Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Photophysics and redox properties of aza-BODIPY dyes with electron-withdrawing groups

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Electrochemical measurements. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on PalmSens[3] potentiostat/galvanostat and was conducted in deoxygenated tetrahydrofuran (THF) prior to the experiments dried with sodium and freshly distilled. Tetrabutylammonium tetrafluoroborate (Fluka, ≥ 99.0 % electrochemical grade) was used as supporting electrolyte (0.1 M). CV and DPV experiments were performed on saturated solutions (5 ml) of the respective compounds. A BioLogic 80 ml water-jacketed glass electrochemical cell with Teflon cap was used. The carbon glassy electrode (5 mm in diameter) was employed as the working electrode. The glassy carbon electrode was polished with alumina abrasive powder followed by rinsing with de-ionized water and acetone. The potentials were measured with respect to the Ag pseudo-reference electrode. The redox potential data were then referenced to the ferrocene/ferrocenium redox couple (added post the measurement). A silver wire served as an auxiliary electrode. All experiments were performed at 25 ± 1 ˚C.

Fluorescence spectra and quantum yields: Steady-state fluorescence spectra of the samples were recorded on an SLM-AMINCO 8100 spectrofluorimeter at room temperature in acetonitrile, THF or toluene. The fluorescence quantum yield (Φ_F) of aza-BODIPYs was determined using the comparative method according to the equation:

$$\Phi_F = \Phi_F^{Std} \frac{F\, A_{Std}\, n^2}{F_{Std}\, A\, n_{Std}^2}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the sample and the standard, A and A_{Std} are the absorbance of the sample and the standard at excitation wavelength and n and n_{Std} are the refractive indices of the solvent used for the sample and the standard, respectively [1]. Unsubstituted zinc phthalocyanine ZnPc (Φ_F^{Std} = 0.2 in DMSO) was employed as the standard [2]. The absorbance of the solutions at the excitation wavelength was in the range of 0.02 - 0.04.

Fluorescence lifetimes: The measurements were performed in deoxygenated solutions using quartz cuvettes with a 1 cm optical path length. Absorbance of main absorption bands of aza-BODIPYs was maintained at 0.2 during experiment. The fluorescence decays for lifetime measurements were fitted using mono-exponential functions taking into account the contribution of the excitation pulse. Pulse diode emitting at 605 nm (pulse width <1.5 ns, power 2 pJ/pulse) was used for time-resolved measurements.

Singlet oxygen quantum yield (Φ_Δ). Φ_Δ of aza-BODIPYs was measured indirectly according to the procedure described elsewhere [3-5]. The procedure was based on the determination of the rates of oxidation of singlet oxygen acceptor photosensitized by a standard molecule (of known quantum yield of singlet oxygen formation) and by the molecule studied. DPBF was applied as an acceptor of singlet oxygen and unsubstituted zinc phthalocyanine (Φ_Δ = 0.58 in toluene) was used as a reference [6]. Typically, 2 ml of the toluene solution containing sensitizer and acceptor was introduced into the quartz cuvette, saturated with oxygen, and irradiated using an Osram® xenon lamp (XBO 75W/2). The absorbance of a sensitizer was maintained at 0.10 at λ_{max} nm and the absorbance of acceptor was maintained at 1.0 at λ 415 nm. A 630 nm glass cut-off filter was used to filter the ultraviolet radiation. The singlet oxygen quantum yield Φ_Δ was calculated based on the following equation:

$$\Phi_\Delta = \Phi_\Delta^{Std} \cdot \frac{R \cdot I_{abs}^{Std}}{R^{Std} \cdot I_{abs}},$$

where Φ_{Δ}^{Std} is the singlet oxygen quantum yield for the standard, R and R^{Std} are the DPBF photobleaching rates in the presence of the aza-BODIPY and in the presence of the reference molecule (zinc phthalocyanine), respectively. I_{abs} and I_{abs}^{Std} are the intensities of light absorbed by the measured sample and the respective standard. The mean intensity of the light absorbed by the samples (I_{abs}, I_{abs}^{std}) was calculated according to the following equation:

$$I_{\text{abs}} = I_{550}\int_{550}^{725} T(\lambda)F(\lambda)\left(1-10^{-A(\lambda)}\right)\mathrm{d}\lambda$$

where $A(\lambda)$ is the absorbance of the sensitizer and $F(\lambda)$ is the spectral distribution of the light emitted by the lamp given as $I(\lambda) = I_{550}F(\lambda)$. Photosensitizer absorbance was maintained at about 0.1. Each experiment was repeated at least three times.

Photostability. THF solutions of the corresponding aza-BODIPY with absorbance ca. 1.0 were irradiated with a xenon lamp (OSRAM) in a quartz cuvette with 1 cm optical path. A 473 nm glass cut-off filter was used for this experiment. The kinetics of photodegradation of aza-BODIPYs were measured in an air atmosphere and were followed using absorption spectroscopy. The intensity of the incident radiation was measured with photo-radiometer HD2102.1 (DELTA OHM) coupled with irradiance probe LP 471 RAD. The following irradiance was measured: 843.0 ± 0.1 Wm^{-2}. The total irradiation time for each sample was 10 hours.

[1] R. Bayrak, H. T. Akçay, M. Pişkin, M. Durmuş and I. DeğirmencioğluI, Dyes Pigments **2012**, 95, 330-337.

[2] A. Ogunsipe, J. Y. Chen and T. Nyokong, New J. Chem. **2004**, 28, 822-827.

[3] M. Nowakowska, M. Kępczyński, M. Dąbrowska, Macromol. Chem. Phys. **2001**, 202, 1679–1688.

[4] M. Kępczyński, A. Karewicz, A. Górnicki, M. Nowakowska, J. Phys. Chem. **2005**, B 109, 1289–1294.

[5] M.D. Maree, N. Kuznetsova, T. Nyokong, J. Photochem. Photobiol. **2001**, A 140, 117–125.

[6] A. Ogunspie, D. Maree and T. Nyokong, J. Mol. Struct. **2003**, 650, 131-140.

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Table S1. Cartesian atomic coordinates and total electronic energies of the ground state optimized geometries of **Ref**, **5**, **6**, **7** and **8.**

Figure S22. A fragment of PES corresponding to the tilts of the proximal rings in the **Ref** molecule. Obtained from a rigid scan with PBE0/6-311G(2d,p) over the geometry optimized at the same level.

Table S2. Contributions (in %) of the aza-BODIPY core, proximal and distal rings in **5**, **6**, **7**, **8** and **Ref** to the frontiers molecular orbitals (for definition of the division refer to **Figure 8** in the manuscript).

Figure S23. Experimental electronic absorption (**blue line**) spectra and computed electronic transitions of **5, 6, 7** and **8** computed by TDDFT with BMK/6-311+G(2d,p) (**green bars**) or by TDDFT with PBE0/6-311+G(2d,p) (**red bars**).

Table S3. Characteristics of the strongest electronic transitions in **5, 6, 7** and **8** as calculated with the BMK/6-311G*//PBE0/6-31G*. Change of the electronic density distribution (%) in the ADPM core, the proximal (P1, P2) and the distal (D1, D2) rings are listed in the last five columns. The analysis was performed with the GaussSum 3.0 program.

^{1}H NMR (600 MHz, THF-d_8) δ (ppm) = 8.34 (d, ^3J = 8.9 Hz, 4H, [1]), 8.31 (d, ^3J = 8.9 Hz, 4H, [2]), 8.18 (d, ^3J = 7.5 Hz, 4H, [3]), 7.50 (t, ^3J = 7.3 Hz, 4H, [4]), 7.46 (t, ^3J = 7.2 Hz, 2H, [5], overlapped with singlet of [6]), 7.45 (s, 2H, [6]).

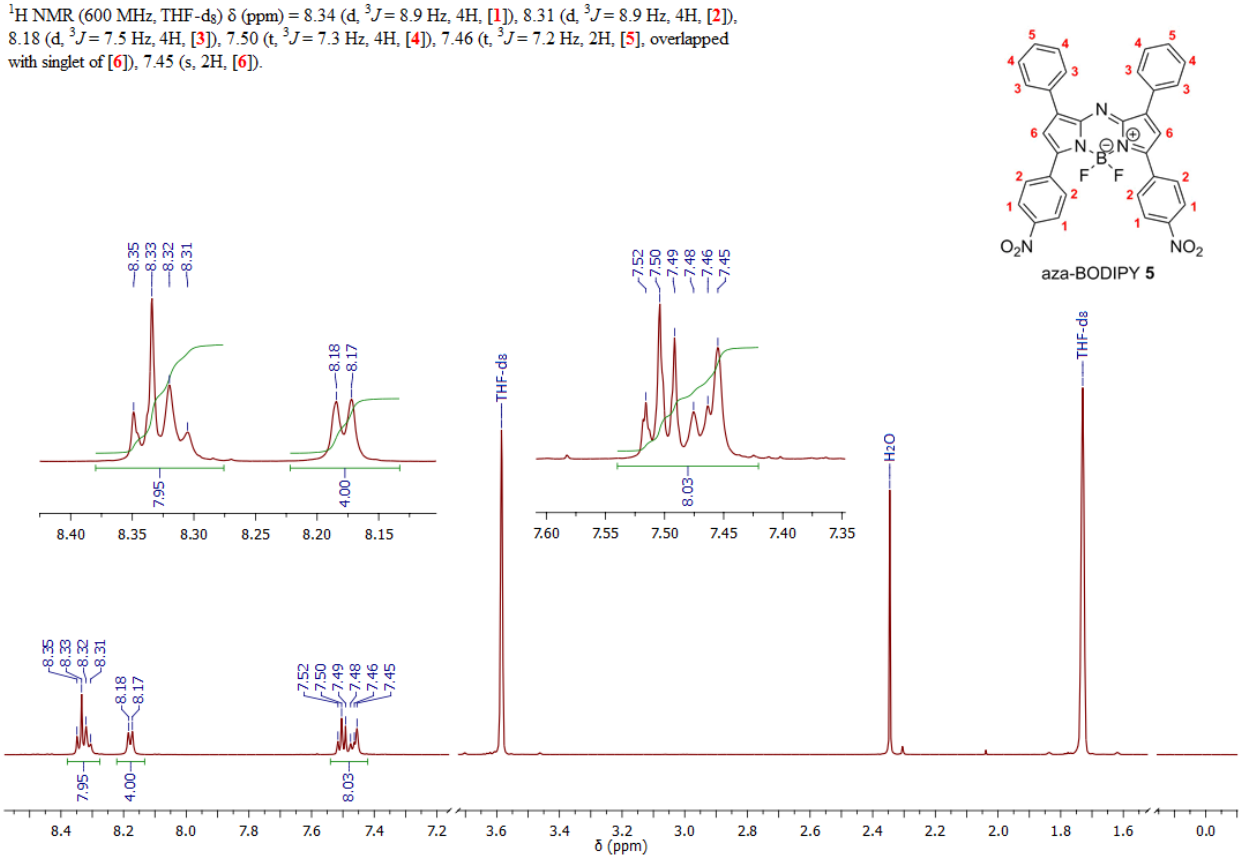

Figure S1. ^{1}H NMR spectrum of aza-BODIPY **5** in THF-d_8 recorded at 52 °C.

^{11}B NMR (96 MHz, $CDCl_3$) δ = 0.67 (t, J=31.1).

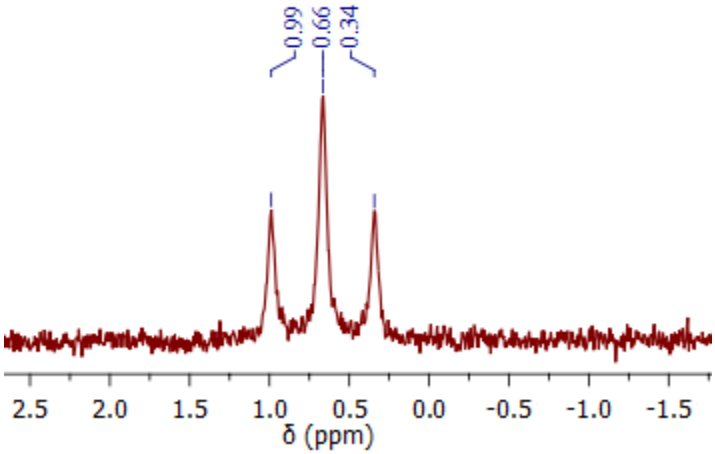

Figure S2. ^{11}B NMR spectrum of aza-BODIPY **5** in $CDCl_3$.

^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = 22.10 (q, $^{1}J_{F\text{-}B}$ = 31.4 Hz, 2F).

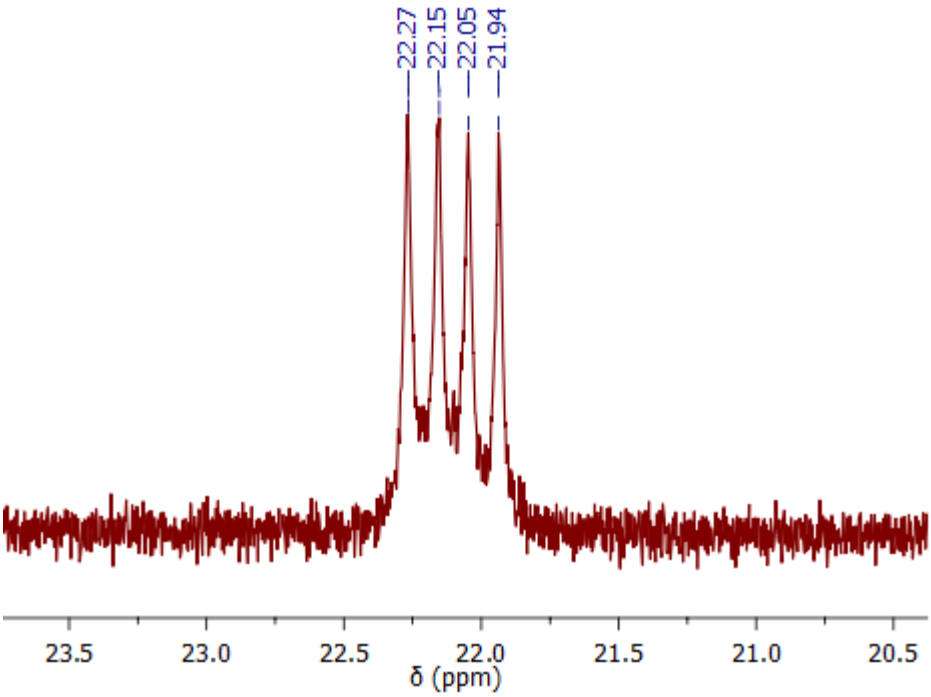

Figure S3. ^{19}F NMR spectrum of aza-BODIPY **5** in $CDCl_3$.

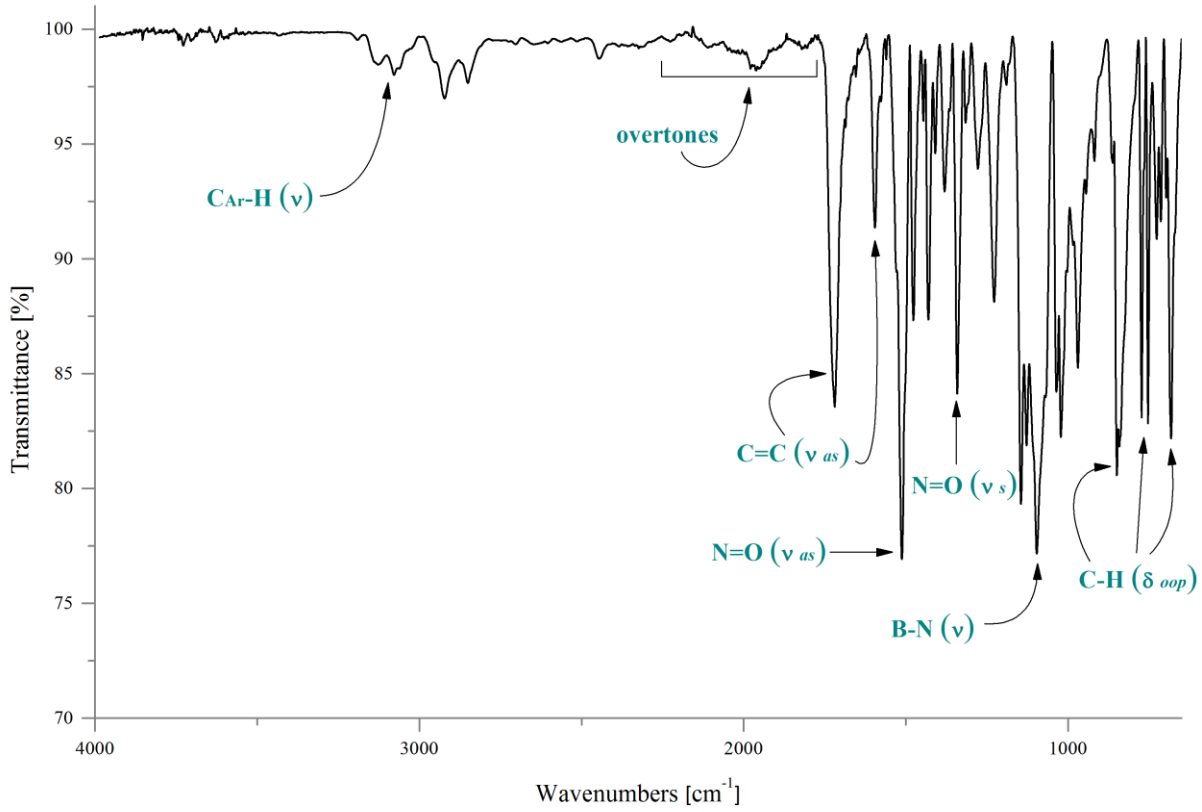

Figure S4. FT-ATR-IR spectrum of aza-BODIPY **5**.

Mass Spectrum List Report

Analysis Info

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Sample Name		Instrument / Ser#	micrOTOF-Q 10258
Comment	MeOH		

Acquisition Parameter

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Scan End	3000 m/z	Set Collision Cell RF	160.0 Vpp	Set Divert Valve	Source

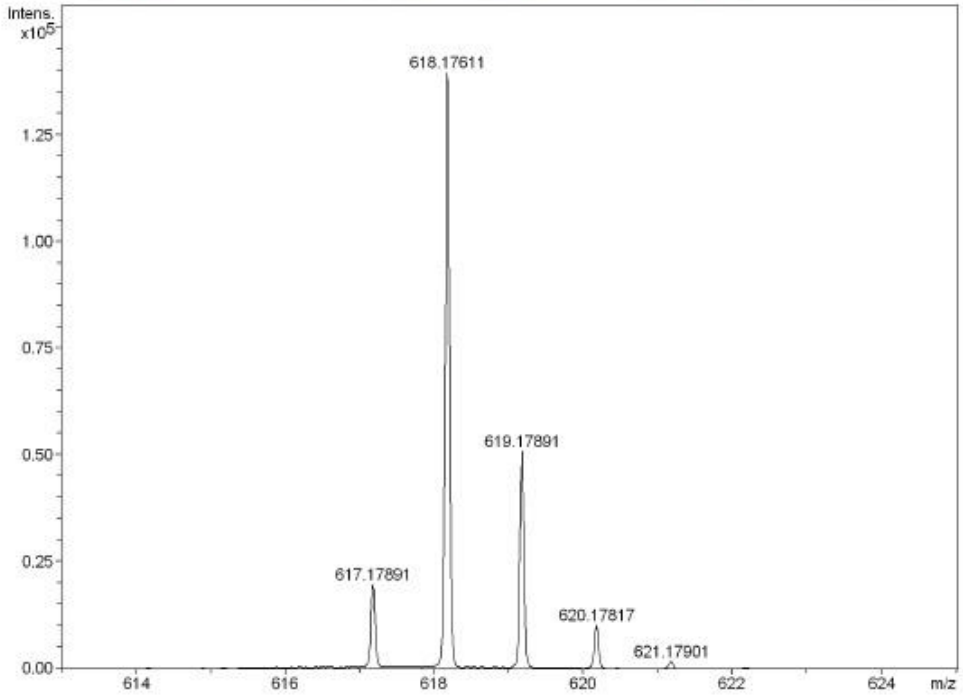

Figure S5. HR-ESI mass spectrum of aza-BODIPY **5**.

^{1}H NMR (600 MHz, Pyr-d5) δ (ppm) = 8.45 (t, ^{3}J = 7.8 Hz, 2H, [1], overlapped with doublet of [2]), 8.44 (d, ^{3}J = 8.9 Hz, 4H, [2]), 8.34 (d, ^{3}J = 8.9 Hz, 4H, [3]), 8.20 (d, ^{3}J = 7.1 Hz, 4H, [4]), 7.68 (s, 2H, [5]), 7.64 (t, ^{3}J = 7.3 Hz, 4H, [6]).

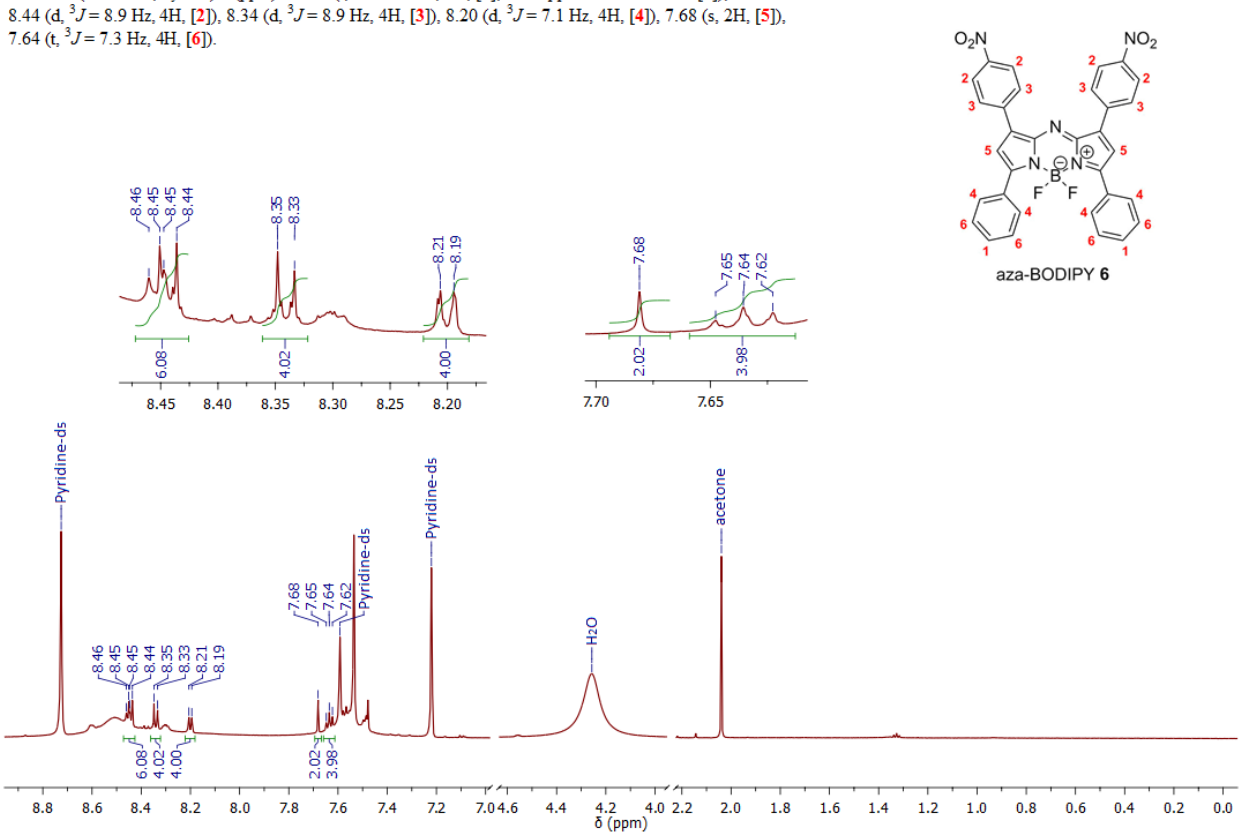

Figure S6. ^{1}H NMR spectrum of aza-BODIPY **6** in Py-D_5 recorded at 80 °C.

^{11}B NMR (96 MHz, $CDCl_3$) δ = 0.79 (t, *J*=30.2).

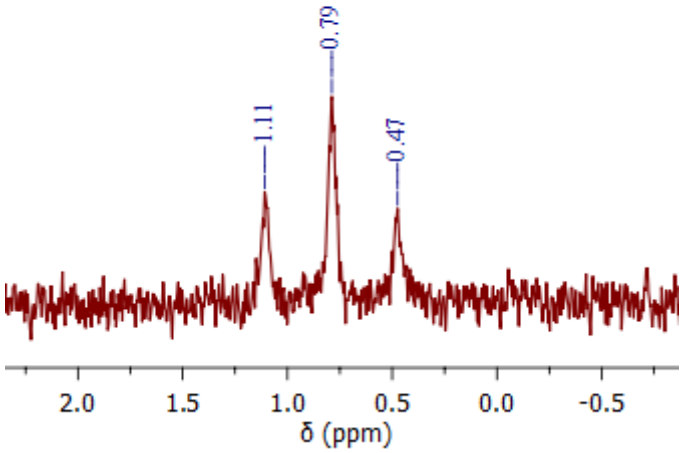

Figure S7. ^{11}B NMR spectrum of aza-BODIPY **6** in $CDCl_3$.

^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = 20.66 (q, $^{1}J_{F\text{-}B}$ = 30.2 Hz, 2F).

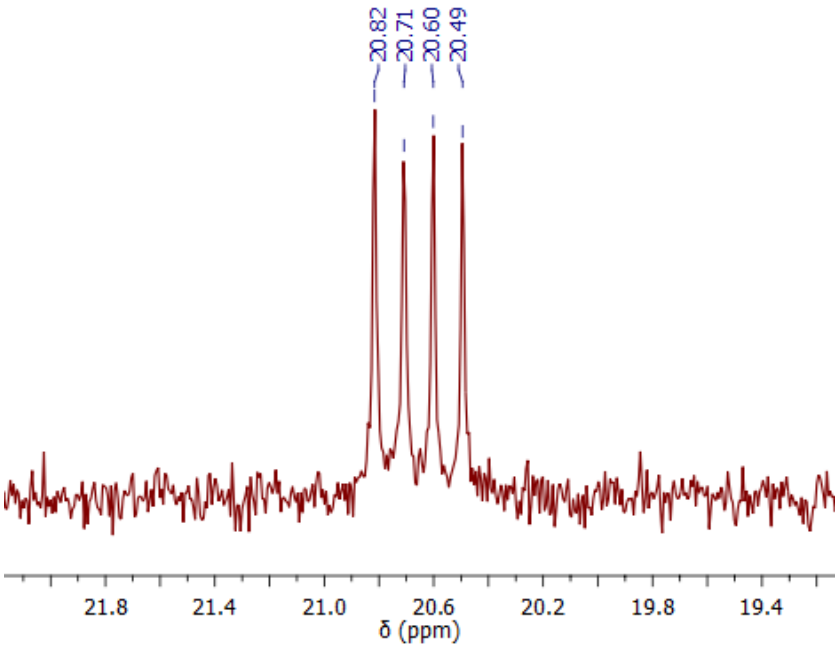

Figure S8. ^{19}F NMR spectrum of aza-BODIPY **6** in $CDCl_3$.

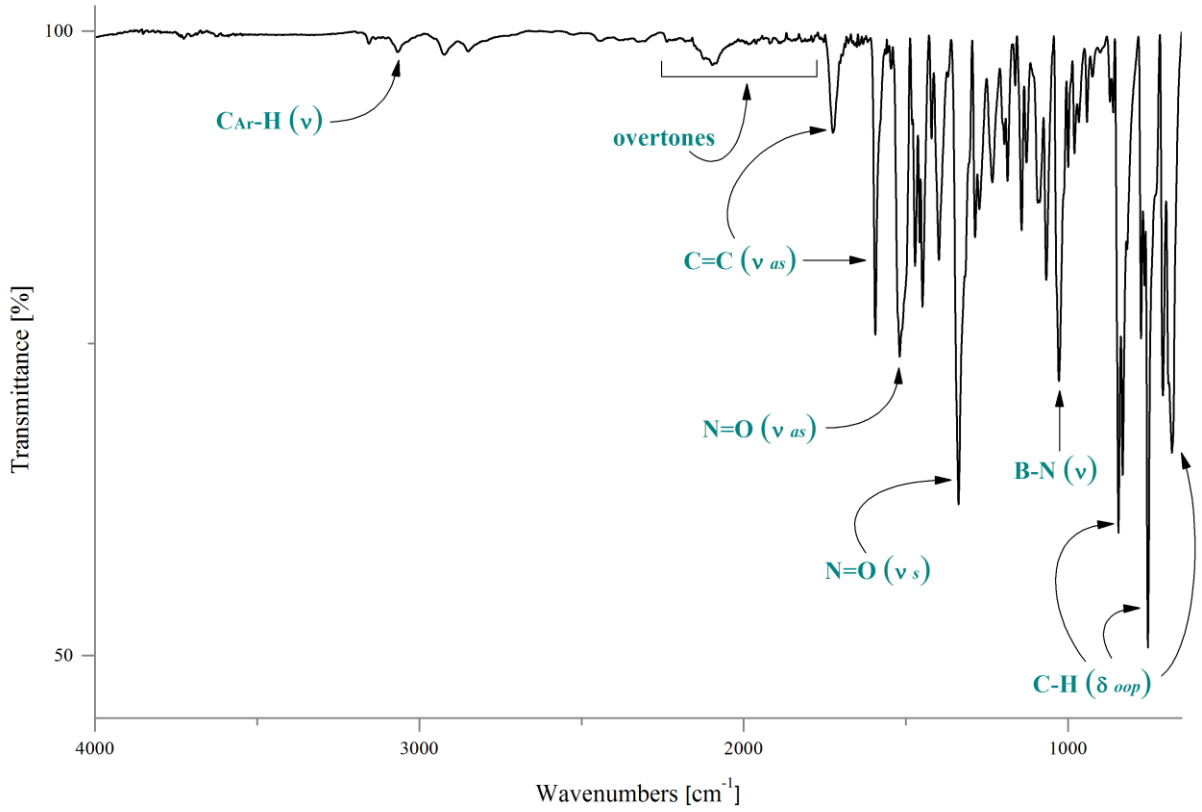

Figure S9. FT-ATR-IR spectrum of aza-BODIPY **6**.

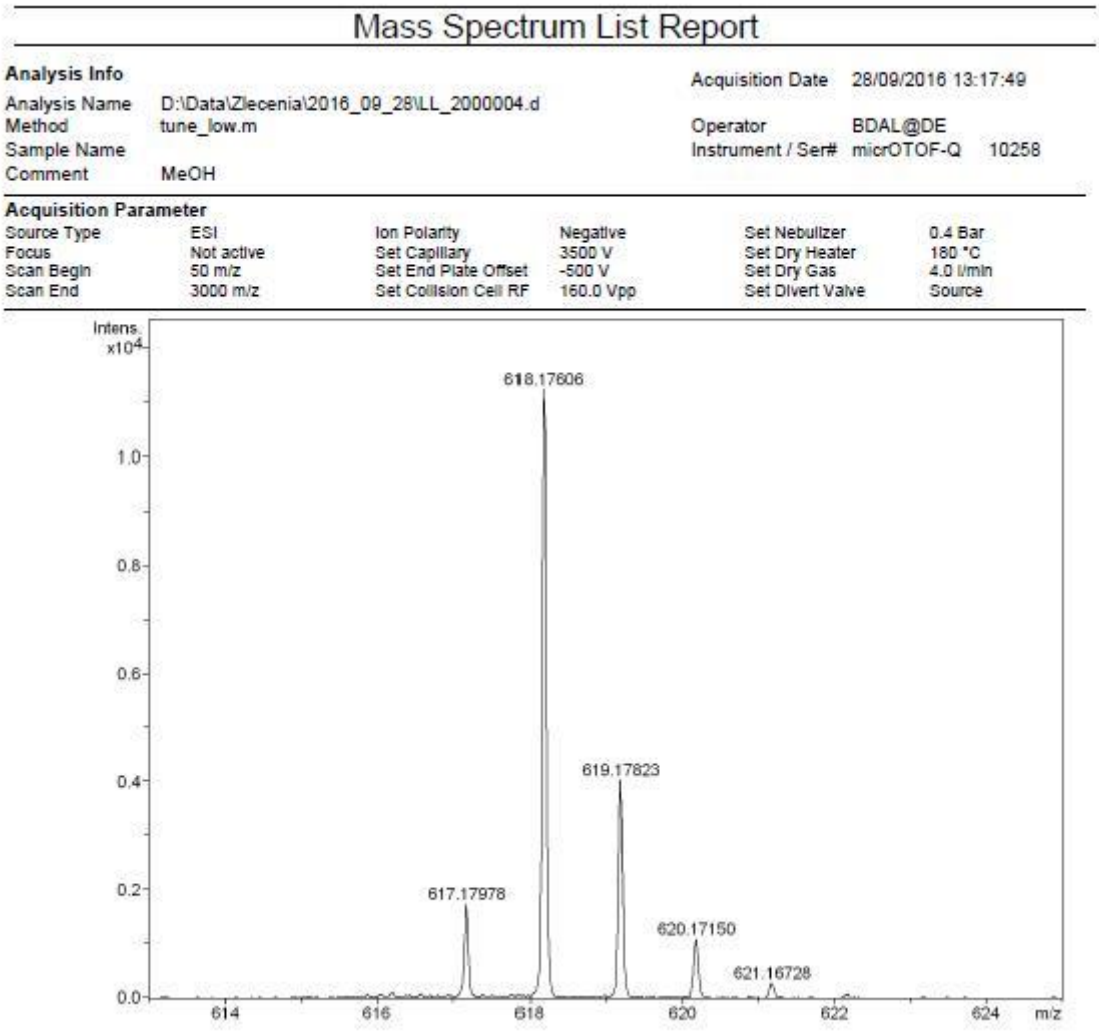

Figure S10. HR-ESI mass spectrum of aza-BODIPY **6**.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.34 (d, ^3J = 9.1, 4H, [1]), 8.18 (d, ^3J = 9.1, 4H, [2]), 8.02 (d, ^3J = 8.7, 4H, [3]), 7.53 (d, ^3J = 8.7, 4H, [4]), 7.05 (s, 2H, [5]), 1.40 (s, 18H, [6]).

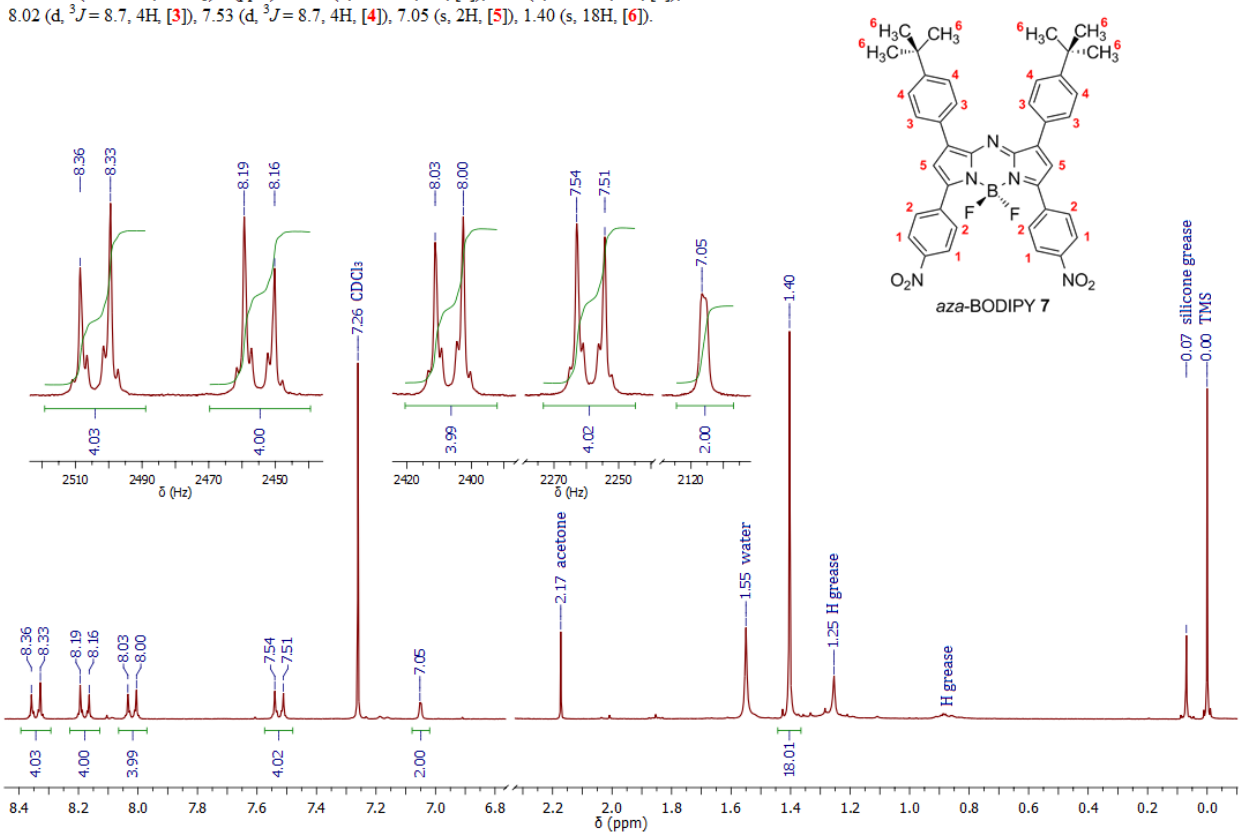

Figure S11. ^{1}H NMR spectrum of aza-BODIPY **7** in $CDCl_3$.

^{11}B NMR (96 MHz, $CDCl_3$) δ = 0.69 (t, *J*=31.4).

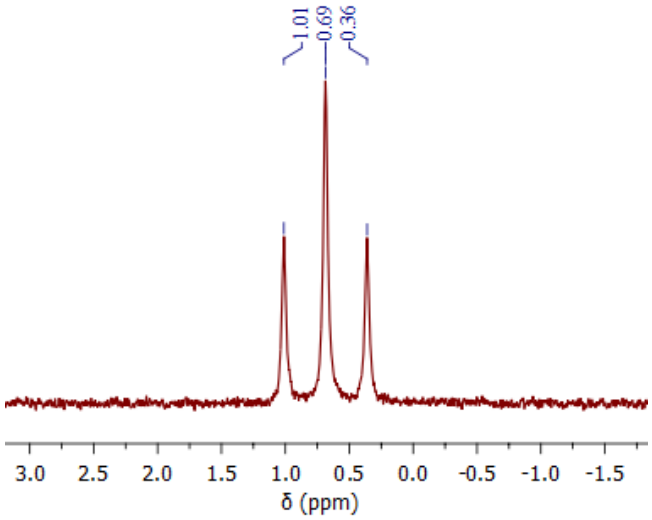

Figure S12. ^{11}B NMR spectrum of aza-BODIPY **7** in $CDCl_3$.

^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = 22.29 (q, $^{1}J_{F\text{-}B}$ =31.3 Hz, 2F).

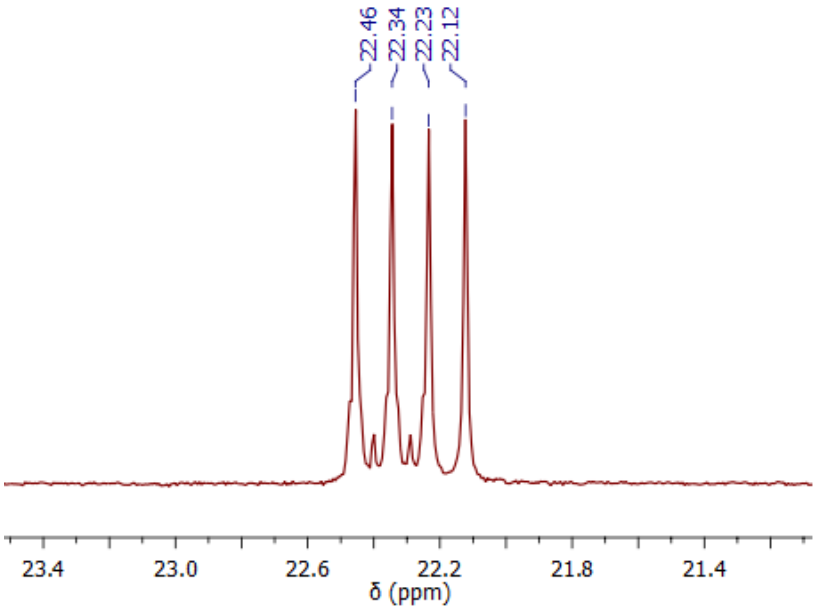

Figure S13. ^{19}F NMR spectrum of aza-BODIPY **7** in $CDCl_3$.

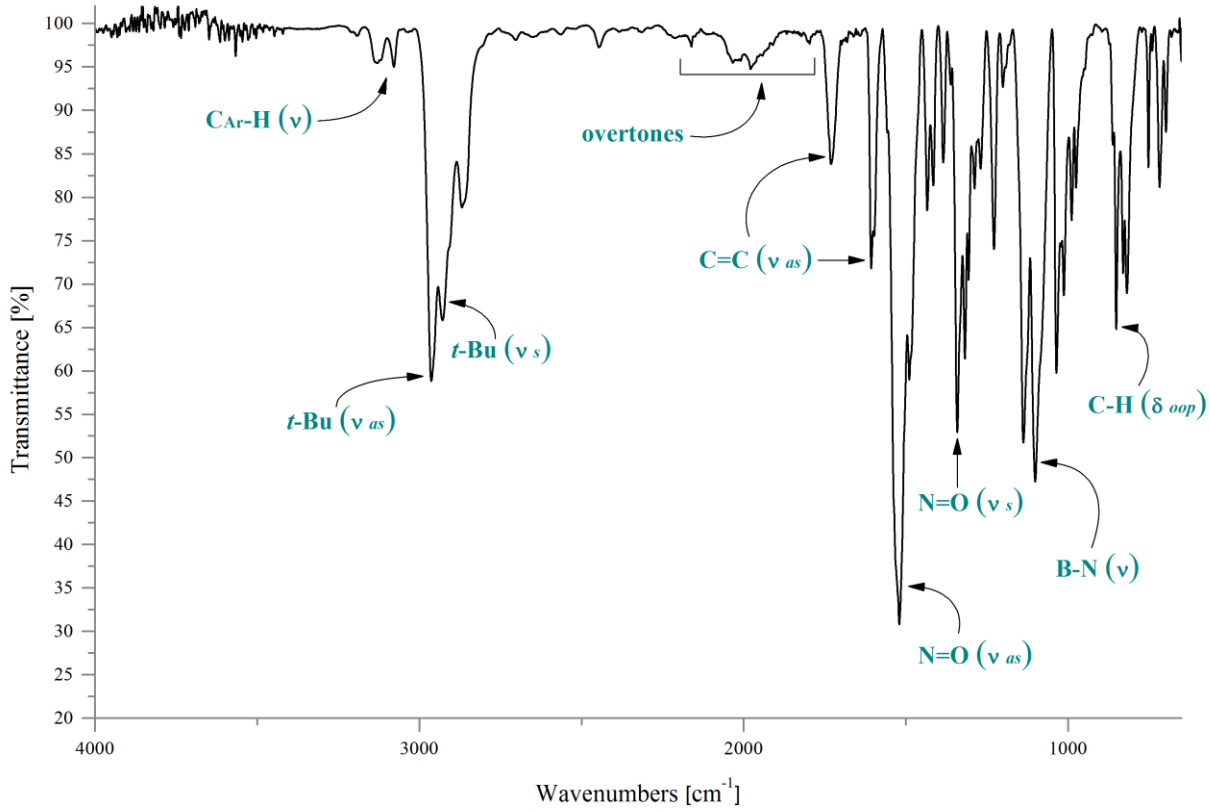

Figure S14. FT-ATR-IR spectrum of aza-BODIPY **7**.

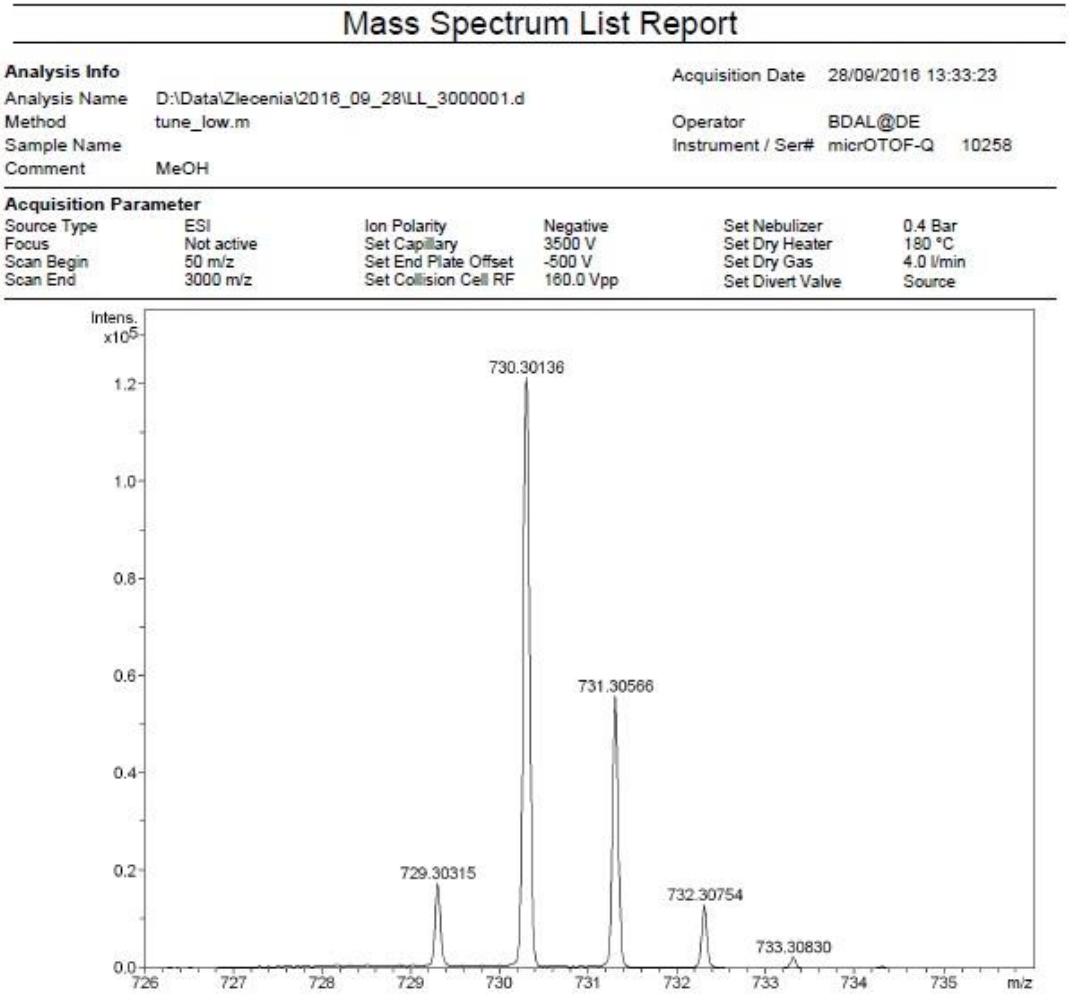

Figure S15. HR-ESI mass spectrum of aza-BODIPY **7**.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.29 (d, ^3J = 8.9, 4H, [1]), 8.12 (d, ^3J = 8.9, 4H, [2]), 8.05 (d, ^3J = 8.6, 4H, [3]), 7.54 (d, ^3J = 8.5, 4H, [4]), 7.17 (s, 2H, [5]), 1.38 (s, 18H, [6]).

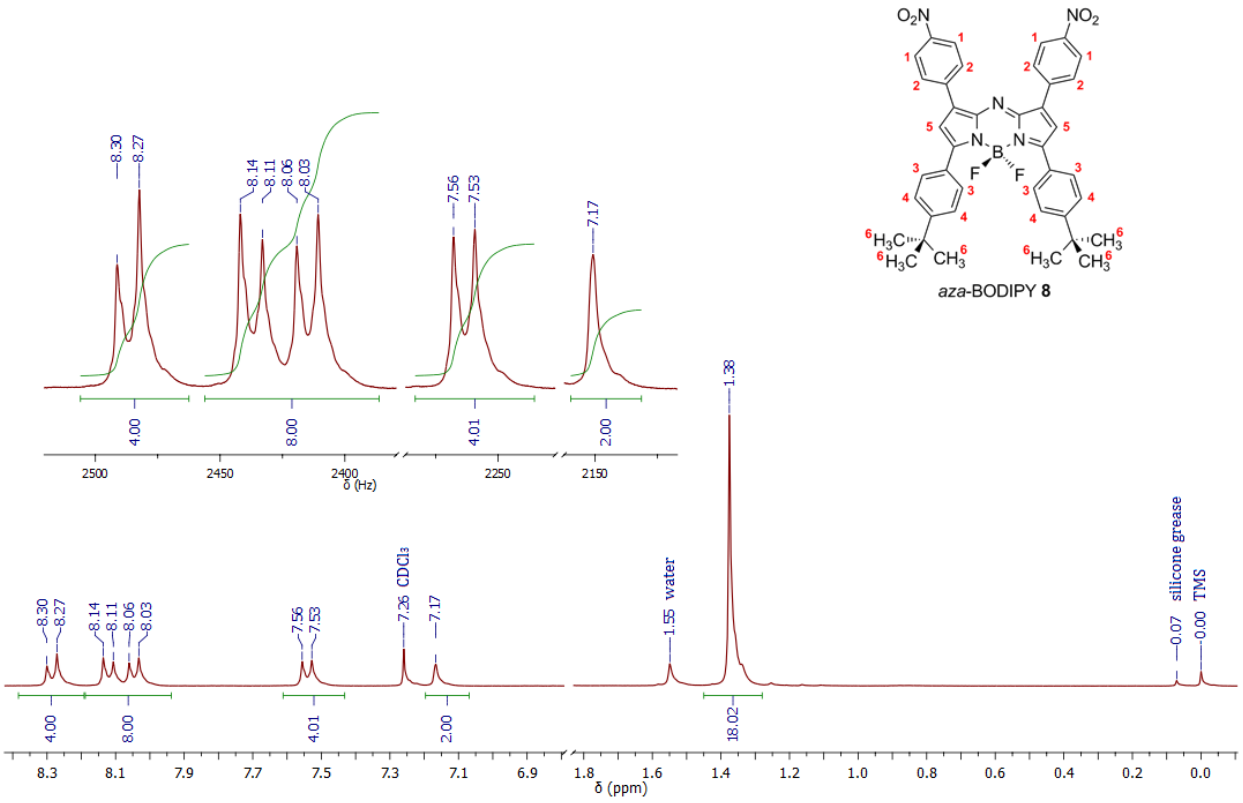

Figure S16. ^{1}H NMR spectrum of aza-BODIPY **8** in $CDCl_3$.

^{11}B NMR (96 MHz, $CDCl_3$) δ = 0.90 (t, *J*=30.6).

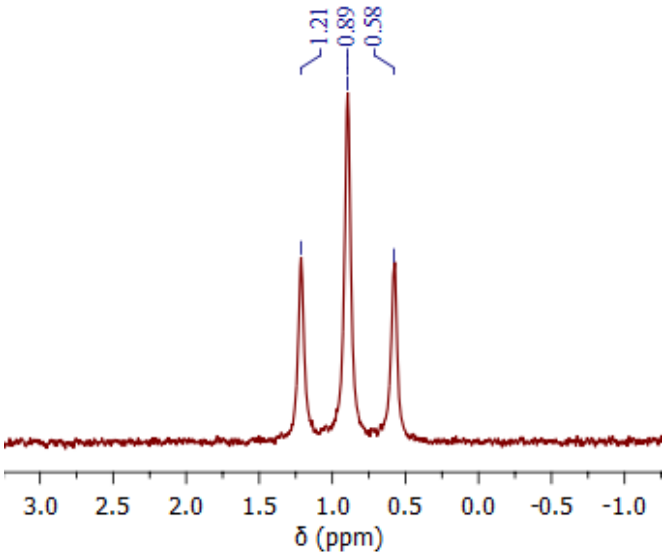

Figure S17. ^{11}B NMR spectrum of aza-BODIPY **8** in $CDCl_3$.

^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = 20.36 (q, $^{1}J_{F\text{-}B}$ = 30.8 Hz, 2F).

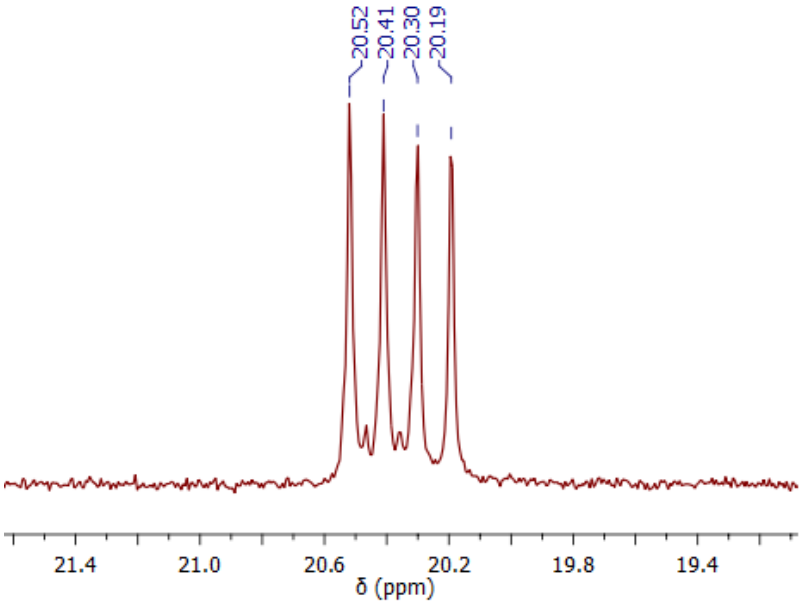

Figure S18. ^{19}F NMR spectrum of aza-BODIPY **8** in $CDCl_3$.

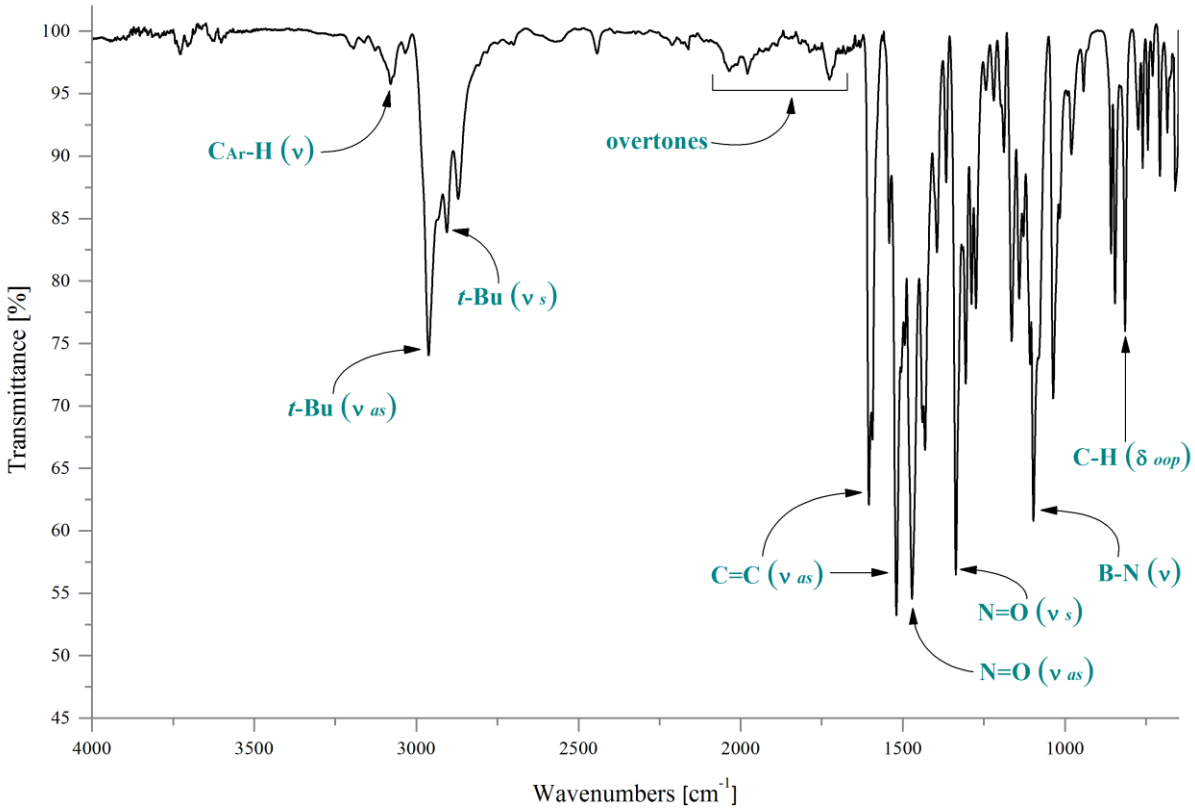

Figure S19. FT-ATR-IR spectrum of aza-BODIPY **8**.

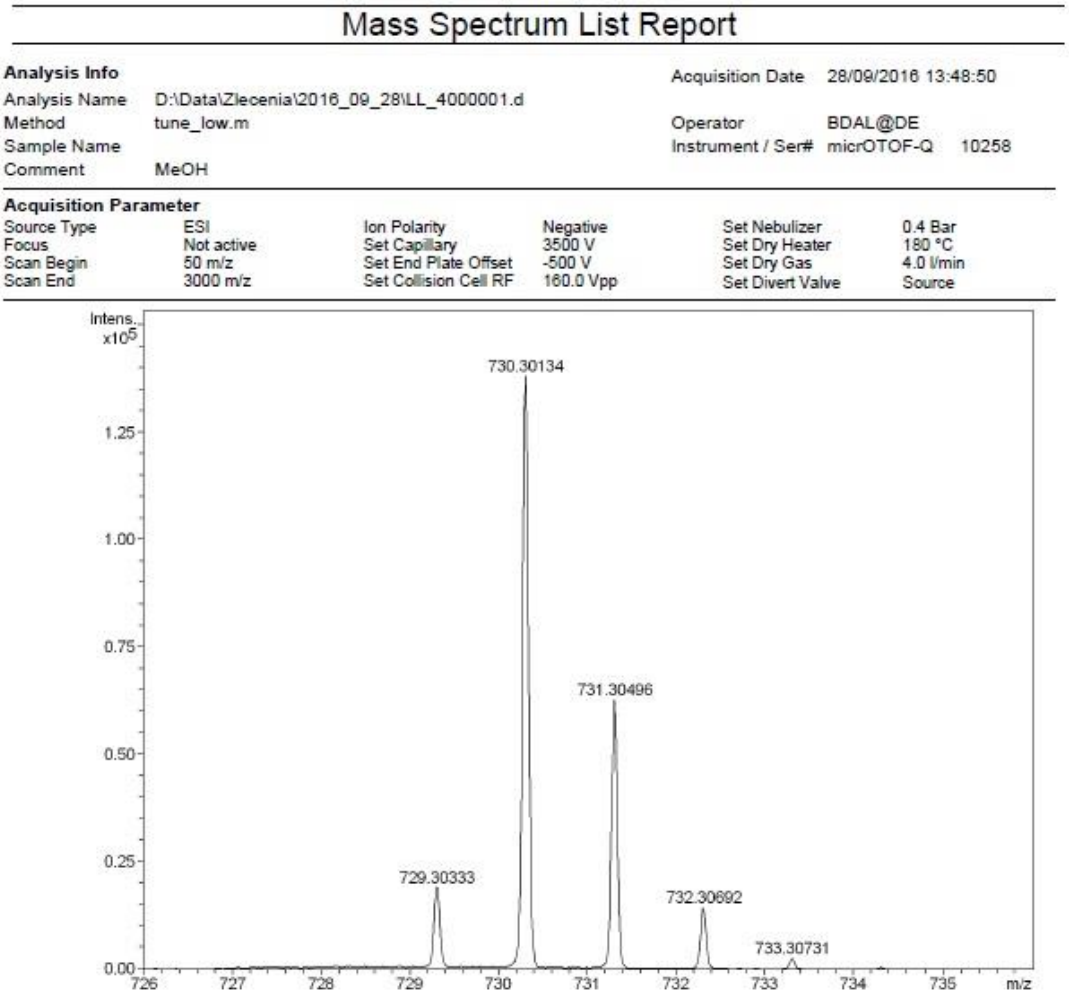

Figure S20. HR-ESI mass spectrum of aza-BODIPY **8**.

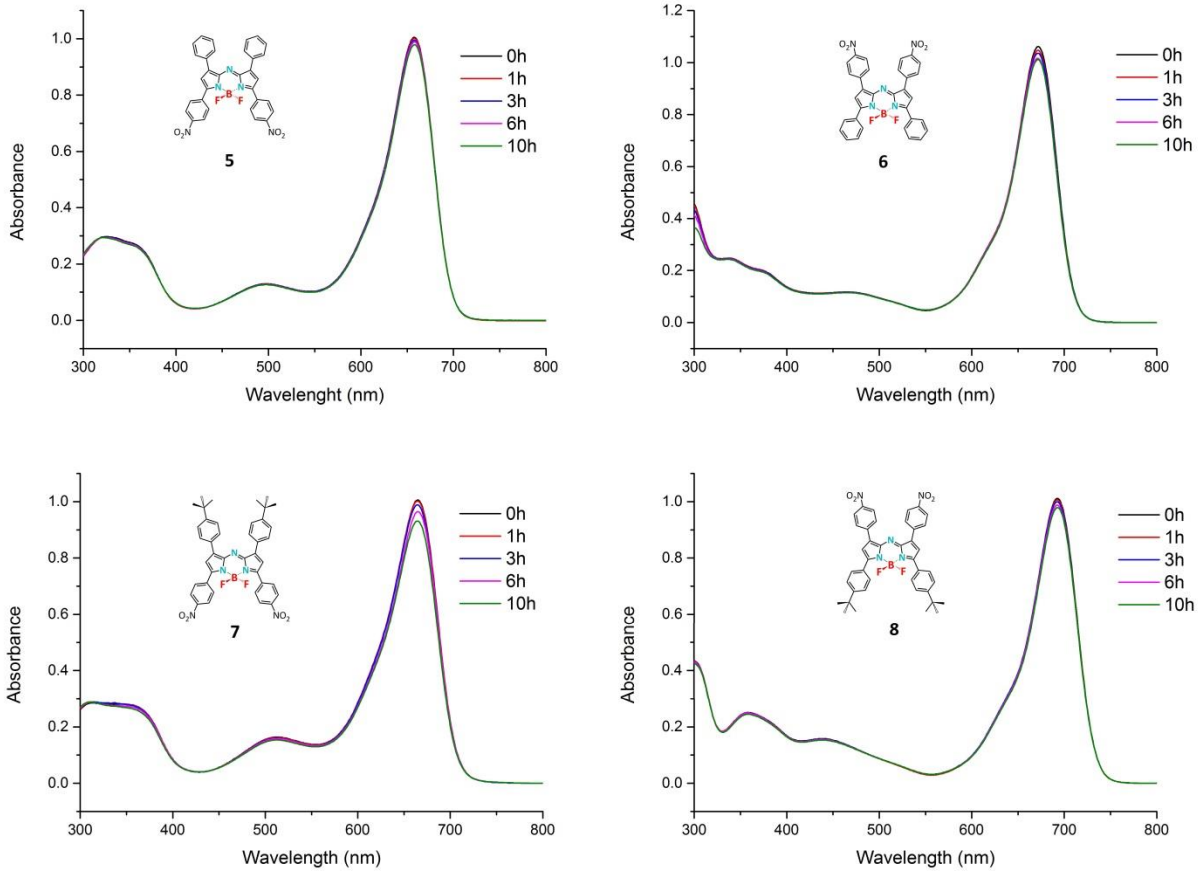

Figure S21. Electronic absorption spectra of THF solution of **5**, **6**, **7** and **8** recorded in air before and after 1, 3, 6 and 10 hours of irradiation with light at λ > 473 nm.

Table S1. Cartesian atomic coordinates and total electronic energies of the ground state optimized geometries of **Ref**, **5**, **6**, **7** and **8.** The energy minimization was performed with Gaussian 09 at the PBE0/6-311G(2d,p) level of theory. PCM model was used to simulate a THF medium. The integration grid was set as "ultrafine". The atomic Cartesian coordinates are reported in Å.

Compound Ref

Energy = -1620.2237383 a.u.

Cartesian atomic coordinates:

atom	X	Y	Z
C	-0.700334	-1.241959	-0.131214
C	-1.002022	-2.562273	-0.108135
C	0.191638	-3.313339	-0.111300
C	1.260991	-2.441049	-0.142074
C	0.681728	-1.132889	-0.119500
N	1.333733	0.000074	0.000055
N	-0.700612	1.241674	0.131484
C	0.681480	1.132928	0.119662
C	1.260446	2.441190	0.142235
C	0.190855	3.313272	0.111487
C	-1.002563	2.561941	0.108408
H	0.232288	-4.390461	-0.159323
H	0.231167	4.390407	0.159555
B	-1.633596	-0.000145	-0.000718
C	-2.332981	-3.160669	-0.084231
C	-3.436036	-2.617498	-0.749773
C	-4.659354	-3.266004	-0.719755
C	-4.809840	-4.457769	-0.023933
C	-3.721612	-5.006460	0.642083
C	-2.494477	-4.369198	0.606601
H	-3.329177	-1.695458	-1.303307
H	-5.502627	-2.836517	-1.249260
H	-5.771646	-4.958207	-0.000825
H	-3.829900	-5.933366	1.194161
H	-1.653998	-4.794990	1.142739
C	-2.333697	3.160019	0.084515
C	-3.435983	2.618000	0.752247
C	-4.659402	3.266346	0.722263
C	-4.810714	4.456784	0.024357
C	-3.723207	5.004358	-0.643752

C	-2.495965	4.367287	-0.608315
H	-3.328496	1.696982	1.307365
H	-5.502079	2.837787	1.253466
H	-5.772599	4.957073	0.001291
H	-3.832119	5.930247	-1.197415
H	-1.655992	4.792188	-1.145967
C	2.678491	-2.778127	-0.173663
C	3.628119	-1.919532	-0.739180
C	4.966317	-2.275915	-0.774117
C	5.383865	-3.491399	-0.248354
C	4.450938	-4.353061	0.314796
C	3.112976	-4.001053	0.350895
H	3.307735	-0.973467	-1.155614
H	5.687909	-1.600534	-1.220812
H	6.432339	-3.767106	-0.277265
H	4.768883	-5.301868	0.732895
H	2.394386	-4.670573	0.810984
C	2.677849	2.778671	0.173852
C	3.627813	1.920184	0.738974
C	4.965900	2.276978	0.773913
C	5.383022	3.492782	0.248553
C	4.449764	4.354347	-0.314198
C	3.111912	4.001927	-0.350300
H	3.307776	0.973863	1.155092
H	5.687742	1.601657	1.220296
H	6.431410	3.768812	0.277470
H	4.767360	5.303411	-0.731981
H	2.393087	4.671399	-0.810089
F	-2.417924	0.172727	-1.130766
F	-2.420129	-0.173147	1.127688

Compound 5

Energy = -2028.944668 a.u.

Cartesian atomic coordinates:

atom	X	Y	Z
N	0.241897	-1.239380	-0.140818
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C	1.132699	-3.313217	-0.128255
C	2.203108	-2.440923	-0.159323
C	1.622716	-1.131839	-0.128552
N	2.274534	-0.000076	0.000452
N	0.241902	1.239194	0.141690
C	1.622729	1.131718	0.129332
C	2.203067	2.440818	0.159355
C	1.132621	3.313048	0.127844
C	-0.057044	2.559364	0.121088
H	1.172669	-4.390168	-0.179500
H	1.172633	4.390021	0.178505
B	-0.692503	-0.000257	0.001893
C	-1.390942	-3.152493	-0.099182
C	-1.557343	-4.358783	0.595464
C	-2.782008	-4.992932	0.632299
C	-3.845586	-4.418652	-0.043499
C	-3.714482	-3.233540	-0.746471
C	-2.486988	-2.600238	-0.770252
H	-0.722147	-4.788741	1.134522
H	-2.925110	-5.916438	1.176416
N	-5.144693	-5.085966	-0.014116
H	-4.567910	-2.823044	-1.268893
H	-2.374267	-1.679852	-1.324665
O	-6.064780	-4.564360	-0.614827
O	-5.233704	-6.127083	0.609192
C	-1.390966	3.152408	0.099103
C	-1.556864	4.359291	-0.594716
C	-2.781419	4.993583	-0.631845
C	-3.845558	4.418841	0.042730
C	-3.715046	3.233075	0.744669
C	-2.487597	2.599672	0.768742
H	-0.721349	4.789588	-1.133001
H	-2.924000	5.917549	-1.175316
N	-5.144539	5.086316	0.013043

H	-4.568843	2.822059	1.266079
H	-2.375449	1.678850	1.322485
O	-6.065122	4.564209	0.612562
O	-5.232973	6.128011	-0.609396
C	3.619198	-2.777365	-0.196398
C	4.567348	-1.912706	-0.755703
C	5.905170	-2.268709	-0.795678
C	6.322936	-3.488782	-0.280764
C	5.391348	-4.356309	0.275894
C	4.053590	-4.005618	0.316332
H	4.246689	-0.963774	-1.165194
H	6.626197	-1.589970	-1.237865
H	7.371351	-3.764030	-0.313524
H	5.710446	-5.308470	0.685049
H	3.336111	-4.679709	0.771259
C	3.619146	2.777361	0.196006
C	4.053386	4.005475	-0.317184
C	5.391138	4.356236	-0.277111
C	6.322881	3.488909	0.279601
C	5.905273	2.268955	0.794925
C	4.567456	1.912893	0.755329
H	3.335810	4.679415	-0.772179
H	5.710104	5.308297	-0.686602
H	7.371290	3.764214	0.312068
H	6.626415	1.590353	1.237133
H	4.246920	0.964048	1.165127
F	-1.479606	0.182683	-1.123314
F	-1.475747	-0.183294	1.129932

Compound 6

Energy = -2028.946571 a.u.

Cartesian atomic coordinates:

atom	X	Y	Z
N	-1.743456	-1.244656	-0.120434
C	-2.047368	-2.563800	-0.084615
C	-0.851551	-3.315659	-0.073550
C	0.214298	-2.442503	-0.110405
C	-0.363817	-1.133918	-0.106530
N	0.289077	-0.000120	-0.000161
N	-1.743160	1.244731	0.120075
C	-0.363568	1.133826	0.106244
C	0.214732	2.442338	0.110490
C	-0.851036	3.315619	0.073880
C	-2.046941	2.563893	0.084677
H	-0.810671	-4.393150	-0.109296
H	-0.810097	4.393097	0.109890
B	-2.679349	0.000097	0.000272
C	-3.376664	-3.161905	-0.059796
C	-3.537703	-4.367090	0.637681
C	-4.765096	-5.002792	0.677164
C	-5.852645	-4.456944	0.007538
C	-5.702105	-3.269564	-0.695898
C	-4.479075	-2.621476	-0.729243
H	-2.698148	-4.790610	1.176941
H	-4.874252	-5.926256	1.234557
H	-6.814540	-4.956944	0.033211
H	-6.544972	-2.843728	-1.228729
H	-4.371816	-1.703936	-1.289942
C	-3.376194	3.162166	0.059717
C	-3.536958	4.367324	-0.637907
C	-4.764217	5.003242	-0.677541
C	-5.851922	4.457671	-0.007906
C	-5.701661	3.270345	0.695639
C	-4.478740	2.622019	0.729129
H	-2.697261	4.790591	-1.177142
H	-4.873209	5.926654	-1.235054
H	-6.813699	4.957893	-0.033686
H	-6.544623	2.844703	1.228476
H	-4.371747	1.704516	1.289942

C	1.631507	-2.777901	-0.134307
C	2.062528	-3.998727	0.400830
C	3.395430	-4.354704	0.375197
C	4.306413	-3.478973	-0.192856
C	3.917079	-2.264403	-0.732618
C	2.580320	-1.918017	-0.702088
H	1.344930	-4.667228	0.861298
H	3.739521	-5.291675	0.791561
N	5.717642	-3.848475	-0.223532
H	4.658651	-1.611718	-1.173144
H	2.261206	-0.975955	-1.126410
C	1.631965	2.777641	0.134367
C	2.062925	3.998851	-0.399961
C	3.395840	4.354764	-0.374368
C	4.306928	3.478588	0.192833
C	3.917665	2.263641	0.731796
C	2.580889	1.917324	0.701317
H	1.345264	4.667727	-0.859781
H	3.739864	5.292031	-0.790121
N	5.718168	3.848011	0.223442
H	4.659312	1.610602	1.171675
H	2.261840	0.974961	1.125012
O	6.500640	-3.063216	-0.724626
O	6.034854	-4.922199	0.253861
O	6.501245	3.062374	0.723824
O	6.035297	4.922070	-0.253259
F	-3.459434	0.163818	-1.130445
F	-3.458406	-0.163372	1.131757

Compound 7

Energy = -2343.1514321 a.u

Cartesian atomic coordinates:

atom	X	Y	Z
N	1.224068	-1.244653	0.111882
C	1.530497	-2.563554	0.065696
C	0.346451	-3.323767	0.059817
C	-0.730626	-2.458516	0.109115
C	-0.157214	-1.145703	0.102359
N	-0.816175	-0.015853	-0.006331
N	1.208223	1.238786	-0.120598
C	-0.171802	1.122240	-0.114320
C	-0.761777	2.427938	-0.123621
C	0.304217	3.306610	-0.071605
C	1.497849	2.561304	-0.074033
H	0.313167	-4.401699	0.090353
H	0.257741	4.384066	-0.102204
B	2.149630	0.003101	-0.002827
C	2.867980	-3.148243	0.031188
C	3.039435	-4.343492	-0.681314
C	4.267374	-4.970284	-0.730930
C	5.330194	-4.399733	-0.050637
C	5.194527	-3.225231	0.669166
C	3.963508	-2.599459	0.706015
H	2.204989	-4.770413	-1.223932
H	4.413705	-5.885184	-1.288577
N	6.632628	-5.059028	-0.093656
H	6.047380	-2.816999	1.194314
H	3.847714	-1.687611	1.273730
O	7.552066	-4.540688	0.511085
O	6.725599	-6.091000	-0.731664
C	2.827824	3.162675	-0.034736
C	2.982079	4.358813	0.680203
C	4.201915	5.000800	0.734740
C	5.273906	4.444658	0.056895
C	5.155178	3.269793	-0.665272
C	3.932176	2.628760	-0.707057
H	2.140655	4.774221	1.220934
H	4.335079	5.916511	1.294349
N	6.567898	5.120050	0.105177

H	6.014702	2.873122	-1.188390
H	3.829507	1.716465	-1.276570
O	7.495714	4.613972	-0.497141
O	6.645897	6.152234	0.744832
C	-2.142735	-2.802266	0.142014
C	-3.105926	-1.946397	0.691112
C	-4.437187	-2.311922	0.722873
C	-4.880311	-3.536658	0.213702
C	-3.916230	-4.384616	-0.329805
C	-2.578261	-4.029300	-0.363651
H	-2.800706	-0.992452	1.101097
H	-5.149311	-1.622329	1.163646
C	-6.361917	-3.894202	0.270546
H	-4.204463	-5.342947	-0.743349
H	-1.862579	-4.708747	-0.814067
C	-2.177773	2.754435	-0.160844
C	-2.628457	3.983135	0.338601
C	-3.966270	4.318074	0.299849
C	-4.924513	3.453440	-0.240792
C	-4.469573	2.235345	-0.741618
C	-3.128315	1.887842	-0.705065
H	-1.920865	4.673472	0.785091
H	-4.271880	5.276081	0.706648
C	-6.393399	3.863191	-0.263520
H	-5.167618	1.532774	-1.179628
H	-2.812119	0.935457	-1.110393
C	-6.651207	-5.264784	-0.338398
C	-6.822094	-3.908707	1.734816
C	-7.166965	-2.841747	-0.504179
H	-8.233162	-3.083093	-0.464474
H	-7.034888	-1.841159	-0.086013
H	-6.863094	-2.812822	-1.554036
H	-7.722493	-5.471393	-0.273846
H	-6.368332	-5.308772	-1.393668
H	-6.127372	-6.064497	0.192222
H	-7.886202	-4.156193	1.789779
H	-6.268414	-4.655233	2.310511
H	-6.678931	-2.937830	2.214572
C	-7.284296	2.791181	-0.888212
C	-6.871433	4.111334	1.173810
C	-6.546131	5.154337	-1.079222
H	-8.322722	3.131924	-0.878390
H	-7.011407	2.590524	-1.927767

H	-7.239132	1.850254	-0.332873
H	-7.595100	5.464165	-1.095811
H	-5.962027	5.973916	-0.654477
H	-6.218505	5.004875	-2.111499
H	-7.922754	4.413435	1.170947
H	-6.779073	3.204815	1.778012
H	-6.297562	4.902444	1.661706
F	2.933403	0.168321	1.128452
F	2.939156	-0.151637	-1.131580

Compound 8

Energy = -2343.1538983 a.u.

Cartesian atomic coordinates:

atom	X	Y	Z
N	-0.405682	-1.244799	-0.124189
C	-0.710516	-2.565446	-0.096347
C	0.487398	-3.315476	-0.090902
C	1.552263	-2.441495	-0.122796
C	0.973602	-1.133459	-0.110882
N	1.626907	-0.000048	0.000028
N	-0.405665	1.244689	0.124254
C	0.973606	1.133377	0.110972
C	1.552271	2.441411	0.123000
C	0.487402	3.315375	0.091219
C	-0.710526	2.565353	0.096593
H	0.530962	-4.392520	-0.134346
H	0.530980	4.392416	0.134752
B	-1.339884	-0.000081	0.000479
C	-2.035693	-3.165813	-0.074581
C	-2.192124	-4.400491	0.572828
C	-3.415364	-5.035426	0.605700
C	-4.542459	-4.487552	-0.016096
C	-4.376932	-3.266490	-0.666357
C	-3.156261	-2.611885	-0.695253
H	-1.348461	-4.850839	1.083429
H	-3.493038	-5.980565	1.131864
C	-5.875321	-5.225693	0.036784
H	-5.214346	-2.803161	-1.172685
H	-3.071548	-1.673271	-1.224132
C	-2.035664	3.165769	0.074824
C	-2.191873	4.400637	-0.572314

C	-3.415060	5.035632	-0.605355
C	-4.542377	4.487614	0.015921
C	-4.377095	3.266384	0.665903
C	-3.156448	2.611733	0.695009
H	-1.348042	4.851094	-1.082536
H	-3.492575	5.980940	-1.131237
C	-5.875190	5.225831	-0.037199
H	-5.214688	2.802913	1.171803
H	-3.071996	1.673040	1.223800
C	2.969672	-2.776245	-0.149598
C	3.918364	-1.912105	-0.711233
C	5.255177	-2.257947	-0.744890
C	5.645221	-3.476491	-0.214500
C	4.734428	-4.356489	0.347384
C	3.401523	-4.000875	0.376284
H	3.598740	-0.966776	-1.127826
H	5.996395	-1.601706	-1.180734
N	7.056182	-3.845435	-0.248504
H	5.078806	-5.296477	0.756672
H	2.684263	-4.672893	0.832150
C	2.969679	2.776182	0.149685
C	3.401430	4.000924	-0.376018
C	4.734331	4.356567	-0.347243
C	5.645227	3.476479	0.214327
C	5.255286	2.257826	0.744543
C	3.918476	1.911962	0.711025
H	2.684095	4.673016	-0.831655
H	5.078624	5.296646	-0.756393
N	7.056189	3.845442	0.248178
H	5.996584	1.601515	1.180149
H	3.598938	0.966551	1.127492
O	7.374090	-4.922462	0.221229
O	7.839018	-3.056669	-0.744565
O	7.839132	3.056554	0.743881
O	7.373992	4.922607	-0.221313
C	-6.982593	-4.475564	-0.700805
C	-5.713128	-6.608375	-0.609565
C	-6.299382	-5.396139	1.502228
H	-7.913063	-5.044802	-0.632779
H	-7.165052	-3.489248	-0.265791
H	-6.749902	-4.346588	-1.761288
H	-7.251980	-5.931199	1.554528
H	-5.563855	-5.966011	2.074496

H	-6.426831	-4.424755	1.987313
H	-6.661379	-7.152098	-0.569549
H	-5.416676	-6.517063	-1.657922
H	-4.960325	-7.211036	-0.096349
C	-6.982772	4.475437	0.699658
C	-5.713192	6.608243	0.609782
C	-6.298693	5.396886	-1.502732
H	-7.913214	5.044699	0.631453
H	-7.165046	3.489278	0.264210
H	-6.750527	4.346076	1.760192
H	-6.661410	7.152015	0.569630
H	-5.417146	6.516482	1.658214
H	-4.960170	7.211091	0.097106
H	-7.251261	5.931985	-1.555158
H	-5.562949	5.966980	-2.074500
H	-6.425983	4.425704	-1.988263
F	-2.121241	0.166663	-1.129961
F	-2.120207	-0.166798	1.131654

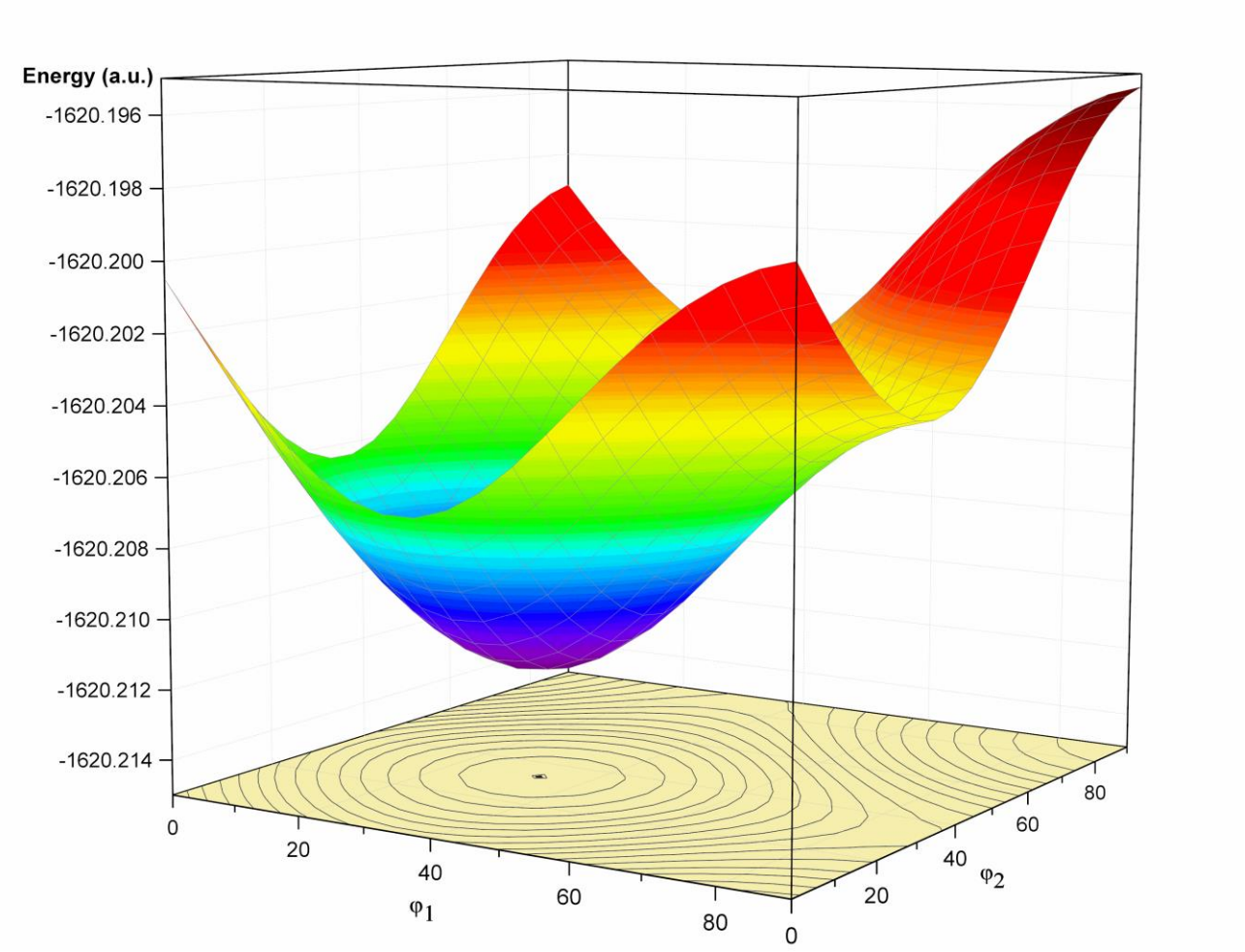

Figure S22. A fragment of PES corresponding to the tilts of the proximal rings in the **Ref** molecule. Obtained from a rigid scan with PBE0/6-311G(2d,p) over the geometry optimized at the same level.

Table S2. Contributions (in %) of the aza-BODIPY core, proximal and distal rings in **5**, **6**, **7**, **8** and **Ref** to the frontiers molecular orbitals (for definition of the division refer to **Figure 8** in the manuscript).

		Aza-BODIPY core	P1	P2	D1	D2
HOMO/LUMO	**Ref**	66/74	11/7	11/7	6/6	6/6
	5	65/66	9/12	9/12	9/5	9/5
	6	66/69	13/7	13/7	4/9	4/9
	7	60/65	8/12	8/12	12/6	12/6
	8	62/67	16/7	16/7	3/9	3/9

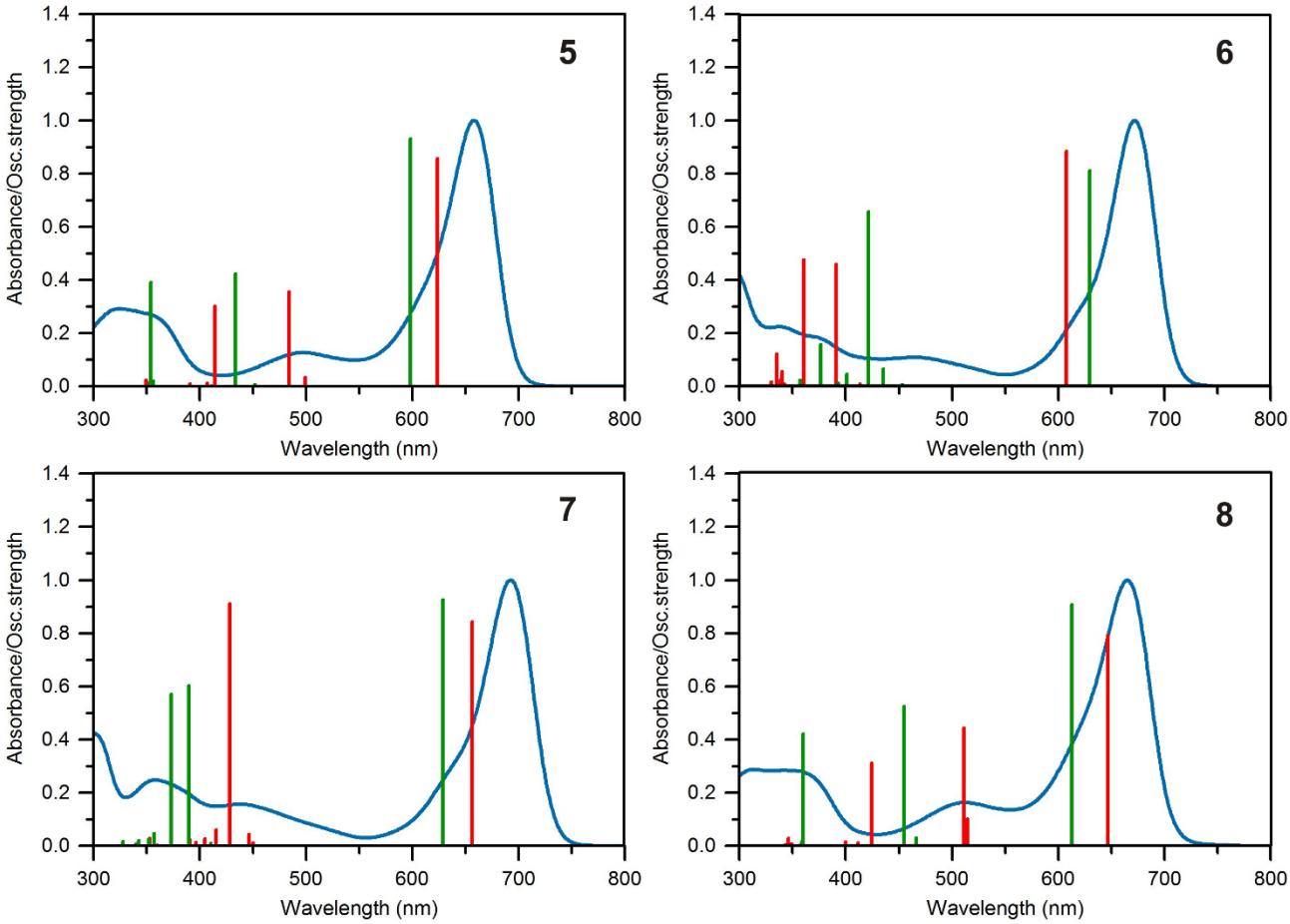

Figure S23. Experimental electronic absorption (**blue line**) spectra and computed electronic transitions of **5, 6, 7** and **8** computed by TDDFT with BMK/6-311+G(2d,p) (**green bars**) or by TDDFT with PBE0/6-311+G(2d,p) (**red bars**).

Table S3. Characteristics of the strongest electronic transitions in **5, 6, 7** and **8** as calculated with the BMK/6-311G*//PBE0/6-31G*. Change of the electronic density distribution (%) in the ADPM core, the proximal (P1, P2) and the distal (D1, D2) rings are listed in the last five columns. The analysis was performed with the GaussSum 3.0 program.

	No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Major contributions	ADPM	P1	P2	D1	D2
	1	16715.0	598.3	0.931	HOMO->LUMO (99%)	65-->66 (1)	9-->12 (3)	9-->12 (3)	9-->5 (-4)	9-->5 (-4)
5	3	23052.1	433.8	0.424	H-2->LUMO (96%)	41-->66 (25)	1-->12 (11)	1-->12 (11)	29-->5 (-24)	28-->5 (-23)
	5	28250.4	354.0	0.392	HOMO->L+1 (92%)	63-->10 (-53)	8-->45 (37)	8-->45 (37)	10-->0 (-10)	10-->0 (-10)
	1	16459.4	607.6	0.883	HOMO->LUMO (99%)	66-->69 (3)	13-->7 (-6)	13-->7 (-6)	4-->9 (5)	4-->9 (5)
6	3	25567.0	391.1	0.459	H-2->LUMO (89%)	44-->69 (25)	7-->7 (0)	7-->7 (0)	21-->9 (-12)	21-->9 (-12)
	4	27735.8	360.5	0.476	HOMO->L+1 (91%)	64-->10 (-54)	14-->1 (-13)	14-->1 (-13)	4-->44 (40)	4-->44 (40)
	1	16318.2	612.8	0.907	HOMO->LUMO (99%)	60-->65 (5)	8-->12 (4)	8-->12 (4)	12-->6 (-6)	12-->6 (-6)
7	3	21976.2	455.0	0.525	H-1->LUMO (95%)	36-->65 (29)	1-->12 (11)	1-->12 (11)	35-->6 (-29)	28-->6 (-22)
	4	27781.8	359.9	0.421	HOMO->L+1 (95%)	60-->8 (-52)	8-->46 (38)	8-->46 (38)	12-->0 (-12)	12-->0 (-12)
	1	15899.6	628.9	0.926	HOMO->LUMO (99%)	62-->67 (5)	16-->7 (-9)	16-->7 (-9)	3-->9 (6)	3-->9 (6)
8	3	25667.0	389.6	0.603	H-3->LUMO (37%), H-1->LUMO (54%)	44-->67 (23)	12-->7 (-5)	12-->7 (-5)	16-->9 (-7)	16-->9 (-7)
	4	26789.7	373.3	0.570	H-1->LUMO (12%), HOMO->L+1 (80%)	60-->17 (-43)	15-->1 (-14)	15-->1 (-14)	6-->40 (34)	6-->40 (34)