Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary Information

Localized Cancer Photodynamic Therapy approach based on Core-Shell Electrospun Nanofibers

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Contents

1. Structural characterization of $TPPF_{16}[S\text{-}CH_2\text{-}COOH]_4$

^1H NMR (300 MHz, DMSO-d_6): δ -3.20 (s, 2H), 4.03 (s, 8H, -CH_2), 9.35 (s, 8H, β-H). ^{19}F NMR (282 MHz, DMSO-d_6): δ -163.44 (dd, J = 10.6 and 26.5 Hz, 8F, Ar-*m*-F), -158.45 (dd, J = 10.6 and 26.5 Hz, 8F, Ar-*o*-F). ^{13}C NMR (126 MHz, CD_3OD): δ 70.3, 105.9, 117.8, 121.3, 126.8, 128.2, 129.7, 136.1, 139.1, 146.7, 147.3, 148.7, 149.3, 157.1, 180.9. HRMS (ESI) *m/z*: calcd for $C_{52}H_{22}F_{16}N_4O_8S_4$ $(M+H)^+$: 1263,0065; found 1263.0084.

NMR spectroscopy

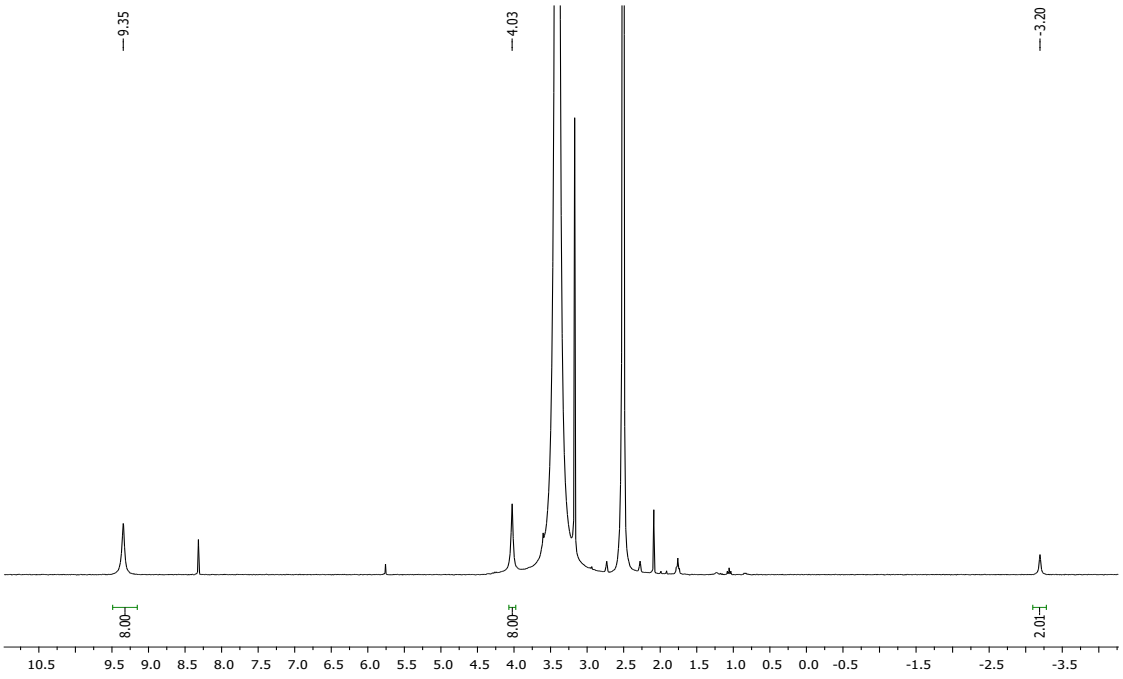

Fig. S1 ^1H NMR spectroscopy of **$TPPF_{16}[S\text{-}CH_2\text{-}COOH]_4$** in DMSO-$d_6$.

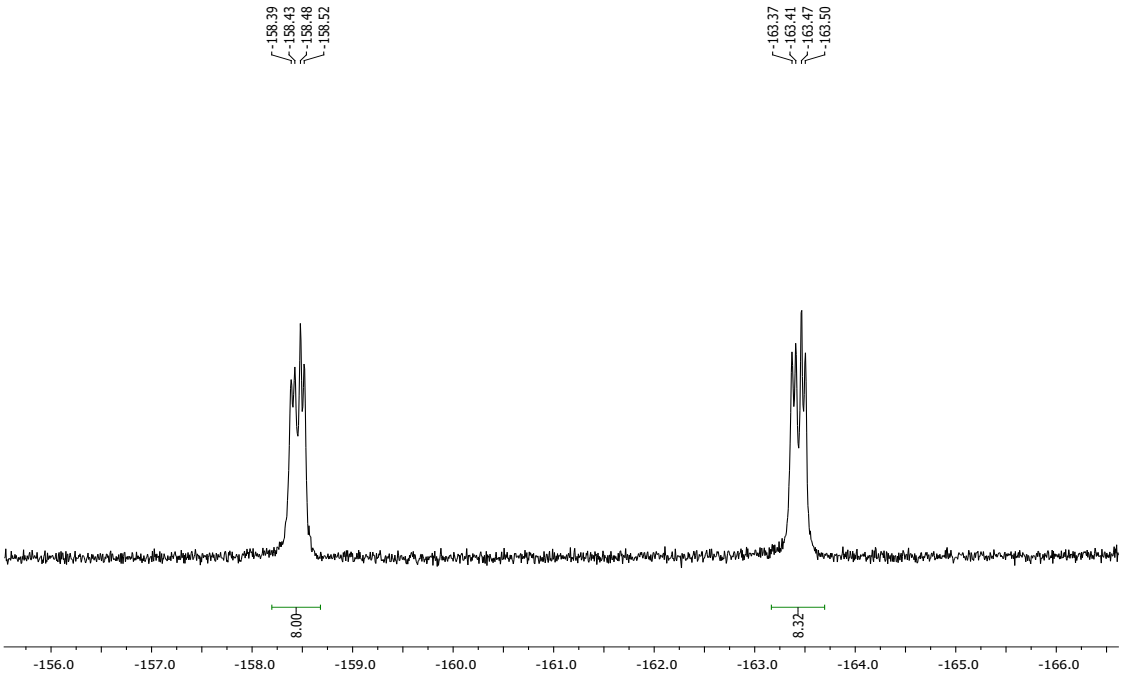

Fig. S2 ^{19}F NMR spectroscopy of **TPPF$_{16}$[S-CH$_2$-COOH]$_4$** in DMSO-d_6.

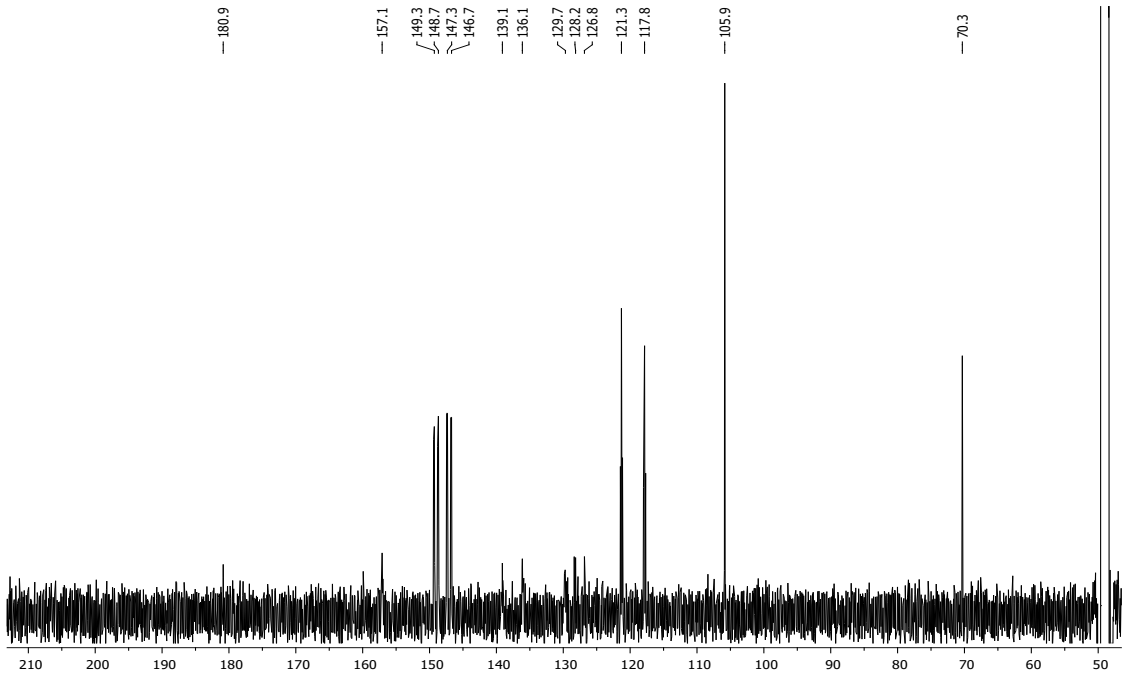

Fig. S3 ^{13}C NMR spectroscopy of **TPPF$_{16}$[S-CH$_2$-COOH]$_4$** in CD_3OD.

<u>High Resolution Mass Spectrometry</u>

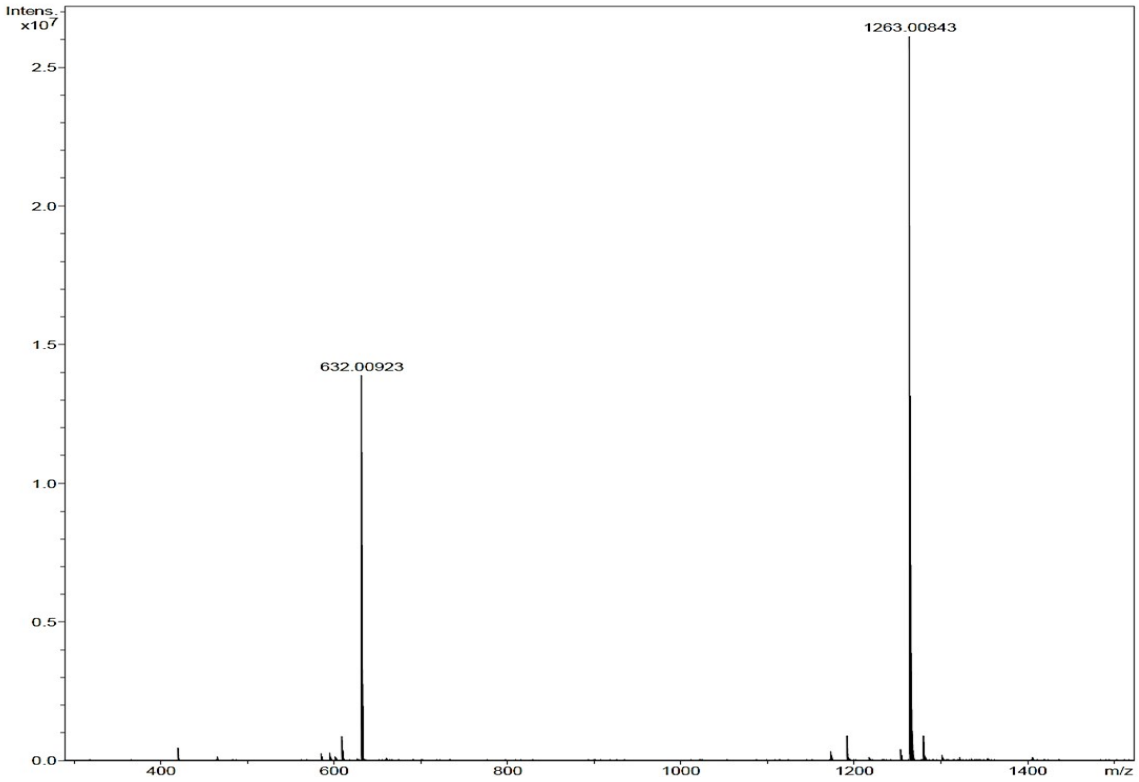

Fig. S4 ESI-HRMS of **TPPF$_{16}$[S-CH$_2$-COOH]$_4$**.

2. Singlet oxygen generation

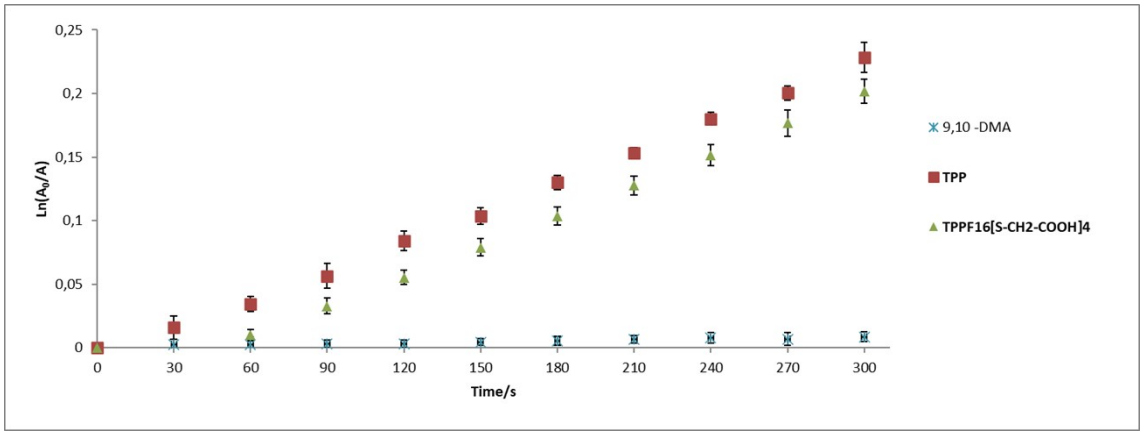

Fig. S5 Time-dependent photodecomposition of 9,10-DMA (~135 µM) alone and in the presence of **$TPPF_{16}[S\text{-}CH_2\text{-}COOH]_4$** at an OD at ~420 nm of ~0.3 in DMF upon irradiation with red light LEDs (418 nm ± 1 nm). Error bars indicate the SD and in some cases are collapsed with the symbols.

3. Confocal Laser Scanning Microscopy (CLSM)

To confirm that the red fluorescence observed in PVA-Gel + Por nanofibers was due to the presence of Por, PVA-Gel nanofibers (without Por) were used as a control. The samples were excited at 405 nm and showed no fluorescence, indicating the absence of Por. Thus, it can be concluded that the red fluorescence detected in Por-loaded PVA-Gel nanofibers was derived from the Por.

Fig. S6 CLSM image of PVA-Gel nanofibers excited at 405 nm and detected at 500-699 nm.