Monolayers Langmuir–Schaefer films and acidichromism of a nonamphiphilic acetone derivative containing carbazole

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Received (in Montpellier, France) 28th June 2001, Accepted 17th September 2001
First published as an Advance Article on the web 20th December 2001

A carbazole-containing compound, di(3-*N*-ethylcarbazoylidene) acetone (dNECa), which has no long substituted alkyl chain, was found to form a stable monolayer at the air–water interface when spread from a chloroform solution. The monolayer can be transferred onto solid substrates by the horizontal lifting method to form a uniform ultrathin film (Langmuir–Schaefer film or LS film). Quartz-crystal microbalance measurements of the transferred LS film confirmed monolayer formation at lower surface pressures (10 mN m^{-1}) and the collapse at higher surface pressures (20 mN m^{-1}). The transferred LS film showed a strong color change from yellow to blue when exposed to HCl gas. The film returns to its original yellow color spontaneously in air or on exposure to NH_3 gas. These color changes can be repeated many times in the transferred films by alternative exposure to HCl and NH_3 gases. It is suggested that the color change or acidichromism is due to the keto–enol tautomerization of the compound in the film. Fluorescence spectra have been used to confirm our conclusions.

Monolayers and Langmuir–Blodgett (LB) techniques, together with the Langmuir–Schaefer (LS) technique, provide elegant ways to assemble molecules in a controlled manner. Such methods are especially useful in fabricating functional ultrathin organic films.[1,2] In order to apply these techniques, however, the choice of molecules is very important. Generally, it is necessary to select amphiphiles, in which hydrophilic groups and hydrophobic long tails are both present, to form stable monolayers and LB films. Long-chain fatty acids, amines and alcohols are typical compounds to form well-defined monolayers and LB films. On the other hand, the functions of LB films have attracted much attention. In order to introduce functional groups into LB films, a long alkyl chain or chains are usually substituted onto them. However, the introduction of long alkyl chains into functional groups often requires tedious synthetic procedures. It would be useful to find simple molecules that form monolayers and LB films. Previously, we have found that some benzimidazole compounds, although having short or even no alkyl chains, can form stable monolayers through an *in situ* coordination with $AgNO_3$ in the subphase.[3] This aroused our interest as it showed that simple molecules can form stable monolayers at the air–water interface which was confirmed through a series of investigations, on some simple molecules without long alkyl chains. In this paper we report the spreading behavior of a carbazole-containing molecule, di(3-*N*-ethylcarbazoylidene)acetone (dNECa, shown in Scheme 1) at the air–water interface.

Diarylideneacetone is a commonly used ligand capable of stabilizing various organometallic compounds.[4–6] While some properties of dNECa have been reported in solution,[7,8] this is the first report on the monolayer and Langmuir–Schaefer films of the compound. In addition, it is interesting to note that the transferred Langmuir–Schaefer films showed acidichromism. Acidichromism refers to color changes that occur with pH variation. In the case of the film, acidichromism was controlled by reaction of the LB films with HCl and NH_3 gases, alternatively. While many chromisms such as photochromism,[9–12] thermochromism[13,14] and electrochromism[15,16] have been extensively investigated in LB films, there are fewer reports on the acidichromism of LB films. In this paper, the monolayer-forming ability and the acidichromism of the transferred LS films of the compound were investigated through surface pressure–area (π-*A*) isotherms, QCM (quartz crystal microbalance) measurements, and UV-vis and fluorescence spectra.

Experimental

dNECa work was synthesized according to a literature method.[7,17] The monolayer was spread from a chloroform solution (1 × 10^{-3} M) onto the water surface and the surface pressure–area isotherms were recorded at 20 °C on a KSV 1100 trough (KSV Instruments, Helsinki, Finland). The monolayer was transferred onto solid substrates by the Langmuir–Schaefer or horizontal lifting method. Quartz plates (Suprasil) were precoated with a monolayer of ferric stearate to make the surface hydrophobic. UV-vis spectra were recorded using a UV-530 system (JASCO, Japan). Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer (Hitachi, Japan).

In order to confirm the monolayer formation, a QCM measurement of the transferred LS film was performed. The QCM employed was a commercially available 9 MHz, AT-cut quartz crystal (0.196 cm^2) from Seiko Instruments. Au electrodes were deposited on both sides of the quartz crystal plates. The QCM was connected to an oscillator and the mass changes were detected as frequency changes. The relationship between the frequency and mass changes is as follows:

$$\Delta m = (-1.05 \pm 0.01)\Delta F \qquad (1)$$

where Δm is the mass change in ng and ΔF is the frequency change in Hz.

In order to investigate the acidichromism in the LS film, the LS films were exposed to HCl and NH3 gas separately for one minute and then the UV-vis spectra were recorded immediately

180 *New J. Chem.*, 2002, **26**, 180–183 DOI: 10.1039/b105694h

after exposure. The concentrations of HCl and NH_3 were estimated to be 2.3×10^{-4} and 0.017 M, respectively.

Results and discussion

Spreading Langmuir films at the air–water interface

Fig. 1 shows the surface pressure–area (π–*A*) isotherm of the spread Langmuir film of dNECa on a water surface. The onset of the surface pressure begins at about 0.6 nm^2 $molecule^{-1}$. After a slight increase to about 1 mN m^{-1}, the surface pressure greatly increases. A hump appeared at 13 mN m^{-1}. After the hump, a slow and continued increase in surface pressure is observed. By extrapolating the linear part of the isotherm before the hump to zero surface pressure, a molecular area of 0.45 nm_2 $molecule^{-1}$ could be obtained. Based on the CPK model, the dimensions of the compound are estimated to be $2.26 \times 0.8 \times 0.34$ nm^3. Three molecular areas of 1.8, 0.768 and 0.27 nm^2 can be obtained, depending on the different orientations. Comparison with the experimental value of 0.45 nm^2 $molecule^{-1}$, suggests that the dNECa molecule, like a cubic brick, is orientated tilted with respect to the water surface along its long axis.

In addition, it has been further found that the appearance of the hump in the isotherm depends on the compression speed. When the π–*A* isotherm was recorded at a slow compression rate, this hump became clearer although the limiting area did not change, meaning that the hump denotes a phase transition of the Langmuir film. Since the molecular area after the hump is very small, it can be considered that the Langmuir film begins to collapse at the hump. It is further noted that the surface pressure kept increasing after the hump. Such pressure increase could be due to overlap of the molecules. The absence of long alkyl chains makes it is easy for the molecules to slip onto neighboring molecules.

In addition, we have investigated the pH dependence of the π–*A* isotherm. No change in isotherms between pH = 2 and 12 was found.

QCM investigation of monolayer formation

In order to make it clear whether the spreading film is a true monolayer or multilayer, we have used the QCM method to monitor the mass change in the film transfer process. The dNECa spreading film could not be deposited by vertical deposition using a hydrophobic substrate. Using a hydrophilic substrate, although the film could be deposited as a Z-type film, the upstroke transfer ratio was only 0.3. Moreover, after several cycles of deposition, the film became inhomogeneous and aggregated at the end of the substrate. For this reason, we transferred the film using the Langmuir–Schaefer or horizontal lifting method. The film was transferred at two different surface pressures onto the Au-coated electrode and the frequency changes were recorded as a function the number of transferred layers shown in Fig. 2. In both cases, the frequency changes are linear with the number of transferred layers, indicating uniform transfer of the film onto the solid substrate. At 10 mN m^{-1}, each transferred layer corresponds to a decrease of 40 Hz, while at of 20 mN m^{-1}, one transferred layer corresponds to −137 Hz. From the above π–*A* isotherm, the molecular areas at 10 and 20 mN m^{-1} were 0.37 and 0.29 nm^2 $molecule^{-1}$, respectively. As the area of the electrode is 0.196 cm^2, a one-layer film transferred at the electrodes should weigh 41.2 and 52.5 ng, respectively. On the other hand, from the frequency changes in the QCM measurements, one layer transferred at 10 and 20 mN m^{-1} can be calculated to weigh 42 and 143.8 ng, respectively, using eq. (1). It is obvious that at 10 mN m^{-1}, a true monolayer is formed, while at 20 mN m^{-1}, a multilayer film is obtained due to film collapse. It should be further noted that while the molecular area at 20 mN m^{-1} is not greatly decreased, the transferred mass increased greatly in comparison with that at 10 mN m^{-1}. This may be because many more layers were transferred due to the instability of the collapsed film.

Traditionally, it is necessary to have a long alkyl chain for the compound to form a stable monolayer at the air–water interface. Although some macrocyclic molecules such as porphyrins,[18] phthalocyanines,[19] calixarenes[20] and macrocyclic poly(esters)[21] have been found to form stable monolayers at the air–water interface, dNECa represents a new type of simple molecule that can form monolayers at the air–water surface.

Characterization and properties of the transferred LS films

UV-vis absorption spectra. Fig. 3 shows the absorption spectra of the LS films transferred at 10 mN m^{-1}. In the UV region, four bands are observed at 241, 285, 326 and 424 nm, respectively. The first three bands can be ascribed to the localized π–π* transition,[22–24] while the band at the longest wavelength can be assigned to the charge transfer band.[7] These absorption bands are essentially similar to those reported in solution. However, the charge transfer band in the film shows a 24 nm red shift in comparison with the absorption bands in solution. This indicates that the molecules undergo inclined or J-aggregation in the LS films, which is in agreement with the above π–*A* measurements.

Acidichromism of the LB film. Our LS films showed an interesting new property, i.e. that is acidichromism. When the

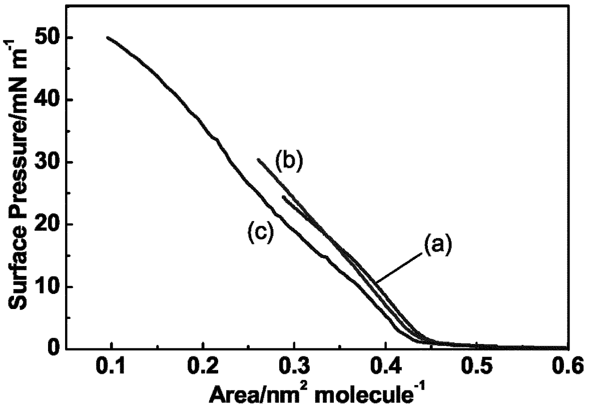


Fig. 1 Surface pressure–area isotherms of the monolayers spread onto a water surface at 20 °C at different compression speeds: (a) 5, (b) 10, and (c) 15 mm min^{-1}.

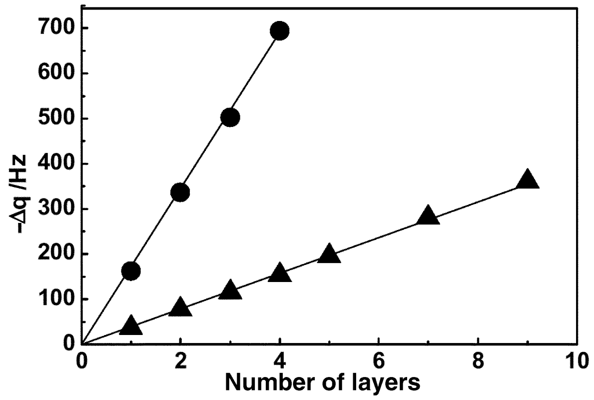


Fig. 2 Frequency change as a function of the number of deposited layers at different surface pressures: (▲) 10 and (●) 20 mN m^{-1}

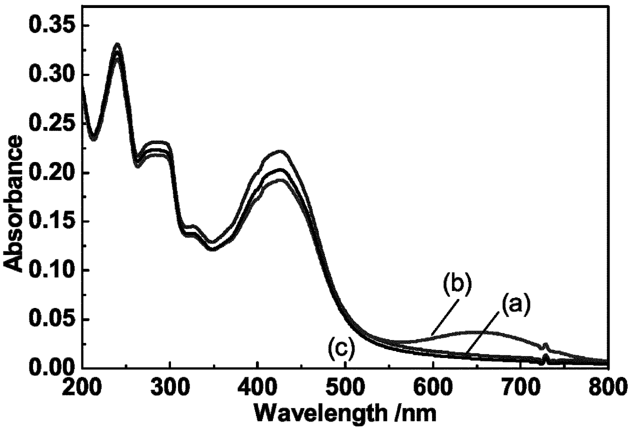


Fig. 3 UV-vis absorption spectra of the LS film: (a) as prepared, (b) after exposure to HCl gas; (c) after exposure of the LS film in (b) to NH_3 gas.

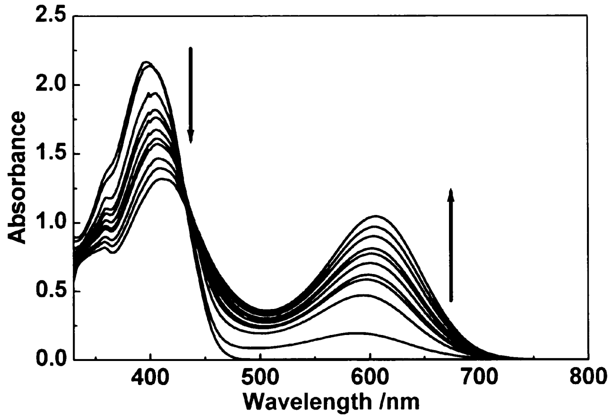
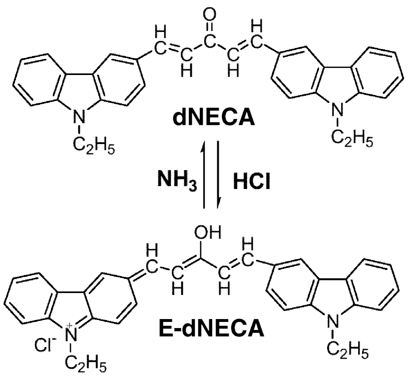


Fig. 5 UV-vis spectra of an acetone solution of dNECa upon adding various amounts of hydrochloric acid (from 0 to 0.85 mol l^{-1}).



Scheme 1

LS film was exposed to HCl gas, it changed color from yellow to blue rapidly. Fig. 3 shows the UV-vis absorption spectra of the film before and after exposure to HCl gas. It is obvious that a new peak appeared at 660 nm after exposure. This blue-colored film was not stable and the absorption intensity diminished by half after 90 s. But it did not return to its original color, even after several hours. Upon exposing the film to NH_3 gas the blue color disappeared completely and the film immediately became yellow. Spectral measurement confirmed that the spectrum returned to its original state after the film was exposed to NH_3 gas. In addition, such color changes could be repeated many times. For a 15-layer LS film, 24 cycles were realized, as shown in Fig. 4.

It is well known that conjugated α,β-unsaturated ketones can undergo keto–enol tautomerism. We checked for tautomerism of our compound in solution first. It was found that the yellow color of an acetone solution of dNECa changed to blue immediately after adding hydrochloric acid solution (Fig. 5). From the spectral changes, the apparent constant for the reaction of $\text{dNECa} + \text{H} \rightleftharpoons \text{E-dNECa}$ can be estimated as 0.812 M^{-1}. It is obvious that in acidic solution, the enol form can be formed as shown in Scheme 1. This form appears to be blue and stable as the conjugation can be extended to the nitrogen atom in the carbazole group. Other strong acids such as sulfuric acid led to similar color changes in solution, but weak acids such as acetic acid could not cause the color change. Therefore, it is suggested that the keto–enol equilibrium causes such acidichromism in the LB film. When the LS film was is exposed to HCl gas, it assumed the blue enol form. However, the enol form is not as stable as the keto form and in air the compound will gradually return to its original color but only partially. When the blue-colored film is exposed to NH_3 gas, the original color is completely restored due to deprotonation.

The above acidichromism of the LS film can be further confirmed through fluorescence measurements. Fig. 6 shows the fluorescence spectrum of the LS film transferred at 10 mN m^{-1}. Upon excitation at 425 nm, strong emission can be observed at 560 nm with a long tail up to 800 nm for the film transferred from a water surface. In addition, a shoulder

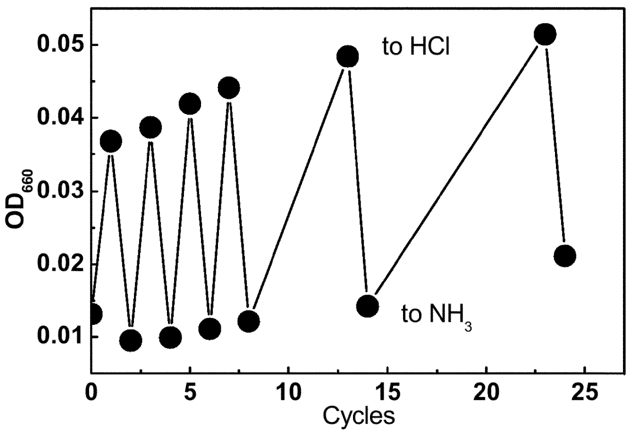


Fig. 4 Change in absorbance at 660 nm as a function of the number of exposure cycles to HCl and NH_3 gases.

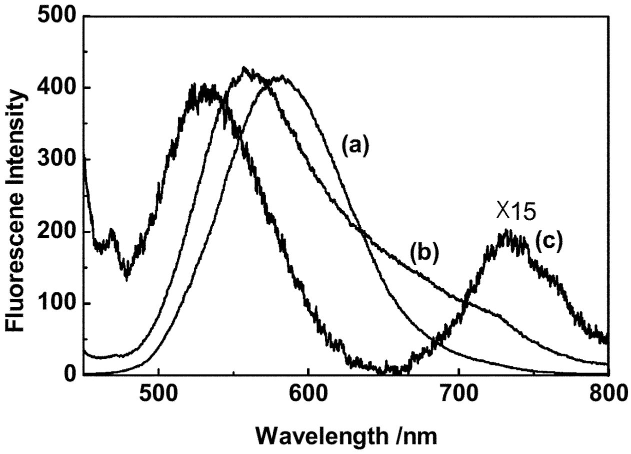


Fig. 6 Fluorescence spectra of the LS film: (a) before and (b) after exposure to HCl gas.

can be observed at 730 nm. The long tail in the LS film indicates the existence of excimers or the emission from aggregates in the LS film due to the ordered arrangement of the functional groups. When the film was exposed to HCl gas, two emission bands were observed at 535 and 730 nm. The fluorescence spectrum of E-dNECa in acetone solution showed a strong emission band at 722 nm. Therefore, the emission at 560 nm can be ascribed to the keto form of the compound, while the emission at 730 nm can be regarded as due to the blue-colored species or enol form. In addition, bleaching of the emission at 560 is observed upon exposure to HCl gas. The shoulder observed at 730 nm in non-exposed films indicates films that these contain a small amount of the enol form.

Conclusions

A carbazole-containing diarylideneketone, which has no substituted long alkyl chain, can form monolayers at the air–water interface. The monolayer can be transferred onto solid substrates by the horizontal lifting method. The transferred LS film shows acidichromism, that is the color can be changed from yellow to blue and returned to yellow by alternative by exposing the LS film to HCl and NH_3 gases, respectively. It is proposed that keto–enol tautomerism of the ketone reason for the acidichromism.

Acknowledgements

This work was supported by the Outstanding Youth Fund, National Natural Science Foundation of China and funds from the Chinese Academy of Sciences.

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