Communication

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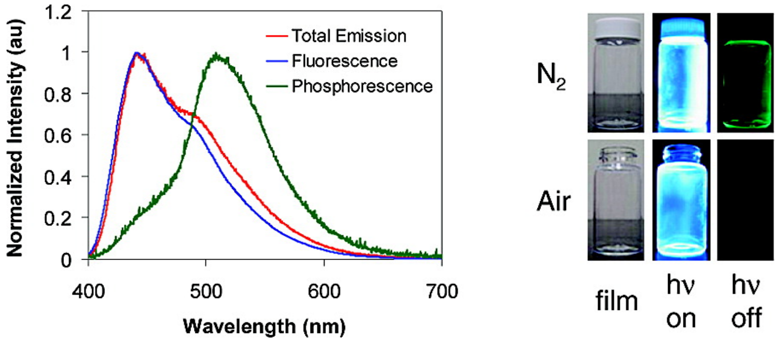

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Multi-Emissive Difluoroboron Dibenzoylmethane Polylactide Exhibiting Intense Fluorescence and Oxygen-Sensitive Room-Temperature Phosphorescence

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When boron difluoride dibenzoylmethane (BF_2dbm) is coupled with poly(lactic acid) (PLA), a biocompatible, biodegradable polymer,[1,2] the fluorescence quantum yield is enhanced and unexpected optical properties emerge, namely, temperature-sensitive delayed fluorescence and oxygen-sensitive room-temperature phosphorescence (RTP). Single-component, multi-emissive materials are rare, and synthesis and fabrication of BF_2dbmPLA are straightforward, offering many advantages over existing materials for imaging and ratiometric sensing.[3]

Fluorescent boron difluoride dyes such as "bodipy"[4] and boron diketonates[5] exhibit large molar extinction coefficients and two-photon absorption cross sections, high emission quantum yields, and sensitivity to the surrounding medium.[6] These features have been exploited in molecular probes,[4] photosensitizers,[7] and lasers.[8] Phosphorescence also offers advantages for optical sensing,[3] including larger Stokes shifts and minimal interference from short-lived fluorescence and scattering. But for these boron systems,[5,9] it is only observed at low temperatures in solid matrices, thus limiting its utility. Though RTP is common for heavy-metal-based luminophores with singlet−triplet state mixing and microsecond−millisecond lifetimes, rigid or organized media and toxic heavy atom assistance (e.g., Pb, Tl, halides) are often required for main group triplet emission,[3,9,10,11] which is longer lived (millisecond−second) and more sensitive to oxygen quenching. Though a liability for certain light emitting materials applications, this sensitivity can be exploited for oxygen sensors[3,12] and photodynamic therapy.[7] Given the limitations of known sensor materials, systems with strong singlet and triplet emission, easy synthesis and fabrication, and good stability and biocompatibility are highly desired.

Hydroxyl-functionalized difluoroboron dibenzoylmethane, BF_2dbmOH (**1**), was prepared for use as an initiator in the ring opening polymerization of lactide to produce BF_2dbm end-functionalized polylactide, BF_2dbmPLA (**2**). The boron complex, **1**, was made from dbmOH[13] and $BF_3{\bullet}Et_2O$ in CH_2Cl_2 (60 °C, 1 h). After recrystallization from acetone/hexanes, air-stable, bright yellow needles were obtained in good yield (75%). The boron polymer, **2**, was generated from BF_2dbmOH and DL-lactide using a tin octoate catalyst (**1**/lactide/$Sn(oct)_2$ = 1:200:1/50; 130 °C). The solvent-free reaction was stopped at ~50% monomer conversion to avoid higher polydispersity indices (PDIs) noted for longer reaction times, due to transesterification and thermal depolymerization. After precipitation, a pale greenish yellow polymer was obtained. Molecular weight data determined by gel permeation chromatography and ^{1}H NMR spectroscopy are in good agreement: M_n(GPC) = 8800, PDI = 1.09; M_n(NMR) = 8600. Furthermore, key proton resonances associated with the boron dbm polymer end group are shifted compared to the initiator (e.g., $BF_2dbmOCH_2CH_2OR$: R = H, 4.04 ppm; R = PLA, 4.54 ppm).

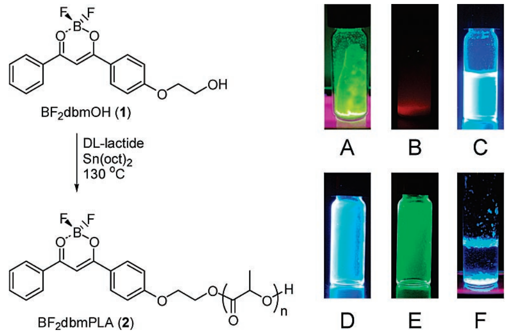

Figure 1. Polymer synthesis and boron initiator and polymer luminescence (λ_{ex} = 365 nm; room temperature in air unless indicated). BF_2dbmOH: (A) solid-state green-yellow fluorescence; (B) red phosphorescence (77 K); (C) blue fluorescent CH_2Cl_2 solution. BF_2dbmPLA: (D) short-lived blue fluorescence and (E) long-lived green phosphorescence for a thin film (N_2); (F) blue fluorescent particle suspension in H_2O after 45 days.

The optical properties of the boron initiator and polymer were investigated in CH_2Cl_2 solution and in the solid state (Figure 1). UV/vis spectroscopic data are similar for BF_2dbmOH (λ_{max} = 397 nm, ϵ = 53 000 M^{-1} cm^{-1}) and BF_2dbmPLA (λ_{max} = 396 nm, ϵ = 50 100 M^{-1} cm^{-1}), showing high molar absorptivities characteristic of this family of compounds. Under black light illumination (λ_{ex} = 365 nm) in air, intense blue fluorescence is observed for BF_2dbmOH (Figure 1C) and BF_2dbmPLA (λ_{em} ~ 436 nm), and in both cases, fluorescence quantum yields, ϕ_F, are very high (**1**: 0.95; **2**: 0.89; compare to BF_2dbm, 0.20, and 1,3-di(4-methoxyphenyl)-propane-1,3-dione, 0.85).[6] Due to the near UV excited fluorescence, solutions appear blue even in ambient light or upon flashlight illumination.

In the solid state, in contrast, BF_2dbmOH displays greenish yellow emission that is sensitive to the solid form (λ_{em}, crystals: 540 nm, Figure 1A; powder: 512 nm).[14] Association in the ground state or excited state (e.g., as dimers or excimers) is likely involved. Fluorescence lifetimes, τ, in air for the initiator **1** (in CH_2Cl_2: 2.0 ns; crystals: 8.9 ns) and polymer **2** (in CH_2Cl_2: 1.9 ns) fit to a single-exponential decay, further verifying sample homogeneity. In the solid state, emission spectra for BF_2dbmPLA also exhibit blue fluorescence (foam: 451 nm; film: 440 nm, Figure 1D; air), but fluorescence lifetimes fit to double-exponential decay (foam: 90% 4.8 ns, 10% 20 ns; film: 90% 1.2 ns, 10% 4.4 ns) perhaps due to heterogeneous polymer microenvironments or fluorophore aggregation. Two-photon absorption with blue emission was also confirmed for BF_2dbmPLA using ~800 nm excitation, demonstrating compatibility with bioimaging technologies that afford greater tissue penetration, reduced cell damage, and minimal interference from biological absorbers.[15] Samples continue to emit strongly even

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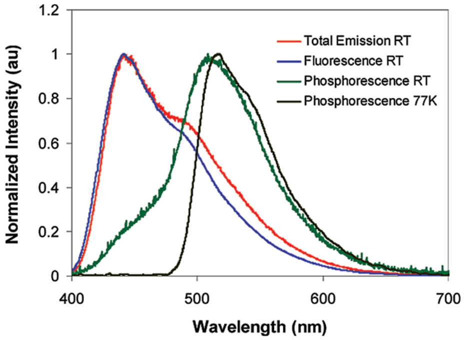

Figure 2. Normalized emission spectra for a BF_2dbmPLA thin film. Room temperature total emission under vacuum (442 nm), fluorescence under air (442 nm), and phosphorescence (509 nm) with delayed fluorescence (∼450 nm) under vacuum after the excitation is turned off. The phosphorescence spectrum at 77 K (517 nm) is also shown. (Note the absence of the ∼450 nm feature in the low-temperature spectrum.) Reported wavelengths represent emission maxima and $\lambda_{ex} = 365$ nm.

after months in aqueous suspension (Figure 1F), conditions under which PLA degradation is known to occur.

Upon deoxygenation, solid BF_2dbmPLA also exhibits long-lived, green room-temperature phosphorescence (RTP) (Figure 1E). (No RTP is observed for solutions.) This is surprising because, normally, phosphorescence is only seen at low temperatures for boron compounds of this type.[5,9] For example, BF_2dbmOH crystals display seconds long red phosphorescence at 77 K (Figure 1B). Triplet thermal decay pathways may be restricted by the rigid polymer medium as in the solid state and solvent glasses. Above the glass transition temperature for BF_2dbmPLA, $T_g = 52$ °C, no phosphorescence is observed. Green RTP is seen for solid BF_2dbmPLA (Figure 1E), including in aqueous suspension, once the excitation source is removed, and can last for as long as 5−10 s.

Room-temperature emission spectra for a BF_2dbmPLA thin film are provided in Figure 2, namely, total emission (fluorescence plus phosphorescence) under vacuum, fluorescence in air where phosphorescence is quenched, and phosphorescence for an evacuated sample following termination of excitation. The green phosphorescence spectrum at 77 K is also shown. Without gating, the primary phosphorescence peak at 509 nm is buried under the much more intense fluorescence peak. In addition to fluorescence and phosphorescence, there is also a shoulder in the phosphorescence spectrum around 450 nm, which closely matches the fluorescence. Given that fluorescence lifetimes are very short and phosphorescence spectra are not collected until after fluorescence has ceased, this feature may be ascribed to delayed fluorescence caused by thermal repopulation from the excited triplet state to the excited singlet state.[16] The shoulder disappears at low temperature, where repopulation may be blocked due to insufficient activation energy, lending support to this proposal. Thus, BF_2dbmPLA serves as a temperature-sensitive material, too.

The long phosphorescence lifetime of BF_2dbmPLA provides a highly sensitive oxygen sensor based on quenching. In the absence of O_2, the RTP decay is complicated, perhaps due to various species or polymer microenvironments in the film. Data can be fit with a triple-exponential giving a preexponential weighted lifetime,[17] τ_{pw0}, of 0.17 s. The lifetime Stern−Volmer plot (τ_{pw0}/τ_{pw} versus air pressure; air = 21% O_2) (Figure 3) is reasonably linear to ∼1 Torr but has complex dynamics beyond that point. With the <1 ms flash lamp, there is a measurable ∼30 ms lifetime at 15 Torr, but above 30 Torr, the RTP is rapidly and entirely quenched. Failure to obtain the typical downward curved Stern−Volmer plot may arise from the complexity of the decay and difficulty in measuring contributions from shorter lived (<10 ms) and very low amplitude long-lived (>0.1 s) components with the present instrumentation. Further investigation is merited.

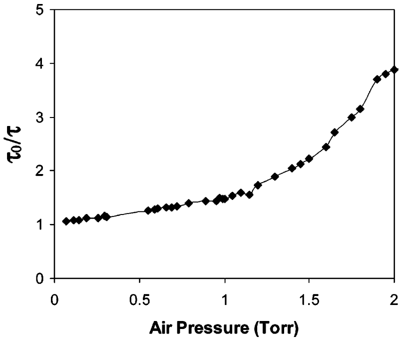

Figure 3. Lifetime Stern−Volmer plot for a BF_2dbmPLA film showing oxygen quenching of room temperature phosphorescence.

By incorporating a classic boron dye into a common biopolymer, a readily processable, single-component, multi-emissive material exhibiting intense fluorescence, delayed fluorescence, and unusual room-temperature phosphorescence is achieved. The optical properties of BF_2dbmPLA are responsive to temperature, oxygen, and the polarity and rigidity of the local medium. Further development of these multifunctional biomaterials for imaging and sensing, including emission color tuning, properties optimization, polymer fabrication, and biological testing, serve as the subjects of future reports.

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Supporting Information Available: Experimental details for the synthesis and luminescence measurements for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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