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## Deep-red electrophosphorescence from a platinum(II)–porphyrin complex copolymerised with polyfluorene for efficient energy transfer and triplet harvesting

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A series of polyfluorene-based polymers with a range of weight percentages (w/w) of a platinum(II)-containing porphyrin, 5,15-dimesityl-10,20-diphenylporphyrinato platinum(II) (**MPP(Pt)**), were synthesised and incorporated into organic light-emitting diodes. All polymers showed emission predominantly in the red/NIR region with only those polymers with porphyrin w/w of less than 2% showing residual tails at wavelengths lower than 600 nm, indicating increased emission from the porphyrin as w/w increases. The 2% loading of **MPP(Pt)** gave the highest efficiency LED (0.48%) and light output (2630 mW/m<sup>2</sup>).

**Keywords:** conjugated polymer; OLED; triplet harvesting; porphyrin; fluorene

### 1. Introduction

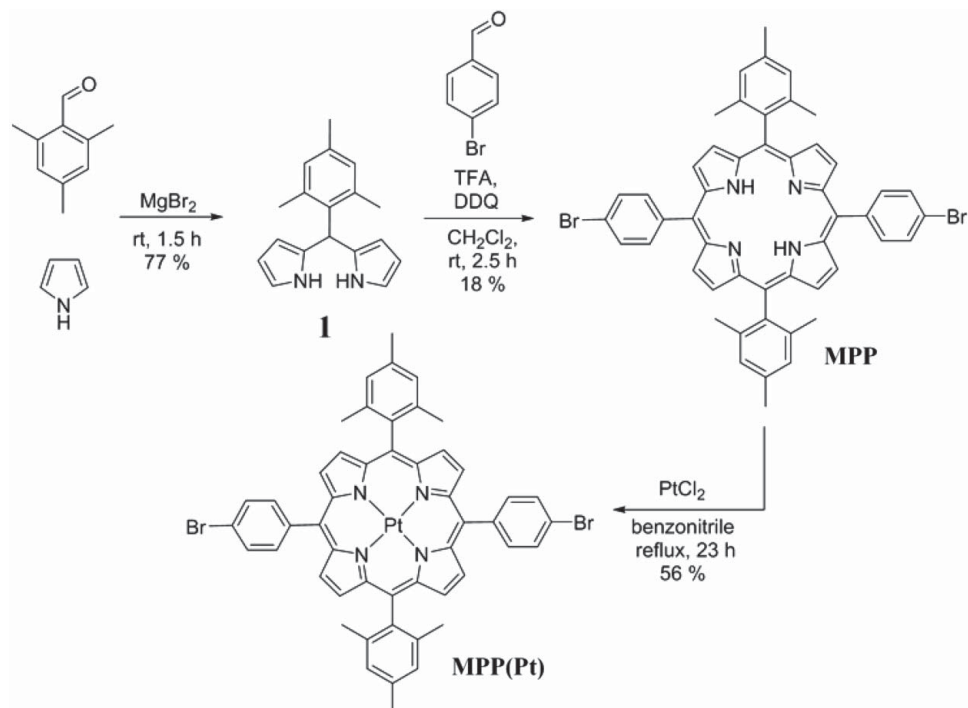
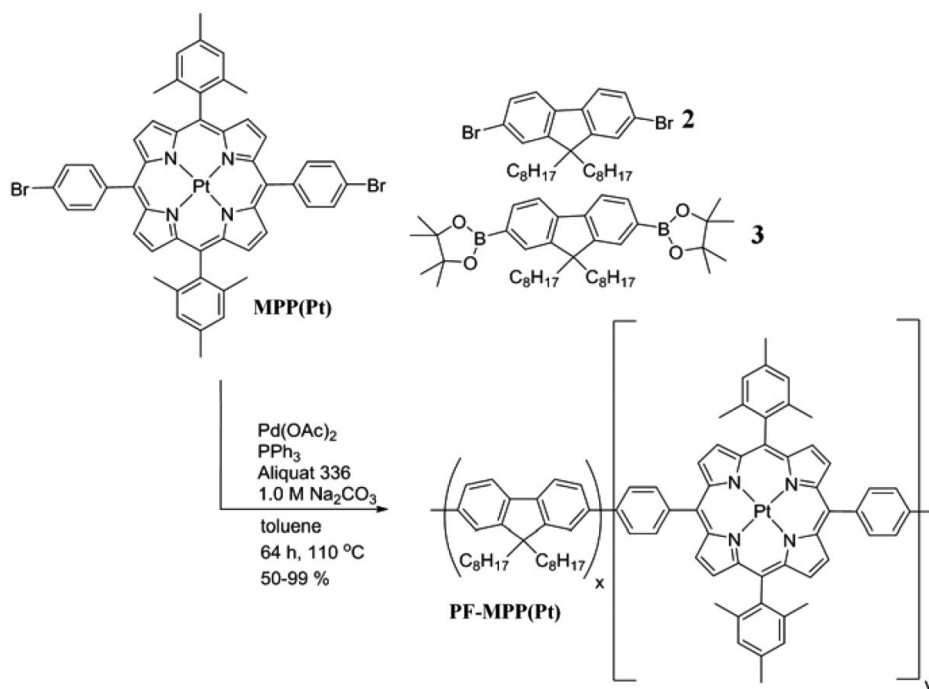
Phosphorescent emitters are of great interest in organic light-emitting diodes (OLEDs) due to their potential to achieve near to 100% internal quantum efficiency.[1] Upon incorporation of heavy metal atoms with strong spin–orbit coupling such as platinum(II) or iridium(III), the system is distorted such that radiative transitions from triplet states, that is, where  $\Delta S \neq 0$ , become feasible. Intersystem crossing from any excited singlet state is also more favourable, resulting in radiative decay from T<sub>1</sub> regardless of the original spin of the exciton. Since the first investigation of the electroluminescence (EL) from Pt(II)–porphyrin complexes [2] and Ir(ppy)<sub>3</sub>, [3] many groups have reported the use of such complexes in blend with a polymer host. However, phosphorescent dopant aggregation and phase separation are disadvantages of blend architecture, due to the increased phosphorescent quenching rate.[4,5] While synthetically more challenging, copolymerisation overcomes these disadvantages.[6,7] Having the dopant covalently bonded to the polymer will both increase the rate of energy transfer and reduce loss processes by maintaining the absorbing and emitting moieties at fixed distance, thus preventing intermolecular interaction between dopant molecules. Solubility of the whole system is also increased facilitating low-cost solution-processed device fabrication. In particular, the incorporation of Pt(II)-complexed

porphyrins into host polymers has been demonstrated to be a viable route, that is, as a side chain in 2-methoxy-5-(20-ethylhexyloxy)-1,4-phenylene vinylene (MEH-PPV). [8–10] These materials are promising candidates for deep-red [11] OLEDs with spectral components extending even into the near-infrared (NIR), [12–15] the focus of increasing attention for application in the biomedical, security and communication sectors. Still few investigations have been reported for the incorporation of Pt(II)–porphyrin directly in the polymer backbone.[16–18] Of the few previously reported polymers, porphyrins are generally incorporated by the  $\beta$ -pyrrolic position.[16,18] Meso incorporation into a polyfluorene polymer has previously been achieved by Xiang but was studied only in the context of oxygen sensing and was synthesised via a less controlled (compared to Suzuki) Yamamoto reaction.[17]

Here, we investigate the inclusion of Pt(II)–porphyrin, a dimesityl diphenyl porphyrin platinum (**MPP-Pt**) in a polyfluorene host polymer, poly(9,9-di-*n*-octylfluorenyl-2,7-diyl) (PFO) where the phosphorescent dopant is covalently linked to the fluorescent host via phenyl groups (**PF-MPP(Pt)**). We also characterised the steady-state and time-resolved photoluminescence (PL) of the materials, which were then incorporated in light-emitting diodes.

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Scheme 1. Synthesis of **MPP(Pt)**.Scheme 2. Suzuki–Miyaura polymerisation of **2**, **3** and **MPP(Pt)** to form **PF-MPP(Pt)**.

## 2. Synthesis

The polymer that forms the basis of this work, **PF-MPP(Pt)**, was prepared via Suzuki–Miyaura cross-coupling reaction of monomers **2**, **3** and **MPP(Pt)** (Scheme 2). Fluorene monomers **2** and **3** were synthesised from a literature procedure from fluorene.[19]

**MPP(Pt)** was synthesised as in Scheme 1 in three steps from pyrrole and mesitaldehyde using a modified procedure of Lindsey that allows the synthesis of trans-A<sub>2</sub>B<sub>2</sub> porphyrins from a relevant dipyrromethane and aldehyde.[20] Mesityldipyromethane **1** was formed by stirring mesitaldehyde with MgBr<sub>2</sub> using pyrrole as

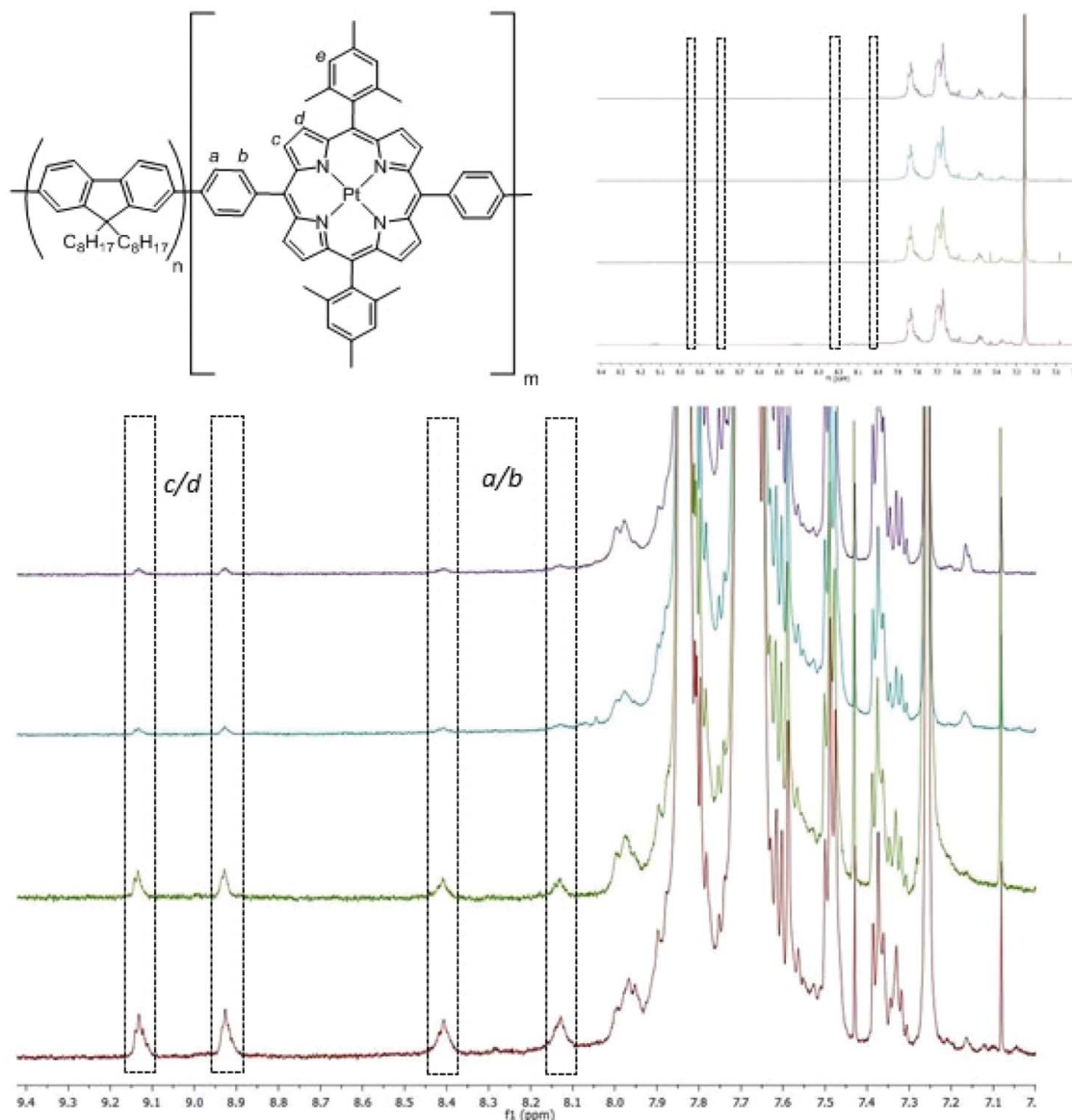


Figure 1.  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  of **PF-MPP(Pt)** containing 0.5% (**P1**, purple, top), 1.0% (**P2**, cyan, second from top), 2.0% (**P3**, green, second from bottom) and 5.0% (**P4**, maroon, bottom) w/w of **MPP(Pt)**. PF observed peaks (top right) were set to the same level. Peaks corresponding to porphyrin protons are shown in dotted boxes.

solvent. Dipyrrromethane **1** was subsequently reacted with bromobenzaldehyde in the presence of TFA and oxidised with DDQ to give **MPP** as purple crystals. Complexation of the free base porphyrin with  $\text{PtCl}_2$  in refluxing benzonitrile resulted in **MPP(Pt)** as a red powder.

Suzuki polymerisation of the monomers was realised using  $\text{Pd}(\text{OAc})_2$  with  $\text{PPh}_3$  as catalyst in the presence of Aliquat 336 and base (Scheme 2). **PF-MPP(Pt)** was prepared with **MPP(Pt)** in several weight percentages (w/w), controlled by varying the ratio of the monomers. The amount of diboronic ester fluorene **3** was always constant while the ratio of fluorene dibromide **2** and **MPP(Pt)** was varied to control the w/w of porphyrin in the final polymer. **MPP(Pt)** was incorporated with w/w of 0.5%, 1.0%, 2.0%

and 5.0% into **PF MPP(Pt)**, giving a range of products that were analysed together (**P1**, **P2**, **P3** and **P4**, respectively). The novel polymers were isolated as dark red solids and were purified by Soxhlet extraction using acetone, hexane and finally chloroform. Gel permeation chromatography of the polymers showed a molecular weight ( $M_w$ ) of 15.0–23.0 kDa with PDIs of 1.6–1.9.

Attempts to determine the percentage incorporation of **MPP(Pt)** into each of the polymers were made by  $^1\text{H}$  NMR spectroscopy. Figure 1 shows how the ratio of porphyrin to PFO signals changes with increasing porphyrin incorporation and it can clearly be seen that the percentage incorporation increases with increased porphyrin feed ratio, and does so in a manner concurrent with the feed

Table 1. Synthetic results of polymerisation.

Polymer	Incorporation ratio		$M_n$ (kDa) <sup>c</sup>	$M_w$ (kDa) <sup>c</sup>	PDI <sup>c</sup>
	w/w porphyrin (%) <sup>a</sup>	Feed ratio <sup>b</sup>			
<b>P1</b>	0.5	0.2	8.0	15	1.8
<b>P2</b>	1.0	0.3	11	20	1.8
<b>P3</b>	2.0	0.9	11	17	1.6
<b>P4</b>	5.0	2.2	12	23	1.9

<sup>a</sup>Determined by reaction stoichiometry.

<sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy.

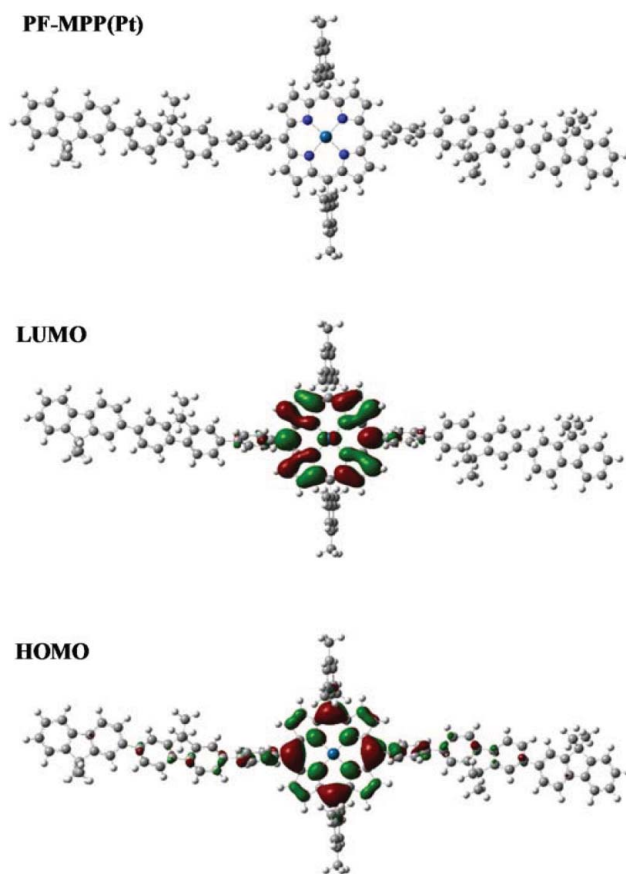
<sup>c</sup>Determined by SEC(PS) using PhCl eluent.

ratios. The estimated incorporation values are shown in Table 1 and are based on the ratio between the alkyl protons closest to fluorene and the most downfield pyrrolic proton peaks, these being the most isolated. As the feed ratio is increased, so does the incorporation ratio by an equivalent amount. This shows good evidence that the polymers are as expected relative to each other and represent a good range of porphyrin incorporation. The values are lower than the corresponding feed ratio, however, low incorporation to feed ratios have been shown before on similar systems.[21] It is thought that this discrepancy is primarily a result of errors associated with the NMR spectra integration, rather than lower than the expected porphyrin incorporation, due to the good solubility of **MPP(Pt)** in toluene. By comparing the **MPP(Pt)** peaks in the polymers to monomeric **MPP(Pt)** and **MPP**, the peaks may be tentatively identified. The four protons *a–d* come at 8.1, 8.4, 8.9 and 9.1 ppm and can be seen as the intensity of the aromatic region is increased. All four shifts are further downfield than **MPP(Pt)** as a monomer. Proton *e* is expected to be under the much larger PFO peaks. The furthest downfield peaks (8.9 and 9.1 ppm) have been assigned as *c* and *d* and the remaining peaks at 8.1 and 8.4 ppm have been assigned as *a* and *b*. These assignments are based on the ordering of peaks of previous compounds (heteroaromatic protons were further downfield than aromatic). As the level of porphyrin incorporation into the polymer is increased from 0.5% to 5.0%, the relative intensities of the proton peaks increase, qualitatively showing that the four porphyrin-containing polymers have a good range of w/w.

Methods for spectroscopy and LEDs are reported in the Electronic Supplementary Information (ESI).

The energy levels and molecular orbitals of **PF-MPP(Pt)** were calculated by DFT B3LYP *in silico* using basis set 6–31G\* for C, H and N and LanL2DZ for Pt. Figure 2 shows the HOMO and LUMO levels of an approximation of a porphyrin-containing portion of the polymer. To reduce calculation times, the octyl chains of PF have been replaced with methyl groups.

What is most apparent from the MO calculations is the degree of localisation of the molecular orbitals to either the

Figure 2. HOMO and LUMO levels of **PF-MPP(Pt)**.

porphyrin or fluorene portion of the molecule. The twist from porphyrin to phenyl to fluorene is such that conjugation across the entire molecule is broken. While this will have an overall negative impact on mobilities of the system, it does mean that the basic electronic characteristics of both moieties are likely to be only mildly affected. However, the HOMO, and to a smaller degree the LUMO, do both show a mild degree of delocalisation from the porphyrin to the main polymer chain, despite the large twist. It is expected therefore that energy transfer will be more facilitated than the analogous blend of porphyrin and PFO. Significant LUMO contribution from the Pt d-orbitals can be observed indicating that its role not only facilitates inter-system crossing but that the electronic transitions have metal-to-ligand charge transfer characteristic.

### 3. Results and discussion

We report the absorption and emission spectra for the copolymers **P1–P4** thin films in Figure 3(b) and 3(c). The copolymers show an intense featureless band at 380 nm due to the absorption of the PFO host polymer. In addition, the samples show two features at about 512 and 540 nm that we attribute to the Q-bands of the metalloporphyrin.[22] These bands increase in intensity as the concentration of **MPP-Pt**

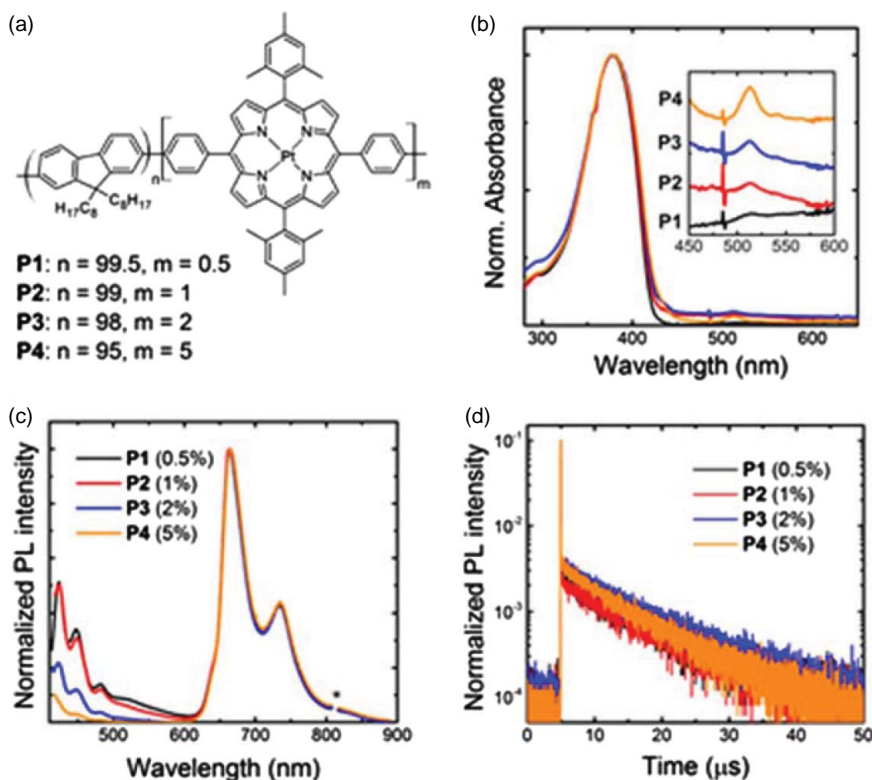


Figure 3. (a) Chemical structure of the PFO-MPP(Pt) copolymers with different MPP(Pt) loading: 0.5% for P1, 1% for P2, 2% for P3 and 5% for P4. (b) Normalised absorption spectra of the copolymers film on fused silica glass. The inset shows MPP(Pt) absorption features, the curves are stacked with Y-offset following the increase in the MPP(Pt) content. (c) Normalised PL spectra of the copolymer films. The '\*' indicates the monochromator second-order transmission of the excitation wavelength. (d) PL time decay taken at the most intense peak emission wavelength of the MPP(Pt) (665 nm) following excitation at 371 nm.

increases and are clearly distinguishable for loadings as low as 1%.

Interestingly, given the small dopant loading, the PL spectra show a dominant emission in the red and NIR region with three components at about 665, 735 and 805 nm and an emission shoulder at 645 nm that we assign to the MPP(Pt) segment. The copolymers also present a lower intensity emission at shorter wavelengths with vibronic peaks at  $\sim 442$ , 467 and 497 nm that we assign to PFO. Interestingly, when increasing the porphyrin content, the intensity of these peaks reduces relative to the porphyrin emission, therefore suggesting an efficient energy transfer from PFO to the porphyrin. Indeed, the good spectral overlap between the MPP(Pt) absorption and the PFO emission (Fig. S1) corroborates this hypothesis: both the Soret band (peaking at 402 nm) and the Q-band of the Pt(II)-porphyrin significantly overlap with the PFO emission. We also note a weak fluorescence emission band between 500 and 600 nm that can be related to the presence of fluorenone defects or aggregates/excimers whose presence is further validated by the TCSPC data.[23,24] In fact, the radiative lifetime of PFO taken at 550 nm (Fig. S2) can be fit with a bi-exponential function yielding time constants of  $\sim 400$  ps and 6.6 ns that are consistent with PFO exciton and fluorenone excimer respectively.[25] The

radiative lifetime taken near the peak emission wavelength of the PFO (440 nm) also confirms the presence of efficient energy transfer from the PFO to the porphyrins. In fact, the lifetime of the pure PFO of about  $\sim 400$  ps is reduced upon loading with the MPP(Pt) and drops below the instrument detection limit ( $\sim 150$  ps). The PL lifetime taken at the emission wavelength of the MPP(Pt) emission (665 nm) are reported in Figure 3(d). The copolymers show lifetime decays in the microsecond scale indicating the triplet nature of the emissive state. Specifically, we found time constants of 9.3  $\mu$ s (P1), 9.2  $\mu$ s (P2), 9.2  $\mu$ s (P3) and 8.6  $\mu$ s (P4).

The PL efficiency is around 4.9% for the MPP(Pt) loading of 0.5% (P1) and slightly decreases (4.5%) upon increasing the amount of porphyrin up to 2% (P2-P3). A drop to a PL efficiency of 2.5% is seen for higher porphyrin content (P4). The trend is consistent with the lifetime values suggesting an increase in the non-radiative deactivation of the exciton for porphyrin concentrations higher than 2%. Note that although these values may appear relatively low in absolute terms, they are comparable to values reported in the literature for similar polymers.[18]

We also incorporated the copolymers in LEDs with ITO/PEDOT:PSS as anode and Ca/Al as cathode. We report the EL spectra in Figure 4(a) in which we note that

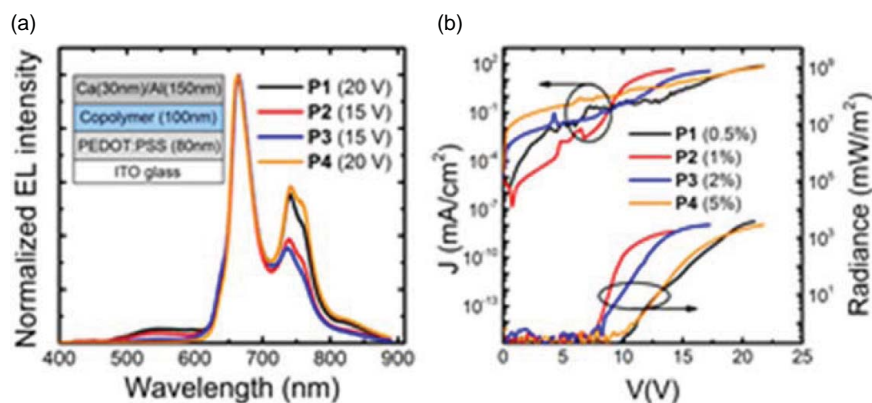


Figure 4. (a) Normalised EL spectra for the copolymers. The LED structure is reported. (b) LED characteristics: current density and radiance versus voltage. The active layer thickness is  $\sim 100$  nm and the device area is  $3.5 \text{ mm}^2$ .

Table 2. Summary of LEDs performances.

Copolymer	EQE <sup>a</sup> (%)	$V_{\text{on}}^b$ (V)	Radiance <sup>a</sup> (mW/m <sup>2</sup> )	Luminance <sup>a</sup> (Cd/m <sup>2</sup> )
<b>P1</b>	$0.17 \pm 0.01$	$10.7 \pm 0.2$	$986 \pm 61$	$14.8 \pm 0.7$
<b>P2</b>	$0.28 \pm 0.04$	$7.6 \pm 0.2$	$1486 \pm 221$	$23.8 \pm 2.9$
<b>P3</b>	$0.48 \pm 0.01$	$8.3 \pm 0.3$	$2630 \pm 38$	$31.1 \pm 0.8$
<b>P4</b>	$0.28 \pm 0.04$	$9.3 \pm 0.4$	$1390 \pm 56$	$9.9 \pm 0.4$

<sup>a</sup>Measured at  $30 \text{ mA/cm}^2$ .

<sup>b</sup>Intercept of the  $I$ - $V$  curve with the  $x$ -axis in a semi-log plot.

the copolymers display an emission predominantly in the red and NIR region. In particular, the EL of **P1** peaks at 665, 736 and 818 nm with a shoulder at 642 nm. We do not observe any shifts of the EL for higher **MPP(Pt)** loadings nor compared to the PL spectra. For copolymer **P1** and **P2**, however, we note a weak EL emission at wavelength below 600 nm. When increasing the content of porphyrin, the intensity of the emission tail decreases with little or no intensity left for loading above 1%. Such emission may be related to oxidative defects on the PFO [23] and to the emission from **MPP(Pt)** singlet state, as reported for similar Pt(II)-porphyrin complexes at 580 nm.[26,27] For **MPP(Pt)** loadings above 1%, copolymers show a pure electrophosphorescence (**P3** and **P4**).

The current-voltage and radiance-voltage characteristics are shown in Figure 4(b), and a summary of the LEDs performance is reported in Table 2. The 2% loading of **MPP(Pt)** (**P3**) gives the highest efficiency LED (0.48%) and light output ( $2630 \text{ mW/m}^2$ ). The result is particularly encouraging compared to what has been reported in the literature up to now, especially when taking into account that the LEDs are not optimised for charge collection and extraction.[16,18] We note an overall improvement of the performance (i.e. lower turn-on voltage, higher efficiency and light output) when increasing the porphyrin loading up to 2%. However, the LEDs performance lowers when the loading exceeds 5%. Given the partial overlap of the **MPP(Pt)** absorption with the PFO emission, we speculate that the EL emission at low voltages is mainly due to

charge trapping in the **MPP(Pt)** segment rather than energy transfer. However, upon a further increase in the applied voltage, charges can be injected directly into the PFO levels and can subsequently migrate to the **MPP(Pt)** moiety and contribute to the phosphorescence emission.

#### 4. Conclusions

We have prepared a series of conjugated copolymers containing **MPP(Pt)**, a platinum(II)-complexed porphyrin, directly into the PFO backbone via the meso position. Emission of the polymers at 665 nm was shown to have a lifetime decay on the microsecond scale, indicating phosphorescence for all porphyrin-containing polymers, with decreased fluorescence from the PFO backbone as the w/w of **MPP(Pt)** was increased. The polymers were incorporated into OLEDs, and 2% w/w of **MPP(Pt)** was shown to have an efficiency of 0.48% and a light output of  $2630 \text{ mW/m}^2$ . Pure **MPP(Pt)** electrophosphorescence is achieved for loading as low as 2%.

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#### Disclosure Statement

No potential conflict of interest was reported by the author(s).

#### Supplemental data

Supplemental data for this article can be accessed [10.1080/21606099.2015.1047473](https://doi.org/10.1080/21606099.2015.1047473).

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