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Carrier mobility of photochromic diarylethene amorphous films

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Naoya Matsui, Tsuyoshi Tsujioka*

Osaka Kyoiku University, Asahigaoka 4-698-1, Kashiwara, Osaka 582-8582, Japan

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ABSTRACT

Photochromic diarylethenes (DAEs) have gained attention as attractive current switching materials by light irradiation in the organic electronics field. We investigated the hole mobility of amorphous films consisting of three types of DAEs using a space-charge-limited current method and a better chemical structure to achieve high mobility. The hole mobility of open-ring (colorless) DAE having benzothiophene rings substituted with triphenylamine (TPA) as an aryl group was 2×10^4 times (2×10^{-6} cm²/V s) larger than that of DAE containing thiophene rings without TPA. When the DAE film was irradiated with ultraviolet (UV) light, the hole mobility decreased temporarily at 4% of closed-ring (colored) isomers and then increased to two-three times of the initial colorless state at 85% of the closed-ring isomers. The temporary decrease in the hole mobility originated in the hole trapping effect of the closed-ring molecules in a matrix consisting of open-ring isomers.

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1. Introduction

Organic electronic devices, such as light emitting devices, thin film transistors and photovoltaic devices are of great interest to the academic and industrial research community because of their potential for application to ubiquitous electronic devices with low cost, light weight, and flexibility [1,2]. Photochromic materials have attracted considerable attention as photo- or electrically controlled current switching materials in the organic electronics field [3]. The reversible change of a π -conjugation molecular system between the colorless state and colored state based on isomerization induces different electronic properties. including energy (highest occupied molecular orbital, (HOMO) and/or lowest unoccupied molecular orbital, (LUMO)) levels [4,5]. The electrical function of photochromic diarylethenes (DAEs) has been applied to various devices, including a photoprogrammable organic lightemitting diode [6], optically switchable organic field-effect

* Corresponding author. Tel./fax: +81 72 978 3633. *E-mail address:* tsujioka@cc.osaka-kyoiku.ac.jp (T. Tsujioka).

http://dx.doi.org/10.1016/j.orgel.2014.06.032 1566-1199/© 2014 Elsevier B.V. All rights reserved. transistors (OFETs) [7–9], a light energy harvesting device [10], and electrically recordable organic semiconductor memory [11–13].

Carrier mobility is an important property in organic electronics, but few studies on DAE mobility have been carried out using an OFET technique [8,9]. The improvement of carrier mobility is essential to achieve improved performance of electrical devices with DAEs. There are various methods to measure carrier mobility, for example, the OFET technique, time of flight (TOF) technique and spacecharge-limited current (SCLC) method. The OFET and TOF methods have been widely used for the mobility measurement of organic materials [14–17]. These methods, however, have some difficulty measuring the mobility of DAEs; the OFET method is not suitable for measuring the very low hole mobility of DAE films and the TOF method induces photoisomerization in the DAE films. In this paper, we report the hole mobility measurement of several kinds of DAE amorphous films using the SCLC method and its change based on photoisomerization in order to better understand the chemical structure of DAEs for obtaining improved performance devices.

2. Colorless DAE films

First, for investigating the influence of the basic chemical DAE structure and functional side groups, we tested three types of DAE, as shown in Fig. 1. An open-ring (cololess) DAE molecule is converted to the closed-ring (colored) isomer by UV irradiation and the closed-ring isomer is reverted to the open-ring isomer by visible irradiation. DAE1 has thiophene rings as an aryl group, which was first reported as a photo-controlled current switching molecule [18]. DAE2 also has thiophene rings, but these are substituted with triphenylamine (TPA) [19], which is a typical hole-transporting base. DAE3 has benzothiophene rings modified with TPA [20]. DAEs with TPA are expected to show better hole mobility compared with that of DAE without TPA groups.

The open-ring state of DAEs has a large ionization potential (*Ip*) of over 6.2 eV [3,18]. The potential barrier for hole injection from the anode into the DAE layer, in general, is large, and electrical contact between the DAE layer and the anode is not ohmic. The key requirement of the SCLC method is the ohmic contact [21] and, therefore, multi-hole-injection layers (HILs) should be introduced between the Au anode and the DAE layer to obtain ohmic contact, as shown in Fig. 2. The gradual potential levels reduce the hole injection barrier and generate ohmic contact. Consequently, the accumulated carriers create a space-charge field and the current is an SCLC.

Hole-only devices with a colorless DAE layer were prepared as follows: DAE (thickness: 1.5 µm), 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl (CBP, HTL4, thickness: 5 nm, *I*p = 6.0 eV), Tris(4-carbazoyl-9-ylphenyl)amine (TCTA, HTL3, thickness: 5 nm, Ip = 5.7 eV), N,N7-Di[(1-naphthyl)-N,N'-diphenyl]-1,1'-biphenyl)-4,4'diamin (NPB, HTL2 thickness: 5 nm, Ip = 5.5 eV), and Copper(II)-phthalocyanine (CuPc, HTL1, thickness: 5 nm, Ip = 5.2 eV) were deposited in turn on an indium tin oxide (ITO) substrate by a conventional vacuum evaporation method. Au was then deposited on the top organic layer. When the voltage was applied to the Au electrode in positive, only holes were injected from the Au electrode into the organic layers; it is difficult to inject electrons from the ITO electrode because of the large potential barrier.

Fig. 3a shows the current-electric field (J-E) characteristics of each colorless DAE device. All the devices demonstrate that *J* is proportional to E^2 in the high electric field region (>300 kV/cm). These results indicate that the injected current is described by the SCLC mechanism,

$$J = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{\bar{E}^2}{L},\tag{1}$$

where *L* is the thickness of the organic layer, μ is the mobility and ε and ε_0 are the relative and vacuum permittivity, respectively [22].

From the results in Fig. 3a, the DAE hole mobility was derived using Eq. (1), as shown in Fig. 3b. The mobility of



Fig. 1. Photochromic reaction of DAEs.



Fig. 2. Energy band diagram of DAE samples.



Fig. 3a. J-E characteristics of colorless samples.



Fig. 3b. Hole mobility of colorless films.

DAE1, DAE2 and DAE3 was calculated to be 9.2×10^{-11} cm2/V s at 350 kV/cm, 1.7×10^{-8} (cm²/V s) at 350 kV/cm and 2.3×10^{-6} (cm²/V s) at 700 kV/cm, respectively. (The relative permittivity ε of DAE1 is 2.9 and that of DAE2 and DAE3 is 3.0. The vacuum permittivity ε_0 is 8.85 × 10^{-12} (F/m²).) The hole mobility of the colorless DAE2, which was modified with TPA, was 2×10^2 times greater than that of DAE1. Furthermore, the hole mobility of the colorless DAE3, which has benzothiophene rings modified with TPA, was 100 times greater than that of DAE2. A dramatic difference in mobility depending on the chemical structure was observed.



Fig. 4a. Vacuum evaporation with UV irradiation.

3. Colored DAE films

Obtaining colored DAE films is not simple and the mobility measurement of the colored films requires a more complicated process. In general, colored DAE films (in the photostationary state (PSS)) are generated by sufficient UV irradiation, but these PSS films are in a mixed state of open-ring and colored-ring isomers for a variety of reasons, including reverse photoreaction at the UV wavelength region and/or incomplete conversion to the closed-ring state in the solid film state. Furthermore, since our samples consist of a thick DAE layer (\sim 1.5 µm), UV irradiation to the DAE layer is not able to isomerize the DAE layer uniformly in depth; a PSS is generated only on the surface region. We, therefore, prepared the colored samples by UV irradiation during DAE evaporation onto the substrate (λ = 254 nm, light power: 0.3 mW/cm², deposition rate: 0.5 nm/s), as shown in Fig. 4a. The samples prepared by this method consisted of uniform-depth isomerized (in PSS) thick DAE films.

Fig. 4b shows the absorption spectra of the DAE1, DAE2, and DAE3 films obtained by the above method, reflecting the isomerization ratio in the DAE films. For the reference, the PSS in toluene solution (solution-PSS) is also displayed. The isomerization ratios to the closed-ring isomer were estimated to be 85% for DAE1, 10% for DAE2 and 6% for DAE3, for which the isomerization ratios coincided with those of the PSS in the thin DAE-film states (film-PSS).



Fig. 4b. Absorption spectra of (a) DAE1, (b) DAE2 and (c) DAE3 obtained by vacuum evaporation with UV irradiation. The dotted lines, solid lines and dashed lines indicate the colorless state, colored film state (film-PSS) obtained by vacuum evaporation with UV irradiation, and solution-PSS in toluene solution state (for the reference), respectively.

Although it is ideally right that current characteristics and mobilities for the colored DAE films should be compared in the same and high isomerization ratios, however, the isomerization ratio in the film-PSS is dramatically reduced compared with the solution-PSS, and the ratio in the film-PSS is strongly depending on DAE species. The DAE1 film showed the high isomerization ratio exceptionally in the film-PSS, but those for DAE2 and 3 were considerably low. The many origins of the reduced isomerization ratio in the film-PSS have been reported: high reverse reaction guantum yield upon UV irradiation, presence of balky substitutes, conformation of aryl groups and/or energy transfer from excited molecules. In this field, it is one of important research subjects even now. Not only the mobility but also the isomerization ratio in the film-PSS, therefore, are important factors as performance of organic semiconductor devices with a photochromic film. In this study, therefore, we compare the current characteristics and mobilities of colored DAE films not in the same isomerization ratio but in their film-PSS.

Fig. 5a shows the *J*–*E* characteristics of the colored DAE samples. *J* was proportional to E^2 in the high electric field region for DAE1 and DAE2, which means that the current



Fig. 5a. J-E characteristics of colored (film-PSS) samples.

is SCLC. On the other hand, *J* of DAE2 was not proportional to E^2 ; the DAE2 showed the thermal emission-type current-characteristic that was caused by the difference in ionization potential depending on DAE species.

Fig. 5b shows the hole mobility of the colored DAE1 and DAE3 films derived from Fig. 5a. The hole mobilities of colored DAE1 and DAE3 were 2.6×10^{-10} (cm²/V s) (at 350 kV/cm) and 9.7×10^{-8} (cm²/V s) (at 700 kV/cm), respectively. The hole mobility of the colored DAE1 film was two-three times that of the colorless DAE1 film, which was caused by the extended π -conjugated molecular system of the closed-ring isomer. However, the mobility of the colored DAE3 film, in which the isomerization ratio was 6%, decreased from that of the colorless film. This decrease in mobility suggests that closed-ring isomers act as hole traps in a colorless matrix consisting of open-ring isomers [23,24].

To investigate whether or not the mobility decrease in the DAE film is a common phenomenon, we studied the isomerization ratio dependence of hole mobility using DAE1, which can achieve various isomerization ratios from 0% to 85% in the amorphous solid film state (see Fig. 4b). DAE1 samples with various closed-ring isomer isomerization ratios were prepared by controlling the DAE1 deposition rate with constant UV light irradiation (λ = 254 nm, light power: 0.3 mW/cm², deposition rate: 20, 5, 1 or 0.5 (nm/s)). Fig. 6a shows the absorption spectra and reflects the isomerization ratios of each sample. For reference, the PSS in the toluene solution state is also displayed in the solid line. The isomerization ratios to the closed-ring isomer were estimated to be 0% (colorless state), 4% (deposition rate: 25 nm/s), 17% (5 nm/s), 40% (1 nm/s), and 85% (0.5 nm/s).

Fig. 6b shows the isomerization ratio dependence of hole mobility for the DAE1 amorphous films. The vertical axis represents the hole mobility at 350 kV/cm and the horizontal represents the isomerization ratio. The hole mobility of the colorless state (0%) was 9.2×10^{-11} (cm²/V s), which decreased temporarily to 1.6×10^{-11} (cm²/V s) at 4% and then increased to 2.4×10^{-10} cm²/V s at 85% according to isomerization. This result reproduces



Fig. 5b. Hole mobility of colored (film-PSS) DAE1 and DAE3 films.



Fig. 6a. Absorption spectra corresponding to DAE1 films obtained by deposition at various deposition rates.



Fig. 6b. Isomerization ratio dependence of hole mobility of DAE1 film (at 350 (kV/cm)).

the decrease of the mobility for the colored DAE3 film with a low isomerization ratio and means that the origin of lowered mobility at a low isomerization ratio is the hole-trapping effect. The lowered mobility for the colored (film-PSS) DAE3 film attribute to the same origin. This result indicates that the mobility increase according to coloring reaction requires a high isomerization ratio in the film-PSS.

4. Conclusion

The hole mobility of several DAEs was estimated using the SCLC method. DAE with benzothiophene rings substituted with TPA (DAE3) showed relatively high hole mobility in the colorless amorphous state. We studied the relation between the isomerization ratio and the hole mobility, and found that mobility decreased temporarily at a low isomerization ratio (<closed-ring isomer 20%) and then increased to two-three times (85%) that of the colorless state (0%) according to the isomerization reaction. This decrease in mobility was caused by a hole-trapping effect on the colored isomers in the colorless matrix. Obtaining a large change in the mobility based on photoisomerization for organic electronics applications requires a large isomerization ratio in the film-PSS. Our results provide a significant perspective in the application of photochromic materials to organic electronics and photonics.

5. Experimental

5.1. Substrate cleaning

ITO substrates (Sigma–Aldrich: 576352-25PAK) were washed by ultrasonication in ethanol (Sigma–Aldrich: 09-0770-3-3L-J, Purity: >99.5%) and acetone (Sigma–Aldrich: 01-0460-3-3L-J, Purity: >99.5%) in turn for 10 min. The substrates were then cleaned using a UV-ozone cleaner.

5.2. Vacuum evaporation

Thermal evaporation of organic or inorganic materials was carried out under 1×10^{-5} Torr at room temperature (20 °C). The deposition thicknesses were monitored and controlled by a quartz thickness monitor during evaporation. The deposition rates of CBP, TCTA, NPB and CuPc were 0.1 nm/s and the thickness was 5 nm. The deposition rate of DAE was 2 nm/s for the samples in Fig. 3 and thickness was 1.5 μ m.

5.3. Vacuum evaporation with UV irradiation

A UV lamp (light power: 0.3 mW/cm² at substrate surface, $\lambda = 254$ nm) was set in the vacuum chamber and irradiated the substrate during DAE deposition. The DAE deposition rate was 0.5 nm/s (Figs. 4b and 5) or varied from 0.5 to 25 nm/s (Fig. 6). The DAE layer thickness was 1.5 μ m.

5.4. J-E measurement

Current–voltage characteristics of the devices were measured using a computer controlled programmable DC source (Keithley, model 6487 Picoammeter, Software: ExceLINX) in the ambient atmosphere under the dark condition.

5.5. Absorption spectra

Absorption for the thick DAE samples displayed in Figs. 4b and 6a were measured as follows: DAE toluene solutions were obtained by dissolving the thick DAE films having various isomerization ratios (including the film-PSS sample), which were formed using the vacuum evaporation method with UV irradiation. The solution-PSS for the reference was generated by sufficient UV irradiation to the DAE solution. Absorption spectra for the DAE solutions were measured using a UV–Vis spectrophotometer (Shimadzu, MultiSpec-1500).

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