Inorg. Chem. **2008**, *47*, 6566−6568

Inorganic Chemistry
Communication

A Novel Solution-Processible Heterodinuclear Al^{III}/Ir^{III} Complex for Host−Dopant Assembly OLEDs

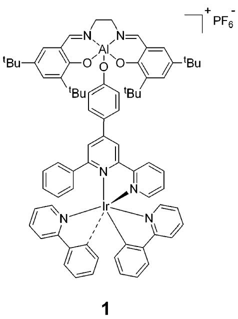
Jung Oh Huh,[†] Min Hyung Lee,[†] Hyosook Jang,[†] Kyu Young Hwang,[†] Jong Soon Lee,[‡] Se Hun Kim,[‡] and Youngkyu Do*,[†]

School of Molecular Science BK-21 and Center for Molecular Design and Synthesis, Department of Chemistry, KAIST, Daejeon 305-701, Korea, and R&D Center, Dongwoo FineChem Company, Ltd., 1177 Pyeongtaek-Si, Gyeonggi-Do 451-764, Korea

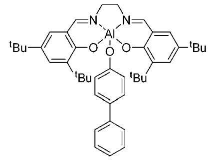
Received February 13, 2008

A discrete heterodinuclear Al^{III}/Ir^{III} complex shows bright-orange light emission when used as an active layer in host−dopant assembly organic light-emitting diodes based on a solution process.

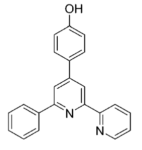
Luminescent metal complexes have been the focus of numerous studies owing to their potential applications in various areas, such as organic light-emitting diodes (OLEDs),[1] chemical sensors,[2] and photovoltaic devices.[3] In OLED applications in particular, the development of new solution-processible phosphorescent small molecules having the multifunctionality of host and emitter properties is extremely attractive. They can be used as light-emitting materials for host−dopant assembly OLEDs[4] based on a solution process, and the efficiency of small molecules can be maximized. Furthermore, easy and cheap fabrication of OLEDs can be achieved, and the drawbacks of phase separation[5] and excimer formation[6] associated with the spin-coating approach of blends of phosphorescent metal complexes[7] and host polymers can be overcome. In the present work, such a challenge has been met by coupling two luminophores, one as a host and the other as a phosphorescent emitter. As a result, an unprecedented heterodinuclear Al^{III}/Ir^{III} complex, $[(3,5\text{-}^t\text{Bu}_2)\text{salenAl}(\mu\text{-hpbpy})\text{Ir}(\text{ppy})_2]^+ [\text{PF}_6]^-$ (**1**), that can serve as a multifunctional light-emitting material for host−dopant assembly OLEDs based on a solution process was discovered as described below.



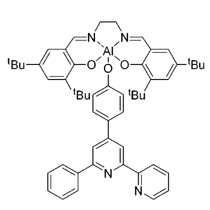
1



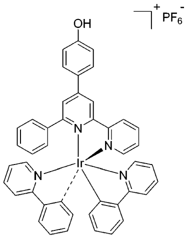
2



3



4



5

Recently, an efficient hole-blocking layer material **2** was developed in the form of a salen-based pentacoordinated Al^{III} complex for a phosphorescent OLED.[8] The HOMO−LUMO energy gap was observed to be 2.9 eV for **2** independent of the type of aryloxy ancillary ligand. Because this energy band gap appears to be suitable for a host, 4′-(4-hydroxyphenyl)-

---

* To whom correspondence should be addressed. E-mail: ykdo@kaist.ac.kr.

[†] KAIST.

[‡] Dongwoo FineChem Company, Ltd.

(1) (a) Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471. (c) Hung, L. S.; Chen, C. H. *Mater. Sci. Eng. Res.* **2002**, *39*, 143.

(2) (a) Cariati, E.; Bourassa, J.; Ford, P. C. *Chem. Commun.* **1998**, 1623. (b) Gao, R.; Ho, D. G.; Hernandez, B.; Selke, M.; Murphy, D.; Djurovich, P. I.; Thompson, M. E. *J. Am. Chem. Soc.* **2002**, *124*, 14828. (c) Badr, I. H. A.; Meyerhoff, M. E. *J. Am. Chem. Soc.* **2005**, *127*, 5318.

(3) (a) Hissler, M.; McGarrah, J. E.; Connick, W. B.; Geiger, D. K.; Cummings, S. D.; Eisenberg, R. *Coord. Chem. Rev.* **2000**, *208*, 115. (b) Jiang, K.-J.; Masaki, N.; Xia, J.-B.; Noda, S.; Yanagida, S. *Chem. Commun.* **2006**, 2460. (c) Rodríguez-Morgade, M. S.; Torres, T.; Atienza-Castellanos, C.; Guldi, D. M. *J. Am. Chem. Soc.* **2006**, *128*, 15145.

(4) (a) Lo, S.-C.; Anthopoulos, T. D.; Namdas, E. B.; Burn, P. L.; Samuel, I. D. W. *Adv. Mater.* **2005**, *17*, 1945. (b) Li, Y.; Rizzo, A.; Salerno, M.; Mazzeo, M.; Huo, C.; Wang, Y.; Li, K.; Cingolani, R.; Gigli, G. *Appl. Phys. Lett.* **2006**, *89*, 061125.

(5) (a) Noh, Y.-Y.; Lee, C.-L.; Kim, J.-J. *J. Chem. Phys.* **2003**, *118*, 2853. (b) Gong, J. R.; Wan, L. J.; Lei, S. B.; Bai, C. L.; Zhang, X. H.; Lee, S. T. *J. Phys. Chem. B* **2005**, *109*, 1675.

(6) D'Andrade, B. W.; Forrest, S. R. *Adv. Mater.* **2004**, *16*, 1585.

(7) (a) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151. (b) Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Pure Appl. Chem.* **1999**, *71*, 2095. (c) Chou, P.-T.; Chi, Y. *Chem. Eur. J.* **2007**, *13*, 380.

(8) (a) Herron, N.; Wang, Y.; Clarkson, L. M. U.S. Patent 2006/0040139 A1, Feb 23, 2006. (b) Hwang, K. Y.; Lee, M. H.; Jang, H.; Sung, Y.; Lee, J. S.; Kim, S. H.; Do, Y. *Dalton Trans.* **2008**, *14*, 1818.

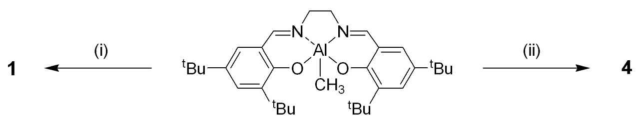
(9) Neve, F.; Crispini, A.; Campagna, S.; Serroni, S. *Inorg. Chem.* **1999**, *38*, 2250.

(10) Cozzi, P. G.; Dolci, L. S.; Garelli, A.; Montalti, M.; Prodi, L.; Zaccheroni, N. *New J. Chem.* **2003**, *27*, 692.

(11) For **5**, the observation of a distinct absorption band at 420 nm and a slight change in the position of an emission maximum are somewhat different from those reported previously.[9] This may be involved with the lower concentration of a solution used in this study. Also see the reference describing the concentration dependence of emission: Cui, Y.; Wang, S. *J. Org. Chem.* **2006**, *71*, 6485.

10.1021/ic8002806 CCC: $40.75

Scheme 1. Synthesis of **1** and **4**[a]



[a] Reagents and conditions: (i) **5**, MeCN, 90 °C, 57%; (ii) **3**, toluene, 120 °C, 83%.

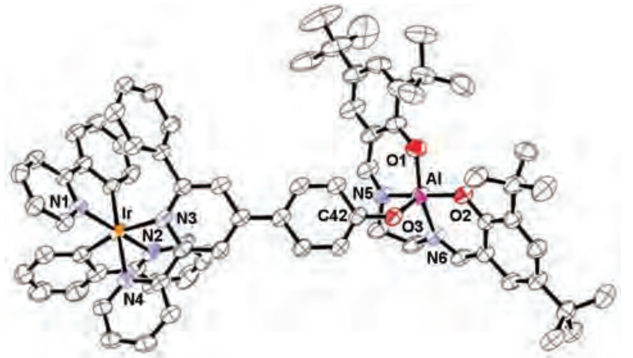


Figure 1. ORTEP diagram of **1** (50% ellipsoids). The counterion (PF_6^-) and H atoms are omitted for clarity.

6′-phenyl-2,2′-bipyridine (Hhpbpy, **3**)[9] was chosen as an aryloxy ancillary ligand to develop a potential host center (3,5-^{t}Bu$_2$)salenAl(hpbpy) (**4**). There are two additional merits of **3**: its Ir^{III} complex [Ir(ppy)$_2$(hpbpy)]$^+$[PF_6^-] (**5**),[9] a potential phosphorescent emitter, is known, and its rigid framework may facilitate efficient energy transfer from the Al host center to the Ir emitter.

Thus, new complexes **1** and **4** were synthesized according to the procedures outlined in Scheme 1.[8]

While ^{1}H and ^{13}C NMR, IR spectroscopy, and elemental analysis results confirm the identity of **1**, a single-crystal X-ray diffraction study clearly establishes the dinuclear nature of **1**, in which the Al and Ir centers are linked via hpbpy, a deprotonated form of **3**, to form a [(3,5-^{t}Bu$_2$)salenAl(μ-hpbpy)Ir(ppy)$_2$]$^+$ cation (Figure 1). Further structural analysis reveals that the Al-salen moiety is bent away from the distorted octahedral Ir center with an Al−O3−C42 angle of 131.7(4)° and retention of the rigid arrangement of both moieties.

The UV−vis absorption and the photoluminescence (PL) spectra of the heterodinuclear complex **1** and its closely related mononuclear complexes **4** and **5** were recorded in a degassed solution of acetonitrile at room temperature (Figure 2). While **4** shows an absorption band centered at 360 nm due to the Al-salen moiety,[10] the absorption spectrum of **5** exhibits lower energy bands at 420 nm assignable to metal-to-ligand charge transfer (MLCT)[11] as well as strong bands from ligand-centered (LC) $\pi-\pi^*$ transitions in a region ranging from 280 to 320 nm.[9,12] On the other hand, the high-energy absorption bands of **1** were slightly broadened by possible overlapping of LC transitions originating from **4** and **5**. In contrast to the distinct transition in **5**, the MLCT transition of **1** appears as a broad tail toward the visible region (ca. 500 nm).

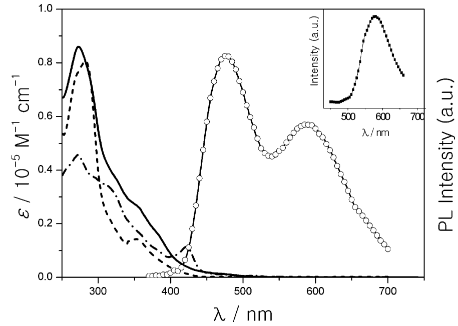


Figure 2. UV−vis absorption of **1** (solid line), **4** (dashed line), and **5** (dash-dotted line) and emission spectrum of **1** (open circles) in acetonitrile (1.0 × 10^{-5} M; λ_{ex} = 360 nm) at room temperature. Inset: emission spectrum of **1** in the solid state.

The room temperature PL spectrum of **1** irradiated at 360 nm (Figure 2) displays emission maxima at 475 and 596 nm, which correspond exactly to those of **4** and **5**, respectively [Figure S2a in the Supporting Information (SI)].[11] Measurement of the lifetime of the emissions at 475 and 596 nm for **1** as <10 and 196 ns, respectively, further reveals that the former is assignable to the Al-centered fluorescence and the latter to the Ir-centered phosphorescence. The PL spectra of **1**, **4**, and **5** with 420-nm excitation (Figures S2b and S3 in the SI) also show invariant appearance of the emission maxima position, indicating the presence of little electronic effect of the Al- and Ir-centered luminophores on the energy band gap of each center, which results in independent emission in the solution. This feature might be a consequence of the unique feature of the nonplanar molecular structure of **1**. It is also consistent with the observation[8] that the energy band gap of mononuclear salen-based aryloxyaluminum complexes is independent of the type of aryloxy ancillary ligand.

A comparison of the emission intensities for **1**, **4**, and **5** at the same concentration reveals decreased intensity of the 475-nm band of **1** compared to **4** and increased intensity of the 596-nm band of **1** compared to **5** (Figure S4 in the SI). This change in intensity suggests the involvement of energy transfer from the Al-centered luminophore to the Ir-centered luminophore in **1**. In order to clarify the energy-transfer pathway, low-temperature PL studies were carried out on **1** and an equimolar mixture of **4** and **5** at 77 K with excitation at 360 nm. The spectra reveal the blue-shifted emission maxima[13] and the relative intensity decrease at 441 nm and increase at 539 nm of the emission peaks from the Al- and Ir-centered luminophores of **1**, respectively, compared to the emission intensities of the mixture (Figure S5 in the SI). This indicates the occurrence of intramolecular energy transfer[14] from the Al-centered luminophore to the Ir-centered luminophore in a rigid matrix. On the other hand, the solid-state PL spectrum of **1** only shows a strong Ir-centered phosphorescent emission (τ = 313 ns) at 583 nm with the quenching of the excited-state lifetime of the Al-centered emission (inset of Figure 2), thus implying that energy transfer takes place completely in the solid state probably via both intra- and intermolecular pathways.[4b]

---

(12) (a) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2001**, *40*, 1704. (b) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7377.

(13) (a) Neve, F.; Crispini, A.; Serroni, S.; Loiseau, F.; Campagna, S. *Inorg. Chem.* **2001**, *40*, 1093. (b) Cavazzini, M.; Pastorelli, P.; Quici, S.; Loiseau, F.; Campagna, S. *Chem. Commun.* **2005**, 5266.

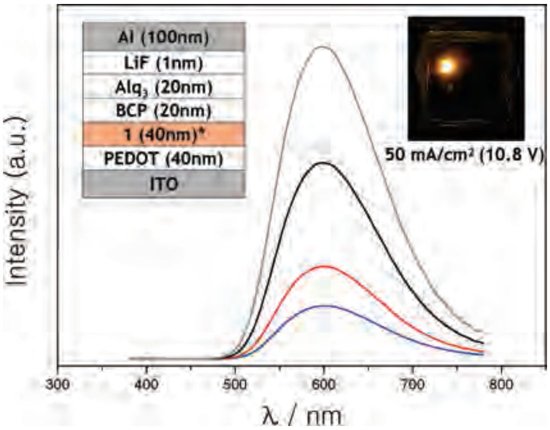


Figure 3. EL spectra of device OLED **1**: 10 mA cm^{-2} (blue line), 20 mA cm^{-2} (red line), 50 mA cm^{-2} (black line), 100 mA cm^{-2} (gray line). Insets: device configuration (left) and a photograph of the working device (right).

Prior to the fabrication of an OLED based on **1** via the solution process, the quality of a spin-coated thin film (40 nm) of **1** on a poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene (PEDOT) layer was explored by atomic force microscopy (AFM), revealing a film surface that is free of pinholes or aggregates (Figure S6 in the SI). The root-mean-square roughness of 0.542 nm further indicates the formation of a uniform film surface. The good film-forming ability of **1** can be ascribed to its high solubility in common organic solvents as well as its poor crystallinity. On the basis of this finding, four electroluminescence (EL) devices using **1**, **2** + **5**, PVK:**1**, and PVK:**5** [PVK:**1** or PVK:**5** = **1** or **5** blended with poly(*N*-vinylcarbazole)] as concomitant host-emitting layer materials were constructed. The OLED configuration is as follows: ITO/PEDOT (40 nm)/**1** or **2** + **5** or PVK:**1** or PVK:**5** (40 nm)/BCP (20 nm)/Alq$_3$ (20 nm)/LiF (1 nm)/Al (100 nm) (BCP = bathocuproine). For OLEDs **1** and **2** + **5**, the emitting layer was directly spin-cast from a 1,2-dichloroethane solution of **1** or an acetonitrile solution of a blend of **2** and **5** onto the spin-coated PEDOT layer.

The EL spectra of **1** with the common maximum at 600 nm, shown in Figure 3, are consistent with its solid-state PL spectrum, which has characteristics of phosphorescence contributed solely from the Ir-based luminophore. This is a clear indication that the heterodinuclear system **1** allows complete energy transfer from the Al-based luminophore to the Ir-based luminophore under electrical excitation. In addition, the observed Commission Internationale de L'Eclairage (CIE) coordinates of (0.54, 0.46) for OLED **1** remain nearly unchanged upon a change of the current density. Figure 4 shows the current density−voltage−luminance (*J*−*V*−*L*) characteristics of the device. Device OLED **1** has a maximum brightness ($L_{\max}$) of 1002 cd m^{-2} at 10.8 V and a luminance efficiency (η_L) of 1.8 cd A^{-1}, external quantum efficiency (EQE) of 0.94%, and a luminous efficiency (LPW) of 0.69 lm W^{-1} at 8.2 V. These results were compared with the devices OLED **2** + **5**, OLED PVK:**1**, and OLED PVK:**5**, revealing an overwhelmingly superior performance of OLED **1** relative to those of OLED **2** + **5**, OLED PVK:**1** (over 500%), and OLED PVK:**5** (over 300%). This might be an indication that device OLED **1** does not suffer from the typical problems of phase separation and excimer formation derived from the host−guest system,[15] while OLED **2** + **5**, OLED PVK:**1**, and OLED PVK:**5** are influenced by the intrinsic properties of individual components such as the charged metal complex.[16]

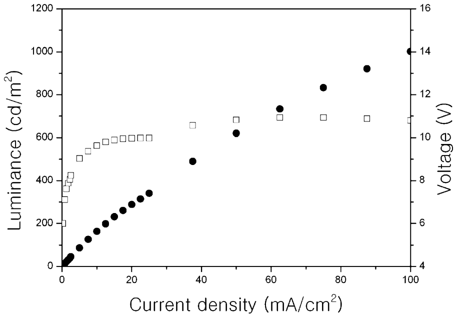


Figure 4. *J*−*V*−*L* characteristics of device OLED **1** (open squares, *J*−*V*; closed circles, *J*−*L*).

Another remarkable feature of OLED **1** is its low turn-on voltage (V_T) of 3.4 V. This is likely the consequence of the good charge-transport property of OLED **1** arising from the ionic nature of **1**: the counterions PF_6^- of **1** are redistributed under electrical excitation, leading to the formation of a high electric field at the electrodes, and thereby the electronic charge injection from the electrodes to the metal complex could be facilitated.[17]

In summary, molecular coupling of a salen-based aluminum complex as a host and a phenylpyridine-based ionic Ir complex as a phosphorescent emitter into a discrete heterodinuclear molecular complex **1** led to unprecedented multifunctional OLED materials for host−dopant assembly OLED based on a solution process. Bright-orange light emission along with stable color purity, low turn-on voltage, and good device performance were thereby obtained. The extension of a family of **1** and the search for new solution-processible molecular multifunctional OLED materials are in progress.

Acknowledgment. We acknowledge the Korea Research Foundation (Grant KRF-2006-312-C00578), the BK21 project, and the PAL (Grant 2007-1041-15). We also thank Prof. Sang Kyu Kim and Dr. Sun Jong Baek for the lifetime measurements.

Supporting Information Available: Experimental details, UV−vis and PL spectra, photophysical data, AFM images, cyclic voltammograms, and *J*−*V*−*L*, thermogravimetric analysis, and differential scanning calorimetry curves. This material is available free of charge via the Internet at http://pubs.acs.org.

IC8002806

---

(14) (a) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836. (b) Speiser, S. *Chem. Rev.* **1996**, *96*, 1953. (c) Schlicke, B.; Belser, P.; Cola, L. D.; Sabbioni, E.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 4207.

(15) You, Y.; An, C.-G.; Lee, D.-S.; Kim, J.-J.; Park, S. Y. *J. Mater. Chem.* **2006**, *16*, 4706.

(16) (a) Plummer, E. A.; van Dijken, A.; Hofstraat, H. W.; Cola, L. D.; Brunner, K. *Adv. Funct. Mater.* **2005**, *15*, 281. (b) Wong, W.-Y.; Zhou, G.-J.; Yu, X.-M.; Kwok, H.-S.; Lin, Z. *Adv. Funct. Mater.* **2007**, *17*, 315.

(17) (a) Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker, S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. *J. Am. Chem. Soc.* **2004**, *126*, 2763. (b) Slinker, J. D.; Koh, C. Y.; Malliaras, G. G.; Lowry, M. S.; Bernhard, S. *Appl. Phys. Lett.* **2005**, *86*, 173506.