

Organic Light Emitting Diodes Using Triphenylene Derivatives as a Hole Transport Material

Shinichi Tanaka, Chihaya Adachi,* Toshiki Koyama, and Yoshio Taniguchi

Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386-8567

(Received May 27, 1998; CL-980407)

We elucidated that hexaalkoxytriphenylenes (HATs) are useful as a hole transport layer (HTL) in organic light emitting diodes (OLEDs). In particular, the insertion of a thin phthalocyanine layer between the anode and HTL drastically improved electroluminescent (EL) performance. Furthermore, we observed that the alkyl chain length of HATs greatly affected carrier transport and EL properties.

Recently, it was revealed that the columnar structure of discotic liquid crystals exhibits extremely high hole mobility.¹ In particular, hexaalkoxytriphenylene (HAT) derivatives showed hole mobilities of 10^{-3} to 10^{-1} cm²/Vs,² which are comparable with some organic single crystals.³⁻⁶ Thus, such a class of these highly ordered molecular aggregates is expected to be used in xerographic, photovoltaic, and organic light emitting diodes (OLEDs) applications.

In previous studies, the low molecular, dimeric, and polymeric triphenylene derivatives were examined as a hole transport layer (HTL) in OLED.⁷⁻⁹ Then, it was revealed that triphenylene cores are useful for HTL. However, HAT derivatives, which are expected to form columnar structures (hexagonal plastic mesophase) with high hole mobility, have not yet been examined thoroughly. Although only the derivative with butoxy side chains was tested,⁷ irreproducible electroluminescent (EL) behavior was observed in the cell structure of an anode/HTL/emitter layer (EML)/cathode.

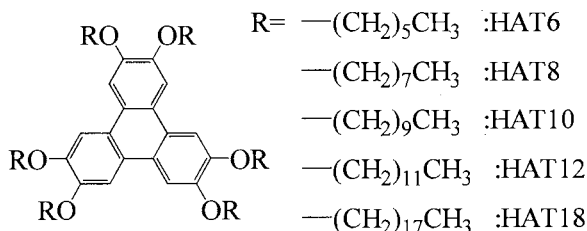


Figure 1. Molecular structures of hexaalkoxytriphenylenes (HATs).

MgAg(200nm)	MgAg(200nm)
Alq(50nm)	Alq(50nm)
HAT(35nm)	HAT(35nm)
ITO(150nm)	CuPc(15nm)
Glass	ITO(150nm)
Dev-1	Dev-2

Figure 2. Two types of OLED cell structures.

Therefore, in this study, we evaluated HATs with various alkyl chain lengths (6, 8, 10, 12, and 18) as an HTL (Figure 1).

Figure 2 shows the two types of device structures, Dev-1 and Dev-2, used in this study. Dev-1 consisted of indium-tin-oxide (ITO) as the anode, 35-nm-thick HTL, 50-nm-thick tris(8-hydroxy-quinoline) aluminum (Alq) as an electron transport and emitting layer, and MgAg as a cathode. Dev-2 consisted of an ITO, 15-nm-thick copper phthalocyanine, 35-nm-thick HTL, 50-nm-thick Alq, and MgAg.¹⁰ These organic layers were deposited onto an ITO substrate at room temperature. HAT6, HAT8, and HAT10 were used as the HTL. In addition, tetraphenyldiaminodiphenyl (TPD) was used as HTL for comparison. The emitting area was 0.2×0.2 cm². Unfortunately, we observed serious decomposition of HAT12 and HAT18 with vacuum deposition, so we could not fabricate devices using HAT12 and HAT18.

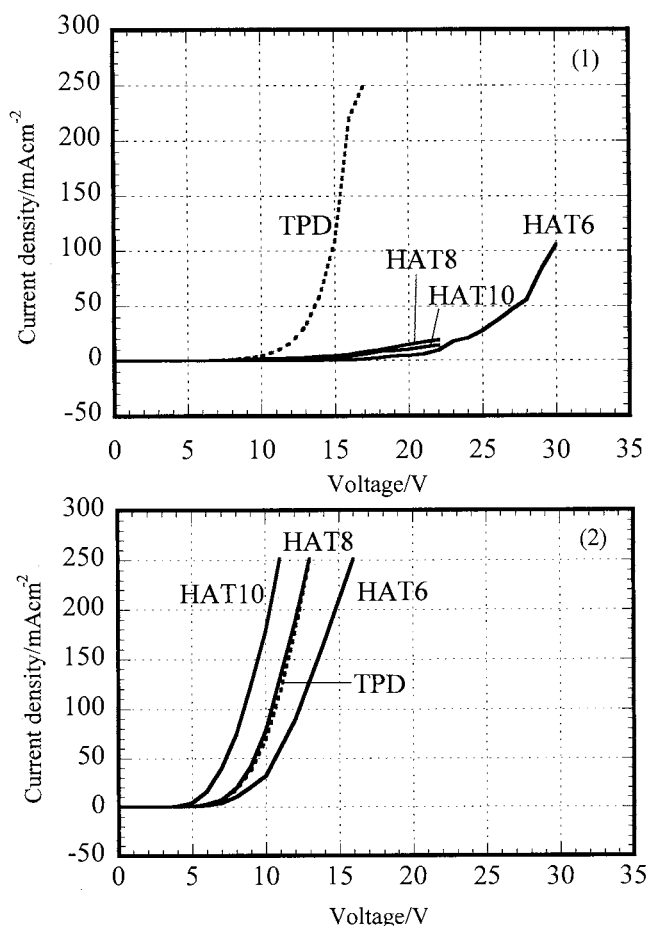


Figure 3.(1) Current density-voltage characteristics of Dev-1 structures with four HTMs.

(2) Current density-voltage characteristics of Dev-2 structures with four HTMs.

Figures 3-1 and 3-2 show the current density versus voltage (J-V) characteristics of Dev-1 and Dev-2 with various HTMs, respectively. In the Dev-1 structures, the devices with HAT8 and HAT10 showed very high resistivity and the current densities were less than 20 mA/cm² at 20 V. Furthermore, when higher voltages were applied, the devices easily broke down. The device with HAT6 was rather stable and we obtained a current density of more than 100 mA/cm² with 30 V. On the other hand, in the Dev-2 structures, which had a thin CuPc layer inserted between the ITO and HTL layers, the J-V characteristics were greatly improved in comparison with those of the Dev-1 structures. The J-V characteristics of the devices using HAT6, HAT8, and HAT10 were greatly enhanced by the presence of a thin CuPc layer in comparison with those of Dev-1 structures. All the Dev-2 structures showed current densities of over 200 mA/cm² at driving voltages under 15 V. In HAT10, in particular, a large current density of 175 mA/cm² was achieved at 10 V. Thus, the longer alkyl chain resulted in a decrease in

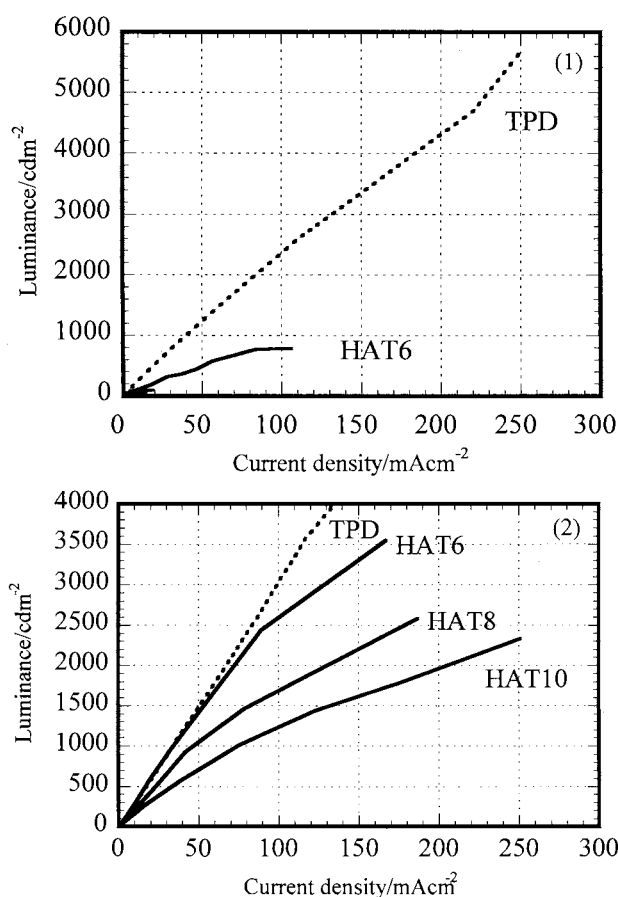


Figure 4.(1) Luminance-current density characteristics of Dev-1 structures with four HTMs. The maximum luminance of HAT8 and HAT10 is less than 50 cd/m².
(2) Luminance-current density characteristics of Dev-2 structures with four HTMs.

driving voltage. We suspect that this phenomenon reflects a difference in inter-molecular stacking of the HAT molecules.

Figures 4-1 and 4-2 show the luminance-current (L-J) characteristics of the Dev-1 and Dev-2 structures, respectively. In Dev-1 with HAT6, although EL was observed with large current injection, the maximum luminance was only 500 cd/m² at J=108 mA/cm². Furthermore, the devices using HAT8 and HAT10 did not show noticeable EL, because of the limit of current injection. On the other hand, the EL efficiency of the Dev-2 structure using HAT6 was three times than that of the Dev-1 structure. Luminance of 1480 cd/m² was achieved at J=50 mA/cm². Thus, the EL efficiency of the device was comparable with that of TPD. In addition, the devices with HAT8 and HAT10 also showed improved EL performance.

This experiment found that EL performance was greatly enhanced by the insertion of a CuPc layer. A separate experiment suggested that the interface morphologies of ITO/HAT and CuPc/HAT were quite different from each other, although the HAT molecules were shown, by IR(ATR) observation of the HAT deposited layers, to be oriented parallel to both the ITO and CuPc substrates.

In this study, the crystalline morphologies of the HAT deposited films have not been revealed yet. The HAT molecules are known to form discotic mesophase at particular temperature. Thus, we have to elucidate the relation between EL performance and the HAT film morphologies. Furthermore, we can expect that the control of the HAT film morphologies will improve OLED device performance.

In conclusion, we observed that HATs with long alkyl chains work as an excellent HTL in Dev-2 structures. These materials do not contain an amine skeleton and are expected to be a promising candidate for a new HTM.

References

- 1 D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher, and K. Siemenmeyer, *Phys. Rev. Lett.*, **70**, 457 (1993).
- 2 D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemenmeyer, K. H. Etzbach, H. Ringsdorf, and D. Haarer, *Nature*, **371**, 141 (1994).
- 3 O. H. Jr. LeBianc, *J. Chem. Phys.*, **33**, 626 (1960).
- 4 R. G. Kepler, *Phys. Rev.*, **199**, 1226 (1960).
- 5 H. Möhwald, D. Haarer, and G. Castro, *Chem. Phys. Lett.*, **32**, 433 (1975).
- 6 N. Karl, J. Ziegler, *Chem. Phys. Lett.*, **32**, 438 (1975).
- 7 A. Bacher, I. Bleyl, C. H. Eedelen, D. Haarer, W. Paulus, and H.W. Schmid, *Adv. Mater.*, **9**, 1031 (1997).
- 8 T. Christ, B. Glösen, A. Greiner, A. Kettner, R. Sander, V. Stümpflen, V. Tsukruk, J. H. Wendorff, *Adv. Mater.*, **9**, 48 (1997).
- 9 T. Christ, V. Stümpflen, and J. H. Wendorff, *Macromol. Rapid Commun.*, **18**, 93 (1997).
- 10 S. A. Van Slyke, C. H. Chen, and C. W. Tang, *Appl. Phys. Lett.*, **69**, 2160 (1996).