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Special properties of monolayer formed by a novel Gemini amphiphile at air–water interface

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Abstract

A novel Gemini amphiphile, *N*,*N*′-bis-(4-decyloxy-2-hydroxybenzylidene)-ethane-1,2-diamine, was synthesized and characterized. This amphiphile is capable of forming stable monolayer at air–water interface. The limiting area has a minimum when the pH value of subphase is 12. The unique behavior is attributed to the formation of intramolecular hydrogen bond between hydroxyl groups. The existence of this hydrogen bond was supported by the FTIR results. With the addition of copper ion into subphase, the limiting area showed a decreasing value, which is quite different from that of the conventional neutral amphiphiles. XPS and UV–vis were also carried out to investigate the effect of copper ion on molecular area.
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Keywords: Gemini amphiphile; Monolayer; Limiting area

1. Introduction

Monolayers at air–water interface are of great importance because of their unusually optical, electronic, magnetic or catalytic properties and extensive potential applications [1–6]. Especially, they can be used as templates in preparing nanomaterials [7,8], which are promising candidates as building blocks for the next generation devices. However, a substantial question encountered is how to actively control molecular area of the monolayer. In recent years, some new types of amphiphiles such as bolaform [9,10] and Gemini [11,12] surfactants emerged and the research on the monolayer of these new kinds of amphiphiles attracted attention due to their unique molecular structures comparing to conventional amphiphiles. For example, Shimomura and coworkers reported that photoirradiation had a significant effect on the pressure–area isotherm of monolayer formed by a synthetic Gemini amphiphile [13]. However, it seemed that no satisfactory solution was found to the question mentioned in the beginning.

In this work, we synthesized a new Gemini amphiphile, *N*,*N*′-bis-(4-decyloxy-2-hydroxybenzylidene)-ethane-1,2-diamine (abbreviated as DBA-OH). For comparison, another Gemini amphiphile, *N*,*N*′-bis-(4-decyloxybenzylidene)-ethane-1,2-diamine (abbreviated as DBA) was also synthesized. Both of them were found to be capable of forming stable monolayer at the air–water interface. And the effects of pH and metal ion in the subphase on the molecular area were investigated in this work.

2. Experimental

2.1. Materials

1-Bromodecane, 2,4-dihydroxybenzaldehyde, 4-hydroxybenzaldehyde and ethylenediamine were obtained commercially. The pH value of subphase was adjusted by potassium hydroxide and potassium bicarbonate. 4-Decyloxy-

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2-hydroxybenzaldehyde and 4-decyloxybenzaldehyde were synthesized according to Ref. [14].

2.1.1. N,N′-Bis-(4-decyloxy-2-hydroxybenzylidene)-ethane-1,2-diamine

1.0 g (3.6 mmol) of 4-decyloxy-2-hydroxybenzaldehyde and 0.108 g (1.8 mmol) of ethylenediamine were dissolved in 20 mL of ethanol. The solution was gently stirred for 6 h at room temperature, and yellow precipitate was observed in the solution. The precipitate was filtered off and thoroughly washed with acetone to give 0.84 g of DBA-OH (80%). FTIR (KBr pellet): 2921, 2852, 1625, 1574 cm^{-1}. 0.88 (t, CH_3, 6H), 1.27 (m, CH_2, 28H), 1.76 (m, CH_2, 4H), 3.84 (s, CH_2N, 4H), 3.94 (t, CH_2O, 4H), 6.35 (d, phenyl ring, 2H), 6.39 (s, phenyl ring, 2H), 7.05 (d, phenyl ring, 2H) and 8.19 (s, CHN, 2H). UV–vis (nm, ethanol): 283, 313, 410.

2.1.2. N,N′-Bis-(4-decyloxybenzylidene)-ethane-1,2-diamine

1.0 g (3.8 mmol) of 4-decyloxybenzaldehyde and 0.114 g (1.9 mmol) of ethylenediamine were dissolved in 20 mL of ethanol. The solution was gently stirred for 6 h at room temperature, and white precipitate was observed in the solution. The precipitate was filtered off and thoroughly washed with acetone to give 0.78 g of DBA (75%). FTIR (KBr pellet): 2924, 2848, 1640, 1607 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): 0.88 (t, CH_3, 6H), 1.27 (m, CH_2, 28H), 1.78 (m, CH_2, 4H), 3.91 (s, CH_2N, 4H), 3.97 (t, CH_2O, 4H), 6.90 (d, phenyl ring, 4H), 7.64 (d, phenyl ring, 4H) and 8.20 (s, CHN, 2H).

2.2. Method

^1H NMR spectra were recorded on a Varian 200 M spectrometer, with tetramethylsilane as internal reference. FTIR spectra were recorded on a Nicolet Magna-IR 750 spectrometer with KBr pellets. UV–vis spectra were recorded on a Shimadzu UV-250 spectrophotometer. The XPS studies were carried out with a ESCA Lab220i-XL (VG Scientific Inc.) spectrometer, using an aluminum anode (Al Kα = 1486.6 eV) and the pressure was 3×10^{-9} mbar. The monolayer and deposition experiments were carried out on a Krüss Film-balance FB-1 with an Alternate Layer Langmuir-Blodgett trough (Type 622). Water was purified by passing through an Easy Pure RF Compact Ultrapure Water system (Barastead, USA). A solution of DBA or DBA-OH in benzene was spread on the subphase. The isotherms were recorded at 30.0 °C. The monolayer compression speeds were 50 cm^2/min. Monolayer depositions from the various subphases were carried out with a dipping speed at 5 mm/min and with an upper delay of 10 min. The pressure was kept constant at 12 mN/m. Transparent supports for spectral investigations were quartz plates, BaF_2 plates or silica plates.

3. Results and discussion

3.1. Synthesis and characterization

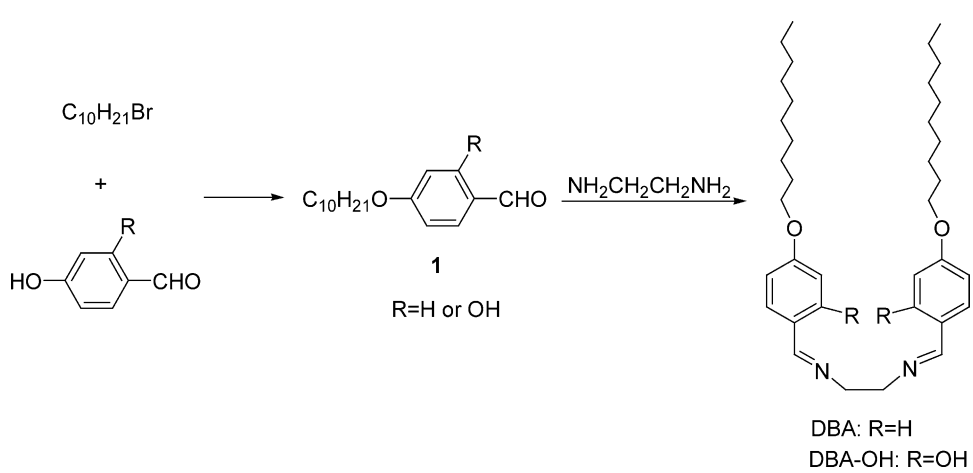
The synthesis route is shown in Scheme 1.

The compound **1** was prepared according to Ref. [13]. After being stirred with ethylenediamine in ethanol for 6 h, **1** was converted into DBA or DBA-OH in a high yield.

The IR spectra of DBA and DBA-OH solid samples are shown in Fig. 1. For DBA-OH, the bands at 2921 and 2852 cm^{-1} are assigned to the antisymmetric (υ_a) and symmetric (υ_b) CH_2 stretching modes of the hydrocarbon chain, respectively. Interestingly, hydroxyl group shows a broad and flat peak ranging from 2300 to 3300 cm^{-1}, which is much less than the normal value of 3650 cm^{-1}. This fact implies the existence of intramolecular hydrogen bond. Furthermore, the wavenumber of C=N stretching mode (1625 cm^{-1}) is much smaller than that of DBA (1640 cm^{-1}), also impling the existence of hydrogen bond in DBA-OH molecule (Scheme 2).

3.2. Effect of pH on A_0

It was found that both DBA-OH and DBA can form stable monolayers at air–water interface. The surface pressure–area



Scheme 1. Synthesis route of DBA and DBA-OH.

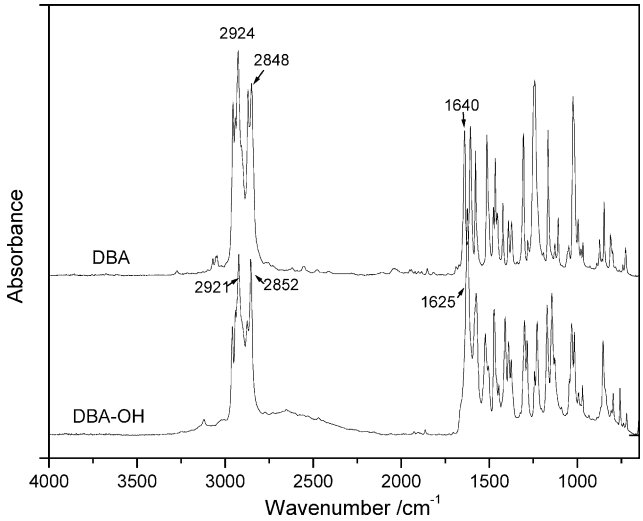
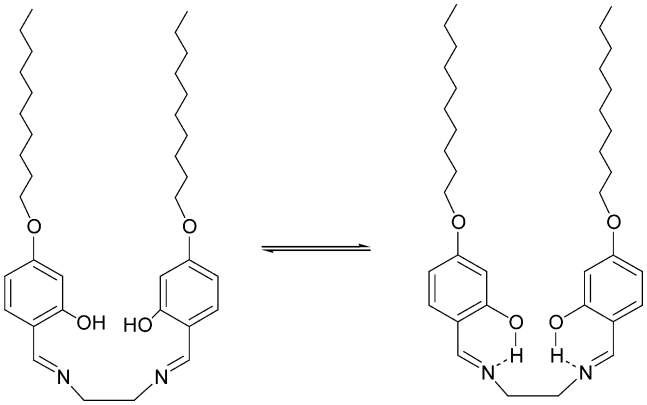


Fig. 1. IR spectra of DBA and DBA-OH solid samples.



Scheme 2. The formation mechanism of intramolecular hydrogen bond in DBA-OH solid sample.

isotherms of monolayers on pure water and subphase of various pH values are shown in Fig. 2. The limiting areas (A_0), obtained by extraploting from the linear parts of the isotherms to zero surface pressure, are listed in Table 1.

The DBA-OH monolayer on the pure water is a typical condensed monolayer. It was obviously affected by the pH value of subphase (Table 1). With the increase of pH value, the limiting area A_0 firstly decreases, then increases after pH is 12, i.e. there exists a minimum for A_0 with the alteration of pH value in the subphase. The result may be attributed to the conformation change, which is elucidated in Scheme 3.

Table 1
The limiting areas (Å) of DBA-OH and DBA monolayers at 30.0 °C on a water subphase with various pH values

	pH						
	6–7 (water)	9	10	11	12	13	14
DBA-OH	108	105	96	93	76	94	162
DBA	119	116	116	115	119	–	118

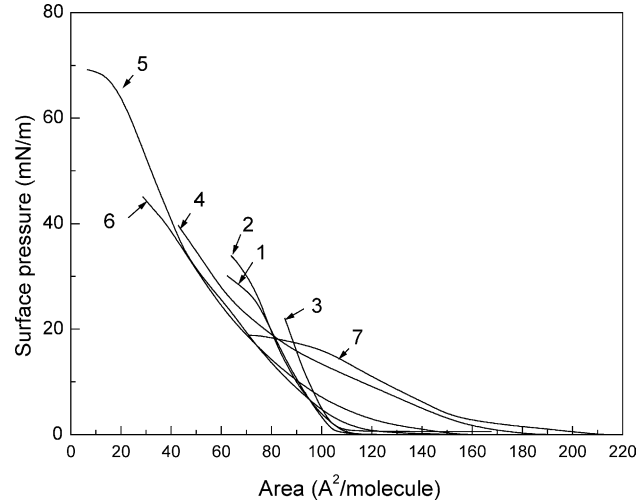


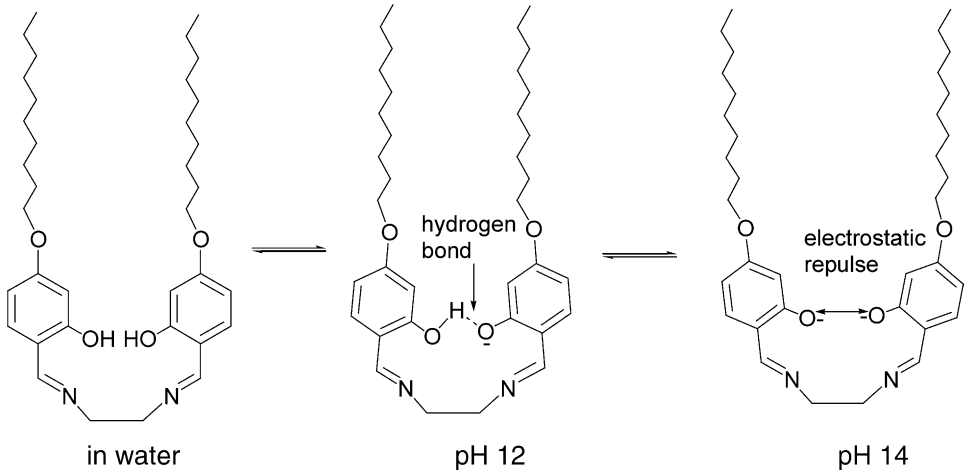
Fig. 2. Surface pressure-area isotherms of DBA-OH monolayer at 30.0 °C on the subphase: (1) pH 6–7 (water), (2) pH 9, (3) pH 10, (4) pH 11, (5) pH 12, (6) pH 13 and (7) pH 14.

The protonation constant pK_a of hydroxyl group on phenyl ring is usually around 12 [15]. Therefore, at pH 12, roughly half of hydroxyl groups are deprotonated. The product, negatively charged oxygen atoms, will attack the hydrogen atoms on the unprotonated hydroxyl groups, resulting in the formation of intramolecular hydrogen bond. Consequently, this bond will pull the aromatic rings together, as a result the molecules in monolayer will be packed more ordered. According to the space filling molecular (CPK) model, the molecular area is $12.7 \times 5.5 = 69.8$ Å^2, which is well consistent with the measured value. However, when pH increases to 14, almost all of hydroxyl groups are deprotonated. The negatively charged oxygen atoms will repulse each other, resulting in the increase of A_0. CPK modeling shows that the calculated molecular area is $18.7 \times 7.7 = 144$ Å^2, which is close to the measured result.

While for DBA, the pH value in subphase has little effect on the limiting area, since hydrogen bond cannot exist in this kind of amphiphiles due to the lack of hydroxyl groups.

FTIR experiments were carried out to investigate the molecular structure of DBA-OH insoluble film. The FTIR spectra of the transferred LB film from the monolayer are shown in Fig. 3. The bands at 2922 and 2853 cm^{-1} are assigned to the antisymmetric (υ_a) and symmetric (υ_b) CH_2 stretching modes, respectively [16]. Previous studies showed that the frequencies of the CH_2 stretching bands are sensitive to conformational ordering of the chain, and lower wavenumber is characteristic of highly ordered conformers of hydrocarbon chains [16].

In our experiment, both $\upsilon_a(CH_2)$ and $\upsilon_b(CH_2)$ frequencies increase in the same sequence: υ (pH 12) < υ (pure water) < υ (pH 14), suggesting that the molecules on pH 12 aqueous solution pack more ordered than the other pH values. As discussed above, the hydrogen bond between hydroxyl group and negatively charged oxygen atom is most easily formed at pH 12. Thus, the highly ordered structure at this



Scheme 3. Conformation changes of DBA-OH molecule on water subphase with different pH values.

pH could be attributed to the existence of hydrogen bond. This result is well consistent with the conclusion drawn from π–A isotherms. The band at 3184 cm^{-1} in pH 14 spectrum is due to KOH in the LB film.

3.3. Effect of copper(II) on A_0

Surface pressure–area isotherms of a monolayer are very sensitive to the interaction between the monolayer and small molecules dissolved in the subphase. Fig. 4 shows the isotherms of monolayers of DBA-OH titrated with copper ion. The obtained limiting areas are listed in Table 2.

With the addition of Cu^{2+} ion, the A_0 of both DBA-OH and DBA have the tendency to decrease. While the decreasing rate of DBA-OH is much faster than that of DBA. This experimental result is quite different from that in the systems of conventional amphiphiles [17]. Usually, when neutral amphiphile molecules bind to transition metal ions, the molecules would repulse each other due to the electrostatic interaction. As a result the limiting area would increase. However, our results show a reverse tendency, because that DBA-OH or DBA molecule can bind to copper ion by the coordination interaction, which will tighten the molecular structure and thus reduce the molecular area.

On the other hand, there exists significant difference between DBA-OH and DBA in term of coordination bind-

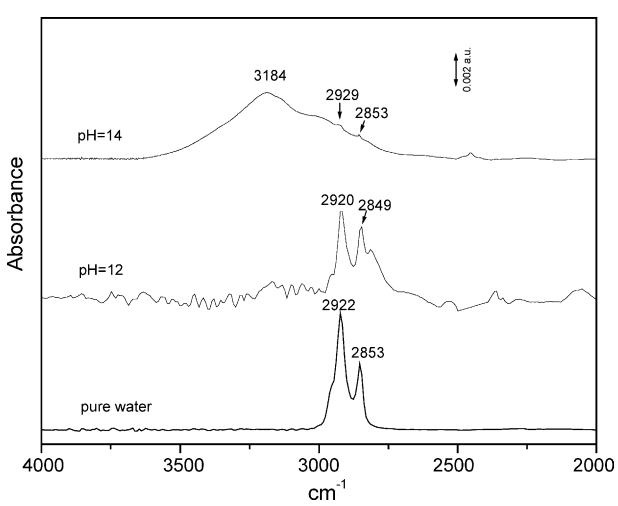


Fig. 3. FTIR spectra of LB films of DBA-OH amphiphiles at different pH values.

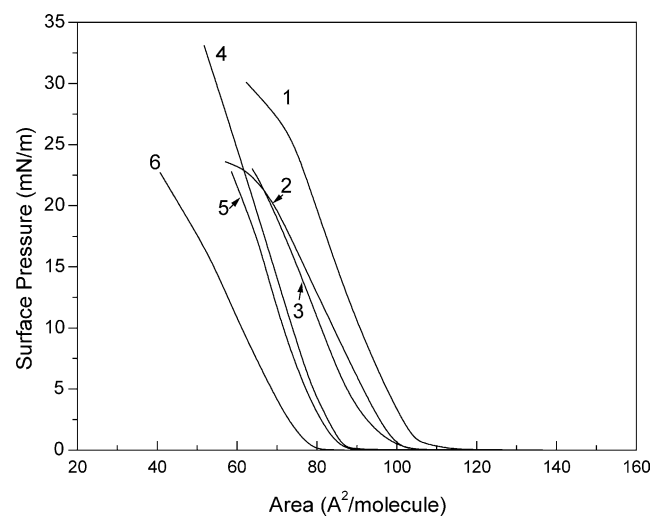
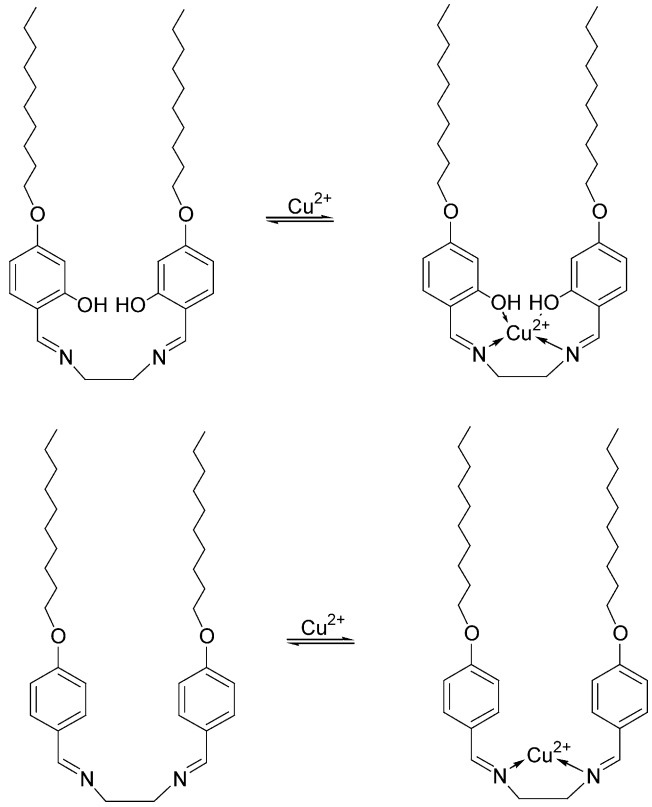


Fig. 4. Surface pressure-area isotherms of DBA-OH monolayer at 30.0 °C on a water surface with Cu^{2+} concentration: (1) 0 (water), (2) $[Cu^{2+}] = 10^{-8}$ mol/L, (3) $[Cu^{2+}] = 10^{-6}$ mol/L, (4) $[Cu^{2+}] = 10^{-5}$ mol/L, (5) $[Cu^{2+}] = 10^{-4}$ mol/L and (6) $[Cu^{2+}] = 10^{-3}$ mol/L.

Table 2
The limiting areas (Å) of DBA-OH and DBA monolayer at 30.0 °C on the water subphase with various Cu^{2+} concentrations

	$[Cu^{2+}]$ (mol/L)					
	0	10^{-8}	10^{-6}	10^{-5}	10^{-4}	10^{-3}
DBA-OH	108	99	88	83	86	83
DBA	119	–	114	104	98	100



Scheme 4. Coordination bindings of DBA-OH and DBA with copper ion.

ing with copper ion. There are four binding sites available in each DBA-OH molecule: two oxygen atoms and two nitrogen atoms. While for DBA, there are only two nitrogen atoms that can act as binding sites. Obviously its interaction with copper ion is much weaker than DBA-OH's. As a result the drop in A_0 is not so fast as that of DBA-OH. This fact is elucidated by a conformation change shown in Scheme 4.

The XPS measurement was carried out to study the LB film of DBA-OH amphiphile. The peak at 935 eV, which is characteristic of copper ion, is clearly shown in Fig. 5 [18]. This result implies the existence of copper in LB film and

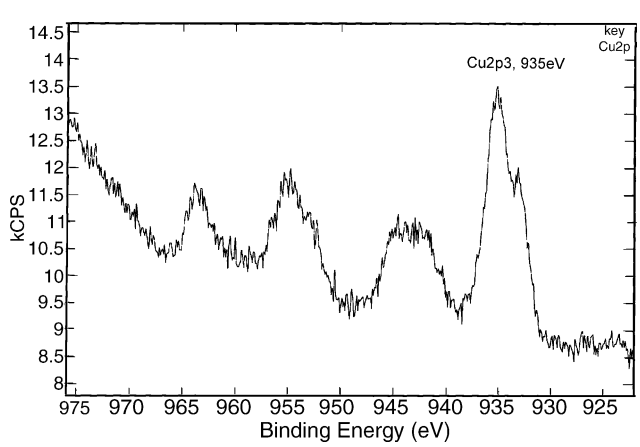


Fig. 5. XPS spectra of LB film of DBA-OH.

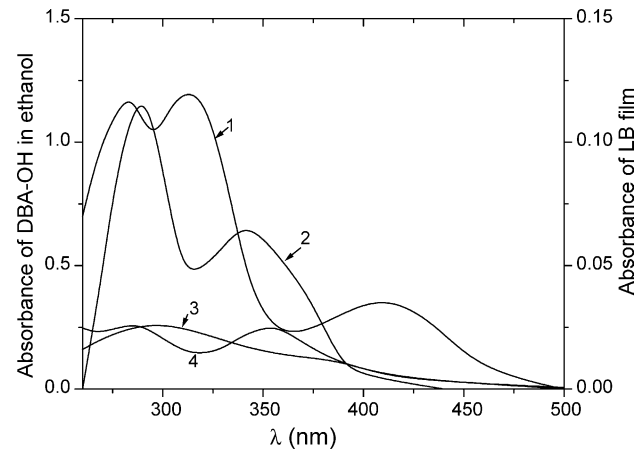


Fig. 6. UV–vis spectra of DBA-OH. Curves (1 and 2) represent with the absence and presence of copper ion in ethanol, respectively. Curves (3 and 4) represent with the absence and presence of copper ion in LB film, respectively.

supports our speculation: it is the interaction between copper ion and DBA-OH that results in the reduction of the limiting areas.

The results of UV–vis spectra also supported our speculation (Fig. 6). The UV–vis spectrum of DBA-OH in ethanol solution shows three characteristic transitions: an n–π^* transition at 410 nm and two π–π^* transitions at 313 and 283 nm [19], which can be attributed to the isomerization shown in Scheme 2. With addition of an excess of $Cu(Ac)_2$ the spectrum of the complex arises with the characteristic complex band around 342 nm, which can be assigned to the charge transfer from the ligand to the copper ion [19]. The similar spectrum was observed with the LB film. After the binding of copper ion, a new band at 355 nm was observed, which is assigned to the charge transfer from ligand to copper ion. This result also suggested that the coordination binding of copper ion with DBA-OH exists in LB film, as well as monolayer at air–water interface.

4. Conclusions

In the present work, a synthetic Gemini amphiphile was employed to form stable monolayer at air–water interface. It was found that the pH value and copper ion in the subphase have significant effects on its limiting area. The area shows a minimum when pH value of subphase is 12. Copper ion could greatly reduce the value of A_0. Models were brought up to elucidate the unique behaviors and the results of IR, XPS and UV–vis spectroscopy also supported the models.

As discussed in this paper, the limiting area, one of the most important factors for monolayer, can be actively adjusted by pH and metal ion in subphase. This result may have extensive potential applications, such as controlling the sizes of nanoparticles. More detailed works are processing in our laboratory.

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References

[1] X.Z. Du, Y.Q. Liang, Langmuir 14 (1998) 3631.
[2] S. Pang, C. Li, J. Huang, Y. Liang, Colloid Surf. A: Physicochem. Eng. Aspects 178 (2001) 143.
[3] J.M. Ouyang, Z.M. Zhang, C.X. Huang, X.Q. Yao, H.Y. Liu, X.M. Hu, Colloid Surf. A: Physicochem. Eng. Aspects 175 (2000) 99.
[4] J.M. Ouyang, W.H. Lin, C.X. Huang, X.Q. Yao, Chem. J. Chin. Univ. 22 (2001) 722.
[5] P. Dynarowicz, N.V. Romeu, J.M. Trillo, Colloid Surf. A: Physicochem. Eng. Aspects 131 (1998) 249.
[6] A. Dhanabalan, N.P. Kumar, S. Major, S.S. Talwar, Thin Solid Films 327–329 (1998) 787.
[7] S. Kuwajima, Y. Okada, Y. Yoshida, K. Abe, N. Tanigaki, T. Yamaguchi, H. Nagasawa, K. Sakurai, K. Yase, Colloid Surf. A: Physicochem. Eng. Aspects 197 (2002) 1.
[8] K.J. Ziegler, R.C. Doty, K.P. Johnston, B.A. Korgel, J. Am. Chem. Soc. 123 (2001) 7797.
[9] J.H. Fuhrhop, H.H. David, J. Mathieu, U. Liman, H.J. Winter, E. Boekema, J. Am. Chem. Soc. 108 (1986) 1785.
[10] D.H. Thompson, K.F. Wong, R. Humphry-Baker, J.J. Wheeler, J.M. Kim, S.B. Rananavare, J. Am. Chem. Soc. 114 (1992) 9035.
[11] F.M. Menger, J.S. Keiper, Angew. Chem. Int. Ed. 39 (2000) 1906.
[12] R. Zana, M. Benrroau, R. Rueff, Langmuir 7 (1991) 1072.
[13] O. Karthaus, M. Shimomura, M. Hioki, R. Tahara, H. Nakamura, J. Am. Chem. Soc. 118 (1996) 9174.
[14] R.M. Claramunt, I. Forfar, P. Cabildo, J. Lafuencente, J. Barberá, R. Giménez, J. Elguero, Heterocycles 51 (1999) 751.
[15] C. Wang, J. Huang, S. Tang, B. Zhu, Langmuir 17 (2001) 6389.
[16] D.A. Myrzakozha, T. Hasegawa, J. Nishijo, T. Imae, Y. Ozaki, Surf. Sci. 427 (1999) 107.
[17] K. Ha, J. Kim, J.F. Rabolt, Thin Solid Films 347 (1999) 272.
[18] R. Buller, T.R. Hagai Cohen, K. Jensen, M. Kjaer, L. Lahav, Leiserowitz, J. Phys. Chem. B 105 (2001) 11447.
[19] G. Hemakanthi, A. Dhathathreyan, D. Möbius, Colloid Surf. A: Physicochem. Eng. Aspects 198 (2002) 443.