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Photovoltaic Properties of Coumarin Dye Films

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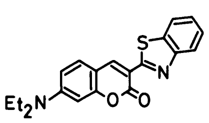
Synopsis. Al/vacuum-deposited dye/Ag(or Au) photocells prepared by using four kinds of coumarin dyes indicate that a Schottky barrier formed at an Al/dye interface is the origin of their photovoltaic effects. Quantum yields of the short-circuit photocurrent of 0.05—0.77% and the photovoltages of 0.30—0.95 V were obtained under 0.1 mW/cm^2 light.

Highly fluorescent coumarin dyes have been frequently used in the studies of the electronic-energy transfer between organic molecules.[1,2] In photoelectric energy-conversion systems, interesting applications can be expected for such coumarin dyes as "antenna pigments" by utilizing their high-emission intensities. For example, Fromherz and Arden have reported[3] a pH-modulated "molecular device" consistig of coumarin monolayer/cyanine monolayer/indium-tin oxide. The photoelectric properties of coumarin dyes themselves, however, have not been investigated so far, although studies of the properties are necessary for further applications of the dyes in photoenergy conversion. We wish to report in this article that some of the coumarin derivatives used in dye lasers act as p-type semiconductors in the photocells of the Al/dye/Ag(or Au) configuration.



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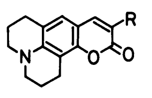

R = COOH **2**
$COOC_2H_5$ **3**
$COCH_3$ **4**

The coumarin dyes **1**—**4** were purchased from Eastman Kodak and were used without further purification. The photocells were formed in the sandwich-type configuration: Al/dye film/Ag(or Au). First, the semitransparent electrode of Al was vacuum-deposited onto a glass substrate, and then the dye was evaporated onto the Al-coated substrate in a vacuum below 5X10^{-4} Pa by heating up to 200 °C. Finally, Ag(or Au) was deposited onto the organic layer to form an effective area of 0.5 cm^2. A 300-W xenon arc lamp equipped with an interference filter was used as the monochromatic light source. The cells were usually illuminated from the Al side except in the illuminating-direction experiment on the Al/dye **1**/Au cell. The photovoltaic parameters were determined for the photocells with dye-layer thicknesses of 0.1—0.3 μm. Reproducible results, little affected by the film thickness, were obtained in this thickness range.

The current-voltage curves of Al/3-(2-benzothiazolyl)-7-diethylaminocoumarin (**1**)/Ag are shown in Fig. 1 as typical examples. For all the photocells in the present work, the Al electrode always became negative against the Ag (or Au) electrode on illumination, and the dark current-voltage curves showed rectification in such a way that negative bias of Al was in a forward direction. This behavior indicates that the coumarin dyes are char-

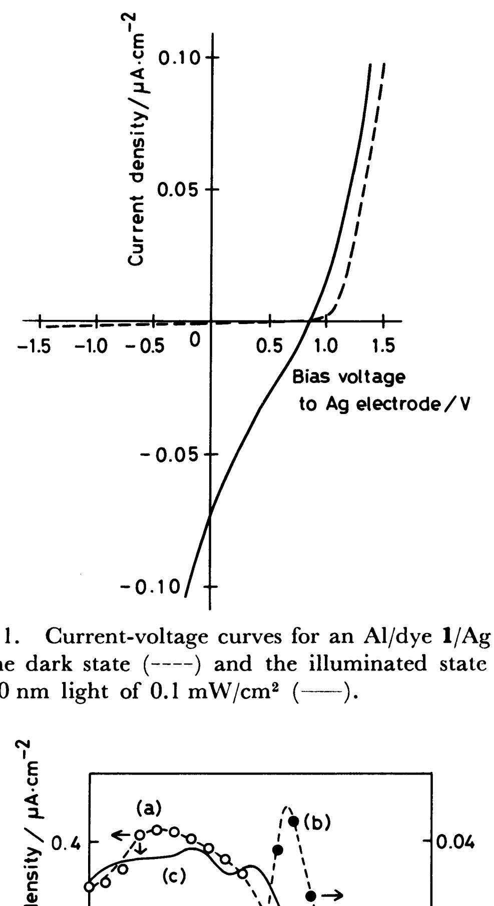

Fig. 1. Current-voltage curves for an Al/dye **1**/Ag cell: The dark state (----) and the illuminated state with 460 nm light of 0.1 mW/cm^2 (——).

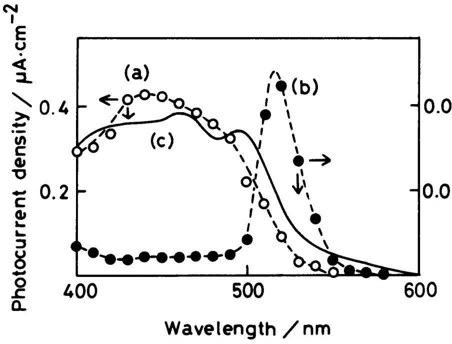

Fig. 2. Action spectra of short-circuit photocurrent for an Al/dye **1**/Ag cell and optical absorption spectrum of a dye **1** film. The values of photocurrent are corrected to the incident photon flux of 1 × 10^{15} photons/cm^2·s.
(a) Action spectrum under the illumination from the Al side. (b) Action spectrum under the illumination from the Au side. (c) Absorption spectrum of a dye **1** film in an arbitrary unit.

acterized as p-type semiconductors forming a Schottky junction at the Al interface and an ohmic contact at the Ag(or Au) electrode. The existence of a photoactive region at the Al/dye interface was confirmed by an illuminating-direction experiment on an Al/dye **1**/Au cell (Fig. 2). The action spectrum of the short-circuit photocurrent obtained on illumination from the Al side resembled the optical-absorption spectrum of a vacuum-deposited **1** film (Fig. 2-(a)). On illumination from the Au side, on the other hand, an optical filtering effect of the dye phase[4] was observed (Fig. 2-(b)), indicating that the photons absorbed near the Al interface contribute mainly to the current generation.

The values of the open-circuit photovoltage (V_{oc}), the quantum yield of the short-circuit photocurrent (Φ_{sc}), and the photoenergy conversion efficiency (η) were determined under a monochromatic light at the peak-absorption wavelength of the dye film (Table 1). When measured, the fill factors were found to be around 0.25, almost independent of the dye structures. Among the four photocells of the Al/dye/Ag configuration, the cell using dye **2**, which has a carboxyl group at the 3-position of the coumarin ring, gave the best values of Φ_{sc} and η. This result is in accordance with the suggestion by Piechowski *et al.*[5] for merocyanine-based photocells that the strong adsorption of the electron-rich end of the dye molecule to Al_2O_3 layer forming over the Al surface is efficient in the cell performance. The comparison of the data for Al/dye **1**/Au with those for Al/dye **1**/Ag in Table 1, on the other hand, demonstrates that the cell performance is fairly much improved by the use of Au in place of Ag as the contact electrode. A tendency for a dye showing a higher fluorescence efficiency in solution to give a higher Φ_{sc} value has been pointed out for merocyanine-based photocells.[5] However, no such tendency was observed for the coumarin dyes.

Table 1. Photovoltaic parameters[a)]

Photocell	V_{oc}/V	Φ_{sc}/%	η/%
Al/dye **1**/Ag	0.84	0.19	0.015
Al/dye **1**/Au	0.95	0.25	0.022
Al/dye **2**/Ag	0.49	0.77	0.033
Al/dye **3**/Ag	0.30	0.046	0.0012
Al/dye **4**/Ag	0.43	0.16	0.0058

a) Under a monochromatic light with an input intensity of 0.1 mW/cm^2. The wavelength of the light is 460 nm for Al/dye **1**/Ag and Al/dye **1**/Au, and 430 nm for the other photocells.

Studies of pH-modulated photoelectrodes utilizing the semiconductor characteristics of coumarin dyes themselves will be published elsewhere.[6]

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