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Benefits of using BODIPY–porphyrin dyads for developing deep-red lighting sources†

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The syntheses, as well as the photophysical and electrochemical characterization, of two novel BODIPY–porphyrin dyads and their first application in lighting schemes are provided. The benefits ascribed to their unique features, namely (i) a good electronic alignment, (ii) a remarkable efficient energy transfer, and (iii) excellent film morphology, lead to deep-red lighting devices with stabilities of around 1000 h and efficiencies of 0.13 Lm W⁻¹.

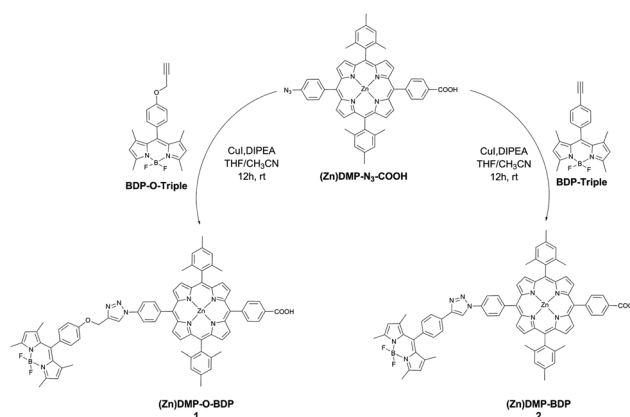
Neutral free-base and metallo-porphyrins have been successfully used in organic light-emitting diodes (OLEDs) and solar cells.^{1–5} This field is mainly driven by their ease of modification to enhance light-harvesting and photoluminescence (PL) properties based on an efficient energy and/or electron transfer process from moieties attached at the periphery to the porphyrin core.

This feature of dyad-like porphyrins is of utmost relevance for lighting schemes, since it could open a new avenue to decouple charge transport and emission processes by only using one active compound. This is more critical in light-emitting electrochemical cells (LECs) than in OLEDs, in which the charge transport is not performed by the emitter, but by a multilayered device architecture.^{6,7} In LECs, the presence of mobile ions in the active single-layer assists the charge injection process, while the charge transport, electron–hole recombination, and emission processes occur *via* the emitter.^{8–10} Thus, to define clear guidelines to design LEC materials that are intrinsically able to decouple charge transport and emission is a challenge in the field.^{8–10}

As an alternative, the host–guest approach by (i) using OLED-host materials doped with ionic liquids,¹¹ (ii) mixtures

of iTMCs,^{12–14} and (iii) using ionic-based small-molecule charge transporters,¹⁵ has been explored in LECs to date. All these approaches show the typical problem of the host–guest strategy, that is, to determine the optimum doping level and effective doping range, which are typically very low and narrow, respectively. Here, a low doping level causes an inefficient energy transfer (ET) from the host to the guest, resulting in a poor color purity and device performance, while a high concentration of the guest leads to the a strong self-quenching of its emission and a prominent phase separation in thin films. The latter are paramount in determining the overall device performance.

Herein, we report on a new concept to decouple charge transport and emission in small-molecule LECs by using only one active compound mixed with an ionic electrolyte. To this end, we took advantage of our mature experience in the synthesis of BODIPY–porphyrin dyads and their implementation in solar cells^{16–19} to further expand their application to lighting schemes, in which the above-mentioned drawbacks of the host–guest approach are circumvented. In detail, two BODIPY–porphyrin dyads have been designed – Scheme 1. On one hand, these dyads fulfill all of the key requirements, such as (i) the energy alignment of the electronic levels between the BODIPY and the porphyrin evokes in a charge



Scheme 1 Synthesis of BODIPY–porphyrin dyads **1** and **2**.

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trapping process at the porphyrin, (ii) there is an almost quantitative ET process from the BODIPY to the porphyrin, (iii) there is a lack of phase separation between both components in thin films as they are linked, and (iv) porphyrins are considered as one of the best candidates for developing narrow emission deep-red OLEDs.^{2,20–27} On the other hand, LECs are ideal devices to demonstrate our concept, as they are single layer devices based on a single active component, allowing to settle clear relationships between molecular design and device performance.^{8–10} In addition, this work provides, to the best of our knowledge, the first example of using this family of dyads in lighting schemes, demonstrating the benefits that state from their unique features.

The synthesis of **1** and **2** is shown in Scheme 1 and details are provided in the ESI.† In short, two new dyads have been prepared through “click” reaction. (Zn)DMP-N₃-COOH was derived from (Zn)DMP-N₃-COOCH₃ though hydrolysis of the ester group,²⁸ while the BDP-Triple and the BDP-O-Triple were prepared according to previously published procedures.^{29,30} The composition of **1** and **2** has been verified by NMR spectroscopy – see Fig. S1–S18 (ESI†). The most noticeable feature is the appearance of the characteristic proton of the newly formed triazole ring at 9.29 and 9.76 ppm for **1** and **2**, respectively.

To investigate the molecular and electronic structures of **1** and **2**, cyclic (CV) and square wave (SQ) voltammetry and computational studies were performed – see the ESI.† The redox features of the dyads and the reference compounds – *i.e.*, the BODIPYs and Zn-porphyrin – are summarized in Table S1 (ESI†), and a representative cyclic voltammogram is shown in Fig. S19 and S20 (ESI†). As an example, **1** shows two reversible oxidation waves at 0.98 and 1.34 V and two reversible reduction waves at –1.18 and –1.4 V. A direct comparison with the references suggests that the first oxidation wave is located at the porphyrin, while the second oxidation is centered at BODIPY. Thus, an efficient hole trapping process in the porphyrin is expected under device operation conditions. In contrast, the assignment of the reduction in the dyads is more elusive, as both references show a similar reduction value at around 1.14 eV – Table S1 (ESI†). In an attempt to elucidate the nature of the reduction process, calculations based on density functional theory (DFT) were performed – see Fig. S21–S24 (ESI†). The electronic structure of the ground state of the dyads consists of a highest occupied molecular orbital (HOMO) located at the porphyrin and separated from HOMO–1 (~0.1 eV) related to the BODIPY moiety. Similar to what has been noted in the CV assays, the dyads feature the first three lowest unoccupied molecular orbitals (LUMO, LUMO+1 and LUMO+2) very close in energy (~0.1 eV), but LUMO and LUMO+1 being located at the porphyrin unit. The same trends are valid for **2** – see the ESI† and Table S1. Hence, this energy alignment suggests that under device operation conditions charge carrier trapping may occur at the porphyrin.

Steady-state and time-resolved spectroscopy assays were performed to shed light on the ET process in the dyads. The absorption and emission features of the references, as well as **1** and **2** are shown in Fig. 1. The absorption spectra of both dyads are the superimposition of the UV-Vis spectra of Zn-porphyrin and BODIPY, namely an intense Soret band in the 420–430 nm

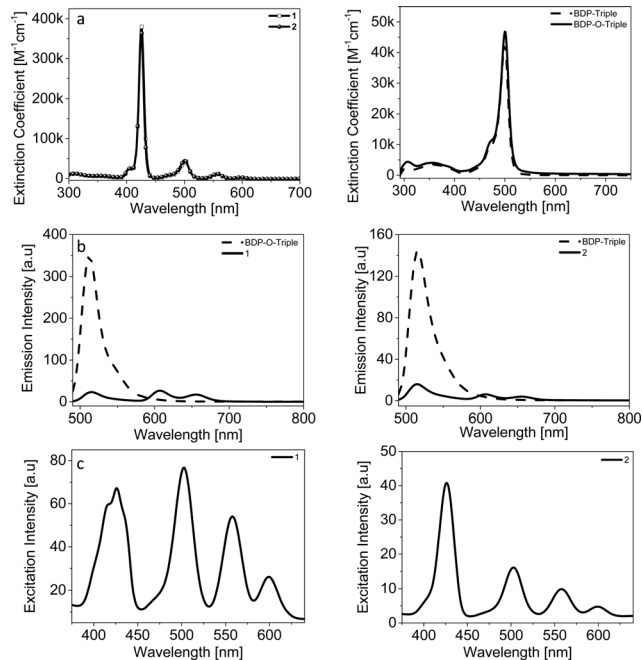


Fig. 1 (a) Absorption spectra of **1** and **2** (left), as well as the BODIPY (right) in THF. (b) Emission spectra of **1** and **2**, as well as the BODIPY in THF upon excitation at 490 nm. (c) Excitation spectra of **1** and **2** in THF when monitoring the emission at 660 nm.

range and two Q-bands in the 555–600 nm range together with a sharp band centered at 500 nm, respectively – Fig. 1a. The first insights into the ET process came from steady-state fluorescence and excitation assays – Fig. 1b and c. Fig. 1b shows that both BODIPY references and the dyads show an intense fluorescence centered at ~510, as well as 610 and 660 nm ($\lambda_{\text{exc}} = 490$ nm). More importantly, both dyads in isoabsorbing solutions compared to the BODIPY reference show an almost quantitative quenching of the BODIPY emission at 510 nm – 98 and 91% for **1** and **2**, respectively – without affecting the Zn-porphyrin emission in terms of, for example, the photoluminescence quantum yields – Fig. 1b and Table S1 (ESI†). In addition, selective excitation of the BODIPY unit in the dyads – *i.e.*, $\lambda_{\text{exc}} \sim 500$ nm – shows a strongly quenched BODIPY-based emission accompanied by the Zn-porphyrin-based emission. In perfect agreement with the latter, the excitation spectra of the dyads when monitoring at 660 nm reveals a pronounced BODIPY absorption feature at ~500 nm – Fig. 1c. This is a clear indication of ET from the $^1\pi-\pi^*$ excited state of the BODIPY to the lower lying singlet excited state of the Zn-porphyrin.

To solidify this notion, transient absorption measurements were performed – see the ESI.† Upon photoexcitation of **1** and **2** at 505 nm, the formation of a transient absorption was dominated by a transient bleaching at around 510 nm, mirror imaging the ground state absorption of BODIPY and a weak transient absorption in the NIR at 1100 nm. These are a good match with those observed for the BODIPY reference – Fig. S25 (ESI†), corroborating the formation of the first excited BODIPY singlet state. But for both dyads this transient feature rapidly decays – *i.e.*, lifetimes of 82 (**1**) and 60 ps (**2**) – compared to 3750 ps for the BODIPY

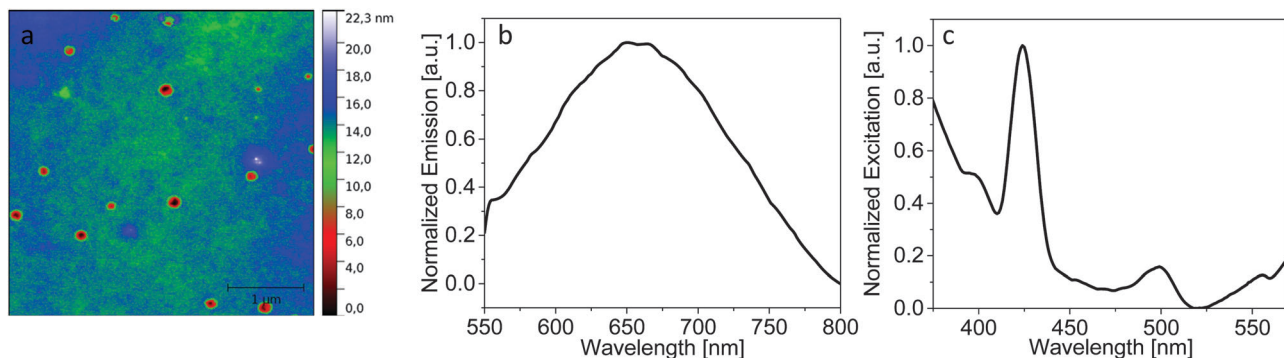


Fig. 2 (a) AFM images of **1** films with a thickness of 110 nm. (b) Emission spectra of **1** films upon excitation at 490 nm. (c) Excitation spectra of **1** films when monitoring the emission at 660 nm.

reference, giving rise to a new set of transient absorptions maximizing at 455, 535, 585, 690, and 835 nm. This indicates the formation of the first excited singlet state located at the porphyrin moiety of the dyads. This finding provides solid evidence for the proposed singlet-singlet ET from the BODIPY to the Zn-porphyrin. Moreover, the ET in **2** occurs quicker than in **1**. This is expected since in **2** both moieties are closely located to each other than in **1**. Finally, the Zn-porphyrin singlet first excited state decays with a lifetime of 2600 ps (**1**) and 2800 ps (**2**) into the corresponding Zn-porphyrin triplet manifold – Fig. S26 and S27 (ESI†).

Next, the morphology and photoluminescence (PL) features of films based on the dyads and the Zn-porphyrin as reference were examined – Fig. 2 and Fig. S28 (ESI†), as well as Table S1 (ESI†). On one hand, the morphology was investigated *via* Atomic Force Microscopy (AFM). The dyad films are homogeneous with no particular aggregation or phase separation features – Fig. 2a. In contrast, the Zn-porphyrin films show zones with small aggregation features, which can act as charge trapping and/or emission quenchers under device operation conditions. On the other hand, the dyad PL behavior is similar to that noted in solution. In detail, they show a broad emission band at around 660 nm with the lack of BODIPY emission upon excitation at 490 nm – Fig. 2b. Please note that the broad and featureless emission band is likely related to the aggregation of the compounds as the film mainly consists of the active component. Indeed, the lack of BODIPY features could be attributed to the poor emission of BODIPY in thin films, but the excitation spectra of the dyad films upon monitoring the Zn-porphyrin emission intensity clearly show a contribution of the BODIPY excitation – Fig. 2c. Thus, the ET from BODIPY to Zn-porphyrin is considered for both solution and films.

As a final step, we took advantage of the excellent features of the dyads to prepare deep-red lighting sources based on the LEC concept. To this end, devices with active layers based on mixtures of an ionic electrolyte matrix with the dyads and the references were investigated – see the ESI.† The latter were prepared onto glass substrates coated with an indium tin oxide (ITO), which were modified by a 100 nm thickness of poly-(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). To finalize the devices, aluminum was evaporated as a top

cathode – see the ESI.† The devices were analyzed using current-voltage-luminance (LIV) assays and were driven using a pulsed current scheme based on a block-wave at 1000 Hz and a duty cycle of 50% – Fig. 3.^{8–10}

To provide a first insight into the electroluminescence (EL) features, LIV assays were performed – Fig. S29 (ESI†). In general, all of the devices feature a moderate low charge injection and turn-on voltages due to the presence of mobile anions. More interesting is, however, the sound differences when analyzing the nature of the EL response between reference and dyad devices. As shown in Fig. 3, BODIPY and Zn-porphyrin devices show yellowish green and deep-red emission with EL spectra located at 545, as well as 630 and 660 nm and color coordinates $x = 0.34/y = 0.53$ and $x = 0.67/y = 0.30$, respectively. This indicates

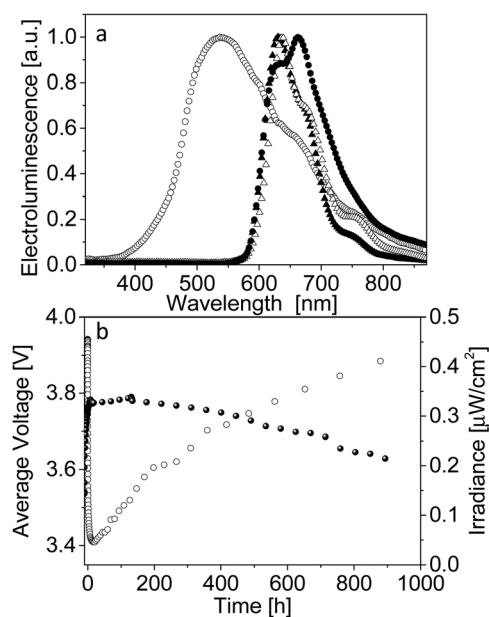


Fig. 3 (a) Normalized EL spectra obtained at 10 V of devices with BODIPY (open circles) and Zn-porphyrin (close circles) references, as well as **1** (open triangles) and **2** (close triangles) devices. (b) Average voltage (open symbols) and irradiance (full symbols) vs. time of **1** device driven by a pulsed current using a block wave at a frequency of 1 kHz with a duty cycle of 50% and an average current of 10 mA.

that for both compounds the EL process arises from an electronic excited state similar to that noted for PL assays. Strikingly enough, devices prepared with the dyads show an EL response purely related to the porphyrin moiety emission 630 and 670 nm with color coordinates $x = 0.67/y = 0.31$ – with a 3–5-fold increase in terms of the maximum irradiance and luminous efficiency compared to the Zn–porphyrin reference device – Fig. S29 (ESI†). Furthermore, we prepared a 1 : 1 molar ratio Zn–porphyrin:BODIPY device that only shows emission from the BODIPY – Fig. S29 (ESI†). Hence, it seems that only in the case of the dyads both the charge trapping and ET processes are beneficial, highlighting the need for having linked both parts.

Finally, the EL response over time of the dyad devices was performed by driving the device at an average pulsed current of 10 mA. In line with the few reports on SM-LECs,^{31–34} Fig. 3 depicts the typical device response features of ionic-based lighting devices. In particular, the voltage required is initially high, providing an immediate EL response – *i.e.*, a turn-on time on the sub-second regime. Then, the applied bias reduces over time followed by an increase of the irradiance until reaching its maximum value, featuring extrapolated lifetimes of around 1000 h. Noteworthy, it is important to state that the device efficiency (0.13 Lm W^{-1}) is comparable to that of state-of-the-art lighting devices based on Zn–porphyrin derivatives.^{21,22} Hence, one must consider that a porphyrin design by, for example, attaching more BODIPYs and/or bulky groups will lead to enhanced efficiencies.

In summary, this work provides the syntheses and comprehensive photophysical, electrochemical, and theoretical characterization of two novel BODIPY–porphyrin dyads. The latter feature (i) an electronic alignment, in which the BODIPY and porphyrin moieties can be considered as the host and the guest, respectively, (ii) the efficient ET process from the BODIPY to the porphyrin, and (iii) the homogenous film morphology that contrasts with that of the references. Herein, we show how to exploit them to expand their application to lighting schemes. As such, small-molecule LECs were for the first time fabricated with these dyads. The device performance indicates that the EL features of the BODIPY–porphyrin family are only ascribed to that of the porphyrin moiety, leading to devices with remarkable stabilities. This might be ascribed to the benefits of decoupling charge transport and emission in LECs. Overall, this work provides a new concept to improve device performance by means of an easy-to-do molecular design.

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