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Comparison of the Photoelectric Responses of Monolayers of Three Fluorescein Derivatives on SnO_2 Coated Substrate

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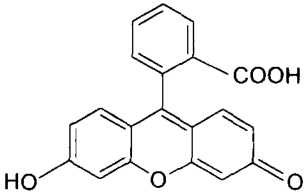
ABSTRACT

Three types of fluorescein derivatives containing long alkyl chain(s) were synthesized and characterized. Their monolayers on SnO_2 coated substrate were fabricated and their photoelectric responses evaluated. Copyright © 1996 Elsevier Science Ltd

Keywords: Fluorescein, L-B film, photoelectric response.

INTRODUCTION

Fluorescein (I) (HO-FL-COOH or FL) is a typical xanthene dye and is a good sensitizer for many photoinduced reactions.[1]



(HO–FL–COOH)

(I)

Intermolecular photoinduced energy transfer and electron transfer reactions between models of fluorescein and electron donors and electron acceptors,

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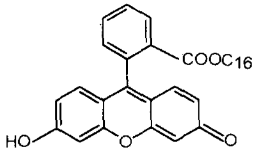
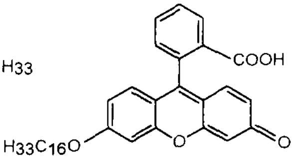
and intramolecular photoinduced reactions of such dyads and triads containing them in solution have been studied. Charge separation products having a lifetime of the order of microseconds were detected by transient absorption spectroscopy.[2–6] Fluorescein has been used in photovoltaic cells as a sensitizer for wide band gap semiconductors to make them responsive to visible light and to increase light energy conversion efficiency.[7] Fluorescein has also been used as a sensitizer for the photogeneration of hydrogen from water.[8] We report here the synthesis of three fluorescein derivatives with long alkyl chain(s), **1**, **2** and **3** and of the fabrication and characterization of their monolayers on SnO_2 coated substrate, together with an evaluation of their photoelectric responses.



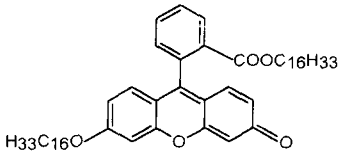
(1)

HO-FL-COOC16



(2)

C16O-FL-COOH



(3)

C16O-FL-COOC16

RESULTS AND DISCUSSION

Langmuir films have been observed and characterized by absorption spectra, fluorescence spectra, fluorescence microscopy, transmission electron microscopy, scanning tunnel microscopy, atom force microscopy, optical ellipsometry, electron diffractometry, X-ray small angle diffractometry, transfer-folding method, IR dichroism, etc.[9] It was found that the films are quite well distributed and ordered; even for multilayers, they are still ordered in two dimensions.

Figure 1 shows the photoresponse curves for compounds **1–3** over 100 s. It is apparent from the figure that when the light was on, the signal was aroused and then quickly disappeared when the light was off; the signals were generally stable over the measured time. Relevant data of the monolayers are listed in Table 1.

The data shown in the Table are average values of at least three experiments. The monomolecular area was obtained from pressure area plot (a routine procedure). Monolayer highness from the substrate surface was

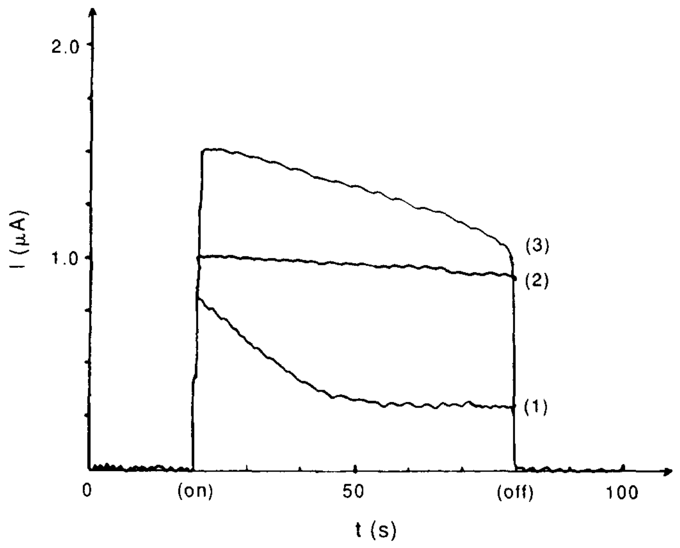


Fig. 1. Photoresponse plots for compounds **1**–**3**.

measured by polarized reflective ellipsometry,[10] X-ray small angle diffractometry,[11] and the transferfolding method by transmission electron microscopy,[12] respectively.

From the Corey-Pauling-Koltun (CPK) molecular model,[13] the plane of the phenyl group of fluorescein is almost perpendicular to the chromophoric plane, the cross-sectional area per molecule being about 70 A^2. It can be seen from the data above that on the monolayer, the fluorescein chromophore of **3** is well matched with the calculated conjugated plane of the dye, and thus lies essentially parallel to the substrate. Compounds **1** and **2**, however, have only one chain and their planes appear to be inclined, to an extent of about 45°, to the substrate plane.

On the monolayer, the long alkyl chains are nearly vertical to the substrate, and because of the close contact of the whole chromophoric plane of the dye with the substrate, the highness of **3** is also a little lower than those of

TABLE 1

Compound structure	1 HO-FL-COOC16	2 C16O-FL-COOH	3 C16O–FL–COOC16
Monomol. area (A^2)	50–55	50–55	70–75
Monohighness (A)	21–24	20–23	20–21
Photovolt. (mV)	10–30	70–150	20–40
Photocurr. (uA/cm^2)	0.3–0.8	0.9–1.0	1.0–1.5

the other compounds. It is interesting, however, that for multilayers, there is an angle of the long chains to the normal line (30–40°).

Compound **3** has better photoresponses, since it has a better contact with the SnO_2 electrode. On the other hand, comparing compounds **1** and **2** which have the same chain, compound **2** has much better photovoltage and photocurrent, indicating that the binding of the free -COOH group to the substrate is much better than that of the -OH group.

The generation of the photoresponses appears to involve a photoelectron injection process (cf. Ref. 14), namely

$$\mathrm{FL} \xrightarrow{h\nu} \mathrm{FL}^*$$

$$\mathrm{FL}^* + \mathrm{TEOA} \longrightarrow \mathrm{FL}^- + \mathrm{TEOA}^+$$

$$\mathrm{FL}^- \longrightarrow \mathrm{FL} + e^- \text{ (into SnO}_2\text{ working electrode)}$$

EXPERIMENTAL

Typically, 0.022 mol hexadecyl bromide and 0.022 mol potassium fluoride were dissolved in 100 ml *N*,*N*-dimethylformamide (DMF) and stirred for 10 min, after which 0.01 mol fluorescein dissolved in 50 ml DMF was then added. The stirred solution was heated at 100°C for 24 h. The solvent was removed under reduced pressure, and the residue was washed three times with water and then dried. The crude product was separated by silica column chromatography (eluted by cyclohexane/ethyl acetate) and three compounds were obtained, namely

Compound **1** was purified by recrystallization from methanol. Yellow rhombic crystals were obtained in 20% yield, mp 80°C.

FAB-MS: 557,333.

UV-vis (nm in methanol): $W_{max} = 510$ (the absorption spectra of this kind of compounds were studied in Ref. 15).

IR (cm^{-1}): 2918, 2849, 1711, 1636, 1600, 1516, 1464, 1375, 1286, 1253, 1211, 1123.

^1H-NMR (in CD_3Cl): 0.86 (t, 3H), 1.0–1.9 (m, 28H), 3.94 (t, 2H), 6.82 (d, 2H), 6.93 (s, 2H), 6.99 (d 2H), 7.30 (d, 1H), 7.68 (t, 1H), 7.73 (t, 1H), 8.27 (d, 1H), 9.0–9.6 (w, 1H).

Compound **2** recrystallized from benzene, giving yellow plates, mp 80°C, yield about 5%.

FAB-MS: 557, 333.

UV-vis (nm): $W_{max} = 460$.

IR (cm^{-1}): 2922, 2850, 1716, 1635, 1592, 1493, 1459, 1381, 1263, 1203, 1105.

^{1}H-NMR: 0.88 (t, 3H), 1.0–1.8 (m, 28H), 3.97 (t, 2H), 6.52 (d, 1H), 6.54 (d, 1H), 6.57 (d, 1H), 6.59 (s, 1H), 6.65 (d, 1H), 6.74 (d, 1H), 7.16 (s, 1H), 7.61 (t, 1H), 7.67 (t, 1H), 8.02 (d, 1H).

Compound **3** was recrystallized from 30 to 60°C, petroleum ether, giving yellow needle crystals, mp 67°C, yield 30%.

FAB-MS: 781, 557, 333, 317, 287, 271.

UV-vis (nm): $W_{max} = 460$.

IR (cm^{-1}): 2918, 2849, 1711, 1636, 1600, 1516, 1464, 1375, 1286, 1253, 1211, 1123.

^{1}H-NMR: 0.90 (t, 6H), 1.0–1.9 (m, 56H), 3.98 (t, 2H), 4.07 (t, 2H), 6.48 (s, 1H), 6.57(d, 1H), 6.76 (d, 1H), 6.90 (d, 1H), 6.94 (d, 1H), 7.32 (d, 1H), 7.36 (s, 1H), 7.70 (t, 1H), 7.75 (t, 1H), 8.28 (d, 1H).

Monolayer fabrication

The film on SnO_2 was fabricated using a JOYCE-LOEBEL Langmuir Trough 4 at 20°C by vertical deposition. The monolayer was spread on a pure water subphase (pH 6.7) from a solution of the fluorescein derivative in chloroform. The pressure and drawing speed were varied from compound to compound and were optimized according to experiments. Generally speaking, compounds **1–3** all had good film-forming characteristics.[9]

Photoelectric response measurements

Photoelectric response measurements were carried out on a computer-controlled microelectric current measurement device, a double cell and double electrode system was used to minimize signal noise.[16] A 500 W Xenon lamp was selected as light source. A filter cut off from 390 nm was used to eliminate the intrinsic response of SnO_2 itself. LiCl (0.1 M) was used as electrolyte and triethanolamine (TEOA) was chosen as sacrificial donor in the solution.

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