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J. Phys. Chem. C, **2007**, 111 (1), 108-115 • DOI: 10.1021/jp0654056 • Publication Date (Web): 01 December 2006

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Optical Properties of Oligo(9,9-diarylfuorene) Derivatives in Thin Films and Their Application for Organic Light-Emitting Field-Effect Transistors

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Received: August 21, 2006; In Final Form: October 15, 2006

We demonstrated that oligo(9,9-diarylfuorene) derivatives have high potential for optoelectronic applications such as organic lasers and light-emitting organic field-effect transistors (LE-OFETs). The oligo(9,9-diarylfuorene) derivatives have high photoluminescence quantum efficiencies up to $\Phi_{\text{PL}} \approx 70\text{--}75\%$ and very low amplified spontaneous emission thresholds (E_{th}) down to $0.5 \mu\text{J}/\text{cm}^2$ in their vacuum-deposited neat films. In particular, the trimer derivatives (B3 and T3) show higher Φ_{PL} and lower E_{th} than those of the dimers (B2 and T2). Efficient deep-blue LE-OFETs with the electroluminescence (EL) peaking at $\lambda_{\text{peak}} = 429 \text{ nm}$ were demonstrated using the ter(9,9-diarylfuorene) as the active layer. Rather high luminance up to $L \approx 150 \text{ cd}/\text{m}^2$ and EL quantum efficiency up to $\eta_{\text{ext}} \approx 0.60\%$ were achieved with the optimum source-drain channel length, indicating bipolar carrier injection in the terfluorene layer under the FET operation.

1. Introduction

Recently, a variety of novel organic semiconducting materials have been widely synthesized for various organic semiconductor device applications such as organic light-emitting diodes (OLEDs),^{1–4} organic transistors,^{5–18} and organic solar cells.^{19–21} OLED development has been especially successful due to extensive research and development during the past two decades, resulting in commercial full-color OLED displays. To further advance OLED displays, active-matrix (AM) driving of OLEDs is now being extensively studied. However, AM-OLEDs require rather complicated electrical circuits and fabrication, and thus simplified device architectures capable of the active-matrix operation are highly desired. One of the most promising solutions is the light-emitting organic field-effect transistor (LE-OFET), i.e., a lateral-type organic light-emitting diode that has field-effect transistor characteristics,¹³ which enables controlling electroluminescence (EL) intensity by operating the field-effect transistor.^{8–18} The details in operation mechanism of LE-FET can be referred to ref 22. Because the LE-OFET structure combines characteristics of both the OLED and the switching thin-film transistors (TFTs), the circuit design of the AM-OLEDs can be simplified to some extent and the aperture of the light-emitting pixels can be increased.

In developing LE-OFETs, however, it is found that development of LE-OFET materials is even more challenging than development of OLED materials. To obtain well-behaved LE-OFET characteristics, LE-OFET materials must (i) be capable of bipolar carrier injection, transport, and accumulation near

the interface between the gate insulator and the organic active layer when a source-drain voltage (V_{d}) and gate voltage (V_{g}) are applied and (ii) possess high photoluminescence (PL) quantum efficiency (Φ_{PL}) in thin films. Most OLED materials widely used nowadays show very low field-effect mobilities, which is due to the amorphous nature of the thin films, so we cannot apply these materials to LE-OFET devices. Instead of using the OLED design rules, we have to prepare LE-OFET materials that have not only high field-effect mobility but also high PL efficiency. Well-packed molecular aggregates often used in organic TFTs show high field-effect mobility, but often also lead to strong concentration quenching of the PL due to strong π – π interactions.¹⁵ For example, the aromatic polyacene derivatives such as anthracene,²³ tetracene,⁸ and pentacene^{5–7} have been previously reported to show unique FET characteristics. However, we found that polyacene derivatives usually do not satisfy at least one of the LE-OFET requirements such as homogeneous thin-film formation, carrier accumulation, or high PL efficiency, etc., which are all critical for obtaining well-behaved LE-OFET characteristics.

In the exploration of LE-OFET materials, we have recently reported on a bright LE-OFET using 1,3,6,8-tetraphenylpyrene (TPPy) as an active layer.¹³ Using TPPy, we demonstrated LE-OFET characteristics that were significantly improved compared to those of previously reported devices.^{8–18} A vacuum-deposited layer of TPPy showed PL efficiency of $\Phi_{\text{PL}} = 68 \pm 3\%$ and a hole mobility of $\approx 10^{-5} \text{ cm}^2/\text{Vs}$, giving the maximum EL quantum efficiency of $\eta_{\text{ext}} \approx 10^{-2}\%$ when used in the LE-OFET. Further, doping a TPPy layer with 1 wt % of rubrene enhanced PL efficiency up to $\Phi_{\text{PL}} \approx 100\%$ and the EL efficiency up to $\eta_{\text{ext}} \approx 0.5\%$. In the studies, it was found that although the TPPy layer has the poor capability of accumulating electrons near the SiO_2 gate insulator interface, electron injection from an Au

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Figure 1. (a) Molecular structures of oligo(9,9-diarylfluorene) derivatives, and (b) schematic view of the LE-OFET structure.

electrode into the TPPy layer occurs at certain combinations of V_d and V_g , giving bright EL.¹³

Although the improvement obtained with rubrene-doped TPPy is impressive, ideally it is desired to achieve efficient LE-OFETs without needing the more complicated doping. Furthermore, since EL from rubrene-doped TPPy is yellow, extending efficient EL from LE-OFETs to other colors, for instance pure blue, is certainly also highly desired and required for practical applications. As such, a few recent findings of intriguing electrical and optical properties of oligo(9,9-diarylfluorene)s are particularly worthy of attention for blue-emitting LE-OFETs. The oligo(9,9-diarylfluorene)s in general show high PL efficiencies from deep blue to near UV in their thin films^{24–26} and high thermal stability with high glass transition temperatures (T_g) over 170 °C. Further, excellent carrier mobilities for both holes and electrons on the order of $\mu \approx 10^{-3}$ cm²/Vs have been identified for these oligofluorenes using the time-of-flight (TOF) method.^{25,27}

In this study, we performed studies on five kinds of oligo(9,9-diarylfluorene) derivatives: B2, bi(9,9'-spirobifluorene); B3, ter(9,9'-spirobifluorene); T2, bi(9,9-ditolylfluorene); T3, ter(9,9-ditolylfluorene); and B3[N2], 4,5-diazafluorene-incorporated ter(9,9-diaryl fluorene), as shown in Figure 1a.^{24–28} We prepared thin films of these compounds using high-vacuum thermal evaporation and investigated their PL and amplified spontaneous emissions (ASE) characteristics. Further, using B3 as an active layer, we fabricated LE-OFET devices with various channel lengths ($L_{SD} = 0.4–10 \mu\text{m}$) (Figure 1b) and investigated the FET and EL characteristics.

2. Experimental Section

Thin films of organic materials were evaporated using a high-vacuum ($<3 \times 10^{-3}$ Pa) thermal evaporation system. The deposition rate for organic materials was monitored using a quartz sensor, and the deposition rates of oligo(9,9-diarylfluorene) derivatives were maintained at 0.1 nm/s. We confirmed that no decomposition of oligo(9,9-diarylfluorene)s occurred during thermal evaporation.

The temperature dependences of the PL intensity and transient lifetime for films of the oligo(9,9-diarylfluorene) derivatives were measured using an N₂ gas laser (MNL 200, Laser Technik Berlin, $\lambda = 337$ nm, pulse width = 500 ps, repetition rate = 20 Hz) as an excitation source and a streak camera (C4334, Hamamatsu) for detection. Fluorescence spectra, absorption spectra, and the Φ_{PL} of the organic layers were measured using a fluorospectrometer (FP-6300, Jasco), a UV/vis spectrometer (UV-3100, Shimadzu), and an absolute PL quantum efficiency measurement system incorporating an integrating sphere. The HOMO levels of the metal and the organic layers were measured using an ultraviolet photoelectron spectroscope, AC-1 (Riken Keiki Co.).

The ASE characteristics of the terfluorenes by optical pumping were measured as follows. A thin film was optically pumped with the nitrogen gas laser with a pulse width of ~ 500 ps and at a repetition rate of 20 Hz by focusing an excitation light with a radiation area of $\sim 1 \times 5$ mm. A cylindrical lens and neutral density filters were used to adjust the excitation intensities. The light emissions were collected from the edge of the film into an optical fiber connected to a spectrometer (PMA-11, Hamamatsu Photonics Co.). The ASE measurements were performed in a nitrogen atmosphere to prevent the film from being degraded by moisture and oxygen.

A schematic view of the fabricated LE-OFET device structure is shown in Figure 1b. A heavily doped n⁺-Si (100) wafer with a 300-nm-thick thermally grown SiO₂ layer ($C_{ox} = 1.18 \times 10^{-8}$ F/cm²) was used as the gate electrode and the gate insulator. Bottom-contact-type S-D electrodes composed of Cr (1 nm)/Au (40 nm) were formed on the SiO₂/n⁺-Si layer using conventional photolithography and lift-off techniques.¹³ The channel lengths between the S-D electrodes were $L_{SD} = 0.4, 0.6, 0.8, 1, 3,$ and $10 \mu\text{m}$ and the channel width was 2 mm. After the photolithography process, the substrate was degreased with acetone and isopropanol and was cleaned before being loaded into the evaporation system. An 80-nm-thick B3 film as an active layer was then deposited in a vacuum of $<1 \times 10^{-3}$ Pa.

All LE-OFET measurements were carried out in a vacuum of $\approx 1 \times 10^{-3}$ Pa at room temperature because the device had unstable TFT characteristics in air. The dependence of the drain current (I_d) on the drain voltage (V_d) and the gate voltage (V_g) were measured using a semiconductor parameter analyzer (Agilent 4145), and the luminance (L) and the quantum efficiency were obtained by using a highly sensitive photon counter (C767, Hamamatsu) and a calibrated Si photodiode. In the measurements, V_d was scanned from 10 to -100 V in steps of -1 V, and V_g was scanned from 0 to -100 V in steps of -20 V. The EL spectra were measured using a multichannel spectrometer (PMA-11, Hamamatsu).

3. Results and Discussion

3.1. PL and ASE Characteristics. The absorption, PL, and ASE spectra of the oligo(9,9-diarylfluorene) derivatives in their thin films (100 nm) are shown in Figure 2, and various photophysical properties extracted are summarized in Table 1. The dependences of ASE characteristics and PL intensity on the excitation power are shown in the insets of Figure 2. Thin films of these oligo(9,9-diarylfluorene) derivatives have fluorescence peaks (λ_{flu}) from the near-UV to the deep blue region (i.e., between 395 and 430 nm). At room temperatures, the deposited films have rather high PL efficiencies of $\Phi_{PL} = 66 \pm 2\%$ in B2, $72 \pm 2\%$ in B3, $47 \pm 2\%$ in T2, $63 \pm 2\%$ in T3, and $52 \pm 2\%$ in B3[N2] (Table 1). In general, the trimer

Figure 2. PL, ASE, and absorption spectra of deposited films of oligo(9,9-diarylfuorene) derivatives: (a) B2, (b) B3, (c) T2, (d) T3, and (e) B3[N2]. Insets show the dependence of emission intensity on the excitation power.

structures (B3 and T3) have higher PL quantum efficiencies than the dimer structures (B2 and T2). The transient lifetimes of fluorescence were also measured and are listed in Table 1. All these oligofluorenes show rather short fluorescence lifetimes of $\tau_f \approx 1$ ns. Correspondingly, the rate constants of radiative fluorescence decay (k_r) are calculated with $k_r = \Phi_{PL}/\tau_f$ and are summarized in Table 1. All the k_r values are on the order of

$\approx 10^9$ s $^{-1}$, which is high compared with conventional organic lasing dyes.²⁹ In general, the trimers show shorter lifetimes and larger rate constants than the dimers. Similar phenomena were observed before for oligomeric systems and can be ascribed to strong dipolar coupling interactions between monomeric units as in the excitonic model of Kasha.^{30,31} Also, in general the trimers exhibit higher PL quantum efficiencies than dimers either

TABLE 1: Optical and Electrical Characteristics of the Oligo(9,9-diarylfuorene), B2, B3, T2, T3, and B3[N2] Films (100 nm): Fluorescence Peak (λ_{flu}), PL Quantum Efficiency (Φ_{PL}), Lifetime of Fluorescence (τ_f), ASE Threshold (E_{th}), Highest Occupied Molecular Orbital/Lowest Unoccupied Molecular Orbital (HOMO/LUMO) Levels, and Field-Effect Hole Mobility (μ_h)

	λ_{flu} peak (nm)	Φ_{PL} (%)	τ_f (ns)	k_r (10^8 s $^{-1}$)	E_{th} (μ J/cm 2)	HOMO/LUMO (eV)	μ_h^a (cm 2 /Vs)
B2	395	66 ± 2	0.95	6.4	5.3 ± 0.5	5.9/2.7	2.0×10^{-6}
B3	430	72 ± 2	0.91	7.8	1.0 ± 0.1	6.1/3.0	2.5×10^{-5}
T2	395	47 ± 2	1.09	4.3	1.1 ± 0.1	5.5/2.2	5.3×10^{-6}
T3	429	52 ± 2	0.89	7.5	0.5 ± 0.1	5.4/2.3	1.0×10^{-5}
B3[N2]	431	52 ± 2	1.02	5.5	2.0 ± 0.2	5.5/2.7	2.5×10^{-7}

^a The LE-OFET with $L_{SD} = 10$ μ m.

Figure 3. Dependence of PL characteristics of oligo(9,9-diarylfuorene) films on the temperature: (a) B2, (b) B3, (c) T2, (d) T3, and (e) B3[N2]. Insets show the radiative decay rate constant for fluorescence.

in solutions or in films,^{23,428} which is probably associated with higher radiative decay rate constants for the trimers and thus weaker influences of nonradiative decay processes.

To get further insights of radiative and nonradiative decay processes, we investigated the temperature dependence of the PL characteristics. The temperature dependence of the PL intensity and the transient lifetime of fluorescence (and also the radiative decay rate constants) of the oligo(9,9-diarylfuorene) films is shown in Figure 3 (and in insets of Figure 3). All these oligofluorenes show certain increase of Φ_{PL} and rather temperature-independent fluorescence lifetimes in decreasing the temperature. As such, it appears that the slight increase of PL efficiencies at low temperatures is associated with the slight increase of the radiative decay rate constants, indicating that enhancement of the molecular rigidity with a decrease of temperature increases an oscillator strength of the oligofluorenes (insets of Figure 3). In addition, we note that the Φ_{PL} values in

these oligofluorene films reach 60–80% at low temperatures, suggesting that 20–40% of the singlet excited energy is lost through certain mechanisms of nonthermal origins (assuming that thermally nonradiative decay from the singlet excited state is completely suppressed at the low temperatures). For instance, transferring to the triplet excited state through intersystem crossing is one possibility.

Due to their rather high PL efficiencies in neat films, these oligo(9,9-diarylfuorene)s also exhibit rather efficient ASE characteristics (Figure 2 and insets of Figure 2). All derivatives showed ASE at the emission peaks corresponding to their 0–1 transitions in fluorescence,²⁹ giving near-UV to deep blue ASE. The ASE thresholds (E_{th}) for these oligofluorenes are very low, ranging from $E_{th} = 0.5$ to $5.3 \mu\text{J}/\text{cm}^2$, as shown in the inset of Figure 2 and in Table 1. In general, the trimers exhibit lower ASE thresholds than those of the dimers. This is consistent with our previous observation that emitters possessing larger radiative

Figure 4. I_d vs V_d characteristics for LE-OFETs with B3 as the active layer and different L_{SD} : L_{SD} = (a) 10 μm , (b) 3 μm , (c) 1 μm , (d) 0.8 μm , (e) 0.6 μm , and (f) 0.4 μm . In measurements, V_g values were varied: V_g = 0 V ($\circ$), -20 V (Δ), -40 V (∇), -60 V (triangle pointing left), and -100 V (triangle pointing right). Inset of panel a shows I_d vs V_d characteristics for LE-OFET with the B3 active layer and L_{SD} of 10 μm . In measurements, V_g were varied: V_g = 0 V ($\circ$), 20 V (Δ), 40 V (∇), 60 V ($\diamond$), 80 V (triangle pointing left), and 100 V (triangle pointing right).

rate constants in general show lower ASE thresholds.²⁹ Still, it is interesting to note that the T3 shows the lowest threshold value of $E_{th} \approx 0.5 \pm 0.1 \mu\text{J}/\text{cm}^2$, although its Φ_{PL} and k_r are lower than those of B3. This may be associated with the weaker absorption at the ASE wavelength for T3 than that for B3 (cf., comparing absorption spectra of Figure 2b,d, which would contribute to a lower waveguiding loss in ASE.²⁹

Finally, we mention the PL and ASE characteristics of B3-[N2]. We observed that B3 possesses slightly better characteristics compared with B3[N2]; the higher PL efficiency and lower ASE threshold in B3. In comparison of temperature dependences of the PL efficiencies in B3 and B3[N2] (Figure 3), although B3 showed almost no temperature dependence, B3[N2] showed a gradual increase between 300–250K, indicating that B3[N2] is susceptible to thermally nonradiative decay.

3.2. LE-OFET Characteristics.

We fabricated LE-OFETs

using these oligo(9,9-diarylfuorene) films with the device structure shown in Figure 1b. Representative FET output characteristics for B3 with L_{SD} = 10 μm are shown in Figure 4a. From these characteristics, the field-effect mobility (μ_{FET}) is extracted by the following equations for the saturation-mode operation of FETs:

$$I_d = \frac{1}{2} \frac{W}{L_{SD}} \mu_{FET} C_{ox} (V_G - V_T)^2 \quad (1)$$

$$\mu_{FET} = \frac{2L_{SD}}{W} \frac{I_d}{C_{ox}(V_G - V_T)^2} \quad (2)$$

where the channel width, W , is 2 mm; the channel length, L_{SD} , is 10 μm ; I_d is the drain current; the capacitance of the SiO_2 insulator, C_{ox} , is $1.18 \times 10^{-8} \text{ F}/\text{cm}^2$; V_g is the gate voltage;

Figure 5. η_{ext} vs I_d characteristics for LE-OFETs with B3 as the active layer and different L_{SD} : L_{SD} = (a) 10 μm , (b) 3 μm , (c) 1 μm , (d) 0.8 μm , (e) 0.6 μm , and (f) 0.4 μm . In measurements, V_g were varied: V_g = 0 V ($\circ$), -20 V ($\triangle$), -40 V (∇), -60 V ($\diamond$), -80 V (triangle pointing left), and -100 V (triangle pointing right).

and V_T is the threshold voltage. The extracted hole mobilities (μ_h) for the devices with L_{SD} = 10 μm are summarized in Table 1. These oligofluorene materials show the field-effect hole mobilities (μ_h) of 10^{-5} to 10^{-7} cm^2/Vs .

Although hole and electron mobilities of 10^{-3} cm^2/Vs were found in previous studies using the time-of-flight method,^{26,27} these FET devices showed rather low FET mobilities with only p-type operation and no n-type operation. However, it should be noted that, in the FET structures, the observed carrier-transport characteristics are usually complicated by issues such as electrodes and the interface characteristics of the gate insulator. In case of B3, for example, since the work function of the Au source/drain electrodes is 4.6 eV, and HOMO and LUMO levels of B3 are 5.9/2.7 eV, the barrier heights for hole and electron injections are 1.3 and 1.9 eV, respectively. Therefore, these large barriers should apparently reduce the FET mobilities, since the calculation of FET mobility tacitly supposes that injection barriers between source/drain electrode and organic

layers are ohmic. Further, significant carrier trapping by the SiO_2 insulating layer also can reduce the FET mobilities.^{32,33} The detailed mechanism on these influences are now in progress.

Among these oligofluorenes, B3 shows the highest $\mu_h \approx 2.5 \times 10^{-5}$ cm^2/Vs , in addition to its highest PL efficiency, and thus was used for further LE-OFET studies. B3 LE-OFETs with various channel lengths were fabricated and characterized. Figure 4 shows the I_d - V_d characteristics for B3 LE-OFETs with various channel lengths: (a) L_{SD} = 10 μm , (b) 3 μm , (c) 1 μm , (d) 0.8 μm , (e) 0.6 μm , and (f) 0.4 μm , under the p-type operation. The LE-OFET with L_{SD} = 10 μm showed typical I_d - V_d characteristics (Figure 4a): linear characteristics in the low V_d region and well-behaved saturation in the high V_d region. On the other hand, the LE-OFETs having short channel lengths of $L_{\text{SD}} \lesssim 3$ μm had unusual I_d - V_d curves similar to those previously observed with the TPPy device. The I_d was greatly enhanced when the channel length was reduced, and no saturation of the I_d - V_d curves, shown in Figure 4b-f, was

Figure 6. EL spectra under $V_d = V_g = -100$ V for LE-OFETs with B3 as the active layer and different L_{SD} : $L_{SD} = 1$ μm , 0.8 μm , 0.6 μm , and 0.4 μm , and a photograph of light emission from a short-channel LE-OFET with $L_{SD} = 0.4$ μm ($V_d = V_g = -100$ V).

observed in the high V_d region. In case of the short channel length devices, due to the high electrical field between the source and drain electrodes (V_d), significant carrier injection would occur from these electrodes. Therefore, the observed current (I_{SD}) is composed of the accumulation current (i.e., FET current) and injection current (i.e., carrier injection similar in OLED), resulting in the divergent current behavior.

Since previous TOF measurements showed that B3 is capable of transporting both holes and electrons, one would expect bipolar operation of the oligofluorene LE-OFETs. Therefore, the I_d - V_d characteristics with positive V_g were also measured and are shown in the inset of Figure 4a. Although the large I_d was observed with $V_g = 0$, I_d decreased with increasing V_g . Such characteristics indicate that no net electron accumulation occurred under the positive V_g and that hole injection from the drain electrode occurs when the larger negative V_D was applied. The mechanism of no electrons accumulation is unclear. We suppose that the large energy barrier for electron injection from the Au electron made electron accumulation difficult, and electron trapping by the SiO_2 insulating layer ruined n-type operation. Introduction of an efficient electron injection electrode such as Al^{34} and Ca^{35} and a novel insulating layer such as BCB^{33} and Dix-C^{35} layers may provide n-type and ambipolar operations.

The external EL quantum efficiency (η_{ext})-drain current (I_d) characteristics for B3 devices with different channel lengths are shown in Figure 6. The η_{ext} of the long-channel LE-OFETs (10 μm and 3 μm) showed very rapid increase with V_d (or I_d). The onset of EL emission in long-channel devices roughly coincides with the onset of the saturation regime, indicating that the formation of a pinch-off region and the building of a high electrical field perhaps enhances electron injection from the drain electrode. In such a case, the gate voltage induces accumulation of the majority carriers (holes) in the B3 layer, while the injection of minority carriers (electrons) increases with increasing V_d . On the other hand, the shorter-channel LE-OFETs ($L_{SD} \lesssim 1$ μm) exhibited a rather gradual increase of η_{ext} with I_d , indicating more balanced bipolar carrier injection. The high electrical field induced by V_d probably significantly enhanced

the electron injection and thus gave more balanced bipolar carrier injection. Among all these devices, the 1 μm and 3 μm devices give the highest η_{ext} of $\sim 0.6\%$. Such efficiency is almost 10 times higher than η_{ext} of the neat TPPy device, perhaps associated with more efficient electron injection for the case of B3. Because the LUMO level of the B3 layer (3.0 eV, Table 1) is 0.3 eV lower than that of a TPPy layer (2.7 eV), electrons might be more efficiently injected from an Au drain electrode into the B3's LUMO level.

We also estimated FET characteristics of B3[N2]. Since the B3[N2] has been well characterized to transport electrons by a time-of-flight method, we expected more efficient electron injection efficiency from a drain electrode. However, B3[N2] showed inferior FET characteristics; the hole mobility was quite low of 10^{-7} cm^2/Vs in the p-type operation, and no n-type operation was observed. EL spectra for B3 LE-OFETs with the channel lengths of $L_{SD} = 0.4$ to 1 μm are shown in Figure 6. These devices showed EL characteristic of B3 emission with the main emission peak at 430 nm and a shoulder peak at 408 nm, which coincides well with the PL of the B3 film (Figure 2b). The shapes of the EL spectra show subtle dependence on the L_{SD} , most probably due to variations in detailed optical effects (e.g., multiple interference) associated with variations in the carrier recombination sites and the source/drain/gate electrode geometry in different device structures. The maximum luminances of ~ 142 cd/m^2 at $L_{SD} = 0.4$ μm , ~ 28 cd/m^2 at $L_{SD} = 0.6$ μm , ~ 3.2 cd/m^2 at $L_{SD} = 0.8$ μm , and ~ 3.1 cd/m^2 at $L_{SD} = 1$ μm were obtained under $V_d = V_g = -100$ V. The inset of Figure 6 shows a photograph of EL from the LE-OFET with $L_{SD} = 0.4$ μm under $V_d = V_g = -100$ V, which is clearly visible under a normal lighting environment.

4. Conclusion

In summary, we reported that the vacuum-deposited oligo-(9,9-diarylfuorene) films have relatively high PL efficiencies of $\Phi_{\text{PL}} = 60$ – 80% and short transient lifetimes of fluorescence, corresponding to relatively high radiative decay rates of $k_r \approx 10^9$ s^{-1} . Consequently, these oligofluorenes exhibited efficient ASE. In particular, T3 [ter(9,9-ditolylfluorene)] showed the

lowest ASE threshold of $E_{th} = 0.5 \mu\text{J}/\text{cm}^2$. Further, using B3 [ter(9,9'-spirobifluorene)] as the active layer, we demonstrated bright deep-blue EL from an LE-OFET structure with a maximum η_{ext} of $\approx 0.60\%$ in the best device structure. Further developments aiming for higher light emission efficiency are now in progress by taking into account of the idea of ambipolar operation.^{33–36} Since we revealed that the oligofluorenes possess both transistor and ASE characteristics, these materials will be a promising candidate for an active media in the future organic laser diodes.

Acknowledgment. This work was supported by the Integrated Industry Academia Partnership of Kyoto University International Innovation Center, and National Science Council of Republic of China. We especially acknowledge Dr. Yoshioka Oku and Mr. Noriyuki Shimoji for assistance in the conventional photolithography and lift-off techniques and Mr. Hajime Nakanotani for ASE measurements.

References and Notes

- (1) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.
- (2) Adachi, C.; Tokito, S.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1988**, *27*, 269.
- (3) Adachi, C.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *Appl. Phys. Lett.* **2000**, *77*, 904.
- (4) Oyamada, T.; Murase, S.; Tominaga, T.; Maeda, C.; Sasabe, H.; Adachi, C. *Appl. Phys. Lett.* **2005**, *86*, 033503.
- (5) Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 4108.
- (6) Brown, A. R.; Jarrett, C. P.; de Leeuw, D. M.; Matters, M. *Synth. Met.* **1997**, *88*, 37.
- (7) Wang, D. X.; Tanaka, Y.; Iizuka, M.; Kuniyoshi, S.; Kudo, K.; Tanaka, K. *Jpn. J. Appl. Phys.* **1999**, *38*, 256.
- (8) Hepp, A.; Heil, H.; Weise, W.; Ahles, M.; Schmechel, R.; von Seggern, H. *Phys. Rev. Lett.* **2003**, *91*, 157406.
- (9) Ahles, M.; Hepp, A.; Schmechel, R.; von Seggern, H. *Appl. Phys. Lett.* **2004**, *84*, 428.
- (10) Capelli, R.; Santato, C.; Loi, M. A.; Roy, V. A. L.; Stallinga, P.; Cicoira, F.; Murgia, M.; Zamboni, R.; Muccini, M.; Rost, C.; Karg, S. *Synth. Met.* **2004**, *146*, 329.
- (11) Sakanoue, T.; Fujiwara, E.; Yamada, R.; Tada, H. *Appl. Phys. Lett.* **2004**, *84*, 3037.
- (12) Oyamada, T.; Okuyama, S.; Shimoji, N.; Matsushige, K.; Sasabe, H.; Adachi, C. *Appl. Phys. Lett.* **2005**, *86*, 093505.
- (13) Oyamada, T.; Uchiuzou, H.; Oku, Y.; Shimoji, N.; Matsushige, K.; Sasabe, H.; Adachi, C. *J. Appl. Phys.* **2005**, *98*, 074506–1.
- (14) Swensen, J. S.; Soci, C.; Heeger, A. J. *Appl. Phys. Lett.* **2005**, *87*, 253511.
- (15) Oyamada, T.; Uchiuzou, H.; Sasabe, H.; Adachi, C. *J. SID* **2005**, *13*, 10.
- (16) Kudo, K. *Curr. Appl. Phys.*, **2005**, *5*, 337.
- (17) Nakamura, K.; Ichikawa, M.; Fushiki, R.; Kamikawa, T.; Inoue, M.; Koyama, T.; Taniguchi, Y. *Jpn. J. Appl. Phys.*, **2005**, *44*, L1367.
- (18) Cicoira, F.; Santato, C.; Melucci, M.; Favaretto, L.; Gazzano, M.; Muccini, M.; Barbarella, G. *Adv. Mater.* **2006**, *18*, 169.
- (19) Tang, C. W. *Appl. Phys. Lett.* **1986**, *48*, 183.
- (20) Kafafi, Z. H. *Proc. SPIE* **2002**, *4465*.
- (21) Rand, B. P.; Peumans, P.; Forrest, S. R. *J. Appl. Phys.* **2004**, *96*, 7519.
- (22) Muccini, M. *Nat. Mater.* **2006**, *5*, 605.
- (23) Ando, S.; Nishida, J.; Fujiwara, E.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *Chem. Mater.* **2005**, *17*, 1261.
- (24) Wong, K. -T.; Chien, Y. -Y.; Chen, R. -T.; Wang, C. -F.; Lin, Y. -T.; Chiang, H. -H.; Hsieh, P. -Y.; Wu, C. -C.; Chou, C. H.; Su, Y. O.; Lee, G. -H.; Peng, S. -M. *J. Am. Chem. Soc.* **2002**, *124*, 11576.
- (25) Wu, C. -C.; Liu, T. -L.; Hung, W. -Y.; Lin, Y. -T.; Wong, K. -T.; Chen, R. -T.; Chen, Y. -M.; Chien, Y. -Y. *J. Am. Chem. Soc.* **2003**, *125*, 3710.
- (26) Chao, T.-C.; Lin, Y.-T.; Yang, C.-Y.; Hung, T.-S.; Chou, H.-C.; Wu, C.-C.; Wong, K.-T. *Adv. Mater.* **2005**, *17*, 992.
- (27) Wu, C. -C.; Liu, T. L.; Lin, Y.; Hung, W.; Ke, T. H.; Wong, K. T.; Chao, T. C. *Appl. Phys. Lett.* **2004**, *85*, 1172.
- (28) Wong, K.-T.; Chen, R.-T.; Fang, F.-C.; Wu, C.-C.; Lin, Y.-T. *Org. Lett.* **2005**, *7*, 1979.
- (29) Aimono, T.; Kawamura, Y.; Goushi, K.; Yamamoto, H.; Sasabe, H.; Adachi, C. *Appl. Phys. Lett.* **2005**, *86*, 071110.
- (30) McRae, E. G.; Kasha, M. *J. Chem. Phys.* **1958**, *28*, 721.
- (31) Anémian, R.; Mulatier, J.-C.; Andraud, C.; Stéphan, O.; Vial, J.-C. *Chem. Comm.* **2002**, *15*, 1608.
- (32) Chua, L. L.; Zaumseil, J. J.; Chang, F.; Ou, E. C. W.; Ho, P. K. H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194.
- (33) Zaumseil, J.; Friend, R. H.; Sirringhaus, H. *Nat. Mater.* **2006**, *5*, 69.
- (34) Sakanoue, T.; Fujiwara, E.; Yamada, R.; Tada, H. *Appl. Phys. Lett.* **2004**, *84*, 3037.
- (35) Yasuda, T.; Tsutsui, T. *Chem. Phys. Lett.* **2005**, *402*, 395.
- (36) Dinelli, F.; Capelli, R.; Loi, M. A.; Murgia, M.; Muccini, M.; Facchetti, A.; Marks, T. J. *Adv. Mater.* **2006**, *18*, 1416.