

# Energy Transfer and Hole Transport Materials for Light-Emitting Diodes of Novel Branched Oligo(thienylphenylamine)s

Jun-Sang Cho, Yojiro Kojima, Kimihisa Yamamoto\*

Kanagawa Academy of Science & Technology (KAST) &

\*Department of Chemistry, Faculty of Science & Technology, Keio University, Yokohama, 223-8522, Japan

Fax: 81-45-566-1718, e-mail: yamamoto@chem.keio.ac.jp

The intramolecular energy transfer characteristics of novel branched amorphous oligo(thienylphenylamine)s (dimer, trimer, and tetramer) were investigated. Moreover, double layer LEDs that used the oligomers as a hole transport material and tris(8-quinolinato)aluminum ( $Alq_3$ ) as an emitting with electron transport material were fabricated. The maximum brightness and the luminous efficiency of the devices increased when the branched tetramer was used compared to the others. This may be due to the fact that the tetramer has a higher carrier mobility and electroactivity compared to the others based on its more branched structure.

Key words: energy transfer; hole transport; light-emitting diodes (LED); oligomers

## 1. INTRODUCTION

Amorphous oligo(thienylphenylamine)s with high a glass transition temperature ( $T_g$ ) have been synthesized and investigated as new hole and/or electron transporting materials for light-emitting diodes (LEDs) in order to increase their thermal durability and simple structure of the devices.<sup>[1-7]</sup> Moreover, hyperbranched polymers or dendrimers have been used in high performance LEDs due to their specific structural and functional properties, e.g., good solubility, energy transfer, and chemical antenna.<sup>[8-15]</sup> We have reported that the branched type of electro-oxidatively polymerized poly(thienylphenylamine)s showed better redox properties which included catalytic activity and electronic conductivity when compared with the linear types.<sup>[16, 17]</sup> Also, some novel branched oligo(thienylphenylamine)s such as 5,5'-{bis[4-di(4-thienylphenyl) amino]phenyl}-2,2'-bithiophene (dimer), 5,5'-{bis[tris(thienylphenyl)amine]}-tris(thienyl)amine (trimer) and 5,5',5''-{tris[tris(thienylphenyl)amine]}-tris(thienyl-phenyl)amine (tetramer) have been synthesized as shown in Figure. 1.

By means of electrochemical measurements (CV; cyclic voltammetry and DPV; differential pulse voltammograms) of the oligomers, it was shown that the more highly branched tetramer showed the lowest oxidation potential of the oligomers. This means that the carrier hopping is promoted on these oligomers. In this study, we focused on the intramolecular energy transfer property of the oligomers. The double layer (oligomers/ $Alq_3$ , tris(8-quinolinato)aluminum) LEDs that used these amorphous materials as a hole transport layer were fabricated and the EL performances of these devices were also investigated.

## 2. EXPERIMENTAL

### 2.1 Materials and measurements

All the compounds were synthesized based on our previously reported methods.<sup>[16, 17]</sup>

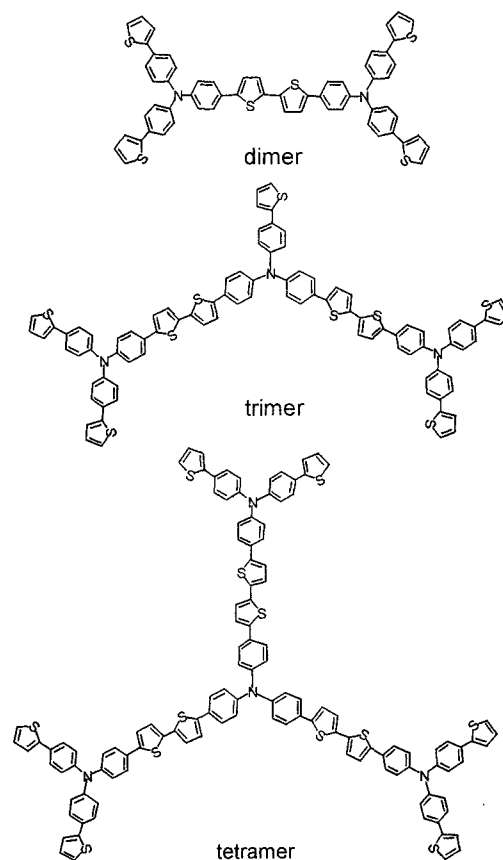


Figure 1. Molecular structure of oligo(thienylphenylamine)s.

The electrochemical analyses and thermal properties of the oligomers were acquired using a BAS Model 660 electrochemical workstation and Rigaku DSC 8230, respectively. The characteristics of the devices such as the current-voltage and luminance-voltage profiles were obtained using an LED measurement system equipped with an Advantest R6243 DC voltage-current source/monitor and a Minolta LS-100 luminance meter. The photoluminescence (PL) and electroluminescence (EL) spectra were measured by a JASCO FP-6500 fluorescence spectrophotometer. The thicknesses of the films were determined using a Sloan Dektak surface profilometer 3030. All electrical and optical measurements of the devices were performed under ambient conditions.

### 2.2 Fabrication of LEDs

The EL devices were fabricated into double layer structures (ITO/oligomers/Alq<sub>3</sub>/CsF/Al) (Figure 2); (Device A (oligomers= dimer), Device B (trimer), Device C (tetramer)). All of the oligomers were spin coated on a patterned ITO glass at about 50 nm. The Alq<sub>3</sub> and cathode were vacuum deposited under 10<sup>-6</sup> Torr with a 3-6 Å/s vaporation rate using an Ulvac VPC-410A vacuum coater with a CRT-5000 deposition controller. An ultrathin CsF (2 nm) layer with Al (100 nm) as the cathode for enhancement of the electron injection balance by vacuum deposition under 10<sup>-6</sup> Torr with a 1-7 Å/s vaporation rate was used. The effective emitting area of the devices was typically 0.09 cm<sup>2</sup>.

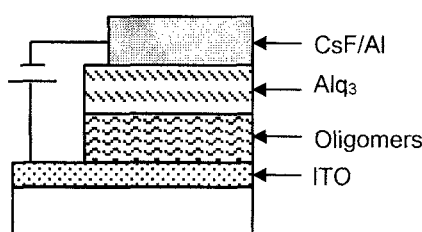


Figure 2. Double layer structure of the EL devices.

### 3. RESULTS AND DISCUSSION

From the differential scanning calorimetry (DSC) measurement of the oligomers, the  $T_g$  of the dimer and trimer were determined to be 135 °C and 137 °C, but the tetramer  $T_g$  was not detectable. This amorphous property is attributed to the rigid terminal thiophene groups and non-planar bithiophene backbone structure.<sup>[3]</sup> The PL spectra of all the oligomers in THF (6 μM) resembled that shown in Figure 3, regardless of the different electronic state result from their structures.<sup>[17]</sup>

In spite of the fact that terminal thiophene moiety is excited at ca. 370 nm, the PL band that originates from the thiophene moiety around 430 nm was not observed, but the maximum emission band was red-shifted around

500 nm with a weak shoulder around 540 nm. This PL characteristic was the same result when the bithiophene moiety was excited at ca. 430 nm.

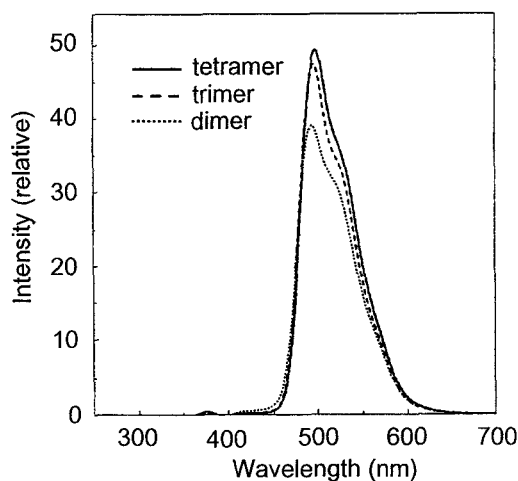


Figure 3. PL spectra of oligo(thienylphenylamine)s. (Excited at 370 nm (dimer), 376 nm (trimer) and 374 nm (tetramer))

It suggested that a singlet exciton of the terminal thiophene moiety effectively transfers to a lower  $\pi-\pi^*$  transition energy state of the bithiophene backbone moiety (Figure 4 (a)).<sup>[18]</sup> Also, the PL intensity was slightly increased for the dimer, trimer, and tetramer and was determined to be 39, 47, and 49, respectively.

From the DPV measurements, the redox potential gap ( $\Delta E$ ) between the amine and bithiophene moiety in the oligomers was confirmed to decrease from the dimer to tetramer.<sup>[17]</sup>

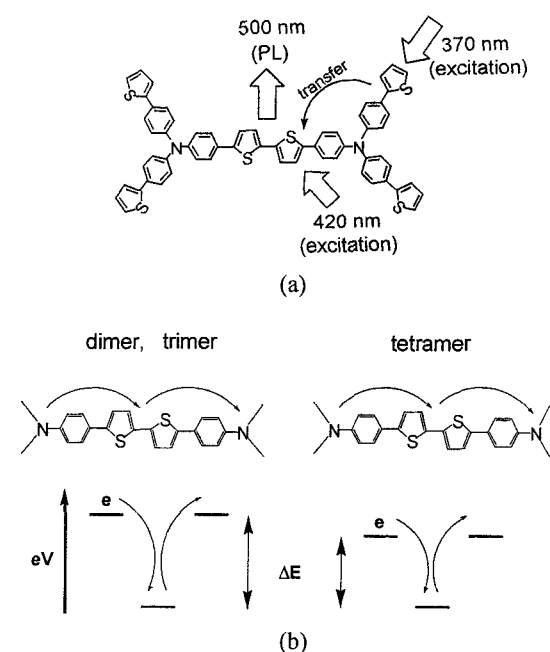


Figure 4. Schematic model of energy transfer (a) and potential gap (b) of oligo(thienylphenylamine)s.

This small  $\Delta E$  means that electron- or hole-hopping from one amine to another amine moiety is promoted by decreasing the potential barrier as shown in Figure 4 (b).

On the other hand, all devices emitted bright green light that corresponds to the PL spectra of  $\text{Alq}_3$  ( $\lambda_{\text{emi}}$  510 nm) when a positive voltage was applied to the ITO electrode. This indicates that the oligomers act as hole transport materials. Figure 5 shows the applied voltage-luminance (L-V) (a) and luminance-current density (L-I) (b) performances of the devices.

The optical and electrical characteristics of the devices are summarized in Table 1. Device C showed a good L-I profile compared to Device A and Device B. As mentioned above, it shows that the tetramer is more advantageous due to its energy transfer ability based on its more branched structure that resulted in an increased recombination rate of holes and electrons.

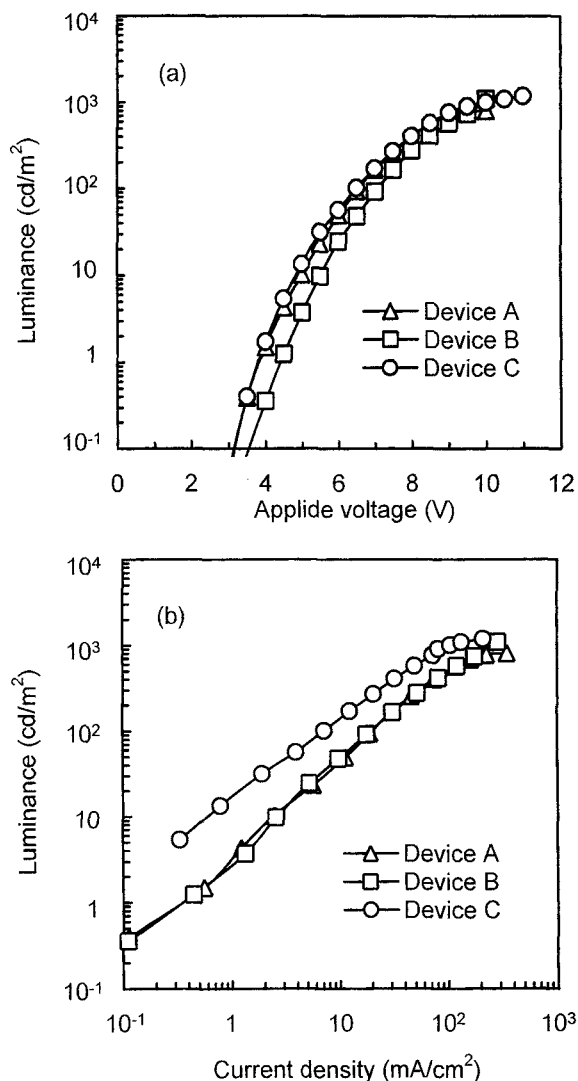


Figure 5. Applied voltage-luminance (L-V) (a) and current density-luminance (I-L) (b) characteristics of EL devices.

The maximum luminance of the devices increased from Device A (806 cd/m<sup>2</sup>) to Device C (1180 cd/m<sup>2</sup>). It is interesting that all the devices showed a lower turn-on voltage at around 3.2 V (at 0.1 cd/m<sup>2</sup>) and a similar voltage at maximum brightness. However, for the luminous efficiency at 300 cd/m<sup>2</sup> for the devices, Device C, which used the tetramer, showed the best efficiency (0.49 lm/W) compared with those of the devices using the dimer (0.19 lm/W) and trimer (0.20 lm/W).

Table 1. Electroluminescence (EL) characteristics of devices.<sup>a)</sup>

Devices	EL $\lambda_{\text{max}}$ (nm)	Turn-on <sup>b)</sup> voltage (V)	Max. brightness (cd/m <sup>2</sup> /at V)	Luminous <sup>c)</sup> efficiency (lm/W)
Device A	509	3.2	806/10	0.19
Device B	510	3.6	1092/10	0.20
Device C	509	3.2	1180/11	0.49

<sup>a)</sup> All devices were two layered (oligomers/ $\text{Alq}_3$ ) types.

<sup>b)</sup> at 0.1 cd/m<sup>2</sup>.

<sup>c)</sup> at 300 cd/m<sup>2</sup>.

#### 4. CONCLUSION

Based on photo-spectroscopic (UV-vis and PL spectra) and electrochemical (CV, DPV) measurements of novel branched oligo(thienylphenylamine)s with high  $T_g$ s, we observed effective intramolecular energy transfer from the terminal thiophene moiety to the bithiophene backbone in the oligomers. Moreover, the double layer LED that used the more branched oligomers as hole transport materials showed the best EL performance, which had the higher luminance and luminous efficiency compared to the others.

#### ACKNOWLEDGEMENT

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