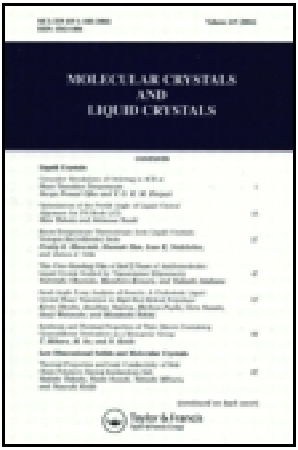

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Fluorene Derivatives with High Hole Mobility

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Fluorene Derivatives with High Hole Mobility

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Fluorene derivatives having electron-releasing carbazole and diphenylamino substituents were demonstrated to possess high hole mobility at the level of $10^{-3}\,cm^2V^{-1}sec^{-1}$ *in their amorphous films from the time-of-flight measurement; for the fluorene derivative with carbazole substituent,* $\mu = 3.1 \times 10^{-3}\,cm^2V^{-1}sec^{-1}$ *at an applied field of* $1.6 \times 10^5\,Vcm^{-1}$.

Keywords: amorphous film; fluorene derivative; hole mobility

Development of carrier-transporting materials with high mobility is indispensable to attain high performance organic electronic devices such as light emitting diode (LED) and organic thin film transistor (TFT). For example, organic LED operates in space charge limited current (SCLC) region. The current (J_{SCLC})–voltage (V) behavior is expressed by the equation $J_{SCLC} = (9/8)\varepsilon\varepsilon_0 V^2\mu/L^3$, where μ is the carrier mobility of sample, L is sample thickness, and ε and ε_0 are the dielectric constant of sample and the permittivity of the free space. The equation suggests that high carrier mobility provides high current density due to injected carriers when the same voltage is applied. In other words, high mobility makes it possible to lower drive voltage of organic LED and leads to improvement of its power efficiency [1].

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For bringing about high speed response time in organic TFT, additionally, organic materials are required to possess high carrier mobility. The response time of organic TFT is limited by the transit time τ of carriers from the source electrode to the drain electrode as described by the equation $\tau \approx L_C^2/\mu|V_d|$, where L_C, μ, and V_d are the channel length, the field effect mobility, and the source-drain voltage, respectively [2].

Recently, various poly(dialkylfluorene)s and related polymers were prepared as organic LED material [3–8], and some of the fluorene-based polymers were demonstrated to exhibit high hole mobility in amorphous and liquid crystalline films [3–5]. The results suggest that the fluorene-skeleton is a promising base-structure in the molecular design of hole conductor. In this work, we prepared fluorene derivatives having electron-releasing substituents, carbazole and diphenylamino groups. From the conventional time-of-flight measurement, the fluorene derivatives were found to possess high hole-transporting capability.

Fluorene derivatives employed in this study are shown in Figure 1. The fluorene derivatives with carbazole or diphenyl amino

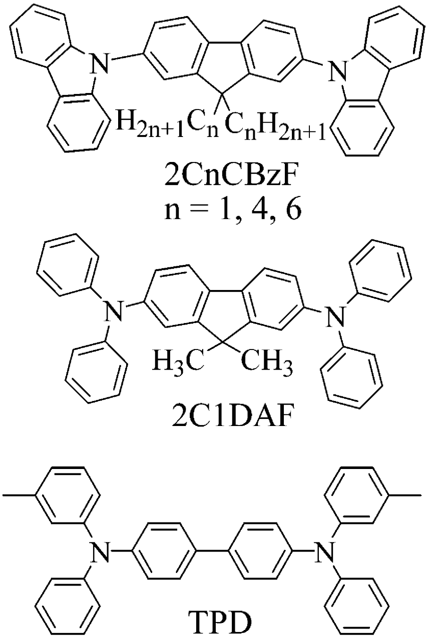

FIGURE 1 Molecular structures of hole-transporting derivatives employed in this study.

substituents, 2CnCBzF and 2C1DAF, were obtained from the palladium-catalyzed coupling of carbazole or diphenyl amine with 2,7-diode-9,9′-dialkyl-fluorene [9]. The crude products were purified using the train sublimation technique [10].

The carrier drift mobility of the fluorene dyes was evaluated by the time-of-flight measurement using a N_2 laser (pulse width = 3 nsec) as excitation light source. Amorphous film samples of the fluorene dyes with a thickness of about 3 μm were prepared on ITO (indium-tin-oxide) electrode-coated glass substrates by vacuum-deposition under a base pressure of 10^{-4} Pa, and then Au electrode was vacuum-deposited as counter electrode. Transient photocurrent was measured when pulse light of the N_2 laser was irradiated to the film sample through the ITO electrode. For comparison, we also measured mobility of a typical hole-conductor, 4,4′-bis[N-(p-tolyl)-N-phenyl-amino] biphenyl (TPD).

The fluorene derivatives, we employed in this study, exhibited large photocurrent due to nondispersive hole transport in their amorphous films while very small photocurrent due to electron transport was observed. Accordingly, we can determine their drift mobility due to hole transport. Figure 2 shows transient photocurrent profiles due to hole transport of a vacuum-deposited 2C1CBzF film. The profiles show apparent plateau regions followed by monotonously decreasing tails, demonstrating nondispersive carrier transport. Then, the transit time t_T were determined from the inflection points from plateau to tail (arrows in Fig. 2). The drift mobility μ was calculated according to the equation $\mu = L/t_T F$, where L is film thickness and F applied field.

Figure 3 shows the electric field dependences of the hole-transporting dyes in their amorphous films. The fluorene dye with carbazole group, 2C1CBzF, exhibits a high hole mobility of $3.1 \times 10^{-3}\,\mathrm{cm^2V^{-1}s^{-1}}$ at $1.6 \times 10^5\ \mathrm{Vcm^{-1}}$. This value is about 4 times larger than that of typical hole conductor TPD at the same electric field. As proposed by Gill [11], the electric field dependence of drift mobility is expressed with the equation $\mu(F) = \mu_0 \exp(\gamma F^{1/2})$, where μ_0 is zero field mobility. For comparison excluding the electric field dependence, then, the zero field mobility of the dyes was estimated from the field dependent data shown in Figure 3. The values of μ_0 were $1.4 \times 10^{-3}\,\mathrm{cm^2V^{-1}s^{-1}}$ for 2C1CBz, $5.0 \times 10^{-4}\,\mathrm{cm^2V^{-1}s^{-1}}$ for 2C1DAF, and $3.0 \times 10^{-4}\,\mathrm{cm^2V^{-1}s^{-1}}$ for TPD; the values of 2C1CBz and 2C1DAF are about 5 times and about twice larger than that of TPD, respectively. The large values of μ_0 are most likely to reveal that the fluorene dyes with electron-releasing substituents possess high potential of hole-transporting.

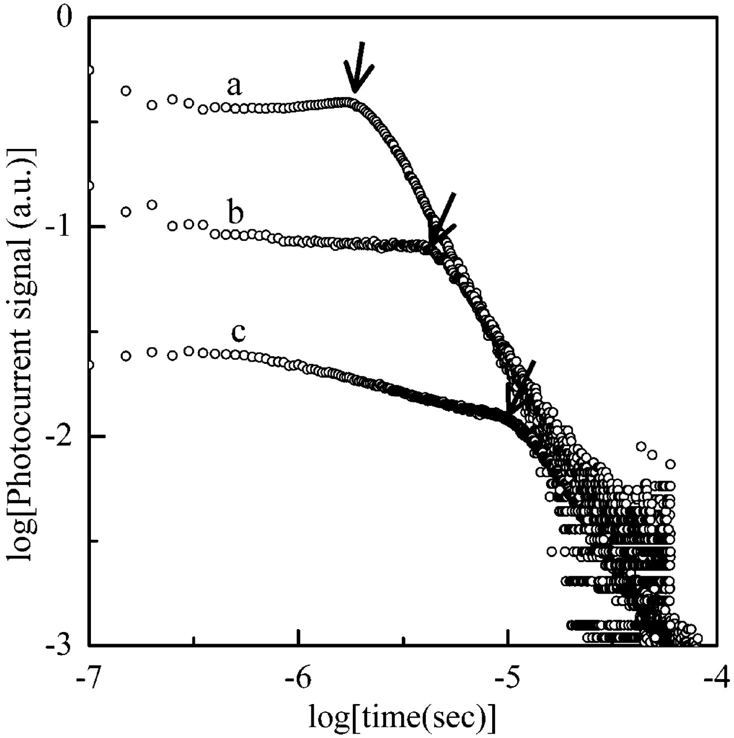

FIGURE 2 Transient photocurrent profiles due to hole transport in 2C1CBz film: profile a; applied field F = 8.4 × 10^5 Vcm^{-1}, profile b; F = 4.2 × 10^5 Vcm^{-1}, and profile c; F = 2.1 × 10^5 Vcm^{-1}. Arrows indicate transit times.

From the calculation of electron transfer rate $\mathbf{k_{el}}$ between aryamines and their radical cations based on Macus theory, Sakanoue *et al.* demonstrated that small structural relaxation of the neutral molecules and the radical cations during the electron transfer provides high electron transfer rate between the neutral molecules and the radical cations, in other words, high hole-transporting rate [12,13]. In 2C1CBz, which gave the highest hole mobility in our study, the molecular structure consisting of fluorene skeleton and carbazole substituents prevents rotational movement of phenyl rings around single bond which exists in biphenyl skeleton and diphenylamino groups of TPD. The rigid molecular structure is expected to make structural relaxation during electron transfer small. As a result, 2C1CBzF may exhibit higher hole mobility, comparing with TPD.

Figure 4 shows the effect of alkyl chain length on hole mobility of the fluorene-derivatives 2CnCBzF. When alkyl chain length of

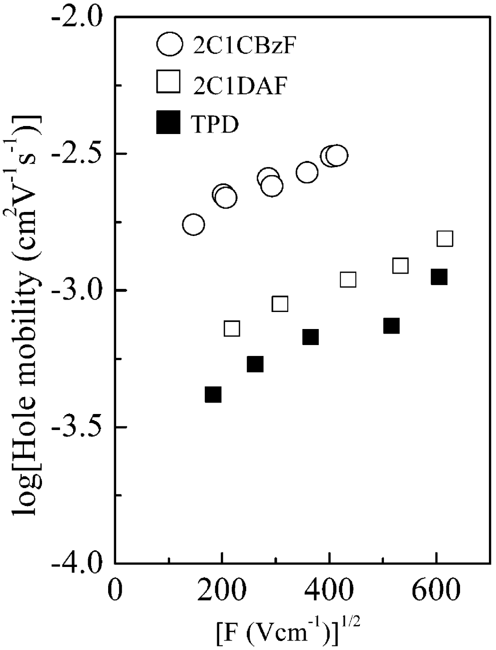

FIGURE 3 The electric field dependences of hole mobility of the dyes employed in this study.

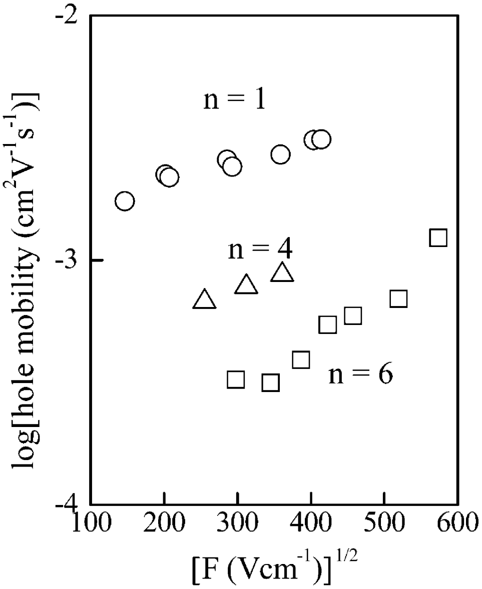

FIGURE 4 The electric field dependences of hole mobility of fluorene derivatives with differenet alkyl chain length, 2CnCBzF.

2CnCBzF is increased from n = 1 to n = 6, hole mobility of the fluorene-derivatives is decreased by about one order of magnitude. The rapid decrease of hole mobility is most likely to be due to elongation of distance between hopping sites by alkyl chains.

In this study, we demonstrated that the fluorene dyes with electron-releasing substituents, carbazole and diphenylamino group, possess high hole transporting capability in their amorphous films. For the development of high performance carrier-transporting materials based on the fluorene skeleton, we are now continuing the study on the relationship between molecular structure of fluorene dye and carrier mobility, in addition to study on origin of high mobility of the fluorene derivatives on the basis of Marcus theory [12–14].

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