

Anisotropic optical properties and molecular orientation in vacuum-deposited ter(9,9-diarylfluorene)s thin films using spectroscopic ellipsometry

Hao-Wu Lin, Chun-Liang Lin, Hsin-Hua Chang,^{a)} Yu-Ting Lin, and Chung-Chih Wu^{b)}

*Department of Electrical Engineering, Graduate Institute of Electro-optical Engineering,
and Graduate Institute of Electronics Engineering, National Taiwan University, Taipei,
Taiwan 10617, Republic of China*

You-Ming Chen, Ruei-Tang Chen, Yuh-Yih Chien, and Ken-Tsung Wong

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10617, Republic of China

(Received 6 August 2003; accepted 29 October 2003)

This article reports on the investigation of anisotropic optical properties of vacuum-deposited thin films of high-efficiency blue-emitting ter(9,9-diarylfluorene)s using variable-angle spectroscopic ellipsometry. Under deposition conditions typical for thin-film organic devices, both real and imaginary parts of refractive indices of vacuum-deposited ter(9,9-diarylfluorene) films exhibit rather significant uniaxial anisotropy with the optical axis along the surface normal. In particular, for the absorption associated with the $\pi-\pi^*$ transition of the terfluorene backbone, they show substantially larger in-plane extinction coefficients than the out-of-plane extinction coefficients. It is thus inferred that the vacuum-deposited ter(9,9-diarylfluorene) molecules tend to align their molecular axes and $\pi-\pi^*$ transition dipole moments along the substrate surface as observed previously in spin-coated films of alkyl-substituted polyfluorenes or oligofluorenes, even though the present ter(9,9-diarylfluorene)s have rigid and bulky aryl substituents on C9, relatively shorter oligomer chains, and very different deposition conditions. © 2004 American Institute of Physics.

[DOI: 10.1063/1.1635991]

I. INTRODUCTION

Thin films of polymeric and molecular organic semiconductors have been subjected to extensive studies in the last 2 decades due to applications in photonics and optoelectronics, such as organic light emitting devices (OLEDs) and displays, photovoltaic cells, photoconductors, nonlinear optical devices, and solid-state lasers.^{1–10} In these applications, knowledge of optical properties of the organic thin films is crucial for modeling and optimizing characteristics of devices. For instance, designs and analyses of organic solid-state lasers with either waveguide or microcavity configurations must be based on the knowledge of complex refractive indices of the organic gain materials.^{11–21} In the case of OLEDs, not only the luminescence efficiency but also the optical constants and the orientation of emitting dipoles of organic films affect the amount of emission that can be collected outside the devices.^{22–26}

On the other hand, interest in optical and photophysical properties of organic films is also stimulated by their subtle relationship with molecular structures and properties afforded by molecular designs and syntheses, and with morphologies in thin films induced by various deposition and treatment techniques and conditions. The optical characterization thus provides a nondestructive approach to probe the

structures in condensed organic systems. In particular, anisotropic optical properties are usually observed when there is preferential orientation or alignment of molecules in condensed organic systems. Therefore, detection of optical anisotropy can provide useful structural and morphological information regarding arrangement of molecules in thin films. For instance, thin films of conjugated polymers often exhibit anisotropic optical properties due to the stiffness of polymer chains and their preferential alignment parallel to the substrate surface with conventional coating techniques such as spin coating.^{26–30} Further, strong optical anisotropy is also observed in molecules that possess strongly anisotropic geometries (e.g., disk-like or rod-like shapes) and can be assembled into somewhat oriented configurations in thin films. Examples include epitaxially grown molecular films,³¹ molecular films composed of liquid-crystalline molecules that can be aligned at elevated temperatures,^{32,33} and thin films consisting of anisotropic oligomers [e.g., oligothiophenes, oligo(phenylenevinylene)s etc.] that can self-organize into some particular packing structures on substrates with vacuum deposition.^{34–37} In spite of these previous reports of optical anisotropy in molecular films and influences of such properties on emission characteristics of devices in polymer OLEDs, we find that in general there is lack of such investigation on low-molar-mass materials that are used in molecular OLEDs and are prepared with vacuum deposition under the nominal deposition conditions for device fabrication. In this article, we report on the studies of anisotropic optical properties of vacuum-deposited oligofluorenes, ter(9,9-

^{a)}Current address: Van Nung Institute of Technology, Chung-Li, Taiwan, Republic of China.

^{b)}Author to whom correspondence should be addressed; electronic mail: chungwu@cc.ee.ntu.edu.tw

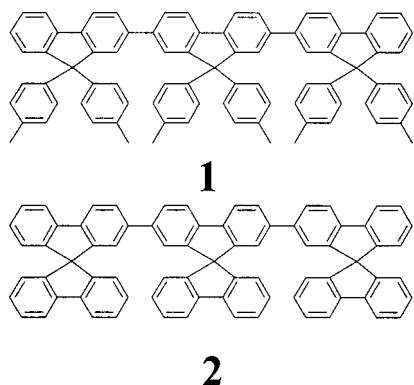


FIG. 1. Chemical structures of ter(9,9-diarylfluorene)s used in this work: TDAF **1** and TDAF **2**.

diarylfluorene)s, that are efficient blue-emitting materials for blue OLEDs.

Fluorene-based polymers or compounds have attracted much interest in recent years as efficient blue emitters for polymeric or molecular OLEDs and for solid-state lasers due to their high luminescence efficiency and flexibility in tuning various physical, optical, and electrical properties through convenient substitution on C9.^{32,33,38–50} There have been a few reports on anisotropic optical properties of polyfluorenes or oligofluorenes. Spin-coated polyfluorene films were found to exhibit uniaxial optical properties with the optic axis along the surface normal due to preferential alignment of polymer chains along the substrate surface.²⁶ Highly polarized electronic transitions were observed for stretched polyfluorene/polyethylene blend films.⁵¹ Polyfluorenes and long oligofluorenes (>5 fluorene units) with lengthy and flexible alkyl C9 substituents were found to exhibit liquid crystallinity.^{32,33,43,52} Due to relatively large molecular weights of these materials, thin films of these materials were fabricated by solution processing such as spin coating. On surfaces with alignment treatments, these liquid-crystalline molecules could be aligned along the defined orientation at elevated temperatures. The aligned configurations could be retained to room temperature by fast enough quenching to avoid perturbation of achieved alignment. The resulting aligned films showed electronic transitions strongly polarized along the alignment orientation and anisotropic optical constants.^{32,33,43,52}

In our previous studies, we have found ter(9,9-diarylfluorene)s (TDAFs) **1** and **2** (Fig. 1) exhibit some intriguing properties promising for blue OLEDs.^{49,50} The introduction of aryl substituents on C9 renders the molecular structures rather bulky, providing steric hindrance to interchromophore packing. As a consequence, these compounds form stable and homogeneous films with vacuum deposition, exhibiting high glass transition temperatures of >200 °C and high thin-film photoluminescence (PL) quantum yields of 90% in pure blue. These TDAFs are electrochemically stable as indicated by both reversible oxidation and reduction. Furthermore, these compounds show unusual nondispersive ambipolar carrier-transport properties with high carrier mobilities on the order of 10^{-3} cm²/(V s) for both holes and electrons.⁵⁰ They had been applied in blue OLEDs as the

emitting layer, exhibiting promising device characteristics.⁴⁹

The TDAFs and corresponding thin films in the present study in many aspects are different from polyfluorenes and oligofluorenes previously reported to exhibit optical anisotropy. First, the molecular structures of the present TDAFs are apparently very different. These TDAFs have substantially shorter main chains, and the peripheral aryl substituents on C9 are much more rigid and bulkier than the lengthy alkyl substituents in previously reported fluorene-based compounds. Second, due to the relatively smaller molecular weights, thin films of the present TDAFs could be deposited with vacuum deposition. In vacuum deposition, molecules receive no lateral force on molecules as in spin coating and no intentional alignment treatment is exerted on substrates in our experiments. With very different molecular structures and deposition conditions, one wonders whether the present TDAFs would have preferential molecular orientation when deposited on a substrate.

In this work, optical constants and anisotropy of vacuum-deposited films of TDAFs are investigated using variable-angle spectroscopic ellipsometry. From the results of optical characterization, one wishes to extract information regarding the arrangement of TDAF molecules in thin films. The article is organized as follows: in Sec. II, experimental methods for material preparation and characterization are described. In Sec. III, results of optical characterization of TDAF films are presented, and the implications of these results are discussed. Finally, Sec. IV concludes results of this work.

II. EXPERIMENT

Ter(9,9-diarylfluorene)s investigated in this work were synthesized through the Suzuki coupling reaction of 2,7-diboronic ester of 9,9'-diarylfluorene and 2-bromo-9,9-diarylfluorene in the presence of Pd(PPh₃)₄ and P^tBu₃ catalysts with high yields (75%–83%). Further details of synthesis and chemical analysis had been previously reported.⁴⁹ Synthesized terfluorenes were subject to purification by temperature-gradient sublimation before use in vacuum deposition. The purity of the purified materials was examined by elemental analysis to be >99.86%.⁴⁹

Thin-film samples of organic compounds for optical characterization were prepared by vacuum deposition in a high-vacuum chamber. The deposition was performed at a rate of 2–3 Å/s with the substrate held at room temperature, i.e., the deposition condition typical for the fabrication of OLEDs. Thin films were vacuum deposited on silicon wafers with ~19 Å native oxide for ellipsometry, and atomic force microscopy. Ultraviolet-visible (UV-vis) absorption spectroscopy were performed on films deposited on fused silica or quartz, PL spectroscopy, and x-ray diffraction.

Variable-angle spectroscopic ellipsometry (VASE) in the reflection mode was used to study the optical constants of thin films of ter(9,9-diarylfluorene)s deposited on Si substrates.^{29,53} Ellipsometry measures the change in polarization of light as a function of incident angle and wavelength. The experimentally determined ellipsometric values are Ψ and Δ , which are related to the ratio of Fresnel reflection

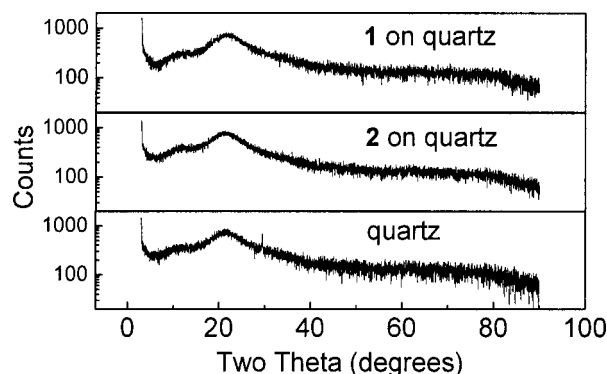


FIG. 2. X-ray diffraction results of the TDAF 1 and TDAF 2 films.

coefficients \tilde{R}_p and \tilde{R}_s for p - and s -polarized light, respectively, by $\tilde{R}_p/\tilde{R}_s = \tan(\Psi)e^{i\Delta}$. Optical constants of the materials are then determined by first constructing an optical model of the sample with physically meaningful structural and optical parameters, and then by iteratively adjusting these parameters to obtain the best fit to the measured ellipsometric data, i.e., the fitting with the minimum mean square error (MSE).⁵⁴

Ellipsometry over a wavelength range of 270–1100 nm in steps of 5 nm were performed in air using the J. A. Woollam V-VASE spectroscopic ellipsometer equipped with a xenon lamp source. The angles of incidence used were between 55° and 75° relative to the surface normal in steps of 5°. The nonlinear regression analysis of the measured ellipsometric data was performed using the J. A. Woollam WVASE32 software. To determine the optical anisotropy in both the transparent region and the absorption region of the spectrum, multiple-sample ellipsometric analysis of thin-film samples with varied thicknesses was employed.^{30,55} Thin-film samples of a compound with different thicknesses were prepared in a single vacuum pump-down without breaking vacuum to ensure high consistency in thin-film properties required in the multiple-sample ellipsometric analysis. The thicknesses of organic films were typically varied from 300 to 2000 Å.

UV-Vis absorption spectra were taken with a Shimadzu UV-1601PC spectrophotometer. Edge photoluminescence of thin-film samples was measured by pumping with a monochromatic light taken from a 75 W xenon arc lamp and by collecting through a polarizer and a fiber bundle connected to a cooled charge-coupled-device spectrograph.

III. RESULTS AND DISCUSSION

Vacuum-deposited thin films of TDAs exhibit a homogeneous appearance. To acquire further information regarding the morphology, x-ray diffraction was performed on TDAF thin films. Figure 2 shows the x-ray diffraction data of thin films of TDAF 1 and TDAF 2 on quartz. The diffraction patterns for both TDAF 1 and TDAF 2 are featureless, indicating no long-range order in the packing of molecules in thin films.

Figure 3(a) and shows the normal-incidence absorption spectra and the front-face PL spectra of TDAs in thin films.

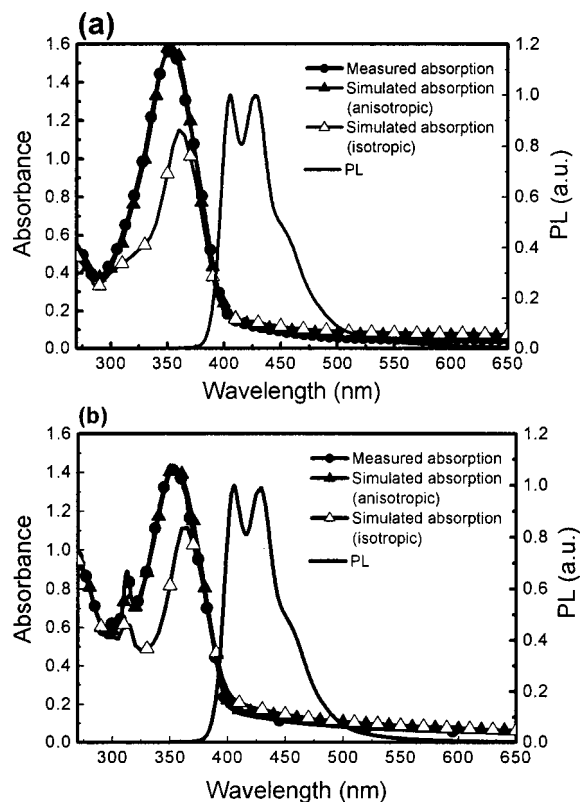


FIG. 3. (a) Normal-incidence absorption and front-face PL spectra of a 1700 Å thick film of TDAF 1 on fused silica. (b) Normal-incidence absorption and front-face PL spectra of a 1400 Å thick film of TDAF 2 on fused silica. For the absorption spectrum of each compound, comparison is made among the measured normal-incidence absorption spectrum, the simulated absorption spectrum using the optical constants extracted with the isotropic model, and the simulated absorption spectrum using the optical constants extracted with the anisotropic model.

Similarly, the optical spectra of TDAF 2 films are shown in Fig. 3(b). The absorption spectra of both terfluorenes exhibit a lowest-energy band peaking around 351 nm. This absorption band is characteristic of the lowest $\pi-\pi^*$ transition of the central terfluorene chromophore,^{46–48,56} and is unaffected by the different aryl substituents on C9 (two tolyls for TDAF 1 or one spiro-linked fluorene for TDAF 2). The tetrahedral C9 carbon thus serves as an effective insulating spacer between the central conjugation backbone and the aryl C9 substituents, consistent with previous studies of spiro-linked chromophores.^{46–48,57,58} In the absorption spectrum of TDAF 2, one observes an additional sharp peak at 309 nm, which is caused by the absorption of the peripheral fluorene units orthogonal to the central terfluorene.⁴⁶ PL of both TDAs exhibits nearly the same blue emission with the two most prominent vibronic peaks around 405 and 430 nm, which are characteristics of emission from the lowest singlet excited states of the terfluorene chromophore.^{46–48,57} The PL quantum yields of both terfluorenes in thin films had been previously determined to be about 90% using an integrating sphere system,⁴⁹ which are among the highest for blue emitters in neat films.^{46–48,57,59,60} These results indicate that in these TDAs the lowest electronic transitions of the terfluorene

TABLE I. Correlation coefficients for single-sample (TDAF film thickness=342 Å) and multiple sample (TDAF film thickness=342, 664, and 1011 Å) analyses for TDAF **1** at wavelength=405 nm. The correlation between parameters when ellipsometry data of three samples are used is significantly reduced compared to that when only single-sample ellipsometry data are used.

	Single sample (405 nm)				Multiple samples (405 nm)			
	n_o	k_o	n_e	k_e	n_o	k_o	n_e	k_e
n_o	1	-0.045	-0.552	-0.76	1	0.065	-0.156	-0.497
k_o	-0.045	1	0.853	-0.608	0.065	1	0.485	-0.337
n_e	-0.552	0.853	1	-0.113	-0.156	0.485	1	-0.043
k_e	-0.76	-0.608	-0.113	1	-0.497	-0.337	-0.043	1

rene backbone is rather intact with the attachment of aryl substituents on C9, yet these rigid and bulky aryl substituents are highly beneficial to prevention of molecular aggregation and to morphological stability in thin films.

In the ellipsometric analysis, initially thin films of TDAFs were treated as isotropic with the real and imaginary parts of the refractive index n and k , respectively. The thickness of thin films was first determined by assuming n in the transparent region (i.e., $k=0$ for the wavelength range of 500–1100 nm) to obey the Cauchy equation in fitting the ellipsometric values in the corresponding region.⁵³ With the determined thickness, n and k were then varied independently across the whole spectral range of interest to fit the ellipsometric values at each wavelength (i.e., point-by-point fitting). Such a procedure works well for molecular materials such as the electron-transport material Alq₃ (tris-(8-hydroxyquinoline)aluminum) and the hole-transport material 4,4-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α -NPD) often used in organic light-emitting devices, indicating thin films of these frequently used compounds are indeed optically isotropic. The fitting for films of TDAFs using the isotropic model, however, was poor, giving a MSE value in excess of 15 for thicker films (>1000 Å). Sometimes in thinner films (<500 Å) the isotropic model seemed to give a reasonable fitting with MSE values below 4. However, the calculated normal-incidence absorption spectra using the thus obtained k show substantial mismatch with the ones measured on fused silica substrates [as illustrated in Figs. 3(a) and 3(b)]. Further, the optical constants thus determined show substantial inconsistency with the Kramers–Kronig relationship.

We then turned to the possibilities of anisotropic distribution of molecular orientation in films and consequent anisotropic optical properties, considering the anisotropic rod-like shape of the terfluorene chromophore in these TDAF molecules. Since no in-plane anisotropy was observed in polarized optical transmission microscopy and the ellipsometric data were the same when rotating the sample in the plane of the films, the films were then treated as uniaxially anisotropic with the optical axis along the surface normal. That is, the optical constants are distinguished by those for the ordinary (in-plane) polarization, $n_o + ik_o$, and those for the extraordinary (out-of-plane) polarization, $n_e + ik_e$. In order to determine optical constants of uniaxially anisotropic films, ellipsometric data obtained at several incident angles are necessary. In principle, Ψ and Δ data from three angles in reflection ellipsometry are sufficient to determine the film

thickness and uniaxial optical constants.²⁹ As usual, the film thickness was first determined using a uniaxially anisotropic Cauchy model to fit the ellipsometric data in the transparent region. Good fittings with MSE values below 2 were routinely obtained at this stage. However, using the reflection ellipsometry data of one sample alone, it was found that the point-by-point fitting process for the whole spectral range of interest, including the transparent and absorption regions, tends to diverge producing incorrect optical constants. Using the data of multiple samples of different thicknesses removed the divergence problem and gave reliable fitting, mainly because the correlation between the fitting parameters (n_o , k_o , n_e , k_e , etc.) is reduced.^{30,55} Such behavior can be understood by examining the correlation coefficients between the different fitting parameters j and k , defined by

$$S_{jk} = \frac{c_{jk}}{\sqrt{c_{jj}}\sqrt{c_{kk}}}, \quad (1)$$

where c_{jk} is the element of the covariance matrix of fitting parameters. A correlation coefficient close to 1 or -1 indicates that the two parameters are highly correlated, i.e., that the overall quality of the fit is insensitive to a change in one parameter, compensated for by a corresponding change in the other parameter. Example correlation coefficients for TDAF **1** (at 405 nm) are shown in Table I for the independent fitting of n_o , k_o , n_e , and k_e using single-sample ellipsometry and using multisample analysis ellipsometry. It is observed that by using multiple-sample ellipsometry, the correlation is substantially reduced, making a reliable fitting. We typically found that 3–6 samples were usually sufficient to obtain good enough fitting results. Figures 4 and 5 show the optical constants for TDAF **1** and TDAF **2** thus acquired, respectively.

The point-by-point fitting procedure described above does not require Kramers–Kronig consistency. A Kramers–Kronig consistent model using a combination of one Cauchy background and several Gaussian oscillators for the ordinary and extraordinary optical constants was therefore also constructed and was used to fit the measured ellipsometric data. That measured Ψ and Δ data can also be well fitted by the Kramers–Kronig consistent model and that good agreement was found between the optical constants extracted from both methods indicate the values shown in Figs. 4 and 5 are Kramers–Kronig consistent. Furthermore, as shown in Figs. 3(a) and 3(b), the simulated normal-incidence absorption spectra for the TDAF films on fused silica, calculated using

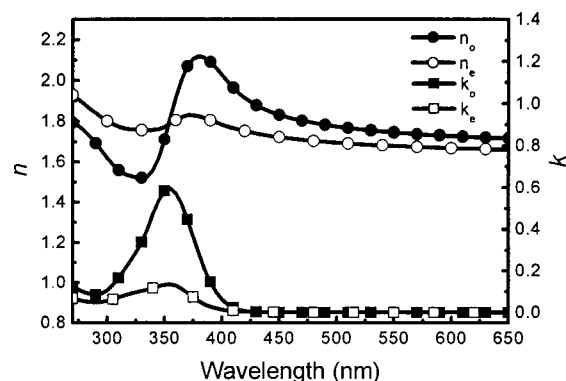


FIG. 4. The ordinary and extraordinary values of n and k determined by ellipsometry for TDAF 1.

the transfer matrix method with the extracted n_o and k_o , the thicknesses of the films, and the known refractive index of fused silica as parameters,⁶¹ met well with normal-incidence absorption spectra measured with a spectrophotometer, giving additional confidence in the optical constants obtained. Further, additional atomic force microscopic analysis of TDAF thin films indicates low root-mean-square (RMS) surface roughness of 2.2–4.2 Å for all the TDAF samples used in ellipsometric analysis (with thickness of 300–2000 Å). Since the RMS roughness is small (<1% of total film thickness) for all samples, it is not considered in the fit of the ellipsometric data and ruled out as a possible explanation of the present finding of optical anisotropy as experimental artifacts due to rough surfaces.³⁰

Vacuum-deposited films of both TDAFs exhibit significant anisotropy in both refractive index and absorption, in view of the fact that they are subject to no intentional alignment. The ratios between ordinary and extraordinary extinction coefficients at the peak of the π – π^* absorption (351 nm) associated with the terfluorene backbone are 4.4:1 for TDAF 1 (Fig. 4) and 5.0:1 for TDAF 2 (Fig. 5), respectively. Previous studies of optical anisotropy in well-aligned polyfluorene films and oligofluorene-based liquid crystals have suggested that the transition dipole moment for the π – π^* transition in polyfluorenes or oligofluorenes is basically along the long chain of the molecules.^{26,32,33,43,51,52} The large ratios between the ordinary and extraordinary extinction coefficients at the π – π^* absorption can therefore be regarded

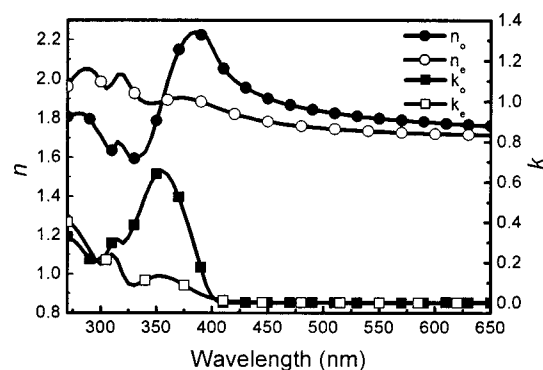


FIG. 5. The ordinary and extraordinary values of n and k determined by ellipsometry for TDAF 2.

as an indication of preferential orientation of these vacuum-deposited TDAF molecules parallel to the surface plane. In the wavelength range of emission, the ordinary (in-plane) polarization shows larger refractive index than the extraordinary (out-of-plane) polarization, and the differences are 0.22 and 0.14 at the two strongest emission peaks 405 and 430 nm for TDAF 1 (Fig. 4), and 0.25 and 0.15 at the two strongest emission peaks 405 and 430 nm for TDAF 2 (Fig. 5). Since the π – π^* transitions and higher transitions of both the central terfluorene chromophores and the peripheral aryl substituents all contribute to the real parts of complex refractive indices, it is therefore not straightforward to extract structural information from these results. However, the larger in-plane refractive index than the out-of-plane one and the known preferential orientation of the terfluorene backbone along the surface indicate that these TDAF molecules in general have higher polarizability along the oligomer main chain in the transparent region, as in many rod-like oligoaryl chromophores (e.g., in many liquid crystal molecules).^{62–64}

The polarization of photoluminescence from the edge of the samples was also measured by pumping films near the substrate edges. For the TDAF films, the intensity of emission polarized parallel to the substrate surface was approximately three times the intensity of emission polarized perpendicular to the substrate. In contrast, the edge emission of Alq₃ films was unpolarized with approximately equal intensities for both polarizations. The results of edge PL suggest that for these TDAF films, the transition dipole moments for emission also lie preferentially parallel to the substrate plane, while in films of ball-like Alq₃ the emitting dipoles can be considered isotropically oriented.

IV. CONCLUSION

In summary, we report the investigation of anisotropic optical properties of vacuum-deposited ter(9,9-diarylfluorene)s thin films using variable-angle spectroscopic ellipsometry. Under deposition conditions typical for thin-film organic devices, both real and imaginary parts of refractive indices of vacuum-deposited ter(9,9-diarylfluorene) films exhibit rather significant uniaxial anisotropy with the optical axis along the surface normal. In particular, for the absorption associated with the π – π^* transition of the terfluorene backbone, they show substantially larger in-plane extinction coefficients than the out-of-plane extinction coefficients. It is thus inferred that the vacuum-deposited ter(9,9-diarylfluorene) molecules tend to align their molecular axes and π – π^* transition dipole moments along the substrate surface as observed previously in spin-coated films of alkyl-substituted polyfluorenes or oligofluorenes, even though the present ter(9,9-diarylfluorene)s have rigid and bulky aryl substituents on C9, relatively shorter oligomer chains, and very different deposition conditions. In addition to thin-film optical properties, such anisotropic molecular orientation may have impacts on electrical properties of thin films. For instance, the high carrier-transport mobility previously reported for ter(9,9-diarylfluorene)s may be related to carrier transport perpendicular to the oligomer chain.⁵⁰ The influences of anisotropic molecular orientation on various physi-

cal, optical, and electrical properties of thin films and further on characteristics of photonic and optoelectronic devices surely are valuable topics worthy of further exploration.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from National Science Council (Grant No. NSC 91-2215-E-002-029) and Ministry of Education of Republic of China.

- ¹L. S. Hung and C. H. Chen, *Mater. Sci. Eng.*, **R**, **39**, 143 (2002).
- ²A. Kraft, A. C. Grimsdale, and A. B. Holmes, *Angew. Chem., Int. Ed. Engl.* **37**, 402 (1998).
- ³N. Tessler, G. J. Denton, and R. H. Friend, *Nature (London)* **382**, 695 (1996).
- ⁴C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- ⁵C. W. Tang, S. A. VanSlyke, and C. H. Chen, *J. Appl. Phys.* **65**, 3610 (1989).
- ⁶C. H. Chen, J. Shi, and C. W. Tang, *Macromol. Symp.* **125**, 1 (1997).
- ⁷J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature (London)* **347**, 539 (1990).
- ⁸G. Horowitz, *Adv. Mater.* **10**, 365 (1998).
- ⁹H. Bleir, in *Organic Materials for Photonics*, edited by G. Zerbi (Elsevier, Amsterdam, 1993), p. 77.
- ¹⁰S. R. Marder, B. Kippelen, A. K. Y. Jen, and N. Peyghambarian, *Nature (London)* **388**, 845 (1997).
- ¹¹M. D. McGehee, R. Gupta, S. Veenstra, E. K. Miller, M. A. Diaz-Garcia, and A. J. Heeger, *Phys. Rev. B* **58**, 7035 (1998).
- ¹²S. V. Frolov, Z. V. Vardeny, and K. Yoshino, *Phys. Rev. B* **57**, 9141 (1998).
- ¹³S. V. Frolov, Z. V. Vardeny, and K. Yoshino, *Appl. Phys. Lett.* **72**, 1802 (1998).
- ¹⁴V. G. Kozlov, G. Parthasarathy, P. E. Burrows, S. R. Forrest, Y. You, and M. E. Thompson, *Appl. Phys. Lett.* **72**, 144 (1998).
- ¹⁵S. V. Frolov, M. Shkunov, Z. V. Vardeny, and K. Yoshino, *Phys. Rev. B* **56**, R4363 (1997).
- ¹⁶F. Hide, M. A. Diaz-Garcia, B. J. Schwartz, and A. J. Heeger, *Acc. Chem. Res.* **30**, 430 (1997).
- ¹⁷V. G. Kozlov, V. Bulovic, and S. R. Forrest, *Appl. Phys. Lett.* **71**, 2575 (1997).
- ¹⁸C. Zenz, W. Graupner, S. Tasch, G. Leising, K. Müllen, and U. Sherf, *Appl. Phys. Lett.* **71**, 2566 (1997).
- ¹⁹V. G. Kozlov, V. Bulovic, P. E. Burrows, and S. R. Forrest, *Nature (London)* **389**, 363 (1997).
- ²⁰N. Tessler, G. J. Denton, and R. H. Friend, *Nature (London)* **382**, 695 (1996).
- ²¹E. K. Miller, M. D. McGehee, M. Diaz-Garcia, V. Srikant, and A. J. Heeger, *Synth. Met.* **102**, 1091 (1999).
- ²²N. C. Greenham, R. H. Friend, and D. D. C. Bradley, *Adv. Mater. (Weinheim, Ger.)* **6**, 491 (1994).
- ²³H. F. Wittmann, J. Grüner, R. H. Friend, G. W. C. Spencer, S. C. Moratti, and A. B. Holmes, *Adv. Mater. (Weinheim, Ger.)* **7**, 541 (1995).
- ²⁴W. M. V. Wan, N. C. Greenham, and R. H. Friend, *J. Appl. Phys.* **87**, 2542 (2000).
- ²⁵A. Boudrioua, P. A. Hobson, B. Matterson, I. D. W. Samuel, and W. L. Barnes, *Synth. Met.* **111–112**, 545 (2000).
- ²⁶M. Tammer, R. W. T. Higgins, and A. P. Monkman, *J. Appl. Phys.* **91**, 4010 (2002).
- ²⁷J. Sturm *et al.*, *Thin Solid Films* **298**, 138 (1997).
- ²⁸L. A. A. Pettersson, T. Johansson, F. Carlsson, H. Arwin, and O. Inganäs, *Synth. Met.* **101**, 198 (1999).
- ²⁹R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1977).
- ³⁰M. Tammer and A. P. Monkman, *Adv. Mater. (Weinheim, Ger.)* **14**, 210 (2002).
- ³¹M. Friedrich, T. Wagner, G. Savlvan, S. Park, T. U. Kampen, and D. R. T. Zahn, *Appl. Phys. A: Mater. Sci. Process.* **75**, 501 (2002).
- ³²Y. Geng, A. Trajkovska, D. Katsis, J. J. Ou, S. W. Culligan, and S. H. Chen, *J. Am. Chem. Soc.* **124**, 8337 (2002).
- ³³Y. Geng, S. W. Culligan, A. Trajkovska, J. U. Wallace, and S. H. Chen, *Chem. Mater.* **15**, 542 (2003).
- ³⁴D. Oelkrug, H. J. Egelhaaf, and J. Haiber, *Thin Solid Films* **284–285**, 267 (1996).
- ³⁵H. J. Egelhaaf, J. Gierschner, and D. Oelkrug, *Synth. Met.* **83**, 221 (1996).
- ³⁶H. J. Egelhaaf, J. Gierschner, J. Haiber, and D. Oelkrug, *Opt. Mater. (Amsterdam, Neth.)* **12**, 395 (1999).
- ³⁷M. K. Debe, *J. Vac. Sci. Technol. A* **10**, 2816 (1992).
- ³⁸M. Fukuda, K. Sawada, and K. Yoshino, *J. Polym. Sci., Part A: Polym. Chem.* **31**, 2465 (1993).
- ³⁹Q. B. Pei and Y. Yang, *J. Am. Chem. Soc.* **118**, 7416 (1996).
- ⁴⁰M. T. Bernius, M. Inbasekaran, J. O'Brien, and W. S. Wu, *Adv. Mater. (Weinheim, Ger.)* **12**, 1737 (2000).
- ⁴¹M. Belletête, M. Ranger, S. Beaupré, M. Leclerc, and G. Durocher, *Chem. Phys. Lett.* **316**, 101 (2000).
- ⁴²M. Redecker, D. D. C. Bradley, M. Inbasekaran, and E. P. Woo, *Appl. Phys. Lett.* **73**, 1565 (1998).
- ⁴³M. Grell, D. D. C. Bradley, M. Inbasekaran, and E. P. Woo, *Adv. Mater. (Weinheim, Ger.)* **9**, 798 (1997).
- ⁴⁴S. Setayesh, A. C. Grimsdale, T. Weil, V. Enkelmann, K. Müllen, F. Meghdadi, E. J. W. List, and G. Leising, *J. Am. Chem. Soc.* **123**, 946 (2001).
- ⁴⁵U. Scherf and E. J. W. List, *Adv. Mater. (Weinheim, Ger.)* **14**, 477 (1997).
- ⁴⁶K.-H. Weinfurter, F. Weissörtel, G. Harmgarth, and J. Salbeck, *Proc. SPIE* **3476**, 40 (1998).
- ⁴⁷D. Katsis, Y. H. Geng, J. J. Ou, S. W. Culligan, A. Trajkovska, S. H. Chen, and L. J. Rothberg, *Chem. Mater.* **14**, 1332 (2002).
- ⁴⁸Y. Geng, D. Katsis, S. W. Culligan, J. J. Ou, S. H. Chen, and L. J. Rothberg, *Chem. Mater.* **14**, 463 (2002).
- ⁴⁹K.-T. Wong *et al.*, *J. Am. Chem. Soc.* **124**, 11576 (2002).
- ⁵⁰C.-C. Wu, T.-L. Liu, W.-Y. Hung, Y.-T. Lin, K.-T. Wong, R.-T. Chen, Y.-M. Chen, and Y.-Y. Chien, *J. Am. Chem. Soc.* **125**, 3710 (2003).
- ⁵¹E. K. Miller, G. S. Maskel, C. Y. Yang, and A. J. Heeger, *Phys. Rev. B* **60**, 8028 (1999).
- ⁵²M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H.-G. Nothofer, U. Scherf, and A. Yasuka, *Adv. Mater. (Weinheim, Ger.)* **11**, 671 (1999).
- ⁵³H. G. Tompkins and W. A. McGahan, *Spectroscopic Ellipsometry and Reflectometry* (Wiley, New York, 1999).
- ⁵⁴G. E. Jellison, *Thin Solid Films* **313–314**, 33 (1998).
- ⁵⁵C. M. Ramsdale and N. C. Greenham, *Adv. Mater. (Weinheim, Ger.)* **14**, 212 (2002).
- ⁵⁶R. Anémian, J.-C. Mulatier, C. Andraud, O. Stéphan, and J.-C. Vial, *Chem. Commun. (Cambridge)* **2002**, 2608 (2002).
- ⁵⁷J. Salbeck, N. Yu, J. Bauer, F. Weissörtel, and H. Bestgen, *Synth. Met.* **91**, 209 (1997).
- ⁵⁸N. Johansson *et al.*, *J. Chem. Phys.* **107**, 2542 (1997).
- ⁵⁹C.-C. Wu *et al.*, *Appl. Phys. Lett.* **81**, 577 (2002).
- ⁶⁰M. R. Robison, S. Wang, G. C. Bazan, and Y. Cao, *Adv. Mater. (Weinheim, Ger.)* **12**, 1701 (2000).
- ⁶¹M. Born and E. Wolf, *Principles of Optics*, 6th ed. (Cambridge University Press, Cambridge, 1980).
- ⁶²I. C. Khoo and S. T. Wu, *Optics and Nonlinear Optics of Liquid Crystals* (World Scientific, Singapore, 1993).
- ⁶³W. Maier and A. Saupe, *Z. Naturforsch. A* **13A**, 564 (1958).
- ⁶⁴J. B. Birk, *Photophysics of Aromatic Molecules* (Wiley, New York, 1970).