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Stilbene-containing amphiphiles in supramolecular assemblies

O. Karthaus [a], K. Ueda [b], A. Yamagishi [b], M. Shimomura [a]

[a] *Research Institute for Electronic Science, Hokkaido University, 060 Sapporo, Japan*
[b] *Faculty of Science, Hokkaido University, 060 Sapporo, Japan*

Abstract

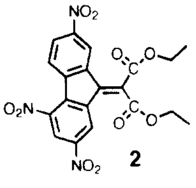
Strong electron donors and acceptors are used in various fields related to optics and electronics. Some exhibit non-linear optical properties and these compounds or their charge transfer complexes are often found to be conductive, photoconductive or electroluminescent. For efficient electron and energy transfer the orientation of the molecules is crucial. In this work, we describe the synthesis of a new type of electron donor/acceptor compound.

Keywords: Stilbene; Amphiphiles; Supramolecular assemblies

1. Introduction

Orientation of molecules in monomolecular layers at the air–water interface offers an efficient and straightforward approach for tailormade molecular assemblies [1]. For this purpose, combined donor–acceptor molecules [2,3] or mixtures of donors and acceptors [4,5] can be used. Transfer of these ordered surface monolayers to solid supports by the Langmuir–Blodgett (LB) technique leads directly to well-defined multilayers which can be used for optical or electronic devices.

Stilbene was chosen as electron donor because it shows efficient energy migration and strong fluorescence in ordered molecular aggregates [6,7]. Linkage via an alkyl spacer to the trinitrofluorenylidene derivative **2** leads to the desired donor–acceptor compound **3**. Compound **2** was chosen as the electron acceptor, because 2,4,7-trinitrofluorenone is a strong electron acceptor which can be used as a sensitizer for polyvinylcarbazole photoconductors.



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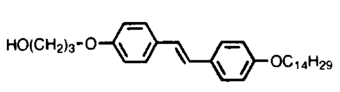

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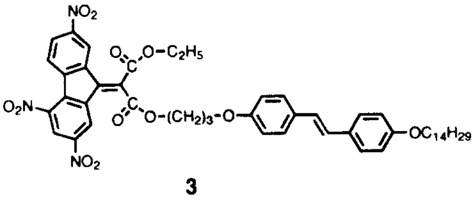

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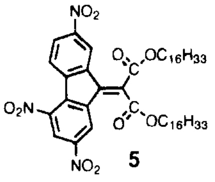

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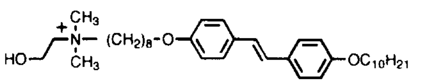

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2. Experimental details

UV and fluorescence spectra were obtained using Jasco Ubest-30 and Jasco FP 770 spectrometers respectively. Monolayers were prepared by spreading a dilute $CHCl_3$ solution (1 mg ml^{-1}) onto a clean water surface (resistance, greater than 18 MΩ). Pressure–area (π–A) isotherms were measured using a computer-controlled film balance (USI Systems) equipped with a Wilhelmy-type pressure pickup system. LB films were prepared by the horizontal lifting method using quartz plates which were hydrophobized with 11 layers of Ba stearate. All measurements were performed at 20 °C.

4,4′-Dihydroxystilbene [8] and 4-hydroxy-4′-tetradecyloxystilbene [6] were synthesized according to the literature.

2.1. 4-(3-Hydroxypropyloxy)-4′-tetradecyloxystilbene (1)

4-Hydroxy-4′-tetradecyloxystilbene (400 mg, 1 mmol) was dissolved in 100 ml of hot ethanol and 142 mg (2.15 mmol) of KOH was added. After the addition of 300 mg (2.16 mmol) of 3-bromopropanol (Tokyo Chemical Industry), the mixture was refluxed for 3.5 h. The hot mixture was

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filtered, evaporated and recrystallized from ethanol. Yield, 138 mg (40%). Clearing point of the anisotropic liquid crystalline melt, 168–170 °C. Thin layer chromatography (TLC) ($CHCl_3$): $R_f = 0.15$.

2.2. *Ethyl-3-(4-oxy-4′-tetradecyloxystilbyl)-propyl-2,4,7-trinitrofluoren-9-ylidenemalonate (3)*

Diethyl-2,4,7-trinitrofluoren-9-ylidenemalonate (74.2 mg, 0.16 mmol) [9] (**2**) and 149 mg (0.32 mmol) of **1** were melted and stirred under an N_2 atmosphere at 145 °C. To the dark red melt, 20 μl of tetraisopropyl orthotitanate (Tokyo Chemical Industry) was added as catalyst. After 15 min incubation, a slight vacuum was applied to remove the resulting ethanol. After an additional 5 min at 1 mbar, the reaction was complete and the reaction mixture was allowed to cool under N_2. The reaction mixture was purified by column chromatography using silica gel (Merck) and $CHCl_3$ as eluent. Yield, 40 mg (20%). The dark purple compound shows a smectic liquid crystalline phase between 110 and 120 °C. TLC ($CHCl_3$): $R_f = 0.54$. Nuclear magnetic resonance (NMR) (60 MHz, $CDCl_3$): 9.2–6.6 ppm (aromatic), 4.5 ppm (OCO-$\underline{CH_2}$), 4.0 ppm (O-$\underline{CH_2}$), 2.0–0.9 ppm (alkyl).

3. Results and discussion

3.1. *Monolayer and LB film*

Fig. 1 shows the π–A isotherm of **3**. It can be seen that the compound forms a stable monolayer at the air–water interface, with a collapse pressure of 20 mN m^{-1}. The shape of the curve, with a slow increase in pressure on compression, is typical of films of liquid crystalline compounds. In addition, a constant or slightly increasing pressure beyond the collapse point is typical of liquid crystals. The collapse area of 0.25 nm^2 per molecule is in good agreement with the calculated area of a stilbene molecule oriented with its long axis perpendicular to the water surface. Although the trinitrofluorenylidene group has no ionic charge, it probably acts as the hydrophilic head group. A schematic model of the orientation of the molecules at the air–water interface is shown in the inset of Fig. 1.

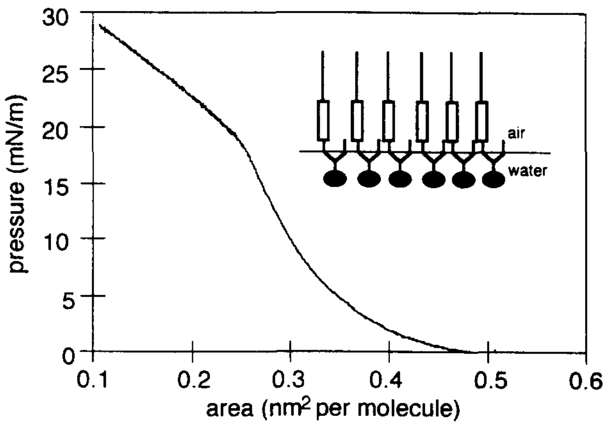

Fig. 1. π–A isotherm of **3** at 20 °C on pure water. The inset shows the proposed model of the orientation of the molecules at the air–water interface.

This film at the air–water interface could not be transferred onto solid substrates by the conventional LB technique. Vertical dipping of hydrophilic or hydrophobic substrates through the monolayer did not lead to a sufficiently reproducible deposition onto the substrate. The horizontal dipping method was the only method which gave reasonable transfer of the film onto hydrophobic substrates.

3.2. *Optical properties in LB and cast films*

The UV spectrum of the LB film shows a linear increase in absorbance with increasing number of layers (Fig. 2(a)) and is significantly different from the spectrum in $CHCl_3$ solution (Fig. 2(b)). The peaks are broadened due to chro-

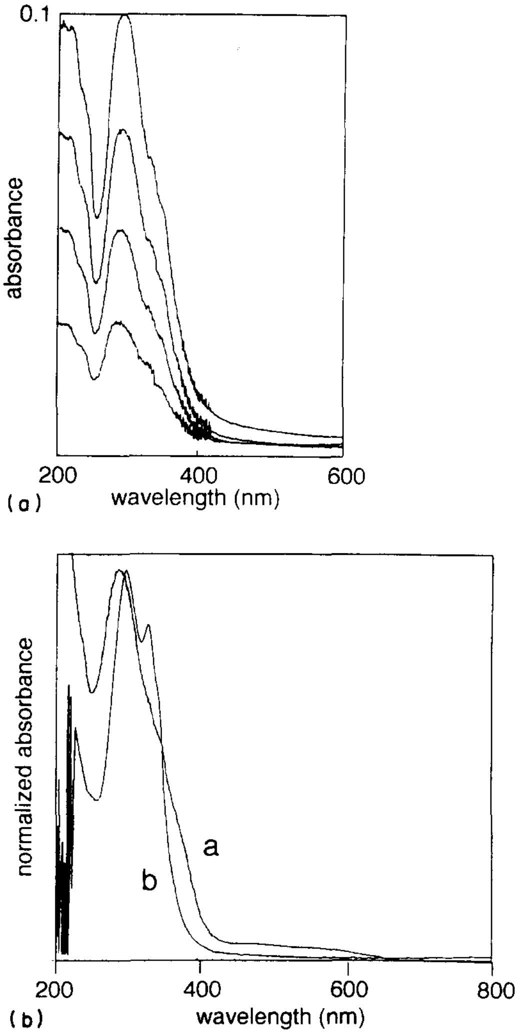

Fig. 2. (a) Absorption spectra of a multilayer film of **3** prepared by the horizontal dipping technique. The spectra after four subsequent transfers are shown. (b) Absorption spectra of a cast film of **3** from chloroform (curve a) and a chloroform solution of **3** (curve b).

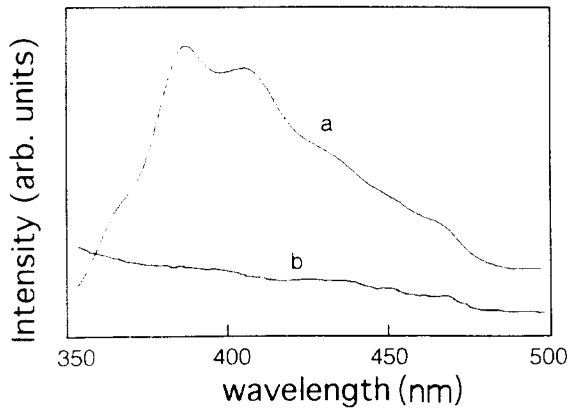

Fig. 3. Fluorescence spectra (λ_{ex} = 320 nm) of an LB film of a 1 : 1 mixture of 4 and 5 (a) and an LB film of 3 (b).

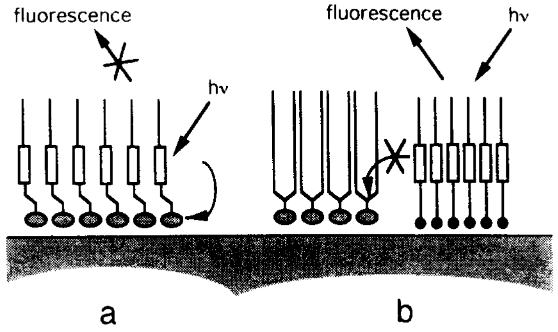

Fig. 4. Schematic representation of intramolecular quenching in a transferred film of 3 (a). In the case of a mixture of 4 and 5, no quenching takes place (b).

mophore interaction and the stilbene absorption is shifted from 300 nm in solution to 285 nm in the LB film.

This blue shift indicates the formation of an H aggregate in the oriented LB film. In addition, no charge transfer band is observed. This provides further evidence for the model proposed in Fig. 1 where, due to the spatial separation of donor and acceptor, no charge transfer band is expected. In contrast, a cast film from chloroform solution shows no aggregation of the stilbene chromophores (absorption at around 300 nm) and an additional weak, broad absorption between 400 and 620 nm, which is due to charge transfer interaction (see Fig. 2(b)).

The LB film of **3** shows only weak fluorescence on excitation of the stilbene moiety with 320 nm light, which is in sharp contrast with an LB film prepared from a 1 : 1 mixture of a stilbene amphiphile **4** and a trinitrofluorenylidene compound **5** [10] which shows strong fluorescence (Figs. 3 and 4).

The π–A isotherm of a 1 : 1 mixture of **4** and **5** is consistent with the formal addition of the isotherms of the two pure compounds, indicating that demixing of both components takes place at the air–water interface. Neither domain formation nor macroscopic demixing of **4** and **5** can be observed at the air–water interface, but the domains may be too small to be observed by optical microscopy. Thus the strong fluorescence of the mixed film indicates that only intramolecular quenching from the excited stilbene to the trinitrofluorenylidene moiety is possible.

3.3. Optical properties in solution

The absorption spectrum of **3** in chloroform shows two absorption maxima at 300 and 330 nm, which are due to the stilbene chromophore. The trinitrofluorenylidene absorption (λ_{max} = 345 nm) can be seen as a shoulder. No charge transfer band can be observed at a concentration of 7.6×10^{-5} M (see Fig. 2(b)). The dark purple crystals dissolve in organic solvents, such as chloroform, ethanol and toluene, to give a slightly yellow solution. Thus the observed charge transfer in the solid state is due to intermolecular complex formation. The intramolecular charge transfer complex, obtained by backfolding of the stilbene unit onto the fluorenylidene moiety, is effectively prevented by the short propylene spacer. However, intramolecular fluorescence quenching can also be observed in solution: the reduced fluorescence intensity of **3** at concentrations lower than 10^{-5} M is constant, leading to the conclusion that energy transfer is purely intramolecular.

4. Conclusions

The first member of a new type of electron donor–acceptor compound has been synthesized, and monolayers at the air–water interface and LB multilayers of this compound have been prepared. The short spacer between the donor and acceptor moieties leads to a spatially separated orientation of the two parts within monomolecular layers, in which the stilbene chromophores form H aggregates. LB multilayers and solutions of **3** in organic solvents show strong fluorescence quenching, which may be due to efficient energy or electron transfer from the donor to the acceptor.

Acknowledgements

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