SUPPORTING INFORMATION

Dual-Emissive Difluoroboron Naphthyl-Phenyl β-Diketonate Polylactide Materials: Effects of Heavy Atom Placement and Polymer Molecular Weight

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Table S1. Polymer Synthesis (**9-12**).

	Sample #	Loading [a]	Time (h)	M_n [b] (kDa)	PDI	M_n [c] (kDa)	Yield [d] (%)
BF_2nbmPLA	9a	1:50:1/50	1.0	5.4	1.05	3.8	0.45
	9b	1:50:1/40	1.0	7.7	1.04	6.6	0.69
	9c	1:180:1/40	1.5	16.1	1.07	13.5	0.59
BF_2n(Br)bmPLA	10a	1:50:1/50	1.5	6.8	1.03	3.9	0.44
	10b	1:50:1/50	2.0	8.8	1.04	7.1	0.54
	10c	1:100:1/50	4.0	11.7	1.04	14.6	0.65
	10d	1:300/1/40	9.0	26.2	1.07	35.7	0.55
BF_2bnmPLA	11a	1:50:1/50	1.0	5.2	1.09	3.3	0.64
	11b	1:100:1/40	1.5	7.5	1.08	7.1	0.56
	11c	1:100:1/40	4.0	9.5	1.04	9.1	0.63
BF_2b(Br)nmPLA	12a	1:50:1/45	1.0	5.6	1.07	4.1	0.40
	12b	1:150:1/40	3.0	12.9	1.04	9.4	0.57
	12c	1:300:1/40	1.5	16.6	1.07	13.5	0.40

[a]Loading (initiator/monomer/cat.). [b]Number-average molecular weight detected by DAD, LS/RI detectors in THF solvent. [c]Number-average molecular detected by ^{1}H NMR. [d]Corrected for monomer conversion.

Table S2. Kinetics Study of Ring Opening Polymerization using BF_2n(Br)bmOH as an initiator.

time	monomer conversion	M_w	M_n	PDI
0	0	0	0	-
5	23	2400	1800	1.33
10	30	3300	2600	1.24
30	51	4800	4700	1.05
60	67	5600	5500	1.04
80	75	6000	5700	1.03
105	83	6100	6000	1.03
135	87	6300	6100	1.03
190	93	6900	6600	1.05

Table S3. Absorption and Emission Data for Boron Initiators and Polymer Samples in CH_2Cl_2.

		λ_{abs} [a] (nm)	ε [b] (M^{-1} cm^{-1})	λ_{em} [c] (nm)	τ_F [d] (ns)	Φ_F [e]	τ_{rad} [f]	Stokes shift (cm^{-1})
BF_2nbmOH	**5**	414	59 000	452	1.55	0.40	3.9	2031
BF_2nbmPLA	**9a**	414	62 000	458	1.73	0.39	4.4	2321
	9b	414	54 000	458	1.75	0.38	4.6	2321
	9c	414	48 000	455	1.75	0.46	3.8	2177
BF_2n(Br)bmOH	**6**	417	65 000	448	0.53	0.19	2.8	1659
BF_2n(Br)bmPLA	**10a**	416	63 000	449	0.52	0.18	2.9	1767
	10b	416	50 000	448	0.52	0.18	2.9	1717
	10c	417	64 000	446	0.50	0.19	2.6	1559
	10d	417	59 000	446	0.51	0.18	2.8	1559
BF_2bnmOH	**7**	418	52 000	505	3.41	0.64	5.3	4121
BF_2bnmPLA	**11a**	418	48 000	504	3.35	0.78	4.3	4082
	11b	418	43 000	501	3.32	0.71	4.7	3963
	11c	418	39 000	501	3.33	0.73	4.6	3963
BF_2b(Br)nmOH	**8**	425	48 000	521	3.33	0.75	4.4	4336
BF_2b(Br)nmPLA	**12a**	425	25 000	514	3.27	0.72	4.5	4074
	12b	425	33 000	514	3.23	0.75	4.3	4074
	12c	425	24 000	512	3.21	0.91	3.5	3998

[a]Absorption maxima. [b]Extinction coefficients calculated at the absorption maxima. [c]Fluorescence emission maxima. [d]Fluorescence lifetime excited with a 369 nm light-emitting diode (LED) monitored at the emission maximum. All fluorescence lifetimes are fitted with single-exponential decay. [e]Relative quantum yield, with anthracene in EtOH as a standard. [f]Radiative lifetime, where $\tau_{rad} = \tau_F / \Phi_F$.

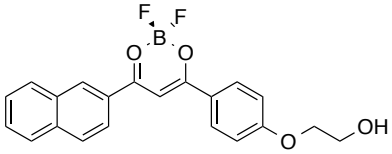
Full Computational Details

All compounds were modeled using the Gaussian 09 suite of programs[1] using density functional theory. We chose B3LYP/6-31+G(d) for ground state geometry optimization with a Tomasi polarized continuum for dichloromethane solvent. 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.[4]

Part I. Gaussian 09 Specifications for Initiators 5-8 in CH_2Cl_2 Solvent.

Table S4. B3LYP/6-31+G(d) optimized structures for future TD-DFT calculation in dichloromethane. Coordinates given in Cartesian, in Angstroms.

5. $BF_2nbmC_2H_4OH$: E (HF) = -1336.17162124



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H, 8.406918, -2.069392, -0.857112
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O, 9.555948, -0.52550, -0.036401
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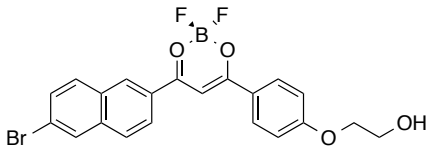
6. BF_2n(Br)bmC_2H_4OH: E(HF) = -3907.30673415



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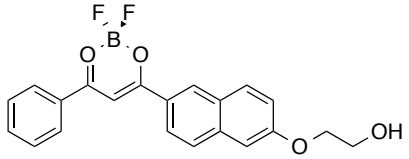
7. BF_2bnmOC_2H_4OH: E (HF) = -1336.17516942



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H, 8.443935, -0.474619, 0.374544
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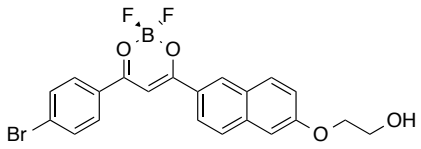
8. BF_2b(Br)nmOC_2H_4OH; E(HF) = -3907.30337535



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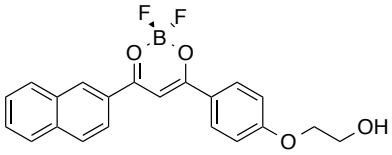
O,-9.950421,-2.096640,1.091018
H,-10.665166,-2.751250,1.051324

Table S5. 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.

5. $BF_2nbmC_2H_4OH$

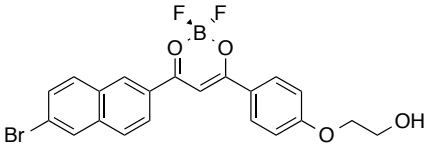


Excited State 1: Singlet-A 2.5736 eV 481.76 nm f=0.6333 <S2>=0.000**
99 ->100 0.70358

Excited State 2: Singlet-A 2.9728 eV 417.06 nm f=1.0186 <S**2>=0.000
97 ->100 0.10141
98 ->100 0.69630

Excited State 3: Singlet-A 3.6424 eV 340.39 nm f=0.0725 <S**2>=0.000
96 ->100 0.11216
97 ->100 0.67779

6. $BF_2n(Br)bmC_2H_4OH$

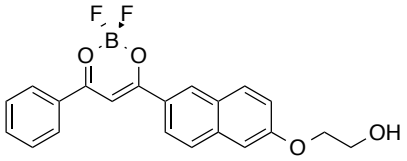


Excited State 1: Singlet-A 2.9230 eV 424.17 nm f=1.1826 <S2>=0.000**
116 ->117 0.70224

Excited State 2: Singlet-A 3.1889 eV 388.80 nm f=0.3501 <S**2>=0.000
114 ->117 0.17290
115 ->117 0.67634

Excited State 3: Singlet-A 3.6507 eV 339.62 nm f=0.0734 <S**2>=0.000
114 ->117 0.66024
115 ->117 -0.17869
116 ->119 0.11843

7. $BF_2bnmOC_2H_4OH$



Excited State 1: Singlet-A 2.6838 eV 461.98 nm f=0.6974 <S2>=0.000**
99 ->100 0.70145

Excited State 2: Singlet-A 3.2668 eV 379.53 nm f=0.5237 <S**2>=0.000
98 ->100 0.69405

Excited State 3: Singlet-A 3.7571 eV 330.00 nm f=0.2364 <S**2>=0.000
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97 ->100 0.64930
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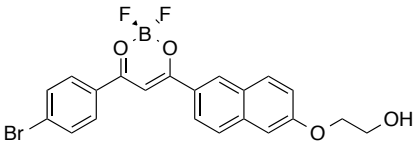
99 ->102 0.17709

8. $BF_2b(Br)nmOC_2H_4OH$



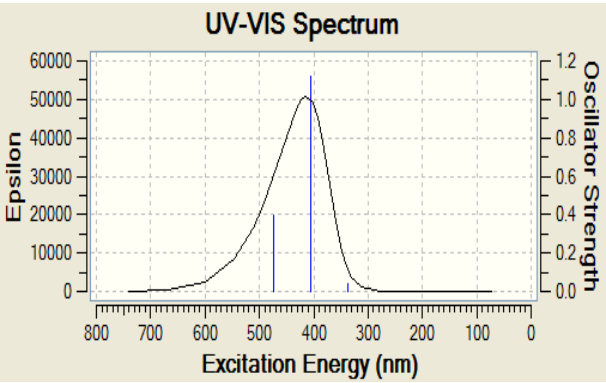
Excited State 1: Singlet-A 2.6327 eV 470.93 nm f=0.7578 <S2>=0.000**
116 ->117 0.70161

Excited State 2: Singlet-A 3.2063 eV 386.69 nm f=0.6128 <S**2>=0.000
115 ->117 0.69568

Excited State 3: Singlet-A 3.6188 eV 342.61 nm f=0.2426 <S**2>=0.000
114 ->117 0.67741
116 ->119 -0.15970

Table S6. Gaussview traces of computed TD-B3LYP/6-311+G(d) absorption spectra for initiators **5-8** in CH_2Cl_2 represented by Tomasi's Polarizable Continuum Model.

5



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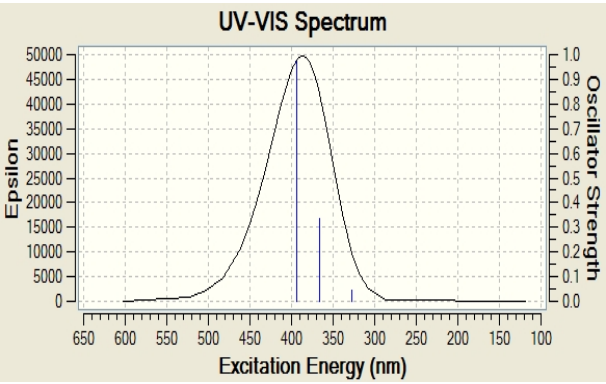

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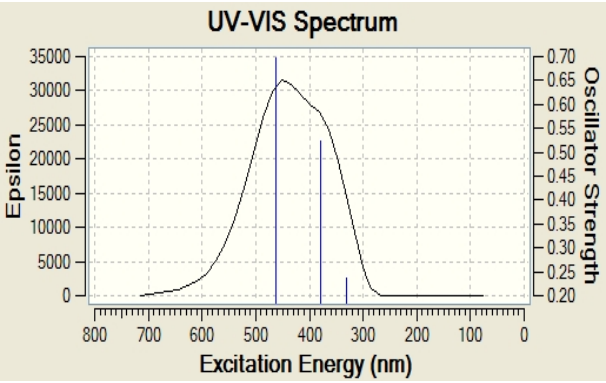

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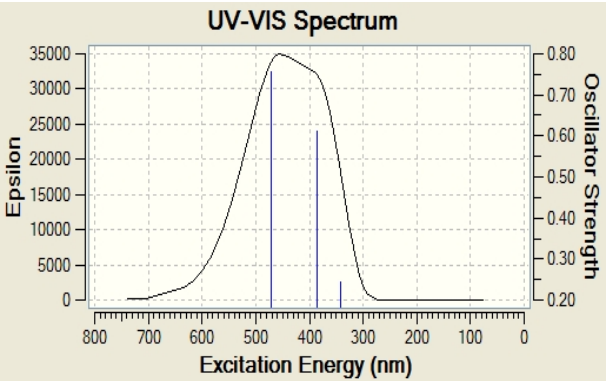

Table S7. Luminescence Data for Films Made from Boron Polymers of Different Molecular Weights.

	Fluorescence					**RTP**			
Polymer	M_n [a] (GPC)	λ_{em} [b] (nm)	τ_F (ns)	%	τ_{pw0} [c] (ns)	λ_{em} [d] (nm)	τ_P (ms)	%	τ_{pw0} [e] (ms)
9a	5.4	526	9.56 2.64 24.50	46.76 21.32 31.92	12.85	558	44.03 132.5 6.24	59.98 32.36 7.66	69.76
9b	7.7	496	6.98 1.78 18.32	47.17 25.00 27.84	8.84	555	8.24 60.04 185.9	5.32 58.63 36.06	102.7
9c	16.1	461	0.64 2.37 8.35	37.56 48.14 14.30	2.57	552	76.87 291.3 20.18	49.09 30.56 20.35	130.9

10a	6.8	491	0.79 2.36 6.82	62.74 29.32 7.94	3.69	568	3.27 10.31 19.89	10.94 78.98 10.08	10.50
10b	8.8	483	0.84 2.58 7.32	64.55 30.14 5.31	1.71	565	1.28 16.85 9.72	4.06 31.34 64.59	11.61
10c	11.7	467	0.71 2.08 5.11	83.07 14.34 2.58	1.02	566	13.89 37.37 3.31	90.09 4.45 5.46	14.36
10d	26.2	444 460	0.63 0.76	100 100	0.63 0.76	565	70.61 6.12 15.37	1.08 13.64 85.28	14.64
11a	5.2	533	2.80 9.89 22.31	12.06 52.81 35.13	13.39	550	16.16 41.47 3.79	69.26 20.98 9.76	20.26
11b	7.5	512	3.04 7.77 18.9	23.74 54.22 22.00	9.10	540	117.2 36.74 7.47	34.73 55.90 9.37	61.94
11c	9.5	505	2.78 7.04 17.89	31.48 49.73 18.78	7.74	545	50.80 185.1 9.96	54.86 33.57 11.56	91.14
12a	5.6	518	1.59 4.49 11.87	23.09 60.91 15.99	5.00	538	19.21 70.67 4.81	55.33 20.00 24.67	25.95
12b	12.9	500	0.74 3.10 8.22	11.35 76.15 12.49	3.47	538	29.59 110.7 7.52	56.04 20.22 23.74	40.76
12c	16.6	495	2.39 5.06 13.2	73.80 24.95 1.17	3.25	539	6.68 28.85 111.82	18.64 55.93 25.43	45.81

[a]Number-average molecular weight detected by DAD, LS/RI detectors in THF solvent. [b]Steady-state fluorescence spectra emission maximum under air. Excitation source: 369 nm xenon lamp. [c]Fluorescence lifetime excited with a 369 nm light-emitting diode (LED) monitored at the emission maximum. All fluorescence lifetimes are fitted with single-exponential decay. [d]Delayed emission spectra maximum under N_2. Excitation source: xenon flash lamp [e]Pre-exponential weighted RTP lifetime. Excitation source: xenon flash lamp; RTP lifetime fit to triple-exponential decay.

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