Supporting Information
BODIPY-Embedded Electrospun Materials in Antimicrobial Photodynamic Inactivation

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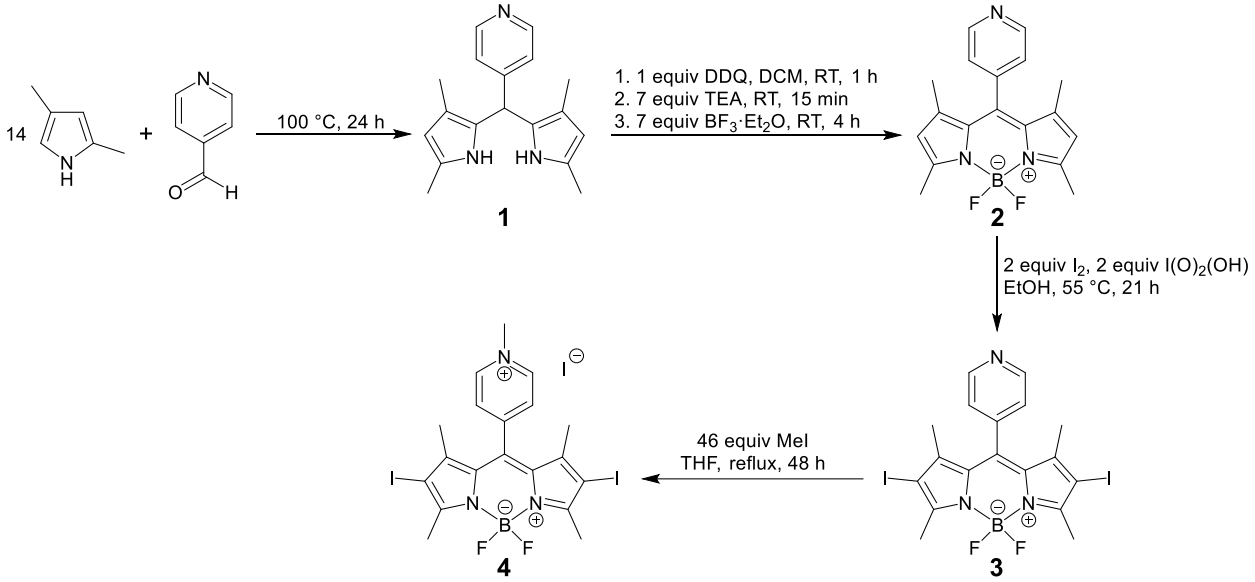
Synthesis of BODIPY$^{(+)}$ Photosensitizer

The cationic BODIPY$^{(+)}$ photosensitizer (Scheme 1) was synthesized per literature protocol,[1-4] with minor modifications as detailed below. All chemicals were minimally reagent grade and purchased from either Fisher Scientific, VWR, or Sigma-Aldrich. ^{1}H-NMR spectra were acquired using a Varian Mercury 400 MHz spectrometer utilizing TMS or the residual solvent peaks as internal standards. UV-visible spectra were acquired on a Varian Cary Bio50 spectrophotometer (Agilent). Mass spectrometry analysis was carried out on a high resolution Thermo Fisher Scientific Exactive Plus Orbitrap mass spectrometer using Heated Electrospray Ionization (HESI) operating in positive ion mode. The samples were diluted in acetonitrile and analyzed via flow injection (200 µL/min) into the mass spectrometer. The mobile phase was 90% CH_3CN with 0.1% formic acid and 10% H_2O with 0.1% formic acid.

Scheme 1. Synthesis of BODIPY$^{(+)}$ photosensitizer.



1,3,5,7-tetramethyl-8-(4-pyridyl)-dipyrromethane (**1**). To a round-bottom flask equipped with a stir bar were added pyridine-4-carboxaldehyde (18.77 mmol, 1.77 mL) and 2,4-dimethylpyrrole (262.76 mmol, 27.06 mL). The reaction mixture was heated under Ar to 100 °C using an oil bath for 24 hours, cooled, and the excess 2,4-dimethylpyrrole was removed under vacuum. Compound **1** was recovered as a reddish-brown solid (5.20 g, >99%) via precipitation from dichloromethane (DCM) upon addition of hexanes. ^{1}H NMR ($CDCl_3$) δ: 1.82 (s, 6H, 2 x CH_3); 2.16 (s, 6H, 2 x CH_3); 5.41 (s, 1H); 5.72 (d, 2H); 7.08 (m, 2H); 7.24 (s, 2H, NH); 8.52 (dd, 2H). ^{13}C NMR ($CDCl_3$) δ: 11.1, 13.1, 40.0,

108.8, 115.7, 123.6, 124.2, 126.2, 150.1, 151.5. UV-vis (CH_2Cl_2): 460 nm (ε = 65 $M^{-1}cm^{-1}$). HRMS (ESI^+) calculated: 280.18082 ($C_{18}H_{22}N_3$, $[M+H]^+$), found: 280.18042. Melting point: 146.8 °C.

1,3,5,7-tetramethyl-8-(4-pyridyl)-4,4'-diflouroboradiazaindacene (**2**). To a round-bottom flask equipped with a stir bar were added 3.17 mmol (0.886 g) compound **1**, 3.17 mmol (0.720 g) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, and 190 mL CH_2Cl_2 under N_2 atmosphere. The reaction mixture was allowed to stir at room temperature for 1 hour, after which 22.19 mmol (3.09 mL) triethylamine was added and stirred for an additional 15 minutes. Then, 22.19 mmol (2.74 mL) $BF_3 \cdot Et_2O$ was added and the reaction mixture was further stirred for 6 hours. Upon completion, the reaction mixture was filtered to remove insoluble material and the solvent was removed under vacuum. The crude reaction was then purified via flash column chromatography (silica, CH_2Cl_2), affording **2** as a reddish-orange solid (502 mg, 49% yield). ^1H NMR ($CDCl_3$) δ: 1.41 (s, 6H, 2 x CH_3); 2.56 (s, 6H, 2 x CH_3); 6.02 (s, 2H); 7.48 (d, 2H); 8.85 (d, 2H). ^{13}C NMR (DMSO-d_6) δ: 14.3, 14.6, 122.3, 123.7, 130.4, 138.8, 142.8, 143.6, 151.1, 156.1. UV-vis (CH_2Cl_2): 505 nm (ε = 85,700 $M^{-1}cm^{-1}$)[2]. HRMS (ESI^+) calculated: 326.16346 ($C_{18}H_{19}N_3BF_2$, $[M+H]^+$), found: 326.16299.

2,6-diiodi-1,3,5,7-tetramethyl-8-(4-pyridyl)-4,4'-diflouroboradiazaindacene (**3**). To a round-bottom flask equipped with a stir bar and reflux condenser were added 35 mL ethanol, **2** (0.55 mmol, 0.1803 g), iodine (1.12 mmol, 0.2876 g), and iodic acid (1.12 mmol (0.1983 g). The reaction mixture was heated via oil bath to 55 °C for 21 hours and the reaction progress monitored by TLC. When starting material was no longer present, the reaction was cooled to room temperature and excess solvent removed under vacuum. The product was precipitated from CH_2Cl_2 upon addition of hexanes, affording **3** as a purple solid (196 mg, 61%). ^1H NMR ($CDCl_3$) δ: 1.42 (s, 6H, 2 x CH_3); 2.65 (s, 6H, 2 x CH_3); 7.30 (dd, 2H); 8.82 (dd, 2H). ^{13}C NMR ($CDCl_3$) δ: 15.9, 17.5, 86.5, 123.6, 130.2, 136.5, 144.2, 144.7, 150.4, 158.0. UV-vis (CH_2Cl_2): 540 nm (ε = 78,800)[2]. HRMS (ESI^+) calculated: 577.95675 ($C_{18}H_{17}N_3BF_2I_2$, $[M+H]^+$), found: 577.95533.

2,6-diiodi-1,3,5,7-tetramethyl-8-(N-methyl-4-pyridyl)-4,4'-diflouroboradiazaindacene (BODIPY$^{(+)}$, **4**). To a round-bottom flask equipped with a stir bar and reflux condenser were added 100 mL tetrahydrofuran, **3** (0.8 mmol, 0.465 g) and methyl iodide (36.8 mmol, 2.29 mL). The reaction was heated to reflux via an oil bath for 48 hours. After cooling to room temperature, the product was precipitated upon addition of 300 mL diethyl ether, filtered, and the solid further washed with diethyl ether, yielding BODIPY$^{(+)}$ (**4**) as a dark purple solid (0.394 g, 83%). ^1H NMR (DMSO-d_6) δ: 1.40 (s, 6H, 2 x CH_3); 2.56 (s, 6H, 2 x CH_3); 4.44 (s, 3H); 8.39 (d, 2H); 9.20 (d, 2H).). ^{13}C NMR (DMSO-d_6) δ: 16.5, 18.2, 49.0, 88.7, 128.3, 129.7, 135.1, 145.1, 147.5, 150.4, 158.4. UV-vis (CH_2Cl_2): 546 nm (ε = 110,000)[2]. HRMS (ESI^+) calculated: 591.97240 ($C_{19}H_{19}N_3BF_2I_2$, $[M^+]$), found: 591.97087.

References

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