Supporting Information

Hydrogen-Bonded Organic Frameworks-stabilized Charge Transfer Co-crystals for NIR-II Photothermal Cancer Therapy

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Figure S1 Schematic illustration of the HUMO-LUMO energy bandgap of the electron donor-acceptor pair used for self-assembling CT cocrystals.
Figure S2 SEM images of PFC-1 and TQC.
Figure S3 SEM images of TBC (a), TBC@PFC-1 (b), DTC (c) and DTC@PFC-1 (d).
Figure S4 PXRD spectra of (a) PFC-1, TBC and TBC@PFC-1; (b) DTC and DTC@PFC-1.
Figure S5 Solid-state absorption spectra of TTF, TCNQ, DBTTF and TCNB.
Figure S6 FT-IR spectra of PFC-1, TTF, TCNQ and TQC@PFC-1.
Figure S7 Raman spectra of TTF, TCNQ and TQC@PFC-1.
Figure S8 X-ray Photoelectron Spectroscopy measurements of TQC@PFC-1. a) N 1s spectrum of TCNQ and TQC@PFC-1. b) S 2p spectrum of TTF and TQC@PFC-1.
Figure S9 Thermogravimetric analyses of PFC-1, TQC and TQC@PFC-1.
Figure S10  Transmission electron microscopy (TEM) image of TQC@PFC-1 and the corresponding EDX mapping of C, O, and S.
Figure S11 The fluorescent spectra of PFC-1 and TQC@PFC-1 (0.025 mg/mL).

The fluorescence spectrum was measured by exciting the sample at 320 nm.
**Figure S12** The PXRD patterns of TQC and TQC@PFC-1 before and after incubation with acetone, CH$_3$OH, or 1 M HCl for 24 h.
**Figure S13** Structural profile of TQC and PFC-1 by cryo-TEM. a) Cryo-TEM image of TQC; b) The amplified cryo-TEM structure and c) the FFT pattern of the selected selected area highlighted in the white frame in a). d) Cryo-TEM image of PFC-1; b) The amplified cryo-TEM structure and c) the FFT pattern of the selected selected area highlighted in the white frame in d)
Table S1 DLS characterizations of PFC-1, TQC and TQC@PFC-1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size (nm)</th>
<th>Zeta potential(mV)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFC-1</td>
<td>228.9 ± 5.7</td>
<td>-32.9 ± 3.0</td>
<td>0.337</td>
</tr>
<tr>
<td>TQC</td>
<td>4380 ± 298</td>
<td>-29.2 ± 1.0</td>
<td>0.526</td>
</tr>
<tr>
<td>TQC@PFC-1</td>
<td>244.8 ± 20.5</td>
<td>-17.4 ± 1.4</td>
<td>0.188</td>
</tr>
</tbody>
</table>
Figure S14 The size distributions of PFC-1, TQC, and TQC@PFC-1 dispersed in water.
Figure S15 UV/Vis absorption spectra of aqueous solutions of PFC-1 and TQC@PFC-1 (1 mg/mL).
The photothermal conversion efficiencies (η) were calculated using equations according to the previous method\textsuperscript{1,2}.

\[
\eta = \frac{hs(T_{max} - T_{surr})}{I(1 - 10^{-A_{1080}})}
\]

h is the heat transfer coefficient; s is the surface area of the container. I is the laser power and A is the absorbance at 1080 nm. Tmax and Tsur are the maximum steady state temperature and the environmental temperature, respectively.

\[
hs = \frac{mC_{water}}{\tau}
\]

m is the mass of the solution containing the photoactive material, C is the specific heat capacity of the solution (C\textsubscript{water} = 4.2 J/(g\textdegree C)), and \(\tau\) is the associated time constant.

\[
t = -\tau \ln(\theta)
\]

\(\theta\) is a dimensionless parameter, known as the driving force temperature.

\[
\theta = \frac{T - T_{surr}}{T_{max} - T_{surr}}
\]

**Figure S16** a) The cooling curve of TQC@PFC-1 (1 mg/mL) after the irradiation of 1080 nm laser (0.8 W/cm\(^2\)) and b) its corresponding time-In\(\theta\) linear curve.
Figure S17 Comparison of the photothermal effect of TQC, physical mixture of TQC and PFC-1, and TQC@PFC-1 aqueous solution (1 mg/mL) under 1080 nm laser irradiation (1.5 W/cm²).
Figure S18 PXRD patterns of TQC@PFC-1 before and after incubation with cell culture medium for 24 h
Flow cytometry analysis was performed to evaluate the delivery efficiency of TQC@PFC-1. HeLa cells were treated with varying concentrations of HOFs for 18 hours, followed by flow cytometry analysis to quantify PFC-1-positive cells.
Figure S20  Cellular uptake study of TQC@PFC-1 by HeLa cells. The cells were incubated with different concentrations of TQC@PFC-1 for 18 h as indicated, followed by flow cytometry analysis to quantify PFC-1 positive cells. The data was presented as mean ± SD (n=3).
Figure S21 Confocal laser scanning microscopy (CLSM) images of HeLa cells incubated with 0.1 mg/mL TQC@PFC-1 at different time points. The endosome/lysosome was stained with 100 nM LysoTracker@Red before CSLM imaging. Scale bar: 20 μm.
Figure S22 The cell apoptosis assay was performed on HeLa cells treated with PBS or TQC@PFC-1 with 1080 nm laser (1.5 W/cm²) irradiation for 5 minutes.
Figure S23 Photothermal ablation of B16F10 cells by TQC@PFC-1. The Viability of B16F10 cells treated with 0.2 mg/mL PFC-1 or 0.2 mg/mL TQC@PFC-1 for 2 h, followed by light irradiation (1080 nm, 1.5 W/cm²) for 5 min. as indicated. The differently treated cells were further incubated for 18 h before the determination of cell viability using MTT assay. The data was presented as mean ± SD (n=3).
Figure S24 Photothermal ablation of 4T1 cells by TQC@PFC-1. The Viability of 4T1 cells treated with 0.2 mg/mL PFC-1 or 0.2 mg/mL TQC@PFC-1 for 2 h, followed by light irradiation (1080 nm, 1.5 W/cm²) for 5 min. as indicated. The differently treated cells were further incubated for 18 h before the determination of cell viability using MTT assay. The data was presented as mean ± SD (n=3).
Figure S25 A representative image of tumors from four groups of mice after different treatments as indicated.
Figure S26 Histological hematoxylin and eosin (H&E) analysis of the major organs of mice received different treatments as indicated. Scale bar 200 µm.
Figure S27  Liver function tests were performed on mice treated with TQC@PFC-1 and laser irradiation.

Reference
