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Boron difluoride complexes of 2’-hydroxychalcones and curcuminoids as fluorescent dyes for photonic applications*

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Abstract
The field of fluorescent boron complexes has witnessed tremendous developments in recent years. In that context, we have investigated two series of boron difluoride complexes based on 2’-hydroxychalcone and curcuminoid ligands that represent naturally occurring pigment structures. The dyes display significantly large Stokes shift values, indicating that an ICT state is involved as lower-energy state in the singlet manifold. Remarkably they are also fluorescent in the solid-state, with emission wavelengths usually in the visible and mainly in the near infrared (NIR). It is especially intriguing that those dyes experience strong π-interactions in the crystal phase. We have observed that the formation of those highly stacked structures was not detrimental to solid-state emission and could even be exploited for the generation of efficient NIR emitters. For example, the boron complexes of curcuminoid ligands can be used to generate NIR fluorescent organic nanoparticles with large cross sections for two-photon absorption. The design of organic dyes displaying NIR emission in solution or in the solid-state remains challenging for applications in bioimaging and organic photonics.

Keywords: curcuminoids, boron complexes, solid-state fluorescence, near infrared, organic nanoparticles

Mathematics Subject Classification: 5.00, 5.04, 6.04

1. Introduction

Fluorescent organic solids are highly sought for applications in many advanced technologies, including chemical sensing, bioimaging, information display and organic photonics [1–3]. For example, they find use in organic lasers, organic light-emitting diodes (OLEDs), and waveguides. Fluorescent organic nanoparticles (FONs) are nanomaterials that display versatile properties amenable to bio-imaging purposes [4, 5]. Currently, small molecules that can be obtained with well-defined structure and high purity represent promising solid-state fluorophores with respect to polymers. Because of their ability to tightly pack in the solid state, most low molecular weight fluorophores are often recognized as poorly efficient emitters in the condensed phase although they are highly emissive in solution. Several approaches have been proposed to increase luminescence efficiency in the crystal state, such as the introduction of bulky substituents or quaternary centers in the vicinity of aromatic rings to limit the formation of π-stacked aggregates. Amorphous organic solids have also been designed [6]. Another important class of chromophores are those capable of undergoing emission enhancement in the aggregated form, functioning according to the aggregation induced emission (AIE) or aggregation induced enhanced emission (AIEE) mechanisms [7, 8]. In such systems, restriction of intramolecular rotation occurring in the aggregate impedes internal conversion and vibrational relaxation processes that otherwise compete with fluorescence emission.

There exists now a wide range of solid-state organic fluorophores [1]. Among them, systems based on boron...
complexes containing a π-conjugated backbone are found particularly efficient [9, 10]. These fluorophores are developed as an alternative to the well-known borondipyrromethene (BODIPY) dyes because BODIPYs are often subject to strong self-quenching in the solid phase. In this lecture, we focus on two series of boron difluoride complexes that are based on the 2′-hydroxychalcone and curcuminoid ligands. We found out that these dyes exhibit outstanding optical properties in the solid state affording fluorescence emission with maxima reaching the near infrared (NIR).

2. Synthesis

Both chalcones and curcuminoids are very well known classes of naturally occurring pigments. Chalcones (scheme 1) are intermediates in the synthesis of many biological compounds, such as flavonoids [11]. They have widely been used in many applications because of their linear and nonlinear optical properties [12–17] and their biological activity [18, 19]. Curcuminoids are also an important class of natural compounds featuring the β-diketone unit embedded in a π-conjugated system (scheme 1) [20]. They derive from the natural curcumin pigment found in turmeric.

Both types of dyes possess in common the arylopropenone moiety. The latter is usually built by the condensation of an enolizable ketone with an aldehyde under mild basic or acid conditions (scheme 2). From the synthetic point of view, the chief asset of these two classes of compounds is to be obtained according to such simple and cheap chemical procedures using nucleophilic additions that proceed in environmentally friendly solvents and do not need the use of expensive catalysts [21, 22]. Another advantage is that tedious purifications required to eliminate traces of reactants and side-products classically encountered in the chemistry of π-conjugated molecules, such as metals, organic or inorganic catalysts, organotin derivatives (used in Stille coupling) etc, can be avoided. Borontrifluoride etherate is used as a source of BF₂ to produce the corresponding dyes under mild conditions as well. As a result, the overall synthetic route allows the generation of a large library of compounds in which a variety of terminal aryl rings with different electron-donating ability can be introduced [21, 22].

2′-Hydroxychalcones and curcuminoids are bidentate negatively charged ligands containing two oxygen atoms as donor atoms (scheme 2). Upon complexation to the boron difluoride unit, they form a six-membered dioxaborine ring that behaves as a strong electron accepting group [23]. Boron complexation is thus a very simple means to tremendously increase the dipolar character of the dye, thus avoiding tedious chemical procedures to introduce substituents with strong electron-withdrawing strength. As such, the BF₂ complexes of 2′-hydroxychalcones and curcuminoids combine electron donating (D) and accepting (A) groups and display the D–A or the D–A–D structure, respectively. Moreover, besides this electronic effect, we could show using computational studies that the BF₂ group is a versatile unit for solid-state molecular assembly and crystal engineering [24].

3. Photophysical properties in solution

Although the solution photophysics of chalcones is well documented [25], the case of boron complexes of 2′-hydroxy-substituted analogues has received little attention [26]. Chalcones usually display a weak fluorescence in solution because their excited-state dynamics is governed by fast intramolecular torsional motions and photoisomerization processes causing nonradiative deactivation of the first singlet excited state, explaining therefore their low efficiency [25]. Following the same trend, none of the free 2′-hydroxychalcone ligands was found to be fluorescent in solution, which is also consistent with the possible occurrence of excited-state intramolecular proton transfer in these compounds [27]. In contrast, the free curcuminoid ligands usually show fluorescence emission, as already reported in literature [28].

BF₂ complexation was observed to produce considerable red shifts (>100 nm) of the maximum absorption wavelength for a large series of 2′-hydroxychalcone compounds as a consequence of the enhanced dipolar character of the difluorodioxaborine-containing species [21].
Concomitantly, BF₂ complexation also leads to a considerable increase of the oscillator strength of the lowest-energy transition band. Weak fluorescence emission in solution is recorded in general, except for the carbazole-containing compound 1 (figure 1) that exhibited bright fluorescence with a quantum yield (Φf) of 79.5% in dichloromethane leading to a high optical brightness of ε × Φf = 45 000 M⁻¹ cm⁻¹ [21]. The boron difluoride complexes of curcuminoids display similar spectral trends but, unlike the chalcones derivatives, they generally give rise to larger values of fluorescence quantum yields (40 to 60% in dichloromethane), making them better fluorophores in solution [22]. The fluorescence emission of those dyes spans the visible region, but also reaches the NIR, as in the case of compound 2 in dichloromethane or acetonitrile (up to 780 nm, figure 2). For both classes of dyes, singlet excited-states are very short-lived with lifetimes in the sub-nanosecond to nanosecond time regime.

Both families of dyes are characterized by intense absorption bands in the visible region with ε values around 50 000–70 000 M⁻¹ cm⁻¹ for chalcones and curcuminoids, giving rise to darkly colored solutions or solids [21, 22]. For example, the boron difluoride complex of a 2′-hydroxychalcone derivative containing a triphenylamine unit as donor end-unit was shown to exhibit an intense and broad absorption band (ε = 70 000 M⁻¹ cm⁻¹) that extended from the UV to the far-red end of the visible spectrum [29]. This panchromatic dye was successfully used as donor material in organic solar cells blended with [6,6]phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) as electron accepting material resulting in a solution-processed solar cells based that showed a PCE of 1.13% [29].

As a consequence of the D–A and D–A–D electronic structure of the dyes, both their electronic absorption and fluorescence emission spectra display positive solvatochromism and lose their vibronic structure in polar solvents, as
illustrated in the case of dye 2 (figure 2) [21, 22]. This observation confirms that emission occurs from a singlet excited state with a strong intramolecular charge transfer character and an excited-state dipole moment larger than that in the ground-state. This behavior is in agreement with that reported for related boron difluoride compounds [30] and is related to the strong electron withdrawing effect of the difluorodioxideborine chelate.

Moreover, we reported the first examples of boron difluoride complexes of meso-aryl-functionalized curcuminoids, i.e., compounds that contain a phenyl ring connected at the central carbon atom of the acetylacetone unit [22]. We showed that the presence of the meso-aryl substituent provides enhanced solubility in organic solvents as compared to the nonsubstituted analogues and further enable the fine tuning of the optical properties of the curcuminoid π-systems. Dynamic 19F NMR allowed to confirm the fact that rotation of the meso-aryl fragment is restricted at room temperature and becomes allowed at higher temperature. The twisted geometry of these dyes has been further confirmed in the solid state by single-crystal x-ray diffraction studies. Interestingly, unlike the case of BODIPY derivatives, meso-substitution with a phenyl ring was shown not to affect the radiative and nonradiative kinetic constants [22].

4. Fluorescence emission in the solid state

The investigation of photophysical properties of photoluminescent organic crystals is highly challenging, for both experiment and theory, because the deep understanding of solid-state photophysics necessitates the establishment of reliable structure–property relationships, which is difficult. Recently, Gierschner et al [31] have provided a critical review on the solid-state excited-state behavior of all-trans para-distyrylbenezene in which they emphasized the role of trap states and rate of exciton migration. While efficient luminescence emission can be obtained from single crystals, polycrystalline solids are usually less emissive because they contain high trap densities as compared to single crystals, located at grain boundaries for example, that quench luminescence. Because polycrystalline organic layers constitute an important basis for the fabrication thin-film devices, it is of paramount importance to identify compounds with optimized luminescence properties in polycrystalline samples.

We discovered that many if not all boron difluoride complexes of the chalcones and curcuminoids we investigated (about 200 compounds) exhibit fluorescence emission in the solid state [21, 22, 32]. Remarkably, the spectra are systematically considerably red-shifted in the solid state relative to solution, leading to maximum emission wavelengths spanning from the far red to the NIR. Unexpectedly high fluorescence emission quantum yields were also obtained for polycrystalline samples, especially for materials exhibiting emission maximum wavelengths located far in the red and in the NIR (up to 855 nm). Indeed, those systems often showed an increase of the luminescence quantum yield in the solid phase relative to the solution case, which hints to an operative AIEE process. Even more important is that i) single crystal x-ray analyses of the boron-containing dyes pointed to the organization of the dipolar molecules in cofacially oriented arrays, and ii) spectroscopic studies conspicuously showed that solid state emission features originated from the strong excitonic coupling between aggregated chromophores.

Boron difluoride complexes of 2′-hydroxychalcone bearing different donors, i.e., molecules with a strong intramolecular push–pull character, were thoroughly investigated and the emission properties are clearly characteristics of tightly packed chromophores (figure 3) [32].

Especially appealing are those dyes that contain the 1-hydroxy-naphth-2-s-carbonyl moiety as scaffold supporting the difluorodioxidoborine ring because they provide unique NIR emission signatures (wavelengths from 736 up to
845 nm) in the condensed phase as well as enhanced chemical stability in solution [32]. For those series of compounds, we investigated the influence of the ground-state dipole moment on the geometry of assemblies of cofacially overlapping chromophores and, in turn, the bathochromic shift of emission spectra. The CT character of the emission transition was also examined as a key factor for NIR emission in the solid state. Strikingly, significant solid-state emission was observed with dyes adopting the H-aggregation mode, thereby exhibiting excimer- or exciplex-like fluorescence emission features. Although this type of intermolecular arrangement is commonly associated with low fluorescence emission ability, the solid-state fluorescence quantum yields remain significant and emissions at 690 nm and 751 nm with 13% and 6.5% efficiencies, respectively, were obtained. Moreover, dye 3 was found to present an emission maximum wavelength at 804 nm and a fluorescence quantum yield value of 2%, which is one of the best NIR solid-state organic emitters to date (scheme 3). Using H-aggregation as a crystal engineering strategy towards solid-state organic emitters combining NIR wavelength and high quantum yield represents a counterintuitive yet interesting approach.

In addition, we could show that the diboron fluoride complexes of curcuminoids are emissive in the solid-state as well, affording emitted light in the visible and NIR [21]. Remarkably, the molecules with a meso-hydrogen atom presented an emission that is red-shifted compared to those containing a phenyl ring. We believe that the steric hindrance induced by the latter group induces a less extended stacking of the curcuminoid backbones. Moreover, these dyes are chemically very stable on the opposite of boron difluoride complexes of chalcones and allow the versatile generation of organic nanoparticles in water. The optical and photophysical properties of these fluorescent organic nanoparticles (FONs) were studied extensively (vide infra) [33].

5. Two-photon excited fluorescence: toward NIR-to-NIR probes

Fluorophores with both large two-photon absorption (TPA) cross section ($\sigma^2$) and high $\Phi_T$ underpin the application of two-photon-excited fluorescence (TPEF) spectroscopy [34–38] in bioimaging technologies [39–43]. One of the advantages of TPEF is to enable excitation of chromophores in the NIR, especially in the so-called biological transparency window (i.e. 700–1000 nm). This is of course mandatory for in vivo and in vitro imaging, but also very useful for other applications requiring in-depth measurements. It occurs that many of the fluorescent dyes used for such applications display large TPEF brightnesses ($B_{\text{max}}^\text{TPEF} = \sigma^2 \Phi_T$) in the visible part of the spectrum, but not in the biological transparency window. There are several families of organic dyes in which one-photon excited fluorescence emission can be tailored to reach the NIR [44, 45], like polymethines [46, 47], but then TPA excitation of such systems is bathochromically shifted and hence occurs at too low energy, out of the biological window. Therefore, dyes combining both NIR TPA and NIR TPEF in the biological transparency window, the so-called NIR-to-NIR dyes, represent challenging materials. Maury et al [48] and Wong et al [49] developed NIR-to-NIR imaging agents based on Yb(III) complexes that absorb at 800 nm and 860 nm, respectively, and emit around 1000 nm. It occurred to us that the boron difluoride complexes of the curcuminoids could present the relevant NIR-to-NIR attributes.

Curcuminoid ligands have been used in imaging applications [50–52], including those based on TPA [53, 54], but reports on boron difluoride-containing curcuminoids are still scarce [55–57]. Because BF$_2$ complexes of curcuminoids display the D–A–D structure frequently found in TPA active chromophores [34–38], we therefore undertook the investigation of the TPEF properties of a series of curcuminoids containing different terminal aromatic groups D [33]. These BF$_2$ complexes possess the C$_{2v}$ symmetry and are related to the V-shaped chromophores that are known as TPA chromophores [58]. Accordingly, the nonlinear absorption band is found strongly blue-shifted for these dyes and does not match the $S_0$–$S_2$ one-photon absorption (OPA) transition [59, 60]. These molecules are found to provide large $\sigma^2$, ranging from 200 to 5000 GM (unpublished data). Because of the increased degree of $\pi$-electron delocalization through the dioxaborine ring, the $\sigma^2$ values are larger than those of the free ligands, which make the BF$_2$-containing dyes valuable TPA fluorophores for imaging purposes.

As mentioned above, the emission of the BF$_2$-curcuminoids is red-shifted in the solid state and can reach NIR region as in the case of compound 4 for example (figure 4). Therefore, it was tempting to investigate the TPEF properties of these dyes in the solid state. To this end, we produce nanoparticles using the reprecipitation method by quickly adding a concentrated THF solution of the dyes into water [61]. Their diameters could be controlled in the range of 50 to 300 nm depending on experimental conditions and dye structure. For example, dye 4 forms nanoparticles with diameter values of about 50 nm that are compatible with cell imaging experiments (figure 4).

In general, FONs that exhibit TPEF have been less investigated than the molecular counterparts because of the generally low fluorescence emission capability of many organic dyes in the condensed phase. Therefore, designing organic nanoparticles having a large TPEF brightness for practical applications remains challenging [62–67]. Nanoparticles of compound 4 exhibited a strong nonlinear response in water and the TPA cross sections in the NIR were found to be 40 to 50% larger than those in DCM as a result of
aggregation. As noticed for solution studies, the two-photon absorption occurs at energy higher than that of the OPA absorption band, which enables setting TPA excitation between 780 and 900 nm (figure 5). The TPEF spectra are recorded beyond 700 nm, in the biological transparency window, and display TPA brightness values larger than 10 GM, which is an adequate value for NIR-to-NIR fluorophores.

6. Conclusion

This work demonstrates the versatile properties of diboron-fluoride complexes of chalcones and curcuminoids. Especially challenging is the synthesis of novel organic solids according to economically viable and environmentally friendly chemical procedures. Ultimately, the exploitation of renewable substitute materials obtained from the biomass could provide a formidable avenue towards the reduction of the impact of feedstock supplies from petroleum chemistry in the generation of advanced organic photonic/electronic materials. In that respect, chalcone and curcuminoid derivatives represent an appealing class of compounds. Future work is directed towards the application of these dyes in organic photovoltaics, bioimaging, and optoelectronics.

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