Organic Phosphorescence | Hot Paper

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Metal-Free Triplet Phosphors with High Emission Efficiency and High Tunability**

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Abstract: *Design of highly efficient phosphorescent emitters based on metal- and heavy atom-free boron compounds has been demonstrated by taking advantage of the singlet fission process. The combination of a suitable molecular scaffold and appropriate electronic nature of the substituents has been utilized to tailor the phosphorescence emission properties in solution, neat solid, and in doped PMMA thin films.*

Molecules that display phosphorescence play a significant role in light- and energy-harvesting systems.[1] This is because the spin statistics theoretically allow for achieving high efficiencies in these systems by harnessing the triplet excitons.[2] In this context, search for new triplet emitters with high quantum yields and tunable emission properties is of major interest for numerous applications such as solar cells, organic light-emitting diodes (OLEDs), photocatalysis, sensors etc.[3] Most of the triplet emitters contain transition metals or heavy atoms that have large spin–orbit coupling to enable efficient intersystem crossing to the triplet states.[4] In contrast to the extensive number of examples of transition metal based triplet phosphors, purely organic materials that show room temperature phosphorescence are quite rare, particularly in solution.[2b,5] Although it has long been established that phosphorescence can be achieved through singlet fission process in purely organic molecules,[6] the design and experimental investigations on new molecular scaffolds are limited.[7] Singlet fission is a process that involves sharing of energy between a singlet-excited state and a ground-state molecule to produce a correlated pair of triplet-excited molecules. In theory, it allows for quantum yields (QY) up to 200% to be achieved.[5a] Recently, an external quantum efficiency of 160% for an organic solar cell device employing pentacene molecules was demonstrated and also a first observation of efficient singlet fission in solution based on a bis(triisopropylsilylethynyl)-pentacene excimer was reported.[8] Boron β-diketonate compounds incorporated into a polylactide polymer were also reported to show phosphorescence, albeit only in the solid-state and the origin for the emission was ascribed to singlet fission.[9] Therefore, until now most investigations on well-defined small molecules have been limited to the acene family and the design of novel chromophores that show singlet fission induced phosphorescence based on purely organic compounds and a systematic tuning of their photophysical and chemical properties remains a major challenge.[5b] A key factor to the successful realization of singlet fission based materials relies on the design of molecules with appropriate electronic structure requirements that enables judicious disposition of the ground state as well as the excited state.[7] The rich photoluminescent properties of organoboron compounds prompted us to pursue them as molecules of choice for our investigations.[10] Moreover, the chemical and the electronic versatility of the molecular scaffold amenable to suitable modifications allows for achieving superior photoluminescent behavior both in the solid state as well as in solution.[11] This work purposedly combines the electronic and structural requirements favoring singlet fission by satisfying different criteria such as presence of strong dipole moments, π–π interactions (see Scheme 1) and appropriate functional groups such as an aromatic nitro group as a part of the conjugate unit that can to some extent exhibit radical character in the excited state.[7,12]

Herein, we report the synthesis, structural and detailed photophysical investigations of a novel family of β-hydroxyvinylimine boron compounds that show singlet fission induced room temperature phosphorescence emission with high efficiency both in solution and when doped in PMMA (poly(methyl methacrylate)) matrix. Two different classes of molecules were chosen and synthesized through a common approach as potential ligand candidates. The first (**1**–**3**) consists of β-hydroxyvinylimines derived from a 3,4-dihydronaphthalene unit with scope for additional modulation of electronic (and dipole moment) changes made possible by varying the R^1 and R^2 substituents. The second set (**4**–**7**) involves β-hydroxyvinylimines derived from a 2*H*-chromene unit in which the donor moiety is already incorporated into the structure (oxa group).

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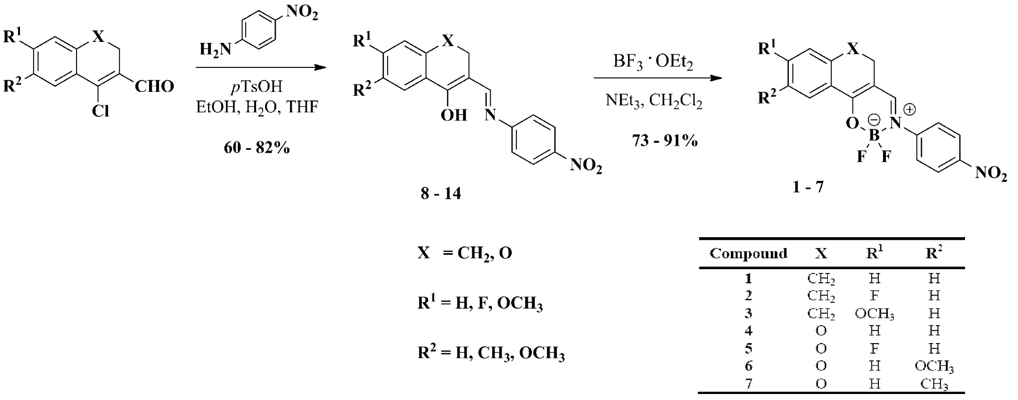

Compound	X	R^1	R^2
1	CH_2	H	H
2	CH_2	F	H
3	CH_2	OCH_3	H
4	O	H	H
5	O	F	H
6	O	H	OCH_3
7	O	H	CH_3

Scheme 1. Synthesis of boron compounds **1–7** from hydroxyvinylimines **8–14**.

The synthesis of the hitherto unknown β-hydroxyvinylimines **8–14** was accomplished by treating β-chlorovinylaldehydes with 4-nitroaniline in ethanol/water/THF, in the presence of *p*-toluenesulfonic acid (*p*TsOH). The corresponding β-chlorovinylimines were not observed under these reaction conditions. Since molecular scaffolds incorporating a nitro group were targeted, the reaction methodology was standardized primarily only for nitro aniline as a substrate in this work. It is important to mention that the above utilized synthetic strategy is previously unknown for accessing β-hydroxyvinylimines and serves as an elegant approach to prepare this family of molecules. In a subsequent step, the β-hydroxyvinylimines precursors were further reacted with $BF_3{\cdot}Et_2O$ in the presence of NEt_3 to give the corresponding boron compounds **1–7** in good to high yields.

Detailed investigations were carried out to evaluate the photophysical properties of **1–7** in solution (Figure 1), in neat solid (powder) and spin-coated PMMA films. The UV/Vis profiles shown in the Supporting Information (Figure S1) reveal a strong influence of the electronic properties of the substituents on the absorption maxima (Figure 2). While compound **7** absorbs at 476 nm, **2** exhibits a strong hypsochromic shift with maxima at 418 nm. All compounds show high molar extinction coefficients in solution with the highest found for compound **3** at 46200 $M^{-1}cm^{-1}$.

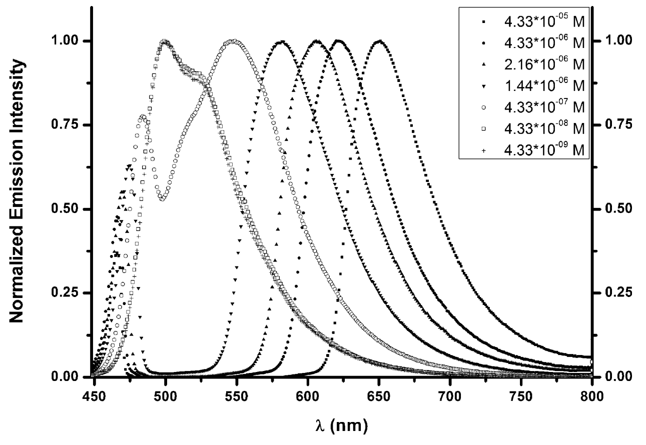

Figure 1. Concentration dependence on the emission wavelengths of **3** in CH_2Cl_2 (RT, under N_2 atmosphere).

Initial examination of the emission properties of **1–7** revealed strong luminescence in solution marked by the presence of two emission bands of different intensities. While the band with the lowest intensity that showed comparably small Stokes shifts (30–81 nm, see Table 1) was attributed to fluorescence, the remarkably high intense band that was significantly shifted bathochromically with substantially large Stokes shifts (140–197 nm at 0.1 OD, see also Tables S3 and S5) was tentatively ascribed to phosphorescence. It is worthwhile to note that such significant Stokes shifts are unprecedented for boron compounds.[9a,13] The excited state lifetimes obtained for the compounds are in the range 1.69–4.79 ns and 1.2–5.4 µs for the low intense band and the high intense band, respectively. This reiterated the nature of the attributed emission to fluorescence and phosphorescence, respectively. In order to further validate the excited-state nature of the long-lived intense band, concentration dependent studies were carried out. A significant shift of the emission wave-

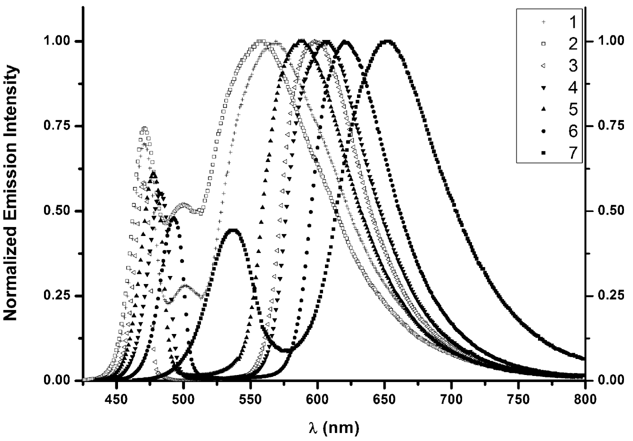

Figure 2. Normalized emission spectra of **1–7** in CH_2Cl_2 (0.1 OD, RT).

Table 1: Photophysical data of **1–7** in CH_2Cl_2 (0.1 OD, RT, under N_2 atmosphere).

Compound	λ_{abs} [nm]	λ_{exc} [nm]	$\lambda_{em,fl}$ [nm]	τ_0^F [ns]	$\lambda_{em,ph}$ [nm]	τ_0^P [ns]	φ_{em} [%]
1	421	423	501	2.07	568	1233	29
2	418	415	500	1.69	558	5413	86
3	440	432	470	2.94	599	1382	104
4	430	430	478	3.77	588	3054	100
5	426	427	493	2.07	621	1311	70
6	439	434	537	4.79	653	2343	98
7	456	446	483	4.73	606	2543	49

length maxima of the long-lived intense band was observed upon varying the concentration of the complexes **1**–**7** in CH_2Cl_2 (Figure 1). For instance, the emission of **3** in CH_2Cl_2 was found to be bathochromically shifted over 150 nm upon increasing the concentration (509 nm at 4.33×10^{-9} M and 659 nm at 4.33×10^{-5} M). This systematic significant shift is quite unique and a rare behavior, which is tentatively ascribed to originate from polarization effects. A local polarization field caused due to the molecular dipole moment interaction with the dipole moment of a neighboring dye molecule. As a consequence, a red shift of the emission band is expected for an excited state with higher polarity than the ground state. This effect decreases with $1/r^3$ and hence is less pronounced for diluted solutions. This behavior was up to now only observed for different concentrations of dye molecules doped into a thin film exhibiting $\Delta\lambda_{em}$ up to 75 nm.[14] While the fluorescence emission maximum was hypsochromically shifted for higher concentrations ($\Delta\lambda_{em} = -33$ nm for **3**), the phosphorescence emission showed an even stronger dependency on concentration ($\Delta\lambda_{em} = 124$ nm for **3**, see Figure 1 and S11–S18). However, neither the absorption wavelength nor the wavelength maximum in the excitation spectrum showed any discernible changes upon varying the concentration, ruling out aggregation induced effects and strongly indicative of formation of an excimer being the origin of the long lived intense emission band (see Figure S3 and S8). This hypothesis is consistent with the single-crystal X-ray diffraction analysis of **2** and **4**, where adjacent molecules are in close proximity allowing π–π stacking interactions between the benzene rings (Figure 3). In the crystal structure of **2**,[15] the crystallographically independent molecules are almost parallel to each other, with an anti-parallel alignment probably favored by the interaction of the dipole moments of the molecules, and are linked through two π–π interactions along the *c* direction (centroid–centroid distances of 3.7568(8) and 3.7834(8) Å). These pairs of molecules are further connected by additional π–π interactions along the *c* axis with centroid–centroid distances of 3.6970(7) and 3.8667(8) Å. In the crystal of **4**,[16] pairs of CH···O interactions generate dimers along the *a* axis (H···O distances of 2.45 and 2.53 Å with the corresponding C···O distances of 3.3027(13) and 3.4556(14) Å). These dimers are further connected by π–π interactions between benzene rings (bearing the NO_2 group) with a centroid–centroid distance of 3.7875(6) Å. These packing arrangements in the solid state can be presumed to be present also in solution leading to the formation of excimers.

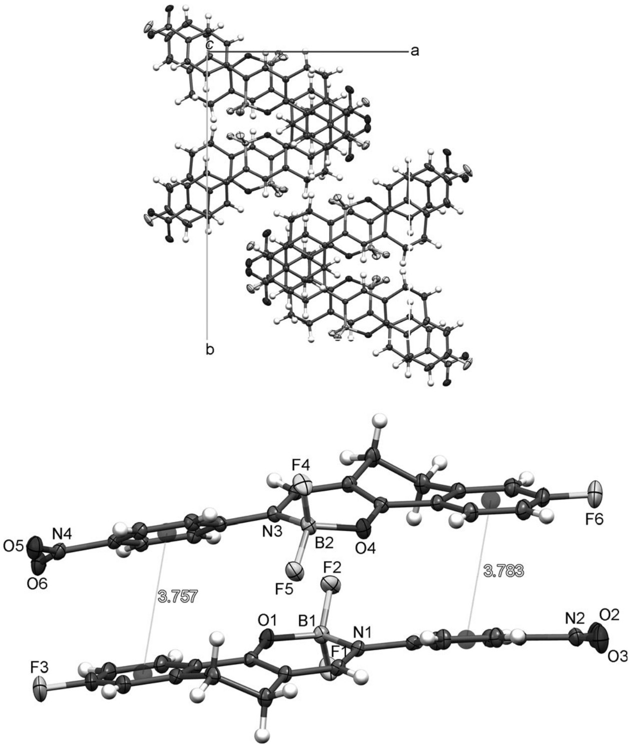

Figure 3. Top: Packing diagram of **2**. Bottom: Measured distance between two molecules of **2** in the crystal structure.

Such an excimer formation favors the sharing of the energy between the molecules in the singlet excited state and the ground state, after which they combine to produce a correlated pair of triplet state excited molecules.[17] These molecules in the triplet excited state then return to the ground state through a radiative decay process resulting in phosphorescence. As a consequence of this series of photophysical events, two photons are being produced through a singlet fission process, which ultimately leads to QY in excess of 100%. This is indeed consistent with the absolute QY found for **3** in solution, which had a maximum value of 114% at 2.16×10^{-6} M in CH_2Cl_2 with lower values observed for more diluted solutions. It has to be mentioned that the QY remained comparably high (35%, see Table S1) even at very low concentrations (4.33×10^{-9} M). On the other hand, significantly higher concentrations also displayed considerably lower QY (see also Table S1) which is most probably due to the non-radiative decay behavior induced by enhanced self-quenching. The phosphorescence was found to contribute between 83.5% (**7**) and 90% (**3**) to the total emission at 0.1 OD with subsequent decrease of the phosphorescence fraction as a consequence of dilution.[18] This finding renders further support to the hypothesis that the observed phosphorescence process depend on the formation of excimers in solution, which becomes less efficient upon dilution. The presence of oxygen showed no significant influence on the photophysical properties, for example, no quenching of the long-lived intense band was observed. This can be attributed to the energetically significantly lower lying T_1 states of the boron compounds compared to the HOMO of O_2.[9a]

Investigations of **1**–**7** in the neat solid (powder) also showed luminescence, albeit with quantum yields that were found to be much lower than in solution or in PMMA ranging between 5.8% and 11.9% (see Table S7). Although **3** exhibits the highest QY of 52.8% in comparison to the other compounds, it was still considerably lower in comparison to what was obtained in solution and PMMA. The creation of low-energy quenching sites due to increased aggregation in conjunction with fast exciton migration in the powder is deemed as a plausible reason for the low quantum yields observed in the neat solid for the compounds. Since the emitter molecules are doped into a matrix for most of the relevant applications, the photophysical behavior of the compounds doped into an inert polymer film such as

PMMA was probed. The studies were carried out by spin-coating a CH_2Cl_2 solution containing 2 wt% of the corresponding boron compound in PMMA. The emission profiles of the boron compounds spin-coated in PMMA resembled the highly diluted samples in solution (Figure S26). However, the quantum yields were found to even exceed the highest solution quantum yields at 0.1 OD in most cases (Table 2) with the exception of the fluorine-containing analogues **2** and **5** for which lower quantum yields were obtained under these conditions than in solution. While a maximum quantum yield of 118% was found for **3**, compounds **4** and **7** exhibited 117% and 106%, respectively, in PMMA. The high quantum yields further lend support to the assumption that in addition to the compounds being well dispersed in the polymer matrix, the vibrational non-radiative decay in the solid state is minimized due to increased rigidity in comparison to solution and suppression of other non-radiative decay pathways that were present in powder.

Table 2: Photophysical data of 2 wt% **1**–**7** in PMMA.

Compound	λ_{exc} [nm]	λ_{em} [nm]	φ_{em} [%]
1	425	512	73
2	424	512	67
3	437	498	118
4	430	528	117
5	426	512	63
6	436	528	63
7	450	556	106

A closer look at the two different series of boron compounds (**1**–**3** and **4**–**7**) highlights the importance of both the electronic properties of the substituents as well as a suitable chromophore scaffold in order to induce efficient singlet fission based phosphorescence. It is evident that the first series with the 3,4-dihydronaphthalene backbone shows a stronger response upon variation of the electronics via R^1 and R^2. Compared to **1**, the substitution with electron-donating groups (**3**) leads to significant increase of the quantum yield, while the substitution with electron-withdrawing groups (**2**) facilitates a moderate augmentation. This is probably due to presence of increased π–π interactions and less vibrational quenching in the former versus the latter. In this series, the parent compound **1** displayed much lower QY in solution. In the second series consisting of the 2*H*-chromene backbone, the parent compound **4** exhibited higher QY in solution and in PMMA than **5**–**7**. Since the donor unit is already incorporated in the chromophore scaffold in these latter compounds, further electronic tuning of R^1 and R^2 leads to less beneficial photophysical properties compared to the parent compound in solution and in PMMA. Interestingly, strong π-donor functional groups like the methoxy groups (**6**) showed similar quantum yields in comparison to **4** in solution but much lower in PMMA. The weaker donor methyl group (**7**) gave only comparable results to the parent compound in PMMA and in powder, which is indicative of the higher non-radiative decay rates in solution. The highest φ_{em} in solution, in PMMA and in solid state observed for **3** in comparison to the other compounds can be rationalized on the basis of the expected highest molecular dipole moment affirmed by the presence of methoxy (donor) and nitro group (acceptor) which are aligned in the direction of the molecular dipole vector of the molecule.

In summary, a new family of β-hydroxyvinylimine boron compounds showing efficient and highly tunable phosphorescent emission at room temperature both in solution and when doped in PMMA have been synthesized. Detailed photophysical investigations confirmed the significantly enhanced phosphorescence efficiency achieved through the systematic variation of the electronic nature of the basic chromophoric scaffold as well as the fine-tuning of the electronic nature of the substituents. Among the investigated complexes, an absolute quantum yield exceeding 100% was obtained for **3** and **4** in solution and for **3**, **4** and **7** in PMMA. The superior efficiencies found for these selected compounds can be explained on the basis of singlet fission favored by amalgamation of factors such as permanent molecular dipole moment, strong π–π stacking interactions and the presence of a functional group that aids to promote radical character in the excited state. The culmination in interesting photoemission properties derived through a rational design approach is expected to pave way for obtaining novel, heavy atom-free compounds exhibiting singlet fission for potential optoelectronic applications. Further investigations are currently ongoing in our group pursuing the applications of the reported compounds.

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[15] CCDC 975346 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See also Figure S34, S35 and S36 and Tables S8 and S9 for X-ray data.

[16] CCDC 975347 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See also Figure S37, S38 and S39 and Tables S8 and S10 for X-ray data.

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