

J-Aggregates of Boron Difluoride β -Diketonates in Polymer Matrix: Formation and Dissociation. Temperature-Dependent Luminescence.

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Abstract

Temperature-dependent luminescence of polymer compositions doped with boron difluoride β -diketonates has been investigated. At room temperature, the luminescence of the samples is yellow-green, and it becomes blue when heated. The mechanism of the temperature-dependent luminescence consists in the dissociation of J-aggregates of dyes at heating. The process of dissociation of J-aggregates is reversible. These boron difluoride β -diketonates have the potential in wide-range applications in the field of temperature sensing.

Trial registration number

Date of registration

Introduction

Luminescent materials whose emission intensities and colors can be adjusted are in high demand for applications in optoelectronic devices as well as sensors and memory storage units [1-6]. However, variation of the solid-state luminescence color is less attainable than in a solution due to the difficulty in obtaining different stable phases in the aggregated state with varied molecular conformations. This task can be solved either by synthesizing a compound crystallizing in different polymorphs or by altering the molecular geometry and/or packing mode by external stimuli, especially by heat [7], solvent vapo [8-10], and mechanical impact [11-13] (including shearing, grinding, smashing, or stretching), thus allowing to control solid state luminescence (thermo-, vapo- and mechanochromism respectively). Reversible color change in substances with variation of temperature is known as thermochromism. A variety of mechanisms are known to be responsible for the thermochromism, for example, a change of the electron configuration in spin-crossover complexes [14-16], changes in coordination geometry and coordination number in transition-metal complexes [17,18], variation of the band gap in semiconductors [19], change of tautomeric equilibrium [20-23], and reversible molecular rearrangement reactions [24,25].

Over the recent years, along with advances in synthetic and materials chemistry, luminescence temperature sensors have also evolved from mere optical thermometers to multifunctional and stimuli-responsive nano-devices, which can also solve highly complex tasks in the biological context [26]

β -Diketonates of boron difluoride represent the types of organic molecules manifesting an unusual luminescence behavior: they demonstrate an improved efficiency in the solid state [27,28]. The solid-state luminescence properties of difluoroboron β -diketonates are related to not only the intrinsic molecular components, but also to the molecular packing modes associated with multiple intermolecular interactions, such as π - π stacking, hydrogen bonding, and dipole-dipole interactions. Changes in the molecular conformation and packing modes cause significant variation in the emission spectra of the solid state [29]. For example, difluoroboron β -diketonates exhibit mechanochromic properties [30-32]

Earlier [33,34], it was shown that the luminescence of concentrated solutions of β -diketonates of boron difluoride was determined by the formation of brightly luminescent aggregates. Here, the low solubility of β -diketonates of boron difluoride with bulky substituents in organic solvents and, as a result, the low concentration of aggregates in solutions leads to the fact that, in most cases no changes are observed in an absorption spectrum of saturated solutions [35-37]. Although the evolution of the excitation and luminescence spectra along with an increase of the solution concentration indicates the formation of aggregates in the solution [35-37]. As opposed to solutions, the mobility of luminophore molecules in a polymer matrix is significantly reduced, and it becomes possible to register the resulting aggregates. We actually managed [34,37] to record the absorption spectra of J-aggregates of β -diketonates of boron difluoride in a polyethylene (PE) matrix.

The present work describes a study of the luminescence and thermochromic properties of PE films doped with β -diketonates of boron difluoride of different structures: with one bulk aromatic substituent (**1**), with two donor aromatic substituents (**2**), and with one donor and one acceptor substituent (**3**) (Scheme).

These polymer materials exhibit peculiar luminescence thermochromic properties, reversibly changing the color of the luminescence from yellow-green at room temperature to bright blue when heated.

Experimental

Samples preparation

The compound **1** was prepared and purified according to [38] **2** – [39], **3** – [40]. Polyethylene (PE) powder (low density, 500 μm) was purchased from Alfa Aesar.

The PE films doped with the compounds **1-3** were prepared according to [34]. The PE powder and boron complex (0.5 wt. %) were mixed thoroughly and compacted using a hydraulic press ($p = 8 \text{ MPa}$, $T = 130^\circ\text{C}$).

Measurements

The absorption spectra were registered using a Shimadzu-UV2550 spectrometer. The luminescence and excitation spectra were registered using a Shimadzu-RF5301 spectrofluorimeter. The measurements of fluorescence lifetime by the method of time-correlated single-photon counting (TCSPC) were performed using a FluoTime 200 device (PicoQuant) with a PDL 800-B (370 nm) excitation source and a TimeHarp device as a SPC controller. The lifetime data were analyzed using the FluorFit 4.0 software from PicoQuant.

The spectra of the heated sample were recorded as follows: the film was heated over an electric stove until PE softened and the luminescence color of the film changed from yellow to blue (90°C). Then the sample was placed in a cuvette holder with temperature control at 60°C , and the spectrum was recorded.

Results And Discussion

The absorption spectrum of 1 in PE at room temperature comprises a band with a maximum at 366 nm and a shoulder at 408 nm. When excited at the maximum of the absorption band, a group of bands in the range 400–450 nm and a wide band with a maximum at 503 nm were observed in the luminescence spectrum. The short-wavelength part of the spectrum was determined by the monomer luminescence of 1, the spectrum of which coincided with the luminescence spectrum of dilute solutions [38]. The second band at 503 nm corresponds to the luminescence of excimers [38]. The presence of two luminescence centers for 1 in PE is corroborated by the different structure of the excitation spectra at different values of λ_{reg} : at 416 nm, there is one band at 360 nm in the excitation spectrum; at 503 nm, the excitation spectrum has a maximum at 412 nm, the spectrum itself is much wider (270–450 nm) and represents a group of bands at 290, 360, and 412 nm. The wide excitation spectrum indicates the presence of several photoprocesses, which result in the excimer luminescence of 1 (Fig. 1a).

When comparing the absorption and excitation spectra of 1 in PE (Fig. 1 a), it was found that the maximum of the absorption spectrum (366 nm) corresponded to the excitation band of the monomer luminescence, whereas the 408 nm shoulder in the absorption spectrum corresponded to the most intense band in the excimer excitation spectrum (412 nm). The authors of [38] showed that, in crystals of 1, the structure of the stacks of molecules corresponded to J-aggregates consisting of dimers. The shoulder in the absorption spectrum of 1 is related to the absorption of J-aggregates and corresponds to the long-wave band of the excimer excitation spectrum. Therefore, at room temperature, the excimer luminescence of 1 in PE is realized by the interaction of two or more molecules that are not separated by hydrocarbon chains of PE. The excimer luminescence of 1 occurs both during the energy transfer from an excited molecule to an unexcited one ($\lambda_{\text{ex}}=360$ nm) and during the excitation of excimer traps (dimers) in the structure of a J-aggregate ($\lambda_{\text{ex}} = 412$ nm). The monomer luminescence of individual molecules of 1 is excited only by the light with $\lambda_{\text{ex}} = 360$ nm.

For 2 and 3 in PE, a similar pattern was observed: a long-wave shoulder related to the absorption of J-aggregates was registered in the absorption spectrum (Fig. 1 b, c). This shoulder in the absorption spectrum corresponds to the intense long-wavelength band of J-aggregates in the excimer luminescence excitation spectrum (Fig. 1 b, c, spectrum 3). When luminescence is excited by the light with a wavelength corresponding to the maximum of the absorption spectrum (380 nm), monomer and excimer luminescence is observed. During the excitation in the absorption band of single molecules (380 nm), both monomer and excimer luminescence are excited. During the excitation in the band of J-aggregates (412 nm), only the luminescence of aggregates (excimers) is observed.

When the sample of 1 in PE is heated, before PE softens ($T = 90^{\circ}\text{C}$), the film is discolored, and the luminescence color changes from yellow-green to blue (Fig. 2). The thermochromism was investigated under UV light ($\lambda = 365$ nm), i.e., in the excitation band of the monomer luminescence. Changes in the spectral properties of the sample under heating are shown in Figures 1 and 2. The long-wavelength shoulder disappears in the absorption spectrum, and the absorption spectrum of the heated film 1

coincides with the excitation spectrum of the monomer luminescence (Fig. 1 a). At the excitation at 360 nm in the luminescence spectrum of the heated film, the intensity of the monomer luminescence bands increases, whereas the intensity of the excimer luminescence decreases (Fig. 2 a). In the excimer luminescence excitation spectrum of 1 in PE, a significant increase in the short-wavelength component is observed during heating (Fig. 1S). The most significant changes were observed in the luminescence spectra recorded at $\lambda_{\text{ex}} = 360$ nm (the maximum of the absorption spectrum of 1). Therefore, when 1 in PE is heated, and the matrix is softened, dissociation of J-aggregates is observed due to an increase in the solubility of 1 in PE, the intensity of excimer luminescence decreases, and the intensity of monomer luminescence increases.

Similar changes were also observed for the complexes 2 and 3 in PE (Fig. 2 b, c): when heated, the film was discolored and the luminescence color changed from yellow-green (2) and from aquamarine (3) to bright blue. Similarly to 1, the discoloration of complexes 2 and 3 in PE is related to the dissociation of J-aggregates under heating (a decrease in the intensity of the long-wave arm in the absorption spectrum (Fig. 1 b, c)). The change in the luminescence color in 2 and 3 is also related to the dissociation of J-aggregates. Indeed, in the excimer excitation spectra of 2 and 3, the decrease of the intensity of the long-wave component related to the excitation of J-aggregates was observed (Fig. 2S, 3S). These processes are characterized by an increase of the intensity of the monomer luminescence bands and a simultaneous decrease of the intensity of the excimer luminescence bands (Fig. 2 b, c). When the film cools down, the color and luminescence color of the films restore to the original ones. The processes of aggregation and dissociation of molecules of 1–3 in PE are reversible and are reproduced in the repeated heating-cooling cycles.

One should mention that the evolution of the absorption spectra and stationary luminescence spectra of complexes 1–3 under heating is identical (Fig. 1, 2). However, unlike the stationary luminescence spectra, the evolution of the time-resolved luminescence spectra of complexes 1–3 is different (Fig. 3, 4).

The luminescence attenuation kinetics was recorded for each sample at two registration wavelengths ($\lambda_{\text{reg}} = 440$ and 500 nm) (Fig. 3), as well as the time-resolved luminescence spectrum (Fig. 4). For 1, the kinetic curves recorded at varied λ_{reg} differ significantly (Fig. 3 a): at $\lambda_{\text{reg}} = 440$ nm, $\tau = 6.9$ ns, three-exponential kinetics (20.5 ns (26.06 %), 2.7 ns (42.00 %), 1.2 ns (31.94 %)); and at $\lambda_{\text{reg}} = 500$ nm, monoexponential $\tau = 19.0$ ns. Both excimer of 20.5 ns and monomer luminescence of 2.7 and 1.2 ns contribute to the kinetics at 440 nm. In the time-resolved luminescence spectrum, as opposed to the stationary one, an intense band of the monomer luminescence and a low-intensity band of the excimer luminescence are registered at room temperature (Fig. 3 a), whereas the excimer band appears 1.2 ns after the system is excited. In the case of 1, the traditional scheme for the excimer formation is observed:





In the heated sample of 1, the lifetime at $\lambda_{\text{reg}}=440$ nm reduced from 6.9 to 4.9 ns by lowering the contribution of a long-lived component. In the time-resolved luminescence spectrum of the heated film of 1, the intensity of luminescence of the excimers decreases significantly and the excimer band is not recorded (Fig. 4 a).

For 2, in contrast to 1, both kinetic curves (Fig. 3 b) are proximate: at room temperature at $\lambda_{\text{reg}}=440$ and 500 nm, the average lifetime equals to 3.8 ns. In both cases, a three-exponential process is registered: the component with $\tau = 16.0$ ns corresponds to the luminescence of excimers; the one with $\tau = 2.9$ and 1.3 ns corresponds to the monomer luminescence. The difference between the luminescence attenuation curves at $\lambda_{\text{reg}}=440$ and 500 nm is determined by the redistribution of the contribution of the components. In the time-resolved spectrum of 2 in PE at room temperature, only excimer luminescence is observed, the intensity of the monomer luminescence is too weak to be registered (Fig. 4 b). For the heated film, on the contrary, only the monomer luminescence is registered in the time-resolved spectrum (Fig. 4 b). For the heated film 2, a component corresponding to the luminescence of excimers with $\tau = 21.0$ ns is observed only at $\lambda_{\text{reg}} = 500$ nm (Table ESI).

For 2, the tendency towards the excimer formation is lower than for 1. This can be related to the structure of a molecule. In the complex 1, a molecule is planar, while a molecule of 2 has two mobile substituents in phenyl rings – methoxy groups, which can cause steric hindrances when overlapping neighboring molecules. Analysis of the crystal structure of 1 [38] and 2 [39] showed that, in crystals of 1, there existed a more complete overlap of the excimer-forming molecules than in 2 (Fig. 4S). A molecule of 3 contains an even more bulky substituent – a bromine atom, which is supposed to create even greater steric hindrances in the formation of excimers. Indeed, unlike the cases of 1 and 2, the lifetime of 3 in the excited state does not depend on the luminescence wavelength and equals to 1.5 ns, the value of τ does not change when heated (Fig. 3 c). In addition, the luminescence band of 3 in PE is narrow, the half-width is only 57 nm (Fig. 2 c, 4 c), which is not typical for the excimer luminescence. Taking into account that there is a long-wavelength shoulder related to the absorption of J-aggregates in the absorption spectrum of 3 in PE, and the excitation spectrum also has a narrow long-wave excitation band of J-aggregates, which is mirror-symmetric to the luminescence spectrum, then the long-wave luminescence of 3 can be attributed to the emission of J-aggregates. When 3 is heated, J-aggregates dissociate (decrease in size), and bands related to the emission of monomers appear in the stationary and time-resolved spectra, simultaneously with the luminescence of the J-aggregates (Fig. 4 c).

Conclusion

To sum up, we have fabricated the samples of PE compositions doped with boron difluoride β -diketonates with various α -substituents. The resulting samples demonstrate interesting luminescent thermochromic properties. At room temperature, the luminescence of the samples is yellow-green, and at heating up to 90°C it becomes blue. The mechanism of the temperature-dependent luminescence

consists in the dissociation of J-aggregates of dyes when heated. The process of dissociation of J-aggregates is reversible. These boron difluoride β -diketonates have the potential in wide-range applications in the field of temperature sensing.

Declarations

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Conflicts of interest/Competing interests

There are no conflicts to declare

Availability of data and material (data transparency)

All data and materials support published claims and comply with field standards.

Code availability (software application or custom code)

Not applicable

Authors' contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Elena V. Fedorenko and Anatolii G. Mirochnik. The first draft of the manuscript was written by Elena V. Fedorenko and Anatolii G. Mirochnik commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Authorship clarified

Anatolii G. Mirochnik made substantial contributions to the conception or design of the work; or the acquisition, analysis, or interpretation of data; or the creation of new software used in the work;

Elena V. Fedorenko drafted the work or revised it critically for important intellectual content and agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.;

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Figures

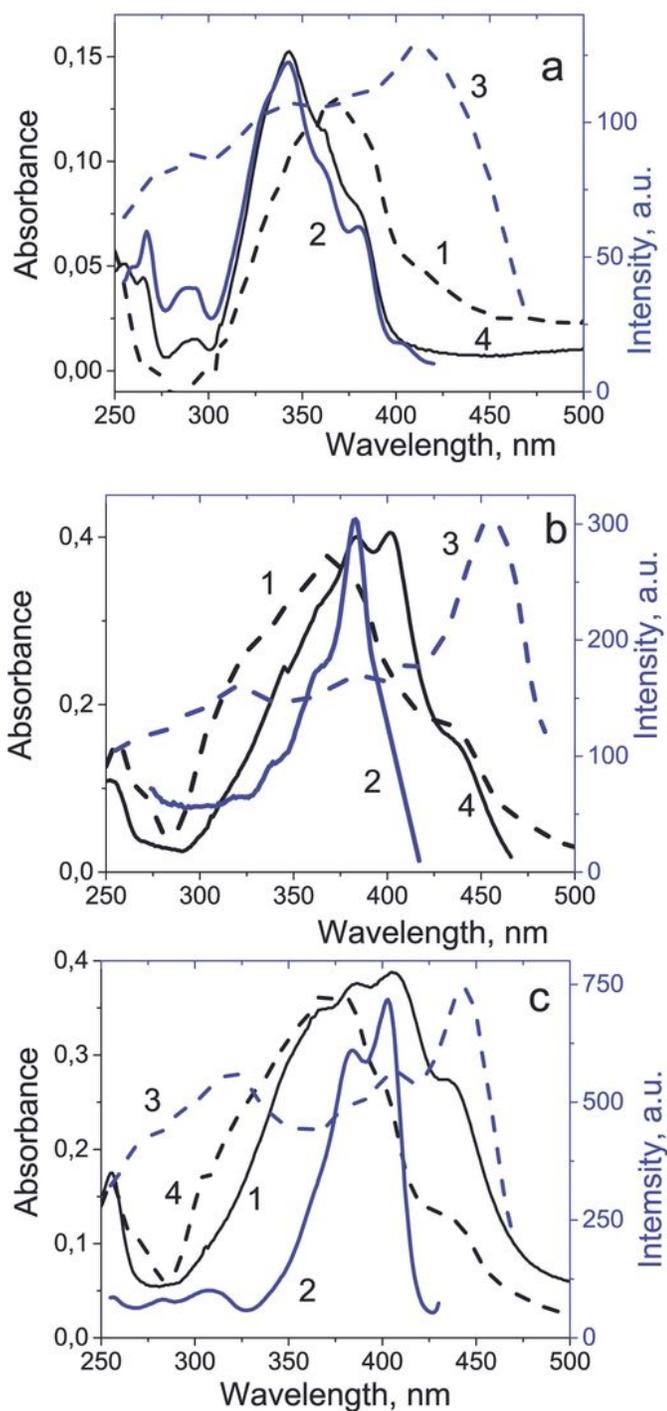


Figure 1

Absorption and excitation spectra of the PE films: 1 – absorption spectrum at 20°C, 2 – excitation spectrum of the monomer luminescence at 20°C, 3 – excimer excitation spectrum at 20°C, 4 – absorption spectrum at 60°C. (a) – complex 1, (b) – complex 2, (c) – complex 3

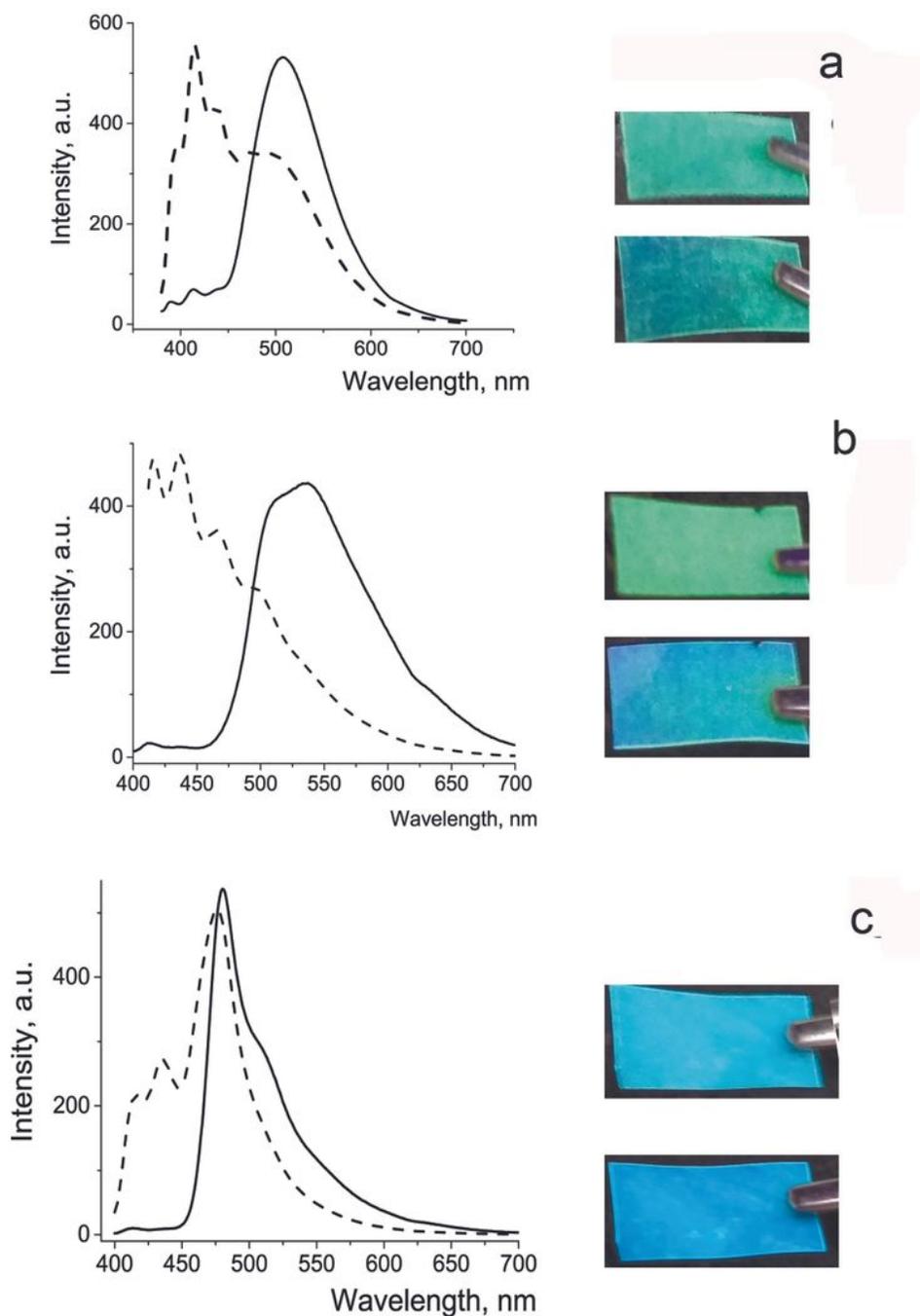


Figure 2

Left: change in the luminescence spectra ($\lambda_{\text{exc}} = 380 \text{ nm}$) with increasing temperature (solid line – at room temperature, dotted line – at 60°C). Right: images of the films under UV irradiation (365 nm): the original sample (top), and the one heated up to 90°C (bottom). (a) – complex 1, (b) – complex 2, (c) – complex 3

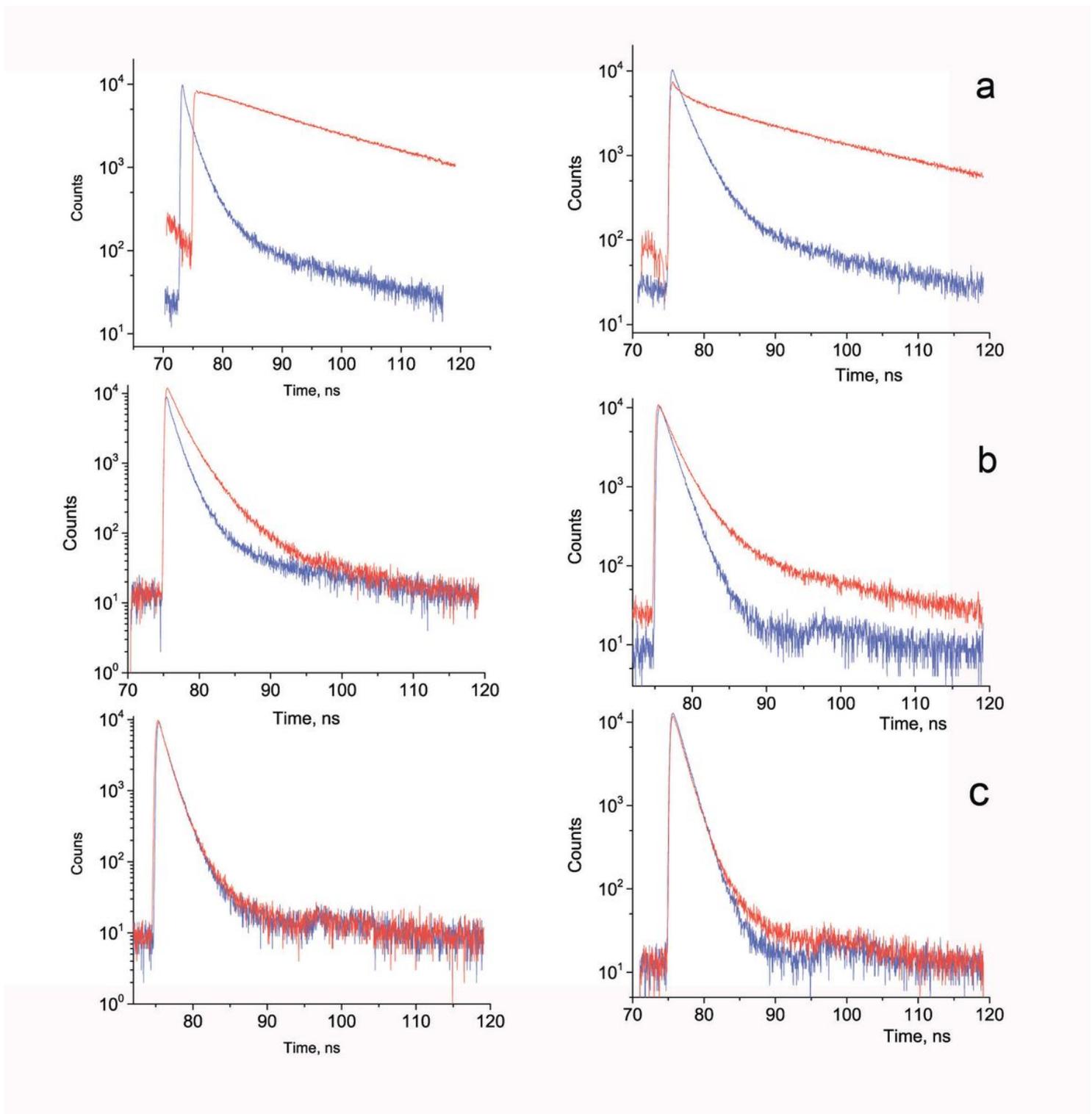


Figure 3

Kinetic curves of luminescence attenuation: left – at room temperature, right – heated film. (a) – complex 1, (b) - complex 2, (c) - complex 3

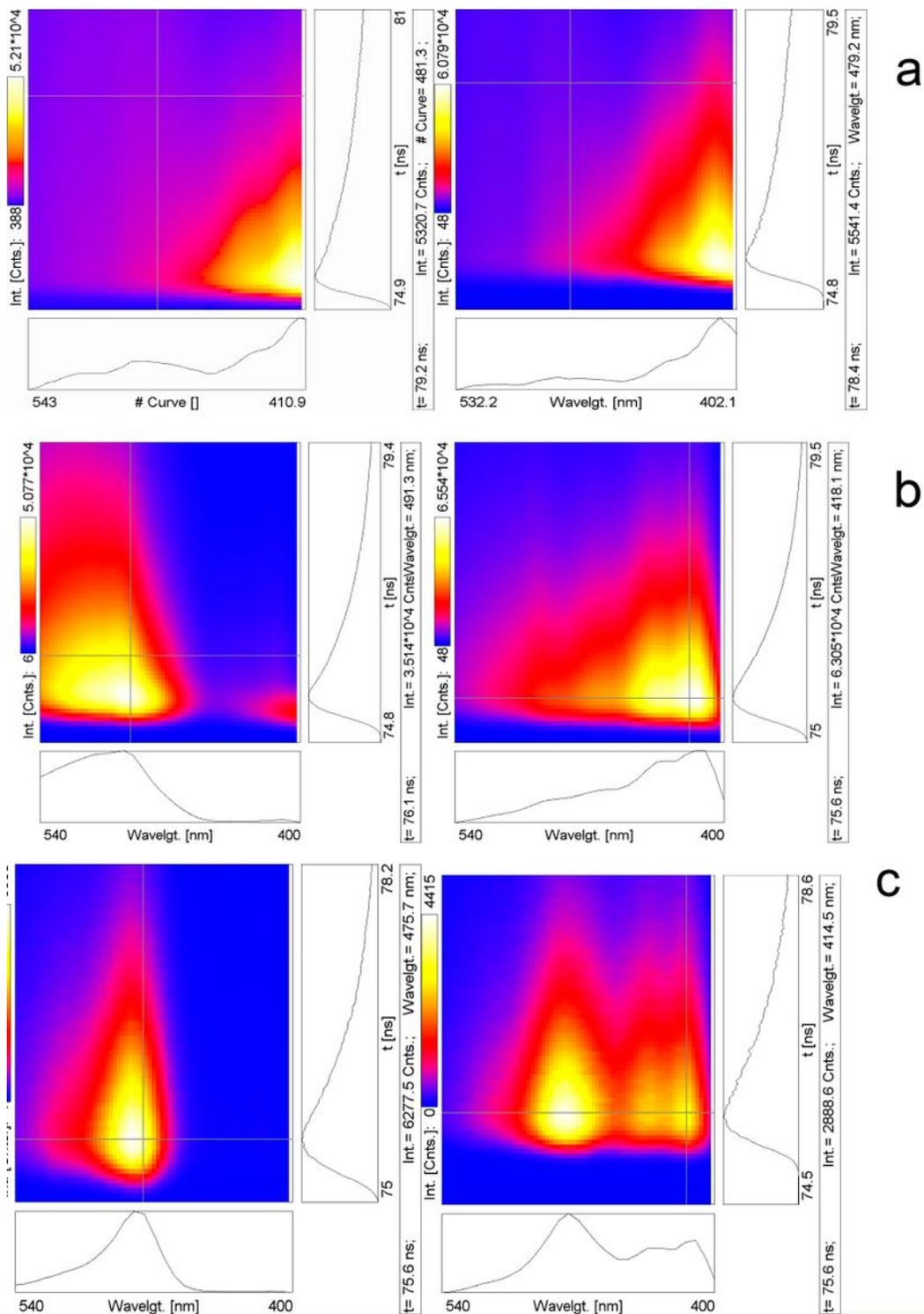


Figure 4

Time-resolved luminescence spectra: left – at room temperature, right – heated film. (a) – complex 1, (b) – complex 2, (c) – complex 3

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