

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230146271>

# Emission Color Tuning with Polymer Molecular Weight for Difluoroboron Dibenzoylmethane-Polylactide

ARTICLE *in* ADVANCED MATERIALS · JUNE 2008

Impact Factor: 17.49 · DOI: 10.1002/adma.200702681

CITATIONS

47

READS

54

## 4 AUTHORS:



**Guoqing Zhang**

University of Science and Technology of Ch...

48 PUBLICATIONS 1,382 CITATIONS

SEE PROFILE



**Steven E Kooi**

Massachusetts Institute of Technology

69 PUBLICATIONS 1,505 CITATIONS

SEE PROFILE



**J. N. Demas**

University of Virginia

205 PUBLICATIONS 9,188 CITATIONS

SEE PROFILE



**Cassandra L Fraser**

University of Virginia

110 PUBLICATIONS 3,176 CITATIONS

SEE PROFILE

DOI: 10.1002/adma.200702681

# Emission Color Tuning with Polymer Molecular Weight for Difluoroboron Dibenzoylmethane-Polylactide\*\*

By Guoqing Zhang, Steven E. Kooi, J. N. Demas, and Cassandra L. Fraser\*

Luminescence color tuning<sup>[1]</sup> is, in essence, the alteration of the transition energy levels of the dye molecules. For organic dyes this change is often effected by chemically modifying the  $\pi$  conjugation or the substituent groups.<sup>[2,3]</sup> Inorganic emitters display different colors by virtue of the metal center<sup>[4]</sup> and ligand set.<sup>[5]</sup> Physically perturbing the dye molecules through aggregation,<sup>[6,7]</sup> energy transfer,<sup>[8]</sup> matrix rigidity,<sup>[9]</sup> and processing conditions<sup>[10]</sup> can also influence emission. These color-tuning strategies have been exploited in OLED displays,<sup>[11]</sup> sensors<sup>[12]</sup> and molecular probes.<sup>[13]</sup>

Another easy approach to dye emission color tuning takes advantage of solvatochromism.<sup>[14]</sup> Polar dyes in particular can be sensitive to the properties of their surroundings. The polarity or dielectric constant of the local medium, whether liquid<sup>[15]</sup> or solid state,<sup>[16,17]</sup> can affect the ground state or excited state energies of fluorophores.<sup>[18,19]</sup> In fact, intermolecular interactions are not restricted to fluorophores and solvents. For polar dyes, fluorophore–fluorophore (F–F) interactions can be so significant that their emission spectra may be adjusted with concentration. For example, emission from the laser dye DCM2 can vary from yellow to red when the relative concentration of DCM2 in TPD thin films changes from 0.9–11 wt%.<sup>[16]</sup> Polyester side chain grafted poly(aryleneethynylene)s also display different solid state emission colors as a function of the polyester/conjugated polymer dye ratio.<sup>[20]</sup> Recently, a single dye species was used to generate multicolor emission on pre-patterned solid substrates, based on the transition energy differences associated with different dye aggregation states.<sup>[7]</sup> These are examples of luminescence color tuning by adjusting the degree of F–F interactions.

A major drawback of two-component dye-substrate systems is that it is hard to control the homogeneity of the doped

materials. Blended dyes are prone to aggregation and can photodegrade due to local temperature buildup.<sup>[21]</sup> These problems may be addressed by covalent attachment of dye molecules to supports such as polymers. Higher relative dye concentrations may be achieved without dye precipitation, and for solvatochromic dyes, color may be tuned across a broader range. Furthermore, covalently attached dyes are less prone to leaching. The dye is better protected from chemical degradation, color fading is minimized, and ambiguity in imaging and sensing schemes due to dye delocalization is reduced.<sup>[22]</sup> Thus, dye stability is enhanced, and material homogeneity and device performance are improved.

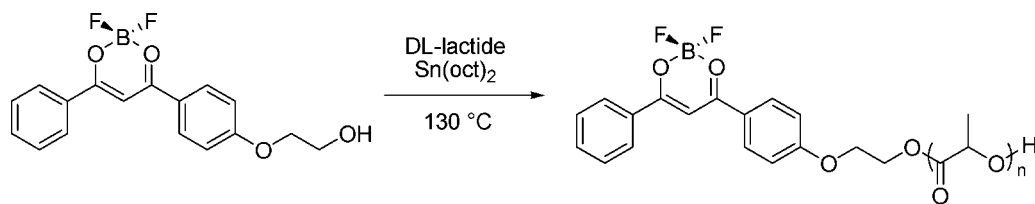
Here we describe a single-component photoluminescent material that is color tunable by varying the polymer molecular weight (MW). Difluoroboron dibenzoylmethane-polylactide, BF<sub>2</sub>dbmPLA, is comprised of a classic fluorescent dye and a common biomaterial.<sup>[23]</sup> Boron difluoride diketone dyes possess large dipole moments (e.g.,  $\mu = 6.7$  Debye for BF<sub>2</sub>dbm<sup>[24]</sup>), and their emission is sensitive to the polarity of the surrounding medium.<sup>[15]</sup> PLA is a biocompatible, biodegradable polymer<sup>[25]</sup> with wide application in biomedicine<sup>[26]</sup> and sustainable plastics.<sup>[27]</sup> When BF<sub>2</sub>dbm is coupled with PLA, a readily processable material with impressive optical properties results. In addition to intense blue fluorescence ( $\lambda_{\text{em}} = 436$  nm, quantum yield = 89% in CH<sub>2</sub>Cl<sub>2</sub>;  $\lambda_{\text{max}} = 440$  nm for solid film), unusual green room temperature phosphorescence (RTP) ( $\lambda_{\text{max}} = 509$  nm), and temperature sensitive delayed fluorescence ( $\lambda \sim 440$  nm) are also observed for BF<sub>2</sub>dbmPLA ( $M_n = 8,800$ , PDI = 1.09).<sup>[23]</sup> In the course of studying the kinetics of this reaction and removing aliquots as the reaction progressed, we noticed that the emission color varied from green to blue as the molecular weight increased. Here we explore this observation in more detail for purified polymers and describe a simple but powerful approach to polymer emission color tuning.

A set of BF<sub>2</sub>dbmPLA samples of different molecular weights was synthesized using Sn(oct)<sub>2</sub>-catalyzed controlled ring-opening polymerization of D,L-lactide with BF<sub>2</sub>dbmOH as the initiator (Eq. 1). Molecular weight data and UV-vis extinction coefficients,  $\epsilon$ , are provided in Table 1. Note that  $\epsilon$  provides a measure of the integrity of the boron center after polymerization. Monodisperse polymers with comparable  $\epsilon$  values<sup>[29]</sup> are obtained using controlled polymerization conditions (1–5). Longer reaction times result in higher MW samples but with broader molecular weight distributions and depressed extinction coefficients (e.g., 6).

[\*] Prof. C. L. Fraser, G. Zhang, Prof. J. N. Demas  
Department of Chemistry, University of Virginia  
Charlottesville, VA 22904 (USA)  
E-mail: fraser@virginia.edu

Dr. S. E. Kooi  
Institute for Soldier Nanotechnologies  
Massachusetts Institute of Technology  
Cambridge, MA 02139 (USA)

[\*\*] This research was supported by grants from the National Science Foundation, CHE 0350121 (C.L.F.), CHE 0410061 (J.N.D.), and a fellowship from the Radcliffe Institute for Advanced Study at Harvard University (C.L.F.). We thank R. C. Somers for assistance with quantum yield measurements, and Profs. D. G. Nocera and E. L. Thomas at MIT. Supporting Information is available online from Wiley InterScience or from the authors.



Equation 1

The fluorescence properties of BF<sub>2</sub>dbmPLA materials **1–6** were examined in solution and the solid state, both for “as precipitated” powders and solvent cast films. In CH<sub>2</sub>Cl<sub>2</sub> solution, BF<sub>2</sub>dbmPLA fluorescence is essentially the same regardless of molecular weight. Polymers **1–6** show intense blue emission ( $\lambda_{\text{em}} = 433 \text{ nm}$ ), high quantum yields ( $\sim 77\text{--}86\%$ ), and fluorescence lifetimes ( $\tau = 1.93\text{--}1.96 \text{ ns}$ ) that fit to single exponential decay (Table 2, Fig. S1). Properties are in accord with those for BF<sub>2</sub>dbmOH ( $\lambda_{\text{em}} = 436 \text{ nm}$ , quantum yield = 95%,  $\tau = 2.0 \text{ ns}$ ).<sup>[23]</sup>

In the solid state, however, purified polymers show a progressive trend from green to blue emission with increasing polymer molecular weight (Fig. 1). The fluorescence of

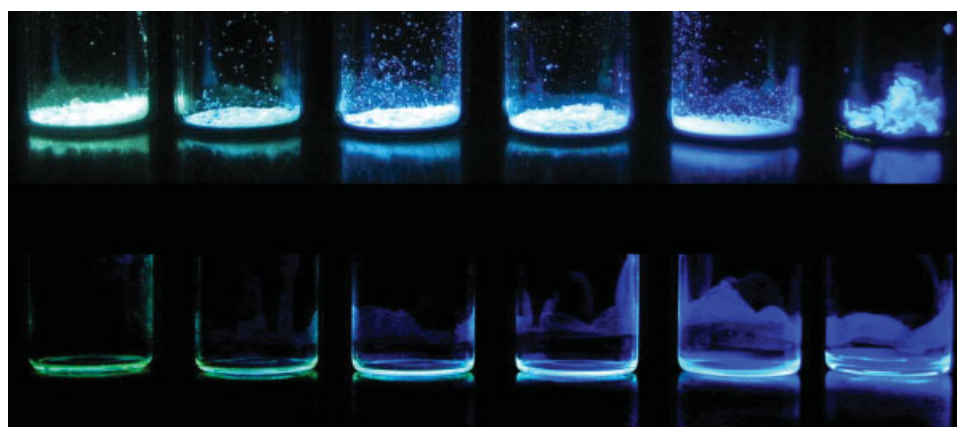
powders was investigated by two different methods and results are in accord: UV lamp excitation ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ) with fiber optic diode array detection (Method A):  $\lambda_{\text{em}}$  (nm) **1**: 502, **2**: 497, **3**: 494, **4**: 465, **5**: 464, **6**: 449 (Fig. 2); 390 nm pulsed laser excitation with imaging spectrograph detection (Method B):  $\lambda_{\text{em}} = 507\text{--}443 \text{ nm}$  (Table 2, Fig. S2). The structureless shape of the bulk emission spectra resembles that of BF<sub>2</sub>dbmPLA obtained in homogeneous solutions and is typical of laser

**Table 2.** Fluorescence data for BF<sub>2</sub>dbmPLA materials **1–6** as powders, films, and solutions [a].

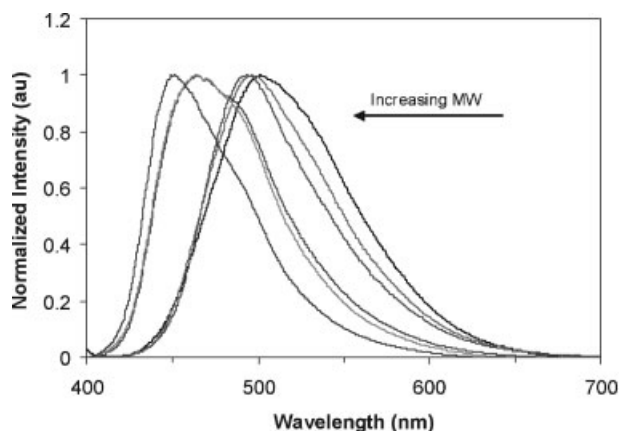
	Powders			Films			Solutions (CH <sub>2</sub> Cl <sub>2</sub> )		
	$\lambda_{\text{em}}$ [nm]	$\tau$ [b] [ns]	%[c]	$\lambda_{\text{em}}$ [nm]	$\tau$ [b] [ns]	%[c]	$\lambda_{\text{em}}$ [nm]	$\tau$ [ns]	$\phi_F$ [%]
<b>1</b>	507	15.4	87	460	14.2	86	432.5	1.94	79
		41.3	13		41.3	14			
<b>2</b>	475	14.5	92	458	12.9	91	432.5	1.96	86
		39.8	8		38.1	9			
<b>3</b>	467	8.8	91	451	11.8	90	432.5	1.96	84
		31.7	9		36.2	10			
<b>4</b>	453	8.2	93	440	8.6	92	432.5	1.93	85
		30.7	7		31.1	8			
<b>5</b>	455	6.4	96	437	7.7	95	432.5	1.94	80
		26.5	4		30.8	5			
<b>6</b>	443	2.7	99	434	3.0	99	432.5	1.95	77
		12.2	1		14.4	1			

[a] Determined by GPC in THF with RI detection vs polystyrene standards (0.58 PLA correction factor)<sup>[28]</sup>. [b] (MW BF<sub>2</sub>dbmOH/ $M_n$  BF<sub>2</sub>dbmPLA)  $\times 100$ . [c] In CH<sub>2</sub>Cl<sub>2</sub> (GPC  $M_n$  used in calculation).

[a]  $\lambda_{\text{ex}} = 390 \text{ nm}$  (Method B). Data were fit to double exponential decay. Percentages represent pre-exponential weighted values.



**Figure 1.** Photographic images showing BF<sub>2</sub>dbmPLA solid-state emission ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ). Top: “as precipitated” bulk polymers. Bottom: thin films. (**1–6** = left to right).



**Figure 2.** Emission spectra for BF<sub>2</sub>dbmPLA bulk polymers 1–6 ( $\lambda_{\text{ex}}$  = 365 nm; Method A).

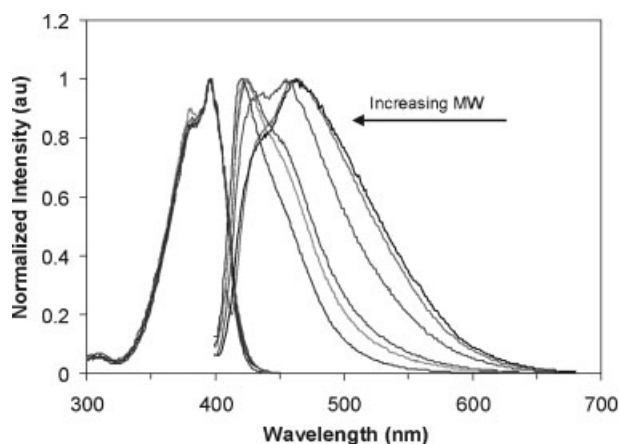
dyes.<sup>[30]</sup> Reasons for the large spectral change between polymers 3 and 4 are not known. It is possible that a change in BF<sub>2</sub>dbmPLA chain conformation or bulk morphology occurs between ~10–13 kDa which likewise affects fluorophore interactions and energy stabilization. Previous studies have demonstrated that polymer molecular weight can affect optical properties of doped dyes. For example, the quantum yield of *p*-(*N,N*-dialkylamino) benzylidene malononitriles increased abruptly for MWs > 10 kDa for the polystyrene support.<sup>[31]</sup> Thus, embedded dyes can provide information about polymer physical properties and morphology at the microscale.

Fluorescence lifetimes were recorded for BF<sub>2</sub>dbmPLA powders (Table 2). In all cases, lifetimes fit to double exponential decay, which may be ascribed to different fluorophore associations or polymer microenvironments in the solid state.<sup>[32]</sup> As the polymer MW increases from 1–6, both longer and shorter lifetimes steadily decrease and the short-lived component contributes more significantly to the decay. For the high MW 20 kDa sample, 6, the lifetime,

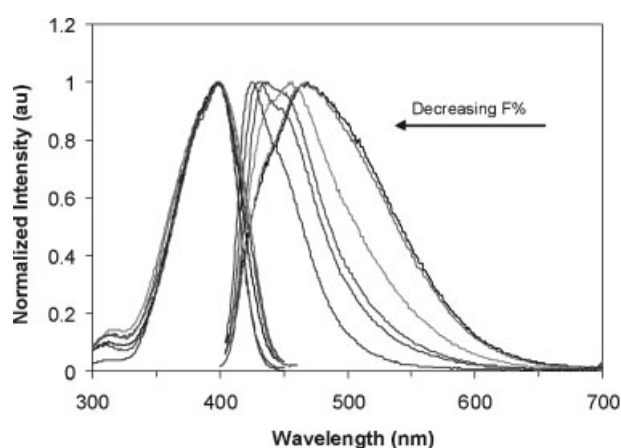
$\tau$  = 2.7 ns, approaches the optically dilute solution value,  $\tau$  = 1.95 ns.

It is well known for conjugated polymeric electronic devices that processing can greatly influence both photoluminescence (PL) and electroluminescent (EL) emission features.<sup>[33]</sup> For instance, Blatchford et al.<sup>[34]</sup> have reported that the PL spectrum of poly(*p*-pyridyl vinylene) powder is different from that of a spin-cast film. To explore the effects of polymer processing on BF<sub>2</sub>dbmPLA PL and test whether color tuning persists for the solid-state polymer in a different form, thin films were prepared. Optically dilute CH<sub>2</sub>Cl<sub>2</sub> solutions of 1–6 were cast onto quartz surfaces, the films were dried, and excitation and emission spectra (Fig. 3) and lifetime data (Table 2) were recorded. Excitation spectra for films of 1–6 are essentially identical; no MW effects or ground-state interactions are noted. But like powders, film emission maxima also exhibit a green to blue progression as BF<sub>2</sub>dbmPLA MW increases. Emission maxima for films with 390 nm laser excitation (Method B) range from  $\lambda_{\text{em}}$  = 460–434 nm for 1–6 (Table 2, Fig. S3). For films cast on the surface of quartz cuvettes and investigated by Method C (spectrofluorimeter,  $\lambda_{\text{ex}}$  = 365 nm, front face detection), emission maxima,  $\lambda_{\text{em}}$  (nm), are as follows: 1: 462, 2: 463, 3: 455 (437 sh), 4: 424 (455 sh), 5: 422 (450 sh), 6: 421 (Fig. 2). Taking into account the differences in signal to noise ratios for these measurement techniques and that smoothing protocols sometimes average maximal and shoulder values in the former approach, data are in agreement for these two methods. Lifetime data for BF<sub>2</sub>dbmPLA films parallel that for powders in both magnitude and trends (Table 2).

We also examined the excitation and emission spectra of BF<sub>2</sub>dbmOH doped PLA films (B1–B6) at similar loadings to covalently attached BF<sub>2</sub>dbmPLA samples 1–6 using Method C (Fig. 4). Compared to BF<sub>2</sub>dbmPLA films, the excitation spectra for dye-doped films are different in two aspects. First, the distinct vibronic shoulders seen in BF<sub>2</sub>dbmPLA spectra are absent perhaps because fluorophores dispersed in PLA have



**Figure 3.** Excitation and emission spectra for BF<sub>2</sub>dbmPLA films 1–6 ( $\lambda_{\text{ex}}$  = 365 nm; Method C).



**Figure 4.** Excitation and emission spectra of polymer blends B1–B6 ( $\lambda_{\text{ex}}$  = 365; Method C); F = Fluorophore.

more degrees of conformational freedom. Secondly, spectra broaden with increased dye loading, suggestive of ground-state association and therefore a less homogeneous environment. Unlike BF<sub>2</sub>dbmPLA dye-polymer conjugates **1–6** that appear homogeneous for all MWs (i.e., dye loadings), slight cloudiness was evident in BF<sub>2</sub>dbmOH doped PLA films at higher dye loadings. Stabilizing arene interactions and fluorine–hydroxyl, F...H–O–, hydrogen bonding are present for BF<sub>2</sub>dbmOH in the solid state.<sup>[35]</sup> Steric hindrance may diminish these effects for BF<sub>2</sub>dbmPLA compared to blends. Despite the difference in excitation spectra, emission spectra for blends are comparable to the corresponding BF<sub>2</sub>dbmPLA films. Dye-doped PLA films also exhibit a concentration dependent green to blue emission color trend (426–469 nm). Emission spectra for blends are likely a combination of ground-state association, excimers and long-range fluorophore–fluorophore interactions.

Changes in emission maxima are typically ascribed to chemical differences, physical phenomena or aggregation effects. Since BF<sub>2</sub>dbmPLA **1–6** are essentially identical in chemical composition and only differ in the length of the PLA chain, we rule out boron binding site and solid state solvent differences as reasons for color shifting. Because rigidochromic effects can affect dye luminescence,<sup>[36]</sup> for the lowest MW sample, **1**, the emission spectrum was also recorded at 77 K. But the emission spectra at liquid nitrogen and room temperatures are essentially the same. Thus, it is unlikely that the spectral changes arise from differences in hardness. Polymer deformation<sup>[37]</sup> and processing conditions<sup>[10]</sup> can influence dye orientation and induce color changes in photoluminescence of dye-polymer systems. However, in this study the same polymer precipitation and film processing methods were employed across the series and no differential mechanical perturbations were applied.

Alternatively, fluorophore–fluorophore (F–F) interactions may be responsible for emission color differences that are observed for **1–6** and **B1–B6**. Short-range F–F interactions may be present in the ground state (gs) or excited state (es); whereas, long-range interactions may occur through the surrounding medium. The fact that all films are colorless and excitation spectra for **1–6** are essentially identical, showing the same maximal value of 396 nm and the same spectral shape with no broadening, suggests that gs interactions are negligible (Fig. 3 left; compare to excitation spectra for blends in Figure 4 left, where evidence of gs interactions is present.) Though the emission spectra for powder samples show a single broad peak that shifts to the blue with increasing polymer MW, the bimodal spectra recorded for films (Method C) is similar to monomer-excimer systems. Unlike monomer-excimer spectra where the relative intensity of two peaks of fixed wavelengths change with concentration, here both peaks display a steady blue shift as the polymer MW increases (i.e., dye concentration decreases). This suggests that the red component in film emission spectra is not likely attributable to the excimer alone. Surface effects may come into play for films compared to the powders.<sup>[38]</sup> Given the low optical density of these films (absorbance < 0.01) and that bulk and thin film samples show

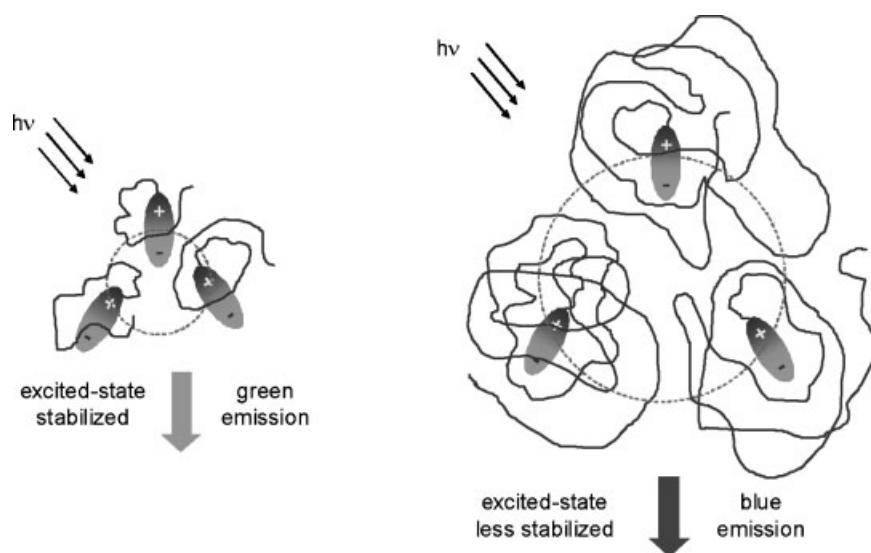
similar emission wavelength and lifetime trends, we also exclude the possibility of self-absorption.

Typically solvatochromism is associated with polarity differences in the surrounding liquid or solid-state medium,<sup>[18]</sup> however, the polarity of the medium can also be affected by different loadings of polar dyes such as BF<sub>2</sub>dbm.<sup>[16]</sup> In the dye-polymer conjugate BF<sub>2</sub>dbmPLA this is reflected in different polymer chain lengths. Just as fluorescence emission of BF<sub>2</sub>dbm derivatives is red-shifted as solvent polarity increases,<sup>[15]</sup> so too is it red-shifted for BF<sub>2</sub>dbmPLA as the dye/polymer loading increases (i.e., overall polymer MW decreases). In solution studies with non-polymeric BF<sub>2</sub>dbm derivatives, excited state solvatochromism was more pronounced than absorbance shifts.<sup>[15]</sup> The same is true for solid state BF<sub>2</sub>dbmPLA (MW range = 2.5–20.2 kDa), which exhibits 64 nm (powders) and 26 nm (films) emission wavelength shifts (Table 1) but essentially no differences in the position and shape of the absorbance and excitation bands. The positive solvatochromism and large Stokes shifts noted for BF<sub>2</sub>dbm derivatives have been ascribed to an increase in dipole moment and significant electronic redistribution upon excitation (i.e., major reorganization of the solvent shell during the excitation lifetime, and large nuclear reorganization prior to emission). Charge transfer coupled to a change in dye geometry in the excited state<sup>[39]</sup> has been advanced as an alternative explanation for difluoroboron diketone emission phenomena.<sup>[15]</sup> In summary, long-range F–F dipolar interactions dependent on the fluorophore distance and dipolar strength may be responsible for the observed luminescence color shift for BF<sub>2</sub>dbmPLA (Fig. 5). Shorter dye–dye distances and a more polar overall medium better stabilize a polar excited state for low MW BF<sub>2</sub>dbmPLA, resulting in lower energy green emission.

This proposal may be further supported by the delayed emission spectra obtained for samples **2** and **5** at 273 K (Fig. 6). These polymers share the same triplet emission maximum (509 nm) but vary in the shape and position of their high energy shoulders, which likely originate from thermally repopulated delayed fluorescence (DF) as previously reported.<sup>[23]</sup> Note that the DF for **2** is slightly red-shifted relative to **5** suggesting a difference in the singlet-triplet energy splitting. The contribution from the red shifted delayed fluorescence may also explain the slight broadening of the phosphorescence for **2**. Shorter phosphorescence lifetimes for polymer **2** ( $\tau$  = 126.2 ms) versus polymer **5** ( $\tau$  = 153.0 ms) point to smaller splitting for **2** and higher probability of back population of the singlet state, which is a significant contributor to triplet decay (Fig. 7). These findings also suggest that color tuning stems from differences in excited state energies, not spectral distortion due to self-absorption.

In summary, a well-defined single-component dye-polymer system exhibiting tunable photoluminescence by varying polymer chain lengths was described. We propose that the “green to blue” color shift observed for BF<sub>2</sub>dbmPLA is a dye concentration effect, which for conjugates is modulated by polymer molecular weight. Analogous to solvatochromism,



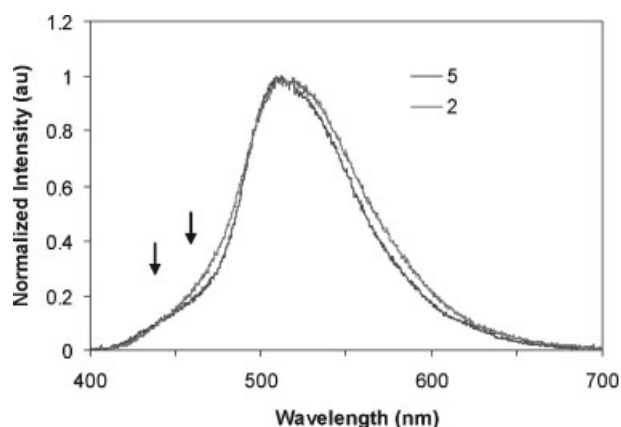


**Figure 5.** Schematic model of F–F interaction in BF<sub>2</sub>dbmPLA.

dyes such as BF<sub>2</sub>dbm with large dipole moments can influence the polarity of the surrounding medium and thus, affect excited state energies in a concentration dependent fashion. Color tunable BF<sub>2</sub>dbmPLA biomaterials show promise for imaging and sensing applications.

## Experimental

**Materials:** D,L-lactide (Aldrich) was recrystallized twice from ethyl acetate and stored under nitrogen. THF and CH<sub>2</sub>Cl<sub>2</sub> solvents were dried and purified by passage through alumina columns. Tin(II) 2-ethylhexanoate (Sn(oct)<sub>2</sub>, Spectrum), and all other reagents and solvents were used as received without further purification. BF<sub>2</sub>dbmOH and BF<sub>2</sub>dbmPLA were prepared as previously described [23].



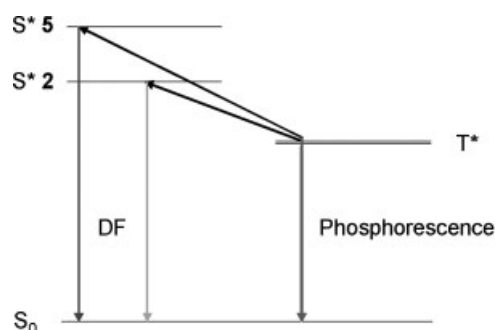
**Figure 6.** Delayed emission of polymer films **2** and **5** at 273 K under deoxygenated conditions (120 mTorr vacuum) (main peak: phosphorescence, high energy shoulders indicated by arrows: delayed fluorescence (DF)).

**Methods:** <sup>1</sup>H NMR (300 MHz) spectra were recorded on a UnityInova 300/51 instrument in CDCl<sub>3</sub>. UV-vis spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer using GPC number average molecular weights,  $M_n$ , to calculate the extinction coefficients [29]. Molecular weights were determined by NMR and by GPC (THF, 20 °C, 1.0 mL min<sup>−1</sup>) vs polystyrene standards with RI and UV/vis detection ( $\lambda = 396$  nm) with a 0.58 correction factor [28,40]. A Hewlett-Packard Series 1100 HPLC, Viscotek software (TriSEC GPC Version 4.1, Viscotek Corp) and Polymer Labs 5  $\mu$ m mixed-C columns were used in the GPC/RI analysis. Photos (Fig. 1) were taken in the dark using a Canon Power Shot SD600 Digital Elph camera with the automatic setting (no flash).

**Fluorescence:** Method A: Powder fluorescence spectra were recorded with an Ocean Optics USB2000 Fiber Optic Spectrometer ( $\lambda_{\text{ex}} = 365$  nm; TLC UV lamp). Method B: Five drops of OD CH<sub>2</sub>Cl<sub>2</sub> polymer solutions (**1–6**) were evaporated on quartz cover slips and dried *in vacuo* for ~10–12 h at RT. Time resolved fluorescence measurements were

performed by exciting solid, OD solution and thin film samples under air with 160 fs pulses at 390 nm, the doubled output of a Coherent RegA Ti:Sapphire amplifier operating at 250 kHz. The resulting fluorescence was spectrally resolved with a Chromex 250is Imaging Spectrograph and temporally resolved with a Hamamatsu C4770 Streak Scope. Data were processed using Hamamatsu, Matlab, and Origin software (Figs. S1–S3). Emission data were collected twice for each sample to ensure reproducibility. Reported lifetimes represent an average of two runs, fitted for the entire emission curves (solid **1**: ~500–650 nm; all other samples: ~405–575 nm). Method C: Several drops of optically dilute (abs < 0.1) CH<sub>2</sub>Cl<sub>2</sub> solutions of **1–6** and the blend samples (**B1–B6**) were cast onto the outside surface of a quartz luminescent cuvette. The resulting film was allowed to air dry for ~10–15 min at RT. Fluorescence excitation and emission spectra of the films were measured on a Spex Fluorolog 2 + 2 spectrofluorometer with front-face detection. Excitation spectra were monitored at 465 nm and emission spectra were acquired with 365 nm excitation. Fluorescence quantum yields,  $\phi_F$ , for BF<sub>2</sub>dbmPLA (**1–6**) in CH<sub>2</sub>Cl<sub>2</sub> were calculated using anthracene as a standard as previously described [23].

**Phosphorescence:** BF<sub>2</sub>dbmPLA samples (**2** and **5**) (~20 mg) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) in 25 mL Kontes tubes. The solvent was evaporated under a stream of N<sub>2</sub> with swirling for ~15 min, standing for 2 h, then drying *in vacuo* for 15 h, giving thin polymer films on the inner walls of the tubes. Phosphorescence spectra were recorded at 273 K (ice



**Figure 7.** Schematic representation of excited state singlet (S\*) and triplet (T\*) energy levels for polymers **2** and **5**.

bath for temperature stability) with a 0.5 s delay using Method A. Phosphorescence lifetimes were recorded as previously described [23].

Received: October 29, 2007  
Revised: December 12, 2007

- [1] A. A. Shoustikov, Y. You, M. E. Thompson, *IEEE J. Sel. Top. Quantum Electron.* **1998**, *4*, 3.
- [2] V. A. Montes, G. Li, R. Pohl, J. Shinar, P. Anzenbacher, Jr., *Adv. Mater.* **2004**, *16*, 2001.
- [3] Y. Qin, I. Kiburu, S. Shah, F. Jäkle, *Org. Lett.* **2006**, *8*, 5227.
- [4] S. Petoud, S. M. Cohen, J.-C. G. Bunzli, K. N. Raymond, *J. Am. Chem. Soc.* **2003**, *125*, 13324.
- [5] J. Li, P. Djurovich, B. D. Alleyne, M. Yousufuddin, N. N. Ho, J. C. Thomas, J. C. Peters, R. Bau, M. E. Thompson, *Inorg. Chem.* **2005**, *44*, 1713.
- [6] H. Zhang, Z. Zhang, K. Ye, J. Zhang, Y. Wang, *Adv. Mater.* **2006**, *18*, 2369.
- [7] W. Hu, N. Lu, H. Zhang, Y. Wang, N. Kehagias, V. Reboud, C. M. S. Torres, J. Hao, W. Li, H. Fuchs, L. Chi, *Adv. Mater.* **2007**, *19*, 2119.
- [8] Y. You, S. Y. Park, *J. Am. Chem. Soc.* **2005**, *127*, 12438.
- [9] B. Dunn, J. I. Zink, *Chem. Mater.* **1997**, *9*, 2280.
- [10] Y. Shi, Y. J. Liu, Yang, *J. Appl. Phys.* **2000**, *87*, 4254.
- [11] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, M. E. Thompson, *J. Am. Chem. Soc.* **2001**, *123*, 4304.
- [12] R. C. Somers, M. G. Bawendi, D. G. Nocera, *Chem. Soc. Rev.* **2007**, *36*, 579.
- [13] A. Bajorek, K. Trzebiatowska, B. Jdrzejewska, M. Pietrzak, R. Gawinecki, J. Peczkowski, *J. Fluoresc.* **2004**, *14*, 295.
- [14] J. Dong, K. M. Solntsev, L. M. Tolbert, *J. Am. Chem. Soc.* **2006**, *128*, 12038.
- [15] E. Cogné-Laage, J. F. Allemand, O. Ruel, J. B. Baudin, V. Croquette, M. Blanchard-Desce, L. Jullien, *Chem. Eur. J.* **2004**, *10*, 1445.
- [16] V. Bulovic, R. Deshpande, M. E. Thompson, S. R. Forrest, *Chem. Phys. Lett.* **1999**, *308*, 317. DCM2 = 2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[*i,j*]quinolizin-9-yl)-ethenyl]-4H-pyran-4-ylidene]propane-dinitrile. TPD = *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-[1,10-biphenyl]-4,4'-diamine.
- [17] C. F. Madigan, V. Bulović, *Phys. Rev. Lett.* **2003**, *91*, 247403.
- [18] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319.
- [19] W. Schuddeboom, S. A. Jonker, J. M. Warman, U. Leinhos, W. Kuehnle, K. A. Zachariasse, *J. Phys. Chem.* **1992**, *96*, 10809.
- [20] Y. Wang, J. S. Park, J. P. Leech, S. Miao, U. H. F. Bunz, *Macromolecules* **2007**, *40*, 1843.
- [21] S. K. Yesodha, C. K. Sadashiva Pillai, N. Tsutsumi, *Prog. Polym. Sci.* **2004**, *29*, 45.
- [22] H. Sun, A. M. Scharff-Poulsen, H. Gu, K. Almdal, *Chem. Mater.* **2006**, *18*, 3381.
- [23] G. Zhang, J. Chen, S. J. Payne, S. E. Kooi, J. N. Demas, C. L. Fraser, *J. Am. Chem. Soc.* **2007**, *129*, 8942.
- [24] N. M. D. Brown, P. Blandon, *J. Chem. Soc. A* **1969**, 526.
- [25] O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* **2004**, *104*, 6147.
- [26] A.-C. Albertsson, I. K. Varma, *Biomacromolecules* **2003**, *4*, 1466.
- [27] a) R. Auras, B. Harte, S. Selke, *Macromol. Biosci.* **2004**, *4*, 835. b) E. T. H. Vink, K. R. Rábago, D. A. Glassner, B. Springs, R. P. O'Connor, J. Kolstad, P. R. Gruber, *Macromol. Biosci.* **2004**, *4*, 551.
- [28] M. Save, M. Schappacher, A. Soum, *Macromol. Chem. Phys.* **2002**, *203*, 889.
- [29] G. Zhang, J. Chen, S. J. Payne, S. E. Kooi, J. N. Demas, C. L. Fraser, *J. Am. Chem. Soc.* **2007**, *129*, 15728.
- [30] I. Garcia-Moreno, A. Coastela, L. Campo, R. Sastre, F. Amat-Guierri, M. Liras, F. Lopez Arbeloa, J. Banuelos Prieto, I. Lopez Arbeloa, *J. Phys. Chem. A* **2004**, *108*, 3315.
- [31] R. O. Loutfy, *Pure Appl. Chem.* **1986**, *58*, 1239.
- [32] E. R. Carraway, J. N. Demas, B. A. DeGraff, *Anal. Chem.* **1991**, *63*, 332.
- [33] B. J. Schwartz, *Annu. Rev. Phys. Chem.* **2003**, *54*, 141.
- [34] J. W. Blatchford, *Phys. Rev. B* **1996**, *54*, 9810.
- [35] G. Zhang, C. L. Fraser, M. Sabat, Unpublished data.
- [36] B. Dunn, J. I. Zink, *Chem. Mater.* **1997**, *9*, 2280.
- [37] C. Löwe, C. Weder, *Adv. Mater.* **2002**, *14*, 1625.
- [38] A. G. Mirochnik, E. V. Fedorenko, V. G. Kuryavyi, B. V. Bukvetskii, V. E. Karasev, *J. Fluoresc.* **2006**, *16*, 279.
- [39] W. Rettig, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 971.
- [40] J. Baran, A. Duda, A. Kowalski, R. Szymanski, S. Penczek, *Macromol. Rapid Commun.* **1997**, *18*, 325.