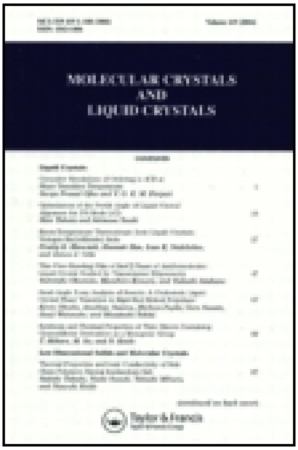

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MOLECULAR DYNAMICS INTERPRETATION OF THE STRUCTURES OF POLYIMIDES FOR ORGANIC ELECTROLUMINESCENT DEVICES

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MOLECULAR DYNAMICS INTERPRETATION OF THE STRUCTURES OF POLYIMIDES FOR ORGANIC ELECTROLUMINESCENT DEVICES

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In this work, we discuss the relative efficiency of the organic electroluminescent devices (OELDs) utilizing various fluorine-containing polyimides in hole transporting layer (HTL) in terms of the structure of the polyimides (PI) by molecular dynamics estimation. Materials for polyimides investigated in this study are; 1,2,4,5-benzentetracarboxylic dianhydride (PMDA), 4,4′-(hexafluoroisopropylidene) diphtalic anhydride (6FDA), 4,4′-oxydianiline (ODA), and 4,4′-(hexafluoroisopropylidene) dianiline (6FDAm). The devices used in this study consist of two organic layers, i.e. ITO-coated glass/TPD-dispersed polyimide/Alq3/Al devices. It was found that the EL efficiency of the OELDs is significantly affected by the molecular structure of polyimides as well as the contents of fluorine atoms in the PI. Molecular dynamics calculation proved that PMDA-6FDAm PI exhibits largest steric hindrance among the four PIs used in this work, due to the largest torsion of benzene rings.

Keywords: molecular dynamics; OELDs; polyimide

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INTRODUCTION

Typical organic electroluminescent devices (OELDs) consist of single or multilayer sublimed dyes and carrier transporting materials. In addition to these types of OELDs, molecularly-dispersed polymer OELDs are also emerging ones since polymers have some advantages such as easy processability, intrinsically good durability and outstanding flexibility [1]. On the other hand, thermal stability is one of the most important requirements in OELDs, since the degradation of OELDs is partly caused by diffusion, crystallization and decomposition of organic layer by Joule-heat during operation. Thermal stability is directly related to the device properties such as current density-voltage-EL intensity (J-V-L) characteristics, electroluminescent spectra, and lifetime.

Kido *et al.* fabricated OELDs introducing a polymer into a hole-transporting layer (HTL) to bind a thermally unstable organic material, such as N,N-diphenyl-N,N-di(m-tolyl)-benzidine(TPD) [2,3]. Similar research has been carried out using some polymer binders such as poly(4,4-oxydiphenylene pyromellitimide) (PMDA-ODA PI) [4] and poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP) [5] in this laboratory. Especially, PMDA-ODA PI was used for giving thermal stability to OELDs [4] and the properties of the OELDs using PVdF-co-HFP were affected by the strong electronegativity of fluorine in HTL [5]. Based on these results, the fluorine-containing polyimide has been introduced to a hole-transporting layer (HTL) in this laboratory for binding a small molecule, such as the triphenylamine derivative [6].

In this work, various fluorine–containing polyimides were synthesized and either of them was selected as a matrix polymer to a HTL because of both the thermal stability of polyimide and the effect of the strong electronegativity of fluorine atom.

OELDs using TPD-dispersed poly(hexafluoropropane dianhydride-co-4,4-oxydiphenylene) (6FDA-ODA PI), poly(hexafluoropropane dianhydride-co-4,4′-(hexafluoroisopropylidene) (6FDA-6FDAm PI), poly (4,4′-oxydiphenylene pyromellitimide) (PMDA-ODA PI) and poly (4,4′-oxydiphenylene-co-4,4′-(hexafluoroisopropylidene) (PMDA-6FDAm PI) with different TPD compositions were fabricated. Molecular dynamics calculation of polyimides were performed in this work to interpret the different EL efficiencies of the devices containing PIs using theoretical stereo chemistry.

EXPERIMENTAL

Materials and Sample Preparation

The chemical structures of materials used in this study are shown in Figure 1. Monomers were purchased from Aldrich chemical Co.; 1,2,4,5-

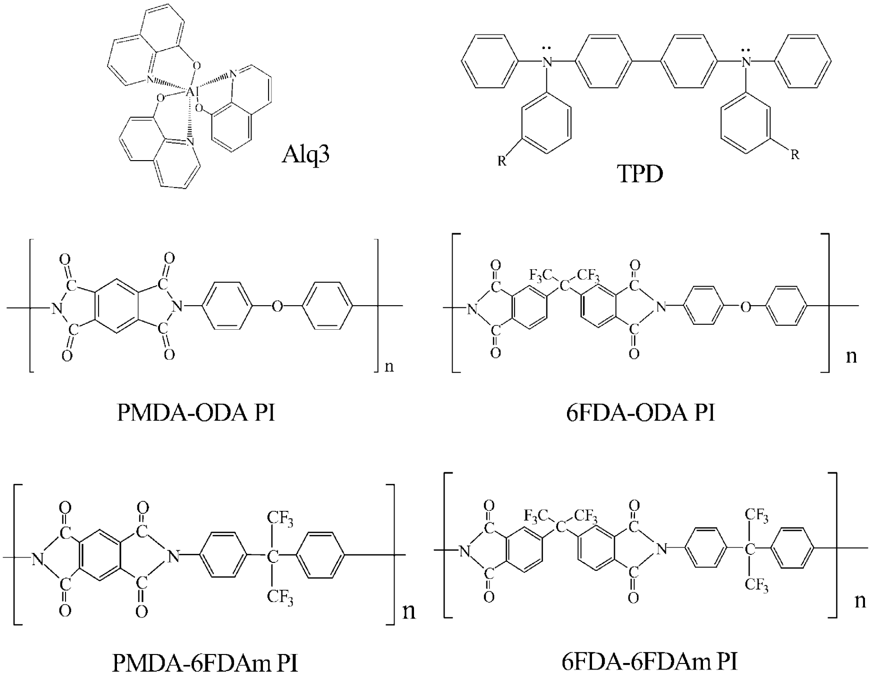

FIGURE 1 The molecular structures of materials used in this study.

benzentetracarboxylic dianhydride (PMDA), 4,4′-(hexafluoroisopropylidene) diphtalic anhydride (6FDA), and 4,4′-oxydianiline (ODA) 4,4′-(hexafluoroisopropylidene) dianiline (6FDAm). 8-hydroxyquinoline aluminium (Alq3) was purchased from TCI. These materials were used without further purification. All solvents also were used as received.

Polyimides were converted via thermal imidization process from their soluble and flexible polyamic acid (PAA) precursors, which were synthesized from dianhydride and diamine in N-methyl-2-pyrrolidone (NMP). PMDA-ODA PI, 6FDA-ODA PI, PMDA-6FDAm PI and 6FDA-6FDAm PI were used as matrix polymers for binding N,N-diphenyl-N,N-di(m-tolyl) benzidine (TPD). The weight ratios of TPD to PAA were 30/70 and 70/30. Overall solid concentration was 1 wt%. The mixture solution was spin-coated onto an ITO-glass substrate at 3000 rpm for 2 min. ITO coated substrate was patterned by acid etching method. Thermal imidization consists of three steps; TPD-dispersed PAA thin film was soft-baked at 80°C for above 30 min and subsequently thermally imidized to PI at 180°C for 1 hr under nitrogen atmosphere. The devices used in this study consist of two organic layers, i.e. ITO-coated glass (150 nm thickness, 15Ω /□) / TPD-dispersed polyimide (50 nm)/Alq3 (60 ~ 70 nm)/Al devices. Then the

Alq3 and aluminum cathode were sequentially prepared by thermal evaporation in a vacuum of ca. 1×10^{-5} Torr.

Measurements and Characterization

Current density-voltage-EL intensity (J-V-L) characteristics of the device were measured using a photomultiplier tube (PMT) (Hamamatsu Photonics Co.) and an electrometer (Keithley 6517).

Stereo Structure in Minimized Energy State

The stereo structure of molecules in minimized energy state was determined by MOPAC (semi-empirical computation) in CS chem3D pro. AM1 (Austin method 1) theory was used for computation [7]. The condition of this calculation is closed shell (restricter) wave function and minimized energy to minimum RMS gradient of 0.100 in window98 me operating system, AMD1.4 GHz process and 40 Gbyte hard disk.

RESULTS AND DISCUSSION

The dependence of EL intensity on the applied voltage of the OELDs is shown in Figure 2. The nomenclatures of PIs in this plot are; PMDA-ODA PI (P-O), 6FDA-ODA PI (6-O), PMDA-6FDA PI (6-6) and 6FDA-6FDAm PI (P-6). When the ratio of TPD and PI is 3:7, the turn-on voltages of the double-layered devices using TPD-dispersed PMDA-ODA PI, 6FDA-ODA PI, PMDA-6FDA PI and 6FDA-6FDAm PI as a HTL were 5.2, 4.6, 6.3 and 3.4 V respectively. It was observed that the TPD/6FDA-6FDAm PI (3:7) device exhibited the best efficiency among all the devices in this work. The 6FDA-6FDAm PI containing device shows the lowest turn-on voltage in comparison to other PI based systems, while the highest turn-on voltage was observed for the PMDA-6FDAm PI based device. The charge injection and turn-on voltage, corresponding to the voltage for the initiation of the charge injection were reduced as the concentration of fluorine atom in PI was increased. It is due to the increase of the hole-transporting ability by the interaction between TPD and the fluorine containing PI. It may be also attributed to the better film formation ability PI in comparison to TPD.

In order to interpret these results, we performed molecular dynamics calculation. Gaussian is a general purpose ab initio molecular electronic structure. Hartree-Fock equation was suggested solving the method of complex Schrődinger equation at multi system, so that the equation is converted to computer code by Gaussian method. The computer code contains programs for the calculation of the required one- and two-electron

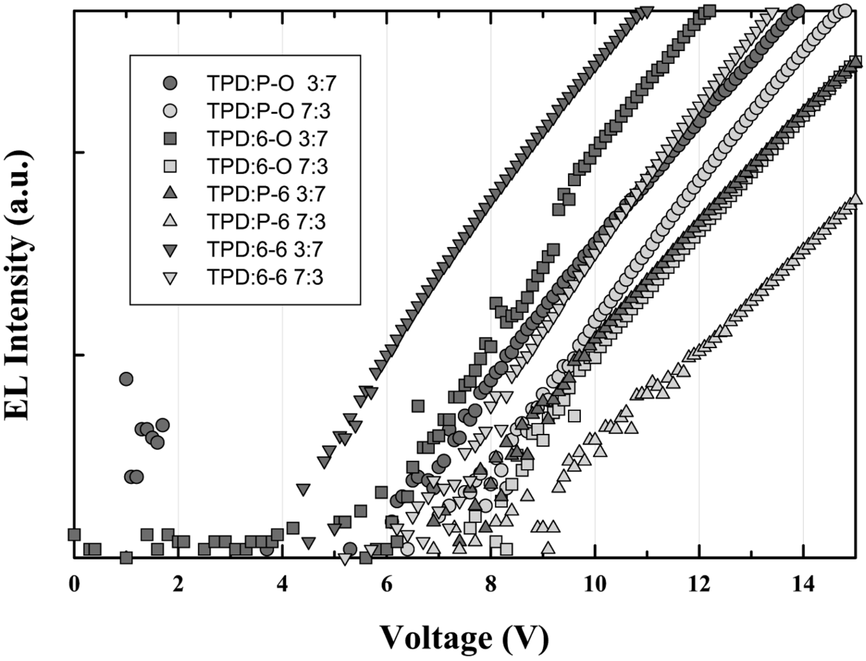

FIGURE 2 Plot of EL intensity vs voltage of each device based on different polyimides with different TPD ratios.

integrals using basis sets of s, p, d, or f Cartesian Gaussian functions. Self-consistent field (SCF) wavefunctions can be determined both for closed and open shell systems within the RHF(restricted Hartree Fock), UHF(unrestricted Hartree Fock), and ROHF (spin-restricted open-shell Hartree Fock) formalism. Post Hartree-Fock correlation methods include Configuration Interaction (CI) with single (CIS), double (CID) or single and double excitations, including correction for triples (CISD, CISD(T)), or Quadratic CI (QCISD, QCISD(T), QCISD(TQ)). Gaussian can predict energies, molecular structures, vibrational frequencies and numerous molecular properties for systems in the gas phase and in solution, and it can model both their ground state and excited states [7–11].

Figure 3 shows a typical 3-dimensional structure of PMDA-6FDAm PI in minimized energy state. It was found from cartesian coordination that the dihedrals of fluorine containing parts are almost same; C(16)-C(7)-C(36)-C(28) = −47.612 (PMDA-6FDAm), C(37)-C(42)-C(43)-C(47) = 49.534 (6FDA-ODA), C(6)-C(17)-C(18)-C(22) = 49.961 (6FDA-6FDAm), but benzene rings have different angles. π-electron clouds in benzene rings comparatively weakly interact with TPD. Thus, it is surmised that the

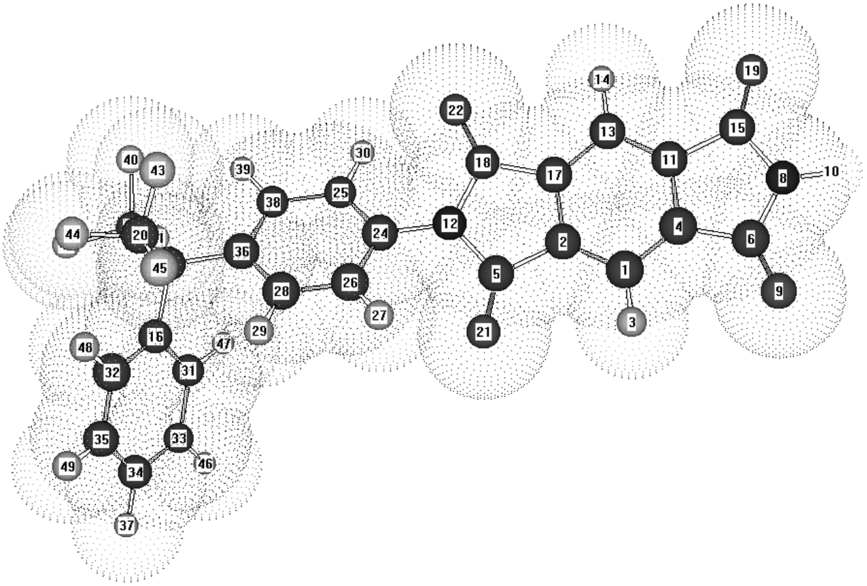

FIGURE 3 The structure of PMDA-6FDAm at minimized energy state by AM1 method.

interaction of TPD and PIs was influenced by not only the fluorine effect but also the torsion of benzene rings. The molecular dynamics calculation proved that PMDA-6FDAm system has the highest steric hindrance. Thus, PMDA-6FDAm system shows worst EL efficiency. Cartesian coordination can offer low data to Gaussian equation for theoretical molecular interaction energy, charge transfer and molecular distance.

Therefore, the EL efficiency in Figure 2 can be explained by the interaction between TPD and π-cloud in benzene rings; i.e. the highest turn-on voltage for PMDA-6FDAm PI in HTL may be attributed to the steric hindrance of PMDA-6FDAm PI.

CONCLUSION

The multilayer OELDs were successfully fabricated utilizing N,N′-diphenyl-N,N′-di(m-tolyl)benzidine (TPD) dispersed poly (4,4′-oxydiphenylene pyromettltimide) (PMDA-ODA PI), poly (hexafluoropropane dianhydride-co-4,4-oxydiphenylene) (6FDA-ODA PI), poly (4,4′-oxydiphenylene-co-4,4′-(hexafluoroisopropylidene) (PMDA-6FDAm PI) or poly(hexafluoropropane dianhydride-co-4,4′-hexafluoroisopropylidene) (6FDA-6FDAm PI). Each polyimide has different fluorine content. In this work, all devices was consisted of two organic layers; ITO coated glass/ TPD:PIs/ Alq3/ Al. The efficiency of the device was found to be governed by the interaction between fluorine in PI and tertiary amine. It was observed that in general the TPD:PI device exhibits higher efficiency as the contents of TPD is lower. It is due to better film formation ability of PI. PMDA-6FDAm PI system performs worst device character. To explain this reason, theoretical stereo chemistry was attempted. The calculation showed that PMDA-6FDAm is most twisted. Thus, it was suggested that PMDA-6FDAm do not possess suitable interaction with TPD.

REFERENCES

[1] Lim, H. T. (2000). Organic electroluminescent devices based on polyurethane derivatives:effects of substituents on electroluminescent and photoluminescent properties, *Thin Solid Films*, *363*, 152–155.

[2] Kido, J. (1992). Organic electroluminescent devices based on the molecularly doped polymers, *Appl. Phys. Lett.*, *61*, 761–763.

[3] Kido, J. (1992). Interband tunneling between valence-band and conduction-band quantum wells in a GaSb/AlSb/InAs/AlSb/GaSb/AlSb/InAs triple-barrier structure, *Jpn. J. Appl. Phys.*, *31*, L960–963.

[4] Lim, H. (1998). Polymeric light-emitting diodes utilizing TPD-dispersed polyimide thin film and organometallic complex, *SPIE*, *3281*, 345–353.

[5] Kang, E. J. (1998). Organic electroluminescent devices using poly(vinylidene fluoride-co-hexafluoropropylene) doped with triphenylamine derivative as a hole-transporting layer, *SPIE*, *3281*, 336–344.

[6] Shin, J. H. (2001). Characterization of organic electroluminescent devices introducing fluorine-containing polyimide to hole-transporting layer, *Mater. Sci. Eng. B.*, *B85*, 195–198.

[7] Cioslowski, J. (1995). Electron intracule densities with correct electron coalescence cusps from Hiller-Sucher-Feinberg-type indentities, *J. Chem. Phys.*, *103*, 6093–6103.

[8] Stefanov, B. B. (1995). An efficient approach calculation of Zero-Flux atomic surface and generation of atomic integration data, *J. Comp. Chem.*, *16*, 1394–14404.

[9] Cioslowski, J. (1994). The atomic softness matrix, *J. Chem. Phys.*, *101*, 366–370.

[10] Cioslowski, J. (1993). Rigorous interpretation of electronic wave functions. 3. Theoretical confirmation of a three-center, two-electron carbon-hydrogen-carbon bond in the in-bicyclo [4.4.4] tetradecyl cation, *J. Am. Chem. Soc.*, *115*, 5177–5179.

[11] Cioslowski, J. (1993). Electronegativities in situ, bond hardnesses, and charge-transfer components of bond energies from the topological theory of atoms in molecules, *J. Am. Chem. Soc.*, *115*, 1084–1088.