

Poling Field Effect on Absorption and Luminescence of Disperse Red-19 and TiO₂ Composites

Byoung-Ju Kim · Un-Jei Hwang · Dong-Hyun Jo · Sae-Han Lim · Kwang-Sun Kang*

Department of New and Renewable Energy, Kyungil University, 50 Gamsilgil Hayangup Gyeongsan, Gyeongbuk 712-701, South Korea

ABSTRACT: Absorption and luminescence characteristics of disperse red-19 (DR-19) and TiO₂ composite have been investigated with various poling electric field strengths. Two step synthetic processes were employed to employ the DR-19 to the TiO₂ sol-gel. Firstly, urethane bond formation between DR-19 (-OH) and 3-isocyanatopropyl triethoxysilane (ICPTES, -N=C=O) performed (ICPDR) prior incorporation to the TiO₂ sol-gel. Secondary, the hydrolysis of the ethoxy group from the ICPTES and condensation reaction between silanol groups from ICPDES and TiO₂ sol-gel were performed. The ICPDR and TiO₂ sol-gel (DRTiO₂) were mixed and stirred for several days. The composite was coated to the ITO coated glass substrate. Corona poling were performed before drying the composite with various electric field strengths. The absorption intensity decreased with the increase of the poling field strength, which resulted in the increase of poling efficiency. The photoluminescence also decreased as the poling field strength increased. There is long luminescence tail for the poled DRTiO₂ film compared with unpoled DRTiO₂ film. The luminescence long tail indicates that the self-trapped excitons and polarons were generated when the DRTiO₂ film was poled with electric field.

Key words: TiO₂, DR-19, Poling, Composite

1. Introduction

Control the molecular orientation in polymers or inorganic matrices has been focused on efforts due to the many interesting properties and potential applications in many optical devices¹⁻⁴. The anisotropic molecule orientation in matrix gives to anisotropic electrical conductivity and nonlinear optical properties including polarized photoluminescence, electroluminescence, and nonlinear optics. The oriented anisotropic molecules produce the material as noncentrosymmetric system, which can generate various second-order nonlinear optical phenomena⁵⁻⁷. One of the methods to obtain highly efficient nonlinear optical materials is poling-induced acentric ordering of the chromophores.

Several techniques have been used to align molecules in a matrix, such as poling by electric field⁸) or laser⁹), rubbing method¹⁰), stretching method¹¹) and self-assembly technique¹²). Stretching is a widely used method to align the molecules. However, the elongation process creates the deformation of the matrix at the micron scale, which makes it limit for wide industrial application. Rubbing is a simple method to orient the

molecules near the surface of the matrix. The limitations of the rubbing method are the difficulty to control the orientation of the molecules and the introduction of the dust and static charge. Poling by electric field is the most widely used technique, which has two different techniques, such as planar and corona poling techniques. Planar poling technique uses plane plate as an electrode and applies high electric field due to the difficulty to obtain the short distance (submicron) between electrode and the sample. The planar electrode is incompatible with the device geometry. The corona poling uses a sharp electrode to apply high corona field to the sample. In this paper we report the poling field effect on the absorption and photoluminescence of disperse red-19 (DR-19). The DR-19 is attached to the 3-isocyanatopropyltriethoxysilane (ICPTES). The synthesized product (ICPDR) was added to the TiO₂ sol-gel. The ICPDR and TiO₂ film was coated to the ITO coated electrodes and poled with various electric fields.

2. Experimental

DR-19 (95%), ICPTES (95%), titaniumisopropoxide (TiISO, 97%), diethanolamine (DEA, 98%), acetic anhydride (98%) were purchased from Sigma Aldrich Co. Ltd. and used without

*Corresponding author: kkang@kiu.ac.kr

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further purification. Schematic view of the synthetic process is depicted in Fig. 1. To the 250 ml round bottom flask with a magnetic stirring bar, 1.2 ml of pyridine, and 30 mg DR-19 were added. Dry nitrogen was purged for 2 h to remove oxygen and water from the reaction flask. ICPTES (280 mg) was added to the reaction flask with stirring, and the temperature was increased to 50°C. The temperature was maintained for 6 h and then naturally reduced to room temperature. The reaction product was poured into aqueous CaCO₃ solution, washed with water and then filtered with 200 nm porous nylon filter. The obtained product was covalently connected ICPTES and DR-19. TiO₂ sol-gel was prepared with the following method. 2-Propanol (25 ml) and DEA (400 mg) were charged to a 100 ml round bottom flask. TiSO (5.69 g) was added to the reaction flask with stirring and then 1.2 g of acetic anhydride was added to the reaction flask. To a round bottom flask, 30 mg of ICPDR and 5 ml of TiO₂ sol-gel was charged with stirring.

The 30 mg ICPDR was added to the TiO₂ sol-gel and aged for two days with stirring. The ICPDR-sol-gel (DRTiO₂) was knife coated to the ITO coated electrode and poled before solidification with various electric fields between 3.0 and 4.0 kV. The ICPTES was directly dropped to the KBr plate and took the FTIR transmission spectrum with Nicolet iS5 FTIR spectrometer. The DR-19 and ICPDR were dissolved in methanol. The solution was dropped and dried to the KBr plate and took the FTIR transmission spectrum. UV-visible spectra were obtained with and without poled samples using Thermo Scientific Genesys 10S UV-visible spectrometer. PL spectra of without and with poled samples were obtained with Hitachi F-450 fluorescence spectrometer.

3. Results and discussion

The functionalized sol-gel precursor of ICPDR was synthesized by a urethane formation reaction between DR-19 and ICPTES. In this reaction, pyridine was used both as a catalyst and a solvent. The reaction route of ICPDR synthesis is depicted in Fig. 1. Since TiO₂ is very quickly hydrolyzed with H₂O, DEA was added to the 2-propanol before addition of TiSO to stabilize the TiSO. Finally the acetic anhydride was added to the reaction solution. This TiO₂ sol-gel was transparent and stable for more than one month.

Fig. 2 shows the transmission FTIR spectra of ICPTES,

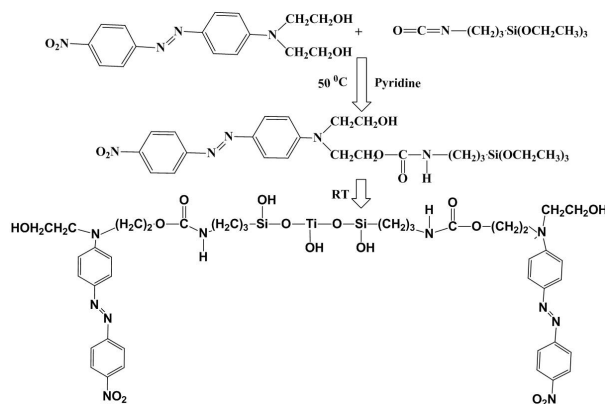


Fig. 1. Schematic view of synthetic process

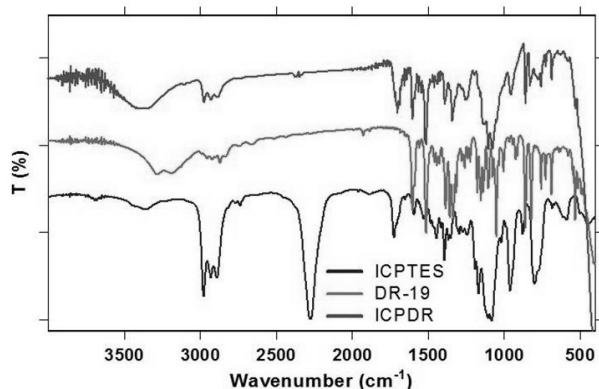


Fig. 2. FTIR spectra of ICPTES, DR-19, and ICPDR

DR-19, and ICPDR. The strong absorption peak at 2270 cm⁻¹ represents the asymmetric stretching vibration of isocyanate for the ICPTES. Disappearance of isocyanate absorption peak and the appearance of the ester absorption peak at 1707 cm⁻¹ indicate the formation of urethane bond. Strong and wide absorption peak between 1000 and 1100 cm⁻¹ for ICPTES and ICPDR implies that the both substance have many Si-O bonds. Moreover, most of the absorption peaks of ICPTES and DR-19 are included in the ICPDR spectrum. These results indicate the ICPTES and DR-19 are well-incorporated in the ICPDR.

The poling was performed at room temperature because the poling was started at semi-liquid state. The poling voltages were 3.0 and 4.0 kV. The distance between electrode and sample and the poling time were 1 cm and 10 min, respectively. The UV-visible spectra for the unpoled and poled DRTiO₂ films with various electric fields were shown in Fig. 3(a). The film color faded with the increase of the poling field strength with the same trend as shown in Fig. 3(a). Since this experiment performed at room temperature, thermochromic correction was not required. Therefore, the color change was due to the purely orientation

effect of the poled molecules. When only the dipole orientation effect exists, the first nontrivial axial order of the dipoles can be described¹³.

$$\Phi = \frac{1}{2}(3\cos^2\theta - 1) \quad (1)$$

The induced birefringence is directly proportional to the order parameter and is due to interaction between the dipoles and the internal electric field. When the transition dipole moment of the molecule is parallel to the molecular dipole moment, it follows the parallel and perpendicular dichroism for the one-dimensional rigid oriented gas model (ROGM)¹⁴ in the absence of induced dipole moments. It gives,

$$\frac{A_{//}}{A_0} = 3\cos^2\theta \quad (2)$$

$$\frac{A_{\perp}}{A_0} = \frac{3}{2}\sin^2\theta \quad (3)$$

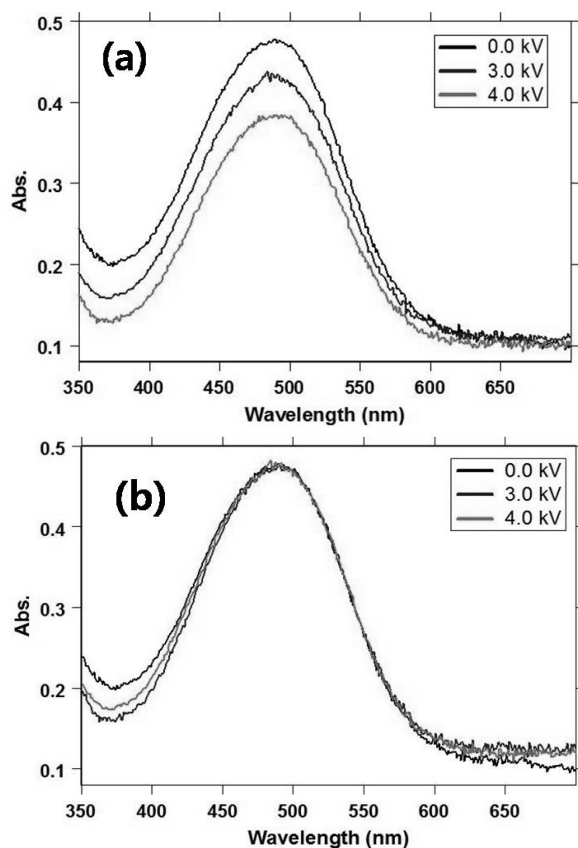


Fig. 3. UV-visible absorption spectra of (a) TiO₂DR19 films poled with 0.0, 3.0 and 4.0 kV and (b) normalized with the spectra (a)

where $A_{//}$ is the absorbance of a poled sample measured with electric field polarized parallel to the poling direction, A_{\perp} is the absorbance of a poled sample measured with electric field polarized perpendicular to the poling direction, and A_0 is the absorbance of an unpoled sample. Absorbance values of $A_{//}$ and A_{\perp} can be measured at λ_{\max} . Using Eqs (1) and (3), the following equation can be obtained.

$$\Phi = 1 - \frac{A_{\perp}}{A_0} \quad (4)$$

The angle between the transition dipole moment and the molecular dipole moment of DR-19 is so small that the transition dipole moment is effectively parallel to the ground-state dipole moment. The one-dimensional ROGM can be used to describe DRTiO₂ films when the doping level is less than 2.74×10^{20} molecules/cm³. The doping density of the ICPDRTiO₂ film was approximately 1.06×10^{18} molecules/cm³. Based on the assumptions and approximations, equation 4 predicts that the DRTiO₂ films have $\Phi = 0.10$ and 0.21 for the poling voltage at 3.0 and 4.0 kV, respectively. The poling efficiency is greatly increased with the increase of the poling field strength. Fig. 3(b) shows the normalized UV-visible spectra of Fig. 3(a). The width of the absorption spectra for the poled samples became slightly narrow compared unpoled absorption spectrum.

TiO₂ is a well-known wide bandgap semiconductor and has demonstrated a good sensitizer to absorb and emit light¹⁵. Although the main UV-visible absorption peak of DR-19 was at 490 nm, PL peak at approximately 350 nm was reported^{16,17}. Fig. 4(a) shows normalized PL spectra of DR-19 in methanol and DRTiO₂ film with excitation wavelength at 300 nm. The luminescence bands for DR-19 in methanol and TiO₂ film are 3.75 and 3.36 eV, respectively. The luminescence intensities of the DRTiO₂ are reduced drastically with the increase of the poling field strength as shown in Fig. 4(b). This phenomenon can be explained by the comparing with the UV-visible absorption spectra. When the poling field strength increased, the UV-visible absorption was drastically decreased and then the luminescence definitely would decrease. However, the normalized relative luminescence intensity of DR-19 peak shows the enhancement of the luminescence intensity with the increase of the poling field strength, as shown in Fig. 4(c). The PL spectrum for the poled film shows long tail compared with unpoled film spectrum. The recombination energy of the main luminescent exciton

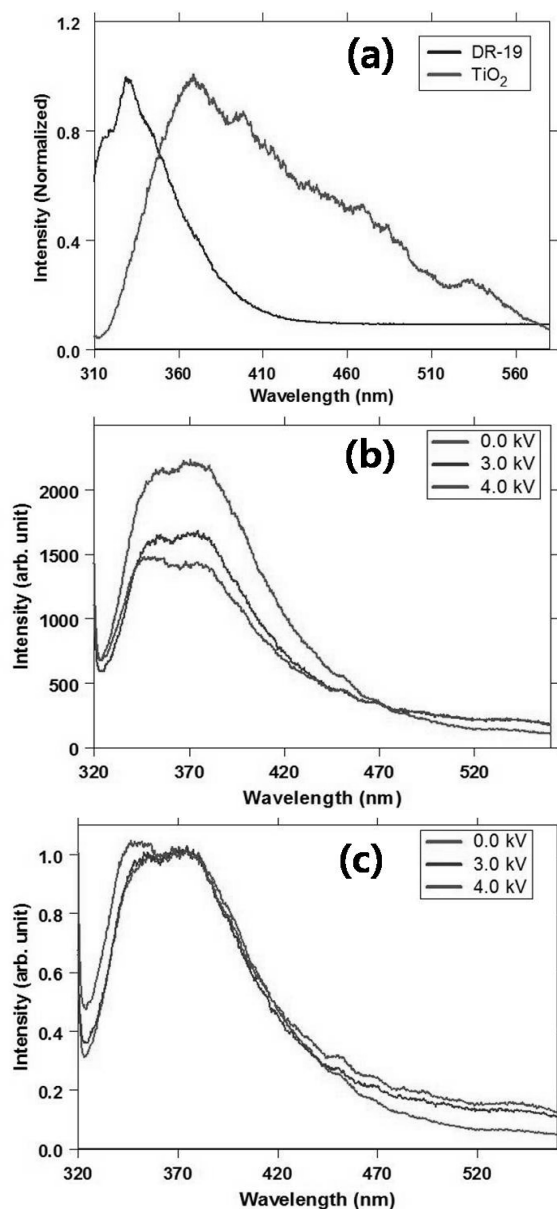


Fig. 4. (a) PL spectra of DR-19 in methanol and TiO₂, (b) poling field strength dependent PL spectra poled with 0.0, 3.0 and 4.0 kV and (c) normalized PL spectra of spectra (b)

(3.44 eV) is greatly exceeds the exciton-lattice coupling energy (<1 eV). The lower energy luminescence causing a Stokes shift is due to the self-trapped exciton. The lowest-energy luminescence is associated with the recombination of separated polarons. In this case, Stokes shift increases with time. According to our result, both self-trapped excitons and localized polarons increased when the DRTiO₂ film was poled with electric field.

4. Conclusions

Absorption and PL of DR-19 were investigated with various

poling electric fields. Poling was performed with semi-liquid state to increase the poling efficiency. The DRTiO₂ film was fabricated with knife coating method, and poling electric field was directly applied to the semi-dried film. The absorption intensity decreased as the poling electric field strength increased with the increase of the poling field strength, which resulted in increase of poling efficiency. The PL intensity decreased with the increase of the poling field strength. Large amount of self-trapped excitons and polarons were generated when the DRTiO₂ was poled with electric field. Write a conclusion text here.

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References

1. Snell, K. E., Stephant, N., Pansu, R. B., Audibert, J. F., Lagugne-Labaarhet, F., Ishow, E. "Nanoparticle organization through photoinduced bulk mass transfer", *Langmuir* Vol. 30, pp. 2926-2935, 2014.
2. Kopyshv, A., Galvin, C. J., Genzer, J., Lomadze, N., Santer, S. "Opto-mechanical scission of polymer chains in photosensitive diblock copolymer brushes", *Langmuir* Vol. 29, pp. 13967-13974, 2013.
3. Bogdanov, A. V., Vorobiev, A. K. "ESR and optical study of photo-orientation in azobenzene-containing liquid-crystalline polymer", *J. Phys. Chem. B* Vol. 117, pp. 12328-12338, 2013.
4. Kaule, T., Zhang, Y., Emmerling, S., Pihan, S., Foerch, R., Gutmann, J., Butt, H. J., Berger, R., Duerig, U., Knoll, A. W. "Nanoscale thermomechanics of water-resilient polymeric bilayer systems", *ACS Nano* Vol. 7, pp. 748-759, 2013.
5. Johnson, P. S., Huang, C., Kim, M., Safron, N. S., Arnold, M. S., Wong, B. M., Gopalan, P., Himpel, F. J. "Orientation of a monolayer of dipolar molecules on graphene from X-ray absorption spectroscopy", *Langmuir* Vol. 30 pp. 2559-2565, 2014.
6. Ojanen, J., Rantala, T. T. "Electronic structure and absorption spectrum of disperse red 1: Comparison of computational approaches", *Open Chem. Phys. J.* Vol. 2, pp. 37-46, 2009.
7. Zhang, L., Cole, J. M., Liu, X. "Tuning solvatochromism of azo dyes with intramolecular hydrogen bonding in solution and on titanium dioxide nanoparticles", *J. Phys. Chem. C* Vol. 117, pp. 26316-26323, 2013.
8. Cremoux, T., Dussauze, M., Fargin, E., Cardinal, T., Talaga, D., Adamietz, F., Rodriguez, V. "Trapped molecular and ionic

- species in poled borosilicate glasses: Toward a rationalized description of thermal poling in glasses”, *J. Phys. Chem. C* Vol. 118, pp 3716-3723, 2014.
9. Buffeteau, T., Labarthe, F. I., Peyolet, M., Sourisseau, C. “Photoinduced orientation of azobenzene chromophores in amorphous polymers as studied by real-time visible and FTIR spectroscopies”, *Macromolecules* Vol. 31, pp. 7312-7320, 1998.
 10. Era, M., Tsutsui, T., Saito, S. “Polarized electroluminescence from oriented p-sexiphenyl vacuum-deposited film”, *Appl. Phys. Lett.* Vol. 67, pp. 2436, 1995.
 11. Dyreklev, P., Berggren, M., Inganäs, M., Andersson, M. R., Wennerström, O., Hjertberg, T. “Polarized electroluminescence from an oriented substituted polythiophene in a light emitting diode”, *Adv. Mater.* Vol. 7, pp. 43-45, 1995.
 12. Elder, D. L., Benight, S. J., Song, J., Robinson, B. H., Dalton, L. R. “Matrix-assisted poling of monolithic bridge-disubstituted organic NLO chromophores”, *Chem. Mater.* Vol. 26, pp. 872-874, 2014.
 13. Petterlin, A., Stuart, H. A. “Über die bestimmung der grobe und form, sowie der elektrischen, optischen und magnetischen anisotropie von submikroskopischen teilchen mit hilfe der kunstlichen doppelbrechung und der inneren reibung”, *Z. Phys.* Vol. 112, pp. 129-147, 1939.
 14. Yamaoka, K., Charney, E. “Electric dichroism studies of macromolecules in solutions. I. Theoretical considerations of electric dichroism and electronchromism”, *J. Am. Chem. Soc.* Vol. 94, pp. 8963-8974, 1972.
 15. Pal, M., Pal, U., Jumenez, J. M. G. Y., Perez-Rodriguez, F. “Effects of crystallization and dopant concentration on the emission behavior of TiO₂:Eu nanophosphors”, *Nanoscale Res. Lett.* Vol. 7, pp. 1-12, 2012.
 16. Zhu, F., Qiu, F., Yang, D., Zhang, R. “Synthesis and third-order nonlinear optical property of poly(urethane-imide)”, *Chinese Optics Lett.* Vol. 7, pp. 527-529, 2009.
 17. Qiu, F. X., Yang, D. Y., Li, P. P., Wang, X. “Preparation and third-order nonlinear optical property of poly(urethane-imide) containing disperse red chromophore”, *Express Polymer Lett.* Vol. 2, pp. 823-828, 2008.