Supporting Information

Synthesis and In Vitro Studies of a Series of Carborane-containing Boron Dipyrromethenes

Sunting Xuan[†], Ning Zhao[†], Zehua Zhou[†], Frank R. Fronczek[†] and M. Graça H. Vicente*[†]

[†]*Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States*

*corresponding author: vicente@lsu.edu

Table of Contents

1. ^{1}H-NMR and ^{13}C-NMR spectra of carboranyl BODIPYs

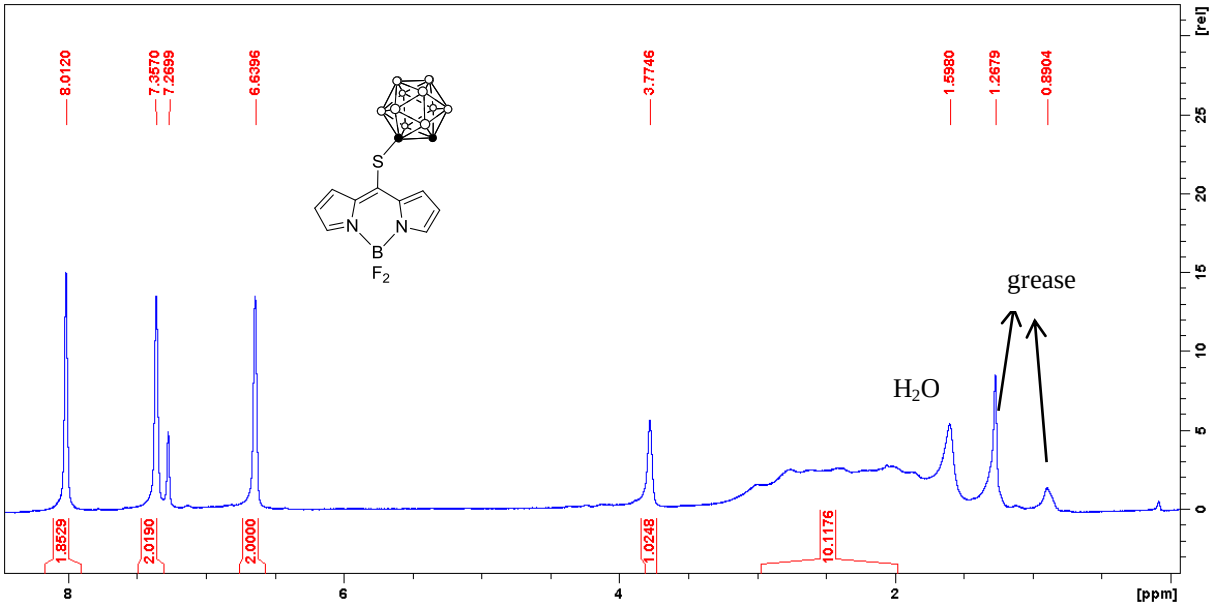


Figure S1. ^{1}H-NMR spectrum of BODIPY**1b**.

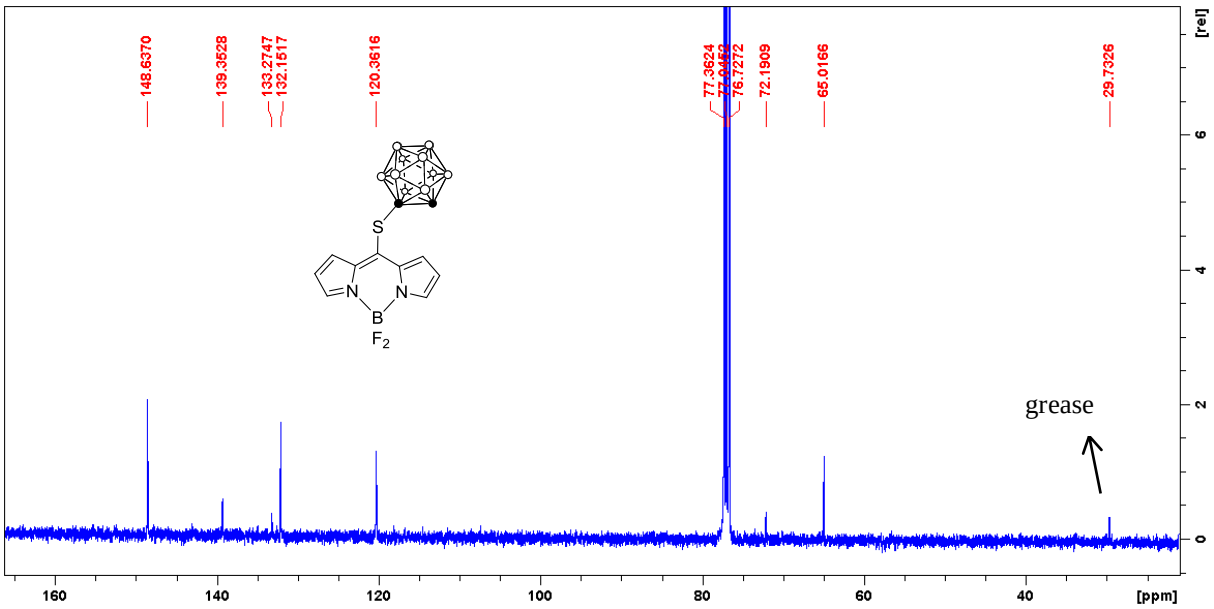


Figure S2. ^{13}C-NMR spectrum of BODIPY**1b**.

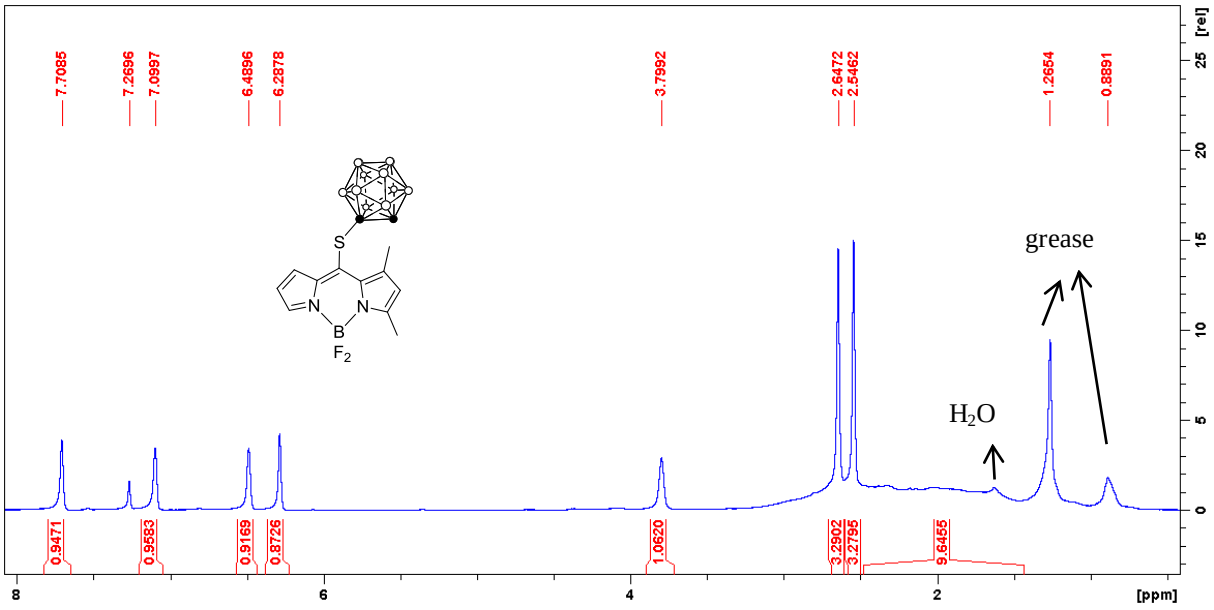


Figure S3. ^{1}H-NMR spectrum of BODIPY**2b**.

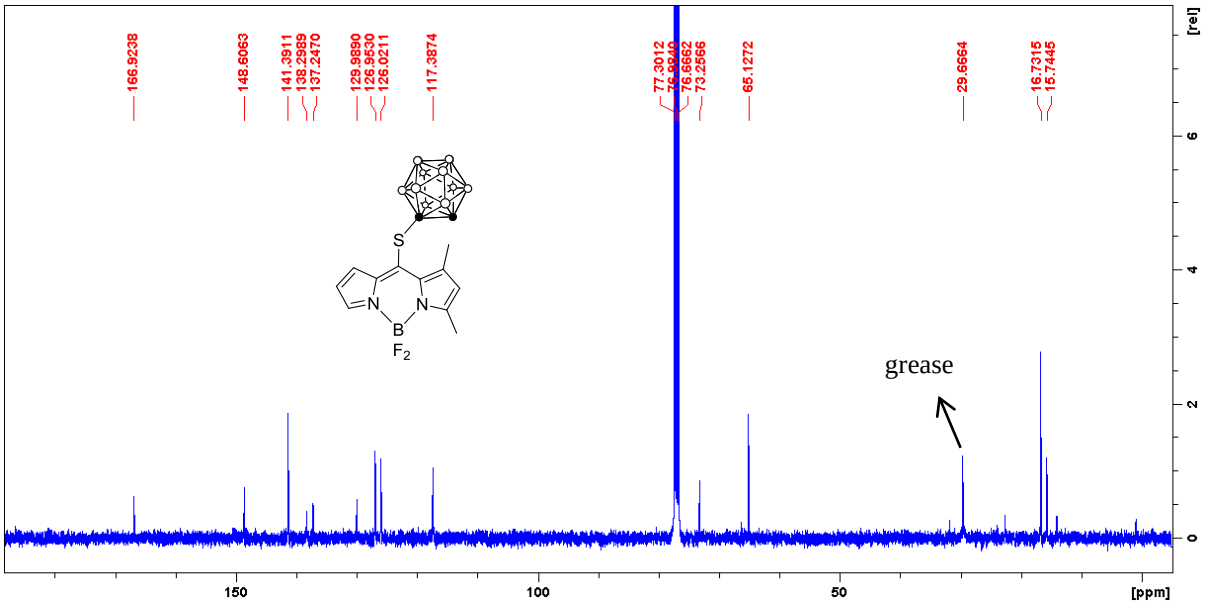


Figure S4. ^{13}C-NMR spectrum of BODIPY**2b**.

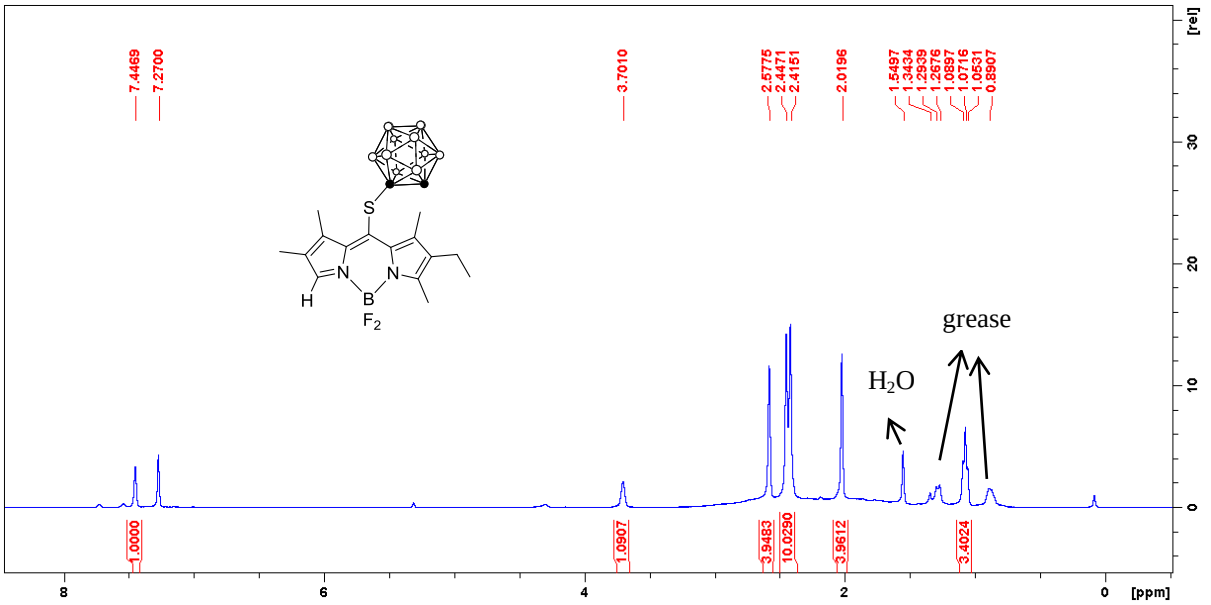


Figure S5. ^{1}H-NMR spectrum of BODIPY **5b**.

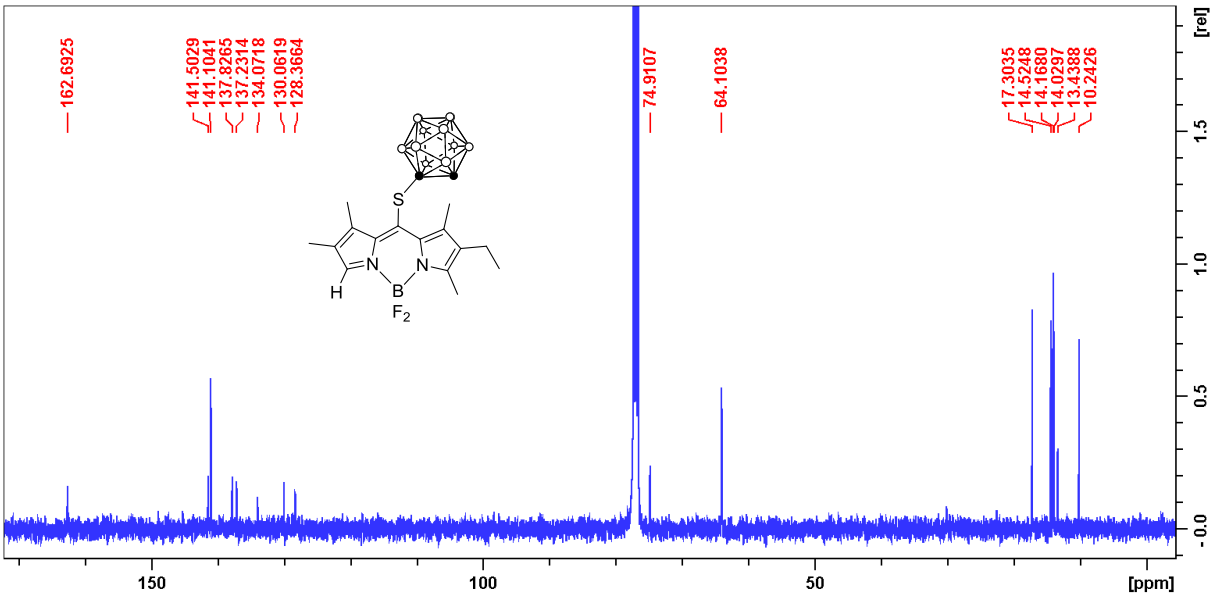


Figure S6. ^{13}C-NMR spectrum of BODIPY**5b**.

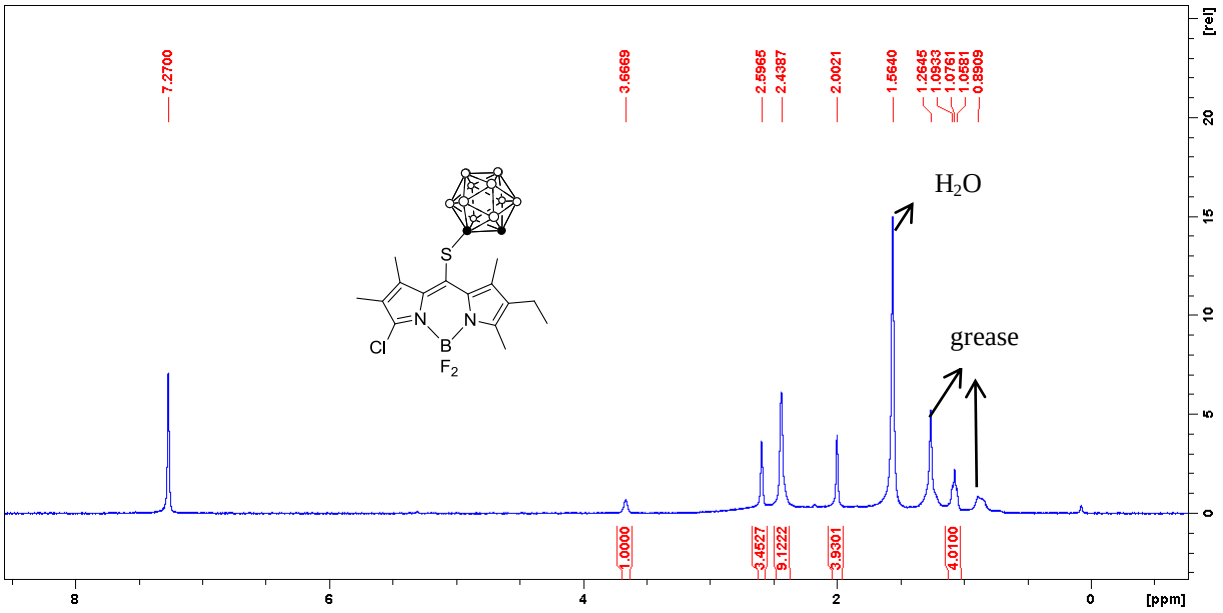


Figure S7. ^{1}H-NMR spectrum of BODIPY**6b**.

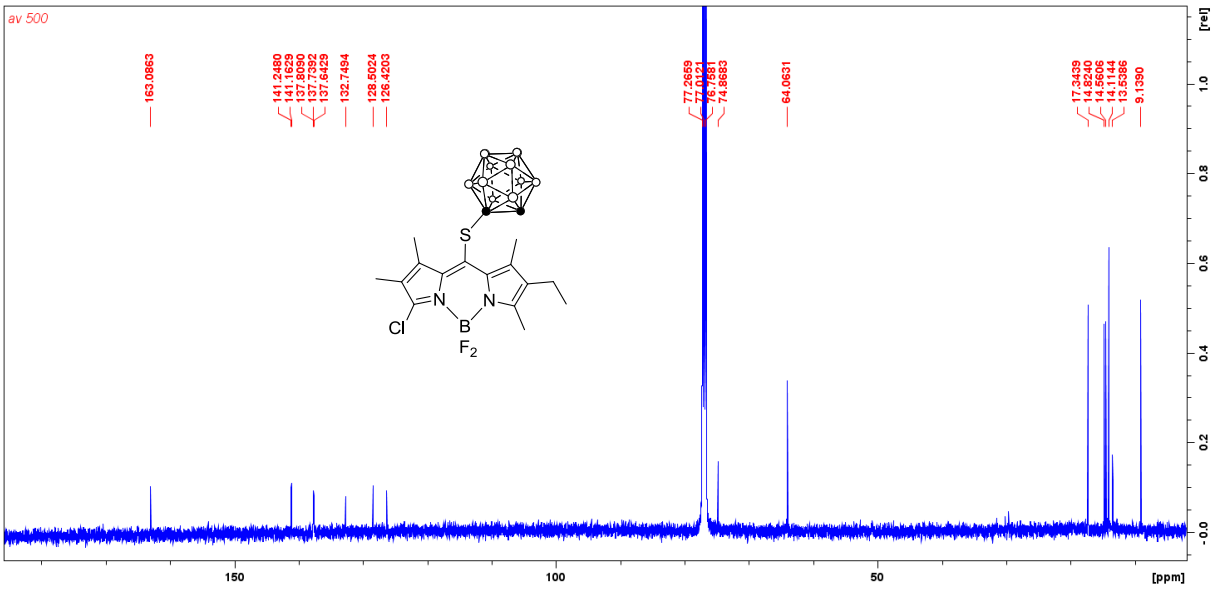


Figure S8. ^{13}C-NMR spectrum of BODIPY**6b**.

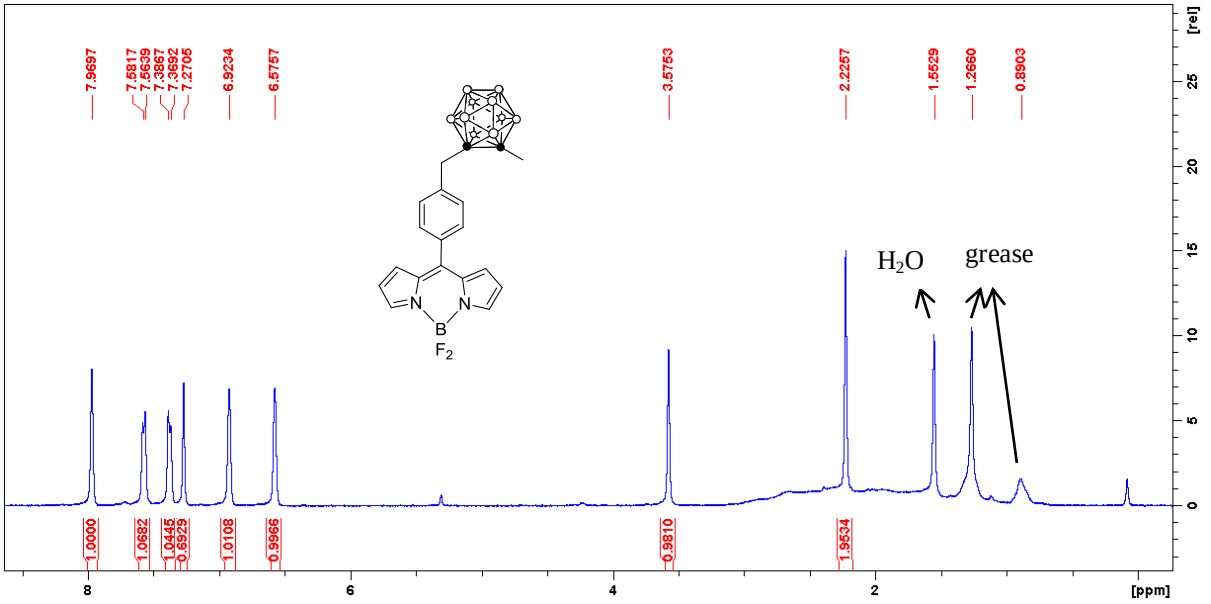


Figure S9. ^{1}H-NMR spectrum of BODIPY**4.**

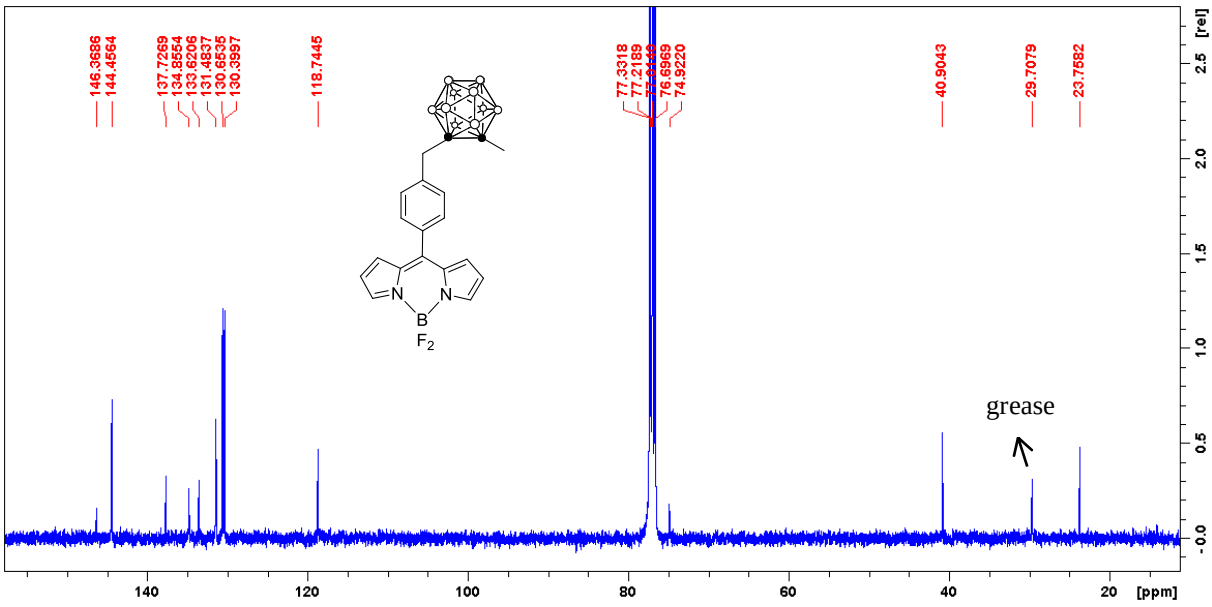


Figure S10. ^{13}C-NMR spectrum of BODIPY**4**.

2. ^{11}B-NMR spectra of carboranyl BODIPYs

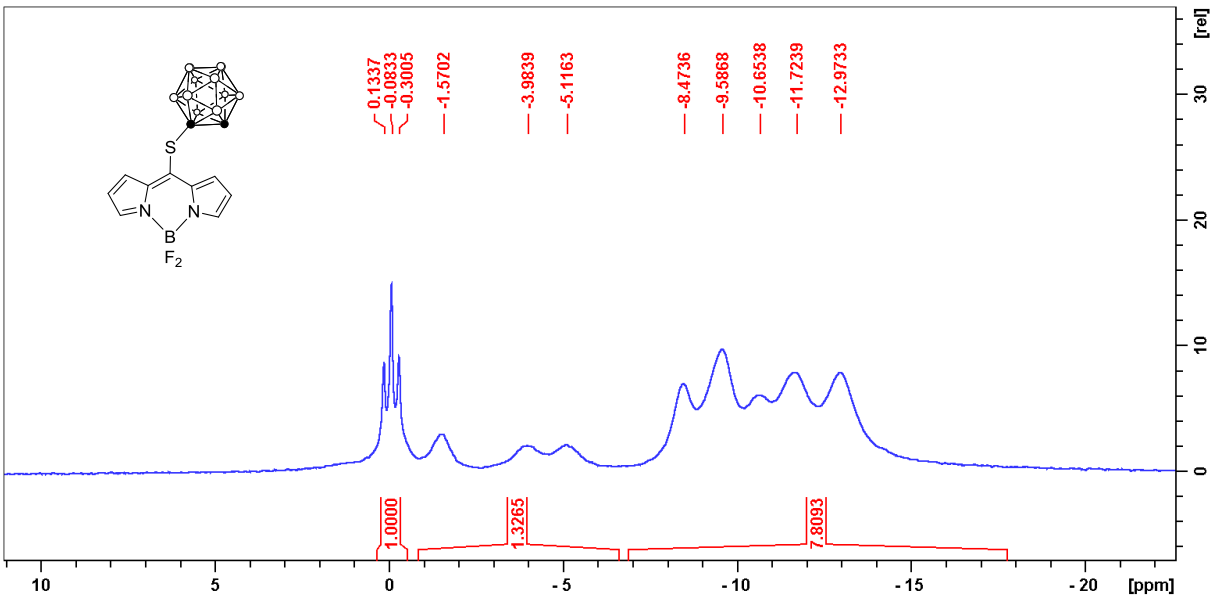


Figure S11. ^{11}B-NMR spectrum of BODIPY **1b**.

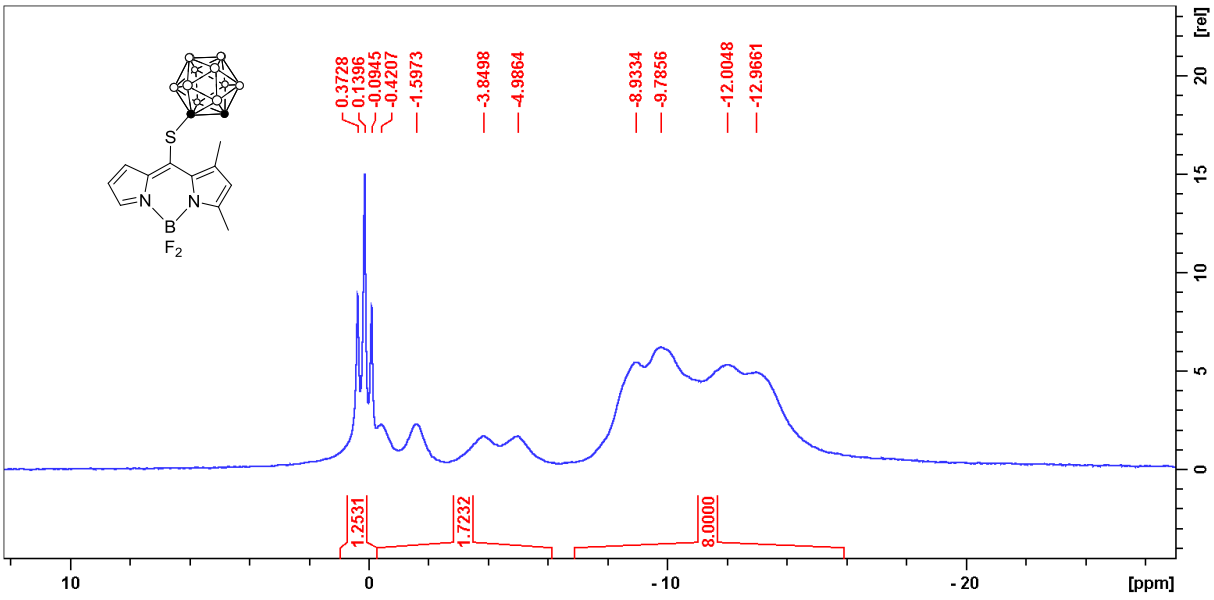


Figure S12. ^{11}B-NMR spectrum of BODIPY **2b**.

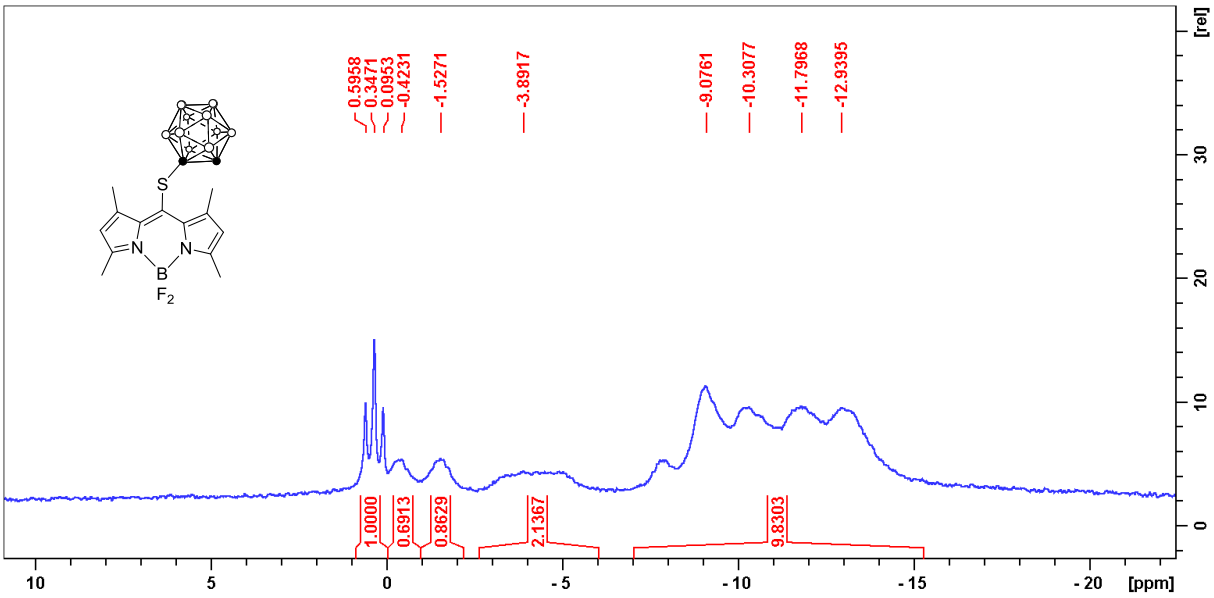


Figure S13. ^{11}B-NMR spectrum of BODIPY**3b**.

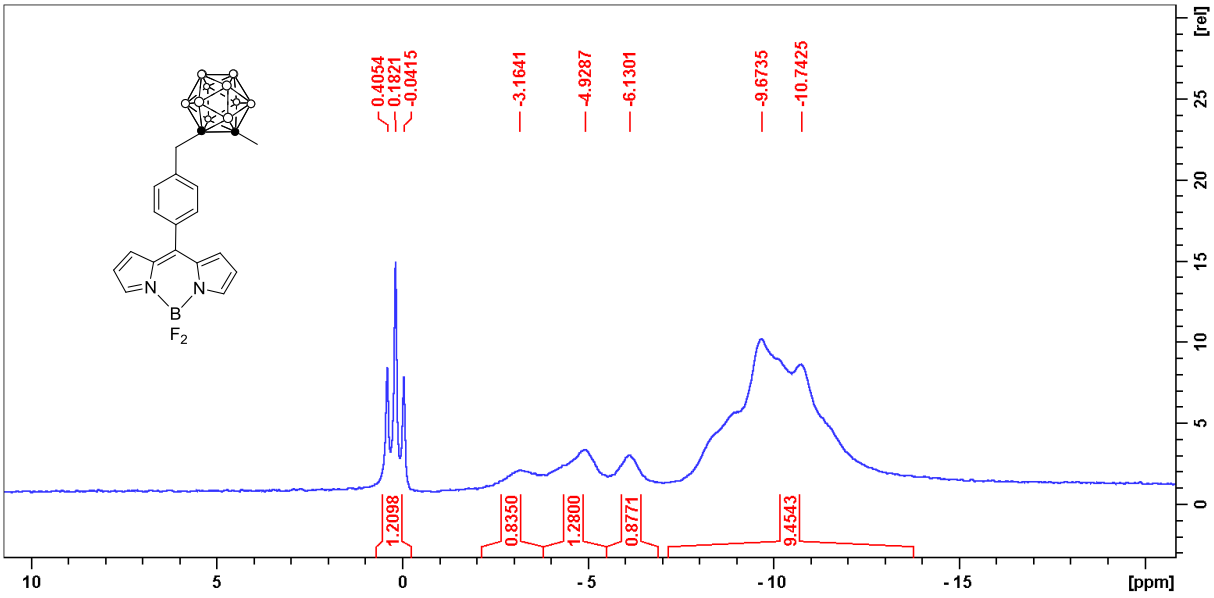


Figure S14. ^{11}B-NMR spectrum of BODIPY **4**.

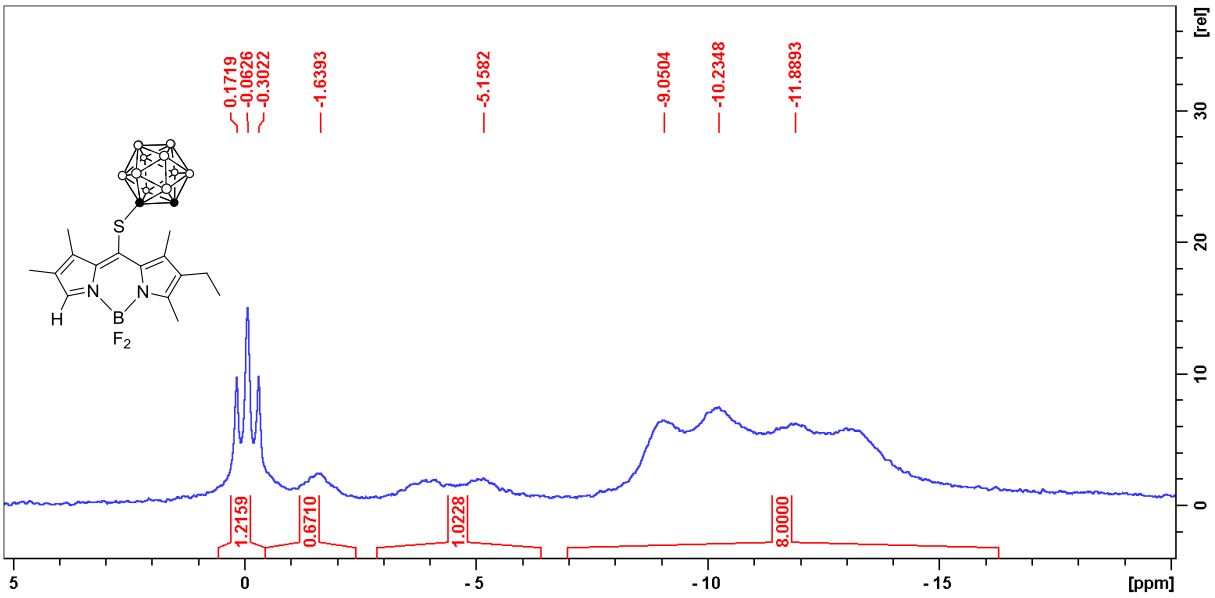


Figure S15. ^{11}B-NMR spectrum of BODIPY **5b**.

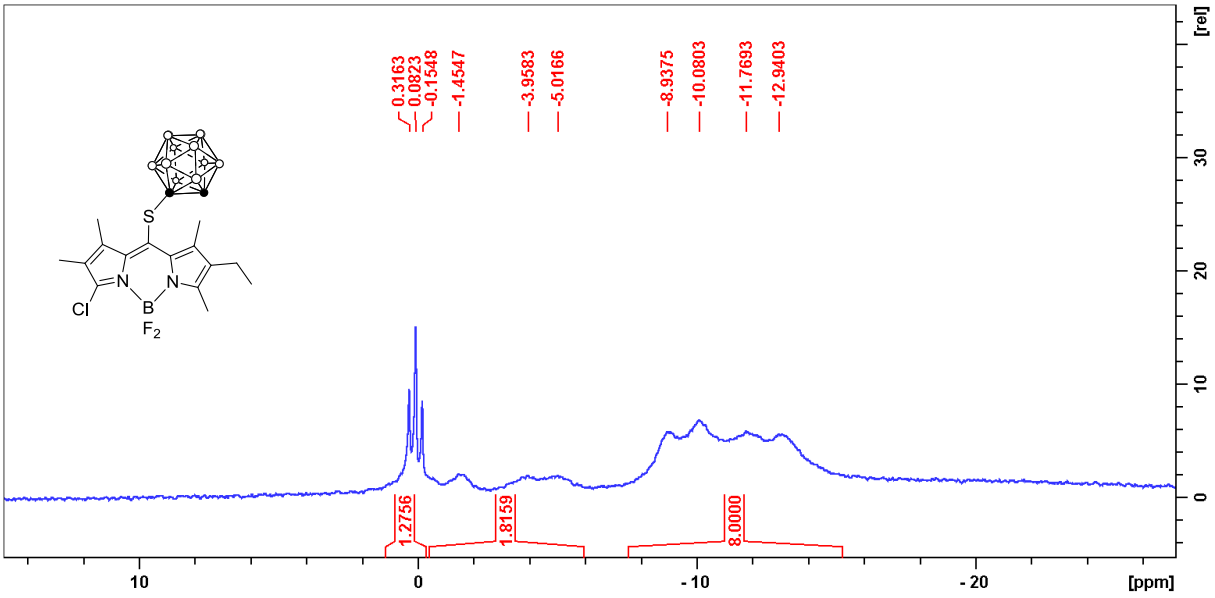


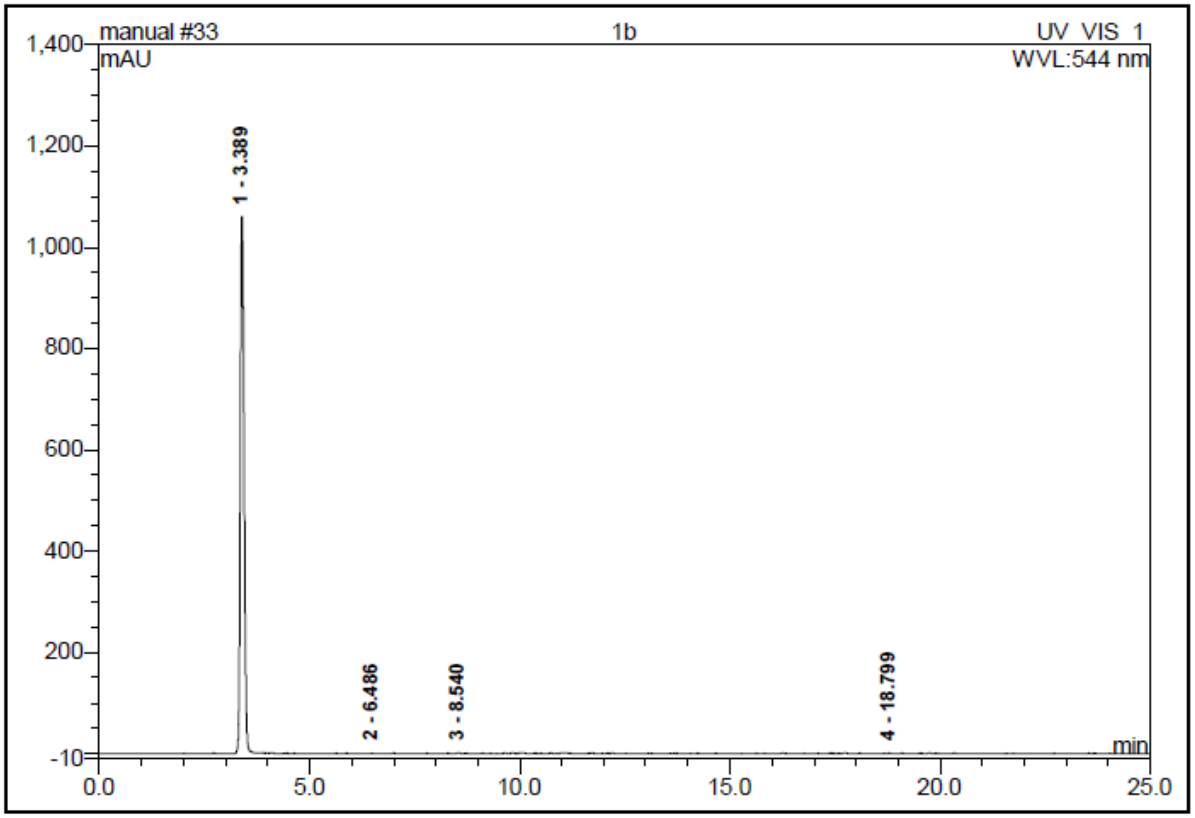
Figure S16. ^{11}B-NMR spectrum of BODIPY **6b**.

3. HPLC conditions

General: Dionex system including a P680 pump and a UVD 340 detector connected to a Dynamax axial compression column packed with Rainin 60 Å irregular silica gel; flow rate: 1mL/min.; injected 20□L; wavelength detection: 544 nm for **1b**, 537 nm for **2b**, 554 nm for **3b**, 502 nm for **4**, 582 nm for **6b** and 521 nm for **7**.

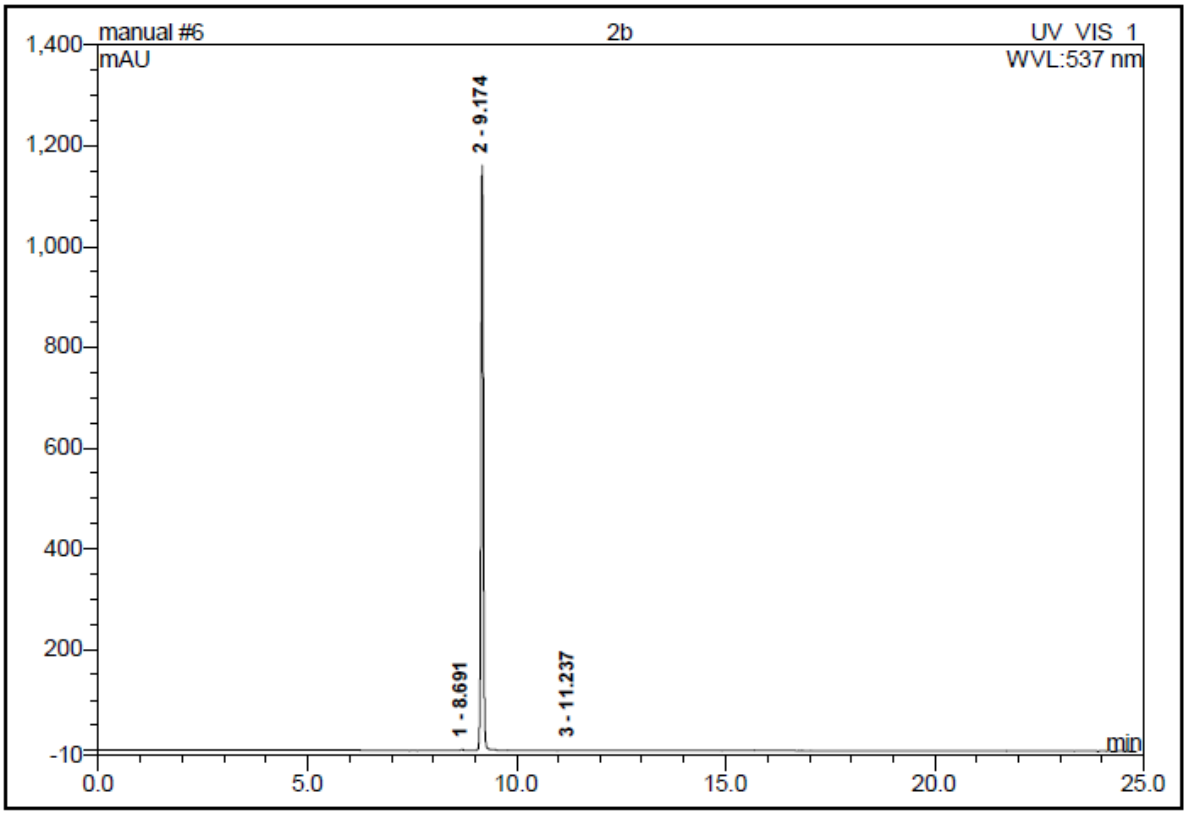
Solvent system 1: stepwise gradient 10% B and 90% A at 0-5 min, 70% B and 30% A at 10-15 min, 10% B and 90% A at 20-25 min. A (hexane), B (EtOAC).

Solvent system 2: stepwise gradient 50% B and 50% A at 0-3 min, 80% B and 20% A at 6-21 min, 50% B and 50% A at 25-27 min. A (hexane), B (EtOAC).



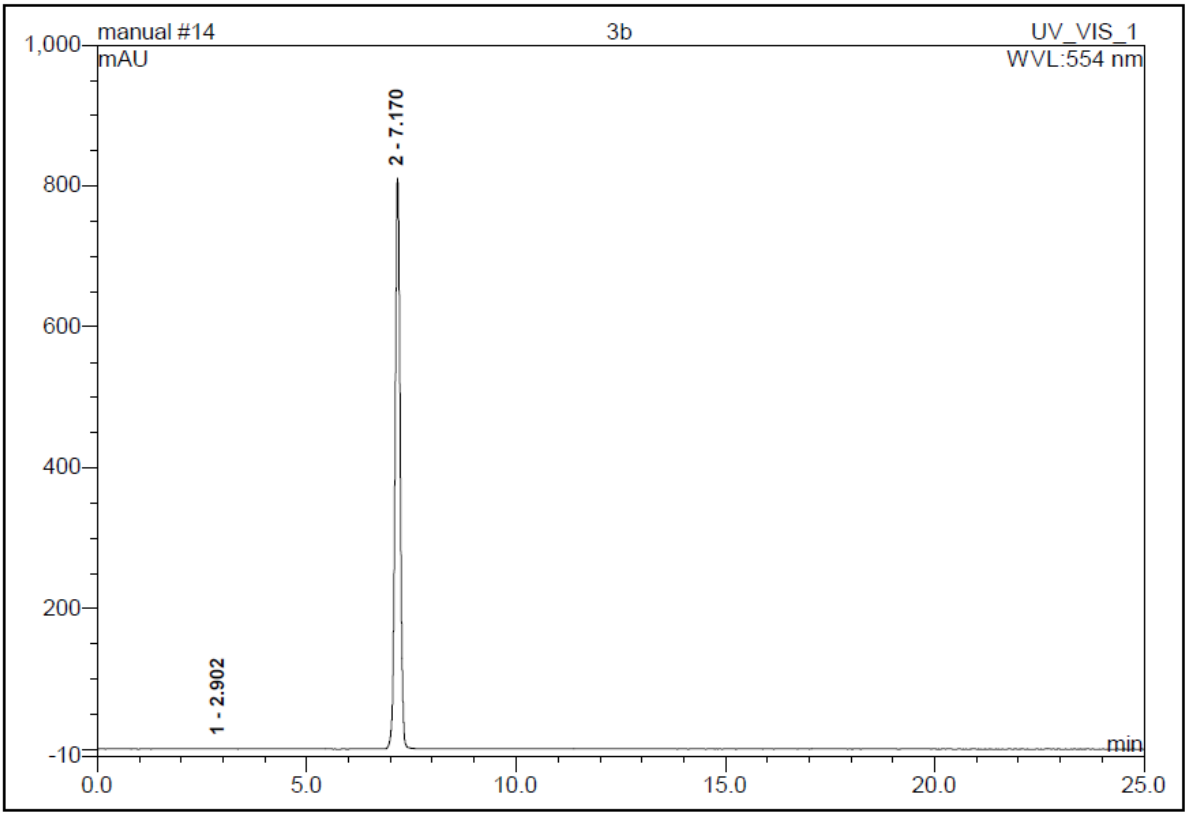
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Pos.	Type
1	3.39	n.a.	1058.790	108.247	99.90	n.a.	BMB
2	6.49	n.a.	0.378	0.033	0.03	n.a.	BMB
3	8.54	n.a.	0.390	0.032	0.03	n.a.	BMB
4	18.80	n.a.	0.316	0.041	0.04	n.a.	BMB
Total:			1059.874	108.353	100.00	0.000	

Figure S17. HPLC trace for BODIPY **1b**, solvent system 2.



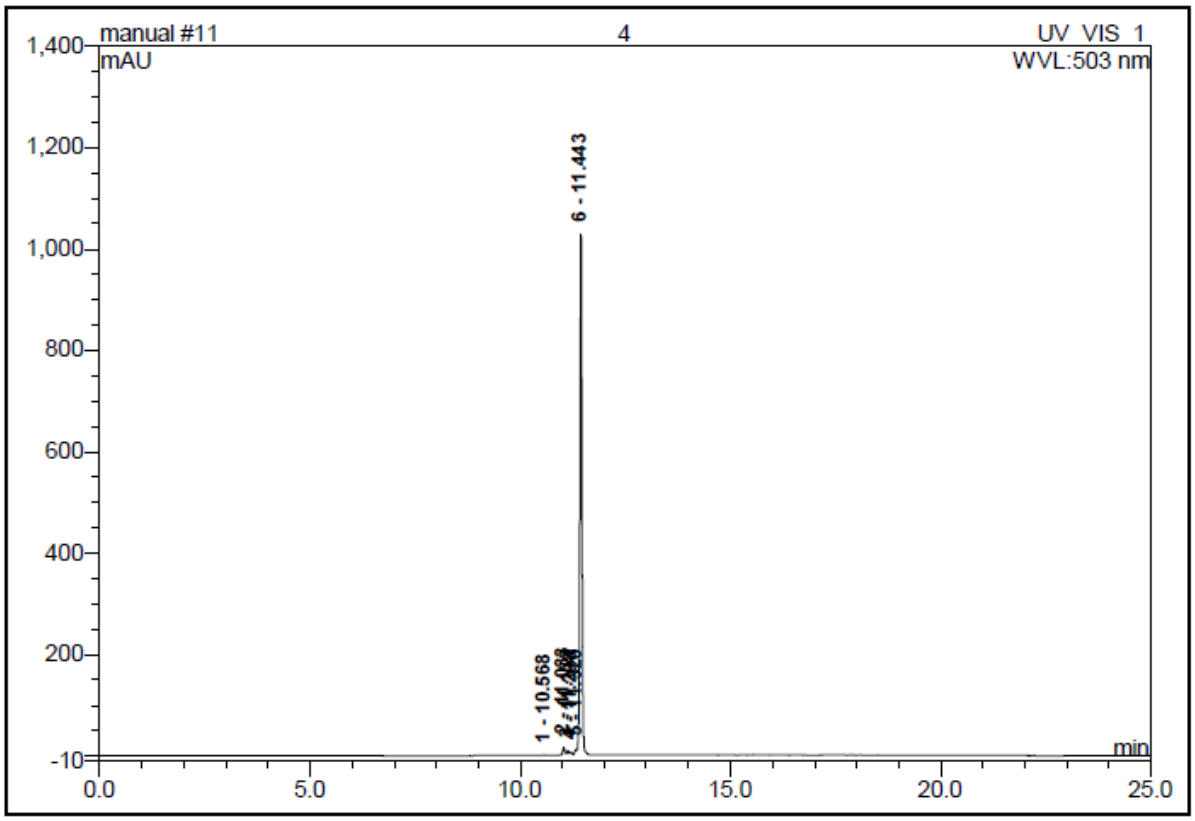
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Pos.	Type
1	8.69	n.a.	1.781	0.145	0.20	n.a.	BMB
2	9.17	n.a.	1158.645	72.917	99.75	n.a.	BMB
3	11.24	n.a.	0.276	0.041	0.06	n.a.	BMB
Total:			1160.702	73.103	100.00	0.000	

Figure S18. HPLC trace for BODIPY **2b**, solvent system 1.



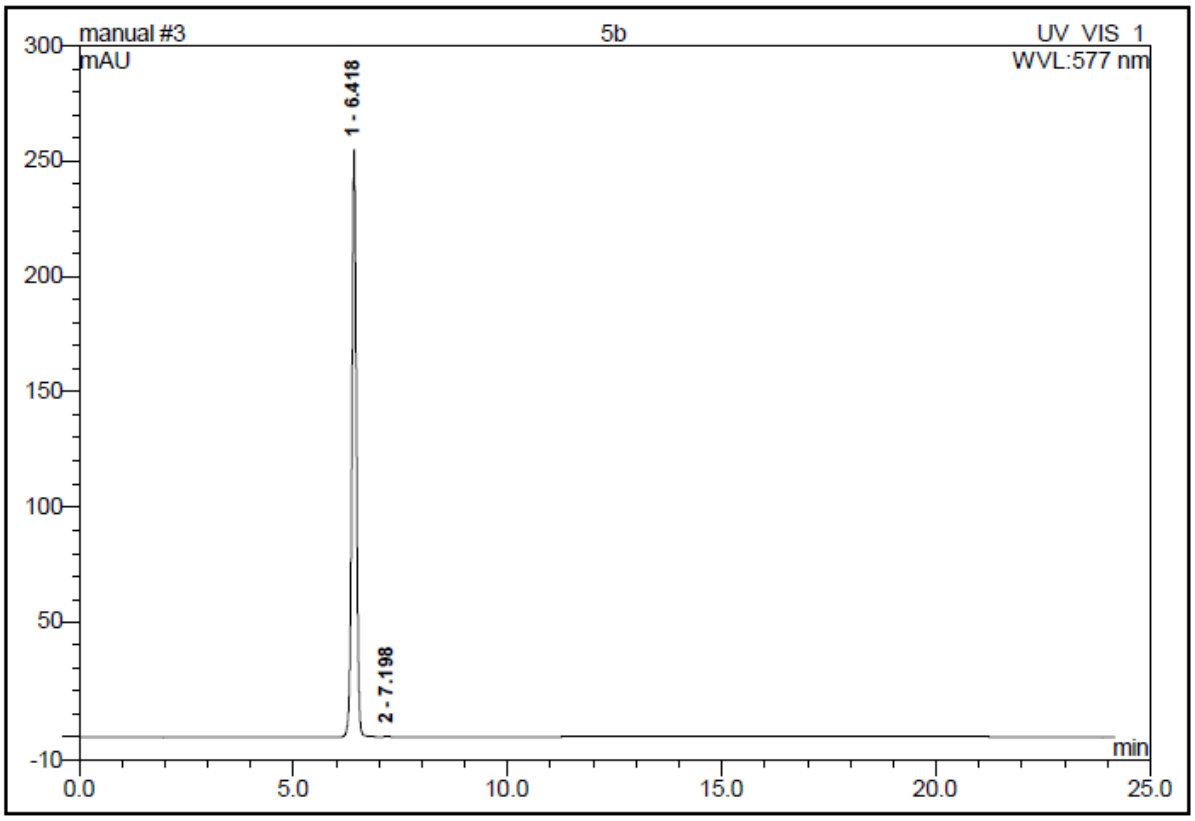
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Pos.	Type
1	2.90	n.a.	0.840	0.076	0.07	n.a.	BMB
2	7.17	n.a.	808.123	113.015	99.93	n.a.	BMB
Total:			808.964	113.090	100.00	0.000	

Figure S19. HPLC trace for BODIPY **3b**, solvent system 1.



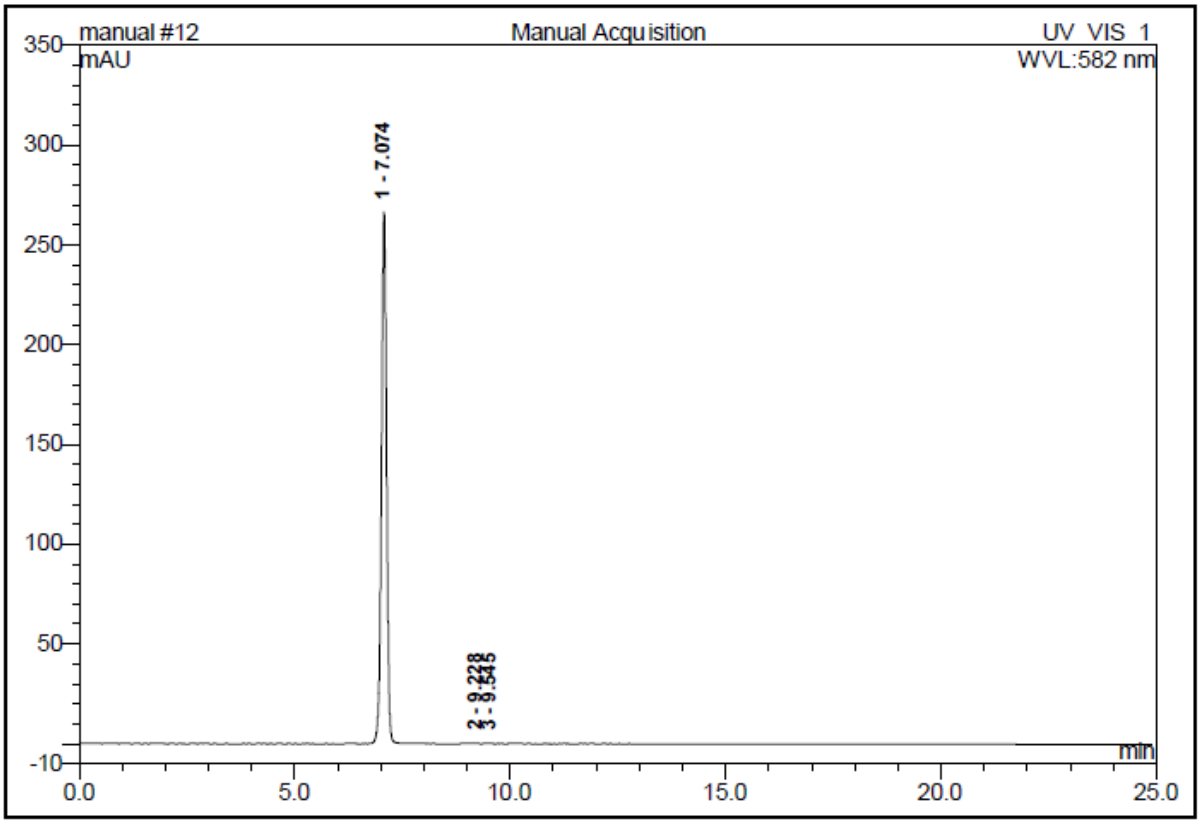
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Pos.	Type
1	10.57	n.a.	0.474	0.042	0.07	n.a.	BMB
2	11.03	n.a.	14.449	0.798	1.34	n.a.	BM
3	11.13	n.a.	7.880	0.421	0.71	n.a.	M
4	11.21	n.a.	4.142	0.193	0.33	n.a.	MB
5	11.32	n.a.	8.984	0.413	0.69	n.a.	BM
6	11.44	n.a.	1023.704	57.500	96.86	n.a.	MB
Total:			1059.633	59.367	100.00	0.000	

Figure S20. HPLC trace for BODIPY **4**, solvent system 1.



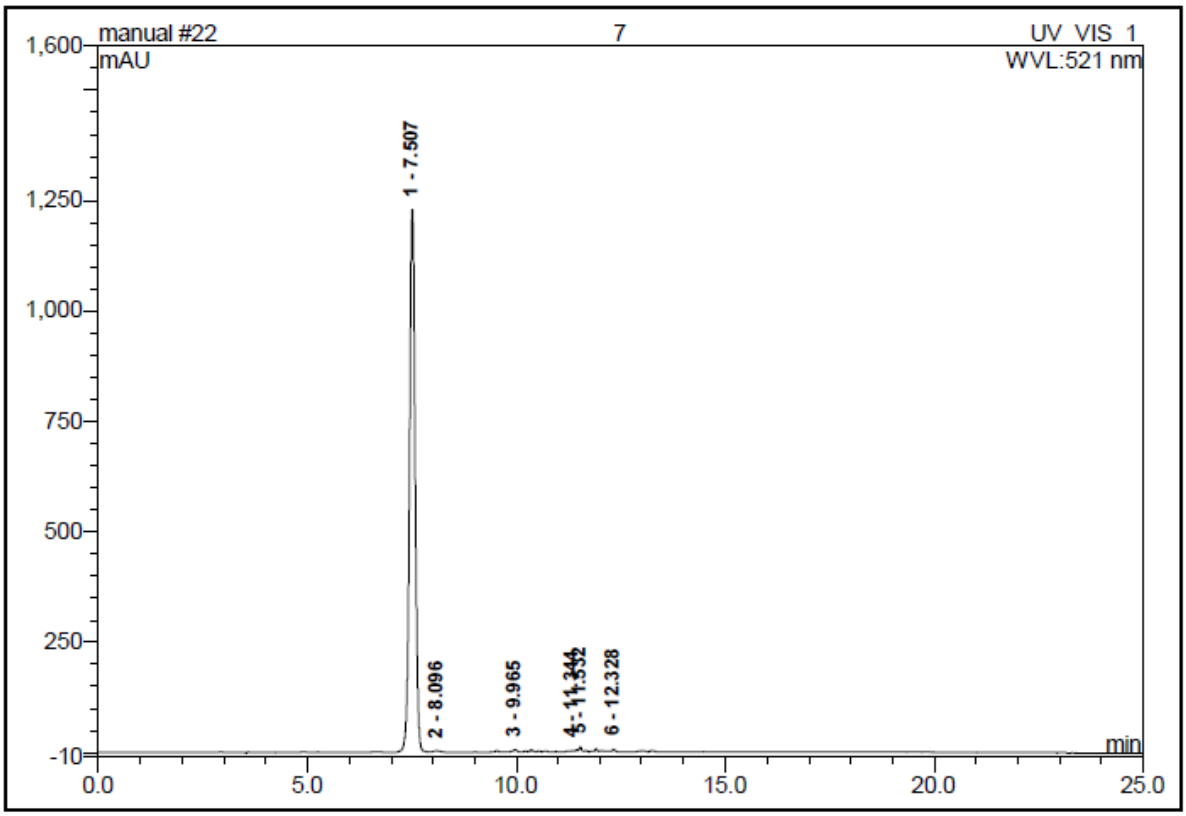
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Pos.	Type
1	6.42	n.a.	254.054	31.278	99.90	n.a.	BMB
2	7.20	n.a.	0.187	0.031	0.10	n.a.	BMB
Total:			254.242	31.309	100.00	0.000	

Figure S21. HPLC trace for BODIPY **5b**, solvent system 1.



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Pos.	Type
1	7.07	n.a.	266.472	36.392	99.62	n.a.	BMB
2	9.23	n.a.	0.176	0.101	0.28	n.a.	BM
3	9.55	n.a.	0.206	0.037	0.10	n.a.	MB
Total:			266.854	36.530	100.00	0.000	

Figure S22. HPLC trace for BODIPY **6b**, solvent system 1.



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Pos.	Type
1	7.51	n.a.	1225.251	192.805	98.91	n.a.	BMB
2	8.10	n.a.	2.630	0.400	0.21	n.a.	BMB
3	9.97	n.a.	4.524	0.416	0.21	n.a.	BMB
4	11.34	n.a.	1.855	0.084	0.04	n.a.	Ru
5	11.53	n.a.	10.341	0.918	0.47	n.a.	BMB
6	12.33	n.a.	5.302	0.316	0.16	n.a.	BMB
Total:			1249.902	194.938	100.00	0.000	

Figure S23. HPLC trace for BODIPY **7**, solvent system 1.

4. Figure of *in vitro* BBB model

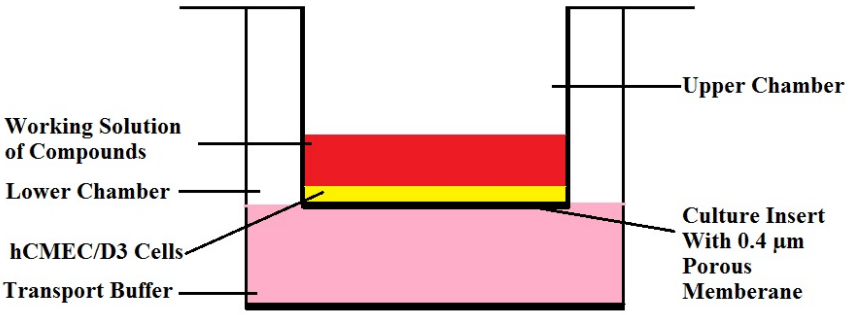


Figure S24. The blood-brain mimic for experimental *in vitro* BBB study. The upper chamber mimics the blood compartment, the lower chamber mimics the cerebral compartment, and the hCMEC/D3 cell monolayer represents the BBB.

5. Dark and phototoxicity graphs

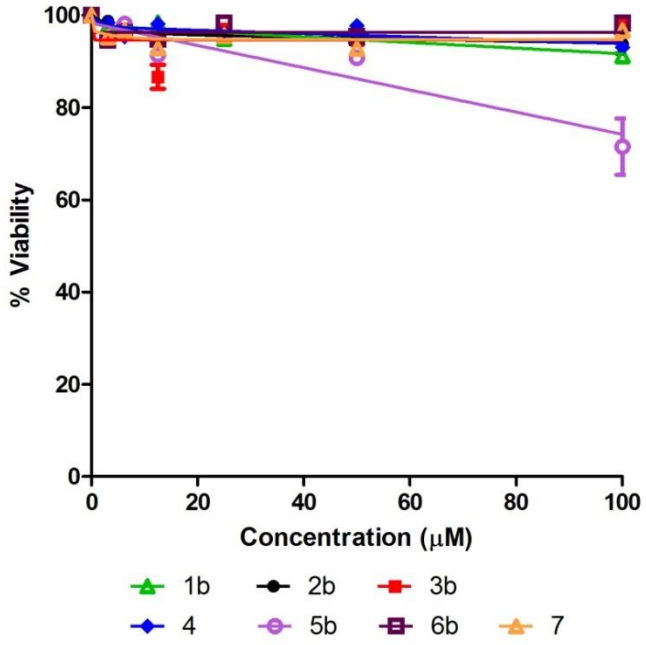


Figure S25. Dark cytotoxicity of **1b-7** using human glioma T98G cells.

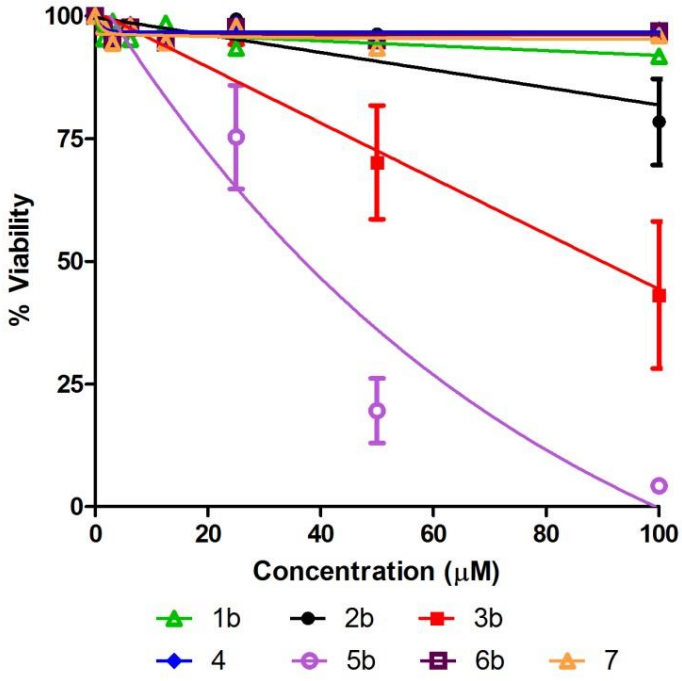


Figure S26. Phototoxicity (~1.5 J/cm^2) of **1b-7** using human glioma T98G cells.

6. Subcellular localization of BODIPY 1b, 2b, 3b, 4, 7.

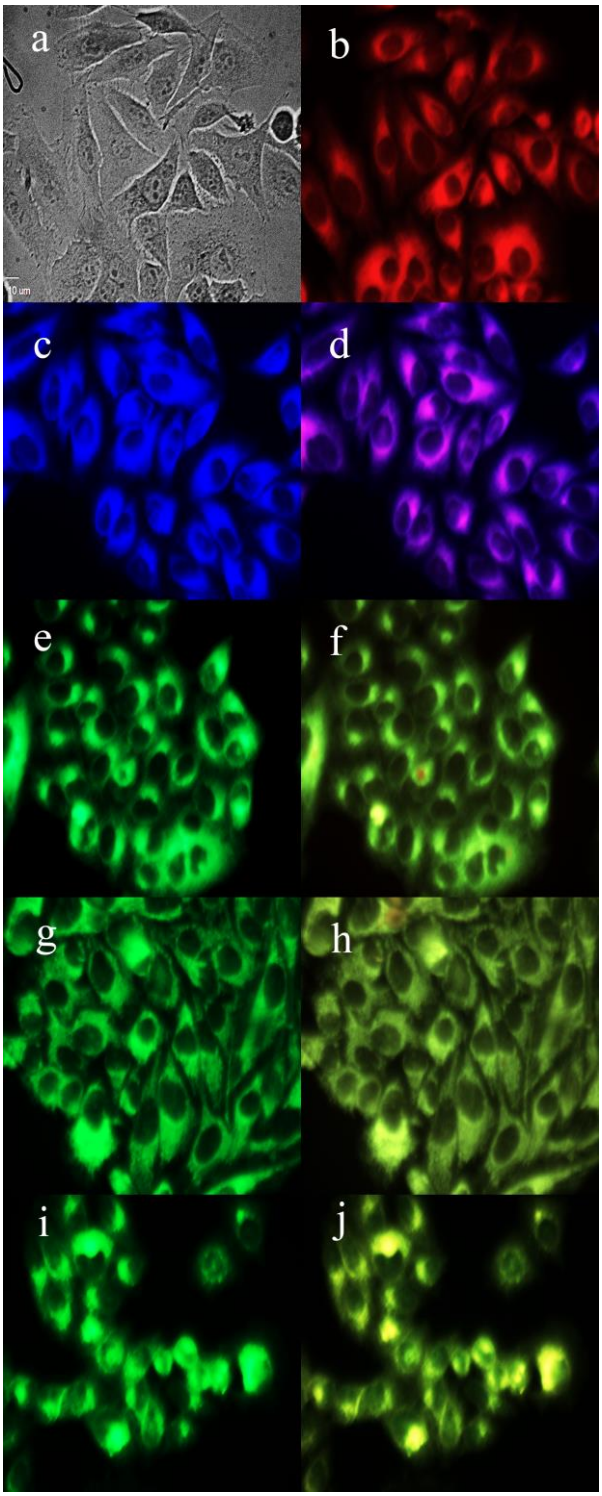


Figure S27. Subcellular localization of BODIPY 2b in HEp2 cells at 10 µM for 6 h. (a) phase contrast. (b) overlay of BODIPY 2b and phase contrast. (c) ER Tracker Blue. (d) overlay of BODIPY 2b and ER Tracker Blue. (e) BODIPY Ceramide. (f) overlay of BODIPY 2b and BODIPY Ceramide. (g) Mito Tracker Green. (h) overlay of BODIPY 2b and Mito Tracker Green. (i) LysoSensor Green. (j) overlay of BODIPY 2b and LysoSensor Green. Scale bar: 10 µm.

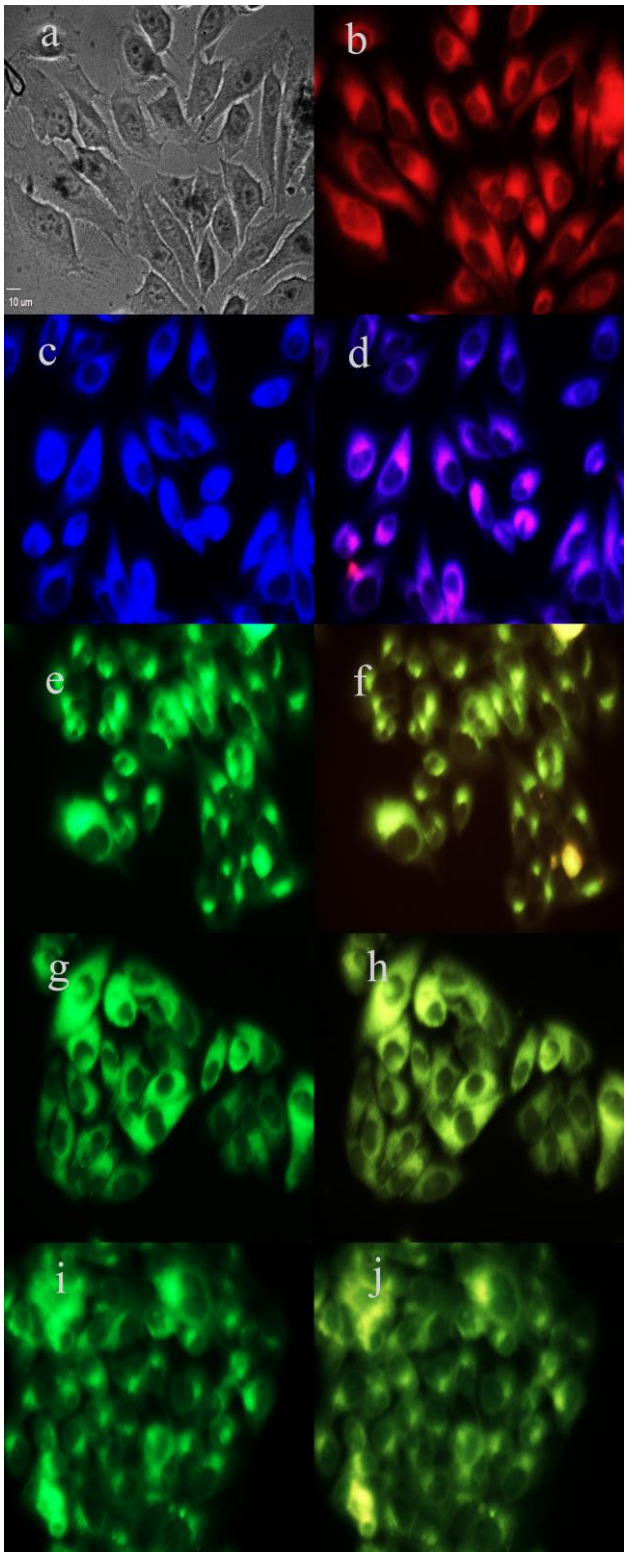


Figure S28. Subcellular localization of BODIPY 3b in HEp2 cells at 10 µM for 6 h. (a) phase contrast. (b) overlay of BODIPY 3b and phase contrast. (c) ER Tracker Blue. (d) overlay of BODIPY 3b and ER Tracker Blue. (e) BODIPY Ceramide. (f) overlay of BODIPY 3b and BODIPY Ceramide. (g) Mito Tracker Green. (h) overlay of BODIPY 3b and Mito Tracker Green. (i) LysoSensor Green. (j) overlay of BODIPY 3b and LysoSensor Green. Scale bar: 10 µm.

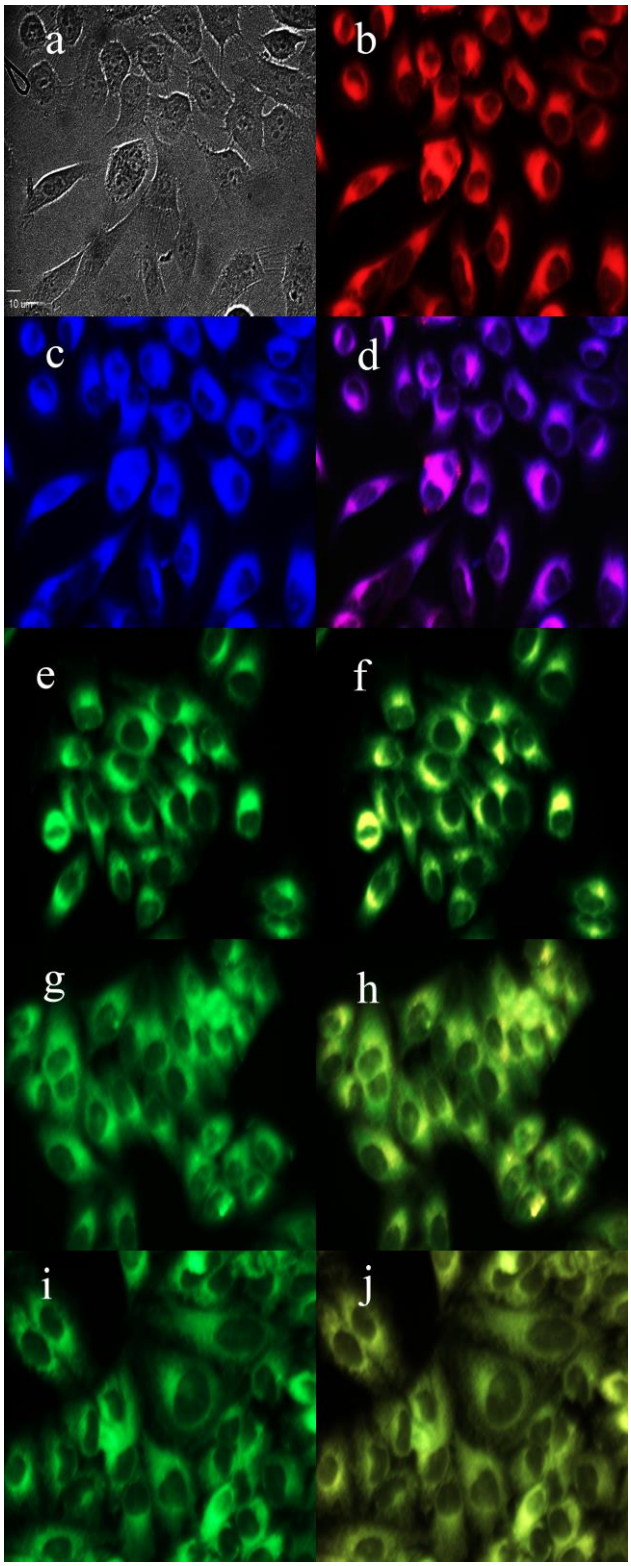


Figure S29. Subcellular localization of BODIPY 4 in HEp2 cells at 10 µM for 6 h. (a) phase contrast. (b) overlay of BODIPY 4 and phase contrast. (c) ER Tracker Blue. (d) overlay of BODIPY 4 and ER Tracker Blue. (e) BODIPY Ceramide. (f) overlay of BODIPY 4 and BODIPY Ceramide. (g) Mito Tracker Green. (h) overlay of BODIPY 4 and Mito Tracker Green. (i) LysoSensor Green. (j) overlay of BODIPY 4 and LysoSensor Green. Scale bar: 10 µm.

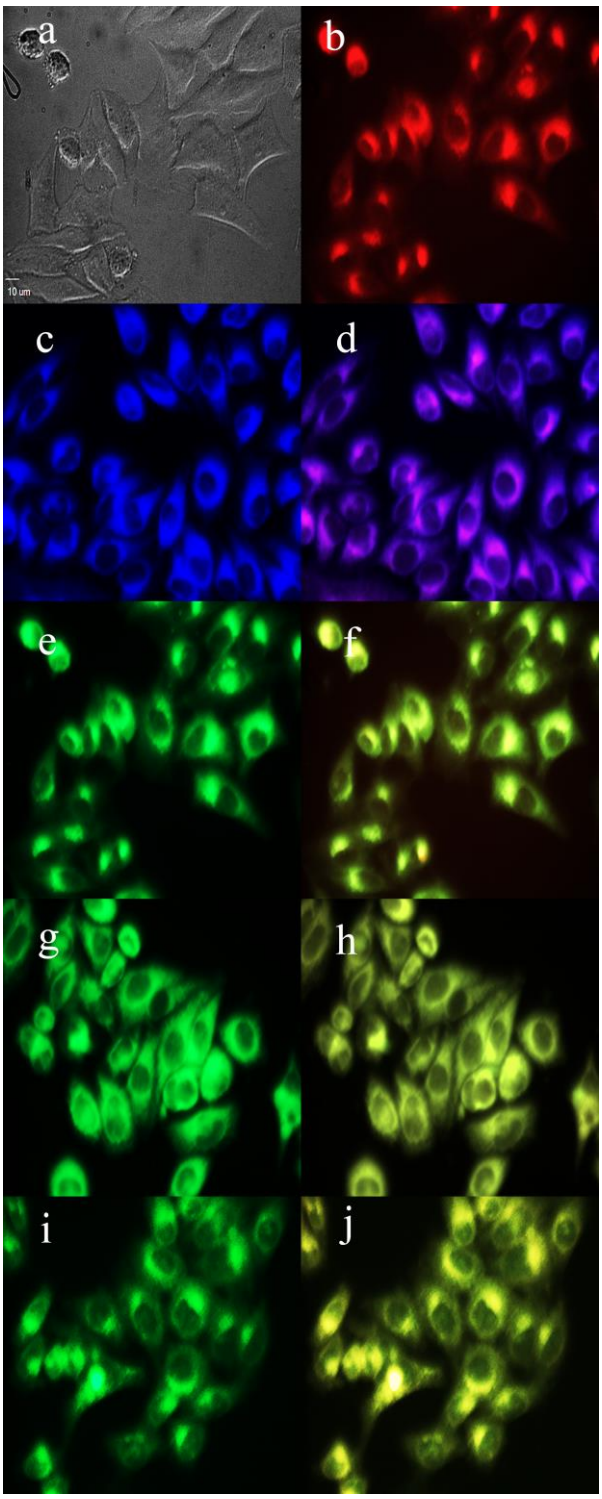


Figure S30. Subcellular localization of BODIPY 6b in HEp2 cells at 10 µM for 6 h. (a) phase contrast. (b) overlay of BODIPY 1b and phase contrast. (c) ER Tracker Blue. (d) overlay of BODIPY 1b and ER Tracker Blue. (e) BODIPY Ceramide. (f) overlay of BODIPY 1b and BODIPY Ceramide. (g) Mito Tracker Green. (h) overlay of BODIPY 1b and Mito Tracker Green. (i) LysoSensor Green. (j) overlay of BODIPY 1b and LysoSensor Green. Scale bar: 10 µm.

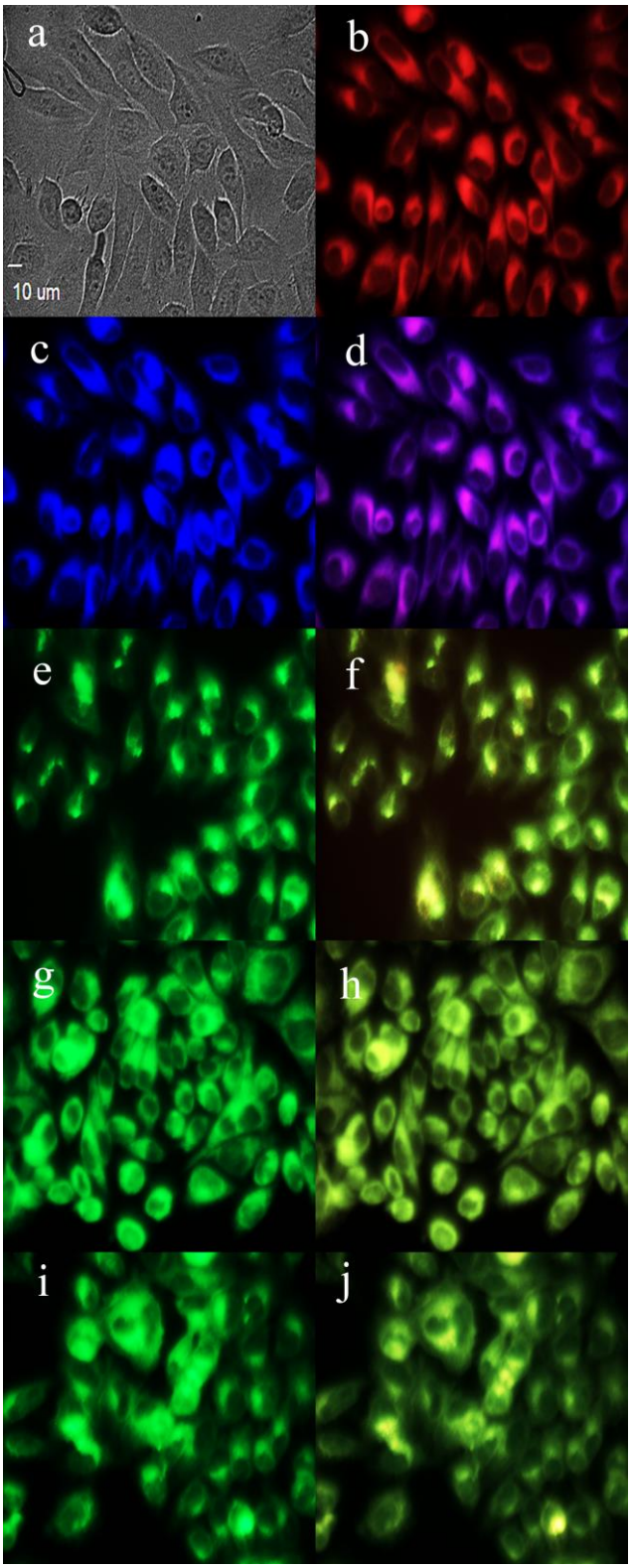


Figure S31. Subcellular localization of BODIPY 7 in HEp2 cells at 10 µM for 6 h. (a) phase contrast. (b) overlay of BODIPY 7 and phase contrast. (c) ER Tracker Blue. (d) overlay of BODIPY 7 and ER Tracker Blue. (e) BODIPY Ceramide. (f) overlay of BODIPY 7 and BODIPY Ceramide. (g) Mito Tracker Green. (h) overlay of BODIPY 7 and Mito Tracker Green. (i) LysoSensor Green. (j) overlay of BODIPY 7 and LysoSensor Green. Scale bar: 10 µm.

7. Absorption and emission spectra of BODIPYs

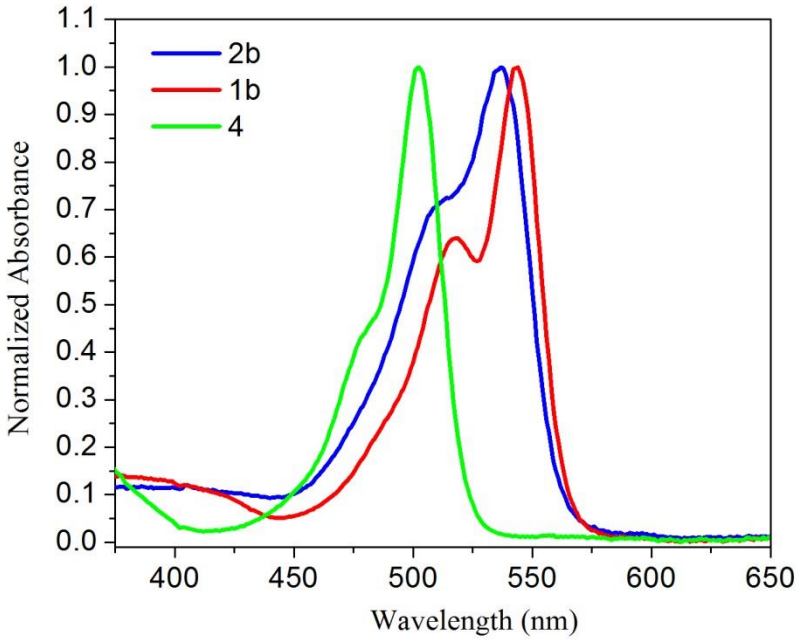


Figure S32. Normalized UV/Vis spectra of BODIPYs **1b** (red), **2b** (blue) and **4** (green) in dichloromethane at room temperature.

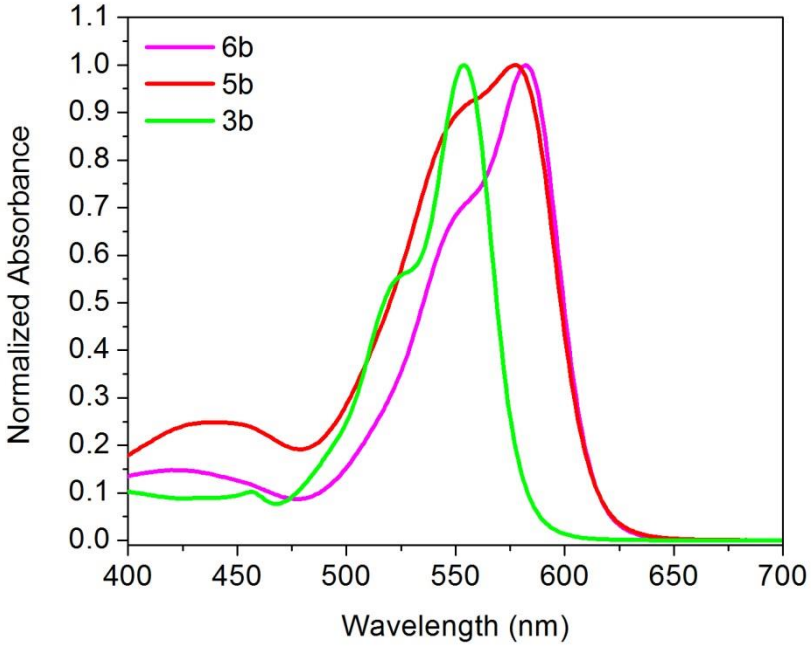


Figure S33. Normalized UV/Vis spectra of BODIPYs **3b** (green), **5b** (red) and **6b** (pink) in dichloromethane at room temperature.

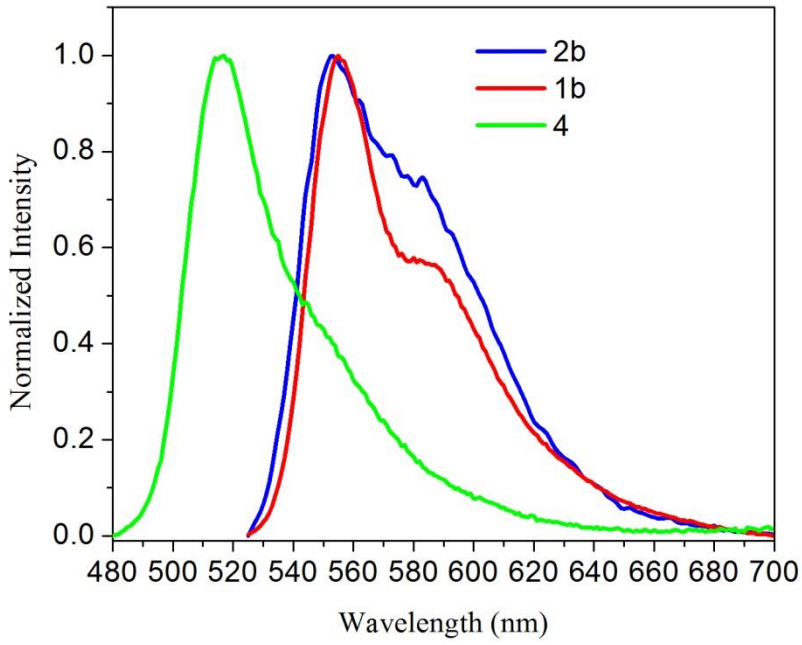


Figure S34. Normalized fluorescence spectra of BODIPYs **1b** (red), **2b** (blue) and **4** (green) in dichloromethane at room temperature.

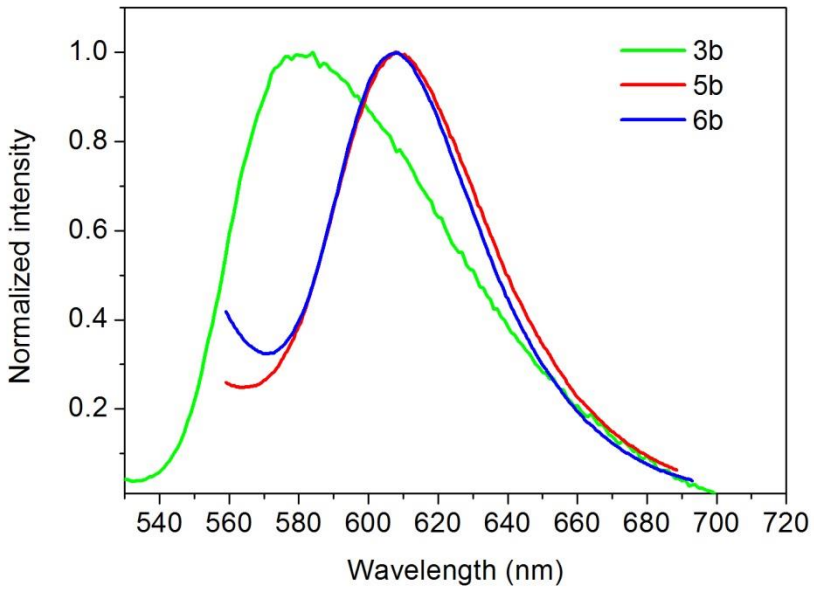


Figure S35. Normalized fluorescence spectra of BODIPYs **3b** (green), **5b** (red) and **6b** (blue) in dichloromethane at room temperature.

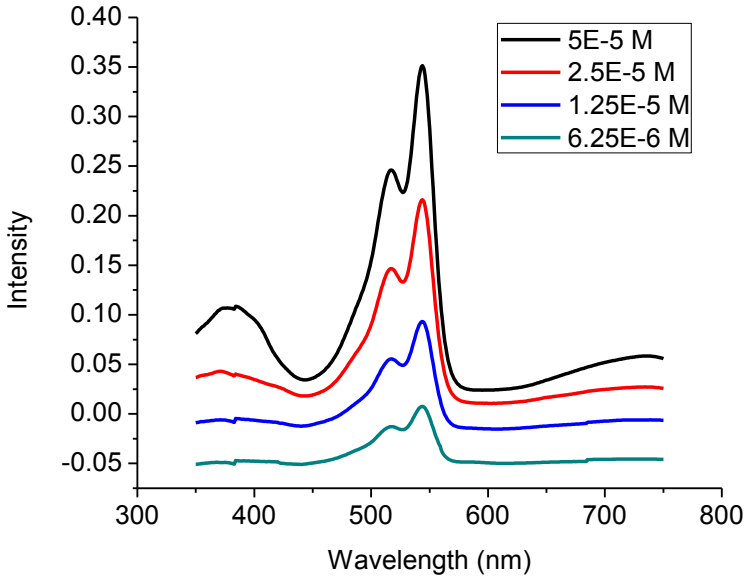


Figure S36. Absorption spectra of BODIPY **1b** at different concentrations in dichloromethane.

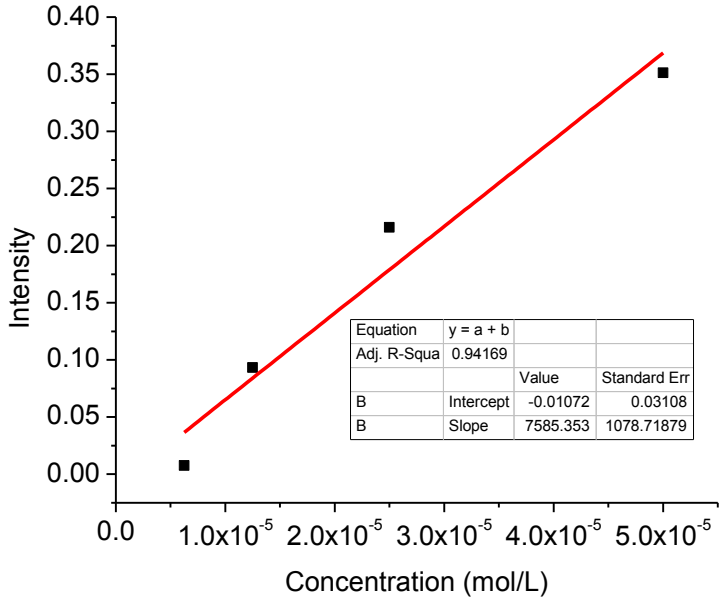


Figure S37. Plot of absorbance intensity of BODIPY **1b** vs. concentration in dichloromethane.

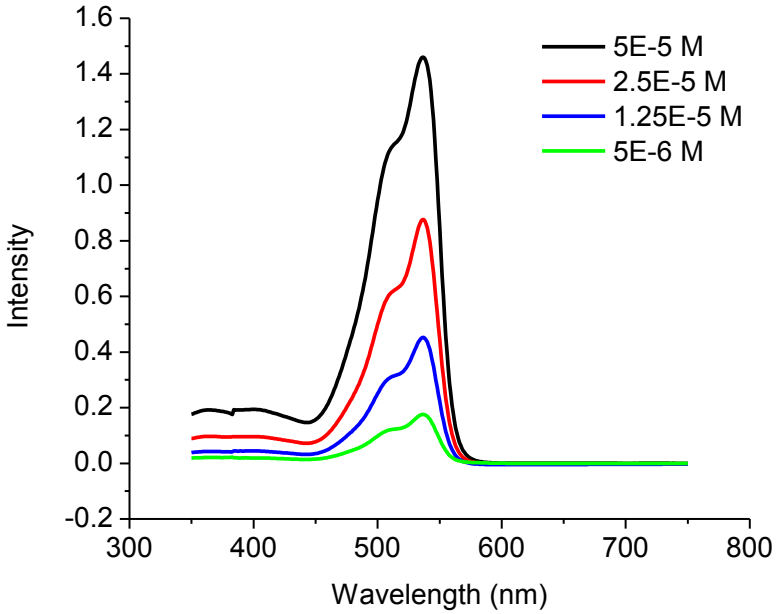


Figure S38. Absorption spectra of BODIPY **2b** at different concentrations in dichloromethane.

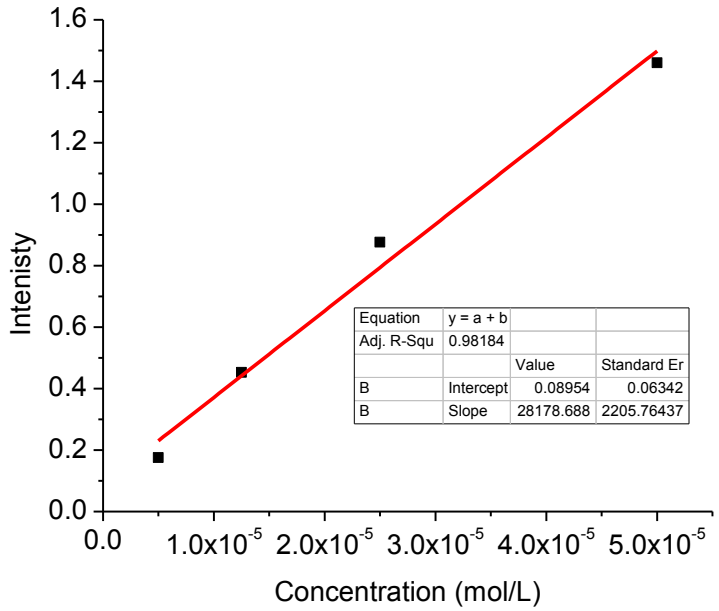


Figure S39. Plot of absorbance intensity of BODIPY **2b** vs. concentration in dichloromethane.

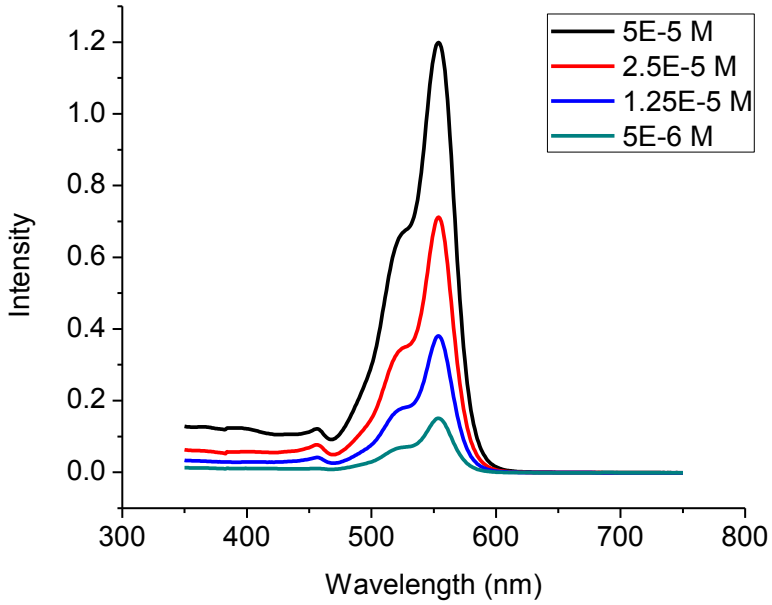


Figure S40. Absorption spectra of BODIPY **3b** at different concentrations in dichloromethane.

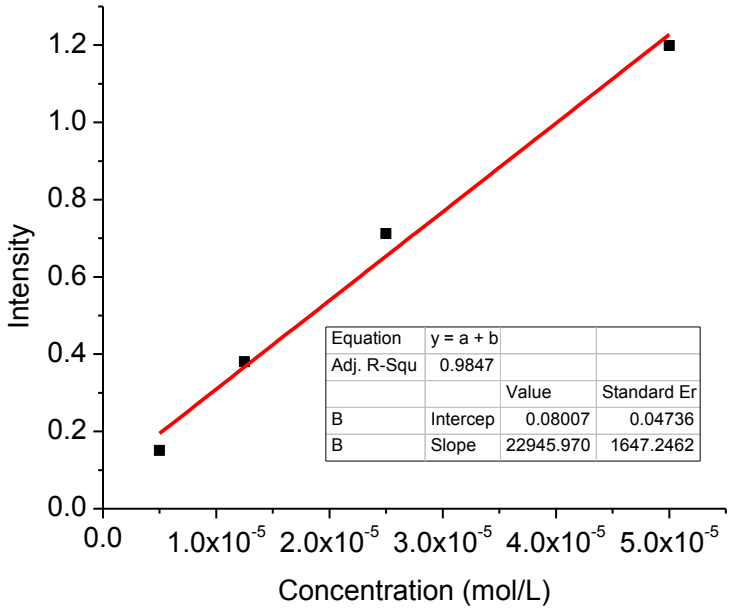


Figure S41. Plot of absorbance intensity of BODIPY **3b** vs. concentration in dichloromethane.

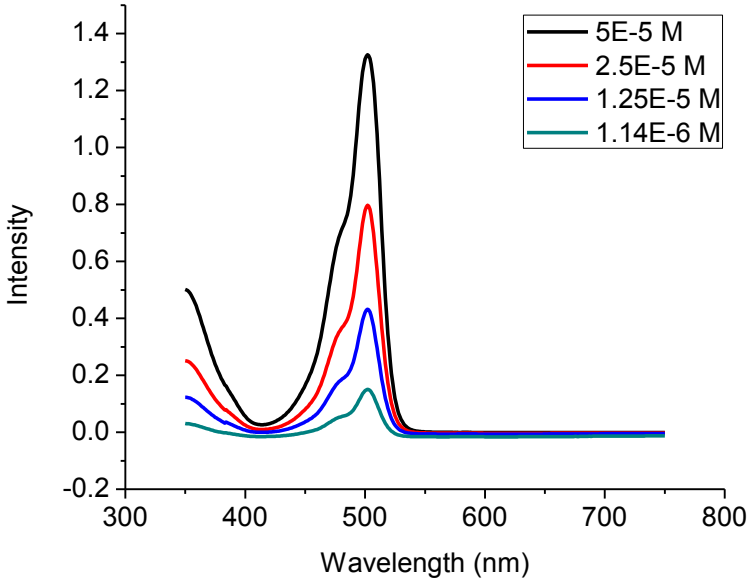


Figure S42. Absorption spectra of BODIPY **4** at different concentrations in dichloromethane.

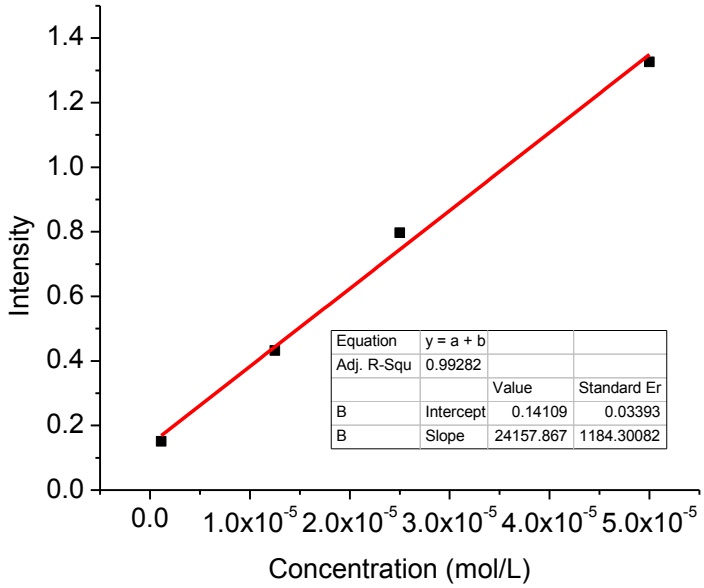


Figure S43. Plot of absorbance intensity of BODIPY **4** vs. concentration in dichloromethane.

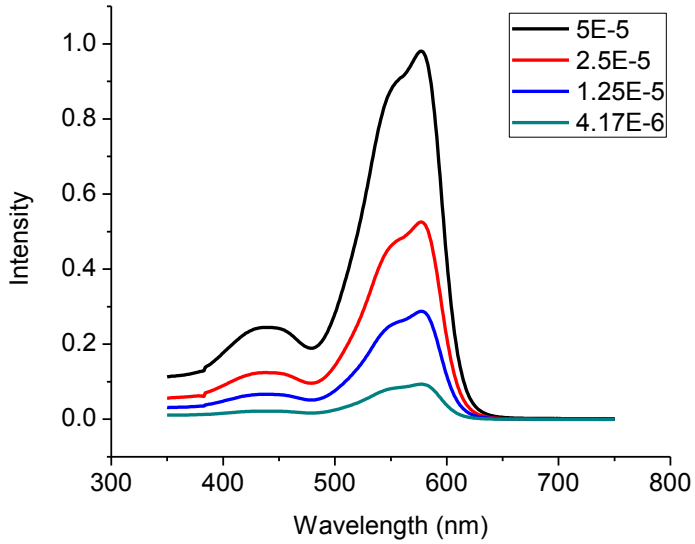


Figure S39. Absorption spectra of BODIPY **5b** at different concentrations in dichloromethane.

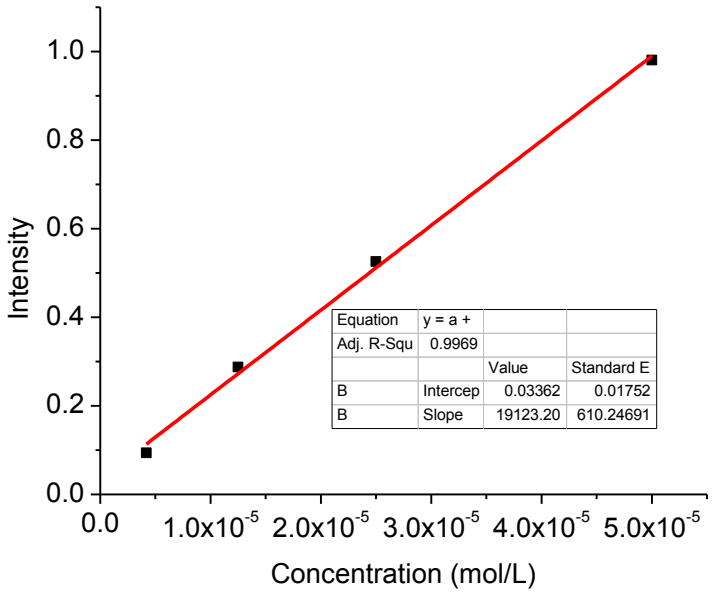


Figure S40. Plot of absorbance intensity of BODIPY **5b** vs. concentration in dichloromethane.

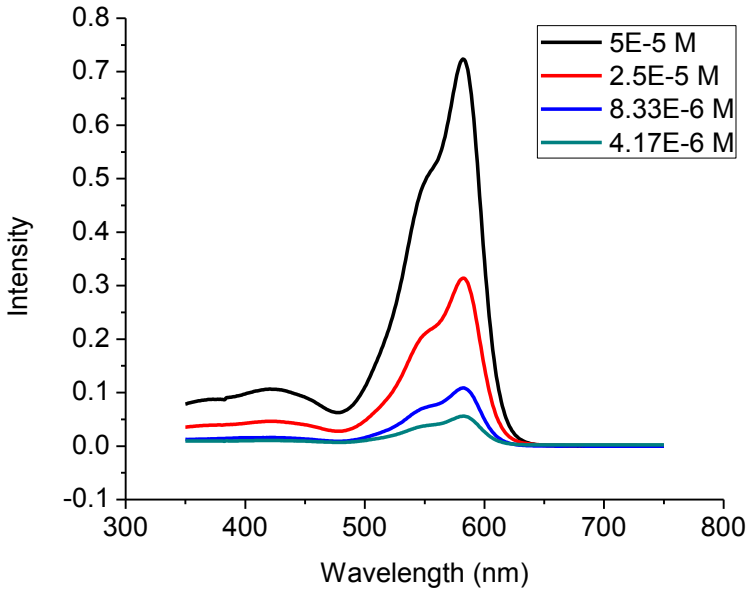


Figure S41. Absorption spectra of BODIPY **6b** at different concentrations in dichloromethane.

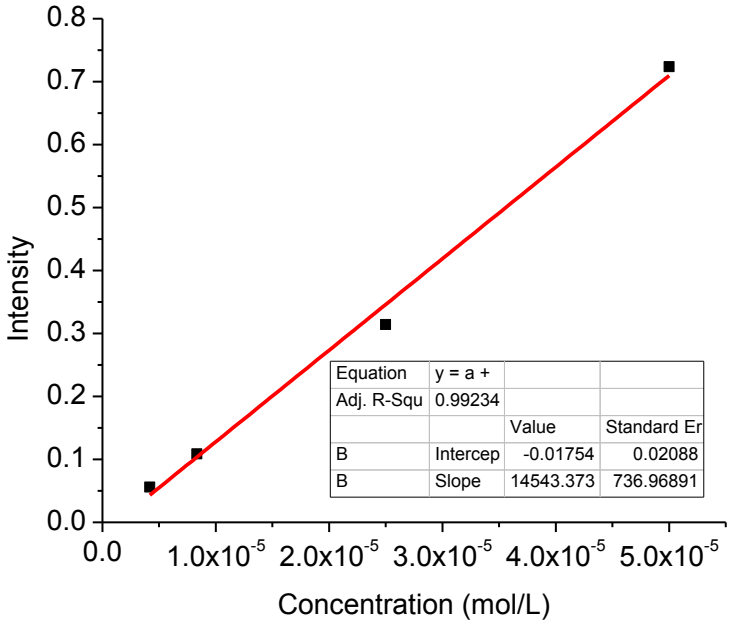


Figure S42. Plot of absorbance intensity of BODIPY **6b** vs. concentration in dichloromethane.

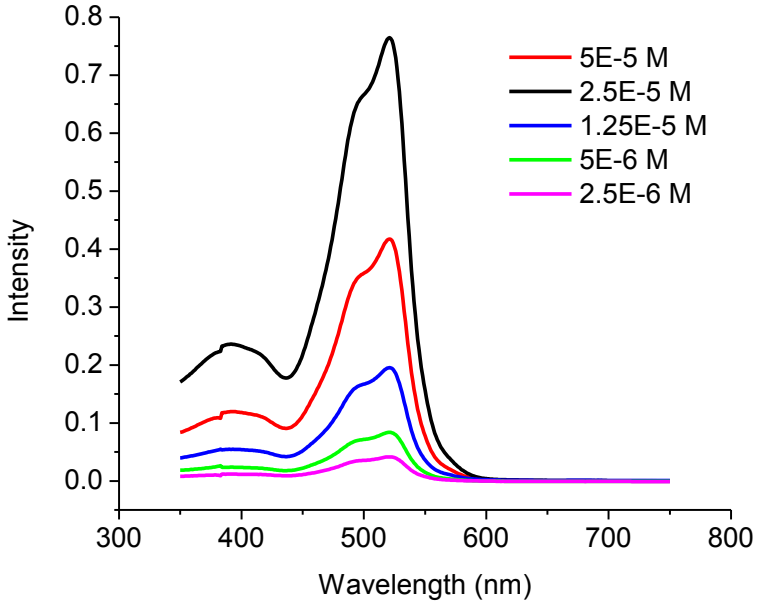


Figure S43. Absorption spectra of BODIPY **7** at different concentrations in dichloromethane.

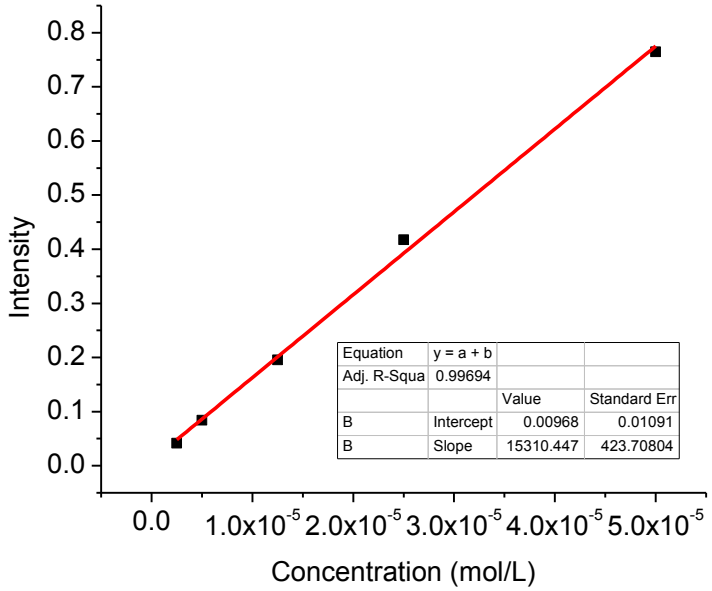


Figure S44. Plot of absorbance intensity of BODIPY **7** vs. concentration in dichloromethane.