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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. ^1H 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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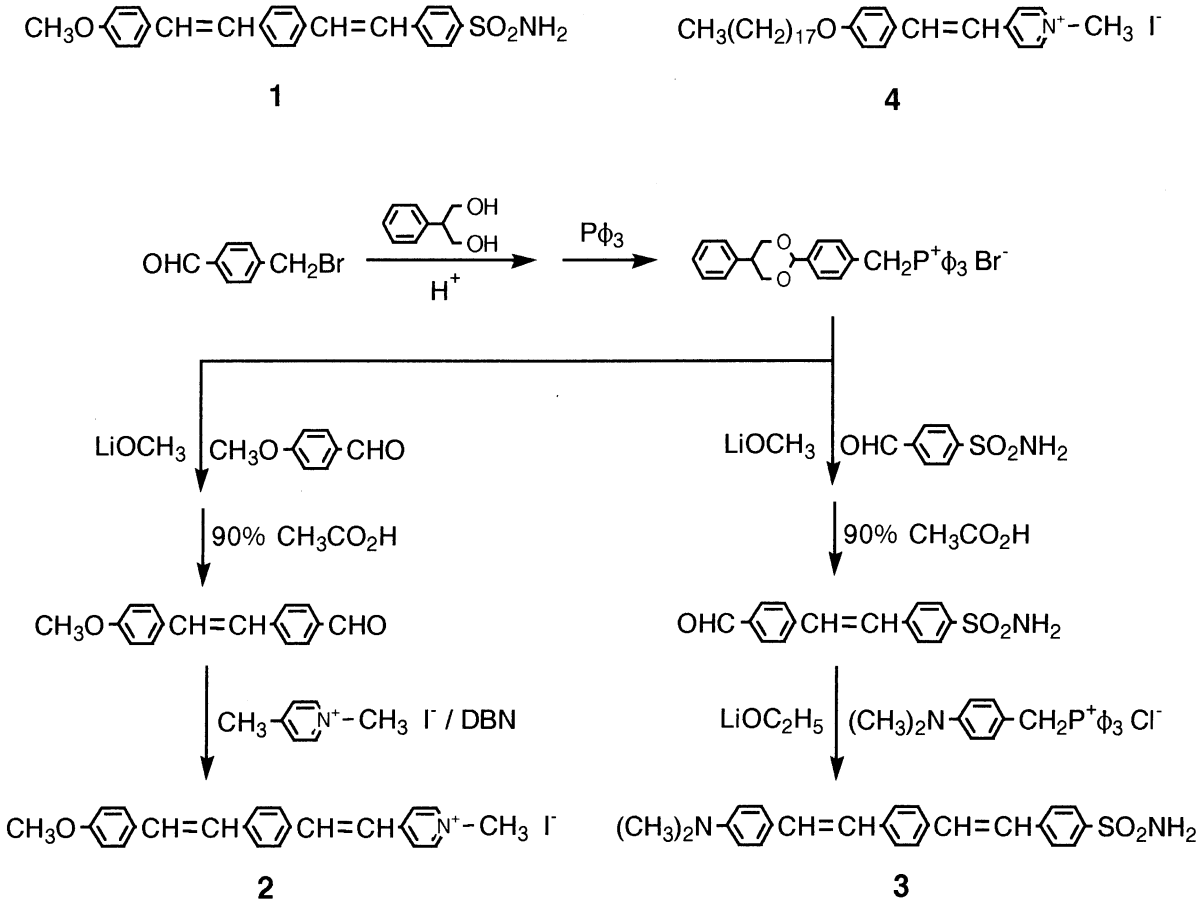

Scheme 1.

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.

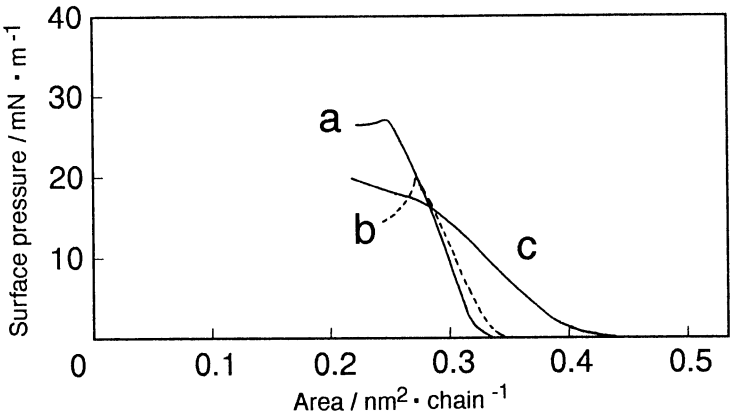

Fig. 1. Pressure-area isotherms of **2** on aqueous anionic polymer solutions. 20.0 ± 0.2 °C. Spreading solution; 0.2 g l^{-1} in chlorform-methanol (4:1 by volume). Subphase polymer concentration; 20 mg l^{-1}. Compression rate; 12 mm / min during the equilibration step. Subphase polymer: a, dextran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

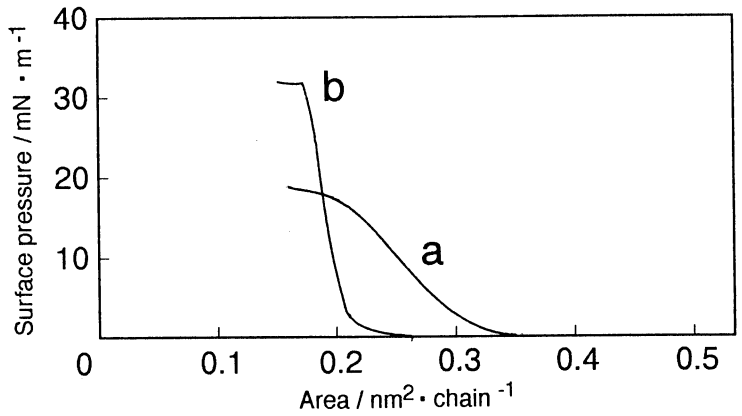

Fig. 2. Pressure-area isotherms of **3** on pure water. 20.0 ± 0.2 °C. Compression rate; 12 mm / min during the equilibration step. a, spreading solution; 0.1 g l^{-1} in benzene-dimethyl sulfoxide (4:1 by volume), monolayer of **3**; b, spreading solution; 0.2 g l^{-1}, equimolar monolayer of **3**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

We demonstrated here superior SHG performance of a monolayer and a Z-type LB film of highly polarizable oligo(phenylene-vinylene) 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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