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Efficient carrier separation from a photochromic diarylethene layer†‡

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Electrical carrier separation from a photoexcited photochromic molecule could be a promising method for controlling the photosensitivity of such a molecule. We report an efficient carrier separation from a photochromic diarylethene (DAE) molecule by adopting a device structure with a heterojunction consisting of an n-type diarylethene layer and a p-type layer of N,N'-di(1-naphthyl)-N,N'-diphenyl-benzidine (NPB). A photocurrent originating from carrier separation for the colored photostationary state was observed, even at zero applied voltage. The efficient carrier separation occurred at the interface between the DAE and NPB layers and was the result of the internal electrical field induced by the pn heterojunction.

Introduction

Photochromism is defined as the reversible change in the color that occurs in certain organic molecules as a result of exposure to light of particular wavelengths. The color change is caused by a reversible isomerization of the molecule.[1,2] In addition to the change in color, various other properties, including fluorescence,[3] crystal shape and surface morphology,[4–8] electrical conductivity,[9–12] hydrophobicity,[13] and metal-deposition properties,[14–17] change as a result of photoisomerization. One of the important applications of photochromism is photon-mode optical memory. Photon-mode memory has a serious problem: the recorded data is destroyed by read-out light irradiation. The problem can be solved if the photosensitivity (quantum yield) is controlled by external stimuli, such as electric field.

Interest in the applications of photochromism in electronics has been growing recently as a result of the dramatic growth in research and development in the field of organic electronics.[18,19] At present, however, research has focused mainly on current switching based on photoisomerization and on the applications of this phenomenon.[9,20–23] This current switching is based on changes in the electric properties, such as the ionization potential, or in the π-conjugation of a molecule as a result of photoisomerization. Many other possibilities can be considered, one of which is the generation of a photocurrent from a photochromic layer.[24] This could be used to control the quantum yield of a photoreaction electronically. In general, when an organic dye molecule absorbs a photon, it is raised to an excited state. In the case of photochromism, the excited molecule is transformed into another isomer, the amount of which will depend on the photoisomerization quantum yield. Free electrons and holes in the excited molecule are on the lowest unoccupied molecular orbital (LUMO) level and the highest occupied molecular orbital (HOMO) level, respectively. When an electric field is applied to the excited molecule, these carriers can be separated from the molecule. As a result, the molecule returns to its ground state, and the separated electrical carriers are detected as an external photocurrent. Returning to the ground state before photoisomerization means that the photoreaction can be suppressed.

In our previous work using a diarylethene (DAE) monolayer,[24] the separation efficiency was very low, and an impracticable electric field of around 1 V nm⁻¹ was required to achieve a high efficiency of carrier separation. The achievement of a high efficiency of carrier separation in photoexcited molecules is therefore an important step in controlling their photosensitivity. Here we report an efficient carrier separation at a low electric field (or low voltage) by improving the design of the molecules used and by adopting a device structure with a heterojunction.

Results and discussion

Device structure

Fig. 1 shows the device structure and DAEs used in the photoabsorbing layer. The device had a multilayered structure with a heterojunction consisted of a DAE absorbing layer, a N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine [NPB; N,N'-di(1-naphthyl)-N,N'-diphenylbiphenyl-4,4′-diamine] hole-transport layer, and a thin tris{4-[3-methylphenyl(phenyl)amino]phenyl}amine [m-MTDATA; N-(3-methylphenyl)-N',N'-bis{4-[(3-methylphenyl)-(phenyl)amino]phenyl}-N-phenylbenzene-1,4-diamine] layer on a indium tin oxide (ITO) electrode. The thicknesses of DAE, NPB, and m-MTDATA layers were 10, 30, and 5 nm respectively, and the size of the device was 2 × 2 mm. The ITO substrate side was irradiated with UV or visible light, which was absorbed by the DAE layer to generate carriers. A NPB layer is normally used to transport holes from the ITO anode in organic light-emitting devices; however, in our device, the NPB layer was used to transport holes formed by carrier separation in the photoabsorbing layer. Various DAEs with symmetrical molecular structures were tested for use in the photoabsorbing layer. DAE-**1a** and DAE-**1b** (Fig. 1) are relatively neutral molecules. DAE-**1b** was used in our previous experiment on photocurrent generation.[24]

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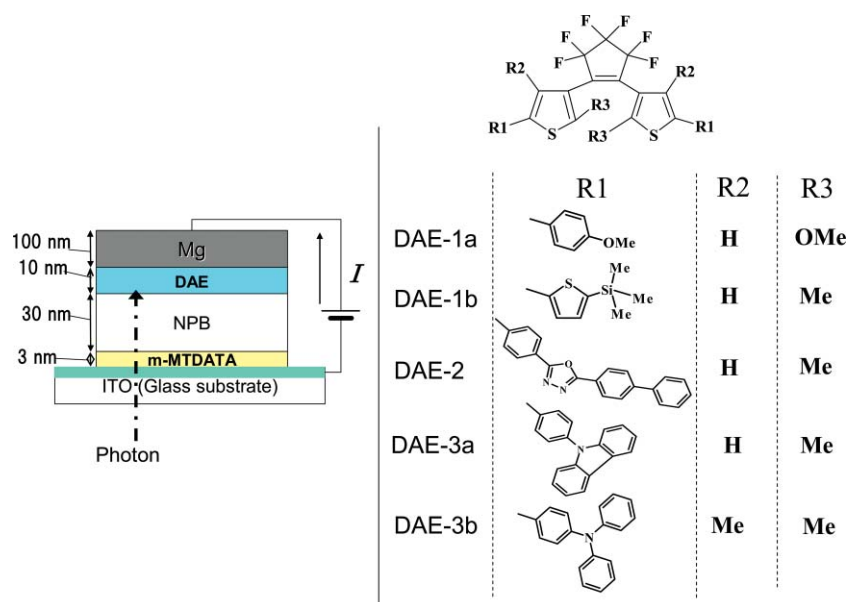
Fig. 1 Structure of the device and the chemical structures of the diarylethenes used.

DAE-**2** with oxadiazole groups is a negative-type (n-type) organic semiconductor molecule that can conduct electrons more easily than it can conduct than holes. DAE-**3a** with phenylcarbazole groups and DAE-**3b** with triphenylamine groups are positive-type (p-type) molecules, conducting holes. The absorption spectra of these DAEs in solution and in film states are presented in the ESI.‡ These spectra show that these DAEs exhibit good photochromism, even in the amorphous film states obtained by vacuum evaporation.

Fig. 2 shows the energy bands for each layer. A reverse-bias voltage, in which the Mg electrode has a positive voltage and the ITO electrode a negative one, is applied to the device. To permit the detection of the small photocurrent, it is necessary to suppress carrier injection from the electrodes. The potential barriers, which are energy-level differences between the ionization potential of the ITO electrode and the LUMO level of m-MTDATA, and between the work function of Mg and the HOMO level of DAE, are sufficiently high to suppress carrier injection from the electrodes.
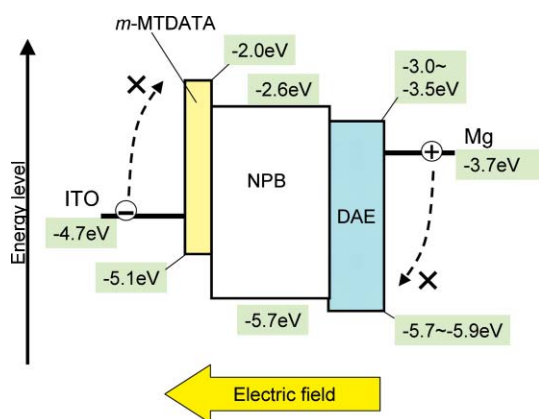
To determine the carrier-separation efficiency at the DAE layer, it is necessary to estimate the number of photons that are absorbed in the layer. For example, when light of a wavelength of 365 nm irradiates the device from the ITO electrode side, the light is absorbed sequentially by the NPB layer and the DAE layer. Light reflected from the Mg electrode is also absorbed by the DAE layer. It is therefore necessary to determine how much light is absorbed by each layer. Fig. 3 shows the absorption spectra for the NPB, DAE-**1b**, and DAE-**2** layers and the inset shows the thicknesses and single-pass absorptions of each of the layers at a wavelength of 365 nm. The solid films of the DAEs, with the exception of DAE-**3b**, show good photochromism, like in the toluene solution (see ESI‡). More than 70% of molecules of DAE-**1a**, -**1b** and -**2** have been photoisomerized even in the solid film state. The DAE layers were of the same thickness in all the devices. All the DAE layers were in the colored state [the photostationary state (PSS) obtained by UV irradiation at 365 nm] and there were no significant differences in the absorptions by the DAE layers. The absorption by the m-MTDATA layer could be ignored because it
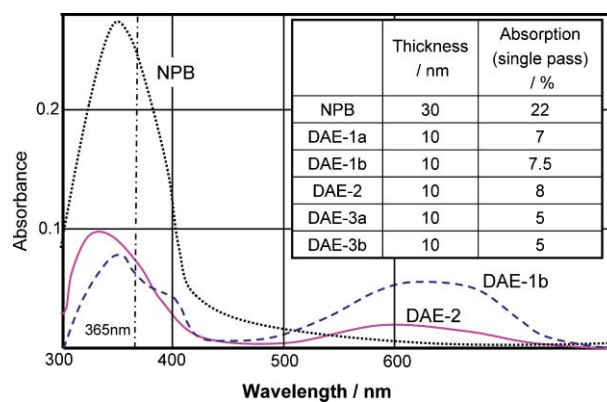

Fig. 2 Energy-band diagram for the device.

Fig. 3 Absorbances of DAE-**1b** and DAE-**2** layers in the photostationary state and of the NPB layer. The inset shows the thicknesses and absorption at 365 nm of each of the layers.

was thin and showed a low absorption. These results allowed us to estimate the number of photons absorbed by the DAE layer, which is equivalent to the number of photoexcited DAE molecules.

Photocurrent from the device with a heterojunction

Fig. 4 shows the photocurrents, which correspond to the PSS, for the reverse-bias voltage range from −1 to +1 V. The current for the device with the DAE-**2** layer in the colored state was considerably higher than those for devices with other DAE layers. Surprisingly, a current of 0.3 µA for the DAE-**2** device was observed even when the voltage was 0 V. The currents for the DAE-**2** and DAE-**3a** devices vanished at voltages of −1.1 and −0.8 V, respectively; the negative values of the current at a negative voltage below −1 V mean that injected carriers from the electrodes becomes dominant in the current.
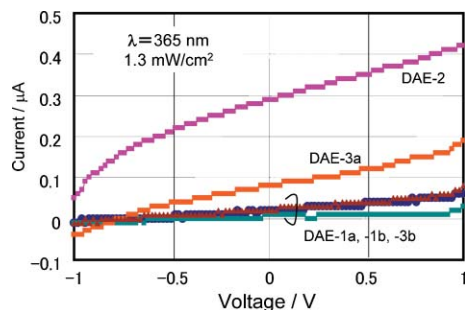
Fig. 4 Photocurrent for the devices in the low voltage region.

To confirm that a current was generated upon light irradiation at 0 V, the light-power dependence of the current for the DAE-**2** device in its colored state was investigated. Fig. 5 shows that the current was proportional to the light power and was therefore generated by light irradiation. Analogous current tendencies were also observed for the other devices.
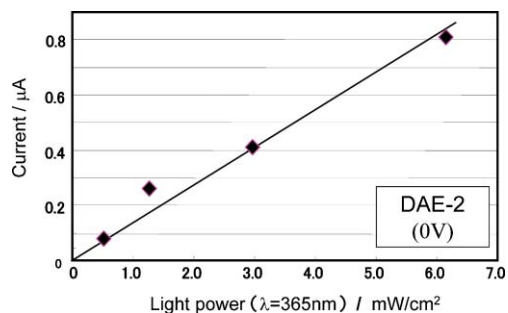
Fig. 5 Light-intensity dependence of the photocurrent for the DAE-**2** device at an applied voltage of 0 V.

Fig. 6 shows the changes in the current with light irradiation at 0 V for the DAE-**2** device. The device was initially in the uncolored (open-ring) state. The current gradually increased from 0.05 µA to 0.13 µA within a few seconds of UV irradiation, and became saturated after 10 s. When UV irradiation was stopped after 20 s, the current rapidly vanished but increased sharply to 0.13 µA upon UV irradiation at 30 s. This result also demonstrates that the current is generated by light irradiation, and that the gradual increase during the initial several few seconds originates from the photoisomerization of the DAE-**2** molecules. The saturated state
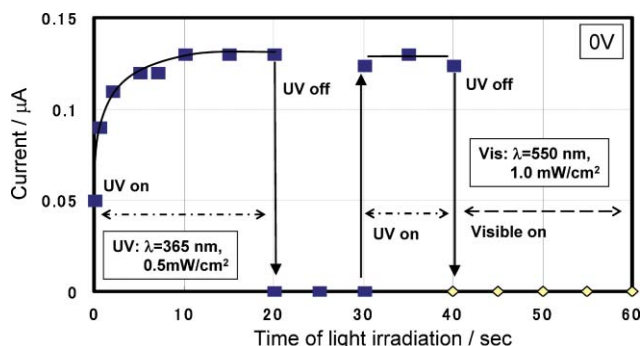
Fig. 6 Irradiation time dependence and on–off characteristics of the photocurrent.

in terms of the current corresponds to the PSS. The closed-ring molecules are stable in the dark, so the current level is unchanged after the interruption of the UV irradiation. At 40 s, the UV irradiation was turned off and the device was irradiated with visible light at a wavelength of 550 nm. No photocurrent as a result of the visible-light irradiation was observed, despite the existence of absorption at 550 nm for the closed-ring molecules. The difference in photocurrent generation between the open- and closed-ring forms of the molecules upon UV irradiation could be attributed to an extension in the π-conjugation of the molecule itself. The closed-ring molecule, with its extended π-conjugation, can conduct an electrical charge more easily than can the open-ring form of the molecule. The observation that there was no current upon irradiation with visible light in the case of the colored form of the molecule can be explained in terms of the high potential barriers between the molecules in the absence of an electric field in the Poole–Frenkel carrier conduction mechanism.[24]

Fig. 7 shows the dependence on the applied reverse-bias voltage of the carrier-separation efficiency, which was defined as the ratio of the number of generated carriers to the number of photons absorbed in the DAE layer. The number of separated carriers was estimated from the detected photocurrent, and the number of absorbed photons was estimated from the light power, the absorption of the layers (as shown in Fig. 3), and the reflectivity of the Mg layer. The photocurrent generated in the NPB layer can be ignored because its absolute value is considerably small compared with the current form the DAE layer and will be described in the next section. The photocurrent for the DAE-**1b** device is shown for reference because we studied a device with a DAE-**1b** monolayer in our previous work.[24] The plots for the DAE-**2** and DAE-**1b** devices show that the current arises by a Poole–Frenkel mechanism. In the low-voltage region (0–4 V), the efficiency of the DAE-**2** device was
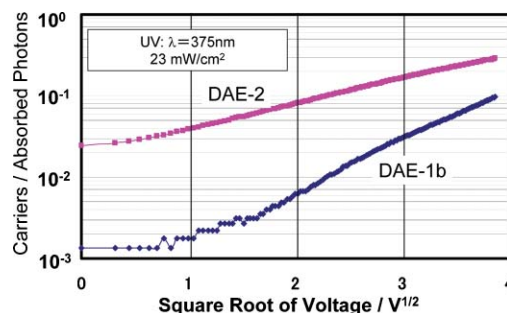
Fig. 7 Carrier-separation efficiency for the DAE-**2** and DAE-**1b** devices.

more than ten times that of the DAE-**1b** device. This shows that the carrier-separation efficiency was greatly improved by adopting an n-type diarylethene.

Origin of the photocurrent at zero-voltage

To determine the site of carrier separation and the origin of the photocurrent at 0 V, we examined the dependence of the photocurrent on the thickness of the DAE-**2** film. If carrier separation occurs throughout the DAE layer, the current should increase with increasing thickness of the DAE layer, because light irradiation should generate a greater number of excited molecules. On the other hand, if carrier separation occurs in the NPB layer (the NPB layer absorbs more photons than does the DAE layer, as shown in Fig. 3), the same magnitude of current should be observed for a device with no DAE layer. (In other words, the DAE layer contributes only to electron transport.) However, the experimental results eliminated these two possibilities, as shown in Fig. 8A. When the thickness of the DAE film was increased from 5 to 20 nm, the current decreased from 0.82 to 0.44 μA. On the other hand, no current was observed for a device with no DAE layer. The remaining possibility, therefore, is that the carriers are generated at the interface between the NPB and DAE layers. Furthermore, the fact that no current was observed for the device lacking the DAE layer shows that the existence of an interface between the DAE layer and the NPB layer is essential. These results demonstrate that the photocurrent at 0 V originates from a carrier-separation effect at the interface as a result of the internal electric field generated by the heterojunction of the NPB layer (p-type) with the DAE-**2** layer (n-type), as shown in Fig. 8B.
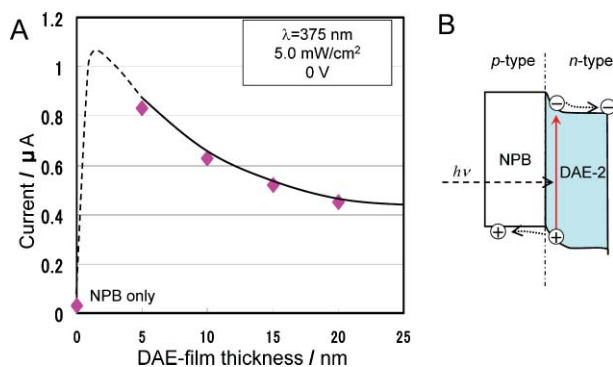

Fig. 8 Photocurrent dependence on the DAE-**2** film thickness (A). Model of carrier separation for the device with the heterojunction (B).

These findings suggest that the photosensitivity of the DAE-**2** molecules at the interface can be effectively controlled by the application of a voltage. Unfortunately, the photosensitivity control based on carrier separation could not be confirmed during our experiments because of the difficulty in detecting the change in absorption in the very thin interfacial region. This is therefore a subject for future study.

Conclusions

We successfully demonstrated efficient carrier separation from photoexited diarylethene molecules. A structure with a heterojunction consisting of an n-type diarylethene layer and a p-type NPB layer was effective in achieving carrier separation at a low voltage. Efficient carrier separation, as obtained here, is an important step toward achieving electrical control of photosensitivity, and the method could be applied in various electronics devices, such as optical memories or switches.

Experimental

Glass substrates with the ITO electrode were cleaned by ultra-sonication in acetone and then by using a UV–ozone cleaner. The organic layers and the metallic Mg electrode layer were deposited sequentially on the substrate by a conventional vacuum-evaporation method at a pressure of 1×10^{-5} Torr. The thicknesses of Mg and organic layers were controlled and were estimated by using a quartz-thickness monitor during evaporation. The samples were irradiated with UV light obtained from a mercury lump with a 365 nm sharp-cut filter through the ITO substrate. The light power was measured by using a light-power meter. Photocurrent was detected by an automatic measurement system with the current–voltage source (ADCMT, 6240A) and the PC software supplied from Sunrise Co., Ltd.

The diarylethenes DAE-**1a**, -**1b** and -**3b** were obtained from KNC Laboratories Co., Ltd. DAE-**2** was prepared by the treatment of 2-(4-biphenyl)-5-[4-(4-bromo-5-methyl-2-thienyl)phenyl]-1,3,4-oxadiazole with butyllithium and octafluorocyclopentene. DAE-**3a** was prepared by the treatment of 3-bromo-2-methyl-5-[4-(N-carbazolyl)phenyl]thiophen with butyllithium and octafluorocyclopentene. Detailed synthetic conditions of DAE-**2** and -**3a** will be reported elsewhere.

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