Synthesis and properties of azulene-functionalized BODIPYs

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1. Absorption spectra of azulene-BODIPY derivatives **1a**, **1b**, **2a**, and **2b** in various solvents.

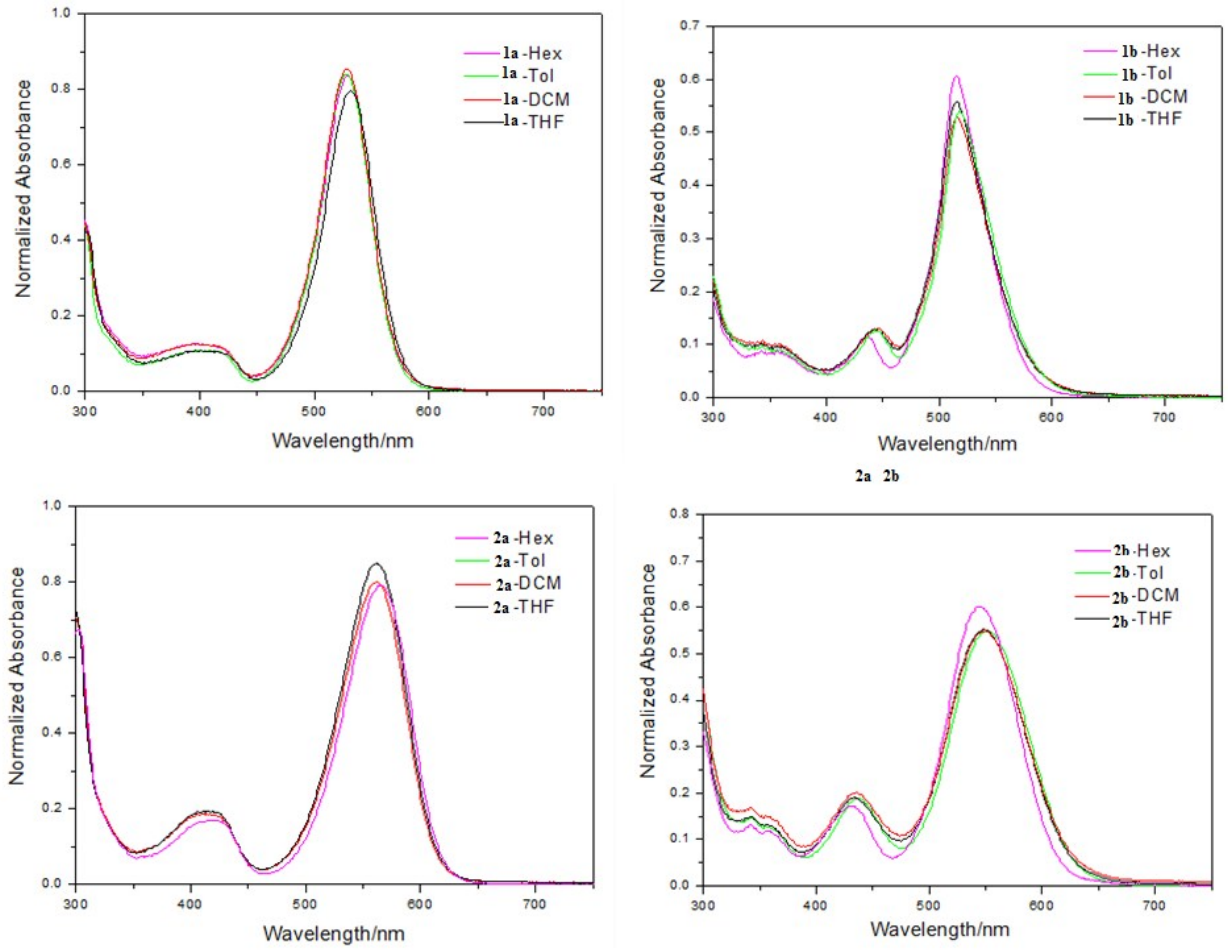


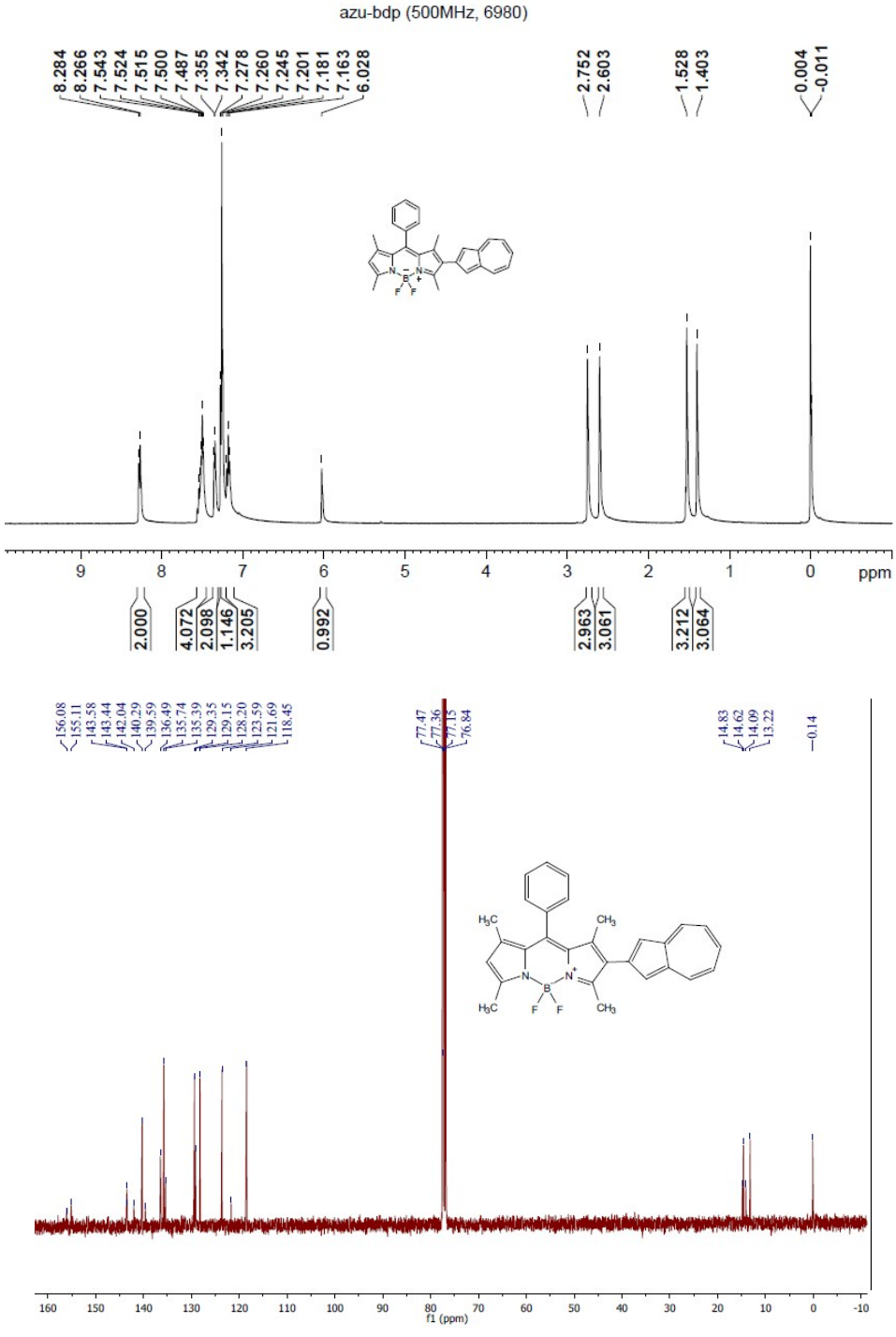
Fig. S1 Absorption spectra of azulene-BODIPY derivatives of **1a**, **1b**, **2a**, and **2b** (10^{-5} M) in hexane, toluene, dichloromethane, and THF.

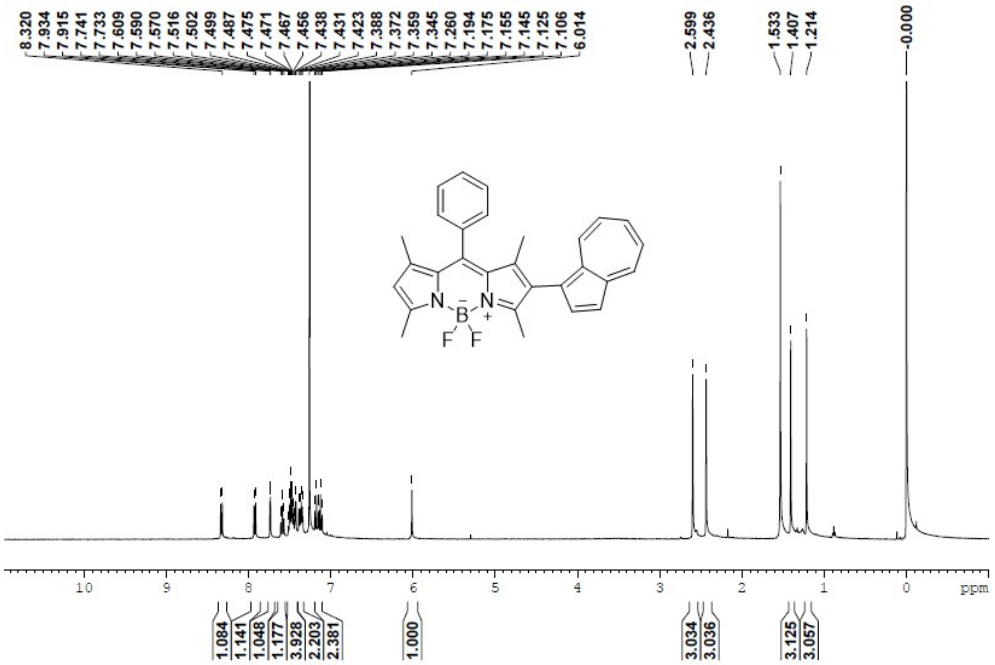
2. X-ray structure determination of **1a.**

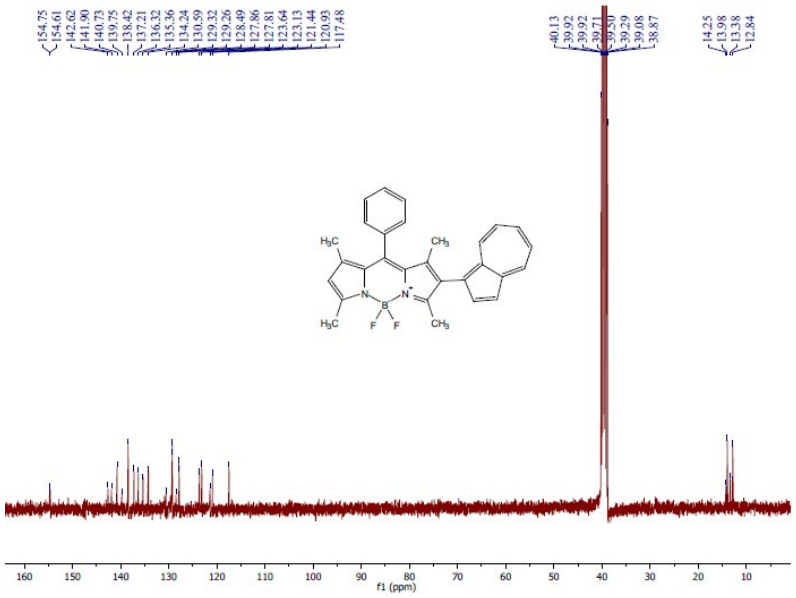
Table S1. X-ray structure determination of **1a**.

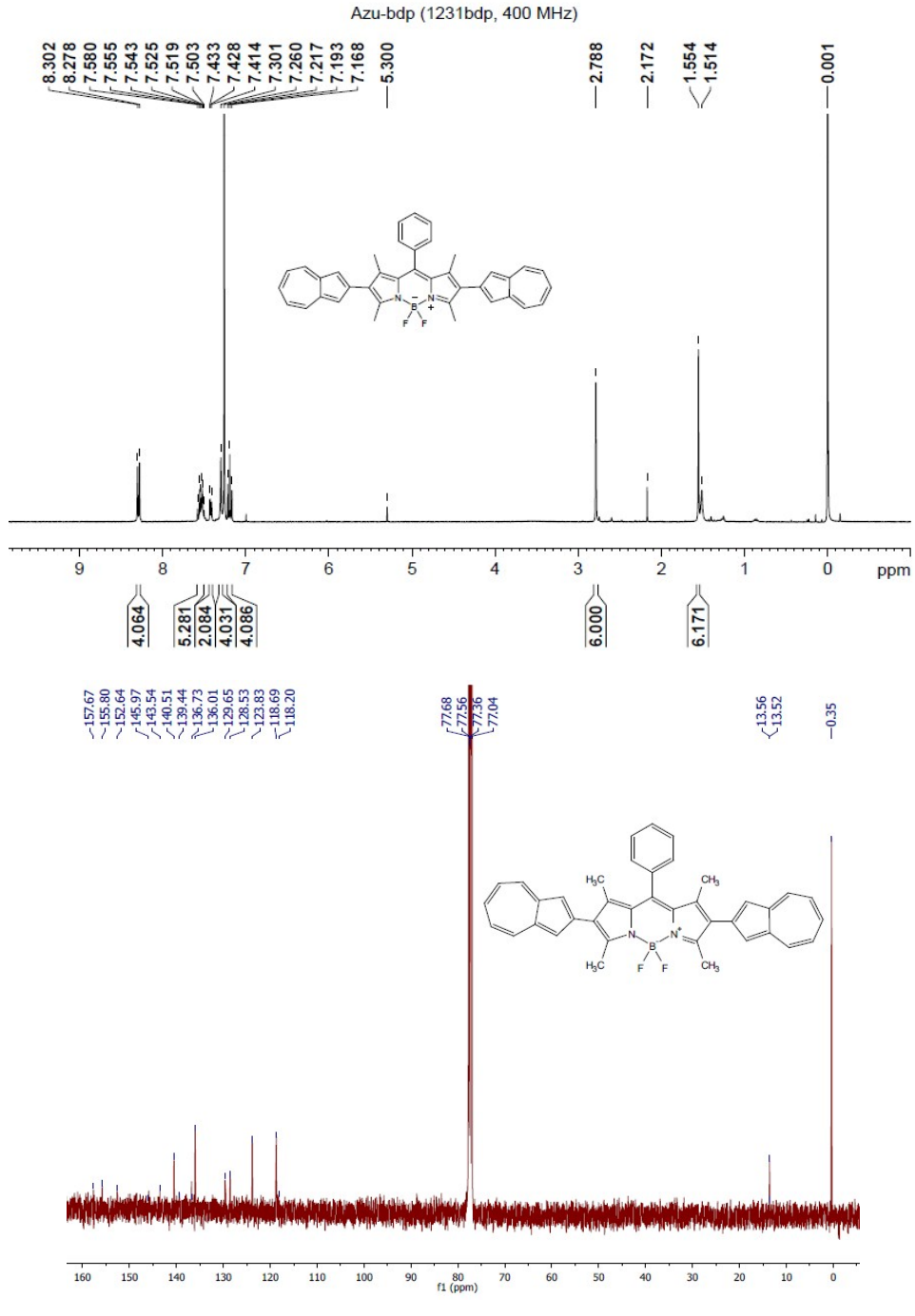
Phase data	
Formula sum	C29 H25 B F2 N2
Formula weight	450.32 g/mol
Crystal system	orthorhombic
Space-group	P n a 21 (33)
Cell parameters	a=16.204(3) Å b=19.565(4) Å c=7.4534(17) Å
Cell ratio	a/b=0.8282 b/c=2.6250 c/a=0.4600
Cell volume	2362.96(90) Å^3
Z	4
Calc. density	1.26575 g/cm^3
Meas. density	
Melting point	
RAll	0.0859
RObs	
Pearson code	oP236
Formula type	NO2P2Q25R29
Wyckoff sequence	a59

3. The ^{1}H NMR spectra of **1a**, **1b**, **2a** and **2b**.




8.320
7.934
7.915
7.741
7.733
7.609
7.590
7.570
7.516
7.502
7.499
7.487
7.475
7.471
7.467
7.456
7.438
7.431
7.423
7.388
7.372
7.359
7.345
7.260
7.194
7.175
7.155
7.145
7.125
7.106
6.014
2.599
2.436
1.533
1.407
1.214
0.000
ppm
1.084
1.141
1.048
1.177
3.928
2.203
2.381
1.000
3.034
3.036
3.125
3.057


154.75
154.61
142.62
141.90
140.73
139.75
138.42
137.21
136.32
135.36
134.24
130.99
129.32
129.26
128.49
127.86
127.81
123.64
123.13
121.44
120.93
117.48
40.13
39.92
39.92
39.71
39.50
39.29
39.08
38.87
14.25
13.98
13.38
12.84
f1 (ppm)


Azu-bdp (1231bdp, 400 MHz)
8.302
8.278
7.580
7.555
7.543
7.525
7.519
7.503
7.433
7.428
7.414
7.301
7.260
7.217
7.193
7.168
5.300
2.788
2.172
1.554
1.514
0.001
ppm
4.064
5.281
2.084
4.031
4.086
6.000
6.171
157.67
155.80
152.64
145.97
143.54
140.51
139.44
136.73
136.01
129.65
128.53
123.83
118.69
118.20
77.68
77.56
77.36
77.04
13.56
13.52
-0.35
f1 (ppm)

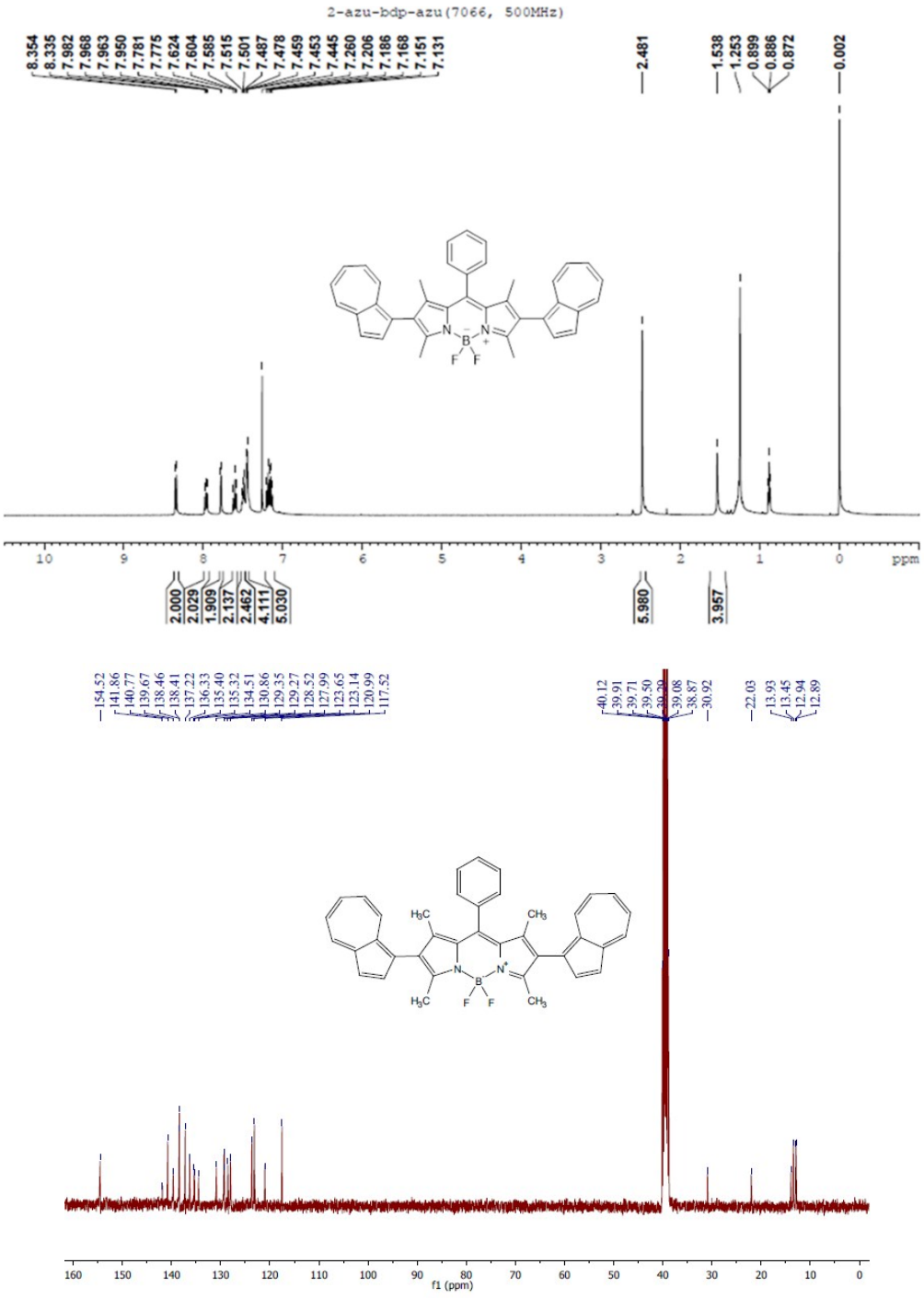


Fig. S2 The ^{1}H NMR spectra of **1a**, **1b**, **2a** and **2b**.

4. HR-MS data for **1a**, **1b**, **2a** and **2b**

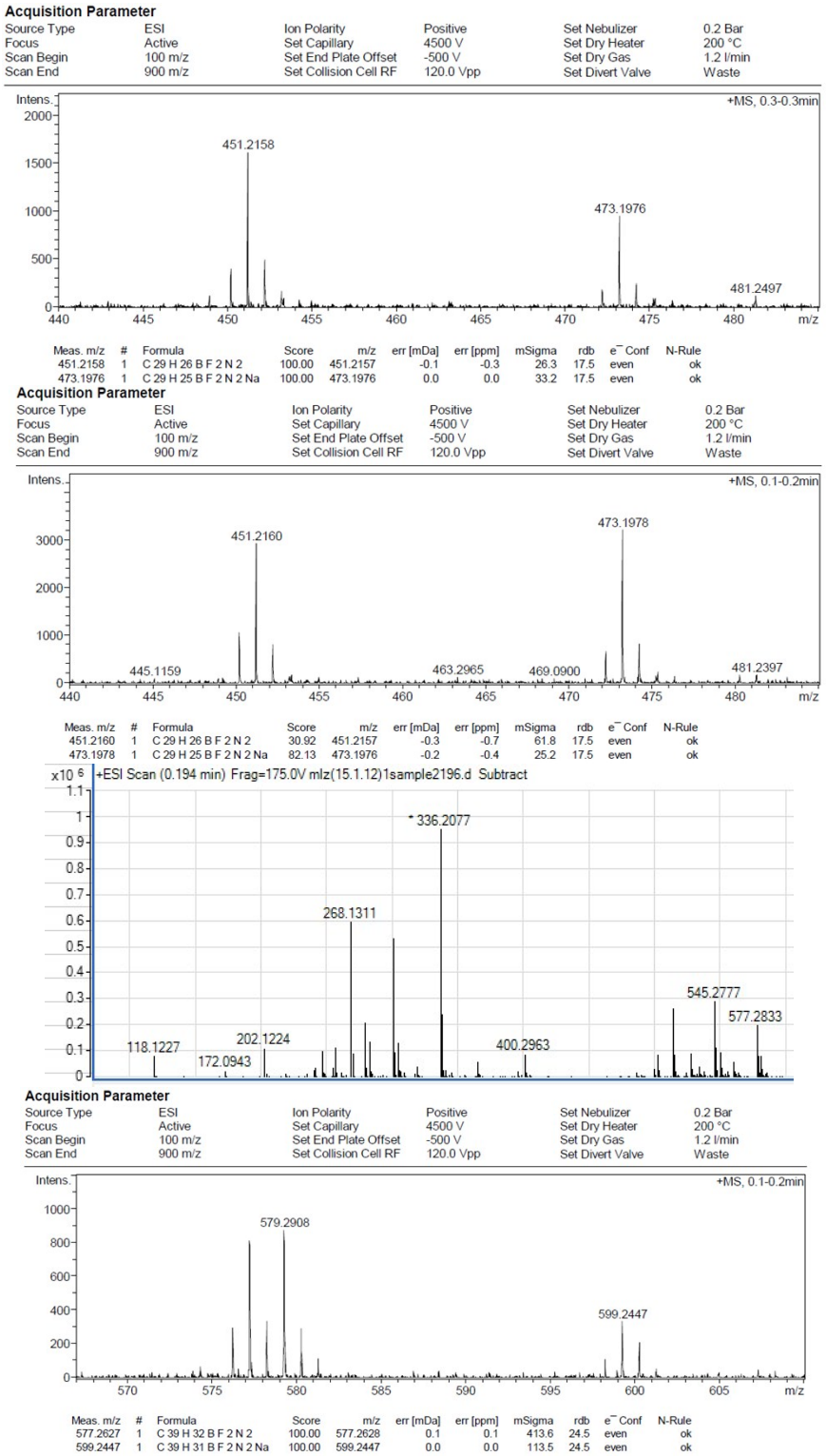


Fig. S3 HR-MS data for **1a**, **1b**, **2a** and **2b**.

5. Details of the TD-DFT calculations for **1a**, **1b**, **2a**, **2b**, **1** + H^+ and **2** + H^+

Table S2. Details of the TD-DFT calculations with the CAM-B3LYP functional and 6-31G(d) basis sets for **1a**, **1b**, **2a**, **2b**, **1** + H^+ and **2** + H^+.

	State[a]	λ [nm (eV)]	*f*[b]	Wavefunction[c] =
1a	S_1	510 (2.43)	0.01	78% |L+1^{Az}←H–1>; 18% |L←H–1>; …
	S_2	439 (2.83)	0.91	**95% |L←H>;** …
1b	S_1	529 (2.35)	0.01	66% |L+1^{Az}←H>; 30% |L+1^{Az}←H–1>; …
	S_2	437 (2.84)	0.65	**83% |L←H>;** 12% |L←H–1>; …
2a	S_1	510 (2.43)	0.01	38% |L+1^{Az}←H–1^{Az}>; 29% |L+2^{Az}←H–2>; 14% |L←H–2>; …
	S_2	510 (2.43)	0.01	38% |L+1^{Az}←H–2>; 29% |L+2^{Az}←H–1^{Az}>; 14% |L←H–1^{Az}>; …
	S_3	463 (2.68)	1.38	**93% |L←H>;** …
2b	S_1	531 (2.34)	0.04	46% |L+1^{Az}←H–1^{Az}>; 35% |L+2^{Az}←H>; 14% |L+2^{Az}←H–2>; …
	S_2	530 (2.34)	0.00	46% |L+2^{Az}←H–1^{Az}>; 36% |L+1^{Az}←H>; 14% |L+1^{Az}←H–2>; …
	S_3	459 (2.70)	0.87	**88% |L←H>;** …
1 + H^+	S_1	478 (2.59)	1.23	87% |L^{Az}←H>; …
	S_3	374 (3.32)	0.27	**50% |L+2←H>;** 35% |L^{Az}←H–1>; …
2 + H^+	S_2	506 (2.45)	1.50	59% |L^{Az}←H–1>; 25% |L^{Az}←H–2>; …
	S_7	394 (3.15)	0.48	**26% |L+2←H–1>;** 22% |L^{Az}←H–1>; 22% |L^{Az}←H–3>; 17% |L^{Az}←H–2>; …

[a] Excited state. [b] Oscillator strength. [c] MOs involved in the transitions, only one-electron transitions with contributions greater than 10% are included. H and L are used to denote the HOMO and LUMO of the entire molecule, respectively. The one-electron transition between the HOMO and LUMO of the BODIPY core are highlighted in bold. A superscript "Az" is used to denote MOs that are localized primarily on the azulene rings.

6. Reference:

1. **Gaussian 09**, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro,M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi,J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar,J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009.**