CHEMISTRY OF MATERIALS

VOLUME 7, NUMBER 6 JUNE 1995

Communications

Second-Order Nonlinear Optical Langmuir–Blodgett Films Based on a Series of Azo Rare-Earth Coordination Compounds

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Received December 21, 1994
Revised Manuscript Received April 3, 1995

LB materials are attracting growing interest in the field of integrated optics because of their variable layer architecture, the exact control of thickness and the high nonlinear optical coefficients especially for second-order processes.[1] The active components in these materials typically consist of conjugated electron systems connecting terminal electron-donor and electron-acceptor moieties. By incorporating different end groups and changing the type of conjugating group, the nonlinear optical activity of a particular system can be adjusted with some degree of predictability.[2] Azo dyes are of particular interest because their system provides excellent conjugation[3] that is necessary for high molecular susceptibilities. Recently, using a lanthanide complex as the counterion of the hemicyanine and spacer within the LB film, we not only improved the film-forming and second harmonic generation properties but also may have created an organic–inorganic superlattice.[4] Here, by combining the azo linker with a strongly electron-donating dihexadecylamino and an electron-accepting pyridinium group, we design and synthesize a new kind of azo dye in which lanthanide complex anions are used as the counterions of an azo cation and also spacers within the LB films, (*E*)-1-methyl-4-(2-(4-(dihexadecylamino)phenyl)azo)pyridinium tetrakis(dibenzoylmethanato)lanthanides(III) (La, Nd, Dy, and Yb). From second harmonic generation (SHG) experiments, the values of second-order molecular hyperpolarizability β of the compounds were estimated to be (1.20–3.03) $\times 10^{-27}$ esu comparable to the largest values known for azo dyes. The air–water interface behaviors and the UV–vis spectra of the four rare-earth complexes are also reported.

The synthetic approach of the four complexes is summarized in Scheme 1. Intermediate products 1 and 2 were synthesized according to the modified literature methods[5,6] and purified by column chromatography on silica gel with petroleum and 1:1 (v/v) petroleum–ethyl acetate as eluents, respectively. Purity was verified by 400-MHz ^{1}H nuclear magnetic resonance spectroscopy. The final products **4** were purified by recrystallization in ethanol–water. Elemental analyses for $C_{104}H_{121}O_8N_4La$: Found: C, 73.76; H, 7.34; N, 3.24. Calcd: C, 73.76; H, 7.15; N, 3.31. $C_{104}H_{121}O_8N_4$-

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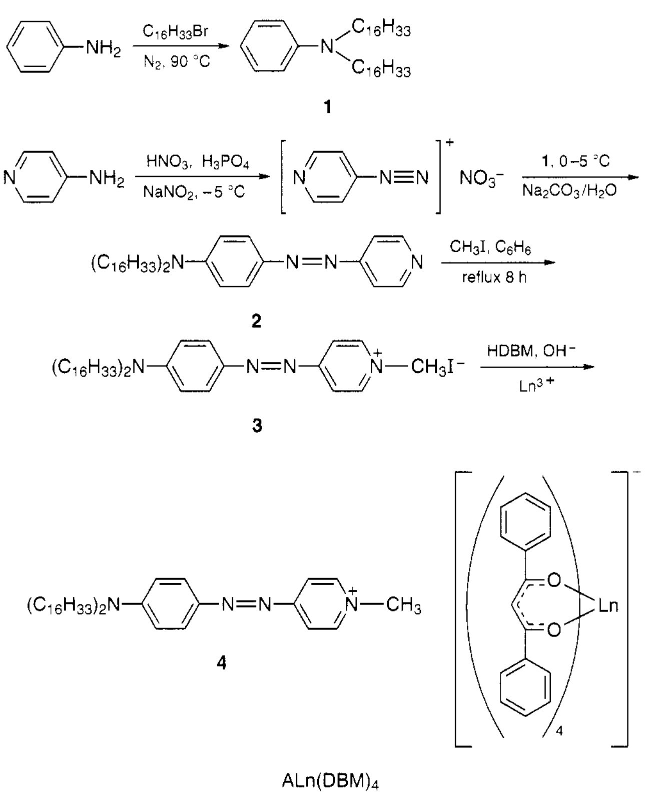
Scheme 1. Synthetic Approach to the Rare-Earth Complexes



Nd: Found: C, 73.30; H, 7.10; N, 3.22. Calcd: C, 73.53; H, 7.13; N, 3.30. $C_{104}H_{121}O_8N_4Dy$: Found: C, 72.60; H, 7.04; N, 3.20. Calcd: C, 72.75; H, 7.05; N, 3.26. $C_{104}H_{121}O_8N_4Yb$: Found: C, 72.11; H, 7.05; N, 3.22. Calcd: C, 72.30; H, 7.01; N, 3.24. For the lanthanum complex, IR (KBr) 2852, 2923 cm^{-1} (ν_{C-H}); 1598 cm^{-1} ($\nu_{C=O}$); 1515 cm^{-1} ($\nu_{C=C}$). UV–vis ($CHCl_3$): λ_{max} 250, 345, and 580 nm. The details of synthesis and characterization of the rare-earth complexes will be published elsewhere.[7] Stable floating monolayers, formed at the pure water subphase (pH 5.6, 18 °C) of a Joyce–Loabl model computer-controlled Langmuir–Blodgett trough by spreading their freshly prepared chloroform solution ((3.7–7.1) × 10^{-4} mol/L), were compressed to 30 mN/m and transferred onto hydrophilically treated fused quartz slides in Z-type mode, at a rate of 5 mm/min. The surface pressure–area isotherms for the four complexes are shown in Figure 1. Each of four complexes exhibits only one solid analogue phase. The collapse pressures are above 42 mN/m, suggesting that the complexes have good film quality. As can be seen from Figure 1 and Table 1, the four complexes have approximately the same molecular areas, indicating the same molecular arrangement within their Langmuir films. The limiting area obtained by the extrapolation of the condensed region to a surface pressure of zero are between 1.30 and 1.57 nm^2/molecule. They are comparable to the sum of area (0.98 nm^2) for the complex anions $Ln(DBM)_4$ and tight packing area (0.4 nm^2) of the two hydrocarbon chains,[8] suggesting that the azo cation and the complex anion are closely packed together "shoulder-to-shoulder".[4]

Figure 2 shows the superposition of UV–visible spectra for the lanthanide complex in $CHCl_3$, the LB film on a quartz substrate, and HDBM in $CHCl_3$. The ultraviolet regions of UV–visible spectra of the complexes in chloroform solution are very similar, exhibiting two peaks centered at 250 and 345 nm, which is the characteristic absorption of ligand HDBM. However, there is only one broader peak centered at ca. 290 nm for the LB film. For the visible regions of the complexes in $CHCl_3$, each of them exhibits one peak at ca. 570 nm due to the charge transfer of azo cation and blue-shifts to 550 nm in the corresponding LB films. These differences are indicative of a lack of intermolecular interaction in the films, as supported by the Figure 2 of ref 4. In addition to the monolayer investigations, preliminary experiments show that multilayers can be prepared via the LB technique by successive deposition of the complex monolayers. Figure 3 shows the UV–visible spectra of LB films of different numbers of layers. The intensities of the absorption spectra show a linear dependence on the number of transferred LB layers (Figure 4), indicating a homogeneous transfer of the multilayers.

The setup of second harmonic generations (SHG) had been described previously.[4] The values of susceptibility $\chi^{(2)}$, the second-order molecular hyperpolarizability (β), and the tilt angle (Φ) to the normal of the film surface were deduced according to the literature methods,[8,9] using refractive index $n_{2\omega} = 1.7$ and $n_{\omega} = 1.5$.[10] The results are given in Table 1 and compared with compounds **5** and **6** reported. As seen from Table 1, the β values of the four complexes are comparable when the experimental errors are taken into account and much larger than those of compounds **5** and **6**. The enhancements in β values may partly originate from the introduction of the rare-earth complex anions[4] and resonance enhancement caused by the absorption of the films at the second harmonic frequency of 532 nm. It should be emphasized that β values were derived based on the SHG data of monolayer films. The monolayer films of the lanthanide complexes we studied have not strong absorption at 532 nm (absorbance is only 0.01 for film area 3 cm^2) due to the low surface densities of the chromophore in the films. This can be easily understood by the large molecular areas of the lanthanide complexes. Also, the films of the four complexes have nearly same peak positions in visible region as that of compound **6**. As a result, the strong push–pulling characteristics of the azo chromophore we studied makes a dominant contribution to the appreciable enhancement in β values of the lanthanide complexes over compounds **5** and **6**. Clearly, the electron-donating and -accepting abilities are both reinforced as the dimethylamino group in compound **5** is changed into dihexadecylamino in the complexes we studied and the cyanine group changed to positively charged pyridinium—the strongest electron-acceptor group so far reported.[8] Furthermore, the presence of two hydrophobic tails on the LB molecules instead of one is expected

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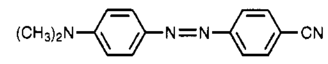
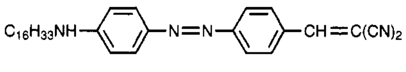
Table 1. Film-Forming Parameters and SHG Results

materials	area per molecule (nm^2)	collapse pressure (mN/m)	Φ (deg)	l^a (nm)	$\chi^{(2)} \times 10^{-6}$ (esu)	$\beta \times 10^{-27}$ (esu)	ref
ALa(DBM)$_4$	1.44	42	39.2	2.90	1.67–3.11	1.63–3.03	this work
ANd(DBM)$_4$	1.35	49	45.2	2.82	1.38–2.56	1.20–2.20	this work
ADy(DBM)$_4$	1.57	49	46.0	2.80	1.26–2.34	1.30–2.42	this work
AYb(DBM)$_4$	1.30	45	41.4	2.88	1.69–3.13	1.45–2.69	this work
compound **5**^{b}						0.36	11
compound **6**^{b}						0.23–0.50	12

[a] l is the film thickness per layer obtained by molecular modeling.
[b] compound **5**:



compound **6**:



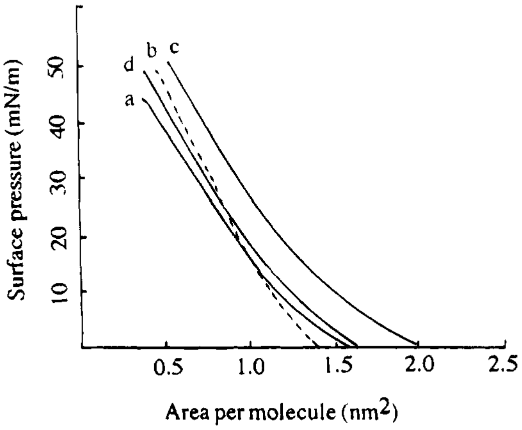


Figure 1. Surface pressure–area isotherms: (a) ALa(DBM)$_4$; (b) ANd(DBM)$_4$; (c) ADy(DBM)$_4$; (d) AYb(DBM)$_4$.

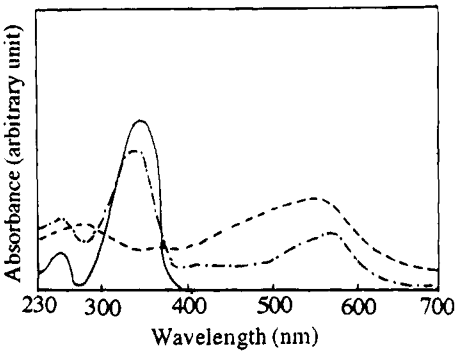


Figure 2. UV–vis spectra: (—) HDBM in CHCl$_3$; (– · –) ALa(DBM)$_4$ in CHCl$_3$; (– – –) LB film (two layers) of lanthanide complex.

to increase the stability and molecular regularity of the films. The films, stored in ambient atmosphere at room temperature for more than 3 weeks, did not show appreciable change in $\chi^{(2)}$ values, showing the good stability of the films. The detailed studies on the stability of this kind of films in different atmosphere will be published elsewhere.[13]

In summary, the rare-earth complexes we studied are a new kind of azo dye with very large second-order

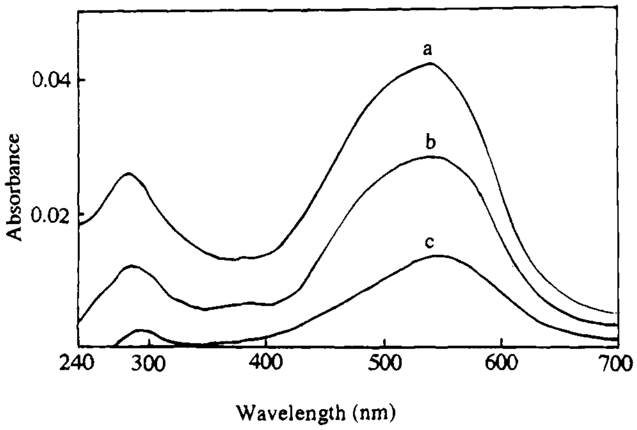


Figure 3. UV–visible spectra of LB films of ALa(DBM)$_4$: (a) five layers; (b) three layers; (c) one layer.

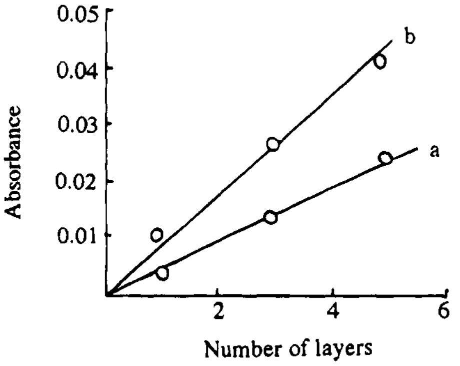


Figure 4. Absorbance change *vs* the number of layers of ALa(DBM)$_4$: (a) λ = 290 nm; (b) λ = 550 nm.

molecular hyperpolarizability β comparable to the highest values known for organic and organometallic compounds. Along with their good film-forming properties, they may be attractive for the application in future optical devices.

Acknowledgment. This project was supported by The Climbing Program, a National Fundamental Research Key Project, and NNSFC.

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