



Tuning solid-state emission properties of pyrene-containing chalcone derivatives



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ABSTRACT

The synthesis and optical properties of chalcone dyes containing pyrene as a donor is described both in solution and in solid-state. With such molecules, we show that, while the ground-state dipole moment is almost zero, the excited state is highly polar resulting in an intramolecular charge transfer excited state. All the chalcone molecules were shown to be emissive in the solid state but the behavior is different as a function of the substituent appended on the aryl group connected to the carbonyl function of the chalcone. We evidenced the beneficial effect of a methoxy function on the aggregation yielding an enhancement of the emission quantum yield in solid-state as compared to the solution.

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1. Introduction

Organic solid-state emitters are currently attracting much attention because of their high potential for applications in organic light emitting diodes,^{1,2} organic field-effect transistors,^{3–5} solid-state lasers^{6–8} or sensors materials.^{5,9} However, the design of efficient organic fluorophores remains challenging since the chemical structure and the electronic properties of the individual molecules, although they are important factors in solution phase, do not allow reliable prediction of the emission behavior in the condensed phase. For instance, molecular assembly can lead to J- or H-aggregates that produce emissive or poorly emissive structures, respectively. The possibility to restrict intramolecular bond rotation can also result in appearance or enhancement of the fluorescence signal in the solid-state as illustrated by Tang et al. (aggregation induced emission, AIE)^{10,11} and Park et al. (aggregation induced enhanced emission, AIEE).¹² Therefore the search for new molecular scaffolds and the understanding of the structure–property relationship is of prime importance to access a range of useful materials.

Chalcones are well-known dyes that have widely been used for decades^{13,14} because of their linear and nonlinear optical properties^{15–20} and their biological activity.^{21,22} However, their luminescence efficiency in solution is usually limited because of the excited-state dynamics that is governed by the occurrence of numerous rotamers, which quenches the photoluminescence by opening nonradiative deactivation pathways.^{23,24} It occurred to us that this property could represent a key feature to base the design of solids emitters involving either AIE or AIEE phenomena. Yet, little is known about the solid-state luminescence of chalcones. Moreover, the introduction of an electron-donating group conjugated with the carbonyl function of the aryl-propenone backbone results in a donor–acceptor structure that enables the expression of large Stokes shifts in solution and possibly in the solid as well. It is known that fluorophores exhibiting small Stokes shifts, such as BODIPYs, for example,^{25,26} undergo efficient reabsorption, which severely offset solid-state emission.

Recently, we reported on boron difluoride complexes of a series of ligands containing negatively charged oxygen donor atoms, such as 2'-hydroxychalcones,^{27,28} curcuminoids,²⁹ and 3-hydroxyflavone.³⁰ Especially the 2'-hydroxychalcone-based complexes were proven to be very effective as solid-state NIR fluorophores, which was attributed to a combination of effects including π -stacking interactions leading to red-shifted emission in the condensed phase with respect to solution state. In addition, we

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have shown recently that the ground-state dipole moment of those dyes is instrumental in determining the solid-state emission wavelength.³¹ While restriction of rotational motions was shown to be operative in those systems,³² the release of NIR emission mostly relied on the fact that boron difluoride complexes of 2'-hydroxychalcones contain the strong electron acceptor dioxaborine ring, favoring the occurrence of a large dipole moment both in the ground and excited states of the push–pull structure. In the course of that work, a pyrene-containing analogue was found to emit light at 755 nm with a fluorescence quantum yield (ϕ_f) value of 15.5% in thin film. This led us to investigate those chalcone derivatives in which the pyrene nucleus is introduced as electron donating unit at the A-side of the propenone skeleton. Here, we report on the synthesis of four related derivatives, compounds **1–4** (Chart 1) that differ by the nature of the B-ring. Phenyl and naphthyl units, and their methoxy-substituted counterparts were considered. We present a study of their photophysical properties in solution and in the solid-state.

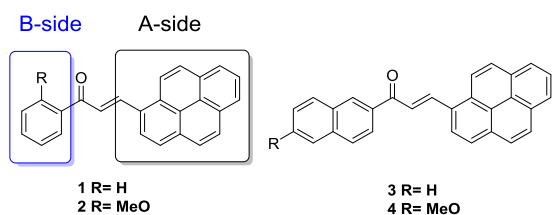


Chart 1. Molecular structures of the synthesized chalcones.

2. Results and discussion

Chalcone derivatives **1–4** were obtained simply by using a Claisen–Schmidt reaction between 1-pyrenecarboxaldehyde and the corresponding acetophenones/acetophenones in EtOH as the solvent and sodium hydroxide as a base (Chart S1). All dyes were recrystallized three times for ethanol, obtained as yellow-orange colored solids and characterized by using ^1H and ^{13}C spectroscopy and HRMS (see Supplementary data and Figs. S1–S4). Compound **1** was already reported in the literature and its X-ray structure determination was described.¹³ We could not obtain suitable single crystals of **2** for X-ray structure analyses, but fortunately evaporation of dichloromethane (DCM) in a mixture with ethyl acetate provided single crystals of **3**³³ and **4**³⁴ that were successfully subjected to X-ray diffraction. Detailed crystallographic parameters are included in Table S1. Figs. S5 and S6 show the molecular structure of **3** and **4**, respectively, with the displacement thermal ellipsoids drawn at the 50% probability level. While dye **3** (P_{bca} , $Z=8$) crystallizes in an orthorhombic system, compound **4** ($P2_1/c$, $Z=2$) crystallizes in a monoclinic crystal system similarly to **1** ($P2_1$, $Z=2$). Noticeably, the π -system of **1**, **3**, and **4** is not planar contrary to boron difluoride of 2'-hydroxychalcones.³¹ The angle between the pyrene unit and the B aromatic ring was measured to be 38.88° , 20.09° , and 9.59° for **1**, **3**, and **4**, respectively. Furthermore, it is important to notice that the experimental powder X-ray diffraction

pattern of the three molecules perfectly matches the one calculated from single X-ray diffraction data (Figs. S7–S9) therefore allowing a reliable comparison between photophysical properties of powders and single crystals.

The UV/visible electronic absorption and fluorescence emission spectra (Fig. 1) of compounds **1–4** were recorded in DCM and the spectroscopic data are collected in Table 1. The electronic absorption spectra of the dyes are similar, which indicates the weak influence of the phenyl or naphthyl B-ring on the ground-state properties. At low energy, a somehow structured band with a sharp peak at 400 nm and a broader one around 420 nm can be seen. The latter band can be attributed to a π – π^* transition with a charge transfer (CT) character that belongs to the push–pull chalcone π -system, while the one at 400 nm has likely a strong styryl-substituted pyrene character by analogy with literature data.^{35,36} The transitions at higher energy, around 300 nm, can also be attributed to the pyrene moiety. It can be noted that the absorption maxima are strongly blue-shifted relative to difluoride complexes of 2'-hydroxychalcone revealing a much less polar S_1 excited state in the pyrenyl-chalcones **1–4**.

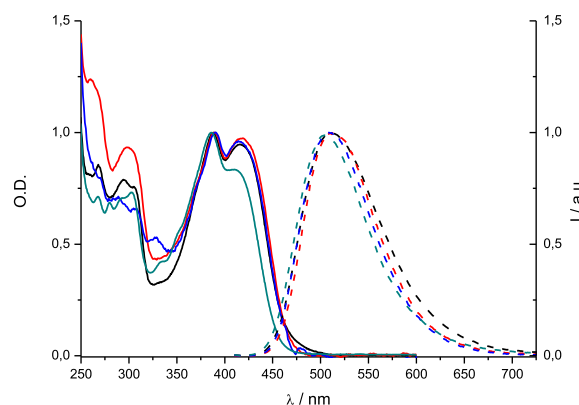


Fig. 1. UV/visible electronic absorption (solid line) and fluorescence emission (dotted line) spectra of compounds **1** (—), **2** (—), **3** (—), and **4** (—) in dichloromethane.

The four compounds were found to be fluorescent in DCM, but the fluorescence emission quantum yields are rather weak, ranging from 3% to 9% (Table 1). Such values associated with the low values of molar absorption coefficient give a rather low brightness for those dyes. The fluorescence lifetimes were found to be in the nanosecond time scale, which leads to an average value of $8.5 \times 10^7 \text{ s}^{-1}$ for the fluorescence radiative constants rate k_f . The non-radiative constant rates k_{nr} are about one order of magnitude higher than the k_f values, reflecting the dominant contribution of vibrational and rotational nonradiative deactivation of the lowest-energy excited singlet state, which is in accordance with the general trend noticed for chalcones.²³ Contrary to electronic absorption, fluorescence emission in DCM is affected by the nature of the B-ring. The ϕ_f values tend to be higher for the naphthyl analogues and smaller for the methoxy-substituted derivatives. The Stokes

Table 1
Photophysical properties of chalcone derivatives **1–4**^{a,b}

| Compound | Dichloromethane solution | | | | | | | | | | | Solid-state | |
|----------|----------------------------------|--|---------------------------------|-------------------------|----------|--------------------------|------------------|-----------------------------|---------------------------------------|---------------------------------|---------------------------------|-------------|--|
| | $\lambda^{\text{abs}}/\text{nm}$ | $\epsilon/\text{M}^{-1} \text{ cm}^{-1}$ | $\lambda^{\text{em}}/\text{nm}$ | $\Delta\nu_{\text{ST}}$ | ϕ_f | $\phi_f \times \epsilon$ | τ/ns | $k_f^b/10^7 \text{ s}^{-1}$ | $k_{\text{nr}}^b/10^7 \text{ s}^{-1}$ | $\sigma^{\text{TPA}}/\text{GM}$ | $\lambda^{\text{em}}/\text{nm}$ | ϕ_f | |
| 1 | 390 | 24,940 | 511 | 6072 | 0.07 | 1746 | 1.00 | 7.0 | 93.0 | 22 | 591 | 0.05 | |
| 2 | 390 | 26,045 | 493 | 5357 | 0.03 | 781 | <0.6 | — | — | 16 | 581 | 0.16 | |
| 3 | 390 | 27,110 | 511 | 6072 | 0.09 | 2440 | 0.90 | 10.0 | 101.0 | 20 | 561 | 0.08 | |
| 4 | 390 | 29,050 | 510 | 6033 | 0.08 | 2324 | 0.76 | 10.5 | 121.1 | 21 | 552 | 0.19 | |

^a The reaction was conducted in aerated conditions.

^b Radiative k_f (10^8 s^{-1}) and nonradiative $k_{\text{nr}}=(1 - \phi_f)/\tau_f$ (10^8 s^{-1}) rate constants.

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