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Supplementary material: The effect of molecular structure of chlorin photosensitizers on photo-bleaching of 1,3-diphenylisobenzofuran—the possible evidence of iodine reactive species formation

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1. Synthetic scheme and identification of PSs

The PSs studied (compounds **1**–**8**, see Figure S1 in the main text) were synthesized, purified and identified in our laboratory with ^{1}H NMR, MS- and UV–Vis spectra. ^{1}H NMR spectra were registered with the Bruker Avance II spectrometer (300 MHz) or Bruker Avance III spectrometer (500 MHz). $CDCl_3$ and DMSO d_6 were used as appropriate solvents and TMS as an internal standard. MS-spectra were obtained with the Thermo finnigan LCQ Flut (ESI) instrument and/or MALDI FAB MS-spectrometer Shimadzu AXIMA Confidence with α-cyano-4-hydroxycinnamic acid (CHCA) and 2,5-dihydroxybenzoic acid (DHB) as a matrix. UV–Vis spectra were obtained with the Drawell D 8 spectrophotometer in a highly diluted solution (~5–8 μmol) at 293 K. The synthetic and identification procedures for compounds **1**, **2**, **5**–**8** are given in detail elsewhere [1–3], while for chlorins **3**, **4** they are presented below.

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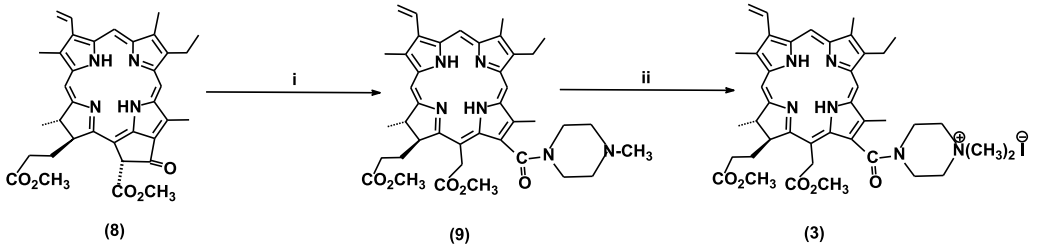
1.1. *Synthesis of compound **3***



i: N-methylpiperazine, $CHCl_3$, 313 K, 2 h; **ii**: CH_3I, CH_2Cl_2, r.t., 1 h.

Supplementary Figure S1. Synthesis of compound **3** *via* methylpheophorbide *a* (compound **8**) functionalization.

1.1.1. *Preparation of pheophorbide a 17(3)-methyl ester (methylpheophorbide a, compound **8**)*

Chemical modification of pheophytin *a*, extracted from the *Spirulina platensis* alga (Germany), to obtain chlorins **3**, **4** was carried out *via* the well-established procedure described in detail in our recent study [4]. The final product was purified by column chromatography, recrystallized from acetone and dried under reduced pressure at 343 K. The total yield of methylpheophorbide *a* from the dry plant material was of 1–1.25 mass %.

^{1}H NMR ($CDCl_3$, 300 MHz, Figure S2), δ(ppm): 9.56 s (1H, 10-H), 9.42 s (1H, 5-H), 8.60 s (1H, 20-H), 8.03 dd (1H, 18.3 and 11.7 Hz, 3-C$\underline{H}$=CH_2), 6.33 dd (1H, 18.3 and 1.5 Hz, 3-CH=CH$\underline{H}_{trans}$), 6.29 s (1H, 13(2)-H), 6.22 d (1H, 11.7 and 1.5 Hz, 3-CH=CH$\underline{H}_{cis}$), 4.50 qd (1H, 7.3 and 2.2 Hz, 18-H), 4.24 br. dt (1H, 8.8 and 2.2 Hz, 17-H), 3.92 s (3H, 13(2)-CO_2CH_3), 3.72 q (2H, 7.3 Hz, 8-CH_2CH_3), 3.72 s (3H, 17-$CH_2CH_2CO_2C\underline{H}_3$), 3.61 s (3H, 12-$CH_3$), 3.44 s (3H, 2-$CH_3$), 3.27 s (3H, 7-$CH_3$), 17-C$\underline{H}_2C\underline{H}_2CO_2CH_3$: 2.74–2.49 m (2H), 2.42–2.20 m (2H), 1.85 d (3H, 7.3 Hz, 18-CH_3), 1.74 t (3H, 7.3 Hz, 8-$CH_2C\underline{H}_3$), 0.59 br. s (1H, 21-NH), −1.58 br. s (1H, 23-NH).

MS (MALDI-TOF-MS, DHB as matrix, Figure S3): molecular formula $C_{36}H_{38}N_4O_5$, calculated $[M]^+$ = 606.7107, found $[M]^+$ = 606.7965, $[M+Na]^+$ = 629.8552, $[M+K]^+$ = 646.8877.

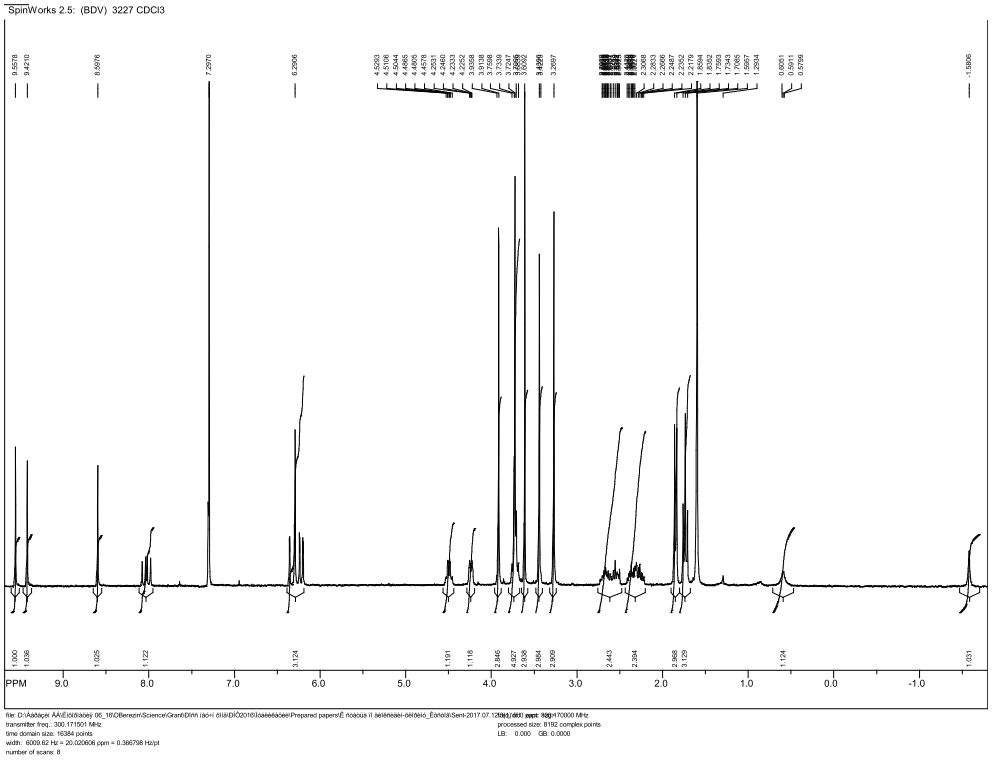
1.1.2. *Synthesis of chlorin e_6 13(1)-(4′-N-methylpiperazinyl)amide 15(2),17(3)-dimethyl ester (**9**)*

Methylpheophorbide *a* (**8**, 0.16 mmol) was treated for 2 h with a chloroform solution (2 ml) contained 6 mmol of N-methylpiperazine at 313 K to obtain chlorin e_6 13(1)-(4′-N-methylpiperazinyl)amide 15(2), 17(3)-dimethyl ester (compound **9**). The final yield of compound **9** was of 53%. The synthesized product was purified and spectroscopically identified.

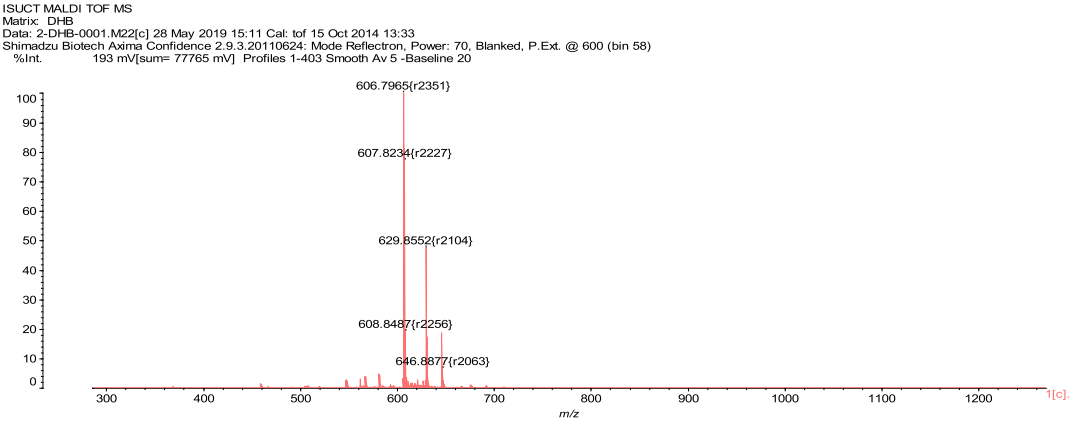
1.1.3. *Synthesis of chlorin e_6 13(1)-(4′-N,N-dimethylpiperazinyl iodide)amide 15(2),17(3)-dimethyl ester (**3**)*

0.1 mL of iodomethane was added to a solution of 50 mg of compound **9** in 5 mL of CH_2Cl_2. The reaction mixture was stirred for 1 h at a room temperature, after that methylene chloride and iodomethane were evaporated under reduced pressure. The product **3** was obtained with a quantitative yield. Chlorins **3** was found to be a mixture of two spatial isomers [5], the structure of which was confirmed with ^{1}H (Figure S4) and 2D COSY ^{1}H–^{1}H (Figure S5) NMR-spectroscopy.

^{1}H NMR ($CDCl_3$), (Figure S4), δ (ppm): Major isomer: 9.59 s (1H, 10-H), 9.48 s (1H, 5-H), 8.81 s (1H, 20-H), 7.70–7.95 m (1H, 3-C$\underline{H}$=CH_2), 6.10 d (1H, 20 Hz, 3-CH=CH$\underline{H}_{trans}$), 5.90 d (1H, 10 Hz, 3-CH=CH$\underline{H}_{cis}$), 4.95 dd (2H, 15÷20 Hz, 15-C$\underline{H}_A\underline{H}_B$$CO_2CH_3$), {13-$CONC_4\underline{H}_8$N: 3.14–2.82 m (2H), 2.64–2.55 m (2H), 2.54–2.43 m (2H), 2.28–2.15 m (2H); 13-$CONC_4H_8N(C\underline{H}_3)_2$: 2.48 s (6H)}, 4.50 q (1H, 5÷10 Hz, 18-H), 4.39 d (1H, 10 Hz, 17-H), 3.62 s (3H, 15-$CH_2CO_2C\underline{H}_3$), 3.60 s (3H, 17-$CH_2CH_2CO_2C\underline{H}_3$), 3.33 s (3H, 12-C$\underline{H}_3$), 3.28 s (3H, 2-C$\underline{H}_3$), 3.18 s (3H, 7-C$\underline{H}_3$), 3.78–3.64 m (4H, 8-C$\underline{H}_2$$CH_3$ and 17-$CH_2C\underline{H}_2CO_2CH_3$), 1.76–1.59 m (8H, 18-C$\underline{H}_3$; 8-$CH_2C\underline{H}_3$; 17-C$\underline{H}_2CH_2CO_2CH_3$), −1.65 br. s (1H, 21-NH), −1.86 br. s (1H, 23-NH); Minor isomer: 9.64 s (1H, 10-H), 9.50 s (1H, 5-H), 8.81 s (1H, 20-H), 7.70–7.95 m (1H, 3-C$\underline{H}$=CH_2),

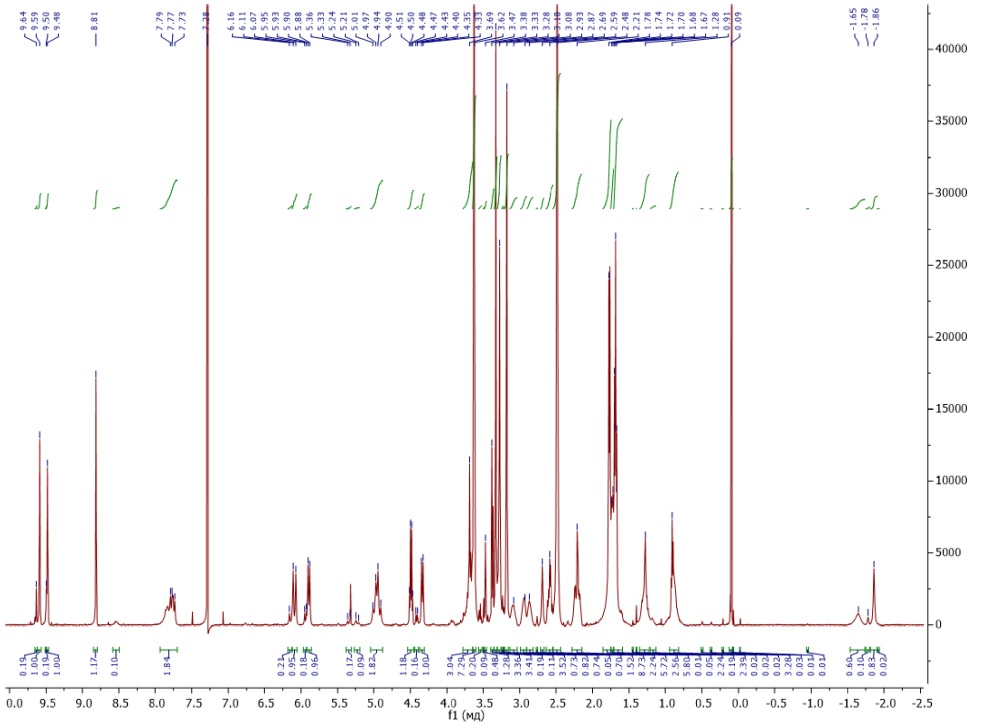


Supplementary Figure S2. ^{1}H NMR spectrum ($CDCl_3$) of pheophorbide *a* 17(3)-methyl ester (compound **8**, methylpheophorbide *a*).

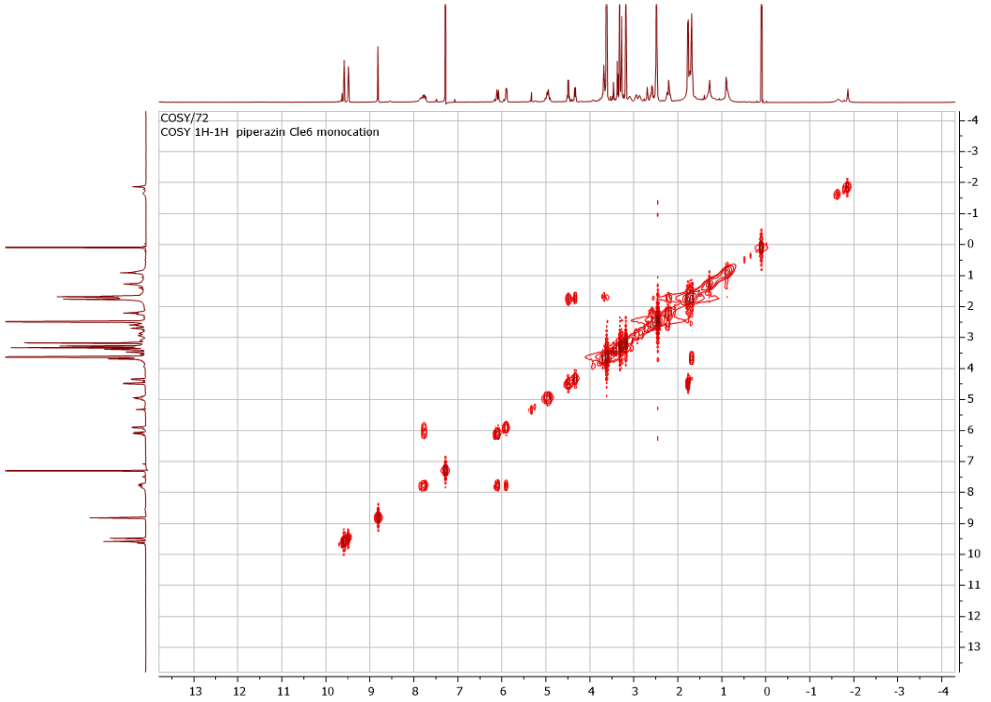


Supplementary Figure S3. MALDI-TOF mass spectrum of pheophorbide *a* 17(3)-methyl ester (methylpheophorbide *a*).

6.15 d (1H, 20 Hz, 3-CH=CH$\underline{H}_{trans}$), 5.95 d (1H, 10 Hz, 3-CH=CH$\underline{H}_{cis}$), 5.30 dd (2H, 15 Hz, 15-C$\underline{H}_2$CO$_2$CH$_3$), {13-CONC$_4\underline{H}_8$N: 3.14–2.82 m (2H), 2.64–2.55 m (2H), 2.54–2.43 m (2H), 2.28–2.15 m (2H); 13-CONC$_4$H$_8$N(C$\underline{H}_3$)$_2$: 2.69 s (6H)}, 4.50 q (1H, 5÷10 Hz, 18-H), 4.42 d (1H, 10 Hz, 17-H), 3.38 s (3H, 12-C$\underline{H}_3$), 3.37 s (3H, 2-C$\underline{H}_3$), 3.19 s (3H, 7-C$\underline{H}_3$), 3.78–3.64 m (10H, 8-C$\underline{H}_2$CH$_3$; 15-CH$_2$CO$_2$C$\underline{H}_3$;



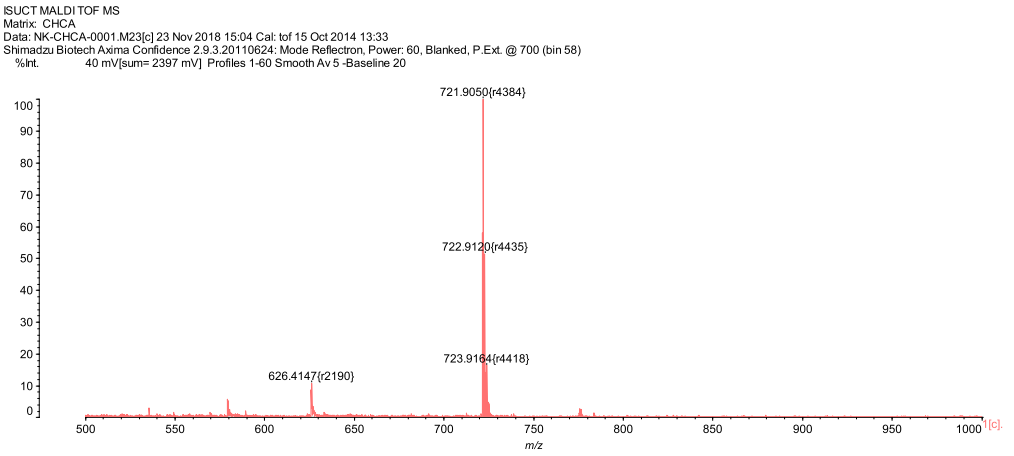
Supplementary Figure S4. ^{1}H NMR spectrum ($CDCl_3$) of chlorin e_6 13(1)-(4′-N,N-dimethylpiperazinyl iodide)amide 15(2),17(3)-dimethyl ester (compound **3**).



Supplementary Figure S5. 2D COSY ^{1}H-^{1}H NMR spectrum ($CDCl_3$) of chlorin e_6 13(1)-(4′-N,N-dimethylpiperazinyl iodide)amide 15(2),17(3)-dimethyl ester (compound **3**).

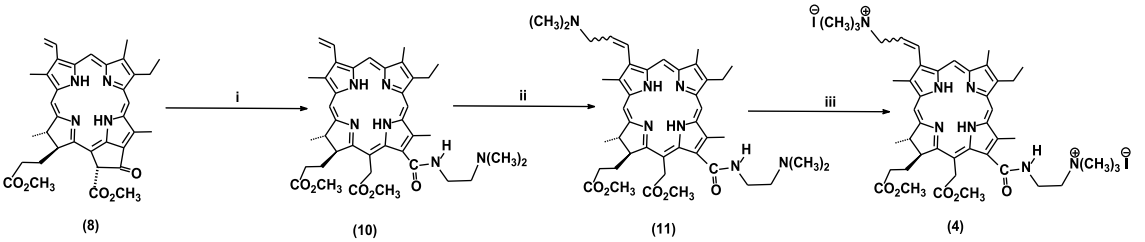
17-$CH_2\underline{CH_2}CO_2\underline{CH_3}$), 1.76–1.59 m (8H, 18-$C\underline{H_3}$; 8-$CH_2\underline{CH_3}$; 17-$C\underline{H_2}CH_2CO_2CH_3$), −1.65 br. s (1H, 21-NH), −1.78 br. s (1H, 23-NH).

MS (MALDI), m/z: (Figure S6): molecular formula $C_{42}H_{53}IN_6O_5$, calculated: $[M^+I^-]$ = 848.8280, $[M - I^-]^+$ = 721.9230, found: 721.9050 $[M]^+$.



Supplementary Figure S6. Mass spectrum of chlorin e_6 13(1)-(4′-N,N-dimethylpiperazinyl iodide)amide 15(2),17(3)-dimethyl ester (compound **3**).

1.2. *Synthesis of compound **4***



i: $NH_2(CH_2)_2N(CH_3)_2$, $CHCl_3$, 313 K, 2 h; **ii**: $[(CH_3)_2N{=}CH_2]^+I^-$, CH_2Cl_2, r.t., 24 h; **iii**: CH_3I, CH_2Cl_2, r.t., 1 h.

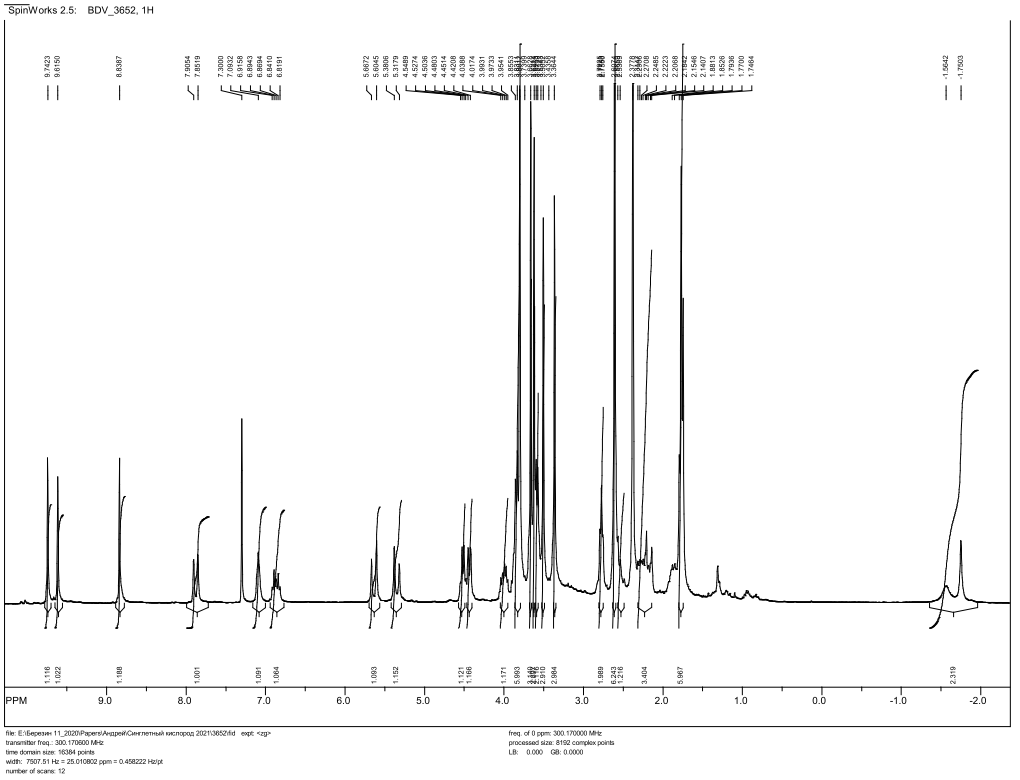
Supplementary Figure S7. Synthesis of compound **4** *via* methylpheophorbide *a* functionalization.

1.2.1. *Synthesis of chlorin e_6 13(1)-N-(2-N′,N′-dimethylaminoethyl)amide 15(2),17(3)-dimethyl ester (**10**)*

Methylpheophorbide *a* (**8**, 0.16 mmol) obtained from pheophytin *a* (see upper Section 1.1.1) was treated for 2 h with a chloroform solution (2 mL) of 6 mmol of N,N-dimethylethylenediamine at 313 K to synthesize chlorin e_6 13(1)-N-(2-N′,N′-dimethylaminoethyl)amide 15(2),17(3)-dimethyl ester (**10**). The final yield of compound **10** was equal to 65%. The synthesized product was purified and identified according to the procedure described elsewhere [6].

1.2.2. *Synthesis of 3(2)-N,N-dimethylaminomethyl chlorin e_6 13(1)-N′-(2-N″,N″-dimethylaminoethyl)amide 15(2),17(3)-dimethyl ester (**11**)*

0.16 mmol of compound **10** dissolved in 5 mL of CH_2Cl_2 and 105 mg (0.58 mmol) of the Eschenmoser reagent were placed in a flat bottom flask.

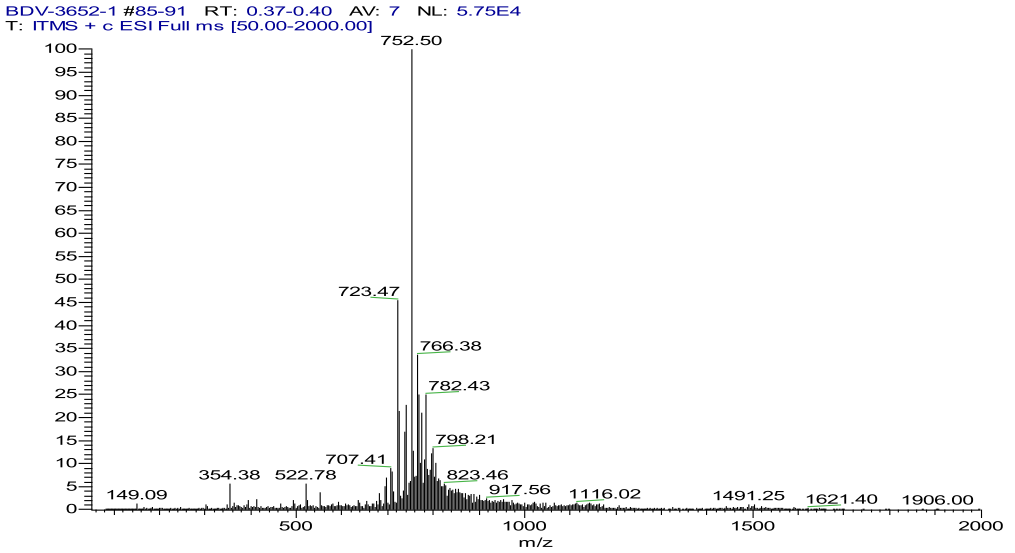


Supplementary Figure S8. ^{1}H NMR spectrum ($CDCl_3$) of 3(2)-N,N-dimethylaminomethyl chlorin e_6 13(1)-N′-(2-N″,N″-dimethylaminoethyl)amide 15(2),17(3)-dimethyl ester (compound **11**).

The mixture was left stirring for 24 h, and the reaction was monitored by TLC on Sorbfil plates using the $CHCl_3$/EtOH binary mixture (9:1) as an eluting solvent. Then, the mixture was diluted by $CHCl_3$ (50 mL), washed with water and dried with anhydrous Na_2SO_4. A liquid was evaporated to dryness under reduced pressure after that the residue was purified by column chromatography on silica gel using the following eluents: CCl_4/acetone, 50:1–1:1, followed by $CHCl_3$/EtOH, 30:1–1:1. The fractions containing the main product of the reaction were collected and dried under reduced pressure. The yield of compound **11** was of 40%.

^{1}H NMR ($CDCl_3$, 300 MHz, Fig S8), δ (ppm): 9.74 s (1H, 10-H), 9.62 s (1H, 5-H), 8.84 s (1H, 20-H), 7.88 d (1H, 16.5 Hz, C$\underline{H}$=CHCH$_2$N(CH$_3$)$_2$), 7.10 br. t (1H, 5.5 Hz, 13-CON$\underline{H}$CH$_3$), 6.87 dt (1H, 15.6 and 6.4 Hz, CH=C$\underline{H}$CH$_2$N(CH$_3$)$_2$), 5.64 d (1H, 19.25 Hz, 15-C$\underline{H}_A$H$_B$CO$_2$CH$_3$), 5.35 d (1H, 19.24 Hz, 15-CH$_A\underline{H}_B$CO$_2$CH$_3$), 4.52 q (1H, 7.3 Hz, 18-H), 4.44 br. d (1H, 9.2 Hz, 17-H), 13-CONHC$\underline{H}_2$CH$_2$N(CH$_3$)$_2$: 4.07–3.94 m (1H) and 3.92–3.82 m (1H); 3.84 q (2H, 7.3 Hz, 8-C$\underline{H}_2$CH$_3$), 3.80 s (3H, 15-CH$_2$CO$_2$C$\underline{H}_3$), 3.66 s (3H, 17-CH$_2$CH$_2$CO$_2$C$\underline{H}_3$), 3.62 s (3H, 12-CH$_3$), 3.58 br. d (2H, 6.4 Hz, CH=CHC$\underline{H}_2$N(CH$_3$)$_2$), 3.51 s (3H, 7-CH$_3$), 3.36 s (3H, 2-CH$_3$), 2.77 t (2H, 6.4 Hz, 13-CONHCH$_2$C$\underline{H}_2$N(CH$_3$)$_2$), 2.61 s (6H, CH=CHCH$_2$N(C$\underline{H}_3$)$_2$), 2.38 s (6H, 13-CONHCH$_2$CH$_2$N(C$\underline{H}_3$)$_2$), C$\underline{H}_2$C$\underline{H}_2$CO$_2$CH$_3$: 2.65–2.51 m (1H) and 2.44–2.11 m (3H); 1.77 t (3H, 7.3 Hz, 8-CH$_2$C$\underline{H}_3$), 1.76 d (3H, 7.3 Hz, 18-CH$_3$), −1.56 br. s (1H, 21-NH), −1.75 br. s (1H, 23-NH).

MS (ESI), m/z (Figure S9): molecular formula $C_{43}H_{57}N_7O_5$, calculated: $[M]^+$ = 751.97, found $[M]^+$ = 752.50 (MH^+), 707.41 ($MH–HN(CH_3)_2)^+$.



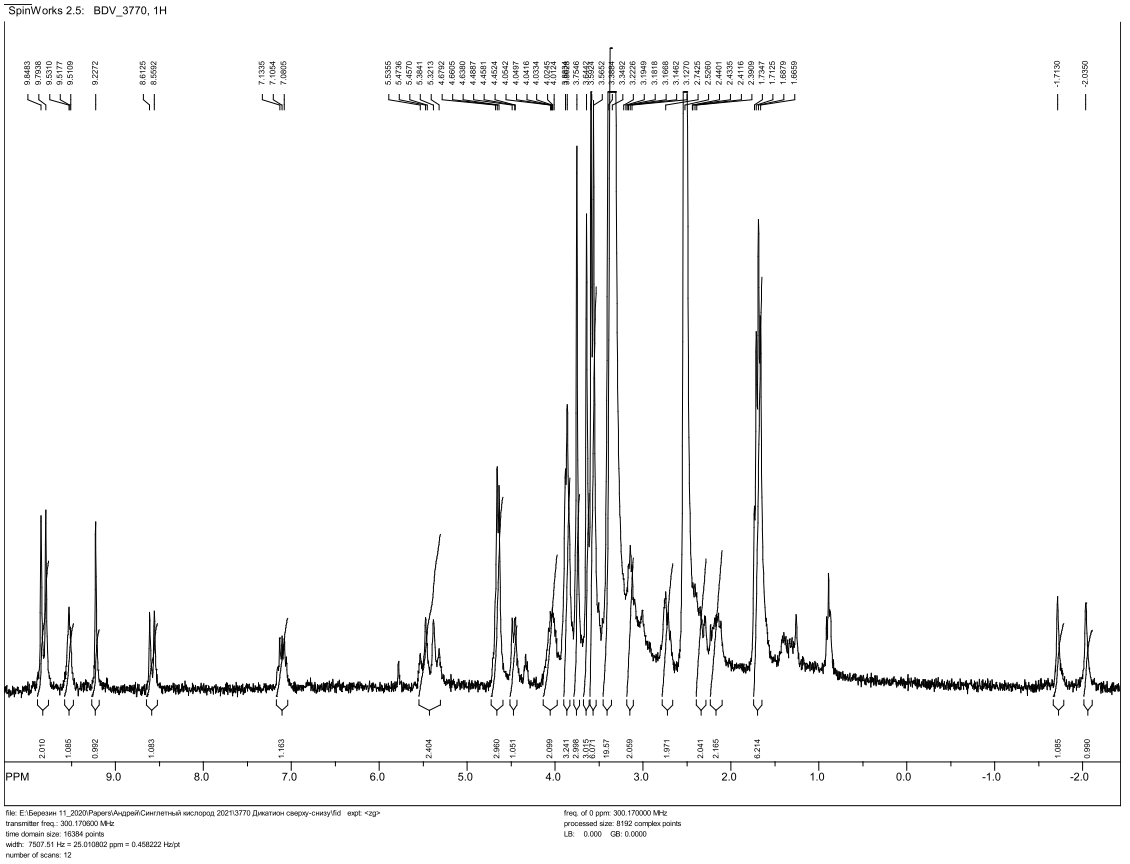
Supplementary Figure S9. Mass spectrum (ESI) of 3(2)-N,N-dimethylaminomethylchlorin e_6 13(1)-N′-(2-N″,N″-dimethylaminoethyl)amide-15(2),17(3)-dimethyl ester (compound **11**).

1.2.3. *Synthesis of 3(2)-(N,N,N-trimethylaminomethyl iodide) chlorin e_6 13(1)-N′-(2-N″,N″,N″-trimethylammonioethyl iodide)amide 15(2), 17(3)-dimethyl ester (**4**)*

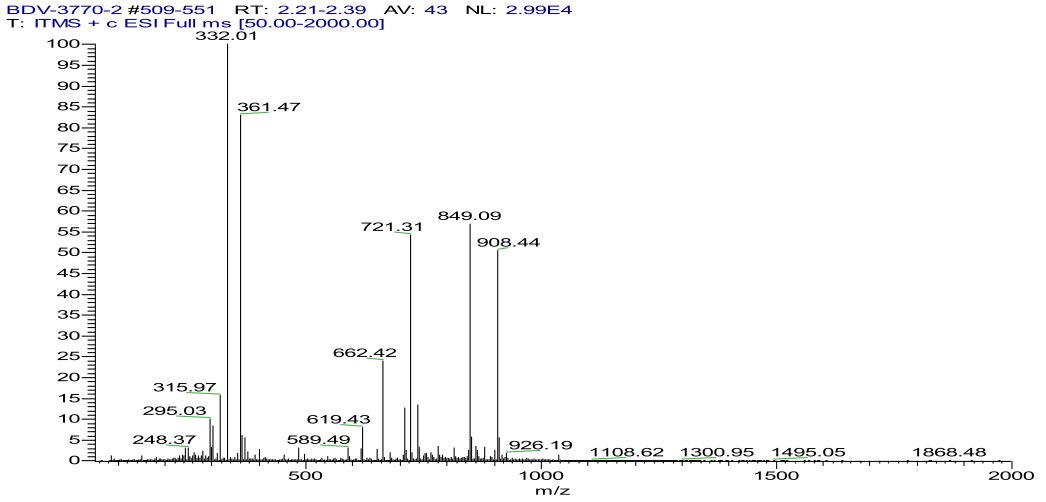
0.1 mL of iodomethane was added to a solution of 50 mg of compound **11** in 5 mL of CH_2Cl_2. The reaction mixture was stirred for 1 h at a room temperature after that methylene chloride and iodomethane were evaporated under reduced pressure. Chlorin **4** was obtained with a quantitative yield.

^{1}H NMR (DMSO-d_6, 300 MHz, Figure S10), δ (ppm): 9.85 s (1H, 10-H), 8.79 s (1H, 5-H), 9.53 br. t (1H, 5.5 Hz, 13-CONHCH$_2$CH$_2$N$^+$(CH$_3$)$_3$I$^-$), 9.23 s (1H, 20-H), 8.58 d (1H, 15.6 Hz, 3-CH=CHCH$_2$N$^+$(CH$_3$)$_3$I$^-$), 7.11 dt (1H, 16.5 and 6.4 Hz, 3-CH=CHCH$_2$N$^+$(CH$_3$)$_3$I$^-$), 5.50 d (1H, 18.3 Hz, 15-CH$_A$H$_B$CO$_2$CH$_3$), 5.33 d (1H, 18.3 Hz, 15-CH$_A$H$_B$CO$_2$CH$_3$), 4.75–4.56 m (1H, 18-H), 4.47 br. d (1H, 8.3 Hz, 17-H), 4.13–3.97 m (2H, 3-CH=CHCH$_2$N$^+$(CH$_3$)$_3$I$^-$), 3.94–3.80 m (2H, 8-CH$_2$CH$_3$), 3.87 s (3H, 15-CH$_2$CO$_2$CH$_3$), 3.76 s (3H, 17-CH$_2$CH$_2$CO$_2$CH$_3$), 3.65 s (3H, 12-CH$_3$), 3.59 s (3H, 7-CH$_3$), 3.57 s (3H, 2-CH$_3$), 13-CONHCH$_2$CH$_2$N$^+$(CH$_3$)$_3$I$^-$ and 3-CH=CHCH$_2$N$^+$(CH$_3$)$_3$I$^-$: 3.39 and 3.36 both s (9H), 3.14 t (2H, 5.5 Hz, 13-CONHCH$_2$CH$_2$N$^+$(CH$_3$)$_3$I$^-$), 2.81-2.66 m (2H, 13-CONHCH$_2$CH$_2$N$^+$(CH$_3$)$_3$I$^-$), 2.44-2.07 m (4H, 17-CH$_2$CH$_2$CO$_2$CH$_3$), 1.71 d (3H, 7.3 Hz, 18-CH$_3$), 1.68 t (3H, 6.4 Hz, 8-CH$_2$CH$_3$), −1.71 br. s (1H, 21-NH), −2.03 br. s (1H, 23-NH).

MS (ESI), m/z (Figure S11): molecular formula $C_{45}H_{63}I_2N_7O_5$, calculated: [M$^+$I$^-$] = 1035.85, [M–2I]$^{2+}$ = 782.03, found: 908.4 [M^{2+}I$^-$]$^+$, 849.1 [M^{2+}I$^-$–N(CH$_3$)$_3$]$^+$, 781.6 [M^{2+}+e]$^+$, 722.7 [M^{2+}+e$^-$–N(CH$_3$)$_3$]$^+$, 721.3 [M^{2+}–H$^+$–N(CH$_3$)$_3$]$^+$, 666.3 [M^{2+}+4H–H$^+$–2N(CH$_3$)$_3$–H$^+$]$^+$, 662.42 [M^{2+}–2N(CH$_3$)$_3$–H$^+$]$^+$, 619.13 [M^{2+}–H–2N(CH$_3$)$_3$–H$^+$–NHCHCH$_2$]$^+$, 390.7 M^{2+}, 361.5 [M^{2+}–N(CH$_3$)$_3$]$^{2+}$, 332.0 [M^{2+}–2N(CH$_3$)$_3$]$^{2+}$.



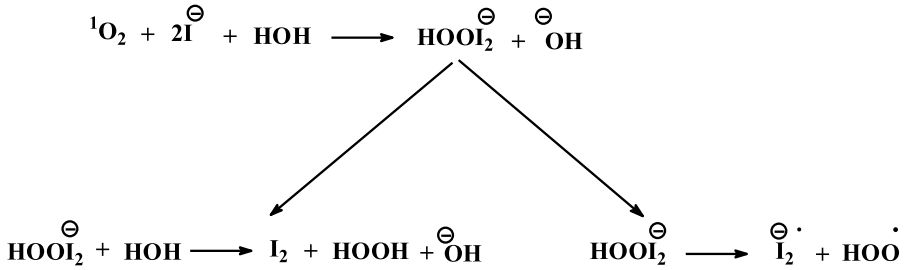
Supplementary Figure S10. ^{1}H NMR spectrum (DMSO d_6) of 3(2)-(N,N,N-trimethylaminomethyl iodide) chlorin e_6 13(1)-N′-(2-N″,N″,N″-trimethylammonioethyl iodide)amide 15(2),17(3)-dimethyl ester (compound **4**).



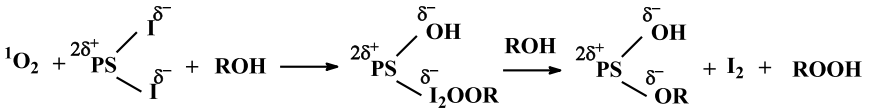
Supplementary Figure S11. Mass spectrum (ESI) of 3(2)-(N,N,N-trimethylaminomethyl iodide) chlorin e_6 13(1)-N′-(2-N″,N″,N″-trimethylammonioethyl iodide)amide 15(2),17(3)-dimethyl ester (compound **4**).

1.3. *Spectral iodine identification in a PS solution*

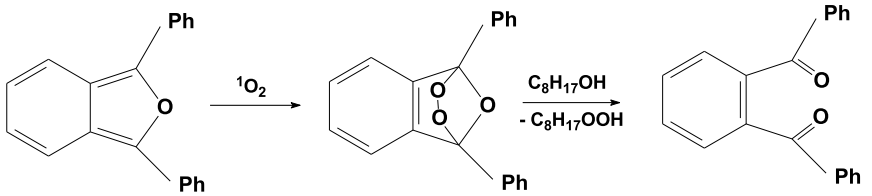
To identify molecular iodine formation during the irradiation session we have prepared several solutions of compound **5** (8×10^{-6} mol·kg^{-1}), ammonium iodide (2×10^{-4} mol·kg^{-1}), I_2+NH_4I (1×10^{-4} mol·kg^{-1} and 2×10^{-4} mol·kg^{-1}, respectively) and NH_4I+ compound **5** (2×10^{-4} mol·kg^{-1} and 8×10^{-6} mol·kg^{-1}, respectively) dissolved in liquid 1-OctOH. Then the solution containing NH_4I+ compound **5** was irradiated by red light with the power density of 3 mW·cm^{-2} (see the main text) during 5, 10, 15, 20, 25, 30, 35 and 40 min. For the last three sessions (between 30 and 40 min) the power density was increased two times. The fact of iodine formation according to Scheme S1 in water [7] and Scheme S2 (I_2/I_3^-) in OctOH is visible from Figure S12, where the solution absorbance at 360 nm increases monotonously with the light dose. The spectrum observed is very similar to that for the I_2+NH_4I solution in 1-octanol (see Figure S12) indicating the formation of molecular iodine in a non-aqueous medium. The possible scheme of 2,5-diphenylisobenzofurane (DPBF) interaction with singlet oxygen in OctOH (R = C_8H_{17}) is shown in Scheme S3.



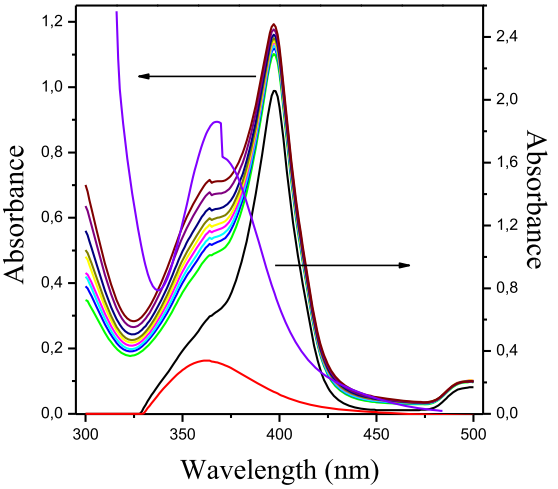
Supplementary Scheme S1. The possible schemes of the interaction between singlet oxygen and iodide ions in water according to Ref. [7].



Supplementary Scheme S2. The possible scheme of the interaction between singlet oxygen and the 3(1),3(2)-*bis*-(N,N,N-trimethylaminomethylvinyl) iodide fragment of cationic PSs (see compounds **5–7** in the main text) in apolar OctOH (R = C_8H_{17}), where PS molecules are mainly in an undissociated form.



Supplementary Scheme S3. The scheme of the interaction between singlet oxygen and DPBF in an apolar phase similar to the scheme given elsewhere [8].



Supplementary Figure S12. (Left-hand scale) Spectral variations of a solution containing both compound **5** and NH_4I between irradiation sessions (see the lines from green to purple) compared to the spectra of the solutions of compound **5** (the black line) and NH_4I (the red line). The violet line illustrates the absorption curve for the solution containing I_2+ NH_4I (the right-hand scale). The green to purple lines refer to the irradiation time of 0, 5, 10, 15, 20, 25, 30, 35 and 40 minutes.

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