

Supporting Information for

RBC Membrane Camouflaged Semiconducting Polymer

Nanoparticles for Near-Infrared Photoacoustic Imaging and

Photothermal Therapy

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S1 Synthesis and Characterization

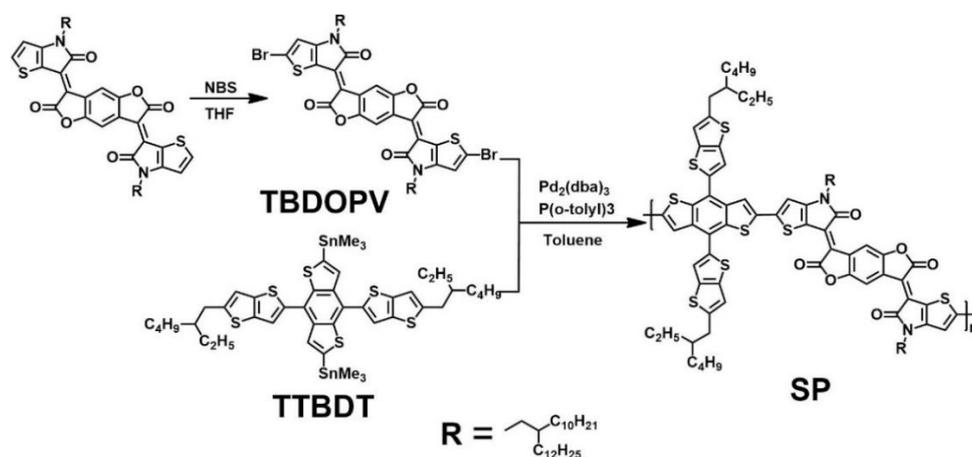


Fig. S1 Synthetic procedure for D-A conjugated semiconducting polymer (SP)

The overall synthesis route was illustrated in Fig. S1. TTBDT was commercially purchased from Suna Tech Inc. (Suzhou, <http://www.sunatech.com.cn/>). TBDOPV was synthesized according to the previous report [S1]. The synthesis procedure of SP were illustrated in Fig. S1.

S2 General Procedure for SP

In Schlenk tube, the TBDOPV (0.1158 g, 0.122 mmol), TTBDT (0.0673 g, 0.122 mmol), $\text{Pd}_2(\text{dba})_3$ (0.0034g, 0.0037 mmol), and $\text{P}(\text{o-tolyl})_3$ (0.0045 g, 0.0146 mmol) were mixed in toluene (10 mL) under nitrogen. The resulting mixture was subjected to three cycles of evacuation and admission of nitrogen. After stirred at 110 °C for 72 h, the solution was cooled down to room temperature, and then poured into stirring methanol to precipitate the polymer product. The precipitated polymer product (SP) was collected by filtration and purified with methanol and DCM in Soxhlet extractions for 24h, respectively. The final polymer product as a blackish green solid was collected.

S3 Characterization of TBDOPV

^1H NMR (CDCl_3 , ppm): δ 8.86 (s, 2H), 6.76 (s, 2H), 3.63-3.62 (d, 4H), 1.81 (m, 2H), 1.33-1.24 (m, 80H), 0.87-0.85 (t, 12H). ^{13}C NMR (CDCl_3 , ppm): δ 169.61, 169.06, 154.27, 151.20, 130.60, 129.76, 125.22, 116.22, 115.87, 115.03, 109.19, 46.31, 37.19, 31.93, 31.45, 29.96, 29.71, 29.66, 29.60, 29.38, 29.36, 26.42, 22.70, 14.13.

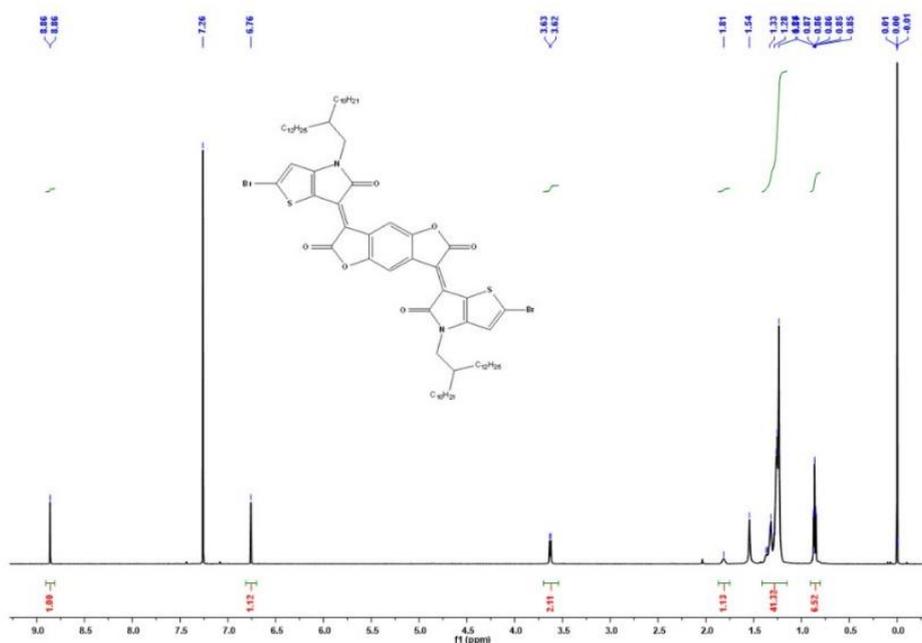


Fig. S2 ^1H NMR spectrum of TBDOPV

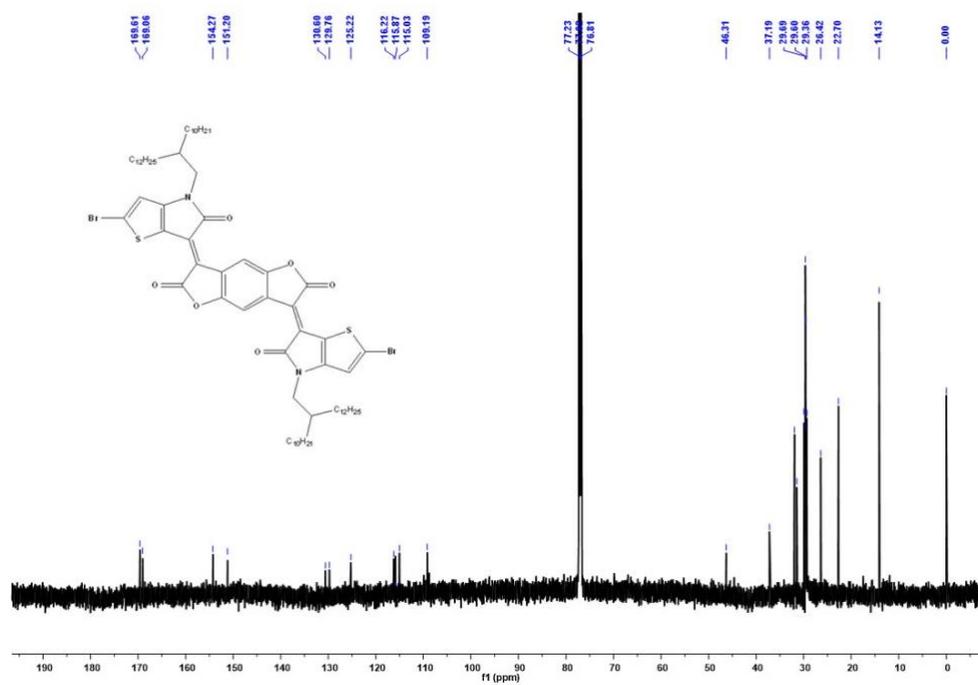


Fig. S3 ^{13}C NMR spectrum of TBDOPV

S4 Characterization of SP

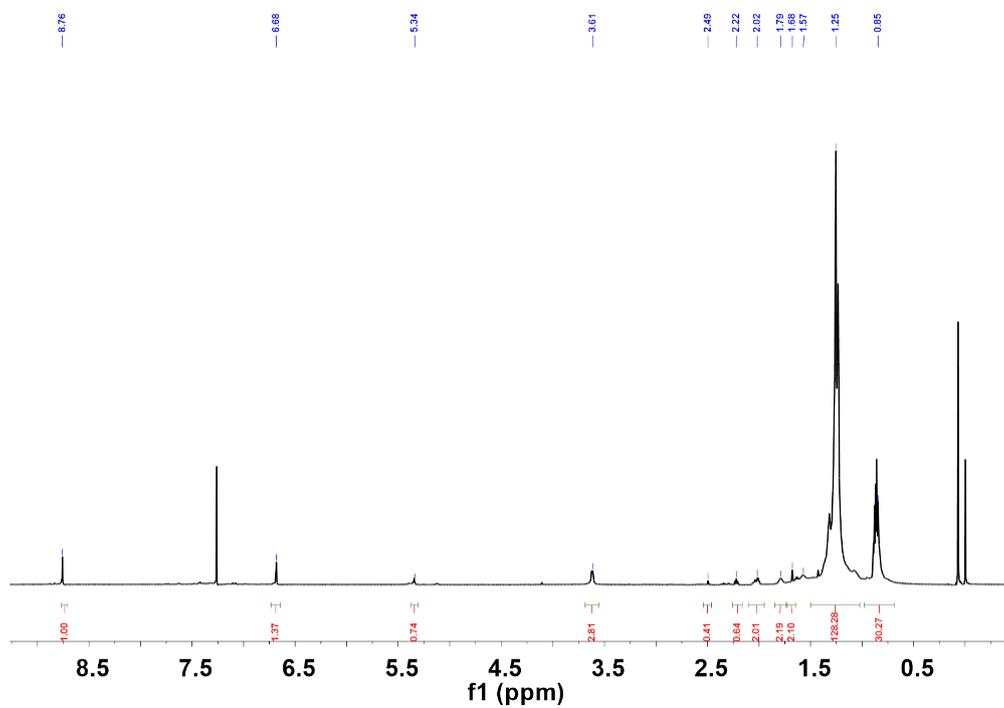


Fig. S4 ^1H NMR spectrum of SP

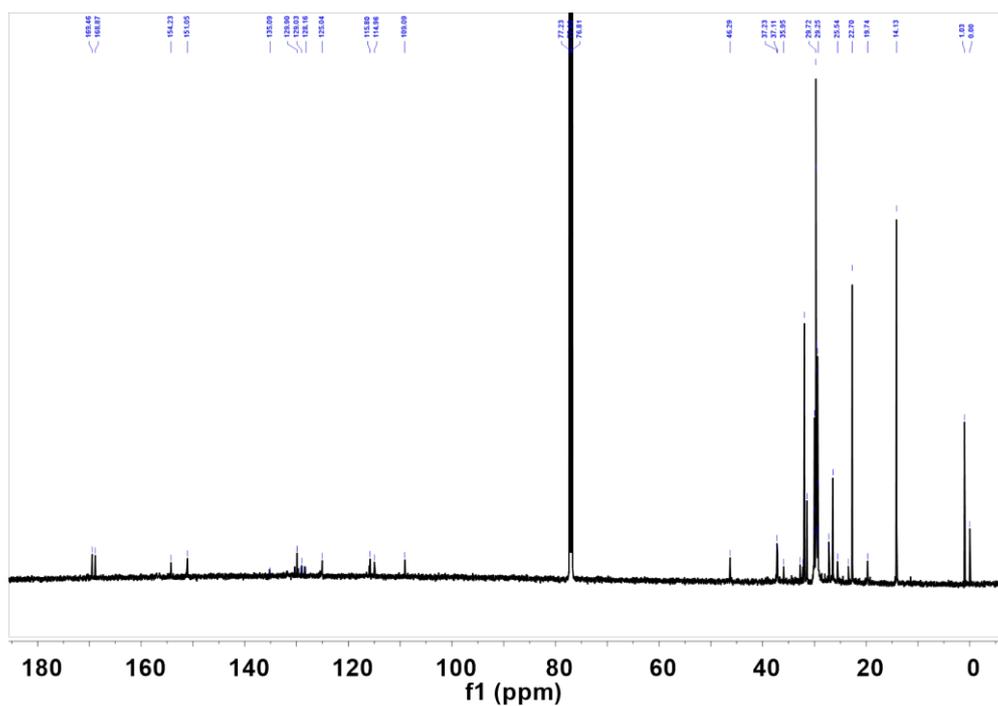


Fig. S5 ^{13}C NMR spectrum of SP

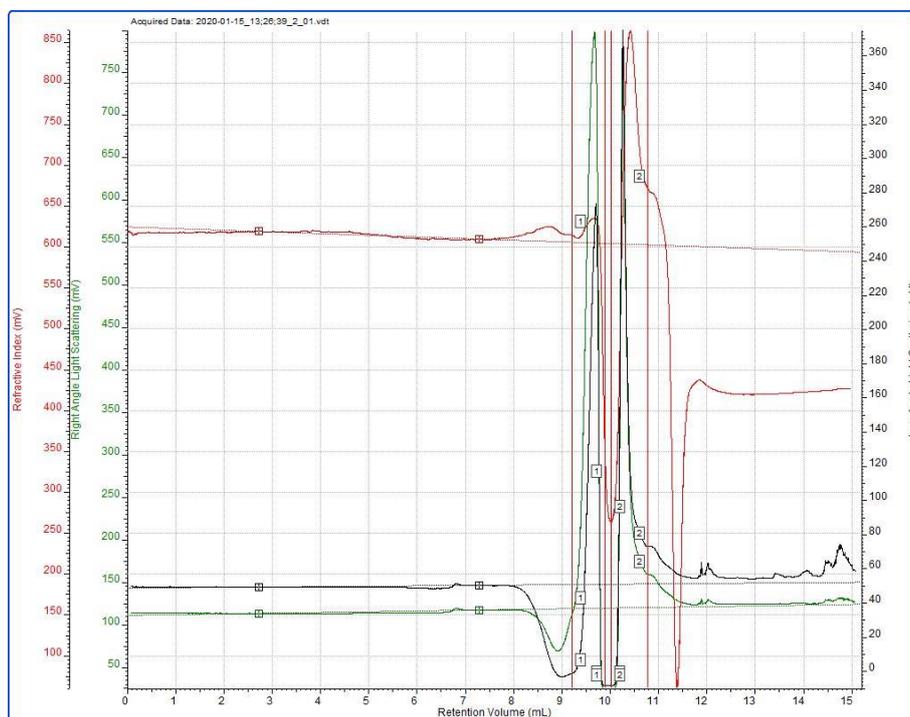


Fig. S6 GPC images of SP. The M_n of SP was determined to 6.366×10^6 , with a polydispersity (M_w/M_n) of 1.668

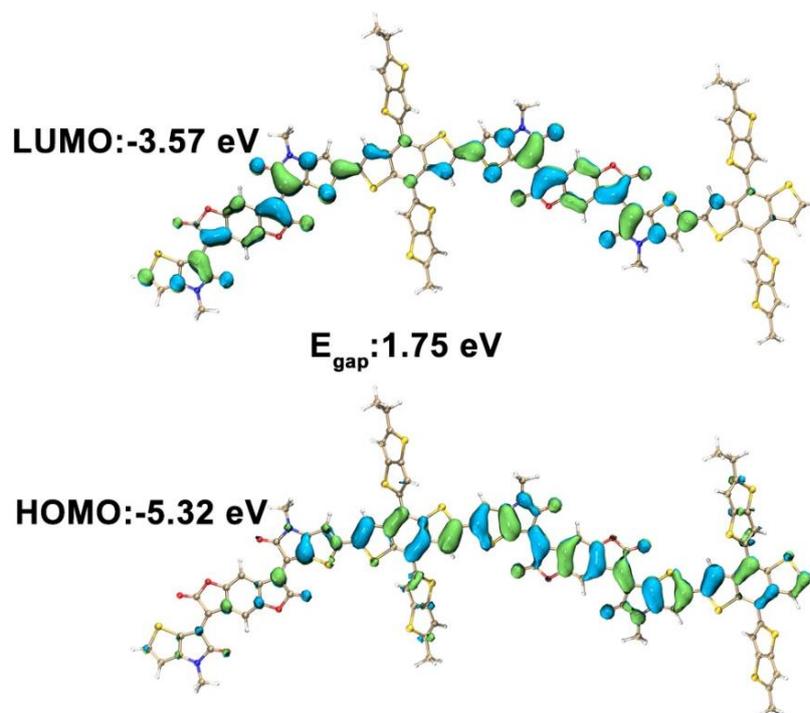


Fig. S7 Density functional theory (DFT) calculated HOMO and LUMO of SP dimer. DFT calculations were performed on the dimer to get insight on the frontier orbital distribution and level of the polymer. All optimizations were done at PBE0/def2-SVP level with Grimme's D3BJ empirical dispersion correction [S2]. The orbital energies and distributions were obtained at same level of theory. All the calculations are performed using Gaussian09 program. $E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$

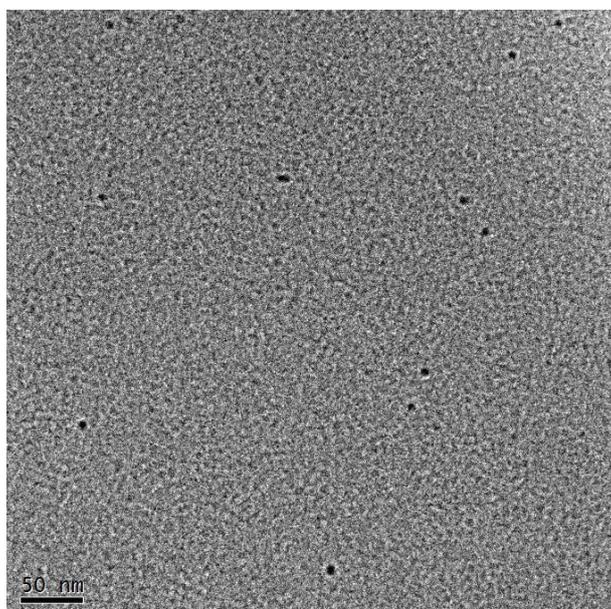


Fig. S8 TEM images of SPN@RBCM

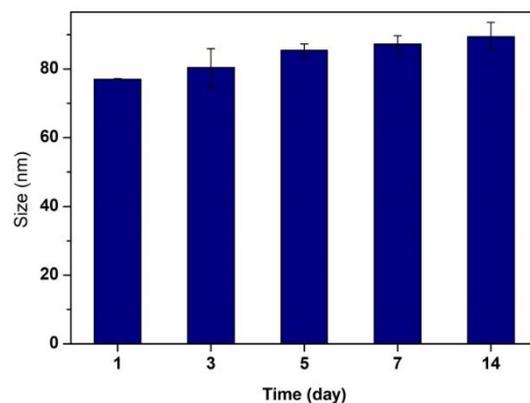


Fig. S9 Colloidal stability of SPN@RBCM in PBS with 10% FBS over a span of 14 days, as determined by DLS

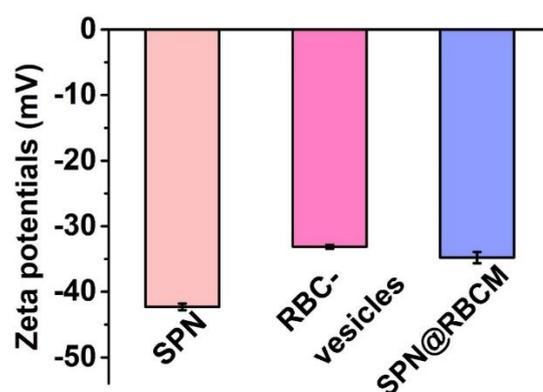


Fig. S10 Zeta potential of SPN, RBC-vesicles and SPN@RBCM

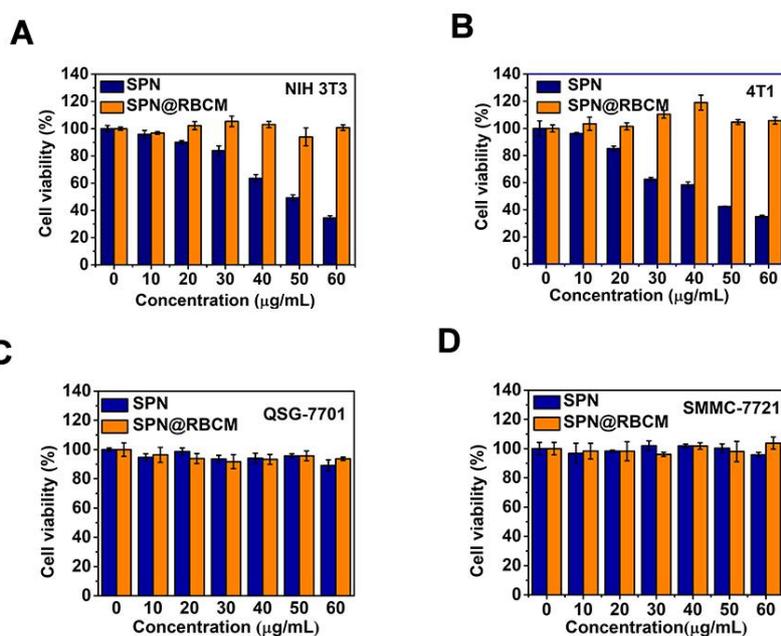


Fig. S11 Cell viability of (A) NIH-3T3, (B) 4T1, (C) QSG-7701, and (D) SMMC-7721 treated with different concentration of SPN or SPN@RBCM

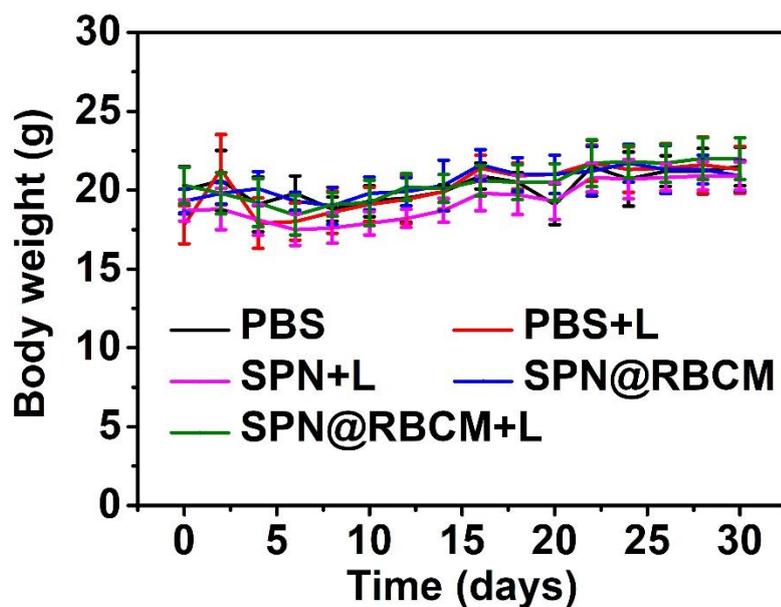


Fig. S12 Body weight variation profiles as a function of time after various treatments

Supplementary References

- [S1]Y. Cao, J.-H. Dou, N.-j. Zhao, S. Zhang, Y.-Q. Zheng et al., Highly efficient NIR-II photothermal conversion based on an organic conjugated polymer. *Chem. Mater.* **29**, 718-725 (2017). <https://doi.org/10.1021/acs.chemmater.6b04405>
- [S2]S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **32**, 1456-1465 (2011). <https://doi.org/10.1002/jcc.21759>