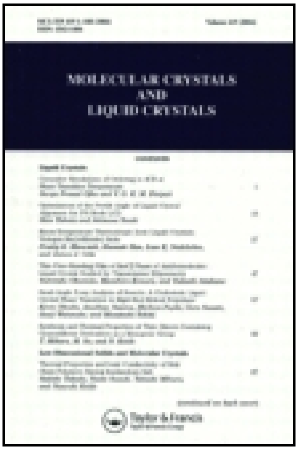

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Langmuir-Blodgett Films of Fullerene Containing β-Diketone Derivatives and Their Coordination Complexes with Rare Earth Metal Ions

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Langmuir-Blodgett Films of Fullerene Containing β-Diketone Derivatives and their Coordination Complexes with Rare Earth Metal Ions

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Two new fullerene-containing β-diketone derivatives are synthesized. Their Langmuir and Langmuir-Blodgett (LB) films are prepared on water and rare earth metal ion solution subphases. The π-A isotherms, UV-Vis and XPS spectra indicate the interaction of rare earth ions with β-diketone moieties.

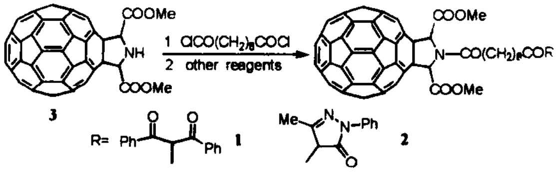
Keywords: fullerene; β-diketone; LB films; rare earth

INTRODUCTION

Studies about the Langmuir and LB films of fullerene derivatives have attracted extensive attention because of their fascinating physical and chemical properties. Several groups reported the formation of stable Langmuir and LB films of fullerene derivatives.[1-3] However, investigations about the effect of metal ion subphases on the formation of fullerene derivatives are still rare. [4, 5] Metal ions in the subphases have been found to have an enormous influence on the Langmuir films. Incorporation of metal ions into LB films can improve applications of LB films as sensors, in catalytical systems[6] and in microelectronical devices.[7] Here we report the syntheses of two new fullerene-containing β-diketone compounds **1** and **2** and their interaction with rare earth ions in Langmuir and LB films.

EXPERIMENTAL

Compounds **1** and **2** are synthesized in a similar procedure as shown in Scheme 1. The following describes the synthesis of compound **1** as an example.



SCHEME 1

Sebacoyl chloride (300 mg, 1.26 mmol) was added at room temperature to a stirred solution of **3** (85 mg, 0.10 mmol)[8] and pyridine (2 ml) in freshly distilled dry toluene (100 ml), which was under nitrogen and protected from light with a tin foil. After the mixture was stirred for 24h, dibenzoylmethane (600 mg, 2.68 mmol) and $Ca(OH)_2$ (800 mg, 10.8 mmol) were added at room temperature to the reaction mixture and stirred for another 3h. After centrifugation and neutralization with acetic acid, The red-brown solution was evaporated. The residue was extracted with toluene and chromatographed on silica gel. Toluene first eluted a little portion of unreacted **3**. The product band was washed out with chloroform. The solvent was evaporated and the residue was washed with methanol and petroleum ether and then dried under vacuum as a brown powder **1** (86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30-1.80 (m, 10H), 1.80-2.00 (m, 2H), 2.54 (t, 2H, J = 7.2Hz), 2.82 (m, 4H), 3.95 (s, 6H), 6.57 (s, 2H), 7.22 (m, 4H), 7.41(m, 4H), 7.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.54, 196.04, 187.28, 172.45, 169.04, 153.60, 150.24, 147.55, 146.45, 146.41, 146.18, 146.14, 145.79, 145.67, 145.60, 145.56, 145.53, 145.41, 145.35, 144.51, 144.45, 144.29, 143.24, 143.17, 142.78, 142.70, 142.31, 142.14, 142.11, 141.88 (broad), 141.85, 140.25, 139.66, 138.94, 137.47, 136.09, 134.14, 133.00, 131.62, 129.34, 128.38, 128.33, 128.20, 114.29, 71.36, 70.22, 52.97, 37.28, 34.36, 29.20, 25.54, 25.03. MALDI-TOF (m/z): 1292 (100%, M^++Na). UV-Vis: 257, 314, 430 nm. Anal.Calcd. for $C_{91}H_{35}O_8N \bullet (0.5H_2O)$:C% 85.44; H% 2.84; N% 1.09; found: C% 85.17; H% 2.54; N% 1.29.

Solutions of compounds **1** (1.57×10^{-5} M) and **2** (1.62×10^{-5} M) in chloroform were spread on pure water subphase and 2×10^{-4} M rare earth ions M^{n+} (M = Ce, Nd and Tb, n = 4 or 3). The absorption spectra were measured by a Shimadzu UV-3100 spetrophotometer. The XPS spectra were obtained with an ESCALAB MARK II photoelectron spectrometer.

RESULTS AND DISCUSSIONS

The π-A isotherms of Langmuir films of **1** and **2** under different subphases are shown in Figure 1. On pure water, compounds **1** and **2** collapse at surface pressure about 30 and 25 mN/m respectively. The observed limiting areas, 81.8 Å^2/molecule for **1** and 88.9 Å^2/molecule for **2**, are relatively small compared with the values of 96 for $C_{60}O$.[9] When a metal ion solution is used as the subphase, significant changes are observed on the isotherms (shown in Figure 1). For compound **2**, limiting areas increase up to 98, 99 and 109 Å^2/molecule for Tb^{3+}, Nd^{3+} and Ce^{4+} subphase respectively. As to compound **1**, when Tb^{3+} and Ce^{4+} are added to the subphase, limiting areas increase up to 91 and 102 Å^2/molecule respectively. The values are close to the theoretical value for these compoundes indicating good monolayer formation. The collapse pressure of the metal ion subphases increases for compound **2** compared to pure water subphase. The opposite is observed for compound **1**. This may be due to the different coordination property of the β-diketone moieties. Compared with monolayers in Tb^{3+} and Nd^{3+} subphases, that on Ce^{4+} subphase collapses at a little higher surface pressure for both **1** and **2**. This is in agreement with the relatively higher positive charge of Ce^{4+} and thus stronger interaction.

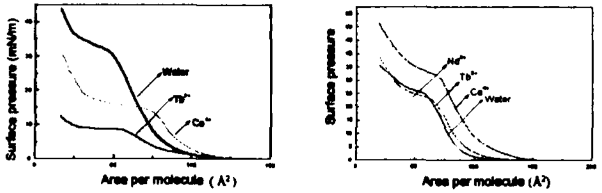


FIGURE.1. Π-A isotherms of 1 (left) and 2 (right) on different subphases
(2 × 10^{-4} M metal salt solutions and pure water), 293K ± 1 K

Langmuir films of compound **2** under different subphases are transferred onto hydrophilic pretreated substrates by compressing the monolayer film to 15 mN/m and then upwardly withdrawing at 3 mm/min. The LB films of **2** on different subphases show similar UV-Vis spectra. Although rare earth ions in the subphase affect the molecule area at the air-water interface, they do not alter the UV-Vis absorption spectra of the films. This indicates that rare earth ions are not close enough to the C_{60} moiety to affect its electronic structure. In the solution of comp-

-ound 2 in $CHCl_3$, three absorptions around 257, 314 and 431 nm are found. However, in the spectra of its LB films, the 257 and 314 nm peaks red-shift to 269 and 343 nm. The absorption at 431 nm almost disappears. These alterations in the absorption are common in fullerene derivative LB films, which may be due to the electronic interaction between the C_{60} moieties of adjacent molecules.

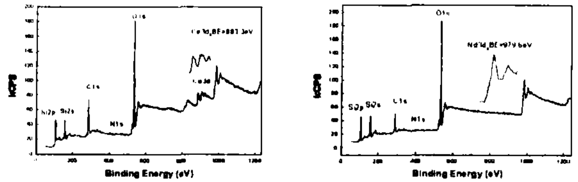


FIGURE 2 XPS spectra of monolayer films of compound **2** on glass plate deposited from Ce^{4+} and Nd^{3+} subphase

X-ray photoelectron spectroscopy (XPS) measurements reveal that the atoms present in the films are carbon, oxygen, nitrogen and the incorporated rare earth metal. Figure 2 shows the XPS spectra of LB films of compound **2** in the Ce^{4+} and Nd^{3+} subphases, from which the presence of Ce^{4+} and Nd^{3+} in the films can clearly be seen. The binding energies of Ce^{4+} and Nd^{3+} are 883.3 eV (Ce $3d_5$) and 979.6 eV (Nd $3d_5$) respectively.

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References

[1] D. Felder, *et al. Angew. Chem. Int. Ed.*, **39**, 201 (2000).
[2] L. Cardullo, *et al. Langmuir.*, **14**, 1955 (1998).
[3] J. F. Nierengarten, *et al. Tetrahedron Letters*, **39**, 5747 (1998).
[4] W. Zhang, *et al.Langmuir*, **15**, 6921 (1999).
[5] S. P. Wang, *et al. Langmuir*, **13**, 1672 (1997).
[6] J. L. Rigaud, *et al. Nature*, **392**, 479 (1998).
[7] M. Fujihira and H. Yamada, *Thin Solid Films*, **160**, 125 (1988).
[8] L.B. Gan et al, *J. Org. Chem.*, **61**, 1954(1996).
[9] N. C. Maliszewskyj, *et al. Langmuir*, **9**, 1439 (1993).