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Electroconductive Organogel. 5. Organic Solar Cells Based on Polymeric Charge-Transfer Complex Gel

Satomi Ohnishi and Yoshihito Osada*

Department of Chemistry, Ibaraki University, Mito 310, Japan

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ABSTRACT: An electroconductive organogel based on a polymeric charge-transfer (CT) complex, cross-linked poly[*N*-[3-(dimethylamino)propyl]acrylamide] (PDMAPAA) gel and tetracyanobenzene (TCNB), was prepared. This gel, swollen in *N*,*N*-dimethylformamide (DMF), showed a power conversion efficiency (η) of 0.18% by irradiating white light and 0.34% by monochromic 400-nm light (14.2 μW cm^2). The two-dimensional alignment of TCNB was also made in the gel by applying a dc, and η of the gel was as high as 0.45%. Such high efficiency could not be obtained in the corresponding liquid (solution) system and showed η of only 10^{-3}% or less. The spectrum of power efficiency largely overlapped the absorption spectrum of the gel, and this suggested that the PDMAPAA cation radical and TCNB anion radical formed by the CT interaction contribute to the photogeneration of carriers.

Introduction

A large number of photovoltaic solar energy conversion systems using organic materials has been reported. They are mostly based on the metal/organic Schottky barrier using low-work function metals or inorganic–organic p–n junction, where organic pigments such as phthalocyanine,[1] merocyanine,[2] and squaric acid derivatives[3] are employed to fabricate organic solar cells. However, their conversion efficiency is far above projected goals. One reason is that changes in the chemical and morphological states of the materials, which critically determine their performance, often happened during film fabrication. However, Tang reported that the two-layered organic photovoltaic cell composed of copper phthalocyanine and perylenetetracarboxylic acid derivative shows a power conversion efficiency of about 1% with a photocurrent density of milliamperes.[4] Since then some organic photovoltaic systems have actively been developed.[5,6]

We report in this preliminary paper a new class of photovoltaic effects based on a solvent-swollen electroconductive polymer gels. This gel is composed of an electrodonating polymeric network and a low molecular weight electron acceptor, like tetracyanobenzene (TCNB), subsequently doped to the polymer network. This kind of organogel based upon charge-transfer (CT) interaction showed a power conversion efficiency of 0.3%–0.5% with more than hundreds of μA cm^{-2} photocurrent density. The polymer gel described here may provide a new class of organic photoresponsive electroconductive materials.

Experimental Section

Synthesis of a cross-linked PDMAPAA gel and subsequent doping of TCNB were carried out by the same procedure as described in the previous paper.[7,8] A cross-linked PDMAPAA gel was prepared by radical polymerization of 3 M DMAPAA in the presence of 0.06 M *N*,*N*′-methylenebis(acrylamide) in DMF. Doping of TCNB was made by immersing PDMAPAA gel in a calculated amount of DMF solution of TCNB (0.5 mol % to repeating unit of PDMAPAA). From the spectral measurement, it was found that all of the TCNB in solution are practically incorporated to PDMAPAA gel. The PDMAPAA–TCNB gel swollen in DMF to 6.5 times its dry state was sandwiched between an indium tin oxide (ITO) coated glass (20 mm × 30 mm) used as a working electrode and a platinum plate (10 mm × 20 mm) used as a reference electrode with a space gap of 3 mm. Light with an intensity 14.2 μW white light) or monochromic light from a 200–550-nm xenon lamp was passed through an IR cut-off filter into a cell through the ITO electrode. Photovoltaic J–V curves were obtained by changing the value of R_L, the load resistance, and characteristic parameters of a photovoltaic cell, namely, open-circuit photovoltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (ff), and energy conversion coefficient (η). η in this report was calculated on the basis of light intensity transmitted through the ITO electrode, which usually showed 40–60% transmittance by the visible-light spectrophotometry method. Upon illumination, Pt became negative relative to the ITO.

Results and Discussion

PDMAPAA gel swollen in DMF is transparent and slightly yellow. However, when 0.5 mol % of TCNB to PDMAPA repeating unit was doped, a thin yellow border initially appeared at the surface of the gel, which gradually spread into the inner part of the polymer network and finally became red without any volume change. The color change of the gel is due to formation of a CT complex, because when TCNB solution is mixed with DMF solution of PDMAPAA, absorptions at 308 and 319 nm are shifted to 410 and 450 nm, and a new absorption appears at 630 nm. Furthermore, when TCNB is mixed with DMAPAA in acetone, new peaks appeared at 401 and 500 nm. According to the literature,[6] TCNB gives a new absorption in a range from 308 to 426 nm when a CT complex is formed with various electrodonating compounds. It is also reported[7] that a broad absorption appears near 650 nm when a CT complex is formed between TCNB and aromatics due to dimer cations of aromatics.

These spectrometric results indicate that TCNB has made a specific interaction with the PDMAPAA network which can be schematically shown as follows:[9,10]

$$\mathrm{PDMAPAA} + \mathrm{TCNB} \rightarrow (\mathrm{TCNB}^{\delta+}\cdots\mathrm{TCNB}^{\delta-})$$

$$\rightarrow (\mathrm{PDMAPAA}^{+} + \mathrm{TCNB}^{\bullet-}) \qquad (1)$$

Figure 1 shows the photo J–V characteristics of a typical cell when irradiated with xenon lamp (14.2 μW cm^{-2}). Several fundamental parameters such as V_{oc}, J_{sc}, ff, and η were extracted from this curve, and the results are summarized in Table I. As seen in Table I, the gel showed a power conversion efficiency as high as 0.18% with a 65 μA cm^{-2} photocurrent density by irradiation with white light. The best power conversion efficiency was 0.31% under illumination of 400 nm, and with correcting for reflection and electrode absorption losses, this value approaches nearly the highest class of efficiencies reported for organic solar cells.

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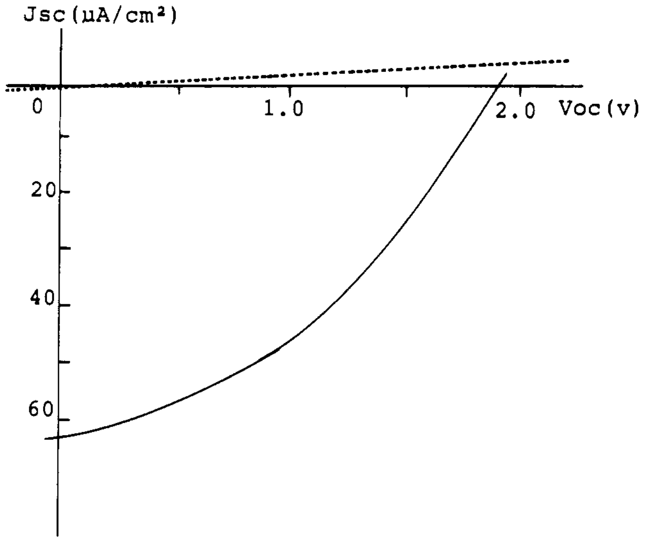

Figure 1. J–V characteristic of PDMAPAA–TCNB gel (solid line) and the corresponding solution (dotted line).

Table I
Photovoltaic Characteristics of Pt/PDMAPAA–TCNB/ITO Cells

light/nm	$P_{in}/\mu W\ cm^{-2}$	$J_{sc}/\mu A\ cm^{-2}$	V_{oc}/V	ff	$\eta/\%$
		solution			
white	14	20	0.021	0.21	6.3×10^{-3}
310	5.9	1.3×10^{-2}	0.010	0.19	1.1×10^{-5}
375	20	19	0.021	0.25	5.1×10^{-3}
500	147	2.8×10^{-2}	0.032	0.21	2.0×10^{-6}
		gel, before alignment			
white	14	65	1.9	0.38	0.18
200	4.1	0.65	0.44	0.25	0.043
300	5.9	3.1	0.41	0.32	0.17
350	13	25	0.43	0.33	0.28
400	37	37	0.78	0.38	0.31
425	68	17	0.35	0.33	0.034
450	91	9.1	0.24	0.31	0.011
550	183	2.4	0.41	0.27	2.5×10^{-3}
		gel, after alignment			
white	14	39	0.21	0.25	0.14
310	5.9	95	0.011	0.26	0.11
350	13	114	0.44	0.28	0.34
375	20	190	0.17	0.28	0.45
400	37	18	0.78	0.38	0.31
450	90	100	0.080	0.27	3.8×10^{-3}

We carried out a similar experiment using a DMF solution of PDMAPAA and TCNB with the same concentration as the gel. The power conversion of solution was as low as $10^{-3}\%$ or lower, the V_{oc} of the solution was 2 magnitudes of order less than that of the gel (Figure 1). Thus, the high efficiency of η could be obtained only in the gel and was not obtained in the corresponding liquid system.

Using the solar cell based on this organogel, a stable and reproducible photocurrent could be observed by repeated irradiation of white light as shown in Figure 2. The corresponding solution again showed an extremely low value for the photocurrent (Figure 2).

Figure 3 shows the photovoltaic spectral response of the ITO/PDMAPAA–TCNB/Au cell, as well as the absorption spectrum of the gel. As seen in this figure, the absorption spectrum of PDMAPAA–TCNB gel largely overlapped the spectrum of power efficiency. The photocurrent spectral response of the gel also showed good coincidence of the absorption spectrum. These facts indicate that the PDMAPAA cation radical and the TCNB anion radical formed by CT interaction contribute to the photogeneration of carriers.

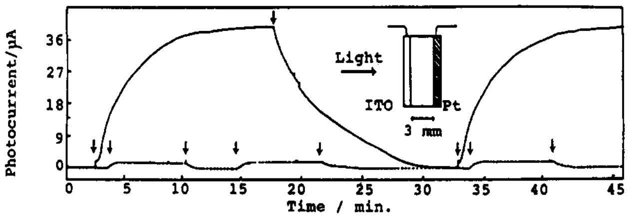

Figure 2. Profile of the photocurrent of PDMAPAA–TCNB gel (solid line) and the corresponding solution (dotted line) (white light 14.2 $\mu W\ cm^{-2}$). Arrows indicate the irradiation of light on and off.

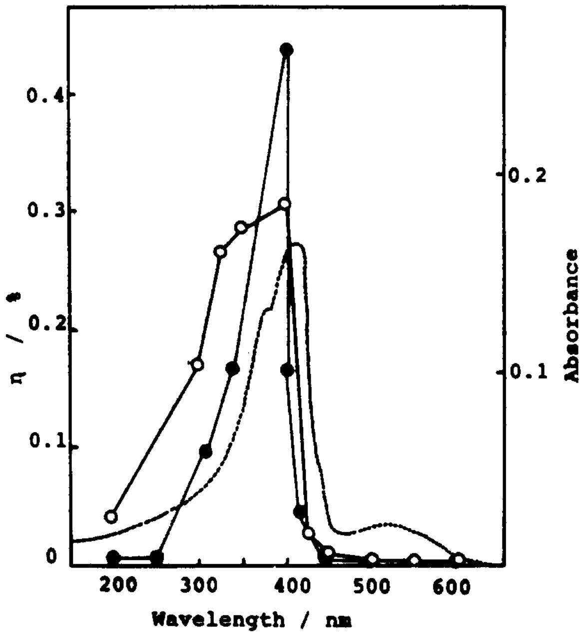

Figure 3. Photovoltaic spectral response (solid line) and the absorption spectrum (dotted line) of PDMAPAA–TCNB gel. (○) before alignment of TCNB; (●) after alignment of TCNB.

Table II
Conductivity of PDMAPAA–TCNB Gel after Applied Electric Field

δ_x (S/cm)	δ_y (S/cm)	δ_z (S/cm)
3.02×10^{-5}	2.36×10^{-8}	2.18×10^{-8}

In a previous communication, we reported that octacyanophthalocyanine (OCPc) doped as an electron acceptor in PDMAPAA gel undergoes electrophoretic migration toward the anode to give a two-dimensional orientation under an electric field.[9] The polymer gel in which OCPc molecules are aligned showed anisotropic electroconductivity with 3 orders of magnitude. This allowed us to investigate the effect of orientation of TCNB molecules on the power conversion efficiency and other photoelectric parameters. Thus, a dc voltage of 10 V was applied to the PDMAPAA–TCNB gel through a pair of platinum electrodes with a distance of 20 mm for 20 h, and then the part of the gel facing the anode electrode was sliced with 2-mm thickness. X-ray diffraction of the specimen showed two-dimensional orientation. This gel also showed an anisotropic electroconductivity with 3 orders of magnitude as shown in Table II. The photovoltaic cell was made in a similar manner using this gel, and the photoresponse was measured under the same conditions. The substantial improvement of η was observed when monochromic light of 375 nm was irradiated and η became 0.45% (Figure 2 and Table I). Since an enhanced conductivity to the direction parallel to the electric field can be associated with increased ionic conduction between neighboring TCNB rings aligned in the PDMAPAA gel, the obtained improvement of the conversion efficiency and photocurrent may be associated with increased mobility of carriers to this direction.

The characteristics of the present electroconductive CT gel is reminiscent of the inorganic p–n junction solar cells, though this preliminary report does not have conclusive evidence to explain the behavior in terms of p–n junction. However, a qualitative model for the operation of the ITO/PDMAPAA/TCNB/Pt cell can be proposed as follows. Since the excitation is created by the light through the absorption band based on the CT complex, the CT complex in a form of ($D^{\delta+}\cdots A^{\delta-}$) or ($D^{+}\cdots A^{\bullet-}$) is presumably the active site for dissociating the excitons. Thus, the light-induced excitons formed at bulk–complex interface subsequently diffuse in the bulk of the gel; the holes are preferentially transported through the PDMAPAA network and collected by the ITO electrode, while the electrons are transported in DMF toward the Pt electrode. In other words, a heterojunction barrier similar to the Schottky type may be formed at the junction of PDMAPAA and TCNB.

At present we do not have enough material to explain why the gel shows high photovoltaic efficiency and the corresponding solution does not. The extremely high local viscosity of the fluid in the gel may induce the effective dissociation of excitons.

Further investigation is required for the elucidation of the photovoltaic process in the gel, and additional work is currently underway.

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