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Description	

Photoinduced change of dielectric permittivity in molecular doped polymer layer

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We demonstrate a large photoinduced change of dielectric permittivity due to the charge separated (CS) state of an electron donor-acceptor linked molecule, 6-[4'-(*N,N*-diphenylamino)phenyl]-3-ethoxycarbonylcoumarin (DPA-CM), doped in a polymethylmethacrylate (PMMA) matrix. Dielectric permittivity of DPA-CM in PMMA film increases from 4.1 to 7.5 under photoirradiation. Electron spin resonance spectra of the films measured under photoirradiation clearly show the formation of the CS state of DPA-CM in PMMA matrix. The origin of the photoinduced change of the dielectric permittivity is ascribed to the realignment of dipole of the CS state of DPA-CM. © 2009 American Institute of Physics. [doi:10.1063/1.3275800]

Organic field-effect transistors (OFETs) using organic semiconductors have attracted much research interests due to their unique advantages, including a variety of molecular designs, light weight, low-cost fabrication, and mechanical flexibility. In particular, research interest in the gate dielectrics is recently increasing since the choice of the gate dielectrics directly affects the electric properties of the OFETs.¹ For example, high-*k* gate dielectrics or very thin gate dielectrics can reduce the operation voltage of the OFETs.^{2,3} The threshold voltage (V_{th}) of the OFETs can be tuned by using polar self-assembled monolayers inserted at the surface of the gate dielectrics^{4,5} and also by using ferroelectric gate dielectrics, where the origin of the shift is due to remnant polarization of the gate dielectrics.^{6,7} Controlling V_{th} was also realized by using the polarized gate dielectrics with charged electrets.⁸ We have reported that the polarization of gate dielectrics can be achieved by the alignment of polar segments (carbonyl groups) of polyurea chains⁹ and a space charge polarization in ion-dispersed gate dielectrics.¹⁰ The polarization of the gate dielectrics induced charged carriers in an organic semiconductor at the semiconductor/dielectric interface and V_{th} shifted toward a lower voltage. These reports indicate that device characteristics of OFETs are significantly affected by the surface or bulk polarization of gate dielectrics. When the gate dielectrics in OFETs reveal a photoinduced polarization due to photoinduced changes of dielectric permittivity and/or a space charge polarization, one can realize organic photoswitches, phototransistors, and photomemories which are key components in optoelectronic circuits.

Photoinduced change of dielectric permittivity was reported in a liquid crystal doped with photosensitive compound.¹¹ A large change of dielectric permittivity up to 60% was achieved by the photoinduced change of the alignment of a liquid crystal. However, it may be difficult to in-

corporate a liquid crystal layer as a gate dielectric in OFET, since the liquid crystals require a rubbing treatment on the electrodes in order to obtain homogeneous alignment. Photoinduced change of dielectric permittivity has been realized by the photoinduced isomerization and reorientation of azo dye molecules in a polymer matrix.¹² Although no rubbing treatment is necessary in the case of azo dye doped in a polymer matrix, the photoinduced change of the dielectric permittivity was limited to 15%.

Recently, we have reported that an electron donor-acceptor linked compound, 6-[4'-(*N,N*-diphenylamino)phenyl]-3-ethoxycarbonylcoumarin (DPA-CM), forms a long-lived charge-separated (CS) state ($DPA^{+ \bullet}-CM^{- \bullet}$) up to milliseconds by intramolecular photoinduced electron transfer from the DPA moiety to the photoexcited state of CM moiety (Fig. 1).¹³ Since the CS state exhibits the large dipole moment, the dielectric permittivity may change by the alignment of the CS state molecules under external electric field. Thus, DPA-CM can be a promising material for photosensitive gate dielectric material. Up to now, there has been no report on the change of dielectric characteristics utilizing a long-lived CS state under photoirradiation. Here, we demonstrate that DPA-CM in polymer matrix film exhibits a large photoinduced dielectric permittivity originated from the CS state of DPA-CM.

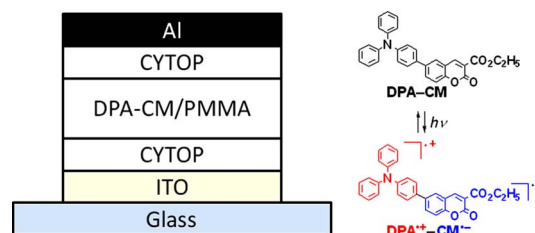


FIG. 1. (Color online) Capacitor structure using DPA-CM in PMMA film and chemical structures of DPA-CM at ground state and CS state after photoirradiation.

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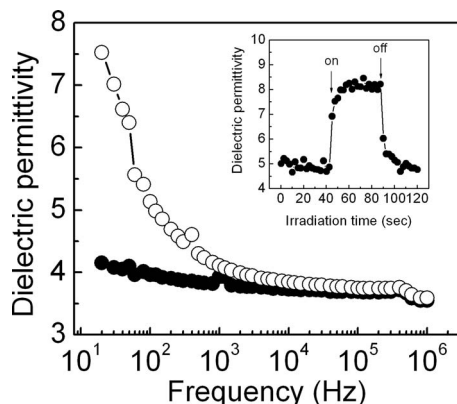


FIG. 2. Frequency dependence of dielectric permittivity of the capacitor using DPA-CM in PMMA film measured under dark conditions (closed mark) and with photoirradiation (open mark). The light intensity was 683 mW/cm^2 . Inset: Reversible change in the dielectric permittivity on photoirradiation.

Details of synthetic method and material characterization of DPA-CM will be reported elsewhere.¹³ Capacitances of the gate dielectrics were measured using a capacitor structure of glass substrate/indium-tin-oxide (ITO) electrode/CytopTM/DPA-CM in polymethylmethacrylate (PMMA)/CytopTM/Al electrode (100 nm), where a perfluoro transparent polymer (CytopTM) and PMMA were used as an insulator layer and as a matrix polymer for DPA-CM, respectively. (Fig. 1) We prepared all the polymer layers by a spin-coating technique on glass substrates coated with a 150 nm thick ITO layer. After fabricating the first layer of CytopTM (200 nm), the surface of CytopTM was treated by a UV-ozone chamber to improve adhesion to the over-coating layer of DPA-CM in PMMA ($3.9 \mu\text{m}$). The molar ratio of the constitutional repeating unit of PMMA to DPA-CM was 2:1 and the solvent of the DPA-CM:PMMA solution was acetonitrile. The second CytopTM layer (200 nm) was formed by spin-coating and the capacitor was completed by the vacuum deposition of Al electrode. The electrode area of the capacitor was $2 \times 2 \text{ mm}^2$. Capacitance was measured with an Agilent 4284A LCR meter and an Omron ZUV UV irradiator ($\lambda=365 \text{ nm}$) was used for photoirradiation.

Figure 2 shows the frequency dependence of the dielectric permittivity of the sample. Without photoirradiation, the frequency dependence of the dielectric permittivity was weak at the frequency range from 20 Hz to 400 kHz. Relatively large decrease in the dielectric permittivity was observed between 400 kHz and 1 MHz. Both of the dielectric permittivity around four and the observed frequency dependence were consistent with those of pure PMMA film.¹² These results indicate that the dielectric permittivity of DPA-CM at the ground state are coincident to that of PMMA. Thus, the dielectric characteristics of DPA-CM doped PMMA film are similar to those of pure PMMA films. On contrary, the dielectric permittivity significantly increases under the photoirradiation at 365 nm, exhibiting strong frequency dependence. The change of the dielectric permittivity was only observed while the light was irradiated to the sample (inset of Fig. 2). A large change in the dielectric permittivity from 4.1 to 7.5 was observed at a low frequency of 20 Hz. The enhanced dielectric permittivity decreased with increasing the frequency up to 10 kHz and then approached to the same value of the sample without photoirra-

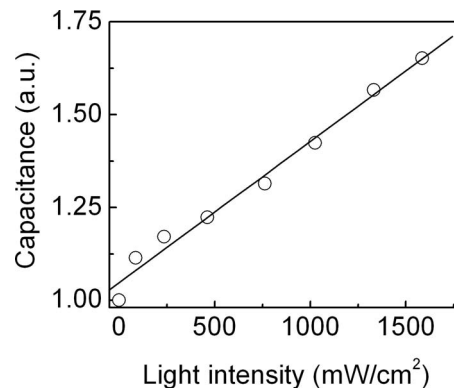


FIG. 3. Light intensity dependence of dielectric permittivity of the capacitor using DPA-CM in PMMA film ($f=20 \text{ Hz}$).

diation. The decrease in the dielectric permittivity with increase of the frequency suggests that the alignment of the CS state molecules no longer respond to the external electric field at a high frequency. Figure 3 shows the light intensity dependence on capacitance measured at 20 kHz. The capacitance was proportional to the incident light intensity. Additionally, a leakage current of the capacitor under dc bias was negligible under photoirradiation. These results clearly suggest that the enhancement of the dielectric permittivity was originated from the CS state of DPA-CM in PMMA film.

To confirm that the formation of CS state of DPA-CM is responsible to the change in the dielectric permittivity, we measured electron spin resonance (ESR) spectra of DPA-CM in PMMA films under photoirradiation. We fabricated a thin film of DPA-CM in PMMA where the molar ratio of the constitutional repeating unit of PMMA to DPA-CM was 2:1. The ESR measurements were performed on a JEOL X-band ESR spectrometer (JES-ME-LX) at 298 K. A film of DPA-CM in PMMA spin-coated on quartz substrate was irradiated in the cavity of the ESR spectrometer with the focused light from a 1000-W high-pressure Hg lamp (Ushio-USH1005D) through an aqueous filter.

The photoirradiation of DPA-CM/PMMA film results in the formation of the CS state of DPA-CM (Fig. 1), which is clearly detected by ESR as shown in Fig. 4(a). In sharp contrast, no ESR signal was observed without the photoirradiation. Based on the ESR signal observation, we confirmed the formation of CS state of DPA-CM ($\text{DPA}^{+}-\text{CM}^{-}$) in PMMA matrix at 298 K. When photoirradiation was performed at 77 K, a typical triplet ESR signal with zero-field splitting due to intramolecular triplet radical ion pair was observed at $g=2.0044$ and 4.02 as shown in Fig. 4(b). Reversible change of ESR signal was observed for the DPA-CM in PMMA film on periodic photoirradiation at 298 K [Fig. 4(c)]. Thus, the plausible mechanism of the change of dielectric permittivity under photoirradiation is realignment of the large dipole of CS state of DPA-CM molecule.

In summary, we have investigated the influence of doping of DPA-CM on the dielectric property of PMMA matrices. The dielectric permittivity measurements show that the DPA-CM molecule significantly enhances the dielectric permittivity of DPA-CM in PMMA film upon photoirradiation. The CS state of DPA-CM is responsible for the photoinduced change of the dielectric permittivity. Unique photosensitive characteristics of DPA-CM make it a promising candidate for the applications to the optoelectronic devices.

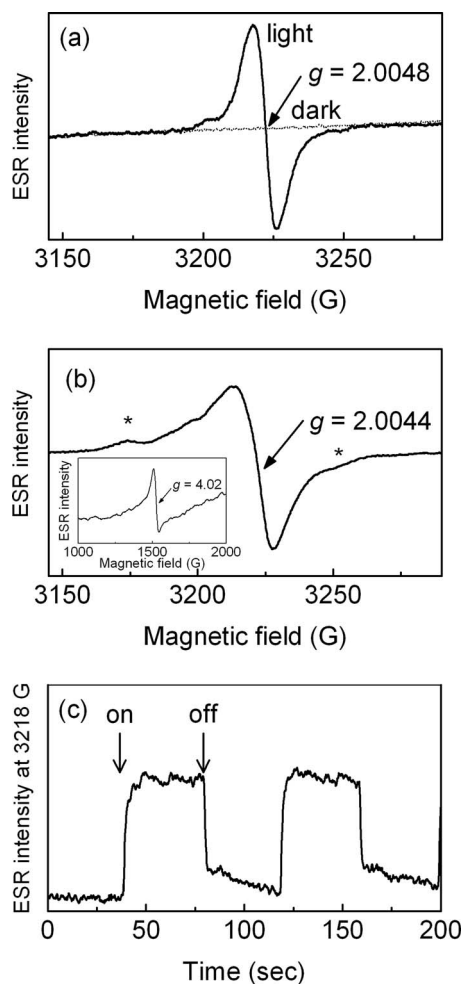


FIG. 4. ESR spectra of DPA-CM (2.5×10^{-1} mol g $^{-1}$) in PMMA (5.0 wt%) film observed (a) under dark conditions (broken line) and with photoirradiation (solid line) at 298 K and (b) after cutting off the photoirradiation at 77 K. Asterisks denote the signals due to zero-field splitting. (c) Time profile of ESR signal intensity at 3218 G observed at 298 K.

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