

Supplementary Information

Blue Thermally Activated Delayed Fluorescence from a Biphenyl Difluoroboron β -Diketonate

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EXPERIMENTAL

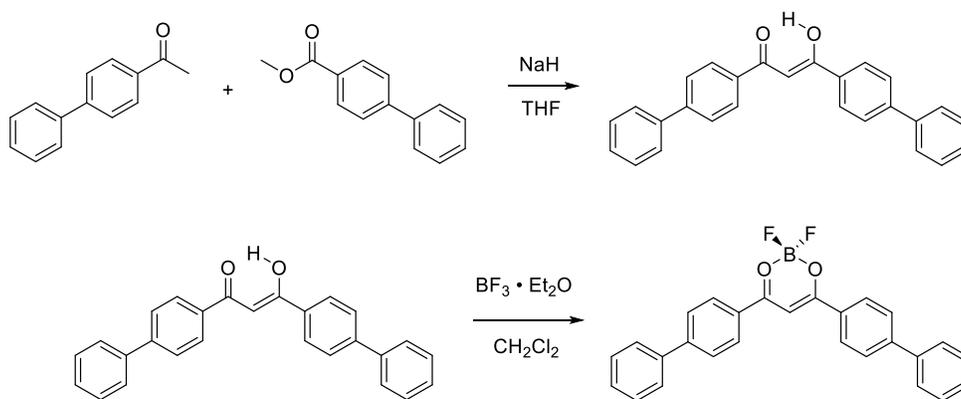
Materials

The polymer (PLA) was prepared as previously described.¹ Diketones and boron dyes were prepared according to literature preparations: BF₂mbm (**1**),² BF₂dbm (**2**),² BF₂bpmm (**3**),³ BF₂bpbm (**4**),⁴ and BF₂dbpm (**5**).⁴ Solvents CH₂Cl₂ and THF were dried and purified over 3 Å molecular sieves activated at 300 °C.⁵ All other chemicals were reagent grade from Sigma-Aldrich and were used without further purification. Thin films of dye/PLA blends were prepared on the inner wall of vials by dissolving dyes and PLA in CH₂Cl₂ to form a homogeneous solution then evaporating the solvent by slowly rotating the vial under a stream of nitrogen. The solution-cast films were then dried *in vacuo* overnight before measurements were performed.

Methods

Steady-state fluorescence emission spectra were recorded on a Horiba Fluorolog-3 Model FL3-22 spectrofluorometer (double-grating excitation and double-grating emission monochromator). A 2 ms delay was used when recording the delayed emission spectra. Time-correlated single-photon counting (TCSPC) fluorescence lifetime measurements were performed with a NanoLED-370 ($\lambda_{\text{ex}} = 369$ nm) excitation source and a DataStation Hub as the SPC controller. Phosphorescence lifetimes were measured with a 1 ms multichannel scalar (MCS) excited with a flash xenon lamp ($\lambda_{\text{ex}} = 369$ nm; duration <1 ms). Lifetime data were analyzed with DataStation v2.4 software from Horiba Jobin Yvon. Fluorescence spectra and lifetimes were obtained under ambient conditions (e.g., air, ~21% oxygen). For phosphorescence measurements, solution cast films in vials were fitted with a 12 mm PTFE/silicone/PTFE seal (Chromatography Research Supplies) connected by a screw cap. Vials were continuously purged with analytical

grade N₂ (Praxair) during measurements. Fluorescence and phosphorescence lifetimes were fit to double or triple exponential decays in solid-state films. For temperature dependent delayed emission spectra, the sample was submerged in liquid N₂ in a coldfinger apparatus (77K) or heated gently with a heat gun for 5 s (~328K). We predict that the sample was heated below the glass transition temperature of PLA (T_g = ~60 °C), because delayed emission was observed.⁶



Scheme 1: Two-step synthesis of BF₂dbpm (**5**).

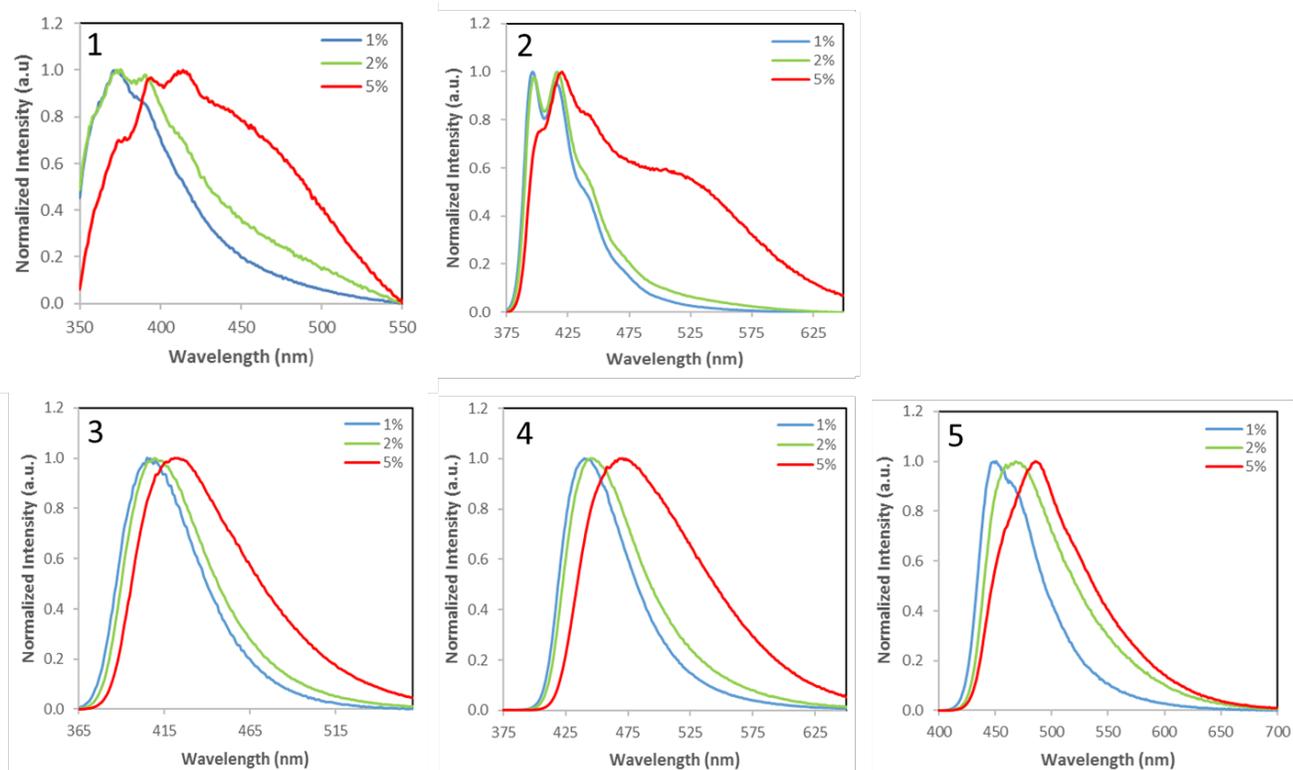


Figure S1. Dye Loading Effects. Emission spectra of 1%, 2% and 5% dye/PLA thin films under air ($\sim 21\% \text{ O}_2$) (i.e. fluorescence) at room temperature (λ_{ex} : **1** = 340 nm; **2-5** = 369 nm).



Figure S2. Images of 1% dye/PLA of BF₂mbm (**1**) BF₂dbpm (**5**) (right) thin films under air (λ_{ex} = 369 nm; UV lamp). Note: Dye **1** has weak fluorescence compared to dye **5**.

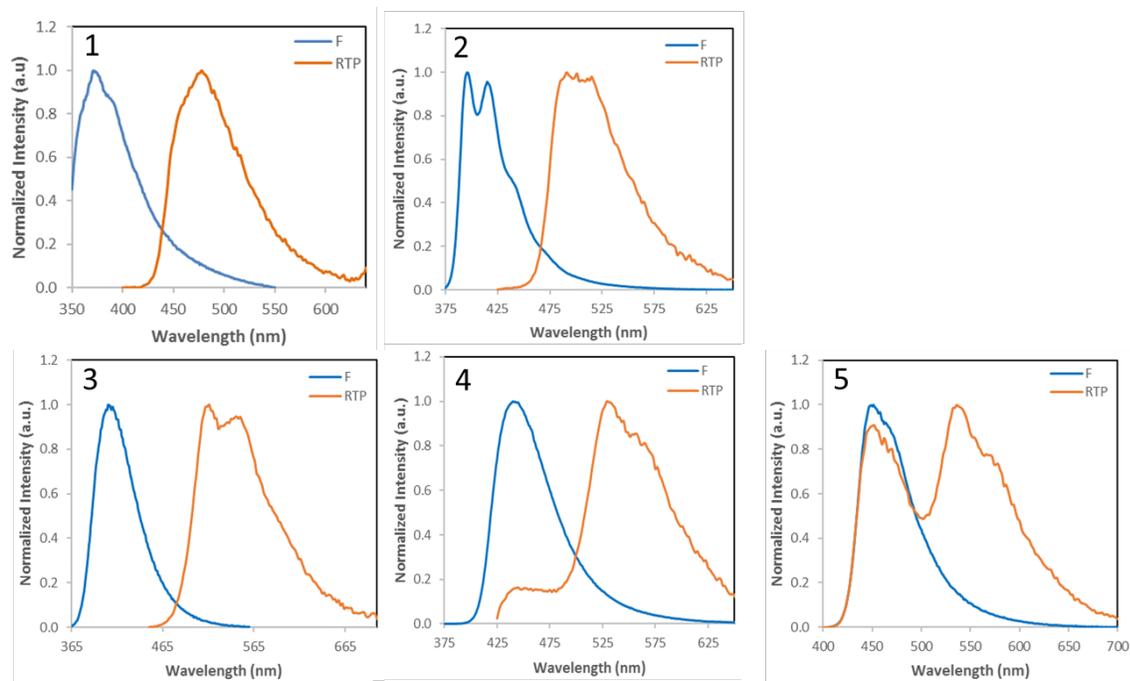


Figure S3. Total emission spectra under air (i.e. fluorescence; F) and delayed emission spectra (1-4: RTP; 5: TADF + RTP) under N_2 for 1% dye/PLA thin films (room temperature; λ_{ex} : 1 = 340 nm; 2-5 = 369 nm). (Note: TADF turns on in dye 5 with a smaller singlet-triplet energy gap and increased number of phenyl rings.)

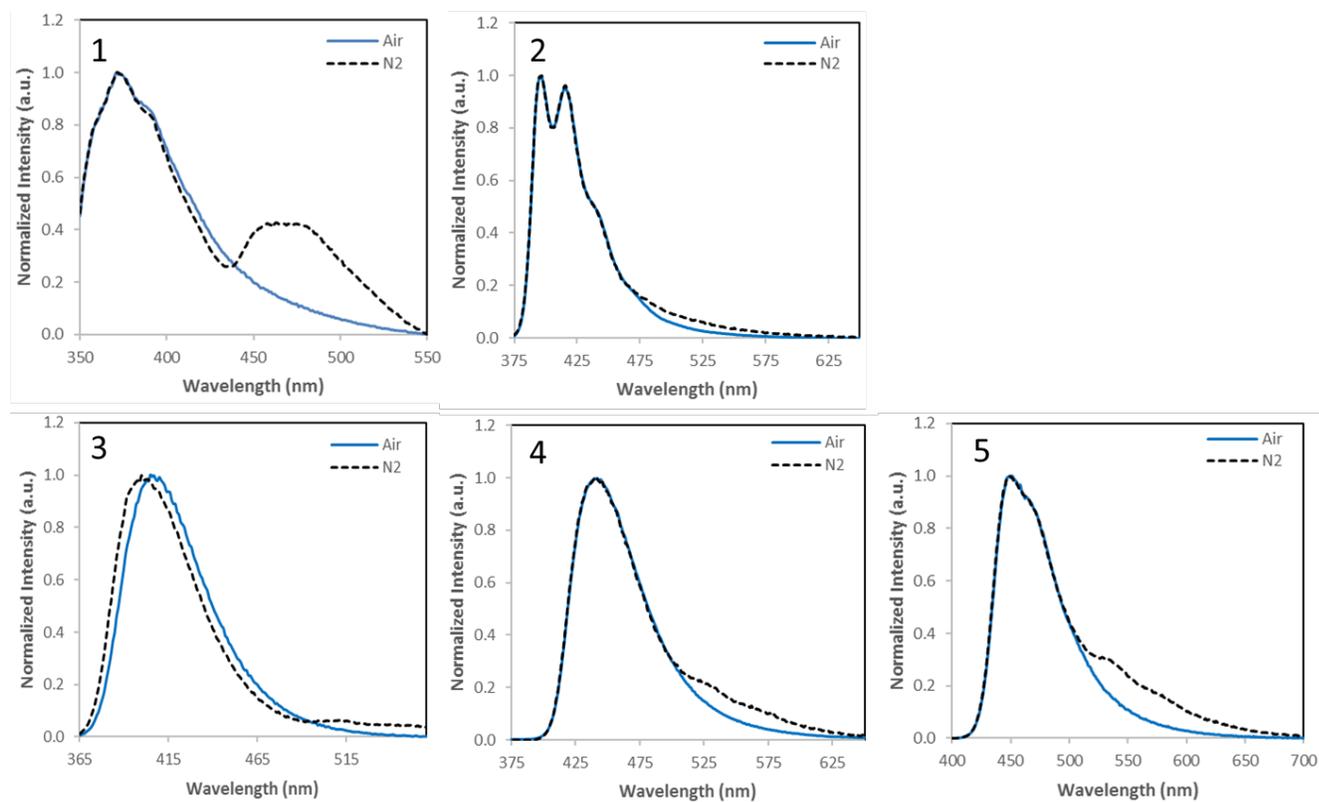


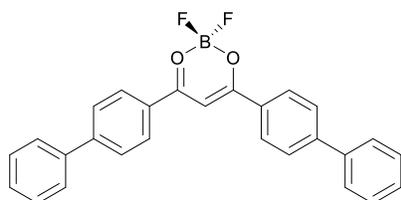
Figure S4. Total emission spectra of 1% dye/PLA thin films under air and N₂ at room temperature. (Note: Delayed emission is weaker than prompt fluorescence.)

Computational Data for Compound 5

The compound was modeled with the Gaussian 09 suite of programs⁷ using density functional theory (DFT) and B3LYP/6-31+G(d) to simulate the B, O, and C atoms. All vibrational frequencies were 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/6-31+G(d) for B, O, and C atoms. Time-dependent density functional theory, TD-B3LYP/6-31+G(d) for B, O, and C atoms, was employed for an estimate of the absorption spectrum at the optimized ground state geometry and the emission spectrum at the optimized S₁ excited state geometry. The emission spectra were computed by calculating the ground state (S₀) energy on the

optimized geometry of the S₁ surface. A Tomasi polarized continuum for dichloromethane solvent was used in each calculation.⁸ Molecular orbital diagrams were depicted using GaussView 5 software.⁹ Coordinates below are given in Cartesian, in Angstroms.

Table S1. Optimized Ground State Geometry



E (HF) = -1415.77051059, μ (Debye) = 11.3917

B, -0.0801, 0., 3.38827
F, 1.30017, -0.00003, 3.85575
F, -0.99757, 0.00003, 4.49655
O, -0.3293, -1.2254, 2.54451
C, -0.03011, -1.21125, 1.23543
C, 0.2047, 0., 0.53696
H, 0.4984, -0.0089, -0.54042
O, -0.3293, 1.2254, 2.54451
C, -0.02329, 1.21125, 1.23543
C, -0.00154, 2.53207, 0.59093
C, 0.07769, 2.68461, -0.80799
C, -0.07636, 3.69344, 1.38605
C, 0.0896, 3.9487, -1.38502
H, 0.10021, 1.8204, -1.46119
C, -0.05777, 4.95506, 0.80337
H, -0.1207, 3.59812, 2.46505
C, 0.02075, 5.11307, -0.59467
H, 0.12268, 4.0325, -2.46702
H, -0.08766, 5.83147, 1.44383
C, -0.01626, -2.53207, 0.59093
C, -0.07769, -2.68461, -0.80799
C, 0.04076, -3.69344, 1.38605
C, -0.0718, -3.9487, -1.38502
H, -0.15361, -1.8204, -1.46119
C, 0.05777, -4.95506, 0.80337
H, 0.0851, -3.59812, 2.46505
C, -0.00295, -5.11307, -0.59467
H, -0.10488, -4.0325, -2.46702
H, 0.08766, -5.83147, 1.44383
C, 0.03073, 6.46103, -1.21493

C, -0.74199, 7.50489, -0.67179
 C, 0.81295, 6.72868, -2.35146
 C, -0.74311, 8.77286, -1.25607
 H, -1.37483, 7.31797, 0.18891
 C, 0.81536, 7.99813, -2.93257
 H, 1.43706, 5.94706, -2.77584
 C, 0.04089, 9.02543, -2.39265
 H, -1.3551, 9.56168, -0.83543
 H, 1.43733, 8.18602, -3.81016
 H, 0.05048, 10.0131, -2.84598
 C, 0.00487, -6.46103, -1.21493
 C, 0.77759, -7.50489, -0.67179
 C, -0.75955, -6.72868, -2.36926
 C, 0.77871, -8.77286, -1.25607
 H, 1.39263, -7.31797, 0.20671
 C, -0.76196, -7.99813, -2.95037
 H, -1.38366, -5.94706, -2.79364
 C, 0.01251, -9.02543, -2.39265
 H, 1.3907, -9.56168, -0.81763
 H, -1.36613, -8.18602, -3.82796
 H, 0.02072, -10.0131, -2.84598

Table S2. Computed Absorption Spectrum Characterization in Dichloromethane

Excited State 1:	Singlet-A	2.8750 eV	431.25 nm	f=1.4977	$\langle S^{*2} \rangle = 0.000$
110 ->111	0.70388				
Excited State 2:	Singlet-A	3.3190 eV	373.56 nm	f=0.1198	$\langle S^{*2} \rangle = 0.000$
109 ->111	0.70353				
Excited State 3:	Singlet-A	3.6842 eV	336.53 nm	f=0.0019	$\langle S^{*2} \rangle = 0.000$
107 ->111	0.65535				
108 ->111	0.23701				

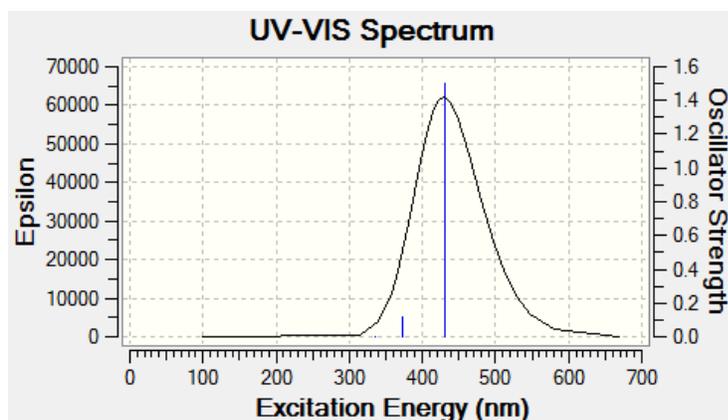
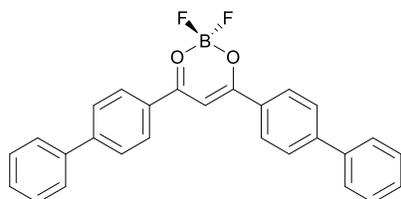


Figure S5. GaussView trace of the computed absorption spectrum.

Table S3. Optimized Excited State Geometry



B, 0.00273, 3.38785, -0.02217
 F, -0.00106, 3.92521, 1.26729
 F, 0.00762, 4.38479, -0.98682
 O, -1.21987, 2.55686, -0.20006
 C, -1.21011, 1.25475, -0.0551
 C, -0.00125, 0.56343, 0.0758
 H, -0.00486, -0.50181, 0.24257
 O, 1.22387, 2.55323, -0.19163
 C, 1.21085, 1.25135, -0.04382
 C, 2.52811, 0.60257, -0.03121
 C, 2.67374, -0.79749, -0.0912
 C, 3.69175, 1.39332, 0.04376
 C, 3.93481, -1.38071, -0.07175
 H, 1.80608, -1.44224, -0.17944
 C, 4.95018, 0.80418, 0.06721
 H, 3.59955, 2.47216, 0.10075
 C, 5.10194, -0.59522, 0.01051
 H, 4.0161, -2.46066, -0.14891
 H, 5.82704, 1.43814, 0.15727
 C, -2.52827, 0.60762, -0.05429
 C, -2.6755, -0.78905, -0.1649
 C, -3.68995, 1.39649, 0.05938

C, -3.9371, -1.37174, -0.15409
 H, -1.8079, -1.43158, -0.26987
 C, -4.94866, 0.80763, 0.07465
 H, -3.59647, 2.47408, 0.13553
 C, -5.10206, -0.58882, -0.03013
 H, -4.0182, -2.45232, -0.22266
 H, -5.82701, 1.4419, 0.14769
 C, 6.44634, -1.2228, 0.03597
 C, 7.54066, -0.61175, -0.60503
 C, 6.65987, -2.44431, 0.70247
 C, 8.80488, -1.20362, -0.5821
 H, 7.39816, 0.31933, -1.14658
 C, 7.92525, -3.03351, 0.72916
 H, 5.8374, -2.92413, 1.22585
 C, 9.00312, -2.41635, 0.086
 H, 9.63364, -0.71989, -1.09246
 H, 8.07002, -3.97133, 1.2591
 H, 9.9878, -2.87572, 0.10548
 C, -6.44739, -1.2148, -0.01114
 C, -7.46993, -0.69915, 0.80758
 C, -6.73362, -2.33826, -0.80954
 C, -8.73516, -1.28897, 0.82909
 H, -7.26781, 0.15273, 1.45096
 C, -8.00053, -2.92468, -0.79158
 H, -5.9692, -2.74083, -1.46843
 C, -9.0064, -2.40351, 0.02879
 H, -9.50699, -0.88105, 1.47652
 H, -8.20334, -3.78487, -1.42425
 H, -9.99192, -2.86126, 0.04408

Table S4. Computed Emission Spectrum Characterization in Dichloromethane

Excited State 1:	Singlet-A	2.8021 eV	442.47 nm	f=1.6201	<S**2>=0.000
110 ->111	0.70196				
Excited State 2:	Singlet-A	3.2739 eV	378.71 nm	f=0.1655	<S**2>=0.000
109 ->111	0.70474				
Excited State 3:	Singlet-A	3.6929 eV	335.74 nm	f=0.0029	<S**2>=0.000
107 ->111	0.65561				
108 ->111	-0.23543				

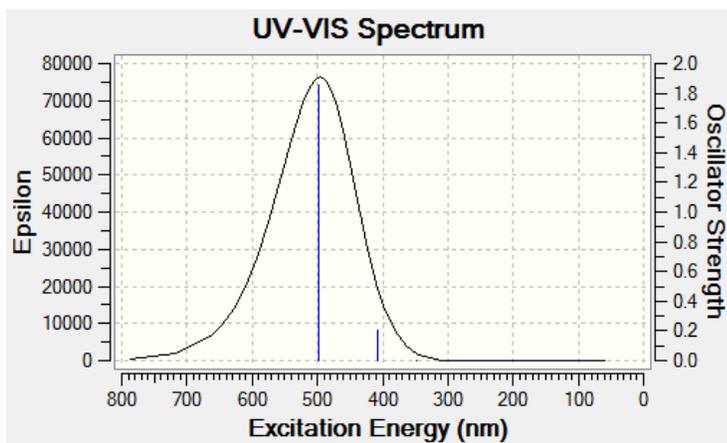


Figure S6. GaussView trace of the computed emission spectrum.

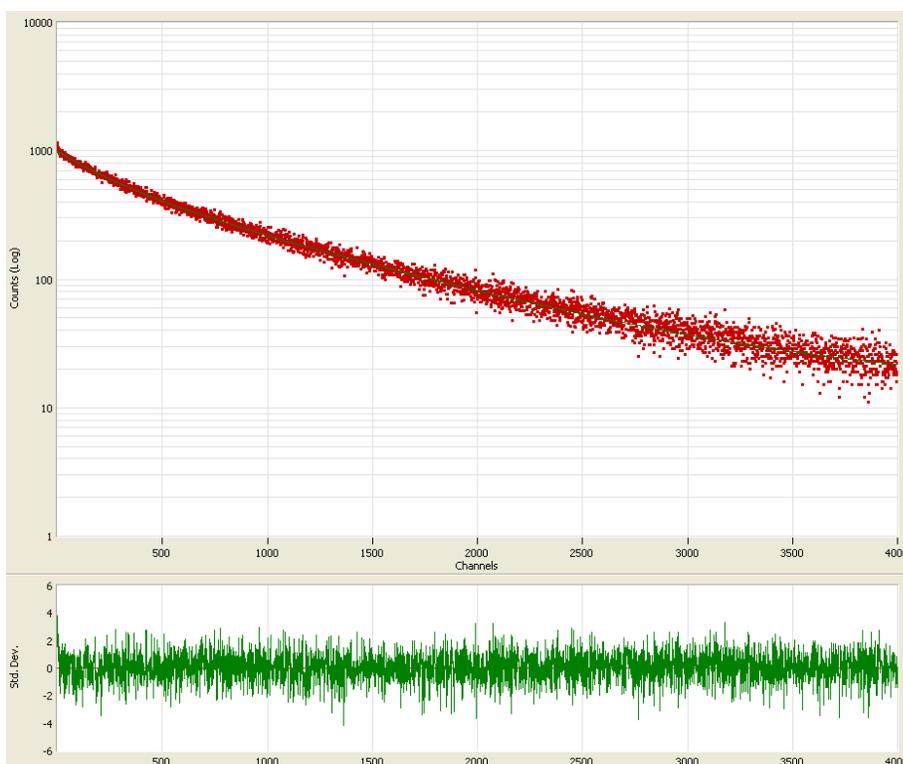


Figure S7. Phosphorescence lifetime decay plot ($\tau_P = 826$ ms) and standard deviation for a 1% BF₂bpbm (4) dye/PLA thin film.

References

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