

Supporting Information

Investigating the Effect of Chemical Structure of Semiconducting Polymer Nanoparticle on Photothermal Therapy and Photoacoustic Imaging

Dongdong Li^{1,*}, Guobing Zhang^{2,*}, Weiguo Xu^{3,*}, Junxia Wang¹, Yucai Wang^{4,✉},

Longzhen Qiu², Jianxun Ding^{3,✉}, Xianzhu Yang^{1,✉}

1. Institutes for Life Sciences, School of Medicine and National Engineering Research Center for Tissue Restoration and Reconstruction, South China University of Technology, Guangzhou, Guandong 510006, P.R. China
2. Academy of Opto-Electronic Technology, Hefei University of Technology, Hefei, Anhui 230009, P.R. China
3. Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130222, P. R. China
4. School of Life Sciences and Medical Center, University of Science & Technology of China Hefei, Anhui 230027, P.R. China

* These authors contributed equally to this work.

✉ **Corresponding Authors:** E-mail: yangxz@scut.edu.cn (Xianzhu Yang), E-mail: jxding@ciac.ac.cn (Jianxun Ding), and E-mail: yucaiwang@ustc.edu.cn (Yucai Wang)

Materials and characterizations:

Chemicals used in this work were purchased from Sigma-Aldrich Chemical Company, Alfa Aesar Chemical Company and Sinopharm Chemical Reagent Co. Ltd, China. Chemical reagents were used as received. Tetrahydrofuran (THF) and toluene were freshly distilled over sodium wire under nitrogen prior to use.

2,5-Bis(trimethylstannyl)thieno[3,2-*b*]thiophene (TT),¹
1,2-bis(5-(trimethylstannyl)-thiophene-2-yl)ethane (TVT),² *N*-(2-decyltetradecyl)-3,6-dibromophthalimide (PhT),³ 1,3-dibromo-5-(2-decyltetradecyl)-4H-thieno[3,4-*c*]pyrrole-4,6-dione (DPT),⁴
3,6-bis(5-bromo-2-thienyl)-2,5-bis(2-decyltetradecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP),¹ and 2,5-dihydro-2,5-dioctyl-3,6-bis[5-(trimethylstannyl)-2-thienyl]pyrrolo[3,4-*c*]pyrrole-1,4-dione⁵ were synthesized via published procedures.

Synthesis of the polymer PDPP-PhT.

Tris(dibenzylideneacetone)dipalladium (Pd₂(dba)₃, 0.005 g, 0.006 mmol) and tri(*o*-tolyl)phosphine (P(*o*-tol)₃, 0.008 g, 0.024 mmol) were added to a solution of 2,5-dihydro-2,5-dioctyl-3,6-bis[5-(trimethylstannyl)-2-thienyl]pyrrolo[3,4-*c*]pyrrole-1,4-dione (0.25 g, 0.30 mmol) and PhT (0.19 g, 0.30 mmol) in toluene (6 mL) under nitrogen. The solution was subjected to three cycles of evacuation and nitrogen filling. The mixture was then heated to 110 °C for 48 h. After cooling to room temperature, the mixture was poured into methanol and stirred for 2 h. A black precipitate was collected by filtration. The product was purified by Soxhlet extractor using methanol

and dichloromethane. The residue was extracted with hot chloroform in an extractor for 24 h. After removing the solvent, a black solid was collected (0.19 g, 42.5%). Elemental Analysis: calcd for C₆₂H₉₁N₃O₄S₂ (%) C: 73.98, H: 9.11, N: 4.17, found (%): C, 73.86, H, 8.56, N: 4.06. The molecular weights and polydispersity index of PDPP-PhT was 42,890 g mol⁻¹ and 2.48, respectively.

Synthesis of the polymer PDPP-TVT.

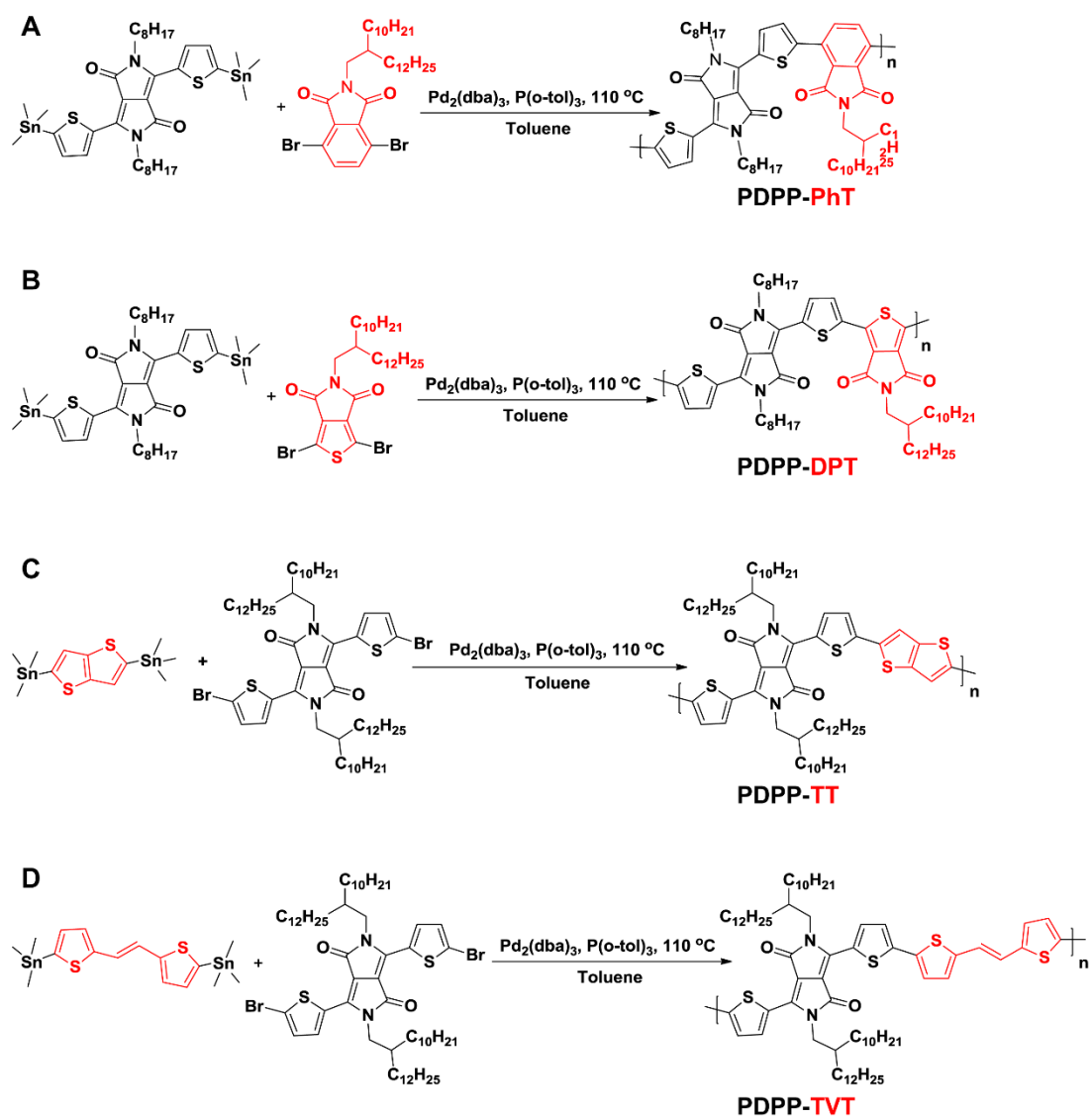
The same procedure was used as PDPP-PhT. The compounds used were Pd₂(dba)₃ (0.095 g, 0.010 mmol), P(*o*-tol)₃ (0.013 g, 0.042 mmol), DPP (0.29 g, 0.26 mmol) and 1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (0.14 g, 0.26 mmol). After the workup, a black solid was collected (0.16 g, 53.0%). Elemental Analysis: calcd for C₇₂H₁₁₀N₂O₂S₄ (%) C: 74.30, H: 9.53, N: 2.41, found (%): C, 73.92, H, 9.15, N: 2.26. The molecular weights and polydispersity index of PDPP-TVT was 40,750 g mol⁻¹ and 2.31, respectively.

Synthesis of the polymer PDPP-DPT.

The same procedure was used as PDPP-PhT. The compounds used were Pd₂(dba)₃ (0.010 g, 0.012 mmol), P(*o*-tol)₃ (0.014 g, 0.048 mmol), 2,5-dihydro-2,5-dioctyl-3,6-bis[5-(trimethylstannyl)-2-thienyl]pyrrolo[3,4-*c*]pyrrole-1,4-dione (0.26 g, 0.30 mmol) and DPT (0.20 g, 0.30 mmol). After the workup, a black solid was collected (0.24 g, 79.2%). Elemental Analysis: calcd for C₆₀H₈₉N₃O₄S₃ (%) C: 71.17, H: 8.86, N: 4.15, found (%): C, 70.67, H, 8.79, N: 3.98. The molecular weights and polydispersity index of PDPP-DPT was 67,980 g mol⁻¹ and 2.80, respectively.

Synthesis of the polymer PDPP-TT.

The same procedure was used as PDPP-PhT. The compounds used were Pd₂(dba)₃, (0.099 g, 0.011mmol), P(*o*-tol)₃ (0.013 g, 0.043mmol), 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (0.13 g, 0.27mmol) and DPP (0.31 g, 0.27mmol). After the workup, a black solid was collected (0.14 g, 46.7%). Elemental Analysis: calcd for C₆₈H₁₀₆N₂O₂S₄ (%): C: 73.46, H: 9.61, N: 2.52, found (%): C, 73.15, H, 9.23, N: 2.21. The molecular weights and polydispersity index of PDPP-TT was 44,050 g mol⁻¹ and 2.11, respectively.



Scheme S1. Synthesis pathways for the SPs: PDPP-PhT (A), PDPP-DPT (B), PDPP-TT (C), and PDPP-TVT (D).

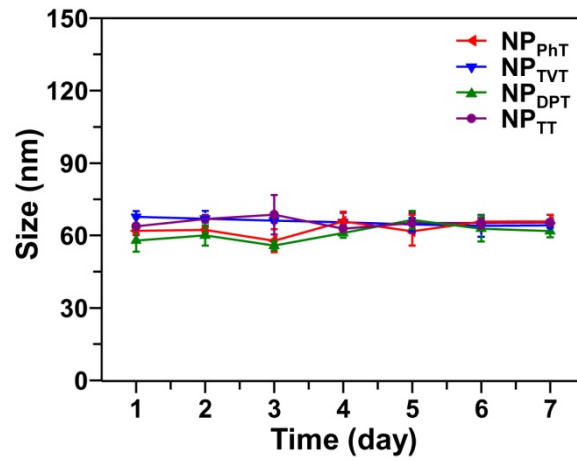


Figure S1. The size change of NP_{TT}, NP_{DPT}, NP_{TVT}, and NP_{PhT} following incubation with PBS which contain 10% FBS.

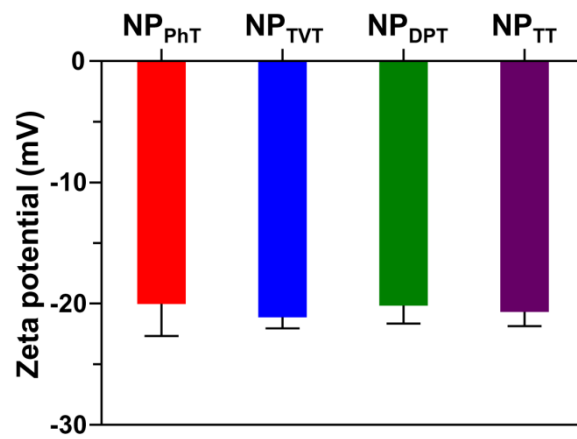


Figure S2. Zeta potentials of NP_{TT}, NP_{DPT}, NP_{TVT}, and NP_{PhT}.

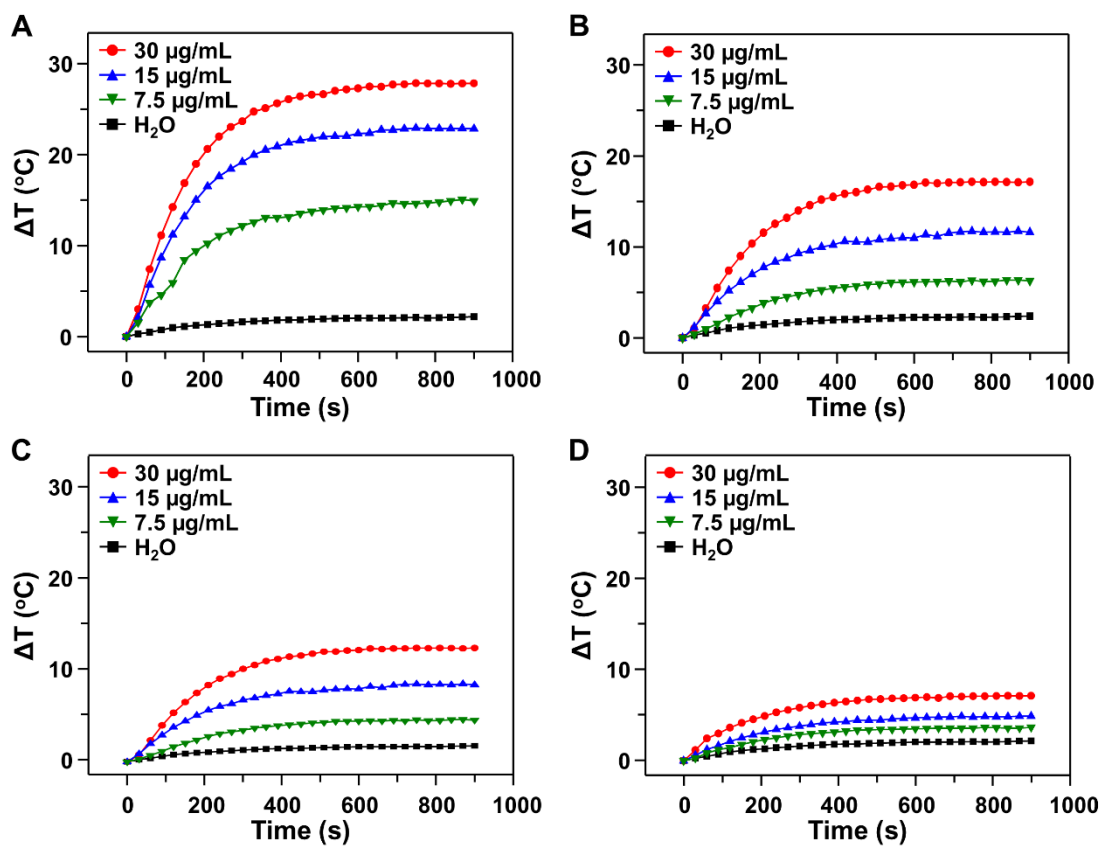


Figure S3. Temperature change curves of NP_{TT} (A), NP_{DPT} (B), NP_{TVT} (C), and NP_{PhT} (D) at different concentrations upon exposure to the NIR laser (808 nm, 1.0 W/cm², 15 min).

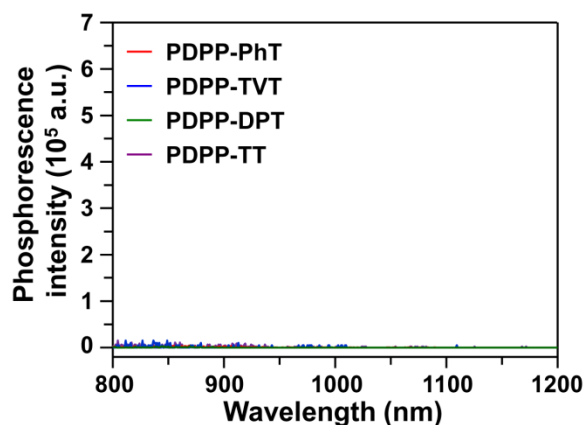


Figure S4. Phosphorescence spectra of NP_{TT}, NP_{DPT}, NP_{TVT}, and NP_{PhT} ([SP] = 10 μg/mL) upon excitation at 808 nm.

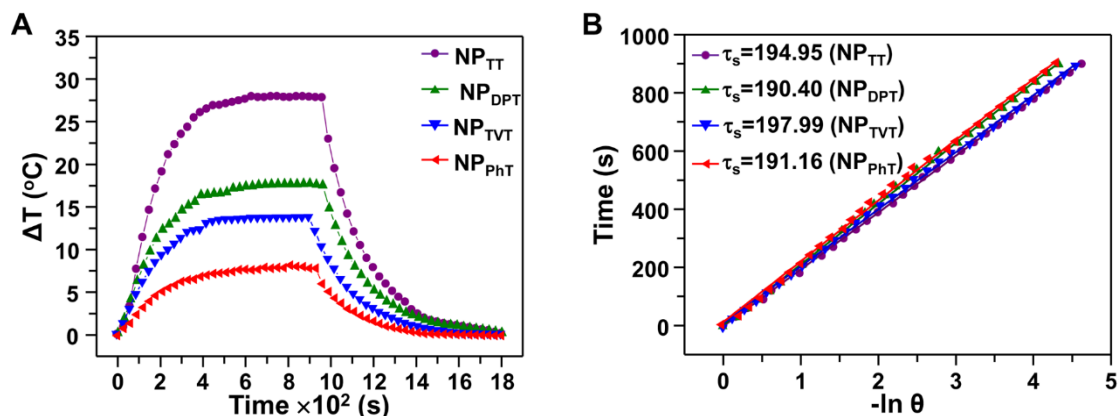


Figure S5. (A) Photothermal effect of the aqueous dispersion of these SP@NP_{PPE} (30 µg/mL) irradiated with 808 laser (a power density of 2.0 W/cm²), in which the irradiation lasted for 15 min, and then the laser was shut off. (B) Time constant for heat transfer from the system is determined to be τ_s by applying the linear time data from the cooling period versus negative natural logarithm of driving force temperature, which is obtained from the cooling stage of panel A.

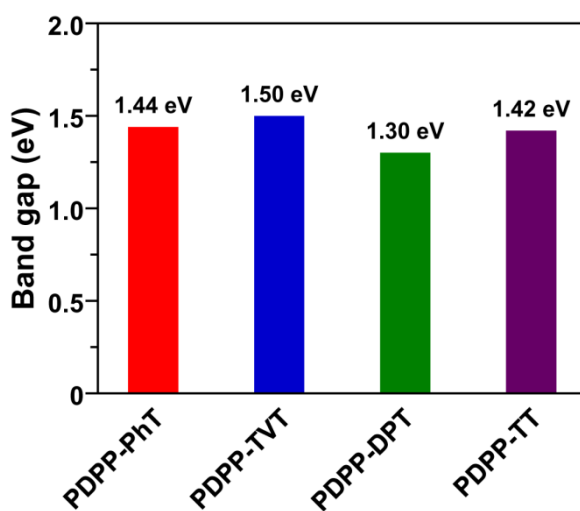


Figure S6. The band gaps of these semiconducting polymers.

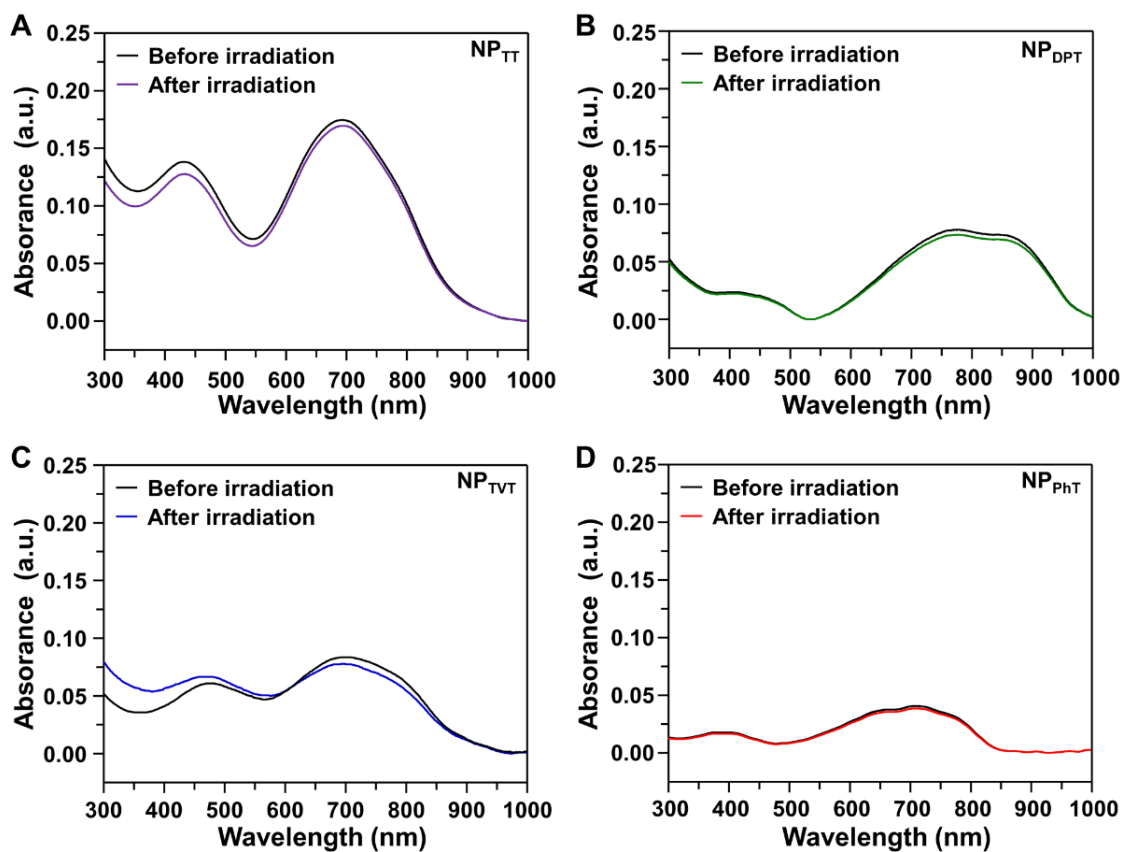


Figure S7. Absorption spectra of NP_{TT} (A), NP_{DPT} (B), NP_{TVT} (C), and NP_{PhT} (D) at a SP concentration of 30.0 $\mu\text{g/mL}$ before and after four laser on/off cycles (808 nm, 1.0 W/cm², 15 min).

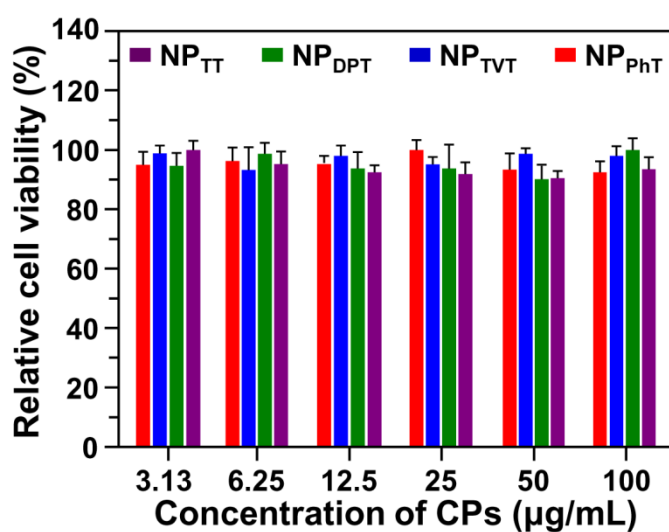


Figure S8. Cytotoxicity of SP@NPs in MDA-MB-231 cells without NIR laser irradiation.

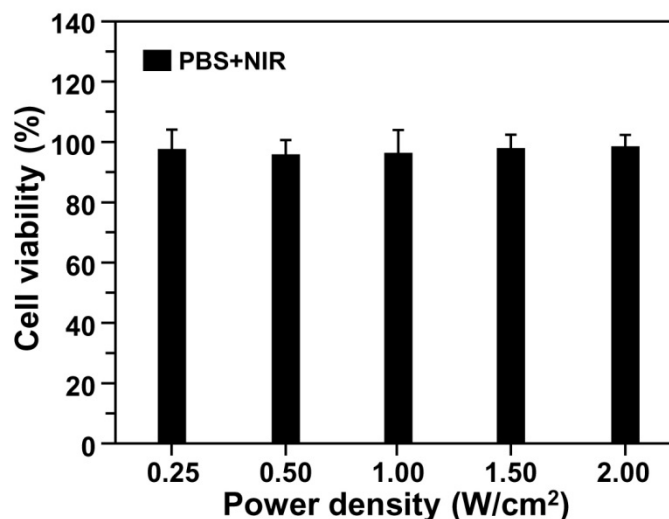


Figure S9. Cytotoxicity of MDA-MB-231 cells after treatment with PBS at different power densities.

References:

1. Zhang G, Fu Y, Xie Z, Zhang Q. Synthesis of low bandgap polymer based on 3,6-dithien-2-yl-2,5-dialkylpyrrolo[3,4-c]pyrrole-1,4-dione for photovoltaic applications. *Sol. Energy Mater. Sol. Cells* 2011; 9: 1168-73.
2. Yun HJ, Choi HH, Kwon SK, Kim YH, Cho K. Conformation-insensitive ambipolar charge transport in a diketopyrrolopyrrole-based co-polymer containing acetylene linkages. *Chem. Mater.* 2014; 2: 3928-37.
3. Zhang G, Fu Y, Zhang Q, Xie Z. Synthesis and photovoltaic properties of conjugated copolymers with benzo[1,2-b:4,5-b']dithiophene and bis(thiophene)phthalimide units. *macromol. Chem. Phys.* 2010; 211: 2596-601..
4. Zhang QT, Tour JM. Alternating donor/acceptor repeat units in polythiophenes. intramolecular charge transfer for reducing band gaps in fully substituted conjugated polymers. *J. Am. Chem. Soc.* 1998; 120: 5355-62..

5. Hu X, Zuo L, Fu W, Larsen-Olsen TT, Helgesen M, Bundgaard E, et al. Incorporation of Ester Groups into Low Band-Gap Diketopyrrolopyrrole Containing Polymers for Solar Cell Applications. *J. Mater. Chem.* 2012, 22, 15710-15716.