Improved Second Harmonic Generation from Langmuir-Blodgett Monolayers of an Ionically Combined Bis-chromophore Zinc Complex

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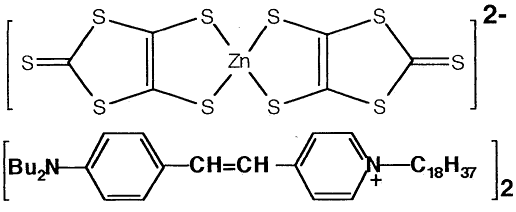
Strong second harmonic generation (SHG) from LB monolayers of a new ionically combined nonlinear optical bis-chromophore zinc complex, bis(E)-N-octadecyl-4-[2-(4-dibutylaminophenyl)ethenyl] pyridinium bis (2-thione-1,3-dithiol-4,5-dimercapto) zinc (**1**), was observed even when the film was transferred at 5 mN/m. The second-order susceptibility ($\chi^{(2)}_{zzz}$) is evaluated to be about 140 pmV^{-1}, which is 2.8 times that of the corresponding dye iodide.

Hemicyanines have attracted much attention due to their large second-order nonlinearities.[1] The SHG from these LB films are strongly counter-anion dependent and sensitive to the extent of molecular aggregation.[2] Our earlier results showed that the replacement of the halide anion in hemicyanines with a large lanthanide complex anion, which maybe used as both spacer and counter-anion, can usually improve the film forming performance and consequently enhance the SHG.[3] Recently, Lupo et al. reported a new class of covalently linked bis-chromophore dyes, but the SHG from their LB films was relatively weak ($\chi^{(2)}_{zzz}$ is smaller than 5 pmV^{-1}).[4] In this letter, by combining two hemicyanines with a bivalent zinc complex anion, a new ionically combined bis-chromophore complex dye, whose molecular structure as depicted, was synthesized. The combination of two chromophores into one molecule probably increases the density of NLO active moieties in a single layer. Thus, stronger SHG from the LB monolayer is obtained even when the film is transferred at a very low surface pressure of 5 mN/m.



Bis (tetrabutylammonium) bis(2-thione-1,3-dithiol-4,5-dimercapto) zinc, Zn(dmit)$_2$.(Bu$_4$N)$_2$), was prepared by the method of Steimecke et al.[5] E-N-octadecyl-4-[2-(4-dibutylaminophenyl) ethenyl]pyridinium iodide was prepared using the method similar to Girling et al.[1a] **1** was synthesized following our earlier procedures:[6] 0.471 g (0.500 mmol) Zn(dmit)$_2$.(Bu$_4$N)$_2$ and 0.688 g (1.00 mmol) E-N-octadecyl-4-[2-(4-dibutylaminophenyl)ethenyl] pyridinium iodide were dissolved in 40 ml acetone and refluxed for 10 min. When it was cooled down to room temperature, 50 ml water was added. The red precipitate was collected and recrystallized from mixed solvents of acetone/water to obtain **1** as a red crystalline solid. Analysis. Found: C, 63.70; H, 8.40; N, 3.62%. Calcd for $C_{84}H_{130}N_4S_{10}Zn$: C, 63.78; H, 8.28; N, 3.54%.

300 μl of **1** in CHCl$_3$ (1.52 × 10^{-4} mol/L) were spread onto the pure water subphase (MilliQ, 18 °C) of one compartment of a NIMA Langmuir trough (model 622),[7] left for 10 min and then compressed at 20 cm^2/min. The surface pressure—area isotherm was recorded and shown in Figure 1. The isotherm shows a plateau-like region around 10 mN/m, with a corresponding area of 0.90 nm^2/molecule. The area is consistent with the van der Waals area of the zinc complex anion,[5] whereas at collapse the area reduces to about 0.35 nm^2/molecule and matches the cross section of the two octadecyl chains (*ca.* 0.40 nm^2). This implies that at low pressures the cationic chromophores stand on a horizontally aligned zinc complex dianion or alternatively, that a vertically aligned dianion separates the chromophores. In contrast, at high pressures, the greatly reduced area per molecule corroborates a vertical arrangement and thus, the plateau region may be attributed to a structural rearrangements which possibly involves a change from horizontal to vertical alignment of the zinc complex anion.

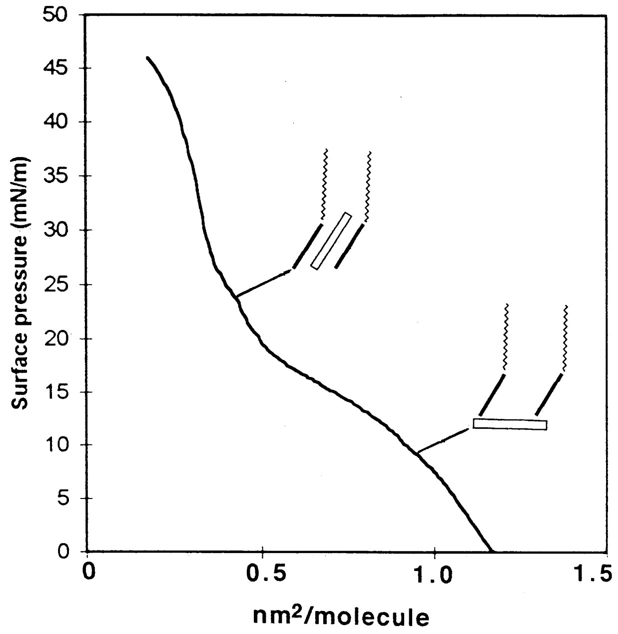


Figure 1. Surface pressure-area isotherm of **1** at the air/water interface. Inserts are the possible arrangements of the molecules at different surface pressure.

The floating film was transferred at constant pressures of 5, 10 and 25 mN/m onto hydrophilically pretreated glass slides [7] on the upstroke at a dipping speed of 5 mm/min. The UV-vis spectra of the LB monolayers transferred at different pressures are almost the same, they all exhibit a broad charge-transfer band of the hemicyanine chromophore with maximum around 484 nm. The absorption maximum is blue shifted by about 30 nm compared with the CHCl$_3$ solution. The monolayer absorbance increases with the increasing of the transferring pressure, for example: 0.0066 at 5 mN/m, 0.0080 at 10 mN/m, 0.0128 at 25 mN/m. 0.0160 at 35 mN/m. This is reasonable, because the area per molecule decreases with the increasing surface pressure. It seems

Table 1. The SHG of the monolayers of **1** at different pressures

Pressure (mN/m)	l (nm)	λ_{max} (nm)	$\chi^{(2)}_{zzz}$ (pmV^{-1})	ϕ (°)	Ref.
5	3.5	484	140	32	This work
10	3.5	484	145	31	This work
25	3.5	485	130	30	This work
35	3.5	480	120	30	This work
35^a	3.4	460	50	36	[7a]

[a] The compound is E-N-octadecyl-4-[2-(4-dibutylaminophenyl) ethenyl]pyridinium $(C_{18}H_{37}SO_4)^-{}_{1/2}(I^-)_{1/2}$. l is the film thickness obtained by molecular modeling.

that the incorporation of the zinc complex gives little affect to the absorbance spectra because its absorption is around 400 nm and very weak.[5]

Second harmonic generation (SHG) was measured in transmission with the Nd:YAG laser beam (λ = 1064 nm) at an angle of 45° to the LB film. The polarization of the fundamental beam was rotated using a half-wave plate and the p-polarized second-harmonic intensity was calibrated against the Maker fringes of a Y-cut quartz reference ($d_{11} = 0.5$ pmV^{-1}). On the assumption that the hemicyanine chromophores have a common tilt angle ϕ, with a random azimuthal distribution and that the second-order molecular hyperpolarizability (β) is dominated by the component along the intramolecular donor-π-acceptor axis, and using the method described in ref.,[7,8] the second-order susceptibility ($\chi^{(2)}_{zzz}$) and tilt angle (ϕ) of the LB film are evaluated and given in Table 1.

The monolayer films of **1** exhibit strong second-order nonlinearities and the SH intensities are almost the same when transferred at different pressures of 5, 10, 25 and 35 mN/m. Typically, the SH intensity is 4 times stronger than its corresponding dye iodide and 7 times stronger than the typical hemicyanine: E-N-docosyl-[4-(2-dimethylaminophenyl)ethenyl]pyridinium bromide, which was first studied by Girling et al.[1a] Apparently, the SH enhancement is not due to the nonlinearity of the zinc complex anion because of its rigid centrosymmetric structure. The enhancement seems to come from the ordered separation of the chromophores by the zinc complex, which may act as both counter-anion and spacer. This is evident from the absorption spectra of the LB films: the absorption maximum of the LB film of the complex dye is blue shifted by about 30 nm compared with its corresponding $CHCl_3$ solution, much smaller than that of the dye iodide (55 nm). The long alkyl chains of the chromophores may pack side-by-side to give an ordered molecular segregation; besides, the dipolar-dipolar interaction of the chromophores is restrained by the large zinc complex anion; furthermore, dependent upon the packing unit, the combination of two chromophores into one molecule probably increases the density of NLO active moieties in the single layer and thus, the SHG from the bis-chromophore LB film is enhanced.

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