Electronic Supplementary Material (ESI) for ChemComm.

Near IR Excitation of Heavy Atom Free Bodipy Photosensitizers Through the Intermediacy of Upconverting Nanoparticles

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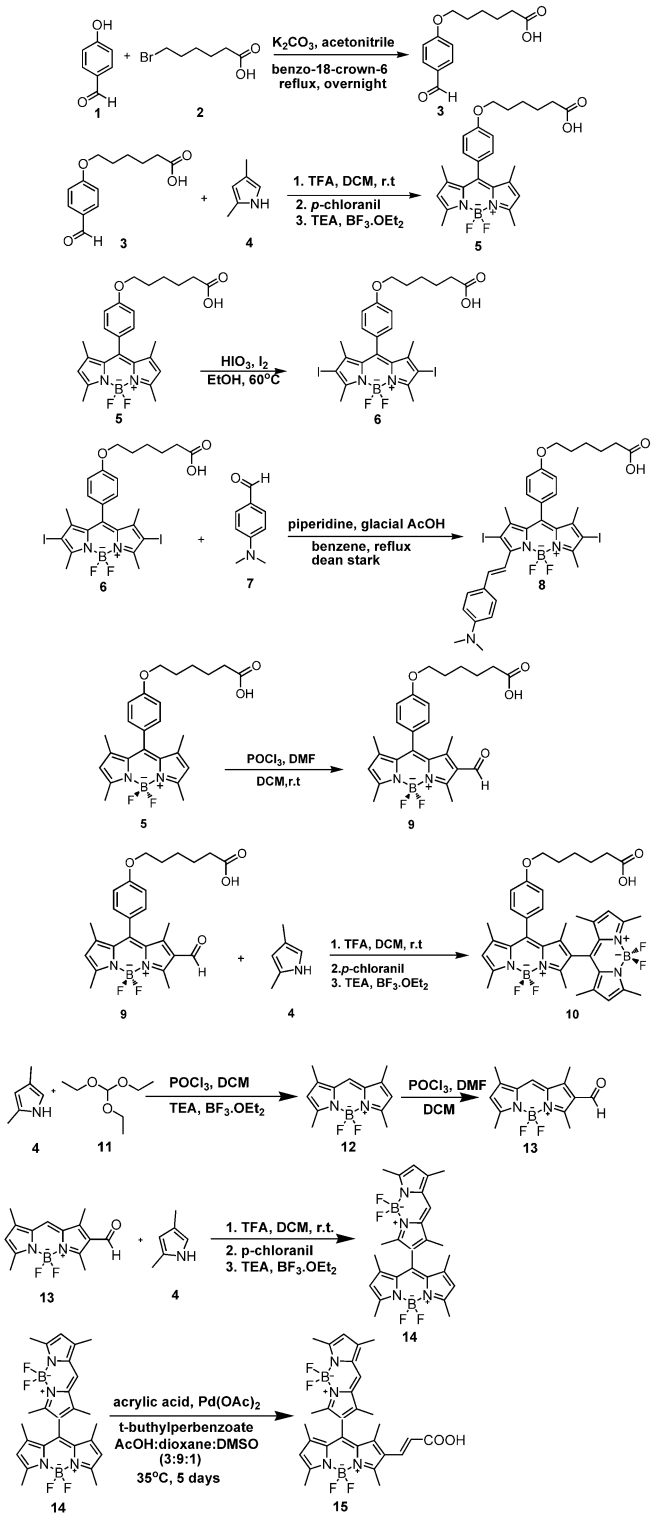
SUPPORTING INFORMATION

1. Materials and methods

All the chemicals and solvents (spectroscopic grade) were purchased from Merck or Sigma and were used without any further purification. Reactions were monitored by thin layer chromatography using Merck TLC Silica gel 60 F254. Silica gel column chromatography was performed over Merck Silica gel 60 (particle size: 0.040-0.063 mm, 230-400 mesh ASTM). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker DPX-400 in $CDCl_3$ solvent with tetramethylsilane as internal standard. All spectra were recorded at 25^{o}C and coupling constants (*J* values) are given in Hz. Chemical shifts are given in parts per million (ppm). Mass spectra were recorded with Agilent Technologies 6224 TOF LC/MS and 6530 Accurate Mass Q-TOF LC/MS. 1,3-Diphenylisobenzofuran was used as a singlet oxygen trap in organic solvent measurements and was purchased from supplier.

The synthesis procedure of the upconverting nanoparticles as follows: In a 100 mL teflon beaker, rare-earth chloride salts $YCl_3.6H_2O$ (0.72 mmol), $YbCl_3.6H_2O$ (0.2 mmol), $ErCl_3.6\ H_2O$ (0.05 mmol), $CeCl_3.6H_2O$ (0.03 mmol) and NaCl (1.0 mmol) were dissolved in 4.0 ml dd water. Polyethyleneimine (PEI, 1 g, MW: 10,000 g/mol) was dissolved in 20.0 ml dd. water and added to the solution of rare earth salts. NH_4F (5 mmol) in 50 ml ethanol was added to the teflon beaker dropwise. After purging of air by bubbling Ar for 20 minutes, the reaction mixture was sealed and heated at 200^{o} C for 3 hours. The upconverting nanoparticles were collected by centrifuge at 10,000 rpm for 10 minutes. The nanoparticles were washed three times with ethanol/water (1:1) and dried *in vacuo* at 40°C.



Scheme S1 Synthetic routes for the carboxy-functionalized dyes: styryl-Bodipy **8**, orthogonal Bodipy dimers **10**, and **15**. The numbering in the ESI is based on this scheme.

2. Synthesis of BODIPY photosentisizers

The numbering of the compounds in the ESI is based on the synthesis scheme on the previous page.

2.a. Synthesis of BODIPY-8: p-Hydroxybenzaldehyde (**1**) (1000 mg, 8.18 mmol) was dissolved in acetonitrile (20 ml). K_2CO_3 (9.58 mg, 49.08 mmol) and a catalytic amount of benzo-18-crown-6 was added to the first solution. Into this solution, 6-bromohexaonic acid (**2**) (2.40 mg, 12.28 mmol) dissolved in asetonitril (15 ml) was added. Reaction mixture was refluxed overnight. Progress of the reaction was monitored by TLC. When all the starting material had been consumed, the reaction mixture was filtered and washed with cold acetonitrile for two times. White crude was dissolved in dd water (15 ml) then neutralized with 4M HCl. White percipitates were filtered and dried. 6-(4-formylphenoxy)hexanoic acid (**3**) were obtained in 58% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.51 (d, 2H, J=8.4 Hz, Ar-CH), 6.70 (d, 2H, J=8.4 Hz, Ar-CH), 3.75 (t, 2H, J= 6.3 Hz, CH_2), 2.01 (t, 2H J= 7.2 Hz, CH_2), 1.56-1.49 (m, 2H, CH_2), 1.41-1.34 (m, 2H, CH_2), 1.25-1.19 (m, 2H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 195.1 (C=O), 176.5 (C=O), 166.0 (C_{ipso}), 136.0 (CH), 130.0 (C_{ipso}), 118.7 (CH), 72.0 (CH_2), 37.8 (CH_2), 32.5 (CH_2), 29.4 (CH_2), 28.4 (CH_2).

In argon bubbled 250 mL dichloromethane, 6-(4-formylphenoxy)hexanoic acid (**3**) (700 mg, 2.96 mmol) and 2,4-dimethylpyrrole (**4**) (564 mg, 5.92 mmol) were mixed. 1 drop of trifluoroacetic acid (TFA) was also added. The reaction mixture was stirred at room temperature overnight. Then *p*-chloranil (800 mg, 3.26 mmol) was added to the reaction medium. After stirring 5 hours at room temperature, TEA (triethylamine) (5 mL) and $BF_3.OEt_2$ (5 mL) was added and stirred again for further 1 hour. The reaction was stopped by extracting with water (3x250 mL). Organic phase was dired over Na_2SO_4 and evaporated. The crude was prufied by column chromatography with MeOH (3%)- $CHCl_3$ yielded the orange product (**5**) (22 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.16 (d, 2H, *J*=8.6 Hz, Ar-CH), 7.00 (d, 2H, *J*=8.6 Hz, Ar-CH), 5.99 (s, 2H, CH), 4.03 (t, 2H, *J=6.4 Hz*, CH_2), 2.56 (s, 6H, CH_3), 2.44 (t, 2H, *J=7.4 Hz*, CH_2), 1.89-1.84 (m, 2H, CH_2), 1.78-1.73 (m, 2H, CH_2), 1.63-1.57 (m, 2H, CH_2), 1,45 (s, 6H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 179.0 (COOH), 159.6 (C_{ipso}), 155.2 (C_{ipso}), 143.2 (C_{ipso}), 141.9 (C_{ipso}),131.9 (C_{ipso}), 129.2 (CH), 127.0 (C_{ipso}), 121.1 (CH), 115.1 (CH), 67.7 (CH_2), 33.9 (CH_3), 28.9 (CH_2), 25.6 (CH_2), 24.5 (CH_2) ve 14.6 (CH_2).

Compound **5** (500 mg, 1,1 mmol) was dissolved in ethanol (200 ml). To this solution, iodide (586.30 mg, 2.31 mmol) and HIO_3 (iodic asit) (483.8 mg, 2.75 mmol) were added, then heated at 60°C for1.5h. Progress of the reaction was monitored by TLC. When all the starting material had been consumed, the reaction was evaporated. The pink crude was dissolved in DCM then extracted with sodium thiosulphate saturated water (100 mlx2). Organic phase was dired over Na_2SO_4 and evaporated. The crude was prufied by column chromatography using MeOH (3%)- $CHCl_3$ solvent mixture yielded the pink product (**6**) (35 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.03 (d, 2H, *J*=8.4 Hz, Ar-CH), 6.93 (d, 2H, *J*=8.4 Hz, Ar-CH), 3.94 (t, 2H, *J= 6.4 Hz*, CH_2), 2.54 (s, 6H, CH_3), 2.29 (t, 2H, *J= 7.4 Hz*, CH_2), 1.81- 1.72 (m, 2H, CH_2), 1.69-1.61 (m, 2H, CH_2) ve 1.52- 1.50 (m, 2H, CH_2), 1.35 (s, 6H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 176.7 (COOH), 160.0 (C_{ipso}), 156.5 (C_{ipso}), 145.4 (C_{ipso}), 141.7 (C_{ipso}),131.7 (C_{ipso}), 129.0 (CH), 128.9 (C_{ipso}), 126.5 (C_{ipso}), 115.4 (CH), 67.9(CH_2), 33.8 (CH_3), 28.9(CH_2), 25.6(CH_2), 25.0(CH_2), 17.2 (CH_3), 16.0(CH_2). MS HRMS (TOF-APCI): *m*/z calcd for $C_{25}H_{27}BF_2I_2N_2O_3$: 705.0172 [M-H$^+$]; found: 705.0111 [M-H$^+$], Δ = 8.6 ppm.

In a 100 mL round-bottomed flask equipped with a Dean-Stark trap and a reflux condenser, 50 mL of benzene, compound **6** (238.2 mg, 0.34 mmol), 4-(*N*,*N*-dimetilamino)benzaldehit (**7**) (125.8 mg, 0.84 mg), acetic acid (AcOH) (0.5 ml, 7.4 mmol) and piperidine (0.5 ml, 5 mmol) were added. The reaction mixture was stirred at reflux temperature and concentrated nearly to dryness. Progress of the reaction was monitored by TLC. When all the starting material had been consumed, water (100 mL) was added and mixture was extracted into $CHCl_3$. The organic layer was dried over Na_2SO_4 and evaporated. The crude was purified by column chromotography using MeOH (5%)- $CHCl_3$ solvent mixture yielded the blue product (**8**) (12 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.15 (d, 1H, *J*= 16.7 Hz, CH), 7.50 (d, 2H, *J*= 8.6 Hz, Ar-CH), 7.45 (d, 1H, *J*= 16.7 Hz, CH), 7.09 (d, 2H, *J*= 8.2 Hz, Ar-CH), 6.97 (d, 2H, *J*=8.2 Hz, Ar-CH), 6.68 ppm'de (d, 2H, *J*= 8.6 Hz, Ar-CH), 3.99 (t, 2H, *J*= 6.0 Hz, CH_2), 2.99 (s, 6H, CH_3), 2.63 (s, 3H, CH_3), 2.32-2.31 (m, 2H, CH_2), 1.82-1.80 (m, 2H, CH_2), 1.69-1.67 (m, 2H, CH_2), 1.54-1.52 (m, 2H, CH_2), 1.40 (s, 3H, *N*-CH_3) 1.45 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 176.7 (COOH), 168.0 (C_{ipso}), 159.9 (C_{ipso}), 154.5 (C_{ipso}), 151.0 (C_{ipso}),142.1 (C_{ipso}), 142.0 (CH) ,139.0 (CH),

129.5 (C_{ipso}), 129.4 (Ar-CH), 129.3 (CH), 127.2 (C_{ipso}), 115.3 (CH), 112.1 (CH), 67.8 (CH_2), 40.3 (CH_3), 33.5(CH_3), 31.6 (CH_2), 28.9 (CH_2), 25.6 (CH_2) ve 24.5 (CH_2), 17.8, 17.1 (CH_3), 17.1(CH_3). MS HRMS (TOF-APCI): *m*/z calcd for $C_{34}H_{36}BF_2I_2N_3O_3$: 836.0907 [M-$H^+$]; found: 836.0851[M-$H^+$], Δ = 6.7 ppm.

2.b. Synthesis of BODIPY-10: In an oven dried 250 ml round bottom flask, $POCl_3$ (10 ml, 100 mmol) and DMF (10 ml, 12 mmol) was stirred in ice bath under argon atmosphere for 15 minutes, then strirred further 30 minutes at room temperature. Compound **5** (200 mg, 0.44 mmol) was dissolved in DCM (100ml) and added slowly to the first solution at room temperature. After 3 hours stirring at room temperature, it was seen that the reaction has been finished by checking with TLC. Then, reaction mixture was poured into cold and saturated $NaHCO_3$ solution slowly in ice-bath. The mixture was stirred for 30 minutes and extracted with DCM (100 mlx3). Organic phase was dried over Na_2SO_4 and evaporated. The crude was purified by column chromotography using MeOH (1%)- $CHCl_3$ solvent mixture yielded the orange product (**9**) (75 %).^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 9.98 (s, 1H, -CHO), 7.12 (d, 2H, J=8.4 Hz, Ar-H), 7.01 (d, 2H, J=8.4 Hz, Ar-H), 6.13 (s, 1H, CH), 4.02 (t, 2H, J=6.3 Hz CH_2), 2.79 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 2.41 (t, 2H, J=7.3 Hz CH_2), 1.87-1.81 (m, 2H, CH_2), 1.75-1.72 (m, 2H, CH_2), 1.69 (s, 3H, CH_3), 1.60-1.54 (m, 2H, CH_2), 1.46 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 186.1 (CHO), 179.2 (COOH), 160.0 (Ar-C_{ipso}), 156.2 (C_{ipso}), 147.1 (Ar-C_{ipso}), 142.7 (C_{ipso}), 130.0 (C_{ipso}), 128.9 (Ar-CH), 126.1 (C_{ipso}), 123.8 (C_{ipso}), 115.0 (Ar-CH), 68.2 (CH_2), 34.1 (CH_3), 29.0 (CH_2), 25.7 (CH_2), 24.4 (CH_2), 15.2(CH_2), 13.1 (CH_3), 11.9 (CH_3).

In argon bubbled 200 mL dichloromethane, compound **9** (173 mg, 0.36 mmol) and 2,4-dimethylpyrrole (**4**) (68.26 mg, 0.72 mmol) were mixed. 1 drop of trifluoroacetic acid was also added. The reaction mixture stirred at room temperature overnight. Then *p*-chloranil (97.36 mg, 0.396 mmol) was added to the reaction medium. After stirring 4 hours at room temperature, TEA (triethylamine) (2 mL) and BF_3.OEt_2 (2 mL) was added and stirred again for further 1 hour. The reaction was stopped by extracting with water (3x200 mL). Organic phase was dired over Na_2SO_4 and evaporated. The crude was prufied by column chromatography with MeOH (3%)-$CHCl_3$ yielded the orange product (**10**) (32 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.16 (d, 2H, *J*=8,4 Hz, Ar-H), 7.00 (d, 2H, *J*=8,4 Hz, Ar-H), 6.07 (s, 1H, CH), 5.98 (s, 2H, CH), 4.00 (t, 2H, *J=6,4 Hz*, CH_2), 2.59 (s, 3H, CH_3), 2.53 (s, 6H, CH_3), 2.41 (t, 2H, *J=8,0 Hz*, CH_2), 2.34 (s, 3H, CH_3), 1.88-1.81 (m, 2H, CH_2), 1.77-1.73 (m, 2H, CH_2) 1.70 (s, 6H, CH_3), 1.60-1.54 (m, 2H, CH_2) 1.26 (s, 6H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 176,2 (COOH), 159.8 (Ar-C_{ipso}), 157.7 (C_{ipso}), 155.1 (C_{ipso}), 150.0 (Ar-C_{ipso}), 145.9 (C_{ipso}), 142.4 (C_{ipso}), 133.8 (C_{ipso}), 131.0 (CH) , 130.0 (CH), 129.1 (Ar-CH), 126.5 (C_{ipso}), 122.1 (C_{ipso}), 121.2 (C_{ipso}), 115.3 (Ar-CH), 67.8 (CH_2), 33.7 (CH_3), 31.5 (CH_3), 28.9 (CH_2), 25.6 (CH_2), 24.5 (CH_2), 14.8 (CH_2), 12.0 (CH_3), 11.9 (CH_3). MS HRMS (TOF-APCI): *m*/z calcd for $C_{38}H_{42}B_2F_4I_2N_4O_3$: 699.3379 [M-$H^-$], ; found: 699.3307 [M-$H^-$], Δ = 10.3 ppm.

2.c. Synthesis of BODIPY-15: In argon bubbled 200 mL dichloromethane, triethyl orthoformate (**11**) (700 mg, 4.73 mmol) and 2,4-dimethylpyrrole (**4**) (900 mg, 9.46 mmol) were mixed and stirred for 15 minutes. To this mixture, phosphoryl chloride ($POCl_3$) (797.6 mg, 0,5 ml) was added and stirred further 2 hours. After stirring 2 h. at room temperature, TEA (5 ml) and BF_3.OEt_2 (5 ml) was added and stirred again for further 1 hour. The reaction was stopped by extracting with water (3x200 mL). Organic phase was dired over Na_2SO_4 and evaporated. The crude was prufied by column chromatography with $CHCl_3$ yielded the orange product (**12**) (67 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 6.97 (s, 1H, Ar-CH), 5.97 (s, 2H, Ar-CH), 2.45 (s, 6H, CH_3), 2.18 (s, 6H, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 156.8 (C_{ipso}), 141.3 (C_{ipso}), 133.5 (C_{ipso}), 120.2 (CH), 119.1 (CH), 14.8 (CH_3), 11.2 (CH_3).

In an oven dried 250 ml round bottom flask, $POCl_3$ (1 ml) and DMF (1 ml) was stirred in ice baht under argon atmosphere for 15 minutes, , then strirred further 30 minutes at room temperature. Compound **12** (621 mg, 2.5 mmol) was dissolved in DCM (100 ml) and added slowly to the first solution at room temperature. After 4 hours stirring at room temperature, when the reaction was checked by TLC, it was seen that the reaction has been finished. Then, reaction mixture was poured into cold and saturated $NaHCO_3$ solution slowly in ice-bath. Mixture was stirred for 30 minutes and extracted with DCM (100 mlx3). Organic phase was dried over Na_2SO_4 and evaporated. The crude was purified by column chromotography using $CHCl_3$ solvent yielded the orange product (**13**) (78 %).^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 9.99 (s, 1H, CHO), 7.17 (s, 1H, Ar-CH), 6.17 (s, 1H, Ar-CH), 2.73 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 1.51 ppm (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 185.5 (CHO), 163.5 (C_{ipso}), 157.2 (C_{ipso}), 145.4 (C_{ipso}), 140.6 (C_{ipso}), 136.4 (C_{ipso}), 131.1 (C_{ipso}), 125.8 (C_{ipso}), 122.0 (CH), 121.4 (CH), 15.2 (CH_3), 12.7 (CH_3), 11.5 (CH_3), 10.4 (CH_3).

In argon bubbled 200 mL dichloromethane, compound **13** (460 mg, 1.67 mmol)and 2,4-dimethylpyrrole (**4**) (313.67 mg, 3.33 mmol) were mixed. 1 drop of trifluoroacetic acid was also added. The reaction mixture stirred at room temperature overnight. Then *p*-chloranil (97.36 mg, 0.396 mmol) was added to the reaction medium. After stirring 4 hours at room temperature, TEA (triethylamine) (2 mL) and $BF_3.OEt_2$ (2 mL) was added and stirred again for further 1 hour. The reaction was stopped by extracting with water (3x200 mL). Organic phase was dired over Na_2SO_4 and evaporated. The crude was prufied by column chromatography with MeOH (3%)-$CHCl_3$ yielded the orange product (**14**) (42 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.16 (s, 1H, CH), 6.14 (s, 1H, CH), 6.01 (s, 2H, CH), 2.55 (s, 3H, CH_3), 2.50 (s, 6H, CH_3), 2.38 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.70 ppm (s, 6H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 160.3 (C_{ipso}), 155.8 (C_{ipso}), 151.5 (C_{ipso}), 143.7 (C_{ipso}), 142.5 (C_{ipso}), 136.6 (C_{ipso}) , 134.7 (C_{ipso}), 133.4 (C_{ipso}), 132.3 (C_{ipso}), 131.8 (C_{ipso}) , 124.2 (C-H) , 121.3 (C-H), 120.7 (C-H), 120.5 (C-H), 14.9 (CH_3), 14.7 (CH_3), 13.9 (CH_3), 12.7 (CH_3), 11.4 (CH_3), 9.8 (CH_3), 8.7 (CH_3).

In a 50 ml round bottom flask, BODIPY **14** (97,24 mg, 0,2 mmol), acrylic acid (72.06 mg, 1 mmol) and *t*-buthlyperbenzoate (77.69 mg, 0.4 mmol) were dissolved in acetic acid: dioxane: DMSO (3:9:1) solvent system. To the reaction mixture, $Pd(OAc)_2$ (8.98 mg, 0.04 mmol) catalyst was added under argon atmosphere. The reaction mixture was stirred at 35°C for 5 days. Progress of the reaction was checked by TLC. After compound **14** has been consumed, reaction was stopped. Reaction solvent was evaporated and purified by column chromatography with ethyl acetate yielded red compound (**15**) (20 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.79 (d, 1H, J= 16.0 Hz, CH), 7.33 (s, 1H, CH), 7.28 (s, 1H, CH), 6.29 (d, 1H, J= 16.0 Hz, CH), 6.06 (s, 1H, CH), 2.74 (s, 3H, CH_3), 2.59 (s, 6H, CH_3), 2.47 (s, 6H, CH_3), 2.19 (s, 3H, CH_3), 1.73 (s, 6H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 178.0 (COOH), 160.3 (C_{ipso}), 156.3(C_{ipso}), 152.3 (C_{ipso}), 148.6 (C_{ipso}), 137.3 (C_{ipso}), 132.1 (C_{ipso}), 131.0 (C_{ipso}), 130.4 (C_{ipso}), 130.0 (CH), 128.7 (C_{ipso}), 126.8 (C_{ipso}), 125.2 (CH), 122.2 (CH), 121.6 (CH), 121.5 (CH), 121.0 (C_{ipso}), 116.4 (C_{ipso}), 29.7 (CH_3), 14.7 (CH_3), 14.0 (CH_3), 13.8 (CH_3), 11.5 (CH_3), 10.0 (CH_3). MS HRMS (TOF-APCI): *m*/z calcd for $C_{29}H_{30}B_2F_4I_2N_4O_2$: 563.2491 [M-H$^-$], ; found: 563.2385 [M-H$^-$], Δ = 18.8 ppm.

3. ^{1}H , ^{13}C -NMR and Mass Spectra

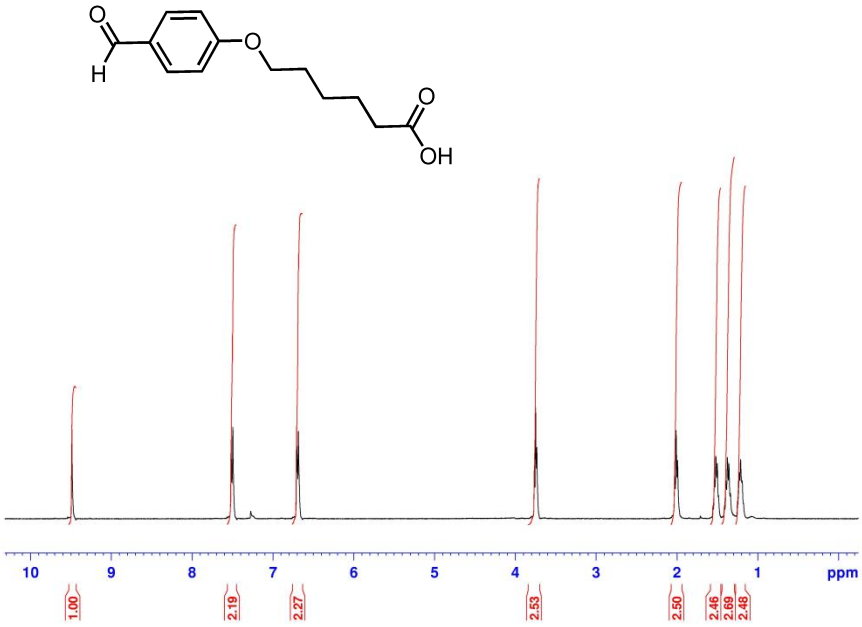


Fig. S1 ^{1}H-NMR spectrum of the compound **3** ($CDCl_3$,400 MHz)

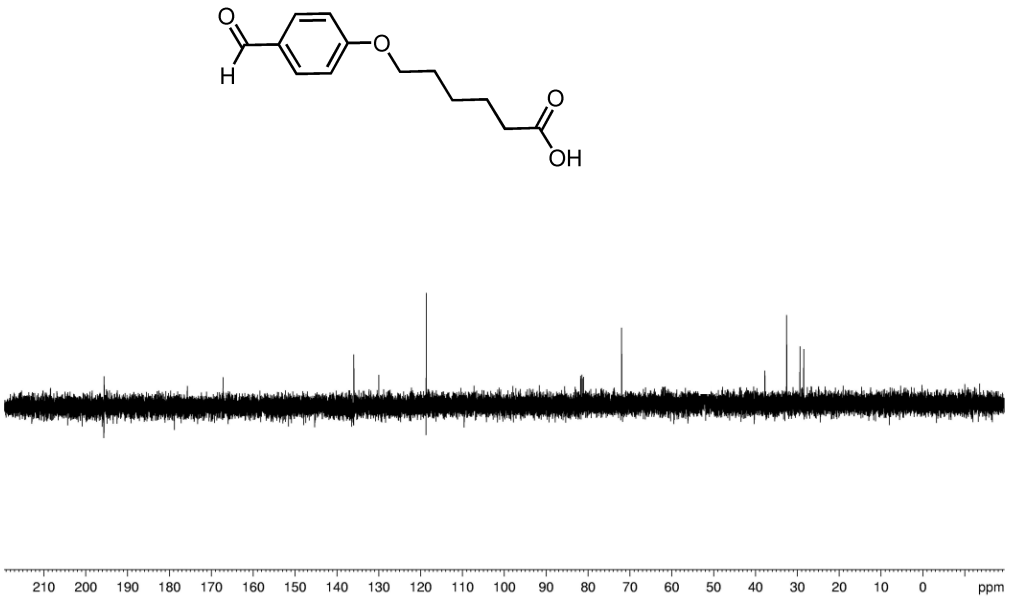


Fig. S2 ^{13}C-NMR spectrum of compound **3** ($CDCl_3$, 100 MHz).

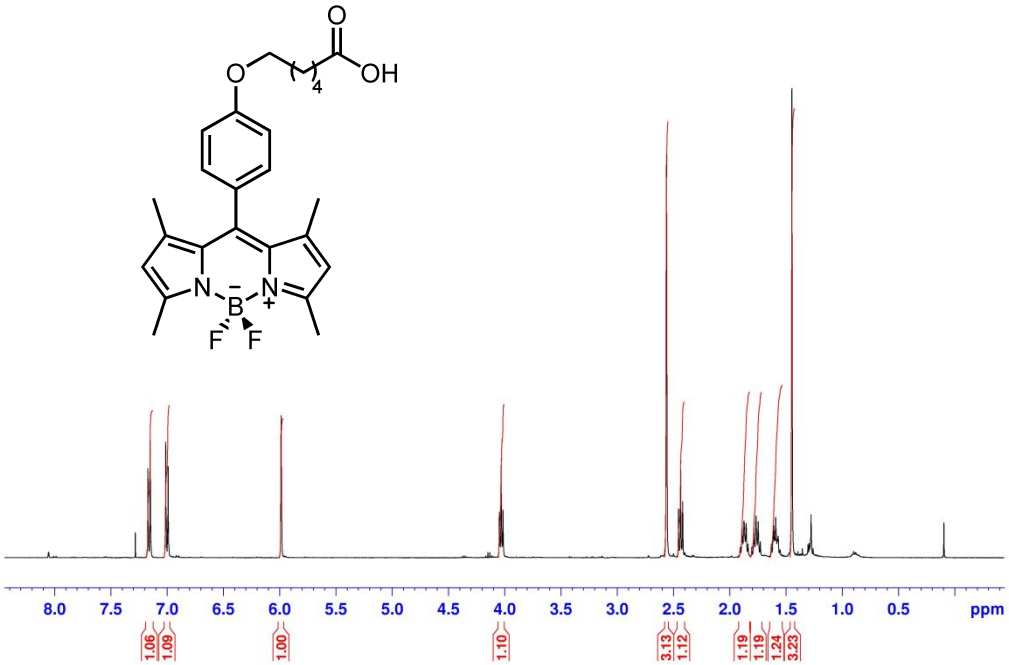


Fig. S3 ^{1}H-NMR spectrum of the compound **5** ($CDCl_3$, 400 MHz)

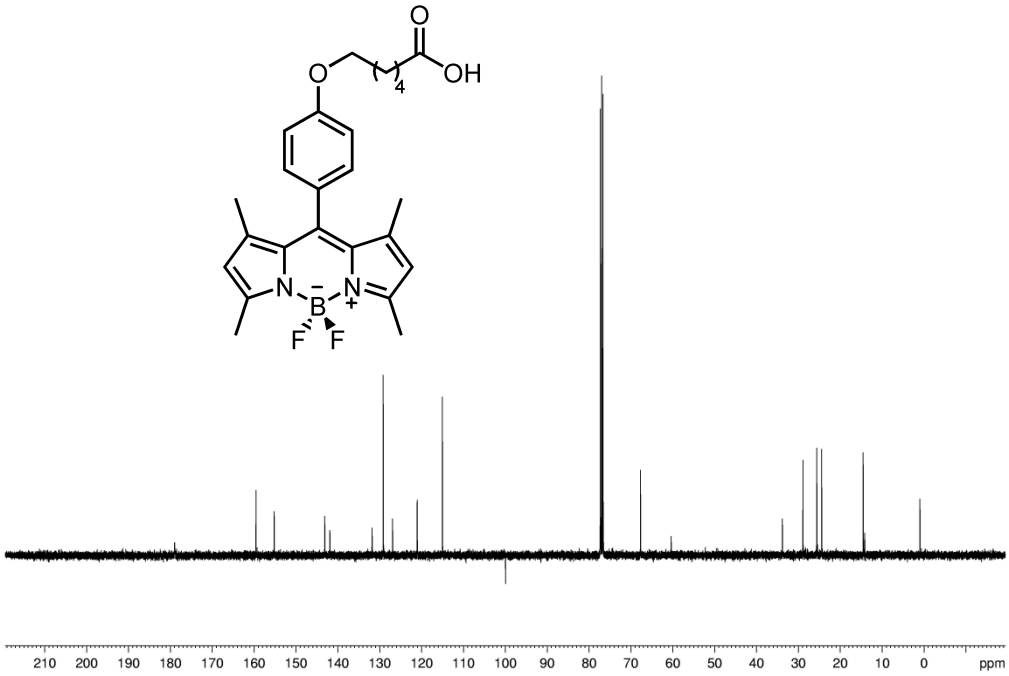


Fig. S4 ^{13}C-NMR spectrum of the compound **5** ($CDCl_3$, 100 MHz)

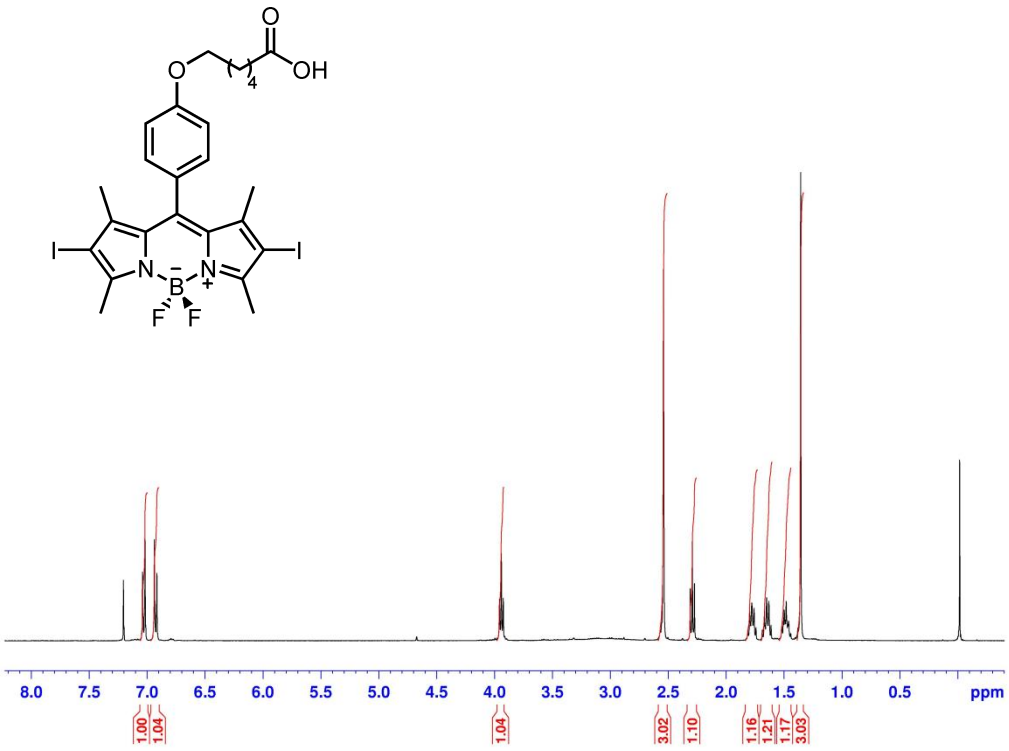


Fig. S5 ^{1}H-NMR spectrum of the compound **6** ($CDCl_3$, 400 MHz)

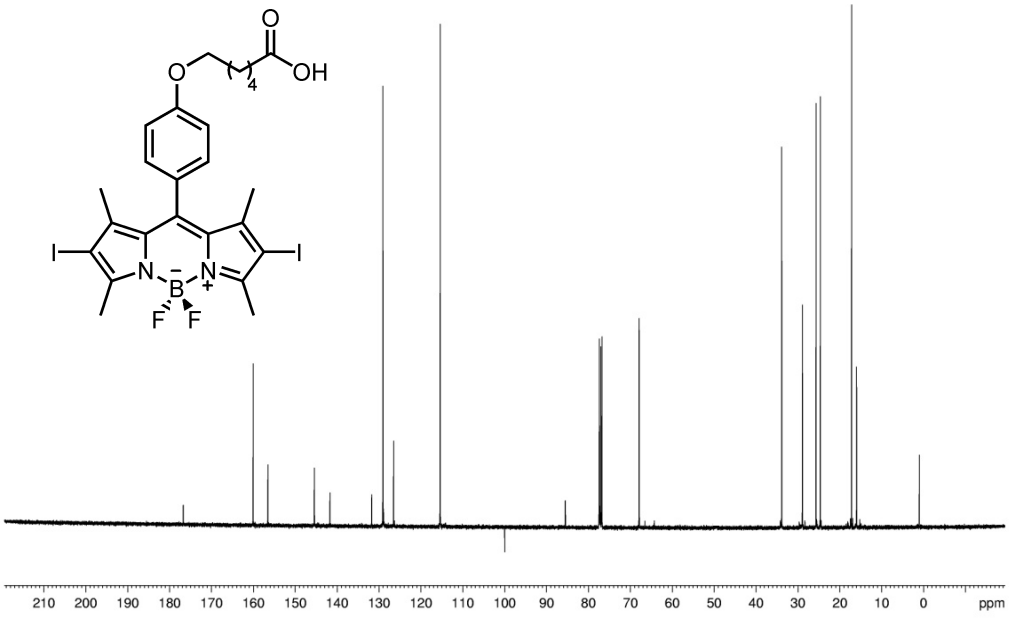


Fig. S6 ^{13}C-NMR spectrum of the compound **6** ($CDCl_3$, 100 MHz)

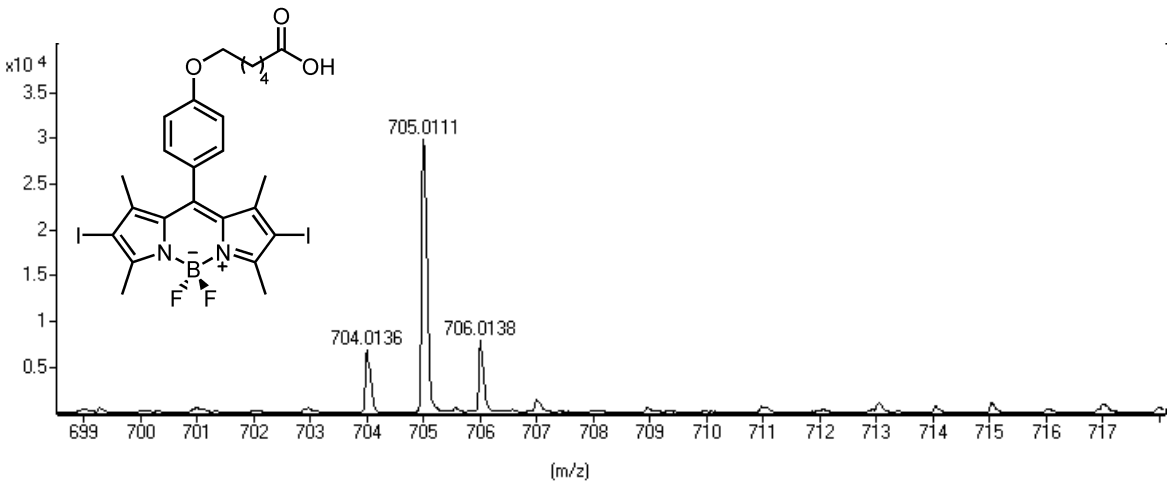


Fig. S7 HR- Mass spectrum of the compound **6** (*m*/z calcd for $C_{25}H_{27}BF_2I_2N_2O_3$: 705.0172 [M-H$^+$]; found: 705.0111 [M-H$^+$], Δ = 8.6 ppm.)

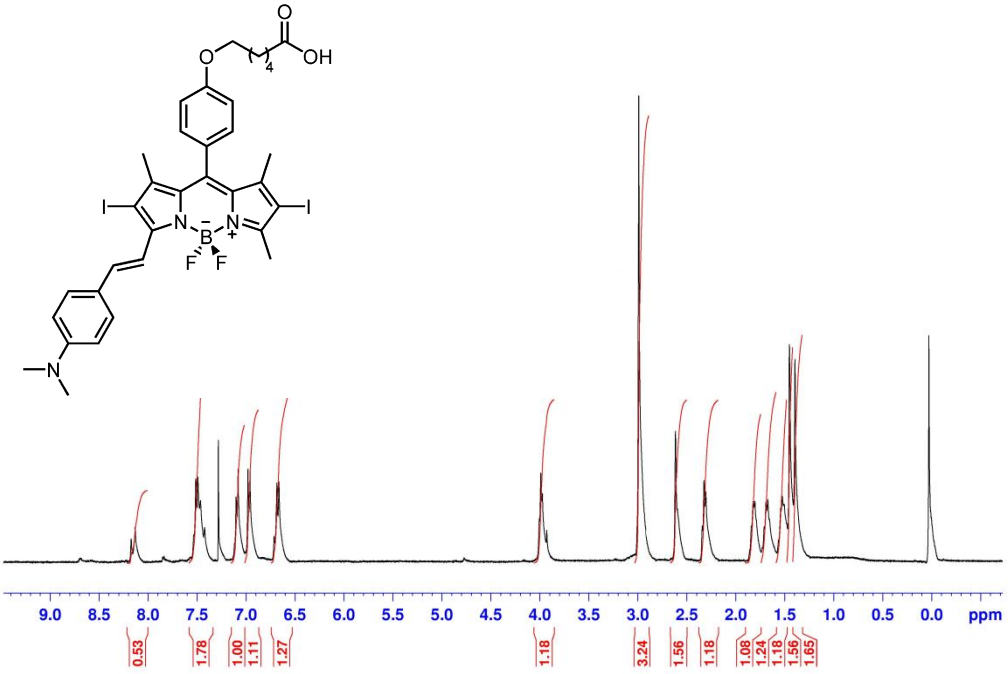


Fig. S8 ^{1}H-NMR spectrum of the compound **8** ($CDCl_3$, 400 MHz)

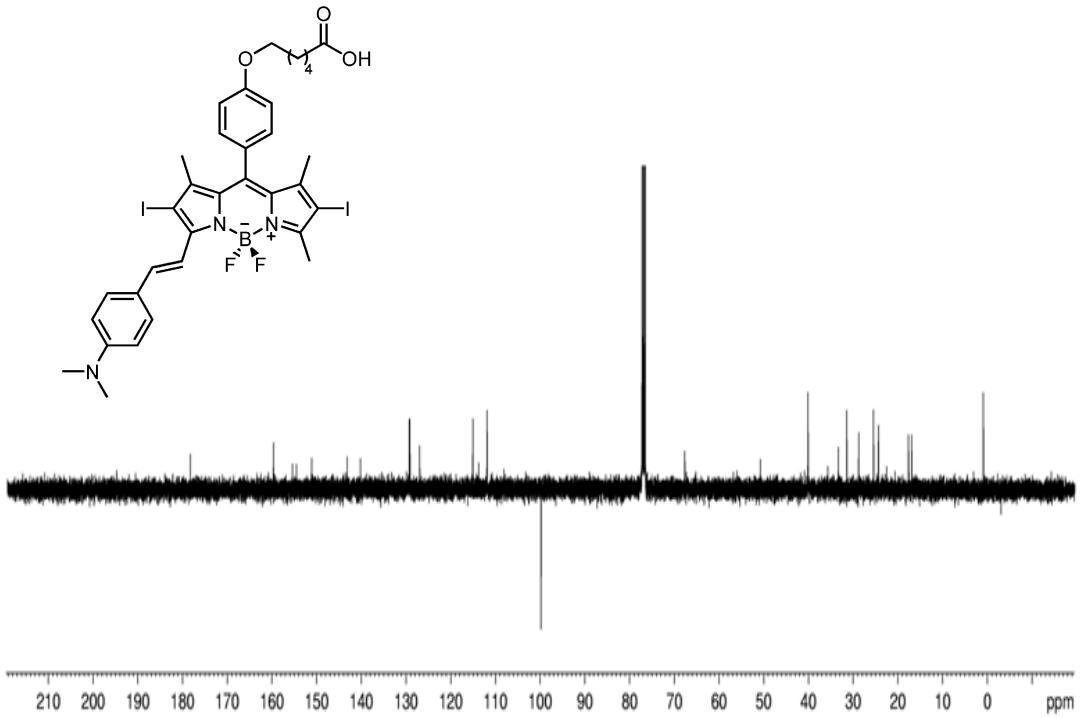


Fig. S9 ^{13}C-NMR spectrum of the compound **8** ($CDCl_3$, 100 MHz)

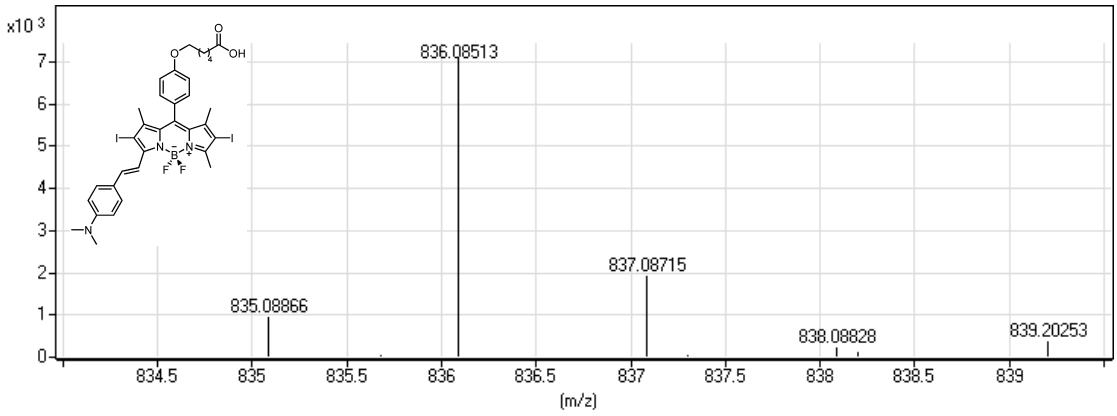


Fig. S10 HR- Mass spectrum of the compound **8** (*m*/z calcd for $C_{34}H_{36}BF_2I_2N_3O_3$: 836.0907 [M-$H^+$]; found: 836.0851[M-$H^+$], Δ = 6.7 ppm.

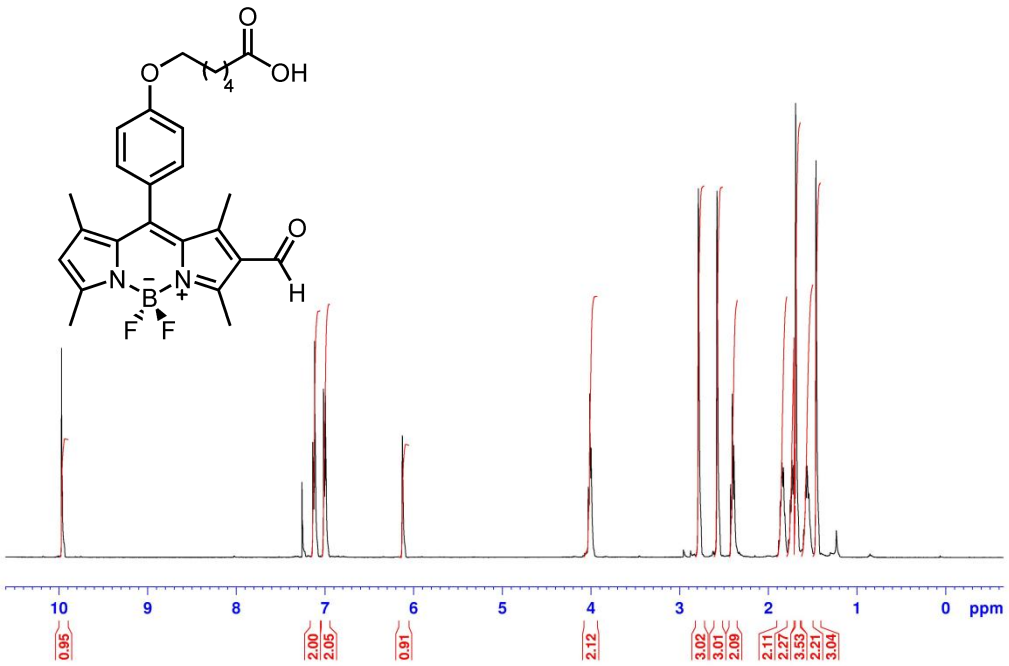


Fig. S11 ^{1}H-NMR spectrum of the compound **9** ($CDCl_3$, 400 MHz)

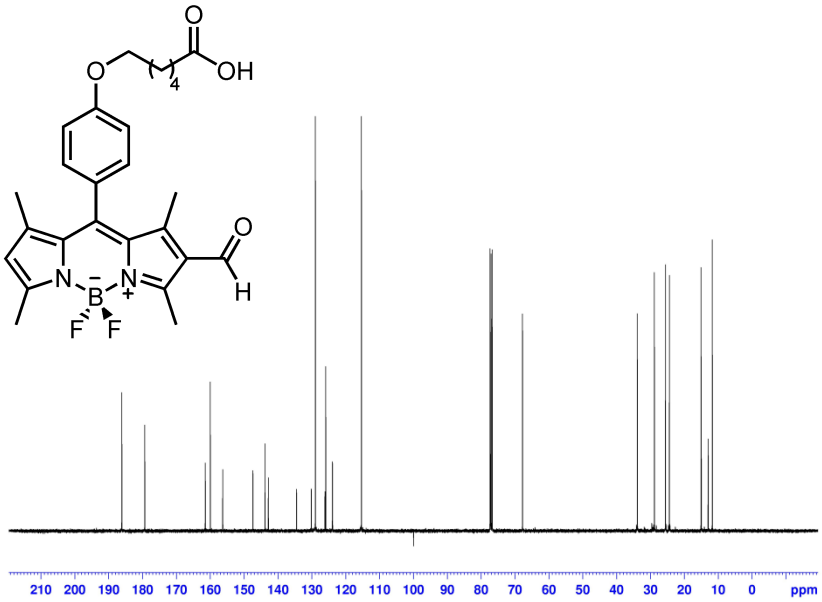


Fig. S12 ^{13}H-NMR spectrum of the compound **9** ($CDCl_3$, 100 MHz)

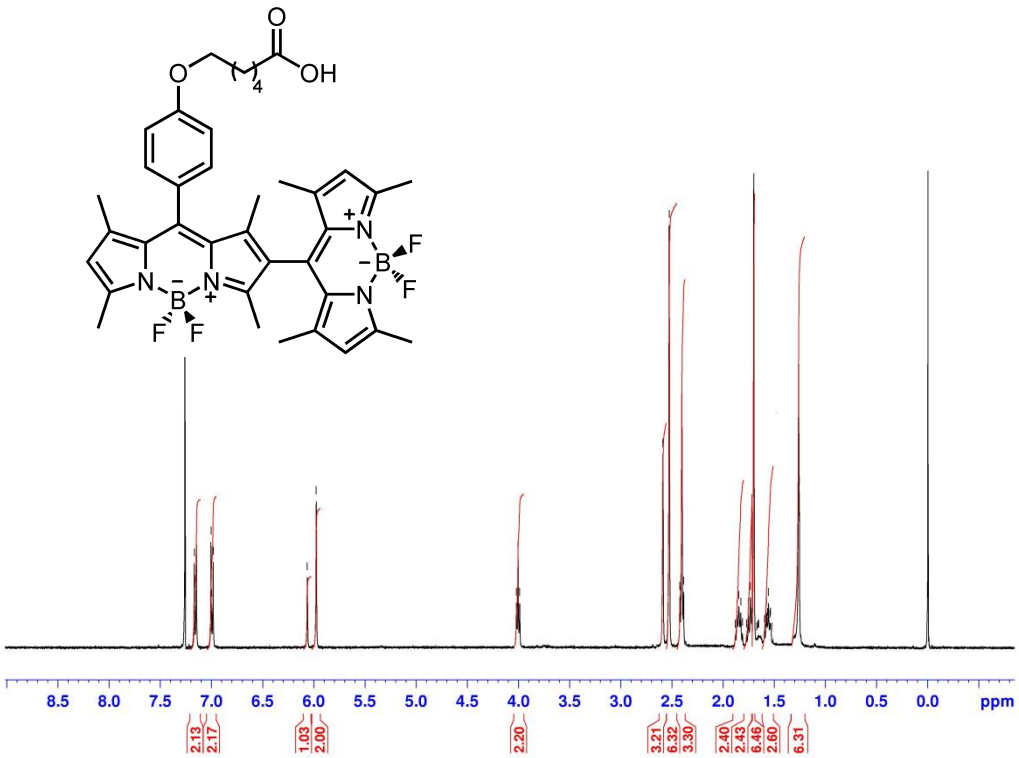


Fig. S13 ^{1}H-NMR spectrum of the compound **10** ($CDCl_3$, 400 MHz)

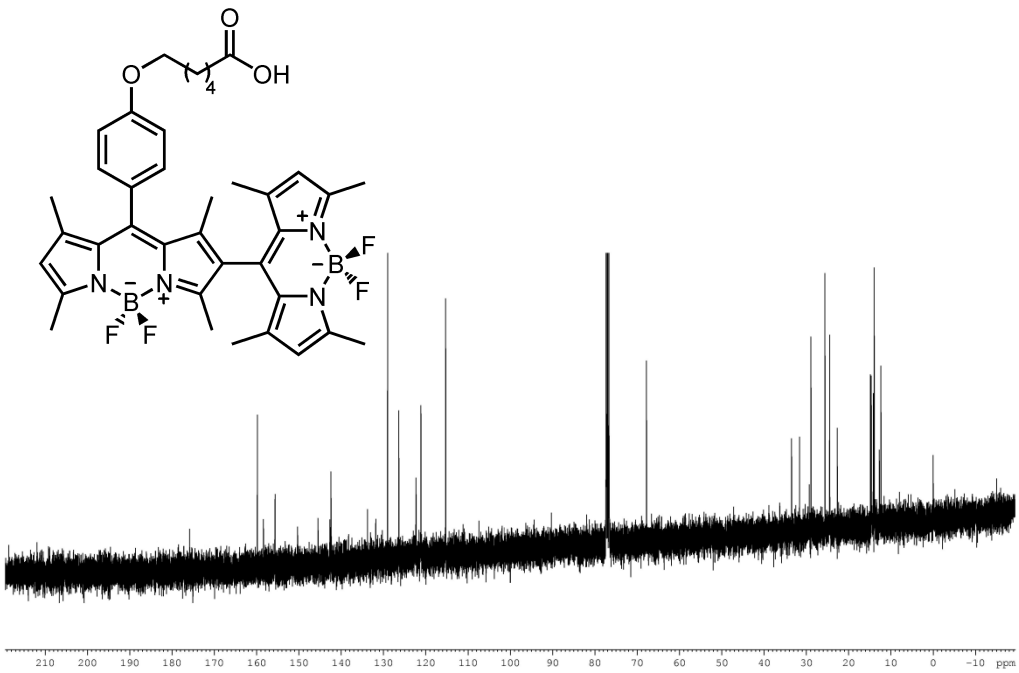


Fig. S14 ^{13}C-NMR spectrum of the compound **10** ($CDCl_3$, 400 MHz)

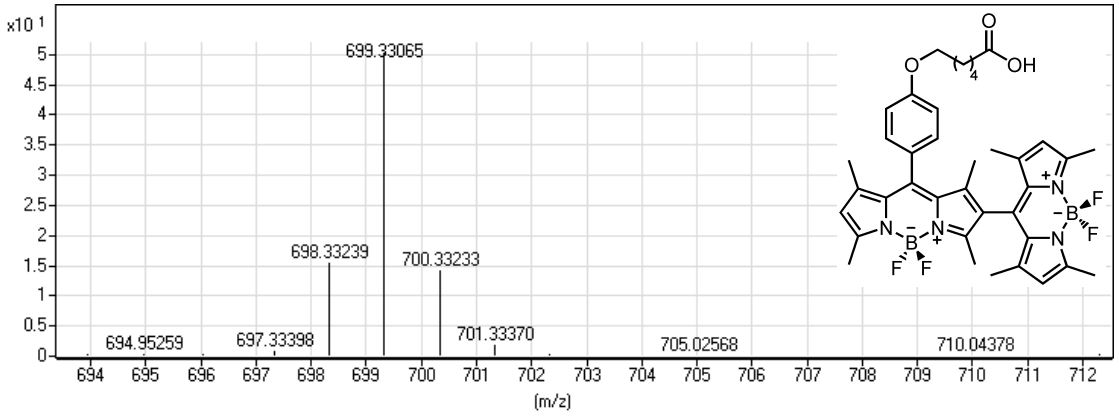


Fig. S15 HR- Mass spectrum of the compound **10** (*m*/z calcd for $C_{38}H_{42}B_2F_4I_2N_4O_3$: 699,3379 [M-H$^-$], ; found: 699,3307 [M-H$^-$], Δ = 10.3 ppm.)

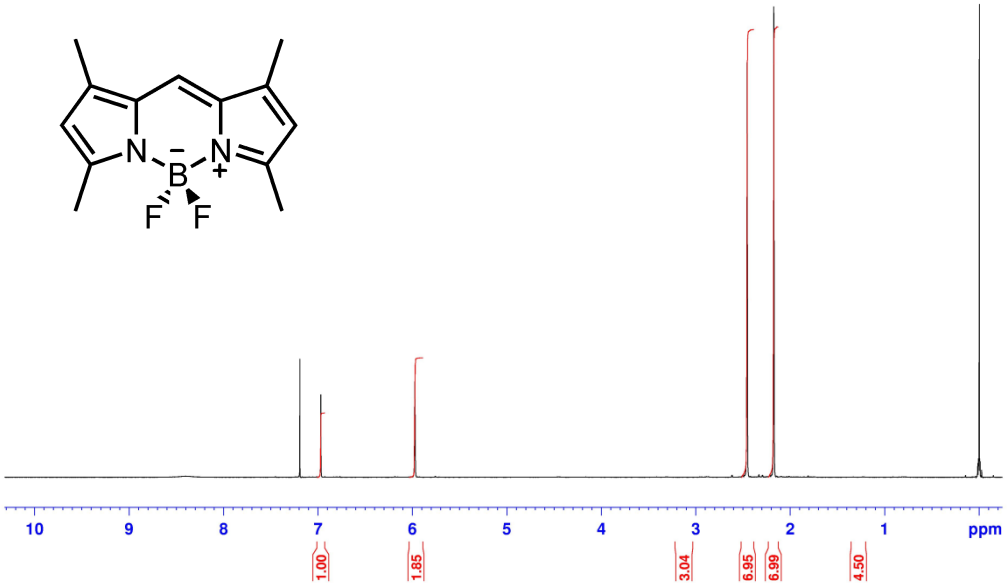


Fig. S16 ^{1}H-NMR spectrum of the compound **12** ($CDCl_3$, 400 MHz)

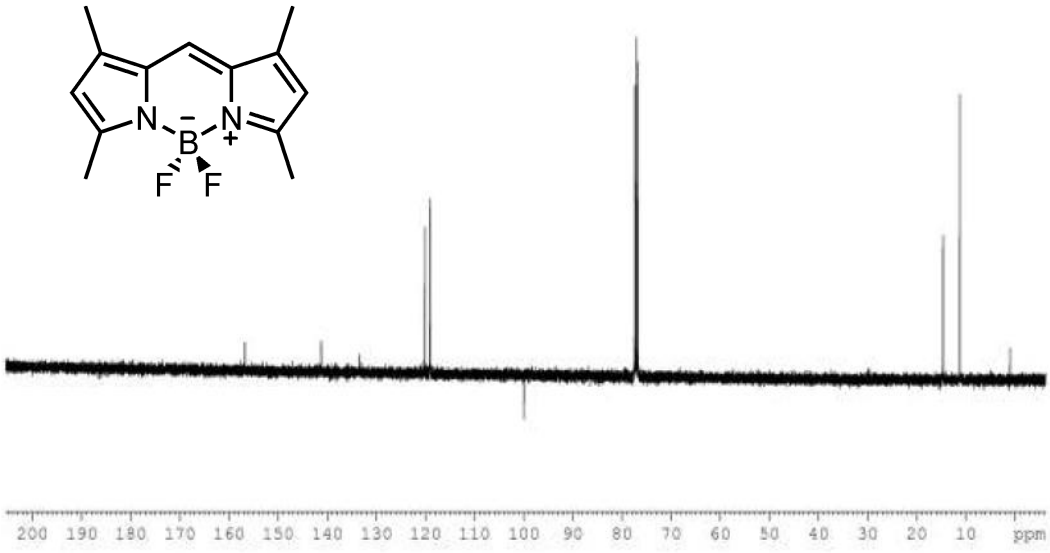


Fig. S17 ^{13}C-NMR spectrum of the compound **12** ($CDCl_3$, 100 MHz)

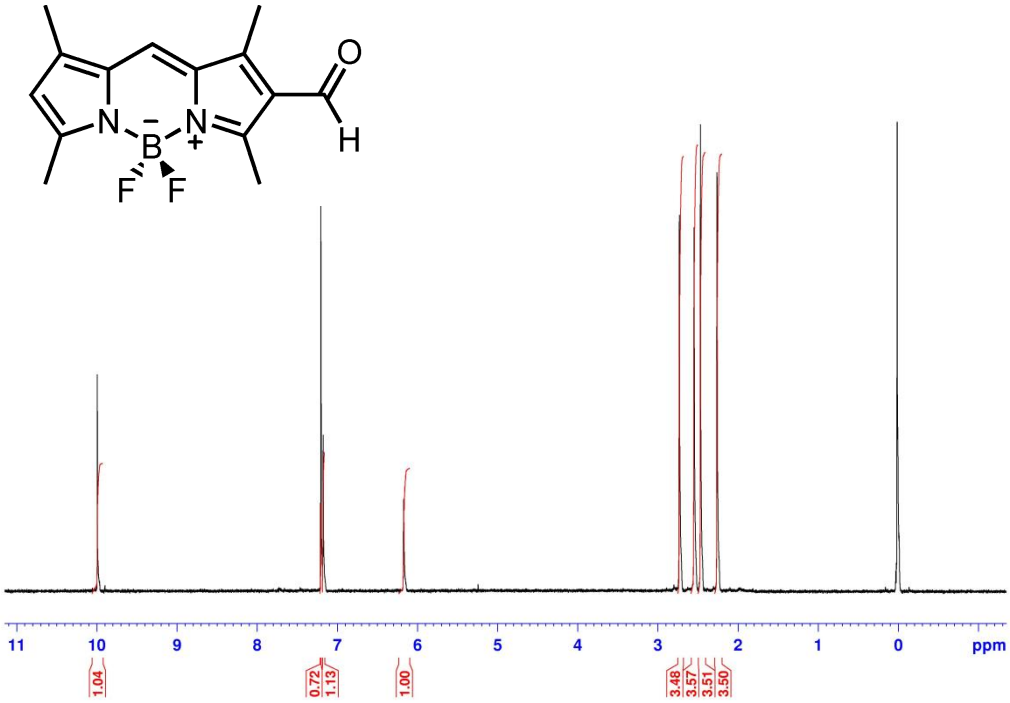


Fig. S18 ^{1}H-NMR spectrum of the compound **13** ($CDCl_3$, 400 MHz)

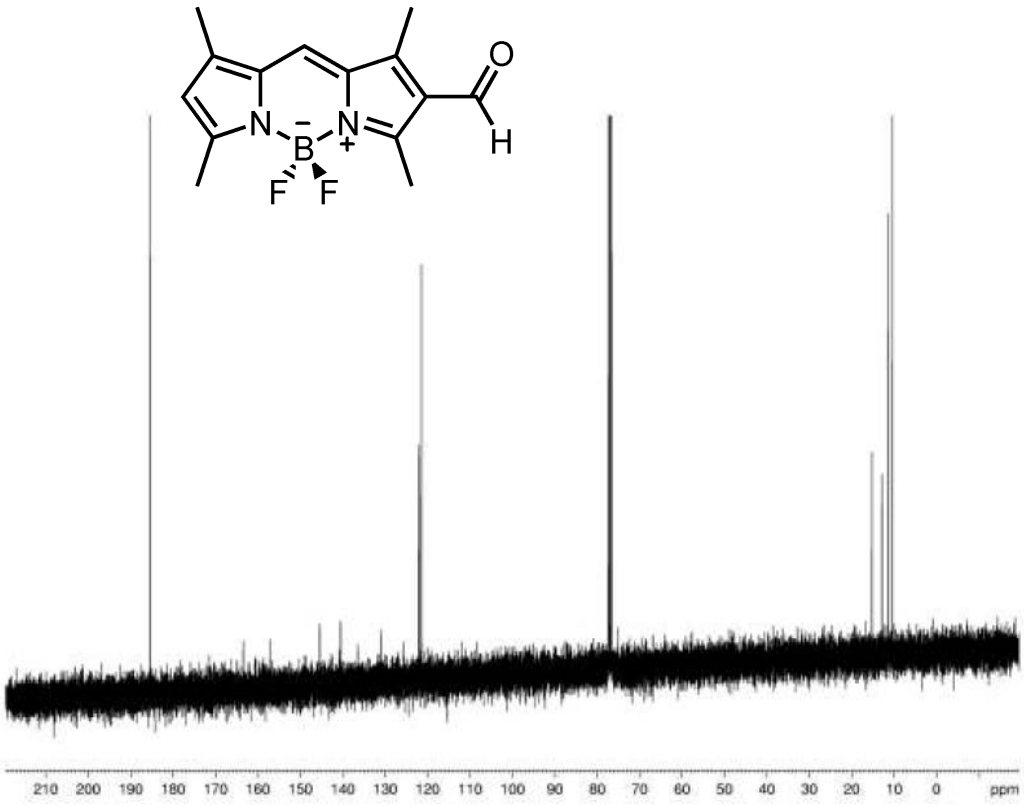


Fig. S19 ^{13}C-NMR spectrum of the compound **13** ($CDCl_3$, 100 MHz)

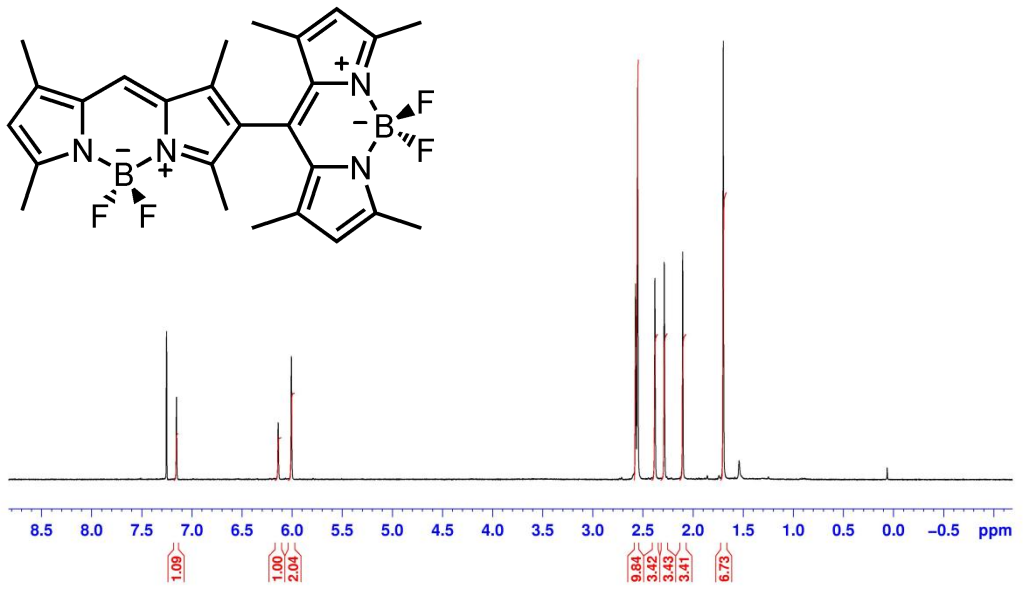


Fig. S20 ^{1}H-NMR spectrum of the compound **14** ($CDCl_3$, 400 MHz)

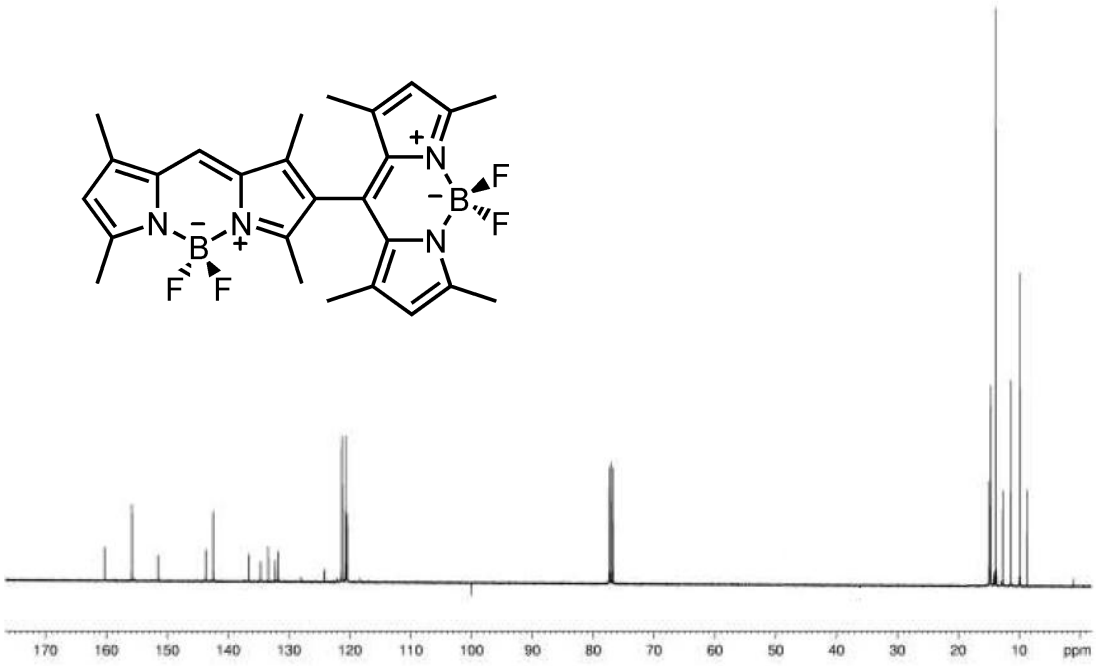


Fig. S21 ^{13}C-NMR spectrum of the compound **14** ($CDCl_3$, 100 MHz)

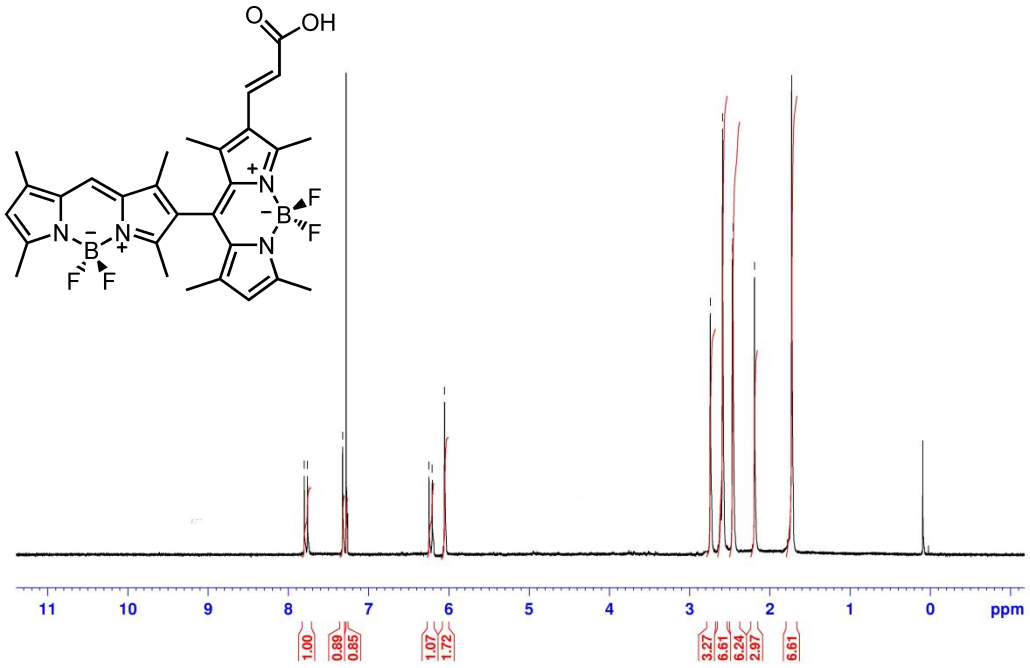


Fig. S22 ^{1}H-NMR spectrum of the compound **15** ($CDCl_3$, 400 MHz)

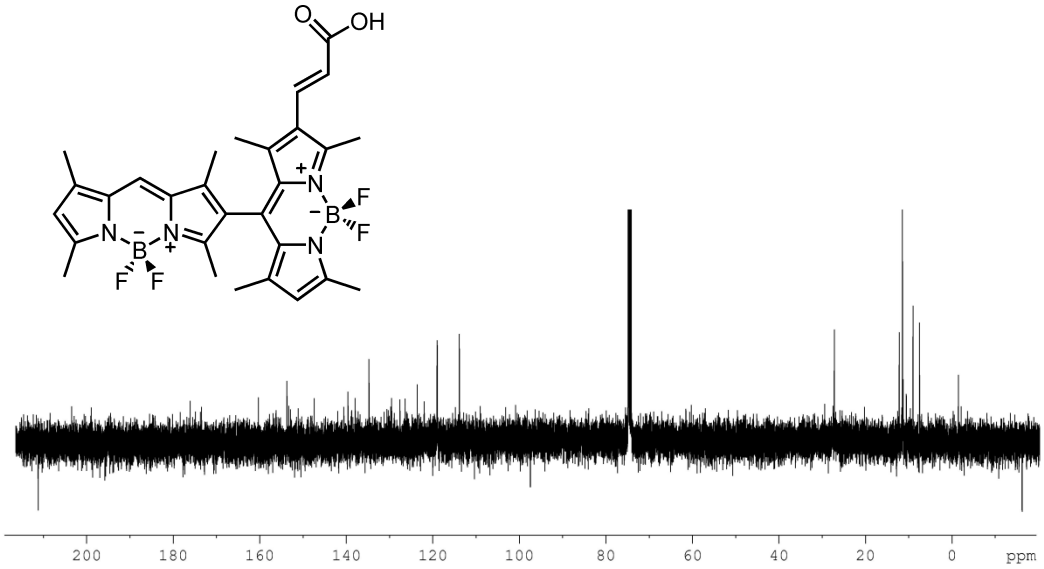


Fig. S23 ^{13}C-NMR spectrum of the compound **15** ($CDCl_3$, 100 MHz)

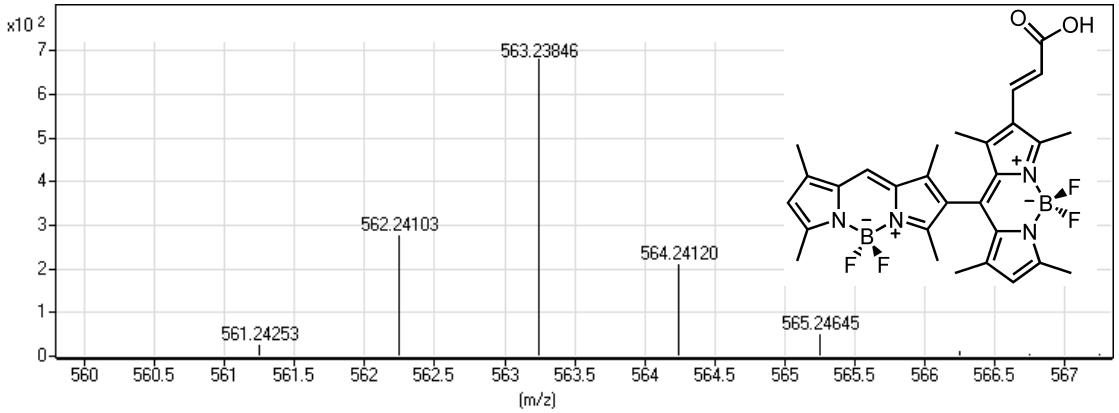


Fig. S24 HR- Mass spectrum of the compound **15** (*m*/z calcd for $C_{29}H_{30}B_2F_4I_2N_4O_2$: 563.2491 [M-H$^-$]; found: 563.2385 [M-H$^-$], Δ = 18.8 ppm.)

4. Characterization of upconverting nanoparticles

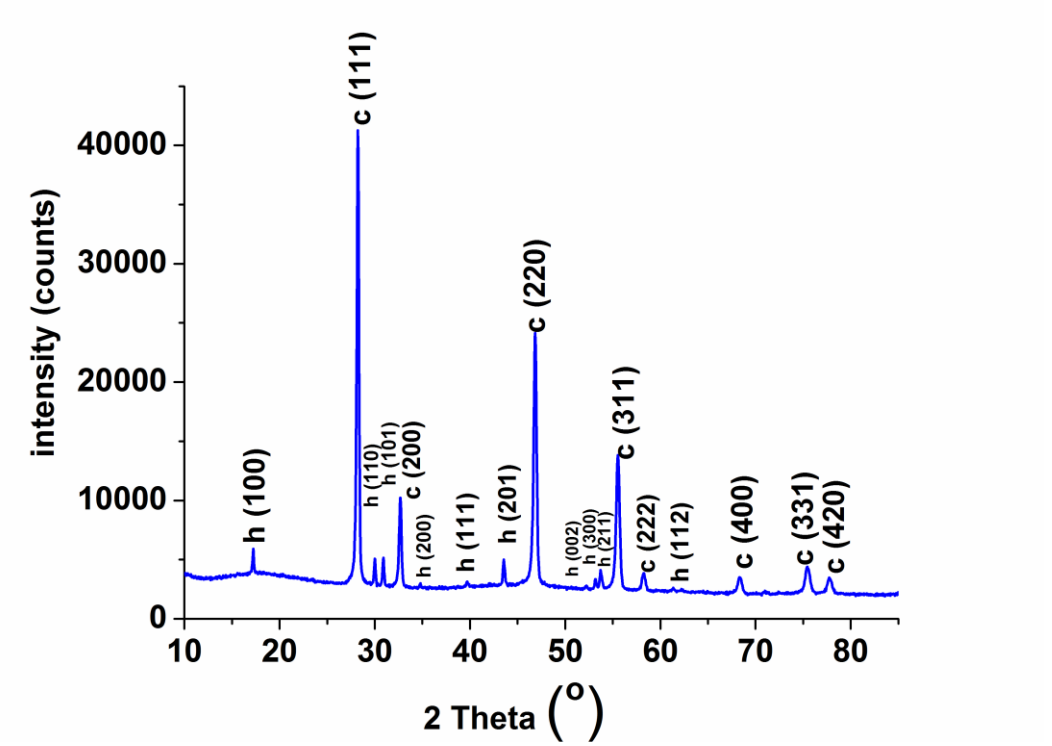


Fig. S25 X-ray Diffraction (XRD) pattern of PEI coated UCNP ($NaYF_4$: Yb^{+3}, Er^{+3}/ Ce^{+3}) h: hexagonal, c:cubic phase peaks

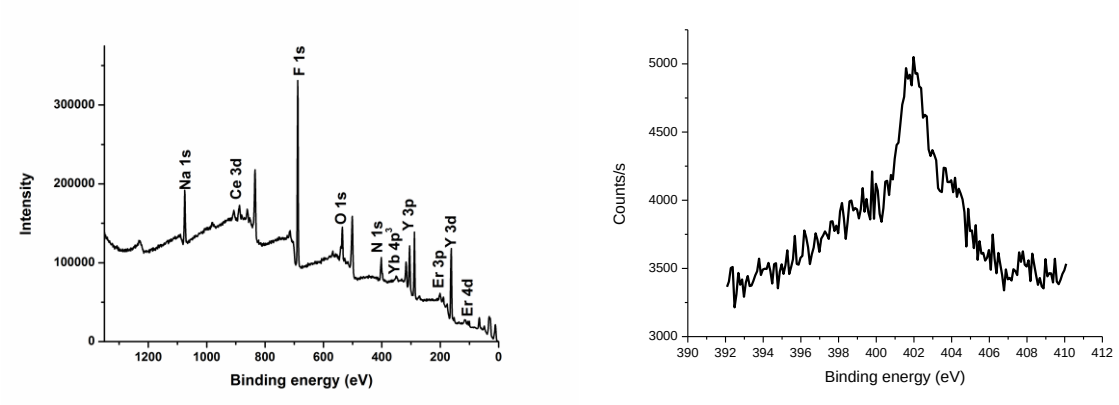


Fig. S26 X-ray photoelectron spectrum (XPS) of PEI coated UCNP (NaYF4: Yb^{+3}, Er^{+3}/ Ce^{+3} (72: 20: 5:3 %). Peak at 402 eV belongs to nitrogen atom which means that PEI was coated on the UCNP.

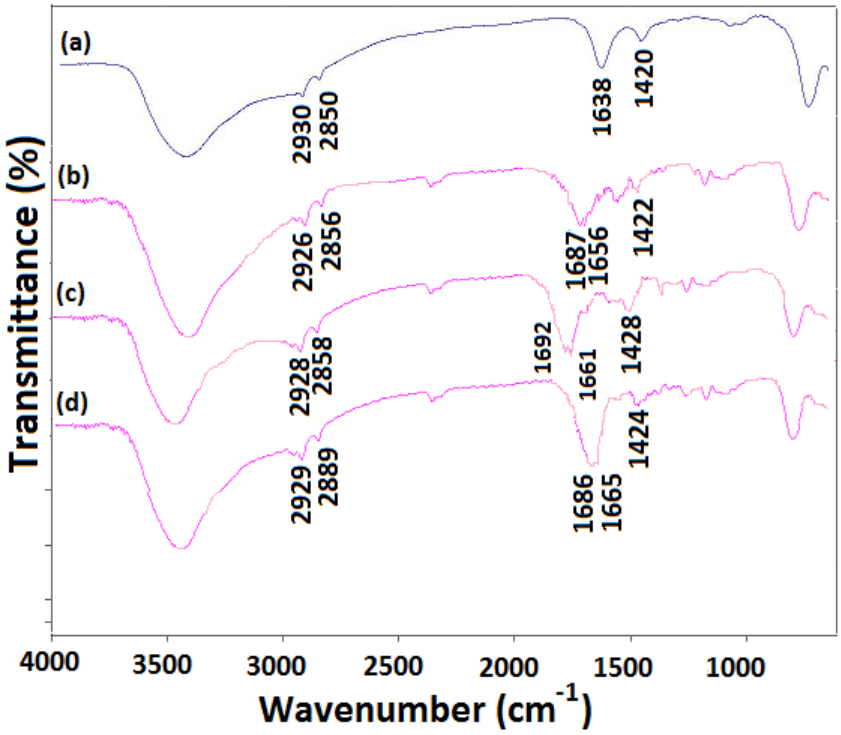


Fig. S27 FTIR spectrum of (a) PEI covered UCNP, (b)BOD**8**-UCNP, (c)BOD**10**-UCNP, (d)BOD**15**-UCNP

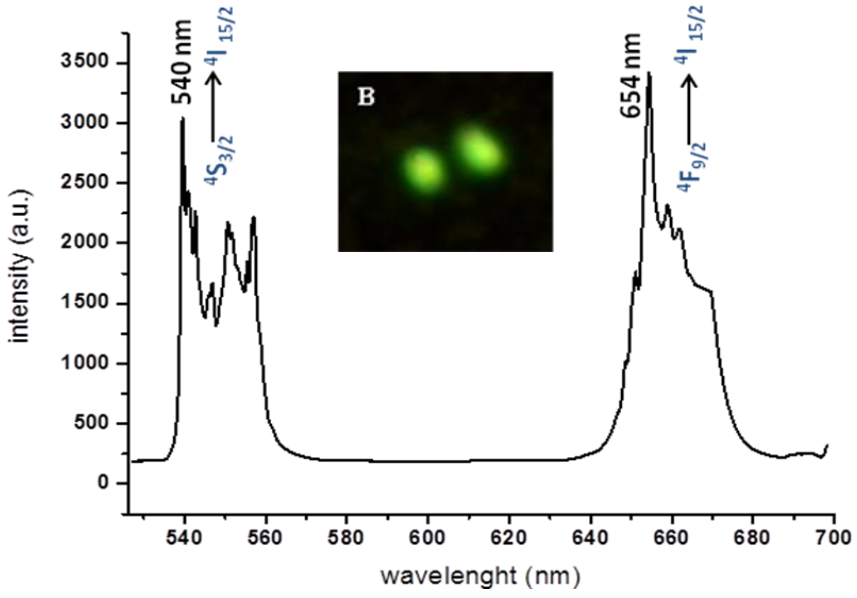


Fig. S28 Room temperature upconversion emission spectra of the $NaYF_4$: Yb, Er/Ce (72:20:5:3 mol %). Inset confocal picture was a photo from raman microscope showing the upconversion luminescence excited by 980 nm laser (50 mW)

5. Singlet oxygen measurements of BODIPY conjugated upconversion nanoparticles

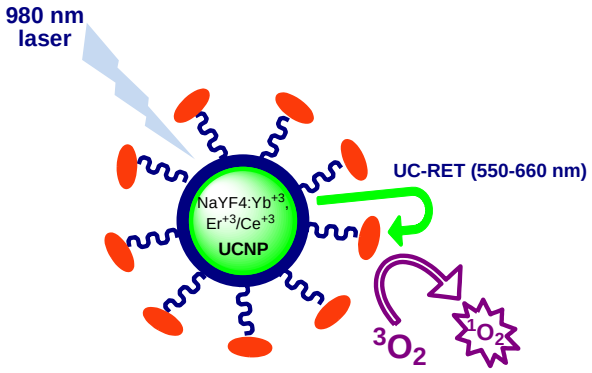


Fig. S29 Schematic illustration of BODIPY-conjugated UCNP

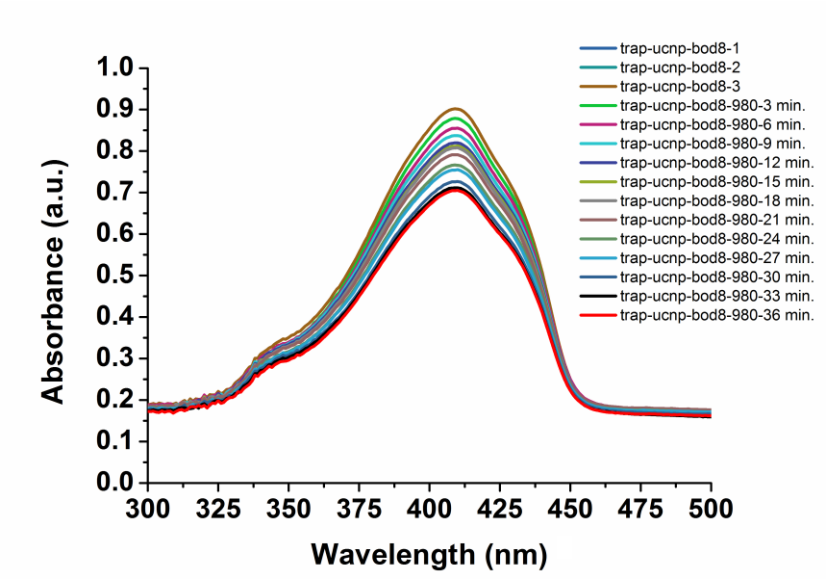


Fig. S30 $^1O_2$ generation from BOD-8@ UCNP under 980 nm laser

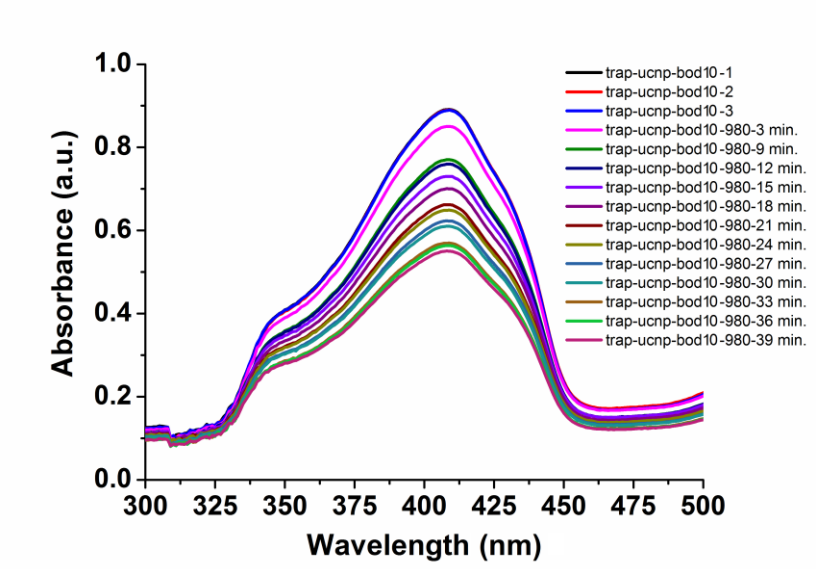


Fig. S31 $^1O_2$ generation from BOD-10 @ UCNP under 980 nm laser

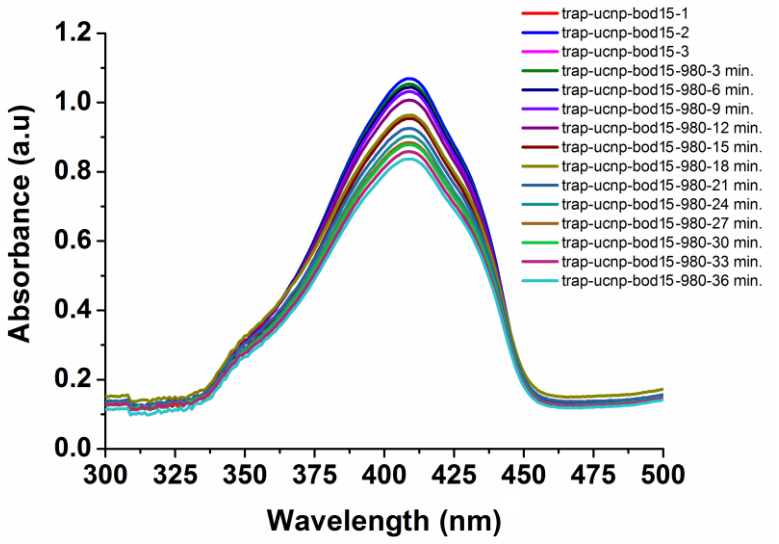


Fig. S32 $^1O_2$ generation from BOD-15 @ UCNP under 980 nm laser

Control experiments

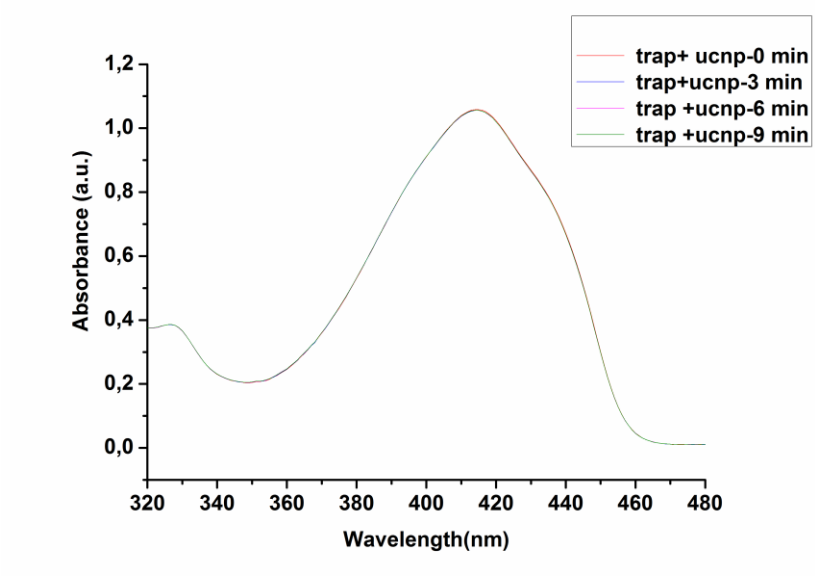


Fig. S33 Control experiment-1: upconverting nanoparticles solution (0.4 mg/ml) without BODIPY dye in trap solution

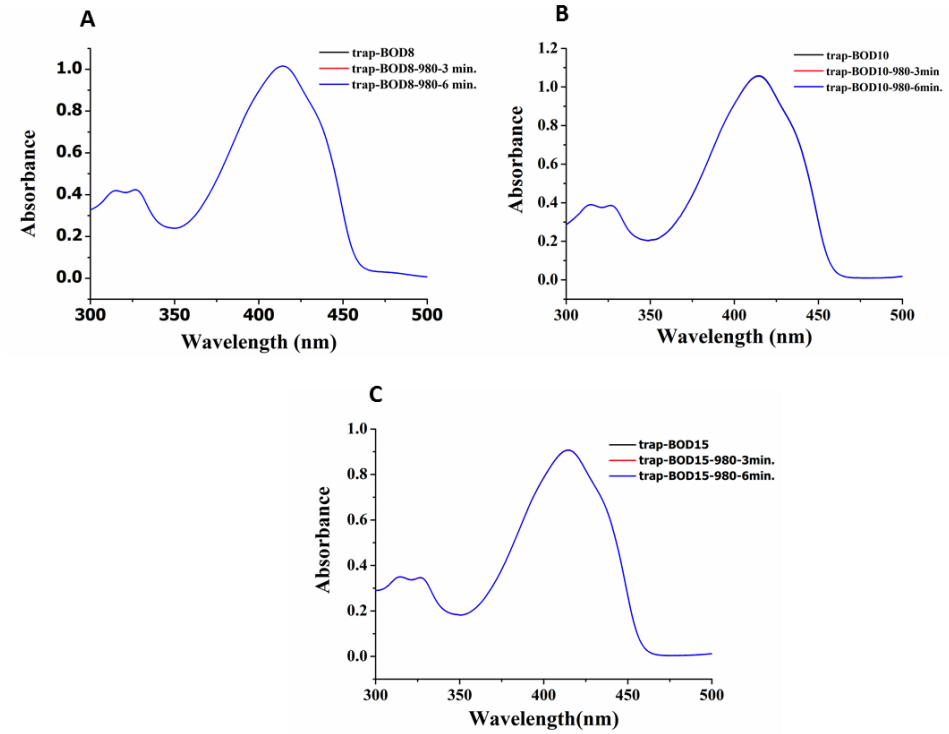


Fig. S34 Control experiment-2: BODIPY dyes in the presence of DPBF trap molecule under 980 nm laser light

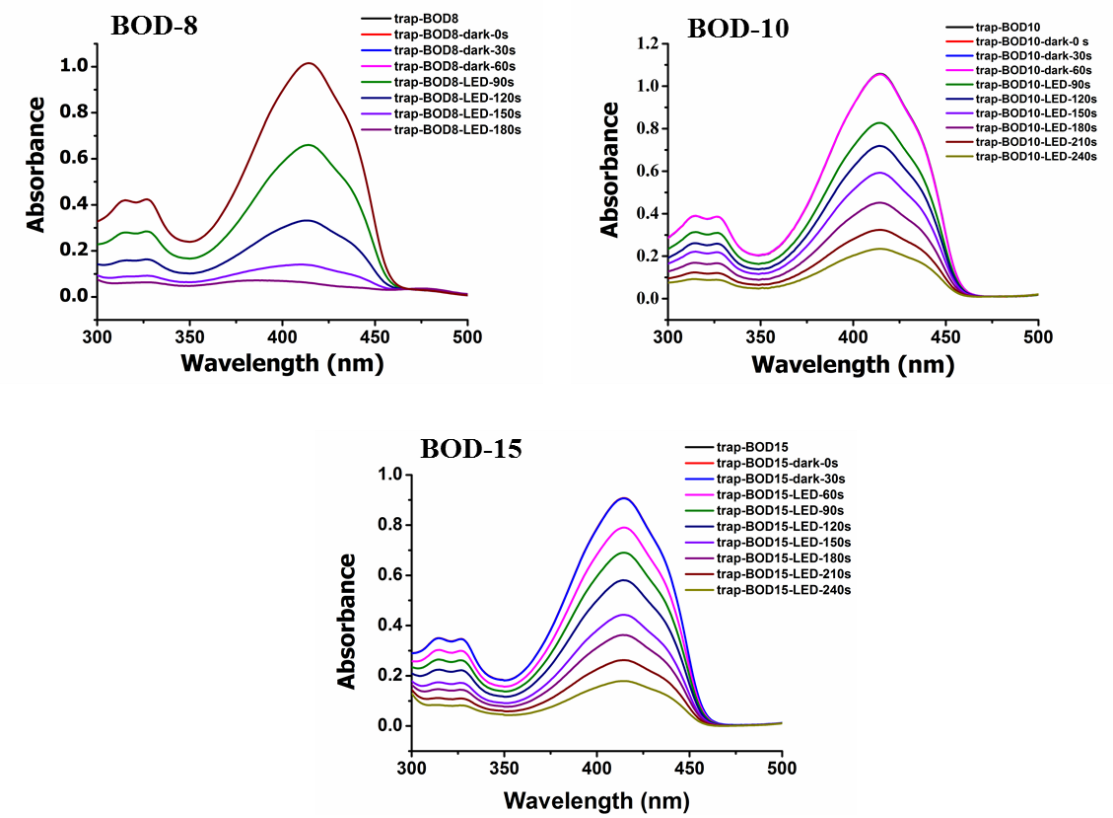


Fig. S35 Singlet oxygen measurements of BODIPY dyes in the presence of DPBF trap molecule under laser light (610nm for BOD 8 and 520 nm for BOD10 and BOD15)

(a)

	A	B	C	D
1	Model	ExpDec1		
2	Equation	y = A1*exp(-x/t1) + y0		
3	Reduced Chi-Sqr	5,09789E-4		
4	Adj. R-Square	0,93089		
5			Value	Standard Error
6	BOD-8	y0	0,64447	0,05414
7	BOD-8	A1	0,31644	0,04778
8	BOD-8	t1	21,0536	7,54473

(b)

	A	B	C	D
1	Model	ExpDecay1		
2	Equation	y = y0 + A1*exp(-(x-x0)/t1)		
3	Reduced Chi-Sqr	1.77598E-4		
4	Adj. R-Square	0.98814		
5			Value	Standard Error
6	BOD-10	y0	0.47134	0.05539
7	BOD-10	x0	0.93778	1.47786E7
8	BOD-10	A1	0.50674	265012.60468
9	BOD-10	t1	28.25884	5.30369

(c)

	A	B	C	D
1	Equation	y = a + b*x		
2	Weight	No Weighting		
3	Residual Sum of Squares	0.00127		
4	Pearson's r	-0.99052		
5	Adj. R-Square	0.97941		
6			Value	Standard Error
7	BOD-15	Intercept	1.00701	0.00562
8		Slope	-0.00634	2.65059E-4

Fig. S36 Equations from the plot (Fig.4) of exponential fit for BOD 8 and BOD10 (a and b) and lineer fit for BOD15.

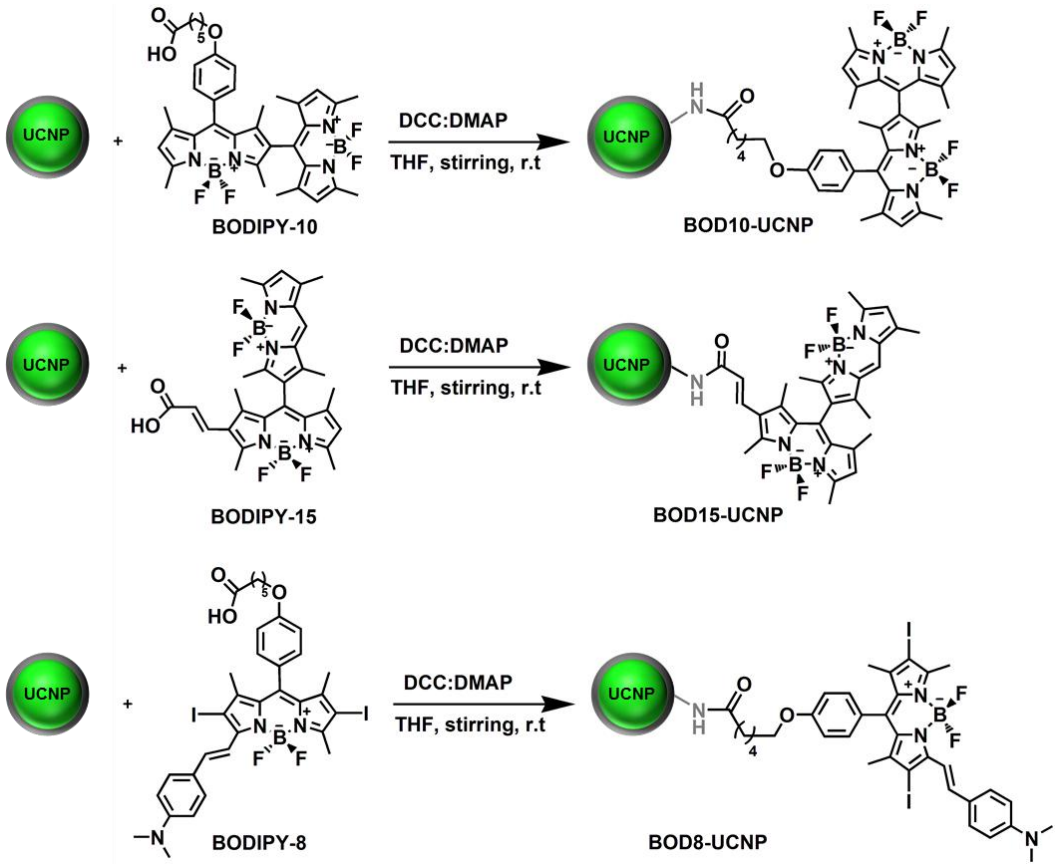


Fig S37. Synthetic procedure for the BODIPY conjugated upconverting nanoparticles.

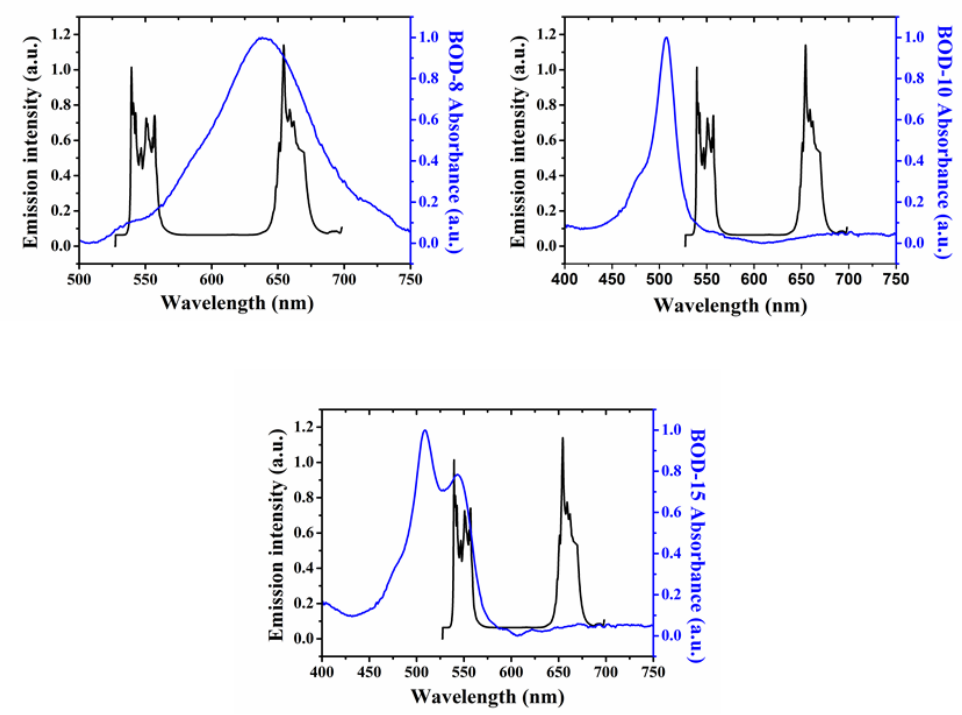


Fig. S38 Overlaid emission spectra of PEI-coated $NaYF_4$:(Yb^{+3},Er^{+3})/Ce^{+3} UCNPs (black line) and absorption spectra of BOD-**8**, BOD-**10** and BOD-**15**, respectively.

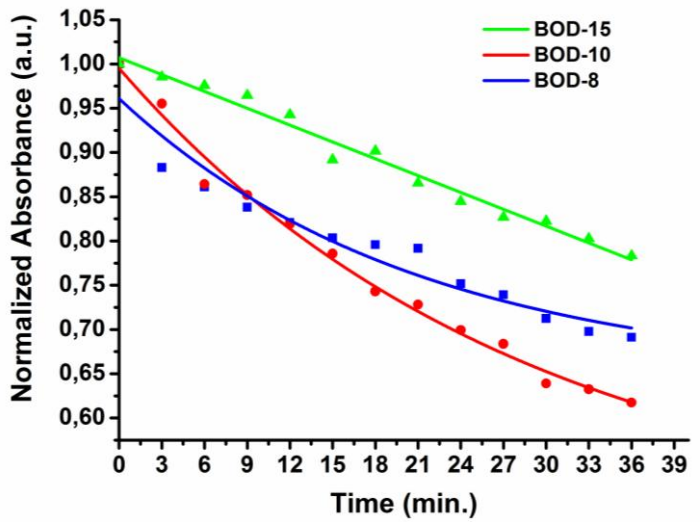


Fig. S39 Changes in the absorption spectrum of the selective singlet oxygen trap 1,3-diphenyl-isobenzofuran (DPBF) in the presence of BODIPY-UCNP (0.4 mg/ml) in methanol solution. Reactions were done in triplicate.