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Monolayers and LB Films of Highly Polarizable Oligo(phenylenevinylene) Derivatives

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Highly polarizable oligo(phenylenevinylene) amphiphiles were synthesized, and their monolayer properties were examined. The corresponding Langmuir-Blodgett films gave optical second harmonic generation.

Optical second harmonic generation (SHG) from Langmuir-Blodgett (LB) films is of great interest,[1-9] since non-centrosymmmetric structures are obtainable from highly polarizable organic molecules by the LB technique. We described previously that stable surface monolayers were obtainable from wholly π-conjugated oligo(phenylenevinylene) amphiphiles.[10] More recently, it was found that a related, more polar derivative, 4-[2-[4-[2-(4-methoxyphenyl)ethenyl]phenyl]ethenyl]benzenesulfonamide (**1**), produced Z-type LB films which displayed SHG property.[11]

In this paper, we extended our study to other highly polarizable analogues, 4-[2-[4-[2-(4-methoxyphenyl)ethenyl]phenyl]ethenyl]pyridinium iodide (**2**) and 4-[2-[4-[2-[4-(dimethylamino)-phenyl]ethenyl]phenyl]ethenyl]benzenesulfonamide (**3**). Compounds **2** and **3** have stronger electron-withdrawing (pyridinium) and electron-donating (dimethylamino) groups, respectively, compared with our previous compound **1**. They were synthesized via Wittig reactions,[12,13] according to Scheme 1. 4-Formylbenzyl bromide, 4-formylbenzenesulfonamide and 4-dimethylaminobenzyltriphenylphosphonium chloride were prepared in ways similar to the reported procedures.[12,14,15] The aldehyde group of 4-formylbenzyl bromide was protected by 2-phenyl-1,3-propanediol[16] which was obtained by reduction of diethyl 2-phenylmalonate with $LiAlH_4$ in THF. The solid acetal intermediate was isolated without contamination of the aldehyde. Protection of the aldehyde by ethylene glycol gave a liquid derivative, which was partially hydrolyzed during the work-up. Oligo(phenylenevinylene) derivative **2**[17] was obtained in 59% yield by condensation of 4-[2-(4-methoxyphenyl)ethenyl]benzaldehyde and 1,4-dimethylpyridinium iodide in refluxing ethanol for 4 h in the presence of 1,5-diazabicyclo[4,3,0]non-5-ene (DBN), followed by recrystallization from methanol. The Wittig reaction of 4-[2-(4-formylphenyl)ethenyl]benzenesulfonamide and 4-dimethylaminobenzyltriphenylphosphonium chloride in the presence of lithium ethoxide in refluxing 95% ethanol for 2 days gave **3**[17] in 43% yield after repeated recrystallization from dimethyl sulfoxide. ^{1}H NMR spectra in the vinylene region of **2** and **3** (DMSO-d^6) were consistent with the all-trans configuration.

Surface pressure-area isotherms were obtained at 20.0 ± 0.2 °C by a film balance FSD-20 (San-esu

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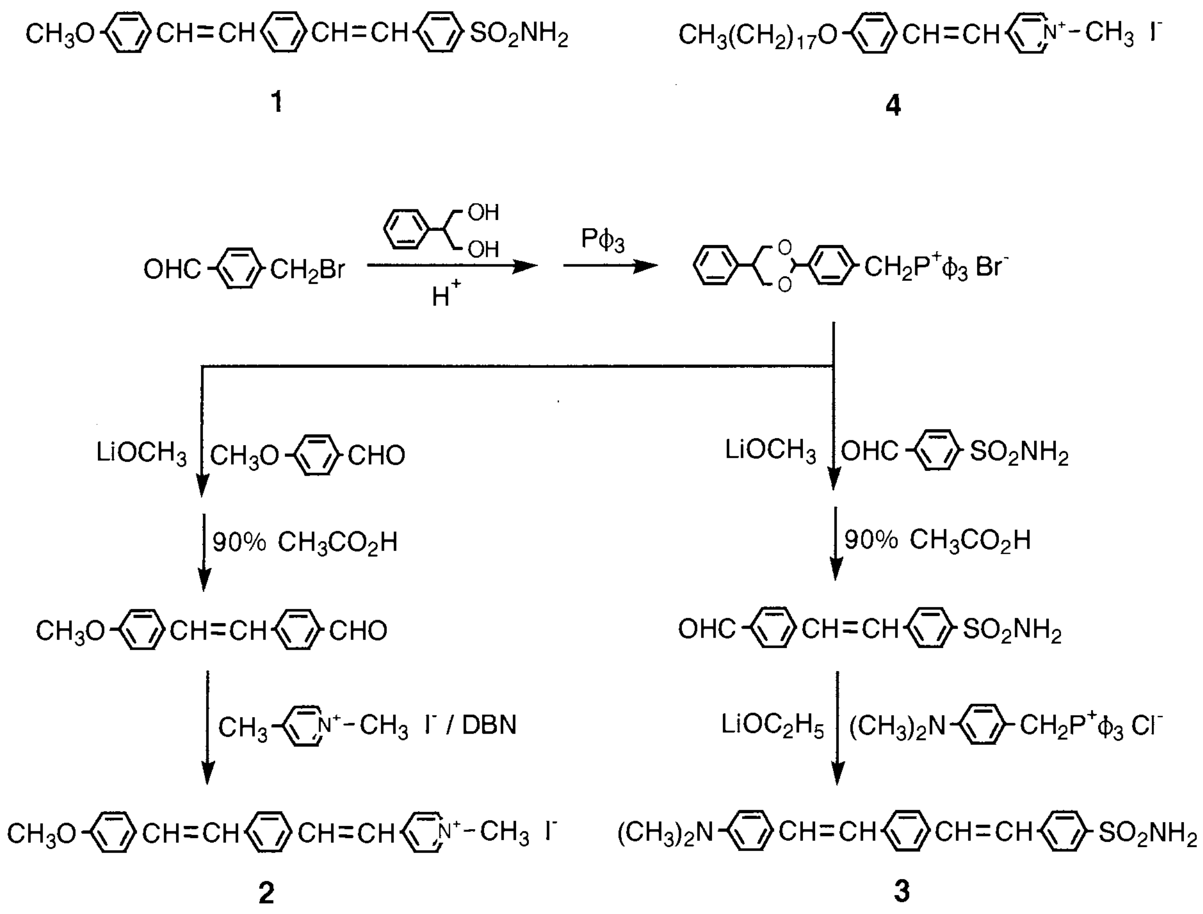

Scheme 1.

Keisoku, Japan). The pressure equilibration mode was used so that the barrier moved only after the pressure variation became less than ± 0.1 mN m^{-1}. Compound 2 did not show any pressure increase on pure water. Its isotherms became measurable in the presence of polyanions in the subphase due to formation of polyion complexes.18) A fairly stable monolayer that contained a condensed region was obtained in the presence of dextran sulfate (MW 5×10^4) (Fig. 1), and it could be transferred onto a quartz plate which had been treated with fuming nitric acid.19) The deposition procedure was performed in the absence of UV light, since the monolayer appeared sensitive to daylight. The deposited monolayer was stored in a colored bottle under nitrogen, and the subsequent measurements were carried out within half a day. SHG measurements were conducted using a Nd/YAG laser (λ=1064 nm, pulse duration 20 ns, 3 mJ $pulse^{-1}$, p-polarized). The value of envelopes of fringes in the θ = 45° transmission geometry was 7.4 times as large as that of 4.4) The longer π-cojugated structure in 2 resulted in more intense second harmonics than the shorter 4, the electron-donating and electron-withdrawing groups being identical in both compounds.

In the case of compound **3**, the collapse pressure was low (Fig. 2), and the attempted deposition onto hydrophilic or hydrophobic (octadecyltrichlorosilane treatment) quartz failed. An equimolar mixture of **3** with palmitic acid produced a stabler monolayer, which could be deposited as Z-type LB films on the hydrophobic quartz except for the first layer. The deposition at 15 mN m^{-1} took place during the first downstroke (100 mm min^{-1}) and the subsequent upstrokes only(10 mm min^{-1}).20) The resulting 7-layered LB film should be comprised of centrosymmmetric two layers which are inactive for SHG, and of noncentrosymmetric five layers which are active for SHG. This mixed multilayer gave approximately 4-fold SHG intensity compared with the monolayer of compound **4** (laser power: 18 mJ pulse^{-1}) and a 5-layered Z-type LB films of **1**.11) The single-component monolayer of **3**, if it could be deposited, would give a much higher (16 times) intensity than the latter.

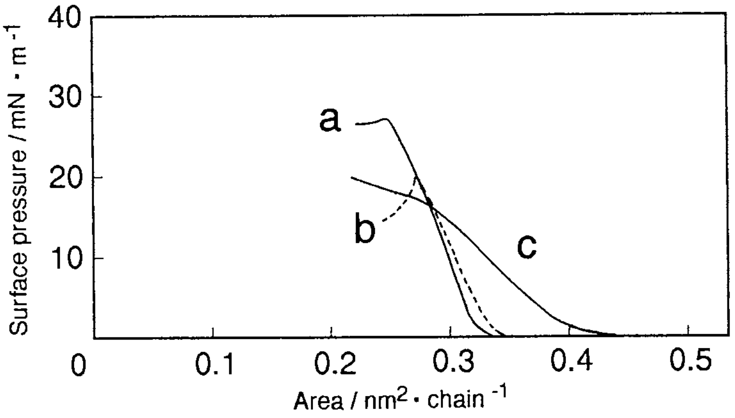

Fig. 1. Pressure-area isotherms of **2** on aqueous anionic polymer solutions. 20.0 ± 0.2 °C. Spreading solution; 0.2 g l^{-1} in chlorform-methanol (4:1 by volume). Subphase polymer concentration; 20 mg l^{-1}. Compression rate; 12 mm / min during the equilibration step. Subphase polymer: a, dextran sulfate (MW 50000); b, dextran sulfate (MW 5000); c, sodium poly-(styrenesulfonate) (MW 18000).

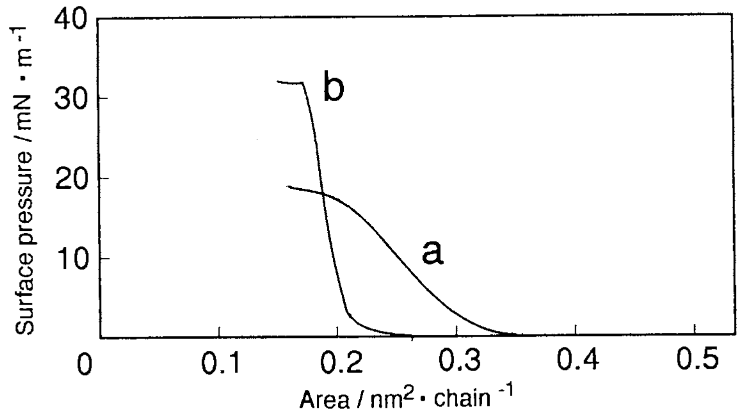

Fig. 2. Pressure-area isotherms of **3** on pure water. 20.0 ± 0.2 °C. Compression rate; 12 mm / min during the equilibration step. a, spreading solution; 0.1 g l^{-1} in benzene-dimethyl sulfoxide (4:1 by volume), monolayer of **3**; b, spreading solution; 0.2 g l^{-1}, equimolar monolayer of **3** and palmitic acid.

We demonstrated here superior SHG performance of a monolayer and a Z-type LB film of highly polarizable oligo(phenylenevinylene) derivatives. The alkoxy pyridinium derivative with two phenylenevinylene units gave a much larger SH intensity than a stilbazium derivative with one phenylenevinylene unit. Non-centrosymmetric LB films of polarizable oligo(phenylenevinylene) derivatives are promising materials for non-linear optical devices.

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17) **2**: dark orange crystal, mp 282 - 285 °C. Anal. Found: C, 60.86; H, 4.88; N, 3.02%. Calcd for $C_{23}H_{22}INO$: C, 60.67; H, 4.87; N, 3.08%; **3**: orange powder, mp >350 °C. Anal. Found: C, 70.93; H, 5.97; N 6.88%. Calcd for $C_{24}H_{24}N_2O_2S$: C, 71.26; H, 5.98; N, 6.92%.

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19) Transfer in the first upstroke: rate, 10 mm / min; surface pressure, 10 mN m^{-1}; transfer ratio; 1.24.

20) Transfer ratio: the first downstroke, 0.86; the subsequent upstrokes, succesively 0.87; 1.05; 1.05; 1.00; 1.01; 0.98.

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