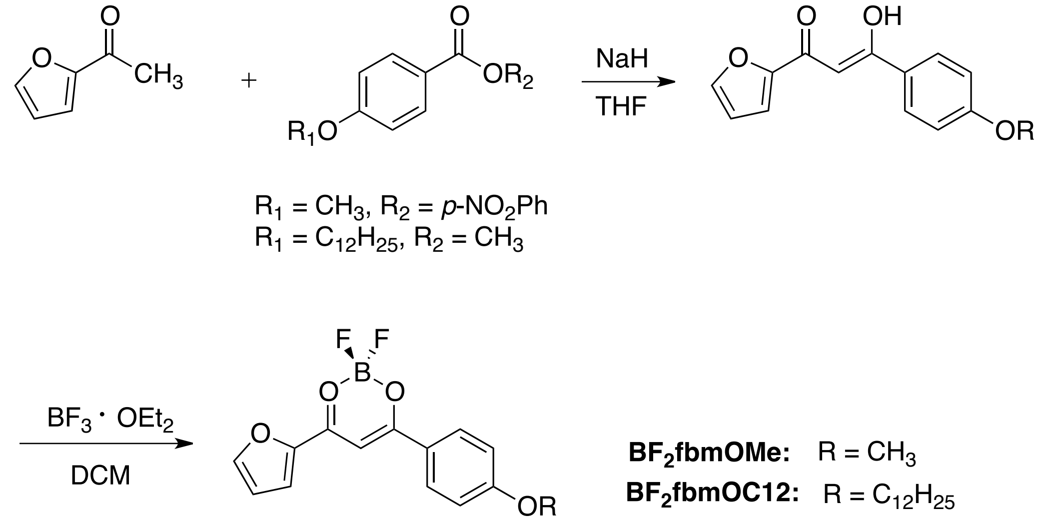
Supporting Information

Stimuli Responsive Furan and Thiophene Substituted Difluoroboron β-Diketonate Materials

*William A. Morris, Tristan Butler, Milena Kolpaczynska, Cassandra L. Fraser**

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904

Scheme S1. Synthesis of Furan-Substituted Difluoroboron β-Diketonate Dyes



BF_2fbmOMe. The ligand fbmOMe[1] was prepared by Claisen condensation of the 2-furyl methyl ketone (0.360 g, 3.27 mmol) and 4-nitrophenyl-4-methoxybenzoate (0.890 g, 3.26 mmol) in THF in the presence of NaH (0.136 g, 5.67 mmol) under a nitrogen atmosphere. The reaction mixture was refluxed for 22 h, allowed to cool to RT, quenched with 1 M HCl, then THF was removed *via* rotary evaporation. The organic layer was extracted with CH_2Cl_2 (2 × 20 mL), washed with H_2O (2 × 20 mL) and brine (10 mL) then dried over Na_2SO_4. After filtration, and concentration *in vacuo*, the residue was purified by column chromatography on silica gel eluting with hexanes/EtOAc (4:1) to give the ligand as a yellow solid: 377 mg (47%) . The fbmOMe ligand (200 mg, 0.82 mmol) was dissolved in

THF (25 mL), and boron trifluoride diethyl etherate (152 μL, 1.23 mmol) was added at room temperature under a nitrogen atmosphere. The reaction mixture was heated at 60° C and monitored by TLC until consumption of ligand substrate was complete (20 h). The reaction mixture was filtered and the solvent was removed *via* rotary evaporation. The product was purified by column chromatography with hexanes:EtOAc (3:1) and an orange powder was obtained: 63 mg (47%). ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.14 (d, 2H, *J* = 12.0 Hz, 2, 6-Phen*H*), 7.75 (broad s, 1H, 2-Fur*H*), 7.55 (d, 1H, *J* = 3.6 Hz, 4-Fur*H*), 7.03 (d, 2H, *J* = 6.0 Hz, 3, 5-Phen*H*), 6.71 (m, 1H, 3-Fur*H*), 6.98 (s, 1H, COC*H*CO), 3.93 (s, 3H, OC*H*$_3$). HRMS (ESI, TOF) m/z calcd for $C_{14}H_{11}BF_2O_4$ 292.07, found 315.0620 $[M + Na]^+$.

BF$_2$fbmOC12. The ligand fbmOC12 was prepared by Claisen condensation of the 2-furyl methyl ketone (1.00 g, 9.08 mmol) and methyl-4-(dodecyloxy)benzoate (2.33 g, 7.28 mmol) in THF in the presence of NaH (0.436 g, 18.17 mmol) under a nitrogen atmosphere. The reaction mixture was heated at 60 °C under a nitrogen atmosphere and monitored by TLC. After 22 h the reaction mixture was removed from the heat and allowed to cool to RT and quenched with 1 M HCl. The THF was removed *via* rotary evaporation. Organics were extracted with CH_2Cl_2 (20 mL × 2), washed with H_2O (20 mL × 2) and brine (10 mL) then dried over Na_2SO_4. After a filtration, and concentration *in vacuo*, the residue run through silica gel column eluting with hexanes/EtOAc (4:1) to give the ligand as a yellow solid. The boron dye, BF$_2$fbmOC12 was made as described for BF$_2$fbmOMe but with the fbmOC12 ligand. The product was purified by recrystallization from hexanes to give a yellow solid: 204 mg (37%). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 8.11 (d, 2H, *J* = 12.0 Hz, 2, 6-Phen*H*), 7.73 (broad s, 1H, 2-Fur*H*), 7.53 (d, 1H, *J* = 3.6 Hz, 4-Fur*H*), 6.98 (m, 3H, 3-Fur*H*, 3, 5-Phen*H*), 6.69 (s, 1H, COC*H*CO), 4.06 (t, 2H, *J* = 6.0 Hz, $\mathrm{OC}\mathit{H}_2\mathrm{C}_{11}\mathrm{H}_{23}$), 1.83-1.81 (m, 2H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}_{10}\mathrm{H}_{21}$), 1.46-1.25 (m, 18H, $\mathrm{OCH_2CH_2C_9}\mathit{H}_{18}\mathrm{CH_3}$), 0.87 (t, 3H, *J* = 6.0 Hz, $\mathrm{CH_2C}\mathit{H}_3$). HRMS (ESI, TOF) m/z calcd for $C_{25}H_{33}BF_2O_4$ 446.24, found 447.2519 $[M + H]^+$ and 469.2337 $[M + Na]^+$.

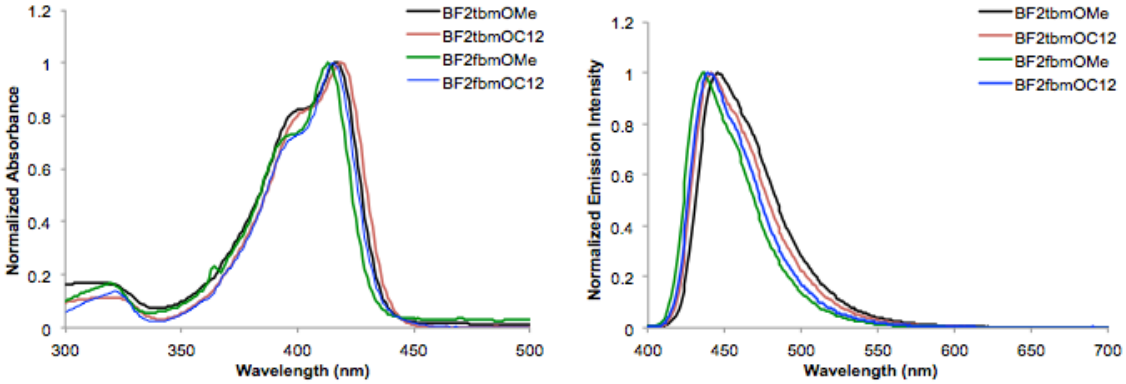


Figure S1. Absorption (left) and fluorescence emission (right) spectra of thiophene and furan-substituted dyes in CH_2Cl_2 solution.

Table S1. Solid State Emission Properties of Boron Dyes as Pristine Powders.

Dye	λ_{em} [a] (nm)	τ_F [b] (ns)	FWHM (nm)
BF_2tbmOMe	593	5.0	105
BF_2tbmOC12	485	3.6	83
BF_2fbmOMe	601	10.7	108
BF_2fbmOC12	594	4.1	N/A

[a] Peak emission wavelength (λ_{ex} = 369 nm), [b] Pre-exponential weighted fluorescence lifetimes excited with a 369 nm light-emitting diode (LED) monitored at the emission maximum. All fluorescence lifetimes are fitted with double-exponential decay.

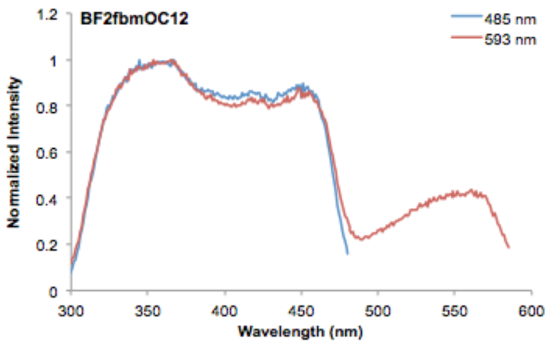


Figure S2. Excitation spectra of the BF$_2$fbmOC12 dye recorded at the indicated emission wavelengths.

Table S2. Optical Properties of Boron Dyes as Films on Both Weighing Paper and Glass Substrates.

	As-Spun			Thermally Annealed			Smeared		
Dye	λ_{em}[b] [nm]	τ_{pw0}[c] [ns]	FWHM[d] [nm]	λ_{em}[b] [nm]	τ_{pw0}[c] [ns]	FWHM[d] [nm]	λ_{em}[b] [nm]	τ_{pw0}[c] [ns]	FWHM[d] [nm]
BF$_2$tbmOC12 (Glass)	525	4.06 (40.57%) 0.81 (17.39%) 13.95 (42.05%) 7.65 (τ_{pw0})	135	486	2.32 (11.57%) 7.65 (88.43%) 7.03 (τ_{pw0})	68	570	6.76 (31.02%) 9.62 (4.08%) 15.39 (64.90%) 12.12 (τ_{pw0})	119
	Heated Green			Heated Orange			TA (125 °C, 10 min)		
BF$_2$fbmOC12 (Paper)	517	0.26 (74.06%) 2.44 (20.61%) 17.48 (29.89%) 0.80 (τ_{pw0})	127	553	4.34 (51.06%) 0.88 (19.11%) 17.48 (29.89%) 7.61 (τ_{pw0})	155	509	3.77 (1.48%) 0.02 (96.66%) 10.44 (4.86%) 0.58 (τ_{pw0})	84

	As-Spun		
	λ_{em}[b] [nm]	τ_{pw0}[c] [ns]	FWHM[d] [nm]
BF$_2$fbmOC12 (Glass)	597	8.47 (9.09%) 29.44 (90.91%) 27.53 (τ_{pw0})	114

[a] λ_{ex} = 369 nm; room temperature, air.
[b] Emission maximum; fluorescence.
[c] Pre-exponential weighted fluorescence lifetime.
[d] Full Width at Half Maximum.

Note: Emission lifetimes were multi-exponential, and the decay traces of emission intensity at λ_{em} and the % weighting factors (WF) were analyzed using DataStation version 2.6 software from Horiba Jobin Yvon. τ_{pw0} was calculated as follows:

$$\tau_{pw0} = \sum_{i=1}^{N} WF_i \cdot \tau_i$$

where N is the number of decay components, WF$_i$ is the weighting factor, τ_i is the component of decay lifetimes, and τ_{PW0} is the pre-exponential weighted lifetime.[2]

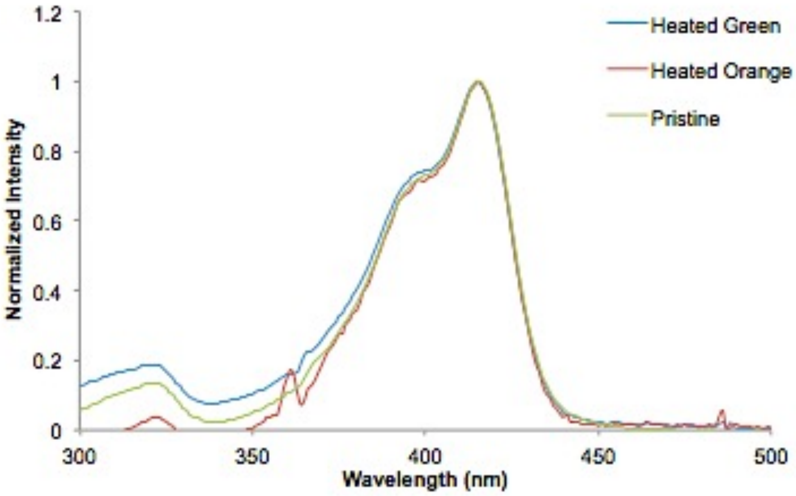


Figure S3. Absorption spectra of BF_2fbmOC12 in CH_2Cl_2 solution. The original spectrum of the pristine powder dissolved in CH_2Cl_2 is compared to the heated green and heated orange forms after they were redissolved and their absorption spectra recorded.

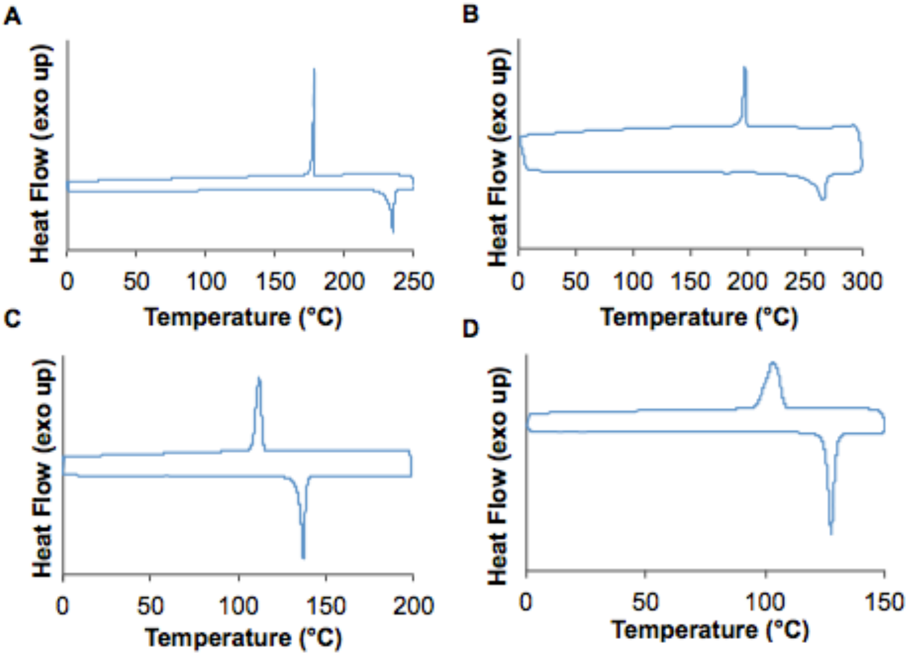


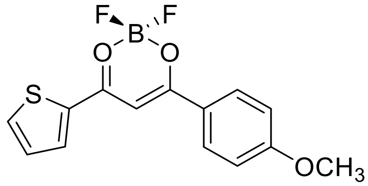
Figure S4. DSC thermograms (ramp rate: 5 °C/min; second heating cycles, after a conditioning cycle) (A = BF_2fbmOMe, B = BF_2tbmOMe, C = BF_2tbmOC12, D = BF_2fbmOC12).

Full Computational Details

All compounds were modeled using the Gaussian 09 suite of programs using density functional theory (DFT).[3] We chose B3LYP/6-31+G(d) for ground state geometry optimization with a Tomasi polarized continuum for dichloromethane solvent.[4] The vibrational frequencies for the optimized geometries were all positive, assuring that the geometries are at least a local minimum. Single point energy calculations were used to generate the molecular orbital diagrams utilizing B3LYP/6-31G(d). We used time-dependent density functional theory, TD-B3LYP/6-311+G(d) for estimates of the absorption spectra, at the respective optimized geometries.2,3 The first three excited states were computed for each compound. Molecular orbitals were depicted by GaussView 5 software.[5]

Table S3. B3LYP/6-31+G(d) optimized structures for future TD-DFT calculations in dichloromethane. Coordinates given in Cartesian, in Angstroms.

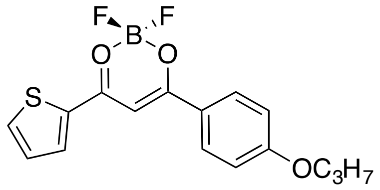
BF$_2$tbmOMe: E (HF) = -1388.75052444



B,	1.047254,	2.282697,	0.017732
F,	1.124661,	2.799166,	1.314774
F,	1.202579,	3.281518,	-0.933151
O,	-0.282447,	1.645663,	-0.170185
C,	-0.477890,	0.355937,	-0.011772
C,	0.614466,	-0.508141,	0.126683
H,	0.464047,	-1.565011,	0.283980
O,	2.133345,	1.278315,	-0.164933
C,	1.912630,	-0.006943,	-0.004006
C,	-1.873414,	-0.079247,	-0.015357
C,	-2.238571,	-1.445633,	-0.016885
C,	-2.902205,	0.882420,	-0.018435

C,	-3.568597,	-1.826026,	-0.016137
H,	-1.481940,	-2.222520,	-0.030323
C,	-4.243255,	0.512697,	-0.016228
H,	-2.642530,	1.935050,	-0.016399
C,	-4.585634,	-0.850540,	-0.014354
H,	-3.849070,	-2.874685,	-0.021573
H,	-5.006502,	1.281865,	-0.013362
C,	3.091296,	-0.843875,	-0.001247
C,	3.181961,	-2.226904,	0.061146
S,	4.682528,	-0.116946,	-0.087821
C,	4.518001,	-2.694602,	0.042766
H,	2.320618,	-2.883097,	0.113641
C,	5.432617,	-1.666741,	-0.036005
H,	4.795000,	-3.741984,	0.083380
H,	6.512350,	-1.742242,	-0.066260
O,	-5.853525,	-1.322099,	-0.012439
C,	-6.944920,	-0.391965,	-0.016536
H,	-7.847203,	-1.003413,	-0.016865
H,	-6.924005,	0.236891,	0.880039
H,	-6.920553,	0.232992,	-0.915734

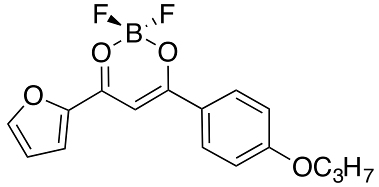
BF_2tbmOC3: E(HF) = -1467.38517722



B,	1.953805,	2.290010,	0.018338
F,	2.049312,	2.798353,	1.317567
F,	2.140271,	3.287382,	-0.928444
O,	0.604035,	1.697146,	-0.170659
C,	0.366378,	0.414672,	-0.009728
C,	1.430839,	-0.483972,	0.128836
H,	1.247355,	-1.535148,	0.288446
O,	3.006392,	1.251532,	-0.169862
C,	2.744037,	-0.025641,	-0.005775
C,	-1.041980,	0.024947,	-0.010705
C,	-1.451350,	-1.328971,	-0.005690
C,	-2.039915,	1.018834,	-0.016502
C,	-2.792797,	-1.666170,	-0.002540
H,	-0.720538,	-2.130276,	-0.015904
C,	-3.392012,	0.692602,	-0.011495
H,	-1.746763,	2.062685,	-0.018794
C,	-3.779662,	-0.659266,	-0.004123
H,	-3.106577,	-2.705409,	-0.003466

H, -4.129490, 1.486399, -0.011121
C, 3.894415, -0.901321, -0.004132
C, 3.938393, -2.286599, 0.057276
S, 5.508989, -0.228339, -0.092033
C, 5.257998, -2.799077, 0.037356
H, 3.055298, -2.913313, 0.109799
C, 6.206714, -1.802630, -0.041747
H, 5.499531, -3.855247, 0.077023
H, 7.283295, -1.914268   -0.073019
O, -5.060415, -1.090053, -0.000753
C, -6.136614, -0.128928, -0.013580
H, -6.055001, 0.512366, 0.873262
H, -6.047389, 0.496887, -0.910680
C, -7.449455, -0.897649, -0.011962
H, -7.481793, -1.542765, 0.875065
H, -7.476940, -1.555444, -0.889782
C, -8.658672, 0.045737, -0.021916
H, -8.660410, 0.685270, -0.913268
H, -9.592725, -0.526316, -0.020253
H, -8.664938, 0.697935, 0.860175

BF$_2$fbmOMe: E (HF) = -1065.77175714



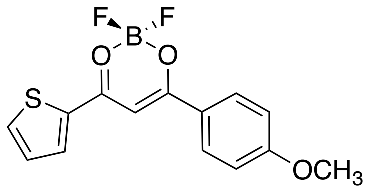
B, -1.358574, 2.226738, 0.012859
F, -1.529753, 3.221209, -0.939848
F, -1.445086, 2.743624, 1.309147
O, -0.017365, 1.612934, -0.173240
C, 0.201948, 0.326534, -0.015932
C, -0.875329, -0.555596, 0.119118
H, -0.711798, -1.611715, 0.270693
O, -2.430252, 1.205581, -0.167665
C, -2.180008, -0.070616, -0.010586
C, 1.605045, -0.083523, -0.017739
C, 1.994301, -1.443174, -0.016333
C, 2.616587, 0.896183, -0.020631
C, 3.330866, -1.799990, -0.013306
H, 1.251679, -2.233531, -0.028886
C, 3.964050, 0.550189, -0.015911
H, 2.338299, 1.944061, -0.020571
C, 4.330515, -0.806704, -0.011548
H, 3.629892, -2.843520, -0.016515
H, 4.713434, 1.332933, -0.013033

C, -3.325855, -0.946011, -0.008985
C, -3.465932, -2.317200, 0.067186
O, -4.566794, -0.366235, -0.098147
C, -4.859809, -2.586287, 0.024174
H, -2.668745, -3.043737, 0.141668
C, -5.477374, -1.366615, -0.076452
H, -5.343678, -3.552179, 0.061361
H, -6.511731, -1.062234, -0.138998
O, 5.606594, -1.255843, -0.007143
C, 6.681325, -0.306603, -0.010065
H, 6.647465, 0.322728, 0.885765
H, 7.594334, -0.901924, -0.007891
H, 6.647818, 0.316911, -0.909961

Table S4. Characterizations of Spectra Computed in Solvent Dichloromethane (PCM-Tomasi as implemented in Gaussian).

Note: Max amplitude is 0.70714 for a pure one-electron excitation. The highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) transitions are in bold.

BF_2tbmOMe

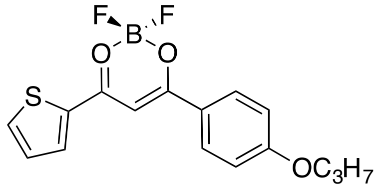


Excited State 1: Singlet-A 3.6394 eV 340.67 nm f=0.7020 <S2>=0.000**
55 -> 56 0.69791

Excited State 2: Singlet-A 4.0132 eV 308.94 nm f=0.0269 <S**2>=0.000
54 -> 56 0.69496
55 -> 56 -0.10029

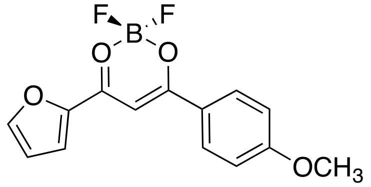
Excited State 3: Singlet-A 4.6387 eV 267.28 nm f=0.0516 <S**2>=0.000
53 -> 56 0.69228
55 -> 57 0.10465

BF$_2$tbmOC3



```
Excited State   1:      Singlet-A      3.0430 eV  407.44 nm  f=1.1477  <S**2>=0.000
      87 -> 88         0.70565

 Excited State   2:      Singlet-A      3.7549 eV  330.19 nm  f=0.0695  <S**2>=0.000
      84 -> 88        -0.19039
      86 -> 88         0.66326

 Excited State   3:      Singlet-A      3.9128 eV  316.87 nm  f=0.0035  <S**2>=0.000
      84 -> 88        -0.19986
      85 -> 88         0.66978
```

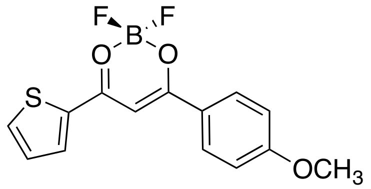
BF$_2$fbmOMe

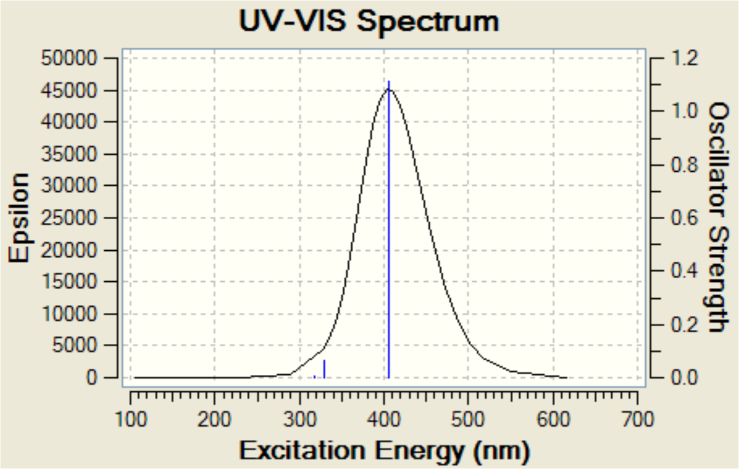


```
Excited State   1:      Singlet-A      3.0808 eV  402.45 nm  f=1.1330  <S**2>=0.000
      75 -> 76         0.70675

 Excited State   2:      Singlet-A      3.8072 eV  325.66 nm  f=0.0738  <S**2>=0.000
      73 -> 76         0.21864
      74 -> 76         0.66300

 Excited State   3:      Singlet-A      4.0112 eV  309.09 nm  f=0.0539  <S**2>=0.000
      73 -> 76         0.65321
      74 -> 76        -0.21043
```

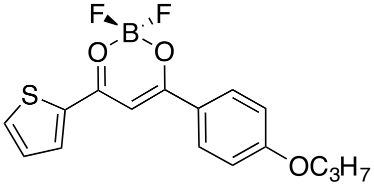
Table S5. Gaussview traces of computed TD-B3LYP/6-311+G(d) absorption spectra for compounds **1-3** in CH$_2$Cl$_2$ represented by Tomasi's Polarizable Continuum Model.

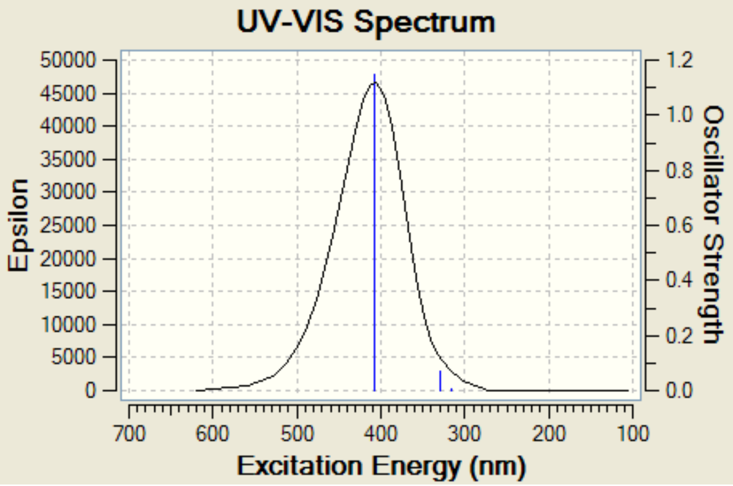
BF$_2$tbmOMe



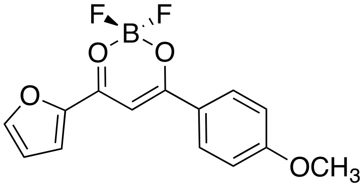


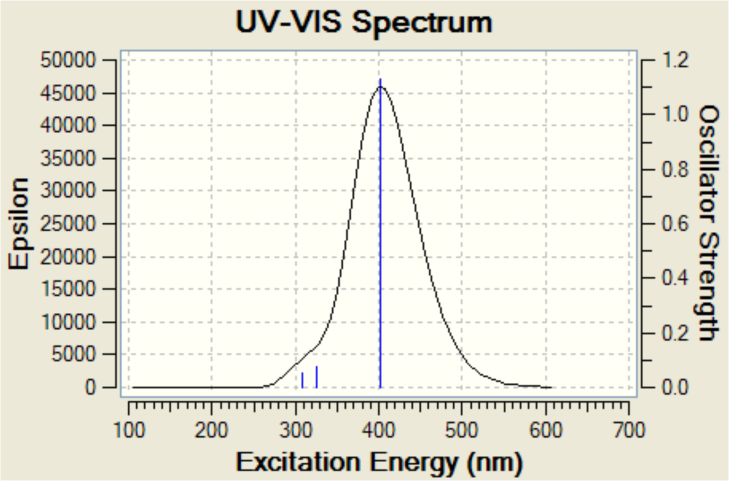
BF_2tbmOC3





BF_2fbmOMe





References

(1) Li, X.; Zou, Y. Q. In *Z. Krist.-New Cryst. St.* **2004**, *219*, 301.

(2) Carraway, E. R.; Demas, J. N.; DeGraff, B. A.; Bacon, J. R. *Anal. Chem.* **1991**, *63*, 337.

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

(4) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999.

(5) Dennington, R. In *Version 5*; Keith, T., Ed.; Semichem Inc.: Shawnee Mission, KS, 2009.