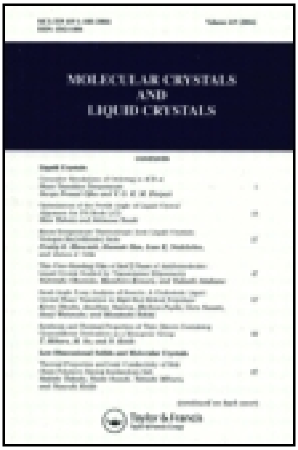

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A New Phosphorescent Iridium Complex and Its Orange and White Light-Emitting Devices

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A new orange phosphorescent iridium complex, Ir(2,4,5-F_3dpq)$_2$(acac), was designed and synthesized, where 2,4,5-F_3dpq represents 2-(2,4,5-trifluorophenyl)-4-phenylquinoline. Its photoluminescence (PL) maxima occurred at 577 nm. The organic light-emitting diode (OLED) device employing Ir(2,4,5-F_3dpq)$_2$(acac) as a dopant in the emitting layer showed orange electroluminescence (EL) centered at 585 nm. The white-OLED (WOLED) was fabricated by combining this orange phosphorescence from Ir(2,4,5-F_3dpq)$_2$(acac) and the blue fluorescence from 2-(2-hydroxyphenyl)benzoxazolato lithium (LiPBO). Combination of orange and blue emission at 585 nm and at 435 nm resulted in white light emission with CIE coordinates of (0.426, 0.360) and (0.376, 0.319) at 8 V and 14 V, respectively.

Keywords: blue fluorescence; iridium complex; orange OLED; orange phosphorescence; white OLED (WOLED)

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) that contain phosphorescent metal complexes as an emitting material have been attracting a great deal of attention because they can exhibit high efficiency in luminescence [1–9]. Recently, there has been a great interest focused on the development of materials for white OLEDs (WOLEDs) [10–17]. Several methods of producing white light from polymer- or

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small molecule-organic devices have been demonstrated [18–22]. Complicated emitting material systems, multilayer structures, and precise fabrication technologies were often necessary to obtain white light efficiently with good color purity [23–25]. The purpose of the present study was the development of an orange phosphorescent iridium(III) complex and its application to WOLEDs.

Kim, *et al*. previously reported that LiPBO (=2-(2-hydroxyphenyl) benzoxazolato lithium) exhibited a broad range of blue fluorescence peaks centered at 430–490 nm [26]. Meanwhile, WOLEDs containing blue fluorescent and red phosphorescent materials have been fabricated [10–13]. Since the ligands in the phosphorescent iridium complex can be designed and prepared for the emission color tuning, an orange phosphor could be designed and obtained from the reaction of the iridium precursor with a suitable ligand. White electroluminescence could then be realized using this phosphor and LiPBO. In this study, we synthesized a new orange light-emitting iridium complex chelated with 2,4,5-F_3dpq ligand, and investigated their luminescence properties. The orange and white OLEDs were prepared, using this iridium complex and/or LiPBO, and their electroluminescence (EL) characteristics were discussed.

2. EXPERIMENTAL SECTION

All reagents were purchased from Aldrich Co., except Ir(III) trichloride hydrate ($IrCl_3 \cdot H_2O$) which was purchased from Strem Co. and used without further purification. All reactions were carried out under an argon atmosphere. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230-mesh, Merck Co). LiPBO was prepared according to the method reported in the literature [26].

2.1. Synthesis of Ligands

2,4,5-F_3dpq. This fluorine-substituted ligand was obtained according to Friedlander reaction with 2-aminobenzophenone (1.972 g, 10.0 mmol) with 2,4,5-trifluoroacetophenone (1.741 g, 10.0 mmol) in 30 ml of glacial acetic acid. The solution was heated to reflux for 20 h at 115°C. The reaction mixture was then cooled and dripped slowly into an ice-cold solution of 50% ammonium hydroxide (140 ml) with stirring. The resultant precipitate was collected by filtration. The solid was chromatographed on a silica gel column with dichloromethane. Yield: 2.891 g, 86.3%.

2.2. Synthesis of Complexes

Ir(2,4,5-F$_3$dpq)$_2$(acac). This complex was obtained via two step reactions. The cyclometallated Ir(III) μ-chloro-bridged dimer, (C^N)$_2$Ir(μ-Cl)$_2$Ir(C^N), was first prepared according to Nonoyama method with slight modification [27]. The following reaction of the dimer with 2,4-pentandione gave Ir(2,4,5-F$_3$dpq)$_2$(acac). The resulting product was recrystallized in CH_2Cl_2/hexane. Yield: 10%.

2.3. Optical Measurements

UV-Vis absorption spectra were measured on a Hewlett Packard 8425 A spectrometer. PL spectra were measured on a Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of iridium complexes were measured in 10^{-5} M dilute CH_2Cl_2 solution.

2.4. Devices Fabrication

OLEDs were fabricated from thermal deposition of organic materials onto the surface of an indium tin oxide (ITO, 30 Ω/□, 80 nm) coated glass substrate under high vacuum (5×10^{-7} Torr.). An orange phosphorescent device and a white light-emitting device were prepared. The structure of the orange OLED containing Ir(2,4,5-F$_3$dpq)$_2$(acac) as a dopant was as follows: indium tin oxide (ITO)/4,4′,4″-tris[2-naphthylphenylamino]triphenylamine (2-TNATA) (60 nm)/4,4′-bis-[*N*-(naphthyl)-*N*-phenyl-amino]biphenyl (NPB) (20 nm)/10% Ir(2,4,5-F$_3$dpq)$_2$(acac) doped in 4,4,*N,N*′-dicarbazolebiphenyl (CBP) (30 nm)/bathocuproine (BCP) (10 nm)/tris-(8-hydroxyquinoline) aluminum (Alq$_3$) (20 nm)/lithium quinolate (Liq) (2 nm)/aluminum (100 nm). The configuration of the white OLED containing the phosphorescent Ir(dpq-2,4,5-F$_3$)$_2$(acac) and the fluorescent LiPBO as an orange and blue dopant, respectively, was indium tin oxide (ITO)/NPB (50 nm)/5% LiPBO doped in 2-methyl-9,10-di(2-naphthyl)anthracene (MADN) (19 nm)/CBP (5 nm)/8% Ir(dpq-2,4,5-F$_3$)$_2$(acac) doped in CBP (2 nm)/CBP (5 nm)/5% LiPBO doped in MADN (20 nm)/4,7-diphenyl-1,10-phenanthroline (BPhen) (30 nm)/lithium quinolate (Liq) (2 nm)/aluminium (100 nm). The active area of the OLEDs was 0.09 cm^2. The current density–voltage (J-V) characteristics of the OLED were measured with a source measure unit (Kiethley 236). The luminance and CIE chromaticity coordinates of the fabricated devices were measured using a chromameter (MINOLTA CS-100A). The electroluminescence (EL) spectrum was measured with a CCD type of spectrometer IVL 2000 of JBS International Corporation. All measurements were performed in ambient conditions under DC voltage bias.

3. RESULTS AND DISCUSSION

The ligand, 2,4,5-F_3dpq, was prepared by the Friedlander Reaction. The synthesis of its iridium complex was straightforward, according to the procedure reported by Nonoyama with slight modification [27], as summarized in Figure 1.

The UV-vis absorption spectra of the complex, Ir(2,4,5-F_3dpq)$_2$(acac), have intense bands appearing below 300 nm, as shown in Figure 2. These bands are assigned to the spin-allowed $^1(\pi \rightarrow \pi^*)$ transitions of the ligand portion in the complex. Due to the perturbation by the iridium center, these transitions were shifted with respect to those of the free ligands. The bands extending into the visible region from 300 to 390 nm are assigned to the spin-allowed metal-ligand charge transfer band (^{1}MLCT), and the weak bands at the longer wavelength than 390 nm are assigned to both spin-orbit coupling enhanced $^3\pi$-π^* and ^{3}MLCT transition. It is noteworthy that the formally spin forbidden ^{3}MLCT gains intensity by mixing with the higher-lying ^{1}MLCT transition through the strong spin-orbit coupling of Ir, which leads to strong absorption comparable to that of the allowed ^{1}MLCT.

The photoluminescence (PL) spectra of Ir(2,4,5-F_3dpq)$_2$(acac) are shown in Figure 3. Its emission maxima occurs at 577 nm where is in the region of orange luminescence. The bathochromic shift is observed in PL of Ir(2,4,5-F_3dpq)$_2$(acac), compared to that of the unsubstituted Ir(2,3-dpq)$_2$(acac). Such a hypsochromic shift could be explained by relative decrease of the HOMO level in the dpq ligand portion upon the ligand substitution: Involvement of an electron-withdrawing group, F, at the phenyl portion of the ligand mainly lowers the HOMO level of the complex. The resulting energy gap between the HOMO and the LUMO of the complex become then increased upon the F-substitution. Therefore, the PL peak of Ir(2,4,5-F_3dpq)$_2$(acac) appears at the shorter wavelength than that of Ir(dpq)$_2$(acac).

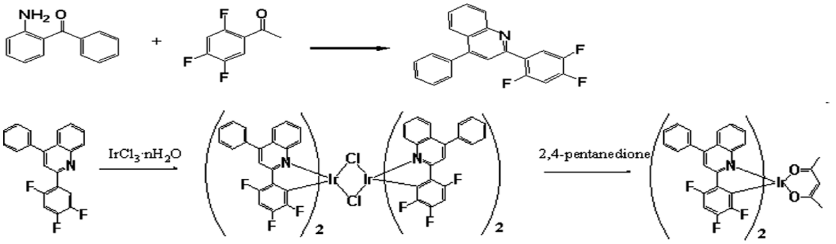

FIGURE 1 The synthesis of 2,4,5-F_3dpq and its iridium complex.

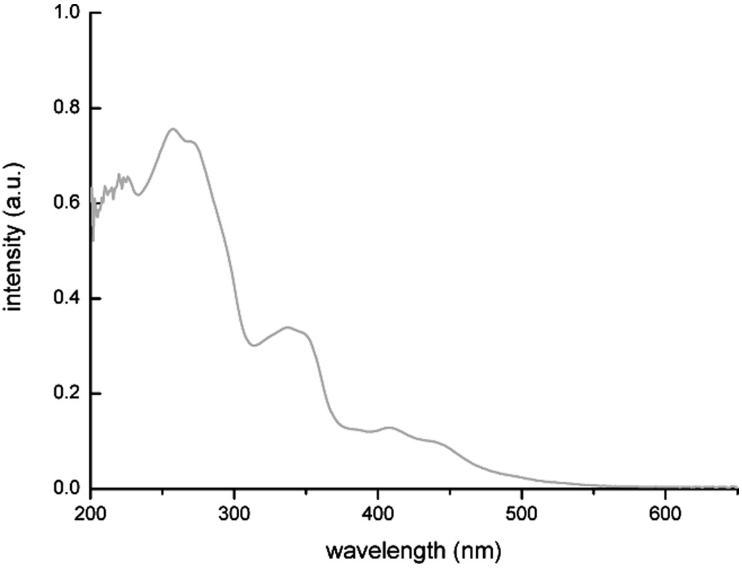

FIGURE 2 UV-Vis absorption spectra of Ir(2,4,5-F_3dpq)$_2$(acac).

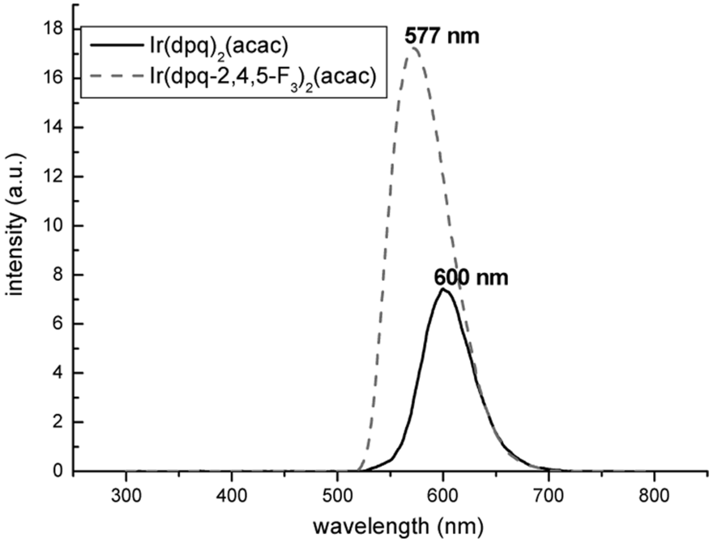

FIGURE 3 PL spectra of Ir(2,4,5-F_3dpq)$_2$ (acac) in a 10^{-5} M CH_2Cl_2 solution.

The orange phosphorescent iridium complex can be applied as a part of white OLEDs (WOLEDs), combined with a proper source of blue light-emitting material [10–17]. The intense luminescence covering a broad range of wavelengths is also required to develop the efficient WOLEDs. Thus, the orange light-emitting material developed in this study and an efficient blue fluorescent LiPBO which was reported to have rather a wide luminescence range are chosen as an orange phosphorescent and a blue fluorescent source for WOLEDs, respectively.

Figure 4 shows the luminances and luminous efficiencies of the orange OLED containing Ir(dpq-2,4,5-F_3)$_2$(acac) and those of the white OLED containing both Ir(dpq-2,4,5-F_3)$_2$(acac) and LiPBO. The luminances of devices are 11800 cd/m^2 and 15600 cd/m^2 for the orange and white OLEDs, respectively, at applied voltage of 14 V. The maximum luminous efficiencies of the orange and white OLEDs are 22.60 cd/A ($J = 1.09$ mA/cm^2) and 19.60 cd/A at ($J = 0.14$ mA/cm^2), respectively. The maximum power efficiencies of these devices are 12.10 lm/W ($J = 0.09$ mA/cm^2) and 13.20 lm/W ($J = 0.04$ mA/cm^2). Such high luminance of Ir(2,4,5-F_3dpq)$_2$(acac) leads to high performance of a WOLED by combination with LiPBO which also shows high luminance of 1500 cd/m^2 at 13 V [26].

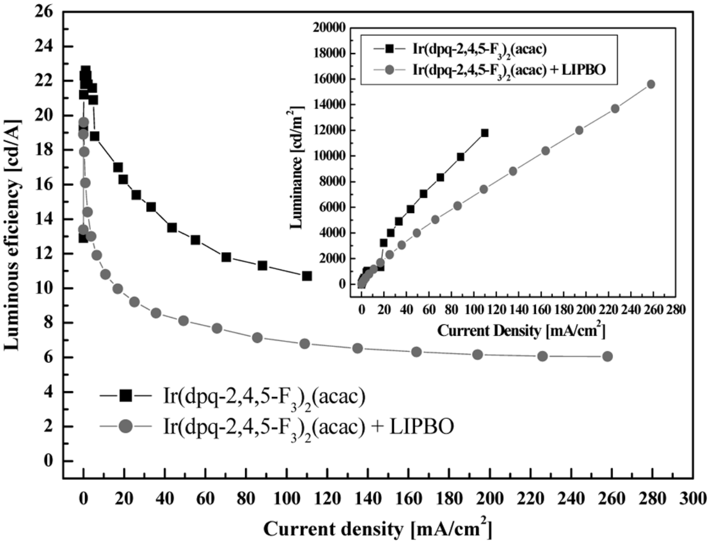

FIGURE 4 Luminous efficiencies (inset: luminance) of an orange and a white OLED vs. current density.

Figure 5 and its inset show the EL spectra of the orange and the white OLEDs depending on voltage, respectively, The monochromatic orange OLED has the emission maximum at 585 nm from phosphorescence of Ir(dpq-2,4,5-F_3)$_2$(acac), which is consistent with its PL peak at 577 nm. The white OLED exhibits both orange and blue emission from Ir(dpq-2,4,5-F_3)$_2$(acac) and LiPBO centered at 585 nm and 435 nm, respectively. The emission color of white OLED is changed as the applied voltage varies (inset of Fig. 5) while that of the orange OLED is independent of applied voltage and maintained with CIE coordinates of (0.538, 0.459) at 14 V (Fig. 6). It is because the intensity of the blue fluorescence from LiPBO becomes dominant over that of the orange phosphorescence from the iridium complex as the voltage increases. In other words, T-T annihilation of Ir(2,4,5-F_3dpq)$_2$(acac) causes the relative diminution of phosphorescence at the high voltage. The CIE coordinates of the white OLED are (0.426, 0.360) and (0.376, 0.319) at 8 V and 14 V, respectively, as shown in Figure 6. Therefore, the increase of voltage of the WOLED yields more whitish emission toward CIE coordinates of (0.33, 0.33) than the orange-white luminescence at lower voltage.

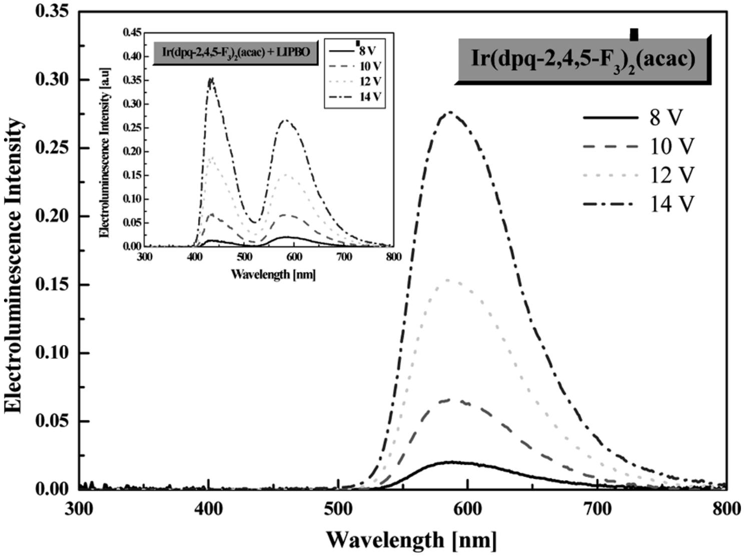

FIGURE 5 Electroluminescence (EL) spectra of an orange OLED with (Ir(2,4,5-F_3dpq)$_2$(acac)) (inset: a white OLED containing both Ir(2,4,5-F_3 dpq)$_2$(acac) and LiPBO) vs. voltage.

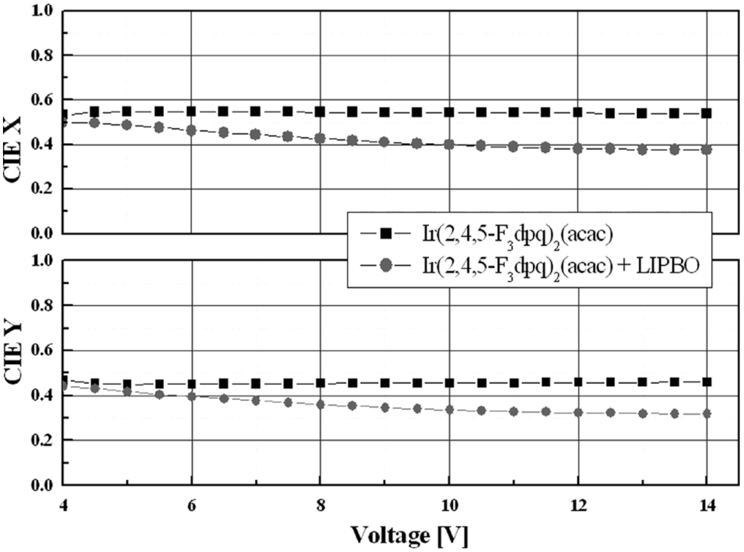

FIGURE 6 CIE Coordinates of the orange and white OLEDs vs. applied voltage.

CONCLUSION

The new orange phosphorescent complex, Ir(2,4,5-F_3dpq)$_2$(acac), was designed and prepared for the application to WOLEDs. Its photoluminescence (PL) maxima occurred at 577 nm. The light-emitting device (OLED) device employing Ir(2,4,5-F_3dpq)$_2$(acac) as a dopant in the device showed an orange electroluminescence (EL) centered at 585 nm with the luminous efficiency of 22.60 cd/A at $J = 1.09\,\mathrm{mA/cm^2}$. A WOLED was fabricated by combining this orange phosphorescence from Ir(2,4,5-F_3dpq)$_2$(acac) and the blue fluorescence from LiPBO. This OLED shows a white luminescence with combination of orange and blue emissions at 585 nm and 435 nm. Its CIE coordinates are (0.426, 0.360) and (0.376, 0.319) at 8 V and 14 V, respectively.

REFERENCES

[1] Baldo, M. A., O'Brien, D. F., You, Y., Shoustikov, A., Sibley, S., Thompson, M. E., & Forrest, S. R. (1998). *Nature*, *395*, 151.
[2] O'Brien, D. F., Baldo, M. A., Thompson, M. E., & Forrest, S. R. (1999). *Appl. Phys. Lett.*, *74*, 442.
[3] Baldo, M. A., Lamansky, S., Burrows, P. E., Thompson, M. E., & Forrest, S. R. (1999). *Appl. Phys. Lett.*, *75*, 4.

[4] Lamansky, S., Djurovich, P., Murphy, D., Adbel-Razzaq, F., Lee, H. E., Adachi, C., Burrows, P. E., Forrest, S. R., & Thompson, M. E. (2001). *J. Am. Chem. Soc.*, *123*, 4304.

[5] Ikai, M., Tokito, S., Sakamoto, Y., Suzuki, T., & Taga, Y. (2001). *Appl. Phys. Lett.*, *79*, 156.

[6] Adachi, C., Baldo, M. A., Thompson, M. E., & Forrest, S. R. (2001). *J. Appl. Phys.*, *90*, 5048.

[7] Tsuzuki, T., Shirasawa, N., Suzuki, T., & Tokito, S. (2003). *Adv. Mater.*, *15*, 1455.

[8] Tsuboyama, A., Iwasaki, H., Furugori, M., Mukaide, T., Kamatani, J., Igawa, S., Moriyama, T., Miura, S., Takiguchi, T., Okada, S., Hoshino, M., & Ueno, K. (2004). *J. Am. Chem. Soc.*, *125*, 12971.

[9] Tsuzuki, T. & Tokito, S. (2007). *Adv. Mater.*, *19*, 276.

[10] Seo, J.-H., Seo, J. H., Park, J. H., Kim, Y. K., Kim, J. H., Hyung, G. W., Lee, K. H., & Yoon, S. S. (2007). *Appl. Phys. Lett.*, *90*, 203507.

[11] Sun, Y., Giebink, N. C., Kanno, H., Ma, B., Thompson, M. E., & Forrest, S. R. (2006). *Nature*, *440*, 908.

[12] Kanno, H., Sun, Y., & Forrest, S. R. (2006). *Appl. Phys. Lett.*, *89*, 143516.

[13] Qin, D. & Tao, Y. (2005). *Appl. Phys. Lett.*, *86*, 113507.

[14] Lee, Y. G., Kee, I. S., Shim, H. S., Ko, I. H., Lee, S., & Koh, K. H. (2007). *Appl. Phys. Lett.*, *90*, 243508.

[15] Kim, Y. M., Park, Y. W., Choi, J. H., Ju, B. K., Jung, J. H., & Kim, J. K. (2007). *Appl. Phys. Lett.*, *90*, 033506.

[16] Tokito, S., Iijima, T., Tsuzuki, T., & Sato, F. (2003). *Appl. Phys. Lett.*, *83*, 2459.

[17] D'Andrade, B. W. & Forrest, S. R. (2004). *Adv. Mater.*, *16*, 1585.

[18] Chao, C. I. & Chen, S. A. (1998). *Appl. Phys. Lett.*, *73*, 426.

[19] Granstrom, M. & Inganas, O. (1996). *Appl. Phys. Lett.*, *68*, 147.

[20] Tasch, S., List, E. J. W., Ekstrm, O., Graupner, W., Leising, G., Schlichting, P., Rohr, U., Geerts, Y., Scherf, U., & Mllen, K. (1997). *Appl. Phys. Lett.*, *71*, 2883.

[21] Berggren, M., Gustafsson, G., Inganas, O., Andersson, M. R., Hjertberg, T., & Wennerstrom, O. (1994). *J. Appl. Phys.*, *76*, 7530.

[22] Jordan, R. H., Dodabalapur, A., Strukelj, M., & Miller, T. M. (1996). *Appl. Phys. Lett.*, *68*, 1192.

[23] Kido, J., Kimura, M., & Nagai, K. (1995). *Science*, *267*, 1332.

[24] Strukelj, M., Jordan, R. H., & Dodabalapur, A. (1996). *J. Am. Chem. Soc.*, *118*, 1213.

[25] Liu, Y., Guo, J., Zhang, H., & Wang, Y. (2002). *Angew. Chem. Int. Ed.*, *41*, 1.

[26] Kim, Y., Lee, J.-G., & Kim, S. (1999). *Adv. Mater.*, *11*, 1463.

[27] Nonoyama, M. (1975). *J. Organomet. Chem.*, *86*, 263.