10.1071/CH15750_AC

Australian Journal of Chemistry 69(5), 537-545

**SUPPLEMENTARY MATERIAL**

# Thienyl Difluoroboron β-Diketonates in Solution and Polylactide Media

*Milena Kolpaczynska, Christopher A. DeRosa, William A. Morris, and Cassandra L. Fraser**

Department of Chemistry, University of Virginia, McCormick Road, Charlottesville, VA 22904, USA

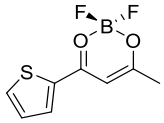
*Corresponding author: Cassandra L. Fraser: fraser@virginia.edu

**Full Computational Details**

All compounds were modeled using the Gaussian 09 suite of programs[1] using density functional theory (DFT). We chose B3LYP/6-31+G(d) for ground state geometry optimization with a Tomasi polarized continuum for dichloromethane solvent.[2] 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.[3]

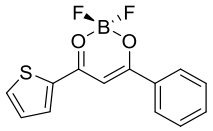
**Table S1.** B3LYP/6-31+G(d) optimized structures for future TD-DFT calculations in dichloromethane. Coordinates given in Cartesian, in Angstroms.

1. **$BF_2$Thio-$CH_3$: E (HF) = -1082.47284568**



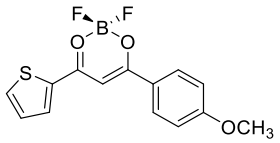

B, 1.91675800, -1.14945100, 0.00984700
F, 2.17867800, -1.69510000, 1.26548600
F, 2.29178400, -2.01241400, -1.00926500
O, 2.67795000, 0.12374600, -0.13083500
C, 2.11144600, 1.29867800, -0.03184300
C, 0.73445800, 1.43965600, 0.06838400
H, 0.29984000, 2.42534300, 0.15464500
O, 0.44622000, -0.89580600, -0.10129300
C, -0.08154500, 0.29766700, -0.00409500
C, -1.52241300, 0.34942500, -0.00167500
C, -2.35260300, 1.46237100, 0.02215000
S, -2.45943000, -1.13028100, -0.03333800
C, -3.72614500, 1.12530300, 0.01739200
H, -1.98754500, 2.48304600, 0.03763200
C, -3.93095400, -0.23809800, -0.01115900
H, -4.53034100, 1.85203000, 0.03293800
H, -4.87744400, -0.76407900, -0.01997900
C, 3.05303200, 2.45835600, -0.05559400
H, 3.63577100, 2.43755400, -0.98418300
H, 2.52404200, 3.41030000, 0.01786000
H, 3.76358700, 2.37152400, 0.77492800

2. **$BF_2$Thio-Ph: E (HF) = -1274.21867029**



B, 0.10957100, 2.22131500, -0.00827300
F, 0.13538100, 2.76126200, 1.27895300
F, 0.17850500, 3.21044400, -0.97685600
O, -1.15650200, 1.46045100, -0.18780200
C, -1.22879600, 0.16151500, -0.02043000
C, -0.06979400, -0.59974300, 0.12999000
H, -0.12725000, -1.66312400, 0.30432500
O, 1.28352900, 1.31313900, -0.17110600
C, 1.18233400, 0.01695000, -0.00146900
C, -2.58933900, -0.40211300, -0.02158800
C, -2.81655000, -1.78985000, -0.10783900
C, -3.69418200, 0.46758800, 0.06422400
C, -4.11616100, -2.29216000, -0.10160300
H, -1.98639200, -2.48221800, -0.19833200
C, -4.99196200, -0.03996600, 0.07330900
H, -3.52499700, 1.53645300, 0.13044700
C, -5.20689200, -1.42000200, -0.00874400
H, -4.27850900, -3.36368400, -0.17417000
H, -5.83571400, 0.64034600, 0.14586400
C, 2.42845000, -0.71128200, 0.01055900
C, 2.63702100, -2.08218900, 0.07532600
S, 3.95176700, 0.15007400, -0.06840400
C, 4.00752600, -2.43291600, 0.06528800
H, 1.83465700, -2.80963400, 0.12205600
C, 4.83051900, -1.32930800, -0.00952900
H, 4.37405800, -3.45220700, 0.10882700
H, 5.91295600, -1.31193400, -0.03278600
H, -6.21915800, -1.81496200, -0.00297600

3. **$BF_2$Thio-Ph$OCH_3$: E (HF) = -1388.75052444**



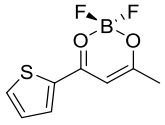
B, 1.04725400, 2.28269700, 0.01773200
F, 1.12466100, 2.79916600, 1.31477400
F, 1.20257900, 3.28151800, -0.93315100
O, -0.28244700, 1.64566300, -0.17018500
C, -0.47789000, 0.35593700, -0.01177200
C, 0.61446600, -0.50814100, 0.12668300

H, 0.46404700, -1.56501100, 0.28398000
O, 2.13334500, 1.27831500, -0.16493300
C, 1.91263000, -0.00694300, -0.00400600
C, -1.87341400, -0.07924700, -0.01535700
C, -2.23857100, -1.44563300, -0.01688500
C, -2.90220500, 0.88242000, -0.01843500
C, -3.56859700, -1.82602600, -0.01613700
H, -1.48194000, -2.22252000, -0.03032300
C, -4.24325500, 0.51269700, -0.01622800
H, -2.64253000, 1.93505000, -0.01639900
C, -4.58563400, -0.85054000, -0.01435400
H, -3.84907000, -2.87468500 -0.02157300
H, -5.00650200, 1.28186500, -0.01336200
C, 3.09129600, -0.84387500, -0.00124700
C, 3.18196100, -2.22690400, 0.06114600
S, 4.68252800, -0.11694600, -0.08782100
C, 4.51800100, -2.69460200, 0.04276600
H, 2.32061800, -2.88309700, 0.11364100
C, 5.43261700, -1.66674100, -0.03600500
H, 4.79500000, -3.74198400, 0.08338000
H, 6.51235000, -1.74224200, -0.06626000
O, -5.85352500, -1.32209900, -0.01243900
C, -6.94492000, -0.39196500, -0.01653600
H, -7.84720300, -1.00341300, -0.01686500
H, -6.92400500, 0.23689100, 0.88003900
H, -6.92055300, 0.23299200, -0.91573400

**Table S2.** 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.

1. **$BF_2$Thio-$CH_3$**

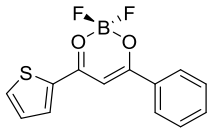



**Excited State 1: Singlet-A 3.6394 eV 340.67 nm f=0.7020 <S**2>=0.000**
**55 -> 56 0.69791**

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

**2. $BF_2$Thio-Ph**

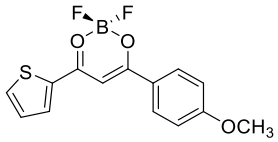



**Excited State 1: Singlet-A 3.2410 eV 382.55 nm f=0.9934 <S**2>=0.000**
**71 -> 72 0.70380**

Excited State 2: Singlet-A 3.7572 eV 329.99 nm f=0.0191 <S**2>=0.000
70 -> 72 0.69768

Excited State 3: Singlet-A 3.8277 eV 323.92 nm f=0.0015 <S**2>=0.000
68 -> 72 0.19548
69 -> 72 0.67312

**3. $BF_2$Thio-Ph$OCH_3$**



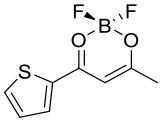

**Excited State 1: Singlet-A 3.0542 eV 405.95 nm f=1.1123 <S**2>=0.000**
**79 -> 80 0.70571**

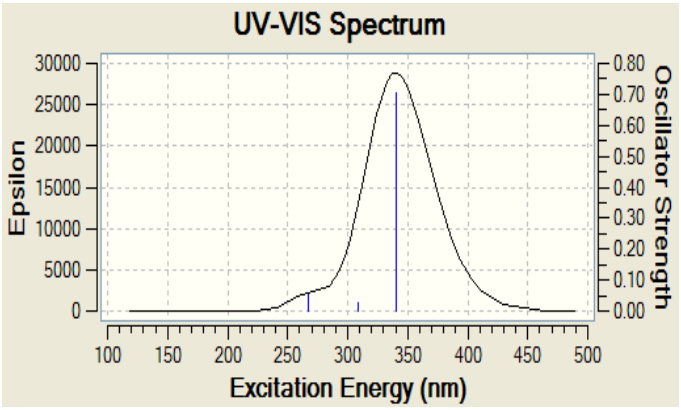
Excited State 2: Singlet-A 3.7605 eV 329.70 nm f=0.0658 <S**2>=0.000
76 -> 80 -0.18491
77 -> 80 -0.11983
78 -> 80 0.66139

Excited State 3: Singlet-A 3.9115 eV 316.97 nm f=0.0048 <S**2>=0.000
76 -> 80 -0.19736
77 -> 80 0.66901

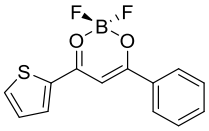
**Table S3.** Gaussview traces of computed TD-B3LYP/6-311+G(d) absorption spectra for compounds **1-3** in $CH_2Cl_2$ represented by Tomasi's Polarizable Continuum Model.

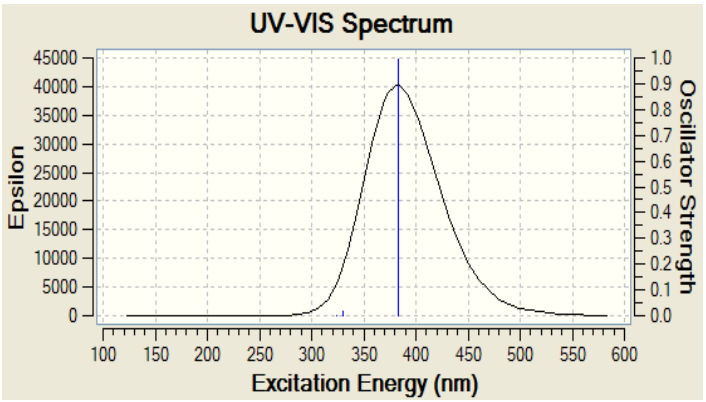
**1. $BF_2$Thio-$CH_3$**



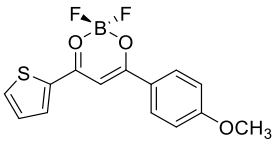




## 2. $BF_2$Thio-Ph




## 3. $BF_2$Thio-Ph$OCH_3$



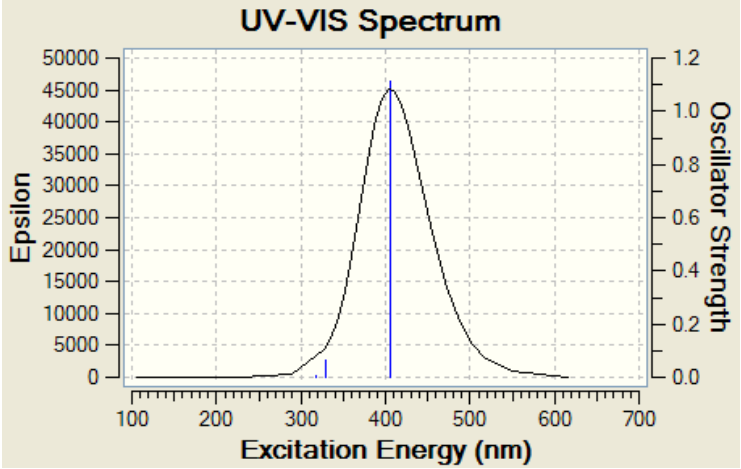



**Table S4.** Computational Data Compared with Experimental Data

| Dye | $E^{*}$ [a.u.] | $\mu^{*}$ [Debye] | $\lambda_{abs}{}^{*}$ [nm] | $\lambda_{abs}{}^{\dagger}$ [nm] | $\lambda_{em}{}^{\dagger}$ [nm] | $\Phi_F{}^{\dagger}$ [%] | Stokes Shift$^{\dagger}$ [$cm^{-1}$] |
|---|---|---|---|---|---|---|---|
| **1** | -1082.47 | 11.11 | 340.67 | 354 | 392 | 0.04 | 2739 |
| **2** | -1274.22 | 11.36 | 382.55 | 401 | 416 | 0.31 | 900 |
| **3** | -1388.75 | 10.71 | 405.95 | 417 | 445 | 0.38 | 1509 |

*Values generated computationally.

$^{\dagger}$Values generated from experiments.

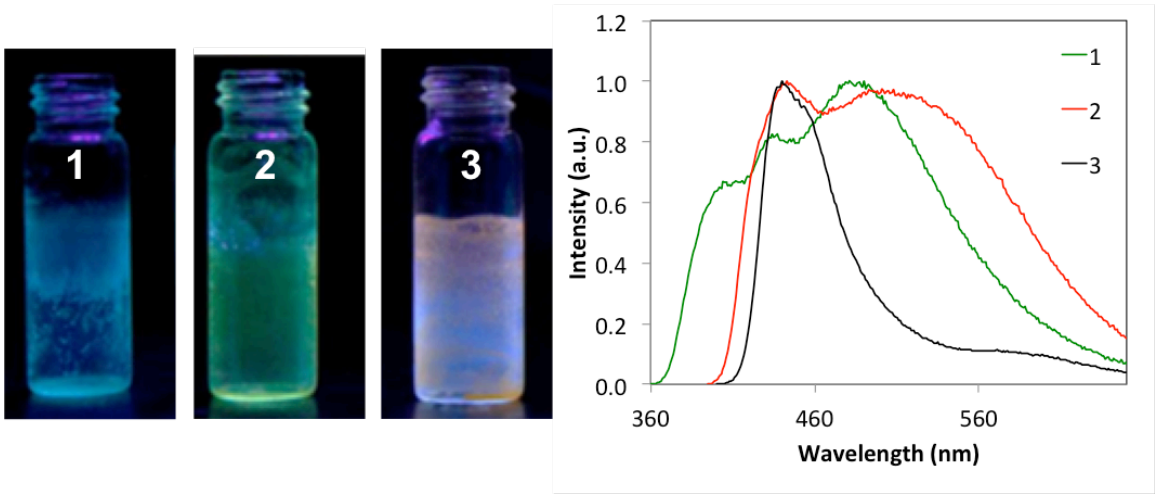



Figure S1. Phase separated dye/PLA blends for **1-3** at 10% dye loading ($\lambda_{ex}$ = 350 nm).

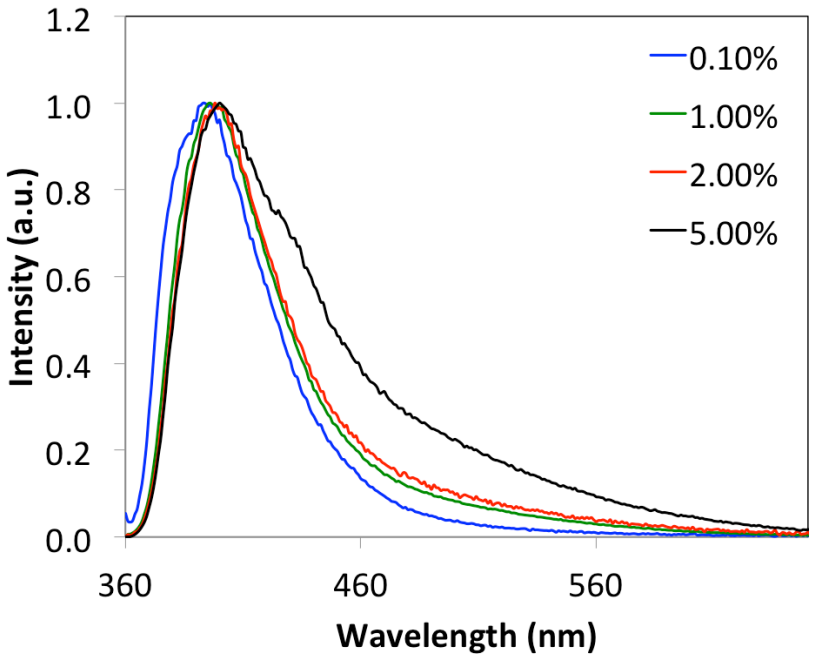



Figure S2. Total emission of $BF_2$mtm (**1**) at various dye loadings in PLA ($\lambda_{ex}$ = 350 nm).

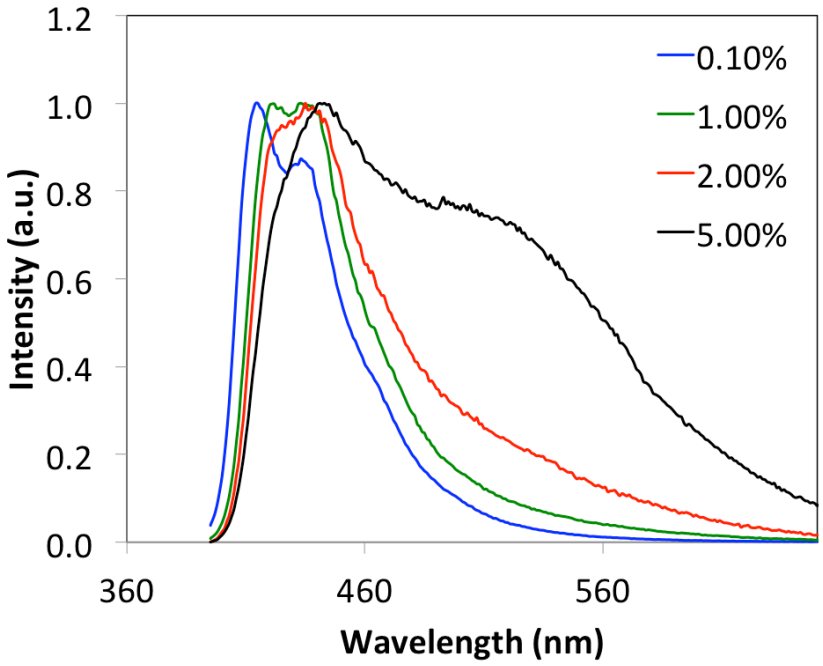



Figure S3. Total emission of $BF_2$tbm (**2**) at various dye loadings in PLA ($\lambda_{ex}$ = 369 nm).

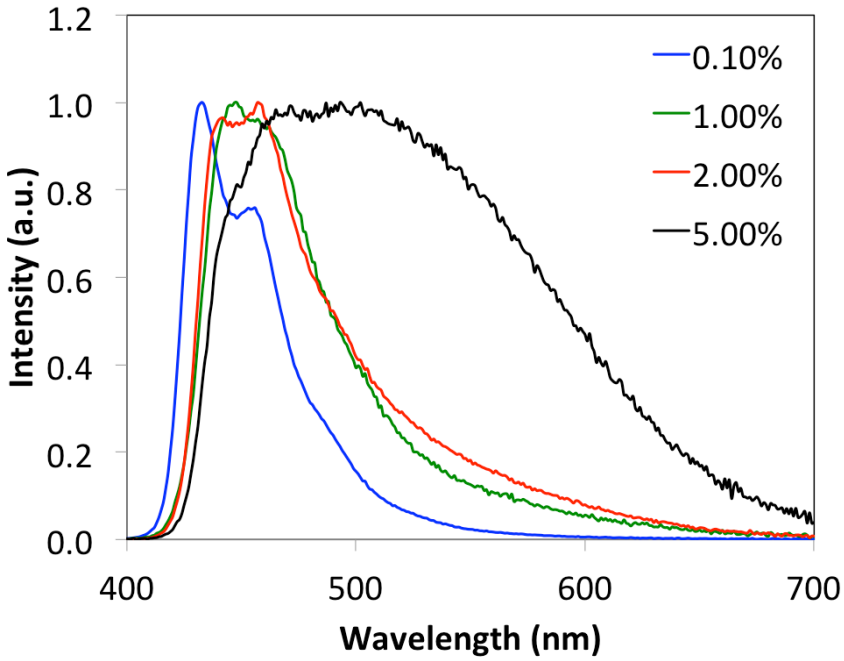



Figure S4. Total emission of $BF_2$dtm (**5**) at various dye loadings in PLA ($\lambda_{ex}$ = 369 nm).

**References**

1) 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.

2) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999-3094.

3) R. Dennington, T. Keith, and J. Millam, Semichem, Inc., Shawnee Mission KS, 2009.