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ARTICLE

## Bis(pyridylpyrazolate)platinum(II): a mechanochromic complex useful as dopant for colour-tunable polymer OLEDs.

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The photoluminescent and mechanochromic behaviour of bis(3-(3,5-bis(dodecyloxy)phenyl)-(5-pyridin-2-yl)pyrazolate)platinum(II) complex PT12, selected from a series of Pt(II) compounds having *N,N'*-pyridylpyrazolate ligands, has been investigated. The electroluminescent properties of polymer OLEDs based on PT12-doped polyfluorene (PFO) are also described. Addition of PT12 induces the formation of PFO  $\beta$ -phase, a much more ordered phase with enhanced colour stability at high bias and high photoluminescence quantum efficiency. Additionally, the characteristic blue emission of PFO is red-shifted for PT12 concentrations equal or higher than 3%. Depending on the dopant concentration and the applied current, the colour coordinates of these polymer OLEDs undergo a broad shift in the CIE colour space. Besides, through the strategic use of keto defect sites, white-emitting devices can be fabricated with a mere addition of PT12.

**Keywords:** organic light-emitting diode, polymer OLEDs, platinum complexes, white-light emitters.

### Introduction

The research of electroluminescent metal complexes has led to several types of emitters based on Ir, Os, Pt or Au metal centres.<sup>1</sup> In particular, Pt(II) complexes result of technological interest for the fabrication of efficient organic light-emitting diodes (OLEDs) on the basis of their interesting photophysical properties.<sup>2</sup> Chelation of platinum centres by selected organic ligands containing delocalised  $\pi$ -systems enhances the generation of an efficient intersystem crossing as a result of spin-orbit coupling, allowing to achieve high quantum yields and long lifetimes of triplet emission. The formation of aggregates through axial contacts (*e.g.* Pt-Pt interactions) is enhanced by their square-planar coordination geometry, which allows inducing metal-metal-to-ligand charge transfer (<sup>3</sup>MMLCT) excited states.<sup>3</sup> In contrast with a metal-to-ligand charge transfer (MLCT), the <sup>3</sup>MMLCT emission is significantly red-shifted,<sup>4-6</sup> this feature being easily obtained by applying an external mechanical stimulus,<sup>7-10</sup> but also with the doping of a polymer matrix.<sup>11-13</sup> So, the greenish emission of these Pt(II) based systems can be transformed in the red luminescence of

the triplet excited state, which results to be potentially useful for the fabrication of colour-tunable OLEDs.<sup>6,14</sup> Additionally, the square-planar Pt(II) complexes has been extensively investigated over the last years because most of them exhibit phosphorescence at room temperature.<sup>15</sup>

Several Pt(II) cyclometalated compounds bearing porphyrins<sup>16,17</sup> and pincer<sup>18,19</sup> ligands have demonstrated to be useful as emissive materials for electroluminescent devices. In such complexes, the strong  $\sigma$  character of the M-ligand bonds enables the development of efficient photoluminescent materials while avoiding the dissociation of the metal.

On the other hand, it is worth establishing that the photophysical properties are often determined by the coordination environment around the metal centre and by the  $\pi$ -conjugation of the ligand. Thus, bidentate ligands containing azole rings and aromatic substituents are being increasingly investigated due to their ability to generate delocalised  $\pi$ -systems with high resonance energies, thus providing photoluminescence enhancement.<sup>15,20-22</sup> Besides, the presence of aromatic rings bearing heteroatoms and/or *N*-donor substituents is a factor especially reflected on phosphorescent boosting.

In this context, we have recently reported a new family of long-chained *N,N'*-pyridylpyrazole ligands that contributes to generate pseudo-cyclometalated Pd(II) and Pt(II) complexes having liquid crystal properties.<sup>23,24</sup> Following the above considerations, we have contemplated the possibility of testing these Pt(II) complexes as dopants of emitting polymers in OLEDs. In order to check this subject, we have selected the complex bis(3-(3,5-bis(dodecyloxy)phenyl)-(5-pyridin-2-yl)pyrazolate)platinum(II) PT12 (Figure 1), a phosphorescent

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† Electronic Supplementary Information (ESI) available: Schematic representation of pplymer-OLED devices and normalised EL spectra of these devices as a function of bias current. See DOI: 10.1039/b000000x.

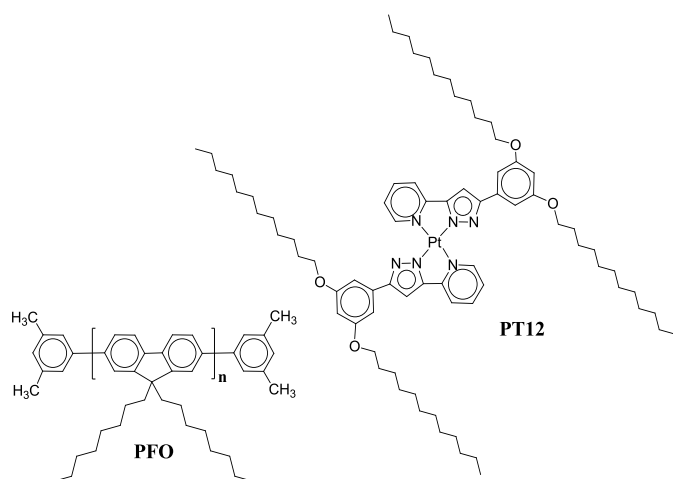


Figure 1. Molecular structures of PT12 and PFO end-capped with DMP

Pt(II) complex previously described by us.<sup>24</sup> Thus, PT12 is employed as a support of neutral species having high conjugation and square-planar environment. The coordination to the platinum centre could favour intraligand, ligand-to-ligand charge transfer, metal-to-ligand charge transfer and <sup>3</sup>MMLCT transitions.

On the other hand, fluorene-based polymers are employed as active materials in polymer organic light-emitting diodes (polymer OLEDs) as well as in other optoelectronic devices such as organic solar cells or organic lasers. In particular, poly(9,9-dioctylfluorene-2,7-diyl), PFO (Figure 1), is widely used due to its high efficiency, its good thermal stability<sup>25</sup> and its convenient solubility,<sup>26,27</sup> therefore potentially being an excellent host material for PT12 doping.

From a morphological point of view, PFO shows different phases such as nematic,  $\alpha$ ,  $\alpha'$  and  $\beta$ .<sup>28</sup> The PFO  $\alpha$ -phase has the fluorene units randomly oriented about the polymer backbone, giving rise to a relatively large band-gap ( $3.11 \pm 0.1$  eV).<sup>29</sup> In contrast, the PFO  $\beta$ -phase shows a planar *zig-zag* conformation that results in an extended conjugation length and a lower energy band-gap ( $2.94 \pm 0.1$  eV). This phase is identified in the absorption spectra by a narrow peak at 433 nm and in the electroluminescence (EL) spectra by a red-shifted emission band compared to  $\alpha$ -phase.<sup>30</sup>

Among all of these,  $\beta$ -phase has gained great attention because of its pure blue emission and its specific electronic and photonic properties. PFO  $\beta$ -phase devices exhibit enhanced carrier mobility,<sup>31-33</sup> improved luminescence<sup>34</sup> and higher efficiency<sup>35</sup> than the corresponding  $\alpha$ -phase devices. Besides,  $\beta$ -phase shows unique spectral characteristics for developing organic lasers.<sup>36,37</sup>

All in all, the combination of Pt(II) complexes enhancing phosphorescence with polyfluorenes or other active polymers seems to be promising for OLED devices. Several works on this subject have been reported: for example, phosphorescent light polarised emitting systems built with Pt(II) complexes and oligofluorene hosts,<sup>38</sup> highly-efficient white emitting devices using PMMA as the host matrix,<sup>3</sup> or OLEDs based on carbazole oligomers and polymers as hosts with improved energy transfer and enhanced efficiency.<sup>39</sup>

In this work we report on the emission properties of several devices based on PFO polymeric matrix doped with different concentrations of PT12 (0-5% w/w). The presence of 2% PT12 induces  $\beta$ -phase formation and triples luminance and efficiency. The emission colour evolves from bluish-green to orange with just 5% of PT12. These results are promising for the development of white light-emitting devices.

## Results and discussion

Bis(3-(3,5-bis(dodecyloxy)phenyl)-(5-pyridin-2-yl)pyrazolate)platinum(II) PT12 was synthesised by refluxing a mixture of  $K_2PtCl_4$  and two equiv. of the 3-(3,5-bis(dodecyloxy)phenyl)-(5-pyridin-2-yl)pyrazole in EtOH for 24 h, according to the procedure previously reported by us.<sup>24</sup> The complex PT12 was isolated as a yellow solid at room temperature. The coordination of the ligand in its pyrazolate form yielded to a neutral Pt(II) complex with a square-planar coordination environment and a high conjugation, both being important structural factors for obtaining a mechanoluminescence material useful as a dopant in OLEDs construction.

### Photophysical and mechanochromic behaviour of PT12

The absorption and emission spectra of PT12 in  $CH_2Cl_2$  solution were similar to those for most platinum azolate complexes, showing the characteristic bands of the monomeric species. Likewise, in the solid state, the fluorescence emission band at 500 nm ( $\tau = 4.5$  ns) was slightly red-shifted with respect to that of the solution, this feature being associated to the presence of self-assembled molecules via  $\pi$ -stacking.<sup>24</sup>

Interestingly, the solid-state photoluminescence of PT12 can be switched in response to several external stimuli. Upon grinding using a pestle or scraping with a spatula, the greenish emission at 500 nm of the crystalline solid turns bright orange ( $\lambda = 614$  nm), so exhibiting a 114 nm mechanochromic shift response. As shown in Figure 2, this colour interconversion is fully reversible and the initial greenish form can be restored by the addition of acetone or by exposure to dichloromethane vapour. On the basis of this behaviour, Figure 3 evidences the

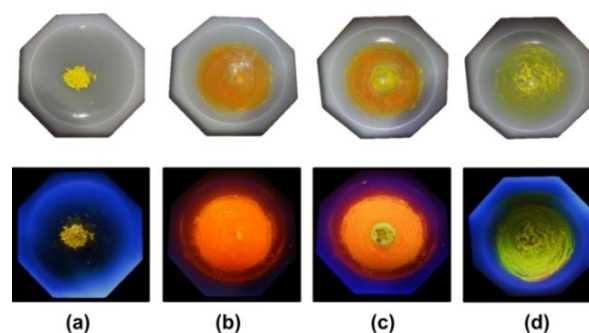


Figure 2. Photographs showing the mechanoluminescence behaviour of PT12 under ambient and UV light (365 nm): (a) crystalline solid, (b) sample after grinding, (c) ground sample after adding a drop of acetone, and (d) ground sample after exposure to  $CH_2Cl_2$  vapour.

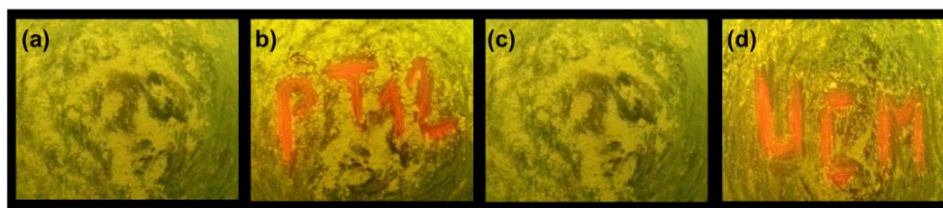


Figure 3. Rewritable data recording system based on mechanochromic and vapochromic properties of PT12: (a) fluorescence emission in the solid state, (b) mechanoluminescence response to write the letters "PT12" with a spatula, (c) natural greenish emission restored by exposure of the sample to  $\text{CH}_2\text{Cl}_2$  vapour, and (d) rewritable mechanochromic behaviour after erased.

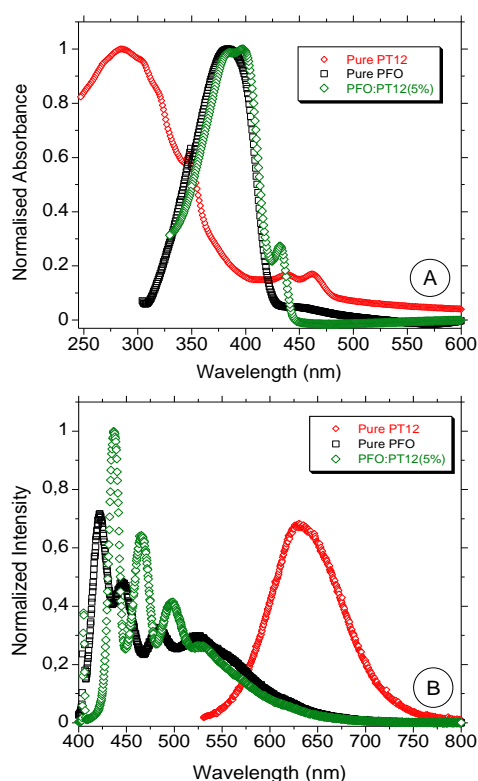


Figure 4. (A) Normalised UV-Vis absorption and (B) photoluminescence spectra of PT12, PFO and PFO:PT12(5%) thin films. The glitch at 350 nm is an artefact of the instrument. Excitation wavelength: 400 nm

rewritable ability of PT12 after being subjected to several cycles of recording and erasing information.

Additionally, the mechanical agitation not only generates a red-shifted emission, but also a change in the photoluminescence nature. The emissive red-shifted band, which can be attributed to a  $^3\text{MMLCT}$  state, together with time-dependent density functional theory calculations<sup>24</sup> evidences the phosphorescence nature of PT12 after grinding. A similar feature had been already observed in the phase transition from solid to the mesophase at 94 °C.<sup>24</sup> Precisely, this change in the emissive excited state will constitute the basis for the fabrication of phosphorescent polymer OLEDs based on PT12 as described below.

#### Photophysical measurements of PFO:PT12 thin-films

The absorption spectra of pure PFO and PT12, as well as of a blend of PFO:PT12(5%) were measured in thin films of *ca.* 100 nm. As seen in Figure 4A, the characteristic absorption band of

the amorphous PFO  $\alpha$ -phase appears at around 382 nm. However, the addition of a small percentage of PT12 results in the appearance of a new band at 438 nm. This peak is associated to formation of the PFO  $\beta$ -phase, in agreement with several studies which point out that doping PFO with low molecular weight materials may favour the formation of this phase.<sup>40</sup> The PFO  $\beta$ -phase has been the subject of many studies due to its greater colour stability at high bias and its high photoluminescence quantum efficiency.<sup>41-45</sup>

In our case, the potential  $\pi$ - $\pi$  interactions between aromatic groups of PT12 and PFO probably induce the latter to adopt a high-ordered coplanar arrangement in film, giving rise to an  $\alpha \rightarrow \beta$  phase transition by addition of PT12. This fact is in agreement with the  $\pi$ -stacking found in the solid state of analogous Pd(II) and Pt(II) complexes.<sup>23,24</sup>

The emission band of PT12 in solid thin films, associated to a  $^3\text{MMLCT}$  transition, was observed at *ca.* 632 nm, showing similar phosphorescence intensity to that of the PFO and a short lifetime of 70 ns (Figure 4B). Doping the PFO film with a 5% of PT12, the three maxima corresponding to the PFO  $\alpha$ -phase (421, 446 and 483 nm) were red-shifted *ca.* 17 nm (438, 466 and 498 nm, respectively). The presence of these well-resolved emission peaks and the small Stokes shift confirm again the existence of PFO  $\beta$ -phase domains in the doped polymer.<sup>46</sup>

On the other hand, the presence of keto defect sites,<sup>47</sup> as evidenced by the presence of an unstructured "green band" in the region of 520-540 nm is negligible in photoluminescence spectra.

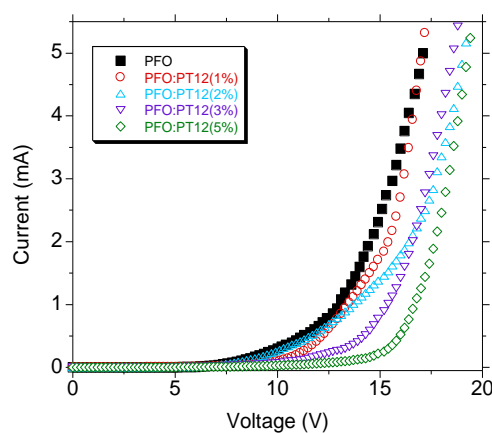


Figure 5. I-V curves of ITO/PEDOT:PSS/Active Layer/Al polymer OLEDs with structures based on PFO, PFO:PT12(1%), PFO:PT12(2%), PFO:PT12(3%), and PFO:PT12(5%). Diode active area: 7 mm<sup>2</sup>.



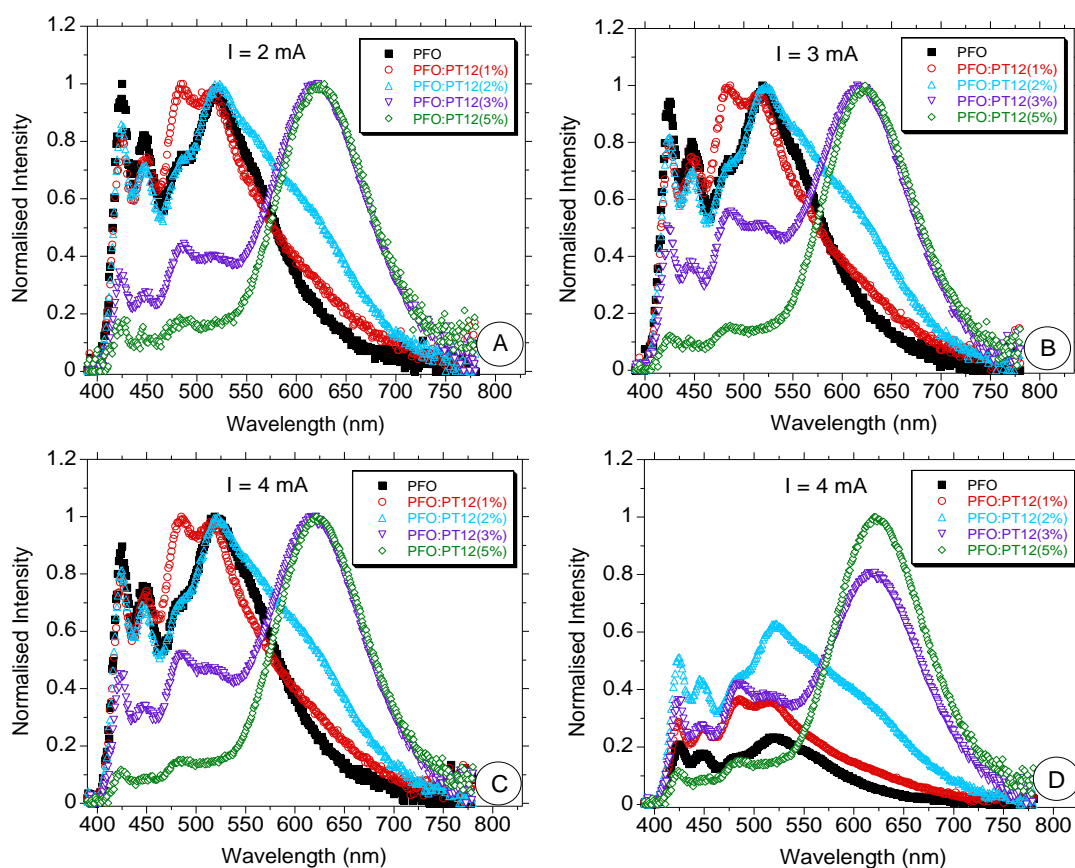


Figure 6. Normalised EL of polymer OLED devices with structures based on PT12-doped PFO for various dopant concentrations. The emission has been recorded at (A)  $I = 2$  mA, (B)  $I = 3$  mA, and (C)  $I = 4$  mA. (D) EL spectra of the devices measured at 4 mA and normalised to the highest peak.

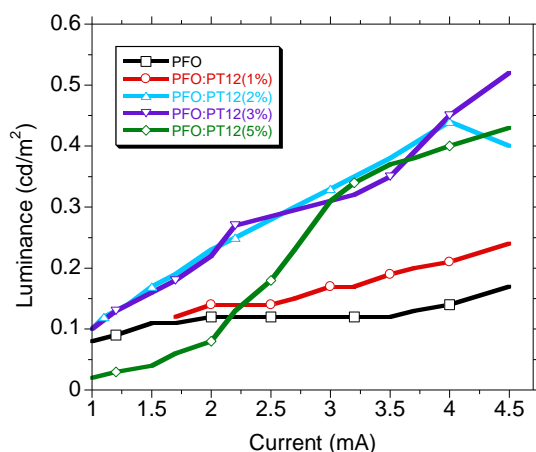


Figure 7. Luminance vs. current for polymer OLED devices based on PT12-doped PFO as a function of dopant concentration.

It is worth mentioning that varying the excitation wavelength modifies the photoluminescence spectra. The spectra shown in Figure 4B were acquired using excitation at 400 nm. If excitation is set at 342 nm, the PFO and PFO:PT12(5%) spectra remain unaffected, but the pure PT12 emission vanishes, becoming almost undetectable. This is apparently contradictory, since the PT12 absorption coefficient at 400 nm is negligible, much lower than its absorption coefficient at 342 nm in any case (Figure 4A).

These results point to the possibility of PT12 is excited by PFO through a radiationless energy transfer (RET) mechanism. Indeed, PFO thin films show an absorption maximum around 400 nm and a much lower absorption at 342 nm. The RET efficiency could be enhanced by the films adopting a stacked configuration. This configuration would be favoured by the planar arrangement of the PFO  $\beta$ -phase and the  $\pi$ -stacking of PT12/PFO.

#### Electrical and optical response of fabricated polymer OLEDs

Several polymer OLED devices with structure ITO/PEDOT:PSS/Active Layer/Al (Figure S1) were prepared with active layers based on PFO, PFO:PT12(1%), PFO:PT12(2%), PFO:PT12(3%), and PFO:PT12(5%). Figure 5 shows the I-V curves of fabricated devices. It can be seen that threshold voltage increases with PT12 concentration. This can be attributed to a poor conductivity of PT12 compared to pure PFO. The I-V curve corresponding to the device based on PFO:PT12(2%) presents a rather high parallel resistance, indicating a non-negligible leakage current at bias below threshold voltage.

Figures 6 and S2 show the electroluminescence (EL) spectra for all devices at different bias currents. EL shows a bathochromic shift from blue ( $\lambda = 425$  nm) for pure PFO to orange-red as the PT12 concentration increases, reaching a maximum at 625 nm for PT12 concentrations equal or higher

Table 1. Integral data of PT12 and PFO contributions to EL spectra at different dopant concentrations and bias currents.

Current [mA]	PT12 concentration [% w/w]	PT12 contribution [a.u.]	PFO contribution [a.u.]
2.5	1	0	0.5
	2	0	0.9
	3	0.2	0.5
	5	0.6	0.2
3.5	1	0	0.7
	2	0.06	1.2
	3	0.6	0.8
	5	1.2	0.3
4.5	1	0	0.8
	2	0.1	1.2
	3	0.9	1.0
	5	1.4	0.3

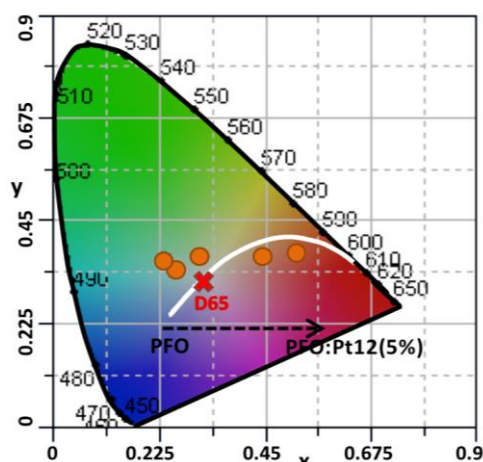


Figure 8. CIE coordinates in ITO/PEDOT:PSS/Active Layer/Al polymer OLEDs with structures based on PT12-doped PFO as in Figure 5. Emission recorded at 2 mA.

than 3%. This is in good agreement with solid state layer luminescence red-shift (see Figure 4B). Additionally, no colour change was occurred with time.

It is interesting to note that a wide band centred at *ca.* 520 nm associated to the presence of fluorenone was observed in all EL spectra.<sup>48</sup>

As it is well known, keto defect sites in polyfluorenes constitute an impediment for the fabrication of devices with a pure blue light emission.<sup>49,50</sup> However, they can play a key role in the design of white polymer OLEDs by doping with a red emitter.<sup>51,52</sup>

In this context, we consider the strategic introduction of fluorenone defects on the active layer during device fabrication. Thus, the EL emission is originated as a result of the recombination of holes and electrons through two mechanisms. First, a direct recombination within the PFO provides blue emission, together with the electron and hole trapping on the fluorenone and the PT12 units. Then, green and orange-red light emissions from fluorenone and the triplet excited state of PT12, respectively, are generated by a

radiative recombination process. The superposition of these colours results in a white electroluminescence.<sup>51,52</sup>

Figure 7 shows that luminance increases with bias current for all devices as expected. It can be noticed that luminance also increases with PT12 concentration, saturating for concentrations higher than 2%. This trend confirms that the incorporation of PT12 to PFO contributes to the formation of  $\beta$ -phase; moreover, the EL can be attributed to phosphorescent mechanisms that enhance the emission rather than quenching it.<sup>3,38</sup>

External quantum efficiency (EQE) has been calculated from the radiance data of Figure 6 taking into account the device area and integrating in the semi-sphere for all wavelengths. The maximum EQE value results in 0.1% and was obtained for the 3% PT12 device, which exhibits a luminous efficiency of  $8,09 \cdot 10^{-4}$  Cd/A at  $0.52$  Cd/m<sup>2</sup> and power efficiency of 19.8 lm/W. As expected, this is in agreement with the highest luminance curve shown in Figure 7.

In order to identify the contribution of each material to emission, the EL curves for all samples and currents have been integrated. Taking the *ca.* 420 nm PFO peak as a reference, and assuming that PT12 contribution to this wavelength is negligible, it is possible to separate the PFO and PT12 contributions to the spectra. Results are shown in Table 1. It can be observed that the PT12 contribution increases with dopant concentration in a higher than linear growth, while the PFO contribution decreases accordingly. This suggests a RET between PFO and PT12, similarly to the case shown in photoemission.

Figure 8 shows the evolution of the *x,y* colour coordinates in a CIE 1931 colour space. The colour coordinates evolve from left to right (*i.e.*, *y* coordinate is substantially constant) for devices increasing PT12 concentration at *I* = 2 mA. The chromaticity coordinates vary from (0.23, 0.36) for the pure PFO device up to (0.51, 0.38) for devices with 5% PT12 concentration. The intermediate PT12 concentrations, between 2% and 3%, intercept the black body curve (white line) close to the D65 (daylight) point. These emissions are perceived as white by the naked eye. This is a promising result for both lighting and display applications since the emission colour can be tuned by only modifying the relative concentration of the blend, covering substantially all the visible range.

## Conclusions

Platinum complexes like bis(3-(3,5-bis(dodecyloxy)phenyl)-(5-pyridin-2-yl)pyrazolate)platinum(II) enhance the emission of polymers like poly(9,9-dioctylfluorene-2,7-diyl) in polymer organic light-emitting diode structures. A mere addition of 2% Pt(II) complex induces the formation of  $\beta$ -phase and triples the emission efficiency. A radiationless energy transfer mechanism is suggested to justify the increasing phosphorescence of this compound with increasing current. At the same time, the emission colour varies substantially evolving from bluish to orange-red, according to the triplet excited state of the Pt(II) complex. Besides, the strategic introduction of keto defect

sites gives rise to a nearly white emission as a combination of the bluish and orange colours, and the green contribution from the fluorenone. It was achieved for intermediate concentrations at which the colour coordinates crossover the blackbody curve in the colour space.

## Experimental section

### Materials

The blue-light emitting poly(9,9-dioctylfluorene-2,7-diyl) (PFO), end-capped with DMP, was purchased from H.W. Sands (USA). Its molecular weight is 91.000 and its polydispersity is 3.0. The Pt(II) complex PT12 was obtained by reaction between the 3-(3,5-bis(dodecyloxy)phenyl)-(5-pyridin-2-yl)pyrazole ligand and  $K_2PtCl_4$  in ethanolic medium, following the procedure described previously.<sup>24</sup>

### Photophysical measurements

Absorption spectra of thin films were measured using a UV-VIS-NIR Spectrophotometer Varian Cary Scan 500. Photoemission (phosphorescence) spectra were acquired using a femtosecond (fs) excitation source and an optical detection apparatus from the Centre for Ultrafast Lasers (CLUR) of the Complutense University. The output of a Ti:sapphire laser was regeneratively amplified (Spitfire, Spectra Physics), resulting in laser pulses at 800 nm (35 fs, 1 kHz), which were directed to an optical parameter amplifier (OPA-800CF, Spectra Physics) to obtain a tunable laser in the range of ca. 400–800 nm. All measurements were recorded with an Ocean Optics USB2000 spectrometer.

### Polymer OLED fabrication

The final device had a structure: ITO/PEDOT:PSS/Active layer/Al. Commercial ITO (indium-tin oxide) coated glass substrates from Glasstone (ITO thickness =  $100 \pm 5$  nm, resistivity  $20 \Omega/\square$  "ohms per square") were first washed in ultrasonic bath for 30 min in bi-distilled water with microfiltered soap and then 15 min in bi-distilled water twice.

Highly transparent, conductive polymer PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) water suspension was filtered (with 0.5 mm PVDF filter) and sonicated for 3 h. PEDOT:PSS was then spin coated for 30 s at 4500 rpm and baked in furnace for 30 min at 120 °C yielding a thickness of 60 nm.

The active layers were spin-coated 1 min at 6000 rpm with 15 s ramp; no baking process was needed in this case. Five types of devices were fabricated with different active layers: pure PFO and PFO blended with PT12 at several percentages: PFO:PT12 (1% w/w), PFO:PT12 (2% w/w), PFO:PT12 (3% w/w), and PFO:PT12 (5% w/w) respectively, dissolved in toluene. The same sequence was used to create thin films of active material for absorption and photoemission measurements.

A cathode layer of Al (100 nm) was deposited by thermal evaporation on top of the device with a vacuum pressure lower than  $10^{-5}$  mbar. The presence of moisture may damage the functionality of the device through hydrolysis, hence the

devices were encapsulated in inert atmosphere using a glass cover attached by a bead of epoxy adhesive. The diode active area was  $7 \text{ mm}^2$ .

### Polymer OLED characterisation

Current-voltage (I-V) characteristic curves were recorded using an Agilent 4155C semiconductor parameter analyser and an Agilent 41501B SMU pulse generator. EL spectra and CIE coordinates were recorded using a CS-2000 Minolta Spectroradiometer. Samples were current driven under pulse conditions with 0.5% duty cycle in order to minimize degradation.

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## Notes and references

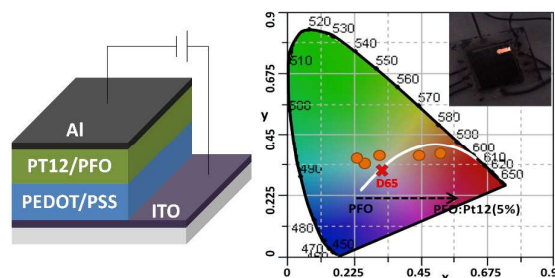
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## Bis(pyridylpyrazolate)platinum(II): a mechanochromic complex useful as dopant for colour-tunable polymer OLEDs.

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A novel metallomesogenic Pt(II) dopant on PFO-matrix allows inducing colour changes from bluish-green to orange-red with just 5% complex concentration.