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Unusual Near-White Electroluminescence of Light Emitting Diodes Based on Saddle-Shaped Porphyrins

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In contrast to the red electroluminescence emission frequently observed in porphyrins based OLED devices, the present devices exhibit a nearly white emission with greenish
15 yellow, yellowish green and blue green hues in the case of $Fe^{II}(TCPPBr_6)$ $(TCPPBr_6$ = β-hexabromo-meso-tetrakis-(4-phenyl carboxyl) porphyrinato), $Zn^{II}(TPPBr_6)$ and $Co^{II}(TPPBr_6)$, respectively.

20 Among the most rapidly developing classes of OLEDs, white-light-emitting-diodes (WOLEDs) are of particular interest. Due to the special properties, WOLEDs offer low-cost alternatives to back-lights in flat panel displays and are considered as future illumination sources which are able to operate at low voltages
25 with high luminescence efficiency [1]. The main approaches to obtain white electroluminescence from organic/inorganic emitters can be classified into two main categories: methods based on the combination of two or more individual emitters of different colours and those using a single material that simultaneously
30 emits light over a wide range of wavelengths of the visible spectrum [2]. On the one hand, as a major drawback, the multiplicity of emitting layers adds complexity to the device manufacture. Also, the operating voltages are superior to those required for WOLEDs with a single emitting layer, due to the
35 increased overall thickness of the multilayer architectures [3]. Furthermore, the design of a single white emitting molecular component is a challenge, since a very careful choice of metal center and ligand functionalization is necessary for successful synthesis of desirable compounds [2]. Accordingly, WOLEDs
40 based on single white emitting molecular components such as metalloporphyrins are strongly desirable to reduce costs, simplify processing, to avoid differential aging of multiple emitters and colour instability caused by morphological changes upon device operation. The porphyrins and their derivatives belong to a very
45 interesting class of molecules which are commonly found naturally in systems that are responsible for energy transfer and electron transport [4]. Many porphyrins are quite stable and are thus suitable for vacuum deposition [5]. As a desirable property, the optical and electronic characteristics of metalloporphyrins can
50 be tuned by the change of the central metal atom, axial lignad, the peripheral substituents and the conformation of the aromatic macrocycle [6]. The stability of porphyrin based chromophores

and the possibility to tailor their optical properties make them
55 promising candidates for active materials in optoelectronic devices such as OLED's, NLO, waveguides and memory devices [7]. Despite the large number of red electroluminescence emission reported for porphyrins, their white electroluminescent properties remain completely unexplored [8]. In particular, the
60 modification of ZnTCPP by substitution of the β-positions with halogen atoms increases the splitting between the key filled and empty frontier orbitals, leading to the enhancement of the red-absorbing Soret and Q bands [9]. In fact, the β-pyrrole halogenated porphyrins seem to be a kind of a "missing link in
65 the family tree" represented by porphyrin emitters for OLED applications.

This commucation systematically introduces a novel approach to obtain white electroluminescence with saddle shaped-porphyrin emitters. Furthermore, the synthesis and characteriztion of the β-
70 substituted meso-tetrakis(4-phenylcarboxyl)porphyrin (H_2TCPP) and some metal complexes are reported. Also, the exciplex trnaformatiom has been used as an unconventional strategy to develop a promising porphyrin based near white light emitting diode. It is noteworthy that a nearly white electroluminescence
75 has been obtained in this work using a well-organized single emissive layer incontrast to the most frequently applied multi layered light emitter ones in white OLED devices. Actually, it appears clear that the research efforts focus on the peripheral substitution of porphyrins as the heart of the progress of WOLED
80 technology. Accordingly, further advancements will largely rely on the ability of scientists to design and synthesis porphyrins with tunable electroluminescence.

Full details regarding the synthesis of complexes are presented in the (ESI†, S1a). H_2TCPP was prepared according to the literature
85 methods [10a]. Briefly, MTCPP, M=Fe(II), Zn(II) and Co(II) complexes were prepared by standard methods by the reaction of the H_2TCPP and metal salts in DMF [10b]. For the synthesis of $MTCPPBr_6$, freshly recrystallised NBS [10c] was added to MTCPP in THF and the reaction mixture was stirred at room
90 temperature for 24 h. Finally, THF was evaporated and the residue was washed with water then purified with chloroform and water by separatory funnel (ESI†, S1a-c).

The degree of bromination of ZnTCPP and the purity of product have been determined by ^{1}H NMR spectrometry based on the
95 ratio of the intensities of the signals corresponding to the protons from $H_β$ and meso substituents ($H_β/H_{ortho}$ and $H_β/H_{meta}$ ratios); in

the case of MTCPPBr$_6$, a value of ca. 0.25 was observed for both the H$_\beta$/H$_{ortho}$ and H$_\beta$/H$_{meta}$ ratios. In the case of the Co(II) and Fe(II) complexes, degree of bromination of the porphyrin ligand was determined after the dematallation with CF$_3$COOH [1c] of
5 metal complexes and extraction of the brominated free base porphyrin, i.e. H$_2$TCPPBr$_6$ (ESI†, S1a). Also, ICP analysis was used to confirm the elemental composition of the brominated metalloporphyrins.

Porphyrins are common emitters because of their two very strong
10 emission bands in region 600-800 nm which could be tuned by different substitutions in the   beta and meso positions of porphyrin ring [11]. The UV–Vis absorption spectra of H$_2$TCPP, FeTCPPBr$_6$, ZnTCPPBr$_6$, and CoTCPPBr$_6$ in THF are shown in Fig. 1. The UV–Vis spectrum of H$_2$TCPP exhibits a strong Soret
15 band at 418 nm and four weak Q-bands at 514, 550, 588 and 644 nm. However, the Soret band of FeTCPPBr$_6$ appears at 424 nm and the weak Q-bands are observed at 476 and 518 nm. In addition, the UV–Vis spectrum of CoTCPPBr$_6$ exhibits a strong Soret band at 444 nm and three moderate Q-bands at 564, 615,
20 671 nm. ZnTCPPBr$_6$, on the other hand, shows a strong absorption band at 488 nm and a broad one at 714 nm. The absorption bands of the latter are broader and red-shifted with respect to those of the other metallporphyrins. As seen in the UV–Vis spectra, the Soret band of FeTCPPBr$_6$, ZnTCPPBr$_6$ and
25 CoTCPPBr$_6$ at 424, 444 and 508 nm are red-shifted by about 6, 46 and 90 nm, respectively compared to that of H$_2$TCPP (ESI†, S2a-d).
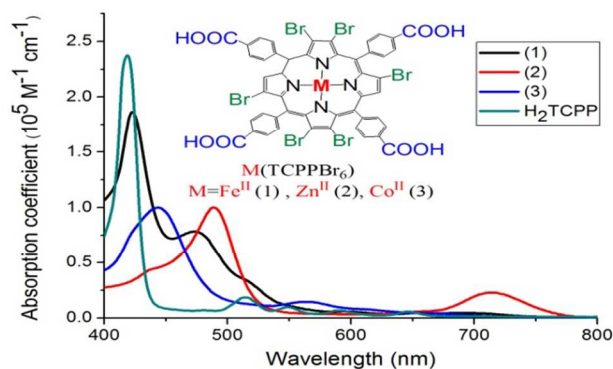

30 Fig.1. Absorption spectra of a 10^{-5} M solution of H$_2$TCPP and M(TCPPBr$_6$) M=Fe^{II}, Zn^{II}, Co^{II} in THF. Inset: Molecular structure of investigated porphyrin derivates

  As was previously reported, the porphyrin geometry can be
35 quantitatively probed by measuring the shift of the Soret band for each MTCPPBr$_x$ derivative [12] (ESI†, S3). As shown in Fig. 1, the results suggest that the Soret and visible absorption bands of the porphyrins are highly sensitive to peripheral substitution pattern of the maacrocycle. However, significant red shifts in the
40 UV-Visible spectra often serve as a signature of porphyrins non-planarity [13]. The saddle distortion of the macrocycle caused by the substitution of Br groups at the β positions is illustrated in Fig. 2. In addition, X-ray structure determination of the β -pyrrole brominated porphyrins proved the saddle-shaped conformation
45 [14].

In general, porphyrin nonplanarity can cause the changes in the a$_{1u}$ and a$_{2u}$ HOMOs levels and the narrowing of the HOMO–LUMO gap, as was observed by reducing the symmetry from D$_{4h}$ to D$_2$ for the metal complexes of β-substituted H$_2$TFPP (TFPP =
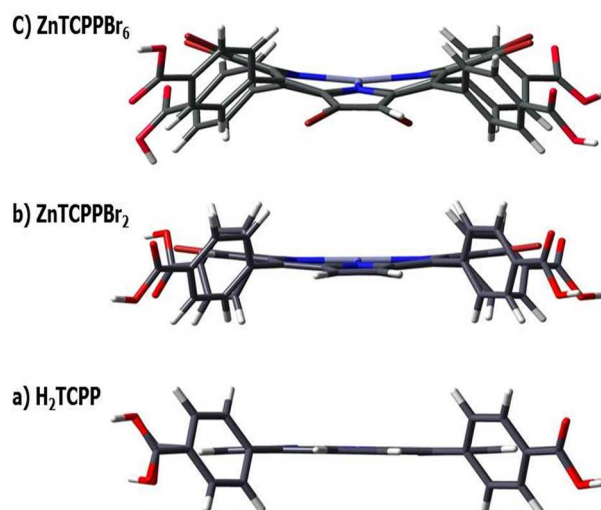50 meso-tetrakis(pentafluorophenyl)porphinato) [15].

Fig. 2. The saddle-shaped ZnTCPP caused by Br atom substitution.

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To further investigate the hole-transporting properties of these new materials, we fabricated the devices with the configuration ITO/PEDOT:PSS/cross-linked   HTM(PVK)/MTCPPBr$_6$/PBD/Al (ESI†,S1d). As shown in Fig. 2, the metal substitution shifts the
60 absorption maxima to a shorter wavelength (from 530 to 450 nm). As a general trend, the EL emission peak shifts to shorter wavelengths from FeTCPPBr$_6$ through ZnTCPPBr$_6$ to CoTCPPBr$_6$ correlating with the increase in the LUMO-HOMO energy gap (2.2, 2.4, and 2.6 eV for MTCPPBr$_6$ where M=Fe, Zn
65 and Co, respectively). All of our devices exhibit a nearly white emission with a greenish yellow hue (0.427; 0.443) in the case of FeTCPPBr$_6$, a yellowish green hue (0.337, 0.406) in the case of ZnTCPPBr$_6$, and a blue green hue (0.225, 0.335) in the case of CoTPPBr$_6$. CIE coordinates are shown in Fig. 2 (CIE =
70 Commission Internationale de L'Eclairage; the ideal white is x= 0.33, y= 0.33). Since the three ETMs have similar molecular structures, the variations in device performance are presumably ascribed to the differences in HOMO-LUMO band gap (ESI†, S4-7). The current density-voltage (J-V) and Luminance-Volatge
75 (L-V) characteristics of the devices are shown in Fig. 3 . Compared to the devices with MTCPPBr$_6$ (M=Fe, Zn, Co) EL, the device based on CoTCPPBr$_6$ exhibited higher performance in term of lower operational voltage, higher maximum luminous efficiency (1.72 cd/A), and higher maximum brightness (1576
80 cd/m^2 at 15 V).

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Table 1. Device EL characteristics of MTCPPBr$_6$, M=Fe ^{II} (1), Zn ^{II} (2), Co ^{II} (3), emitters.

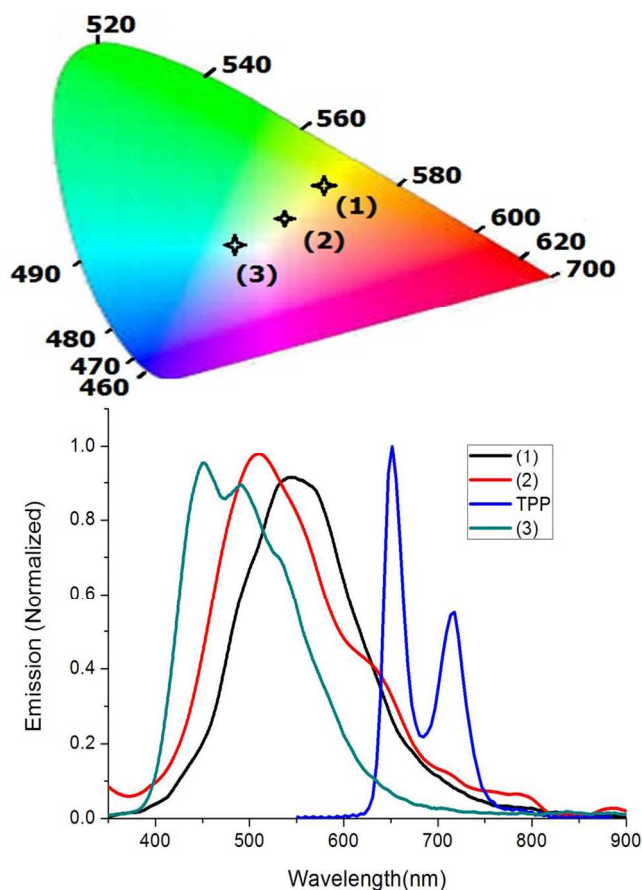| No.	EL$_{max}$ [nm]	CIE [x, y]	FWHM [nm]	Maximum current density, at 15 V	Turn-on V	Luminous efficiency [cd A^{-1}] at 150V	Luminance [cd m^{-2}] at 15 V	EQE (%)
(1)	553	(0.42, 0.44)	136	235	6.2	1.21	1135	0.6
(2)	510	(0.33, 0.41)	139	415	5.5	0.88	592	1.1
(3)	451	(0.27, 0.33)	137	240	5.1	1.72	1576	0.8

Fig. 2. EL spectra of TPP,(1), (2) and (3). Upper: Emission colors of devices based on (1), (2) and (3) in a CIE chromaticity diagram.

It is useful to note, the efficiency of the devices increases with increasing porphyrin concentration from 6 to 8 wt.%, but decreases when the dopant concentration is more than 8 wt. All devices with 8 wt.% dopant have the highest luminance and current efficiency.

The observation of white electroluminescence in β-brominated porphyrin emitter is of interest in the study of the fundamental electron transfer of this class of macromolecule-light emitting diodes. Here, the concept of Exciplex formation in the energy transfer mechanism has been a useful one. The red-shifted region of EL emission contributions to white light can be attributed to the formation of Exciplex. External quantum efficiencies (EQE) of 1.1% , 0.8% and 0.6 % at current densities of 25 mA/cm^2 were achieved in ZnTCPPBr$_6$, CoTCPPBr$_6$ and FeTCPPBr$_6$ devices, respectively. The external quantum efficiencies of three devices

decreased by the increasing current densities, which is possibly caused by the saturation of emission sites.

According to the band gap arrangement, it is reasonable to ascribe this anomalous emission to an Exciplex formed at the interface between the electron donor PVK and the electron acceptor MTCPPBr$_6$. At the interface of PVK/Porphyrin, the whole injection barriers at PVK/ MTCPPBr$_6$ (M= Fe^{II}, Zn ^{II} and Co^{II}) are 0.5, 0.4 and 0.6 eV, respectively, which are large enough and close to the brink for whole injection into the porphyrin layer [16]. Many papers on the Exciplex formation process and Exciplex emission properties being affected by an external electric field has been reported. However, Exciplex emission in porphyrin family is not fully explored [17]. It should be noted that Exciplex formation process and Exciplex emission properties being affected by an external electric field have been reported [16]. However, Exciplex emission in porphyrin family has not fully explored. The Exciplex formations and emission mechanisms under an applied electric field including the generation of charge carriers, can be described by Scheme 1 and Fig. 4. In scheme 1, Porphyrin* (an excited state of Porphyrin) forms an encounter complex (PVK···Porphyrin*) in the presence of PVK (I), and then a radical ion pair (PVK$^+$ ···Porphyrin $^-$) is produced by an intermolecular electron transfer from the PVK to Porphyrin* (II) [18]. Relaxation of the radical ion pair to an Exciplex state (PVK$^+$ Porphyrin $^-$)* (III) occurs in competition with a dissociation into free carriers: PVK $^+$+Porphyrin$^-$(IV).
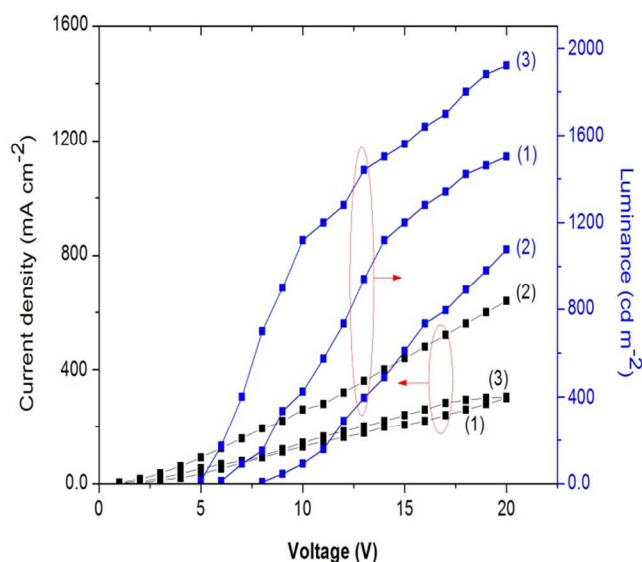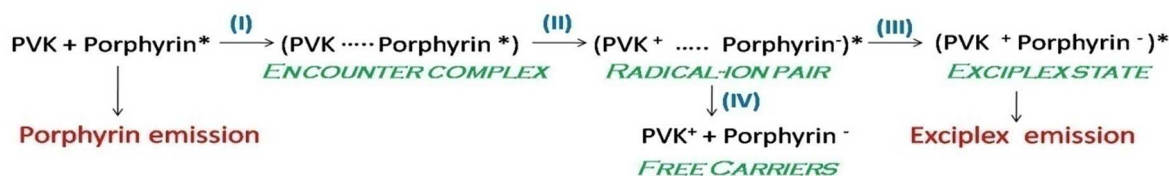

Fig. 3. Current density and luminance versus applied voltage for devices (1-3).

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Scheme 1: Exciplex formations and emission mechanisms under applied electric field.

Therefore, the red-shifted region of EL spectra of PVK-porphyrin layers are largely affected by intermolecular interaction between porphyrin excitons and PVK at the PVK/Porphyrin interface. Fig. 5 represents the producing of exciplex emission with regard to the HOMO and LUMO energy levels of the compounds.

It is useful to note, the Excimer transfer generates from the aggregation of two neighbouring identical molecules one being in the excited and the other in the ground state. In addition, the heavy atom such as Pt enhances the singlet-triplet intersystem crossing rate constant, thus leading to the formation of triplet Excimers. However, the triplet excited state of Zn, Fe and Co atoms is relatively inactive and the singlet-triplet intersystem crossing is impossible (ESI.S8).
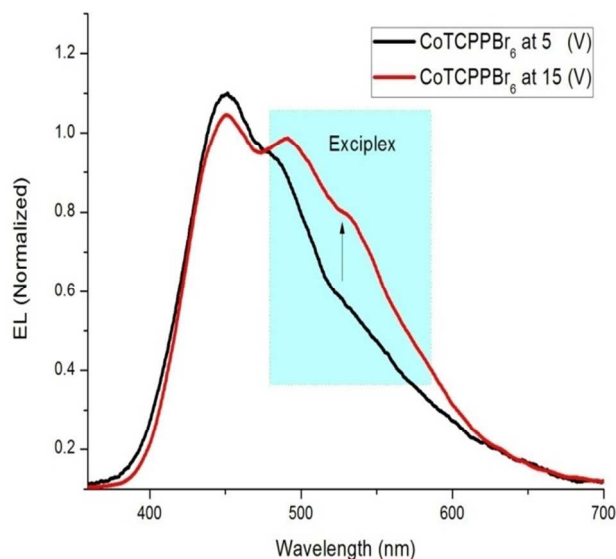
Fig. 4. EL spectra of $CoTCPPBr_6$ at different applied voltage. The Exciplex transfer is highlighted.

We conclude that Soret band contributes to produce Forster transfer due to the overlap of the absorption spectrum of porphyrin with the PL spectrum of PVK. Beside, the origin of Exciplex transfer can be attributed to Q band which is red-shifted to Soret band (ESI. S9).
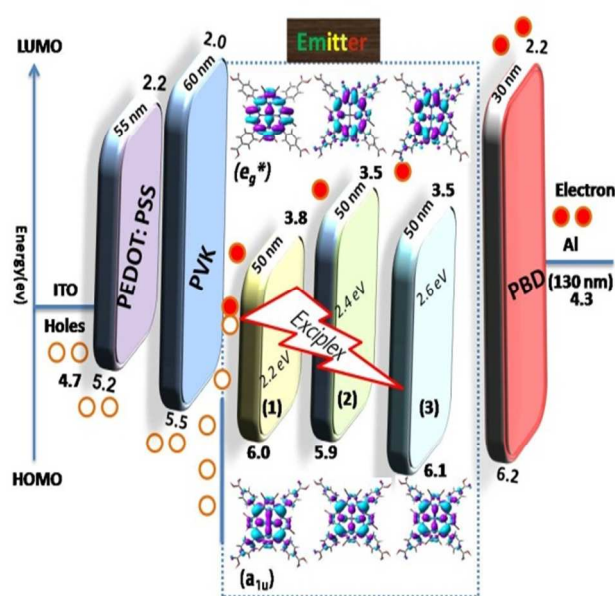

Fig. 5. Schematic illustration of the energy levels of the device and the dynamic process of emission. The HOMO-LUMO energy levels of the investigated emitters and other materials used for LED device production are also shown.

The good performance characteristics of this interesting class of porphyrins compared to other porphyrin family provide the basis to expect that the metal complexes of β-pyrrole brominated porphyrins as emissive materials would have a significant impact on the development of WOLEDs.

In conclusion, contrary to the most frequently applied multi layered light emitting structures in white OLED devices, all our single emitter layer devices with a neat emissive layer based on 1-3 emit a bright and nearly white light with greenish yellow hue (0.427; 0.443) in the case of $FeTCPPBr_6$, a yellowish green hue (0.337, 0.406) in the case of $ZnTCPPBr_6$, and a blue green hue ($CIE_{x,y} = 0.225, 0.335$) in the case of $CoTPPBr_6$. This paper opens the new avenue for a more in depth investigation of halogenated-porphyrin emitters for use as WOLEDs.

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Graphical Abstract

For

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