1. Introduction

Biluminescence refers to compounds able to simultaneously emit fluorescence and phosphorescence. These emitters are also referred to as dual-state emitters.[1] Such materials have, of late, been in the focus of an intense research effort due to the large and versatile set of potential applications: oxygen sensing in biological media,[2,3] anti-counterfeiting,[4] delayed electroluminescence,[5] etc. Nowadays, most of widely developed phosphorescent emitters are based on organometallic complexes containing precious metals such as iridium or platinum.[6] Such metals enable a strong spin–orbit coupling necessary to ensure proper intersystem crossing (ISC) from $S_1$ to $T_n$ and efficient room-temperature phosphorescence (RTP). But they tend to be quite expensive and potentially harmful. Consequently, the development of competitive biluminescent pure-organic derivatives seems essential. Nonetheless, to achieve RTP from pure organic molecules implies to overcome three major challenges: First ensure an efficient ISC to populate the triplet state, second suppress as much as possible any energy dissipation through vibrational motion, and third avoid quenching of the triplet state by molecular oxygen. Recently, several groups have introduced different approaches to tackle those issues.

ISC can be favored by incorporating carefully chosen chemical units, such as carbonyl units, or heavy atoms, such as halogens.[7–11] But in the past years many phosphorescent halogen-free small conjugated organic molecules not satisfying El-Sayed rule have also been reported. It is reported that for highly symmetrical planar aromatic derivatives, where the fluorescence decay rate $k_f$ is reduced due to symmetrically forbidden transition dipoles in the $S_1$-$S_0$ transition, the intersystem crossing is therefore the more favorable transition, leading to pronounced phosphorescence.[12]

The suppression of vibrational motion and protection against molecular oxygen can be carried out either by trapping the phosphors in crystalline structures or by embedding them in rigid host matrices.[13–15] Since the crystallization process can prove daunting and necessitates stringent conditions, our attention is focused on the latter systems. Several times it has been reported that RTP of amorphous organic derivatives in host matrices is obtained because of host-guest and/or guest–guest intermolecular interactions to further rigidify the phosphor. In one example, an amorphous pure-organic derivative hexa-(4-carboxyl-phenoxy)-cyclotriphosphazene functionalized with six carboxylic acid...
moieties is developed to enable the formation of H-bonds with the PVA host. Here it is shown that those host–guest interactions are necessary for the phosphorescence emission to appear. At first weakly emissive, the casted films need to be exposed to strong ultraviolet (UV) irradiation (254 nm, 65 min), leading to an increased rigidification of the host through the formation of cross-linked bonds, to reach intense and long-lived phosphorescence. However, this long-duration and high photon energy post-treatment is unwanted and prevents practicable applications of such systems. As described in the work above, H-bonds intermolecular host-guest interactions are of the utmost importance either for the appearance of the phosphorescence or for the enhancement of previously existent luminescent properties (such as quantum yield or lifetimes).

In parallel our group recently published a new method to obtain perfectly smooth and transparent thin-films which can be used as programmable luminescent tags (PLTs) under aerated atmosphere. Here, the films are prepared in two steps: after dissolution of the organic biluminescent derivatives in anisole and mixing with PMMA (poly(methyl methacrylate)), the solution is spin coated on quartz substrates. The PMMA films are then covered by an Exceval layer, which is a water-soluble ethylene vinyl alcohol (EVOH) polymer. This second layer, which acts as an oxygen barrier, is essential for the luminescence properties of our films and for their use in aerated media.

2. Synthesis and Experimental Methods

To further simplify the fabrication process of the films, that is, to suppress the use of organic solvents, we decided to develop a water-soluble derivative able to display the biluminescent properties mentioned above. Hence, this material can be dissolved directly into the oxygen barrier material, leading to a reduced device complexity combined with easier and less harmful processing. One well-known biluminescent molecule is tetraphenylbenzidine (TPB). Here, TPB was redesigned with 4 carboxylic acid moieties introduced on the side parts to lead to TCATPB (Figure 1). The carboxylic acid units have been introduced to induce the needed water solubility. Additionally, this design is beneficial to maximize RTP because these units can also be expected to interact through multiple H-bonds with the Exceval polymer. Important for future use scenarios, where the exposure to the functional materials represents a possible danger, TPB is known as a not hazardous substance or mixture according to the globally harmonized system; we expect the same for TCATPB.

TPB was synthesized according to a previously detailed procedure. TCATPB was synthesized in three steps. First, 4,4′-bis(methoxycarbonyl)triphenylamine 1 was synthesized from aniline and methyl-4-bromobenzoate through a double Buchwald–Hartwig palladium coupling. 2 was obtained from 1) following an oxidative coupling with methanesulfonic acid and chloranil in dichloromethane. This step was followed by a saponification using a large excess of LiOH in a THF/water medium leading to the desired target with excellent yields (overall yield 67%) (Figure 1) (see Supporting Information for more details).

For the following study three samples were prepared. Samples S-1 and S-2 were made following the old procedure: the molecules TPB or TCATPB are respectively dissolved in anisole and mixed in a solution of PMMA. Then 150 µL are collected and spin coated on quartz plate (Figure 2A). These samples are designed as control systems where no host-guest H-bonds interactions are possible. For the third sample S-3:TCATPB is dissolved in a water/KOH solution before been mixed in an aqueous solution of Exceval and spin coated (Figure 2A). In this case the deprotonated carboxylate function enable the use of Exceval as host and has the possibility to engage in strong intermolecular H-bonds. In each case, the dopant is dispersed in a host matrix with a constant concentration of 17 mm. (see Supporting Information for detailed procedures). The spectroscopic properties of each sample were investigated and measurements were performed under ambient conditions unless otherwise specified. A first look at both Figure 2B and Table 1 proves that the introduction of the four carboxylic acid moieties has a moderate impact on the absorption and emission characteristics. TPB absorption spectrum displays two absorption bands in the UV with a maximum located at 351 nm.

3. Results and Discussion

TCATPB shows a single absorption band, fitting the most red-shifted band of TPB and shares the same absorption maximum. The fluorescence spectra of TPB and TCATPB have the same shape but the TCATPB spectra are accompanied with a 11 nm (68 cm⁻¹) red-shift compared to TPB (λ_em max = 396 nm). The phosphorescence spectra are also almost identical for the three samples with a common maximum centered around 525 nm. Thus, the triplet energy is not impacted by the carboxylic acid

Figure 1. A) Structures of both derivatives: TPB and TCATPB. B) Synthesis of TCATPB with yields.
units which is in accordance with previous observations suggesting that the triplet energy is mainly affected by modifications performed on the core of such molecules.[19] The study of their photoluminescence quantum yield (PLQY) [21] (fluorescence $\Phi_{\text{Fluo}}$ and phosphorescence $\Phi_{\text{Phos}}$) leads to the first noticeable differences linked to the embedding media. Whereas the $\Phi_{\text{Fluo}}$ value barely fluctuates whatever the conditions and the host:guest system, $\Phi_{\text{Phos}}$ is substantially altered. In PMMA, $\Phi_{\text{Phos}}$ is slightly higher for S-2 (4.1%) compared with S-1 (3.0%). However, the use of Exceval as a host (S-3) leads to a further increase of $\Phi_{\text{Phos}}$ up to 6.2% (Table 1).

The analysis of the lifetime values[22] also suggests the ability of TCATPB to engage in H-bonds intermolecular interactions. Indeed, the lifetimes of TPB or TCATPB in PMMA are very similar, with values of 590 and 585 ms, respectively. But the lifetime of TCATPB in Exceval displays a 100 ms (Table 1) increase compared to the control systems. Thus, the sample S3 displays both the longest lifetime and highest $\Phi_{\text{Phos}}$ compared with both control samples S1 and S2. This ascertainment tends to confirm the presence of host-guest H-bonds interactions between TCATPB and Exceval. Those interactions which would be responsible for an increased rigidification of the molecular structure through host:guest interactions and would further suppress non-radiative deactivations of the triplet manifold can explain both to the increase of the lifetime values and phosphorescence quantum yield, in accordance with earlier reports.[16] As mentioned earlier, strong UV radiation is sometimes needed to activate efficient RTP.[17] In our case, no particular post treatment is needed to obtain strongly emissive films, be it in PMMA or Exceval. Out of curiosity, and since Exceval and PVA structures are similar, we exposed our films to strong UV which led to no change in the previously discussed characteristics (Figure S1, Supporting Information). We further investigated the impact of the concentration of the emitter molecules on the luminescent properties of the thin-films. For this study, five samples were prepared with different doping concentrations: 0.2, 0.5, 2.0, 5.0, and 10.0 wt% for each case: PMMA:TPB/Exceval, PMMA:TCATPB/Exceval, and Exceval:TCATPB. Once again absorption and emission

Table 1. Summary of the maximum of absorption and emission (fluorescence and phosphorescence) of the different targets: Sample S-1: PMMA:TPB/Exceval, Sample S-2: PMMA:TCATPB/Exceval, and sample S-3: Exceval:TCATPB along with the measured fluorescence and phosphorescence lifetimes and quantum yields (see Supporting Information for details).

| Sample | $\lambda_{\text{Abs}}$ [nm] | $\lambda_{\text{Fluo}}$ [nm] | $\lambda_{\text{Phos}}$ [nm] | $\tau_{\text{Fluo/Phos}}$ [ns/ms] | $\Phi_{\text{Fluo}}$ [%] | $\Phi_{\text{Phos}}$ [%] |
|--------|----------------|----------------|----------------|----------------|----------------|----------------|
| S-1    | 351            | 396            | 528            | 0.5/590        | 31.7 a)        | 3.0 a)        |
| S-2    | 354            | 407            | 523            | 1.0/580        | 32.1 a)        | 4.1 a)        |
| S-3    | 351            | 407            | 528            | 0.8/670        | 31.8           | 6.2           |

a) Measured under nitrogen of samples without Exceval top layer.

Excitation wavelength 365 nm. All measurements were performed under air unless otherwise specified.
spectra, $\Phi_{\text{Phos}}$ and phosphorescent lifetimes were measured (Figures 3 and 4). As expected, the absorption strengths of the films keep on growing with increasing concentration of the dopants (Figure 4, top). In contrast, the emission, $\Phi_{\text{Phos}}$ (Figure 4, bottom) and phosphorescence lifetimes (Figure 4, middle) do not follow such a simple trend. Regarding the fluorescence, in every case, an increase of the dopant concentration leads to a red-shift of the emission maxima and a broadening of the spectra which is specific for emitter aggregation. On the contrary, the phosphorescence spectra (Figure 3, insets) are not significantly modified but their intensity which, in a first instance raises, starts to decrease for concentration of 5.0 wt% and above. This can be explained by both the rise of triplet-triplet annihilation (TTA) which can no longer be considered as negligible and by more possible motion among the emitter species, causing an effective de-rigidification. For the samples dispersed in PMMA, lifetimes and $\Phi_{\text{Phos}}$ values are quite stable up to a dopant concentration of 2.0 wt% (Figure 4). TPB and TCATPB are characterized by mean $\Phi_{\text{Phos}}$ and lifetime values of 2.8% and 573 ms, and 4.2% and 590 ms, respectively. Those values are dropping at the highest concentrations (5.0 and 10.0 wt%) with respective values of 1.7% and 302 ms for TPB and 2.4% and 464 ms for TCATPB at 10 wt%. The thin-films from TCATPB mixed with Exceval are much more sensitive to the dopant concentration. For the lowest concentration (0.5 wt%), lifetimes up to 800 ms with a $\Phi_{\text{Phos}}$ of 8.8% were measured, which are quite substantial values for phosphorescent organic molecules.

However, the weak absorbing ability induces a low brightness of the systems. The lifetime and $\Phi_{\text{Phos}}$ values steadily decrease to reached 616 ms and 3.8%, respectively, for the 10.0 wt% sample. Overall, the 2 wt% samples display the best equilibrium between all the previously discussed characteristics regardless of the host and dopant used.

Therefore, the 2 wt% films containing TCATPB (either dispersed in PMMA or Exceval) were chosen in the following to study their emission properties in more detail and to fabricate various samples (thin films and 3D objects for demonstration).

As discussed in the beginning of the article, the bilayers materials, constituted of doped PMMA covered with Exceval can be
Indeed, the Exceval top layer enables the control of the oxygen concentration inside the PMMA film which lead to the possibility to encrypt information with high resolution (Figure 5C). An intense LED or a laser is used to locally consume the molecular oxygen contained inside the emitting layer letting the phosphorescence appears after some time on a precise area.

But those films can only be used so for short term display, (few hours to several days) since the phosphorescence signal tends to disappear after some time due to the slow diffusion of oxygen through the Exceval layer into the PMMA matrix.[18] This observation limits their use for applications which require both immediate and steady luminescence emission over days, months or years as for the protection of official papers such as passports or bank notes.

Accordingly, the films containing TCATPB dispersed in PMMA need to be activated to reveal their phosphorescence properties, as can be seen in Figure 5A. The full phosphorescence of the film is obtained after 40 s of continuous irradiation with a 365 nm UV lamp (2.3 mW cm⁻²). Of course, this activation depends on both the chosen wavelength and the intensity of the excitation light. Surprisingly, for the monolayer materials, only constituted of TCATPB doped Exceval, no activation is needed: the strong phosphorescence appears instantly at room temperature and under ambient atmosphere (Figure 5A). The luminescent properties of the films (phosphorescence intensity and lifetime) were monitored up to 9 weeks and were globally preserved (Figure 3; full details in Supporting Information). No specific precautions were taken for the preparation or storing of the samples. The differences perceived may result from deviations in the error range of the measurement set-up, for example, in sample mounting, ambient conditions, or excitation source stability deviations. (Figure 5B). It appears that, even though oxygen can penetrate through an Exceval layer, as highlighted in the PMMA host/Exceval bilayers system,[18] it seems unable to reach the emitting species inside the designed based only on Exceval:TCATPB layer. Thus, the phosphorescence of films based only on Exceval, used as both oxygen barrier and host matrix, is preserved and can be detected at will for a long time. Similar results, revealing a stability of the phosphorescence signal up to several months, have only been reported for a special system where a phosphorescent dopant is dispersed in a cholesterol matrix.[24,25] However, this material system is not so easy to handle for large scale applications. In our system, stability up to 2 months has been demonstrated (see Supporting Information for more details), in an easily processable, environmental and user-friendly matrix. The doped polymer could even be conveniently used for 3D printing as shown Figure 5D. Even after heating at 190 °C during the printing process, the material is not damaged, and the phosphorescence properties are preserved (see Supporting Information). This type of process was realized with a very low doping concentration of 0.1 wt% and keeps on displaying strong and long-lasting luminescence. This new system appears to be perfectly suited for the previously unreachable applications such as anti-counterfeiting.

4. Conclusion

In summary, we have reported the rational design, synthesis, and analysis of a new biluminescent emitter (TCATPB) able to be involved in non-covalent intermolecular H-bonds interactions and soluble in both organic and aqueous media. This
enabled the investigation of its phosphorescence characteristics after dispersion in either PMMA or in a water-soluble ethylene vinyl alcohol (Exceval) polymer. It was highlighted that the nature of the host had a direct impact on the phosphorescence properties (lifetimes and quantum yields). Indeed, the ability of the dopant to be involved in intermolecular H-bondings with the Exceval host, lead to an increase of both phosphorescence lifetime and $\Phi_{\text{Phos}}$ compared with PMMA where such interactions are impossible. Then the biluminescent qualities of both films (TCATPB in PMMA covered with Exceval and TCATPB in Exceval) were compared and very different trends were highlighted leading to a large variety of completely distinct and complementary accessible applications. In PMMA host the phosphorescence of films needs to be activated by direct illumination of the sample for a couple of seconds, leading to the ability to activate only locally the phosphorescence signal. However, after some time the signal disappear and will need to be reactivated, all previous printed information being lost. Thus, this first system can be used for short-term information process nor in the storage conditions. Strong phosphorescence associated with long lifetime were preserved even after more than one month making those films suitable for information storage or data encryption. Furthermore, the system can be used in 3D printing to obtain phosphorescent materials of all kind and shapes.

**Keywords**

3D printing, biluminescence, pure-organic derivatives, room-temperature phosphorescence, water soluble

---

**Supporting Information**

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

**Acknowledgements**

This project received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No. 679213 “BILUM”).

**Conflict of Interest**

The authors declare no conflict of interest.

**Author Contributions**

M.L. and H.T. contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

---

[1] S. Reineke, N. Seidler, S. R. Yost, F. Prins, W. A. Tisdale, M. A. Baldo, *Appl. Phys. Lett.* **2013**, *103*, 093302.

[2] G. Zhang, M. G. Palmer, W. M. Dewhirst, C. L. Fraser, *Nat. Mater.* **2009**, *8*, 747.

[3] S. Wu, Z. Pan, R. Chen, X. Liu, *Long Afterglow Phosphorescent Materials, SpringerBriefs in Materials*, Springer, Berlin **2017**.

[4] Y. Katsurada, S. Hirata, K. Totani, T. Watanabe, M. Vacha, *Adv. Opt. Mater.* **2015**, *3*, 1726.

[5] R. Kabe, N. Notsuka, K. Yoshida, C. Adachi, *Adv. Mater.* **2016**, *28*, 655.

[6] Y. Kawamura, K. Goushi, J. Brooks, J. J. Brown, H. Sasaki, C. Adachi, *Appl. Phys. Lett.* **2005**, *86*, 071104.

[7] W. Zhao, Z. He, J. W. Y Lam, Q. Peng, H. Ma, Z. Shuai, G. Bai, J. Hao, B. Z. Tang, *Chem 2016*, *1*, 592.

[8] Z. He, J. W. Y Lam, W. Zhao, Q. Peng, H. Ma, G. Liang, Z. Shuai, B. Z. Tang, *Nat. Chem.* **2017**, *8*, 416.

[9] Y. Xie, Y. Ge, Q. Peng, C. Li, Q. Li, Z. Li, *Adv. Mater.* **2017**, *29*, 1606829.

[10] L. Xia, H. Fu, *Chem. - Eur. J.* **2019**, *25*, 714.

[11] S. Cai, H. Shi, D. Tian, H. Ma, Z. Cheng, Q. Wu, M. Gu, L. Huang, Z. An, Q. Peng, W. Huang, *Adv. Funct. Mater.* **2018**, *28*, 1705045.

[12] S. Hirata, *Adv. Opt. Mater.* **2017**, *5*, 1700116.

[13] A. Forni, E. Lucenti, C. Botta, A. Cariati, *J. Mater. Chem. C* **2018**, *6*, 4603.

[14] C. Salas Redondo, P. Kleine, K. Roszeitis, T. Achenbach, M. Kroll, M. Thomschke, S. Reineke, *J. Phys. Chem. C* **2017**, *121*, 14946.

[15] K. Junai, R. Kabe, C. Adachi, *Adv. Mater.* **2018**, *30*, 1800365.

[16] S. M. Kwon, D. Lee, S. Seo, J. Jung, J. Kim, *Angew. Int. Chem. Ed.* **2014**, *53*, 11177.

[17] Y. Su, Z. F. S. Phua, Y. Li, X. Zhou, D. Jana, G. Liu, Q. W. Lim, W. K. Ong, C. Yang, Y. Zhao, *Sci. Adv.* **2018**, *4*, eaas9732.

[18] M. Gmelch, H. Thomas, F. Fries, S. Reineke, *Sci. Adv.* **2019**, *5*, eaau7310.

[19] M. Louis, H. Thomas, M. Gmelch, A. Haft, F. Fries, S. Reineke, *Adv. Mater.* **2019**, *31*, 1807887.

[20] S. Maddala, S. Mallick, P. Venkatakrishnan, *J. Org. Chem.* **2017**, *82*, 8958.

[21] C. J. De Mello, H. F. Wittmann, R. H. Friend, *Adv. Mater.* **1997**, *9*, 230.

[22] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd ed., Springer, Berlin **2008**.

[23] S. Reineke, T. C. Rosenow, B. Lüssem, K. Leo, *Adv. Mater.* **2010**, *22*, 3189.

[24] S. Hirata, K. Totani, J. Zhang, T. Yamashita, H. Kaji, R. S. Marder, T. Watanabe, C. Adachi, *Adv. Funtct. Mater.* **2013**, *23*, 3386.

[25] S. Hirata, K. Totani, H. Kaji, M. Vacha, T. Watanabe, C. Adachi, *Adv. Opt. Mater.* **2013**, *1*, 438.