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Unsymmetrical boron diketonates containing strong electron-donating groups as mechanochromic fluorescent solids

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Abstract: New π -conjugated unsymmetrical β -diketones were synthesized thanks to a modular synthetic approach involving *in situ* generated acylketenes through thermal degradation of 1,4-dioxin-2-ones. This method gave access to a family of new chromophores featuring either an indoline or a benzothiazole as electron-donating groups in one side and various aromatic moieties in the other side. After complexation with boron difluoride, BDK (Boron DiKetonates) compounds were obtained featuring fluorescence in non-polar solvents. These compounds were also found to be fluorescent in solid state with quantum yield up to 0.22, and their emission wavelength was very sensitive to their crystallinity. Two of these compounds were successfully recrystallized to provide small single crystals and emission spectra were recorded in crystal phase and ground state which showed mechanochromism with a spectral shift of 37 nm.

1. Introduction

β -diketones are ligands commonly used to stabilize metals which can also act as antenna for their photosensitization. Their complexation with boron species gives rise to boron diketonates (BDK) which find many applications as photoluminescent dyes¹ in the fields of photoactive materials and biological imaging.²⁻⁶ For example, they have been applied in optoelectronic materials such as OLEDs playing a role of emitters,⁷⁻⁹ as luminescent liquid crystals,¹⁰ as laser dyes,⁷ or as photoswitches.¹¹ Extended π -conjugated BDK can be used as two photon absorbing chromophores because complexation with boron makes diketones strong electron accepting groups suitable for the design of D- π -A or D- π -A- π -D dipolar or pseudo quadrupolar chromophores.¹²⁻¹⁸ Many BDK fluorophores can also stabilize their excited state as the triplet state thanks to efficient intersystem crossing. As such, when embedded within polymers they have been used as ratiometric room temperature oxygen sensors.¹⁹⁻²⁰ Indeed, in absence of oxygen they can exhibit both fluorescence and phosphorescence, this latter emission being inversely proportional to environmental oxygen concentration allowing to discriminate hypoxia in living tissues.

In many BDK application, the conformational restrictions play a crucial role, for example, such fluorophores have been applied in fluorescence imaging for the detection of Amyloid- β deposits;²¹ dimers of BDK compounds presented excimer emission,²² or inside polymer boron moieties can create

intermolecular bridges inducing modulation of their optical properties.²³ This phenomenon was also exploited in aggregation induced fluorescence.^{24,25} In addition, solid state luminescence studies showed that many BDK compounds present mechanochromic properties, their emission wavelength being correlated to their solid structure.^{26–37} BDK compounds, in solid state, were also applied for the detection of volatile amines because these latter can interact with difluoroboron moiety, lowering their acceptor character, leading to blue shifted emission and increase of fluorescence quantum yields.

38–40

The development of synthetic methods producing unsymmetrical β -diketone compounds can give access to push pull chromophores i.e. molecules featuring electron withdrawing and donating groups on either side of the diketo moiety. These compounds favor excited state intramolecular charge transfer ICT inducing a shift of absorption and emission toward the red part of the visible spectrum while keeping a relatively small size. This shift can be useful for adjusting the excited state energy level for lanthanide sensitization.⁴¹

Here unsymmetrical β -diketones were designed with on one side an aromatic ring functionalized with either an electron donating or a withdrawing group and on the other side either an indoline or a benzothiazole group, acting as electron-donating moieties. This assembly is a merocyanine, and as such, can either gives rise to push-pull or cyanine dyes behavior depending on the resonance form (Figure 1), the cyanine form is also referred in literature as dioxaborazine.^{42,43}

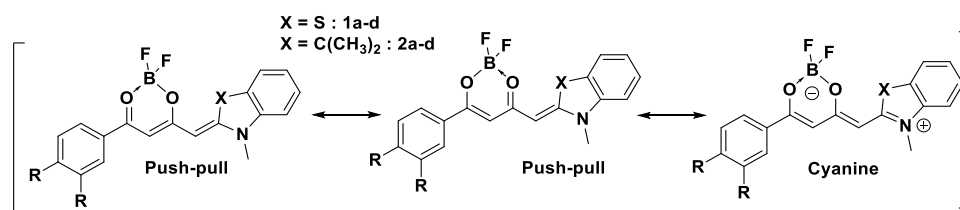


Figure 1. BDK compounds and resonance forms, equilibrium between push-pull and cyanine forms.

2. Experimental

2.1. Material and methods:

Microwave reactions were carried in a monovave 300 (Anton Paar). Column chromatography purifications were performed on silica gel (40–63 μ m). TLC (Thin-layer chromatography) analyses were carried out on Merck DC Kieselgel 60 F-254 aluminum sheets. The spots were visualized with UV lamps ($\lambda = 254$ nm and 360 nm). IR spectra were recorded with a universal ATR sampling accessory. ^1H and ^{13}C NMR spectra (C13APT or C13CPD experiments) were recorded on a Bruker 300 MHz spectrometer. Chemical shifts are expressed in parts per million (ppm) from the residual non-deuterated solvent signal contained in CDCl_3 ($\delta\text{H} = 7.26$, $\delta\text{C} = 77.16$), and in DMSO-d_6 ($\delta\text{H} = 2.50$, $\delta\text{C} = 39.52$). Multiplicities are described as s (singlet), d (doublet), t (triplet), brs (broad peak). Coupling constants, J values, are reported in Hz. High-resolution mass spectra (HRMS) were obtained using an orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer equipped with an electrospray source and in the positive and negative modes (ESI+/-). Absorption UV-visible spectra were recorded with a Cary 60 (Agilent) and fluorescence spectra with a Fluorolog3 (Horiba). Solution fluorescence measurements were carried with an optical density $\text{OD} < 0.1$. Solid spectra were measured with a GMP8 integrating sphere (General Microtechnology & Photonics).

2.2. Synthesis

Dioxinones **8 a-d** were synthesized following our reported procedure.^{44,45}

General protocol A: Diketone synthesis. In a 10 ml microwave tube flushed with argon, the corresponding dioxinone **8a-d** (1eq), diisopropylethylamine (2 eq) and 2,3-Dimethylbenzothiazolium iodide **5** or 1-Ethyl-2,3,3-trimethyl-3*H*-indolium iodide **6** (3 eq) were introduced followed by toluene and molecular sieve. The tube was sealed and heated 5 min at 50°C then 20 min at 120 °C under microwave irradiation. After cooling to room temperature, water was added and the mixture was extracted 3 times with dichloromethane the combined phases were then dried with MgSO₄ and concentrated under vacuum. The crude residue was then purified by flash chromatography on silica gel.

General protocol B: Boron difluoride complex formation. To a solution of diketone **3a-d** or **4a-d** (50 mg, 0.150 mmol, 1eq.) a solution of boron trifluoride diethyl etherate (40 μL, 0.3 mmol, 2 eq.) in 2 mL of chloroform was added, the mixture was then heated under reflux for 30 min. After cooling to room temperature, water was added and the mixture extracted three times with dichloromethane. The combined organic layers were then washed with a saturated solution of NaCl. The organic layer was dried with anhydrous MgSO₄, filtered and concentrated under vacuum. The product was purified by flash column chromatography to give **1a-d** or **2a-d**; characterization data for each compound is provided in the supplementary information.

2.3. Optical properties studies

Absorption spectra were recorded with a Cary 60 (Agilent) in 1 cm quartz cuvettes (4ml), using a baseline correction (optical density OD ≈ 1, c ≈ 10⁻⁵ M). Fluorescence was recorded with a Fluorolog 3 (Horiba) (PMT R13456) using a correction factor. Fluorescence measurements in solvents were carried out with 4 ml quartz cuvette, with optical density below 0.1 (c ≈ 10⁻⁶ M) in order to avoid inner filter effects. Relative fluorescence quantum yields in solutions were measured with coumarin 153 in ethanol as standard (QY = 0.53) (excitation wavelength 420 nm).⁴⁶ Time resolved spectroscopy was carried out with a 405 nm EPL LASER diode (Edinburgh) with a 200 ns repetition rate. Solid spectra were recorded with an integrating sphere GMP G8 (GMP), a correction curve was applied; in this sphere, small crystals or ground powders were introduced inside of quartz capillaries. The quantum yield is given by Equation 1.

Equation 1. Fluorescence quantum yield calculation in integrating sphere.

$$\varphi_c = \frac{f \left(F_c - F_s \left(\frac{L_c}{L_s} \right) \right)}{L_c - L_s}$$

To measure solid state fluorescence quantum yield, four spectra are required. Excitation wavelength is fixed at 430 nm. **L_c** and **L_s** are integrated signals of the lamp recorded between 420 nm and 440 nm in presence of a filter at the excitation side (five averaged measurements), **L_c** is the measure of the compound, while **L_s** is measured with an empty capillary. **f** is the attenuation factor of the filter at 430 nm. **F_c** is integral of the luminescence signal measured between 525 nm and 800 nm in presence of the compound in the capillary. **F_s** is measured in the same conditions with an empty capillary. In order

to take into account of the excitation filter effect due to the compound, F_s was multiplied by the fraction L_c/L_s . All signals are corrected with a correction curve.

Solid spectra $F(\lambda)$ are obtained by subtracting the blank signal of the sphere $B_s(\lambda)$ corrected with the filter effect of the compound (L_c/L_s). In order to get normalized results $F_n(\lambda)$ this signal was divided by the area under the curve and multiplied by the quantum yield ϕ_c . In Figure 5 the amplitude of the most fluorescent compounds was arbitrary fixed at 1.

Equation 2. Blank correction and normalization in order to get spectral curves representative of fluorescence quantum yields.

$$F(\lambda) = F_c(\lambda) - B_s(\lambda) \times \frac{L_c}{L_s} \quad F_n(\lambda) = \frac{F(\lambda)}{\int F(\lambda)} \phi_c$$

3. Results and discussion

3.1. Synthesis

Unsymmetrical β -diketones were synthesized by condensation of either an indolinium **5** or a benzothiazolium **6** on an acylketene (Figure 2) at the reflux of toluene and in presence of triethylamine. Indeed, acylketenes are highly electrophilic species that we already used in the synthesis of fluorophores or biologically active molecules; they can easily be generated by thermal fragmentation of dioxinones **8**.^{44,45,47} These dioxinones were chosen for their diversity, they contain electron-poor, electron-rich or neutral aromatic moieties (Ar). Moreover, furan diketones are very classical ligand in coordination chemistry, therefore it was interesting to introduce this heteroaromatic group in presence of more unusual electron donating moieties based on either an indoline or a benzothiazole.⁴⁸

For the clarity of the discussion, the two substituents on both sides of the diketo central core will be called "aromatic moiety" for substituents introduced via the dioxinone and "electron-donating moiety" for benzothiazole or indoline moieties.

Eight β -diketones **3a-d** and **4a-d** were obtained in good yields, ranging from 53 to 95%, they are in equilibrium with their corresponding keto-enol forms with a ratio depending mostly on the nature of the substituents on the aromatic moiety (Ar) and, to a lesser extent, on the electron-donating moiety (benzothiazole *versus* indoline).

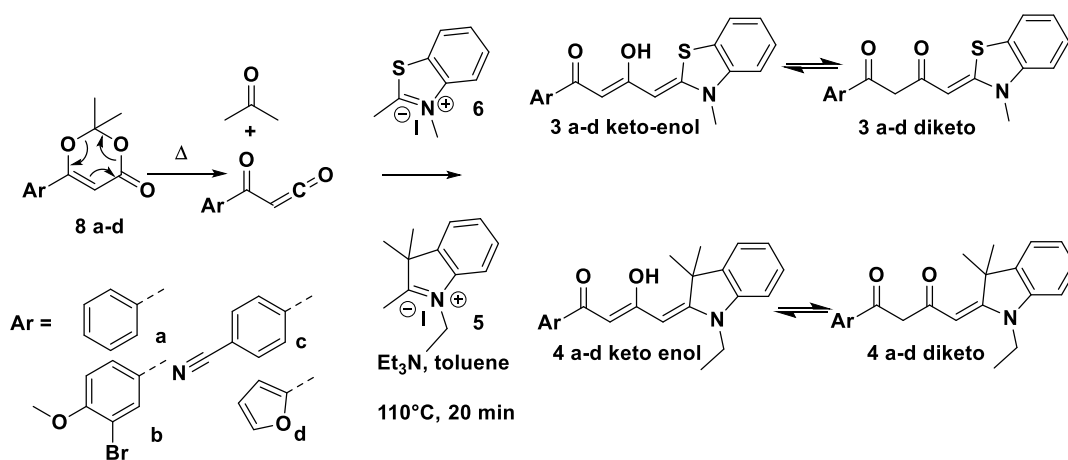


Figure 2. thermal degradation of dioxinone and trapping by indolinium or thiazolium nucleophile to generate diketones.

It should be noted that this synthetic route was already explored by Konovalova *et al.*; however, they only described the structure of the diketone adducts and did not further convert them to their corresponding boron diketonates, neither did they study their photophysical properties.⁴⁹

The ¹HNMR analysis of **3a-d** and **4a-d** showed the presence of two main tautomers (diketo and keto-enol) and traces of a third tautomer (other keto-enol).⁵⁰ The position of the carbonyl group in the major keto-enol tautomer was assigned using carbon-hydrogen NMR 2D experiments. The tautomeric equilibrium is affected by the nature of the aromatic moiety, the presence of an electron-withdrawing group stabilizing the keto enol form as in **3c** and **4c** (Table 1).

	Yield	Keto-enol	Diketone		Yield	Keto-enol	Diketone
3a	88%	63 %	37%	4a	95%	83%	15%
3b	90%	63%	37%	4b	53%	67%	33%
3c		x	x	4c	55% ^a	95%	5%
3d	58%	42%	58%	4d		x	x

Table 1. Reaction yield and tautomer equilibrium in CDCl₃ measured by ¹HNMR. ^a crude yields

Compounds **3 a-d** and **4 a-d** were then reacted with boron trifluoride diethyl etherate in chloroform to give the corresponding BDK final products **2 a-d**, **1 a-d** (Figure 3). After purification on silica gel column, the products were obtained as fluorescent powders. Samples of these powders were then recrystallized in dichloromethane (with diethyl ether vapors) to produce orange or red crystals.

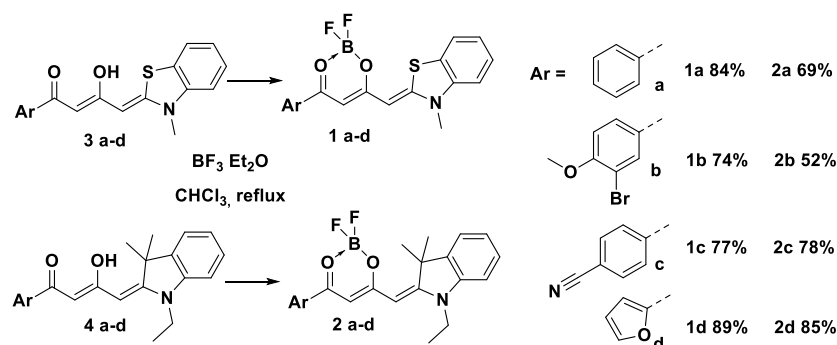


Figure 3. Borylation of diketones.

3.2. Optical properties in dilute solutions.

The optical properties of boron complexes **1a-d** and **2a-d** were studied in toluene and dichloromethane. In toluene, both compounds featured highly structured absorption and emission spectra with prominent vibronic substructures and small Stokes shifts; these two features are typical of local state emission, which is quite unexpected because of the strong electron donating character of the indoline moiety. In dichloromethane the vibronic structures were retained, the emission solvatochromism is low in the case of compounds **1a-d**, while the Stokes shifts increased in the case of compounds **2a-d**. In all molecules but **1c** and **2c**, the shapes of absorption and emission are very similar; the presence of a methoxy group on the aromatic moiety of **1b** and **2b** does not affect at all the spectra. However, introduction of an electron withdrawing nitrile group on the aromatic moiety of **1c** and **2c** leads to a small red shift in absorption and a larger red shift in emission and modifies the shape of their absorption spectra. Interestingly, the nature of the electron-donating moiety, either indoline of

benzothiazole, has no impact on absorption and emission spectra in toluene indicating that these two moieties have close electronic effect in this while in dichloromethane a small emission solvatochromism effect is observed for compounds **1a-d**.

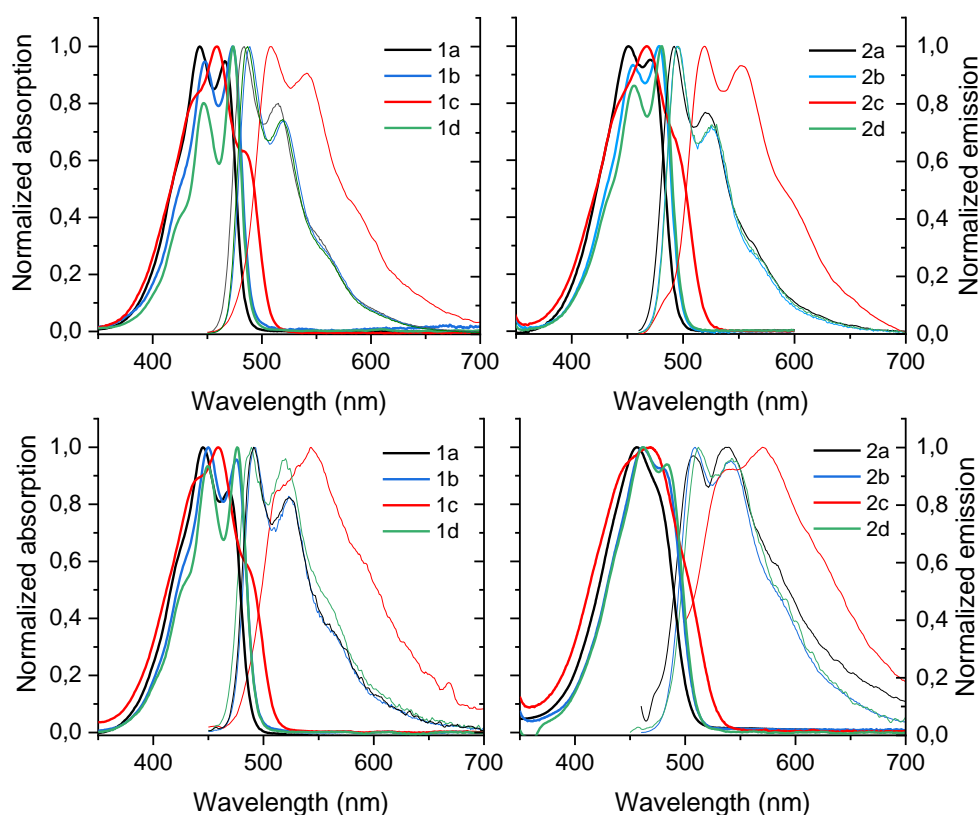


Figure 4. Absorption and emission of compounds **1 a-d** and **2 a-d** in toluene (top) and dichloromethane (bottom) ($\lambda_{exc} = 440$ nm).

The fluorescence quantum yields of compounds **1a-d** and **2a-d** were then measured in toluene and ranged from 0.03 to 0.90 (Table 2). Generally, molecules **2a-d** are more fluorescent than **1a-d**, but the fluorescence quantum yields depend most significantly on the nature of the substitution of the aromatic moiety, with highest quantum yields for molecule **1b** (0.68) and **2b** (0.90) substituted by a 3-bromo-4-methoxy phenyl group. On the contrary, the presence of a nitrile group in **1c** and **2c** leads to a strong fluorescence quenching (QY < 0.05) concomitantly with a red-shifted emission. To understand better this phenomenon, quantum yields were also measured in dichloromethane, in which this quenching effect was then observed for all compounds, dropping fluorescence quantum yields below 0.03. Polarity induced fluorescence quenching in BDK compounds was previously observed by Ma et al.⁵¹ Surprisingly, in compounds **1a-d** this phenomenon does not come along with a fluorescence red-shift as absorption and emission spectra in toluene and dichloromethane are perfectly superimposable; no significant solvatochromism was observed.

	$\Phi_F(\text{Tol})^a$	$\lambda_{abs}/\lambda_{em}^b$	ϵ^c	$\langle\tau_F\rangle^d$	k_F . 10^{-9}s^{-1c}	k_{nr} . 10^{-9}s^{-1c}	$\Phi_F(\text{DCM})^a$
1a	0.33	444/483	32000	0.86	0.38	0.78	0.01
1b	0.68	447/488	35000	0.79	0.86	0.41	0.03
1c	0.04	459/509	45000	x	x	x	<0.01
1d	0,24	473/487	42000	1.40	0.17	0.54	0.02
2a	0,62	450/492	52000	1.84	0.34	0.20	0,02

2b	0,90	479/495	60000	2.11	0.43	0.04	0,02
2c	0,03	466/519	49000	x	x	x	<0.01
2d	0,70	480/495	48000	1.97	0.36	0.12	<0.01

Table 2. Optical properties in solution. a. ϕ_F were measured at 420 nm using coumarine 153 in ethanol as reference ($\phi_F = 0.53$).⁴⁶ b. λ given in nm, c. molar extinction ($L \cdot mol^{-1} \cdot cm^{-1}$), d. average lifetime in toluene in ns, the fluorescence lifetime of **1c** and **2c** were too short (below 0.3 ns).

The fluorescence lifetimes were measured in toluene (Table 2) and are generally quite short, even for strongly fluorescent compound **2b** (2,1 ns, $\phi_F = 0.90$). For weakly fluorescent molecules **1c** and **2c** the fluorescence lifetimes were too short (below 300 ps) to be measured with our TCSPC setup which is totally in accordance with their low fluorescence quantum yields. The calculated k_F are almost constant, ranging from $0,17 \cdot 10^9 s^{-1}$ to $0,43 \cdot 10^9 s^{-1}$. On the other hand, k_{nr} is strongly varying and the fluorescence quantum yields are closely correlated to the amount of non-radiative pathways. In dichloromethane, in which the dyes are poorly fluorescent, the fluorescence lifetimes were also very short (below 300 ps) for all compounds. Transferring the dyes from toluene to more polar dichloromethane enhances non-radiative de-excitation pathways without inducing any solvatochromism. Such behavior might be related to intersystem system crossing (ISC) efficiency, as some BDK compounds de-excite through this process, and also because ISC efficiency depends strongly on interactions with solvent. To investigate the formation of a triplet state, the luminescence of singlet of singlet oxygen was measured at 1270 nm but no signal was detected in both solvents for all compounds. This indicates that the fluorescence quenching occurs through another process such as electron transfer; this may happen through twisting at the excited state, which can break π -conjugation at the level of the BDK bridge. This is corroborated by the fact that the indoline or benzothiazole moieties act as electron-donors, while the aromatic moiety acts as electron acceptor. Indeed, for the more electron poor the aromatic moiety (**1c** or **2c**) the quenching is the strongest. In addition, dichloromethane stabilizes separated charge states generated by electron transfers; explaining the strong quenching observed in dichloromethane.

3.3. Optical properties in solid ground powder.

The fluorescence of solid BDK compounds was measured using an integrating sphere. The results obtained with the product isolated directly from the synthesis were not consistent, they varied strongly from batch to batch as some were obtained as fine powder and other as polycrystalline mixture. Indeed, the luminescence of solid BDK compounds have been reported to be strongly dependent on their crystalline phase.^{26,52} In order to solve this problem these samples were finely ground before measurements presented in (Figure 5), this treatment allowed to get reproducible results. The emission of ground powders of compounds **1a-d** ranged from 575 to 650 nm and those of **2a-d** from 575 to 610 nm. Compounds **1d** and **2d** were poorly emissive (Table 4). Two distinct behaviors were observed, **2b** and **2c** and in less extend **2a** and **1c** present narrow band and a shoulder in the red side of their spectra by comparison to the others. This spectral shape is representative of a cyanine character. As expected **2c** is more red-shifted than **2b** due to the presence of an electron withdrawing group. However, this trend is not found in molecules **1b** and **1c** as, surprisingly, **1b** is more red-shifted, this emphasizes that both molecule are certainly not in the same crystalline phase. In order to investigate this issue, the products were then recrystallized.

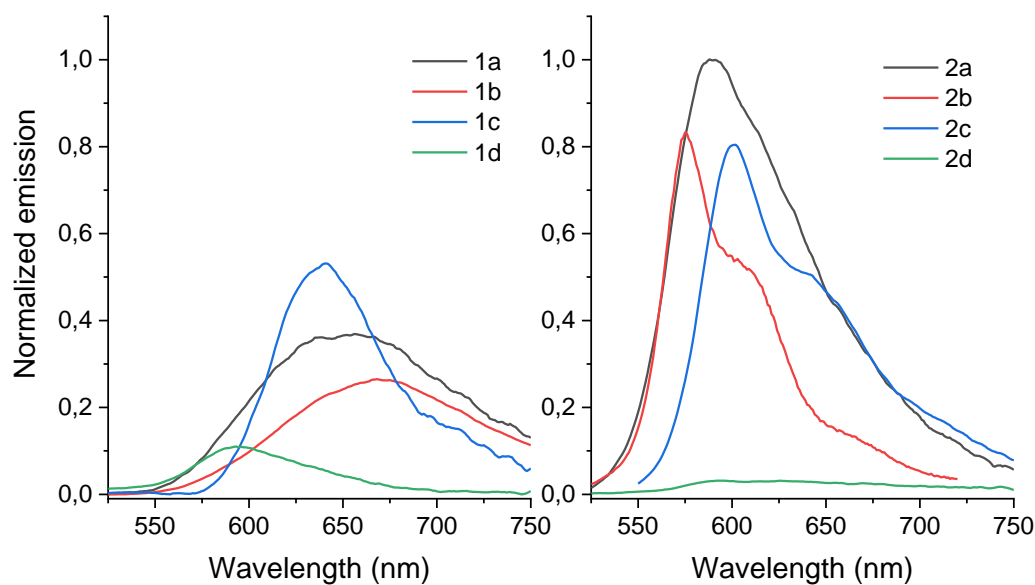


Figure 5. Normalized spectra of compounds 1a-d and 2a-d (ground powders). The area under the curves is proportional to their fluorescence quantum yield.

3.4. Crystal structures of 2b and 2c and mechanochromism.

The products were then recrystallized by slow diffusion of diethyl ether in concentrated dichloromethane solutions. This method enabled red single crystals to be obtained for compounds **2b** (CCDC2181345), **4b** (CCDC2181374) and **2c** (CCDC2181383) only. Their structure was analyzed by X-Ray diffraction.

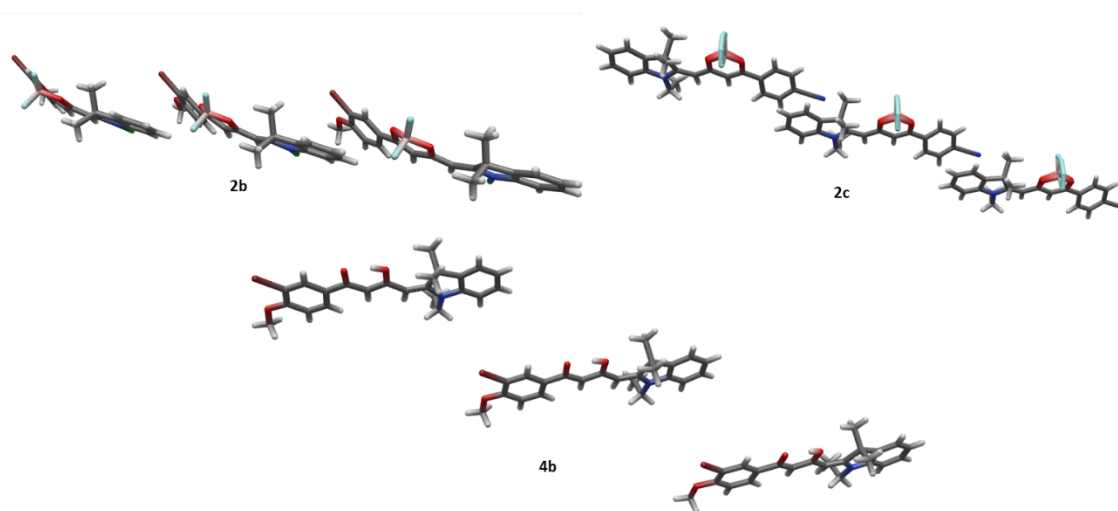
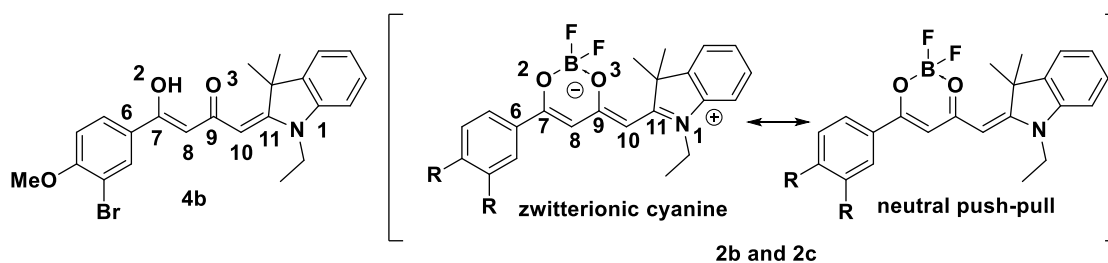


Figure 6. Crystalline structure of 2b, 2c and 4b.

Crystalline structures of **2b**, **2c** and **4b** show colinear arrangement where indoline moieties interact with the aromatic sides of neighbor molecules (Figure 6). In **2b** the position of the ethyl chain of the

indoline is disordered. While the structure of molecule **2c** and **4b** are very flat, there is a torsion in **2b** due to the repulsion between the large bromine atom of one molecule and the *gem*-dimethyl moiety of another. This repulsion is not observed in **4b** because molecules are more shifted from each other and the bromine atom interacts with the benzene part of the closest indoline groups. The bond lengths were studied to understand better the optical properties of the crystals (Table 3). The crystallographic structure of **4b** reveals that the equilibrium of the diketone moiety leans toward the keto-enol form where the carbonyl bond is localized between carbon C(9) and oxygen O(3). Atom-to-atom distances in compounds **2b** and **2c** are very similar and can be treated together as they follow exactly the same trends. The bond lengths between oxygen and carbon atoms O(2)-C(7) and O(3)-C(9) are of the same order (1.318 ± 0.016 Å) and are both longer than expected for carbonyl function; they both feature an enolate character. Bonds between carbons C(6)-C(7) and C(8)-C(9) are clearly single bonds while C(7)-C(8) and C(9)-C(10) feature double bond character. More interestingly, the bond C(10)-C(11) is quite short (1.381 ± 0.002 Å) and is of the same length than C(9)-C(10) bond. This suggests that there is an equilibrium between a zwitterionic cyanine and a push-pull form. The carbon nitrogen bond C(11) - N(1) is also quite short which is compatible with this hypothesis.



	C(6)-C(7)	C(7)-C(8)	C(8)-C(9)	C(9)-C(10)	C(10)-C(11)	O(2)-C(7)	O(3)-C(9)	C(11)-N(1)
2b	1.464	1.342	1.421	1.391	1.383	1.334	1.317	1.327
4b	1.490	1.377	1.416	1.430	1.366	1.300	1.284	1.374
2c	1.469	1.349	1.410	1.387	1.379	1.323	1.303	1.345

Table 3. Tautomer form in observed in crystal, and bond lengths (Å).

Then, the fluorescence of crystals of **2b** and **2c** was measured using an integrating sphere and their fluorescences were also measured after meticulous grinding in fine powder. Under UV-lamp, breaking the crystal structure leads to an obvious color change for **2b**, while this effect is not visible to the eyes with **2c** (Figure 7). However, the spectral change is very noticeable (Figure 7); the spectra of both compounds featured a red shifted emission in crystal state by comparison with powder with a maximum of 612 nm for **2b** in crystal state vs 575 nm in powder ($\Delta\lambda = 37$ nm) and a maximum of 637 nm for **2c** in crystal vs 600 nm in powder ($\Delta\lambda = 37$ nm). In crystal form, the emission is broader with no vibronic sub-structure. Their spectral shapes in powder were more structured with a distinct shoulder in the red side as commonly observed with cyanine compounds. This cyanine character was previously observed in solution but the emission wavelength is higher by 75 nm in powder than in solution. No reversibility could be observed after grinding, the optical properties of the ground powders **2b** and **2c** remains stable after ageing or warming and cooling process.

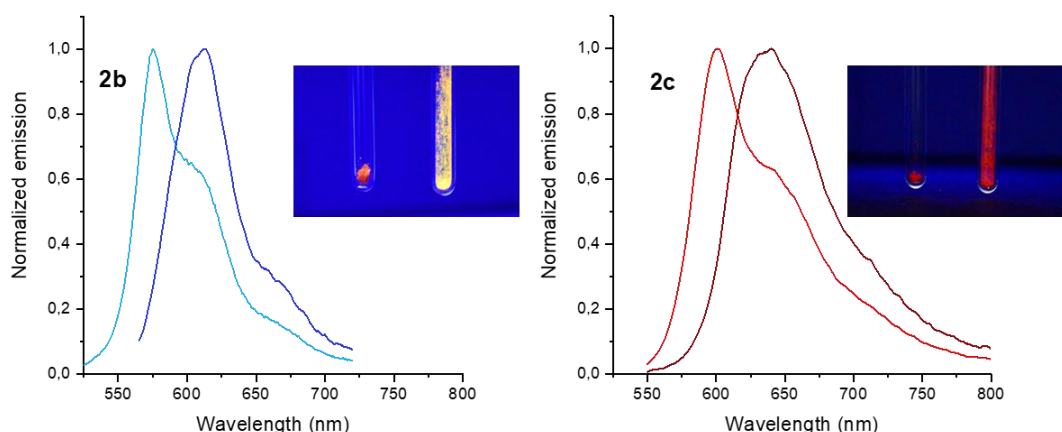


Figure 7. Left : emission of **2b** single crystals (dark blue) and ground crystal (light blue). Right : emission of **2c** crystals (dark red) and ground crystals (light red). On the photos the capillaries show crystal before (left) and after grinding (right).

The quantum yields of both powders and crystals were measured (Table 4), the values for powders were obtained after fine grinding of the solid. Generally, compounds **2a-c** featuring indoline were more luminescent than their benzothiazole counterparts **1a-c**. The presence of the nitrile function in **1c** and **2c** does not result in emission quenching; this support our previous hypothesis of a quenching effect caused by twisting in solution when the aromatic moiety of BDK is electron deficient. The absence of any substituents on the phenyl group in **1a** and **2a** enhances the fluorescence quantum yields. In the case of **2b** and **2c** the fluorescence quantum of crystals and powders are very similar. Surprisingly the fluorescence of **1d** and **2d** remained low in solid state.

	1a	1b	1c	1d	2a	2b	2c	2d
Powder	0.15	0.07	0.10	0.02	0.22	0.12	0.16	0.01
Crystals	-	-	-	-	-	0.13	0.10	-

Table 4. Absolute solid state fluorescence quantum yields measured by integrating sphere.

4. Conclusion

New β -diketone compounds were synthesized through an uncommon reaction pathway relying on the capture of an “*in situ*” generated acylketene. This highly electrophilic intermediate is generated via thermal degradation of 1,3-dioxin-4-one and efficiently reacts with nucleophilic indolium or benzothiazolium. Using this method, a library of eight unsymmetrical β -diketones was obtained using four 1,3-dioxin-4-one decorated with either electron neutral, withdrawing or donating groups. The nature of this substituent affects the keno-enol equilibrium, especially the electron withdrawing nitrile group in **2c** shifts the tautomer equilibrium toward the keto-enol form. Complexation of these molecules with boron trifluoride, provided BDK compounds which showed fluorescence only in non-polar solvents in absence of electron withdrawing groups in the aromatic side. The shape of their absorption and emission spectra and their low solvatochromism demonstrated that they behave as cyanines. Noteworthy, the majority of these molecules proved to be fluorescent in solid state, in particular **2a** showed a high quantum yield in ground powder ($\phi_f = 0,22$). Two of these molecules, **2b** and **2c** were successfully recrystallized to provide single crystals. The comparison of their optical properties in crystal state and powder demonstrated that they feature promising mechanochromism with $\Delta\lambda = 37$ nm, and fluorescence quantum yield in both crystal and ground crystal state comprised between 0,10 and 0,16. Further work is ongoing to optimize these molecules in order to make them

easier to crystallize, or to make them suitable for mechanochromism in thin film by modulation of the size of their side alkyl chains.

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- (1) Nagai, A.; Kokado, K.; Nagata, Y.; Arita, M.; Chujo, Y. Highly Intense Fluorescent Diarylboron Diketonate. *J. Org. Chem.* **2008**, *73* (21), 8605–8607. <https://doi.org/10.1021/jo8017582>.
- (2) Tanaka, K.; Chujo, Y. Recent Progress of Optical Functional Nanomaterials Based on Organoboron Complexes with β -Diketonate, Ketoiminate and Diiminate. *NPG Asia Mater.* **2015**, *7* (11), e223–e223. <https://doi.org/10.1038/am.2015.118>.
- (3) Chen, P.-Z.; Niu, L.-Y.; Chen, Y.-Z.; Yang, Q.-Z. Difluoroboron β -Diketonate Dyes: Spectroscopic Properties and Applications. *Coord. Chem. Rev.* **2017**, *350*, 196–216. <https://doi.org/10.1016/j.ccr.2017.06.026>.
- (4) Chandrasekar Murali, A.; Nayak, P.; Venkatasubbaiah, K. Recent Advances in the Synthesis of Luminescent Tetra-Coordinated Boron Compounds. *Dalton Trans.* **2022**, *51* (15), 5751–5771. <https://doi.org/10.1039/D2DT00160H>.
- (5) Collot, M. Recent Advances in Dioxaborine-Based Fluorescent Materials for Bioimaging Applications. *Mater. Horiz.* **2021**, *8* (2), 501–514. <https://doi.org/10.1039/D0MH01186J>.
- (6) Gerasov, A.; Shandura, M.; Kovtun, Y.; Losytskyy, M.; Negrutskya, V.; Dubey, I. Fluorescent Labeling of Proteins with Amine-Specific 1,3,2-(2H)-Dioxaborine Polymethine Dye. *Anal. Biochem.* **2012**, *420* (2), 115–120. <https://doi.org/10.1016/j.ab.2011.09.018>.
- (7) D'Aléo, A.; H. Sazzad, M.; H. Kim, D.; Y. Choi, E.; W. Wu, J.; Canard, G.; Fages, F.; Ribierre, J.-C.; Adachi, C. Boron Difluoride Hemicurcuminoid as an Efficient Far Red to Near-Infrared Emitter: Toward OLEDs and Laser Dyes. *Chem. Commun.* **2017**, *53* (52), 7003–7006. <https://doi.org/10.1039/C7CC01786C>.
- (8) Kim, D.-H.; D'Aléo, A.; Chen, X.-K.; Sandanayaka, A. D. S.; Yao, D.; Zhao, L.; Komino, T.; Zaborova, E.; Canard, G.; Tsuchiya, Y.; Choi, E.; Wu, J. W.; Fages, F.; Brédas, J.-L.; Ribierre, J.-C.; Adachi, C. High-Efficiency Electroluminescence and Amplified Spontaneous Emission from a Thermally Activated Delayed Fluorescent near-Infrared Emitter. *Nat. Photonics* **2018**, *12* (2), 98–104. <https://doi.org/10.1038/s41566-017-0087-y>.
- (9) D'Aléo, A.; Felouat, A.; Fages, F. Boron Difluoride Complexes of 2-Hydroxychalcones and Curcuminoids as Fluorescent Dyes for Photonic Applications. *Adv. Nat. Sci. Nanosci. Nanotechnol.* **2014**, *6* (1), 015009. <https://doi.org/10.1088/2043-6262/6/1/015009>.
- (10) Sánchez, I.; José Mayoral, M.; Ovejero, P.; Antonio Campo, J.; Vicente Heras, J.; Cano, M.; Lodeiro, C. Luminescent Liquid Crystal Materials Based on Unsymmetrical Boron Difluoride β -Diketonate Adducts. *New J. Chem.* **2010**, *34* (12), 2937–2942. <https://doi.org/10.1039/C0NJ00503G>.

- (11) Li, Z.; Dai, Y.; Lu, Z.; Pei, Y.; Chen, H.; Zhang, L.; Duan, Y.; Guo, H. Efficient Green Light-Excited Switches Based on Dithienylethenes with BF₂-Doped π -Conjugated Systems. *Chem. Commun.* **2019**, 55 (89), 13430–13433. <https://doi.org/10.1039/C9CC06838D>.
- (12) Cogné-Laage, E.; Allemand, J.-F.; Ruel, O.; Baudin, J.-B.; Croquette, V.; Blanchard-Desce, M.; Jullien, L. Diaroyl(Methanato)Boron Difluoride Compounds as Medium-Sensitive Two-Photon Fluorescent Probes. *Chem. – Eur. J.* **2004**, 10 (6), 1445–1455. <https://doi.org/10.1002/chem.200305321>.
- (13) Kamada, K.; Namikawa, T.; Senatore, S.; Matthews, C.; Lenne, P.-F.; Maury, O.; Andraud, C.; Ponce-Vargas, M.; Le Guennic, B.; Jacquemin, D.; Agbo, P.; An, D. D.; Gauny, S. S.; Liu, X.; Abergel, R. J.; Fages, F.; D'Aléo, A. Boron Difluoride Curcuminoid Fluorophores with Enhanced Two-Photon Excited Fluorescence Emission and Versatile Living-Cell Imaging Properties. *Chem. – Eur. J.* **2016**, 22 (15), 5219–5232. <https://doi.org/10.1002/chem.201504903>.
- (14) Kim, E.; Felouat, A.; Zaborova, E.; Ribierre, J.-C.; Wu, J. W.; Senatore, S.; Matthews, C.; Lenne, P.-F.; Baffert, C.; Karapetyan, A.; Giorgi, M.; Jacquemin, D.; Ponce-Vargas, M.; Guennic, B. L.; Fages, F.; D'Aléo, A. Borondifluoride Complexes of Hemicurcuminoids as Bio-Inspired Push–Pull Dyes for Bioimaging. *Org. Biomol. Chem.* **2016**, 14 (4), 1311–1324. <https://doi.org/10.1039/C5OB02295A>.
- (15) D'Aléo, A.; Felouat, A.; Heresanu, V.; Ranguis, A.; Chaudanson, D.; Karapetyan, A.; Giorgi, M.; Fages, F. Two-Photon Excited Fluorescence of BF₂ Complexes of Curcumin Analogues: Toward NIR-to-NIR Fluorescent Organic Nanoparticles. *J. Mater. Chem. C* **2014**, 2 (26), 5208–5215. <https://doi.org/10.1039/C4TC00543K>.
- (16) Halik, M.; Wenseleers, W.; Grasso, C.; Stellacci, F.; Zojer, E.; Barlow, S.; Brédas, J.-L.; Perry, J. W.; Marder, S. R. Bis(Dioxaborine) Compounds with Large Two-Photon Cross Sections, and Their Use in the Photodeposition of Silver. *Chem. Commun.* **2003**, No. 13, 1490–1491. <https://doi.org/10.1039/B303135G>.
- (17) Lanoë, P.-H.; Mettra, B.; Liao, Y. Y.; Calin, N.; D'Aléo, A.; Namikawa, T.; Kamada, K.; Fages, F.; Monnereau, C.; Andraud, C. Theoretical and Experimental Study on Boron β -Diketonate Complexes with Intense Two-Photon-Induced Fluorescence in Solution and in the Solid State. *ChemPhysChem* **2016**, 17 (14), 2128–2136. <https://doi.org/10.1002/cphc.201600178>.
- (18) Ju, C.; Zhou, Y.; Semin, S.; Yang, G.; Tinnemans, P.; Duan, Y.; Feng, Y.; Rasing, T.; Xu, J. Solvent Dependent Linear and Nonlinear Optical Properties of Triphenylamine Unit Incorporated Difluoroboron β -Diketonate Complexes. *Dyes Pigments* **2019**, 162, 776–785. <https://doi.org/10.1016/j.dyepig.2018.11.002>.
- (19) Zhang, G.; Chen, J.; Payne, S. J.; Kooi, S. E.; Demas, J. N.; Fraser, C. L. Multi-Emissive Difluoroboron Dibenzoylmethane Polylactide Exhibiting Intense Fluorescence and Oxygen-Sensitive Room-Temperature Phosphorescence. *J. Am. Chem. Soc.* **2007**, 129 (29), 8942–8943. <https://doi.org/10.1021/ja0720255>.
- (20) Zhang, G.; Palmer, G. M.; Dewhirst, M. W.; Fraser, C. L. A Dual-Emissive-Materials Design Concept Enables Tumour Hypoxia Imaging. *Nat. Mater.* **2009**, 8 (9), 747–751. <https://doi.org/10.1038/nmat2509>.
- (21) Ran, C.; Xu, X.; Raymond, S. B.; Ferrara, B. J.; Neal, K.; Bacskai, B. J.; Medarova, Z.; Moore, A. Design, Synthesis, and Testing of Difluoroboron-Derivatized Curcumins as Near-Infrared Probes for in Vivo Detection of Amyloid- β Deposits. *J. Am. Chem. Soc.* **2009**, 131 (42), 15257–15261. <https://doi.org/10.1021/ja9047043>.
- (22) Catherin, M.; Uranga-Barandiaran, O.; Brosseau, A.; Métivier, R.; Canard, G.; D'Aléo, A.; Casanova, D.; Castet, F.; Zaborova, E.; Fages, F. Exciton Interactions, Excimer Formation, and $[2\pi+2\pi]$ Photodimerization in Nonconjugated Curcuminoid-BF₂ Dimers. *Chem. – Eur. J.* **2020**, 26 (17), 3818–3828. <https://doi.org/10.1002/chem.201905122>.
- (23) Tanaka, K.; Chujo, Y. Modulation of the Solid-State Luminescent Properties of Conjugated Polymers by Changing the Connecting Points of Flexible Boron Element Blocks. *Polym. J.* **2020**, 52 (6), 555–566. <https://doi.org/10.1038/s41428-020-0316-y>.

- (24) Wang, L.; Zhang, Z.; Cheng, X.; Ye, K.; Li, F.; Wang, Y.; Zhang, H. Red Emissive Diarylboron Diketonate Crystals: Aggregation-Induced Color Change and Amplified Spontaneous Emission. *J. Mater. Chem. C* **2015**, *3* (3), 499–505. <https://doi.org/10.1039/C4TC02070G>.
- (25) Mirochnik, A. G.; Fedorenko, E. V.; Karasev, V. E. Size-Dependent Luminescence of Boron Difluoride β -Diketonates. *Russ. Chem. Bull.* **2008**, *57* (6), 1190–1193. <https://doi.org/10.1007/s11172-008-0149-x>.
- (26) Louis, M.; Brosseau, A.; Guillot, R.; Ito, F.; Allain, C.; Métivier, R. Polymorphism, Mechanofluorochromism, and Photophysical Characterization of a Carbonyl Substituted Difluoroboron- β -Diketone Derivative. *J. Phys. Chem. C* **2017**, *121* (29), 15897–15907. <https://doi.org/10.1021/acs.jpcc.7b01901>.
- (27) Mechanofluorochromism of NIR-Emitting Dyes Based on Difluoroboron β -Carbonyl Cyclic Ketonate Complexes. *Dyes Pigments* **2018**, *156*, 140–148. <https://doi.org/10.1016/j.dyepig.2018.03.069>.
- (28) Louis, M.; Guillot, R.; Métivier, R.; Allain, C. β -Diketone Derivatives: Influence of the Chelating Group on the Photophysical and Mechanofluorochromic Properties. *Photochem. Photobiol. Sci.* **2018**, *17* (6), 822–828. <https://doi.org/10.1039/C8PP00070K>.
- (29) Liu, T.; D. Chien, A.; Lu, J.; Zhang, G.; L. Fraser, C. Arene Effects on Difluoroboron β -Diketonate Mechanochromic Luminescence. *J. Mater. Chem.* **2011**, *21* (23), 8401–8408. <https://doi.org/10.1039/C0JM04326E>.
- (30) Li, M.; Han, Y.; Zhang, Z.; He, X.; Chen, Y. The Effect of Substituent Number on Mechanochromic Luminescence of β -Diketones and the Corresponding Boron Complexes. *Dyes Pigments* **2019**, *166*, 159–167. <https://doi.org/10.1016/j.dyepig.2019.03.022>.
- (31) Liu, Z.; Jiang, Z.; Xu, C.; Chen, B.; Zhu, G. Fluorenyl-Difluoroboron- β -Diketonates with Multi-Stimuli Fluorescent Response Behavior and Their Applications in a Thermochromic Logic Gate Device. *Dyes Pigments* **2021**, *186*, 108990. <https://doi.org/10.1016/j.dyepig.2020.108990>.
- (32) Liu, W.; Wang, Y.; Yang, J.; Li, X.; Wang, X.; Ma, L. The Abnormal Solvatochromism, High-Contrast Mechanochromism and Internal Mechanism of Two AIEE-Active β -Diketones. *Dyes Pigments* **2020**, *175*, 108149. <https://doi.org/10.1016/j.dyepig.2019.108149>.
- (33) Saotome, S.; Suenaga, K.; Tanaka, K.; Chujo, Y. Design for Multi-Step Mechanochromic Luminescence Property by Enhancement of Environmental Sensitivity in a Solid-State Emissive Boron Complex. *Mater. Chem. Front.* **2020**, *4* (6), 1781–1788. <https://doi.org/10.1039/C9QM00719A>.
- (34) Guieu, S.; Pinto, J.; Silva, V. L. M.; Rocha, J.; Silva, A. M. S. Synthesis, Post-Modification and Fluorescence Properties of Boron Diketonate Complexes. *Eur. J. Org. Chem.* **2015**, *2015* (16), 3423–3426. <https://doi.org/10.1002/ejoc.201500318>.
- (35) Wang, L.; Wang, K.; Zou, B.; Ye, K.; Zhang, H.; Wang, Y. Luminescent Chromism of Boron Diketonate Crystals: Distinct Responses to Different Stresses. *Adv. Mater.* **2015**, *27* (18), 2918–2922. <https://doi.org/10.1002/adma.201500589>.
- (36) Poggi, B.; Bodelot, L.; Louis, M.; Métivier, R.; Allain, C. Quantification of Mechanofluorochromism at the Macroscale via Colorimetric Analysis of Controlled Mechanical Stimulation. *J. Mater. Chem. C* **2021**, *9* (36), 12111–12117. <https://doi.org/10.1039/D1TC02274A>.
- (37) Zhai, L.; Sun, M.; Liu, M.; Shu, Y.; Sun, J.; Zhang, F.; Zhao, J.; Lu, R. β -Diketone Difluoroboron Complexes-Based Luminescent π -Gels and Mechanofluorochromic Dyes with Low-Lying Excited States. *Dyes Pigments* **2019**, *160*, 467–475. <https://doi.org/10.1016/j.dyepig.2018.08.025>.
- (38) Zhai, L.; Liu, M.; Xue, P.; Sun, J.; Gong, P.; Zhang, Z.; Sun, J.; Lu, R. Nanofibers Generated from Nonclassical Organogelators Based on Difluoroboron β -Diketonate Complexes to Detect Aliphatic Primary Amine Vapors. *J. Mater. Chem. C* **2016**, *4* (34), 7939–7947. <https://doi.org/10.1039/C6TC01790H>.

- (39) Zhang, X.; Liu, X.; Lu, R.; Zhang, H.; Gong, P. Fast Detection of Organic Amine Vapors Based on Fluorescent Nanofibrils Fabricated from Triphenylamine Functionalized β -Diketone-Boron Difluoride. *J. Mater. Chem.* **2011**, *22* (3), 1167–1172. <https://doi.org/10.1039/C1JM14187B>.
- (40) Liu, X.; Zhang, X.; Lu, R.; Xue, P.; Xu, D.; Zhou, H. Low-Dimensional Nanostructures Fabricated from Bis(Dioxaborine)Carbazole Derivatives as Fluorescent Chemosensors for Detecting Organic Amine Vapors. *J. Mater. Chem.* **2011**, *21* (24), 8756–8765. <https://doi.org/10.1039/C0JM04274A>.
- (41) Seob Baek, N.; Hee Kim, Y.; Kyung Eom, Y.; Hwan Oh, J.; Kyu Kim, H.; Aebischer, A.; Gumy, F.; Chauvin, A.-S.; G. Bünzli, J.-C. Sensitized Near-IR Luminescence of Lanthanide Complexes Based on Push-Pull Diketone Derivatives. *Dalton Trans.* **2010**, *39* (6), 1532–1538. <https://doi.org/10.1039/B915893F>.
- (42) Polishchuk, V.; Stanko, M.; Kulinich, A.; Shandura, M. D- π -A- π -D Dyes with a 1,3,2-Dioxaborine Cycle in the Polymethine Chain: Efficient Long-Wavelength Fluorophores. *Eur. J. Org. Chem.* **2018**, *2018* (2), 240–246. <https://doi.org/10.1002/ejoc.201701466>.
- (43) Choi, K.-R.; Kim, D. H.; Lee, Y. U.; Placide, V.; Huynh, S.; Yao, D.; Canard, G.; Zaborova, E.; Mathevet, F.; Mager, L.; Heinrich, B.; Ribierre, J.-C.; Wu, J. W.; Fages, F.; D'Aléo, A. Effect of the Electron Donating Group on the Excited-State Electronic Nature and Epsilon-near-Zero Properties of Curcuminoid-Borondifluoride Dyes. *RSC Adv.* **2021**, *11* (60), 38247–38257. <https://doi.org/10.1039/D1RA08025C>.
- (44) Peixoto, P. A.; Boulangé, A.; Leleu, S.; Franck, X. Versatile Synthesis of Acylfuranones by Reaction of Acylketenes with α -Hydroxy Ketones: Application to the One-Step Multicomponent Synthesis of Cadiolide B and Its Analogues. *Eur. J. Org. Chem.* **2013**, *2013* (16), 3316–3327. <https://doi.org/10.1002/ejoc.201300166>.
- (45) Boulangé, A.; Parraga, J.; Galán, A.; Cabedo, N.; Leleu, S.; Sanz, M. J.; Cortes, D.; Franck, X. Synthesis and Antibacterial Activities of Cadiolides A, B and C and Analogues. *Bioorg. Med. Chem.* **2015**, *23* (13), 3618–3628. <https://doi.org/10.1016/j.bmc.2015.04.010>.
- (46) Rurack, K.; Spieles, M. Fluorescence Quantum Yields of a Series of Red and Near-Infrared Dyes Emitting at 600–1000 Nm. *Anal. Chem.* **2011**, *83* (4), 1232–1242. <https://doi.org/10.1021/ac101329h>.
- (47) Boulangé, A.; Peixoto, P. A.; Franck, X. Diastereoselective IBX Oxidative Dearomatization of Phenols by Remote Induction: Towards the Epicocconone Core Framework. *Chem. – Eur. J.* **2011**, *17* (37), 10241–10245. <https://doi.org/10.1002/chem.201101681>.
- (48) Zhang, H.; Liu, C. Synthesis and Properties of Furan/Thiophene Substituted Difluoroboron β -Diketonate Derivatives Bearing a Triphenylamine Moiety. *Dyes Pigments* **2017**, *143*, 143–150. <https://doi.org/10.1016/j.dyepig.2017.04.022>.
- (49) Konovalova, V. V.; Shklyayev, Yu. V.; Slepukhin, P. A.; Maslivets, A. N. Five-Membered 2,3-Dioxo Heterocycles: LXXVIII. Acylation of Fischer's Base with Aroylketenes. Crystalline and Molecular Structure of (1E, 3Z)-4-(4-Chlorophenyl)-4-Hydroxy-1-(1,3,3-Trimethyl-2,3-Dihydro-1H-Indol-2-Ylidene)but-3-En-2-One. *Russ. J. Org. Chem.* **2011**, *47* (7), 1062. <https://doi.org/10.1134/S1070428011070153>.
- (50) Bassetti, M.; Cerichelli, G.; Floris, B. Substituent Effects in Keto-Enol Tautomerism. Part 3.1 Influence of Substitution on the Equilibrium Composition of β -Dicarbonyl Compounds. *Tetrahedron* **1988**, *44* (10), 2997–3004. [https://doi.org/10.1016/S0040-4020\(88\)90039-7](https://doi.org/10.1016/S0040-4020(88)90039-7).
- (51) Ma, Q.; Zhang, Y.; Jiao, Y.; Zhang, T.; Chu, Q.; Xiao, H.; Zhou, Z.; Liu, Y. New β -Diketone-Boron Difluoride Based near-Infrared Fluorescent Probes for Polarity Detection. *Analyst* **2021**, *146* (19), 5873–5879. <https://doi.org/10.1039/D1AN00912E>.
- (52) Galer, P.; Korošec, R. C.; Vidmar, M.; Šket, B. Crystal Structures and Emission Properties of the BF₂ Complex 1-Phenyl-3-(3,5-Dimethoxyphenyl)-Propane-1,3-Dione: Multiple Chromisms, Aggregation- or Crystallization-Induced Emission, and the Self-Assembly Effect. *J. Am. Chem. Soc.* **2014**, *136* (20), 7383–7394. <https://doi.org/10.1021/ja501977a>.