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Raman Spectra of Molecularly-Ordered 1-TNATA Thin Films and Organic Electroluminescence Device Properties

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A molecularly-ordered thin film of vacuum deposited 1-TNATA(4,4′,4″-tris (N-(1-naphthyl)-N-phenylamino) triphenylamine) as a hole injection layer (HIL) is placed between indium tin oxide (ITO) electrode and a hole transporting layer (HTL) in multi-layered organic electroluminescence (EL) diodes. The molecular ordering of 1-TNATA thin film was obtained by thermal annealing and electromagnetic field after vacuum deposition and the film was investigated by the Raman spectra, XRD, and AFM. It was found that the current density-voltage (J-V) and luminance-voltage (L-V) characteristics of the multi-layered diodes were improved due to the ordering of 1-TNATA molecules, which could enhance the charge carrier mobility and luminance efficiency among the organic molecules in the molecularly-ordered film.

Keywords: 1-TNATA; electromagnetic field; molecular ordering; OLED; Raman spectra

INTRODUCTION

Many efforts have been made in recent years to improve the performance and stability of the multi-layered organic light-emitting diodes (OLEDs) because of their potential application in flat panel displays [1–6]. In general, a layered diode structure is that it facilitates injection, balances the transport of electron and holes, and

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removes the emission region from the metal contacts. This generally results in higher efficiency and luminance at low operating voltages [7]. A hole-injecting buffer layer typically plays the role of improving the performance of the diodes. It is known that enhanced hole injection from ITO into the HTL lowers the operating voltage and, thus, improves performances of the diodes including the L-V characteristics. Recently, it is known that highly ordered organic thin films are of great importance for OLEDs, organic TFTs and organic solar cells because charge injection and mobility through the layers in the devices are improved [8,9]. The molecular ordering of vacuum-deposited organic thin films can be achieved by means of thermal annealing and electromagnetic field induction since many macrocyclic organic materials like metal phthalocyanine possess magnetic behavior [10,11]. In this study, the molecular ordering of vacuum-deposited 1-TNATA(4,4′,4″-tris(N-(1-naphthyl)-N-phenylamino)triphenylamine), widely used as a hole injection material in OLEDs, thin films were investigated and then these films were placed between the ITO and HTL to improve the performance of the multi-layered diodes.

EXPERIMENTAL

Material

As an organic material, 4,4′,4″-tris(N-(1-naphthyl)-N-phenylamino) triphenylamine(1-TNATA) was sublimed to obtain thin films via vacuum process and the chemical structure of 1-TNATA (formula: C66H48N4, molecular weight: 897.08, melting point: 249∼251°C, T_g: 112°C, H. W. Sands Corp.) is shown in Figure 1. Other materials used are 4,4′bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPD) (formula: $C_{44}H_{32}N_2$, molecular weight: 576.078, melting point: >277°C, T_g: 96°C, T H.W. Sands Corp.), Alq_3 (tris(8-hydroxyquinoline)aluminum, formula: $C_{27}H_{18}AlN_3O_3$, molecular weight: 459.437, melting point: >410°C, T_g: 174°C, Aldrich), and Lithium fluoride (LiF) (molecular weight: 25.9374, melting point: 870°C, Tokyo Kasei Kogyo Co. Ltd).

Formation of Molecularly-Ordered 1-TNATA Films

Vacuum deposition technique by thermal evaporation was used to obtain a homogeneous layer with well-controlled thickness. Before deposition, the ITO-coated glass was treated by acid solution followed by rinsing with de-ionized water and acetone and dried under nitrogen gas for cleaning the ITO-coated glass. 1-TNATA was deposited onto the pre-patterned ITO glass and the deposition rate was controlled

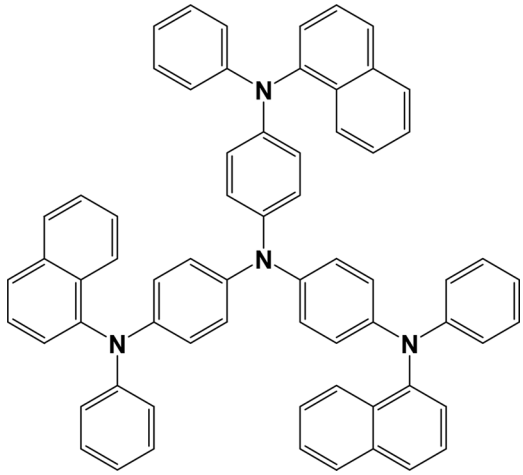

FIGURE 1 Chemical structure of 1-TNATA (4,4′,4″-tris(N-(1-naphthyl)-N-phenylamino)triphenylamine).

to 0.45 nm/min to obtain 50 nm thickness of the 1-TNATA films. At this deposition rate the surface of the deposited films were found to be uniform throughout the deposition experiments in this study. The deposition of all the organic materials was carried at a base pressure of 10^{-6} torr and the substrate was not intentionally heated during the device fabrication process. The cathode in all devices was composed of 100 nm aluminum. The active area of the all devices was subject to the pre-patterned ITO glass.

In addition, 1-TNATA thin films were deposited under electromagnetic field (∼6 mT) and without electromagnetic field to investigate the effect of electromagnetic field on the ordering of 1-TNATA molecules during deposition process. After deposition, thermal annealing of the deposited 1-TNATA thin films was performed in a cylindrical furnace in which electromagnetic field (∼6 mT) was selectively applied as well. During thermal annealing, temperature was 110°C and the duration was 1 hr. The film annealed in electromagnetic field was compared to both the as-deposited sample and the sample annealed at the same temperature but without electromagnetic field.

Fabrication of Multi-Layered Diodes

The multi-layered ITO/1-TNATA/NPD/Alq_3/LiF/Al devices were fabricated as shown in Figure 2 and the luminance-voltage (L-V)

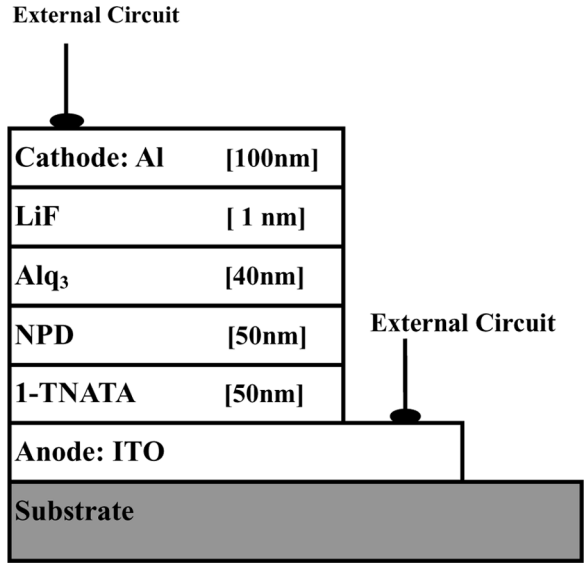

FIGURE 2 Configuration of multi-layered diodes.

characteristics were measured to investigate the effect of the molecular ordering of 1-TNATA on the enhancement of hole injection from ITO (Indium Tin Oxide) into HTL (Hole Transporting Layer) through a well-ordered 1-TNATA layer.

Analysis and Measurements

Film thickness was measured with a profilometer model Alpha-step 100 (KLA-Tencor Co. Ltd.) and SEM (HITACHI S-4200). The luminance-voltage (L-V) characteristics and luminance efficiency of the fabricated OLEDs were measured using a source multi-meter (KEITHLEY 236) and a HP semiconductor parameter analyzer (HP-4155). XRD (Rigaku Model D/Max 2400), RAMAN (Bruker IFS 66) and AFM (Nanoscope III-a, Digital Instruments Co. Ltd.) analysis were employed to characterize the molecular orientation and topology of the 1-TNATA thin films, respectively.

RESULTS AND DISCUSSION

Cross-sectional views and surface images of 1-TNATA thin films before and after thermal annealing were shown in Figures 3 and 4. Thermal annealing was carried out at 110°C, which is near the glass

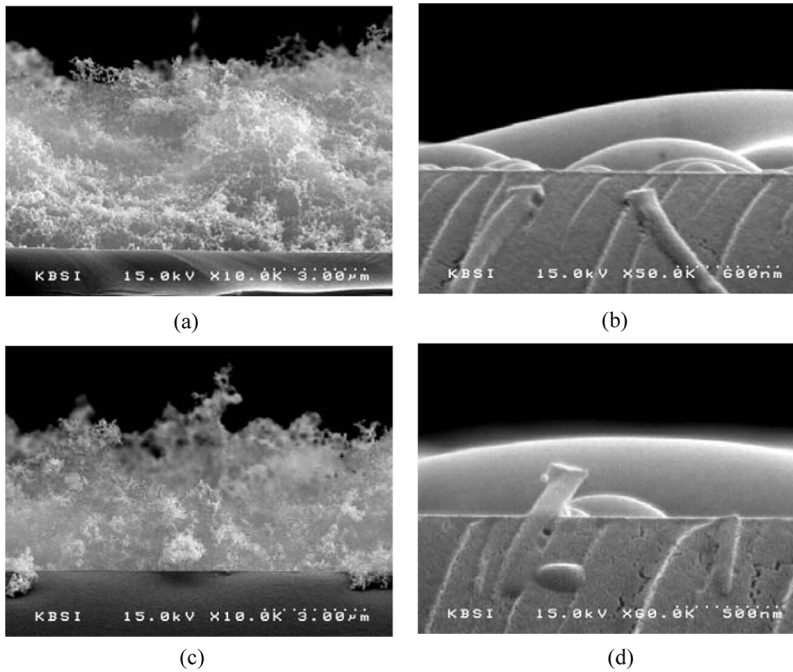

FIGURE 3 SEM images(cross-sectional view) of 1-TNATA films: (a) as-deposited film (film thickness: 3.5 μm), (b) thermal annealing at 110°C for 1 hr (film thickness: 500 nm), (c) electromagnetic field (∼6 mT) during deposition (film thickness: 2.5 μm), and (d) thermal annealing at 110°C for 1 hr with electromagnetic field (film thickness: 400 nm).

transition temperature of 1-TNATA. Molecularly-ordered films of organic materials can be obtained by thermal annealing at near the glass transition temperature, as shown in some reports [7,8]. After thermal annealing at 110°C for 1 hr, it was found that the surface roughness decreased and the lowered grains on the surface were observed. Smooth surface was obtained by means of thermal annealing at near glass transition temperature. According to the cross-sectional views of 1-TNATA films, it seems like that thermal annealing participates to increase the interaction of 1-TNATA molecules, which leads to closer packing of molecules and thus the treated films become denser compared to as-deposited films.

The Raman spectra of 1-TNATA films are shown in Figure 5. For the aromatic ring containing organic materials, typical Raman bands are observed at 1609, 1594, 1574, 1530, 1374, 1288, 1222, and 1198 cm^{-1} [8,9]. The 1609 cm^{-1} band is attributed to a ring stretch

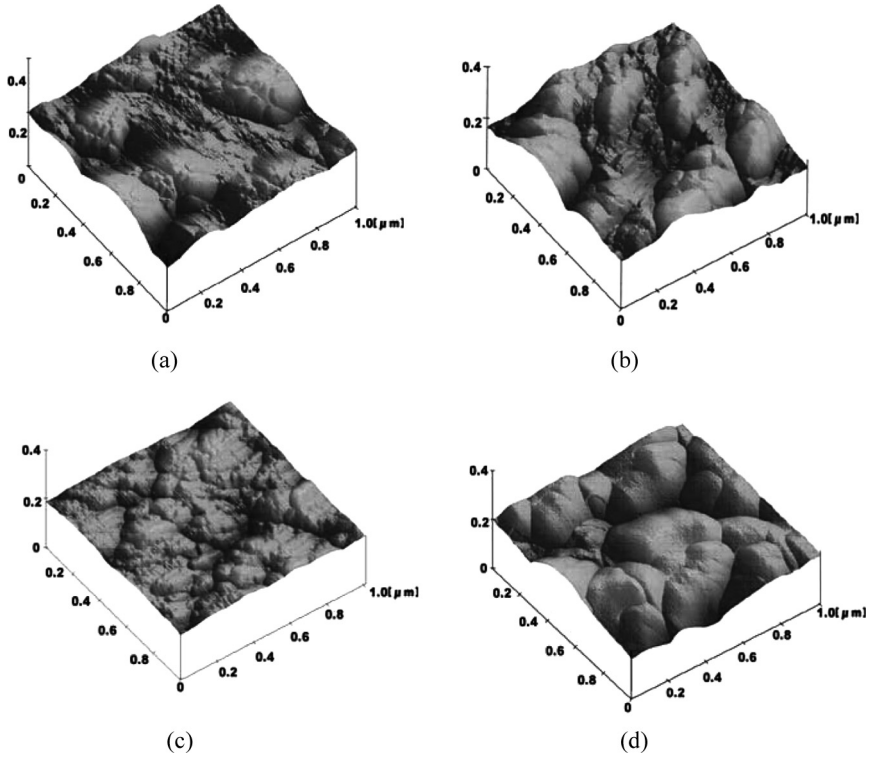

FIGURE 4 AFM images (3D) of 1-TNATA film surfaces: (a) as-deposited film (R_a: 14.0 nm, $R_{r.m.s.}$: 16.5 nm), (b) thermal annealing at 110°C for 1 hr (R_a: 7.2 nm, $R_{r.m.s.}$: 9.6 nm), (c) electromagnetic field (~6 mT) during deposition (R_a: 12.5 nm, $R_{r.m.s.}$: 15.5 nm), and (d) thermal annealing at 110°C for 1 hr with electromagnetic field (R_a: 4.0 nm, $R_{r.m.s.}$: 5.0 nm).

and the 1288 cm^{-1} band to the inter-ring C-C stretch. The 1198 cm^{-1} band is assignable to the CH band. It has been reported that the width of each band in the amorphous state is broader than that in the crystalline state of some organic materials used in OLEDs as hole injection and transport materials. In some reports, it was found that the position and width of Raman bands had been changed after thermal annealing of the films. The observed intensity of each band arising from an organic layer mainly depends on the thickness of the organic layer and the cross-section of the Raman band(resonance Raman effect). In addition, the overlapping of π-bond of macrocyclic organic materials leads to the enhanced absorption intensity in Raman spectra [12]. The overlapping of π-bond of macrocyclic organic materials can be

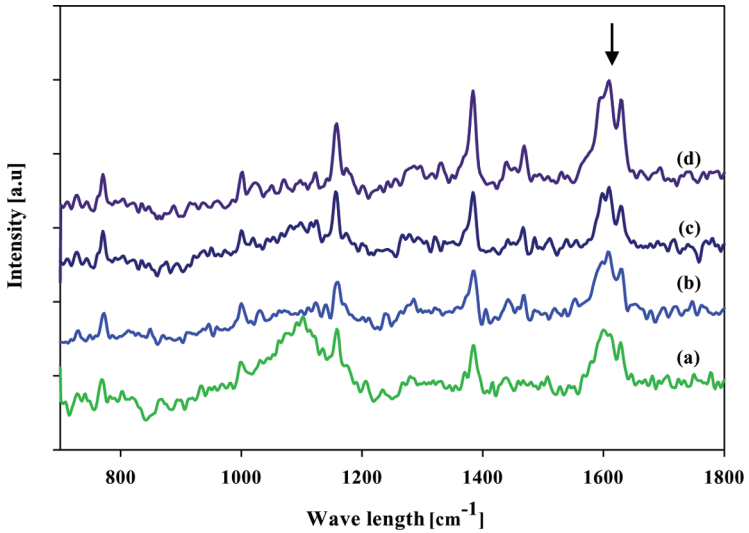

FIGURE 5 Raman spectra of the 1-TNATA films with various treatments: (a) as-deposited film, (b) thermal annealing at 110°C for 1 hr, (c) electromagnetic field (~6 mT) during deposition, and (d) thermal annealing at 110°C 1 hr for with electromagnetic field.

arisen from the closer packing of the organic materials. In this study, it was observed that the peak intensities at 1609 cm^{-1} in Figure 5 become higher and sharper with increasing temperature during thermal annealing as well as electromagnetic field treatment. However, in Figure 5(d), the change of peak intensity at 1609 cm^{-1} was much clearly observed compared to the change of peak intensities in Figures 5(a)–(c). These higher intensities at 1609 cm^{-1} indicate that 1-TNATA molecules come closer since thermal annealing participates to increase the interaction of 1-TNATA molecules, which can be attributed to the molecular ordering of 1-TNATA thin films [10,11]. No additional peaks were observed for all films after treatments, which indicates that there should be no reaction during the treatments.

Figures 6 and 7 show the current density-voltage (J-V) and luminance-voltage (L-V) characteristics of the multi-layered diodes with organic layers. It can be seen that both current density and luminance are increased depending on the treatment methods. In general, the diodes with higher annealing temperature has better performance but the temperature increases up to 110°C, which is near the glass transition temperature of 1-TNATA in this study. Electromagnetic fields can also affect on the interaction of 1-TNATA molecules since

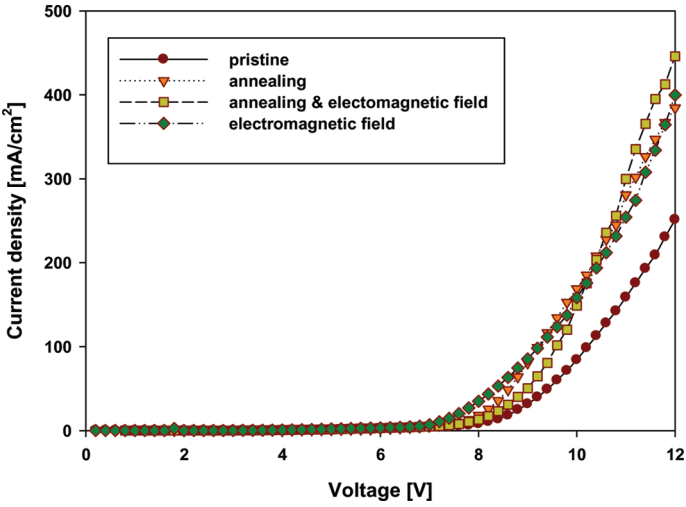

FIGURE 6 J-V characteristics of ITO/1-TNATA/Al devices fabricated at various conditions: (●) as-deposited film, (▼) thermal annealing at 110°C for 1 hr, (◆) electromagnetic field (~6 mT) during deposition, and (■) thermal annealing at 110°C 1 hr with electromagnetic field.

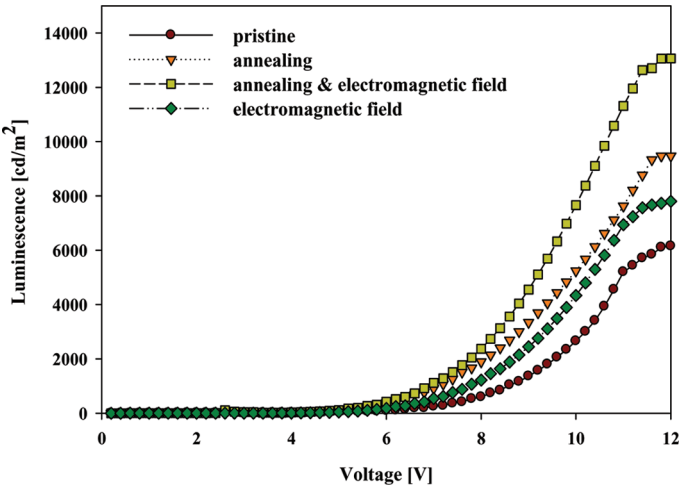

FIGURE 7 L-V characteristics of ITO/1-TNATA/NPD/Alq_3/LiF/Al devices fabricated at various conditions: (●) as-deposited film, (▼) thermal annealing at 110°C for 1 hr, (◆) electromagnetic field (~6 mT) during deposition, and (■) thermal annealing at 110°C 1 hr with electromagnetic field.

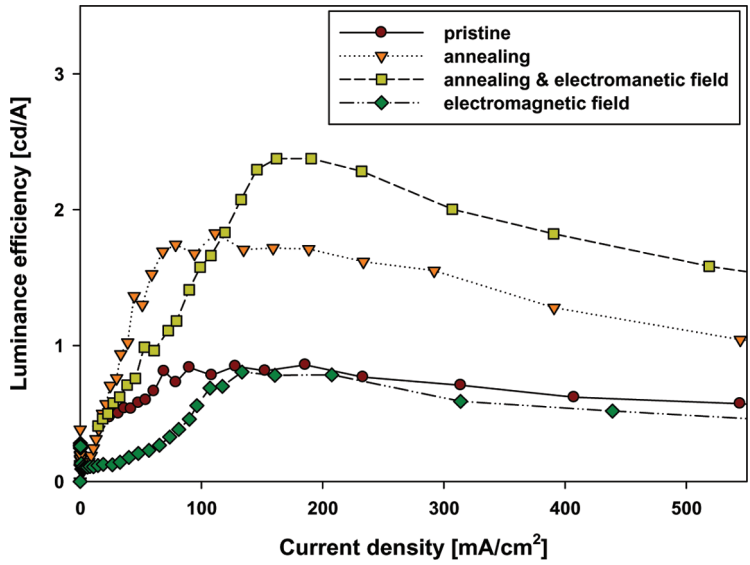

FIGURE 8 Luminescence efficiency-current density (LE-J) characteristics of ITO/1-TNATA /NPD/Alq_3/LiF/Al devices fabricated at various conditions: (●) as-deposited film, (▼) thermal annealing at 110°C for 1 hr, (◆) electromagnetic field (~6 mT) during deposition, and (■) thermal annealing at 110°C 1 hr with electromagnetic field.

most of macrocyclic organic materials posses polar and/or magnetic behavior, which can be attributed to the molecular ordering of 1-TNATA thin films. After the thermal annealing and electromagnetic field treatment, the luminance, turn-on voltage, driving voltage, and current density were significantly improved as shown in Figures 6 and 7. Furthermore, luminance efficiency-current density (LE-J) characteristics, shown in Figure 8, indicate that improved performance of the current diodes can be achieved to be due to the closer packing and molecular ordering of the organic film which is a hole injection layer of organic light-emitting diodes.

CONCLUSIONS

The results of Raman spectra show that the 1-TNATA films are molecularly ordered after thermal annealing at the temperature of to 110°C as well as electromagnetic field treatment. The increase of peak intensities in Raman spectra indicates that 1-TNATA molecules come closer and eventually are molecularly ordered in the films.

A molecularly-ordered 1-TNATA thin layer has had an important role in improving J-V and L-V characteristics of the organic light-emitting diodes. The multi-layered diodes have higher current density and luminance at even lower driving voltage after simultaneous or individual treatment of thermal annealing and electromagnetic field in this study.

REFERENCES

[1] Bao, Z., Lovinger, A. J., & Dodabalapur, J. (1996). *Appl. Phys. Lett.*, *69*, 3066.
[2] Bialek B., Kim, I. G., & Lee, J. I. (2003). *Thin Solid Films*, *436*, 107.
[3] Collins, G. E., Williams, V. S., Chau, L.-K., Nebesny, K. W., England, C., Lee, P. A., Lowe, T., Fernando, Q., & Armstrong, N. R. (1993). *Synth. Met.*, *54*, 351.
[4] El-Nahass, M. M., El-Gohary, Z., & Soliman, H. S. (2003). *Opt. Laser Technol.*, *35*, 523.
[5] Khrishnakumar, K. P. & Menon, C. S. (2001). *Mater. Lett.*, *48*, 64.
[6] Yanagiya, S., Nishikata, S., Sazaki, G., Hoshino, A., Nakajima, K., & Inoue, T. (2003). *J. Cryst. Growth.*, *254*, 244.
[7] Giebeler, C., Antoniadis, H., Bradley, Donal D. C., & Shirota, Y. (1999). *J. Appl. Phys. 85*(1), 608.
[8] Chen, B. J., Sun, X. W., Wong, T. K. S., Hu, X, & Uddin, A. (2005). *Appl. Phys. Lett.*, *84*, 063505.
[9] Sugiyama, T., Furukawa, Y., & Fujimura, H. (2005). *Chem. Phys. Lett.*, *405*, 330.
[10] Boamfa, M. I., Christianen, P. C. M., Maan, J. C., Engelkamp, H., & Nolte, R. J. M. (2001). *Physcia B*, *294–295*, 343.
[11] Ji, Z. G., Wong, K. W., Tse, P. K., Kwok, R. W. M., & Lau, W. M. (2002). *Thin Solid Films*, *402*, 79.
[12] Hawkridge, A. M. & Pemberton, J. E. (2003). *J. Am. Chem. Soc.*, *125*, 624.