JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Highly Efficient Blue Electrophosphorescent Polymers with Fluorinated Poly(arylene ether phosphine oxide) as Backbone

Shiyang Shao,[†,‡] Junqiao Ding,*[,†] Lixiang Wang,*[,†] Xiabin Jing,[†] and Fosong Wang[†]

[†]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

[‡]Graduate School, Chinese Academy of Sciences, Beijing 100039, P. R. China

Supporting Information

ABSTRACT: In view of the tolerance of F atoms in FIrpic to the nucleophilic aromatic substitution polymerization, an activated fluorinated poly(arylene ether phosphine oxide) backbone is used to construct novel blue electrophosphorescent polymers containing FIrpic as the blue emitter, because they can be synthesized under a milder temperature of 120 °C. Compared with the counterparts prepared at high temperature (165 °C), unexpected bathochromic shift is successfully avoided, and a state-of-art luminous efficiency as high as 19.4 cd A^{-1} is achieved. The efficiency is comparable to the corresponding physical blend system, which indicates that the fluorinated poly(arylene ether phosphine oxide) has the potential to be used as the platform for the development of high-performance all-phosphorescent white polymer based on single polymer system.

Electrophosphorescent polymers,[1] where the phosphorescent dyes are incorporated into the polymeric main chain or side chain via covalent bonds, have attracted considerable interest since they can not only harvest both singlet and triplet excitons to achieve nearly 100% internal quantum efficiency, but also be fabricated by low-cost wet processes, such as spin-coating and inkjet printing. Most importantly, compared with the physical blends of polymer hosts and phosphors, the risk of phase segregation[2] can be effectively prevented for electrophosphorescent polymers. To date, much effort has been paid to the development of red and green electrophosphorescent polymers, and their luminous efficiencies have reached up to 26.7[1f] and 50.5 cd A^{-1},[1k] respectively. By contrast, the highest reported efficiency of blue electrophosphorescent polymers has remained 5.5 cd A^{-1} since the discovery in 2003,[1b,e,3] which is far inferior to that of the corresponding physical blend system.[4] On the other hand, as one of the three primary colors, blue electrophosphorescent polymers are indispensable components for low-cost full-color displays as well as white light sources. In view of these two points, it is highly desirable to design efficient blue electrophosphorescent polymers. Nevertheless, this is a challenging task due to the lack of the polymer hosts with suitable triplet energy level and HOMO/LUMO levels used as their backbones.

To achieve efficient blue electrophosphorescence, in principle, some critical criteria have to be taken into account for the backbone of blue electrophosphorescent polymers. Of primary importance is to increase the triplet energy of the polymeric backbone to be higher than 2.75 eV,[5] so that triplet excitons can be effectively confined on the phosphor.[6] Simultaneously, appropriate HOMO and LUMO levels should match well with the Fermi levels of the electrodes to facilitate charge injection. However, it is very difficult to meet these two requirements at the same time, because the polymer with high triplet energy will usually suffer from charge injection problems.[7] For example, poly(*N*-vinylcarbazole) (PVK) with a high triplet energy of 3.0 eV is often used as the backbone for blue electrophosphorescent polymers. However, it has a deep HOMO level of −5.9 eV and a shallow LUMO level of −2.1 eV, which leads to large charge injection barriers for air stable electrodes, and thus poor device performance (5.5 cd A^{-1}).[3c]

In our previous work, a trade-off between HOMO/LUMO levels and triplet energy has been realized on a novel bipolar polymer host, PCzPO, by adopting a poly(arylene ether phosphine oxide) scaffold.[4a] Compared with PVK, its HOMO and LUMO levels are tuned to −5.7 and −2.3 eV, respectively, to improve the charge injection capability while the triplet energy remains as high as 2.96 eV. With PCzPO as the host of a typical blue phosphor, iridium(III)[bis(4,6-difluorophenyl)-pyridinato-N,C^2]-picolinate (FIrpic), a luminous efficiency of 23.3 cd A^{-1} is attained, which indicates that PCzPO is a promising polymer host for FIrpic.

To realize efficient blue emission using electrophosphorescent polymer rather than physical blend system, we attempt to directly introduce FIrpic to the side chain of PCzPO through a covalent linkage for the construction of blue electrophosphorescent polymers (Scheme 1a). Unfortunately, the resultant polymer PB′-0.05 exhibits a bathochromic shift of 11−18 nm relative to the corresponding physical blend that is composed of 5 mol % FIrpic mixed with PCzPO (Figure S1). This observed abnormal emission of PB′-0.05 may be ascribed to the displacement of the F atoms in FIrpic by nucleophilic attack under the harsh polycondensation condition that involves the adoption of a base in a polar aprotic solvent at a high temperature (165 °C).

In this communication, we report the usage of a different fluorinated poly(arylene ether phosphine oxide) as the backbone and its attachment to the same Ir complex, FIrpic (Scheme 1b). This change allows the successful preparation of high-efficiency blue electrophosphorescent polymers with

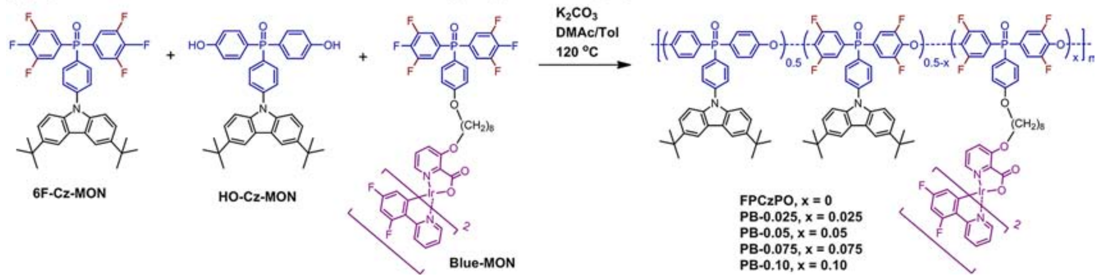
Received: June 11, 2012
Published: September 6, 2012

dx.doi.org/10.1021/ja305634j | *J. Am. Chem. Soc.* 2012, 134, 15189−15192

Scheme 1. Comparison of the Synthetic Routes for Blue Electrophosphorescent Polymers

(a) Synthetic route of PCzPO-based blue electrophosphorescent polymers

(b) Synthetic route of FPCzPO-based blue electrophosphorescent polymers



normal triplet emission from FIrpic. Here several issues should be noted as follows: (1) Owing to the activation of the monomer 6F-Cz-MON induced by the incorporated four electron-withdrawing F atoms adjacent to the C−F bonds para to P atom, the nucleophilic aromatic substitution polymerization can be carried out smoothly at a moderate temperature of 120 °C. Consequently, FIrpic is compatible with this milder condition, and unwanted color alteration of blue electrophosphorescent polymers can be avoided. (2) Although six C−F bonds exist, the nucleophilic reaction occurs merely on the two activated C−F bonds para to P atom. This is in accordance with the literature,[8] and supported by the fact that only one strong singlet peak appears at −8.02 ppm (vs fluorobenzene) in the ^{19}F NMR spectrum of FPCzPO (Figure S2). If the C−F bonds meta to P atom take part in the polymerization, there would be at least two sets of signals. (3) The incorporation of additional F atoms almost does not affect the original electronic properties of the main chain. As presented in Figure S3, the triplet energy and HOMO/LUMO levels of FPCzPO are estimated to be 2.96 and −5.7/−2.3 eV, respectively. These values are comparable to those of PCzPO, implying that FPCzPO can act as a suitable host for FIrpic as PCzPO does.

On the basis of the above-mentioned modified backbone and milder polymerization condition, a series of blue electrophosphorescent polymers (PB-0.025 ~ PB-0.10) have been synthesized by tailoring the feed ratio between 6F-Cz-MON and Blue-MON. Workup of simply washing by water, and then precipitating in methanol affords these polymers pure enough to be used in PLEDs without any residual catalyst contamination, which is always a big trouble in transition-metal-catalyzed conjugated polymers.[9] These polymers possess good solubility in common organic solvents together with high decomposition temperatures (T_d) above 370 °C. Meanwhile, the actual content of FIrpic in the polymer is quantified by comparing the integration of the ^{1}H NMR signals at 3.95−4.10 ppm from -CH_2O- groups in the alkyl spacer with the singlet peak at 8.10 ppm related to the protons of carbazole units (Figure S4). As listed in Table S1, the Ir loading is found to be slightly lower than the feed ratio, consistent with the literature.[10]

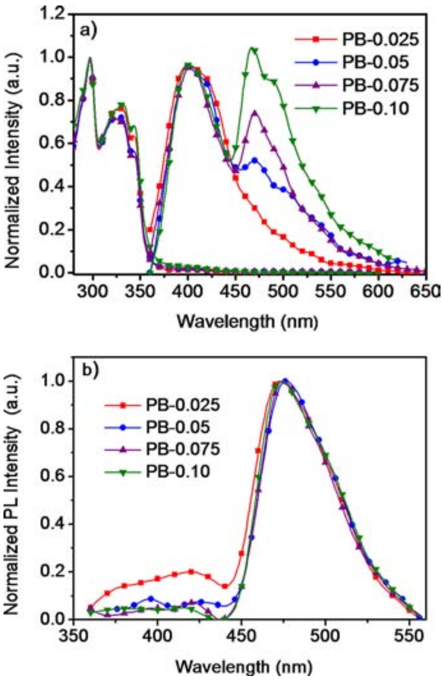


Figure 1. The absorption and PL spectra of PB-0.025 ~ PB-0.10 in DCM solutions (a), and their PL spectra in films (b).

Figure 1 shows the absorption spectra in dichloromethane (DCM) solutions of PB-0.025 ~ PB-0.10 and their photoluminescent (PL) spectra both in DCM solutions and solid states. All the polymers display strong $\pi-\pi^*$ absorption peaks at 297/329/344 nm, similar to those of FPCzPO. And the low energy absorption bands at 375−450 nm corresponding to the metal-to-ligand charge transfer (MLCT) transition of FIrpic are too weak to be discernible due to the low Ir loading. As can be clearly seen in Figure 1a, there exist two distinct PL peaks at about 402 and 472 nm, which are assigned to the emissions of

FPCzPO and FIrpic, respectively. It is worthy noting that, unlike PB′-0.05, PB-0.025 ~ PB-0.10 have normal phosphorescence from FIrpic, indicative of the successful introduction of FIrpic into the FPCzPO side chain without destroying the structure of FIrpic. Furthermore, with the increasing Ir loading, the relative emission intensity ratio between FIrpic and FPCzPO increases noticeably. This demonstrates that intramolecular Förster energy transfer can happen from FPCzPO to FIrpic, because there is a good overlap between the absorption spectrum of FIrpic and PL spectrum of FPCzPO (Figure S5).[11]

On going from solutions to solid states, the emission of FIrpic further dominates the whole PL profiles (Figure 1b), suggesting the contribution from both intra- and intermolecular Förster energy transfer. Even in PB-0.025, noticeably, the emission of FPCzPO is quenched to a large extent. It differs from PCzSiIr2.5,[3b] where the emission of the polymeric host, 3,6-carbazole-alt-tetraphenylsilane copolymer (P36HCTPSi), is much more intense albeit the same incorporated Ir complex content. This difference can be reasonably explained by the higher triplet energy of FPCzPO than P36HCTPSi, which prevents the loss of triplet excitons.

To evaluate their electroluminescent (EL) performance, PB-0.025 ~ PB-0.10 are used as the emitting layer (EML) to fabricate electrophosphorescent devices with a configuration of ITO/PEDOT:PSS (40 nm)/EML (40 nm)/TPCz (50 nm)/LiF (1 nm)/Al (100 nm), where TPCz[12] acts as an electron transporting and hole blocking material. Figure 2a presents the EL spectra of PB-0.025 ~ PB-0.10 at a driving voltage of 8 V. They all reveal similar EL feature with a Commission Internationale de L'Eclairage (CIE) coordinates of (0.18, 0.33). Moreover, the EL spectra are very close to their PL counterparts, and no additional emissions from FPCzPO or TPCz are observed. It is believed that, different from red electrophosphorescent polymers,[13] Förster energy transfer rather than charge trapping is mainly responsible for the EL process. This hypothesis can be further confirmed by the Ir complex concentration dependence of the current density (*J*) versus voltage (*V*) characteristics shown in Figure S6. Except for PB-0.025, the *J*−*V* curves shift toward a lower driving voltage with the increasing Ir loading for PB-0.05, PB-0.075 and PB-0.10.

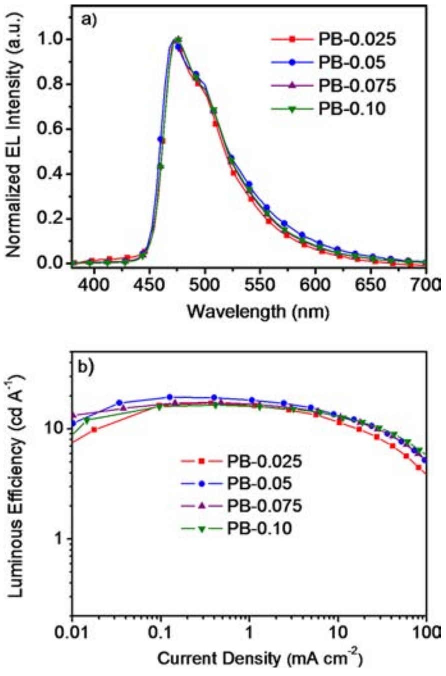


Figure 2. EL spectra of the polymers at a driving voltage of 8 V (a), and the luminous efficiency versus current density curves of PB-0.025 ~ PB-0.10 (b).

As depicted in Figure 2b and Table 1, the influence of Ir loading on device performance in this case is not as strong as that observed in red electrophosphorescent polymers. The luminous efficiency first rises from 17.1 cd A^{-1} of PB-0.025 to 19.4 cd A^{-1} of PB-0.05, and then decreases to 16.5 cd A^{-1} of PB-0.10. And a variance of about 15% is observed when the Ir loading changes in the range of 2.5−10 mol %. Among these blue electrophosphorescent polymers, PB-0.05 gives the best performance with a peak luminous efficiency of 19.4 cd A^{-1}, a peak power efficiency of 10.0 lm W^{-1}, a peak external quantum efficiency (EQE) of 9.0% and a maximum brightness of 5508 cd m^{-2}. Even at a brightness level of 1000 cd m^{-2}, the luminous efficiency still remains as high as 14.5 cd A^{-1} (EQE 6.7%), indicating a gentle roll-off of device efficiency at high current density. To our best knowledge, this is the highest efficiency for blue electrophosphorescent polymers ever reported, which nearly approaches that of the physical blend of PCzPO and FIrpic. In addition, an about 3.5-fold improvement of the luminous efficiency has been realized by comparison to the blue electrophosphorescent polymers with PVK as the main chain.[1b] Considering that the grafted guest is the same in these studies (FIrpic), we propose that the state-of-art performance of the resulting polymers can be attributed to the use of a fluorinated poly(arylene ether phosphine oxide) backbone.

Table 1. Device Performance of the Blue Polymers

polymer	V_{on}[a] [V]	$\eta_{l,max}$[b] [cd A^{-1}]	$\eta_{p,max}$[c] [lm W^{-1}]	EQE[d] (%)	L_{max}[e] [cd m^{-2}]	CIE[f] (*x*, *y*)
PB-0.025	5.1	17.1	9.0	8.0	3927	(0.18, 0.33)
PB-0.05	5.3	19.4	10.0	9.0	5508	
PB-0.075	5.3	17.3	8.9	8.0	5531	
PB-0.10	5.3	16.5	8.8	7.6	6367	

[a] Turn-on voltage at a brightness of 1 cd/m^2. [b] Maximum luminous efficiency. [c] Maximum power efficiency. [d] Maximum external quantum efficiency. [e] Maximum brightness. [f] CIE coordinates at a voltage of 8 V.

In conclusion, novel blue electrophosphorescent polymers with a fluorinated poly(arylene ether phosphine oxide) as their backbone have been successfully synthesized under a compatible condition with FIrpic because of the activation of the monomer resulting from the fluorine substituents. Most importantly, the resulting polymers emit normal phosphorescence from FIrpic, and show a promising luminous efficiency as high as 19.4 cd A^{-1}. We believe this work will pave the way for the development of high-performance blue electrophosphorescent polymers as well as all-phosphorescent single white polymers[14] in the future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

AUTHOR INFORMATION

Corresponding Author

junqiaod@ciac.jl.cn; lixiang@ciac.jl.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful to the 973 Project (2009CB623601 and 2009CB930603), National Natural Science Foundation of China (Nos. 20923003, 21174144 and 21074130), and Science Fund for Creative Research Groups (No.20921061) for financial support of this research.

REFERENCES

(1) (a) Chen, X. W.; Liao, J. L.; Liang, Y. M.; Ahmed, M. O.; Tseng, H. E.; Chen, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 636−637. (b) Tokito, S.; Suzuki, M.; Sato, F.; Kamachi, M.; Shirane, K. *Org. Electron.* **2003**, *4*, 105−111. (c) Furuta, P. T.; Deng, L.; Garon, S.; Thompson, M. E.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 15388−15389. (d) Jiang, J. X.; Xu, Y. H.; Yang, W.; Guan, R.; Liu, Z. Q.; Zhen, H. Y.; Cao, Y. *Adv. Mater.* **2006**, *18*, 1769−1773. (e) You, Y.; Kim, S. H.; Jung, H. K.; Park, S. Y. *Macromolecules* **2006**, *39*, 349−356. (f) Chien, C. H.; Liao, S. F.; Wu, C. H.; Shu, C. F.; Chang, S. Y.; Chi, Y.; Chou, P. T.; Lai, C. H. *Adv. Funct. Mater.* **2008**, *18*, 1430−1439. (g) Liu, J.; Pei, Q. *Curr. Org. Chem.* **2010**, *14*, 2133−2144. (h) Park, M.-J.; Kwak, J.; Lee, J.; Jung, I. H.; Kong, H.; Lee, C.; Hwang, D.-H.; Shim, H.-K. *Macromolecules* **2010**, *43*, 1379−1386. (i) Poulsen, D. A.; Kim, B. J.; Ma, B.; Zonte, C. S.; Fréchet, J. M. J. *Adv. Mater.* **2010**, *22*, 77−82. (j) Ma, Z.; Chen, L.; Ding, J.; Wang, L.; Jing, X.; Wang, F. *Adv. Mater.* **2011**, *23*, 3726−3729. (k) Liu, J.; Yu, L.; Zhong, C.; He, R.; Yang, W.; Wu, H.; Cao, Y. *RSC Adv.* **2012**, *2*, 689−696.

(2) (a) Chen, F. −C.; He, G.; Yang, Y. *Appl. Phys. Lett.* **2003**, *82*, 1006−1008. (b) Chen, F. −C.; Chang, S. −C.; He, G.; Pyo, S.; Yang, Y.; Kurotaki, M.; Kido, J. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 2681−2690. (c) Noh, Y. −Y.; Lee, C. −L.; Kim, J. −J.; Yase, K. *J. Chem. Phys.* **2003**, *118*, 2853−2864.

(3) (a) Kimyonok, A.; Domercq, B.; Haldi, A.; Cho, J.-Y.; Carlise, J. R.; Wang, X.-Y.; Hayden, L. E.; Jones, S. C.; Barlow, S.; Marder, S. R.; Kippelen, B.; Weck, M. *Chem. Mater.* **2007**, *19*, 5602−5608. (b) Fei, T.; Cheng, G.; Hu, D.; Dong, W.; Lu, P.; Ma, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 1859−1865. (c) Tokito, S.; Suzuki, M.; Sato, F. *Thin Solid Films* **2003**, *445*, 353−357.

(4) (a) Shao, S.; Ding, J.; Ye, T.; Xie, Z.; Wang, L.; Jing, X.; Wang, F. *Adv. Mater.* **2011**, *23*, 3570−3574. (b) Earmme, T.; Ahmed, E.; Jenekhe, S. A. *Adv. Mater.* **2010**, *22*, 4744−4748. (c) Li, L.; Liu, J.; Yu, Z.; Pei, Q. *Appl. Phys. Lett.* **2011**, *98*, 201110.

(5) (a) Holmes, R. J.; Forrest, S. R.; Tung, Y. J.; Kwong, R. C.; Brown, J. J.; Garon, S.; Thompson, M. E. *Appl. Phys. Lett.* **2003**, *82*, 2422−2424. (b) Brunner, K.; van Dijken, A.; Borner, H.; Bastiaansen, J.; Kiggen, N. M. M.; Langeveld, B. M. W. *J. Am. Chem. Soc.* **2004**, *126*, 6035−6042.

(6) Sudhakar, M.; Djurovich, P. I.; Hogen-Esch, T. E.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7796−7797.

(7) Tao, Y.; Yang, C.; Qin, J. *Chem. Soc. Rev.* **2011**, *40*, 2943−2970.

(8) Bernal, D. P.; Bankey, N.; Cockayne, R. C.; Fossum, E. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1456−1467.

(9) (a) Nielsen, K. T.; Bechgaard, K.; Krebs, F. C. *Macromolecules* **2005**, *38*, 658−659. (b) Hou, Q.; Niu, Y.; Yang, W.; Yang, R.; Yuan, M.; Cao, Y. *Acta Polym. Sin.* **2003**, *1*, 161−166. (c) Tu, G.; Liu, Z.; Wang, L.; Ma, D.; Jing, X.; Wang, F.; Wu, H.; Peng, J.; Cao, Y. *Chin. J. Polym. Sci.* **2004**, *22*, 395−398. (d) Liu, R.; Zeng, W.; Du, B.; Yang, W.; Hou, Q.; Shi, W.; Zhang, Y.; Cao, Y. *Chin. J. Polym. Sci.* **2008**, *26*, 231−240.

(10) Evans, N. R.; Devi, L. S.; Mak, C. S. K.; Watkins, S. E.; Pascu, S. I.; Koehler, A.; Friend, R. H.; Williams, C. K.; Holmes, A. B. *J. Am. Chem. Soc.* **2006**, *128*, 6647−6656.

(11) Förster, T. *Discuss. Faraday Soc.* **1959**, 7−17.

(12) Ding, J.; Wang, Q.; Zhao, L.; Ma, D.; Wang, L.; Jing, X.; Wang, F. *J. Mater. Chem.* **2010**, *20*, 8126−8133.

(13) Ma, Z.; Ding, J.; Zhang, B.; Mei, C.; Cheng, Y.; Xie, Z.; Wang, L.; Jing, X.; Wang, F. *Adv. Funct. Mater.* **2010**, *20*, 138−146.

(14) (a) Wang, L.; Jing, X.; Wang, F. *Acta Polym. Sin.* **2009**, *1*, 980−991. (b) Bian, C.; Jiang, G.; Cheng, Y.; Xie, Z.; Wang, L. *Acta Polym. Sin.* **2012**, *0*, 334−346.