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Second—Harmonic Generation from the Monolayers of Rare Earth Complexes $Et_2NC_6H_4CH{=}CHC_5H_4NC_{16}H_{33}Ln(TTA)_4$ (Ln=La、Nd、Dy、Yb)

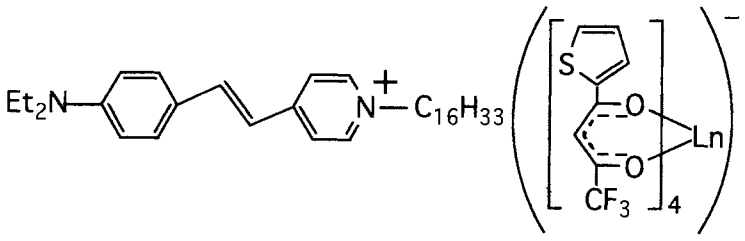
Ke Zhi WANG, Wei JIANG, Chun Hui HUANG,* Guang Xian XU,
Ling Ge XU,† Tian Kai LI,† Xin Sheng ZHAO,†† and Xiao Ming XIE††
State Key Laboratory of Rare Earth Material Chemistry and Applications,
Peking University, Beijing 100871,China
† Institute of Photographic Chemistry, Academia Sinica, Beijing 100101,China
†† Chemistry Department, Peking University, Beijing 100871,China

The LB films of four hemicyanine salts with rare earth complex anions were prepared. From second — harmonic generation experiments, the second — order molecular hyperpolarizability β was evaluated to be about 2×10^{-27}e. s. u. Enhanced second — order nonlinearity compared with the hemicyanine bromide was discussed according to the crystal structure of a model complex. The results of UV —Vis, IR and low angle X—ray diffraction for the LB films are also reported.

The Langmuir—Blodgett (LB) films which exhibit second—order nonlinearity are of potential applications in various areas of opto—electronics including optical communications, electro—optical devices and laser scanning.[1] So far, the research interests have been focused on organic materials, but few of them were on metal coordination complexes.[2] For the first time nonlinear optical and strong fluorescent LB films based on rare earth complexes have been investigated in our laboratory.[3-4]

The monolayer and LB films of hemicyanines have been extensively investigated.[5-12] The second —harmonic generation (SHG) properties of these films showed strong counter—anion dependent and sensitivity to the extent of molecular aggregation.[9-11] In some case, dye molecules were interspersed with an inert phase,[10-12] such as stearic acid, to improve the film—forming properties and reduce inferior J aggregation, but this may cause the danger of phase separation. Here use of the complex anion as both the counterion and spacer may result in an ordered separation of the hemicyanine chromophores without the danger of the phase separation. Apart from these considerations, we are also in a attempt to prepare the magnetic LB films of rare earth complexes. In this paper, the air—water interface behaviors, ultraviolet spectra, IR, low angle X—ray diffraction and second—harmonic generation(SHG) of the LB films for amphiphilic rare earth complexes (*E*) — N — hexadecyl — 4 — (2 — (4 — diethyl — aminophenyl) ethenyl) pyridinium tetrakis (α — thenoyltrifluoroacetonato) lanthanide (Ⅲ) (their

molecular structure are shown as follows) are reported.



(abbreviated to $ALn(TTA)_4$)

where Ln=La, Nd, Dy, Yb

The materials were synthesized according to the previously reported method.[4] Stable floating monolayers formed on pure water subphase (pH 5.4, 18 °C) of NIMA Technology of Joyce—Loeble trough by spreading 50 μl of their chloroform solution (1.07~1.65 mg/ml), were transferred onto hydrophilic substrates of quartz and calcium floride at a constant surface pressure of 15 mN/m.

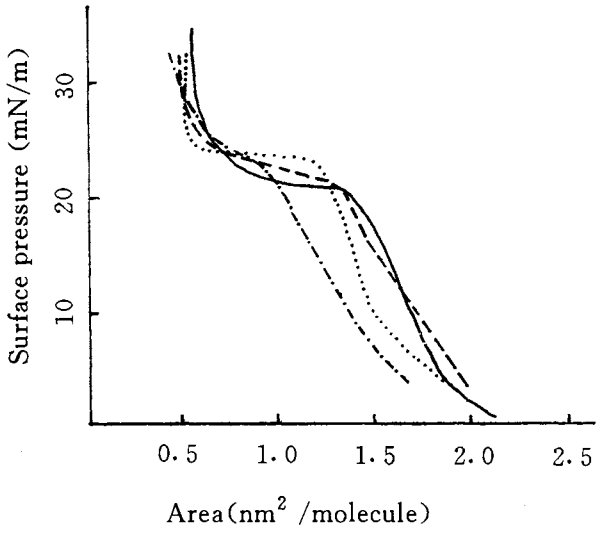


Fig. 1. Surface pressure—area isothems for $ALn(TTA)_4$ La(——); Nd(……); Dy(— • — • —); Yb(— — —).

Their surface pressure — area isotherms (shown in Fig. 1) exhibit two "condense regions", one ocurres at above 20 mN/m, and the other locates between ca. 3~20 mN/m, from which their molecular areas ranged from 1.85~1.95 nm^2 / molecule were obtained by extrapolation to zero surface pressure. This implies that packing within the monolayer is controlled by both hemicyanine cation and complex anion, they are closely packed together "shoulder" to "shoulder".

UV spectrum for chloroform solutions of each of the four complexes peaks at 272 and 336 nm, the former is usually assigned to $\pi \rightarrow \pi^*$ transition in thenyl ring of ligand TTA, but the monolayer films of the complexes are subjected to a large blue shift to 240 nm, this may be due to the strong interaction between the thenyl rings in the film. The latter is generally attributed to $\pi \rightarrow \pi^*$ transition in the carbonyl group of the TTA and basically remain unchanged in the spectra of the films.

Low angle X—ray diffration for 50 layer LB films of Dy complex on CaF_2 substrate exhibits only one peak at 2θ 9.4°, which was resulted from the organized lamellar structure of the film.

IR spectrum for 50 layer LB film of Dy complex is similar to that of powder complex. C=O stretch band of free HTTA (α—thenoyltrifluoroacetone) at 1661 and 1642 cm^{-1} red shifts to 1639 and 1609 cm^{-1} in the spectrum of powder complex and nearly a singlet at 1634 cm^{-1} in that of the LB film of complex. This is indicative of the coordination of oxygen in the carbonyl of TTA and no occurence of free HTTA. Therefore, it can be concluded that the film was formed by the target complex, and that

it can be deposited safely without side reaction such as the hydrolyses of metal ions, but the hydrolyses of metal ions happened in the LB films of rare earth stearate.[13]

SHG was measured in transmission with a Y—cut quartz plate as reference. The light of Nd:YAG laser at 1.064 μm linearly polarised either parallel (p) or perpendicular (s) to the plane of incidence was directed at 45° to the film. P—polarized double—freqency signal intensity $I_{2\omega}^{s\rightarrow p}$ generated by s—polarized incidence and $I_{2\omega}^{p\rightarrow p}$ generated by p—polarized incidence from the monolayers were measured. On assuming that the chromophores have a common tilted angle, Φ, with respect to the surface normal 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, then the Φ was calculated according to equation (1):[9]

$$\tan(\Phi)=[(I_{2\omega}^{p\rightarrow p}/(I_{2\omega}^{s\rightarrow p})^{1/2}-3/2]^{-1/2} \qquad (1)$$

By comparing SH signals from monolayer of the complexes with that from the quartz reference (d_{11}, 0.5pm/V), the susceptibility $\chi^{(2)}$ and β were obtained according to the literature.[9] These values are given in Table 1.

Table 1. the SHG results for the monolayers of ABr and $ALn(TTA)_4$

Compound	$I_{2\omega}^{p\rightarrow p}/I_{2\omega}^{s\rightarrow p}$	Φ(°)	$\chi^{(2)}$(e.s.u)$\times 10^6$	β(e.s.u)$\times 10^{27}$
ABr	7.2	42.6	0.74	0.76
$ALa(TTA)_4$	6.4	44.6	1.3	2.3
$ANd(TTA)_4$	6.5	44.3	1.5	2.2
$ADy(TTA)_4$	6.2	45.1	1.2	2.0
$AYb(TTA)_4$	8.2	40.6	1.2	1.7

It is noteworthy that nonlinearity of the films is complex anion—dependent, β values enhance ca. 2 times compared with hemicyanine bromide. It was reported that SHG intensity is dependent on the extent of molecular aggregations,[9,10] which can be restrained by diluting the chromophore layer with an inert phase such as behenic acid,[9] a 1 : 1 film of the hemicyanine and behenic acid exhibits a large bathochromic shift of the absorption band from 439 nm to 477 nm and 44—fold increase in SHG intensity. This is due in part to resonant enhancement. But, the complexes have nearly same spectral overlap at the harmonic wavelength as the hemicyanine bromide. As a result, the enhanced SH signals are not responsible for the resonant enhancement and most likely due to the use of the bulky rare earth complex anions which force charge separation and cause more charge delocalization in the hemicyanine.

In order to demonstrate this point of view, the crystal structure of metal complex $Me_2NC_6H_4CH=CHC_5H_4NC_2H_5La(TTA)_4$ was determined. The crystal belongs to space group C2/c, with unit cell constants a=2.7356(6), b=1.0414(2), c=2.4032(5) nm, β=129.95(2)°, V=5.249(5)nm^3, Z=4. The packing diagram of the complex illustrated in Fig. 2 is in accord with what discussed above, the bulky complex anion both seperate and screen the dipolar chromophores from one to another. Thus it

is possible for the complex anions in the films to cause more charge delocalization in the hemicyanine.

In conclusion, we prepared the LB films of a rare earth metal complex with large second-order molecular hyperpolarizability. This is most likely due to the fact that chromophores in the film are orderly charge separated by the rare earth complex anions. In the meantime, magnetic rare earth ions were introduced into the film, studies on related properties are under way.

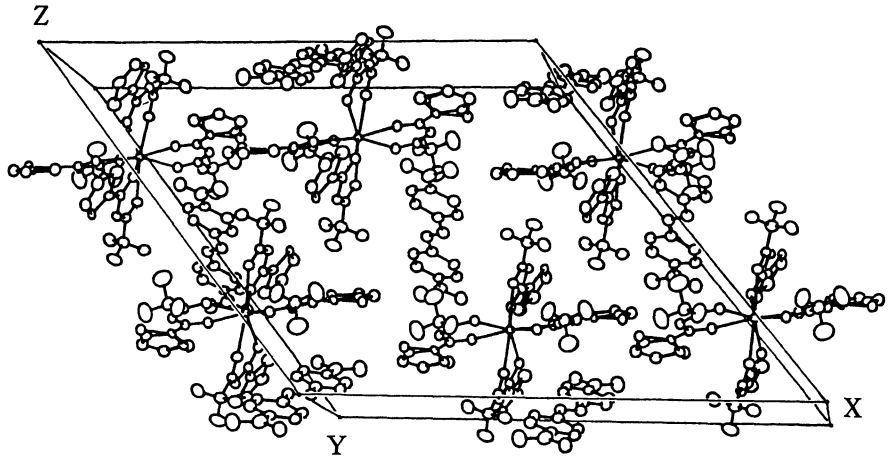


Fig. 2. Packing diagram of complex $Me_2NC_6H_4CH=CHC_5H_4NC_2H_5La(TTA)_4$.

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