

NOTE

Carrier Mobility for π -Conjugated Dendrimer Composed of Phenylene-vinylene Dendron and Triphenylamine Surface Group

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Carrier transport property of π -conjugated dendrimer is of current scientific and technological interest because of a molecular architecture for organic semiconductor materials and because of a variety of practical applications such as light emitting diodes, thin film transistors, and photo-voltaic cells.^{1–6}

Previously, we reported the carrier transport property of the soluble π -conjugated three-generation dendrimer which is composed of phenylene-vinylene as a dendron group and triphenylamine as a soluble surface group (G3D3-PV(TPA)) as shown in Figure 1b.⁷ The carrier of transporting across the G3D3-PV(TPA) dendrimer film was preferentially hole with an indium-tin-oxide (ITO)/G3D3-PV(TPA)/Mg-Al cell. The Mg-Al is the opposite electrode composed of alloy of Mg and Al. The hole mobility was 10^{-5} (cm²/(V·s)) order at 25 °C, which is the same order as that of poly(*p*-phenylene-vinylene) reported by Lebedev and co-workers though the dendrimer is surrounded by the triphenylamine surface group.⁸ According to the results reported previously, the triphenylamine surface group covalently attached to the dendron did not show the carrier transport property.⁷ This result indicates that the phenylene-vinylene molecules with different dendrimer are comparably close to each other. We have estimated the structure of the G3D3-PV(TPA) dendrimer was comparably planar shape rather than globular shape.⁷

If the above conclusion is not contradicted, the dendrimer of the lower generation number is expected to become higher mobility because the dendron and surface groups are less restricted by each moiety, and the dendrimer would be more planar shape. To examine the effect of steric constraints by decrement of the generation number on the carrier mobility, we prepared a soluble π -conjugated two-generation dendrimer G2D3-PV(TPA) as shown in Figure 1a, where the phenylene-vinylene dendron and the triphenylamine surface group are less restricted. In this dendrimer, the structure is expected to be more planar under less constraining condition than in the case of the G3D3-PV(TPA) dendrimer.

In this paper, we have reported the carrier transport property of the G2D3-PV(TPA) dendrimer with the ITO/G2D3-PV(TPA)/Mg-Al cell by a time-of-flight (TOF) method focusing on the comparison of the three-generation dendrimer.

EXPERIMENTAL

The chemical structure of the two-generation dendrimer (G2D3-PV(TPA)) used in this study is shown in Figure 1a. The synthesis procedure was reported previously.⁹ The weight and number average molecular weights measured by GPC were 4,500 and 4,300, respectively, and the molecular weight distribution was 1.05.⁹ The standard polymer and eluent for GPC evaluation were polystyrene and THF, respectively. For comparison, we also used the three-generation dendrimer G3D3-PV(TPA) shown in Figure 1b.

The solutions of the dendrimers were prepared in chloroform at concentrations of 10 mg/mL. The ITO substrates were masked, patterned and cleaned in ultrasonic of NaOH and deionized water. Films of the dendrimers, typically 1 μ m thick, were formed by spin-coating from the chloroform solutions onto the cleaned ITO substrates at 25 °C. A vacuum evaporator was used for the thermal evaporation of the alloy of 10 wt% Mg and 90 wt% Al (Mg-Al) onto the desired ITO glass plates deposited with the 1 μ m dendrimer films.

TOF measurements for the ITO/dendrimer/Mg-Al cells were carried out with a conventional setup as described previously.⁷ The measurements were performed at 25 °C in vacuum condition (10^{-3} Torr). The current generated as a result of photocarrier drift was collected across a 50 Ω resistor upon the application of an external bias voltage for 100 ms. The carrier mobility was determined by the following relation;

$$\mu = \frac{L^2}{T_{tr}V} \quad (1)$$

where μ is the carrier mobility, L is the thickness of the

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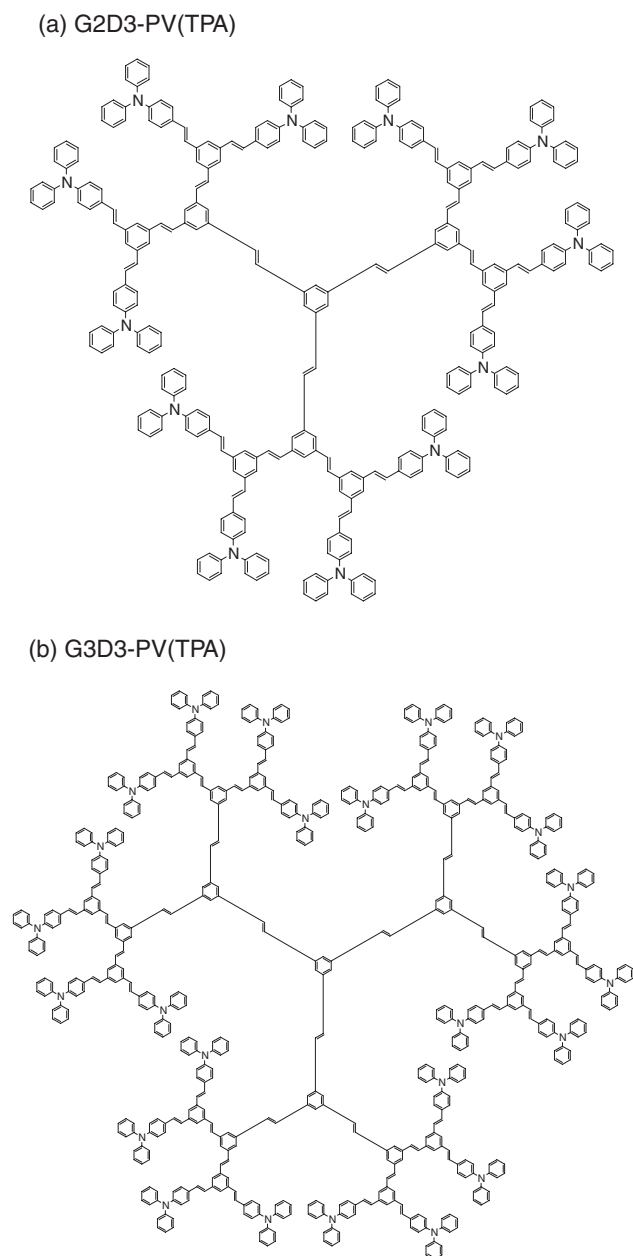


Figure 1. (a) G2D3-PV(TPA) dendrimer used in this study and (b) G3D3-PV(TPA) dendrimer for comparison as a reference in this study.

dendrimer film, V is the applied bias voltage, and T_{tr} is the transit time derived from the double logarithmic plot of the transient photocurrent.⁷

RESULTS AND DISCUSSION

By illuminating a pulsed N₂ laser (337.1 nm, pulse width 0.7 ns) from the ITO side of the ITO/dendrimer/Mg-Al cell, photoexcited carriers of hole and electron generate at the surface of the dendrimer film since the absorption of the dendrimer occurs at 337.1 nm shown in Figure 2. As we reported previously, the absorption centered at 370 nm is from the phenylene-vinylene site and that centered at 300 nm is from

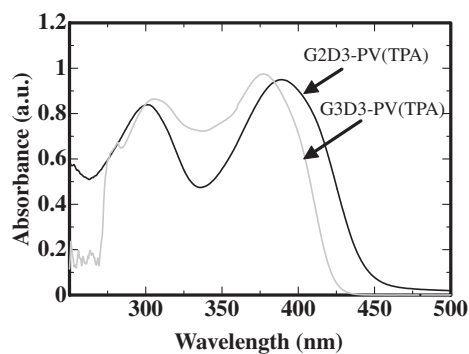


Figure 2. UV absorption spectra for G2D3-PV(TPA) and G3D3-PV(TPA).

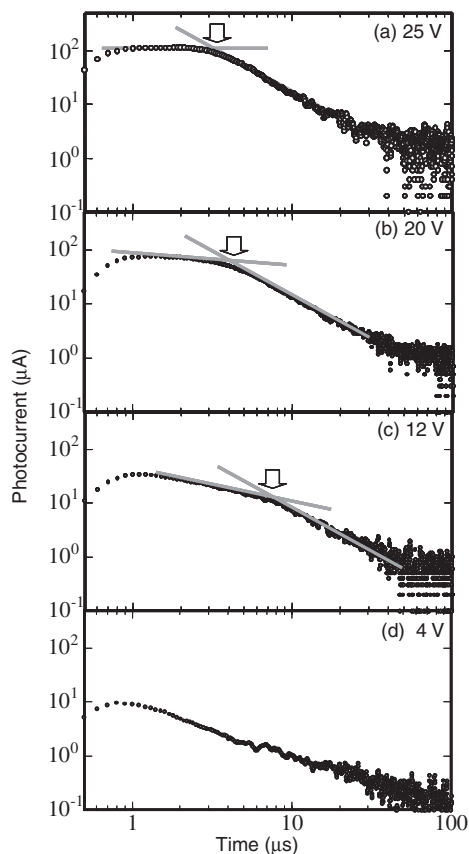


Figure 3. Profiles of double logarithmic transient photocurrent plots for ITO/G2P3-PV(TPA)/Mg-Al device at applied voltage of (a) 25 V, (b) 20 V, (c) 12 V, and (d) 4 V.

the triphenylamine group.⁷ In the case that the positive bias voltage was applied at the ITO side, transient photocurrent was observed, indicating the hole drift occurred from the ITO side to the Mg-Al side. On the other hand, when the negative bias voltage was applied at the ITO side, transient photocurrent was not observed, implying the electron did not drift. The double logarithmic plots of the transient photocurrents of the hole for the ITO/G2D3-PV(TPA)/Mg-Al cell in the V range from 25 V to 4 V are shown in Figure 3a–3d. T_{tr} , which is determined from the intercept of two tangential lines before and after the inflection point of the photocurrent, is clearly observed at

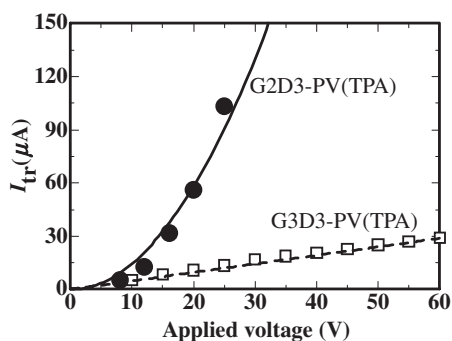


Figure 4. Current at the transit time I_{tr} for G2D3-PV(TPA) and G3D3-PV(TPA) as a function of V .

comparably high V whereas it becomes difficult to distinguish T_{tr} with decreasing V as shown in Figure 3d. The fact that the inflection point becomes unobservable with decreasing V implies that the hole disappears before arriving at the Mg-Al side. One of the reasons for the disappearance is that the recombination occurs preferentially between the hole and the electron at the surface of the dendrimer film at low V since the transport velocity of the hole is small. On the other hand, as V becomes high, the transport velocity becomes high and the rate of the recombination becomes low.

Figure 4 shows the current value at the inflection point (I_{tr}) for G2D3-PV(TPA) as a function of V . For comparison, I_{tr} for G3D3-PV(TPA) is also shown in this figure. The I_{tr} values for G2D3-PV(TPA) are much higher than those for G3D3-PV(TPA). There are two reasons of this. One is that the mobility for G2D3-PV(TPA) is higher than that for G3D3-PV(TPA), the other is that the number of the carrier drifting across the dendrimer film for G2D3-PV(TPA) is higher than that for G3D3-PV(TPA). The result leads to the fact that the steric structure of G2D3-PV(TPA) is strikingly different from that of G3D3-PV(TPA) owing to the less restricted steric barrier. This implies the possibility that the mobility or the number of the carrier drifting across the film increases nonlinearly with increasing V for G2D3-PV(TPA).

The hole mobility, which was determined with eq 1, for G2D3-PV(TPA) and G3D3-PV(TPA) as a function of the square root of the applied bias voltage $V^{1/2}$ are depicted in Figure 5. The mobility for G2D3-PV(TPA) is about three times higher than that for G3D3-PV(TPA) in the $V^{1/2}$ range from $2.8 V^{1/2}$ to $5 V^{1/2}$. The higher mobility for G2D3-PV(TPA) is induced by the easier carrier hopping compared with the case of G3D3-PV(TPA). We estimate that the distance between the phenylene-vinylene dendrons with the different dendrimer molecule for G2D3-PV(TPA) is more close to each other than that for G3D3-PV(TPA). As those dendrimers are surrounded by the triphenylamine surface group, the dendrimers need to be planar structure for the dendron site, which is the carrier transporting site, to become close to each other and show high mobility. According to the comparisons for I_{tr} and hole mobility between G2D3-PV(TPA) and G3D3-PV(TPA), the degree of the planar structure for G2D3-PV(TPA) is estimated

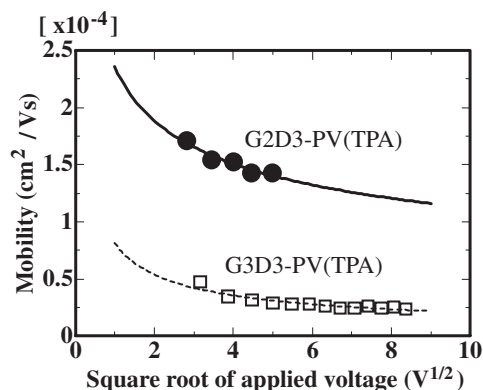


Figure 5. Hole Mobility for G2D3-PV(TPA) and G3D3-PV(TPA) as a function of $V^{1/2}$.

to be higher than that for G3D3-PV(TPA). Here, the mobility for both the dendrimers decreased with increasing the application voltage. Concerning this, Bassler proposed a model to explain the various electric field dependence of the mobility by the Monte Carlo simulation of random carrier walk.¹⁰ Based on the model, in the case of low bias voltage application, some of the carriers transport to the opposite electric field direction, resulting in the negative electric field dependence of the mobility.

We succeeded to improve the carrier mobility for the π -conjugated dendrimer having soluble surface group to 10^{-4} ($\text{cm}^2/(\text{V}\cdot\text{s})$) order by decreasing the generation number of the dendron site. This is owing to the facts that less restricted structure is formed and that the distance between the π -conjugated dendron sites with the different dendrimer is more close to each other.

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