

Synthesis of Novel Amphiphilic Poly(ester-amine) Dendrimers and Their Recognition of Hg^{2+} at the Air/Water Interface

SHEN, Liang^a(申亮) LI, Fu-You^b(李富友) SHA, Yao-Wu^{*a}(沙耀武)
PAN, Zheng-Zheng^a(潘铮铮) HONG, Xiao-Yin^a(洪啸吟) HUANG, Chun-Hui^b(黄春辉)

^a Department of Chemistry, Tsinghua University, Beijing 100084, China

^b State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University, Beijing 100871, China

Two novel amphiphilic poly(ester-amine) dendrimers were synthesized and characterized by ^1H NMR, ^{13}C NMR and IR spectra. Their properties of Langmuir film were investigated at the air/water interface. The relationship between the surface pressure and area isotherms of the dendrimers was found to be dependent on the nature of subphases. Interaction between HgCl_2 and the dendrimers was observed, indicating that the amphiphilic dendrimers could act as a sensor for Hg^{2+} .

Keywords amphiphilic poly(ester-amine) dendrimer, Langmuir films, ion recognition

Introduction

Dendrimers can provide powerful building blocks for the construction of giant macromolecular and supramolecular systems with complex architecture and precise shape and functionality.¹ In the past years, a wide range of “designer” dendrimers have been developed. Their chemical and physical properties in solution have also been studied.² Recently, the application of dendrimers in surface and interface chemistry has grown quickly.³ In order to probe interfacial behaviors such as shape, compressibility and the localization of end groups at air/water interface, several research groups have studied the property of Langmuir monolayer of amphiphilic dendrimers.⁴ However, the dependence of dendrimer Langmuir film property on different subphases has not yet been reported. We have reported the synthesis of new aliphatic poly(ester-amine) dendrimers bearing peripheral hydroxyl or acrylate groups.⁵ Herein, two novel amphiphilic dendrimers were designed and synthesized and their behaviors at air/water interface with different subphases were studied.

Results and discussion

Synthesis and characterization of amphiphilic dendrimers

Two different generations of poly(ester-amine) den-

drimers, PEA-dendri-(OH)_n, **G_{OH}1** with four peripheral hydroxy groups and **G_{OH}2** with eight peripheral hydroxy groups, were acylated respectively with heptadecanoyl chloride and the corresponding **G_R1** and **G_R2** amphiphilic dendrimers were obtained (Scheme 1). Structural characterization of the products with ^1H NMR, ^{13}C NMR and IR spectroscopy showed complete acylation of the hydroxyl groups. Dendrimer **G_R1** was further characterized with mass spectroscopy and the calculated mass peak was shown. No defect due to incomplete acylation could be observed in the mass spectrum. For **G_R2**, no proper mass spectrum could be observed, probably due to the low ionization degree of the high-molecular-mass compound during the ESI-MS measurement. All dendrimers showed good solubility in apolar organic solvents.

Characterization of LB monolayer

The surface pressure-area (π -A) isotherms of two novel amphiphilic dendrimers' s monolayer on subphase were measured and shown in Fig. 1. It could be seen that the π -A isotherms of the dendrimer monolayer were distinctive with the change of generation, and the limiting molecular areas were obtained by extrapolating the vertical rise of the curve down to zero surface pressure. On the pure water, the collapse pressures of **G_R1** (isotherm a) and **G_R2** (isotherm b) were 53.2 and 46.0 $\text{mN}\cdot\text{m}^{-1}$ respectively, which revealed that the dendrimers have good film formation property at the air/water interface. The limiting molecular areas of **G_R1** and **G_R2** were 0.86 and 1.52 nm^2 , respectively, extrapolated from the π -A curves under 35 $\text{mN}\cdot\text{m}^{-1}$. The areas per end group of the dendrimer **G_R1** and **G_R2**, with four and eight long alkyl chains, were 0.215 and 0.190 nm^2 respectively. They are only slightly larger than the typical 0.18 nm^2 cross-sectional area of an alkyl chain. This suggested the tight parallel arrangement of hydrophobic long chain and the insertion of hydrophilic

* E-mail: shayw@mail.tsinghua.edu.cn; Tel.: 86-10-62795866, Fax: 86-10-62795866

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Scheme 1 Brief synthetic procedures of the amphiphilic dendrimers

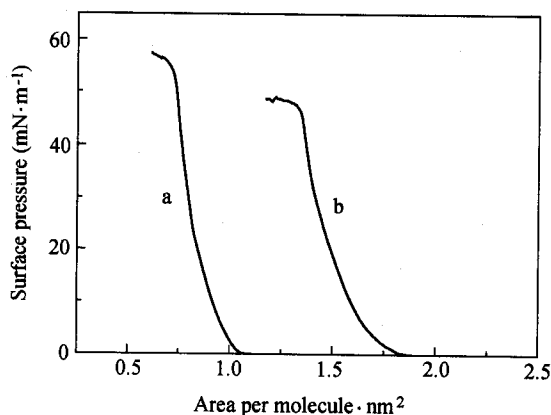
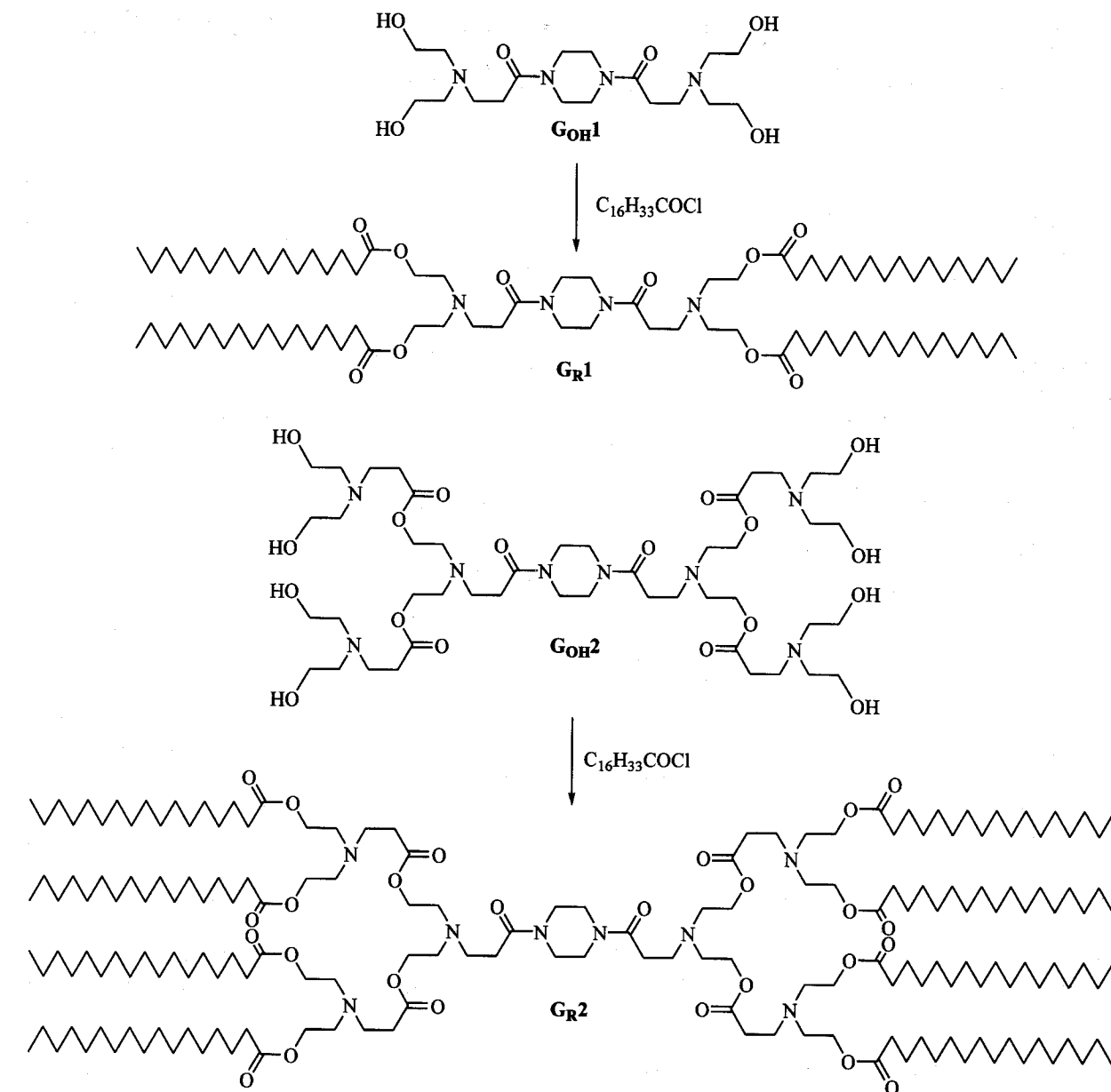


Fig. 1 Surface pressure versus area isotherms of G_{R1} (a) and G_{R2} (b) at the air/water interface at $(20 \pm 1) ^\circ C$.

part into water. Similar results have been reported.^{4a}

As shown in Fig. 2, the limiting areas and the collapse pressures of G_{R2} were dependent on the changes of the subphase. When the concentration of $HgCl_2$ in subphase reached $10^{-7} \text{ mol} \cdot \text{L}^{-1}$, the limiting area increased to 1.56 nm^2 and the collapse pressure increased to $47.5 \text{ mN} \cdot \text{m}^{-1}$ (isotherm d). Increasing the concentration of $HgCl_2$ to $1 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ and $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ would result in an expansion of limiting area to 1.64 nm^2 and to 1.75 nm^2 respectively, and the collapse pressure increased to $48.7 \text{ mN} \cdot \text{m}^{-1}$ and $49.6 \text{ mN} \cdot \text{m}^{-1}$ (isotherms e and f, respectively). However, further increasing of $HgCl_2$ concentration to $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ in the subphase would show little effect on the limiting area and the collapse pressure (isotherm g). These experimental results indicated that the addition of $HgCl_2$ into the water subphase could change the dendrimer film properties in a certain range.

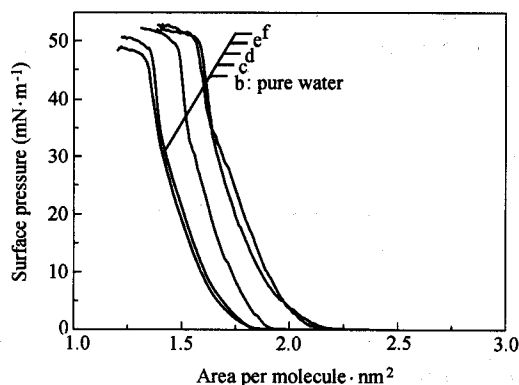


Fig. 2 Surface pressure versus area isotherms of **GR2** at the air/water interface with different subphases. b: pure water; c: $[\text{HgCl}_2] = 10^{-7} \text{ mol} \cdot \text{L}^{-1}$; d: $[\text{HgCl}_2] = 10^{-6} \text{ mol} \cdot \text{L}^{-1}$; e: $[\text{HgCl}_2] = 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; f: $[\text{HgCl}_2] = 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

XPS measurements

To further clarify this interaction, XPS technique was used to study the binding energy of dendrimer with Hg atoms under different conditions. It could be seen in Fig. 3 that the dendrimer-**GR2** film showed characteristic peak of $\text{Hg}4f_{7/2}$, but the binding energy of $\text{Hg}4f_{7/2}$ was changed from 100.1 eV for the pure HgCl_2 (Curve HgCl_2) on ITO electrode to 102.0 eV for the dendrimer-**GR2** film, which suggested that the coordination surrounding of Hg atom had been changed.

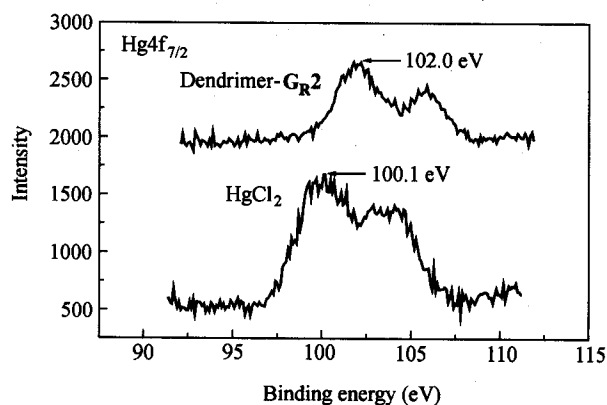


Fig. 3 XPS spectra of Hg^{2+} in the dendrimer **GR2** LB film and in HgCl_2 .

In summary, two novel amphiphilic dendrimers were synthesized and characterized by ^1H NMR, ^{13}C NMR and IR spectra. The Langmuir film property was investigated at the air/water interface. The relationship between the surface pressure and area isotherms of the dendrimers was dependent on the HgCl_2 concentration of subphase. An interaction between dendrimer monolayer and HgCl_2 was observed, which indicated that the amphiphilic dendrimer could act as a sensor for Hg^{2+} .

Experimental

General methods and materials

The melting points were measured with micro melting point apparatus and the thermometer was uncorrected. The spectra of ^1H NMR and ^{13}C NMR were recorded on Bruker AM 500 instrument and TMS was used as internal standard for chemical shifts. ESI mass spectra were recorded with Bruker Esquire-LC ion trap mass spectrometer operated in positive ion mode. IR spectra were recorded with Nicolet 560 FTIR spectrophotometer. The model 622 NIMA Langmuir-Blodgett trough was employed for the Langmuir monolayer study. Water obtained from an EASY pure RF system was used as the subphase (R ca. $18 \text{ M}\Omega \cdot \text{cm}$, pH ca. 5.6). The substrates (ITO slide and quartz) were all pretreated as following: the plate was firstly immersed in a saturated sodium-methanol solution for 2 d and then thoroughly rinsed with pure water under ultrasonication for several times. X-Ray photoelectron spectra (XPS) were measured with VG ESCA LAB 5 Multitechniques photoelectron spectrometer (VG Co., UK), and Al was used as the target of X-ray source.

CH_2Cl_2 was distilled over P_2O_5 . Pyridine was distilled over KOH. Heptadecanoyl chloride (Aldrich, 98%), 4-dimethylaminopyridine (DMAP) (Acros, 99%) and chloroform were used as received. Poly(ester-amine)-dendrimer(OH) $_n$ ($n = 4, 8$) were prepared according to the reported method.⁵

Typical procedure for the preparation of heptadecanoyl-functionalized dendrimers (**GR2**)

Poly(ester-amine)-dendrimer(OH) $_8$ (210 mg, 0.2 mmol) and 6 mg (0.049 mmol) of DMAP were dissolved in 10 mL dry CH_2Cl_2 and then added 1 mL of dry pyridine. Heptadecanoyl chloride (693 mg, 2.4 mmol) dissolved in 5 mL of dry CH_2Cl_2 was added slowly over a period of 15 min at room temperature. The reaction mixture was stirred for 15 h at 39°C and then diluted with 20 mL of CH_2Cl_2 . The organic phase was extracted with $2 \times 20 \text{ mL}$ of NaHSO_4 ($1 \text{ mol} \cdot \text{L}^{-1}$), $2 \times 20 \text{ mL}$ of Na_2CO_3 (10%) and $1 \times 20 \text{ mL}$ of brine, and then dried over MgSO_4 . After distillation of solvent and column chromatography separation on silicon gel, the pure product was obtained as white wax solid (**GR2**, 355 mg, 58%).

GR1 White powder, yield 64%, m. p. $53\text{--}55^\circ\text{C}$; ^1H NMR (CDCl_3 , 500 MHz) δ : 0.88 (t, 12H, CH_3), 1.26 (brs, 102H, CH_2), 1.43 (s, 2H, CH_2), 1.61 (s, 8H, $\text{O} = \text{CCH}_2\text{CH}_2\text{CH}_2$), 2.29–2.33 (m, 8H, $\text{O} = \text{CCH}_2\text{CH}_2\text{CH}_2$), 2.52 (t, 4H, $\text{O} = \text{CCH}_2\text{CH}_2\text{N}$), 2.80 (s, 8H, $\text{O} = \text{CCH}_2\text{CH}_2\text{N}$), 2.94 (t, 4H, $\text{O} = \text{CCH}_2\text{CH}_2\text{N}$), 3.49–3.66 (q, 8H, $\text{NCH}_2\text{CH}_2\text{N}$, piperazine), 4.13 (s, 8H, $\text{O} = \text{COCH}_2\text{CH}_2\text{N}$); ^{13}C NMR (CDCl_3 , 500 MHz) δ : 178.82, 173.70, 62.07, 53.00, 50.83, 45.25, 41.57, 34.24, 33.99, 31.90, 31.58,

30.30, 29.67, 29.48, 29.43, 29.28, 29.24, 29.17, 29.09, 24.92, 24.73, 22.66, 14.07; IR (KBr) ν : 2918, 2848, 1734 (s), 1630 (s), 1471 (s), 719 (s) cm^{-1} ; ESI-MS m/z : calcd for $(M + H)^+$ 1414.6, found 1414.7.

G_{R2} M.p. 51–52 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 0.88 (t, 24H, CH_3), 1.26 (brs, 202H, CH_2), 1.43 (s, 6H, CH_2), 1.60 (s, 16H, $\text{O} = \text{CCH}_2\text{-CH}_2\text{CH}_2$), 2.29 (t, 16H, $\text{O} = \text{CCH}_2\text{CH}_2\text{CH}_2$), 2.45 (t, 8H, $\text{O} = \text{CCH}_2\text{CH}_2\text{N}$), 2.52 (t, 4H, $\text{O} = \text{CCH}_2\text{CH}_2\text{N}$), 2.78 (s, 16H, $\text{O} = \text{COCH}_2\text{CH}_2\text{N}$), 2.79 (s, 8H, $\text{O} = \text{COCH}_2\text{CH}_2\text{N}$), 2.89 (t, 8H, $\text{O} = \text{CCH}_2\text{CH}_2\text{N}$), 2.93 (s, 4H, $\text{O} = \text{CCH}_2\text{CH}_2\text{N}$), 3.50–3.65 (q, 8H, $\text{NCH}_2\text{-CH}_2\text{N}$, piperazine), 4.11 (s, 16H, $\text{O} = \text{COCH}_2\text{CH}_2\text{N}$), 4.12 (s, 8H, $\text{O} = \text{COCH}_2\text{CH}_2\text{N}$); ^{13}C NMR (CDCl_3 , 500 MHz) δ : 173.62, 172.04, 62.30, 62.22, 52.68, 50.35, 45.26, 41.58, 34.21, 32.94, 31.88, 30.27, 29.65, 29.45, 29.30, 29.26, 29.16, 24.90, 22.63, 14.04; IR (KBr) ν : 2918, 2850, 1736 (s), 1643 (s), 1468 (s), 721 (s) cm^{-1} .

LB film formation

The solution of **G_{R2}** in chloroform ($0.18 \text{ mg} \cdot \text{mL}^{-1}$) was spread drop-by-drop from a chloroform-cleaned glass micro syringe onto the pure water or HgCl_2 solution subphase (from 10^{-7} to $10^{-3} \text{ mol} \cdot \text{L}^{-1}$) at $(20 \pm 1) \text{ }^\circ\text{C}$. After evaporation of solvent for 15 min, the monolayer was compressed at a rate of $40 \text{ cm}^2 \cdot \text{min}^{-1}$ and the surface pressure (π)-area (A) isotherms were recorded. For deposition of the LB films, the hydrophilic pretreated substrate was immersed into the subphase, the monolayer was formed at the surface pressure of $40 \text{ mN} \cdot \text{m}^{-1}$ and then transferred onto

transparent electrodes of indium-tin oxide (ITO)-coated borosilicate glass (the resistance was $250 \Omega \cdot \text{cm}^{-2}$) with a pulling rate of $5 \text{ mm} \cdot \text{min}^{-1}$ (vertical dipping) and transfer ratio (1.0 ± 0.1).

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