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Synthesis of Calix[4]arene Derivatives Containing a Nucleobase and their Interaction with Complementary Nucleosides at the Air–Water Interface

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Amphiphilic calix[4]arene derivatives with a nucleobase on the lower rim have been synthesized in good yields by the condensation of calix[4]arenediamine {5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-aminoethoxy)-26,28-dihydroxycalix[4]arene} with uracilo-*N*-acetic acid, thymino-*N*-acetic acid and adenino-*N*-propionic acid in the presence of CDI in DMF. Monolayers of the amphiphilic calix[4]arene-nucleobase derivatives on the surface of pure water, the aqueous subphases containing complementary nucleosides, were studied by film balance measurement and relaxation experiments. LB films deposited from all subphases were investigated by UV spectra and FT-IR spectroscopy. All the results indicate that the interaction between the nucleobases in the headgroup of amphiphilic *p-tert*-butylcalix[4]arene derivatives and the complementary nucleosides in the subphase takes place through multiple hydrogen bonding and the nucleosides can be transferred to solid substrates along with their monolayers.

Keywords: Calix[4]arene; Nucleoside; Synthesis; Monolayers, Langmuir–Blodgett films

INTRODUCTION

Molecular recognition plays a central role in biological systems. It is a process in which the functional groups of receptors form supramolecules with substrates by non-covalent interaction, such as hydrogen bonding, electrostatic interaction, and so on [1–4]. 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 [5–11]. Unlike biological molecular recognition, most of these artificial systems are effective only in non-aqueous media due to strong hydrogen bonding with water [12]. For example, monomeric nucleic acids cannot form complementary pairs in water [13]. Fortunately, the organized molecular monolayers assembled by the Langmuir–Blodgett technique can provide a unique environment resembling biological membrane systems for molecular recognition of water-soluble biomolecules in aqueous media *via* interfacial intermolecular interactions [12]. Some examples of interfacial recognition of typical amphiphiles for biomolecules have been reported before [14–17]. Especially in the last few years, much attention has been paid to the monolayer-forming amphiphilic receptors that bear nucleobase head groups because they can efficiently bind complementary nucleobases, nucleosides and nucleotides from the aqueous subphase [18–22].

Calix[4]arenes were introduced into the field of interfacial science due to their outstanding ability to include neutral molecules and ions [23]. Langmuir monolayers and LB films formed by amphiphilic calixarenes have their advantages in molecular recognition, transportation and separation [14,24–26]. Recently, we introduced two alkyl

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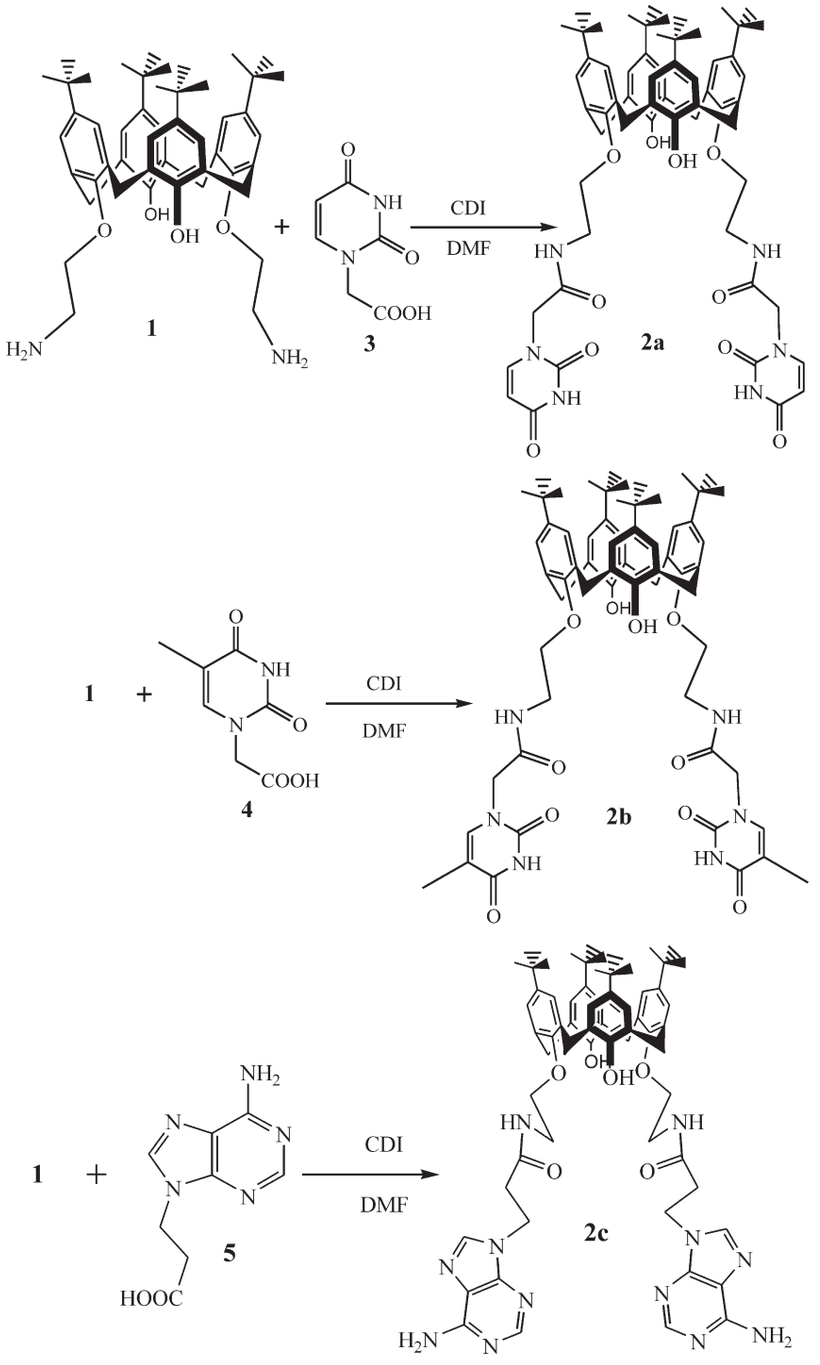
guanidinium groups onto the lower rim of the *p-tert*-butylcalix[4]arene molecule [27] and the resulting interfacial properties were carefully studied by means of Langmuir–Blodgett techniques. Investigations showed that the derivative can form stable monolayers at the air–water interface and bind complementary nucleotides efficiently from the aqueous subphase [28]. Encouraged by these results, we explored the synthesis of new amphiphilic calix[4]arene derivatives with nucleobases on the lower rim and their interaction with nucleosides at the air–water interface. This study may also allow us to shed light on recognition processes in biological systems and to develop novel film materials for accumulating, storing and reproducing information.



SCHEME 1

RESULTS AND DISCUSSION

Synthesis of Amphiphilic Calix[4]arene Derivatives containing a Nucleobase on the Lower Rim

Calix[4]arene derivatives containing a nucleobase on the upper rim have been synthesized and their self-assembly through complementary hydrogen bonding in organic solvents studied independently by de Mendoza *et al.* [29] and Huang *et al.* [30]. However, calix[4]arene derivatives with a nucleobase on the lower rim have never been reported. Here we report the introduction of nucleobase groups onto the lower rim of *p-tert*-butylcalix[4]arene (Scheme 1). With the coexistence of the hydrophobic upper rim of *p-tert*-butylcalix[4]-arene and hydrophilic nucleobases groups within their structures, compounds **2a**, **2b** and **2c** can all form stable monolayers at the air–water interface and can transfer complementary nucleosides to solid substrates from the aqueous subphases.

Compounds **2a**, **2b** and **2c** were obtained *via* a three step synthesis, in which *p*-tetra-*tert*-butyl-calix[4]arene was selectively *O*-alkylated with bromoacetonitrile, reduced with $LiAlH_4$, and then condensed with uracilo-*N*-acetic acid, thymino-*N*-acetic acid or adenino-*N*-propionic acid in the presence of the condensing agent CDI (1,1′-carbonyl-diimidazole) in DMF, respectively. Purification of the products was achieved by flash chromatography through a silica gel column, followed by crystallization from ethyl acetate/petroleum. Yields were 60–70%. Mono-nucleobase-calix[4]arene derivatives were found in only trace amount. Compounds **2a**, **2b** and **2c** were characterized by ^{1}H NMR, ^{13}C NMR, ESIMS and elemental analysis. In ^{1}H NMR spectra, the peaks of protons of $ArCH_2Ar$ appeared as doublets at 3.25–3.40 (H_{exo}) and 3.99–4.24 (H_{endo}), which is consistent with the cone conformation [31,32].

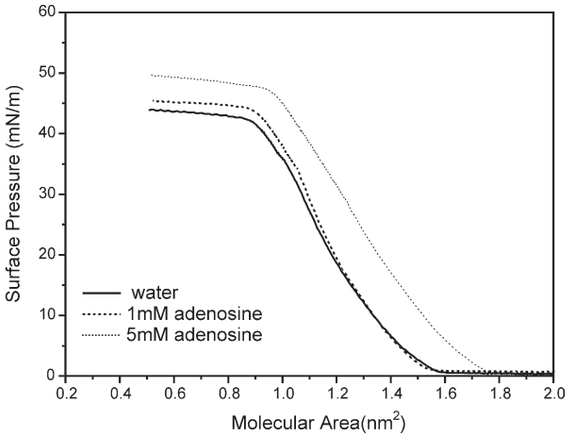


FIGURE 1 π–A isotherms of monolayers of **2a** on the surfaces of pure water, 1.0 and 5.0 mM adenosine aqueous solution.

π–A Isotherms of the Monolayers of Compounds 2a, 2b, 2c on Different Subphases

Fig. 1 shows the π–A isotherms of the monolayers of **2a** on the subphase of pure water and an aqueous solution of the adenosine with a concentration of 1.0 mM and 5.0 mM. On pure water, the monolayer of **2a** gives a limiting molecular area of 1.50 nm^2. Because of the molecular structure of **2a**, 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. Just as reported before [24], 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. Therefore, **2a** molecules in this state may also adopt a *cone* or *pinched-cone* conformation at the air–water interface.

From Fig. 1, it can be seen that the π–A isotherms of **2a** monolayers change noticeably when adenosine is added to the subphase. On the subphase of 1.0 mM adenosine solution, the limiting molecular area (1.52 nm^2) and collapse pressure (46 mN/m) are little greater than those on the pure water (1.50 nm^2 and 44 mN/m). On the subphase of 5.0 mM adenosine solution, the π–A isotherm is much more expanded than that on pure water, giving a limiting molecular area of 1.75 nm^2 and a higher collapse pressure of 50 mN/m. It indicates that adenosine in the subphase can interact effectively with headgroup uracils of **2a** molecules through the hydrogen bonding of complementary base pairs. Therefore, the monolayer becomes more stable and a higher collapse pressure can be observed. Moreover, with the concentration of adenosine increasing in aqueous subphase, the limiting molecular area and collapse pressure of **2a** increase and rise prominently, because of the fuller interaction between the monolayer of **2a** and the complementary nucleobase adenosine in the subphase.

Similar phenomena can be observed from π–A isotherms of **2b** and **2c** monolayers on the subphase of pure water and aqueous solution of the corresponding complementary nucleosides. On the subphase of 5.0 mM adenosine solution, the limiting molecular area and collapse pressure of **2b** are 1.73 nm^2 and 52 mN/m respectively, which are higher than that on pure water (1.53 nm^2 and 45 mN/m). Similarly, the limiting molecular area (1.70 nm^2) and collapse pressure (52 mN/m) of **2c** on the subphase of 5.0 mM uridine solution are much larger and higher than that on pure water (1.51 nm^2 and 46 mN/m). These results further indicate that

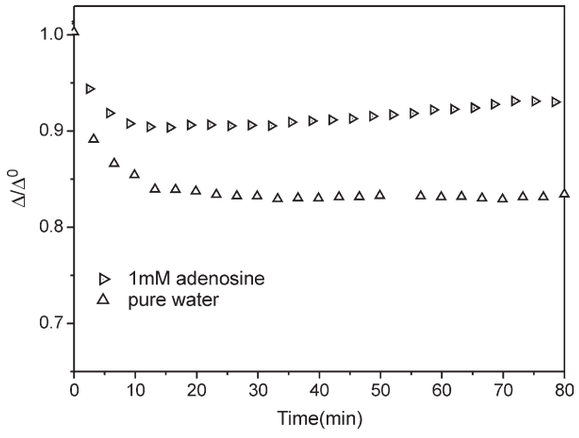


FIGURE 2 Relaxation experiment plots showing the changes in surface pressure over time for **2a** monolayers at 30 mN/m.

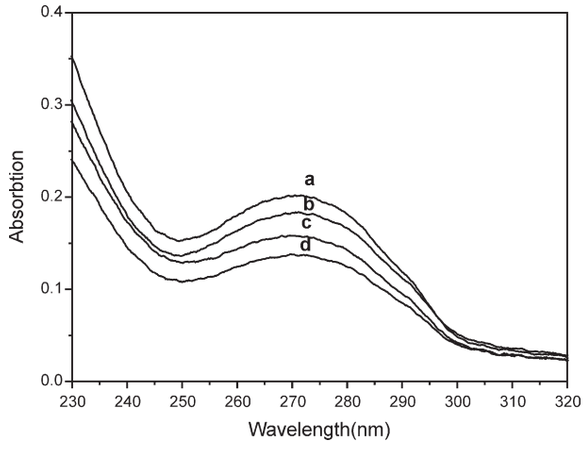


FIGURE 3 UV-VIS spectra of LB films of **2a** deposited on quartz substrates from the surfaces of pure water: (a) 40-layer; (b) 30-layer; (c) 20-layer; (d) 10-layer.

the nucleobase groups of *p-tert*-butylcalix[4]arene-nucleobase derivatives are stuck out into the water phase to a certain extent, and interact with the corresponding nucleosides *via* complementary hydrogen bonding.

Experiments on the $\pi-A$ isotherms of the monolayers on the aqueous solution of the some non-complementary nucleosides were also performed under the same conditions. The results indicate that the interaction between the nucleobases in the headgroup of *p-tert*-butylcalix[4]arene derivatives and the non-complementary nucleoside is weaker. For example, on the subphase of 1.0 mM cytidine or guanosine, the limiting molecular area and collapse pressure of **2c** show no change. On the subphase of 5.0 mM cytidine or guanosine, the limiting molecular area (1.55 nm^2 or 1.57 nm^2) is only slightly increased compared with that on the pure water (1.51 nm^2), and the collapse pressures did not rise. Therefore, the interaction between the nucleobases in the headgroup of *p-tert*-butylcalix[4]arene derivatives and the corresponding complementary nucleosides is remarkably stronger than that for non-complementary nucleosides.

Relaxation Experiments

Relaxation experiments were carried out to study the stability of the monolayer of *p-tert*-butylcalix[4]-arene-nucleobase derivatives on different subphases. Fig. 2 shows the corresponding results of **2a** on two subphases at 30 mN/m. When the initial surface pressure is 30 mN/m, the surface pressure of the monolayer on pure water quickly decreases once the barriers stop. The surface pressure showed no decrease after twenty minutes and remained constant thereafter. π/π^0 is about 0.83. On the subphase of 1.0 mM adenosine solution, the initial surface pressure is decreased only within ten minutes and π/π^0 is about 0.92, which is different from that on pure water. Similar results were also obtained from the same relaxation experiments for the **2b** and **2c** monolayers on the subphase of pure water and aqueous solutions of corresponding complementary nucleosides. These phenomena suggest that **2a**, **2b** and **2c** monolayers are more stable due to larger hydrophilic nucleobases groups, and the nucleosides in the subphase can further improve the stability of the monolayers because of the intermolecular hydrogen bonding interaction between the nucleoside in the subphases and the complementary nucleobases of the monolayers.

UV Spectra of LB Films

UV spectra of 10-, 20-, 30- and 40-layer LB films of **2a** deposited on quartz substrates from the surface of pure water are shown in Fig. 3. It can be seen that the absorption intensities of the bands increase directly

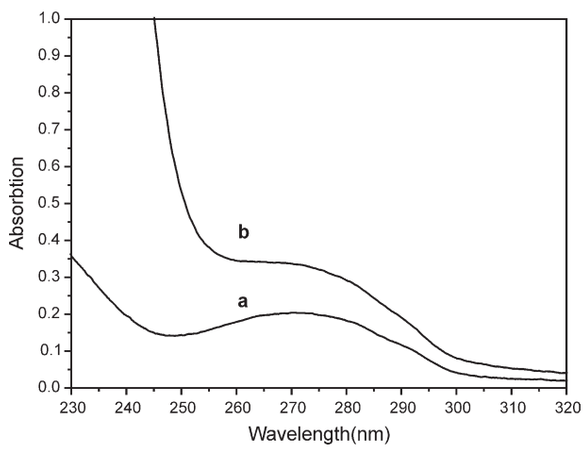


FIGURE 4 UV-VIS spectra of 40-layer LB films of **2a** deposited on quartz substrates: (a) from the surface of pure water; (b) from 5.0 mM adenosine aqueous solution.

with the number of layers, and the absorption maximum of headgroup uracil shifts to 270 nm compared with that of the chloroform solution (264 nm). This shift may indicate $\pi-\pi$ stacking interaction of the headgroups of **2a** [33]. UV spectra of 40-layer LB films of **2a** deposited on quartz substrates from the subphase of pure water and 5.0 mM adenosine solution are displayed in Fig. 4. It can be seen that the absorption intensities of the bands increase noticeably in the UV spectra of LB films deposited on the subphase of 5.0 mM adenosine solution compared with that of LB films prepared from the surface of pure water, and the absorption maximum shows a shift to 267 nm compared with that of headgroup uridine (270 nm) and the aqueous adenosine solution (260 nm).This can be ascribed to the overlap of the similar bands of the headgroup uracil of **2a** and the adenosine. So the conclusion can be drawn that the headgroup uracils of amphiphile **2a** are capable of interacting with adenosines in the subphase at the air–water interface, and adenosines can be transferred to solid substrates along with the monolayer of **2a**.

Similar cases can be observed from UV spectra of the LB films for **2b** and **2c** from the subphase of pure water and aqueous solution of corresponding complementary nucleosides. The absorption intensities of the bands increase noticeably in the UV spectra of LB films of **2b** and **2c** from the subphase of 5.0 mM adenosine/uridine solution compared with that of the LB film prepared from the surface of pure water, respectively. The absorption maximum of the LB film for **2b** from the subphase of 5.0 mM adenosine solution shows a shift to 269 nm compared with that of LB film from pure water (headgroup thymine 274 nm) and the aqueous adenosine solution (260 nm). Similarly, the absorption maximum of the LB film of **2c** from the subphase of 5.0 mM uridine solution shows a shift to 267 nm compared with that of the LB film from pure water (headgroup adenine 261 nm) and aqueous uridine solution (270 nm). Therefore, all of the UV spectral features demonstrate that the complementary nucleosides in the subphase can be bound by *p-tert*-butylcalix[4]arene-nucleobase derivatives through hydrogen bonding and incorporated into the LB films.

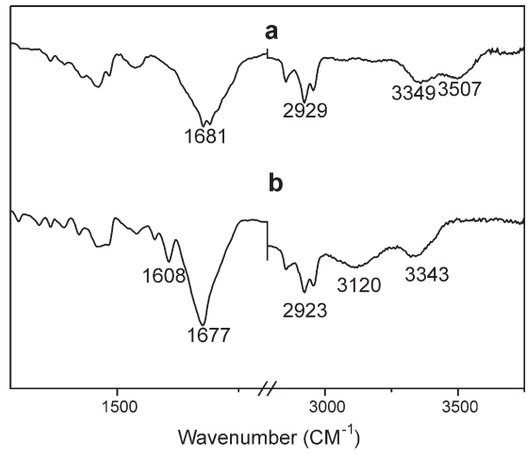


FIGURE 6 FT-IR spectra of 40-layer LB films of **2a** deposited on CaF_2 substrates: (a) from the surface of pure water; (b) from 5.0 mM adenosine aqueous solution.

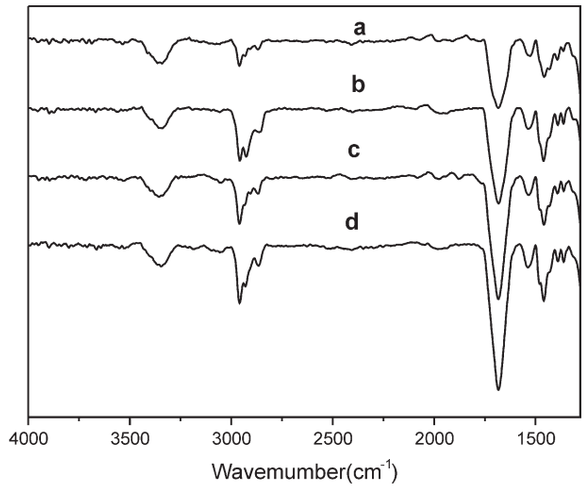


FIGURE 5 FT-IR spectra of LB films of **2a** deposited on CaF_2 substrates from the surface of pure water: (a) 10-layer; (b) 20-layer; (c) 30-layer; (d) 40-layer.

FT-IR Spectra of LB Films

Fig. 5 shows FT-IR spectra of 10-, 20-, 30- and 40-layer LB films of **2a** deposited on CaF_2 substrates from the surface of pure water. All the spectra are very similar to each other except for the band intensities, which increase with increasing number of monolayers. Fig. 6 shows the FT-IR spectra of 40-layer LB films of **2a** deposited from the surface of pure water and 5.0 mM adenosine solution. The diversity of spectral features between the adenosine-containing LB films of **2a** and the LB films deposited from pure water subphase can be clearly observed. In Fig. 6b, the broad band observed in the 3500–3000 cm^{-1} region is due to multiple hydrogen bonding between the uracil moiety in the headgroup of **2a** and adenosine, which is experimental evidence of the formation of a complementary base-base complex. In Fig. 6a, the band at 1681 cm^{-1} is attributed to the C=O and C=N stretching mode in the headgroup of **2a**. This band becomes remarkably stronger for the adenosine-containing LB films of **2a**. Moreover, the peak undergoes a red-shift to 1677 cm^{-1}. These

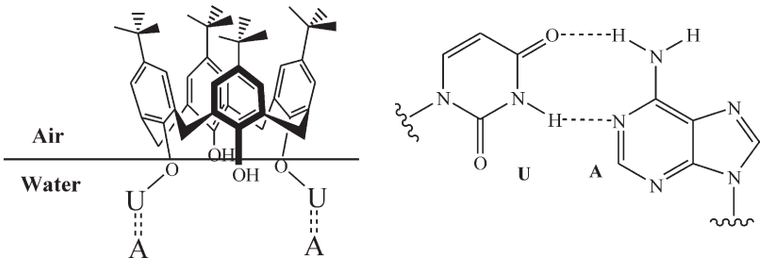


FIGURE 7 Schematic interaction patterns of **2a** with adenosine at the air–water interface.

changes mainly result from the overlap of the C=O, C=N stretching mode in the headgroup and the C=N, C=C stretching mode in the adenine ring and the influence of hydrogen bond formation of the complementary nucleobases [34]. Similar changes are also observed from the FT-IR spectra of 40-layer LB films of **2b** with the thymine headgroup deposited from the surface of pure water and 5.0 mM adenosine aqueous solution. In the FT-IR spectra of 40-layer LB films of **2c** deposited from 5.0 mM uridine, a broad band in the 3550–3000 cm^{-1} region is also observed because of the formation of multiple hydrogen bonding between complementary nucleobases. In the FT-IR spectra of 40-layer LB films of **2c** deposited from the surface of pure water, the band at 1642 cm^{-1} is the C=N, C=C stretching mode in the headgroup adenine ring. The peak becomes stronger for uridine-containing LB films of **2c** and shifts to 1678 cm^{-1} due to the overlap with the C=O, C=N stretching mode in the uridine as well as the formation of multiple hydrogen bonds between complementary nucleobases [34]. Therefore, the molecular recognition between the nucleobases in the headgroup of *p-tert*-butylcalix[4]arene-nucleobase derivatives and the complementary nucleosides in the subphase takes place through multiple hydrogen bonding, for example the interaction pattern between the headgroup uracil of **2a** and adenosine in the subphase (Fig. 7), and the nucleosides can be transferred to solid substrates along with the monolayer of *p-tert*-butylcalix[4]-arene-nucleobase derivatives. These results are consistent with the results obtained from the π–A isotherm, relaxation experiments and UV spectra.

CONCLUSIONS

Three amphiphilic calix[4]arene derivatives with a nucleobase on the lower rim were synthesized in good yields by the condensation of calix[4]arenediamine (5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-aminoethoxy)-26,28-dihydroxycalix[4]-arene) with uracilo-*N*-acetic acid, thymino-*N*-acetic acid and adenino-*N*-propionic acid in the presence of CDI in DMF. The interfacial interaction of the amphiphilic calix[4]arene-nucleobase derivatives with the complementary nucleosides in the subphase was studied by Langmuir–Blodgett techniques. All the results indicate that the amphiphilic calix[4]arene derivatives can form stable monolayers at the air–water interface. The complementary nucleosides in the subphases are efficiently bound to the monolayers at the air–water interface and they can be readily transferred onto solid substrates along with the monolayers, because of the strong intermolecular interactions by multiple hydrogen bonding, just as occurs in nucleic acids.

EXPERIMENTAL

Synthesis of Calix[4]arene Derivatives with Nucleobases

Melting points were determined on a Yanaco micro melting point apparatus (uncorrected). Elemental analyses were determined by means of a Perkin Elmer 240C. ^1H NMR and ^{13}C NMR were recorded on Bruker AM 300 (Germany) instruments. Mass spectra were recorded on an electrospray mass spectrometer (LCQ, Finnigan) in the negative mode. Preparative column chromatographic separations were performed on G60 silica gel, while precoated silica gel plates (GF_{254}) were used for analytical TLC. All solvents were purified by standard procedures. All other chemicals were purchased from Sigma or Aldrich. Compound **1** [35,36] and compounds **3** [37], **4** [37], **5** [38] were synthesized according to literature procedures.

A solution of compound **3** (**4** or **5**) (6.0 mmol) and CDI (6.0 mmol) in anhydrous DMF (50 ml) was stirred for 0.5 h under N_2 at rt, then *p*-tetra-*tert*-butylcalix[4]arenediamine **1** (2.0 g, 2.72 mmol) was added. The mixture was stirred for 4 days at rt. Then the mixture was evaporated to dryness *in vacuo*. The residue was dissolved in $CHCl_3$ (50 ml) and a small amount of insoluble suspension was removed by filtration. The mixture was washed consecutively with saturated Na_2CO_3 solution (3 × 25 ml) and water (3 × 25 ml), and then the organic layer was

dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by column chromatography ($CHCl_3$–CH_3OH, 10:1). The products were further purified by crystallization from ethyl acetate–petroleum to give a white powder **2a** (**2b** or **2c**, respectively).

5,11,17,23-Tetra-tert-butyl-25,27-bis[2-(uracilo-N-acetamido)ethoxy]-26,28-dihydroxycalix[4]arene (2a)

Yield: 60%. Mp 220–223°C. ^{1}H NMR ($CDCl_3$, 20°C): δ 9.60 (s, 2H, 2 × CONHCO), 8.63 (s, 2H, 2 × –CONH), 7.63 (s, 2H, 2 × OH), 7.25 (d, 2H, $J = 8.0$ Hz, –CH=CH–) 7.23 (s, 4H, 2 × HO-Ar*H*), 6.95 (s, 4H, 2 × RO-Ar*H*), 5.65 (d, 2H, $J = 8.0$ Hz, –CH=CH–), 4.48 (s, 4H, 2 × –$COCH_2$N–), 4.24 (d, 4H, $J = 12.9$ Hz, 4 × *endo*-ArCH_2Ar), 4.14 (m, 4H, 2 × –OCH_2CH_2NH–), 3.93 (m, 4H, 2 × –OCH_2CH_2NH–), 3.40 (d, 4H, $J =$ 12.9 Hz, 4 × *exo*-ArCH_2Ar), 1.27 (s, 18 H, 2 × ROAr-*t*-C_4H_9), 1.06 (s, 18H, 2 × HOAr-*t*-C_4H_9). ^{13}C NMR ($CDCl_3$, 20°C): δ 167.2 (CONH), 164.6, 151.9 (uracil CONH), 149.8, 149.1, 148.4, 145.7, 143.4, 135.3, 132.9, 128.2, 126.4, 126.0, 121.9, 102.8 (aromatic C), 77.8 (O*C*H_2CH_2), 75.3 (N*C*H_2CO), 51.1 (NH*C*H_2CH_2), 40.0, 34.5, 34.3, 32.3, 31.9, 31.4 [–$C(CH_3)_3$, Ar*C*H_2Ar]. MS (ESIMS): $m/z = 1037.8$ ([M − H]$^-$, calcd. 1037.5). Anal. Calcd. for $C_{60}H_{74}N_6O_{10}$: C, 69.33; H, 7.18; N, 8.09. Found: C, 69.59; H, 7.26; N, 7.88.

5,11,17,23-Tetra-tert-butyl-25,27-bis[2-(thymino-N-acetamido)ethoxy]-26,28-dihydroxycalix[4]arene (2b)

Yield: 67%. Mp 231–233°C. ^{1}H NMR (*d*-DMSO, 20°C): δ 11.32 (s, 2H, 2 × CONHCO), 8.54 (s, 2H, 2 × CONH), 8.47 (s, 2H, 2 × HO), 7.27 (s, 2H, 2 × CH=C, in pyrimidyl), 7.17 (s, 4H, 2 × HO-Ar*H*), 7.15 (s, 4H, 2 × RO-Ar*H*), 4.41 (s, 4H, 2 × –$COCH_2$N–), 4.17 (d, 4H, $J = 12.5$ Hz, 4 × *endo*-ArCH_2Ar), 4.14 (m, 4H, 2 × –OCH_2CH_2-NH–), 3.79 (m, 4H, 2 × –OCH_2CH_2NH–), 3.48 (d, 4H, $J = 12.5$ Hz, 4 × *exo*-ArCH_2Ar), 1.56 (s, 6H, 2 × –CH_3), 1.17 (s, 18H, 2 × ROAr-*t*-C_4H_9), 1.13 (s, 18H, 2 × HOAr-*t*-C_4H_9). ^{13}C NMR (*d*-DMSO, 20°C): δ 168.7 (CONH), 165.2 (CONH, in pyrimidyl), 151.9 (CONH, in pyrimidyl), 150.2, 150.0, 148.3, 142.8, 142.7, 134.1, 128.6, 126.6–126.3 (aromatic C), 109.4 (CH_3–*C*, in pyrimidyl), 79.9 (OCH_2CH_2), 75.4 (NCH_2CO), 50.7 (CH_2CH_2NH), 41.1, 34.8, 34.5, 32.1, 31.7, 31.5 [–$C(CH_3)_3$, ArCH_2Ar], 12.5 (–CH_3). MS (ESMS): $m/z = 1065.3$ ([M − H]$^-$, calcd. 1065.6). Anal. Calcd. for $C_{62}H_{78}N_6O_{10}$: C, 69.76; H, 7.37; N, 7.88. Found: C, 69.50; H, 7.38; N, 7.63.

5,11,17,23-Tetra-tert-butyl-25,27-bis[2-(adenino-N-propionamido)ethoxy]-26,28-dihydroxycalix[4]arene (2c)

Yield: 65%. Mp 240–242°C. ^{1}H NMR ($CDCl_3$, 20°C): δ 8.67 (s, 2H, 2 × CONH), 8.48 (s, 2H, 2 × OH), 8.19 (s, 2H, adenine H), 7.96 (s, 2H, adenine H) 7.00 (s, 8H, Ar*H*), 5.93 (s, 4H, 2 × NH_2), 4.57 (s, 4H, 2 × $COCH_2CH_2$N–), 3.99 (d, 4H, $J = 12.6$ Hz, 4 × *endo*-ArCH_2Ar), 3.84 (m, 4H, 2 × –OCH_2CH_2NH–), 3.44 (m, 4H, 2 × –OCH_2CH_2NH–), 3.25 (d, 4H, $J = 12.6$ Hz, 4 × *exo*-ArCH_2Ar), 2.88 (m, 4H, 2 × $COCH_2CH_2$N–), 1.24 (s, 18H, 2 × ROAr-*t*-C_4H_9), 1.15 (s, 18H, 2 × HOAr-*t*-C_4H_9). ^{13}C NMR (*d*-DMSO, 20°C): δ 170.6 (CONH), 156.7, 153.2, 150.2, 149.9, 148.3, 142.7, 141.8, 134.0, 128.4, 126.6, 126.3, 119.5 (aromatic C), 75.6 (OCH_2CH_2), 58.3 (OCH_2CH_2N), 36.1, 34.9, 34.5, 32.2, 31.9, 31.7, 31.5 [$COCH_2CH_2$N, –$C(CH_3)_3$, ArCH_2Ar]. MS (ESMS): $m/z = 1111.3$ ([M − H]$^-$, calcd. 1111.6). Anal. Calcd. for $C_{64}H_{80}N_{12}O_6$: C, 69.04; H, 7.24; N, 15.10. Found: C, 69.26; H, 7.31; N, 15.46.

Surface Pressure–Area Isotherm 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 25 µl of a 5×10^{-4} M chloroform solution of receptor **2a** (**2b** or **2c**) onto the surface of deionized water (purified by the Milli-Q system, >18 MΩ, pH ~ 5.6) and the aqueous subphases containing different nucleosides, respectively. A period of 30 min was given for the evaporation of the spreading solvent and the interaction between nucleoside and receptor. The π–A isotherms were measured three times at a barrier speed of 4 mm/min and were found to be reproducible.

Relaxation Experiments

Relaxation experiments were carried out at constant molecular area and at an initial surface pressure of 30 mN/m. When the surface pressure rose to the desired magnitude during compression, the barriers were stopped and the surface pressure was recorded over a period of 80 min thereafter.

Characterization of LB Films

All the LB films were prepared at a surface pressure of 30 mN/m by the horizontal lifting method. The transfer ratio was close to 0.9 ± 0.1. UV spectra of LB films deposited on quartz plates (40 layers) were measured on a JASCO V-530 spectrophotometer. FT-IR spectra (transmission-absorption spectrum mode) of LB films deposited on CaF_2 plates

(40 layers) were measured using a Bruker IFS 66v spectrometer with a resolution of 4 cm^{-1}.

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