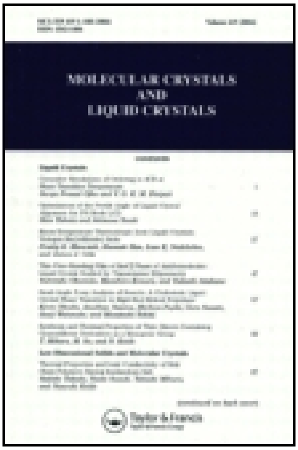

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Material Design of Polymers with Chromophores in Skeletons for Electroluminescent Devices

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MATERIAL DESIGN OF POLYMERS WITH CHROMOPHORES IN SKELETONS FOR ELECTROLUMINESCENT DEVICES

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Abstract As the extension of molecular design concept of low molar mass dyes for vacuum-sublimed multilayer electroluminescent devices, concept of material design for electroluminescent polymers with charge transport and emissive chromophores on their skeletons were described. A 9,10-bis[4-(N,N-diphenylamino)-styryl]anthracene chromophore, which has both charge transporting and emissive capabilities was used as a model system.

INTRODUCTION

Much progress has been shown in the research and development in organic and polymeric electroluminescent (EL) materials and devices in these several years. Today, it is known that varieties of materials such as vacuum-sublimed dye films, fully π-conjugated polymers, polymers with chromophores on skeletal-chains or side-chains and polymer-dispersed dye films are useful for EL materials.[1,2] Among varieties of EL devices, multilayer-structure EL devices made of vacuum-sublimed dye films exhibit the highest performances. We have investigated the meaning of multilayer structures in multilayer EL devices which were composed of sublimed dye films, because the designs of both device structures and constituent dye molecues in multilayer-dye EL devices have high flexibility.[3,4] As the extension of our study on multilayer-dye EL devices, we have reported the experimental work on molecularly-dispersed polymer films and have shown that very similar material design concept was applicable for the cases of dye-polymer composite systems: The usage of the words such as hole and electron transport molecules and emissive molecules are valid in molecularly doped polymer films.[5,6] Thus we expect that the molecular design concept on dye molecules is further extended to the chromophores incorporated in polymer chains.

Since the first demonstration of electroluminescent (EL) diodes made of fully π-conjugated polymers[7], the use of polymeric materials for emissive layers in thin-film EL diodes attracted considerable attentions. Varieties of polymer systems, such as fully π-conjugated polymers[8-12], polymers with chromophore on main-chains or side-chains [13-16] and molecularly doped dye-polymer composites[5, 17-19] have been used. Polymeric materials, in general, are assumed to have intrinsically high durability and good film-processability in comparison with low molar mass compounds. Much effort has been paid for the synthesis of polymeric EL materials which are processable via solution processes. Two different strategies have been used: One is to introduce long aliphatic side chains to enhance solubility in organic solvents and the other is to introduce flexible linkage groups in main chains. One of the major problems in both cases has been the deficiency of mechanical strength due to the introduction of long side chains and/or flexible linkage groups.

Another important issue in designing EL polymers is how to introduce both emissive and charge transporting functionality in chromophores incorporated in skeletal chains. Some trails have been reported but the attainment of balanced injection and transport of positive and negative charges in single component polymer films has not been reported so far. We have performed experimental studies on the design of soluble polymers with emissive and charge transporting chromophores in skeletal chains[20-22]. We have discussed about the design concept for incorporating both emissive and charge transporting chromophores in the same polymer skeletons and concluded that the introduction of both electron-donating and electron-withdrawing groups is one of the key issues for balanced charge injection and transport.

In this article, we describe one of our studies on molecular design of low molar mass dyes and polymers which have a common chromophore of 9,10-bis[4-(N,N-diphenylamino)-styryl]anthracene (BSA) unit.

MULTILAYER DEVICES MADE OF SUBLIMED DYE FILMS

Figure 1 shows molecular structures of BSA-2 as an emissive layer material, TPD as a hole transport material and OXD-7 as an electron transport material. Using these three dyes, we fabricated four types of EL devices; a single-layer (SL) device, two double-layer devices (DL-H and DL-E) and a triple-layer device (TL). The structures of the SL, DL-H, DL-E and TL devices are ITO/BSA-2(100 nm)/MgAg, ITO/TPD(50 nm)/BSA-2(100 nm)/MgAg, ITO/BSA-2(100 nm)/OXD-7(50 nm)/MgAg and ITO/TPD(50 nm)/BSA-2(100 nm)/OXD-7/MgAg, respectively. ITO and MgAg mean transparent indium-tinoxide anode and co-deposited MgAg alloy cathode, respectively.

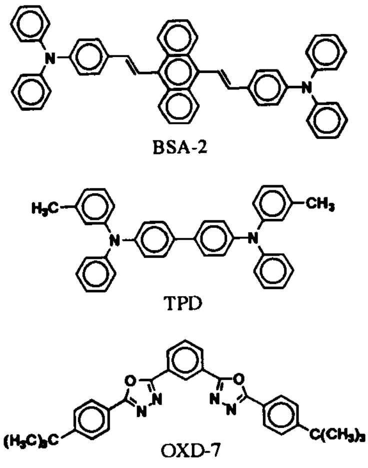


FIGURE 1 Molecular structures of BSA-2, TPD and OXD-7 used for vaccum-sublimed multilayer EL devices.

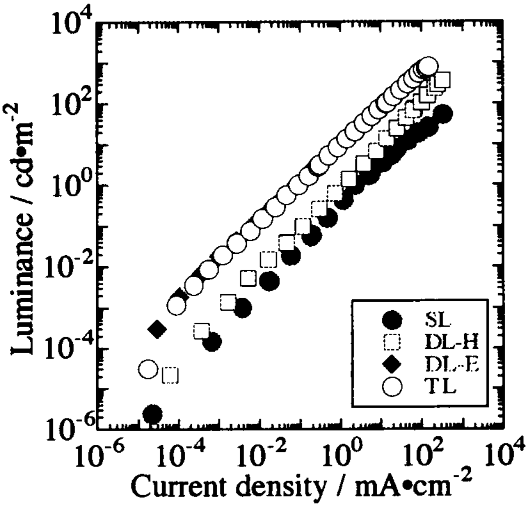


FIGURE 2 Luminace-current density relationships in SL, DL-H, DL-E and TL type devices with BSA-2 as an emissive layer.

Figure 2 demonstrate luminance-current density relationships in four types of devices with the same BSA-2 emissive layer. The TL and DL-E devices exhibited highest quantum efficiencies among four types of devices. This is due to the attainment of balanced charge injection and transport in the TL and DL-E devices. Hole blocking effect of the OXD-7 layer as an electron transport layer plays a key roles for that purpose. It should be noted also that even the SL devices showed good performances.

The quantum efficiency of the SL device is 1/20 for those of the TL and DL-E devices. This fact indicates that the balance of injected holes and electrons is fairly good even in the single layer devices of BSA-2. BSA-2 molecules have two triphenylamine units and this causes the introduction of hole transporting capability in BSA-2.

As the BSA-2 molecule was proved to have bipolar charge transport capability in addition to its emissive function, we selected a BSA-2 chromophore which served as charge transport and emissive units in polymer chains.

POLYMERS WITH BSA-2 CHROMOPHORE IN SKELETONS

Figure 3 shows chemical structures of the polymer with the BSA chromophore in its skeletal chain and two related polymers with similar chemical structures. Details of syntheses of those polymers were described in previous papers.

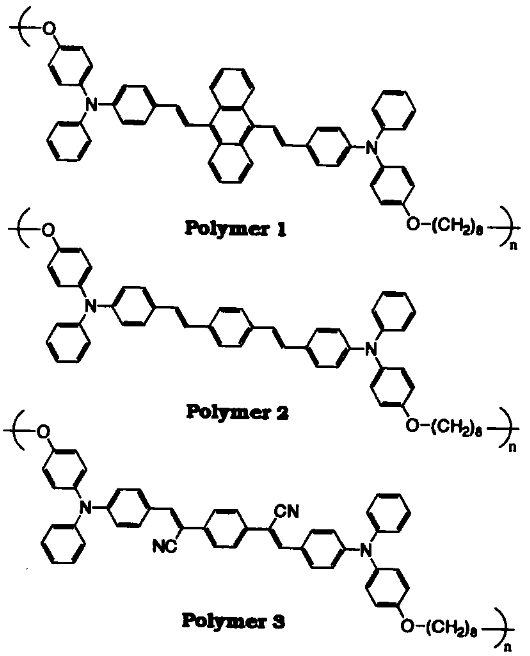
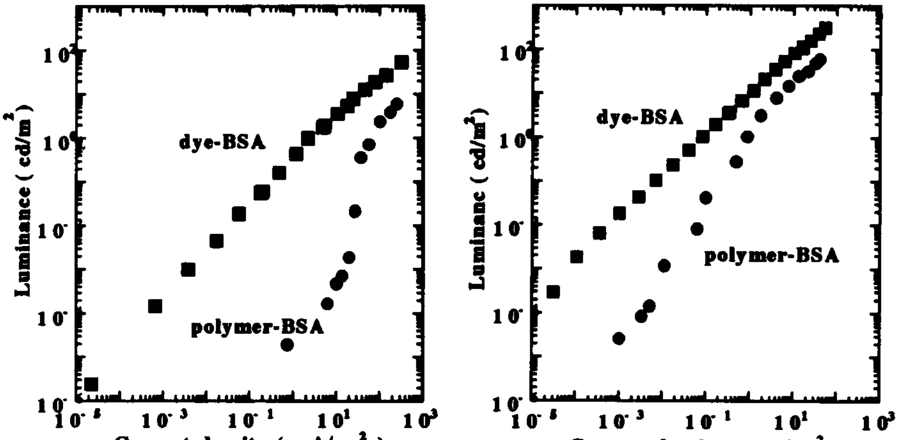


FIGURE 3 Chemical structures of three polymers with charge transporting and emissive chromophres in skeletal chains.

Polymer 1 has exactly the same chromophore with BSA-2, except for an alkylether linkage group. In polymer 2, the anthracene unit in the BSA chromophore was replaced by a phenylene ring, and in the case of polymer 3 an electron-withdrawing cyano group was attached for the purpose of enhancing electron injection/transport tendency.

Figure 4(a) compares the luminance-current density relationship of the single layer device made of polymer 1 with that of the single layer device made of the BSA-2 dye. Although large difference was observed at a low current density region due to large leakage current in the device made of spin-coated polymer 1 films, the luminance values in the polymer device at the higher current desity region was close to that in the vacuum-sublimed dye device. Figure 4(b) compares the luminance-current density relationship of the double layer device made of polymer 1 (ITO/polymer 1/OXD-2/MgAg) with that of the double layer device made of the BSA-2 dye (ITO/BSA-2/OXD-2/MgAg). About 20-fold increases in quantum efficiencies were observed in both devices. The increase is ascribed to the improvement in balanced injection of electrons and holes due to the insertion of the hole blocking OXD-7 layer. The luminance values in the polymer devices are found to be very close to those in the sublimed-dye devices. These observations demonstrate the validity of our material design concept in polymer systems.



(a) (b)

FIGURE 4 Luminance-current density relationships in single-layer (a) and double layer (b) EL devices with BSA as emissive chromophres. For the case of double layer devices, a vacuum-sublimed OXD-7 layer was used as electron transport layer.

CONCLUDING REMARKS

We have domonstrated that molecular design concept for charge transporting and emissive chromophores in vacuum-sublimed dye films can be extended to the design of chromophores incorporated in polymer skeletons. Thus we can conclude that the design and synthesis of varieties of polymers for EL devices are open for further study and the fabrications of high performance EL devices in future are promising.

One of the major issues to be studied is the design of flexible spacer groups which have a role of connecting chromophores. Design of connecting groups are expected to bring about the improvements in thermal and mechanical stabilities as well as processability of polymer films.

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