Control of molecular ordering in guanidinium-functionalized monolayer by carboxylate template molecules

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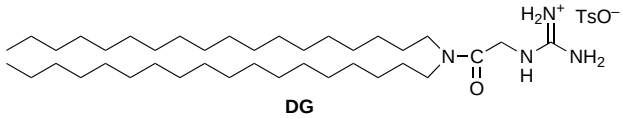
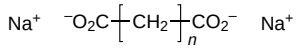
Electron diffraction studies of a [(dioctadecyl)carbamoylmethyl]guanidinium toluene-*p*-sulfonate (DG) monolayer reveal that the regularity of the molecular arrangement and the size of crystalline domains are controlled through binding of aqueous α,ω-dicarboxylates with various spacer lengths.

Morphological and structural control of monolayers at the air–water interface is crucial for their applications in molecular electronics, optical devices and biomedical uses.[1,2] It has been demonstrated that patterning of monolayer components within a monolayer is realized through molecular recognition between monolayer components and aqueous templates.[3,4] We describe here that this concept is extended to control of regularity of the molecular arrangement in a monolayer. Dialkylguanidinium monolayers have been shown to strongly bind aqueous sodium α,ω-dicarboxylates through hydrogen and ionic bonding.[5] These interactions are expected to affect molecular packing, as inferred from π-*A* isotherms. Diffraction techniques are a powerful tool for evaluating the molecular packing in a monolayer.[3,6,7]



DG



dicarboxylate

Figs. 1(*a*)–(*f*) show electron diffraction (ED) patterns† of a **DG** monolayer‡ on pure water and on 0.1 mM aqueous solutions of sodium oxalate (n = 0), malonate (n = 1), succinate (n = 2), glutarate (n = 3) and adipate (n = 4).§ Each monolayer was transferred by the horizontal drawing-up method[6] onto a hydrophilic SiO substrate,¶ after compressing up to a surface pressure of 30 mN m^{-1}.‖ The ED pattern of the **DG** monolayer on pure water was an amorphous halo, indicating that the monolayer is in an amorphous state. This may be caused by electrostatic repulsion among ionic hydrophilic groups of the **DG** molecules.[7] The elemental ratio of oxygen and nitrogen atoms (O/N) obtained by X-ray photoelectron spectroscopic analysis of a multilayered film of the monolayer revealed that the hydrophilic groups of the **DG** molecules are dissociated, with TsO^- replaced with a OH^- counterion.** On the other hand, the ED pattern of the monolayer on aqueous sodium oxalate displays a crystalline arc, indicating that crystallization of the monolayer is induced by the oxalate template. Apparently, electrostatic repulsion among the positive hydrophilic groups is weakened by tight binding of the rigid oxalate template, inducing transformation from the amorphous to the crystalline state. **DG** monolayers on aqueous malonate and succinate are also in the crystalline state. However, the arc of these ED patterns is broader along the azimuthal direction than that of the monolayer on oxalate. This broadening suggests reduction in the size of the crystallites†† formed in the monolayer and a random alignment of the crystallographical axes of the crystallites. It appears that the bridging effect of two neighbouring monolayer components is lessened owing to the relatively flexible methylene spacers connecting the two carboxylate groups in malonate and succinate. In the cases of glutarate and adipate with longer methylene spacers, the corresponding ED patterns are again amorphous haloes. The bridging effect must be reduced even more due to the longer methylene chains between the two carboxylate units. These

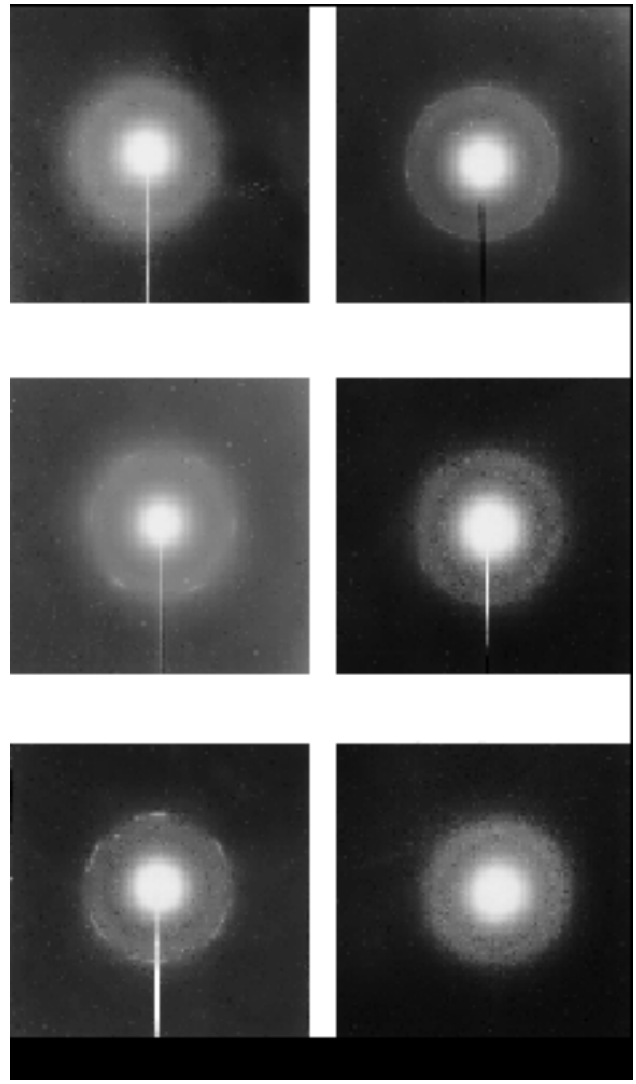


Fig. 1 ED patterns of each **DG** monolayer (*a*) on pure water, (*b*) on aqueous oxalate, (*c*) on aqueous malonate, (*d*) on aqueous succinate, (*e*) on aqueous glutarate and (*f*) on aqueous adipate

structural changes based on ED pattern analyses were reflected in the π-*A* isotherms, as shown in Fig. 2. The shapes of these π-*A* isotherms‡‡ are affected by the presence and the nature of the dicarboxylates: the averaged molecular area of the monolayers on oxalate and malonate at a surface pressure of 30 mN m^{-1} was smaller than that on pure water, and again increased as the number of the spacer methylene groups in the dicarboxylates increased from succinate to adipate. Therefore, the molecular area of the monolayer, evaluated from π-*A* isotherms, is smaller in the crystalline state (on aqueous oxalate, malonate and succinate) than that in the amorphous one (on pure water, aqueous glutarate and adipate). The expanded region observed in the π-*A* isotherm on pure water was much reduced on aqueous dicarboxylates. This change supposedly comes from suppression of free molecular translational movement at low surface pressures by binding of the hydrophilic groups of the **DG** molecules to dicarboxylates.

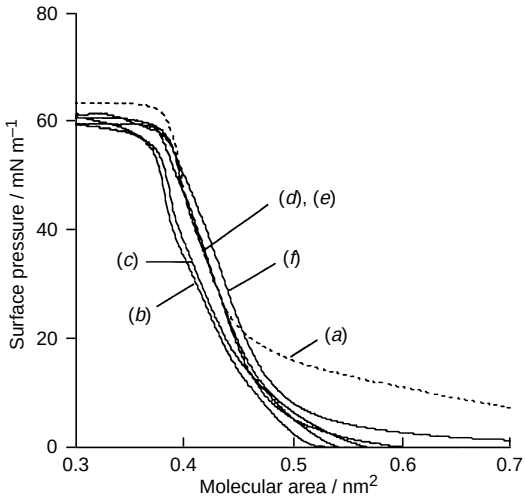


Fig. 2 π-*A* Isotherms of each **DG** monolayer (*a*) on pure water, (*b*) on aqueous oxalate, (*c*) on aqueous malonate, (*d*) on aqueous succinate, (*e*) on aqueous glutarate and (*f*) on aqueous adipate

Fig. 3 shows a schematic representation of the relationship between the mode of host–guest interaction and the monolayer morphology. **DG** molecules are randomly arranged in the monolayer on pure water, because the **DG** monolayer can not crystallize owing to electrostatic repulsion among the cationic head groups. In the case of the **DG** monolayer on a template molecule without a spacer group, the **DG** monolayer crystallizes and the molecules form large crystalline domains, because the cohesive effect among the hydrophobic groups in **DG** molecules and the tight bridging of the two monolayer components act cooperatively. In the case of the **DG** monolayer on template molecules with spacer groups, the bridging effect is lessened, and the monolayer is composed of small crystalline domains and/or the positional order in the monolayer deteriorates.

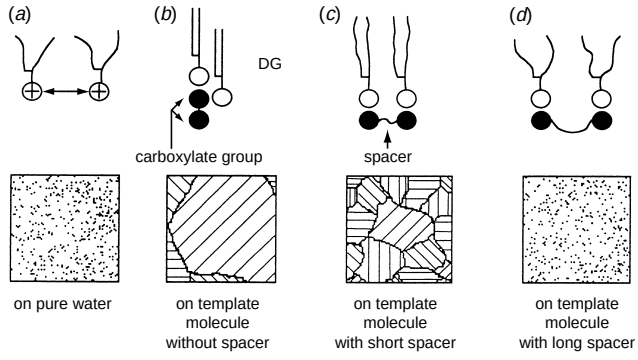


Fig. 3 Schematic representation of the aggregation structure of each **DG** monolayer. Points and lines express the random and the regular molecular arrangement of **DG** molecules in the monolayer, respectively.

In summary, the molecular ordering and the size of crystalline domains in guanidinium monolayers can be controlled by aqueous dicarboxylates with different methylene bridge lengths. Preliminary observation of the monolayer by atomic force microscopy also confirms the presented results. The details on their molecular images are now under investigation.

Footnotes

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† ED patterns in this study are for a monolayer transferred onto the hydrophilic SiO substrate, not for a floating monolayer on a water surface. However, the structure of the transferred monolayer is considered to be the same as that of the floating monolayer (see ref. 6). ED patterns were recorded with a Hitachi H-600S transmission electron microscope, operating at an acceleration voltage of 75 kV and with a beam current of several μA. The electron beam was several μm in diameter.

‡ Benzene–ethanol (80 : 20) was used as the spreading solvent. Compression was started 10 min after spreading at a rate of 0.2 mm s^{-1} by using a computer-controlled film balance system FSD-50 (USI System, Fukuoka). The subphase temperature was kept at 293 ± 0.2 K. Surface pressures were measured by a Wilhelmy plate which was calibrated with the transition pressure of an octadecanoic acid monolayer.

§ Subphase pH was *ca.* 6 and the strongly basic **DG** was protonated. Dicarboxylates were added with equivalent NaOH into subphase, thus they must be the sodium salt (see ref. 5).

¶ The hydrophilic SiO substrate was prepared by vapour deposition of SiO onto a Formvar thin layer, with which an electron microscope grid was covered on a glass slide.

‖ The transfer ratio for each monolayer was unity, indicating that the SiO substrate is completely covered with each monolayer.

** Replacement of the TsO^- counterion by OH^- was strongly suggested by the absence of an S atom and the O/N ratio of 0.44 in the XPS data of the transferred LB film.

†† The broadness of arc along the azimuthal direction on the ED pattern results from the existence of a large number of crystalline domains with different crystallographical axes. The diameter of the electron beam was constant in this study. Therefore, the broader arc observed on the present ED pattern indicates a size reduction of the crystalline domain in monolayer.

‡‡ Highly water-soluble dicarboxylates do not make any contribution to the molecular area. Thus, the molecular area (abscissa in Fig. 2) is based on the number of **DG** molecules.

References

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