Second-Order Nonlinear Optical Langmuir-Blodgett Films Made of a Series of Ferrocenyl Lanthanoid Complexes

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A series of lanthanoid complexes (*E*)-1-ferrocenyl-2-(*N*-hexadecylpyridinium-4-yl)ethylene tetrakis(dibenzoylmethanato)-lanthanoides(III) (La, Nd, Dy and Yb) have been newly synthesized for second-order nonlinear optical LB materials. The monolayer behaviors at the air-water interface, ultraviolet spectra and second-harmonic generation (SHG) of the films have been reported.The values of second-order molecular hyperpolarizability β of the complexes were estimated to be $(1.37\text{-}1.58)\times10^{-28}$ esu.

Organic materials for second-order nonlinear optical Langmuir-Blodgett (LB) films have been intensively investigated.[1,2] However, the LB films based on metal complexes are very rare.[3-6] Previously, using the lanthanoid complexes as the counter ions of hemicyanions, we improved both the film-forming and second-harmonic generation properties.[7,8] Also, probably organic-inorganic superlattice containing lanthanoid complexes was created.[9] Here we reported on the LB films of a series of novel lanthanoid complexes.

Film-forming materials with molecular structures shown in Figure 1, (*E*)-1-ferrocenyl-2-(*N*-hexadecylpyridinium-4-yl)ethylene tetrakis(dibenzoylmethanato)lanthanoides(III) (abbreviated to FcLn(DBM)$_4$, Ln=La, Nd, Dy, and Yb) were synthesized as follows: 1 mmol of La(NO$_3$)$_3$ aqueous solution was added dropwise under vigorous stirring to a mixture of 4 mmol of dibenzoylmethane(HDBM) in 20 ml of ethanol neutralized with 2 ml of NaOH (2.0 mol dm^{-3}) aqueous solution and 1 mmol of (*E*)-1-ferrocenyl-2-(*N*-hexadecylpyridinium-4-yl)ethylene bromide (FcBr).[7] The precipitate formed on cooling was filtered and washed with hot ethanol repeatedly, and then recrystallized in chloroform-ethanol to afford the target complexes with good purity.[10]

The lanthanoid complexes were spread from their chloroform solutions (4.6×10^{-4} mol dm^{-3}) onto a pure aqueous subphase (pH5.6, 18 °C) of a NIMA LB trough. At a constant surface pressure of 25 mN m^{-1}, the floating monolayer films were transferred onto hydrophilic quartz substrates[9] by the vertical dipping method, with a substrate up-stroke (Z type mode) of 2 mm/min. The surface pressure-area isotherms were recorded at a speed of 10 mm/min. The apparatus and methods of spectral and SHG (a Q-switched 1064 nm Nd:YAG laser as fundamental frequency) measurements are same as those described previously.[7]

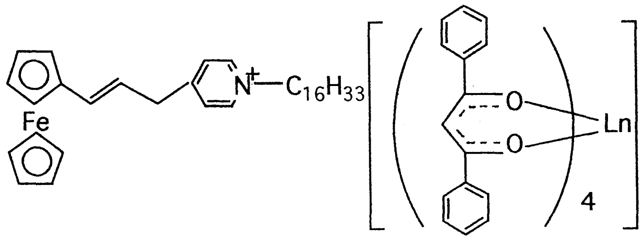

Figure 1. The molecular structure of the FcLn(DBM)$_4$ in which Ln=La, Nd, Dy and Yb.

The surface pressure-area(π-A) isotherms for the four complexes are shown in Figure 2. As can be seen from Figure 2, each exhibits one well-defined solid analog phase. The collapse pressures are above 38 mN m^{-1}; the curves rise steeply on compression of the monolayers, indicating that the complexes have good monolayer-forming properties. The limiting areas, obtained by the extrapolating of the condensed region to π=0 are (1.02-1.11) nm^2/molecule, much larger than that for the FcBr(0.56 nm^2), indicating that packing within the monolayer is governed by both the lanthanoid anions and the ferrocenyl

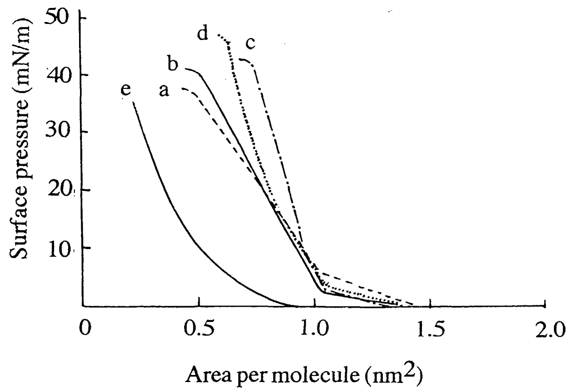

Figure 2. Surface pressure-area isotherms of the FcLn(DBM)$_4$ and FcBr (a) Ln=La (b) Ln=Nd (c) Ln=Dy (d) Ln=Yb (e) FcBr.

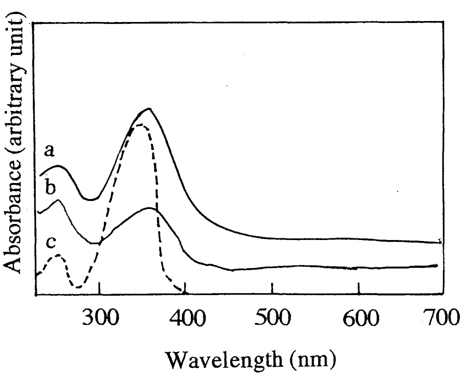

Figure 3. UV-vis spectra (a) FcLn(DBM)$_4$ in CHCl$_3$ (b) 5-layer FcLn(DBM)$_4$ film (c) HDBM in CHCl$_3$.

cation, namely, the four complexes have approximately the same molecular arrangements, the "shoulder" by "shoulder" configuration of the lanthanoid complex anion and the ferrocenyl cation within their monolayer films.

Figure 3 shows the superposition of UV-visible spectra for the lanthanoid complex in $CHCl_3$, the 5-layer LB film on a quartz substrate and HDBM in $CHCl_3$. The ultraviolet spectra of the complexes in chloroform solution and their corresponding LB films are very similar, exhibiting two peaks centered at approximately 250 and 344 nm respectively, which is the characteristic absorption of ligand HDBM. The former peak which is usually assigned to π–π^* transition on aromatic ring remain unchanged in the spectra of $FcLn(DBM)_4$; the latter one, ascribed to π–π^* transition on carbonyl, are subjected to a small red shift to 349 nm. The UV absorption of ferrocenyl counter cation is obscured by the strong absorption of complex anion $Ln(DBM)_4$. According to our previous result,[7] H-aggregations exist in the films of the FcBr and FcI. However, when replacing Br^- or I^- by $Ln(DBM)_4$, we found that there is no evidence of H-aggregation because large complex anions take a role of segregation of the chromophores. Also, the complexes $FcLn(DBM)_4$ have better transparency in double-frequency region (532 nm) than the hemicyanine[9] and azo congener,[11] suggesting that $FcLn(DBM)_4$ are promising candidates for applications in nonlinear optical devices.

On the assumption that the chromophores have a identical tilt 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 following equation can be obtained:[7-9]

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

In which $I_{2\omega}(p\rightarrow p)$ is p-polarized double-frequency signal intensity with p-polarized incidental fundamental light; $I_{2\omega}(s\rightarrow p)$ is p-polarized double-frequency signal intensity with s-polarized incidental fundamental light. By the comparison of polarization-dependent SH signals from the monolayer films with that from quartz reference (d_{11}, 0.5 pm V^{-1}), the susceptibility $\chi^{(2)}$ and β were then derived using eq. (2) according to the literatures.[12,13]

$$\chi^{(2)}=Nf_{2\omega}(f_{\omega})^2\beta \qquad (2)$$

The results are given in Table 1. It is noteworthy that the β for the lanthanoid complexes 1.3 times that for FcBr.[7] Because the monolayers of the complexes hardly absorb at the fundamental region, the enhanced nonlinearity is obviously not due to the resonant enhancement and most probably due to the use of the bulky lanthanoid complex anions which force charge separation and cause more charge delocalization in the ferrocenyl chromophores.[9]

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Table 1. Film-Forming parameters and SHG results of the complexes $FcLn(DBM)_4$

Ln	Area per molecule (nm^2)	Φ (deg.)	$\chi^{(2)}$ $\times 10^{-7}$ (esu)	β $\times 10^{-28}$ (esu)
La	1.11	38.5	2.3	1.58
Nd	1.02	45.6	2.2	1.37
Dy	1.03	40.1	2.4	1.50
Yb	1.02	39.8	2.9	1.44

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10 Analysis Calcd for $C_{93}H_{92}NO_8FeLa$: C, 72.23; H, 5.95; N, 0.91%. Found: C, 71.96; H, 6.07; N, 0.87%. Analysis Calcd for $C_{93}H_{92}NO_8FeNd$: C, 71.98; H, 5.93; N, 0.90%. Found: C, 71.74; H, 6.17; N, 0.84%. Analysis Calcd for $C_{93}H_{92}NO_8FeDy$: C, 71.15; H, 5.87; N, 0.89%. Found: C, 71.14; H, 6.01; N, 0.87%. Analysis Calcd for $C_{93}H_{92}NO_8FeYb$: C, 70.67; H, 5.83; N, 0.89%. Found: C, 70.39; H, 5.97; N, 0.87%. $\nu_{C=O}$ (KBr): 1597(La); 1598(Nd); 1600(Dy); 1599 cm^{-1} (Yb).

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