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### Cunning metal core: efficiency/stability dilemma in metallated porphyrin based light-emitting electrochemical cells<sup>+</sup>

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The syntheses, photophysical/electrochemical characterizations of different metallated porphyrins – *i.e.*,  $Zn^{2+}$ ,  $Pt^{2+}$ ,  $Pd^{2+}$ , and  $Sn^{4+}$  porphyrins – as well as their first application in light-emitting electrochemical cells are provided. A direct comparison demonstrates that depending on the metallation either efficient (Pt-por) or stable (Zn-por) devices are achieved, demonstrating that the choice of the metal core is a key aspect for future developments.

Metallated porphyrins have been successfully applied to develop deep-red lighting sources based on the organic lightemitting diode  $(OLED)^{1-10}$  and the light-emitting electrochemical cell  $(LEC)^{11}$  concepts. One of the most important advantages of porphyrins is the mature control of their photophysical features by means of a proper molecular design, namely (i) the expansion of the  $\pi$ -conjugation of the pyrrole unit to red-shift the emission to the near-infra red region,<sup>3</sup> (ii) the use of substituents at the *meso* position in order to enhance the photoluminescence quantum yields  $(\phi)$ ,<sup>4</sup> to promote self-assembling,<sup>8,10</sup> and/or to open up the preparation of porphyrin dyads with efficient energy/electron transfer processes,<sup>2,6,9,11-14</sup> and (iii) the use of different metal cores to provide new photoluminescence (PL) mechanisms like phosphorescence  $^{2,5,6,8}$  and thermally activated delayed fluorescence (TADF).  $^7$ 

Recently, we have demonstrated that an efficient energy transfer process from peripheral BODIPY units to the zinc porphyrin core in dyad-like compounds can be exploited to decouple charge transport and emission processes in LECs.<sup>11</sup> This leads to very stable deep-red emitting devices, but with a moderate efficiency. The latter might be limited by the spin statistics that indicate the formation of excitons with a 1:3 spin distribution of singlets and triplets upon electron-hole recombination. Since both the PL and electroluminescence (EL) behaviours are related to a fluorescence mechanism, the management of the formed excitons is therefore not optimized. In addition, films prepared with mixtures of zinc porphyrin and ionic polyelectrolyte feature the formation of aggregates that act as both emission quenching and charge carrier disruptor centers.<sup>11</sup>

As state-of-the-art red-emitting LECs, several groups have explored a few more systems, such as polymers,<sup>15,16</sup> coordination complexes,<sup>17-19</sup> dyads based on small-molecules linked to a coordination complex,<sup>20</sup> and, more recently, small molecules.<sup>21-23</sup> Despite efforts, the design of stable and efficient red-emitting electroluminescent compounds still remains as one of the contemporary challenges in LECs. Herein, we investigate a new strategy to enhance porphyrins towards efficient LECs. In view of the above-mentioned, this contribution demonstrates how to increase the efficiency of porphyrin-based LECs by changing the metal core in combination with bulky phenyl substituents attached to the meso positions - Scheme 1. On one hand, we provide a direct comparison between different metallated porphyrins, that is, zinc (Zn-por), tin (Sn-por), platinum (Pt-por), and palladium (Pdpor) porphyrins. As a matter of fact, each metal core opens up new exciton radiative mechanisms involving one - i.e., fluorescence (Zn-por) or phosphorescence (Pt-por) - or two - i.e., dual emission (Pd-por) or TADF (Sn-por) - excited states. On the other hand, all the porphyrins are decorated with bulky tetraphenyl groups - i.e., 3,5 di-tert-butyl phenyl substituents -

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Scheme 1 Chemical structures and synthetic protocol of the metallated porphyrins.

placed at the *meso* position – Scheme 1. The latter might enhance the quality of the film morphology, while preventing self-quenching due to close proximity between porphyrins.

Hence, this work reveals the impact of the metal core in a new porphyrin skeleton on the LEC performance, providing a much clearer prospect of this type of compounds for developing single-layer deep-red emitting sources. These results are supported by a comprehensive photophysical and electrochemical characterization in solution and/or solid-state in concert with a device analysis by means of electrochemical impedance spectroscopy (EIS) and long-term device measurements. Overall, we show that although the device efficiency can be enhanced up to one order of magnitude – *e.g.*, Pt-por *vs*. Zn-por based LECs, there is a trade-off related to the device stability due to the electrochemical features of the Pt-por that might affect both injection and transport processes.

The synthesis of the metallated porphyrins is shown in Scheme 1 and details are provided in the ESI.† In short, Zn-por<sup>24</sup> and Sn-por<sup>25</sup> were synthesized according to previous reported literature procedures. For the synthesis of Pt-por and Pd-por, free-base porphyrin (H2-por) was added in refluxing solution of benzonitrile containing either PtCl<sub>2</sub> or PdCl<sub>2</sub>. The new compounds Pt-por and Pd-por were fully characterized on the basis of their <sup>1</sup>H and <sup>13</sup>C NMR spectra - Fig. S1-S4,† MALDI-TOF mass spectra, and elemental analysis. The corresponding data for Zn-por and Sn-por were in perfect agreement with the literature. The most noticeable feature in the <sup>1</sup>H NMR spectra is the lack of the characteristic peaks of inner protons of H2-por. Pt-por was also characterized by means of single-crystal X-ray crystallography - Fig. S5 and Tables S1-S4.† The compound exhibits a planar molecular structure with four-fold symmetry and Pt-N bond lengths of 1.975(8) and 2.021(7) Å.

As a first step, cyclic (CV) and square wave (SQ) voltammetry assays were performed in THF to investigate the impact of the metal substitution on the electronic structure of this series – see ESI.† Their redox features are summarized in Table S5, while Fig. S6–S9† display the CV and SQ graphs. In particular, the Zn-por shows two reversible oxidation processes at 1.04 and 1.31 V vs. SCE and one reversible reduction process at -1.41 V vs. SCE. Similar features were noted for the Pd-por, that is, reversible oxidation and reduction processes centered at 1.43 and -1.19 V vs. SCE, respectively. In stark contrast, the Pt-por and Sn-por show an irreversible oxidation wave at 1.53 V *vs.* SCE and a featureless graph in the applied positive voltage window, respectively. However, both compounds show quasireversible reduction processes centered at -1.24 and -1.70 V *vs.* SCE, as well as -0.79 and -1.33 V *vs.* SCE for Pt-por and Sn-por, respectively. These values are in good agreement with the literature.<sup>26–28</sup> Taking into account that all the processes in LECs – *i.e.*, the charge injection, charge transport, electron-hole recombination, and emission processes – are performed by the electroluminescent material, we can postulate that the Zn-por and Pd-por are highly suitable for this lighting concept, while stability problems might be noted for Pt-por and Sn-por devices.

Next, the absorption and emission features of the metallated porphyrins were determined – Fig. 1 and S10–S13.† The former consist of an intense Soret band located at 375–450 nm range and two Q-bands in the 475–600 nm – Fig. S10.† This series show emission features in aerated solutions spanning from the deep-red to the near-infrared regions of the visible spectrum – Fig. 1 and S11.† In detail, the Zn-por shows an emission band with two peaks at around 600 and 650 nm that corresponds to a fluorescence process as suggested by the  $\phi$  of 3.8% and a monoexponential excited state lifetime ( $\tau$ ) of 1.9 ns. Similar emission features are noted for Sn-por with a fluorescence band centered at 610 and 665 nm associated to  $\phi$  of 1.2% and  $\tau < 1$  ns. In contrast, the Pd-por shows the typical dual-emission from fluorescence and phosphorescence processes located at 565–610 nm and



**Fig. 1** PL spectra of Zn-por, Sn-por, Pt-por and Pd-por in THF at rt (top) and in thin films with the composition of the device at rt and 77 K (bottom).

700 nm, respectively. Here, we noted two  $\phi$  of 0.047 and 0.0013% and two  $\tau$  of around 1 and 600 ns depending on the probed wavelength - *i.e.*, 610 and 700 nm, respectively. Finally, the Pt-por shows a pure phosphorescence emission with maxima at ca. 675 and 730 nm with  $\phi$  of 0.095% and  $\tau$  of 681 ns. Corroborating the nature of the emission processes, Fig. S12<sup>†</sup> displays the emission spectra of the porphyrins in degassed solutions, showing a similar spectra shape for Zn-por, Sn-por, and Pt-por, but only the phosphorescence feature located at around 700 and 775 nm for Pd-por. Importantly, we also noted a strong increase of  $\phi$  and  $\tau$  values up to 0.3% and 9 µs, as well as 3% and 6 µs for Pd-por and Pt-por, respectively, while they remain almost constant for Zn-por and Sn-por - Table S6.† Finally, a similar emission spectra shape featuring red- (Zn-por) and blue-shifted (Pt-por, Pd-por, and Sn-por) maxima were noted at 77 K - Fig. S13.† This is accompanied by the phosphorescence feature at around 750-800 nm for the Zn-por and Sn-por, suggesting that a TADF process could be involved in the PL process.<sup>7</sup>

Similar spectroscopic investigations were also carried out in thin films. The latter were prepared via spin-coating from THF solution with a mixture of the porphyrins with the ionic polyelectrolyte as used in the device fabrication - see ESI.<sup>†</sup> To the naked eye, the Zn-por, Sn-por, and Pt-por films show a homogenous morphology that is suitable for device fabrication, but despite our efforts, we were unable to prepare homogenous Pd-por films - see ESI for details and Fig. S14.<sup>†</sup> This incident seems to be common since, in general, there is a lack of lighting devices prepared with Pd-por derivatives. More in detail, the morphology of the Zn-por, Sn-por, and Pt-por films was investigated via Atomic Force Microscopy (AFM) - Fig. 2. Although all the films look homogeneous, the morphology of Zn-por and Sn-por films show a less and a more prominent phase separation along with aggregates and holes, respectively. In contrast, the Pt-por shows no phase separation, but the presence of small aggregates. This is reflected in the PL features of the Pt-por, Sn-por, and Zn-por films - Fig. 1. Here, the Sn-por and Zn-por films show broad and red-shifted (15-30 nm) emission bands with different relative peak intensities compared to those in solution - Fig. 1. This is expected

Fig. 2 AFM images of Zn-por (left), Sn-por (middle), and Pt-por (right) films as used in devices.

100

80 60

due to the above-mentioned phase separation and/or aggregation features that typically lead to a red-shifted emission and a further PL quenching – e.g.,  $\phi$  of 0.34% and 2.30% for Sn-por and Zn-por films, respectively. Indeed, the Pt-por films show a very similar emission spectra to that in solution with the highest  $\phi$  (5.78%), corroborating the lack of phase separation. Finally, the emission spectra of the films measured at 77 K were similar to those at room temperature with a slight redshift - Fig. 1. Noteworthy, none of the phosphorescence features were noted for Sn-por and Zn-por films, suggesting a lack of TADF in the films.<sup>7</sup> To further support this notion, we monitored the changes in the emission intensities upon increasing the temperature from 77 to 430 K in an attempt to accelerate the back intersystem crossing from the triplet to the singlet excited states that might lead to an increase in the fluorescence intensity.<sup>7</sup> As shown in Fig. S15,† the emission intensity gradually reduces with the increase of the temperature due to the enhancement of the thermally activated vibrational deactivation mechanism. As last complement, we also performed theoretical calculations to qualitatively describe the energy splitting between the singlet and triplet excited states of Sn-por. We notice that this value is around 5000  $\text{cm}^{-1}$  (Tables S7 and S8<sup>†</sup>) that is far beyond the maximum value for TADF (ca. 800  $\text{cm}^{-1}$ ). Hence, we can state that no TADF features are observed in this series, even though the Sn-por substituted with fluorine atoms poorly showed this process.<sup>7</sup>

As a final step in our study, the EL features of Zn-por, Pt-por, and Sn-por were directly compared in LECs - see ESI<sup>+</sup> for more details. Fig. 3 displays the EL response over time and representative EL spectra, pointing out three main conclusions. Firstly, the EL spectra of Zn-por and Sn-por devices are broader than the PL in thin films with emission bands at ca. 650 nm, while Pt-por devices show a well-structured EL emission band centred at 650 and 750 nm - Fig. 1 and 3. As expected, the x/y colour coordinates are 0.65/0.32, 0.68/0.29, and 0.64/0.32 for Zn-por, Pt-por, and Sn-por devices, confirming that they are deep-red lighting sources. Secondly, all the devices show a similar electronic behaviour, that is, an initial applied voltage at around 4-5 V that raises over time up to steady values of 8-9 V for Zn-por and Sn-por devices and 5.5 V for Pt-por devices. The lower applied voltage and the welldefined structure of the EL spectrum of the latter highlight the better morphology of the films. Concerning the emission response, the devices show an instantaneous irradiance that maximizes in less than one hour for Sn-por (~5 min) and Ptpor (~45 min) devices and several hours for Zn-por devices. This is related to the differences in the ion conductivity - vide infra. Thirdly, as expected from the PL features, the irradiance maxima increases going from Sn-por, to Zn-por, and to Pt-por devices. The latter shows the highest external quantum efficiency (EQE) with a value of 0.16%, but with the drawback of a low lifetime of only a few hours. In stark contrast, the Zn-por and Sn-por devices feature EQE of 0.017% and 0.0061% with lifetimes of hundreds of hours. Noteworthy, the Pt-por device shows similar EQEs to those of both small-molecules LECs<sup>21-23</sup> and porphyrin OLEDs.<sup>1,2,4,5</sup>

25.0 20.0 15.0



**Fig. 3** Average voltage (symbols) and irradiance (line) vs. time of Zn-por (top), Pt-por (central), and Sn-por (bottom) devices driven by an average pulsed current of 7.5 mA. Inset: Normalized EL spectra obtained at the maximum irradiance.

The efficiency differences between the Sn-por and Zn-por devices are expected from the  $\phi$  in thin films, but that between Zn-por and Pt-por devices might be related to both a better  $\phi$  and film morphology. Strikingly enough is the low lifetime of the Pt-por devices that we relate to its intrinsic poor redox stability – *vide supra*. To unveil the impact of the latter on the device mechanism, static EIS assay was performed at the beginning (fresh) and the end (dead) of the long-term measurements – see ESI.† Fig. S16† shows that the resistance trends are similar for the fresh devices upon increasing the applied voltage. However, it is worth to notice that the conductivity of Zn-por devices is much lower than that of Pt-por and Sn-por devices – *i.e.*,  $6.0 \times 10^{-10}$  vs.  $7.0 \times 10^{-9}$  and  $3.7 \times 10^{-7}$  S cm<sup>-1</sup>, respectively. This explains the differences in the time needed to reach the maximum irradiance – Fig. 3.

The same EIS analysis of the dead devices show that the resistance increases for the Pt-por device in one order of magnitude, while those of Sn-por and Zn-por devices show a decrease of two orders of magnitude. This points to the formation of degraded products in Pt-por devices. They are likely related to the oxidized species that might affect both the charge injection and transport, limiting the device stability.

In summary, this work describes a comprehensive comparison of different metallated porphyrins - *i.e.*, Zn<sup>2+</sup>, Pt<sup>2+</sup>, Pd<sup>2+</sup>, and Sn<sup>4+</sup> cores – with respect to their EL responses towards efficient and stable deep-red LECs. This is assessed by the thoughtfully analysis of the photophysical/electrochemical features, the film morphology, and the electronic device behaviour. Overall, although the metal cores rule the PL nature, they also have a detrimental impact on the electrochemical features and the film morphology when mixed with a standard ionic polyelectrolyte - e.g., the lack of homogeneous Pd-por films and the prominent phase separation in Sn-por films. As such, either efficient (Pt-por) or stable (Zn-por) devices can be achieved, demonstrating that the choice of the metal core is a key aspect for future developments. In this context, the design of redox stable Pt-por along with derivatives to decouple charge transport and emission processes is ongoing.

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#### Notes and references

- 1 V. A. Montes, C. Perez-bolivar, N. Agarwal, J. Shinar and P. Anzenbacher, *J. Am. Chem. Soc.*, 2006, **128**, 12436.
- 2 V. A. Montes, C. Perez-bolivar, N. Agarwal, J. Shinar and P. Anzenbacher, *J. Am. Chem. Soc.*, 2007, **129**, 12598.
- 3 J. R. Sommer, R. T. Farley, K. R. Graham, Y. Yang, J. R. Reynolds, J. Xue and K. S. Schanze, *ACS Appl. Mater. Interfaces*, 2009, **1**, 274.
- 4 M. Ikai, F. Ishikawa, N. Aratani, A. Osuka, S. Kawabata, T. Kajioka, H. Takeuchi, H. Fujikawa and Y. Taga, *Adv. Funct. Mater.*, 2006, **16**, 515.
- 5 R. C. Kwong, S. Sibley, T. Dubovoy, M. Baldo, S. R. Forrest and M. E. Thompson, *Chem. Mater.*, 1999, **11**, 3709.
- 6 Y. Li, A. Rizzo, M. Salerno, M. Mazzeo, C. Huo, Y. Wang,
  K. Li, R. Cingolani and G. Gigli, *Appl. Phys. Lett.*, 2006,
  89, 24.
- 7 A. Endo, M. Ogasawara, A. Takahashi, D. Yokoyama, Y. Kato and C. Adachi, *Adv. Mater.*, 2009, **21**, 4802.
- 8 J. C. Ostrowski, K. Susumu, M. R. Robinson, M. J. Therien and G. C. Bazan, *Adv. Mater.*, 2003, **15**, 1296.

- 9 X. Wang, H. Wang, Y. Yang, Y. He, L. Zhang, Y. Li and X. Li, *Macromolecules*, 2010, **43**, 709.
- 10 O. Fenwick, J. K. Sprafke, J. Binas, D. V. Kondratuk, D. Stasio, H. L. Anderson and F. Cacialli, *Nano Lett.*, 2011, 11, 2451.
- 11 M. D. Weber, V. Nikolaou, J. E. Wittmann, A. Nikolaou, P. A. Angaridis, G. Charalambidis, C. Stangel, A. Kahnt, A. G. Coutsolelos and R. D. Costa, *Chem. Commun.*, 2016, 52, 1602.
- 12 C. Stangel, C. Schubert, S. Kuhri, G. Rotas, J. T. Margraf,
  E. Regulska, T. Clark, T. Torres, N. Tagmatarchis,
  A. G. Coutsolelos and D. M. Guldi, *Nanoscale*, 2015, 7, 2597.
- 13 M. K. Panda, T. Lazarides, G. Charalambidis, V. Nikolaou and A. G. Coutsolelos, *Eur. J. Inorg. Chem.*, 2015, 468.
- 14 T. Lazarides, G. Charalambidis, A. Vuillamy, M. Reglier,
  E. Klontzas, G. Froudakis, S. Kuhri, D. M. Guldi and
  A. G. Coutsolelos, *Inorg. Chem.*, 2011, 50, 8926.
- 15 Z. Yu, L. Li, H. Gao and Q. Pei, *Sci. China: Chem.*, 2013, **56**, 1075.
- 16 J. L. Rodríguez-Redondo, R. D. Costa, E. Ortí, A. Sastre-Santos, H. J. Bolink and F. Fernández-Lázaro, *Dalton Trans.*, 2009, 9787.
- 17 A. R. Hosseini, C. Y. Koh, J. D. Slinker, S. Flores-Torres, H. D. Abruña and G. G. Malliaras, *Chem. Mater.*, 2005, 17, 6114.

- 18 R. D. Costa, E. Ortí, H. J. Bolink, F. Monti, G. Accorsi and N. Armaroli, *Angew. Chem.*, *Int. Ed.*, 2012, 51, 8178.
- S. B. Meier, D. Tordera, A. Pertegás, C. Roldán-Carmona,
   E. Ortí and H. J. Bolink, *Mater. Today*, 2014, 17, 217.
- 20 R. D. Costa, F. J. Céspedes-Guirao, E. Ortí, H. J. Bolink, J. Gierschner, F. Fernández-Lázaro and A. Sastre-Santos, *Chem. Commun.*, 2009, 3886.
- 21 S. Tang, W.-Y. Tan, X.-H. Zhu and L. Edman, *Chem. Commun.*, 2013, **49**, 4926.
- 22 D. Tordera, J. J. Serrano, E. Orti and H. J. Bolink, J. Am. Chem. Soc., 2013, 135, 18008.
- 23 M. D. Weber, M. Adam, R. R. Tykwinski and R. D. Costa, *Adv. Funct. Mater.*, 2015, **25**, 5066.
- 24 G. Di Carlo, A. Orbelli Biroli, M. Pizzotti, F. Tessore, V. Trifiletti, R. Ruffo, A. Abbotto, A. Amat, F. De Angelis and P. R. Mussini, *Chem. – Eur. J.*, 2013, **19**, 10723.
- 25 M. J. Crossley, P. Thordarson and R. A.-S. S. Wu, J. Chem. Soc., Perkin Trans. 1, 2001, 2294.
- 26 J. Takeda and M. Sato, Chem. Lett., 1995, 939.
- 27 A.-M. Manke, K. Geisel, A. Fetzer and P. Kurz, *Phys. Chem. Chem. Phys.*, 2014, **16**, 12029.
- 28 P. Chen, O. S. Finikova, Z. Ou, S. A. Vinogradov and K. M. Kadish, *Inorg. Chem.*, 2012, **51**, 6200.