Red-Emitting OLEDs

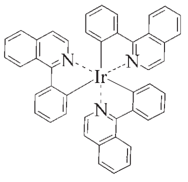
DOI: 10.1002/anie.200604094

Triphenylamine-Dendronized Pure Red Iridium Phosphors with Superior OLED Efficiency/Color Purity Trade-Offs**

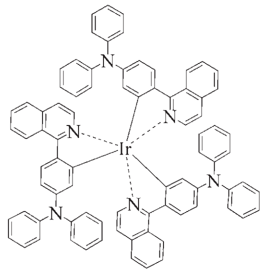
Guijiang Zhou, Wai-Yeung Wong, Bing Yao, Zhiyuan Xie,* and Lixiang Wang*

Since the first synthesis of red-phosphorescent metal complexes for use in highly efficient organic light-emitting diodes (OLEDs),[1] the scope and diversity of studies on metal–organic phosphors in color tuning have continued to expand at an exponential rate.[2,3] While great success has been achieved in green-light phosphors, the design and synthesis of efficient red emitters is intrinsically more difficult, in accordance with the energy-gap law.[4] Many red organic dyes currently in use do not show a good compromise between device efficiency and color purity because of the nature of red-light emitters.[4] Typically, efficient and bright dopants are not red enough, and red-enough dopants are not efficient and bright. Optimization of the OLED efficiency/color purity trade-offs is therefore a key consideration for the realization of highly efficient phosphors of good color purity for pure red OLEDs.

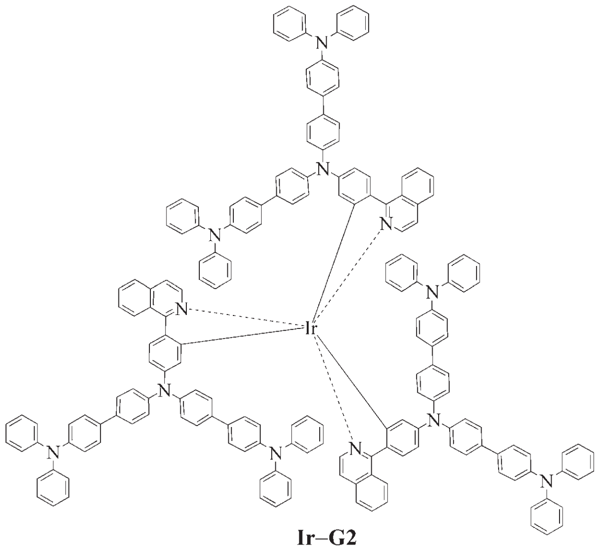
Recent research endeavors in the field of OLED devices have focused on solution-processable phosphorescent dendrimers and polymers owing to their advantages as low-cost, large-area displays and lighting sources.[5] In this regard, however, only a limited number of examples of phosphorescent dendrimers have been developed,[6] and their solution-processed OLEDs show a maximum external quantum efficiency (η_{ext}) of 5.7% for red light.[6c] In such cases, the first-generation molecules are not very effective in relieving molecular interactions among the emissive cores,[6e] although higher-generation dendrimers can usually reduce the carrier mobility substantially.[7] Despite this situation, the apparently poorer performance of the OLEDs fabricated by spin-coating than that of their vacuum-deposited counterparts suggests the need for more efforts in developing highly amorphous Ir^{III} complexes with new dendritic frameworks. Generally, a large hole-injection (HI) barrier for organic materials often limits the device efficiency. Since most of the hole-transporting (HT) materials reported are derived from aromatic amines,[8] the incorporation of arylamine units into the dendritic wedges should improve the HI/HT properties and the morphological stability of the Ir^{III} phosphors.



Ir–G0



Ir–G1



Ir–G2

In light of this, pure red-emitting bifunctional Ir^{III} complexes with triphenylamine dendrons (**Ir-G1** and **Ir-G2**) have been synthesized and compared with **Ir-G0**. The new dendrimers were isolated as highly amorphous ($T_g \approx 145$–$220\,^{\circ}$C) and thermally stable (decomposition starts above 417 °C) solids. The T_g value increases gradually with dendron size.

The Ir^{III} dendrimers show two major absorption bands in their UV/Vis spectra (Figure 1). The intense bands below 380 nm are assigned to the spin-allowed intraligand $^{1}\pi$–π^{*} transitions. The weaker, lower-energy features in the visible region are due to the ^{1}MLCT and ^{3}MLCT (metal–ligand charge transfer) excitations induced by the strong spin-orbital coupling between the singlet and triplet manifolds. Upon light irradiation at 420 nm, all Ir complexes show deep-red photo-

---

[*] Dr. G.-J. Zhou, Dr. W.-Y. Wong
Department of Chemistry
Hong Kong Baptist University and
Centre for Advanced Luminescence Materials
Waterloo Road, Kowloon Tong, Hong Kong (P.R. China)
Fax: (+852) 3411-7348
E-mail: rwywong@hkbu.edu.hk

B. Yao, Prof. Z.-Y. Xie, Prof. L.-X. Wang
State Key Laboratory of Polymer Physics and Chemistry
Changchun Institute of Applied Chemistry
Chinese Academy of Sciences
Changchun 130022 (P.R. China)
Fax: (+86) 431-5684937
E-mail: xiezy_n@ciac.jl.cn

[**] This work was supported by a CERG Grant from the Hong Kong Research Grants Council (HKBU 202106P) and a Faculty Research Grant from the Hong Kong Baptist University (FRG/04-05/II-59). OLED: organic light-emitting diode.

Supporting Information for this article is available on the WWW under http://www.angewandte.org or from the author.

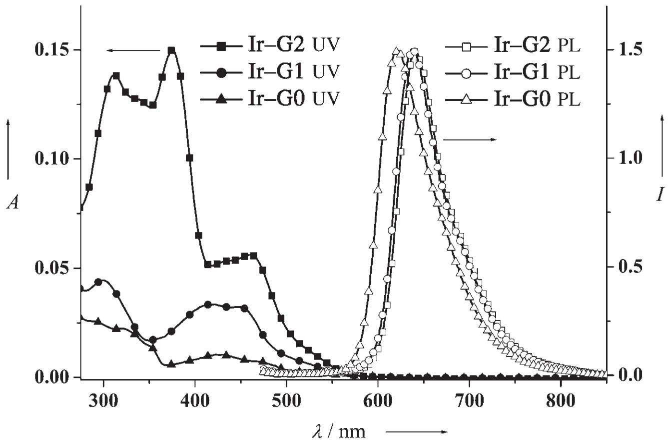


Figure 1. Absorption (left) and PL spectra (right) of iridium dendrimers in CH_2Cl_2 (conc. approximately 10^{-5} M).

luminescence (PL) in CH_2Cl_2, at 620 nm for **Ir-G0**, 636 nm for **Ir-G1**, and 641 nm for **Ir-G2** (Figure 1), and lifetimes as short as 0.81–1.40 μs in degassed toluene. A substantial increase of PL intensity with increasing dendritic generation can be seen in the PL spectra of neat films of the dendrimer complexes. This increase indicates that the dendritic structures will block the self-quenching of the triplet emission core effectively.

Table 1: Performance of iridium-containing dendrimer-based red OLEDs.

Device	Phosphor dopant	$V_{\text{turn-on}}$ [V]	Luminance L [cd m^{-2}][a]	η_{ext} [%][a]	η_{L} [cd A^{-1}][a]	η_{p} [Lm W^{-1}][a]	$\lambda_{\max}$ [nm][b]
A	**Ir-G1** (8 wt%)	4.4	7451 (17)	11.65 (5)	5.82 (5)	3.65 (5)	640 (0.70, 0.30)
B	**Ir-G1** (10 wt%)	4.3	6239 (18)	10.25 (5)	5.07 (5)	3.18 (5)	640 (0.70, 0.30)
C	**Ir-G1** (12 wt%)	4.0	5890 (17)	5.43 (6)	2.83 (6)	1.77 (5)	640 (0.70, 0.30)
D	**Ir-G2** (8 wt%)	4.7	6162 (16)	4.58 (9)	2.35 (9)	0.90 (8)	640 (0.70, 0.30)
E	**Ir-G2** (10 wt%)	4.7	6143 (16)	7.36 (6)	3.72 (6)	2.29 (5)	640 (0.70, 0.30)
F	**Ir-G2** (12 wt%)	4.7	6205 (17)	6.42 (7)	3.18 (7)	2.08 (7)	640 (0.70, 0.30)

[a] Maximum values of the devices. Values in parentheses are the voltages at which they were obtained. [b] Data were collected at 10 V; CIE coordinates in parentheses.

In the cyclic voltammograms, there is one reversible anodic redox couple for **Ir-G0**, two for **Ir-G1**, and five for **Ir-G2** (see the Supporting Information). The HOMO energy levels determined from the redox data for **Ir-G1** (−4.99 eV) and **Ir-G2** (−4.96 eV) are notably higher than that of **Ir-G0** (−5.11 eV). These data show that incorporation of the aromatic amine dendrons into the Ir^{III} core in **Ir-G1** and **Ir-G2** has a great impact on the self-quenching problem of the phosphors and can improve their HI/HT properties.

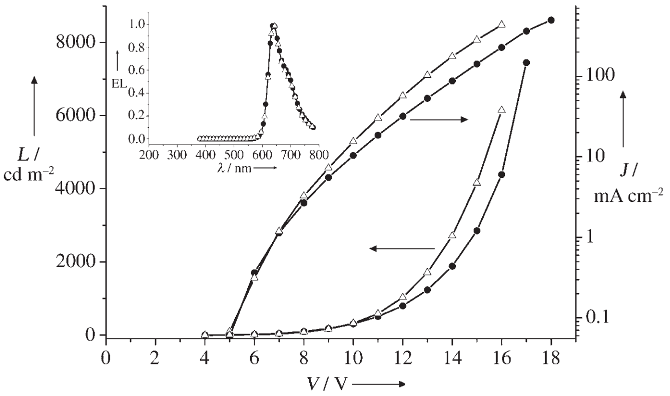


Figure 2. The *L–V–J* characteristics of device **A** (●) and device **E** (△) and their EL spectra (inset).

Deep-red OLEDs **A**–**F** were fabricated from **Ir-G1** and **Ir-G2** in the configuration ITO/PEDOT:PSS/x% Ir:CBP/BCP/Alq_3/LiF/Al (PEDOT = poly(3,4-ethylenedioxythiophene), PSS = poly(styrene sulfonate), CBP = 4,4′-*N*,*N*′-dicarbazole-biphenyl, BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, Alq_3 = tris(8-hydroxyquinoline)aluminum). The active dendrimer:CBP blend layer was deposited by spin-coating to give uniform thin films. It should be noted that CBP itself cannot be spin-coated from solution to form good-quality thin films. When the dendrimer concentration is below 5 wt% the CBP host is prone to crystallize in the as-prepared films and the devices short. This situation illustrates the ability of the dendritic architecture to enhance the processing properties of the materials for spin-coating. All of these devices emit pure red light with an electroluminescence (EL) maximum at around 640 nm and excellent CIE color coordinates of (0.70, 0.30; CIE: Commission International de L'Eclairage). The EL spectrum is consistent with the PL spectrum and indicates that the EL originates from the triplet states of the dendrimer. No emission from CBP or Alq_3 is observed, which suggests an efficient energy transfer from the host exciton to the phosphor molecule upon electrical excitation and the effective hole-blocking effect of BCP.

The device data are given in Table 1. The best device performance for devices **A**–**C** is achieved for **A** with a doping level of 8 wt%. The luminance–voltage–current density (*L*–*V*–*J*) characteristics for this device are shown in Figure 2. The device has a turn-on voltage of 4.4 V, a maximum brightness of 7451 cd m^{-2} at 17 V, an η_{ext} of 11.65% at 5 V, a luminance efficiency (η_{L}) of 5.82 cd A^{-1} at 5 V, and a power efficiency (η_{p}) of 3.65 Lm W^{-1} at 5 V. The EL spectrum of each device does not change substantially with the applied voltage (see inset of Figure 2 and the Supporting Information).

Devices **D**–**F** differ in their **Ir-G2** doping levels. Device **E**, with 10 wt% of **Ir-G2** as dopant, shows the best performance, with a turn-on voltage of 4.7 V, a maximum brightness of 6143 cd m^{-2} at 16 V, an η_{ext} of 7.36% at 6 V, an η_{L} of 3.72 cd A^{-1} at 6 V, and an η_{p} of 2.29 Lm W^{-1} at 5 V. Device **E** shows analogous *L*–*V*–*J* and EL characteristics to that of device **A** (Figure 2), although its current density is generally higher than that of device **A**, which may be ascribed to the better HI/HT characteristics of the dendritic array in **Ir-G2** than in its **Ir-G1** counterpart. In other words, the triphenylamine dendritic ligands might overcome the classical problem of carrier-mobility reduction with increasing dendron generation.[6f,7] Furthermore, the detrimental intermolecular interactions between the emission cores are reduced with increasing dendron generation. This can be seen by the observation of an excimeric emission band resulting from the intermolecular interaction in the excited state owing to concentration quenching in the EL spectrum of the device made from the neat film of **Ir-G1**, which is absent for **Ir-G2** (see the Supporting Information).

The sudden drop of η_{ext} for devices made from **Ir-G1** at a higher doping level (η_{ext} for device **B** is 10.25 % while that for device **C** is just 5.43 %) relative to that of **Ir-G2**-doped devices (7.36 % for device **E** and 6.42 % for device **F**) clearly shows the role of increasing dendron generation in reducing the quenching effect among the emissive cores. Hence, **Ir-G2** is a very promising pure red electrophosphor in spite of its slightly lower EL efficiencies compared with those of **Ir-G1**. The lower luminosity of these red-emitting devices is due to their characteristic pure red emission in a spectral region where the eye has poor sensitivity. The efficiencies of our devices with CIE (0.70, 0.30; $\eta_{ext} = 11.65\,\%$ for **Ir-G1** and 7.36 % for **Ir-G2**) are some of the highest reported for pure red spin-coated devices and are even superior or comparable to those of vacuum-deposited devices with a similar CIE color.[9]

The performance of device **A** compares well with the efficiency reported by Cao et al. for phosphorescent polymer LEDs with saturated red emission (about 12 %)[10] and is much better than those for first-generation red-emitting Ir dendrimers based on *meta*-bonded phenylene in terms of EL efficiency (5.70 and 4.25 %) and color purity ((0.64, 0.36) and (0.67, 0.30)).[6c] Device **A** also outperforms the best vacuum-evaporated device with the dopant **Ir-G0** in CBP, which has an η_{ext} of about 10.3 % and CIE (0.68, 0.32).[11] We attribute this excellent performance to the fact that the hole-trapping triphenylamine dendritic structure of the Ir^{III} complexes shows more favorable HI/HT properties.

In conclusion, we have synthesized two highly efficient pure red Ir^{III} phosphors. The EL efficiencies based on these metallodendrimers are some of the highest ever reported for solution-processed devices and are not far from those of the best evaporated devices with a comparable CIE. More importantly, these materials should provide an avenue for the synthesis of metal phosphors with the optimized EL efficiency/color purity trade-offs needed for pure red light, which is still a great challenge in the field of red-emitting materials.

Received: October 5, 2006

Keywords: dendrimers · iridium · OLEDs · optical properties · phosphorescence

[1] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151.

[2] a) V. Adamovich, J. Brooks, A. Tamayo, A. M. Alexander, P. I. Djurovich, B. W. D'Andrade, C. Adachi, S. R. Forrest, M. E. Thompson, *New J. Chem.* **2002**, *26*, 1171; b) W. Lu, B.-X. Mi, M. C. W. Chan, Z. Hui, C.-M. Che, N. Zhu, S.-T. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 4958; c) Y.-H. Niu, Y.-L. Tung, Y. Chi, C.-F. Shu, J. H. Kim, B. Chen, J. Luo, A. J. Carty, A. K.-Y. Jen, *Chem. Mater.* **2005**, *17*, 3532; d) Y.-L. Tung, S.-W. Lee, Y. Chi, L.-S. Chen, C.-F. Shu, F.-I. Wu, A. J. Carty, P.-T. Chou, S.-M. Peng, G.-H. Lee, *Adv. Mater.* **2005**, *17*, 1059; e) R. C. Evans, P. Douglas, C. J. Winscom, *Coord. Chem. Rev.* **2006**, *250*, 2093.

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

[4] a) C.-T. Chen, *Chem. Mater.* **2004**, *16*, 4389; b) S. D. Cummings, R. Eisenberg, *J. Am. Chem. Soc.* **1996**, *118*, 1949.

[5] a) S. Tokito, M. Suzuki, F. Sato, M. Kamachi, K. Shirane, *Org. Electron.* **2003**, *4*, 105; b) A. J. Sandee, C. K. Williams, N. R. Evans, J. E. Davies, C. E. Boothby, A. Köhler, R. H. Friend, A. B. Holmes, *J. Am. Chem. Soc.* **2004**, *126*, 7041; c) F.-I. Wu, H.-J. Su, C.-F. Shu, L. Luo, W.-G. Diau, C.-H. Cheng, J.-P. Duan, G.-H. Lee, *J. Mater. Chem.* **2005**, *15*, 1035.

[6] a) S.-C. Lo, N. A. H. Male, J. P. J. Markham, S. W. Magennis, P. L. Burn, O. V. Salata, I. D. W. Samuel, *Adv. Mater.* **2002**, *14*, 975; b) J. P. J. Markham, I. D. W. Samuel, S.-C. Lo, P. L. Burn, M. Weiter, H. Bässler, *J. Appl. Phys.* **2004**, *95*, 438; c) T. D. Anthopoulos, M. J. Frampton, E. B. Namdas, P. L. Burn, I. D. W. Samuel, *Adv. Mater.* **2004**, *16*, 557; d) S.-C. Lo, G. J. Richards, J. P. J. Markham, E. B. Namdas, S. Sharma, P. L. Burn, I. D. W. Samuel, *Adv. Funct. Mater.* **2005**, *15*, 1451; e) S.-C. Lo, E. B. Namdas, P. L. Burn, I. D. W. Samuel, *Macromolecules* **2003**, *36*, 9721; f) J. P. J. Markham, S.-C. Lo, S. W. Magennis, P. L. Burn, I. D. W. Samuel, *Appl. Phys. Lett.* **2002**, *80*, 2645.

[7] J. M. Lupton, I. D. W. Samuel, R. Beavington, M. J. Frampton, P. L. Burn, H. Bässler, *Phys. Rev. B* **2001**, *63*, 5206.

[8] Y. Shirota, *J. Mater. Chem.* **2000**, *10*, 1.

[9] a) D. K. Rayabarapu, B. M. J. S. Paulose, J.-P. Duan, C.-H. Cheng, *Adv. Mater.* **2005**, *17*, 349; b) J. Gao, H. You, J. Fang, D. Ma, L. Wang, X. Jing, F. Wang, *Synth. Met.* **2005**, *155*, 168; c) K. R. Justin Thomas, M. Velusamy, J. T. Lin, C.-H. Chien, Y.-T. Tao, Y. S. Wen, Y.-H. Hu, P.-T. Chou, *Inorg. Chem.* **2005**, *44*, 5677.

[10] C. Jiang, W. Yang, J. Peng, S. Xiao, Y. Cao, *Adv. Mater.* **2004**, *16*, 537.

[11] A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, *J. Am. Chem. Soc.* **2003**, *125*, 12971.