Molecular recognition of nucleotides by a calix[4]arene derivative with two alkyl guanidinium groups at the air–water interface

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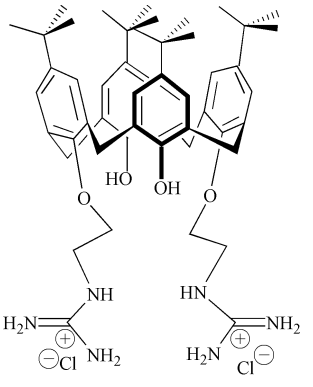
Monolayers of 5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-guanidinoethoxy)-26,28-dihydroxy calix[4]arene hydrochloride (BGC) on the surface of pure water and of aqueous subphases containing 5′-AMP^{-} and 5′-GMP^{2-} were studied by film balance measurements and relaxation experiments. LB films deposited from the monolayers on the three kinds of subphases were investigated by ultraviolet visible spectra (UV), circular dichroism spectra (CD), Fourier transform infrared spectra (FT-IR) and X-ray photoelectron spectra (XPS). All the results indicate that BGC can form stable monolayers on these different subphases. Moreover, BGC can effectively bind with 5′-AMP^{-} and 5′-GMP^{2-} dissolved in the subphase by complementary hydrogen bonding and electrostatic interactions in 1 : 1 and 2 : 1 molar ratios, respectively. Two intermolecular interaction patterns are proposed and the binding constants are estimated to be $1 \pm 0.5 \times 10^{6}$ and $6 \pm 1 \times 10^{5}$ M^{-1}, respectively.

Molecular recognition is a general activity of biological systems. It is a process in which the functional groups of receptors form supramolecules with substrates by non-covalent interactions, such as hydrogen bonding, electrostatic interactions and hydrophobic interactions.[1–3] It is therefore not surprising that artificial molecular recognition systems are attracting much attention, especially for bio-molecules such as nucleotides, amino acids, peptides and proteins.[4–6] Nucleotides, existing normally as anions in neutral conditions, have several subunits that can interact with corresponding structures of other molecules *via* non-covalent interactions. More recognition sites in receptor molecules for a substrate would lead to a higher effectiveness of the system.

Calix[4]arenes were introduced into the field of interfacial science due to their outstanding ability of include neutral molecules and ions.[7] Langmuir monolayers and LB films formed by calixarenes have their advantages in molecular recognition, transportation and separation.[7–11] Lower rim ester derivatives of calixarens with different ring sizes can recognize Na^{+} and K^{+} at the air–water interface,[10] while LB films of calix[8]larene were found to have the ability to bind with transition metal ions selectively.[11] The results all demonstrate that calixarene monolayers and LB films are promising materials in the field of sensors. Moreover, as calixarenes have multiple sites that can be modified by functional groups, they can offer more recognition sites for substrates.

Guanidinium, as a common anion recognition site,[12–14] can efficiently associate with carboxylate and phosphate anions *via* electrostatic forces and multiple hydrogen bonds. Moreover, it also can form hydrogen bonds with nucleobases.[15] Kunitake *et al.*[16–18] have used long-chain amphiphiles with guanidinium to recognize nucleotides at the air–water interface *via* the electrostatic and hydrogen bonding interactions between phosphate anion and guanidinum cation, and the hydrogen bonds between the nucleobase and guanidinium group. Moreover, they also used the mixed monolayer formed by two kinds of amphiphiles bearing guanidinium and nucleobase groups, respectively, to recognize nucleotides. In this case, the guanidinium group interacts only with phosphate anions, while the base group interacts with the base part of nucleotides.

We have introduced two guanidinium groups onto the lower rim of a calix[4]arene molecule, with the expectation, that the two groups can act as recognition sites for both phosphate anion and the nucleobase of nucleotides. Since the two recognition sites are exactly the same, the two subunits of a nucleotide molecule, phosphate anion and nucleobase, can interact not only with the guanidinium groups in the same calix[4]arene molecule, but also can interact with those coming from different receptor molecules.



BGC

In this work the interfacial properties of bis(alkyl guanidinium) calix[4]arene derivative (BGC) were carefully studied. Investigations show that although BGC is not a typical amphiphile with a long alkyl chain, it can form stable monolayers at the air–water interface. Moreover, its different binding behavior to 5′-AMP^- and 5′-GMP^{2-} at the air–water interface were also studied by means of π–A isotherms, relaxation curves, and UV, CD, IR and XPS of the LB films.

Experimental

Materials

The bis(alkyl guanidinium) calix[4]arene derivative (BGC) was synthesized *via* three steps from simple calix[4]arene and characterized by ^{1}H NMR, ^{13}C NMR (Bruker AM 500), electrospray mass (LCQ, Finniigan) spectrometry and elemental analysis (Perkin–Elmer 240C).[19] 5′-AMP monosodium salt and 5′-GMP disodium salt were purchased from Sigma. Chloroform used as spreading solvent was of analytical grade.

Surface pressure–area isotherms experiments

Surface pressure-area isotherms (π–A isotherms) were determined on a KSV 5000 (mini trough). The temperature was kept at 20 ± 0.2 °C. Monolayers were formed by spreading 36 μL of a 5×10^{-4} M chloroform solution of BGC onto the surface of deionized water (purified by a Milli-Q system, >18 MΩ, pH ≈ 5.6) and on the aqueous subphases containing 5′-AMP monosodium salt and 5′-GMP disodium salt, respectively. The concentration of the nucleotides varied from 10^{-2} to 10^{-4} M. Thirty minutes was allowed for evaporation of the spreading solvent and the interaction between the nucleotides and BGC. The π–A isotherms were measured three times at a barrier speed of 4 mm min^{-1} and were found to be reproducible.

Relaxation experiments

Relaxation experiments were carried out at constant molecular area and at different initial surface pressures. When the surface pressure rose to the desired magnitude during compression, the barriers were stopped and the surface pressure was recorded for a period of 80 min thereafter.

Characterization of LB films

All the LB films were prepared at a surface pressure of 15 mN m^{-1} by the horizontal lifting method. The transfer ratio was near 0.9 ± 0.1. UV and CD spectra of LB films deposited on quartz plates (40 layers) were measured on a Jasco V-530 spectrophotometer and Jasco J-720 spectropolarimeter, respectively. FT-lR spectra (transmission-absorption spectrum mode) of LB films deposited on CaF_2 plates (40 layers) were measured using a Bruker IFS 66v spectrometer. The resolution is 4 cm^{-1}. X-Ray photoelectron spectra (XPS) of LB films deposited on glass plates (30 layers) were measured on a VG ESCALAB MKII. The X-ray source was Mg-Kα (1253.6 eV). Repeated scans over the same surface region at a take off angle of 45° gave reproducible spectra. The elemental composition was obtained by dividing the observed peak area by the intrinsic sensitivity factor of each element.

Results and discussion

π–A isotherms on subphases with different nucleotides at different concentrations

When BGC is spread from chloroform solution onto water surface and aqueous subphases containing 5′-AMP^- and 5′-GMP^{2-}, stable monolayers can be formed. Fig. 1(a) shows the

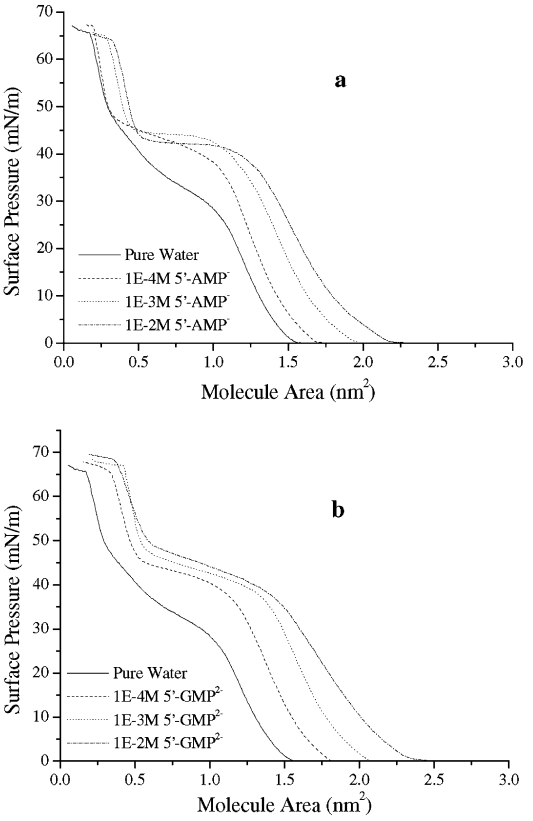
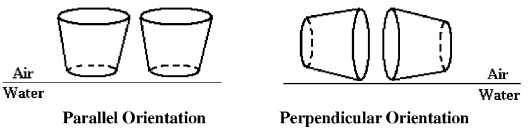


Fig. 1 π–A isotherms of a monolayer of BGC: (a) on the surfaces of pure water, 10^{-4}, 10^{-3} and 10^{-2} M 5′-AMP^- aqueous solution; (b) on the surfaces of pure water, 10^{-4}, 10^{-3} and 10^{-2} M 5′-GMP^{2-} aqueous solution.

π–A isotherms of the BGC monolayers on pure water and aqueous subphase containing 5′-AMP^-. On pure water, it is observed that the limiting molecular area of BGC is 1.47 nm^2. According to the molecular structure of BGC, the limiting area is mainly determined by the cross-sectional area of the upper rim of calix[4]arene, therefore the conformation of calix[4]arene is essential to the limiting areas. As we proposed before,[20] calix[4]arene can attain a *pinched-cone* conformation (two opposite phenyl rings are almost parallel, while the other two opposite phenyl rings form a somewhat bigger dihedral angle) in which its cross-sectional area is 1.40–1.65 nm^2. The surface pressure of monolayer increases quickly and a compression plateau appears from 28 to 47 mN m^{-1} during compression. At higher surface pressure (above 47 mN m^{-1}), the area per molecule is much lower than that expected for calix[4]arene lying flat on the water surface (0.65 nm^2). Molecular reorientation or multilayer formation may be a reasonable explanation for this. According to the proposal of Coleman *et al.*,[21] calix[4]arene can assume two kinds of molecular orientations at the air–water interface. One is the parallel orientation: calix[4]arene molecules can exist in the normal cone or anamorphic cone conformation with its lower rim anchoring into the water; the limiting area is over 1.0 nm^2. The other orientation is the perpendicular one: calix[4]arene molecules may take an orientation parallel to the air–water interface with the lateral side contacting with water; the molecular area is under 0.7 nm^2 (Scheme 1). In this way, the



Scheme 1

compression plateau is a process in which the calix[4]arene molecules are re-oriented. Similar phenomena and hypotheses have been also discussed for calix[6]arene and calix[8]arene by other scientists.[11,22]

In contrast, the π–A isotherms of BGC on the surface of a 10^{-4} M aqueous solution of 5′-AMP^{-} shows that the molecular limiting area is 1.55 nm^2. The larger limiting area may be caused by the interaction between the BGC molecules and nucleotide molecules. Moreover, there is a higher and more obvious compression plateau (from 38 to 47 mN m^{-1}). When the concentration of the subphase containing 5′-AMP^{-} becomes higher, although the shape of the isotherms does not show any intrinsic changes, larger limiting molecular areas and longer compression plateaus are observed. To check the effect of the ionic strength of the subphase, we also spread BGC on a 5′-AMP^{-} (10^{-4} M) buffer solution, to which NaCl is added (9×10^{-4} M) to make the ionic strength roughly equal to that of a 10^{-3} M 5′-AMP^{-} solution. We found that the limiting molecular area of BGC increased by about 16–18 Å^2. According to this result, the concentration effect on the isotherm of a BGC monolayer may be mainly caused by the greater ionic strengths of the subphases.

Similar phenomena can be observed for the BGC monolayers on 10^{-4}, 10^{-3} and 10^{-2} M 5′-GMP^{2-} aqueous solutions [Fig. 1(b)]. A molecular limiting area of 1.65 nm^2 is observed from the π–A isotherms on the 10^{-4} M subphase. Moreover, the compression plateau of the π–A isotherm measured on the 5′-GMP^{2-} subphase appears at above 40 mN m^{-1}, which is much higher than that on pure water. Similarly, although higher concentrations of the subphase do not cause much difference in the shape of their π–A isotherms, the π–A isotherms extend out to larger molecular areas indicating strong interactions of the monolayer with 5′-GMP^{2-}. Comparing the isotherms of BGC monolayers on the subphases of 5′-AMP^{-} and 5′-GMP^{2-}, it can be seen that the molecular areas on aqueous 5′-GMP^{2-}-containing subphases are larger than those in the case of 5′-AMP^{-}. This may imply that BGC interacts differently with 5′-AMP^{-} and 5′-GMP^{2-}.

From Fig. 1(a) and (b) it can be seen that the π–A isotherms obtained on subphases containing nucleotides always inflect to the compression plateau at higher surface pressures, compared with that on pure water. These results indicate that nucleotide-containing subphases favor the parallel orientation of BGC at the air–water interface and the re-orientation to the perpendicular orientation is delayed. In the parallel orientation, BGC can assume the pinched-cone conformation at the air–water interface with the guanidinium groups sticking into the water phase and the hydrophobic calix[4]arene skeleton stretching out of the water. Furthermore, BGC as the surfactant can interact strongly with 5′-AMP^{-} and 5′-GMP^{2-} in the subphase at the air–water interface and the intermolecular interaction between BGC and the nucleotides *via* complementary non-covalent interactions stabilizes the parallel orientation of BGC molecules at the air–water interface.

Relaxation experiments

In order to investigate the stability of the monolayers in different compression states, surface pressure relaxation experiments at constant area were carried out. For initial surface pressures of 22 and 42 mN m^{-1}, the relaxation experiment results on pure water and 10^{-4} M nucleotides are shown in Fig. 2(a) and (b) respectively. Just as we discussed above, when the initial surface pressure is 22 mN m^{-1}, the BGC molecule exists in a pinched-cone conformation at the air–water interface (parallel orientation). Therefore, the guanidinium groups of the BGC molecules are submerged in water and interact more readily with nucleotides in the subphase. In Fig. 2(a), when nucleotides are introduced into the subphase, the smaller decrease in surface pressure implies that the stability of the

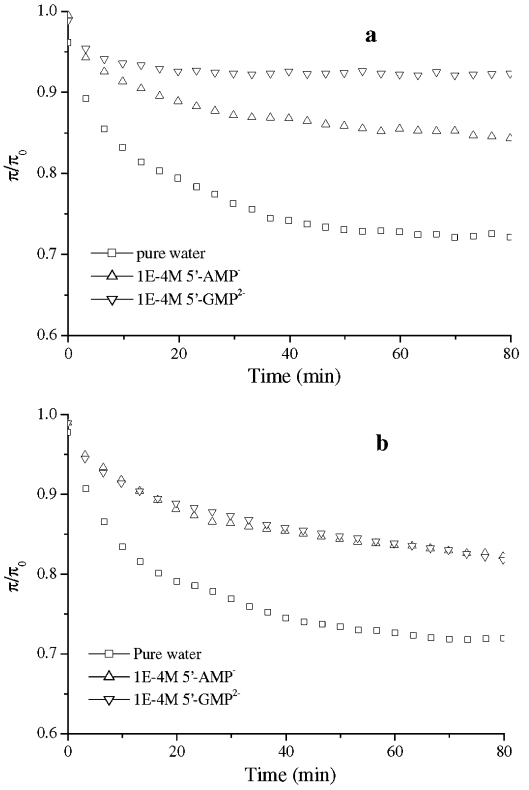


Fig. 2 Relaxation experiment plots showing the changes in surface pressure over time for a BGC monolayer at (a) 22 and (b) 42 mN m^{-1}.

monolayers is substantially improved since BGC interacts with both nucleotides *via* non-covalent interactions. Moreover, it seems that the stability of the monolayer on the subphase containing 5′-GMP^{2-} is better than that on the subphase containins 5′-AMP^{-} at low surface pressure. This may originate from different interaction modes between BGC molecules and the two nucleotides. It also suggests that 5′-GMP^{2-} may facilitate the self-assembly of BGC molecules at surface pressures around 22 mN m^{-1}. This result is in accordance with the π–A isotherm measurements.

When the initial surface pressure is at the plateau ($\pi = 42$ mN m^{-1}), the monolayer is in a transition phase [Fig. 2(b)]. In this case, the two molecular orientations (parallel and perpendicular) coexist. When compared with pure water, the two nucleotides can still improve the stability of the monolayer, but the capacity of 5′-GMP^{2-} to stabilize the monolayer is reduced to be similar to that of 5′-AMP^{-}. In addition, on the same subphase, the monolayer shows better stability at lower pressure than at higher pressure. This suggests that the parallel orientation at lower pressure is more stable.

UV and CD spectra of LB films

UV and CD spectra of LB films of BGC deposited on pure water and 10^{-4} M nucleotide-containing subphases are shown in Fig. 3 and Fig. 4 respectively. It can be seen that the absorption intensity of the band near 200 nm clearly increases in the UV spectra of LB films deposited on subphases containing 5′-AMP^{-} (LB–AMP) and 5′-GMP^{2-} (LB–GMP), compared with that of the LB film prepared from the surface of pure water (LB–W). This is due to overlap of similar wavelength bands of BGC and the nucleotides. In addition, because of the chirality of nucleotides this band is also observed as a positive Cotton effect in the corresponding CD spectra (Fig. 4). Similarly, the absorption intensities of the bands in the range from 250 to 290 nm in the UV spectra of the LB films prepared from nucleotide-containing subphases also

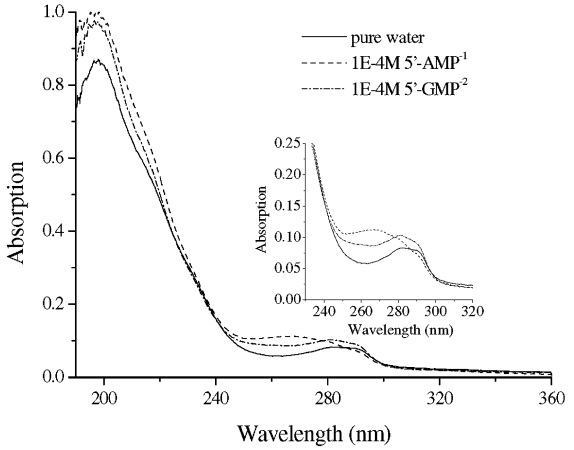


Fig. 3 UV-visible spectra of LB films of BGC deposited from the surfaces of pure water, 10^{-4} M 5′-AMP^{-} aqueous solution and 10^{-4} M 5′-GMP^{2-} aqueous solution and 10^{-4} M 5′-GMP^{2-} aqueous solution. The inserted small figure is the magnification for the bands in the range of 230–320 nm.

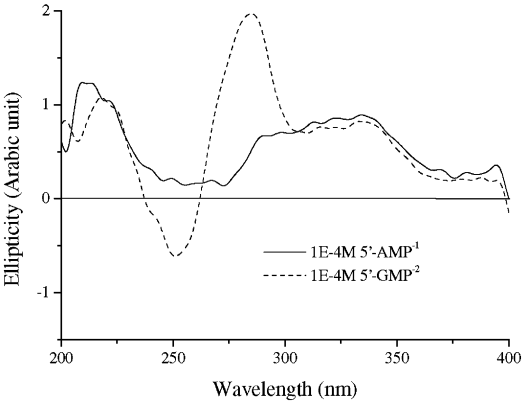


Fig. 4 CD spectra of LB films of BGC deposited from the surfaces of 10^{-4} M 5′-AMP^{-} aqueous solution and 10^{-4} M 5′-GMP^{2-} aqueous solution.

increase notably. Moreover, the absorption maximum of the band in this range shifts from 282 nm for LB–W to 269 nm for LB–AMP and the absorption at 280 nm for LB–GMP gets stronger. These changes are mainly attributed to the absorption bands of 5′-AMP^{-} (259 nm) and 5′-GMP^{2-} (253 and 273 nm); the interaction of BGC with the nucleotides makes the corresponding peaks undergo a red-shift. On the other hand, the corresponding CD spectra show that the band at 253 nm of 5′-GMP^{2-} gives a negative Cotton effect, while the band at 273 nm shows a positive Cotton effect. However, the Cotton effect of the band at 259 nm of 5′-AMP^{-} is too weak to be found in the CD spectra. All these spectral features demonstrate that BGC is able to bind with the nucleotides in the subphase by complementary non-covalent interactions to form supramolecular entities and both 5′-AMP^{-} and 5′-GMP^{2-} can be transferred onto solid substrates along with the monolayers of BGC.

FT-IR spectra of LB films

The assignments of some IR bands for LB films of BGC deposited on pure water and 10^{-4} M nucleotide-containing subphases are listed in Table 1. When compared with the IR spectra for LB–W, a broader band in the 3100–3600 cm^{-1} region is observed in the IR spectra of LB–GMP, while for LB–AMP, the absorption maximum of the band in this range shifts

Table 1 IR band assignments[a] for BGC in 40-layer LB films[b] on CaF_2

Pure water	5′-AMP^{-}	5′-GMP^{2-}	Assignment[c]
3348s, br	3353s, br	3347s, br	ν_{as}(NH)
3199w, br	3211w, br	3205m, br	ν_{as}(OH)
3054w	3050w	3052w	ν(=C–H)
1733w	1737w		δ(=C–H)
1669vs	1647vs, br	1675vs, br[d]	ν(C=N)
1544w	1547m	l542m	ν(C=C)
1295w	1296w	1300w	δ(O–H)
1200s	1200s	1200s	ν(C–O)

[a] vs, very strong; s, strong; m, medium; w, weak; br, broad. [b] LB films deposited on pure water and 1×10^{-4} M nucleotide aqueous solutions. [c] ν, stretch; δ, bend; as, antisymmetric. [d] Including the red-shifted band of the C=O stretching mode of guanine

from 3348 cm^{-1} for LB–W to 3353 cm^{-1}. This is due to the formation of multiple hydrogen bonds between the guanidinium groups of BGC and the nucleotides in the subphase, and the different changes between LB–GMP and LB–AMP imply that the two nucleotides interact with guanidinium groups in a different way. The difference should be mainly ascribed to the different number of negative charges in 5′-AMP^{-} and 5′-GMP^{2-}. The former will interact with one guanidinium group, while the latter with two. This will lead to a difference in the hydrogen bonding between phosphate anion and guanidinium group and finally cause a difference in their IR spectra. On the other hand, the effect of different hydrogen bonding between the nucleobase and guanidinium group can not be excluded.

As shown in Table 1, the band at 1669 cm^{-1} of LB–W is attributed to the C=N stretching mode of BGC. This band becomes clearly broader and the intensity increases remarkably for LB–GMP. Moreover, the peak undergoes a blue-shift to 1675 cm^{-1}. This may be caused by the guanidinium groups accepting electrons from the phosphate anion. The broadening of this band is also the result of the overlap of the C=N stretching mode of the guanidinium group and the C=O stretching mode of the guanine ring of 5′-GMP^{2-} (1695 cm^{-1} for 5′-GMP^{2-} itself). The red-shift of the C=O stretching band further suggests that C=O is bound to the BGC molecules. For LB–AMP, the C=N stretching band of BGC shifts to 1647 cm^{-1} and the intensity is also increased. These changes mainly result from the overlap of the C=N stretching modes of guanidinium and the adenine ring of 5′-AMP^{-} (1655 and 1607 cm^{-1} for 5′-AMP^{-} itself). Certainly, the effect of the intermolecular interaction between phosphate anion and guanidinium group cannot be excluded. All the results indicate that the nucleotides in the subphase can bind with BGC mainly by complementary hydrogen bonds and electrostatic interactions, and the nucleotides can be transferred to solid substrates along with the monolayer of BGC. They also suggest that the interaction modes of BGC with 5′-AMP^{-} and 5′-GMP^{2-} are different. These results are consistent with the results obtained from π–A isotherms, relaxation experimens, UV and CD spectra.

XPS of LB films and the possible interaction modes

The extent of nucleotide binding was determined by X-ray photoelectron spectroscopy (XPS) of LB films of BGC prepared on the subphases containing nucleotides in different concentrations (10^{-7}–10^{-3} M). The ratio of nucleotide to BGC was obtained from the relative ratio of P_{2p}/N_{1S} in the XPS data. Fig. 5 describe the binding behavior of BGC with 5′-AMP^{-} and 5′-GMP^{2-}. From these binding curves, it is observed that the binding of BGC with 5′-AMP^{-} arrives at saturation at 10^{-5} M, while the binding of BGC with 5′-GMP^{2-} becomes saturated at 10^{-4} M. Moreover, the respective molecular fraction at saturation are 0.9

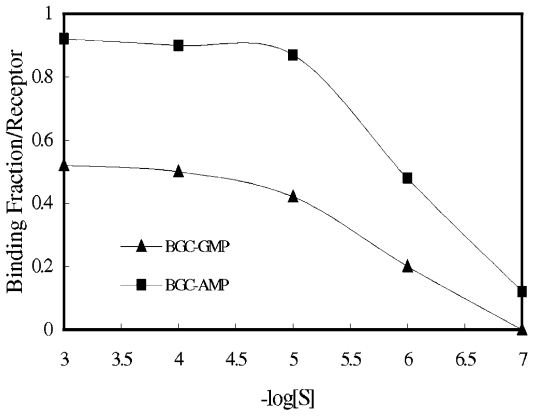


Fig. 5 The binding curves of BGC with 5′-AMP^{-} and 5′-GMP^{2-} obtained from the XPS data of LB films deposited on nucleotide-containing subphases of different concentrations (10^{-3}–10^{-7} M).

and 0.5. This reveals that 5′-AMP^{-} is bound to the BGC monolayer in a 1 : 1 ratio, while 5′-GMP^{2-} binds to the BGC monolayer in a 1 : 2 ratio. A general adsorption isotherm[23] was employed to analyze the binding behavior and gave binding constants of $1 \pm 0.5 \times 10^{6}$ and $6 \pm 1 \times 10^{5}$ M^{-1} for 5′-AMP^{-} and 5′-GMP^{2-}, respectively.

Based on the binding behaviors of 5′-AMP^{-} and 5′-GMP^{2-}, two possible interactions between BGC and nucleotides are proposed. Like typical amphiphiles with guanidinium,[16–18] both 5′-AMP^{-} and 5′-GMP^{2-} are mainly bound to the BGC monolayers by the formation of the guanidinium/phosphate pair. However, because of the differences in their valence and in the functional groups on the heterocycle of the two nucleotides, there are some distinctions in their interaction patterns with BGC at the air–water interface. In the interaction of 5′-AMP^{-} and BGC [Fig. 6(a)], the guanidinium cation/phosphate anion pair are connected *via* two hydrogen bonds and electrostatic interactions to form a stable 8-membered cycle.[16] Certainly, it cannot be excluded that the adenine of 5′-AMP^{-} forms a hydrogen bond with the other guanidinium group of the same host molecule. In the case of 5′-GMP^{2-} [Fig. 6(b)], as each guanidinium unit contains one positive charge, the divalent anion should interact with two guanidinium cations to maintain electrical neutrality. In addition, the carbonyl group of the guanine ring in 5′-GMP^{2-} also forms hydrogen bonds to the guanidinium groups of another host molecule, similar to the interaction pattern put forward by Kunitake *et al.*[16] Therefore, a 1 : 2 interaction pair is formed.

In addition, these interaction patterns accord with the results of the π–A isotherms and relaxation experiments. At lower pressure, BGC molecules adopt a parallel orientation at the air–water interface. This orientation allows the BGC monolayer to bind 5′-AMP^{-} and 5′-GMP^{2-} in the two proposed patterns. Once the supramolecular entities are formed, they also will facilitate the stabilization of this orientation. This is in agreement with the higher and longer compression plateaus of the π–A isotherms on nucleotide-containing subphases. Moreover, 5′-GMP^{2-} can also improve self-assembly of BGC molecules due to its binding to two BGC molecules simultaneously. Therefore, 5′-GMP^{2-} in the subphase has a higher capability to stabilize the BGC monolayer at lower pressures. This argument also accords with the relaxation experiments at lower pressure.

Conclusions

All the results indicate that BGC can form a stable monolayer at the air–water interface. 5′-AMP^{-} and 5′-GMP^{2-} in the subphase are efficiently bound to BGC monolayers at the air–water interface and they can be easily transferred onto solid substrates along with the monolayers of BGC, because of the strong intermolecular interactions. The recognition of 5′-AMP^{-} and 5′-GMP^{2-} in the subphase by BGC is realized by multiple hydrogen bonding and electrostatic interactions. The molar ratio of the intermolecular interaction pattern mainly depends on the differences in valence state and the nucleobase of the two nucleotides; it is 1 : 1 for BGC–5′-AMP^{-} and 2 : 1 for BGC–5′-GMP^{2-}. Moreover, XPS analysis on the LB films fabricated from the subphases with different concentrations of nucleotides revealed that the binding constants of BGC with 5′-AMP^{-} and 5′-GMP^{2-} are $1 \pm 0.5 \times 10^{6}$ and $6 \pm 1 \times 10^{5}$ M^{-1}, respectively.

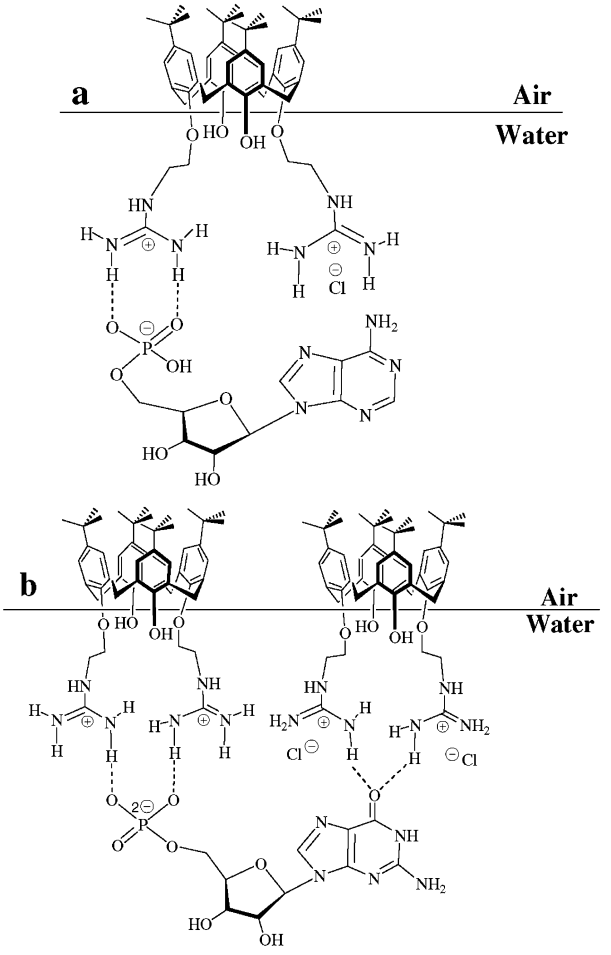


Fig. 6 The interaction patterns of BGC with two nucleotides at the air–water interface: (a) with 5′-AMP^{-} and (b) with 5′-GMP^{2-}.

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