Mechanochromic Luminescence Quenching: Force-Enhanced Singlet-to-Triplet Intersystem Crossing for Iodide-Substituted Difluoroboron-Dibenzoylmethane-Dodecane in the Solid State

3 AUTHORS, INCLUDING:

Guoqing Zhang
University of Science and Technology of China

48 PUBLICATIONS   **1,378** CITATIONS

Cassandra L Fraser
University of Virginia

110 PUBLICATIONS   **3,150** CITATIONS

Inorganic Chemistry

Communication

Mechanochromic Luminescence Quenching: Force-Enhanced Singlet-to-Triplet Intersystem Crossing for Iodide-Substituted Difluoroboron−Dibenzoylmethane−Dodecane in the Solid State

Guoqing Zhang,[†] Jiwei Lu,[‡] and Cassandra L. Fraser*,[†]

[†]*Department of Chemistry and* [‡]*Department of Materials Science and Engineering, University of Virginia, Charlottesville, Virginia 22904*

A lipid derivative of difluoroboron−iododibenzoylmethane (BF$_2$-dbm(I)OC$_{12}$H$_{25}$) was synthesized via Claisen condensation and boronation. Green photoluminescence is observed for the complex in the solid state. Unlike the previously reported difluoroboron−avobenzone (BF$_2$AVB) complex, which exhibited significantly red-shifted fluorescence upon mechanical perturbation, the emission of a BF$_2$dbm(I)OC$_{12}$H$_{25}$ solid film is quenched when the sample is smeared under air but becomes orange under nitrogen. Spectroscopic and lifetime studies suggest that smearing brings the singlet excited state closer to the triplet state, thus increasing the coupling between the two states. As a result, intersystem crossing from the singlet to the triplet excited state is facilitated, and the total luminescence intensity is quenched at room temperature.

Piezochromism or mechanochromism refers to the color change of materials in response to pressure or other mechanical stimuli. These color changes are often highly dependent on the solid-state morphology and can be induced by material structural changes such as bond breaking or forming[1] on the molecular level or by larger-scale dye aggregation,[2] or domain spacing effects.[3,4] Specifically, if mechanical perturbation causes a change in emission, it is called mechanochromic luminescence (ML).[5,6] Recently, we discovered that a simple boron−sunscreen complex, BF$_2$AVB, exhibits polymorphism and thermally reversible ML.[7] A significantly red-shifted fluorescence spectrum was observed when solid samples were ground or smeared. Crystalline or ordered BF$_2$AVB corresponds to higher energy emission, while the amorphous state is responsible for lower energy emission. Although the mechanism of BF$_2$AVB ML is not entirely understood, these findings indicate that singlet excited-state energy can be altered by mechanical processes.

BF$_2$dbm molecules display strong excited-state interactions that can affect fluorescence. Previously, this phenomenon was studied in a polymer matrix, where BF$_2$dbm was covalently attached to a polylactide (PLA) chain. The singlet excited-state energy dropped most dramatically for short BF$_2$dbmPLA chains (i.e., stronger fluorophore−fluorophore interactions).[8] A material with tunable fluorescence-to-phosphorescence (F/P) ratios was also achieved based on this model. When the polymer chain is shorter, the excited-state interactions are stronger, the singlet state energy decrease is more significant, and the singlet-to-triplet intersystem crossing is enhanced, especially in the presence of an iodide internal heavy atom.[9] This material design concept was successfully applied to ratiometric oxygen sensing for optical tumor hypoxia imaging with the versatile boron dye−polymer system fabricated as nanoparticles. If the singlet excited-state energy can also be lowered after mechanical stimulation, enhanced intersystem crossing is expected here too. Here we extend the F/P tuning concept to nonpolymeric boron diketone complexes in the solid state, where the triplet process is enhanced mechanically.
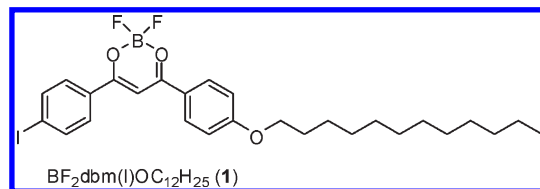
BF$_2$dbm(I)OC$_{12}$H$_{25}$ (**1**)

The luminescent boron complex BF$_2$dbm(I)OC$_{12}$H$_{25}$ (**1**) was synthesized via Claisen condensation followed by

*To whom correspondence should be addressed. E-mail: fraser@virginia.edu.
(1) Davis, D. A.; Hamilton, A.; Yang, J.; Cremar, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martinez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. *Nature* **2009**, *459*, 68–72.
(2) Crenshaw, B. R.; Burnworth, M.; Khariwala, D.; Hiltner, A.; Mather, P. T.; Simha, R.; Weder, C. *Macromolecules* **2007**, *40*, 2400–2408.
(3) Arsenault, A. C.; Clark, T. J.; von Freymann, G.; Cademartiri, L.; Sapienza, R.; Bertolotti, J.; Vekris, E.; Wong, S.; Kitaev, V.; Manners, I.; Wang, R. Z.; Sajeev, J.; Wiersma, D.; Ozin, G. A. *Nat. Mater.* **2006**, *5*, 179–184.
(4) Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. *Chem. Rev.* **2009**, *109*, 5755–5798.
(5) Recent review:Sagara, Y.; Kato, T. *Nat. Chem.* **2009**, *1*, 605–610.
(6) Selected examples: (a) Lee, Y. A.; Eisenberg, R. *J. Am. Chem. Soc.* **2003**, *125*, 7778–7779. (b) Ito, H.; Saito, T.; Oshima, N.; Kitamura, N.; Ishizaka, S.; Hinatsu, Y.; Wakeshima, M.; Kato, M.; Tsuge, K.; Sawamura, M. *J. Am. Chem. Soc.* **2008**, *130*, 10044–10045. (c) Sagara, Y.; Mutai, T.; Yoshikawa, I.; Araki, K. *J. Am. Chem. Soc.* **2007**, *129*, 1520–1521. (d) Chung, J. W.; You, Y.; Huh, H. S.; An, B.-K.; Yoon, S.-J.; Kim, S. H.; Lee, S. W.; Park, S. Y. *J. Am. Chem. Soc.* **2009**, *131*, 8163–8172.

(7) Zhang, G.; Lu, J.; Sabat, M.; Fraser, C. L. *J. Am. Chem. Soc.* **2010**, *132*, 2160−2162.
(8) Zhang, G.; Kooi, S. E.; Demas, J. N.; Fraser, C. L. *Adv. Mater.* **2008**, *20*, 2099–2104.
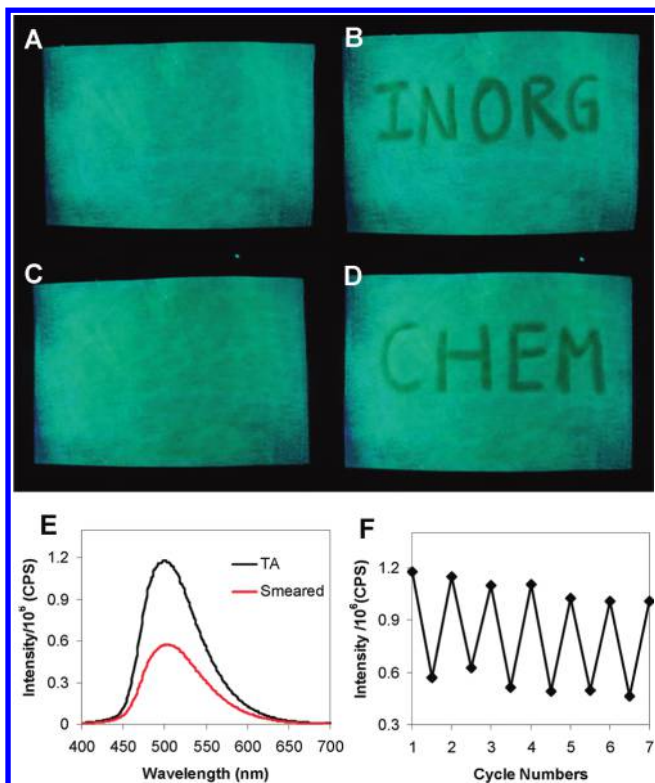(9) Lower, S. K.; El-Sayed, M. A. *Chem. Rev.* **1966**, *66*, 199–241.

Figure 1. Reversible MLQ (λ_{ex} = 365 nm) of a thermally annealed solid film of **1** on a piece of weighing paper (A), "INORG" written with a cotton swab tip seen as shadow areas (B), background emission restored by heating the film for 1 min in a 110 °C oven (C), and rewritable MLQ demonstrated by "CHEM" generated with a cotton swab tip (D). Steady-state luminescence spectrum under air showing an intensity decrease after smearing (E) and the fluorescence emission intensity monitored at 500 nm under air versus smearing/thermal erasing of the cycle number (F).

boronation in CH_2Cl_2 (Supporting Information). A bright-yellow waxy solid (mp = 144−146 °C) was obtained after silica gel chromatography. The lipid derivative was chosen to increase both the solubility of the iodide dye and the possible organization of the boron complexes in the solid state, given that material ordering can play an important role in ML.[5] The optical properties of **1** were studied in a CH_2Cl_2 solution. The absorption (λ_{max} = 409 nm) and emission (λ_F = 446 nm) spectra (Figure S1 in the Supporting Information) are similar to those for a reported $BF_2dbm(I)$[10] derivative, but the fluorescence lifetime (τ_F = 1.50 ns) and quantum (Φ_F = 0.67) yield of **1** have increased values.

In the solid state, ML was observed for a film of **1** on a piece of weighing paper (~3 mg smeared on 2 × 2 in^2). After thermal annealing at 110 °C for 1 min, the solid film showed green luminescence under UV light. When the solid film was rubbed with a cotton swab, the smeared regions turned darker; with brief thermal treatment, the dark regions were restored. This reversible ML quenching (MLQ) is illustrated in Figure 1A−D. Despite the reduction in the emission intensity from steady-state spectroscopy (Figure 1E), normalized emission spectra of **1** before and after smearing are almost superimposable. The smeared solid spectrum has a slightly larger high-energy shoulder and a small shift in the maximum intensity (Figure 2A; before, λ_F = 496 nm; after, λ_F = 500 nm). Similar to BF_2AVB, the ML of **1** was found to recover

(10) Zhang, G.; Palmer, G. M.; Dewhirst, M. W.; Fraser, C. L. *Nat. Mater.* **2009**, *8*, 747–751.
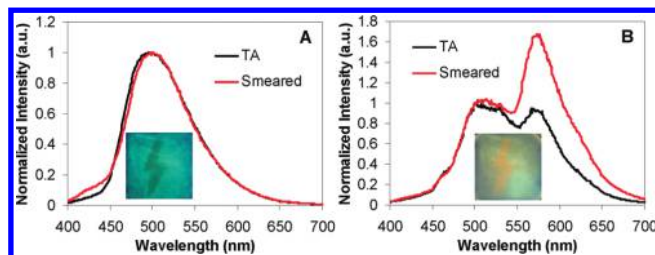

Figure 2. Normalized steady-state emission spectra of **1** solid film on a piece of weighing paper at room temperature (RT) under air (A) and at 77 K (B) (λ_{ex} = 369 nm). TA: thermally annealed. The image insets show smearing-induced emission "turn off" (i.e., MLQ in dark region) at RT under air (A) and red-shifted phosphorescence "turn on" (i.e., orange region) at 77 K (λ_{ex} = 365 nm).
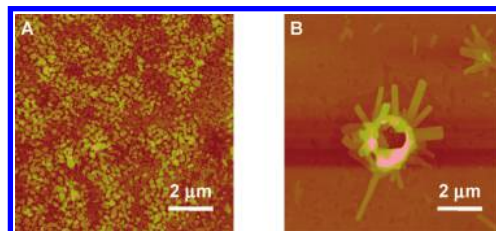

Figure 3. AFM images of films of **1** spin-cast from dilute CH_2Cl_2 onto glass before (A) and after heating (B) for 1 min in a 110 °C oven.
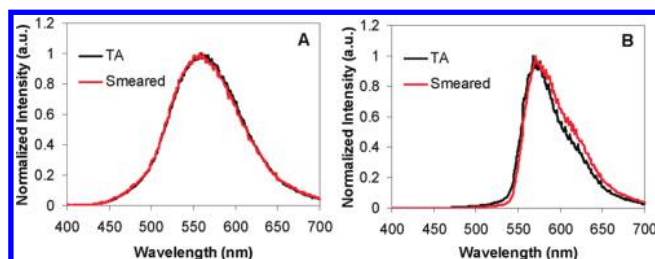

Figure 4. Normalized delayed emission spectra of a solid film of **1** on a piece of weighing paper at room temperature (A) and 77 K (B) (λ_{ex} = 369 nm, delay time 1.0 ms, under nitrogen) TA: thermally annealed.

spontaneously at room temperature or much faster at elevated temperature (~3−5 s with a heat gun). The thermal reversibility was also demonstrated by monitoring the luminescence emission at 500 nm, where a cyclic drop and rise in the intensity was recorded (Figure 1F). The recovery may be related to the strong tendency of **1** to form ordered aggregates, as evidenced by atomic force microscopy (AFM) images (Figure 3).

If this MLQ behavior at room temperature is indeed due to increased triplet quenching (e.g., oxygen or collisional), an increase in the relative phosphorescence intensity would be expected at low temperature, where these processes are hindered. At room temperature, the normalized emission spectra of **1** before and after smearing are similar. At 77 K, however, the smeared sample shows a much stronger peak around 570 nm (Figure 2).[11] To confirm that the lower-energy peak corresponds to phosphorescence, delayed emission spectra (Δt = 1 ms) were collected for the thermally annealed and smeared films of **1** both at room temperature under nitrogen and at 77 K (Figure 4). At room temperature,

(11) MLQ caused by an increase in the surface area during smearing has been ruled out. This was supported by the fact that the fluorescence loss at room temperature is roughly 60% and the phosphorescence gain at 77 K is also roughly 60%.

the two delayed spectra are almost identical, with emission maxima at 560 and 558 nm, respectively. At 77 K, however, the maxima are red-shifted by ∼10 nm to 567 and 571 nm. The red shift in delayed emission spectra at lower temperatures has been previous ascribed to a diminished contribution from delayed fluorescence (blue-shifted relative to the phosphorescence peak), where thermal back-population from triplet to singlet excited states is inhibited.[8] Overlapped excitation spectra at 77 K monitored at the two peak intensities ($\lambda_F = 500$ and $\lambda_P = 570$ nm) also indicate that these features arise from the same species (Figure S2 in the Supporting Information).

These results suggest that, for smeared solid films of **1**, the triplet excited-state population is indeed increased. As has been discussed before, eq 1 explains how a decreased energy gap in the presence of a heavy atom can enhance the singlet ($^1\Psi$)−triplet ($^3\Psi$) mixing and, thus, the intersystem crossing.[9,10] For BF$_2$AVB, without a heavy-atom effect, only a bathochromic shift in fluorescence was observed upon mechanical perturbation. In the case of a solid film of **1**, mechanical force is likely to induce the same singlet energy drop; however, with iodide substitution, this also corresponds to an increased fraction of the singlet excited-state species crossing over to the triplet excited state. At room temperature, the triplet excited state for the dye-lipid derivative may be quenched by oxygen or may preferentially decay by thermal pathways.

$$\delta = \frac{\langle ^3\Psi | H_{so} | ^1\Psi \rangle}{|E_1 - E_3|} \tag{1}$$

If this hypothesis is true, enhanced intersystem crossing may also be reflected in a reduced fluorescence lifetime (τ_F) for the smeared sample. Indeed, when monitored at the peak intensity (500 nm), a reduction of τ_F from 1.63 to 1.31 ns was recorded after smearing. However, the decrease in τ_F could be due to enhanced intersystem crossing from increased excited-state interactions or due to exciton migration. To better understand the mechanism, τ_F of BF$_2$dbmOC$_{12}$H$_{25}$, a control compound of **1** without iodide substitution, was also measured. Comparison of the τ_F values in CH$_2$Cl$_2$ [**1** (1.50 ns) vs control (2.05 ns)] indicates a higher intersystem-crossing efficiency for **1**. When monitored at the emission maximum, $\lambda_F = 466$ nm, for solid films, the control τ_F increases from 6.69 to 11.27 ns upon smearing, suggesting changes in the excited-state energy. To explore whether exciton migration is also involved, we measured τ_F of the control at a higher
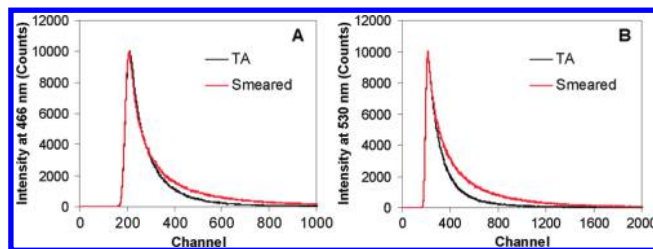

Figure 5. Fluorescence lifetime decays of a BF$_2$dbmOC$_{12}$H$_{25}$ (control) solid film on a piece of weighing paper monitored at 466 nm (A) and 530 nm (B) ($\lambda_{ex} = 369$ nm LED). TA: thermally annealed.

wavelength. A consistent increase in the lifetime from 7.26 to 13.28 ns was also recorded when the emission was monitored at 530 nm, but no initial rise in the decay profile characteristic of exciton migration was observed (Figure 5). This does not rule out exciton migration, however, given that our lifetime instrument (> 200 ps) may not reveal fast processes.

In summary, we have described a heavy-atom-substituted difluoroboron−dibenzoymethane−lipid dye that exhibits mechanosensitive intersystem crossing and reversible MLQ in the solid state. Under UV excitation, the relative ratio of singlet-to-triplet excited-state populations is decreased when a solid film of the dye is smeared or scratched. One possible explanation is that mechanical processes lower the singlet excited-state energy level and thus increase the degree of singlet and triplet state coupling according to perturbation theory. Luminescence under nitrogen at room temperature and 77 K shows that the relative intensity of phosphorescence increases in the smeared solid film. This increase corresponds nicely to the drop in the fluorescence intensity at room temperature under air, suggesting near-complete singlet quenching upon mechanical perturbation. This unique force-induced method of altering the intersystem crossing may be useful in the design of luminescent mechanical sensors.

Supporting Information Available: Methods, experimental details, and solution absorption and emission spectra (Figure S1) and solid-state excitation spectra (Figure S2) of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.