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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
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White Electroluminescence from All-Phosphorescent Single Polymers on a Fluorinated Poly(arylene ether phosphine oxide) Backbone Simultaneously Grafted with Blue and Yellow Phosphors

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Ⓢ *Supporting Information*

ABSTRACT: On the basis of a fluorinated poly(arylene ether phosphine oxide) backbone with both high triplet energy and appropriate HOMO/LUMO levels, highly efficient all-phosphorescent single white-emitting polymers were designed and successfully synthesized via a "two-step addition" strategy. Simultaneous blue and yellow triplet emissions were achieved to generate white electroluminescence with a promising luminous efficiency as high as 18.4 cd/A (8.5 lm/W, 7.1%) and CIE coordinates of (0.31, 0.43).

Single white-emitting polymers (SWPs)[1] have attracted great attention because of their advantages of no potential phase segregation and excellent spectral stability over physical-blend systems. The basic molecular design of these SWPs involves covalent tethering of chromophores with either two complementary colors (blue and yellow; named as two-color SWPs)[2] or three primary colors (red, green, and blue; named as three-color SWPs)[3] to the main or side chain of a polymer host at the same time. In other words, one macromolecule contains two or three chromophores, forming an intramolecular dopant/host system. Through fine-tuning of their doping contents at a very low level to manage the energy transfer and charge trapping, individual emissions from all of the incorporated chromophores can be achieved simultaneously, resulting in a continuous electroluminescence (EL) spectrum close to that of standard white light.

As shown in Figure 1 (where for clarity only side-chain SWPs with a linear architecture are presented), two-color SWPs can be divided into three classes according to the nature of the generated excitons: (I) all-fluorescent SWPs with only singlet blue and yellow emitters; (II) fluorescent/phosphorescent hybrid SWPs with both singlet blue and triplet yellow emitters; and (III) all-phosphorescent SWPs with only triplet blue and yellow emitters. Early in 2004, our group reported the first all-fluorescent SWPs and realized a luminous efficiency of 5.3 cd/A with Commission Internationale de L'Eclairage (CIE) coordinates of (0.25, 0.35).[2a] To utilize both singlet and triplet excitons, fluorescent/phosphorescent hybrid SWPs with a luminous efficiency of 6.1 cd/A and CIE coordinates of (0.32, 0.44) were subsequently developed in 2006 by the Cao

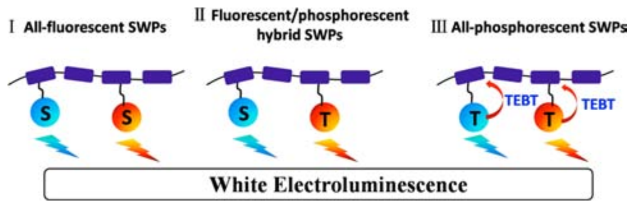

Figure 1. Schematic diagram of three kinds of two-color SWPs. S and T represent singlet and triplet emitters, respectively.

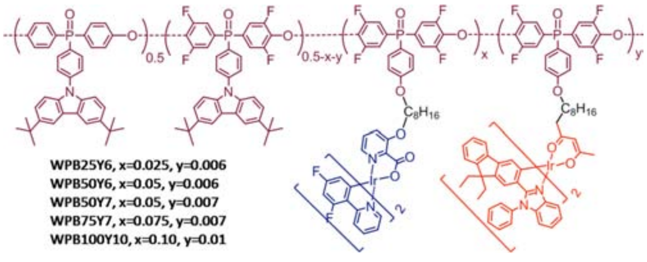

Figure 2. Molecular structures of the all-phosphorescent SWPs.

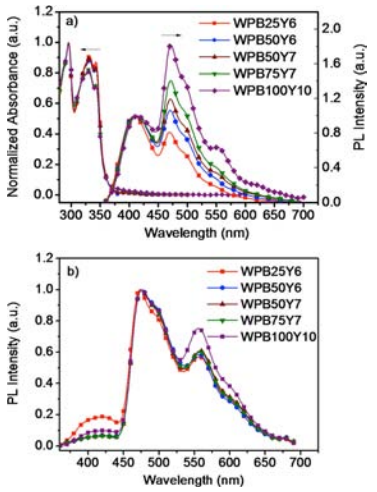

Figure 3. (a) Absorption (in CH_2Cl_2) and PL (in toluene) spectra of WPB25Y6−WPB100Y10 in solution and (b) their PL spectra in films.

Received: October 14, 2012
Published: December 6, 2012

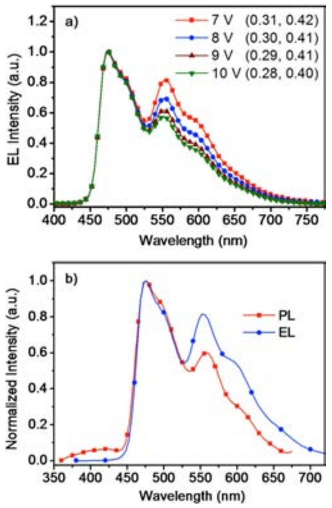

Figure 4. (a) EL spectra at various voltages and (b) a comparison of the PL and EL spectra at 7 V for WPB75Y7.

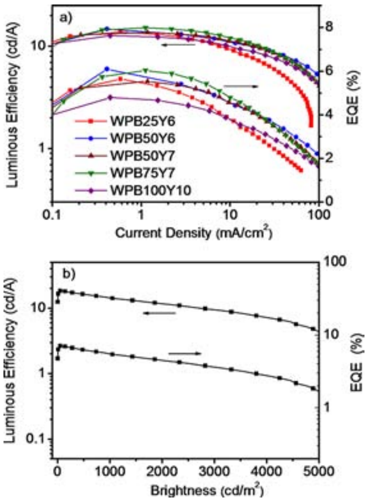

Figure 5. Luminous efficiency and EQE as functions of (a) current density for devices using TPCz as the ETM and (b) brightness when SPPO13 was used as the ETM.

group.[3a] Since then, a significant amount of work has been devoted to the design of all-fluorescent and fluorescent/phosphorescent hybrid SWPs, and their reported highest efficiencies have reached to 12.8 cd/A (5.4%)[2c] and 10.7 cd/A (5.4%),[2f] respectively. However, progress on all-phosphorescent SWPs remains challenging, although an interesting site isolation to produce white EL in phosphorescent bichromophoric block copolymers was attained in 2010.[2g] The lack of progress is likely due to the lack of suitable polymer hosts with high triplet energies above 2.75 eV as well as HOMO/LUMO levels matched with the Fermi levels of the electrodes.

In the case of all-phosphorescent SWPs, to prevent triplet-energy back-transfer (TEBT)[4] from the blue and yellow phosphors to the polymer host (Figure 1), the triplet energy of the polymer host should be at least 2.75 eV [0.1 eV higher than that of the typical blue phosphor bis[2-(4,6-difluorophenyl)-pyridinato-*κN*,*κC*](picolinato)iridium(III) (FIrpic)[5]]. However, enhancing the triplet energy would inevitably increase the HOMO−LUMO energy gap of the polymer host, leading to a large barrier for charge injection. This intrinsic contradiction,[6] we believe, undoubtedly has limited the development of efficient all-phosphorescent SWPs.

We very recently demonstrated a tradeoff between triplet energy and HOMO/LUMO levels in a fluorinated poly(arylene ether phosphine oxide) scaffold [FPCzPO; Figure S1 in the Supporting Information (SI)].[7] In the case of the obtained high triplet energy (2.96 eV), the HOMO/LUMO levels of FPCzPO can be adjusted to −5.7/−2.3 eV to facilitate charge injection. On the basis of this advantage, FPCzPO-based blue electrophosphorescent polymers exhibit a state-of-art efficiency of 19.4 cd/A, indicating that FPCzPO is a promising platform for all-phosphorescent SWPs.

In this communication, we report that highly efficient all-phosphorescent SWPs can be realized by grafting FPCzPO with blue and yellow phosphors simultaneously. The molecular structures of the designed all-phosphorescent SWPs are shown in Figure 2. Here FIrpic and bis[2-(9,9-diethyl-9*H*-fluoren-2-yl)-1-phenyl-1*H*-benzimidazolate-*κN*,*κC*](acetylacetonato)-iridium(III) [$(\mathrm{fbi})_2\mathrm{Ir(acac)}$][8] were selected as the blue and yellow phosphors, respectively, because their combination has been applied in the fabrication of highly efficient white organic light-emitting diodes (WOLEDs).[9] Meanwhile, in view of the compatibility of FIrpic, a similar low-temperature polycondensation (120 °C) was adopted.[7b]

The synthesis of these SWPs was challenging, as it seemed problematic to add both of the complex monomers, **Blue-MON** and **Yellow-MON**, together with the other monomers (**HO-Cz-MON** and **6F-Cz-MON**) at the initial stage of the polymerization (the "one-step addition" method; Scheme S1 in the SI). As indicated in Figure S2a, the EL emission from the yellow chromophore in the resulting polymer, WP′-B100-Y10, displayed a hypsochromic shift of 10 nm relative to the yellow electrophosphorescent polymer PY-10 (Figure S1). This abnormality may have been caused by ancillary ligand exchange between **Blue-MON** and **Yellow-MON**, as the replacement of the acetylacetonate ligand with picolinate would lead to a similar blue shift.[10] Further experiments would be needed to verify this hypothesis but were beyond the scope of this work.

Table 1. SWP Device Performance

polymer	V_{on} (V)[c]	$\eta_{\mathrm{l,max}}$ (cd/A)[d]	$\eta_{\mathrm{p,max}}$ (lm/W)[e]	EQE (%)[f]	L_{max} (cd/m²)[g]	CIE (*x*, *y*)[h]
WPB25Y6[a]	6.5	13.8	6.0	5.6	2243	(0.32, 0.39)
WPB50Y6[a]	6.1	14.8	6.7	6.1	5782	(0.28, 0.39)
WPB50Y7[a]	6.3	13.7	6.0	5.5	4194	(0.36, 0.41)
WPB75Y7[a]	6.1	15.2	6.7	6.0	4331	(0.30, 0.41)
WPB100Y10[a]	6.3	12.7	5.5	4.8	4406	(0.37, 0.43)
WPB75Y7[b]	5.8	18.4	8.5	7.1	5100	(0.31, 0.43)

[a]TPCz was used as the ETM. [b]SPPO13 was used as the ETM. [c]Turn-on voltage at a brightness of 1 cd/m². [d]Maximum luminous efficiency. [e]Maximum power efficiency. [f]Maximum external quantum efficiency. [g]Maximum brightness. [h]CIE coordinates at 1000 cd/m².

To avoid the negative color change, a "two-step addition" strategy was employed (Scheme S2). **Blue-MON** was first copolymerized with **HO-Cz-MON** and **6F-Cz-MON**, after which **Yellow-MON** was added to continue the polymerization. With this modified method, a series of all-phosphorescent SWPs (WPB25Y6–WPB100Y10) were successfully prepared by tailoring the feed ratios of **Blue-MON** and **Yellow-MON**. It should be noted that unlike WP′-B100-Y10, all of the polymers showed normal yellow emission from $(fbi)_2Ir(acac)$. For example, the yellow part in the EL spectrum of WPB100Y10 matched well with that of PY-10 (Figure S2b).

Figure 3a presents the absorption and photoluminescence (PL) spectra of WPB25Y6–WPB100Y10 in solution. They exhibited nearly identical absorption spectra in CH_2Cl_2 with peaks at 296, 333, and 343 nm. The metal-to-ligand charge transfer (MLCT) transitions from the Ir complexes were too weak to be discernible because of the low loadings of the complexes. As can be clearly seen in Figure 3a, two strong peaks at 410 and 472 nm accompanied by a shoulder at 568 nm were found in the PL spectra in toluene for all of the polymers, which can be ascribed to the emissions from FPCzPO, FIrpic, and $(fbi)_2Ir(acac)$, respectively. Moreover, the emission intensities of FIrpic and $(fbi)_2Ir(acac)$ increased gradually with the contents of the Ir complexes. This indicates that efficient intramolecular Förster energy transfer[11] from the polymer host to the Ir complexes can happen, as supported by the good overlap between the absorption spectra of FIrpic and $(fbi)_2Ir(acac)$ and the PL spectrum of FPCzPO (Figure S5).

In constrast to their behavior in solution, the emissions from both FIrpic and $(fbi)_2Ir(acac)$ became dominant in the thin-film PL profiles, while the FPCzPO emission almost disappeared (Figure 3b). This observation implies that there exists both intra- and intermolecular energy transfer in the films. Noticeably, the relative intensity ratio of the yellow to the blue emission is much higher than that in solution. According to our previous work, the energy transfer from FPCzPO to $(fbi)_2Ir(acac)$ is not as effective as that to FIrpic.[7b,12] Therefore, apart from the direct FPCzPO to $(fbi)_2Ir(acac)$ energy transfer, we speculate that a cascade process through the FIrpic sensitizer also contributes to this enhancement.[13] This is reasonable since the reduction in the distance between FIrpic and $(fbi)_2Ir(acac)$ in going from solution to the solid state would favor Dexter energy transfer[14] from FIrpic to $(fbi)_2Ir(acac)$.

To investigate their EL performance, white polymer light-emitting diodes (WPLEDs) were fabricated with WPB25Y6–WPB100Y10 as the emitting layer (EML). A double-layer device configuration of ITO/PEDOT:PSS (40 nm)/EML (40 nm)/TPCz (50 nm)/LiF (1 nm)/Al (100 nm) (Figure S6a) was used, where 3,6-bis(diphenylphosphoryl)-9-[4-(diphenylphosphoryl)phenyl]-9*H*-carbazole (TPCz) acts as an electron transport material (ETM).[15] The EL spectra of WPB75Y7 at various applied voltages (Figure 4a) showed almost bias-independent white EL, which is of key importance for practical applications. When the driving voltage was changed from 7 to 10 V, the CIE coordinates slightly shifted from (0.31, 0.42) to (0.28, 0.40).

In addition, a decline in the emission from $(fbi)_2Ir(acac)$ with increasing voltage was observed, suggesting that more charges are trapped on $(fbi)_2Ir(acac)$ at low operating voltages. This mechanism is consistent with the HOMO/LUMO levels of $(fbi)_2Ir(acac)$ and FPCzPO (Figure S6b) and is further proved by the difference between the PL and EL spectra of WPB75Y7 (Figure 4b). The intensity of the $(fbi)_2Ir(acac)$ emission relative to FIrpic in the EL spectrum turns out to be stronger than that in the PL, indicating the existence of charge trapping. Together with the above-mentioned energy transfer routes under light excitation, three possible processes may be involved in the WPLEDs: (1) Förster energy transfer from FPCzPO to FIrpic and $(fbi)_2Ir(acac)$; (2) direct charge trapping on $(fbi)_2Ir(acac)$; and/or (3) Dexter energy transfer from FIrpic to $(fbi)_2Ir(acac)$. With the synergistic effect of these possibilities, simultaneous emissions from FIrpic and $(fbi)_2Ir(acac)$ can be generated to create standard white EL.

Figure 5a shows the current density dependence of the luminous efficiency and external quantum efficiency (EQE) for WPB25Y6–WPB100Y10, and their device data are summarized in Table 1. Interestingly, we first note that the efficiency and CIE coordinates are not very sensitive to the contents of the Ir complexes. For instance, when the feed ratios of FIrpic and $(fbi)_2Ir(acac)$ were modulated from 2.5 to 10 mol % and 0.6 to 1 mol %, respectively, the luminous efficiencies gently varied within the range 14.0 ± 1.2 cd/A with CIE coordinates of (0.33 ± 0.05, 0.41 ± 0.02). Second, the typical chromophore doping concentration in all-phosphorescent SWPs (0.6–10 mol %) is 1–2 orders of magnitude higher than that in all-fluorescent SWPs (0.01–0.1 mol %),[2a−c] and the actual content of FIrpic can be estimated from the ^1H NMR spectrum (Figure S3). These two features are very beneficial for decreasing the batch-to-batch variation in the synthesis of SWPs and enhancing the reliability and reproducibility during the fabrication of WPLEDs. Furthermore, the higher doping concentration relative to all-fluorescent SWPs also helps to relieve the quandary in SWPs that the actual samples are mixtures of polymer chains containing chromophores with those containing no chromophores as a result of the extremely low doping level.

Among WPB25Y6–WPB100Y10, WPB75Y7 exhibited the best device performance, with a maximum luminous efficiency of 15.2 cd/A, a maximum power efficiency of 6.7 lm/W, and a peak EQE of 6.0%. The somewhat low power efficiency can be attributed to the high turn-on voltage of ca. 6 V, which is understandable when considering that there is still a hole injection barrier of 0.5 eV between the PEDOT:PSS layer and the EML (Figure S6b). This problem may be overcome by either elevating the HOMO level of the polymeric host (or blue phosphor) through rational molecular design[16] or inserting an additional hole transport layer on PEDOT:PSS.[17]

When 9,9′-spirobis(fluorine)-2,7-diylbis(diphenylphosphine oxide) (SPPO13)[18] was used as the ETM in place of TPCz, an optimized luminous efficiency of 18.4 cd/A (8.5 lm/W, 7.1%) was obtained (Figure 5b). Even at a brightness of 1000 cd/m^2, the luminous efficiency still remains as high as 14.2 cd/A, indicating a slow efficiency rolloff at high current density. To the best of our knowledge, this is the highest performance ever reported for all-phosphorescent SWPs. Relative to the phosphorescent bichromophoric block copolymers with non-conjugated polystyrene as the backbone (1.5%),[2g] the efficiency was improved ca. 4.7-fold. Furthermore, it was also much better than those of all-fluorescent and fluorescent/phosphorescent hybrid SWPs (5.4%), shedding light on the significance of all-phosphorescent SWPs.

In conclusion, with a fluorinated poly(arylene ether phosphine oxide) backbone that has a high triplet energy and appropriate HOMO/LUMO levels, we have synthesized a series of all-phosphorescent SWPs via a "two-step addition" strategy. Tuning their incorporated contents of FIrpic and (fbi)$_2$Ir(acac) resulted in the generation of individual blue and yellow emissions to give standard white EL with a prominent efficiency as high as 18.4 cd/A. Since even higher efficiencies have been realized for physical blend systems,[19] these all-phosphorescent SWPs bear a promising potential for further improvement. Also, related work on developing novel blue and yellow phosphors to replace FIrpic and (fbi)$_2$Ir(acac) is now under way.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, structural characterization data, and photophysical and EL properties of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the 973 Project (2009CB623602 and 2009CB930603), the National Natural Science Foundation of China (20923003, 21174144, and 21074130), and the Science Fund for Creative Research Groups (20921061) for financial support of this research.

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