

Theoretical and Experimental Study on Boron β-Diketonate Complexes with Intense Two-Photon-Induced Fluorescence in Solution and in the Solid State

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Three boron diketonate chromophores with extended π -conjugated backbone were prepared and their spectroscopic features were investigated through a combined theoretical/experimental study. It was shown that these complexes, which undergo very large electronic reorganization upon photoexcitation, combine large two-photon absorption cross section with an emission energy and quantum efficiency in solution that is strongly dependent on solvent polarity. The strong positive influence of boron complexation on the magnitude of the twophoton absorption was clearly established, and it was shown that the two-photon absorption properties were dominated by the quadrupolar term. For one of the synthesized compounds, intense one- and two-photon-induced solid-state emission (fluorescence quantum yield of 0.65 with maximum wavelength of 610 nm) was obtained as a result of antiparallel J-aggregate crystal packing.

1. Introduction

Chromophores that combine large two-photon absorption cross sections with high solid-state fluorescence quantum yields are valuable candidates for applications ranging from optoelectronics (upconversion lasing) to biophotonics (ultrabright nanosized fluorescent contrast agent).^[1] Yet, reports on such molecules are relatively scarce in the literature.^[2]

It was recently established by different groups that boron difluoride complexes of a variety of organic ligands present exceptional solid-state luminescence properties.^[3] It has been proposed that these exceptional features are most likely a consequence of restrictions of the rotational/torsional mobility arising from the formation of a boron chelate.^[4] Alternatively, it has also been suggested that steric hindrance induced by the substituents attached to the boron complex can also participate in reducing molecular interactions in the crystal packing,

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thus avoiding the formation of aggregates, which are in the most general cases detrimental to emission efficiency.^[5]

In parallel, the two-photon-induced fluorescence (TPIF) properties of various boron complexes have been quite extensively studied by different groups. Besides archetypical boron–dipyrromethene (BODIPY), used in bioimaging since the early 2000s and almost immediately investigated in the context of TPIF,^[6] other types of boron compounds, particularly trivalent ones, have received considerable attention.^[7] In 2003 and 2004 successive reports by the groups of Marder and Blanchard-Desce showed that fluorophores based on β -(diketonato)boron moieties displayed, in spite of a short π -conjugated backbone, unexpectedly large cross section values up to 200 GM (Göppert Meyer unit, 1 GM = 10^{-50} cm⁴ s photon⁻¹).^[8]

As a consequence, it can be anticipated that similar boron complexes could constitute an interesting basis to be used as two-photon solid-state emitters. Indeed, recent studies by D'Aléo, Fages, and co-workers have clearly established that borylated curcuminoid derivatives are particularly attractive candidates in this regard, as they combine relatively large two-photon cross sections with significant fluorescence quantum yields in solution and in the solid state, with emission that can reach the near-IR region in the condensed phase.^[4f, 9]

In the present paper, we show that a boron complex of 1,3diphenylpropane-1,3-dione—a scaffold that has already been used in the context of solid-state fluorescent materials^[10]—for which both phenyl groups are halogenated in their *para* positions, can be used as a convenient and highly reactive electron-deficient synthetic intermediate towards a variety of twophoton-absorbing boron diketonate complexes with tunable absorption and emission wavelengths (λ_{abs} and λ_{em}). We took



advantage of this approach to introduce three different end groups with varying electron-donating abilities, namely, a strong dialkylaniline donor, a weaker alkoxyphenyl moiety, and an intermediate alkoxyfluorene; these groups constitute some of the most archetypical electron-donating groups used in nonlinear optical chromophores. As a consequence of their electronic dissymmetry, the resulting compounds possess significantly large two-photon absorption cross sections, above 1000 GM for the best compound within the series. Their fluorescence is highly solvatochromic, and its efficiency is very dependent on the polarity of the solvent. For one of these complexes, 6b, a very intense solid-state emission centered around 610 nm is obtained by using both one- and two-photon excitation, which is in good compliance with bioimaging requirements. The origin of this luminescence is discussed on the basis of its crystal-packing parameters, and we show that it can be achieved by using either one- or two-photon excitation.

2. Results and Discussion

2.1. Synthesis

The syntheses of all target molecules (Scheme 1) relied on a similar strategy that involved key intermediate boron complex **4**, which we obtained through a classical literature procedure.^[11] First, condensation of commercially available *p*-bromobenzaldehyde and (*p*-bromophenyl)methyl ketone by using the standard Claisen–Schmidt procedure afforded β -enone **1**. This compound was then treated with bromine to afford addition product **2**. Reaction of compound **2** with sodium methanoate followed by acidolysis afforded diketone ligand **3**, which was involved in complexation with boron trifluoride to afford target intermediate **4** in a satisfactory overall yield of 66%.

Target chromophores **6a**, **6b**, and **6c** were finally obtained through a very efficient Sonogashira cross-coupling step with alkynes **5a**,^[12] **5b**,^[13] and **5c**, respectively.^[14] Owing to the presence of the strong electron-withdrawing boron diketonate group, this last step, which usually requires relatively strong heating over several hours, was readily achieved in a couple of minutes at room temperature. In the cases of **6a** and **6b**, the target chromophores precipitated during the course of the reactions and were isolated in good yields and with good analytical purities after simple filtration and precipitation in a dichloromethane/pentane mixture. For **6c**, additional column chromatography was required. In all cases, the identities and purities of the compounds were confirmed by a variety of analytical techniques (see Sections S1–S5 in the Supporting Information).

2.2. Spectroscopy

The spectroscopic features of these three complexes in solutions were then investigated in detail (the data are gathered in Table 1). In all cases, broad structureless absorption bands were observed, characteristic of an intramolecular charge transfer (ICT) electronic transition (see Sections S8–S10).^[15] For all compounds, the absorption band was slightly affected by the solvent's polarity, whereas all the chromophores displayed marked positive solvatochromism of their emission (Figure 1). This clearly indicated a strong increase in their dipole moments between their ground and excited states,^[16] which could only



Scheme 1. Synthesis of compounds 6a-c.

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Compd	Solvent	λ_{abs} [nm]	λ_{em} [nm]	$arPsi_{f}^{[a]}$	Stokes [cm ⁻¹]
6 a ^(b)	cyclohexane	520	544	0.72	850
	1,4-dioxane	510	672	0.30	4730
	toluene	515	620	0.62	3290
	CHCl₃	540	753	0.05	5240
6 b ^[34]	cyclohexane	426	465	0.69	1970
	1,4-dioxane	440	504	1	2890
	toluene	442	487	1	2090
	CHCl₃	448	542	1	3870
	1,2-dichlorobenzene	455	568	0.94	4370
	THF	442	563	0.88	4860
	EtOAc	436	553	0.91	4850
	MeOH	440	628	0.018	6800
6 c ^(c)	cyclohexane	450	497	0.74	2100
	dioxane	458	575	0.68	4440
	toluene	462	543	0.74	3230
	CHCl₃	468	666	0.25	6350
	1,2-dichlorobenzene	472	707	< 0.01	7040
	THF	462	694	0.025	7230

be related to transfer of electron density from the peripheral donor groups to the central boron diketonate moiety. A Mataga–Lippert plot^[17] of the Stokes shift of compound **6b** versus the solvent polarity allowed us to estimate the dipole moment variation between the ground and excited states $(\Delta \mu_{\rm ce})$ to be about 18 D, which confirmed this hypothesis.

Beside this emission solvatochromism, the emission quantum efficiency also showed a strong dependence on the solvent's polarity. As a general statement, upon increasing the solvent polarity, a marked decrease in the luminescence efficiency was observed. This behavior, sometimes referred to as "positive solvatokinetics",^[18] is classical behavior for such charge-transfer (CT) chromophores and can be attributed to increased vibronic contributions to the nonradiative de-excitation pathways as the emission energy is decreased.^[18,19] It was previously reported, and found to be particularly marked, in other boron complexes.^[20]

The extent of this emission quenching process turned out to be markedly dependent on the substitution parameters (Figure S11). Thus, whereas methoxy-substituted **6b** presented a fluorescence quantum yield (Φ_f) that remained high in a variety of solvents with polarities ranging from cyclohexane to ethyl acetate, the drop in luminescence quantum efficiency was much more pronounced in the case of dialkylamino-terminated compound **6a**, the emission of which was the most redshifted within the series: a rapid drop in the fluorescence quantum efficiency was observed upon going from cyclohexane (0.72) to dioxane (0.28) and dichloromethane (0.05), and fluorescence was not observed in solvents of higher polarities.

Moreover, intermediate behavior was observed for **6c**, for which fluorescence was not seen in ethyl acetate or methanol. This suggested that, more than the solvent's polarity, the position of the maximum emission wavelength determined the efficiency of the fluorescence process. Indeed, for such CT chro-

mophores with large Stokes shifts, it is well documented that excited-to-ground-state vibronic couplings can play an important role in nonradiative decay of the excited state at low emission energies, which often results in important luminescence quenching.^[21] In the present case, this led to a rapid decrease in the emission of the studied compounds above a certain threshold, typically located between wavelengths of 600 and 650 nm.

Whereas **6b** displayed distinctively high solid-state emission (Figure 2), with a quantum yield of 0.65 and a maximum emission wavelength of 610 nm, the other two complexes did not display any detectable solid-state emission. In addition to the abovementioned ground-to-excited-state vibronic coupling, intermolecular vibrational and dipolar coupling processes may also contribute to emission quenching in the solid state in the latter.^[22]

2.3. Crystal Structure

Crystals suitable for X-ray diffraction were obtained as long, thin, bright orange-like needles by slow diffusion of diisopropyl ether into a chloroform solution of **6b**. An orthorhombic crystal structure was obtained. Its main crystal parameters are summarized in Section S17.

The crystal structure shows that, as expected, the molecule consists of an essentially flat V-shaped π -conjugated backbone, in which the two oxygen atoms of the central β -diketonate moieties complex a single boron atom. Fluoride substituents lie in a plane orthogonal to the plane of the rest of the molecule. An attractive interaction seem to take place between the fluoride groups and the aromatic protons of the neighboring chromophore, as illustrated by the presence of short contact distances (2.40 Å, compared with the sum of van der Waals radii, 2.67 Å; Figure 3 b). Such H···F bonds of similar lengths have been thoroughly reported and described in the past,^[23]







Figure 1. Emission spectra of a) compound 6a, b) compound 6b, and c) compound 6c in solvents of different polarities.



Figure 2. Crystalline powder sample of $6\,b$ under left) natural and right) UV-A ($\lambda\!=\!365$ nm) light.

including in related dioxazoborine-based compounds;^[24] in the present case, it certainly contributes, along with the strong di-



Figure 3. Crystal structure of compound **6b**. a) Structure of an individual molecule of **6b** within its crystal cell; hydrogen atom are omitted for clarity. b) Close up of the H---F short contact; (methoxy)phenylethynyl moieties are omitted for clarity. c) Crystal packing diagram of **6b** shown down the direction of the *b* axis.

polar interactions classically encountered in such boron diketonate complexes, to stabilizing the antiparallel and partly offset stacking of molecules along the *b* axis of the cell, with an interplanar distance of 3.49 Å (Figure 3 c).

This kind of "antiparallel J-aggregate" configuration accounts for the high luminescence efficiency of the solid, in agreement

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with published works, $^{\rm [25]}$ including examples on related boron diketonate complexes. $^{\rm [26]}$

2.4. Two-Photon Absorption

Two-photon cross sections were then systematically evaluated for compounds **6a-c** by using TPIF spectroscopy.^[27] In the cases of compounds 6a and 6c, for which the two-photon spectrum envelope exceeded the limit of the working wavelength of the laser used for the TPIF measurements, the twophoton absorption cross section values were cross-checked by an additional Z-scan measurement^[28] to fill the missing points and ascertain the accuracy of the TPIF measurement. Toluene was used as a common solvent for the entire study, as all complexes possessed good emission efficiency in this solvent, which thus facilitated the TPIF measurements. All three complexes displayed significantly high two-photon cross section values, in the range of 200 to 1300 GM (Figure 4). As expected, an increase in the strength of the terminal electron donor or in the conjugation length resulted in an enhancement in the cross section value. This trend was, however, particularly marked here: dialkylamino-substituted 6a possessed a cross section (1300 GM) almost one order of magnitude higher than that of its methoxy counterpart 6b (170 GM), whereas substitution of the phenyl group by a fluorenyl group in 6c resulted in a threefold increase in the two-photon efficiency (570 GM).

Comparison between the one- and two-photon absorption spectra of all complexes showed unambiguously that the twophoton transition was systematically blueshifted relative to that of the one-photon transition; thus, the one- and twophoton transitions are mutually exclusive. This behavior is generally associated with centrosymmetric chromophores, in which the zero permanent dipole moment cancels the dipolar term in the third-order hyperpolarizability equation.^[29] Strictly, the molecules studied here are not centrosymmetric; nevertheless, the blueshift suggests that the quadrupolar term is dominant in the two-photon absorption processes of 6a-c. Similar observations have already been reported for other V-shaped chromophores such as various polymethines^[30] and (aza)-BODIPY derivatives,^[6b] and this trend seems to be a general characteristic of curcuminoids and diketonate boron complexes.[31]

2.5. Theoretical Calculations

To clarify the nature of the transitions involved in the one- and two-photon processes, quantum-chemical calculations were performed for model molecules **6a**' and **6c**', in which the hexyl groups of **6a** and **6c** were replaced with methyl groups to save computational costs (Figures 5 and S16). Geometry optimization and calculations of the excited states were performed in the gas phase at the B3LYP//6-31G(d) level of theory with the Gaussian09 program (details of the calculation results and the geometries are given in the Supporting Information, see Section S16). As shown in Figure 5, the first intense two-photon absorption (TPA) transition can be assigned to the transition from the ground state to the S₂ excited state that

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Figure 4. Two-photon absorption spectra by TPIF (red marks) overlapped with the corresponding one-photon absorption spectrum (full, black) for compounds **6a–c** in toluene. For compounds **6a** and **6b**, accuracy of the TPIF measurement was ascertained by a complementary Z-scan measurement (blue marks). The typical Z-scan traces can be found in Figures S15-1 and S15-2. σ^{TPA} =two-photon absorption cross section; ε =molar extinction coefficient.

has gerade-like symmetry against the vertical symmetric plane of the molecule, whereas the first and third excited states (S_1 and S_3) have ungerade-like symmetry and are responsible for the one-photon absorption (OPA) bands. These calculations



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Figure 5. Structures of model compounds 6a' and 6c' with the orbital patterns involved in the optical transitions to the first three excited states [transition energy, oscillator strength (f), and approximate symmetry are shown in parentheses]. The number next to the arrow stands for the orbital component of the configuration to the transition. The u and g attached to the orbital names are the approximate symmetries, that is, ungerade- and gerade-like, respectively, against the vertical symmetry plane of the molecule.

clearly ascertained the CT character of the one- and twophoton transitions, with a shift in the electronic density from the peripheral donors to the central boron complex.

The energy of the OPA-allowed lowest-lying excited state (S_1) was nicely reproduced [e.g. calcd value of 2.316 eV for **6a**' vs. exptl values of 2.26 (in dichlorobenzene) to 2.43 eV (in dioxane) for **6a**], and calculations showed that this transition possessed dominant HOMO — LUMO (with symmetry inversion, i.e. ungerade-like) character. Conversely, the second lowest lying excited state (S₂) mainly corresponded to a HOMO $-1 \rightarrow$ LUMO (with symmetry conservation, i.e. gerade-like) electronic transition, the energy of which closely matched our experimental value for the two-photon transition [e.g. calcd value of 2.54 eV for 6a' vs. exptl values of 2.58 (TPIF) and 2.64 eV (Z-scan) for 6a], which confirmed the dominant quadrupolar nature of the electronic transitions. The above discussion is limited to the planar structure, as obtained by the geometrical optimization. However, rotational motion around the triple bond can be activated at room temperature. Thus, we checked the influence of rotational motion of the end groups on the optical properties by calculating some selected rotational conformers. These results clarified that rotation from the planar structure diminishes the one- and two-photon absorption bands because of decreasing overlap of the orbital (see Section S16 for details), which suggests that the planar and planar-like structures are responsible for the observed TPA band.

2.6. Comparison with Benchmark Compounds

With the aim to evaluate the influence of boron complexation on the two-photon absorption cross sections of the complexes, we synthesized compound **7** (see Section S2 and S6), a nonborylated analogue of **6a** (most efficient complex within the series in terms of two-photon efficiency).

Moreover, compound **8** (see Section S2 and S7) was also evaluated as a dipolar counterpart of **7**, which allowed us to

obtain additional insight into the influence of symmetry (Figure 6). The absorption and emission profiles of **7** and **8** in various solvents are given in Sections S12 and S13.

The two-photon absorption cross sections of both molecules were evaluated by TPIF spectroscopy (Figure 7). The beneficial influence of boron complexation on the TPA efficiency of the molecule was clear, as the TPA cross section dropped by almost one order of magnitude upon going from 6a (1300 GM) to 7 (200 GM). This effect may arise from the largely increased electron-withdrawing ability that results from boron complexation but also from stabilization of the fully conjugated enol, relative to the ligand, in which both the enol and ketol forms may coexist. The second hypothesis seems to be ruled out by examination of the ¹H NMR spectrum of the latter, which clearly reveals the exclusive presence of a single methylene proton signal associated to the enol form at a chemical shift ($\delta = 6.89$ ppm) that is not markedly different from that of the complex (δ = 7.15 ppm), and in close match with that in the literature.^[11] This indicates that the enol form is also predominant in the ligand.

In contrast, dipolar compound **8** displayed a two-photon efficiency (90 GM) that was lowered only by a factor of two relative to that of its quadrupolar counterpart **7** (200 GM), which, given the difference in size between both compounds, corresponds to a very similar two-photon efficiency per π electron. However, a difference exists in the nature of the transition involved in both cases, as **8** shows superimposition of its one-photon and two-photon transitions, whereas the two-photon spectrum was significantly blueshifted in the case of **7**, as it was in complex **6a**. This is in good agreement with an electronic transition fully delocalized over the entire chromophore backbone, which gives it pseudoquadrupolar character; this is consistent with the purely enol nature of the molecule as suggested above.

Finally, we tested the relevance of our approach for applications requiring two-photon solid-state emitters. To this end,

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Figure 6. Structure and overlaid one- and two-photon absorption spectra in toluene for benchmark compounds a) 7 and b) 8.

a powder sample of compound 6b was compressed into a tablet, which was placed in a TPIF setup. By varying the incident laser wavelength, we were able to obtain a solid-state two-photon excitation spectrum (Figure 7).^[32] In contrast with the one-photon excitation spectrum, which showed a broad structureless band, characteristic of molecular aggregates, the spectrum consisted in a narrow band, the maximal twophoton excitation wavelength of which was centered around 790 nm, in close match with the solution data.

λ^2 / (nm) 600 800 1000 1200 1400 1600 1800 4.00E+008 excitation intensit

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Figure 7. Solid-state one-photon (black, full) and two-photon (red marks) excitation and emission (black, dotted) spectra of a powdered sample of 6b. Solid-state emission upon one-photon excitation is featured as a dotted gray line for comparison.

3. Conclusions

In the course of this study, we synthesized three new diketonate boron complexes as potential candidates for applications dealing with two-photon-induced solid-state emission. Through a detailed spectroscopic study we clearly established that all three compounds display intense two-photon absorption (200 to 1200 GM) in the near-IR range ($\lambda = 700-1100$ nm), along with emission quantum yields that exceed 0.6 and that can reach unity in toluene. However, this luminescence was found to be extremely sensitive to environmental parameters, such as solvent polarity and solid-state interactions. These results were rationalized on the basis of theoretical calculations, which clearly ascertained the strong charge-transfer character of the low-energy electronic transition $(S_1 \leftarrow S_0)$ and the dominant quadrupolar character of the two-photon-allowed transition $(S_2 \leftarrow S_0)$. This last feature was also confirmed by complementary spectroscopic measurements and comparisons on model compounds 7 and 8, which also clearly established the importance of boron complexation in the magnitude of the two-photon absorption cross section.

For one of the complexes, that is, **6b**, intense solid-state emission with a quantum yield of 0.65 could be achieved. TPIF measurements were performed on a crystalline powder sample of this complex: a very intense TPIF signal was obtained, which further demonstrated the applicability of complex **6b** as a two-photon solid-state emitter. More specifically, because of its orange-red fluorescence, and because of the tremendous interest and growing use of curcuminoid complexes in the framework of biomedical applications,^[33] we believe that $\mathbf{6b}^{[34]}$ could constitute a very appealing chromophore towards the making of organic nanoparticles for two-photon laser scanning microscopy bioimaging.



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 Theoretical and Experimental Study on Boron β-Diketonate Complexes with Intense Two-Photon-Induced Fluorescence in Solution and in the Solid State



Getting excited! The linear and nonlinear optical properties of three two-photon-absorbing, fluorescent boron diketonate complexes are unraveled through a combined spectroscopic and computational study. All three compounds display intense two-photon absorption (200–1200 GM) in the near-IR range (λ = 700–1100 nm), along with emission quantum yields that exceed 0.6 and that can reach unity in toluene.