On the Origin of the Red-Shifted Optical Spectra Recorded for aza-BODIPY Dyes

Supporting Information

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Table of Contents

Gaussian Deconstruction of Absorption and Emission Spectra

Deconstruction of the absorption and emission spectra for aza-BOD and BOD, respectively, was accomplished by fitting each spectral trace to a minimum number of Gaussian curves of a common full-width at half-height (FWHM). It was determined that the spectra recorded for both compounds consistently fitted to the highest accuracy (measured by R^2 values) as the sum of five Gaussian components. The resultant absorption and emission spectra are presented below (Figures S1-6). The y-axis is presented in units of wavenumber.

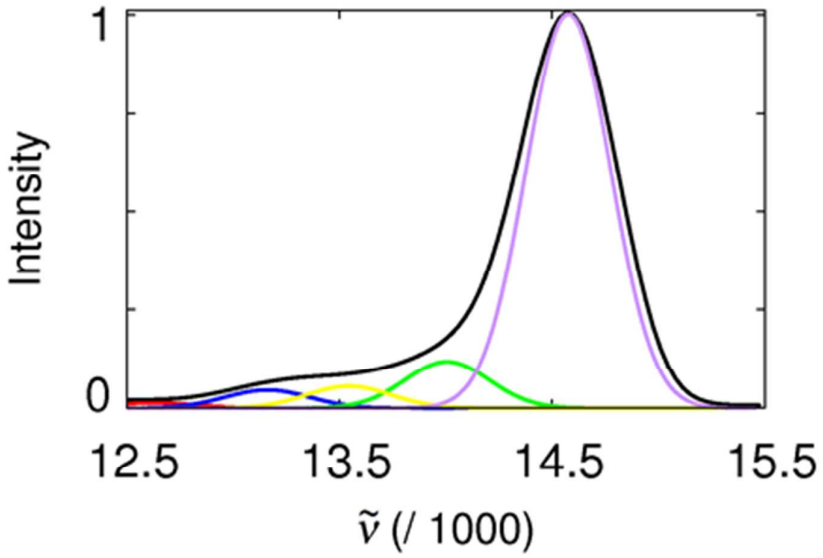


Figure S1. Low-temperature (77K) fluorescence spectrum recorded for aza-BOD.

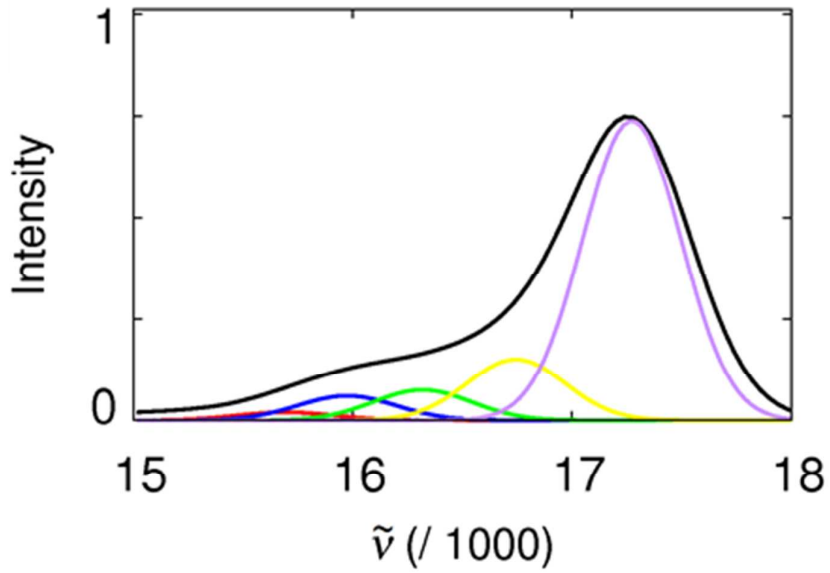


Figure S2. Low temperature (77K) fluorescence spectrum recorded for BOD.

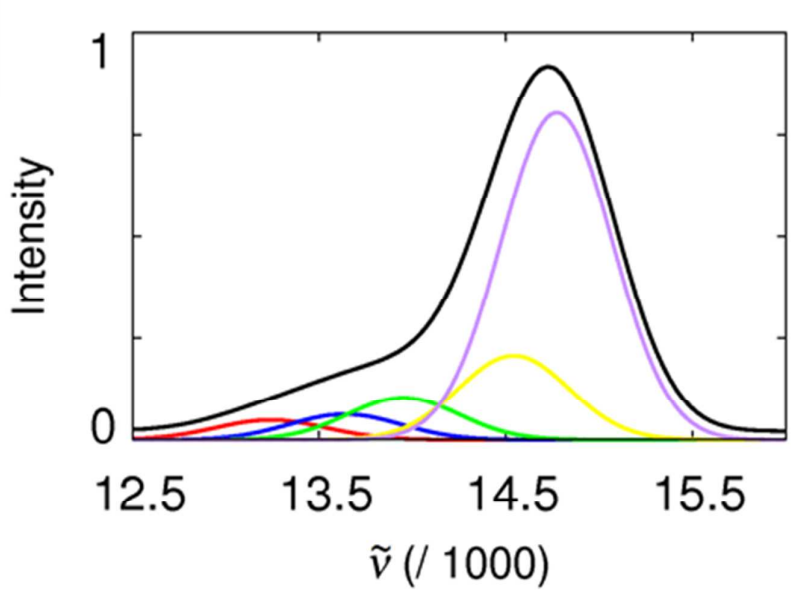


Figure S3. Room-temperature fluorescence spectrum recorded for aza-BOD.

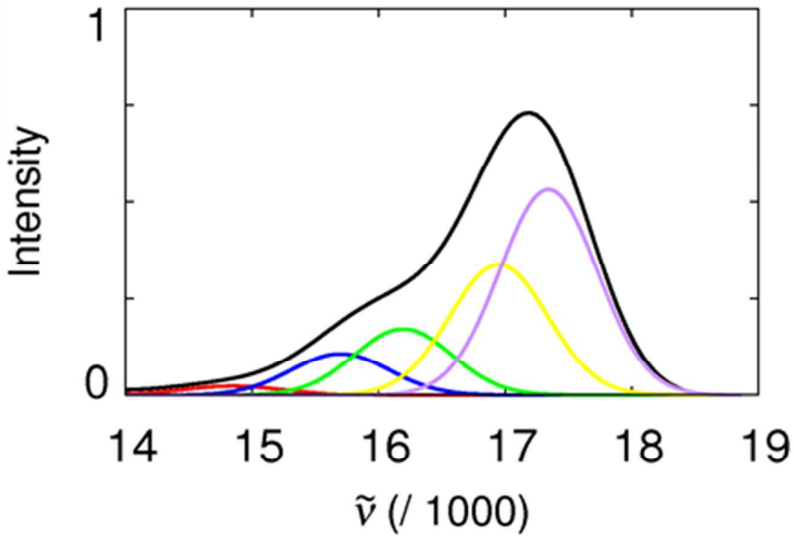


Figure S4. Room-temperature fluorescence spectrum recorded for BOD.

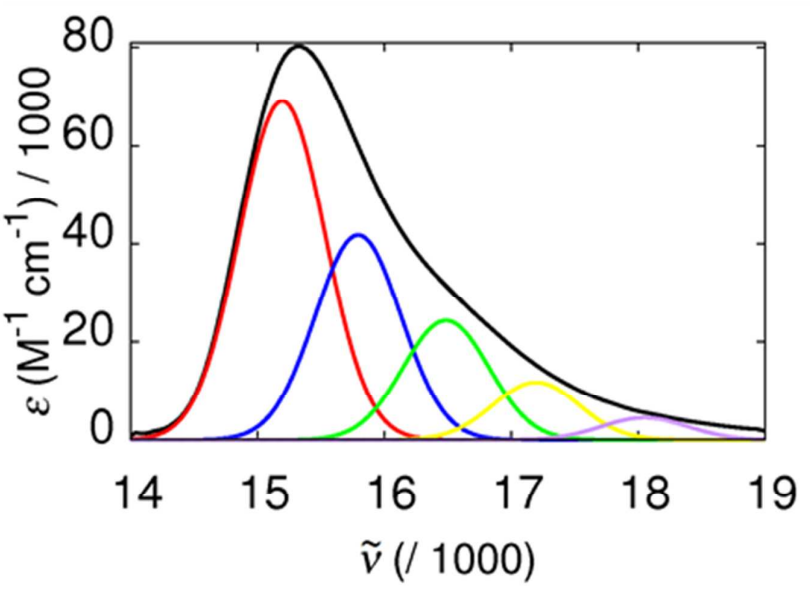


Figure S5. Absorption spectrum recorded for aza-BOD.

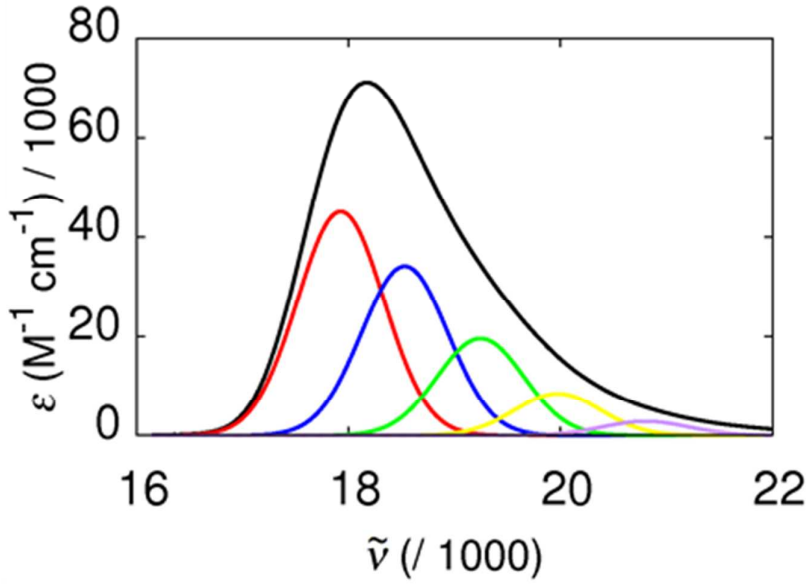


Figure S6. Absorption spectrum recorded for BOD.

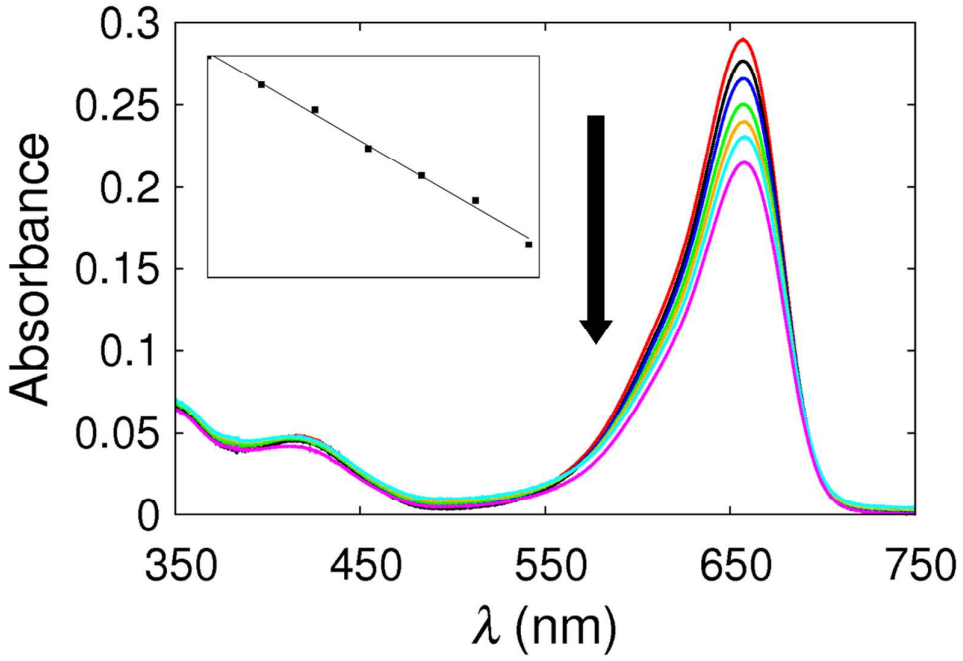


Figure S7. Steady-state photo-bleaching of aza-BOD in deaerated DMF. Absorption spectra recorded at equal periods between 0 and 6 hours. A semi-log plot (inset) of absorbance as a function of time (x) reveals bleaching consistent with first-order kinetics. On this basis, the rate constant for photo-bleaching was determined as 6.0 x 10^{-7} M h^{-1} (error limits ±10%).

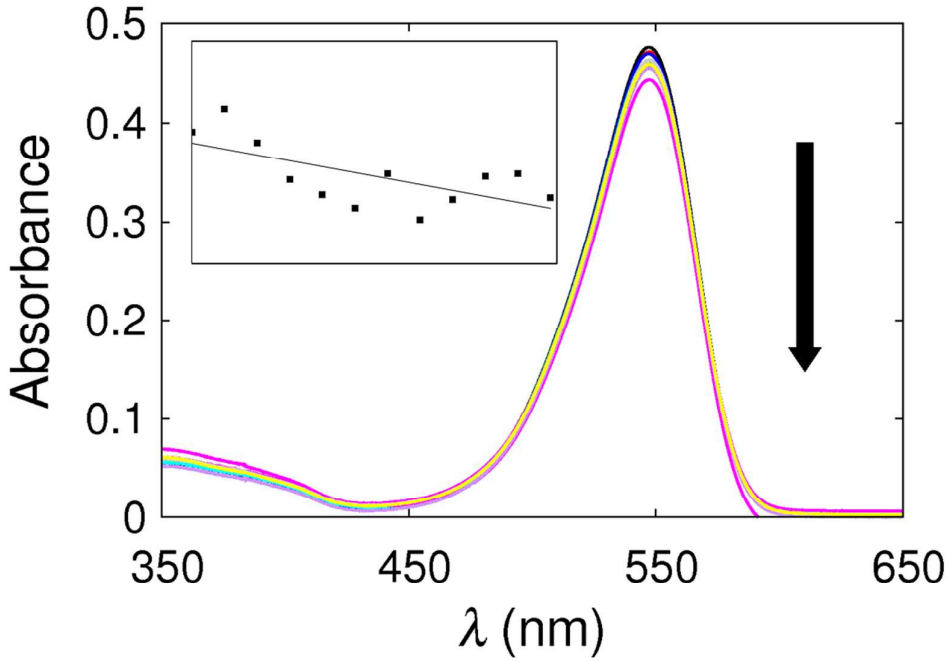


Figure S8. Steady-state photo-bleaching of BOD in deaerated DMF. Absorption spectra recorded at equal intervals between 0 and 10 hours. A semi-log plot of absorbance values as a function of time is given as the inset. Negligible bleaching was observed in comparison with aza-BOD.

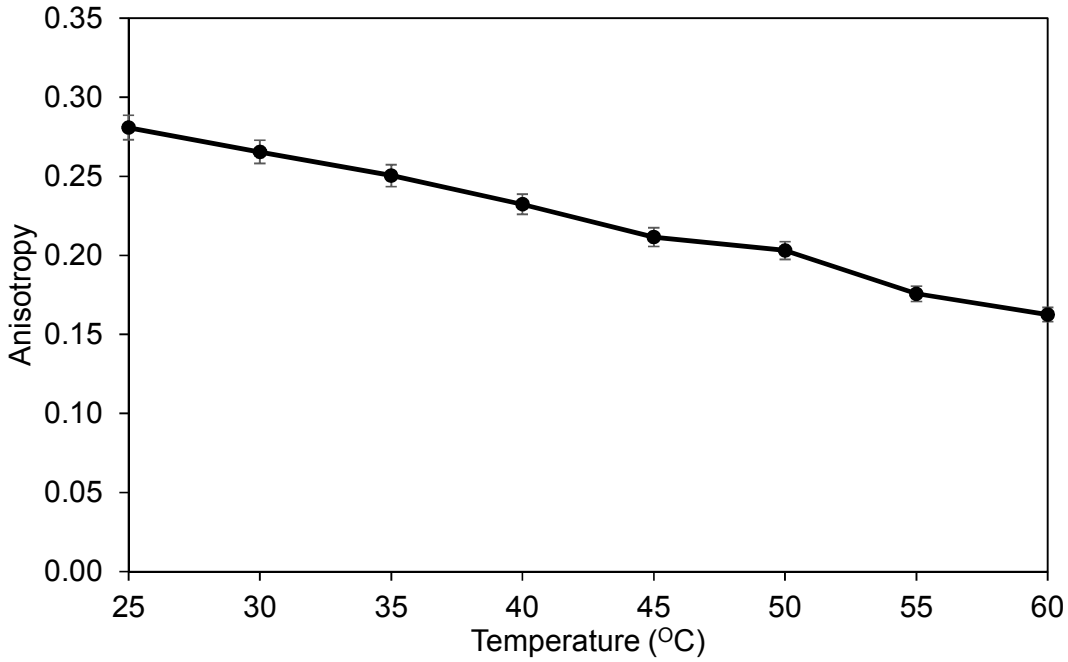


Figure S9. Steady-state fluorescence anisotropy measurements for aza-BOD in glycerol as a function of temperature. Measurements were repeated 8 times with an average experimental error of 2.8%. Modelling suggests the limiting anisotropy value for aza-BOD is 0.37, which is consistent with literature values for somewhat related compounds.

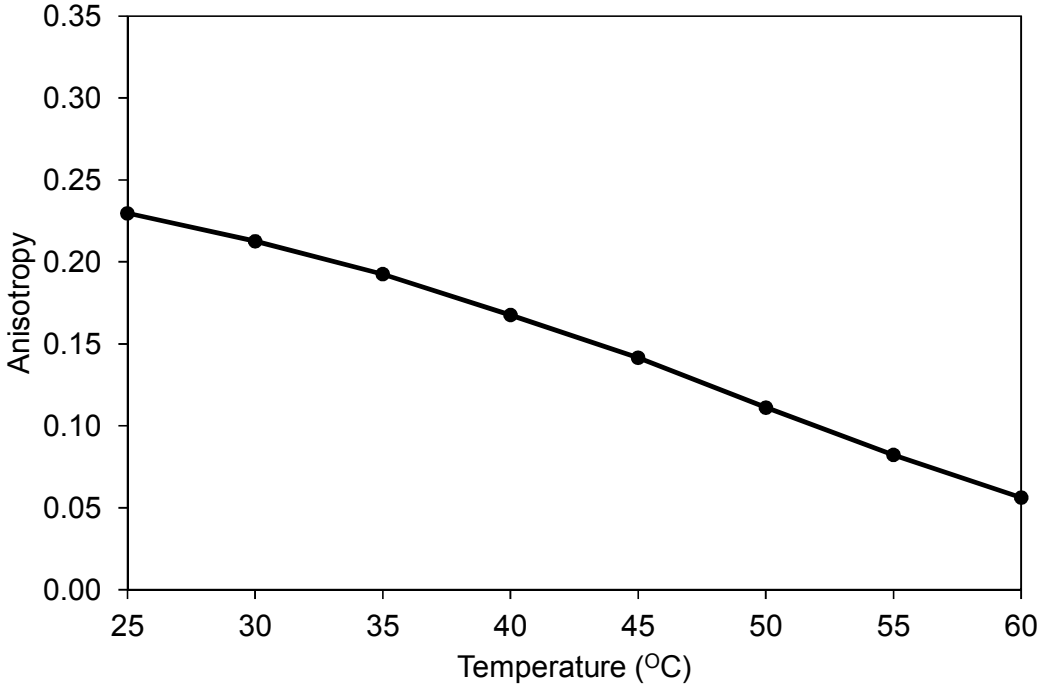
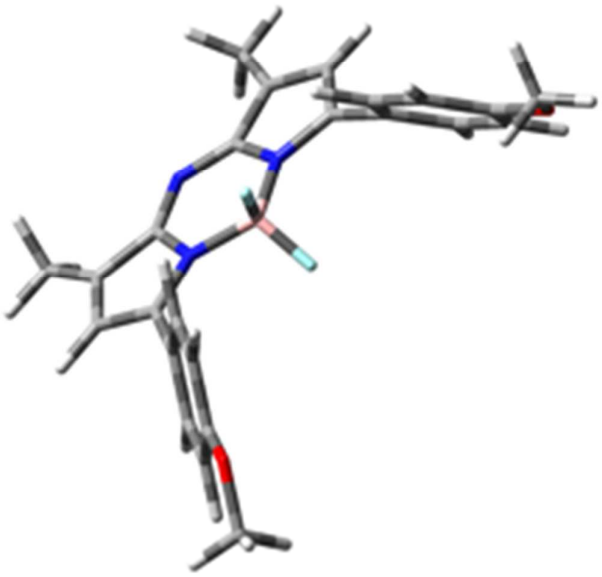


Figure S10. Steady-state fluorescence anisotropy measurements for BOD in glycerol as a function of temperature. Measurements were repeated 8 times with an average experimental error of 0.9%.

Energy-minimized geometry for aza-BOD



CARTESIAN COORDINATES

NO.	ATOM	X	Y	Z
1	C	0.00000000	0.00000000	0.00000000
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3	B	2.26079986	1.34519977	0.00000000
4	N	1.24199963	2.53860005	-0.04560001
5	C	-0.19070019	2.30000008	-0.04570001
6	N	-0.75770032	1.09559983	-0.02010000
7	C	1.45769962	3.87080010	-0.11630001
8	C	0.18209921	4.55640031	-0.16160003
9	C	-0.82960035	3.61580042	-0.11290003
10	C	-0.41459975	-1.40350057	-0.01430000
11	C	0.73780017	-2.16700005	-0.03600001
12	C	1.88350012	-1.28080036	-0.02540000
13	C	-2.28230021	3.82550041	-0.12500003
14	C	-1.81309968	-1.84940096	-0.00340000
15	C	3.28340058	-1.70580050	-0.05110001
16	C	2.77000002	4.51710031	-0.15030001
17	F	3.12690010	1.39829980	-1.06850030
18	F	3.06259965	1.43259975	1.11639968
19	C	3.67981297	4.34973412	0.90397380
20	C	4.92310611	4.98392189	0.87216871
21	C	5.24119826	5.78121055	-0.23481297
22	C	4.33734588	5.96579194	-1.30425160
23	C	3.10506160	5.33030217	-1.25257292
24	C	4.16137441	-1.35056715	0.99221348
25	C	5.48370519	-1.77288455	0.96672889
26	C	5.92760246	-2.55239960	-0.12301259

27 C	5.06874610	-2.91834835	-1.16841057
28 C	3.74207559	-2.48893117	-1.12193504
29 O	7.25399173	-2.89375048	-0.02824146
30 C	7.83119997	-3.70861047	-1.08309041
31 O	6.41968897	6.46295846	-0.41123295
32 C	7.44298288	6.34260090	0.61271864
33 H	0.08059923	5.62500007	-0.21900001
34 H	0.81230046	-3.23920005	-0.05340001
35 H	-2.56190033	4.88910089	-0.17740006
36 H	-2.75980040	3.31920022	-0.98310035
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38 H	-2.39890001	-1.38360095	-0.81560028
39 H	-1.91619933	-2.94040054	-0.10909995
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41 H	3.41518203	3.72798635	1.76341644
42 H	5.62082536	4.84858913	1.69552809
43 H	4.61846161	6.59584567	-2.14682211
44 H	2.39110646	5.45649015	-2.07063622
45 H	3.79855980	-0.75070951	1.83093006
46 H	6.17866340	-1.51266082	1.76384664
47 H	5.41484213	-3.52101051	-2.00492142
48 H	3.05756671	-2.76323105	-1.92893681
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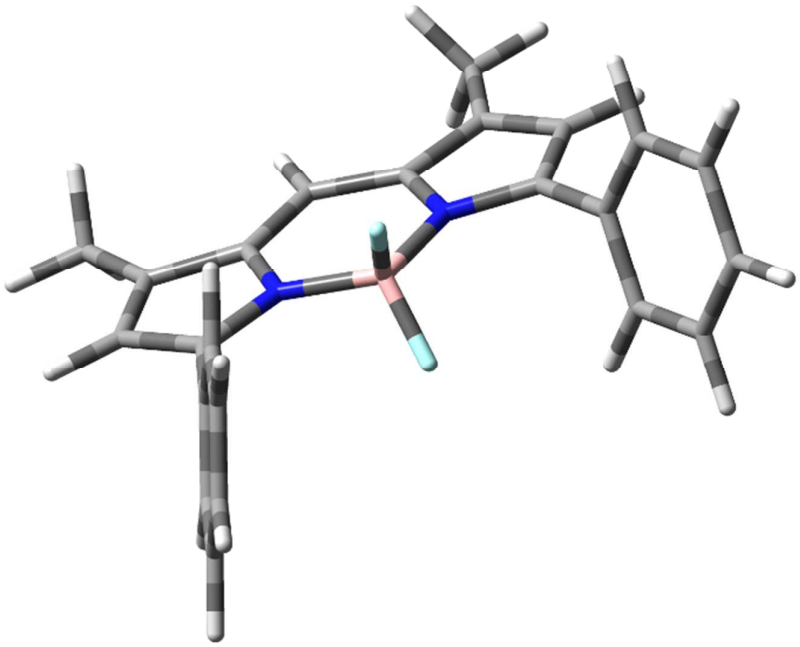
52 H	8.24939549	6.96596870	0.20274109
53 H	7.07909205	6.74720160	1.56187928
54 H	7.76412045	5.30111394	0.70930467

Energy-



minimized geometry for BOD

CARTESIAN COORDINATES

NO.	ATOM	X	Y	Z
1	C	0.00000000	0.00000000	0.00000000

2 N	1.43140000	0.00000000	0.00000000
3 B	2.26279983	1.32499971	0.00000000
4 N	1.30610003	2.55979948	0.07910000
5 C	-0.11830042	2.42199946	0.06860000
6 C	-0.73570025	1.17810041	0.02700002
7 C	1.61480004	3.87779950	0.14510001
8 C	0.39820040	4.64709927	0.17940002
9 C	-0.67089946	3.76069938	0.12970003
10 C	-0.42090014	-1.38740045	-0.00630001
11 C	0.72869950	-2.16770019	-0.00110000
12 C	1.86569990	-1.28379969	0.00120000
13 C	-2.10809906	4.07449928	0.13440005
14 C	-1.82120058	-1.83810059	-0.01260001
15 C	3.27569957	-1.69809957	0.00950000
16 C	2.97940009	4.42259952	0.18350002
17 F	3.04729959	1.40049968	-1.13279964
18 F	3.15729997	1.33569970	1.04970015
19 C	3.78474445	4.34512898	-0.96337926
20 C	5.09142216	4.83678249	-0.92391670
21 C	5.59456679	5.40165029	0.25285507
22 C	4.79006982	5.47734137	1.39384435
23 C	3.48037818	4.99004965	1.36392173
24 C	4.04631583	-1.49182069	1.16431475
25 C	5.37912856	-1.90867538	1.18913562
26 C	5.94165061	-2.53090812	0.06957442
27 C	5.17148242	-2.73611018	-1.07909761
28 C	3.83746475	-2.32091648	-1.11452215
29 H	-1.83369987	1.12470043	0.02240002
30 H	0.35930039	5.71809947	0.23270003
31 H	0.79369947	-3.23879971	-0.00090001
32 H	-2.30489902	5.15439894	0.22840002
33 H	-2.60319887	3.74159942	-0.79369957
34 H	-2.63659899	3.58159934	0.96729996
35 H	-2.38060040	-1.43730072	-0.87429971
36 H	-1.91210059	-2.93510065	-0.05740002
37 H	-2.36110057	-1.51220060	0.89269999
38 H	3.38927629	3.90806857	-1.88080787
39 H	5.71935209	4.78070925	-1.81372497
40 H	6.61532030	5.78454880	0.27960224
41 H	5.18271202	5.91955222	2.31003326
42 H	2.85089893	5.05385004	2.25234049
43 H	3.60672806	-1.00422052	2.03510101
44 H	5.98152138	-1.74742936	2.08369136
45 H	6.98265643	-2.85529631	0.09295080
46 H	5.61147405	-3.21998751	-1.95172706
47 H	3.23755786	-2.47943864	-2.01151725

Table S1. The Aryl Ring Dihedral Angle Calculated for aza-BOD in a Solvent Reservoir from Optimized Geometries Obtained at a Few Different Levels

Method	N-C-aryl / ^{0}
HF/6-31G**	54.1
MP2/6-31G**	53.2
CCD/6-31G**	53.5
B3LYP/cc-pVDZ	54.2
B3LYP/cc-pVTZ	54.3
B3LYP/6-31G**	54.2

Table S2. Compilation of the Structural Parameters Calculated for the Two Dyes at the Ground State and Excited State Levels.[(a)]

Parameter	BOD (S_0)	BOD (S_1)	BOD (T_1)	aza-BOD (S_0)	aza-BOD (S_1)	aza-BOD (T_1)
C-X-C / ^{0}	121.6	121.7	119.2	116.2	119.6	116.8
N-B-N / ^{0}	110.1	109.1	107.7	108.3	107.3	106.0
F-B-F / ^{0}	104.8	106.8	106.7	105.3	107.1	107.2
N-C-Ph / ^{0}	59.3	55.4	60.2	54.1	52.0	57.3
C-X / Å	1.398	1.389	1.403	1.332	1.330	1.364
N-B /Å	1.564	1.572	1.573	1.570	1.575	1.578
B-F / Å	1.380	1.373	1.372	1.377	1.370	1.369
X-B / Å	3.002	3.034	3.034	3.030	3.045	3.077
C_1-C_7 / Å	5.921	5.932	5.930	5.700	5.701	5.697

(a) S_0 refers to the ground state; S_1 refers to the first-excited singlet state; T_1 refers to the first-allowed triplet state. Calculations made in a solvent reservoir with dielectric constant of 10.

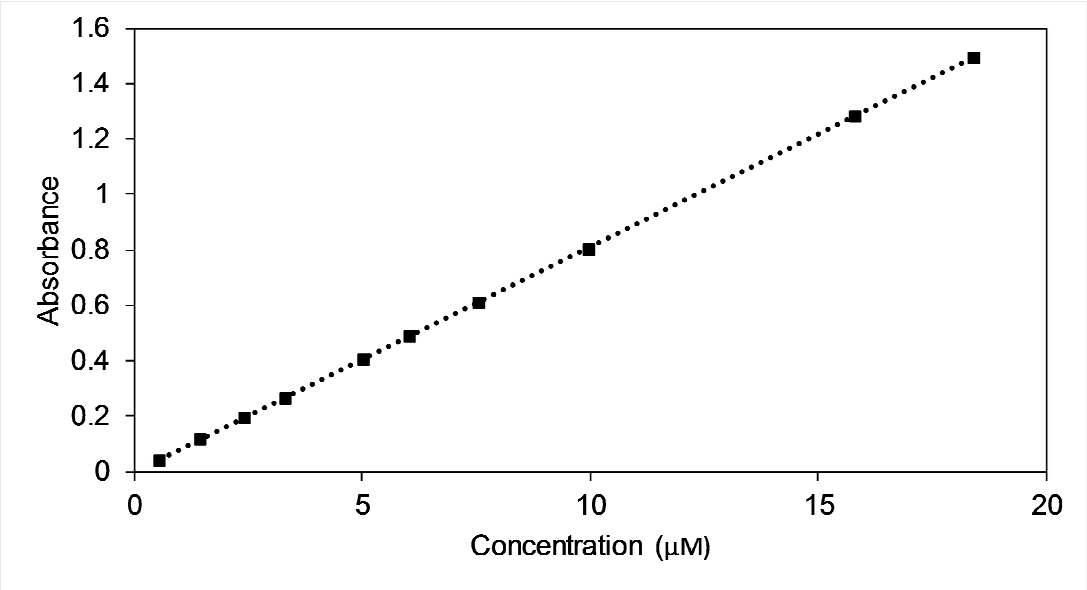


Figure S11. Example of a Beer's law plot made for aza-BOD in N,N-dimethylformamide at room temperature.