

# Potential End-Use of a Europium Binary Photoluminescent Ink for Anti-Counterfeiting Security Documents

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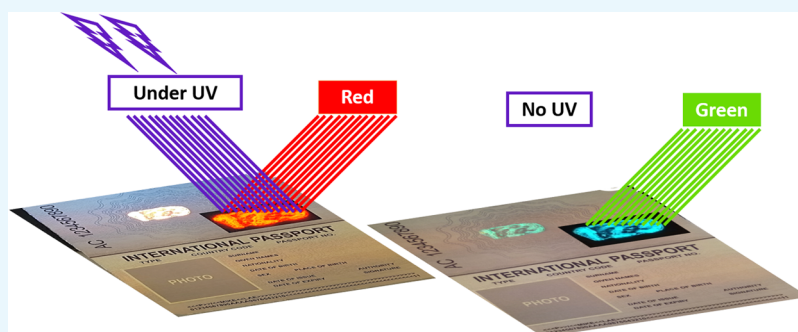
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**ABSTRACT:** Composed of two europium complexes doped in polyvinyl butyral as the host material, a novel photoluminescent ink has been formulated by synthesizing  $\text{Eu}(\text{FAC})_3\text{Phen}$  as a red luminescent down-shifting emitter and employing  $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$  as a long persistent green phosphor. Both emitters are incorporated to design a photoluminescent ink with binary emission under a single UV excitation wavelength, where a red light is emitted when exposed under 325 nm, subsequently becoming green upon the UV light being switched off. The concept presented here is unequivocally distinct from the classical dual-mode emission, which requires a second extra near-infrared excitation around 980 nm to produce a binary luminescence. This work demonstrates the effortlessness of using one UV excitation for dual-mode visible emission while rendering the counterfeiting of confidential documents more onerous.

## 1. INTRODUCTION

There are currently several high-security techniques proposed for the prevention of document and identity fraud, namely, invisible personal information (IPI) technology containing a special filter integrated within the polycarbonate data page, rendering concealed personalized data visible. Likewise, Kinigram uses costly materials, such as customized gold foils, with forensic features for personal data protection. The drive to eliminate identity fraud and the need to “become the most trusted source of identity verification” translate into Secure’s ability to secure funding of \$96 million. This commitment to provide diverse security printing methods comes with its own set of challenges, especially regarding the use of expensive materials. Moreover, while single-fluorescence luminescent materials may be widely integrated as part of the forensic features, they are nonetheless susceptible to potential counterfeiting.

More recent dual-fluorescence mode techniques have been implemented as alternatives in anti-counterfeiting applications using a lanthanide-doped  $\text{NaLuF}_4/\text{Y}_2\text{O}_3$  composite,<sup>1</sup> which, upon exposure to excitation with a laser at 980 nm and with UV light at 254 nm, results in a multicolor dual emission. The two mechanisms behind these types of photoluminescence are up-conversion (UC), via excitation in the near-infrared region

(NIR) and collecting luminescence in the visible, and luminescent down-shifting (LDS) where excitation is applied in the UV–vis region with emission occurring in the visible region.<sup>2–10</sup> Chen et al.<sup>11</sup> demonstrated that the lanthanide-based material  $\text{Yb}/\text{Ln}/\text{Mn}:\text{Na}_3\text{ZrF}_7$  enables simultaneous red and multicolor emissions upon excitation of UV light and a NIR laser, respectively, with the material displaying bifunctional emissions for anti-counterfeiting applications. These studies indicate the possibility of using a combination of UC and LDS as a luminescent ink under two near-infrared and UV excitation wavelengths.

The concept presented here focuses on designing a new luminescent ink composed of LDS and afterglow complexes, which release separate emissions under one excitation wavelength and, consequently, simplify the use of the more

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complex concept of up-converted near-infrared luminescent materials.

In contrast to traditional europium(III)  $\beta$ -diketonate complexes as luminescent down-shifting agents,<sup>12–15</sup> the complex synthesized in this study is  $\text{Eu}(\text{FAC})_3\text{Phen}$  whose photoluminescence properties suggest that it exhibits a very strong red emission at 612 nm under UV light at 325 nm. Under the same excitation wavelength, the  $\text{SrAl}_2\text{O}_4\cdot\text{Eu}$ , Dy releases a very strong green emission several minutes after removal of the UV excitation (Figure 1). The luminescent ink



**Figure 1.** Photoluminescent ink (a) under UV–vis light and (b) under visible light; UV light is switched off. In this concept, the dual emission is clearly visible and only one excitation of light at 325 nm is employed without the need for near-infrared laser excitation light (photo taken by O.M.).

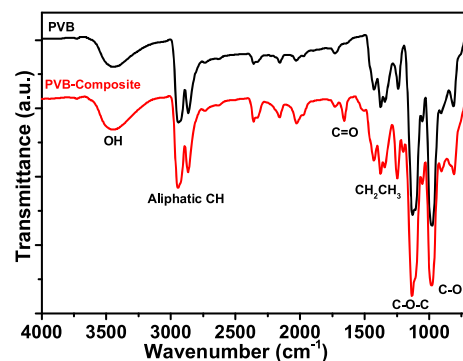
containing  $\text{Eu}(\text{FAC})_3\text{Phen}$  and  $\text{SrAl}_2\text{O}_4\cdot\text{Eu}$ , Dy in PVB is prepared and applied by screen-printing on a passport page model. Possessing very good stability and homogeneity at 65 °C, the ink displays red luminescence under 325 nm excitation UV light, and a visible afterglow green emission after the excitation light is switched off. This points toward the prospective future application of bifunctional luminescent materials via low-cost screen-printing and inexpensive materials for anti-counterfeiting purposes.

## 2. RESULTS AND DISCUSSION

**2.1. Morphology and FTIR Stability Test.** Scanning electron microscopy (SEM) images (Figure 2) reveal the morphology and the temperature effect of the composite of two europium complexes into the PVB matrix. The complexes are incongruously dispersed at 40 °C in Figure 2a compared to Figure 2b at 65 °C. An increase in temperature improved the penetration of the complex  $\text{Eu}(\text{FAC})_3\text{Phen}$ , which is highly soluble in the PVB matrix. In contrast, the complex  $\text{SrAl}_2\text{O}_4\cdot\text{Eu}$ , Dy, known for its insolubility in organic solvents, is in fact highly insoluble in a PVB matrix. Further microscopy images (Figure S1) of a pure PVB polymer compared to the composite at 65 °C evidently prove that the dual complex PVB mixture is homogeneous as suggested by the change in color

from white to yellowish white as a result of the temperature increase.

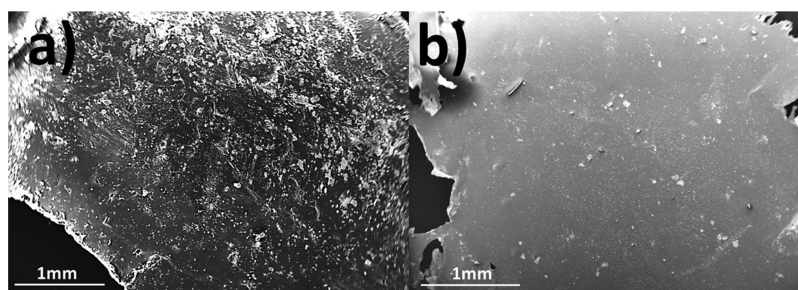
This temperature change led us to check the stability of the matrix with Fourier transform infrared (FTIR) (Figure 3), and



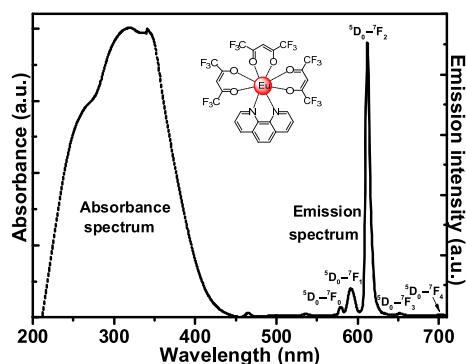
**Figure 3.** FTIR spectra of PVB and the PVB composite (photoluminescent ink including the two europium complexes and the PVB host polymer).

it was found that the IR bands of PVB-free and PVB-containing ink remain the same with the following distribution: 3500  $\text{cm}^{-1}$  (OH stretching), 2950  $\text{cm}^{-1}$  (aliphatic CH stretching), 1440  $\text{cm}^{-1}$  ( $\text{CH}_2$  bending), 1377  $\text{cm}^{-1}$  ( $\text{CH}_3$  bending), 1131  $\text{cm}^{-1}$  (C–O–C stretching), and 999  $\text{cm}^{-1}$  (CO stretching). This demonstrates that the stability of the PVB matrix is unaffected by the temperature-induced color change. Furthermore, the high solubility of the two complexes in the PVB matrix at 65 °C can be determined by their dispersion inside the PVB matrix, which is also confirmed by energy-dispersive X-ray spectroscopy mapping in Figure S2a,b. Notably, the dispersion of two complexes is higher at 65 °C (Figure 2b).

**2.2. Optical Properties.** The UV–vis absorbance spectrum is recorded from 210 to 500 nm (Figure 4) with the two clear bands visible around 235 nm and at 325 nm attributable to the absorbance of FAC and Phen ligands, respectively. Under excitation at 325 nm, the emission is recorded from 500 to 700 nm. The emission peaks of  $\text{Eu}(\text{FAC})_3\text{Phen}$  are localized at 579, 591, 612, 652, and 702 nm and can be ascribed to  ${}^5\text{D}_0\text{--}{}^7\text{F}_0$ ,  ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ ,  ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ ,  ${}^5\text{D}_0\text{--}{}^7\text{F}_3$ , and  ${}^5\text{D}_0\text{--}{}^7\text{F}_4$  transitions, respectively.<sup>16</sup> The complex exhibits a very strong red emission at 612 nm due to the hypersensitive  ${}^5\text{D}_0\text{--}{}^7\text{F}_2$  transition, which is the most dominating transition. The ligand to metal charge transfer (LMCT) is the mechanism behind the electronic transition responsible for the luminescence of  $\text{Eu}^{3+}$  through an intramolecular process by pumping the phenanthroline ligand absorption bands (Scheme 1).

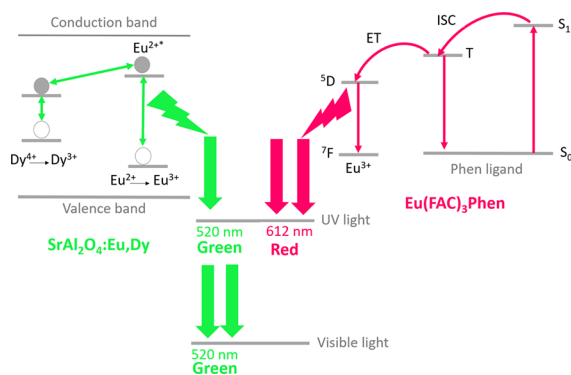


**Figure 2.** SEM images of the photoluminescent ink (a) at 40 °C and (b) at 65 °C.



**Figure 4.** Absorbance and emission spectra of  $\text{Eu}(\text{FAC})_3\text{Phen}$  excited at 325 nm. Inset, the chemical structure of  $\text{Eu}(\text{FAC})_3\text{Phen}$ .

### Scheme 1. Schematic Illustration of the Dual-Mode Emission Effect of the Photoluminescent Ink



In addition, the chelating of ligands with high intense absorption can be transferred intermolecularly to the  $\text{Eu}^{3+}$  ion, improving its photoluminescence properties. In this work,  $\text{Eu}(\text{FAC})_3\text{Phen}$  was selected for its ease of synthesis and very strong total photoluminescence quantum yield (PLQY) close to 40% with a lifetime of 1.3 ms in PMMA.<sup>12</sup> Moreover, the Eu complex, as shown previously, can be dissolved easily in PVB and other host materials, resulting in a homogeneous film.<sup>13</sup>

On the other hand, the Eu-based complex  $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$  is known for its persistent afterglow properties. The strontium aluminate phosphors activated by  $\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$  ions have attracted a lot of attention with their exceptional properties such as high quantum efficiency, long persistence of phosphorescence, and good stability. The energy transfer processes of the green emission are composed of fluorescence, phosphorescence, and afterglow. Generally, in these types of complexes, the triplet states are populated through the singlet–triplet intersystem crossing (ISC). The triplet excitons are quickly stabilized resulting in the formation of triplet excited states with the extended lifetime required for afterglow phosphorescence. The mechanism of long-lasting luminescence has been studied widely to delay the duration and intensity of afterglow properties. Thanks to the work of Spustaka et al.<sup>17</sup> discussing all the scenarios behind the persistent luminescence of the  $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$  complex, several mechanisms are highlighted to explain the causes of the luminescence. The clearest scenario is that  $\text{Eu}^{3+}$  centers are created during excitation, and electrons are localized in trapping centers by Dy. After the thermal release of electrons from the trapping centers, they recombine with  $\text{Eu}^{3+}$  creating an excited  $\text{Eu}^{2+}$  and a radiative  $\text{Eu}^{2+}$  transition to the ground

state.<sup>17</sup> Nevertheless, investigations are still ongoing to understand the role of  $\text{Dy}^{3+}$  and its implication in the photoluminescence of the complex.

**2.3. Anti-Counterfeiting Passport Security Applications.** A viscous composite of the  $\text{Eu}(\text{FAC})_3\text{Phen}$ ,  $\text{SrAl}_2\text{O}_4:\text{Eu}$ , Dy, and PVB has been screen-printed on the surface of a passport page model. After 30 min, the composite solidified at room temperature (Figure 5a), and when exposed to UV light, it emits a very strong red light (Figure 5b).



**Figure 5.** 123 numbers screen with the anti-counterfeiting photo-luminescent ink of  $\text{Eu}(\text{FAC})_3\text{Phen}$ ,  $\text{SrAl}_2\text{O}_4:\text{Eu}$ , Dy, and PVB added on top of the passport's image showing a dual-mode emission effect under similar UV excitation wavelength. (a) Composite under normal light, (b) under UV light, red emission is clear, and (c) green afterglow luminescence persisted, lasting for a few minutes, upon removal of the UV light (photo taken by O.M.).

Under the same wavelength, with the UV light switched off, a green afterglow emission is observable lasting for a few minutes (Figure 5c).

### 3. CONCLUSION AND PERSPECTIVES

In light of the complexities regarding the photophysical mechanisms of the two Eu-based complexes, this work clearly demonstrates that binary emission under single excitation is possible using simple, inexpensive screen-printing techniques and that the integration of two highly green and red phosphorescent europium complexes into a PVB polymer results in a very stable luminescent ink, which can be applied as an anti-counterfeit material. The synthesis of the  $\beta$ -diketonate  $\text{Eu}(\text{FAC})_3\text{Phen}$  complex is simple exhibiting a very strong red emission at 612 nm due to the hypersensitive  ${}^5\text{D}_0\text{--}{}^7\text{F}_2$  transition. The development of a new ancillary ligand with high  $\pi$ -conjugated systems can improve not only the brightness of the red emission but also the absorbance characters and the PLQY of the europium. The afterglow  $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$  is the highest green emitter with high delayed persistent luminescence showing some issues of solubility, which is resolved by increasing the temperature to 65 °C, thus enabling it to dissolve partially in the PVB polymer as demonstrated by SEM. The composite was added by low-cost screen-printing on the top of the first page of a passport model showing a red and green dual emission under the same excitation UV wavelength around 325 nm. Other techniques, such as printing or coating, can also be used to improve the surface smoothness and film formation of the photoluminescent ink. This study clearly demonstrates that this technology can be applied effortlessly to enhance high-security data protection and personalization of passport and ID documents.



## 4. EXPERIMENTAL SECTION

**4.1. Materials.** H<sub>2</sub>O and ethanol (for analysis, Sigma-Aldrich) were used without further purification. Potassium *tert*-butoxide (KOtBu), hexafluoroacetylacetonate (hfac), 1,10-phenanthroline (99%+), EuCl<sub>3</sub>·6H<sub>2</sub>O, strontium aluminate, europium and dysprosium doped, and polyvinyl butyral (PVB) were procured from Sigma-Aldrich.

**4.2. General Instrumentation and Procedures.** Infrared measurements were conducted with a Jasco FTIR-4600 spectrometer, and Spectra Manager software was used to plot the curves. An interferometer system was used with the latest digital signal processing (DSP) control technology, including an integrated attenuated total reflection (ATR) for sample measurements. ATR is a single reflection 1.8 mm monolithic diamond model with a wide spectral range (7800–350 cm<sup>-1</sup>) and a maximum resolution of 0.7 cm<sup>-1</sup>. The absorbance spectrum was recorded with a Jasco V-770-UV/VIS/NIR single monochromator with a wavelength range between 190 and 3200 nm. The emission spectrum was scanned by a FP-8500 spectrofluorometer with a wavelength range of 200–850 nm. <sup>1</sup>H NMR spectra were performed at 293 K on a Bruker 600M Avance III spectrometer. The morphology of the LDS layers was inspected with scanning electron microscopy (SEM; ZEISS EVO 10) at 10 kV, and all samples were vacuum-coated with gold. Microscopy images were taken with an Olympus DSX 1000.

**4.3. Synthesis of Eu(FAC)<sub>3</sub>Phen.** The complex Eu(FAC)<sub>3</sub>Phen was prepared according to the work carried out by Moudam et al.<sup>12</sup> with some of the following changes: hfac (3 mmol) and KOtBu (3 mmol) were mixed together in ultrapure water (5 mL) at 60 °C for 30 min to form a transparent solution before adding the salt of EuCl<sub>3</sub>·6H<sub>2</sub>O. A white precipitate was subsequently obtained and dissolved in 3–5 mL of ethanol. The mixture was stirred for an extra 30 min before mixing the 1,10-phenanthroline (1 mmol) in a solution to form a white precipitate, which was filtered off, washed with cold water (100 mL), and dried under vacuum for 6 h. The final compound Eu(FAC)<sub>3</sub>Phen was obtained as white crystals in a 69% yield. The compound was characterized by <sup>1</sup>H NMR spectroscopy (Figure S3).

**4.4. Preparation of the Photoluminescent Ink.** PVB (100 mg) was dissolved in dichloromethane for 30 min at 40 °C, then, 20 mg of Eu(FAC)<sub>3</sub>Phen 10% (w/w) was added, and the mixture was stirred for an extra 30 min. Strontium aluminate, europium and dysprosium doped was added to the mixture and stirred for an hour at 40 °C. A few drops of dichloromethane (DCM) were added to adjust the solvent level. The same procedure was repeated at 65 °C to optimize the doping quality of the two complexes into PVB.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c03949>.

Response: compound characterized by microscopy, EDX, and <sup>1</sup>H NMR spectroscopy; Figure S1: microscopy images taken with an Olympus DSX 1000 for free PVB and PVB-based luminescent ink; Figure S2: EDX mapping at 40 and 65 °C; and Figure S3: <sup>1</sup>H NMR spectra of Eu(FAC)<sub>3</sub>Phen in CDCl<sub>3</sub> at 600 MHz (PDF)

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### Notes

The authors declare the following competing financial interest(s): Omar Moudam and Omar Lakbita are inventors of this technology under Patent number MA52845 which was filed on the 7th April 2021 at the Moroccan Office of Industrial and Commercial Property (OMPIC).

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## ■ REFERENCES

- (1) Chen, X.; Yao, W.; Wang, Q.; Wu, W. Designing Multicolor Dual-Mode Lanthanide-Doped NaLuF<sub>4</sub>/Y<sub>2</sub>O<sub>3</sub> Composites for Advanced Anticounterfeiting. *Adv. Opt. Mater.* **2020**, *8*, 1901209.
- (2) Evangelista, A. J.; Ivanchenko, M.; Myers, A. F.; McNulty, L. N.; Payne, G. K. M.; Jing, H. Multi-Shelled Upconversion Nanostructures with Enhanced Photoluminescence Intensity via successive Epitaxial Layer-by-Layer Formation (SELF) Strategy for High-Level Anticounterfeiting. *J. Mater. Chem. C* **2020**, *8*, 5692–5703.
- (3) Meruga, J. M.; Cross, W. M.; Stanley May, P.; Luu, Q.; Crawford, G. A.; Kellar, J. J. Security Printing of Covert Quick Response Codes Using Upconverting Nanoparticle Inks. *Nanotechnology* **2012**, *23*, 395201.
- (4) Liu, Y.; Han, F.; Li, F.; Zhao, Y.; Chen, M.; Xu, Z.; Zheng, X.; Hu, H.; Yao, J.; Guo, T.; Lin, W.; Zheng, Y.; You, B.; Liu, P.; Li, Y.; Qian, L. Inkjet-Printed Unclonable Quantum Dot Fluorescent Anti-Counterfeiting Labels with Artificial Intelligence Authentication. *Nat. Commun.* **2019**, *10*, 2409.
- (5) Han, Y.; Li, H.; Wang, Y.; Pan, Y.; Huang, L.; Song, F.; Huang, W. Upconversion Modulation through Pulsed Laser Excitation for Anti-Counterfeiting. *Sci. Rep.* **2017**, *7*, 1320.
- (6) Huang, H.; Chen, J.; Liu, Y.; Lin, J.; Wang, S.; Huang, F.; Chen, D. Lanthanide-Doped Core@Multishell Nanoarchitectures: Multimodal Excitable Upconverting/Downshifting Luminescence and High-Level Anti-Counterfeiting. *Small* **2020**, *16*, 2000708.
- (7) Zhang, Z.; Ma, N.; Kang, X.; Li, X.; Yao, S.; Han, W.; Chang, H. Switchable up and Down-Conversion Luminescent Properties of Nd(III)-Nanopaper for Visible and near-Infrared Anti-Counterfeiting. *Carbohydr. Polym.* **2021**, *252*, 117134.
- (8) Liu, J.; Rijckaert, H.; Zeng, M.; Haustraete, K.; Laforce, B.; Vincze, L.; Van Driessche, I.; Kaczmarek, A. M.; Van Deun, R. Simultaneously Excited Downshifting/Upconversion Luminescence from Lanthanide-Doped Core/Shell Fluoride Nanoparticles for Multimode Anticounterfeiting. *Adv. Funct. Mater.* **2018**, *28*, 1707365.
- (9) Kumar, P.; Singh, S.; Gupta, B. K. Future Prospects of Luminescent Nanomaterial Based Security Inks: From Synthesis to Anti-Counterfeiting Applications. *Nanoscale* **2016**, *8*, 14297–14340.

- (10) Ma, C.; Liu, H.; Ren, F.; Liu, Z.; Sun, Q.; Zhao, C.; Li, Z. The Second Near-Infrared Window Persistent Luminescence for Anti-Counterfeiting Application. *Cryst. Growth Des.* **2020**, *20*, 1859–1867.
- (11) Chen, D.; Liu, Y.; Chen, J.; Huang, H.; Zhong, J.; Zhu, Y. Yb<sup>3+</sup>/Ln<sup>3+</sup>/Mn<sup>4+</sup> (Ln = Er, Ho, and Tm) Doped Na<sub>3</sub>ZrF<sub>7</sub> Phosphors: Oil-Water Interface Cation Exchange Synthesis, Dual-Modal Luminescence and Anti-Counterfeiting. *J. Mater. Chem. C* **2019**, *7*, 1321–1329.
- (12) Moudam, O.; Rowan, B. C.; Alamiry, M.; Richardson, P.; Richards, B. S.; Jones, A. C.; Robertson, N. Europium Complexes with High Total Photoluminescence Quantum Yields in Solution and in PMMA. *Chem. Commun.* **2009**, *43*, 6649–6651.
- (13) Wang, X.; Wang, T.; Tian, X.; Wang, L.; Wu, W.; Luo, Y.; Zhang, Q. Europium Complex Doped Luminescent Solar Concentrators with Extended Absorption Range from UV to Visible Region. *Sol. Energy* **2011**, *85*, 2179–2184.
- (14) Mei, J. F.; Lv, Z. P.; Lai, J. C.; Jia, X. Y.; Li, C. H.; Zuo, J. L.; You, X. Z. A Novel Photo-Responsive Europium(III) Complex for Advanced Anti-Counterfeiting and Encryption. *Dalton Trans.* **2016**, *45*, 5451–5454.
- (15) Hasegawa, Y.; Kitagawa, Y.; Nakanishi, T. Effective Photosensitized, Electrosensitized, and Mechanosensitized Luminescence of Lanthanide Complexes. *NPG Asia Mater.* **2018**, *10*, 52–70.
- (16) Freund, C.; Porzio, W.; Giovanella, U.; Vignali, F.; Pasini, M.; Destri, S.; Mech, A.; Di Pietro, S.; Di Bari, L.; Mineo, P. Thiophene Based Europium  $\beta$ -Diketonate Complexes: Effect of the Ligand Structure on the Emission Quantum Yield. *Inorg. Chem.* **2011**, *50*, 5417–5429.
- (17) Vitola, V.; Millers, D.; Bite, I.; Smits, K.; Spustaka, A. Recent Progress in Understanding the Persistent Luminescence in SrAl<sub>2</sub>O<sub>4</sub>:Eu, Dy. *Mater. Sci. Technol.* **2019**, *35*, 1661–1677.