Electronic Supplementary Information

Green-light photocleavable meso-methyl BODIPY building blocks for macromolecular chemistry

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Synthesis:

Poly(Jeffamine M-1000 – propargylamine)phosphazene: The poly(organo)phosphazene was synthesised in the glove box under Ar according to slightly adapted literature procedure[1]. Briefly, dichlorotriphenylphosphorane (43.3 mg, 0.13 mmol, 1 eq.) was dissolved in ~0.5 ml anhydrous DCM and added to a solution of the monomer (N-trimethylsilyl)phosphorimidoyl trichloride (1.4594 g, 6.50 mmol, 50 eq.) in 0.5 ml anhydrous DCM, previously synthesized according to literature[1]. The reaction was stirred at room temperature for 24 h to synthesis a poly(dichloro)phosphazene with a number of repeating units n=50. Jeffamine M-1000 (6.5 g, 6.50 mmol, 50 eq.) and triethylamine (1.5 ml, 10.76 mmol, 82 eq.) were dissolved in ~50 ml anhydrous THF and the poly(dichloro)phosphazene solution was dropped in slowly, resulting in a cloudy, white solution. After stirring for 24 h, propargylamine (0.5 ml, 7.65 mmol, 60 eq.) and triethylamine (1.5 ml, 10.76 mmol, 82 eq.) in 2 ml anhydrous THF were added to the solution and again stirred for 24 h. The solution was transferred out of the glove box, the precipitate was filter of and the solvent was evaporated. Finally, a dialysis (MWCO 6-8kDa) was carried out in ethanol (72 h) and Milli-Q water (30 h). Freeze drying served the product as a waxy solid with a yield of 38.6 % (2.7567 g).
^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.15 (s, 9 H), 2.25 (s, 1 H), 3.38 (s, 3 H), 3.38 (s, 2 H), 3.65 ppm (s, 85 H); ^{31}P-NMR (202 MHz, $CDCl_3$, δ): 0.29 ppm

Jeffamine - hydrogel: The whole reaction was carried out under argon in the dark. Jeffamine ED-2003 (157.54 mg, 82.25 µmol, 3 eq.) was dissolved in 3 ml dry toluene and H_{12}-MDI (13.20 mg, 50.26 µmol, 1.82 eq.) was added. After stirring over night at room temperature, poly(hexamethylene diisocyanate) (10.63 mg, 22.19 µmol, 1.2 eq) was added upon which the reaction was stirred vigorously until gelation. The produced transparent, elastic gel was washed with acetone and deionized water and stored in the dark in deionized water.

NMRs:

8-Acetoxymethyl-2,6-diethyl-1,3,5,7-tetramethyl pyrromethene fluoroborate, BODIPY, 1:

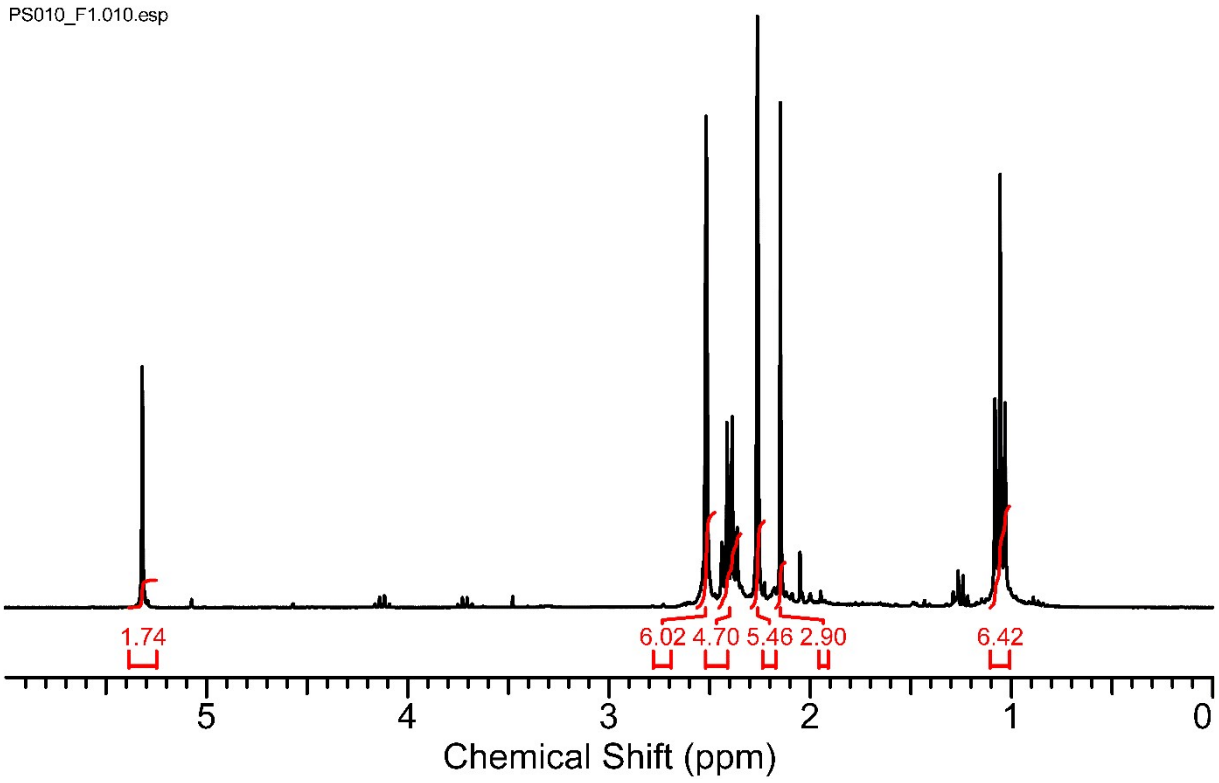


Figure ESI 1: 1H-NMR spectrum of the BODIPY compound (**1**) in CDCl3.

2,6-Diethyl-8-hydroxymethyl-1,3,5,7-tetramethyl pyrromethene fluoroborate, BODIPY-OH, 2:

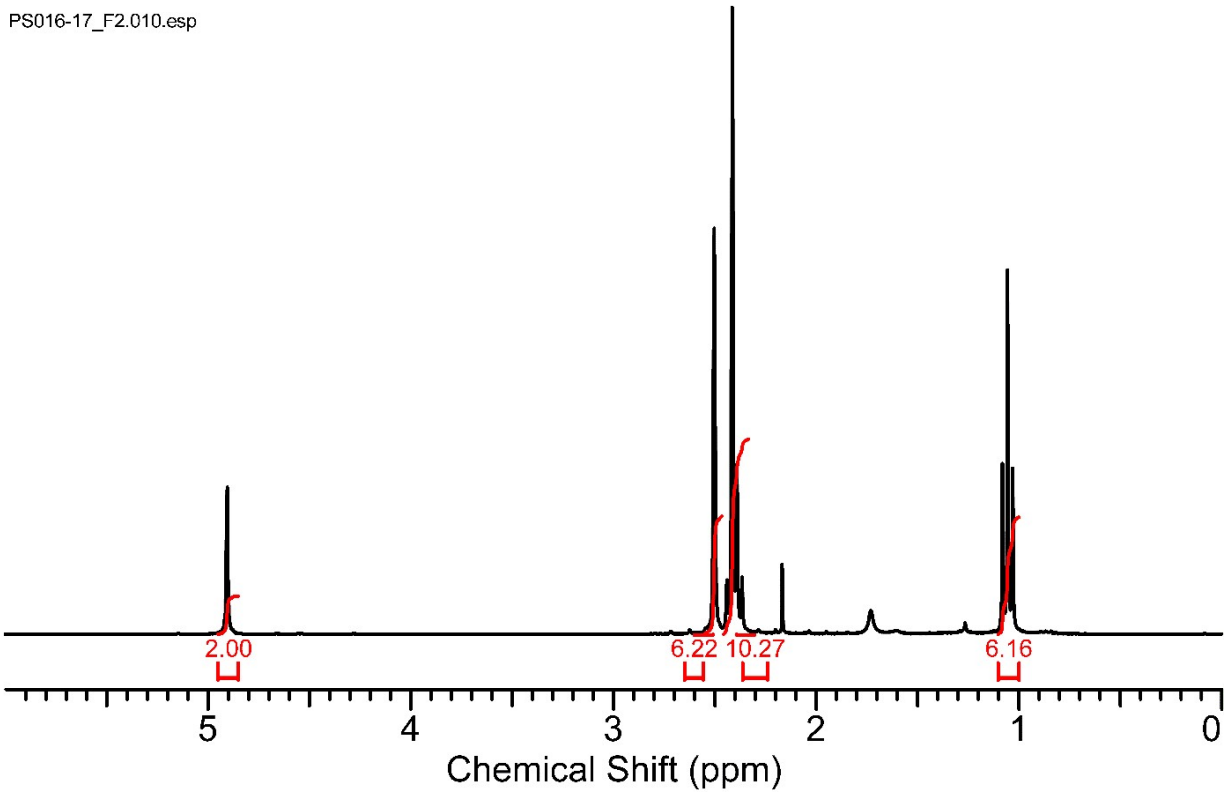


Figure ESI 2: ^{1}H-NMR spectrum of the BODIPY-OH compound (***2***) in $CDCl_3$.

2,6-Diethyl-5,8-dihydroxymethyl-1,3,7-trimethyl pyrromethene fluoroborate, BODIPY-diol, 3:

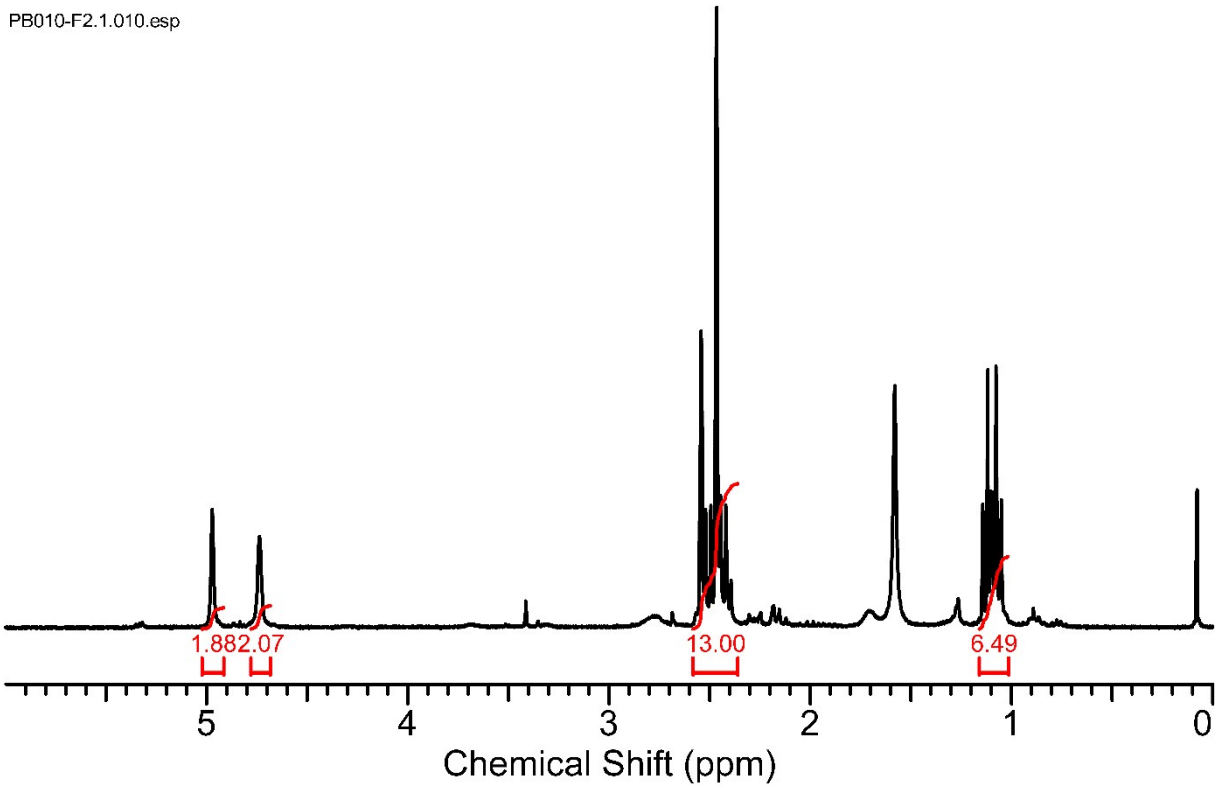


Figure ESI 3: ^{1}H-NMR spectrum of the BODIPY-diol compound (**3**) in $CDCl_3$.

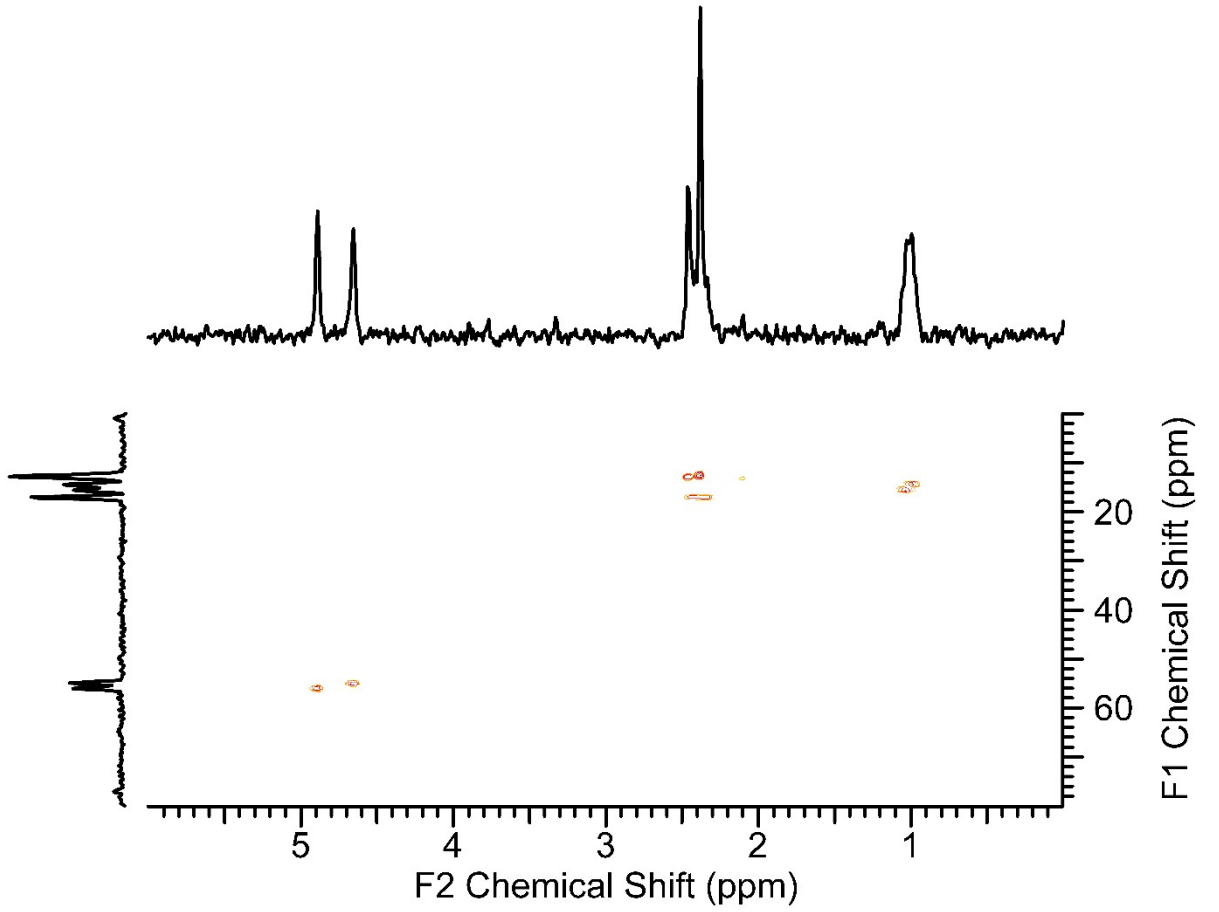


Figure ESI 4: HSQC-NMR spectrum of BODIPY-diol compound (**3**) in $CDCl_3$.

5-Azidomethyl-2,6-diethyl-8-hydroxymethyl-1,3,7-trimethyl pyrromethene fluoroborate, BODIPY-azide, 4:

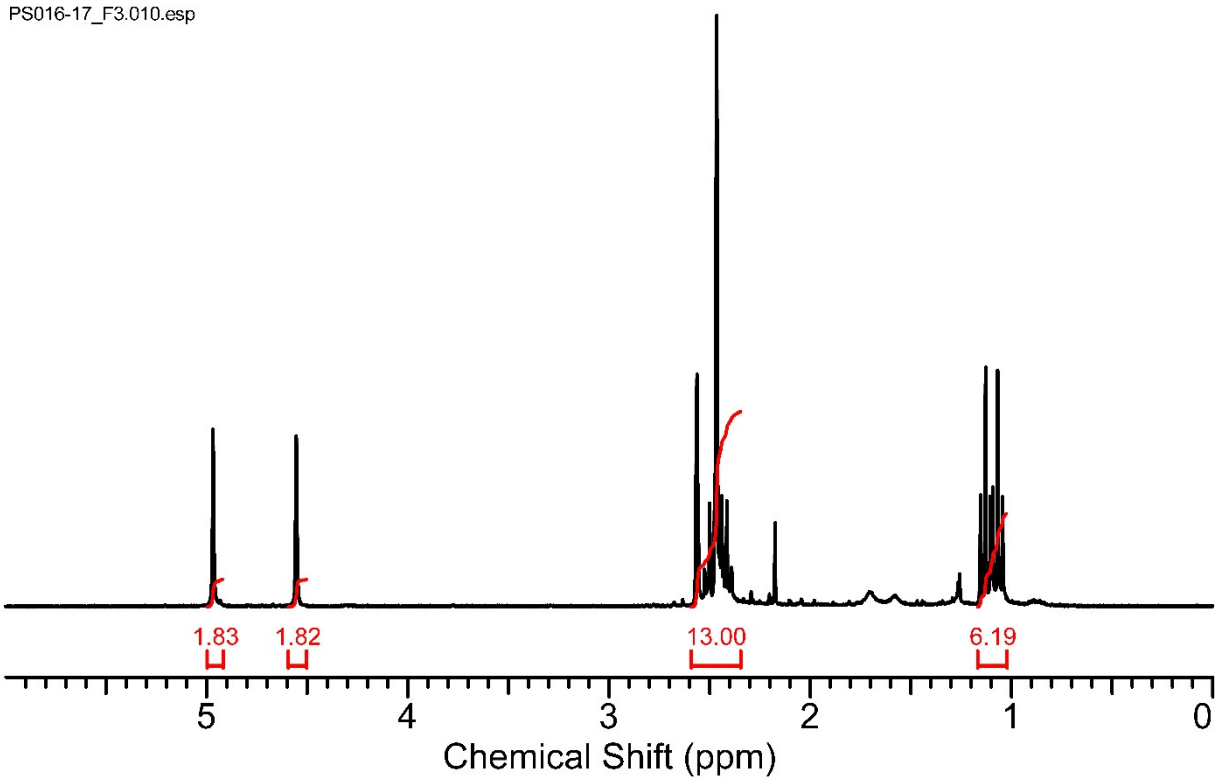


Figure ESI 5: ^{1}H-NMR spectrum of BODIPY-azide compound (**4**) in $CDCl_3$.

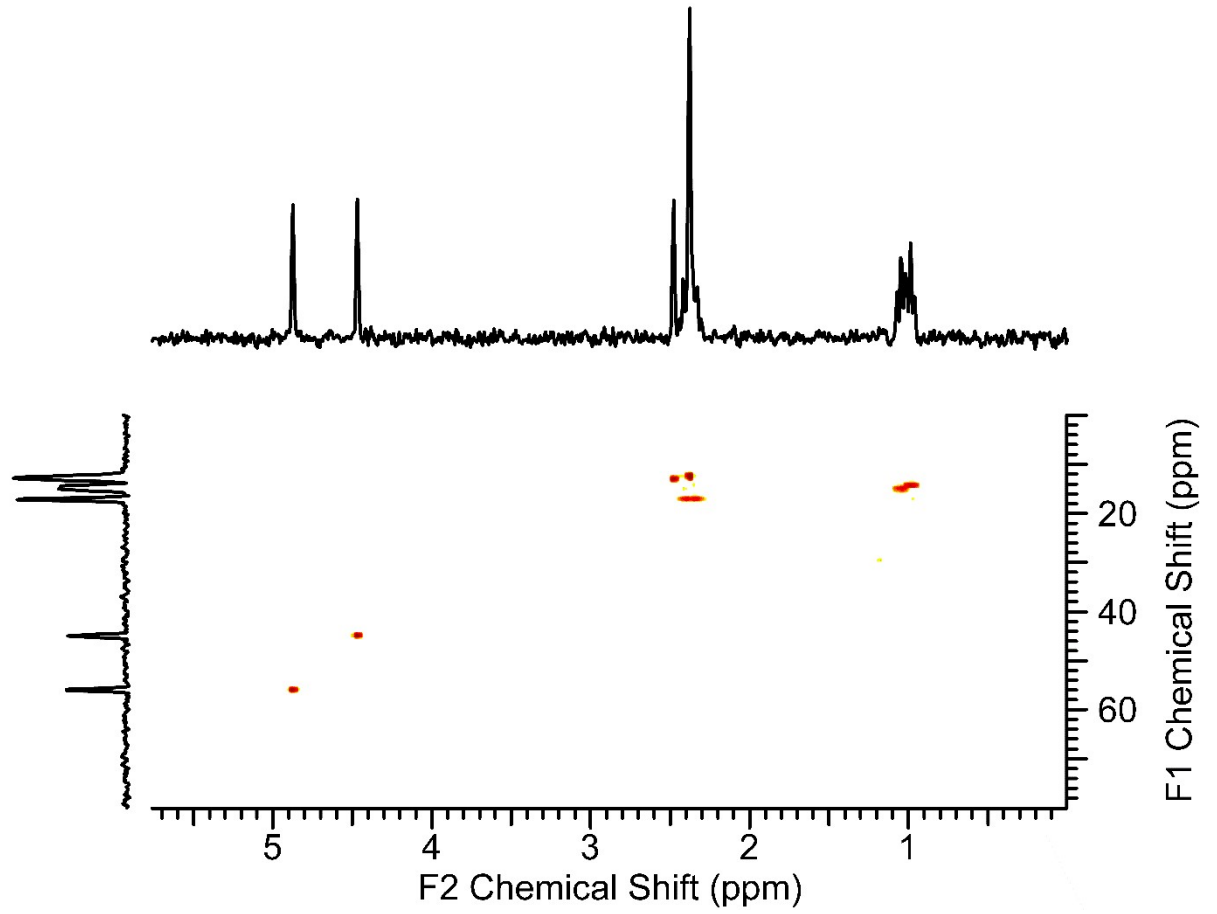


Figure ESI 6: HSQC-NMR spectrum of BODIPY-azide compound (**4**) in $CDCl_3$.

5,8-Bis(((benzylcarbamoyl)oxy)methyl)-2,6-diethyl-1,3,7-trimethyl pyrromethene fluoroborate, BODIPY-diol-model, 5:

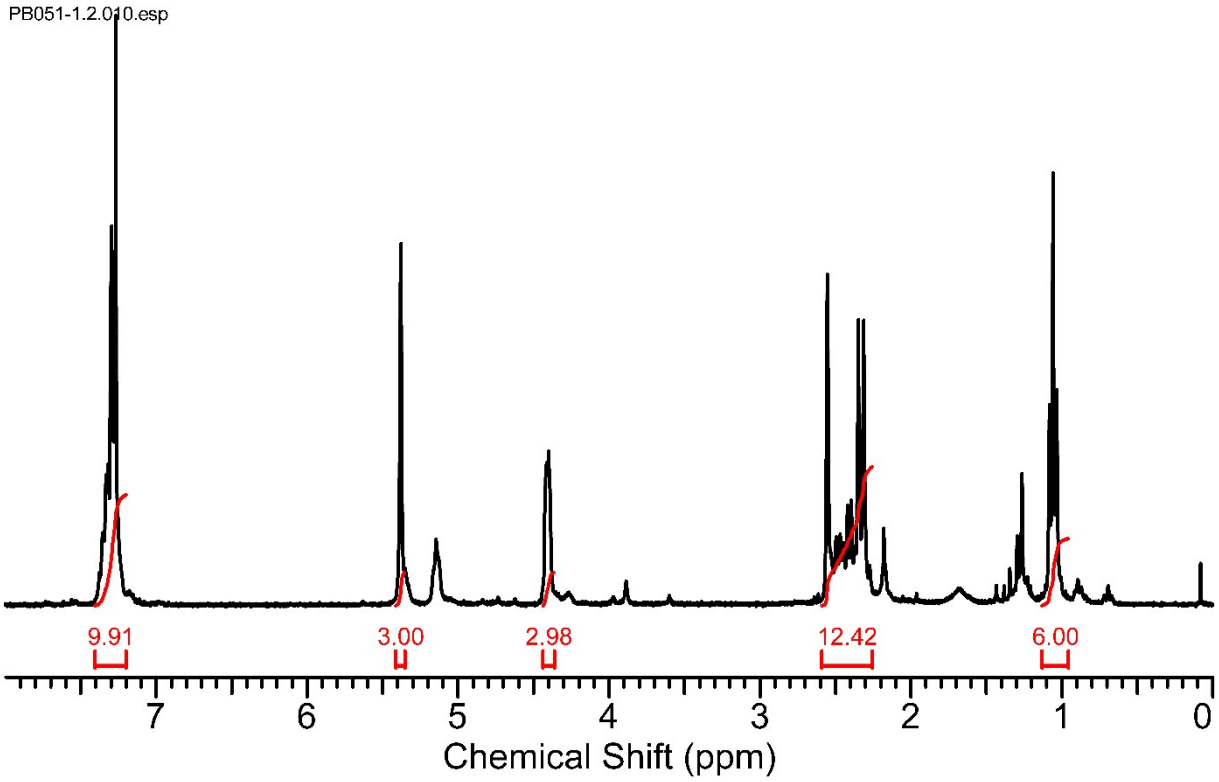


Figure ESI 7: ^{1}H-NMR spectrum of BODIPY-diol-model compound (**5**) in $CDCl_3$.

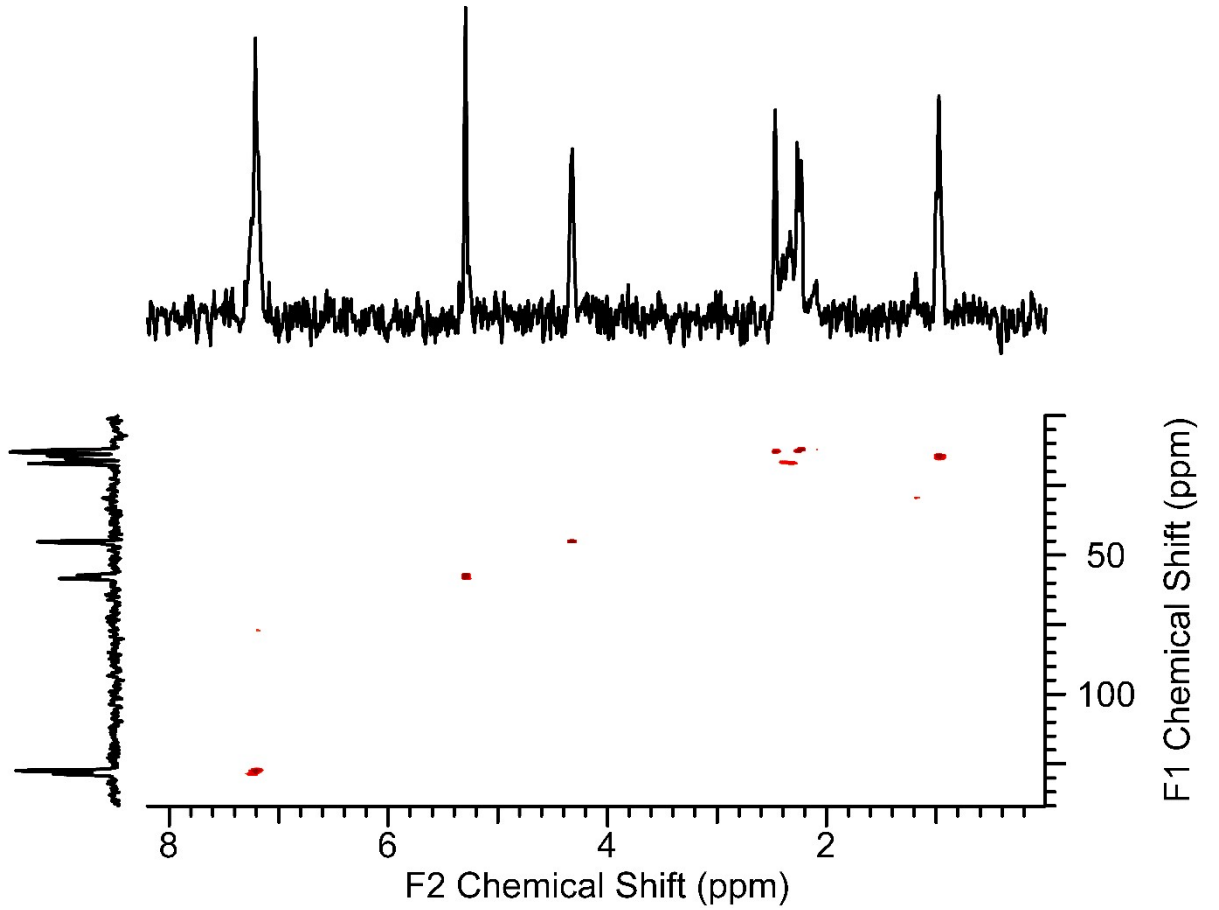


Figure ESI 8: HSQC-NMR spectrum of BODIPY-diol-model compound (**5**) in $CDCl_3$.

5-((4-Propyl-1H-1,2,3-triazol-1-yl)methyl)-8-(phenylacetoxymethyl)-2,6-diethyl-1,3,7-trimethyl Pyrromethene Fluoroborate, BODIPY-azide-model, 6:

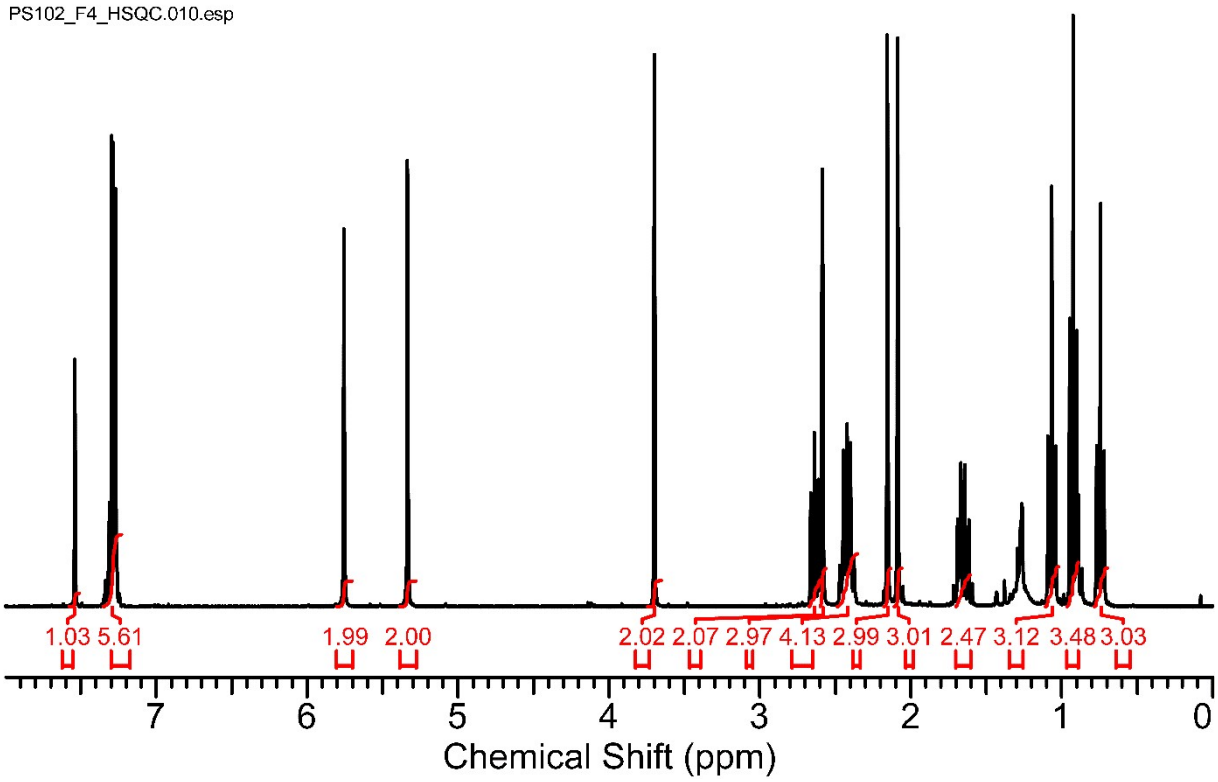


Figure ESI 9: ^{1}H-NMR spectrum of BODIPY-azide-model compound (**6**) in $CDCl_3$.

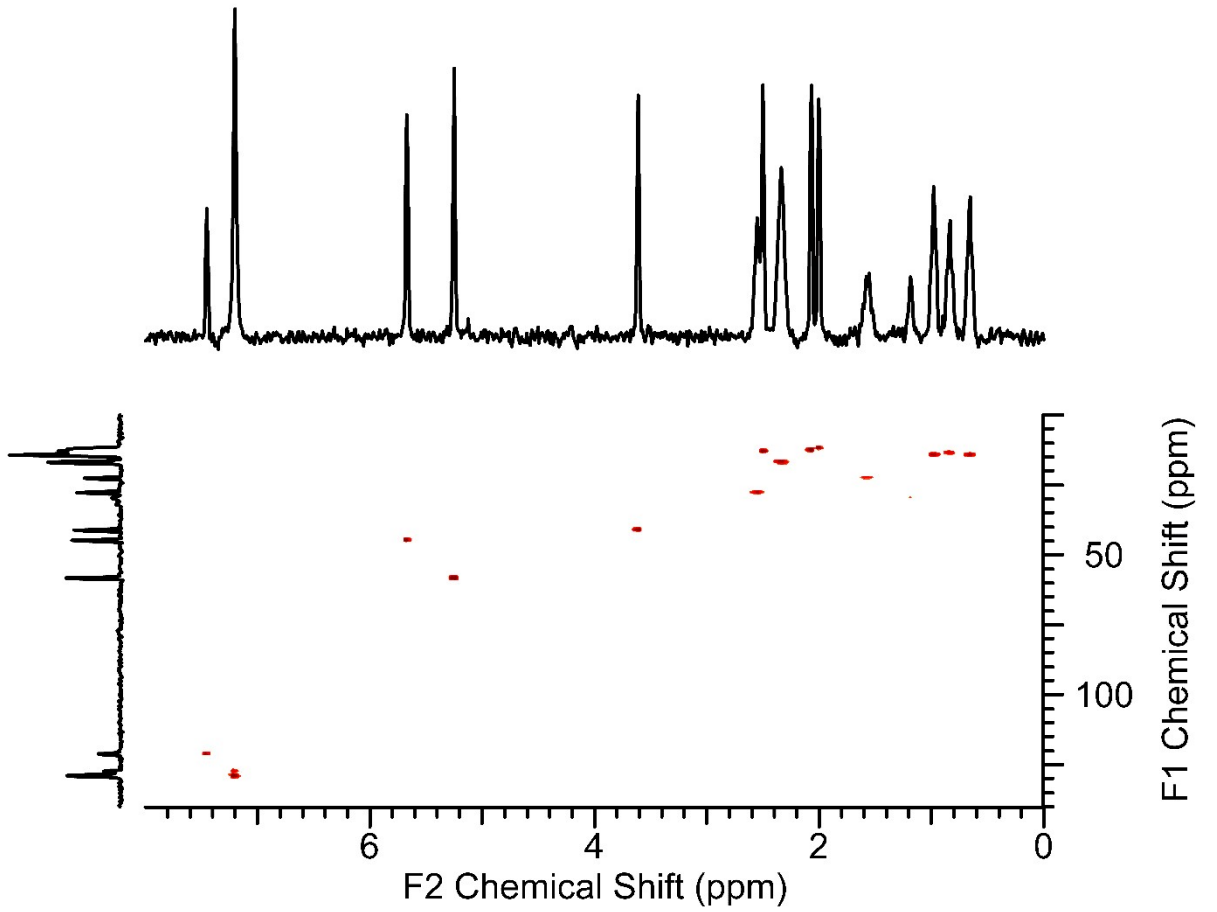


Figure ESI 10: HSQC-NMR spectrum of BODIPY-azide-model compound (**6**) in $CDCl_3$.

5-((4-Propyl-1H-1,2,3-triazol-1-yl)methyl)-8-hydroxymethyl-2,6-diethyl-1,3,7-trimethyl pyrromethene fluoroborate, BODIPY-pentyne, 6a:

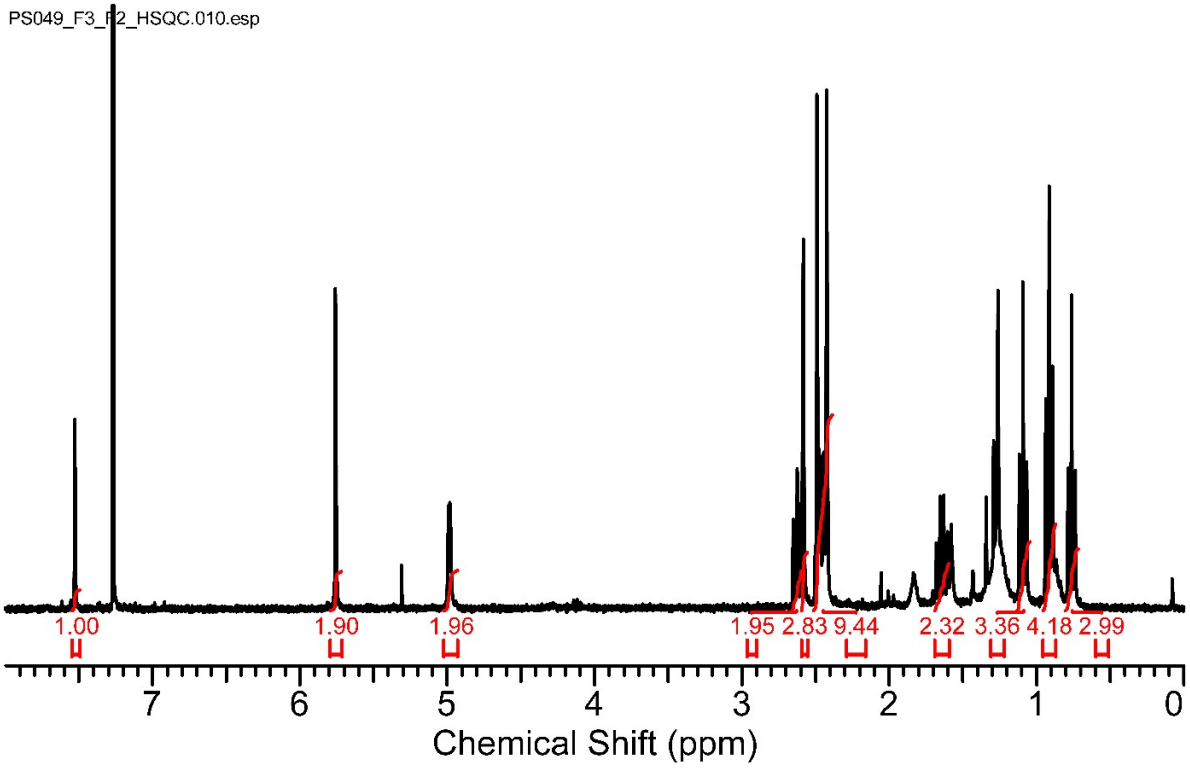


Figure ESI 11: ^{1}H-NMR spectrum of BODIPY-pentyne compound (**6a**) in $CDCl_3$.

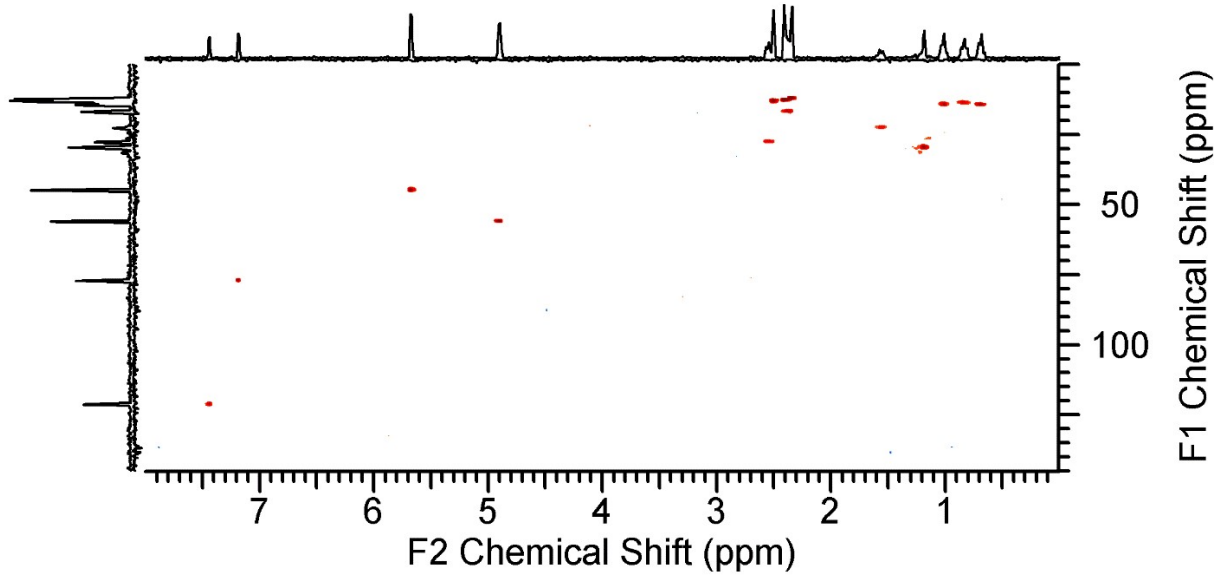


Figure ESI 12: HSQC-NMR spectrum of BODIPY-pentyne compound (**6a**) in $CDCl_3$.

5-Azidomethyl-8-(phenylacetoxymethyl)-2,6-diethyl-1,3,7-trimethyl pyrromethene fluoroborate, caged linker BODIPY-azide, 7:

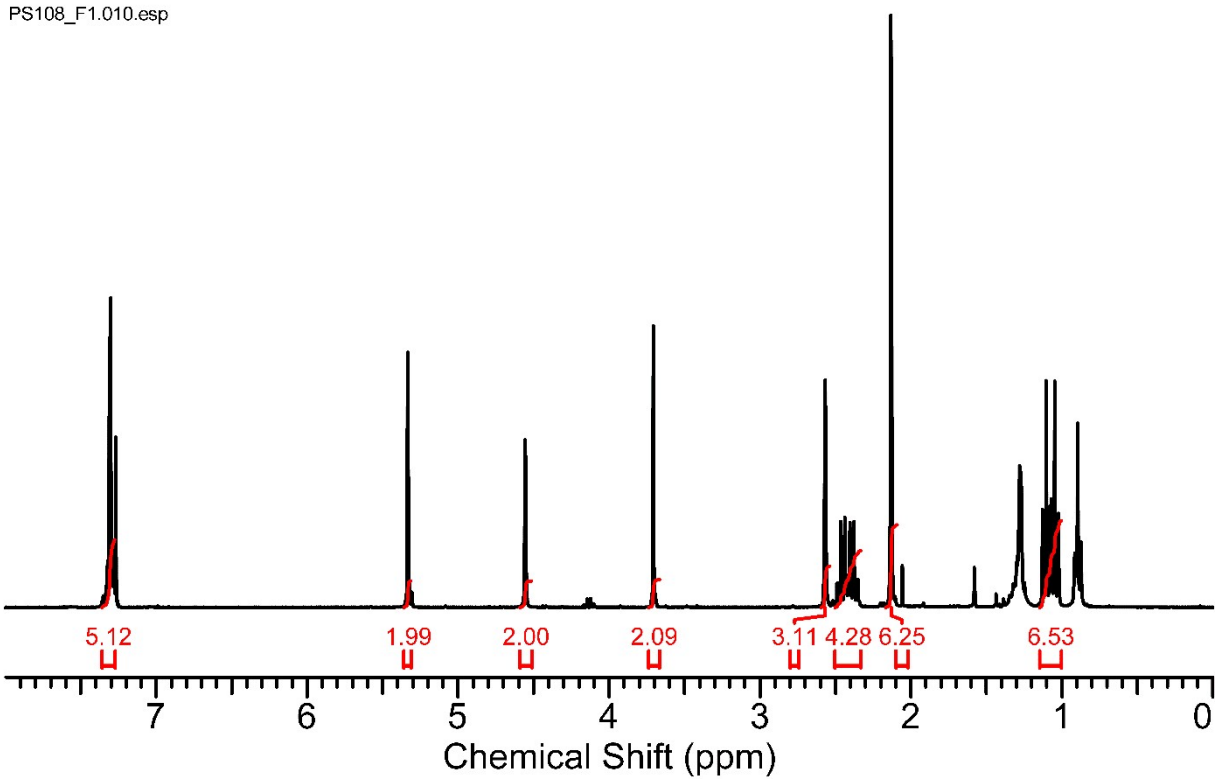


Figure ESI 13: ^{1}H-NMR spectrum of the caged linker BODIPY-azide compound (**7**) in $CDCl_3$.

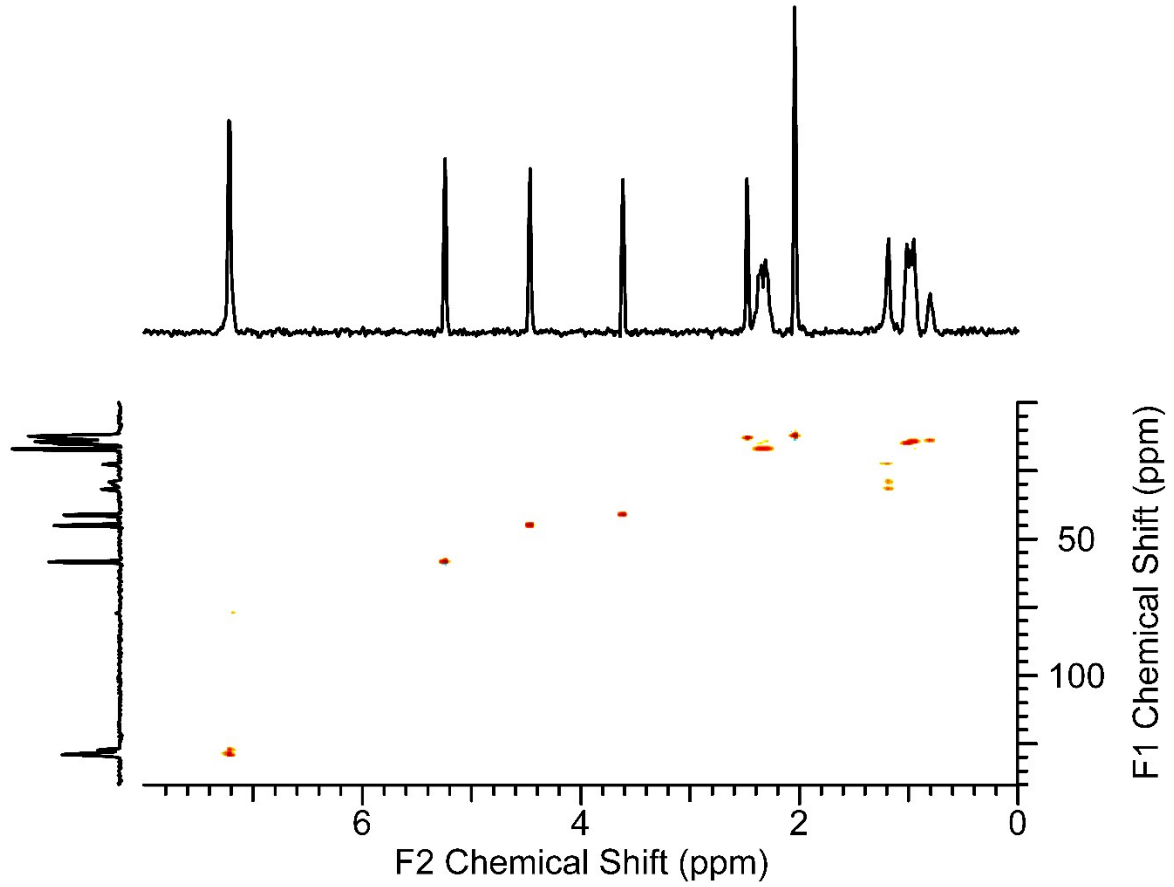
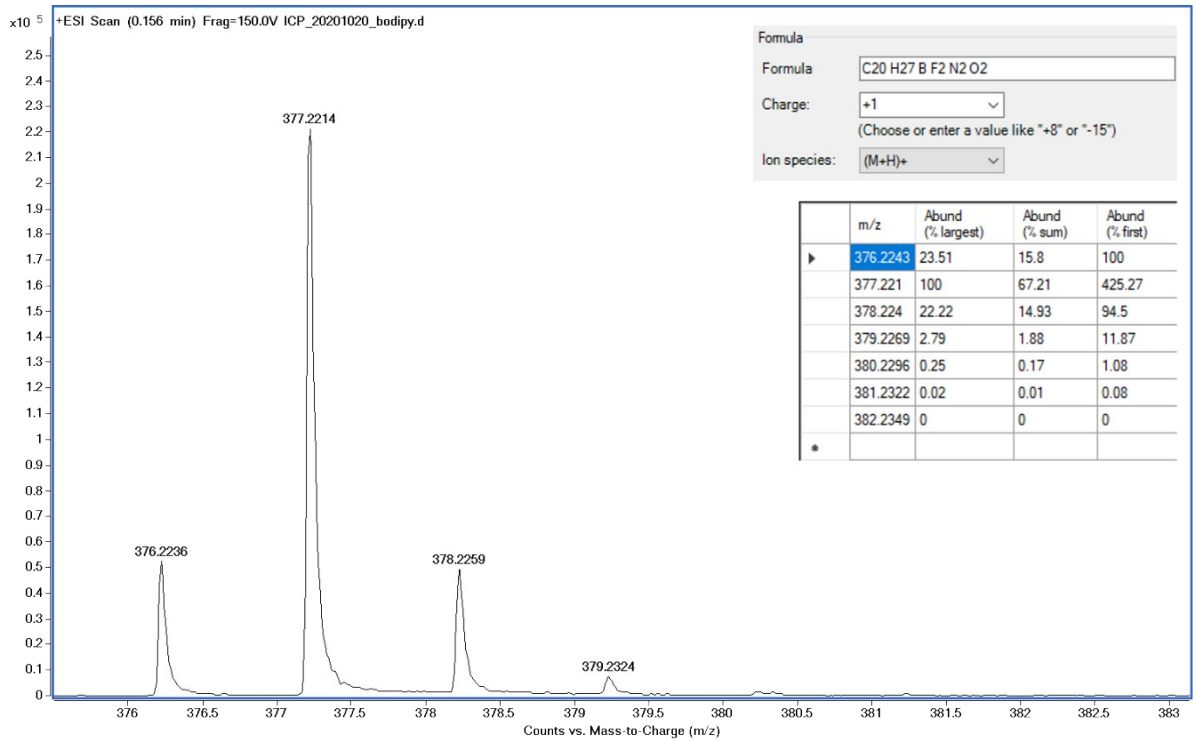


Figure ESI 14: HSQC-NMR spectrum of the caged linker BODIPY-azide compound (**7**) in $CDCl_3$.

MS:

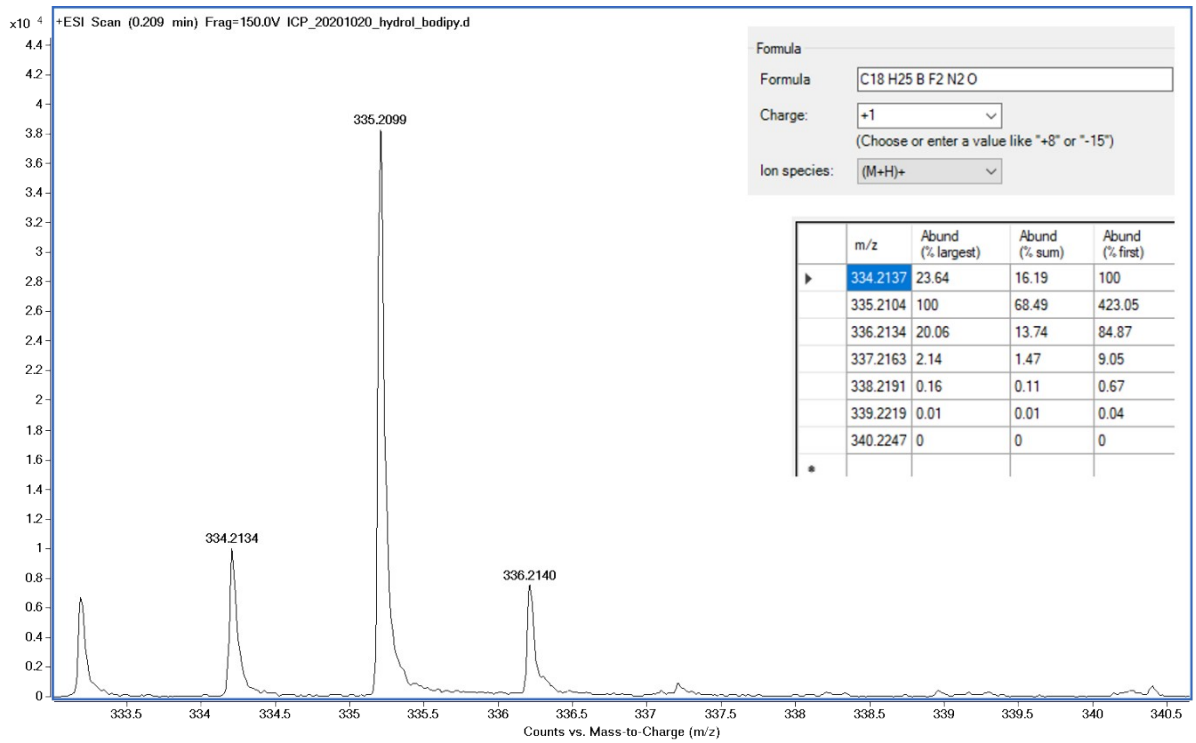
8-Acetoxymethyl-2,6-diethyl-1,3,5,7-tetramethyl pyrromethene fluoroborate, BODIPY, 1:



m/z	Abund (% largest)	Abund (% sum)	Abund (% first)
376.2243	23.51	15.8	100
377.221	100	67.21	425.27
378.224	22.22	14.93	94.5
379.2269	2.79	1.88	11.87
380.2296	0.25	0.17	1.08
381.2322	0.02	0.01	0.08
382.2349	0	0	0

Figure ESI 15: High-resolution mass spectrum (ESI-QTOF) of BODIPY compound **1**.

2,6-Diethyl-8-hydroxymethyl-1,3,5,7-tetramethyl pyrromethene fluoroborate, BODIPY-OH, 2:



m/z	Abund (% largest)	Abund (% sum)	Abund (% first)
334.2137	23.64	16.19	100
335.2104	100	68.49	423.05
336.2134	20.06	13.74	84.87
337.2163	2.14	1.47	9.05
338.2191	0.16	0.11	0.67
339.2219	0.01	0.01	0.04
340.2247	0	0	0

Figure ESI 16: High-resolution mass spectrum (ESI-QTOF) of BODIPY-OH **2**.

2,6-Diethyl-5,8-dihydroxymethyl-1,3,7-trimethyl pyrromethene fluoroborate, BODIPY-diol, 3:

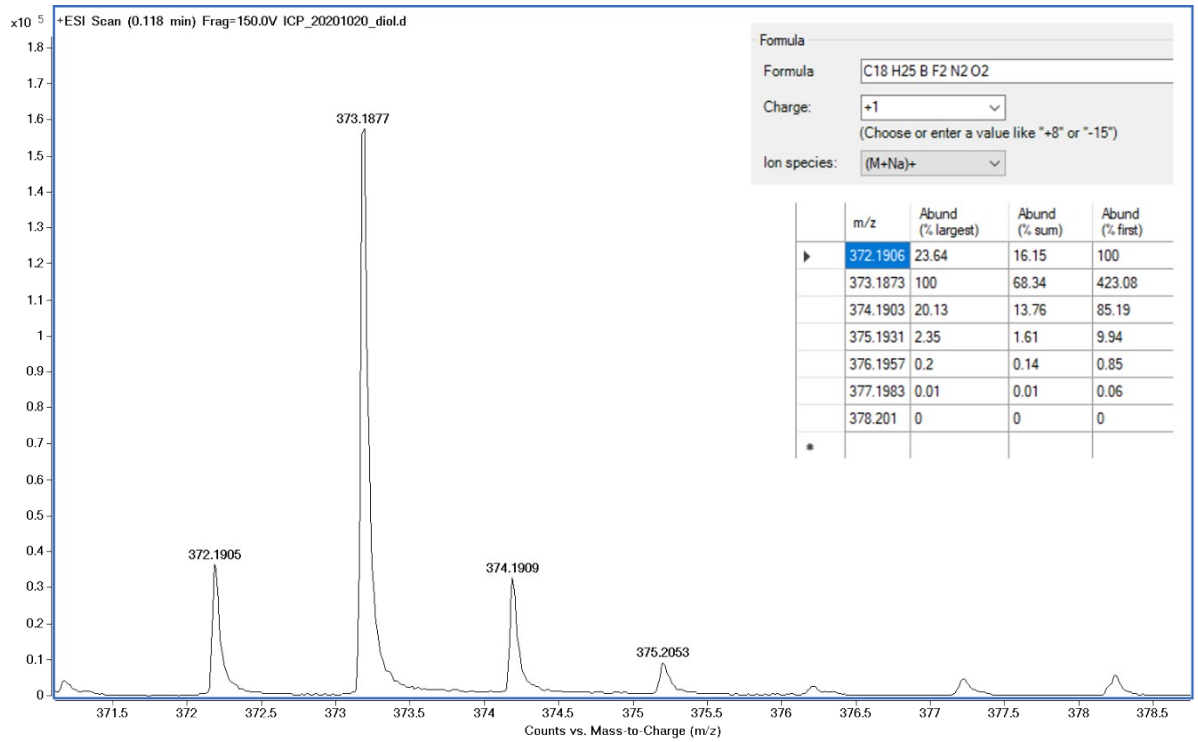


Figure ESI 17: High-resolution mass spectrum (ESI-QTOF) of BODIPY-diol **3**.

5-Azidomethyl-2,6-diethyl-8-hydroxymethyl-1,3,7-trimethyl pyrromethene fluoroborate, BODIPY-azide, 4:

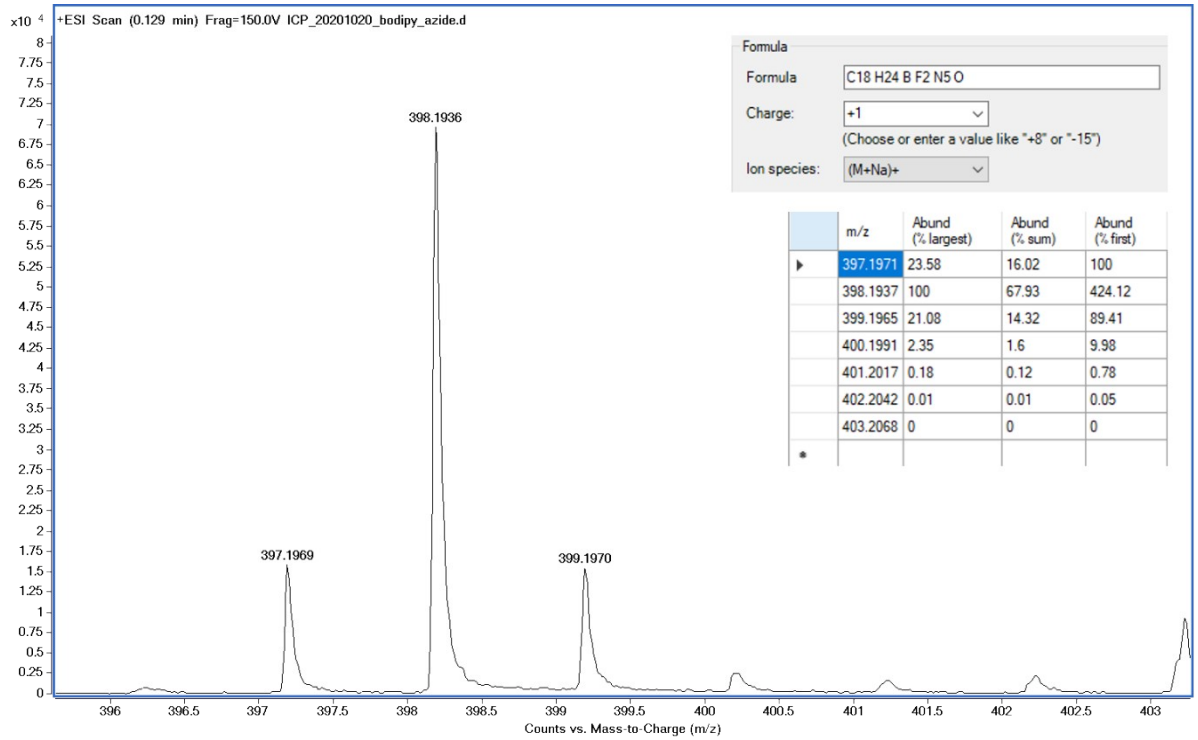


Figure ESI 18: High-resolution mass spectrum (ESI-QTOF) of BODIPY-azide **4**.

UV/Vis:

8-Acetoxymethyl-2,6-diethyl-1,3,5,7-tetramethyl pyrromethene fluoroborate, BODIPY, 1:

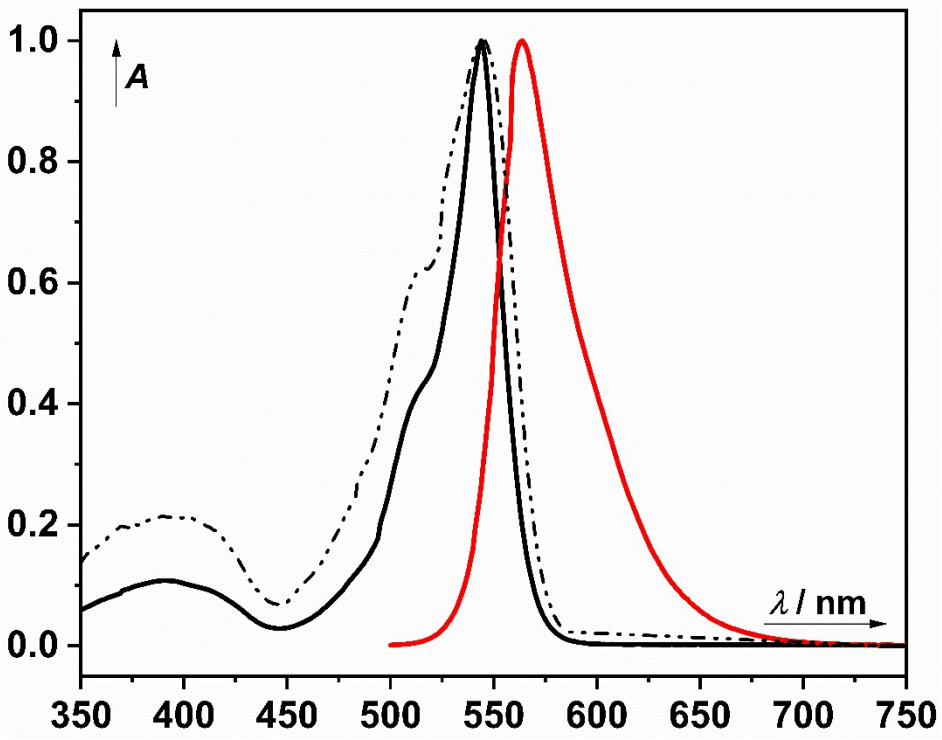


Figure ESI 19: Normalized absorption (solid black line), normalized emission (solid red line, excitation wavelength: 485 nm) and normalized excitation (dash-double doted black line, emission wavelength: 595 nm) spectra of BODIPY compound **1** in methanol.

2,6-Diethyl-8-hydroxymethyl-1,3,5,7-tetramethyl pyrromethene fluoroborate, BODIPY-OH, 2:

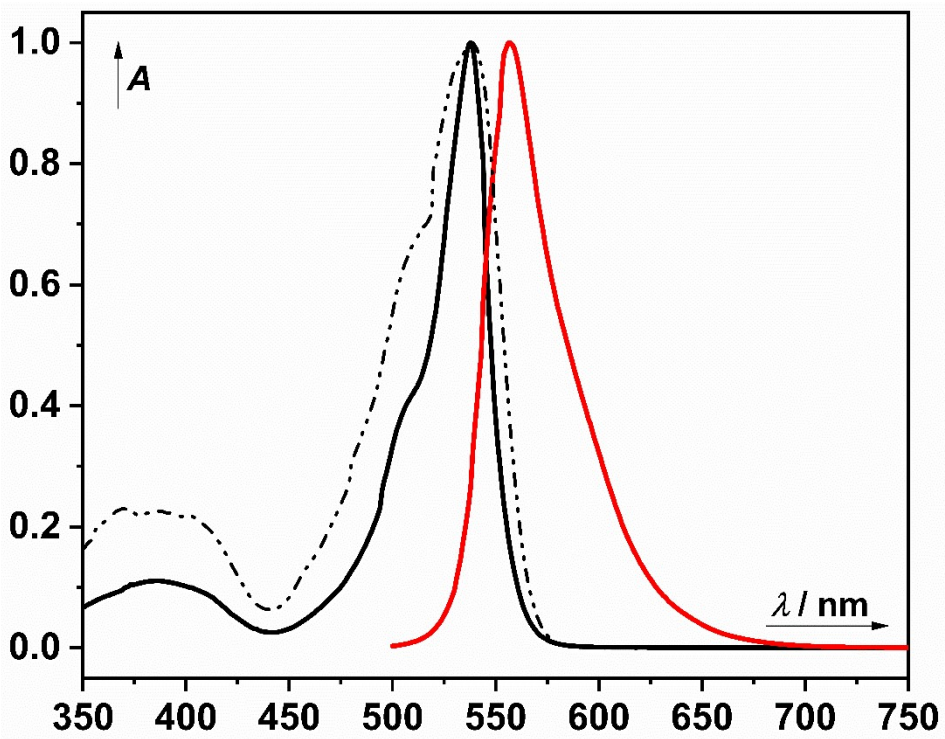


Figure ESI 20: Normalized absorption (solid black line), normalized emission (solid red line, excitation wavelength: 485 nm) and normalized excitation (dash-double doted black line, emission wavelength: 595 nm) spectra of BODIPY-OH **2** in methanol.

2,6-Diethyl-5,8-dihydroxymethyl-1,3,7-trimethyl pyrromethene fluoroborate, BODIPY-diol, 3:

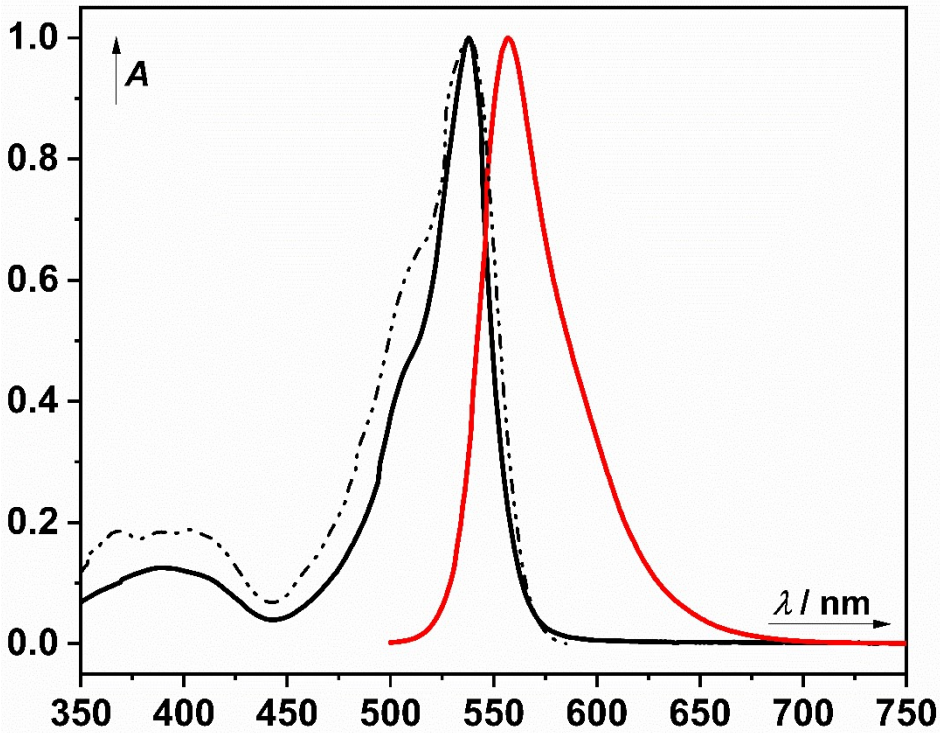


Figure ESI 21: Normalized absorption (solid black line), normalized emission (solid red line, excitation wavelength: 485 nm) and normalized excitation (dash-double doted black line, emission wavelength: 595 nm) spectra of BODIPY-diol **3** in ethanol.

5-Azidomethyl-2,6-diethyl-8-hydroxymethyl-1,3,7-trimethyl pyrromethene fluoroborate, BODIPY-azide, 4:

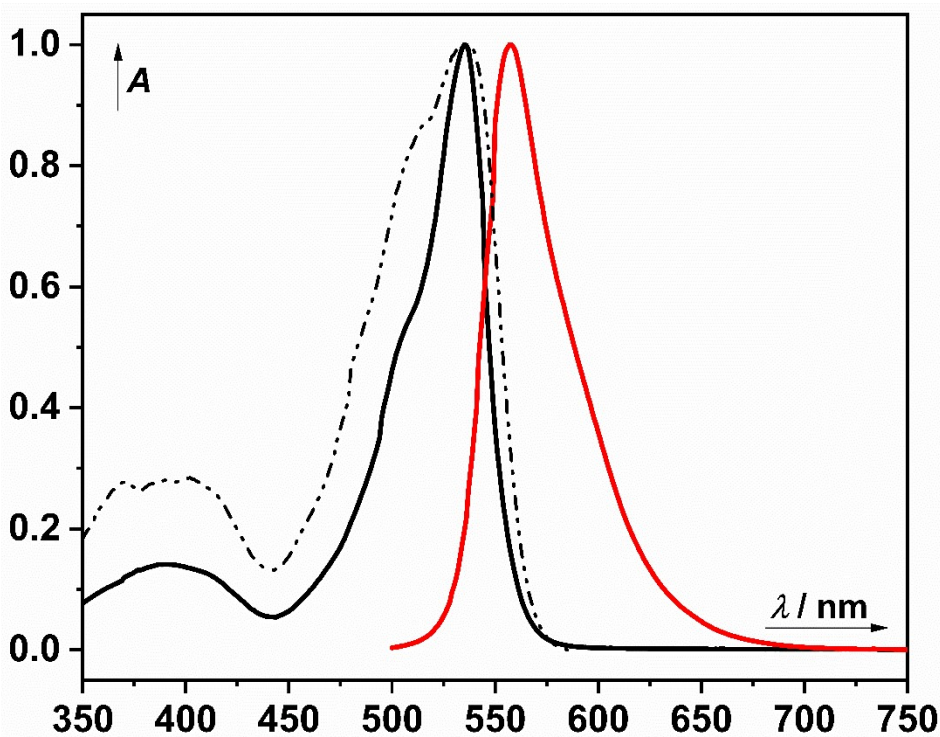


Figure ESI 22: Normalized absorption (solid black line), normalized emission (solid red line, excitation wavelength: 485 nm) and normalized excitation (dash-double doted black line, emission wavelength: 595 nm) spectra of BODIPY-azide **4** in ethanol.

5,8-Bis(((benzylcarbamoyl)oxy)methyl)-2,6-diethyl-1,3,7-trimethyl pyrromethene fluoroborate, BODIPY-diol-model, 5:

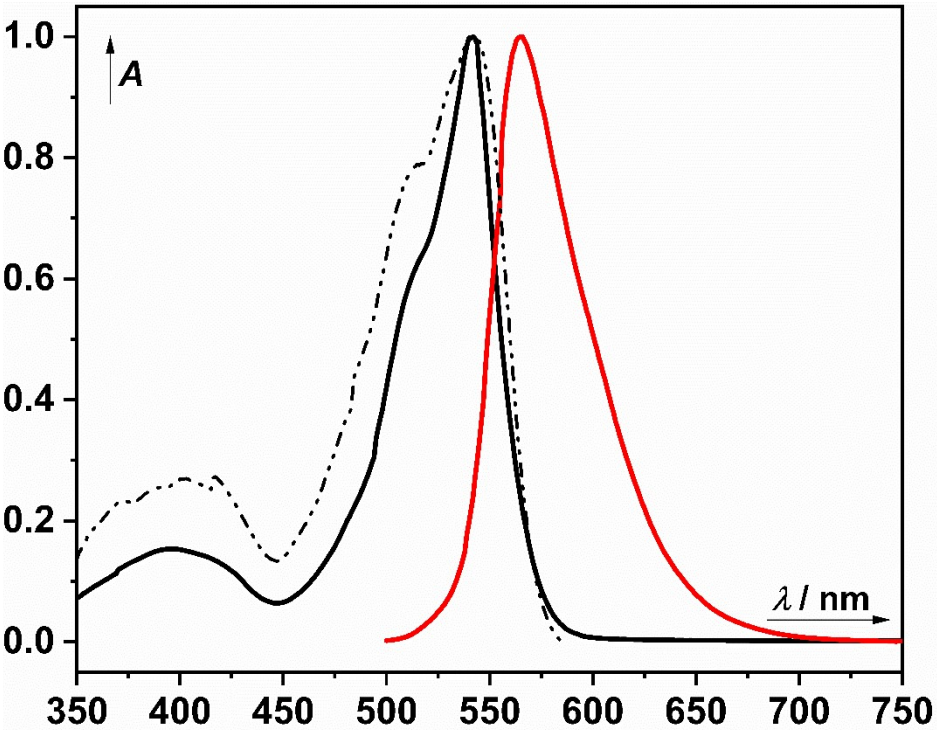


Figure ESI 23: Normalized absorption (solid black line), normalized emission (solid red line, excitation wavelength: 485 nm) and normalized excitation (dash-double doted black line, emission wavelength: 595 nm) spectra of BODIPY-diol-model **5** in methanol.

5-((4-Propyl-1H-1,2,3-triazol-1-yl)methyl)-8-(phenylacetoxymethyl)-2,6-diethyl-1,3,7-trimethyl pyrromethene fluoroborate, BODIPY-azide-model, 6:

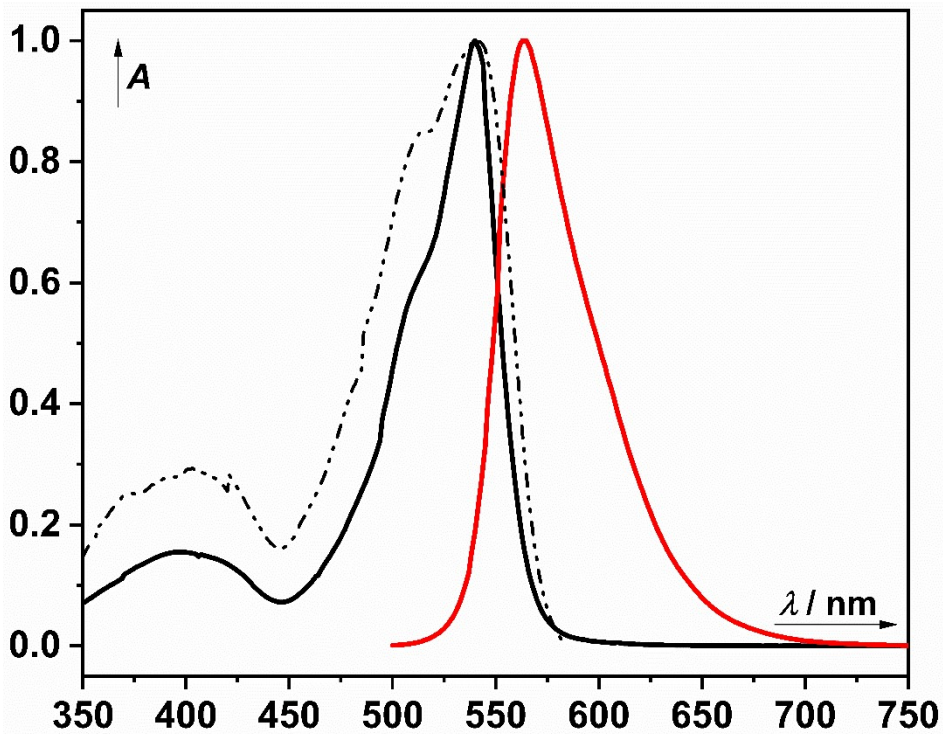


Figure ESI 24: Normalized absorption (solid black line), normalized emission (solid red line, excitation wavelength: 485 nm) and normalized excitation (dash-double doted black line, emission wavelength: 595 nm) spectra of BODIPY-azide-model **6** in ethanol.

Kinetic study of the photoreaction of BODIPY-diol-model 5 and BODIPY-azide-model 6:

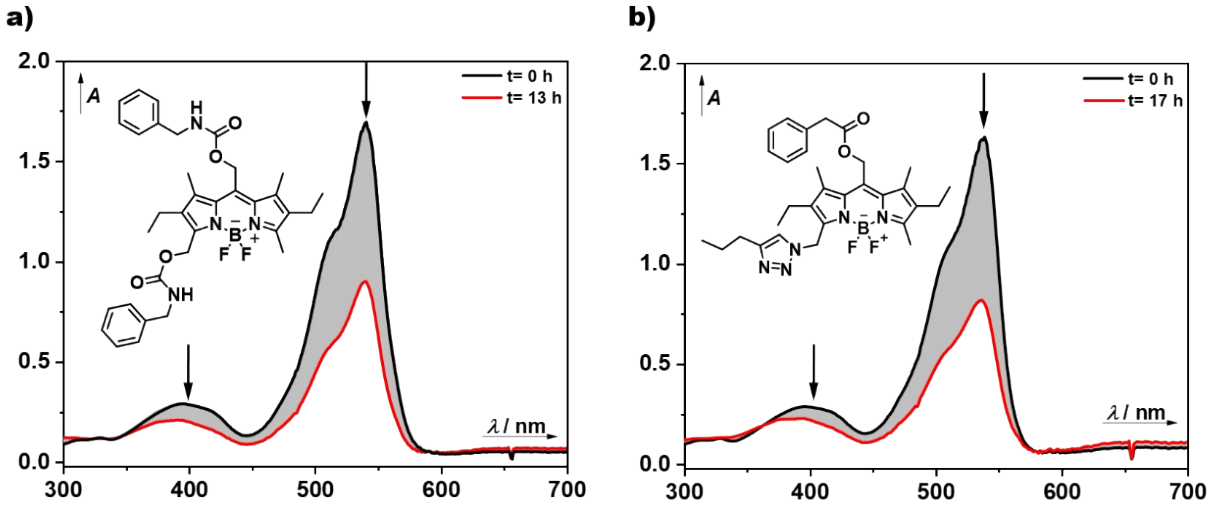


Figure ESI 25: Kinetic study of the photoreaction of BODIPY-model compound **5** (a) and **6** (b) in degassed methanol solution ($4*10^{-5}$ M and $6*10^{-5}$ M in MeOH, respectively) upon 505 nm LED irradiation for the indicated time.

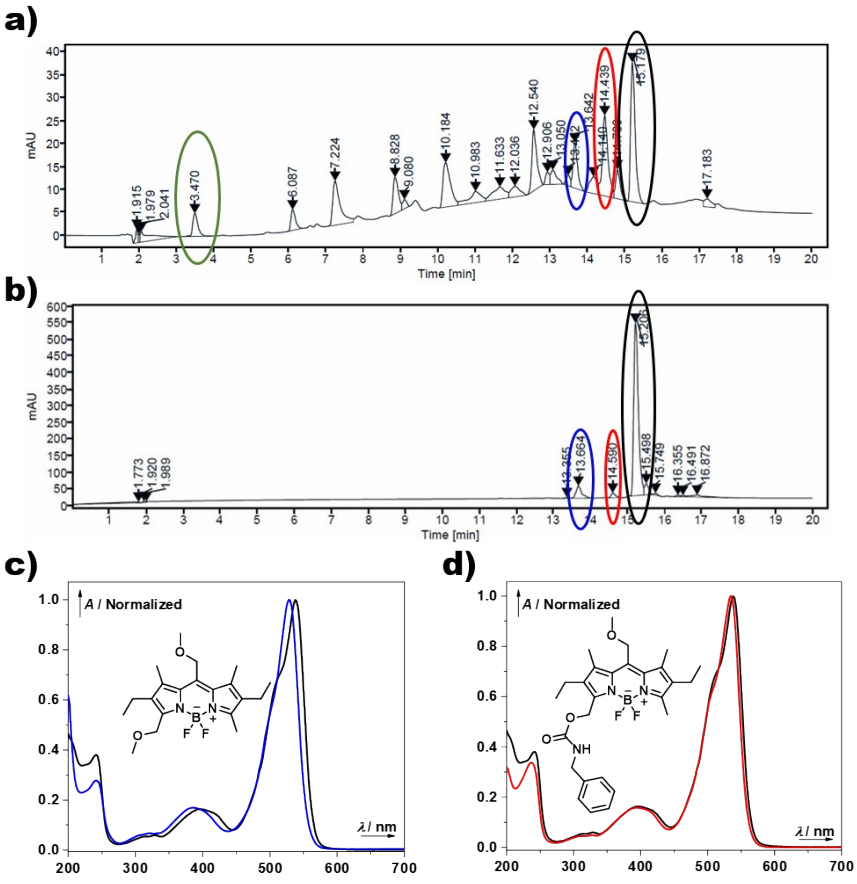


Figure ESI 26:. Representative HPLC traces of the release of the leaving group benzylamine (encircled in green) upon photoreaction of BODIPY-model compound **5** (encircled in black) in degassed solution irradiated to 80% conversion, c_{init} = 1.0 x 10^{-3} M. Exemplary BODIPY degradation products are encircled in blue and red, for further information on the degradation behavior one may be referred to additional literature[2-4]. (a) HPLC trace with UV-Vis detector wavelength = 260 nm. (b) HPLC trace with UV-Vis detector wavelength = 500 nm. (c) UV-Vis spectrum of the photodegradation product (blue, λ_{max} = 528 nm, suggested structure according to literature) of BODIPY-model compound **5** (black, λ_{max} = 538 nm) after release of the leaving group in *meso*-position and position 3. (d) UV-Vis spectra of the supposed photodegradation product (red, λ_{max} = 534 nm, suggested structure according to literature) of BODIPY-model compound **5** (black, λ_{max} = 538 nm) after release of the leaving group in *meso*-position.

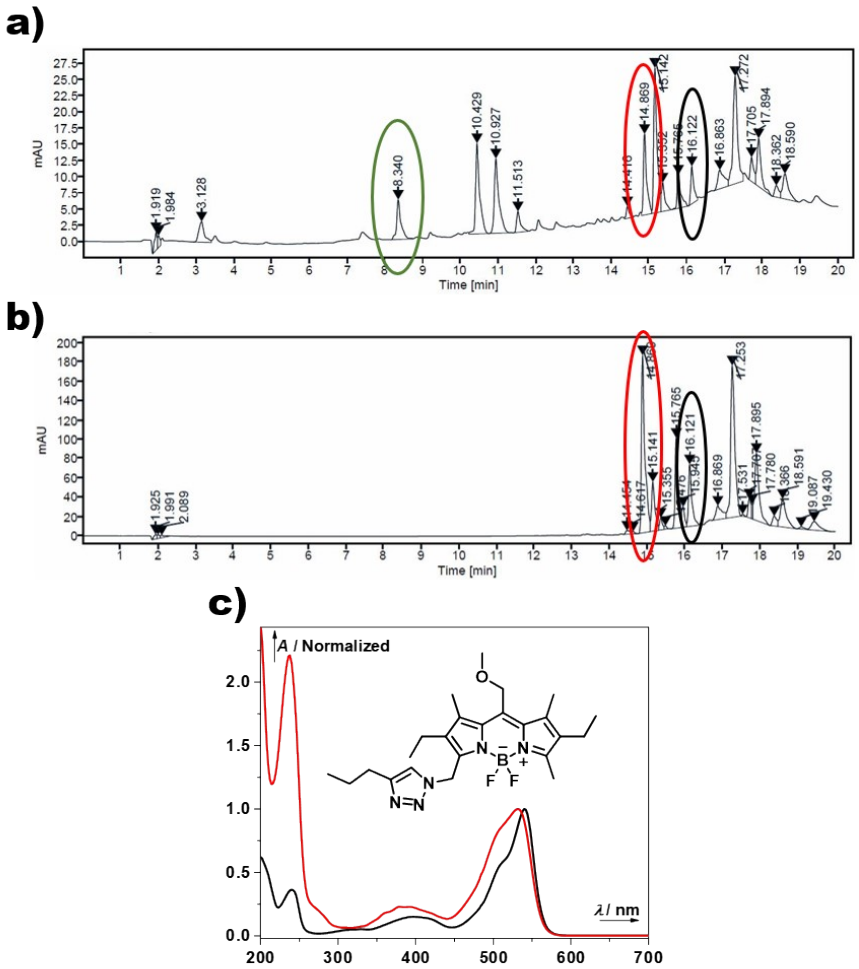


Figure ESI 27: Representative HPLC traces of the release of the leaving group phenylacetic acid (encircled in green) upon photoreaction of BODIPY-model compound **6** (encircled in black) in degassed solution irradiated to 80% conversion, c_{init} = 1.7 x 10^{-3} M. An exemplary BODIPY degradation product is encircled in red, for further information on the degradation behavior one may be referred to additional literature[2-4]. (a) HPLC trace with UV-Vis detector wavelength = 260 nm. (b) HPLC trace with UV-Vis detector wavelength = 500 nm. (c) UV-Vis spectra of the photodegradation product (red, λ_{max} = 532 nm, suggested structure according to literature) of BODIPY-model compound **6** (black, λ_{max} = 540 nm) after release of the leaving group in *meso*-position

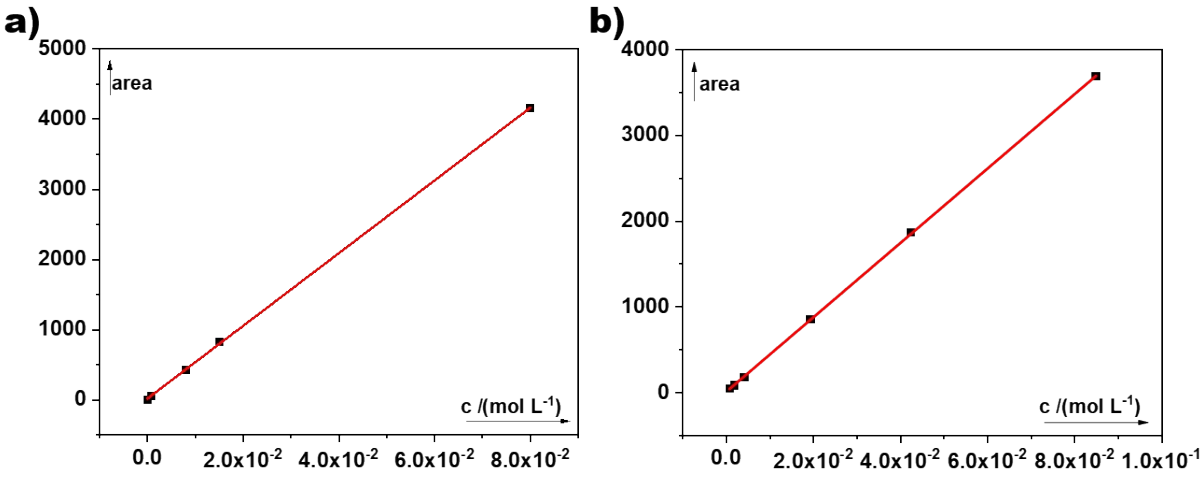


Figure ESI 28: HPLC calibration curves of benzylamine (a) (R^2 = 0.99983) and phenylacetic acid (b) (R^2 = 0.99993), the leaving groups of compound **5** and **6**, respectively, using a C-18 column and MeOH/H_2O as eluent.

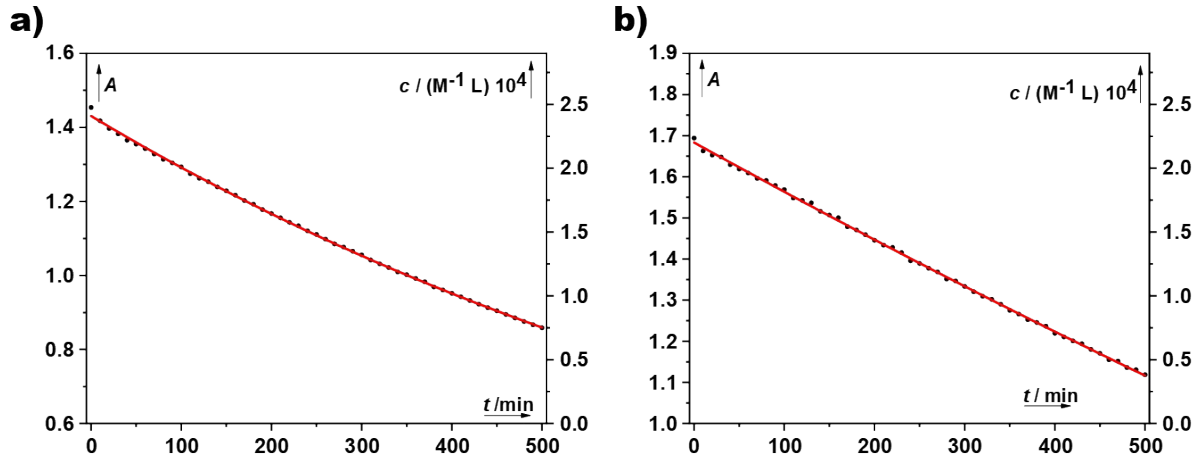


Figure ESI 29: Kinetic studies of the photodegradation of compound **5** in aerated (a) and degassed (b) methanol showing the decrease of the absorbance/concentration (λ_{em} = 541 nm) over time (black) and its exponential fit (red, (a) R^2 = 0.99945, (b) R^2 = 0.9995).

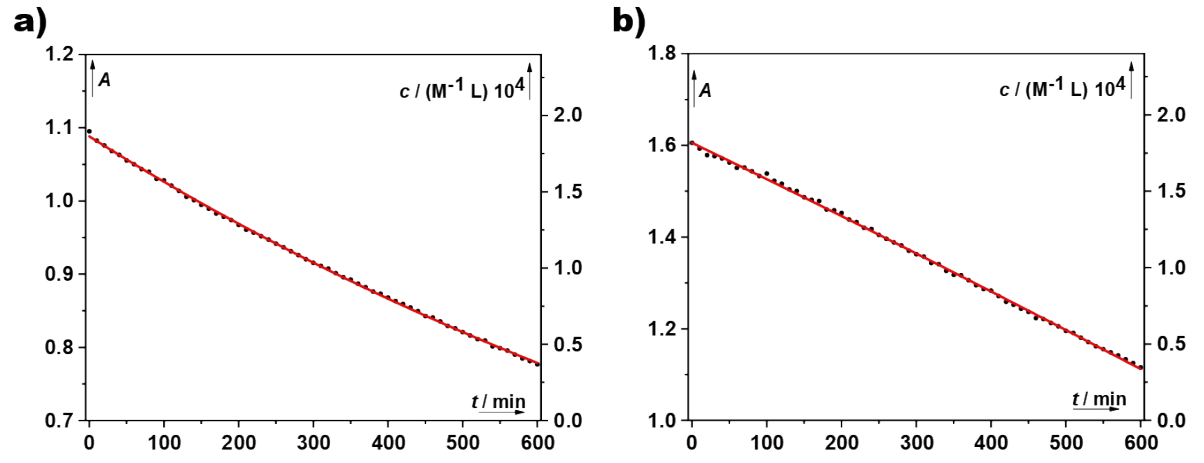


Figure ESI 30: Kinetic studies of the photodegradation of compound **6** in aerated (a) and degassed (b) methanol showing the decrease of the absorbance/concentration (λ_{em} = 538 nm) over time (black) and its exponential fit (red, (a) R^2 = 0.99969, (b) R^2 = 0.99922).

Dark stability tests of of BODIPY-diol-model 5 and BODIPY-azide-model 6:

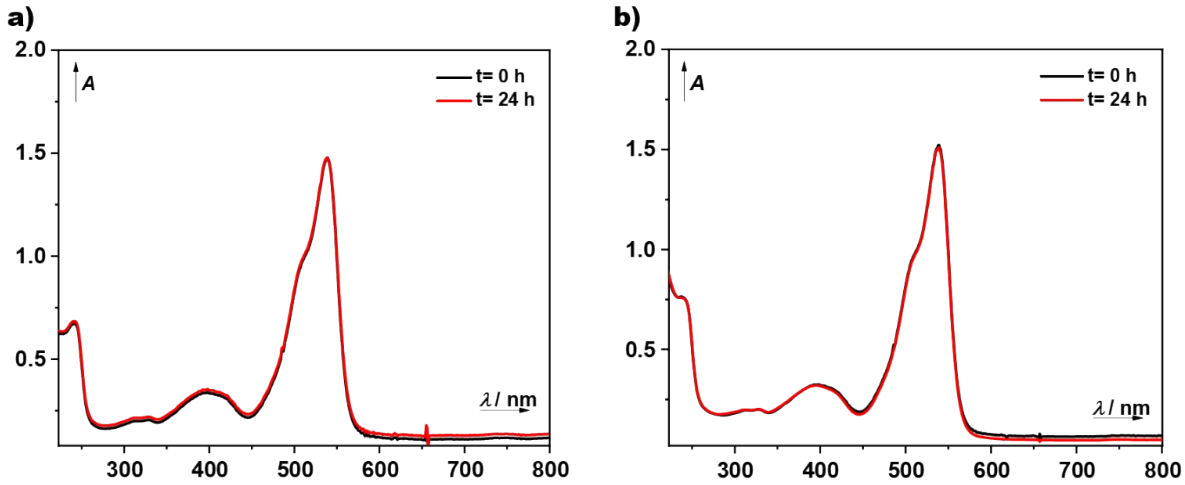


Figure ESI 31: Stability of the BODIPY-model compounds **5** (a) and **6** (b) (c ~ 5x 10^{-5} M) in a stirred methanol solution in the dark for 24 h.

Kinetic study of the photodegradation of the BODIPY-diol containing hydrogel:

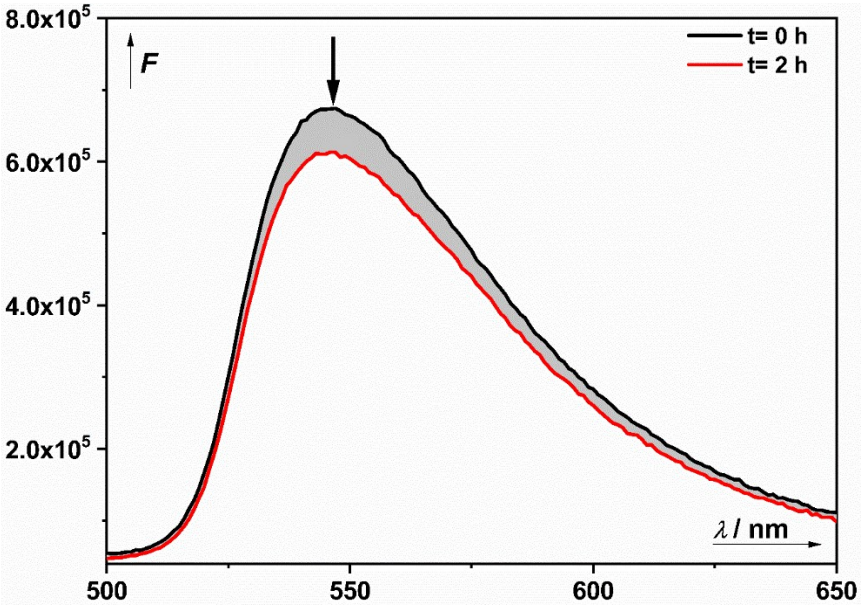


Figure ESI 32: Kinetic study of the photodegradation of the BODIPY-diol **5** containing hydrogel by irradiation of the BODIPY- hydrogel at 365 nm for 2 h in the fluorolog and determination of the decrease in fluorescence intensity.

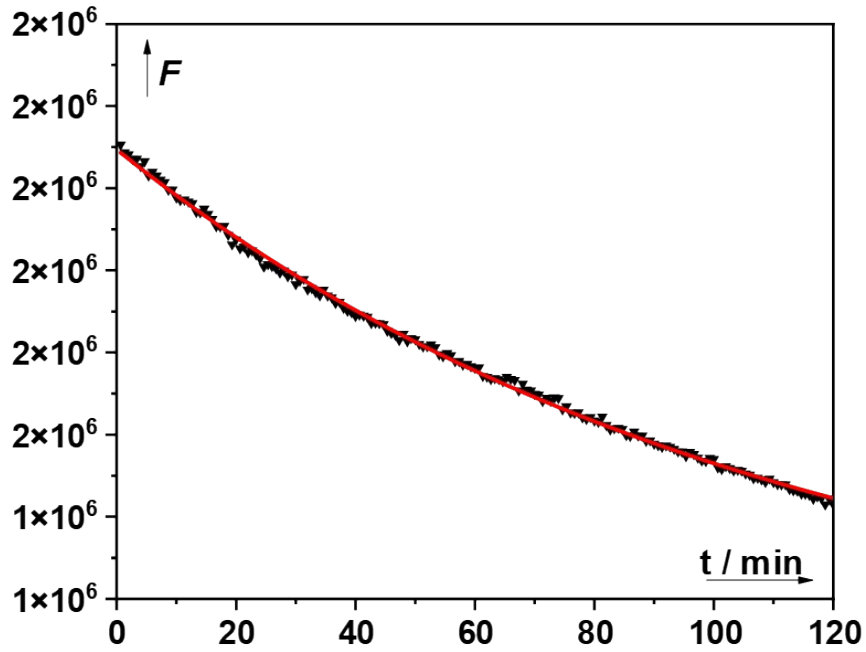


Figure ESI 33: Kinetic studie of the photodegradation of the BODIPY-diol containing hydrogel showing the decrease of the fluorescence intensity (λ_{em} = 543 nm) over time (black) and its exponential fit (red, R^2 = 0.99844).

Kinetic study of the photodegradation of the BODIPY decorated poly(organo)phosphazene:

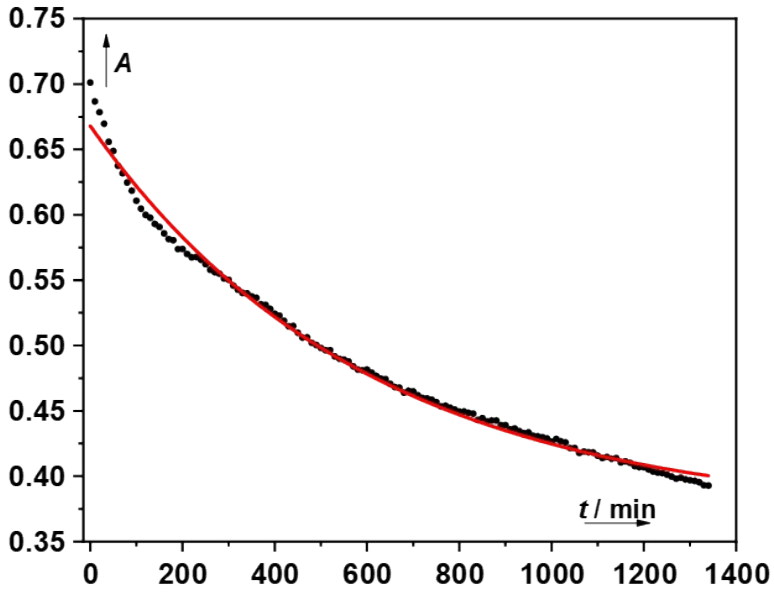


Figure ESI 34: Kinetic studie of the photodegradation of the BODIPY decorated poly(organo)phosphazene in aerated methanol showing a decrease of the absorbance (λ_{em} = 522 nm) over time (black) and its exponential fit (red, R^2 = 0.99319).

Aqueous size exclusion chromatography (SEC):

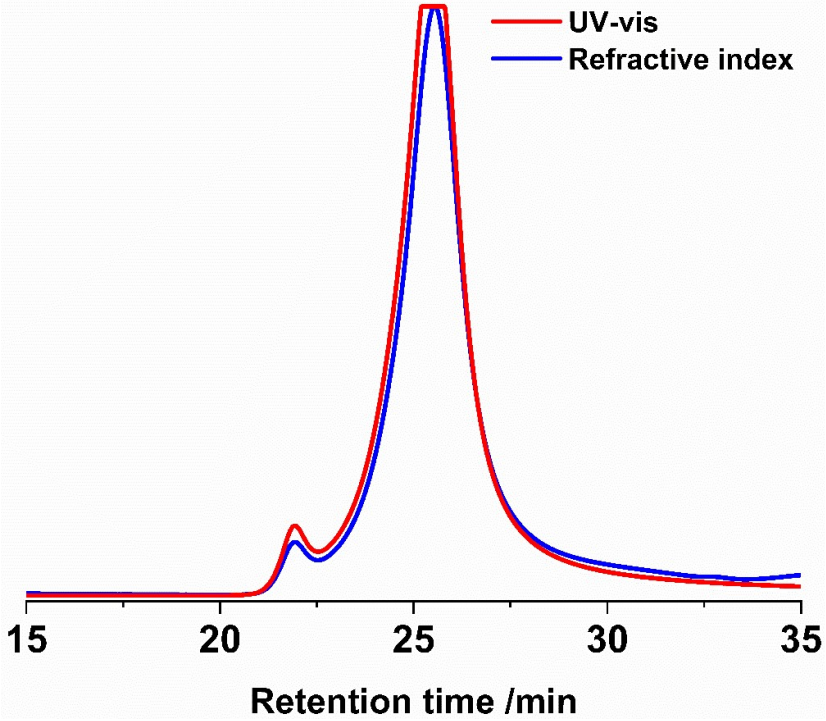


Figure ESI 35: SEC-traces of the UV-Vis (540 nm) and the refractive index detectors, showing an overlap of the signals and hence a successful loading of the BODIPY-azide **4** onto the poly(organo)phosphazene carrier.

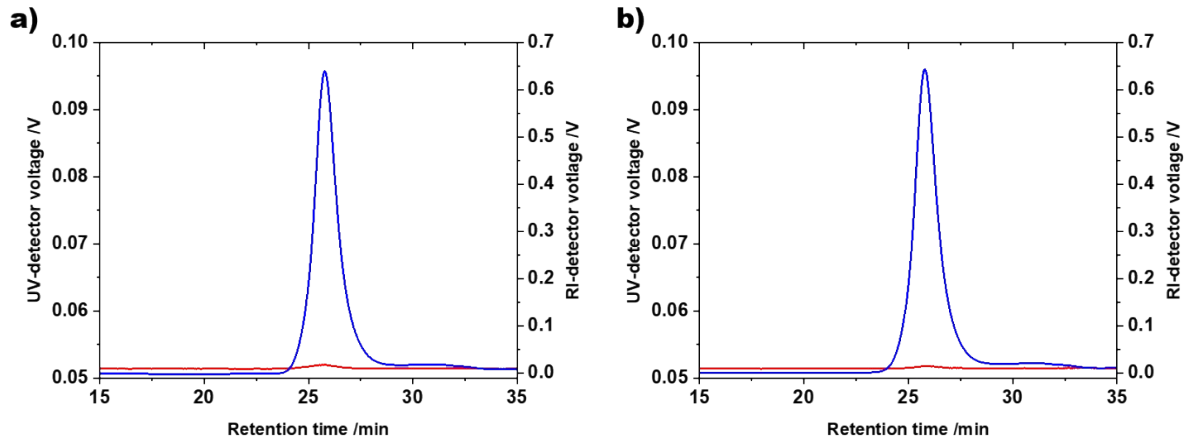


Figure ESI 36: SEC-traces of the UV-vis (red, 540 nm) and the refractive index (blue) detectors of the poly(organo)phosphazene carrier without any conjugated BODIPY before (a) and after irradiation at 550 nm over night (b). The spectra show no degradation of the polymer carrier upon irradiation, as well as only small absorbance of the polymer at 540 nm in the UV-vis detector.

FT-IR spectra:

5-Azidomethyl-2,6-diethyl-8-hydroxymethyl-1,3,7-trimethyl pyrromethene fluoroborate, BODIPY-azide, 4:

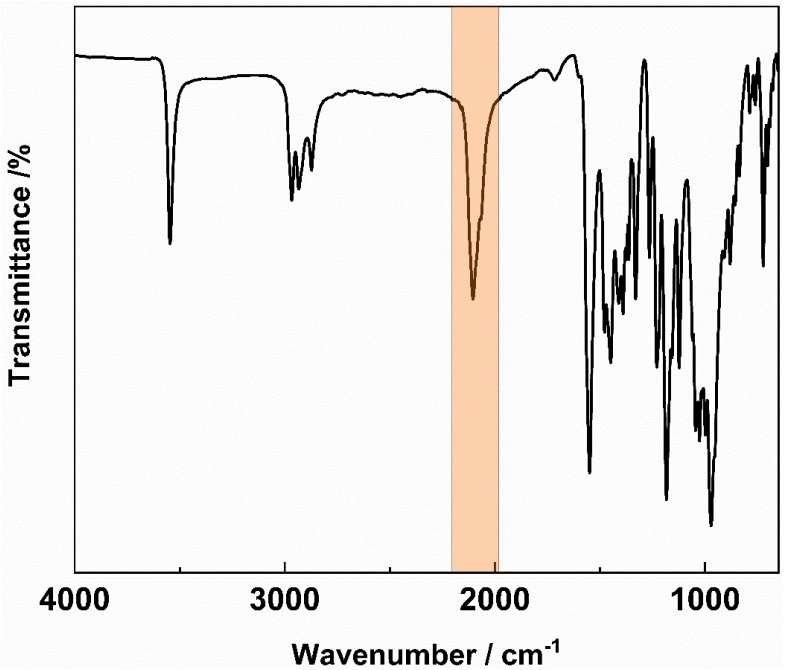


Figure ESI 37: FT-IR spectrum of the BODIPY-azide **4**; N=N=N stretching highlighted in orange.

5-((4-Propyl-1H-1,2,3-triazol-1-yl)methyl)-8-hydroxymethyl-2,6-diethyl-1,3,7-trimethyl pyrromethene fluoroborate, BODIPY-pentyne, 6a:

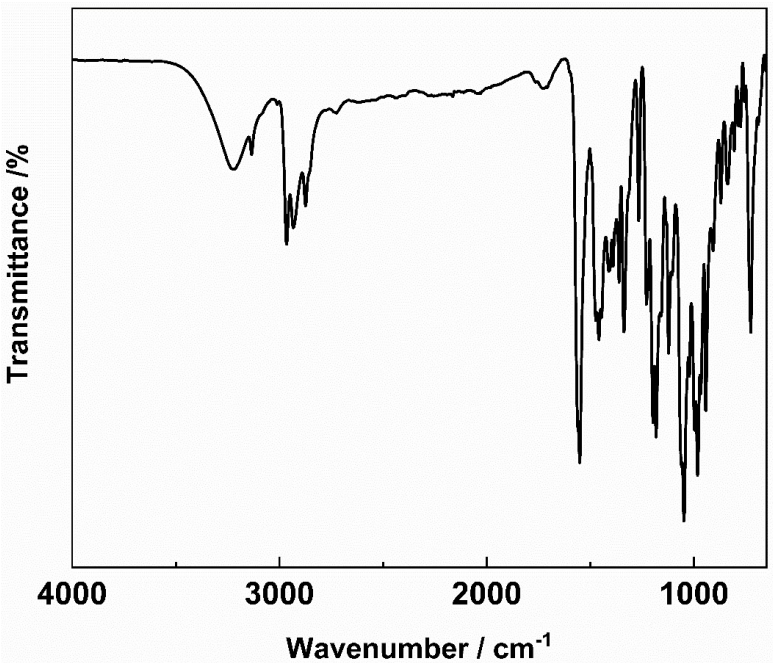


Figure ESI 38: FT-IR spectrum of the BODIPY-pentyne **6a**.

X-Ray diffraction crystal data:

Table ESI 1: X-ray diffraction crystal data, data collection and structure refinement for the compounds **1** and **4**.

Compound	BODIPY, 1	BODIPY-Azide, 4
Empirical formula	$C_{20}H_{27}BF_2N_2O_2$	$C_{18}H_{24}BF_2N_5O$
Formula weight (g mol^{-1})	376.24	375.23
Crystal system	monoclinic	triclinic
Space group	*C*2/*c*	$P\bar{1}$
Temp (K)	293	293
a (Å)	17.1373(13)	8.7126(10)
b (Å)	11.7136(9)	10.0034(12)
c (Å)	20.6062(15)	11.8736(14)
α (°)	90	69.381(2)
β (°)	99.0463(10)	80.082(2)
γ (°)	90	76.862(2)
V (Å^3)	4085.03	938.372
Z	8	2
ρ_{calc} (g cm^{-3})	1.224	1.328
Reflns collected	21027	11484
Indep. reflns	3500	4017
Obs. reflns [I > 2σ(I)]	2485	2534
Param. refin./restr.	251 / 0	250 / 0
Absorption correction	multi-scan	multi-scan
R_1	0.066	0.058
wR_2	0.197	0.190
CCDC No.	2109137	2109136

References:

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