BODIPY-Pt-Porphyrins Polyads for Efficient Near-Infrared Light-Emitting Electrochemical Cells

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1. Introduction

The search for deep-red and near-infrared (NIR) small molecule emitters for solid-state lighting devices is an ongoing quest. Among the solid-state lighting approaches, light-emitting electrochemical cells (LECs) are of particular interest as they consist of a simple structure, that is, a layer of ionic and neutral electroluminescent materials with ionic additives, sandwiched between two electrodes. The working mechanism involves the initial formation of electric double layers (EDLs) upon applying external bias, leading to an efficient charge injection from air stable electrodes and the subsequent formation of p- and n-doped regions flanking the emitting undoped (i) region, in which hole–electron recombination forms radiative excitons. This working mechanism is named p–i–n junction. Importantly, the device performance does not strictly depend on the electrode material, allowing for low-cost and high-throughput solution-based fabrication under ambient air.

While several red emitters have already been implemented in LECs, the best NIR-emitting LECs rely on ionic transition metal complexes. Here, porphyrins could stand out due to their easy synthesis and modification toward NIR emission. Indeed, several groups have recently shown interesting advances in porphyrin-based LECs. In 2016, our group first reported on the effect of the metal core (Zn$^{2+}$, Sn$^{2+}$, Pd$^{2+}$, and Pd$^{2+}$), of porphyrins on the LEC figures-of-merit, achieving red-emitting devices that were either stable and low efficient (Zn-porphyrin) or highly efficient but poorly stable (Pt-porphyrin). In detail, Pt-porphyrin-based LECs exhibited good efficiencies caused by the heavy metal-induced phosphorescent emission, but also a pronounced electrochemical degradation, leading to low stabilities of a few minutes. This issue can be overcome using a host–guest system to decouple charge transport and exciton recombination.

In this context, the chemical binding of host–guest units in a dyad-type structure is desired over simple physical blending toward stable and efficient LECs. For instance, we reported on intramolecular host–guest systems binding 1 BODIPY (BDP) unit to the periphery of a Zn-porphyrin that yielded deep-red LECs with one order of magnitude enhanced stabilities (>1000 h) keeping the low irradiance of the reference devices with the Zn-porphyrin reference.
realizing NIR emission ($\approx 900$ nm) along with good irradiances of $36 \mu\text{W cm}^{-2}$ and stabilities of tens of minutes.$^{[15]}$

In view of these earlier reports, the molecular design of low-energy emitters following a host–guest strategy is very appealing toward realizing highly performing NIR LECs. Herein, we present the design of a series of Pt-porphyrin-BDP polyads by connecting 1, 2, 3, and 4 BDP units to the central porphyrin macrocycle through tetra-fluorophenyl triazole spacers (i.e., $\text{PtBDP-x-y}$ in which $x$ is the number of BDP and $y$ is the number of F atoms) along with two reference Pt-porphyrins that bear either zero ($\text{Pt-0}$) or 20 F atoms at their peripheral substituents (Pt-20) (Figure 1). The rationale of this design is twofold. On one hand, the functionalization with fluorine and/or hexyloxy groups is an effective strategy to control the electronic properties that are further correlated to the LEC performance. Thus, we can elucidate clear relationships about the effect of coupling/decoupling charge transport process between the BDP and Pt-porphyrin units and the ionic conductivity in thin film via dipole–dipole interactions$^{[11]}$ on the device behavior. On the other hand, the covalent binding of increasing BDP units to the Pt-porphyrin core allows us to maximize the energy transfer from the BDP to the Pt-porphyrin in thin films.$^{[30–32]}$ This is supported by comprehensive spectroscopic, electrochemical, and microscopic studies that enable the correlation between molecular structure and electroluminescence features in LECs, namely, 1) the number of BDP units and the efficient energy transfer to the Pt-porphyrin to increase device efficiency, 2) the number of F atoms and the ionic conductivity in thin films allowing a well-balanced charge injection and transport to realize high irradiances and stable operation at low currents, and 3) the changes in the electronic structure toward an efficient host:guest design to decouple charge transport and recombination processes toward stable devices.

Among the members of this family, the best performing emitter was the $\text{PtBDP-2-8}$, exhibiting remarkable irradiances of $80 \mu\text{W cm}^{-2}$, efficiencies of $0.12 \text{lm W}^{-1}$, and stabilities of $1 \text{h or 11 mJ}$, along with a NIR electroluminescence output centered at 780 nm. Overall, this work provides important guidelines for the design of highly performing porphyrin-based NIR LECs, highlighting how their rich chemical functionalization allows us to control charge transport, energy transfer, and ionic conductivities.

Figure 1. Chemical structures of reference compounds BDP, Pt-0 and Pt-20 as well as the new $\text{PtBDP-x-y}$ polyads.
2. Results and Discussion

2.1. Synthesis

The synthesis of the PtBDP-1-4 is shown in Scheme 1. Porphyrin 1 was metallated with Pt, providing derivative 2, which was subsequently reacted with sodium azide in order for the para-fluorine atom to be replaced by the desired azide group, forming azide-porphyrin 3. The final step was a click reaction between the azide bearing intermediate 3 and the alkyne-substituted BDP compound, using CuI complex as the catalyst in a THF/CH$_3$CN (1:1) mixture, yielding PtBDP-1-4. This particular BDP compound was selected based on our previous study of Zn-porphyrin-BDP dyads, where the LECs with this nonconjugated (triazolyl)methoxy group between the BDP and the porphyrin outperformed the dyad, in which the two components were directly linked through the triazole ring.

The experimental approach regarding PtBDP-2-8 is shown in Scheme 2. At first, the trans-\text{A}_2\text{B}_2 porphyrin derivative 6 was prepared via a condensation reaction between dipyrromethane 4 and aldehyde 5 under mild conditions and the use of two oxidative reagents (BF$_3$OEt$_2$ and DDQ). The following two steps involved the insertion of the platinum metal center in the macrocycle core (7) and a nucleophilic aromatic substitution (SNAr) reaction for the substitution of para-fluorine atoms with $\text{-N}_3$ groups (8), forming the PtBDP-2-8. Finally, a copper-catalyzed (CuI) azide–alkyne cycloaddition was performed in a THF/CH$_3$CN (1:1) mixture, producing the PtBDP-2-8.

The first step for the preparation of PtBDP-3-12 was the synthesis of tri-pentafluorophenyl-porphyrin 10 (Scheme 3). For this reaction, aldehydes 5 and 9 along with dipyrromethane 4 were stirred vigorously in a CHCl$_3$ solution for 44 h with the consecutive addition of BF$_3$OEt$_2$ (24 h) and DDQ (20 h). Then, we performed a metalation (porphyrin 11) and a SNAr reaction (azide-containing intermediate 12). The last step was a CuAAC reaction, but with modified experimental conditions. More specifically, the tri-azide-substituted Pt-porphyrin 12 was connected with the alkyne-BDP compound in the presence of sodium ascorbate and CuSO$_4$·5H$_2$O in a mixture of N,N-dimethylformamide (DMF) and water under heating at 40 °C. The reaction was completed after 3 days providing the desired product (PtBDP-3-12) with an 11% isolated yield.

Finally, the synthesis of the PtBDP-4-16 hybrid is shown in Scheme 4. The reference porphyrin derivative Pt-20 reacted with NaN$_3$ to form the symmetric tetra-$\text{N}_3$-porphyrinic compound 13.
Lastly, for the preparation of PtBDP-4-16 hybrid a click reaction between porphyrin 13 and BDP was performed, using the same experimental conditions as previously stated in the case of PtBDP-3-12.

The synthetic routes followed for the preparation of the reference porphyrins are shown in Scheme 5. In short, aldehyde 5 along with pyrrole underwent a typical Alder–Longo condensation reaction producing the symmetrical porphyrinic compound 14. The following step is mutual for the synthesis of both reference complexes. Particularly, the free base porphyrins 14 and 15 were metallated with platinum(II) chloride in benzonitrile under reflux, yielding the desired products Pt-0 and Pt-20, respectively.

The successful formation of all the intermediate and final products was verified through matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry and nuclear magnetic resonance (NMR) spectroscopy (1H, 19F, and 13C) (Figure S1–S51, Supporting Information). Concerning the reference derivatives, their NMR spectra show typical peaks that correspond to symmetrical Pt-metallated porphyrins. In the 1H NMR spectra of the final polyads, the characteristic proton signal of the formed triazole ring appeared at 8.33, 8.34, 8.36, and 8.38 ppm for PtBDP-1-4 (Figure S13, Supporting Information), PtBDP-2-8 (Figure S28, Supporting Information), PtBDP-3-12 (Figure S42, Supporting Information), and PtBDP-4-16 (Figure S48, Supporting Information), respectively. Finally, a characteristic quadruple BDP-based signal at approximately –146.3 ppm was detected in the 19F NMR spectra of the final hybrids, along with two additional signals (around –134.2 and –147.9 ppm), originating from the ortho- and meta-fluorine atoms of the porphyrin’s peripheral phenyl groups.

2.2. Spectroscopic Studies in Solution and Thin Films

The UV–vis absorption features of the reference and polyads in both solution (THF) and thin films used for devices, namely, blends of each emitter with trimethylol propane ethoxylate (TMPE), and lithium triflate (LiOTf) in a mass ratio of emitter:TMPE:LiOTf 1:0.15:0.03, were studied (Figure 2) and Table 1. The ionic matrix was selected owing to the encouraging results obtained in the prior art. The BDP shows the typical sharp and structured absorption band centered at 500 nm and an almost featureless spectrum in the high-energy region. However, the absorption spectra in thin films consist of two broad bands centered at 500 and 500 nm. This suggests that the films are highly aggregated, and they, are, indeed, formed of crystalline domains as confirmed by optical microscopy images (Figure S52, Supporting Information). In stark contrast, the reference Pt-porphyrins exhibit a similar absorption band.

![Scheme 4](image)

**Scheme 4.** Synthetic approach for PtBDP-4-16. Conditions: i) NaN3, DMF, 60 °C, 2 h; ii) CuSO4·5H2O, Sodium ascorbate, DMF/H2O, 40 °C, 5 d.

![Scheme 5](image)

**Scheme 5.** Synthetic scheme for the preparation of Pt-0 and Pt-20. Conditions: i) pyrrole, propionic acid, 3 h, reflux; ii) PtCl2, PhCN, reflux, 3 h.

![Figure 2](image)

**Figure 2.** Absorption spectra of the reference and the polyad compounds (see legend) in THF 10⁻⁵ M (left) and thin-film onto quartz (right).
shape in thin film and solution. They consist of a Soret band centered around 400 nm and well-structured Q-bands peaking at 500, 540, and 580 nm (Figure 2). Importantly, there is no absorption features in the range of 450–480 nm, in which the BDP can exclusively be excited. In addition, the presence of the fluorine atoms in Pt-20 leads to red-shifted absorption features, while the absorption spectra of the thin films are slightly red-shifted compared with those in solution. Indeed, atomic force microscopy (AFM) images confirm that both films show a homogeneous morphology containing some aggregation features (Figure S53, Supporting Information). On the other hand, the PtBDP dyads feature a homogeneous film morphology without any aggregation that results in very similar absorption features in both solution and thin films (Figure 3). In short, characteristic peaks of both the Pt-porphyrin (400 nm and two less intense bands at 550 and 580 nm) and the BDP (500 nm) moieties are clearly detected. Thus, the absorption spectra can be described as a superimposition of the UV–vis spectra of the polyad constituents. As expected, the only difference in the absorption spectra of the final polyads concerns the intensity

| Compound | $\lambda_{abs}$ \[^b\] [nm] | $\lambda_{abs}$ \[^h\] [nm] | $\lambda_{em}$ \[^b, c\] [nm] | $\tau$ \[^b\] [ns] | $\tau$ \[^h\] [ns] | PLQY \[^b, d\] [%] | $k_r \times 10^9$ [s$^{-1}$] | $k_{nr} \times 10^9$ [s$^{-1}$] |
|----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| BDP      | 495            | -              | 510$^h$        | 3.5$^h$        | -              | -              | -              | -              |
| Pt-0     | 388            | 390            | 650, 729, 789  | -              | 8.2            | 4.8$^g$        | 5.8            | 115.3          |
| PtBDP-1-4| 401            | 404            | 511, 557, 653, 729 | 3.1            | 9.7            | 3.8            | 3.9            | 104.4          |
| PtBDP-2-8| 400            | 402            | 515, 552, 653, 729 | 1.3            | 9.9            | 3.5            | 3.5            | 96.3           |
| PtBDP-3-12| 399           | 399            | 515, 555, 654, 718 | 0.9            | 11.8           | 4.5            | 3.8            | 80.6           |
| PtBDP-4-16| 400           | 392            | 515, 552, 654, 718, 775 | 13.1           | 4.3            | 3.3            | 3.3            | 73.4           |
| Pt-20    | 402            | 407            | 650, 708, 788  | -              | 32.6           | 9.4$^g$        | 2.9            | 27.9           |

$^a$THF solution; $^b$Thin film; $^c\lambda_{exc} = 490$ nm; $^d\lambda_{exc} = 490$ nm, $\lambda_{exc} = 400$ nm.

Figure 3. AFM images (10 × 10 μm) of the active layers of PtBDP-1-4 (top left), PtBDP-2-8 (top right), PtBDP-3-12 (bottom left), and PtBDP-4-16 (bottom right) as used in devices.
of the BDP-centered peak that tends to increase in relation to the increasing number of the peripheral BDP units that are connected to the porphyrin core (Figure 4).

As far as the photoluminescence in thin film is concerned, BDP and Pt-porphyrin references show the typical well-structured emission bands peaking at 500–600 and 600–800 nm, respectively (Figure 4 and S54, Supporting Information). The excitation spectra of Pt-0 and Pt-20 films show an intense peak around 510 nm, highlighting the possibility of an efficient energy transfer from the BDP to the porphyrin core in the polyads. Indeed, excitation at the BDP moiety ($\lambda_{\text{exc}} = 450$ nm) in PtPBD films leads to a dual emission centered at 515 nm (BDP) and at 650, 720, and 775 nm (Pt-porphyrin core) (Figure 4). Noteworthy, the high-energy emission band intensity decreases with respect to the overall emission spectrum upon increasing number of BDP units (e.g., 1 for PtBDP-1-4 and 0.11 for PtBDP-4-16) (Figure 4). In addition, normalizing the data to the counts at $\lambda_{\text{em}} = 515$ nm shows a gradual increase in the emission intensity up to tenfold for PtBDP-4-16 compared with PtBDP-1-4 (Figure 4). Noteworthy, all these experiments were performed in thin films, in which the molecular conformations are frozen, and the energy transfer may lose efficiency compared with those in solution. However, it is in our interest to characterize the emitters in forms that resemble our devices.

To further corroborate the energy transfer process in thin films, the average excited-state lifetimes $<\tau>$ upon excitation at 395 nm and probing at 515 nm were measured. The BDP reference films showed a $<\tau>$ of 3.5 ns, while PtBDP arrays with 1, 2, and 3 BDP units showed a gradual decrease from 3.1, 1.3, and 0.9 ns, respectively. PtBDP-4-16 did not show any detectable emission features at 515 nm and, in turn, any $<\tau>$ value (Table 1 and Figure S55, Supporting Information). The $<\tau>$ values related to the phosphorescence processes were investigated exciting with a microsecond lamp ($\lambda_{\text{exc}} = 400$ nm) and probing at 650 nm. The Pt-0 and Pt-20 films showed $<\tau>$ values of 8.2 and 32.6 $\mu$s, respectively. The longer $<\tau>$ in Pt-20 is ascribed to a correspondent increase in the number of fluorine atoms in its periphery, which may stabilize the excited state via negative hyperconjugation.[41] Indeed, the PtBDP films showed an increasing trend in $<\tau>$ upon increasing the number of F atoms (Table 1 and Figure S56, Supporting Information).

Finally, the Pt-0 and Pt-20 films showed photoluminescence quantum yield (PLQY) ($\lambda_{\text{exc}} = 490$ nm) values of $\approx$5% and 10%, respectively. In contrast, the PLQY of the PtBDP films ($\lambda_{\text{exc}} = 490$ nm) was around 4%, as a more efficient energy transfer leads to an enhanced Pt-porphyrin emission along with a concomitant increase in the number of photon absorbed from the BDP units.
Nevertheless, these PLQY values render them as appealing candidates for NIR LECs compared with those previously reported.\[42\]

### 2.3. Electrochemical Characterization in Solution and Thin Films

The electrochemical properties of all reference compounds (Pt-0, Pt-20, and BDP) as well as the final polyads (PtBDP-1-4, PtBDP-2-8, PtBDP-3-12, and PtBDP-4-16) were determined by cyclic and square wave voltammetry in freshly distilled and deoxygenated dichloromethane with tetrabutylammonium hexafluorophosphate (TBAPF\(_6\)) as supporting electrolyte (Figure S57–S62, Supporting Information). All the electrochemical data are shown in Table 2.

In line with the literature, BDP presents one reversible oxidation and one reversible reduction peak at +1.22 and −1.24 V versus saturated calomel (SCE), respectively. Those peaks are present in the cyclic voltammograms of all final PtBDP polyads (Figure 5). The quasi-reversible redox waves that were shown for the two reference porphyrins (Pt-0 and Pt-20) were located at different regions due to the effect of their different peripheral substituents. Particularly, Pt-0 presents two oxidation waves at +0.84 and +1.46 V and a reduction wave at −1.64 V (Figure S57, Supporting Information), while Pt-20 bearing 20 F atoms to the redox peaks were significantly anodically shifted (Figure S58, Supporting Information), namely, one oxidation (+1.50 V) and one reduction wave (−0.90 V). Accordingly, the porphyrin-based redox potentials for the polyads also exhibit anodic shifts in relation to the increasing number of F atoms. This is ascribed to the electron withdrawing properties of the fluorine atoms, resulting in a shift of the oxidation and reduction processes at higher and lower voltages, respectively (Figure 5).

Table 2. Summary of the electrochemical and EIS features of the reference compounds and PtBDP polyads. Electrochemical redox data were recorded in degassed CH\(_2\)Cl\(_2\) versus SCE with TBAPF\(_6\) as electrolyte. Ferrocene (FcH/FcH\(^+\)) (E\(^{1/2}\)\(_{\text{FcH}}\) = 0.47 V) was used as the internal standard.

| Compound | Ox1BP [V] | Ox1Pur [V] | Ox2Pur [V] | Red1BP [V] | Red1Pur [V] | Red2Pur [V] | \(\sigma \times 10^{-8} \text{S m}^{-1}\) |
|----------|-----------|-----------|-----------|------------|------------|------------|-------------------|
| BDP      | 1.22      | −         | −         | −1.24      | −          | −          | −                 |
| Pt-0     | −         | 0.84      | 1.46      | −1.24      | −1.64      | −          | 5.93              |
| PtBDP-1-4 | 1.23      | 1.07      | 1.64      | −1.22      | −1.50      | −          | 3.21              |
| PtBDP-2-8 | 1.23      | −         | −1.23     | −1.77      | −1.08      | −1.58      | 0.91              |
| PtBDP-3-12 | 1.19     | 1.47      | −1.22     | −1.08      | −1.58      | −          | 0.52              |
| PtBDP-4-16 | 1.18     | 1.55      | −         | −0.86      | −          | −          | 0.97              |
| Pt-20    | −         | 1.50      | −         | −0.90      | −1.39      | −          | −                 |

Figure 5. Monitoring the anodically shifted redox potentials in the cyclic voltammograms of our reported systems according to the increasing number of the peripheral fluorine atoms. Green box indicates the stable BDP-centered oxidation and reduction waves, while purple and magenta asterisks highlight the shifts of the first porphyrin-based oxidation and reduction potentials, respectively.

While hole and electron transport processes should be expected via Pt-porphyrin and BDP units, respectively. In stark contrast, a single reversible oxidation and reduction wave at +1.23 and −1.23 V were noted for PtBDP-2-8, indicating that features from both BDP and the Pt-porphyrin core are very close and, in turn, hole and electron injection might occur in the BDP moiety as expected in a good hostguest system (Figure 6 and Figure S60, Supporting Information). Conversely, this is not the case for PtBDP-3-12 that showed the first reversible oxidation and reversible reduction peaks at the BDP and the Pt-porphyrin core, respectively (Table 2 and Figure S61, Supporting Information). Thus, hole and electron transport processes will be ruled by the BDP and Pt-porphyrin units, respectively. Likewise, PtBDP-4-16 presents a BDP-centered reversible first oxidation at +1.18 V, and a reversible reduction at −0.86 V that is related to the Pt-porphyrin core (Figure S62, Supporting Information) because it is almost the same with the value recorded for Pt-20 (−0.90 V).

These values were used to calculate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels through the formula \(E_{\text{HOMO/LUMO}} = \)
and Pt-porphyrin reference compounds. With the exception of PtBDP-1-4, whose HOMO energy levels are the same to the BDP one, indicating that hole injection and transport processes will take place at this moiety. In contrast, the LUMO of PtBDP-1-4 and PtBDP-2-8 also corresponds to the BDP unit, while for PtBDP-3-12 and PtBDP-4-16 their LUMO energy levels are located at the Pt-porphyrin due to the larger number of tetra-fluorophenyl triazole linkers. Thus, only PtBDP-2-8 shows the best electronic structure to ensure an efficient host-guest scheme that should result in the most stable devices—vide infra.

Finally, electrochemical impedance spectroscopy (EIS) assays were conducted in devices with a standard sandwich architecture (ITO/PEDOT:PSS (70 nm)/active layer (70 nm)/Al) to determine the ionic conductivity ($\sigma$) at 0 V—see Experimental Section and Figure S63 and S64, Supporting Information, for the circuit model and Nyquist plots as well as Table S1, Supporting Information. The reference Pt-porphyrin devices showed $\sigma$ values of $5.3 \times 10^{-8}$ S m$^{-1}$ (Pt-0) and $9.7 \times 10^{-9}$ S m$^{-1}$ (Pt-20). This is expected due to the strong interaction between fluorine and the lithium atoms present in the electrolyte. Indeed, there is a clear trend in the PtBDP series, in which the $\sigma$ reduces from $3.2 \times 10^{-8}$ to $3.1 \times 10^{-8}$ to $9.1 \times 10^{-9}$ and to $5.2 \times 10^{-9}$ S m$^{-1}$ upon increasing the number of F atoms (Table 2). Thus, the increase in the number of the peripheral fluorine atoms may lead to less efficient charge injection and transport affecting the device efficiency—vide infra.

2.4. Device Characterization

As indicated earlier, LECs were prepared with a standard sandwich architecture and measured at a pulsed driving current of 20 mA (Figure 7). The figures-of-merit of devices are shown in Table 3. Note that the BDP device was discarded due to the crystalline morphology of the films. In addition, films consisting of the physical blended BDP and Pt-porphyrin reference compounds did not show a homogenous film morphology suitable for device fabrication.

Regardless of the type of emitter, the devices showed the standard LEC behavior as derived from the static EIS assays in the range of 0–4 V. Here, the LEC resistance ($R_{LEC}$) was plotted against the applied bias, revealing two different slopes, namely, one below the bandgap of the emitters, i.e., 0–2.5 V, and one above it, i.e., 2.5–3 V. The earlier shows a monoeponential slope that resembles the unique feature of LECs with respect to the EDL formation that ultimately lowers the charge injection resistance. In detail, it reduces until 1.5 V and reaches a plateau up to 2.5 V. At applied voltages beyond the bandgap of the emitter, a linear slope is related to an effective ohmic charge injection process that causes the growth of the doped layer. As a result, the electrical resistance in the nondoped region of the film is further reduced, as this region is getting thinner.

In line with the static EIS, all the devices showed a similar electroluminescence behavior at pulsed current functioning conditions, that is, a high initial voltage that decreases to a minimum plateau as the p- and n-doped regions are formed and the recombination becomes autosustained in the i zone (Figure 7). Finally, the average voltage can arise over time depending on the degradation mechanism and the morphology of the active layer. In parallel, the irradiance rises over time until it reaches its maximum value, and it slowly decreases until it reaches half of its maximum. This is defined as lifetime ($\tau_{1/2}$). Owing to the differences in irradiance values between devices, the device stability is better compared considering the total emitted energy ($E_{tot}$) of the devices until the irradiance reaches one-fifth of its maximum.

Pt-0- and Pt-20-based LECs feature similar irradiances (65 and 48 $\mu$W cm$^{-2}$), luminous efficiencies (0.09 and 0.07 lm W$^{-1}$), and external quantum efficiencies (EQE) (0.014% and 0.010%) (Table 3). In both devices, the electroluminescence spectra cover the region from 600 to 900 nm (Figure 8). The fresh spectrum shows a well-defined vibrational structure peaking at ≈660 and 790 nm, while the dominant contribution over time is the low-energy emission feature. Compared with the prior examples in porphyrin-based LECs, e.g., 36 $\mu$W cm$^{-2}$ at $\lambda_{max}$ = 900 nm, these devices already exhibited a remarkable NIR electroluminescence.

All the devices based on the PtBDP polyads outperformed the reference devices with both Pt-porphyrins, highlighting the benefits of this molecular design (Table 3 and Figure 7). In detail, the PtBDP devices featured a decreasing trend in irradiance and luminous efficiency upon increasing the number of BDP units and F atoms (Figure 9 and Table 3). This is in line with the reduction in ionic conductivity (Table 2) that leads to higher average voltages to hold the applied current. In addition, the stability ($\tau_{1/2}$) maximizes for the devices based on PtBDP-2-8 and linearly reduces within the series (Figure 8 and Table 3). Thus, the most balanced devices, showing irradiances of 83 $\mu$W cm$^{-2}$, efficiencies of 0.12 lm W$^{-1}$, EQEs of 0.03%, and stabilities of 11.1 h, are met using the PtBDP-2-8 compound (Figure 7 and Table 3). This is expected considering the energy levels and the optimized energy transfer processes in thin films (Figure 4 and 6). Within the series, PtBDP-2-8 exhibits an energy alignment that allows both hole and electron transports to take place at the BDP moiety and an efficient energy transfer from the BDP to the Pt-porphyrin core, retaining a sufficiently high ionic conductivity—vide supra.

Similar to the reference Pt-porphyrin devices, the electroluminescence spectra show a well-defined emission band located at 660, 720, and 790 nm, with the latter peak’s intensity increasing...
Table 3. Figures-of-merit of devices based on Pt-0, Pt-20, and PtBDP polyads.

| Compound | \( \text{Irradiance}_{\text{max}} \) [\( \text{μW cm}^{-2} \)] | \( t_{\text{max}}^{\text{a}} \) [h] | \( t_{\text{1/2}}^{\text{b}} \) [h] | Efficiency [ImW\(^{-1}\)] | EQE\(^{\text{c}} \) [%] | \( E_{\text{tot}}^{\text{d}} \) [mJ] | \( \lambda_{\text{max}} \) [nm] |
|----------|--------------------------|----------------|----------------|-----------------|----------------|----------------|----------------|
| Pt-0     | 65.9                     | 0.07           | 0.20           | 0.09            | 0.014          | 2.37           | 656, 765       |
| PtBDP-1-4| 96.8                     | 0.03           | 0.25           | 0.15            | 0.067          | 4.04           | 608, 656, 724, 777 |
| PtBDP-2-8| 82.8                     | 0.01           | 0.81           | 0.12            | 0.030          | 11.1           | 600, 656, 722, 778 |
| PtBDP-3-12| 55.7                     | 0.52           | 1.1            | 0.06            | 0.022          | 10.7           | 610, 656, 778   |
| PtBDP-4-16| 49.1                     | 0.03           | 1.0            | 0.06            | 0.012          | 8.81           | 528, 600, 656, 791 |
| Pt-20    | 48.2                     | 0.10           | 0.92           | 0.06            | 0.010          | 7.39           | 542, 610, 656, 778 |

\(^{\text{a}}\text{Turn on time: time to reach the maximum luminance; }^{\text{b}}\text{Lifetime: time to reach 50\% of the maximum luminance; }^{\text{c}}\text{EQE: it describes the ratio of emitted photons per injected electrons; }^{\text{d}}\text{Total emitted energy: calculated from integration of the radiant flux of the device versus time from } t = 0 \text{ to } t = t_{1/2}.\)
Electroluminescence spectra of 2021 polyads (right, see legend) and 2000188 (10 of 12) © 2021 The Authors. Advanced Photonics Research published by Wiley-VCH GmbH (left, see legend), and www.adpr-journal.com

Pt-BDP

780 nm. This result is attrib- for of 11 mJ, and at a low-energy electrolumines-

ition as shown by Gao

mizing driving scheme using, for example, intermittent opera-

the radiative rates of the vibrational states of the excited state

could be related to interference effect from the device optical

structure, self-absorption of doped species, and the changes in

the radiative rates of the vibrational states of the excited state

carried out by the effects of external and local electrical fields.

Overall, the high irradiance values (e.g., 83 μW cm−2 for

PtBDP-2-8) are considerably high for a pure NIR emission, while

the limited stability of the material could be overcome by optimizing driving scheme using, for example, intermittent operation as shown by Gao’s group.31

3. Conclusions

We report on the synthesis, characterization, and LEC device application of a series of NIR-emitting Pt-porphyrin-based systems including two reference Pt-por and four PtBDP polyads, in which the number of BDP groups and fluorine atoms gradually increases. This rules the energy transfer process from BDP to Pt-porphyrin core, the electronic structure toward an effective host-guest scheme, and the ionic conductivity in thin films. This was established via a one-to-one comparison of the spectroscopic and electrochemical features in accordance to the device behavior within this series. In general, the PtBDP polyad design led to devices outperforming the Pt-porphyrin references. In particular, the PtBDP containing two BDP units and eight F atoms led to superior devices with irradiance of 83 μW cm−2, efficiencies of 0.12 lm W−1, Etot of 11 mJ, and at a low-energy electroluminescence maximum centered at λmax ≈ 780 nm. This result is attributed to a trade-off between the electronic alignment toward an effective intramolecular host–guest system, an efficient energy transfer, and a reduction of the ionic conductivity to achieve high irradiances and stabilities. Overall, this work gives important molecular design guidelines on the preparation of efficient low-energy emitting sustainable porphyrin-based emitters for application in NIR lighting technologies.

4. Experimental Section

Materials and Techniques: All chemicals and solvent were purchased in reagent grade from commercial suppliers and directly used, unless other- wise stated. NMR spectra were recorded on a Bruker AVANCE III-500 MHz spectrometer, selecting the deuterated solvent peak as the internal standard. Mass spectra were obtained with an UltraFleXtreme matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectrometer (Bruker), selecting trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyli- den] malononitrile (DCTB) as matrix. In the Supporting Information, we provide further information regarding the synthesis of all intermediate and final derivatives.

Fabrication and Characterization of Solutions and Thin Films: A Shimatsu 2700-I UV–Vis spectrometer was used to acquire UV–vis spectral data. Photoluminescence spectra and PLQY values were obtained with a FSS spectrofluorometer with integrating sphere (Edinburgh Instruments), while average excited states lifetimes (τ) were measured with an Edinburgh Instruments TCSPC and exciting with either a diode laser (λexc = 377 nm) or a microsecond lamp (100 Hz frequency).

The average lifetime was calculated with the following formula:32

\[ R(t) = \sum_{i=1}^{n} A_i e^{-\frac{t}{\tau_i}} \]

where A is constant. In our case (double-component decay), the average lifetime equals to:

Figure 8. Irradiance and total emitted energy versus the number of F atoms in Pt-0 and Pt-20 and PtBDP polyads. The circle highlights the area including the devices, in which both parameters are maximized. The intersection between the two curves corresponds to a number of fluorine substituents of 8.8, as highlighted in the graph.

Figure 9. Electroluminescence spectra of Pt-0 and Pt-20 (left, see legend), and PtBDP polyads (right, see legend).
(r) = \frac{A_1 r_1^2 + A_2 r_2^2}{A_1 r_1 + A_2 r_2} \quad (1)

To achieve thin films on a quartz substrate, a THF solution of the emitter with a concentration of 12 mg mL\(^{-1}\) was used to spin-coat thin films under nitrogen pressure with the following three-step procedure: 700 rpm for 30 s, 1600 rpm for 30 s, and 3000 rpm for 10 s. The resulting thickness was 70 nm. The used spin-coater is a Laurell WS-650mmz-23npbb. The morphology of the thin films was checked via AFM assays with a Park XE150 instrument (Park Systems Corp., Suwon, South Korea).

**Electrochemical Characterization in Solution:** Cyclic and square wave voltammetry assays were performed with an AutoLab PGSTAT204 potentiostat, using a scan rate of 100 mV s\(^{-1}\) in deoxygenated CH\(_2\)Cl\(_2\) solutions featuring tetrabutylammonium hexafluorophosphate 0.1 M (TBAPF\(_6\)) as supporting electrolyte. The cell setup consisted in a glassy carbon working electrode, a SCE reference electrode, and a platinum wire as counter electrode. The ferrocene/ferrocinium couple was employed in all cases as reference (0.46 V vs SCE).

**Device Preparation and Characterization:** ITO substrates (130 nm thick) (Naranjo Substrates) were carefully cleaned by bathing them in soap, water, ethanol, and isopropanol in an ultrasonic bath for 15 min each. Then, they were put in a UV–ozone cleaner for 8 min. Right after this step, a PEDOT: PSS layer (70 nm) was spin-coated on top of the clean substrates. In detail, the PEDOT: PSS (Clevios AI 4083) was mixed with isopropanol in a volumetric ratio of 3:1.3, and spin-coated onto the plates at 1700 rpm for 60 s. An annealing step followed (30 min, 120 °C). The BDP-Pt-por polyad were spin-coated on top of the PEDOT: PSS from a 10 mg mL\(^{-1}\) THF solution containing the electrolyte matrix in a weight ratio of polyad:TMPE (M\(_w\), 450 000):LiOTf \(1:0.15:0.03\). This spin coating procedure consisted in three steps: 700 rpm for 30 s, 1600 rpm for 30 s, and 3000 rpm for 10 s. The thickness of the layers was of 70 nm, as measured from an AlphaStep 500 profilometer (KLA Tencor). The devices were dried under vacuum for 2 h before being inserted in a glove box (<0.1 ppm O\(_2\) and H\(_2\)O, Angstrom Engineering), where 90 nm-thick aluminum cathodes were evaporated under physical vapor deposition as a high vacuum Angstrom Covap evaporator. The device active area was of 10 mm\(^2\). The so-fabricated LECs were measured with the coupled Avantes spectrophotometers AvaSpec-ULS2048L-US2B and AvaSpec-ULS2048C-CL-EVO for high UV–Vis and NIR sensitivity, respectively, and a calibrated integrated sphere Avsphere 30-Irrad and a Botest OLT OLED Lifetime Test System, as described in previous contributions.\(^{[11,12]}\)

EIS assays were conducted with a potentiostat/galvanostat PGSTAT204 (Metrohm µAutolabIII) with EIS frequency response analyser module (FRA2). The applied voltage ranged from 0 to 4 V. The obtained data were fitted with the novel software 1.1 using the circuit model shown in Figure S63, Supporting Information, as described in previous contributions.\(^{[13]}\)

**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.

**Data Availability Statement**

Research data are not shared.

**Keywords**

carrier trapping, host:guest, light-emitting electrochemical cells, near-infrared emission, porphyrin polyads

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