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Synthesis and spectral characteristics of halogen-substituted *meso*-carboxypropyl-BODIPYs as effective photosensitizers

Yulya V. Eremeeva, Galina B. Guseva and Elena V. Antina

Contents

General

The organic solvents used in the work were purchased from Sigma-Aldrich, J&K Scientific and were used without further purification. Mass-spectrometric measurements were carried out on a MALDI TOF Shimadzu Biotech Axima Confidence spectrometer. NMR spectra were recorded on a Bruker AVANCE-II-500 spectrometer with operating frequencies of 500 MHz (for ^{1}H) and 125 MHz (for ^{13}C) in $CDCl_3$ solvent using standard Bruker pulse programs. The internal standard is the solvent residual peak. The spectra are shown in Supplementary Materials. The electronic absorption and fluorescence spectra were recorded i on a spectrofluorimeter CM2203 (Minsk, Belarus). The value $\Phi\Delta$ was determined from the emission spectra of $^{1}O_2$ at 1270 nm using a Fluotime 300 (PicoQuant) spectrometer.

Synthesis.

BODIPY **1** (*M* = 334.17) ^{1}H NMR spectrum ($CDCl_3$), δ, 6.06s (2H, 4,4'-H); 3.02–3.05 m (2H, *meso*-CH_2); 2.52 s + 2.56 t (6 + 2 H, J = 7.6 Hz, CH_3 + CH_2CO); 2.43 s (6H, CH_3); 1.95–2.01 m (2H, CH_2). Mass spectrum, *m*/*z*: 334.21 $[M]^+$. Found, %: H 6.37, C 75.50, N 8.41. Calculated, %: H 6.33, C 75.48, N 8.38 (Figure S1, S6).

BODIPY **2** and **3** were obtained using a similar technique. The precursor BODIPY **1** (0.025 g, 0.0748 mmol and 0.027 g, 0.0808 mmol, respectively, for **2** and **3**) was dissolved in dichloromethane (20 ml). A solution of *N*-bromosuccinimide (0.1077 g, 0.6048 mmol) or *N*-iodosuccinimide (0.1088 g, 0.4836 mmol) in anhydrous DMF (5 ml) was slowly added to the precursor solution, respectively. The reaction mixture was stirred at 40 °C for 2 days. After that, the crude mixture was extracted with ethyl acetate and washed with water. The organic layers were dried over Na_2SO_4 and concentrated on a rotary evaporator. The crude mixture was purified by column chromatography on silicon dioxide using dichloromethane/hexane/ethanol (1:1:0.1) as an eluent to obtain the products as red powders.

BODIPY **2** (*M*=491.97).

Yield 0.0206 g (0.0419 mmol, 56%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.13-3.11 m (2H, CH_2); 2.60–2.52 m (*J* = 7.5 Hz *J* = 2+2H, *meso*-CH_2 + CH_2CO); 2.50 s (*6*H, CH_3); 2.49 s (6H, CH_3);. Mass spectrum, m/z: 491.36 $[M+H]^+$. Found, %: H 3.86, C 41.47, N 5.69. Calculated, %: H 3.89, C 41.50, N 5.69 (Figure S2, S4, S7).

BODIPY **3** (*M* = 585.97).

Yield 0.0285 g (0.0486 mmol, 60 %). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.09-3.16 m (2H, CH_2); 2.61 s (6H, CH_3); 2.59–2.52 m (*J* = 7.5 Hz *J* = 2+2H, *meso*-CH_2 + CH_2CO); 2.50 s (*6*H, CH_3);. Mass spectrum, m/z: 586.89 $[M]^+$. Found, %: H 3.24, C 34.81, N 4.77. Calculated, %: H 3.27, C 34.85, N 4.78 (FigureS3, S5, S8).

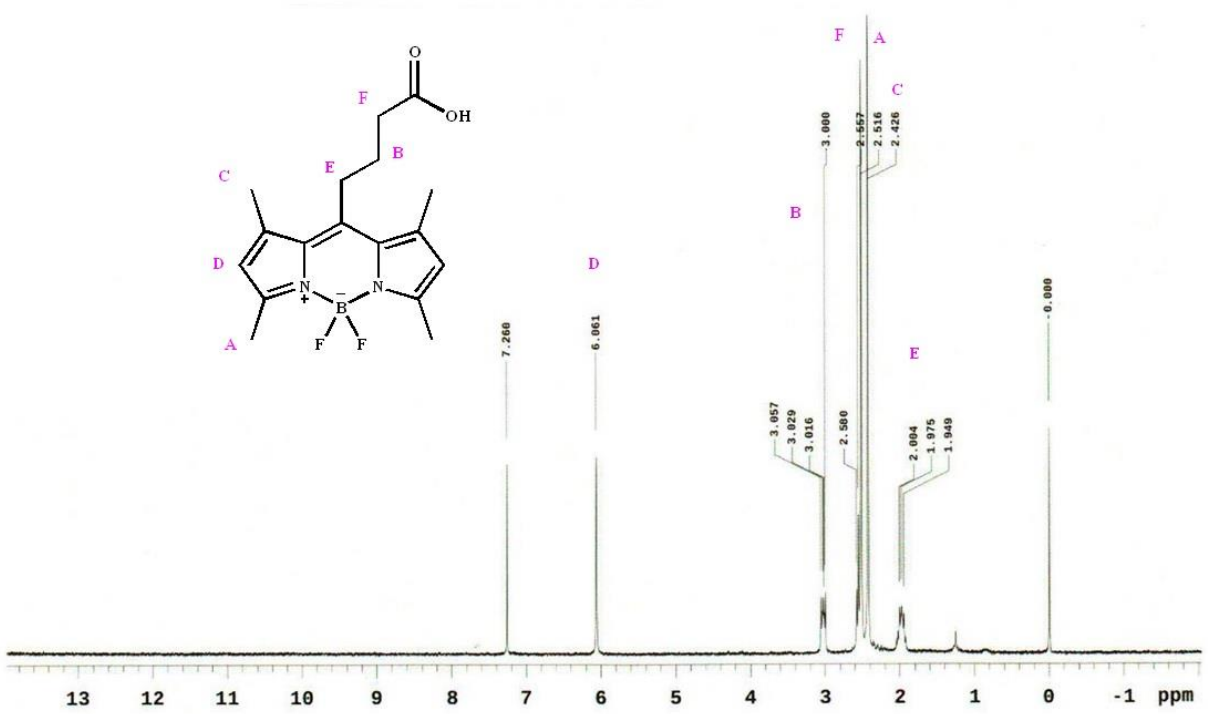

Figure S1 ^{1}H NMR spectrum of BODIPY **1** in $CDCl_3$.

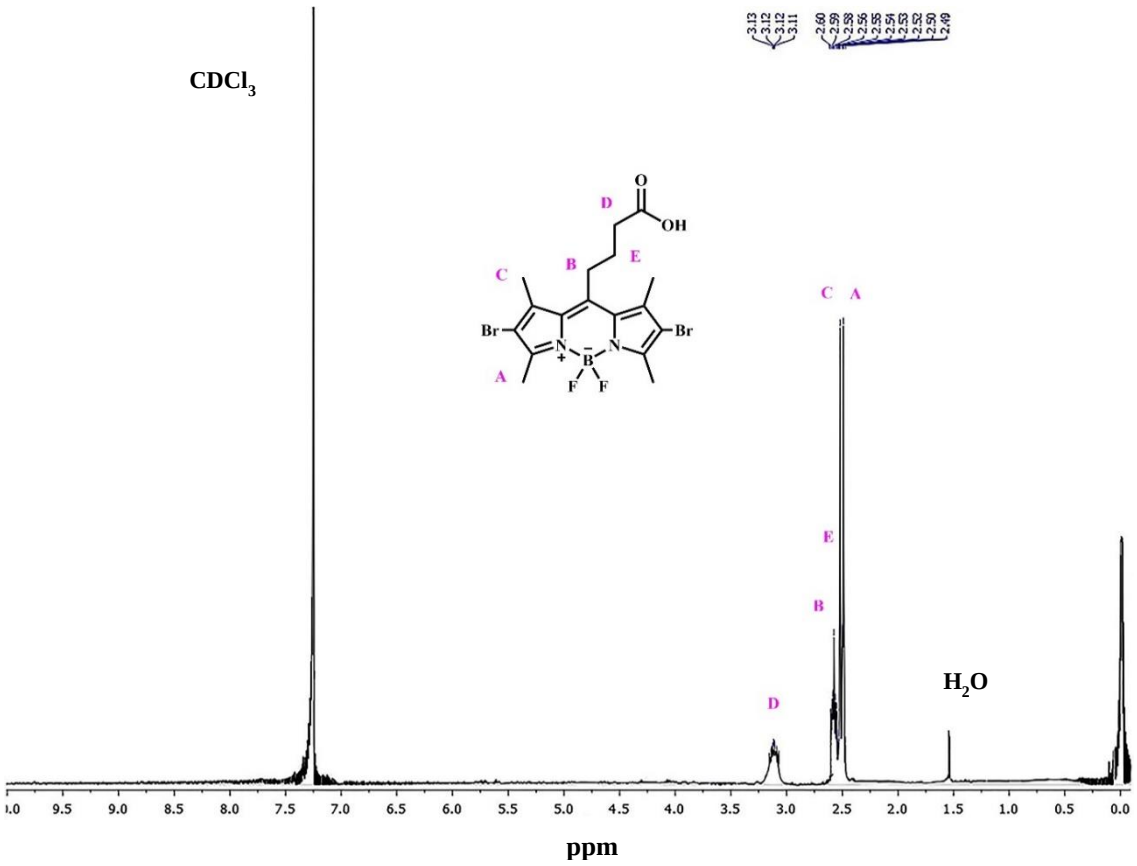

Figure S2 ^{1}H NMR spectrum of BODIPY **2** in $CDCl_3$.

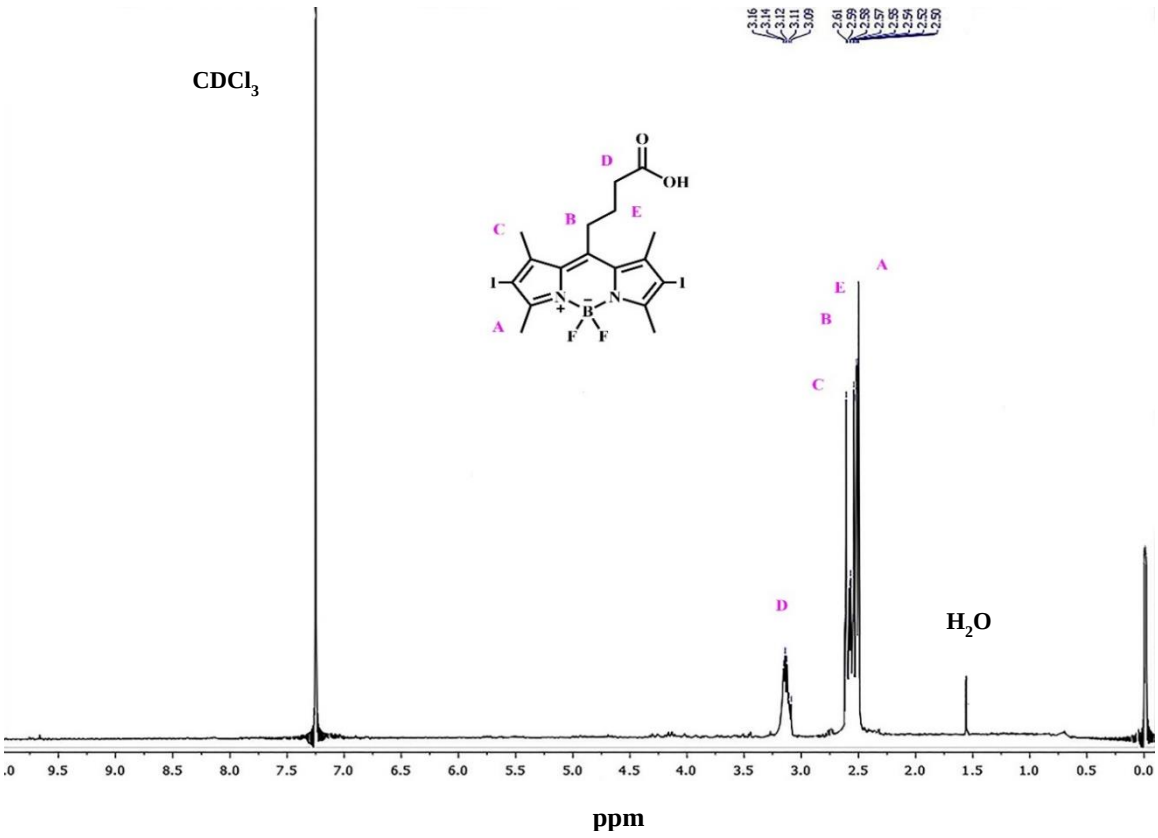

Figure S3 ^{1}H NMR spectrum of BODIPY **3** in $CDCl_3$.

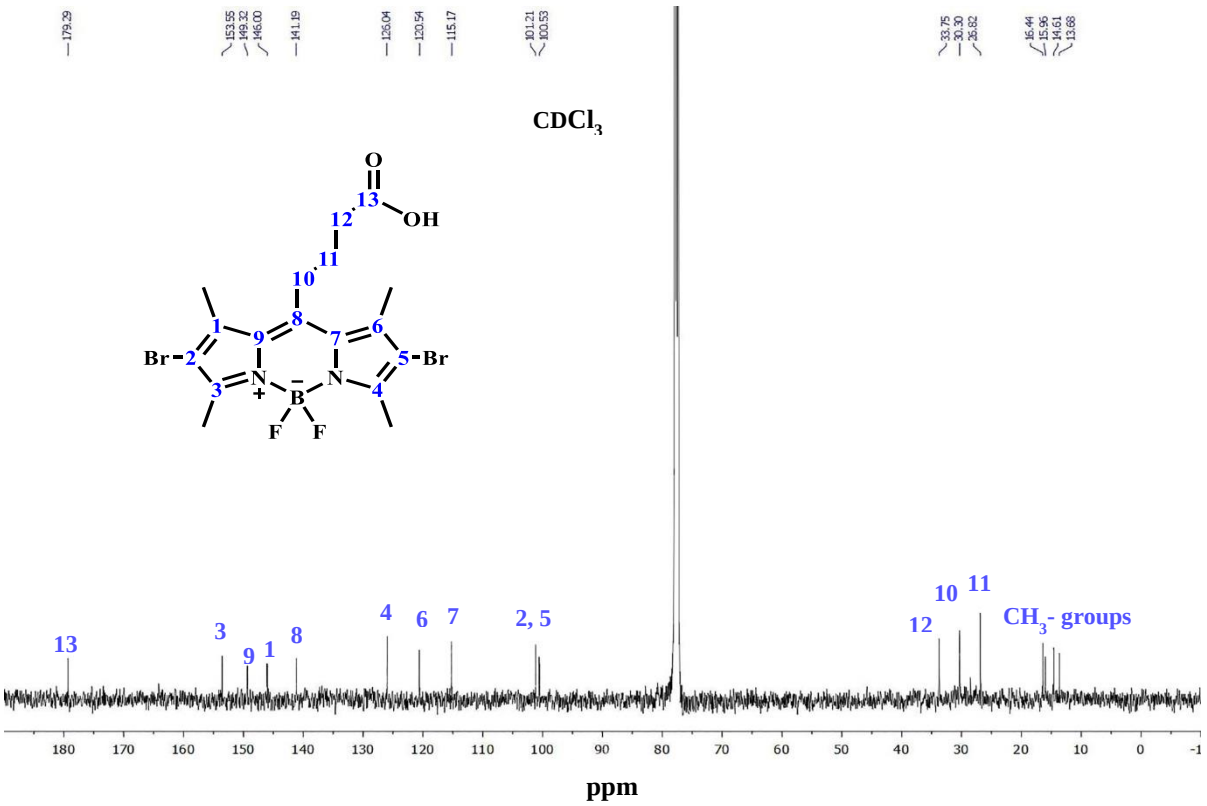

Figure S4 ^{13}C NMR spectrum of BODIPY **2** in $CDCl_3$.

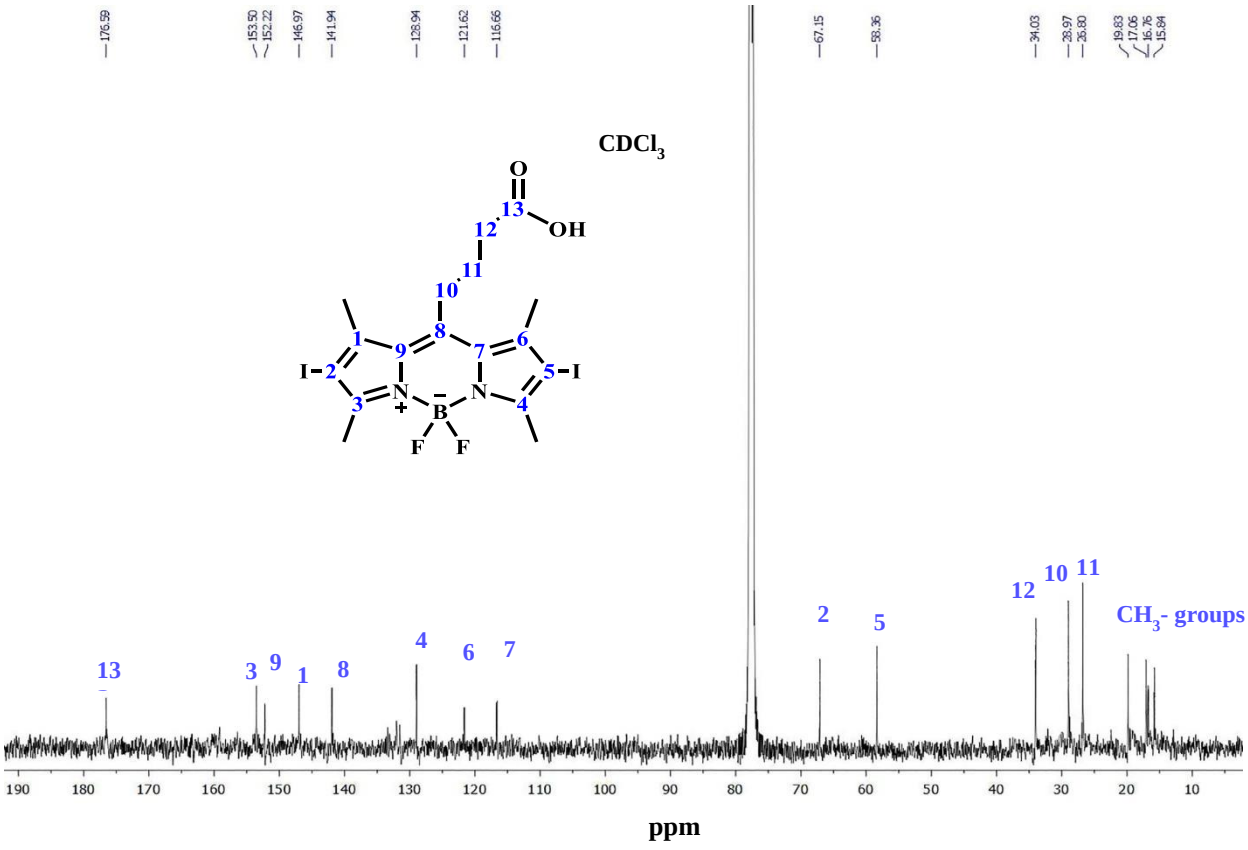

Figure S5 ^{13}C NMR spectrum of BODIPY **3** in $CDCl_3$.

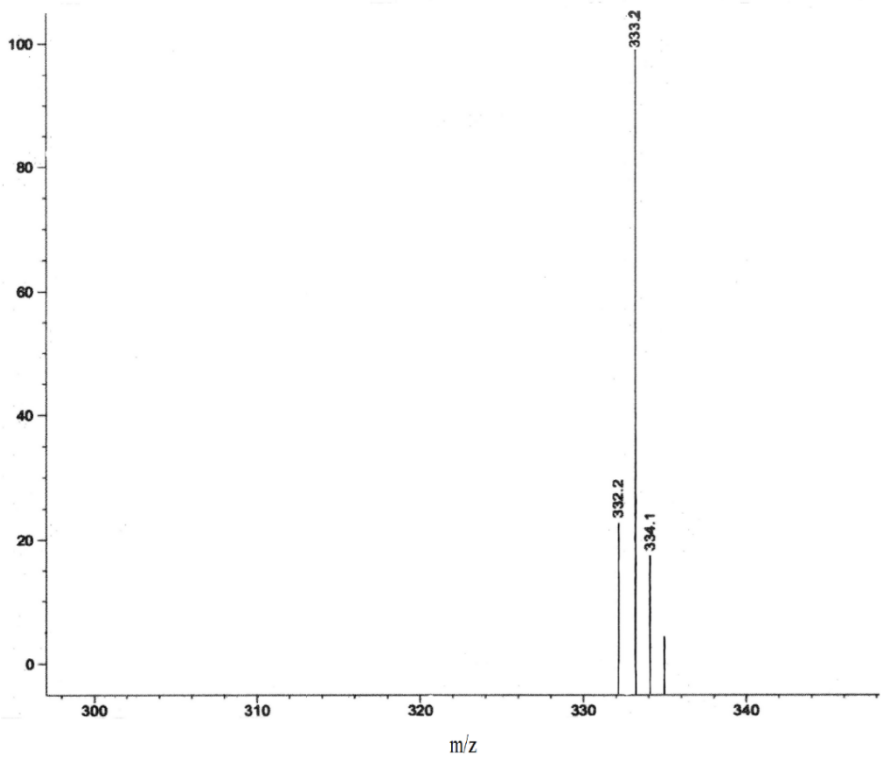

Figure S6 MALDI -TOF spectrum of BODIPY **1**.

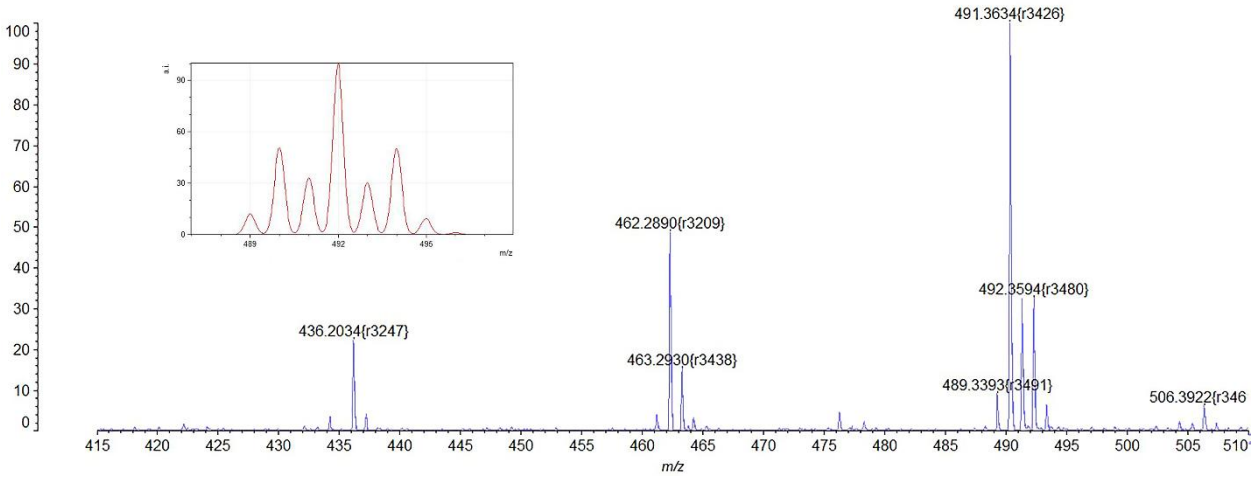

Figure S7 MALDI -TOF spectrum of BODIPY **2**.

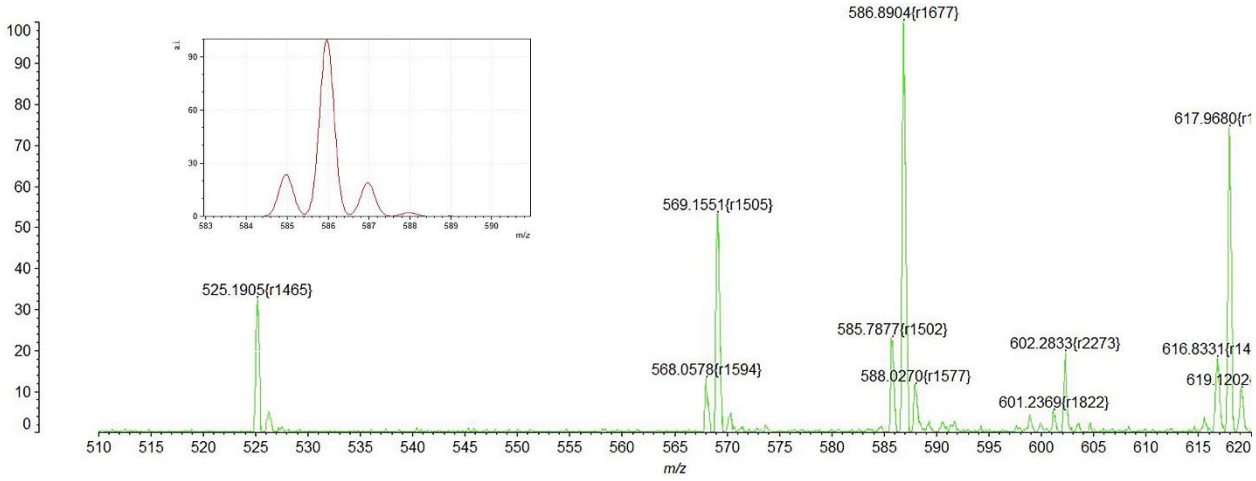

Figure S8 MALDI -TOF spectrum of BODIPY **3**.

Spectral-luminescent measurements. The electronic absorption and fluorescence spectra of BODIPYs **2**, **3** in organic solvents were recorded in quartz cuvettes (1 cm) at 25°C in the wavelength range of 300–600 nm on a spectrofluorimeter CM2203 (Minsk, Belarus). The relative fluorescence quantum yield (φ^{fl}) was calculated according to the literature method [S1] using the equation: $\varphi^{fl} = \varphi^{st} \cdot (\frac{S^x}{S^{st}}) \cdot (\frac{A^{st}}{A^x}) \cdot (\frac{n^x}{n^{st}})^2$, where φ^{fl} and φ^{st} are the quantum yields of the sample and standard, S^x и S^{st} are the area under the emission spectrum of the sample and standard, A^x и A^{st} – are the optical density in the absorption spectrum of the sample and standard at the excitation wavelength, n is the refractive index of the solvent. As a standard for determining the quantum yield, we used a solution of Rhodamine 6G with a known value of the quantum yield φ^{st} = 0.94 in ethanol [S2].

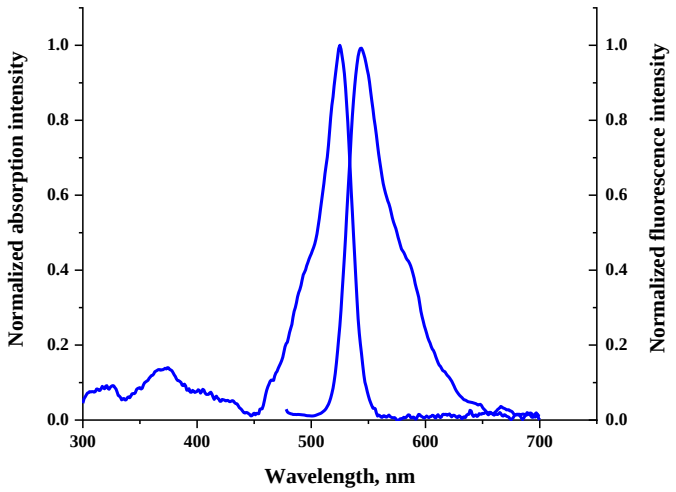

Figure S9 The normalised electronic absorption and fluorescence spectra of BODIPY **2** (c ~$1.2 \cdot 10^{-5}$ mol/L) in an ethanol-water binary mixture at a ratio of (1:1).

Singlet oxygen generation. The study of singlet oxygen formation was carried out according to the methodology detailed in [S3]. The value $\Phi\Delta$ was determined from the emission spectra of $^1O_2$ at 1270 nm using a Fluotime 300 (PicoQuant) spectrometer, equipped with an infrared detector, with an LDH-P-C-500 (PicoQuant) laser as an excitation source. Diluted solutions of dyes and standard (TPP) with absorbance $A \approx 0.25–0.3$ (at λ = 530 nm) were prepared in ethanol. $\Phi\Delta$ was calculated using the equation: $\Phi_\Delta = \Phi_{\Delta st} \cdot (\alpha_{st}/\alpha) \cdot (Se/Se_{st})$, where $\Phi_{\Delta st}$ is the quantum generation yield of the $^1O_2$ standard ($\Phi\Delta$ = 68%, [S4]); coefficient $\alpha = 1*10^{-Abs}$, corrects for the different number of photons absorbed by the sample (α_{PS}) and the standard (α_{st}); coefficient *Se* is intensity of the $^1O_2$ phosphorescence signal of the sample (Se) and the standard (Se_{st}) at 1270 nm. The accuracy of the determination of $\Phi\Delta$ was ~10–12%.

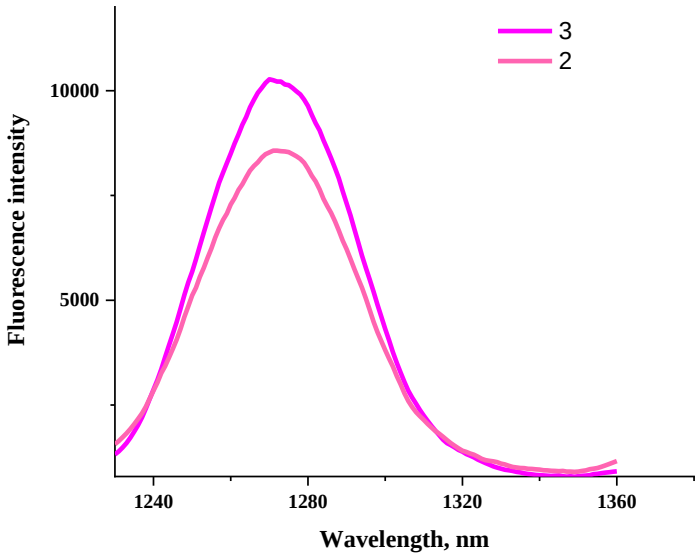

Figure S10 NIR emission of singlet oxygen at 1270 nm in an air-saturated ethanol solution of **2, 3** with excitation at 500 nm (absorbance 0.30).

References

S1. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd edn., Springer, New York, 2006; https://doi.org/10.1007/978-0-387-46312-4.

S2. M. Fischer and J. Georges, *Chem. Phys. Lett.*, 1996, **260**, 115; https://doi.org/10.1016/0009-2614(96)00838-X.

S3. W. Hu, R. Zhang, X.-F. Zhang, J. Liu and L. Luo, *Spectrochim. Acta, Part A*, 2022, **272**, 120965; https://doi.org/10.1016/j.saa.2022.120965.

S1. C. Mchiri, S. Dhifaoui, K. Ezzayani, M. Guergueb, T. Roisnel, F. Loiseau and H. Nasri, *Polyhedron*, 2019, **171**, 10; https://doi.org/10.1016/j.poly.2019.06.055.