Luminescent Poly(vinylidene fluoride)-Based Inks for Anticounterfeiting Applications

Daniela Maria Correia, Rita Polício, Nelson Pereira, Carmen Rial Tubio, Marita Cardoso, Gabriela Botelho, Rute A. S. Ferreira, Senentxu Lanceros-Méndez, and Verónica de Zea Bermudez

1. Introduction

Counterfeiting is a global ever-growing problem of immense magnitude that represents a menace to security, economy, and health at a worldwide level. Herein, a new luminescent security ink composed of poly(vinylidene fluoride) (PVDF) and the home-made ionic liquid (IL) 1-butyl-3-methylimidazolium tetra(thienyltrifluoroacetonato)europate(III) ([Bmim][Eu(tta)₄]) is reported. The optimized PVDF/[Bmim][Eu(tta)₄] composite is processed by the doctor blade method as a micrometer-thick film invisible under white light, with porous texture. The material exhibits high thermal stability, high chemical stability (inertness with respect to ethanol), high photostability, and intense red emission when excited with long UV radiation (365 nm) with a maximum quantum yield value of 0.10 ± 0.01. A test of the PVDF/[Bmim][Eu(tta)₄] ink screen-printed on a medical N95 protection mask performed under irradiation with white light and with a commercial 365 nm LED demonstrates its suitability to combat fraud. The exciting possibilities offered by PVDF/luminescent IL pair in terms of chemical modification of PVDF (copolymerization or functionalization) and IL (cation type/lanthanide ion/ligand type) for the tuning of the ink properties allow envisaging the production of tailor-made tri- or biluminescent security inks, for authentication purposes.
3M, one of the largest American producers of N95 masks, suffered a counterfeiting attack. As part of an extensive fraud investigation, 1 million counterfeit N95 masks with the 3M stamp were apprehended by agents of the USA Department of Homeland Security.\cite{1}

The development of anticounterfeiting technological platforms is a top priority to protect documents (passports, identification cards, credit cards,DRAMs, and certificates), currency (bank notes), edible products (packaging), pharmaceuticals, and high-value branded products.\cite{2} In this context lanthanide-doped luminescent security inks have attracted much attention.\cite{3–9} Lanthanide ions (Ln$^{3+}$) possess several unique luminescent features of high technological interest: long luminescence lifetimes (μs to ms), fingerprint emission profiles, fine emission bands, and large pseudo-Stokes shifts. However, their low luminescence intensity, due to the parity forbidden nature of 4f–4f transitions, represents a major drawback. A successful strategy to overcome this disadvantage is the complexation of the Ln$^{3+}$ transitions, which in turn undergoes the corresponding radiative emission. The whole process is known as antenna effect.\cite{14,15} Lanthanide complexes, especially β-diketonate chelates, exhibit intense quasi-monochromatic emission, and long emission lifetimes over a wide range of wavelengths (UV/visible/near-infrared [NIR]) upon UV light irradiation. Apart from potential applications in tuneable lasers, luminescence displays, and amplifiers for optical communications, lanthanide complexes are particularly suitable candidates for the production of anticounterfeiting luminescent security elements (tags, markers, security codes/bars, and labels).\cite{16–19} Recently, biluminescent security inks incorporating lanthanide complexes were proposed. Kumar et al.\cite{20} prepared poly(vinyl chloride) (PVC)-based inks incorporating the [Eu(tta)3Phen] (where Eu is europium, tta$^{−}$ is 2-thenyltrifluoroacetate, and Phen is phenantroline) complexes, which exhibited strong red and green emission under 367 and 445 nm excitations, respectively. Andres et al.\cite{21} developed [Eu(dpa)$_3$]$^{3−}$ and [Tb(dpa)$_3$]$^{3−}$ (where Tb is terbium and dpa$^{2−}$ is dipicolinate) complexes which were printed onto paper with a commercially available desktop inkjet printer. In combination with a commercial blue luminescent ink, the red-emitting luminescent ink containing [Eu(dpa)$_3$]$^{3−}$ and the green-emitting luminescent ink containing [Tb(dpa)$_3$]$^{3−}$ reproduced accurate full color images which were invisible under white light and visible upon excitation of a 254 nm UV light. Ramalho et al. proposed novel luminescent QR codes\cite{19,22,23} based on supermodules spatial multiplexed with the triple storage capacity of an analogous size black/white QR code, acting as a smart-tag ensuring restrict access\cite{22,24} and trackability.\cite{19} The supermodules were printed using luminescent low-cost and eco-friendly inks based on organic–inorganic hybrids modified by lanthanides with multiplexed color emission in the orthogonal red–green–blue (RGB) space. The access to the restrict information was attained only under UV irradiation and encrypted for secure transmission.\cite{19}

The incorporation of luminescent security elements in genuine articles for authentication purposes is usually performed through printing of the luminescent inks.\cite{25} Such inks must fulfill a number of requirements: 1) high stability; 2) ease of availability at low cost; 3) ability to disperse luminescent nanomaterials; 4) high luminescent intensity; 5) printability ability; and 6) sticky nature on different surfaces.\cite{19} The knowledge of the ink’s wettability (hydrophobic or hydrophilic behavior) prior to being applied on surfaces is advisable. The choice of the medium is of high relevance for ink fabrication.

Poly(methyl methacrylate) (PMMA),\cite{26} poly(vinyl alcohol) (PVA),\cite{27} and PVC\cite{28} have been widely used to disperse luminescent nanomaterials homogenously and yield suitable colloidal suspensions. Very recently, colloidal suspensions of highly luminescent lanthanide-based coordination polymer molecular alloys for inkjet printing and tagging of technical liquids were reported.\cite{29}

In the current work, we present the production of a nontoxic luminescent security ink with high photo-, thermal, and chemical stability, and strong red emission upon excitation with a commercial LED. To achieve this goal, we synthesized a new ink composed of poly(vinylidene fluoride) (PVDF) (Scheme 1a) doped with the home-made luminescent ionic liquid (IL) 1-butyl-3-methyl imidazolium tetra(2-thenyltrifluoroacetate) europate(III) ([Bmim][Eu(tta)$_3$]) (Scheme 1b). This IL was first introduced by Yi et al.\cite{30} Here, to prepare it we used a two-stage synthesis procedure that resulted in the formation of a precursor

![Scheme 1](https://www.advancedsciencenews.com)
compound sharing the same complex anion: Na[Eu(tta)₄][31] (Scheme S1, Supporting Information). An ink based on the latter compound was also prepared for comparison purposes.

To the best of our knowledge the approach proposed here is unprecedented for two reasons. First of all, reports of luminescent PVDF-based materials are rather scarce in the literature and targeted different technological applications. Sui et al.[32] developed flexible multifunctional composite films based on PVDF and dysprosium (Dy³⁺) with interest for sensing, optoelectronics, and coupling devices. Itankar et al.[33] produced polymeric nanofibers based on PVDF doped with europium chloride (EuCl₃) for photoluminescent fabrics, contributing to the design of smart textiles, protective textiles for soldiers, and medical textiles. More recently, Bispo-Jr. et al.[34] demonstrated the potential of PVDF composites comprising buriti oil and europium oxide (Eu₂O₃) particles in low-temperature sensor platforms. Secondly, although the combination of PVDF with ILs has been explored in the last few years,[35–39] doping PVDF with luminescent ILs had never been tried before.

The rationale for the design of the PVDF/Na[Eu(tta)₄] and PVDF/[Bmim][Eu(tta)₄] composites was threefold: 1) The incorporation of a lanthanide complex into a polymer matrix allows circumventing several critical problems associated with the former compounds, in particular low thermal stability, poor mechanical properties, solubility issues, and photodegradability. Semicrystalline PVDF[32] was chosen on account of its extremely attractive features, which include nontoxicity, excellent chemical and thermal stability, excellent mechanical properties, high optical transparency, and high UV resistance.[40–41] Its piezoelectricity can be considered an additional advantage because it provides extra functionality to the final composite.[41] 2) The introduction of the Ln³⁺ ion as an anionic complex, including four β-diketone ligands instead of the stoichiometric three, aimed at promoting the reduction of quenching effects and the enhancement of quantum efficiency because the first coordination sphere of the Eu³⁺ ion in [Eu(tta)₄]⁻ accommodates eight carbonyl (C=O) oxygen atoms versus only six in Eu(tta)₃.[30,31,42,43] Moreover, this procedure may be beneficial in terms of the photo-, mechanical, and thermal stability. 3) The lanthanide complex anion was introduced as an IL. ILs are environmentally friendly compounds defined as salts entirely composed of ions with melting points usually below 100 °C.[44–46] They have drawn significant attention in the last two decades[47,48] owing to their unique physical–chemical properties, including high negligible vapor pressure, thermal, mechanical, chemical, and electrochemical stabilities, and a wide liquid range.[49–52] Due to their transparency throughout nearly all visible and NIR spectral regions, ILs are particularly useful solvents of optically active compounds.[53,54]

The synthesis of the PVDF/Na[Eu(tta)₄] and PVDF/[Bmim][Eu(tta)₄] composites was straightforward and fast (Figure 1). Large-area films were produced from the corresponding inks by means of the doctor blade method (Figure 1a) and screen-printing (Figure 1b). The morphology, structure, thermal behavior, chemical stability, luminescence properties, and

![Figure 1](https://www.advancedsciencenews.com/2022.3.2100151/2100151-3-of-10.jpg)

**Figure 1.** Synthesis of the luminescent PVDF/Na[Eu(tta)₄] and PVDF/[Bmim][Eu(tta)₄] composites, and film processing of the corresponding inks by a) doctor blade and b) screen-printing.
photostability were evaluated. The optimized composite was tested targeting applications in anticounterfeiting.

The exciting results obtained with PVDF/[Bmim][Eu(tta)₄] allow enlarging the range of applications of PVDF-based composites to the field of anticounterfeiting inks. A large technological potential is offered by the present concept, arising from the combination of two versatile components with high multifunctionality and tuneable design. While the production of PVDF copolymers is well known,[41] the possibility of changing the IL cation and anion chemical composition offers a wide range of possibilities.[55] These inks encompass two major benefits in terms of printing processing: 1) no emitting micro/nanoparticles are incorporated, thus avoiding the nonhomogeneity of many printing solutions resulting from heterogeneous nanoparticles dispersion, particles sedimentation and clogging; 2) due to the presence of the IL, the volatility is null. Owing to these attributes, such inks are particularly attractive for the quick preparation of complex designs at reduced cost and high resolution by ink-jet printing, as they guarantee an extremely high stability of the whole printing process, and ensure the deposition of droplets with controlled volumes in a reproducible way through either continuous or drop-on-demand methodologies.[56] Moreover, the inclusion of more than one lanthanide ion and different ligands expands the usefulness of the PVDF/IL composites for the development of efficient bi- or triluminescent security inks. The different lanthanide ions might be incorporated simultaneously in the same material or introduced separately via multiscreen printing or ink-jet printing.[19] Very recently, the former sort of strategy was successfully demonstrated by some of us to produce an electrochromic device with dual emission in the visible (red color) and NIR spectral regions as a result of the coexistence in the electrolyte of appropriate amounts of [Eu(tta)₄]⁻ and [Nd(tta)₄]⁻ (where Nd is neodymium) species.[57]

2. Results and Discussion

2.1. Structure and Morphology

To evaluate the influence of Na[Eu(tta)₄] and [Bmim][Eu(tta)₄] on the morphology of PVDF, the samples were analyzed by scanning electron microscopy (SEM). PVDF is known to crystallize into a homogeneous nonporous structure when processed from the melt.[39] Figure 2a,b shows that the doped materials exhibit, however, a porous texture. This finding is a manifestation of the occurrence of strong interactions between Na[Eu(tta)₄] and [Bmim][Eu(tta)₄] with the polymer solution in the early stages of the synthesis of the composites which led to phase separation, and subsequent entrapment of the dopant compounds within the pores created upon evaporation of dimethylformamide (DMF). A similar effect was previously reported for PVDF and other polymer matrices incorporating ILs.[58] The cross-sectional SEM images reveal that the incorporation of Na[Eu(tta)₄] into PVDF promoted the development of a composite film thicker (Figure 2a) than that formed with [Bmim][Eu(tta)₄] (Figure 2b).

The topographical 3D atomic force microscopy (AFM) images shown in Figure 2c,d denote that the surface of the PVDF/Na[Eu(tta)₄] film is considerably rougher than that of the

Figure 2. a,b) Cross-sectional SEM and c,d) 3D AFM images of the PVDF/Na[Eu(tta)₄] (left column) and PVDF/[Bmim][Eu(tta)₄] composites (right column), respectively.
PVDF/[Bmim][Eu(tta)4] film (estimated average roughness (R_a) values of 79.4 ± 31.6 and 32.2 ± 6.30 nm, respectively).

Comparison of the attenuated total reflectance/Fourier transform infrared (ATR/FT-IR) spectra of PVDF (Figure 3a, black thick line), Na[Eu(tta)4] (red thin line), [Bmim][Eu(tta)4] (Figure 3a, blue thin line), PVDF/Na[Eu(tta)4] (Figure 3a, red thick line), and [Bmim][Eu(tta)4] (Figure 3a, blue thick line) allows concluding that the addition of Na[Eu(tta)4] and [Bmim][Eu(tta)4] to PVDF did not exert major structural modifications in the host polymer. The characteristic bands of the two most relevant crystalline phases of PVDF (976, 855, 796, and 765 cm⁻¹ for the α phase, and 1232 and 840 cm⁻¹ for the β phase) remained unshifted in the ATR/FT-IR spectra of the doped samples. No significant changes occurred either in the PVDF electroactive β phase content in the presence of both these compounds, as observed from the absorption band intensity at 840 cm⁻¹.

2.2. Thermal Behavior

In the differential scanning calorimetry (DSC) curve of Na[Eu(tta)4] (Figure 3b, red thin line), two broad endothermic peaks centered at 120 °C (onset at 107 °C) and 136 °C are detected. The second melting transition might be associated with the occurrence of a liquid crystalline phase. In contrast, the DSC curve of [Bmim][Eu(tta)4] (Figure 3b, blue thin line) does not exhibit any melting event below 200 °C. The weak, broad, and asymmetric endothermic peak centered at about 77 °C (onset at 55 °C) is associated with the reversible thermotropic gauche/trans transition of the butyl group of the imidazolium ring. It might also receive the contribution of the loss of occluded tetrahydrofuran (THF). In addition, several weak peaks of unknown nature are detected around 120 °C.

The DSC curve of PVDF (Figure 3b, black thick line) exhibits a sharp and strong melting peak centered at 170 °C (onset at 163 °C). In the case of PVDF/Na[Eu(tta)4] and PVDF/[Bmim][Eu(tta)4] (Figures 3b, red and blue thick lines, respectively), the same thermal event persisted unchanged, revealing the presence of pure PVDF in both these samples. However, PVDF/Na[Eu(tta)4] produced a second endotherm centered at 166 °C (onset at 163 °C) (Figure 3b, red thick line), confirming that a fraction of the Na⁺ ions interacted with PVDF leading to the formation of crystalline domains with melting temperature slightly lower than that of pristine PVDF.

The thermogravimetric analysis (TGA) curve of PVDF shows that the degradation of this polymer, associated with the scission of C–H and C–F bonds, was initiated at about 435 °C, with a single, abrupt weight loss of ≈ 60% (Figure 3c, black thick line). At 700 °C, ≈ 20% of this polymer remained to be decomposed. The degradation process of Na[Eu(tta)4] (Figure 3c, red thin line) and [Bmim][Eu(tta)4] (Figure 3c, blue thin line) started already at about 120 °C with a minor weight loss, followed by a dramatic drop at about 250 °C, corresponding to a weight loss of approximately 50%. At the highest temperature examined, about 30% and 40% of these two samples remained to be decomposed, respectively. The thermal decomposition of PVDF/Na[Eu(tta)4] (Figure 3c, red thick line) and PVDF/[Bmim][Eu(tta)4] (Figure 3c, blue thick line) was a multistep process. The first step
of the thermal degradation of both doped samples began around 267 °C, leading to weight loss values of 10% and 20%, respectively. Beyond ≈ 300 °C, the TGA curve of PVDF/Na[Eu(tta)₄] (Figure 3c, red thick line) showed a plateau which persisted until the onset of PVDF decomposition was attained around 465 °C. We may infer from this result that Na[Eu(tta)₄] exerted a stabilizing effect on PVDF in a nonoxidizing atmosphere. In the case of PVDF/[Bmim][Eu(tta)₄] (Figure 3c, blue thick line), the first degradation stage ended at 330 °C and the second one ended with PVDF degradation. At this point, the TGA curves of PVDF and PVDF/[Bmim][Eu(tta)₄] were superimposed. At 700 °C, about 30% and 25% of the composites remained to be decomposed, respectively.

2.3. Optical Properties

The invisible PVDF/Na[Eu(tta)₄] and PVDF/[Bmim][Eu(tta)₄] films and imprinted inks show red emission visible at the naked eye when irradiated with UV radiation (Figure 4, left and right, respectively). Video S1, Supporting Information, illustrates the appearance of the PVDF/[Bmim][Eu(tta)₄] film. To reveal the luminescent label, the UVA (365 nm) excitation was selected, following the methodology used nowadays to detect safety elements in currency notes.[19] For instance, in the case of Euro bills, fibers embedded in the paper in specified areas show different colors under standard UVA irradiation. The EU flag, small circles, and large stars glow yellow on the front of the banknote, whereas on the back a quarter of a circle glows green, and the serial number and a vertical stripe glow red.[62]

The red emission from PVDF/Na[Eu(tta)₄] and PVDF/[Bmim][Eu(tta)₄] arises from the Eu³⁺ lines associated with the 5D₀ → 7F₂,₄ transitions (Figures 5a–d). The hypersensitive 5D₀ → 7F₂ transition is the most intense transition (613 nm) on account of the high polarizability of the chelating β-diketonate tta⁻ ligands.[14] Independently of the excitation wavelength, the PVDF intrinsic emission formed by a broad band in the blue/green spectral region (Figure S1, Supporting Information) is absent, in good agreement with efficient PVDF-to-tta⁻/Eu³⁺ energy transfer.

The excitation spectra were selectively monitored revealing for PVDF/Na[Eu(tta)₄] and PVDF/[Bmim][Eu(tta)₄] (Figure 5e) a broad band with three components at 260, 320, and 390 nm. The latter two components are ascribed to the π-π* electronic transition of the tta⁻ ligands.[63,64] The contribution of the PVDF excited states cannot be discarded as they lie in the UV spectral around 315, 325, 360, and 425 nm. The absence of the intrinsic emission of the PVDF in the emission spectra (Figures 5a–d) is an additional argument supporting PVDF-to-complex energy transfer. The aforementioned four components were previously correlated with the electronic transition occurring in single C–F bonds,[65] involving the promotion of electrons in σ and π-orbitals from the ground state to higher energy states.[66] In both spectra, the intra-4f⁶ lines display negligible relative intensity, reinforcing the efficient ligands-to-Eu³⁺ energy transfer. This situation contrasts with that observed in the excitation spectra of the isolated complexes Na[Eu(tta)₄] (Figure S2b, Supporting Information) and [Bmim][Eu(tta)₄] (Figure S2d, Supporting Information) where the intra-4f⁶ transitions (′F₂₋→D₇₋₂) are clearly discerned, suggesting that the incorporation in the PVDF medium favors the D₇₀ population via ligand sensitization, rather than direct intra-4f⁶ excitation. The decrease in the relative intensity of the intra-4f⁶ lines is an evidence that a more efficient sensitization process is promoted when the complexes are incorporated into PVDF.

The emission decay curves were monitored under UV excitation (388 nm) denoting a single exponential behavior (Figure S3, Supporting information) with lifetime values of 0.188 ± 0.001 ms for PVDF/Na[Eu(tta)₄] and 0.226 ± 0.001 ms for PVDF/[Bmim][Eu(tta)₄]. The different lifetime values may be rationalized based on the following reasoning. The experimental transition probability may be expressed as τ⁻¹ = τₙᵣ⁻¹ + τᵣ⁻¹, where τₙᵣ and τᵣ represent the nonradiative and radiative lifetimes, respectively, and usually, the radiative contribution can be calculated from the relative intensities of the 5D₀ → 7F₀₄ transitions.[67] Considering that the intensities of the 5D₀ → 7F₀₄ transitions are analogous for both materials because the emission spectra overlap (Figure 5a–d), the larger τ value found for PVDF/[Bmim][Eu(tta)₄] may be ascribed to the nonradiative lifetime. In particular, it points out that [Bmim]⁺ contributes to the decrease of the nonradiative transition probability with respect to that of PVDF/Na[Eu(tta)₄]. We note that the lifetime values reported for [Bmim][Eu(tta)₄] and Na[Eu(tta)₄] were 0.521 ms[68] and 0.289 ms[31] respectively.

The absolute emission quantum yield was measured under UV excitation demonstrating maximum values of 0.020 ± 0.002 for PVDF/Na[Eu(tta)₄] and 0.10 ± 0.01 for PVDF/[Bmim][Eu(tta)₄]. The fivefold increase in the [Bmim]⁺-based material is another experimental argument supporting the active role of [Bmim]⁺ in protecting the Eu³⁺ ions from nonradiative channels. The higher absolute emission quantum yield of PVDF/[Bmim][Eu(tta)₄] can be correlated with the formation of a hydrogen bond between the C–H group of a [Bmim]⁺ ion and a C=O group of the tta⁻ ligand, which, according to Yi et al.,[68] leads to the improvement of the energy transfer efficiency due to a decrease in the nonradiative transition.

![Figure 4](image-url)
deactivation. The boost in luminescence and stability in europium β-diketonate materials induced by the formation of hydrogen bonds with imidazolium ions was also reported by other authors.\cite{69,70}

The better optical performance of PVDF/[Bmim][Eu(tta)4] was the rationale to further study its potential as active layer in smart labeling for anticounterfeiting. A relevant issue in this context is the photostability under daylight conditions. The emission intensity dependence under continuous AM1.5G irradiation (Figure S4, Supporting Information) demonstrated that, despite a maximum decrease around 20% in the initial 2 h of irradiation, the emission intensity remained constant in the following 8 h, where nearly 80% of the initial intensity was still detected, ensuring that the red emission was visible under the naked eyes (Figure S4, Supporting Information).

### 2.4. Anticounterfeiting Ability

Prior to evaluating the viability of the optimized luminescent ink for anticounterfeiting, we checked the chemical stability of the PVDF/[Bmim][Eu(tta)4] film by exposing it to ethanol, a polar solvent with antiseptic and disinfectant properties, which might wipe out the ink. The digital images taken before and after the chemical exposure under 365 nm UV light, at different ethanol immersion times (30–90 min) (Figure 6a) revealed that no noticeable changes occurred in the luminescence intensity, and that the patterns remained fully intact.\cite{20} This demonstrates that it is possible to use ethanol to disinfect surfaces coated with the luminescent PVDF/[Bmim][Eu(tta)4] inks without removing the latter or jeopardizing their luminescent features.

An invisible luminescent ink was prepared with a DMF solution of PVDF/[Bmim][Eu(tta)4] with appropriate viscosity\cite{71} (cf., Experimental Section), and subsequently screen-printed (Figure 1b) on a medical N95 brand protection mask. Figure 6b and Video S2, Supporting Information, demonstrate the potential of the PVDF/[Bmim][Eu(tta)4] material as security ink to combat fraud, both as imprinted ink and film, respectively, under white light (invisible) and under irradiation with a low-cost and readily available 365 nm LED (intense red emission).
3. Conclusions

PVDF-based materials doped with two luminescent home-made compounds ([Bmim][Eu(tta)4]) IL and its precursor [Na(Eu(tta)4)] were synthesized for the first time. They were processed as large-area films by doctor blade and or screen-printing onto a substrate. The incorporation of dopants led to the increase in the roughness of the PVDF film but did not globally affect its physical–chemical properties. The PVDF/[Bmim][Eu(tta)4] composite exhibits superior optical properties than PVDF/Na(Eu(tta)4). The relative magnitude of the lifetime/absolute emission quantum yield (measured under UV excitation) values (0.188 ± 0.001 ms/0.020 ± 0.002 and 0.226 ± 0.001 ms/0.10 ± 0.01, respectively) demonstrates that [Bmim]⁺ efficiently protects the Eu³⁺ ions from nonradiative channels. PVDF/[Bmim][Eu(tta)4] displays high photostability, and intense red emission when excited with long UV irradiation (365 nm). In addition, it is thermally stable up to approximately 267 °C and does not dissolve in ethanol. On account of the aforementioned features, PVDF/[Bmim][Eu(tta)4] emerged as an attractive candidate as active layer in smart labeling to combat fraud. We provide here the proof of concept with a test of the PVDF/[Bmim][Eu(tta)4] ink screen-printed on a medical N95 protection mask, upon irradiating the latter with white light (invisible) and with a commercial 365 nm LED (intense red emission). The present PVDF/IL design approach opens exciting new avenues in the very challenging field of anticounterfeiting inks. As far as PVDF is concerned, a noteworthy thermal robustness and the possibility of easily introducing tailor-made chemical modifications represent two of its most attractive assets. Its piezoelectricity, characterized by the development of an electric potential variation in response to an applied mechanical stress and vice versa, can be considered an additional potential advantage to be further investigated because it provides extra functionality to the final composite, allowing to foresee the development of sensing/actuating materials with luminescent/identification ability. The second component, the luminescent lanthanide-based IL, offers countless opportunities in terms of tuning of the chemical–physical properties, which at this early stage remain largely unexplored. For instance, the good solvating ability and inherent green nature of ILs allow us envisaging the replacement of the solvent used in the preparation of the inks proposed here (i.e., DMF) by an appropriate IL enabling in parallel the fine adjustment of the ink’s viscosity. A parameter that should be optimized in future is the reduction of the emitter concentration down to the minimum level that does not jeopardize the luminescence intensity.

4. Experimental Section

Synthesis: Poly(vinylidene fluoride) (PVDF-6010, M_w 30 000–33 0000 Da, Solvay), N,N-dimethylformamide (DMF, 99.5%, Merck), 1-butyl-3-methylimidazolium chloride (Bmim)C (98% Solvionic), europium(III) chloride hexahydrate (EuCl₃·6H₂O, 99.99%, Sigma-Aldrich), 2-thienyltrifluoroacetone (Htta) (99%, Sigma-Aldrich), ethanol (EtOH) (99.8%, Fisher Chemical), tetrahydrofuran (THF, Sigma-Aldrich), and sodium hydroxide (NaOH, Merck) were used as received.

Preparation of the Luminescent ILs: Sodium tetra(2-thienyltrifluoroacetone)europate(III) ([Bmim][Eu(tta)4]) (Scheme 1b) were synthesized on the basis of the procedure described in detail elsewhere (Scheme S1, Supporting Information, and Scheme 1).[21]

The preparation of Na(Eu(tta)4) involved the dissolution of Htta in ethanol, followed by deprotonation with NaOH (molar ratio Htta:NaOH= 1:1) at 50–60 °C for 2 h. To this solution EuCl₃·6H₂O, dissolved in ethanol, was added dropwise (molar ratio Htta:NaOH:EuCl₃·6H₂O = 1:1:0.25). This mixture was kept at 50–60 °C for 1 h and then ethanol was evaporated under reduced pressure in a rotary evaporator. The resulting salt was dried for 3 days at 50 °C.

To obtain [Bmim][Eu(tta)4], Na(Eu(tta)4) was reacted with [Bmim]Cl in THF under nitrogen atmosphere (molar ratio Na(Eu(tta)4)·[Bmim]Cl=1:1). The sodium chloride (NaCl) salt formed was removed by precipitation and centrifugation (3 times at 3000 rpm) of the solution. [Bmim][Eu(tta)4], obtained as a yellow powder, was dried for several hours. Its structure (Scheme 1b, Supporting Information) was confirmed by elemental analyses: C₄₀H₃₇Cl₂EuF₁₂N₂Na₂O₁₁S₄. Calculated: C, 35.67; H, 2.77; S, 9.52. Found: C, 35.66; H, 2.66; S, 9.63.

Preparation of the Composite Films: The nondoped and doped PVDF-based films were prepared by doctor blade following the guidelines reported previously (Figure 1a).[21] A neat PVDF film was obtained through dissolution of PVDF in DMF (15.85 wt%) at room temperature and under magnetic stirring. The resulting solution was cast onto a glass substrate and allowed to dry at 210 °C in an air oven for 10 min to ensure DMF evaporation. To prepare the doped films, a similar procedure was adopted. Prior to polymer dissolution, 20 wt% of Na(Eu(tta)4) and [Bmim][Eu(tta)4] was dissolved in DMF. Transparent composite PVDF/[Bmim][Eu(tta)4] and PVDF/[Bmim][Eu(tta)4] films with a thickness of ~42 and 46 μm, respectively, were produced.

Printing of the Luminescent Inks: The viscosity of the luminescent PVDF/Na(Eu(tta)4) and PVDF/[Bmim][Eu(tta)4] inks was first adjusted (1.08 Pa·s at shear rate of 100 s⁻¹) through the addition of DMF (Figure 1b). The inks were then screen-printed on a 100 μm-thick polyethylene terephthalate (PET) film (Dupont Teijin) using a semiautomatic printing equipment (model DX-3050D from DSTAR) and a printing speed of 0.3 m s⁻¹. A polyster screen (circular pattern) with a mesh of 100 threads per cm was used at 3 mm distance from the substrate. Prior to printing the substrates were cleaned with ethanol to remove any particle. After being printed, the inks were cured at 80 °C for 1 h in an electric Convection Forced Oven (JP Selecta 2005163).

SEM: The morphology of PVDF and of the PVDF-based composite films were evaluated with SEM using a SEM Hitachi S-4800 with an accelerating voltage of 5 kV. For the SEM analysis, the samples were previously fractured using liquid nitrogen, and coated with a thin gold layer by means of sputter coating with a Polaron, model SC502.

AFM: Surface morphology and roughness of the PVDF and of the PVDF-based films (20 μm × 20 μm) were studied by AFM using a Nano-Observer CSI. The provided average roughness (R_a) values represent the arithmetic average of the deviations from the center plane of the sample.

ATR/FT-IR Spectroscopy: ATR/FT-IR spectra of the samples were acquired at room temperature in a JASCO FT/IR-4100 in ATR mode. The spectra were collected in the 4000–600 cm⁻¹ range by averaging 64 scans at a resolution of 4 cm⁻¹.

DSC: DSC measurements performed using a Perkin-Elmer DSC 8000 apparatus. A mass of ~4.5 mg was placed in a 30 μL aluminum pan. The latter was hermetically sealed and the thermogram was recorded. The samples were heated from 30 to 200 °C at a heating rate of 10 °C min⁻¹.

TGA: TGA measurements were performed using a TGA/SDTA 851e Mettler Toledo apparatus operating between 25 and 800 °C at a heating rate of 20 °C min⁻¹. The purge gas was high purity nitrogen supplied at a constant 10 mL min⁻¹ flow rate.

Photoluminescence Spectroscopy: The photoluminescence spectra were recorded at room temperature with a modular double-grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to a R928 Hamamatsu.
The authors declare no conflict of interest.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
The manuscript was written with the contributions of all authors. All authors approved the final version of the manuscript.

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