

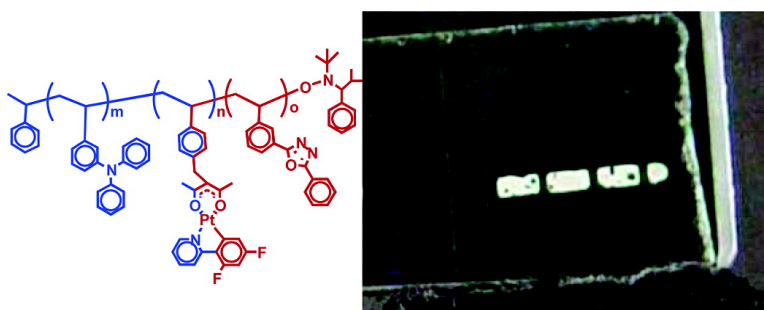
Communication

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Platinum-Functionalized Random Copolymers for Use in Solution-Processible, Efficient, Near-White Organic Light-Emitting Diodes

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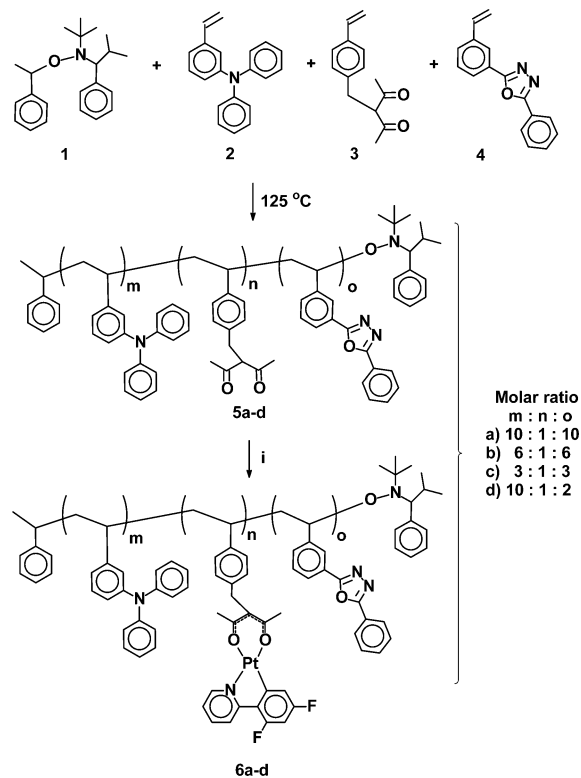
Electroluminescent devices based on cyclometalated metal complexes of Pt¹ and Ir² are of considerable interest due to their high quantum efficiencies (QE). The strong spin-orbit coupling of the heavy metal ions results in intersystem crossing from singlet to triplet excited state, allowing the complexes to utilize both singlet and triplet excitons, theoretically approaching 100% internal QE.³ Due to ligand effects and excimer emission, complexes based on Pt can emit over a wide range of wavelengths,^{1c,4} thus enabling the fabrication of organic light-emitting devices (OLEDs) in a range of colors, including white.⁵

Efficient white light devices are of particular interest, as they may be useful in a wide range of applications from backlight for displays in portable devices to broad area illumination sources for room lighting. Such white OLEDs have been prepared by both solution⁶ and vacuum^{5,7} deposition methods with best efficiencies recorded for devices obtained by vacuum deposition of small molecules.

We now report on near-white phosphorescent polymer OLEDs based on a single luminescent dopant, anchored to a polymer chain, which emits simultaneously from monomer (blue) and aggregate (orange) states. White polymer OLEDs have involved luminescence from different species, either uniformly dispersed in a single layer^{6a,d} or in separate layers,^{6b} resulting in a current-dependent color balance. Unfortunately, white light-emitting devices based on multiple independent emitters are expected to change color throughout the life of the device, due to differential aging of the different components. We have previously reported that vacuum-deposited OLEDs utilizing (2-(4',6'-difluorophenyl)pyridinato-N,C^{2'})(2,4-pentanedionato)Pt(II) dopant (FPt) emit white light from simultaneous blue FPt "monomer" emission and red emission from the excimer or aggregate FPt emission, with the ratio of blue to red emission controlled by the total FPt concentration (high concentration favors red emission). The excimer lacks a bound ground state, limiting energy transfer between dopants. Since the stability of both emitting species depends on only a single complex, the age-dependent color shifts should decrease.

In addressing the challenge of making a solution-processed device, which emits white light from a combination of monomer and excimer/aggregate states, we now report the synthesis of a multifunctional polymer-containing electron- (ET) and hole-transporting (HT) moieties as well as emitter complexes. First, a series of random terpolymers **5** containing triphenylamine (TPA), oxadiazole, and β -diketonate units was prepared by polymerization of various ratios of monomers **2**, **3**,⁸ and **4**⁹ using alkoxyamine initiator¹⁰ **1** at 125 °C. This living polymerization system¹¹ was chosen due to its compatibility with the various functional monomers and its ability to form predictable molecular weight polymers with low polydispersity. It should be noted that other

Scheme 1^a



^a Conditions: (i) 2-ethoxyethanol, anisole, [Pt-2-(4',6'-difluorophenyl)pyridinato(μ -Cl)]₂, Na₂CO₃, 80 °C.

living polymerizations such as ATRP involving metal catalysts might not be well suited for the preparation of **5**, as the presence of catalyst residues might impair device performance. Conjugated polymer systems containing phosphor complexes can suffer from quenching of phosphorescence for wavelengths lower than red,¹² which is the reason for choosing polymers with a photoinert backbone. The diketonate moieties of terpolymers **5a-d** were then metalated (Scheme 1) using [Pt-2-(4',6'-difluorophenyl)pyridinato(μ -Cl)]₂⁴ and Na₂CO₃ in a 2-ethoxyethanol/anisole mixture at 80 °C to give the final Pt-containing polymers **6a-d**. These air-stable metalated terpolymers have good solubility, enabling solution processing, and can be stored at room temperature.

All solution process steps were performed in air. OLEDs were prepared on indium-tin oxide (ITO)-coated glass substrates, upon which a 450 Å layer of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) was spin-coated and baked (90 °C for 45 min) prior to addition of polymers **6a-d**. The polymer layers (**6a-d**, 1000 Å) were spin coated from a chloroform solution, followed by thermal vacuum evaporation of 150 Å of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 250 Å aluminum-tris(8-

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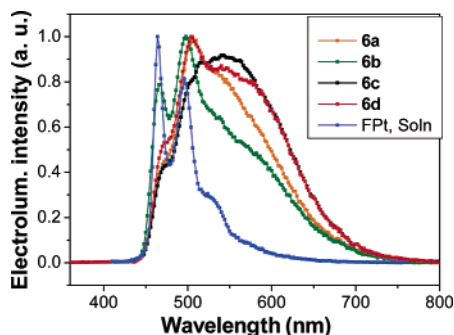


Figure 1. EL spectra of devices **6a–d** and the PL spectrum of FPt.

Table 1. Devices **6a–d** Performance, Color, and Composition

polymer	turn on voltage, V	EQE %	CIE coordinates	ratio of <i>m:n:o</i>
6a	7.8	4.6	$x = 0.33; y = 0.50$	10:1:10
6b	8.0	3.2	$x = 0.36; y = 0.48$	6:1:6
6c	8.1	3.0	$x = 0.38; y = 0.50$	3:1:3
6d	8.1	3.5	$x = 0.30; y = 0.43$	10:1:2

hydroxyquinolate) (Alq₃), and finally 1000 Å of LiF/Al for the cathode. The combined BCP/Alq₃ layers act as an efficient electron injecting contact.^{1a,13}

To achieve the goal of white light emission,¹⁴ two different forms of the Pt complex must be present within the polymer film: the monomeric form for blue monomeric emission and the aggregate form for orange excimer emission. Therefore, in addition to intrinsic structural features of the polymer, the concentration of the Pt complex⁵ will largely determine the extent of FPt–FPt interaction within the polymer. Figure 1 shows the electroluminescence (EL) spectra of devices made from polymers **6a–d**. Polymers **6a**, **6b**, and **6c** have the same HT/ET balance of 1:1, but have a Pt complex loading that increases from 6 to 10 and 18 wt %. A comparison of the EL of **6a** and **6b** shows that the latter has a broader spectrum beyond 550 nm. This is due to the higher concentration of complex, leading to an increased proportion of FPt with strong FPt–FPt interaction, hence the stronger emission in the orange to red part of the spectrum. This effect is much greater in **6c**, where the blue and green bands of the complex are nearly absent compared to the orange-red excimer/aggregate emission. Interestingly, while the loading of the Pt complex in **6b** and **6d** are identical (10 wt % each), the spectrum of **6d** with its large proportion of HT units has a noticeable contribution of the blue and blue-green monomer emission and less of the excimer emission than both **6b** and **6a**, even though the concentration of Pt complex is higher in **6d** than in **6a**. This appears to be an effect of the polarity of the environment, where the higher ratio of nonpolar TPA to polar oxadiazole favors the monomer complex emitting species over the excimer, compared to **6a–c**.

As mentioned previously, the colors emitted by devices made from **6a**, **6b**, and **6d** differ slightly, and this is reflected in their CIE coordinates (Table 1). However, all devices appear nearly white to the eye (pure white is $x = 0.33, y = 0.33$). Device **6c**, having greater excimer emission, was orange-white in color. The spectra were reproducible for each device made with the same polymer. The devices give EL spectra consistent with only dopant emission;

there is no copolymer backbone, HT, or ET emission observed at any bias level. The ratio of monomer/aggregate contributions in the EL spectra is also invariant with the applied voltage, leading to a voltage-independent, good quality, near-white broad emission. The performance of the devices also depended on the concentration of Pt complex, with **6a** having the best efficiency (4.6%) as well as the lowest turn on voltage (7.8 V); the other devices likely suffer Förster losses from high complex loading.

In conclusion, we have demonstrated that a random terpolymer, containing HT, ET, and phosphorescent Pt complex moieties, can be spin cast from solution to fabricate near-white light-emitting diodes with up to 4.6% external quantum efficiency (EQE), which is among the highest values reported for a solution-processed white-emitting device. Further changes in the composition ratio could potentially tune the emission closer to pure white.

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Supporting Information Available: Experimental and characterization data of polymers **5a–d** and **6a–d** and OLED structure, characterization, and performance data for all devices (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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