Supporting Information
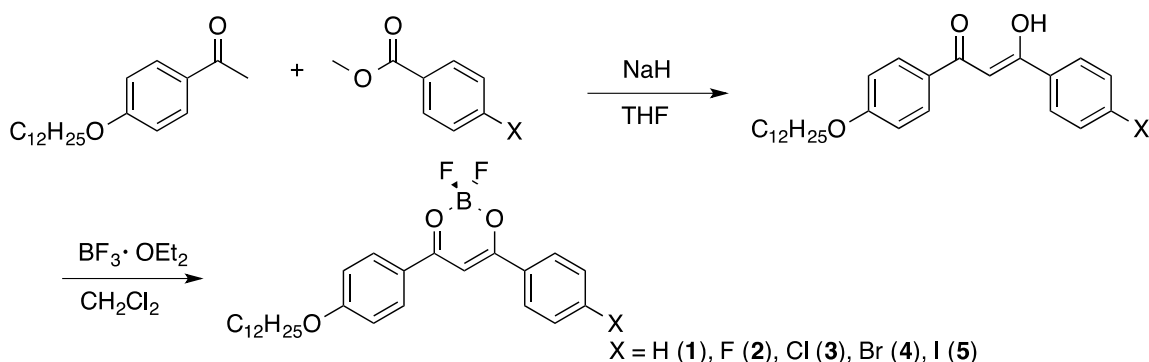**Mechanochromic Luminescence of Halide-substituted Difluoroboron β-Diketonate Dyes**

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X = H (**1**), F (**2**), Cl (**3**), Br (**4**), I (**5**)

Synthesis of β-Diketones. The β-diketone ligands were prepared by Claisen condensation in the presence of NaH as previously described.[1] A representative synthesis is as follows. **Dbm(F)OC$_{12}$H$_{25}$.** 4-Acetophenone (500 mg, 4.16 mmol), ethyl 4-fluorobenzoate (841 mg, 4.99 mmol) and THF (20 mL) were added sequentially to a 50 mL round bottom flask. After stirring the mixture for 10 min, a suspension containing NaH (157 mg, 6.24 mmol) in THF (10 mL) was added dropwise at room temperature under N$_2$. The mixture was stirred and refluxed at 60 °C for 20 h. After cooling to room temperature, saturated aqueous NH$_4$Cl (1 mL) was added to quench the reaction. The aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 20 mL). The combined organic layers were washed with distilled water (2×10 mL) and brine (10 mL), and dried over Na$_2$SO$_4$ before concentration *in vacuo*. The residue was purified by column chromatography on silica gel eluting with hexanes/ethyl acetate (6:1) to give crude 4-fluorobenzoyl 4′-dodecyloxybenzoylmethane as a white solid. The crude product was used for the next step without further purification.

Difluoroboron Diketonate Complex Synthesis. A representative synthesis is as follows. **BF$_2$dbm(F)OC$_{12}$H$_{25}$ (2).** Boron trifluoride diethyl etherate (627 μL, 4.99 mmol) was added to a solution of the fluoro ligand in 20 mL CH$_2$Cl$_2$ at room temperature under N$_2$. The mixture was stirred for 12 h. The solvent was removed *in vacuo*. The residue was recrystallized from hexanes/acetone (4:1) to give **2** (418 mg, 71%) as a yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.18 - 8.12 (m, 4H, 2, 6-Ar*H*, 2′, 6′-Ar*H*), 7.26 - 7.19 (m, 2H, 3, 5-Ar*H*), 7.03 (s, 1H, COC*H*CO), 7.01 (d, 2H, *J* = 9.0 Hz, 3′, 5′-Ar*H*), 4.08 (t, 2H, *J* = 6.3 Hz, OC*H$_2$*C$_{11}$H$_{23}$), 1.88 − 1.78 (m, 2H, OCH$_2$C*H$_2$*C$_{10}$H$_{21}$), 1.49 - 1.27 (m, 18H, OCH$_2$CH$_2$C$_9$*H$_{18}$*CH$_3$), 0.88 (t, 3H, *J* = 6.3 Hz, CH$_2$C*H$_3$*); MS (MALDI): m/z calculated for C$_{16}$H$_{12}$BF$_3$O$_3$ 474.26; found 497.15 [M+Na].

BF₂dbmOC₁₂H₂₅ (1). This compound has been previously synthesized and characterized.[2] This compound was synthesized as previously described.[2] ^{1}H NMR (300 MHz, CDCl₃) δ 8.16 - 8.12 (m, 4H, 2, 6-Ar*H*, 2′, 6′-Ar*H*), 7.68 (t, 1H, *J* = 6.0 Hz, 4-Ar*H*), 7.55 (t, 2H, *J* = 7.8 Hz, 3, 5-Ar*H*), 7.10 (s, 1H, COC*H*CO), 7.02 (d, 2H, *J* = 9.0 Hz, 3′, 5′-Ar*H*), 4.08 (t, 2H, *J* = 6.0 Hz, OC*H₂*C₁₁H₂₃), 1.88 - 1.78 (m, 2H, *J* = 6.0 Hz, OCH₂C*H₂*C₁₀H₂₁), 1.50-1.27 (m, 18H, OCH₂CH₂C₉*H₁₈*CH₃), 0.88 (t, 3H, *J* = 6.0 Hz, OC₂₄H₂₂C*H₃*).

BF₂dbm(Cl)OC₁₂H₂₅ (3). The same method for **2** was used with the ligand for **3**. Recrystalization over hexanes/acetone (3:1) to give **3** (361 mg, 74%) as a yellow solid. ^{1}H NMR (300 MHz, CDCl₃) δ 8.14 (d, 2H, J = 9.0 Hz, 2′, 6′-Ar*H*), 8.06 (d, 2H, *J* = 8.7 Hz, 2, 6-Ar*H*), 7.52 (d, 2H, *J* = 8.7 Hz, 3, 5- Ar*H*), 7.05 (s, 1H, COC*H*CO), 7.01 (d, 2H, *J* = 9.0 Hz, 3′, 5′-Ar*H*), 4.08 (t, 2H, *J* = 6.3 Hz, OC*H₂*C₁₁H₂₃), 1.88 - 1.79 (m, 2H, OCH₂C*H₂*C₁₀H₂₁), 1.49 - 1.27 (m, 18H, OCH₂CH₂C₉*H₁₈*CH₃), 0.88 (t, 3H, *J* = 6.3 Hz, CH₂C*H₃*); MS (MALDI): m/z calculated for C₂₇H₃₄BClF₂O₃ 490.23; found 513.14 [M+Na].

BF₂dbm(Br)OC₁₂H₂₅ (4). The same method for **2** was used with the ligand for **4**. Recrystalization over hexanes/acetone (3:1) to give **4** (524 mg, 67%) as a yellow solid. ^{1}H NMR (300 MHz, CDCl₃) δ 8.13 (d, 2H, *J* = 9.3 Hz, 2′, 6′-Ar*H*), 7.96 (d, 2H, *J* = 8.7 Hz, 2, 6-Ar*H*), 7.67 (d, 2H, *J* = 8. 7 Hz, 3, 5- Ar*H*), 7.05 (s, 1H, COC*H*CO), 7.00 (d, 2H, *J* = 9.0 Hz, 3′, 5′-Ar*H*), 4.08 (t, 2H, *J* = 6.3 Hz, OC*H₂*C₁₁H₂₃), 1.88 - 1.79 (m, 2H, OCH₂C*H₂*C₁₀H₂₁), 1.50 - 1.27 (m, 18H, OCH₂CH₂C₉*H₁₈*CH₃), 0.88 (t, 3H, *J* = 6.3 Hz, CH₂C*H₃*); MS (MALDI): m/z calculated for C₂₇H₃₄BBrF₂O₃ 534.18; found 557.08 [M+Na].

BF₂dbm(I)OC₁₂H₂₅ (5). This compound has been previously synthesized.[3] The same method for **2** was used with the ligand for **5**. Recrystalization over hexanes/acetone (2:1) to give **5** (620 mg, 68%) as a yellow solid. ^{1}H NMR (300 MHz, CDCl₃) δ 8.14 (d, 2H, *J* = 9.0 Hz, 2′, 6′-Ar*H*), 7.91 (d, 2H, *J* = 8.7 Hz, 2, 6-Ar*H*), 7.81 (d, 2H, *J* = 8. 7 Hz, 3, 5-Ar*H*), 7.05 (s, 1H, COC*H*CO), 7.01 (d, 2H, *J* = 9.0 Hz, 3′, 5′-Ar*H*), 4.08 (t, 2H, *J* = 6.6 Hz, OC*H₂*C₁₁H₂₃), 1.88 - 1.79 (m, 2H, OCH₂C*H₂*C₁₀H₂₁), 1.50 - 1.27 (m, 18H, OCH₂CH₂C₉*H₁₈*CH₃), 0.88 (t, 3H, *J* = 6.0 Hz, CH₂C*H₃*); MS (MALDI): m/z calculated for C₂₇H₃₄BIF₂O₃ 582.16; found 605.07 [M+Na].

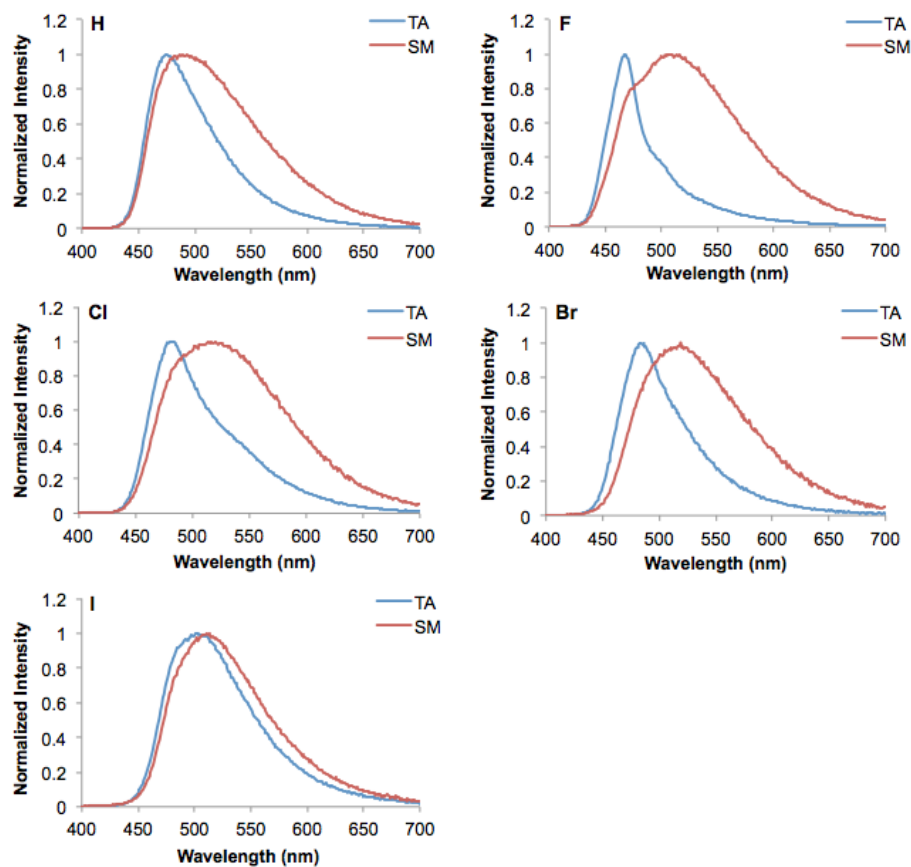**Table S1.** Melting Points of Difluoroboron β-Diketonate Dyes **1-5**.

Compound	Melting Point (°C)
1	133-135
2	140-142
3	148-150
4	151-154
5	145-148
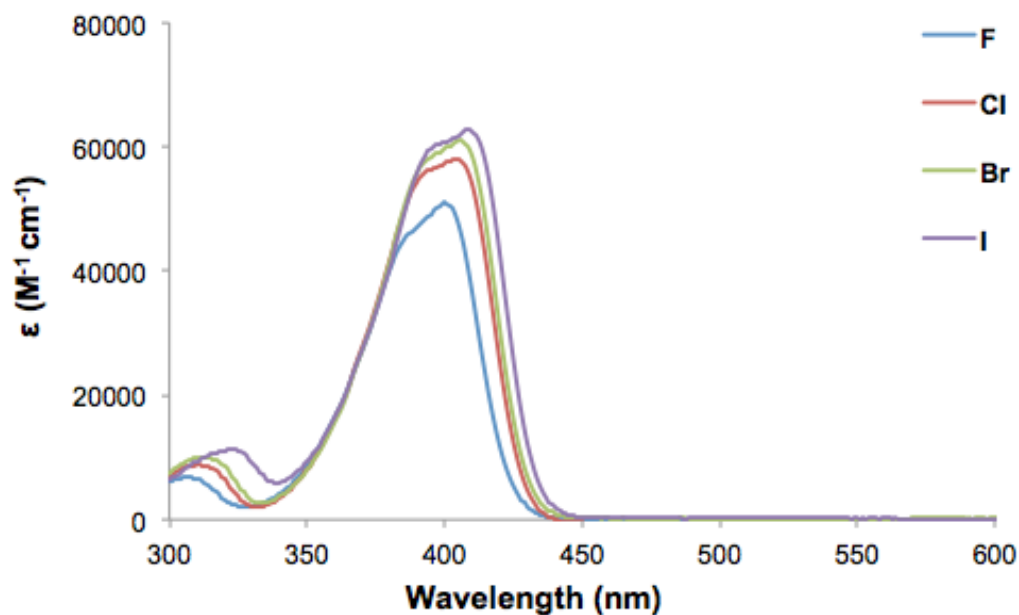
Figure S1. UV/vis absorption spectra of $BF_2dbm(X)OC_{12}H_{25}$ (X = F, Cl, Br, I) dyes in CH_2Cl_2 solution.
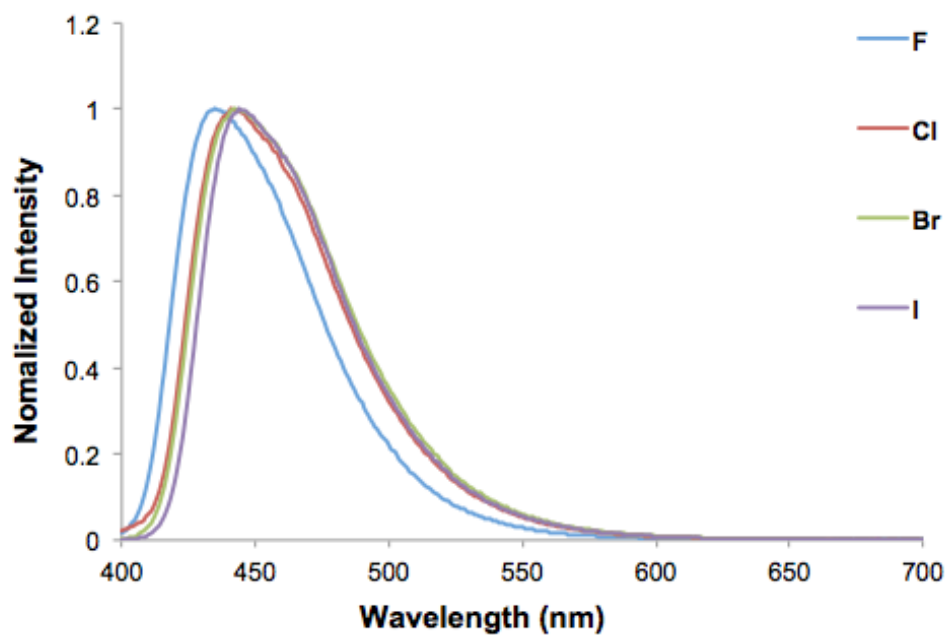
Figure S2. Steady-state fluorescence spectra of $BF_2dbm(X)OC_{12}H_{25}$ (X = F, Cl, Br, I) dyes in CH_2Cl_2 solution.

Figure S3. Normalized emission spectra of $BF_2dbm(X)OC_{12}H_{25}$ dyes as films on weighing paper comparing thermally annealed (TA) and smeared (SM) states (λ_{ex} = 369 nm) (room temperature, air).

Table S2. Emission Maxima and Lifetimes with % Weighting Factors for the Dyes as Films on Weighing Paper at Room Temperature under Air.[a]

Dye	Thermally Annealed λ_{em}[b] [nm]	Thermally Annealed τ[c] [ns]	Smeared λ_{em} [nm]	Smeared τ [ns]	$\Delta\tau_{PW0}$[d] [ns]
H	475	0.42 (7.30%) 5.30 (59.50%) 12.7 (33.20%) 7.40 (τ_{pw0})	487	7.36 (45.76%) 0.89 (8.20%) 27.2 (46.05%) 16.0 (τ_{pw0})	8.60
F	467	0.35 (16.98%) 2.54 (75.44%) 11.24 (7.58%) 2.83 (τ_{pw0})	507	9.58 (39.13%) 1.23 (7.75%) 30.4 (53.11%) 20.0 (τ_{pw0})	17.2
Cl	483	0.39 (9.18%) 4.35 (67.77%) 9.31 (23.05%) 5.13 (τ_{pw0})	514	7.25 (53.31%) 0.87 (9.04%) 25.2 (37.65%) 13.4 (τ_{pw0})	8.27
Br	483	0.97 (89.75%) 5.16 (10.25%) 1.40 (τ_{pw0})	519	4.27 (49.87%) 0.56 (15.09%) 12.7 (35.04%) 6.66 (τ_{pw0})	5.26
I	502	0.23 (31.45%) 1.61 (63.60%) 3.99 (4.94%) 1.29 (τ_{pw0})	513	0.36 (52.21%) 1.40 (43.48%) 4.94 (4.31%) 1.01 (τ_{pw0})	-0.28

[a] λ_{ex} = 369 nm.

[b] Emission maximum; fluorescence.

[c] Fluorescence lifetime.

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.[4]
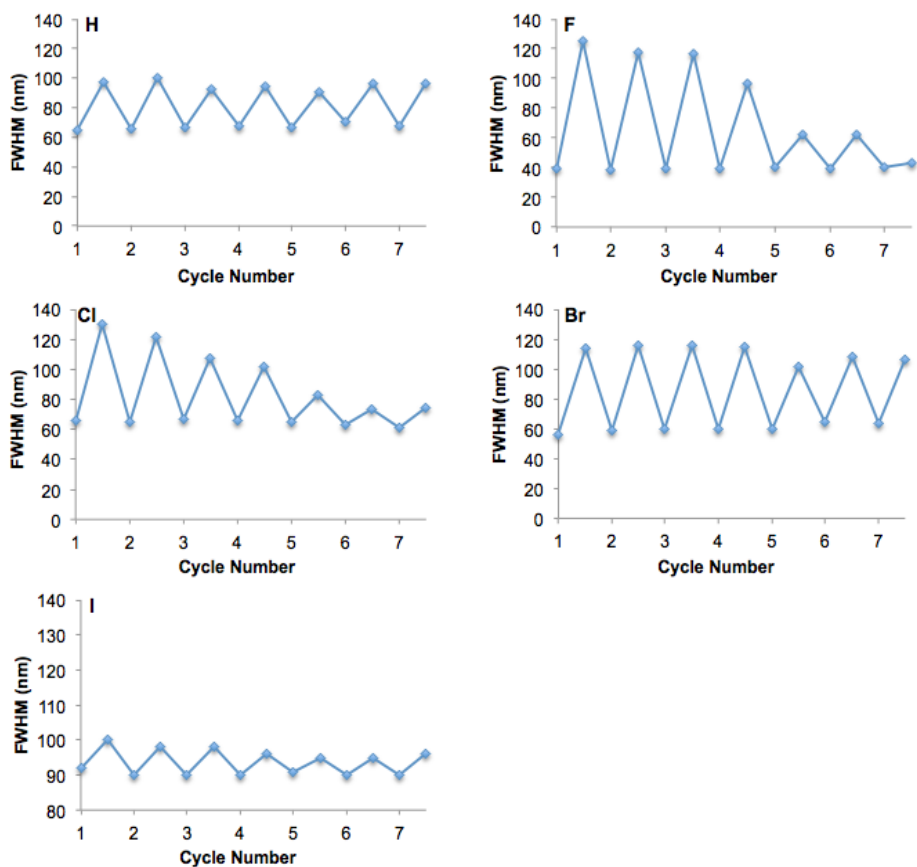
Figure S4. Full width at half maximum (FWHM) values for emission peaks monitored through annealing and smearing cycles (λ_{ex} = 369 nm) (room temperature, air).
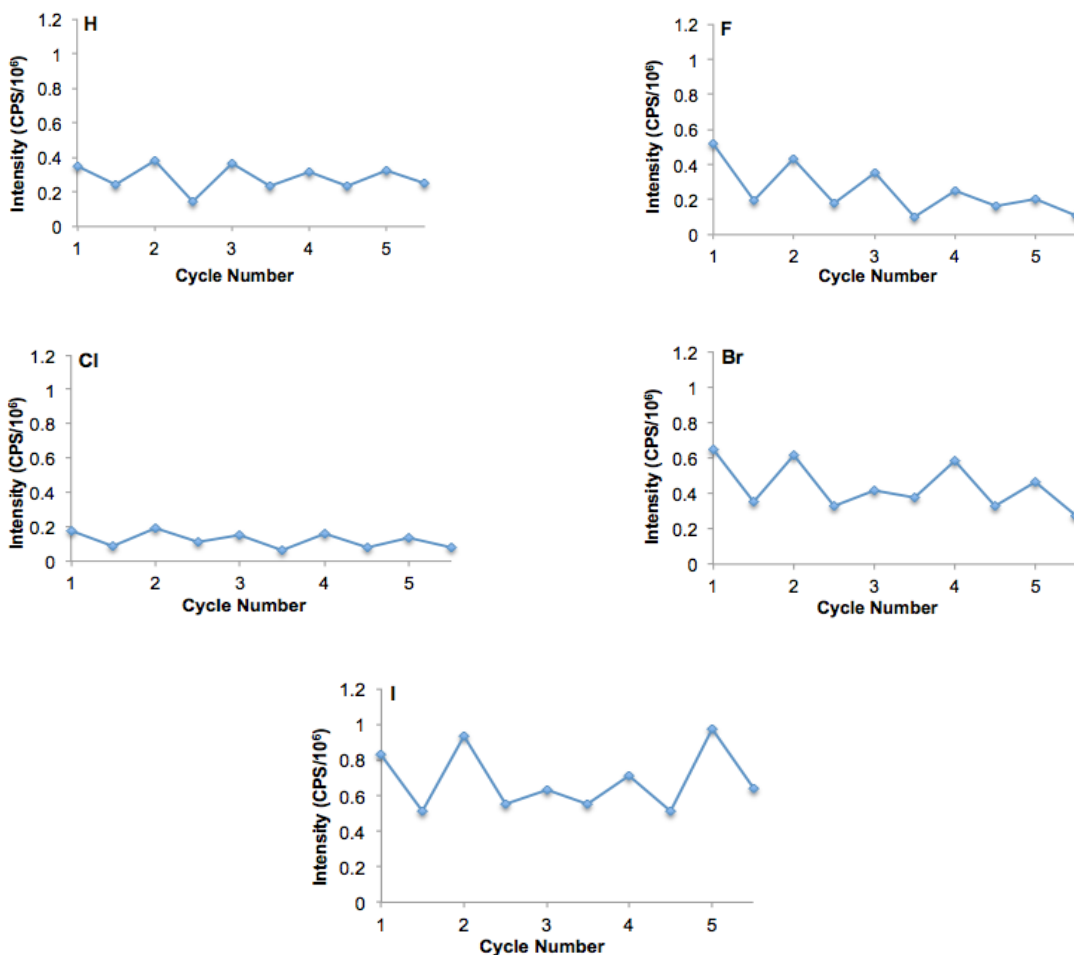
Figure S5. Emission intensities of dyes as films on weighing paper monitored through cycles of smearing and annealing at room temperature in air (λ_{ex} = 369 nm). The intensities were recorded in photon counts per second (CPS) and shown as CPS/10^6.

Table S3. Total Emission for Boron Dyes as Films on Weighing Paper at 77K in liquid N_2.[a]

Dye	Thermally Annealed		Smeared	
	λ_{em}[b] [nm]	FWHM[c] [ns]	λ_{em} [nm]	FWHM [nm]
H	504	71	506	79
F	474	49	521	89
Cl	497	67	530	68
Br	497[d]	67	535[f]	123
I	489[e]	84	502[g]	88

[a] λ_{ex} = 369 nm.

[b] Emission maximum; fluorescence.

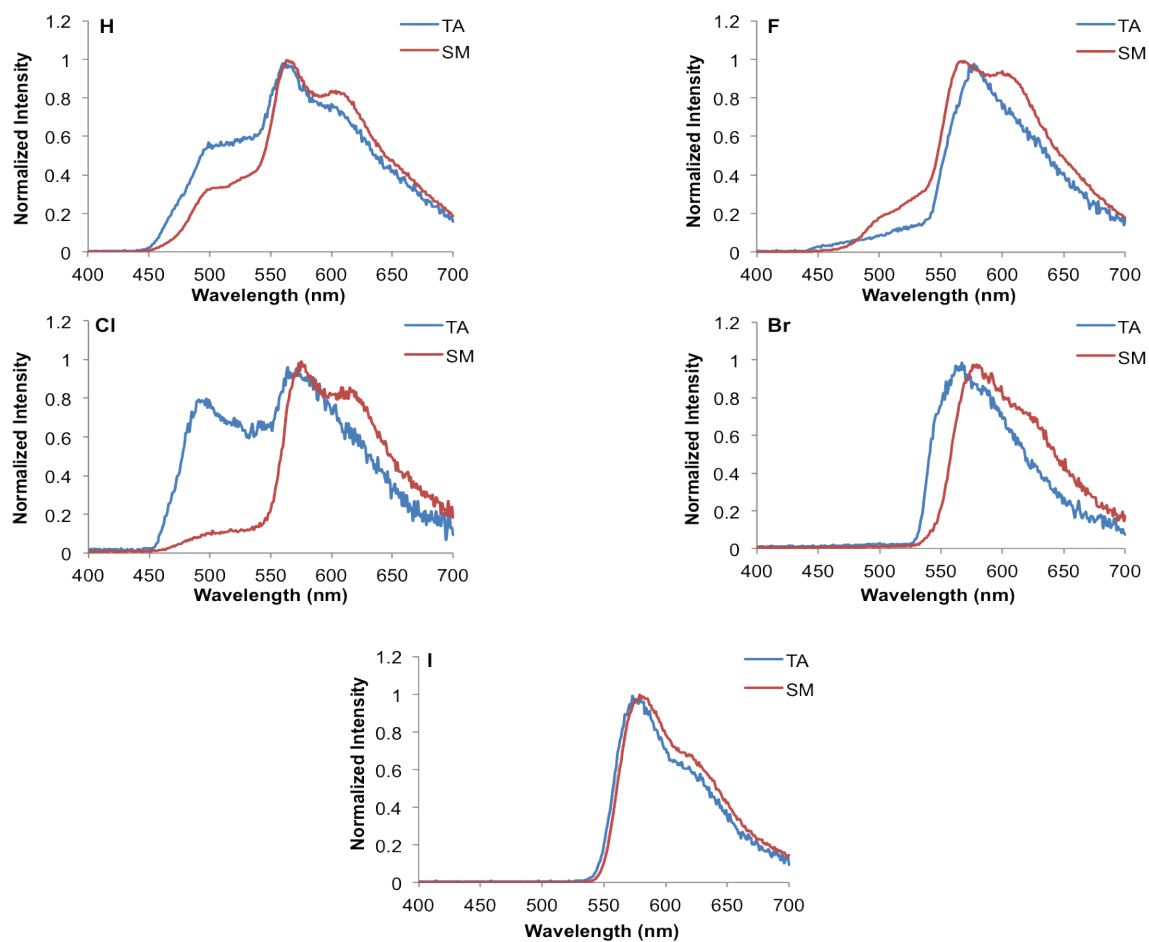[c] Full Width at Half Maximum.

[d] Phosphorescence evident; λ_{phos} = 564 nm.

[e] Phosphorescence evident; λ_{phos} = 570 nm.

[f] Phosphorescence evident: λ_{phos} = 561 nm.

[g] Phosphorescence evident: λ_{phos} = 579 nm.

Figure S6. Normalized delayed emission spectra of $BF_2dbm(X)OC_{12}H_{25}$ dyes on weighing paper in both thermally annealed (TA) and smeared (SM) states at 77K in liquid N_2 (λ_{ex} = 369 nm).

Table S4. Delayed Emission Maxima and Lifetimes with % Weighting Factors for the Dyes as Films on Weighing Paper at 77K in liquid N_2.[a]

Dye	Thermally Annealed λ_{phos}[b] [nm]	Thermally Annealed τ_{phos}[c] [ms]	Smeared λ_{phos} [nm]	Smeared τ_{phos} [ms]	$\Delta\tau_{PW0}$ [ms]
H	562	107 (18.43%) 10.3 (11.47%) 748 (59.16%) 1.25 (10.93%) 463 (τ_{pw0})	563	194 (13.04%) 1010 (81.68%) 17.1 (3.37%) 1.47 (1.92%) 851 (τ_{pw0})	388
F	577	44.1 (47.05%) 545 (40.90%) 3.80 (12.05%) 244 (τ_{pw0})	569	143 (10.22%) 18.7 (4.19%) 1050 (83.93%) 1.28 (1.66%) 897 (τ_{pw0})	653
Cl	564	8.80 (26.49%) 65.1 (20.71%) 553 (34.62%) 1.40 (18.18%) 208 (τ_{pw0})	578	83.2 (9.15%) 581 (81.75%) 8.50 (5.05%) 1.98 (4.05%) 483 (τ_{pw0})	275
Br	567	3.94 (6.61%) 22.7 (50.02%) 218 (3.56%) 58.4 (39.80%) 42.6 (τ_{pw0})	580	44.5 (33.33%) 4.62 (3.28%) 106 (63.39%) 82.0 (τ_{pw0})	39.4
I	573	1.57 (14.20%) 17.6 (31.85%) 233 (1.87%) 8.10 (52.08%) 14.4 (τ_{pw0})	580	96.1 (0.52%) 1480 (1.37%) 14.7 (98.11%) 35.2 (τ_{pw0})	20.8

[a] $\lambda_{ex} = 369$ nm.

[b] emission maximum; phosphorescence.

[c] Phosphorescence lifetime.
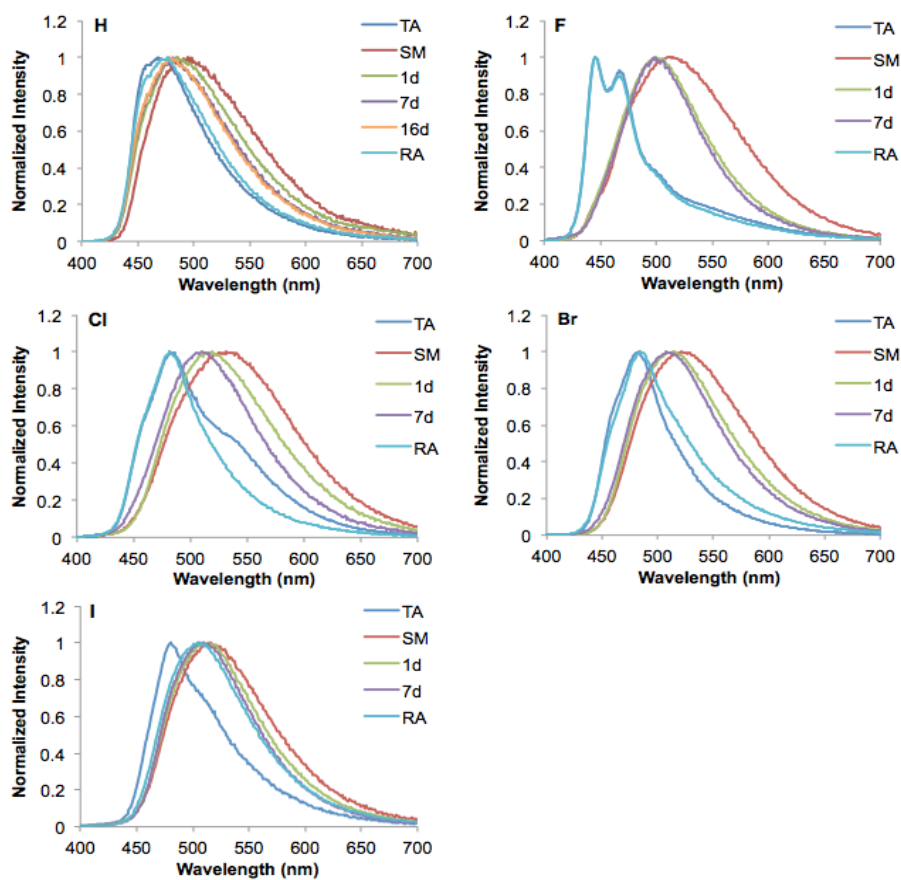
Figure S7. Emission spectra of boron dyes as spin-cast films on glass (λ_{ex} = 369 nm) (room temperature, air). The dyes were thermally annealed (TA), smeared (SM), and then the emission spectra were monitored over time. After three weeks, the films were re-annealed (RA). Note: d = days.

| Dye	As-spun λ_{em} [nm]	As-spun τ [ns]	As-spun FWHM [nm]	Thermally Annealed λ_{em} [nm]	Thermally Annealed τ [ns]	Thermally Annealed FWHM [nm]	$\Delta\tau_{PW0}$ (ns)
H	524	16.6 (29.75%) 2.83 (3.51%) 40.9 (66.74%) 32.3 (τ_{pw0})	131	468	2.12 (16.07%) 6.54 (54.42%) 16.4 (29.50%) 8.74 (τ_{pw0})	74	-23.6
F	517	13.3 (38.23%) 37.7 (61.77%) 28.4 (τ_{pw0})	113	445	1.52 (90.99%) 8.77 (9.01%) 2.17 (τ_{pw0})	48	-26.2
Cl	538	11.3 (62.35%) 34.8 (37.65%) 20.1 (τ_{pw0})	124	484	5.20 (56.21%) 8.70 (43.79%) 6.73 (τ_{pw0})	74	-13.4
Br	520	1.25 (13.76%) 5.60 (60.48%) 14.3	105	483	1.05 (95.70%) 5.43 (5.30%) 1.28 (τ_{pw0})	63	-5.96
I	515	0.74 (87.99%) 2.89 (12.01%) 1.00 (τ_{pw0})	106	480	1.66 (54.02%) 3.05 (45.98%) 2.30 (τ_{pw0})	72	1.30

[a] λ_{ex} = 369 nm.

[b] Emission maximum; fluorescence.

[c] Fluorescence lifetime.

Table S5. Emission Maxima and Lifetimes with % Weighting Factors for the Dyes as Spin-cast Films on Glass at Room Temperature under Air.[a]
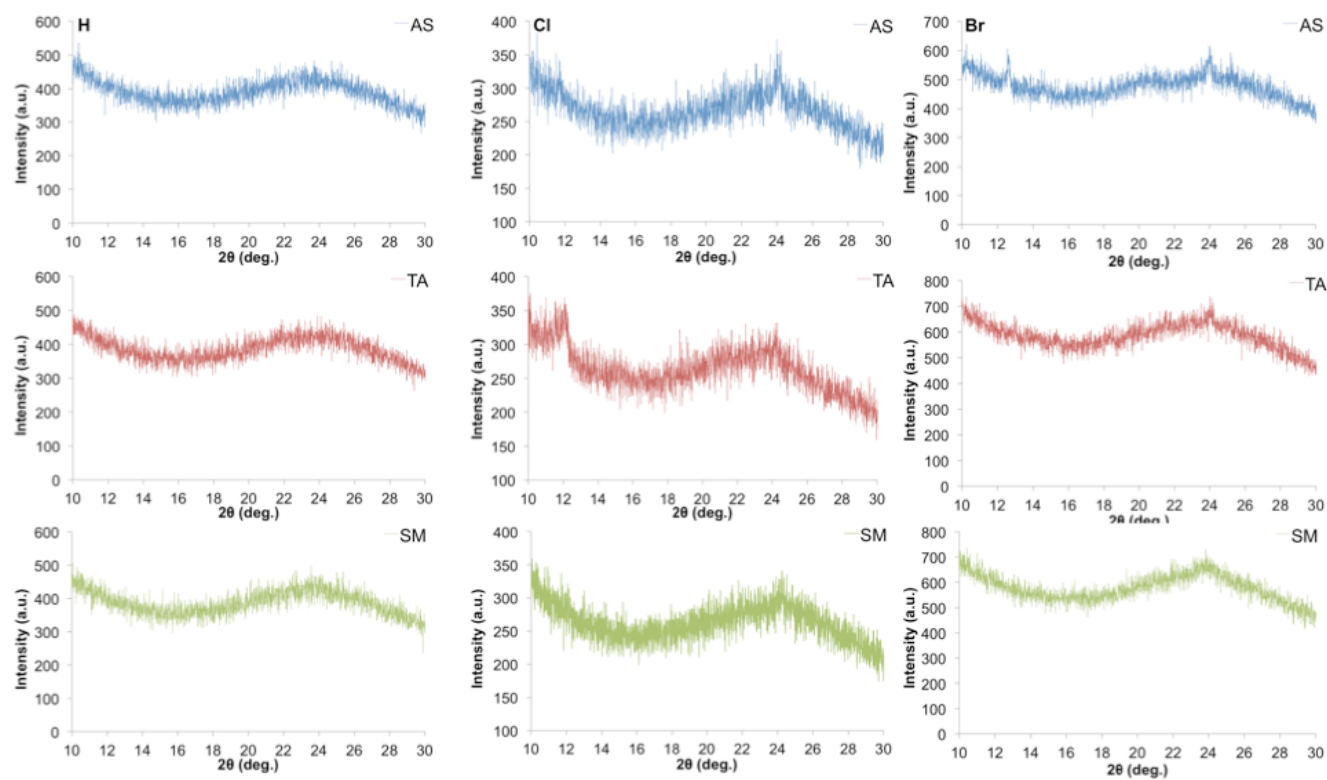
Figure S8. X-ray diffraction patterns of the H, Cl, and Br dyes as-spun (AS), thermally annealed (TA), and smeared (SM).
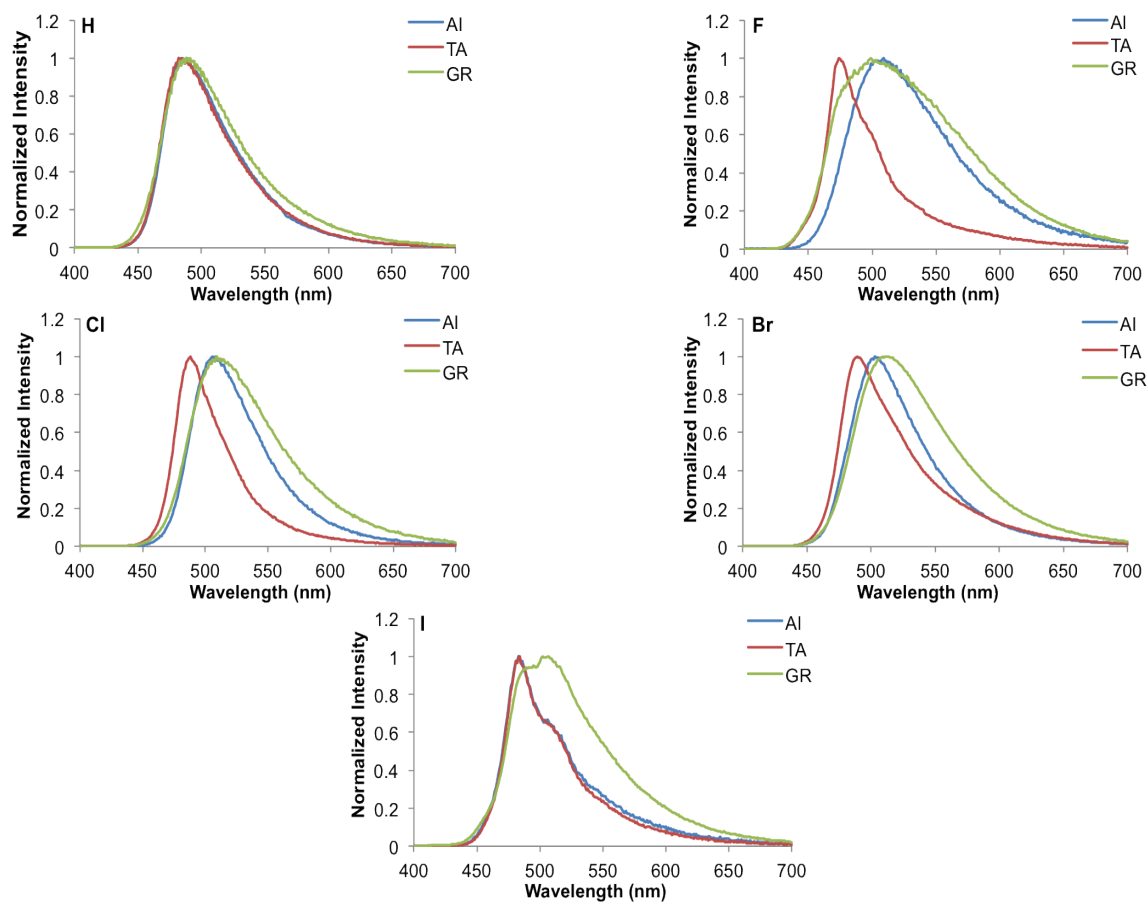
Figure S9. Emission spectra of boron dyes as bulk powders (λ_{ex} = 369 nm) (room temperature, air). As-isolated (AI), thermally annealed (TA), and ground (GR) powders are compared.
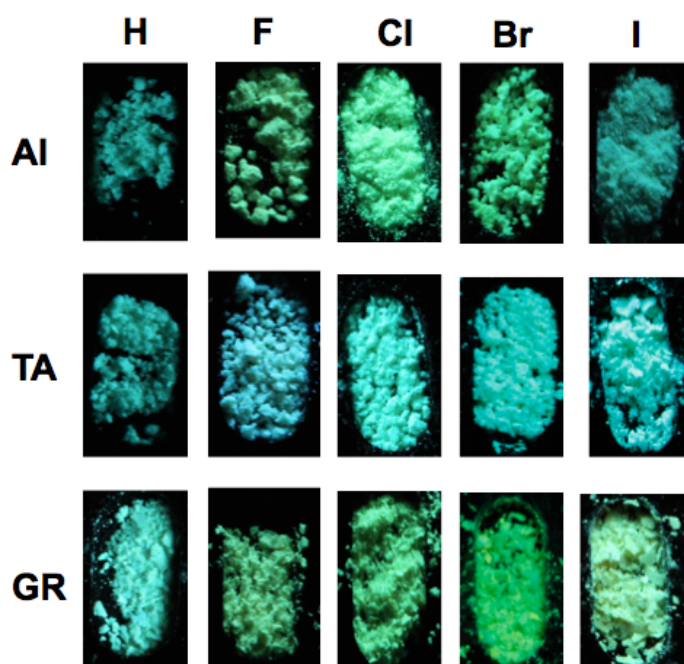
Figure S10. The $BF_2dbm(X)OC_{12}H_{25}$ dyes as bulk powders. As-isolated powders (AI) from acetone/hexanes were thermally annealed (TA) at the their respective optimum annealing temperatures for 3 hours. AI powders were also ground (GR) vigorously for ~30 minutes using a mortar and pestle.
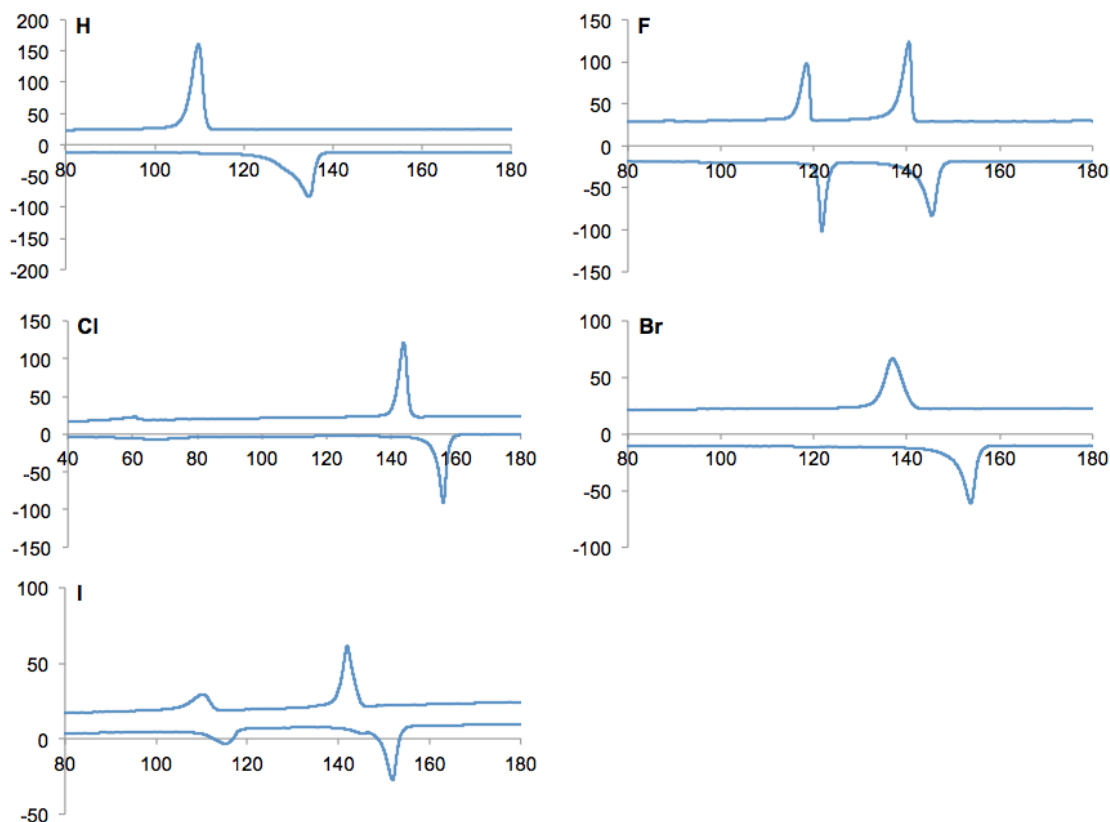
Table S6. Fluorescence Properties of the Boron Dyes as Bulk Powders.[a]

Dye	As-Isolated		Thermally Annealed		Ground	
	λ_{em}[b] [nm]	FWHM[c] [nm]	λ_{em}[b] [nm]	FWHM[c] [nm]	λ_{em}[b] [nm]	FWHM[c] [nm]
H	485	62	482	61	488	69
F	509	89	474	43	503	79
Cl	506	63	488	45	509	81
Br	504	66	489	56	511	85
I	483	52	484	50	506	82

[a] λ_{ex} = 369 nm.

[b] emission maximum; fluorescence.

[c] Full Width at Half Maximum.

Figure S11. Differential scanning calorimetry (DSC) thermograms of all dyes. The 2nd cycle is shown for all samples.

References

(1) Zhang, G.; Fiore, G. L.; St. Clair, T. L.; Fraser, C. L. *Macromolecules* **2009**, *42*, 3162.

(2) Nguyen, N. D.; Zhang, G.; Lu, J.; Sherman, A. E.; Fraser, C. L. *J. Mater. Chem.* **2011**, *21*, 8409.

(3) Zhang, G.; Lu, J.; Fraser, C. L. *Inorg. Chem.* **2010**, *49*, 10747.

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