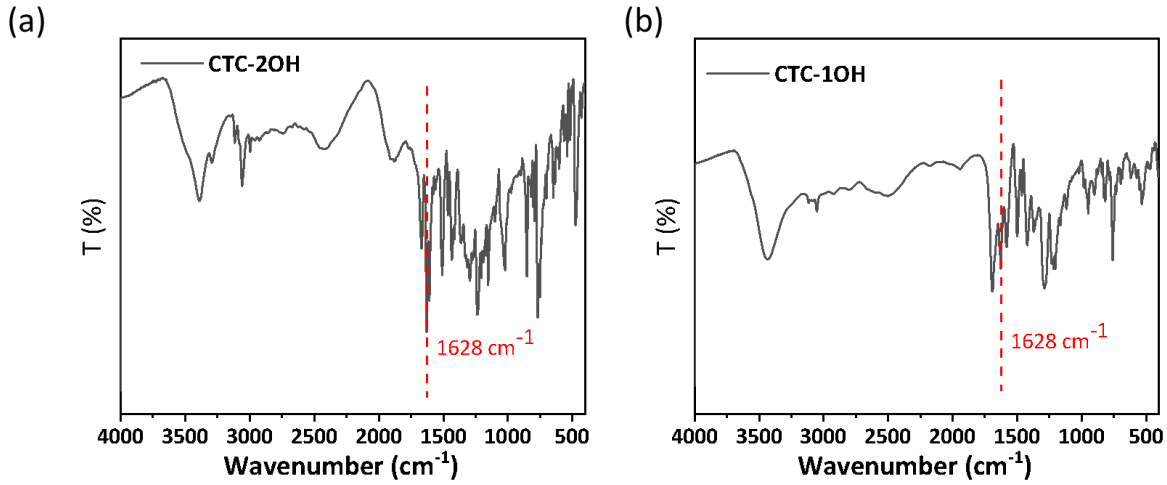

Fig. S2 FT-IR spectra of **CTC-2OH** (a) and **CTC-1OH** (b)**.**

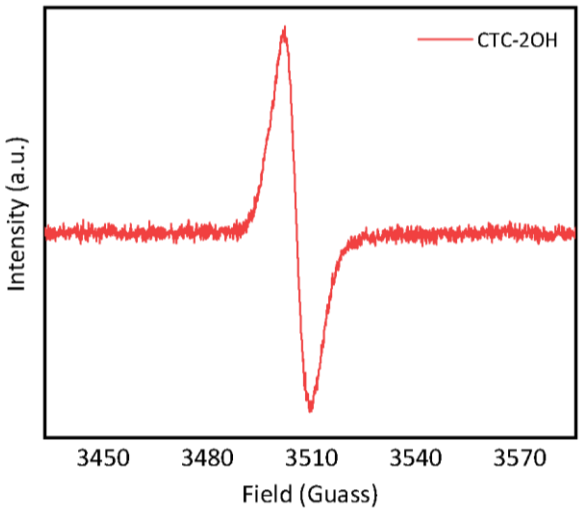

Fig. S3 ESR spectrum of **CTC-2OH** in the solid-state under an air atmosphere at room temperature.

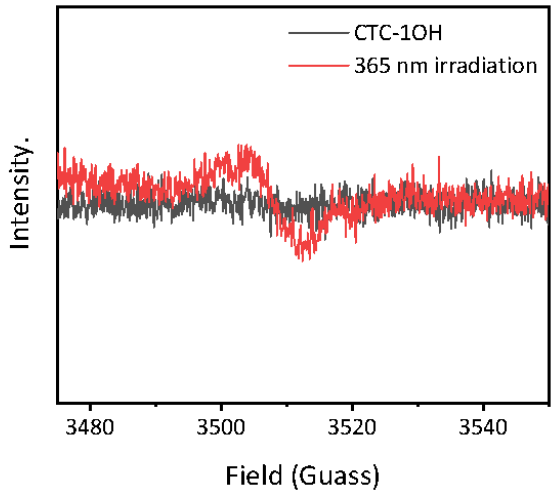

Fig. S4 ESR spectra of **CTC-1OH** in the solid-state before and after 365 nm light irradiation.

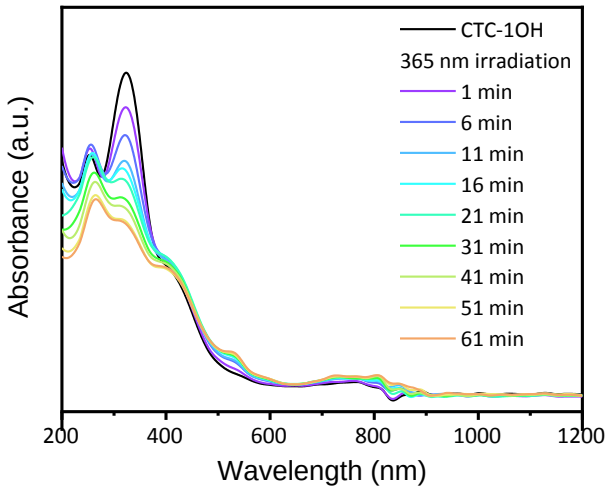

Fig. S5 Time-dependent UV-Vis-NIR spectral change of **CTC-1OH** in solid state upon 365 nm light irradiation.

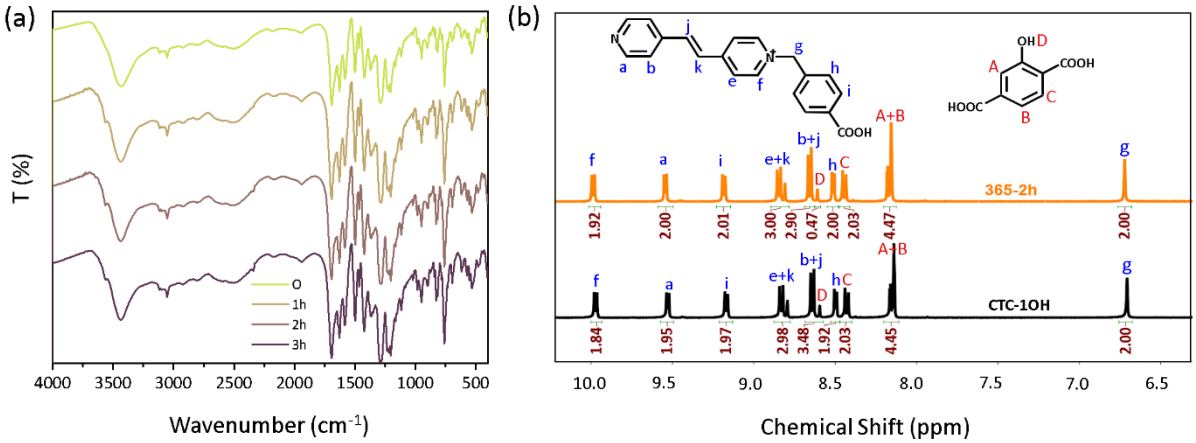

Fig. S6 (a) IR and (b) ^{1}H NMR spectra of **CTC-1OH** before and after 365 nm light irradiation.

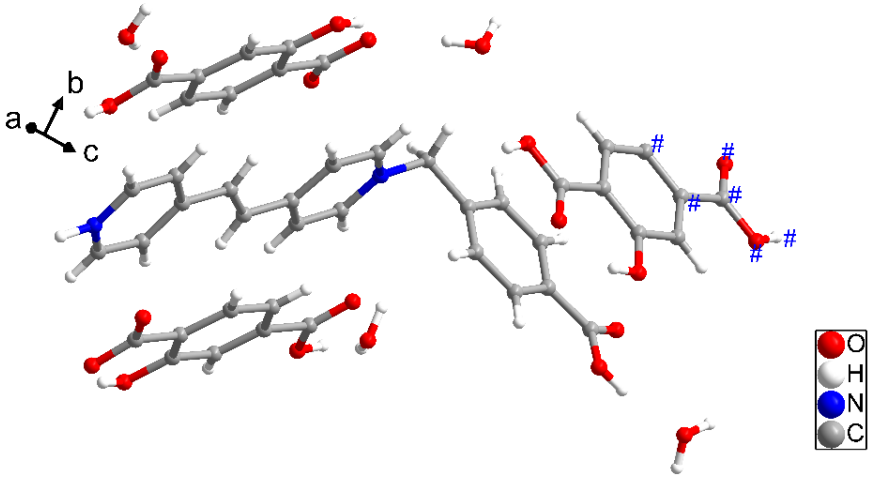

Fig. S7 The crystallographically asymmetric unit in **CTC-1OH** (The atoms marked # are generated by symmetric operation).

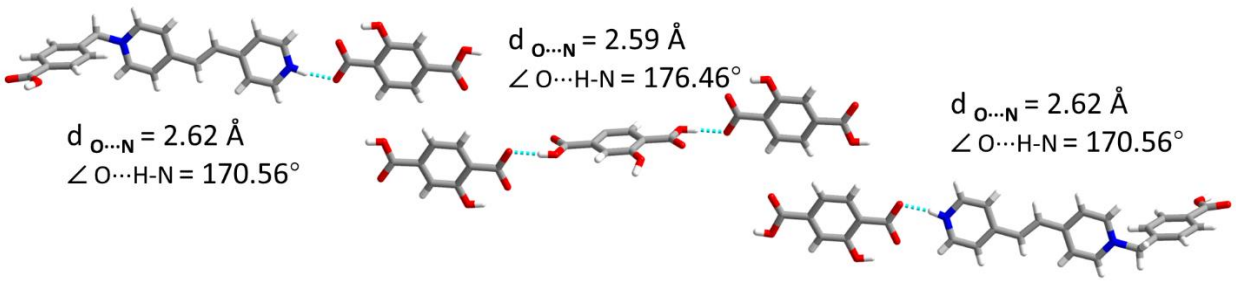

Fig. S8 The hydrogen bonds between adjacent H_2BCbpe^{2+}, $Hbdc\text{-}OH^{-}$ and $H_2bdc\text{-}OH$ in **CTC-1OH**.

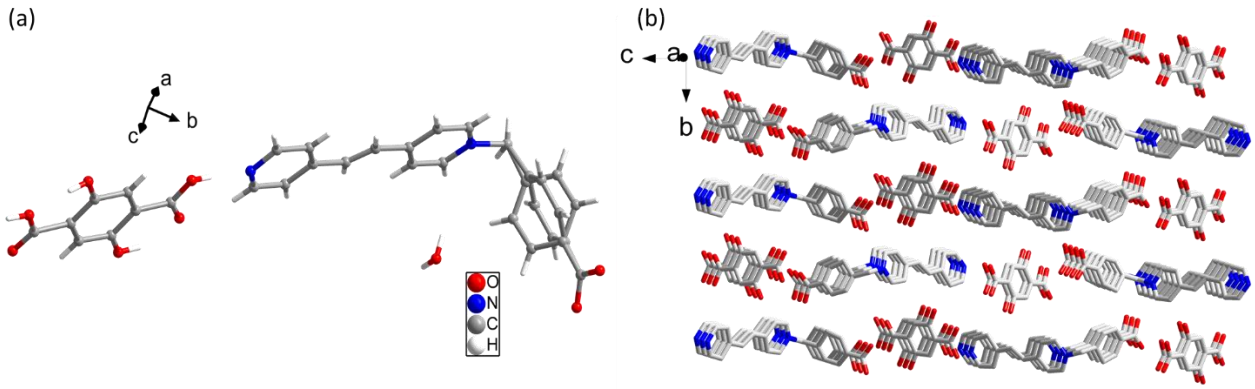

Fig. S9 (a) The crystallographically asymmetric unit and (b) three-dimensional supramolecular stacking of **CTC-2OH.**

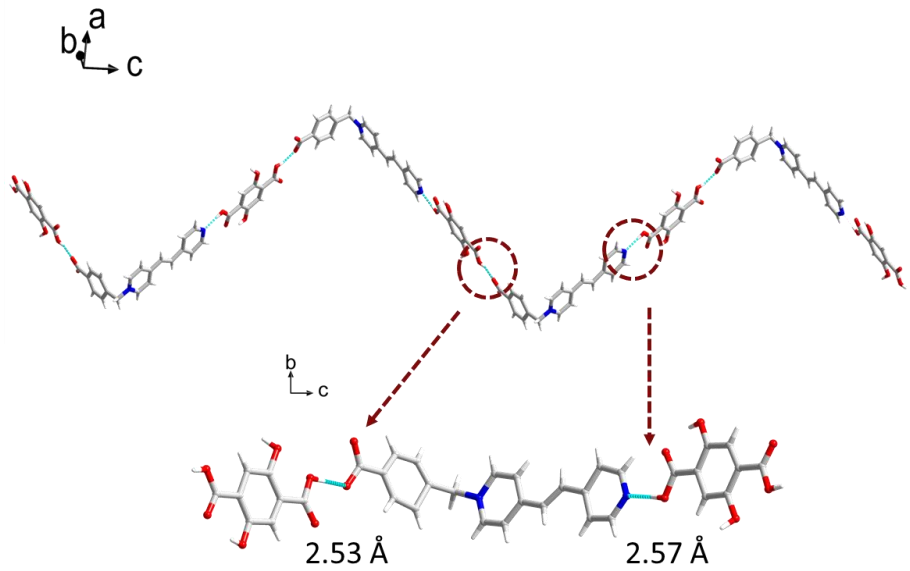

Fig. S10 The hydrogen bonds between adjacent BCbpe and $H_2bdc\text{-}(OH)_2$ in "Z" type chain. The "head" and "tail" moieties of BCbpe are connected to $H_2bdc\text{-}(OH)_2$ by two types of hydrogen bonds: O-H· ·O hydrogen bonds ($d_{O\text{-}O}$ = 2.53 Å) and O-H· ·N hydrogen bonds ($d_{O\text{-}N}$ = 2.57 Å) in **CTC-2OH**.

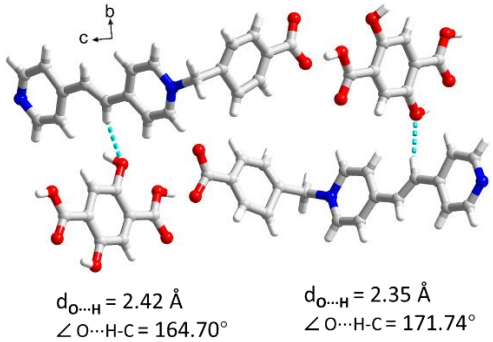

Fig. S11 The adjacent BCbpe ligands and $H_2bdc\text{-}(OH)_2$ ligands are connected by interchain hydrogen bonds: C-H· ·O hydrogen bonds ($d_{C\text{-}O}$ = 2.66 Å) in **CTC-2OH**.

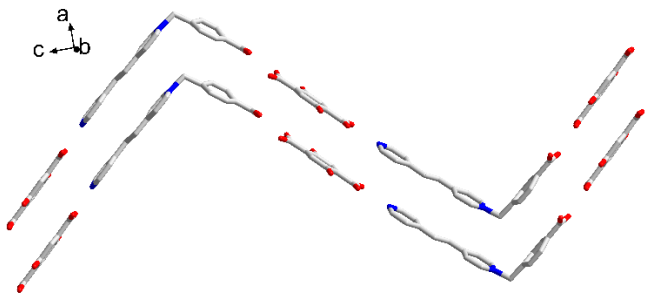

Fig. S12 pile-up sequences and Z-shaped arrangement in **CTC-2OH.**

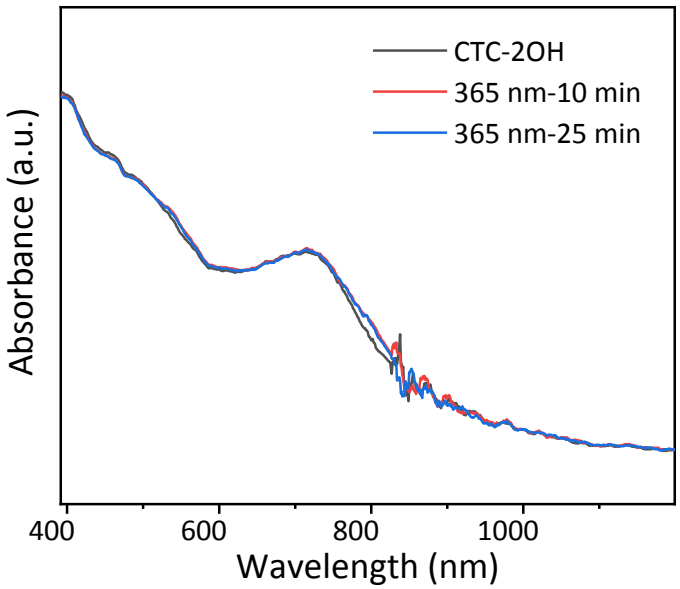

Fig. S13 UV-Vis-NIR spectral change of **CTC-2OH** in the solid-state-upon 365 nm light irradiation.

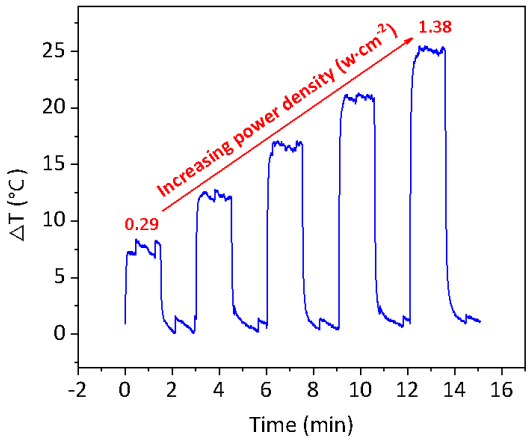

Fig. S14 Photothermal conversion curves of **CTC-1OH** co-crystal upon exposure to NIR laser at varied power densities.

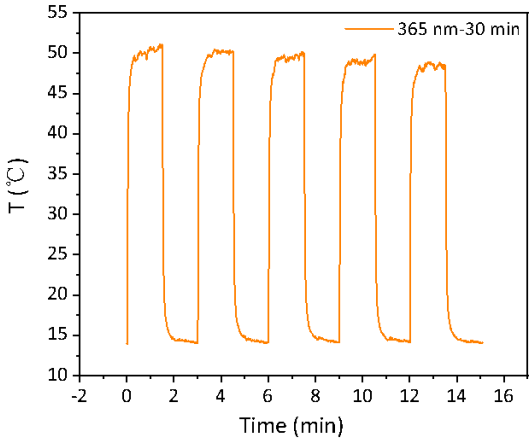

Fig. S15 Photothermal conversion curves of the photo-irradiated **CTC-1OH** (365 nm light for 30 min) during five cycles of heating and cooling processes.

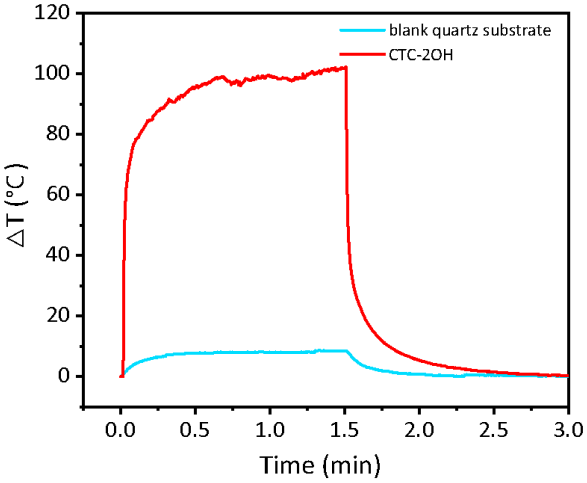

Fig. S16 Temperature transformation curves of **CTC-2OH** co-crystal and its blank quartz substrate upon exposure to 808 nm laser with power density of 1.38 W·cm^{-2}.

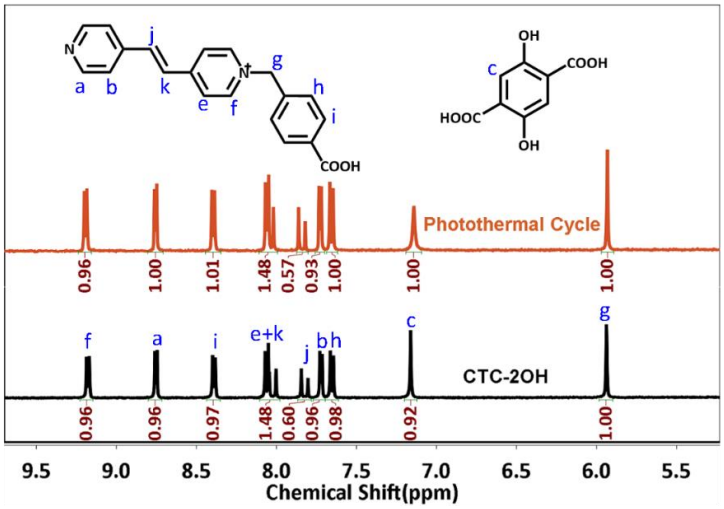

Fig. S17 ^{1}H NMR spectra and the attribution of characteristic peaks of **CTC-2OH** after 10 photothermal cycles via 808 nm laser.

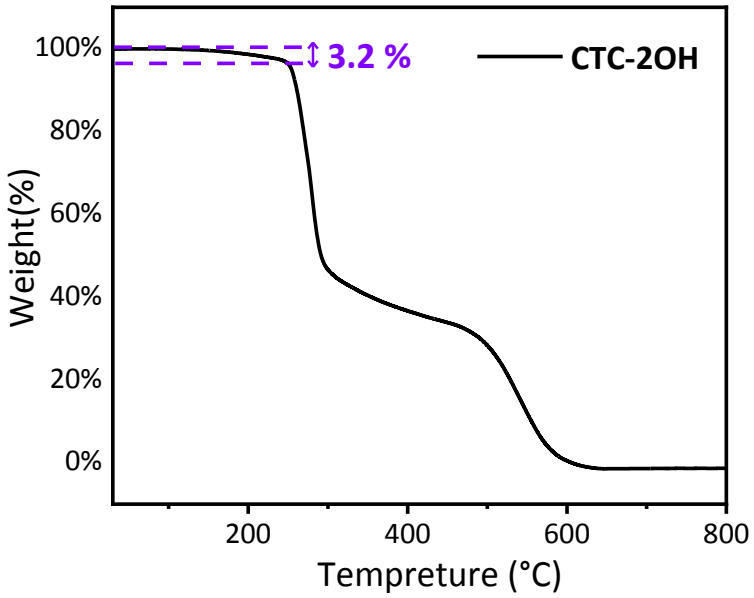

Fig. S18 Thermogravimetric curve of **CTC-2OH.**

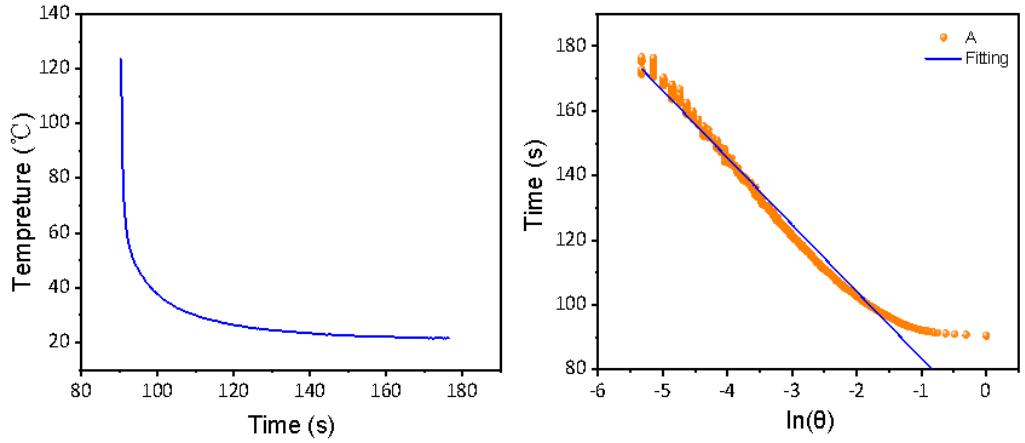

Fig. S19 Cooling curve (a) of the **CTC-2OH** irradiated by 808 nm laser (1.38 W·cm^{-2}) and its corresponding time-lnθ linear curve; the calculated value of τ_s is 29.7 s.

Calculation of photothermal efficiency ($\eta_{CTC\text{-}2OH}$)

The photothermal conversion efficiency (η) is obtained according to Equation (1).

$$\eta = \frac{hA(T_{Max} - T_{surr}) - Q_{Dis}}{I(1 - 10^{-A808})} \quad (1)$$

In equation (1), T_{Max} is the maximum steady-state temperature(123.4 °C), T_{surr} represents the surrounding temperature (20.1 °C); I represents the power of incident laser (0.39 w); A_{808} is the absorbance of the sample at 808 nm (0.19); h, the heat transfer coefficient; A, the surface area of the container and the value of hA is obtained by equation (2); Q_{Dis} is the heat dissipation of light absorbed by the quartz sample cell, obtained by formula (3).

$$hA = \frac{m_D C_D}{\tau_s} \quad (2)$$

$$Q_{Dis} = \frac{m_D C_D (T_{max} - T_{surr})}{\tau_s} \quad (3)$$

m_D and C_D are the mass (8 mg) and heat capacity (0.8 J/g) of the sample respectively, τ_s (the time constant of heat transfer in the system) can be obtained from equation (4).

$$t = -\tau_s ln\theta = -\tau_s ln(\frac{T_t - T_{surr}}{T_{Max} - T_{surr}}) \quad (4)$$

The variable t in equation (4) is the cooling time point after continuous irradiation, T_t is the temperature at the corresponding time point in the cooling process, and τ_s is 29.7s. By calculation, the photothermal efficiency of compound **CTC-2OH** is 35.4 %.