Electroluminescence Device with Novel Hole-transporting Materials Having Metal Collecting Sites 1

Atsushi Kimoto, Jun-Sang Cho and Kimihisa Yamamoto

Kanagawa Academy of Science & Technology (KAST), and Department of Chemistry, Faculty of Science & Technology, Keio University, Yokohama, 223-8522, Japan

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1. Introduction

Hole-transport materials are important components for electronic devices such as organic light-emitting diodes (OLEDs) and photo cells [1,2]. Efforts have been ongoing to develop novel hole-transport polymers for advanced electronic devices which is a key material to improve the turn-on voltage, luminescence intensity, operation lifetime, full color display capability, durability, reasonable power efficiency, etc. Such high-performance devices are obtained by developing sequential HOMO/LUMO energy gradients in the device by introducing a multi-layered structure fabricated by repeatedly making thin films. For instance, introducing another layer on the ITO electrode, with a HOMO energy level between that of the hole-transporting layer and of the electrode, that is a hole-injecting layer, lowers the energy barrier for hole injection. This approach involves placing onto the ITO injecting layers, such as copper phthalocyanine (CuPc) [3], 4, 4', 4''-tris(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA) [4], polythiophene (PEDOT) [5], thus producing an enhanced EL efficiency. Recently, we developed another approach to enhance the EL property. This is to attach metal-coordination sites to the hole-transporting material, the complexation of which changes the properties of the film, thus resulting in higher EL efficiency [6].

2. Method

2.1. Synthesis of the Materials

We synthesized three phenylazomethine structural isomers designated as CNCN, CNNC, and NCCN (Fig. 1). The CNNC and CNCN isomers were obtained using the literature methods [7,8]. The

NCCN isomer was synthesized by the dehydration of 1,4-dibenzoylbenzene and aniline using titanium tetrachloride (TiCl_4) as the dehydrating agent and 1,4-diazabicyclo-[2.2.2]octane.

Fig. 1. Structure of the phenylazomethine isomers

2.2. Fabrication of the OLEDs

For the two-layer OLEDs, the phenylazomethine isomers, and their complexes with SnCl_2 films were employed as the hole-transporting layer in order to evaluate their performance as the hole-transporting material. To a solution of phenylazomethine in chloroform was added a solution of SnCl_2 in acetonitrile (1 eqv.). The yellow solution turned a deep orange based on the complexation which evaporated to dryness to give the phenylazomethine-Sn complex [9,10]. The films (50 nm thick for the hole-transporting layer) were obtained by spin-coating their solutions in N-methyl-pyrrolidone on an ITO-coated glass anode. Alq (60 nm), CsF (~3 nm) and Al (100 nm) were sequentially vacuum deposited on top of

the hole-transporting layer, where Alq is tris(8-hydroxyquinoline) aluminum.

3. Results and Discussion

3.1. Electroluminescence Properties

Using the azomethine complexes as the hole-transporting layer (HTL), the characteristic green light from the Alq layer was observed when applying a voltage (Fig. 2). Using azomethine itself as the HTL, the device having the CNCN and CNNC oligomers showed better EL properties than that of NCCN. This is due to the difference in the conductivity of the isomers with various framework. Complexing the SnCl_2 to the imine sites, the turn-on voltage was reduced and the maximum luminescence was enhanced 10 or more times by just complexing with SnCl_2 (Table 1). This result indicates that the complexation results in a *p*-type doping into the oligophenyl-azomethines, thus increasing the hole-injection efficiency from the electrode and reducing the driving voltage of the device.

Generally, hole-injection is enhanced by *p*-type doping in the charge-transporting layer, for example, *p*-type doping in aromatic diamines by various oxidizing reagents such as SbCl_5 . However, limited compounds for the hole-transporting layer have prevented the development of advanced materials. This new enhancement method can be followed by only preparing various aniline derivatives.

Table 1. Electroluminescence data for the compounds

HTL	Turn-on voltage [V]	Maximum brightness [cd/m^2]
NCCN	6	1.12 (13 V)
CNCN	4	6.78 (9 V)
CNNC	5	8.42 (10 V)
NCCN+ SnCl_2	5	23.9 (11 V)
CNCN+ SnCl_2	4	62.3 (11 V)
CNNC+ SnCl_2	4	107 (11 V)

4. Summary

In summary, we have synthesized three phenyl-azomethine isomers as a metal collecting unit. These isomers have the ability to collect metal ions such as Sn^{2+} and Eu^{3+} . The physical property of the film such as conductivity can be easily changed by complexation without any drastic structural changes. The use of the phenylazomethine - SnCl_2 complex provides a homogeneous film, which enhanced the performance of the electroluminescence device in comparison with only the oligomer as the hole-transporting

Fig. 2. *L-V* characteristics for electroluminescence device, which the CNNC oligomer and its complex with SnCl_2 were employed as a hole-transporting layer.

layer.

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References

1. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913.
2. U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer and M. Grätzel, *Nature* **1998**, *395*, 583.
3. S. A. VanSlyke, C. H. Chen and C. W. Tang, *Appl. Phys. Lett.* **1996**, *69*, 2160.
4. Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami and K. Imai, *Appl. Phys. Lett.* **1994**, *65*, 807.
5. S. A. Carter, M. Angelopoulos, S. Karg, P. J. Brock and J. C. Scott, *Appl. Phys. Lett.* **1997**, *70*, 2067.
6. A. Kimoto, J.-S. Cho, M. Higuchi and K. Yamamoto, *submitted*.
7. M. Higuchi, A. Kimoto, S. Shiki and K. Yamamoto, *J. Org. Chem.* **2000**, *65*, 5680.
8. M. Higuchi, S. Shiki, K. Ariga and K. Yamamoto, *J. Am. Chem. Soc.* **2001**, *123*, 4414.
9. K. Yamamoto, M. Higuchi, S. Shiki, M. Tsuruta and H. Chiba, *Nature* **2002**, *415*, 509.
10. T. Imaoka, H. Horiguchi and K. Yamamoto, *J. Am. Chem. Soc.* **2003**, *125*, 340.