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Electroluminescent Properties of Anthracene Chromophore with Naphthylethenyl Substituents

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Abstract : New electroluminescent materials based on anthracene chromophore with naphthylethenyl substituent, 9,10-bis(α-naphthylethenyl)anthracene (a-BNA), as well as four kinds of its derivatives were synthesized, and luminescent properties of these materials were investigated. Electroluminescent(EL) emission band was discussed based on their substituent structure differences. It was found that the emission band strongly depends on the molecular structure of introduced substituent. It can be tuned from 557 nm to 591 nm by changing the substituent structures. On the other hand, the anthracene chromophore with bulky substituent possessed high melting point and they gave stable films through vacuum-sublimation. The double layer EL device of ITO/TPD/emission layer/Mg:Ag was employed, and exhibited efficient orange light originating from emitting materials. EL emission with a maximum luminance was observed in the b-BNA emitting material, : maximum luminance was about 8,060 cd m^{-2} at an applied voltage of 10 V and current density of 680 mA/cm^2. In conclusion, the electroluminescent properties also showed good difference with their substituent structure.

Keywords : *organic electroluminescent devices, anthracene chromophore, substituent difference.*

1. Introduction

Organic electroluminescent(EL) devices based on organic fluorescent materials have been the subject of many recent publications because of their potential to produce emissions of all colors ranging from blue to red in accordance with the wide selection of organic emitting materials, and their possible application as large-area light-emitting displays, which are difficult to realize using inorganic light-emitting cells. Generation of light in these systems is the result of recombination of holes and electrons injected from the electrodes. Such recombination in the emitting layer excites the emitter materials. Such recombination in the emitting layer, then, excites the emitter material. The emitting layer can be either low molecular weight materials or high molecular weight polymeric materials. In organic materials, Tang and co-workers[1,2] were the first to demonstrate that the use of a hole transport layer for hole injection from the electrode into

the emitting layer significantly lowers the drive voltage to a value of a few volts. Since then, a variety of organic materials, fluorescent dye[3-5], metal complex[6,7] and π-conjugated polymer[9-13] have been applied to EL devices as emitting material, and efficient EL properties have been attained in all visible region including the three primary colors[14-16]. Although these organic materials have been newly synthesized and used as emitting materials in EL devices, currently the biggest problem of the organic EL devices is the short operating lifetime[19]. The degradation mechanism in the organic EL devices is not fully understood, but a preliminary study indicates that the degradation is partly caused by crystallization of organic layers including the emissive layer due to heat produced in the device[3,15]. In EL devices, generally, the organic materials are used in amorphous state because one can easily obtain uniform thin films with less macroscopic defects which degrade device performance. Therefore, the improvement of morphological stability in the amorphous film is indispensable to develop stable and high performance organic EL devices. For this purpose, introducing bulky substituents into

aromatic compounds is a promising material design : the bulky substituent is assumed to give an ability to form a stable amorphous film in addition to highly efficient emissive ability of aromatic compounds.

This research was aimed to elucidate the molecular structure dependency of the emission bands of anthracene chromophore with naphthylethenyl substituent[17,18]. we designed and synthesized five kinds of bis-(arylethenyl)anthracene derivatives (BArA's) to be used as emitting materials for organic EL devices. In addition that BArA's exhibit efficient photoluminescence, they possesses a flexibility in material design: a modification of their emissive and electric properties is possible by replacement of arylethenyl substituents. In this study, our objective is to develop the BArA's with morphological stability of their amorphous film. We synthesized five kinds of antharcene chromophore derivatives with bulky substituent and examined their EL properties, they are called b-BNA, a-BNAmo, b-BNAmo and BQA. Their molecular structures and synthetic route are shown in scheme 1.
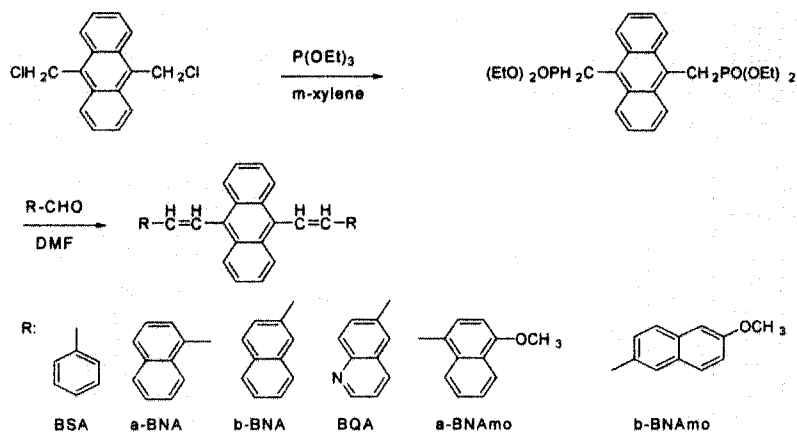
Scheme 1. Synthetic route of material used.

2. Experimental

All the anthracene chromophore with naphthylethenyl bulky substituent were newly synthesized through the Wittig-reaction according to the route shown in scheme 1. For comparison, an anthracene-based dye with small substituents, 9,10-bis(styryl) anthracene (BSA) was also prepared[6]. The reaction mixtures were poured into water, and the obtained precipitates were filtered and washed several times with pure water and ethanol. The final products were purified by recrystallization from chlorobenzene, and dried in a vacuum oven, and it was finally purified by the train sublimation method and the molecular structure was conformed by DSC and elemental analyses. All reagents employed in this experiments were purchased from Tokyo Kasei Company (Japan) and used without further purification.

For evaluation as an emitting material of newly synthesized derivatives, we fabricated double layer (DL) type EL devices consisting of indium-tin-oxide anode (ITO), hole-transporting layer of a diamine derivative (TPD), emissive layer of the newly synthesized derivatives and MgAg (10:1) cathode as shown in Fig. 1. The structure of DL devices was ITO / TPD (50nm) /emissive layer(50nm)/MgAg. The organic layers were successively vacuum-deposited onto an ITO-coated glass substrate at about 1.0×10^{-6} torr, and then MgAg (10:1) alloy was

deposited as cathode. The size of emitting area was 2 x 2 mm^2. ITO-coated glasses, having a sheet resistance of 15 Ω/square, were purchased from Asahi Glass Co., Ltd.

EL devices were set in a vacuum cryostat with quartz windows, and all EL characteristics were conducted at room temperature under vacuum for avoiding bad effects of moisture in the air. The measurements of brightness were conducted using a photon counter(Hamamatsu photonics, C767, Japan). Relative EL intensity values were changed into absolute luminance meter(Topcon BM-8, Japan). EL spectrum were obtained through a 100mm monochrometer and a photon counter (Hamamatsu photonics, PMA-11, Japan). The photoluminance (PL) spectrum of organic thin films were measured by a conventional fluoro spectrophotometer (Hitachi 650/60, Japan). All data were measured within one minute for reducing thermal effect during EL operation.

3. Results and Discussion

The number of organic materials suitable for multilayer organic-based electroluminescent devices is somewhat limited by this technology's material requirements. The organic thin films must be morphologically, electrochemically, and photochemically stable. They must also have
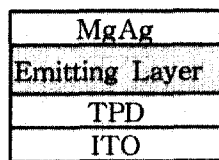
(a)
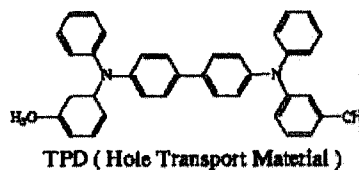
(b)

Fig. 1. (a) Structure of double layer EL devices.
(b) Molecular structures of hole transporting material(TPD).

the required transport and junction characteristics. The layer designed to encompass the recombination zone must also be fluorescent[3]. Another complication that arises is due to the donor-acceptor nature of the carrier transport layers and their propensity to form exciplexes with one another, usually leading to a shift of the EL emission towards lower energy as well as an accompanying decrease in quantum efficiency[4-6]. Table 1 summarizes the value of some typical PL and EL properties of these derivatives. The anthracene derivatives with bulky substituents exhibit high melting points in comparison with BSA. Further, all the materials with bulky substituents formed stable amorphous films through vacuum-sublimation, while BSA formed a polycrystalline film[17,18]. These results suggest that the introduction of bulky substituents surely improves the morphological stability of amorphous film in the derivatives with naphthylethenyl bulky substituents[3]. And the emission band on each EL spectrum is different, it changed from 557 nm, a yellow color, to 591 nm, a orange color, due to the difference of the substituent. The EL spectra of organic light-emitting devices (OLEDs) with these emitting materials are similar to the corresponding PL spectra, indicating that these materials really act as emissive centers in the OLEDs.

In this study, therefore, we fabricated DL devices with a diamine derivative (TPD) which possesses relatively low Ip (5.5 eV), as a hole transporting layer[3,17]. When we used the anthracene chromophore with naphthylethenyl substituent, which formed stable amorphous films and exhibited strong PL as an emissive layer. As shown in Fig. 2, the maximum EL spectrum of devices with emissive layer of these materials was observed intense and efficient yellow and orange light emission at wide range of the visible region from 591 nm to 581 nm. As shown in the Table 1 and Fig. 2, the emission wavelength is not exactly the same with that of PL spectrum. The difference between EL and PL spectrum demonstrate interference effect of both emissive layer and hole transport material. Compared with the EL spectrum of BSA having small substituent, the EL spectra of these emitting materials are red shifted. This is due to the extended π-conjugation of the substituents, which causes narrower energy gap between the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) of these emitting materials compared with that of BSA[8]. Although BSA exhibited strong PL, EL performance of the device using BSA was very low : maximum luminescence of device was less than 1 cd m^{-2}. The polycrystalline texture in BSA vacuum-sublimed films may affect the device performance[17,18].

Table 1. Melting Points of the Anthracene Chromophore and Their Morphology, Elctroluminance, Photoluminance in Vacuum-Sublimed Films

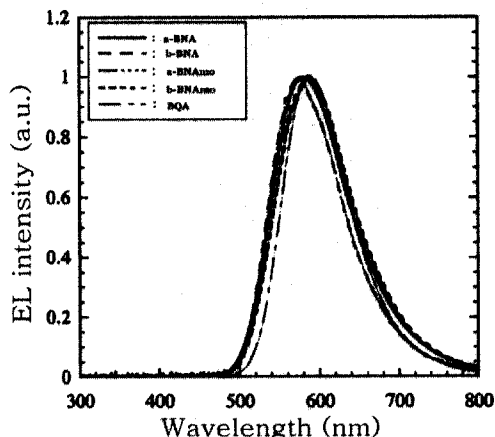| Materials	T_m[K]	Morphology of sublimed film	$\lambda_{max,EL}$[nm]	$\lambda_{max,PL}$[nm]	PL Intensity
BSA	554	polycrystalline	−	520	strong
a-BNA	580	amorphous	585	557	strong
b-BNA	598	amorphous	581	560	strong
a-BNAmo	597	amorphous	587	580	strong
b-BNAmo	603	amorphous	585	576	strong
BQA	515	amorphous	591	586	strong

Fig. 2. Electroluminescence spectra of the double layer EL devices made of naphthylethenyl derivatives.

Fig. 3 shows the current density-luminance characteristics of the double layer EL devices using naphthylethenyl derivatives. The luminance of the devices using these materials revealed linearly increase with current density over 1 mA cm^{-2}. In the result, the maximum luminance of double layer EL devices using these naphthylethenyl derivatives, a-BNA, b-BNA, a-BNAmo, b-BNAmo and BQA, was detected about 5,110 cd m^{-2}, 8,060 cd m^{-2}, 1,491 cd m^{-2}, 3,350 cd m^{-2} and 4,660 cd m^{-2} at a current density of 525 mA cm^{-2}, 683 mA cm^{-2}, 400 mA cm^{-2}, 650 mA cm^{-2} and 500 mA cm^{-2}, respectively. Fig. 4 shows the applied voltage – luminance characteristics for the double layer EL devices using naphthylethenyl derivatives. As shown in Fig. 3-4, the emission started at a driving voltage as low as 2~5 V for EL devices and luminance increases with increasing injection current as well as bias voltage. This lower drive voltage was made possible by the low work function of the contact electrode[14,15]. The maximum luminance of these naphthylethenyl derivatives, a-BNA, b-BNA, a-BNAmo, b-BNAmo and BQA, was reached at an applied voltage of about 8~10V.
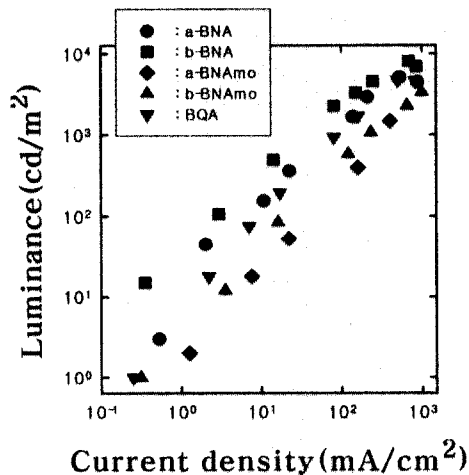

Fig. 3. Luminance-Current density characteristics in double layer EL devices made of naphthylethenyl derivatives.
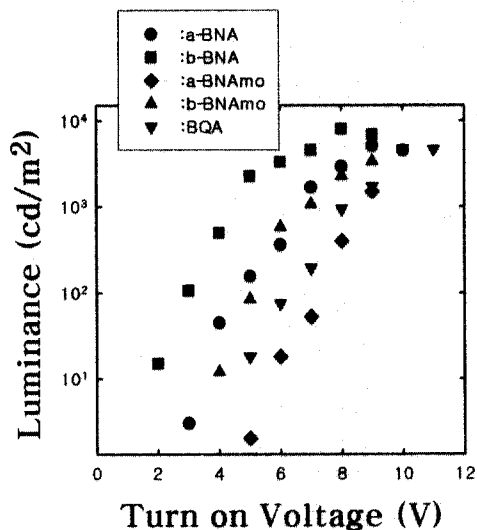

Fig. 4. Voltage-Luminance characteristics in double layer EL devices made of naphthylethenyl derivatives.

Fig. 5 shows the plots of luminous efficiency(η) for double layer devices as a function of current density[8]. The luminous efficiency is estimated as, $\eta = \pi \cdot L/V \cdot J$,

where L, V and J are the luminance, the applied voltage and the current density, respectively. The luminous efficiency of the EL devices is largely dependent on the recombination efficiency of electrons and holes in the organic layer. It is also dependent on the generation efficiency of the fluorescent exited state, which is formed as the result of carrier recombination, and on the fluorescence efficiency of the exited state[16-18]. The luminous efficiency of these naphthylethenyl derivatives, a-BNA, b-BNA, a-BNAmo, b-BNAmo and BQA, as emitting material in double layer device is rapidly increased with increased of the current density up to $3 \sim 5$ mA/cm^2 and remains or slowly decreases as the current density increases further. and the maximum luminous efficiency of these naphthylethenyl derivativesas is $0.37 \sim 3.8$ lm/W. In conclusion, the bright and efficient EL suggests that the
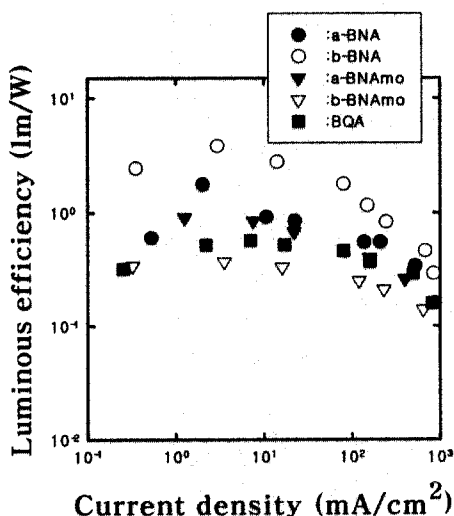

Fig. 5. Luminous efficiency - Current density characteristics in double layer EL devices made of naphthylethenyl derivatives.

balance of injected carriers and carrier confinement in the emissive layer was

improved in the multi layer devices, since the anthracene-based dyes played not only a role as a good emissive material but a role as a hole blocking material by combination with TPD.

4. Conclusions

We synthesized new electroluminescent dyes, a-BNA, b-BNA, a-BNAmo, b-BNAmo and BQA, based on anthracene-chromophore. Introducing bulky substituents such as naphthylethenyl, methoxynaphthylethenyl and quinolinyl groups into the anthracene-based dye exhibited high melting point, and made the formation of stable amorphous film possible. In case of using these anthracene derivatives as an emissive material, intense and efficient EL was attained in the double layer devices, and which formed stable amorphous films and exhibited strong PL in the amorphous films. In the present study, a novel amorphous molecular material containing a naphthylethenyl and methoxynaphthylethenyl substituent, which formed stable and good morphological stability, was shown to function as orange and yellow emitting material in organic EL devices.

Acknowledgement

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