Supplementary Materials

Exploring BODIPY *meso*-enamines as singlet-oxygen photosensitizers for PDT.

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Description: Supplementary Methods, Supplementary Figure and Supplementary References.

Supplementary Methods

1. General

Synthesis: All starting materials and reagents were obtained commercially, unless otherwise indicated, and used without further purifications. Common solvents were dried and distilled by standard procedures. Flash chromatography was performed using silica gel (230-400 mesh). NMR spectra were recorded using DMSO at 20 ºC. ^{1}H NMR and ^{13}C NMR chemical shifts (δ) were referenced to internal solvent DMSO (δ = 2.51 and 39.97 ppm, respectively). DEPT 135 experiments were used to determine the type of carbon nucleus (C vs. CH vs. CH_2 vs. CH_3). FTIR spectra were obtained from neat samples using the ATR technique. High resolution mass spectrometry (HRMS) were performed using the EI technique.

Photophysical properties: Photophysical properties were obtained for every enamine in dichloromethane. The UV/Vis absorption spectra were recorded on an Agilent Technologies Spectrophotmeter (CARY 7000) in transmittance mode. Emission spectra were recorded on a spectrofluorimeter Edinburgh Instruments (FLSP920 model) with a xenon flash lamp 450 W as the excitation source.

Singlet oxygen quantum yield: The production of singlet oxygen was determined by direct measurement of the luminescence at 1276 nm of the singlet oxygen with a NIR detector (InGaAs detector, Hamamatsu G8605-23) integrated in the spectrofluorimeter (Edinburgh Instruments, model FL920). The singlet oxygen reference is 5-dimethyl-2,6-diiodo-8-thiomethyl-pyrromethene (MeSBDP-2I) in dichloromethane (Φ_Δ=0.87).[1]

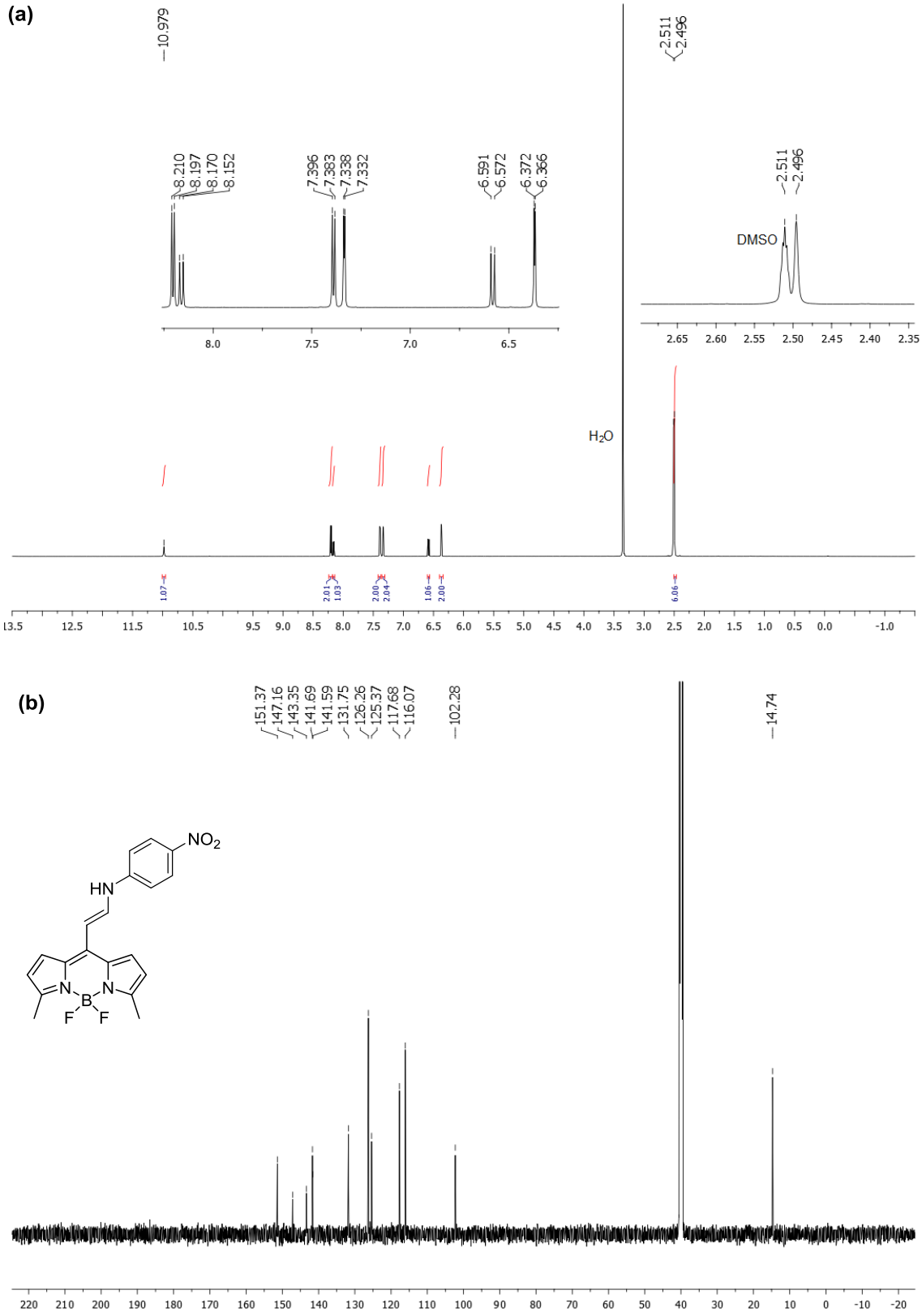
2. Synthetic procedure and characterization data

Synthesis of meso-enamine 3: A solution of *meso*-enamine **2a**[2] (29 mg, 0.1 mmol), 4-nitroaniline (41.4 mg, 0.3 mmol) and AcOH (0.5 mL) in dichloromethane (3 mL) was stirred at r.t. for 36 h. The solvent was evaporated under vacuum and the reaction mixture was dissolved in EtOAc and washed with water. The organic layer was dried over $MgSO_4$, filtered, and concentrated to dryness. Flash chromatography using hexane/EtAcO (9:1) afforded **3** (32 mg, 84%) as a red solid.

^{1}H NMR (700 MHz, DMSO) δ 10.98 (s, 1H, NH), 8.21 (d, *J* = 9.1 Hz, 2H, 2CH), 8.16 (d, *J* = 12.6 Hz, 1H, CH), 7.39 (d, *J* = 9.1 Hz, 2H, 2CH), 7.33 (d, *J* = 4.2 Hz, 2H, 2CH), 6.58 (d, *J* = 12.6 Hz, 1H, CH), 6.37 (d, *J* = 4.2 Hz, 2H, 2CH), 2.50 (s, 6H, $2CH_3$) ppm; ^{13}C NMR (176 MHz,

DMSO) δ 151.4, 147.2, 143.3 (CH), 141.7, 141.6, 131.7, 126.3 (CH), 125.4 (CH), 117.7 (CH), 116.1 (CH), 102.3 (CH), 14.7 (CH_3) ppm; FTIR ν 3349, 2961, 2744, 1625, 1577, 1217, 1176, 952 cm^{-1}; HRMS-EI *m/z* 382.1407 (382.1413 calcd for $C_{19}H_{17}BF_2N_4O_2$).

Supplementary Figures



Supplementary Figure S1. (a) ^{1}H (700 MHz, DMSO) and (b) ^{13}C (176 MHz, $CDCl_3$) spectra of **3.**

Supplementary References

1. Epelde-Elezcano, N.; Martínez-Martínez, V.; Peña-Cabrera, E.; Gómez-Durán, C. F. A.; Arbeloa I. L.; Lacombe, S. Modulation of singlet oxygen generation in halogenated BODIPY dyes by substitution at their *meso* position: towards a solvent-independent standard in the vis region. *RSC Adv.* **2016**, *6*, 41991-41998. DOI: 10.1039/c6ra05820e.

2. Palao-Utiel, E.; Montalvillo-Jiménez, L.; Esnal, I.; Prieto-Montero, R.; Agarrabeitia, A. R.; García-Moreno, I.; Bañuelos, J.; López-Arbeloa, I.; de la Moya, S.; Ortiz, M. J. Controlling Vilsmeier-Haack processes in *meso*-methylBODIPYs: a new way to modulate finely photophysical properties in boron dipyrromethenes. *Dyes Pigm*. **2017**, *141*, 286-298. DOI: 10.1016/j.dyepig.2017.02.030.