Electrostatically Driven Guest Binding in Self-Assembled Porous Network at the Liquid/Solid Interface

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ABSTRACT

We present here the construction of a self-assembled two-dimensional (2D) porous monolayer bearing a highly polar 2D space to study guest co-adsorption through electrostatic interactions at the liquid/solid interface. For this purpose, a dehydrobenzo[12]annulene (DBA) derivative, **DBA-TeEG**, having tetraethylene glycol (TeEG) groups at the end of the three alternating alkoxy chains connected by *p*-phenylene linkers was synthesized. As a reference host molecule, **DBA-C10** having non-polar C₁₀ alkyl chains, at three alternating terminals was employed. As guest molecules, hexagonal phenylene-ethynylene macrocycles (PEMs) attached by triethylene glycol (TEG) ester and hexyl ester groups, **PEM-TEG** and **PEM-C6**, respectively, at each vertex of the macrocyclic periphery were used. STM observations at the 1,2,4-trichlorobenzene/HOPG interface revealed that **PEM-TEG** was immobilized in the pores formed by **DBA-TeEG** at higher probability due to electrostatic interactions such as dipole-dipole and hydrogen bonding interactions between oligoether units of the host and guest, in comparison to **PEM-C6** with non-polar groups. These observations are discussed based on molecular mechanics simulations to investigate the role of the polar functional groups. When a non-polar host matrix formed by **DBA-C10** was used, however, only phase separation and preferential adsorption were observed; virtually no host-guest complexation was discernible. This is ascribed to the strong affinity between the guest molecules which form by themselves densely packed van der Waals networks on the surface.

INTRODUCTION

Two-dimensional (2D) molecular assembly on solid surfaces has become a subject of keen interest because of prospects in the field of nanoscience and nanotechnology such as molecular-scale electronics, highly selective sensors, and tailor-made catalyses.¹⁻⁵ Among various 2D structures, porous networks attract a great deal of interest because various molecules and molecular clusters can be immobilized in the surface-confined pore space as guests in size-, shape-, symmetry-, and function-selective manner.⁶⁻¹⁰ In most cases, the main driving forces for guest immobilization in the pores are vertical van der Waals interactions between a guest molecule and the substrate surface in addition to lateral van der Waals interactions between the periphery of a guest molecule and the edge of the 2D pore; the latter frequently serve to generate selectivity. In this respect, matching in size and shape between a guest molecule and the 2D porous space plays a very important role for guest binding. To gain crucial information on the host-guest events on surfaces, scanning tunneling microscopy (STM) has been used as a powerful tool by visualizing the molecular assemblies with sub-molecular level under ultrahigh vacuum conditions as well as the liquid/solid interfaces.¹¹⁻¹³

In view of prospects in nanoscale patterning and sensing based on host-guest recognition, the modification of not only the physical environment such as the size and shape of pores but also the chemical environment to bind a specific guest molecule via guest-specific noncovalent interactions is one of the challenges in this field. For example, binding small positively charged ions¹⁴⁻¹⁹ and

negatively charged species^{20,21} has been reported. However, for immobilization of neutral organic guests, although a few studies on the size- and shape-modification of the 2D pores with space-controlling groups have been reported,^{22–25} little has been done for chemical modification of pore space. Recently, we demonstrated the construction of porous space modified by fluoroalkyl groups of a honeycomb type network formed by a dehydrobenzo[12]annulene (DBA) and its guest recognition ability toward guests via fluorophilicity at the liquid/solid interface.²⁶ In order to study host-guest binding driven by other intermolecular interactions at the solid/liquid interface, we describe herein the construction of polar pores outlined with oligoethylene glycol (OEG) units which possess a permanent dipole moment.^{27,28} In three dimensional (3D) space, OEG groups have been used to create a polar environment in which guest molecules are immobilized by dipole-dipole interactions.^{29–31} However, the construction of 2D pores that can bind a guest molecule by electrostatic interactions has not been reported yet.

For the construction of 2D pores equipped with OEG units at the liquid/solid interface, we planned to use a supramolecular honeycomb structure of a DBA derivative as a host matrix. To this end, we designed and synthesized **DBA-TeEG** (Figure 1a). To place three tetraethylene glycol (TeEG) units at the periphery of the pore, the TeEG unit was connected by a *para*-phenylene linker at the end of a C₁₀ alkyl chain. The three other alkyl chains were tetradecyloxy groups (C₁₄). As a reference host molecule, **DBA-C10**²⁶ having non-polar C₁₀ alkyl chains, instead of polar TeEG groups, at three

alternating terminals was employed. As guest molecules, two phenylene-ethynylene macrocycles (PEMs), **PEM-TEG**³² having six peripheral triethylene glycol (TEG) units and **PEM-C6**³³ surrounded by six C₆ alkyl chains, respectively, were chosen (Figure 1a). 1,2,4-Trichlorobenzene (TCB) was used as a solvent in view of its moderate affinity to both polar and nonpolar host/guest molecules to minimize bias due to solvent polarity. Prior to experiments, molecular modeling studies indicated that the porous space formed by **DBA-TeEG** is not large enough to accommodate a guest with extended side chains, suggesting that the side chains of either the host matrix (the TeEG units) or the guest molecules (the TEG or C₆ units) may not be adsorbed on the surface, but exposed to the solution phase (Figure 2).

It should be pointed out, however, that the guest molecules, **PEM-TEG** and **PEM-C6**, are capable of forming self-assembled networks of their own. In the previous study,³³ we revealed that **PEM-TEG** formed dense packed monolayers (tentatively called dense hexagonal and zigzag structures) on the surface stabilized by hydrogen bonds between the carbonyl oxygen and aromatic hydrogen atoms. The TEG units did not adsorb on the HOPG surface. **PEM-C6** formed a honeycomb structure driven by van der Waals interactions between the interdigitated alkyl chains of neighboring molecules at the liquid/solid interface. Therefore, **PEM-TEG** and **PEM-C6** would not only act as guest molecules but also assemble by themselves in competition with the networks of the host molecules. Indeed, there are a few examples of co-existence of host-guest events and phase separation in bicomponent

systems.^{34–36} In binary systems, there are following four possible outcomes of the phase behavior; (1) phase segregation,^{37–39} (2) preferential adsorption,^{40–42} (3) random mixing,^{43–45} and (4) cocrystallization.^{14,26,46–50} Phase segregation means co-existence of domains of host networks and guest networks in the present case. The host-guest networks in which a guest molecule is co-adsorbed in the pores without affecting the host network structure^{9,10,51–56} can be regarded as preferential adsorption of a host. Though co-crystallization including cooperative interactions of both components is principally possible in view of the presence of the phenylene-ethynylene units as a common scaffold in both host and guest molecules, it is unlikely because of the mismatch in the chain lengths. As a consequence, we report here not only the host-guest events but also the phase behavior in the binary system consisting of DBAs and PEMs (Figure 2), and the controlling factors that govern the outcome of molecular assembly at the liquid/solid interface.

Figure 1. Chemical structures of **DBA-TeEG**, **DBA-C10**,²⁶ **PEM-TEG**,³² and **PEM-C6**.³³

Figure 2. Schematic models for the formation of a honeycomb type network of DBAs (a) and a dense packed network of PEMs (b), and host-guest event and phase behavior in binary system (c) by self-assembly on a surface. In the networks, the side-chains of PEMs are omitted for clarity reason.

EXPERIMENTAL SECTION

Synthesis. Syntheses of **DBA-C10**,²⁶ **PEM-TEG**,³² and **PEM-C6**³³ were reported previously.

DBA-TeEG was prepared by the same method as that reported for **DBA-C10** (See Supporting Information).

Details of STM Observations at the Liquid/Solid Interface. All experiments were performed at 23–27 °C using a Nanoscope IIIa (Digital Instruments Inc.) or a Nanoscope V (Bruker AXS) with an

external pulse/function generator (Agilent 33220A) with negative sample bias. All STM images were acquired in the constant current mode. Tips were mechanically cut from Pt/Ir wire (80%/20%, diameter 0.25 mm). During scanning, electric pulses from -1.6 to -2.8 V with a pulse width of 880 ns were occasionally applied using a pulse/function generator to clean the point end of an STM tip.

Prior to imaging, compounds were dissolved in commercially available 1,2,4-trichlorobenzene (TCB) at several solute concentrations described in the text. Immediately before use, highly oriented pyrolytic graphite (HOPG) substrate (grade ZYB, Momentive Performance Material Quartz Inc., Strongsville, OH) was cleaved using adhesive tape. A homemade liquid cell placed on HOPG substrate was employed to minimize the effect of solvent evaporation using a sample solution of 30 μL . All STM observations of the monolayers were performed at the interface between TCB and HOPG after the solution was subjected to the cell without annealing treatment within a 3 h period or after annealing treatment at 70°C for 1 h in an oven to attain thermodynamic equilibrium.⁵⁷ By changing the tunneling parameters during the STM imaging, namely, the voltage applied to the underlying HOPG substrate, it was possible to switch from the visualization of the adsorbate layer to that of the substrate. This enabled us to correct for drift effects by the use of SPIP (scanning probe image processor) software (version 6.2.4., Image Metrology A/S, Hørsholm). Unit cell parameters are determined from more than 30 experimental values of at least two calibrated STM images.

Details of Molecular Mechanics Simulations. Molecular mechanics (MM) simulations were performed with the Materials Studio 8.0 using the Forcite module with COMPASS force field. The initial structures of monolayers were built from the respective molecular models which were optimized by the semiempirical PM3 method. Then, the orientation of the alkyl chains relative to the π -system was adjusted based on that observed in the STM images. The molecules were placed 0.35 nm above the first layer of a periodic two-layer sheet of graphene with an interlayer distance of 0.335 nm to mimic graphite. The two-layer graphene structure was frozen during the simulations, and a cutoff of 2.0 nm was applied for the van der Waals interactions (Lennard-Jones type). Periodic boundary conditions (PBC) for simulations are described in the figure captions.

RESULTS AND DISCUSSION

STM observations of monolayers formed by DBA-TeEG or DBA-C10 at the TCB/graphite interface. A high resolution STM image of a self-assembled monolayer formed by **DBA-TeEG** at the TCB/HOPG interface (1.0×10^{-5} M) after annealing treatment at 70 °C for 1 h is shown in Figure 3a. A large-scale image is given in Figure S1a. In the STM image, the triangular shaped bright features correspond to the conjugated cores of **DBA-TeEG**, while the darker parts between the DBA cores are assigned to four interdigitated alkyl chains,⁵⁸ revealing the formation of a honeycomb structure. Small bright features located at the corners of the pores correspond to the phenylene linkers (indicated by the yellow arrow in Figure 3a). The dim fuzzy rods at the rim of the pores indicated by the green arrow in Figure 3a are assigned to the TeEG units, though they are not visualized clearly, probably due to the low tunneling efficiency of the ethylene glycol units^{59,60} or the mobility owing to weak interactions with the HOPG substrate.⁶¹ Unit cell parameters are $a = b = 5.0 \pm 0.1$ nm, $\gamma = 60 \pm 1^\circ$. In some of the pores, dim fuzzy features are observed, which are ascribed to a self-adsorbed⁶² **DBA-TeEG** molecule or co-adsorbed TCB molecules. Figure 3b displays a molecular model built by molecular mechanics (MM) simulations of the honeycomb structure of **DBA-TeEG** in which six TeEG units were placed in the pores.

STM observation of a self-assembled monolayer formed by **DBA-C10** (1.0×10^{-5} M in TCB) after annealing revealed a similar honeycomb structure wherein the phenylene linkers and the terminal

alkyl chains placed at the rim of the pores are clearly visualized (Figures 3c and S1b). A network model optimized by MM simulations is displayed in Figure 3d. The unit cell parameters ($a = b = 5.0 \pm 0.1$ nm, $\gamma = 60 \pm 1^\circ$) were identical to those of the honeycomb structure of **DBA-TeEG**, indicating that the terminal groups in the DBAs (TeEG and C₁₀ alkyl) do not participate in the honeycomb network formation.

Figure 3. STM images and molecular models of honeycomb structures of **DBA-TeEG** (a, b) and **DBA-C10** (c, d) formed after annealing at 70 °C for 1 h at the TCB/graphite interface (concentration = 1.0×10^{-5} M, tunneling parameters: $I_{\text{set}} = 28$ pA and $V_{\text{set}} = -88$ mV for a and $I_{\text{set}} = 41$ pA and $V_{\text{set}} = -200$ mV for c). White arrows indicate the directions of the main symmetry axes of underlying graphite, and yellow and green arrows in (a) and (b) indicate the small feature corresponding to the phenylene linker and the dim fuzzy rod due to the TeEG unit, respectively. Unit cell parameters for both structures are $a = b = 5.0 \pm 0.1$ nm, $\gamma = 60 \pm 1^\circ$. Molecular models were optimized by MM simulations on a graphene bilayer under periodic boundary conditions (PBC): $a = b = 4.97$ nm, $\gamma = 60.0^\circ$. Color code for atoms: blue; C of **DBA-TeEG** and **DBA-C10** molecules, grey; C of the graphene bilayer, red; O, white; H.

STM observations of monolayers formed by a mixture of DBA-TeEG and PEM-TEG at the TCB/graphite interface. Figures 4 displays STM images of a self-assembled monolayer of a mixture of **DBA-TeEG** (1.0×10^{-5} M) and **PEM-TEG** (1.0×10^{-5} M) in a 1 : 1 molar ratio at the TCB/HOPG interface after annealing. STM images before annealing are shown in Figure S2. In both cases, the surface was covered by the honeycomb structure formed by **DBA-TeEG** and in some of the pores **PEM-TEG** molecules were observed as cyclic features. The unit cell parameters of the honeycomb structure ($a = b = 5.0 \pm 0.1$ nm, $\gamma = 60 \pm 1^\circ$) were identical to those of the network formed by **DBA-TeEG** alone, indicating that co-adsorption of **PEM-TEG** does not affect the host network structure. The pore spaces are classified into four categories, according to appearance: *filled pore* containing a single **PEM-TEG** molecule which is observed as an apparent cyclic feature, *partly filled pore* in which an incomplete cyclic feature is observed, *fuzzy pore* with a fuzzy feature, and *open pore* in which any bright features are observed (Figure 4c). These pores are indicated by red, green, yellow, and white hexagons, respectively, in Figures 4d and S2c. From a statistical analysis of the STM images before annealing, the distribution of these types of pores was determined to be 42% for *filled pores*, 7% for *partly filled pores*, 2% for *fuzzy pores*, and 49% for *open pores* (Table 1). Annealing did not change the distribution significantly; 40% *filled pores*, 3% *partly filled pores*, 4% *fuzzy pores*, and 52% *open pores*.

Figure 4. (a, b) STM images of monolayers formed by a mixture of **DBA-TeEG** and **PEM-TEG** (each 1.0×10^{-5} M) after annealing at 70 °C for 1 h at the TCB/graphite interface (tunneling parameters: $I_{\text{set}} = 32$ pA and $V_{\text{set}} = -60$ mV for a, $I_{\text{set}} = 26$ pA and $V_{\text{set}} = -160$ mV for b). Unit cell parameters are $a = b = 5.0 \pm 0.1$ nm, $\gamma = 60 \pm 1^\circ$. White arrows indicate the directions of the main symmetry axes of underlying graphite. (c) Representative images for *filled pore*, *partly filled pore*, *fuzzy pore*, and *open pore*. (d) The same STM images as b with the color-coded hexagons: red; *filled pores*, green; *partly filled pores*, yellow; *fuzzy pores*, and white; *open pores*.

When the ratio of **PEM-TEG** relative to **DBA-TeEG** was increased to 2.6 (1.0×10^{-5} M for **DBA-TeEG** and 2.6×10^{-5} M for **PEM-TEG**), the phase segregation between the domains of the honeycomb structure of **DBA-TeEG**, containing immobilized **PEM-TEG** as a guest, and those of

closely packed structures of **PEM-TEG** was observed regardless of the annealing treatment (Figures S3a and S4a). The relative area of the domains, however, was different before and after annealing. By analysis of 14 STM images of a $100 \times 100 \text{ nm}^2$ area, the areas of the domains of the monolayers of **DBA-TeEG** and **PEM-TEG** were estimated to be approximately 1 : 1 before annealing, whereas the populations changed to 3 : 7 after annealing (determined from 6 STM images of a $100 \times 100 \text{ nm}^2$ area). In the honeycomb structure of **DBA-TeEG** (Figures S3b, S3c before annealing, and S4b, S4c after annealing), the guest occupancy was determined by statistical analyses before and after annealing (Table 1). For example, the proportions of *filled pores* were 47% and 60% before and after annealing, respectively. The distribution of *filled pores* did not increase significantly in spite of the increased ratio of **PEM-TEG**, because the concentration of the guest does not increase as much due to its adsorption on HOPG forming domains consisting solely of the guest.

In the domain of the self-assembled monolayer of **PEM-TEG**, two different types of 2D patterns, dense hexagonal and zig-zag patterns,³³ were observed irrespective of annealing treatment (Figures S5a, S5b before annealing, and S5c, S5d after annealing). These patterns are identical to those observed by self-assembly of **PEM-TEG** under similar conditions as reported previously.³³ Figures S5e, S5f show molecular models of the dense hexagonal and zigzag structures, respectively, of a PEM derivative in which the TEG ester groups are replaced by ethyl groups. The molecules are connected by hydrogen bonds between the ester carbonyl oxygen and the aromatic hydrogen atoms of

neighboring molecules.

STM observations of monolayers formed by a mixture of DBA-TeEG and PEM-C6 at the TCB/graphite interface. In order to investigate the effect of the polarity of the guest molecule, STM observations of a self-assembled network formed by a mixture of **DBA-TeEG** (1.0×10^{-5} M) and **PEM-C6** (1.0×10^{-5} M) was performed in a 1 : 1 molar ratio in TCB. Before annealing treatment (Figure 5a), phase segregation between the domains of the honeycomb structure of **DBA-TeEG** and a self-assembled monolayer of **PEM-C6**³³ was observed in an approximate ratio of 7 : 3 (estimated from 6 images of a 100×100 nm² area and 2 images of a 200×200 nm² area). By contrast, after annealing (Figure S6) the surface coverage of a monolayer formed by **PEM-C6** increased to more than 95% (from 9 images of a 100×100 nm² area and 4 images of a 200×200 nm² area). Thus, after annealing treatment, **PEM-C6** was adsorbed preferentially over **DBA-TeEG**.

In the domain of the honeycomb structure of **DBA-TeEG** (Figures 5b, 5c), the guest occupancy distribution was determined as follows: 9% *filled pores*, 3% *partly filled pores*, 4% *fuzzy pores*, and 84% *open pores* (Table 1). The distribution of co-adsorbed guest (**PEM-C6**) in the pores decreased significantly in comparison with the case of **PEM-TEG** guest. Figures S7 and S6b show STM images of domains consisting of **PEM-C6** observed before and after annealing, respectively. The network pattern is assigned to a honeycomb structure of **PEM-C6** containing self-adsorbed **PEM-C6**

molecules in some of the pores, as described in our previous report.³³

Figure 5. (a, b) STM images of monolayers formed by **DBA-TeEG** (1.0×10^{-5} M) and **PEM-C6** (1.0×10^{-5} M) before annealing at the TCB/graphite interface (tunneling parameters: $I_{\text{set}} = 61$ pA and $V_{\text{set}} = -320$ mV). Unit cell parameters of the honeycomb structure of **DBA-TeEG** are $a = b = 5.0 \pm 0.1$ nm, $\gamma = 60 \pm 1^\circ$. White lines indicate the domain boundaries between the monolayers of **DBA-TeEG** and **PEM-C6**. White dotted lines and arrows indicate the domain boundaries of the honeycomb structure of **DBA-TeEG** and the directions of the main symmetry axes of underlying graphite, respectively. (c) The same STM image as (b), in which red, green, yellow, and white hexagons indicate *filled pores*, *partly filled pores*, *fuzzy pores*, and *open pores*, respectively.

STM observations of monolayers formed by a mixture of DBA-C10 and PEM-TEG at the TCB/graphite interface. Next, STM observations using a 1 : 1 mixture of **DBA-C10** (1.0×10^{-5} M) and **PEM-TEG** (1.0×10^{-5} M) were performed (Figure S8 before annealing and Figure 6 after annealing). In both cases, a honeycomb structure formed by **DBA-C10** with **PEM-TEG** barely co-adsorbed in the pores was observed. The unit cell parameters are $a = b = 5.0 \pm 0.1$ nm, $\gamma = 60 \pm 1^\circ$, which are identical to those of the honeycomb structure of **DBA-C10**. No self-assembled monolayer of **PEM-TEG** was observed, indicating the preferential adsorption of **DBA-C10**. Statistical analyses of the distribution of the pores showed <1% *filled pores*, <1% *partly filled pores*, 1–2% *fuzzy pores*, and 97% *open pores* for the both conditions (Table 1).

Figure 6. (a, b) STM images of monolayers formed by a mixture of **DBA-C10** (1.0×10^{-5} M) and **PEM-TEG** (1.0×10^{-5} M) after annealing at 70 °C for 1 h at the TCB/graphite interface (tunneling parameters: $I_{\text{set}} = 41$ pA and $V_{\text{set}} = -210$ mV for a, $I_{\text{set}} = 40$ pA and $V_{\text{set}} = -189$ mV for b). Unit cell parameters of the honeycomb structure of **DBA-C10** are $a = b = 5.0 \pm 0.1$ nm, $\gamma = 60 \pm 1^\circ$. White arrows indicate the directions of the main symmetry axes of underlying graphite. (c) The same STM images as (b), in which red, yellow, and white hexagons indicate *filled pores*, *fuzzy pores*, and *open pores*, respectively.

By increasing the molar ratio of **PEM-TEG** to 2.6 relative to **DBA-C10**, phase segregation was observed as shown in Figures 7a (after annealing) and S9a (before annealing). The domains of the honeycomb structure of **DBA-C10** and the self-assembled monolayers of **PEM-TEG** were found in an approximate ratio of 7 : 3 (estimated from 10 STM images of a 100×100 nm² area) before annealing. However, the ratio changed to approximately 3 : 7 (estimated from 16 STM images of a 100×100 nm² area) after annealing. Figures S9b–c and 7b–c show STM images of the honeycomb

structure of **DBA-C10** observed before and after annealing, respectively. Analyses of STM images revealed 1–2% *filled pores*, 2–3% *partly filled pores*, 4% for *fuzzy pores*, and 92% for *open pores* (Table 1). In the domains of **PEM-TEG**, the dense hexagonal and zigzag structures were observed (Figure S10).³³

Figure 7. (a, b) STM images of monolayers formed by a mixture of **DBA-C10** (1.0×10^{-5} M) and **PEM-TEG** (2.6×10^{-5} M) after annealing at 70 °C for 1 h at the TCB/graphite interface (tunneling parameters: $I_{\text{set}} = 55$ pA and $V_{\text{set}} = -330$ mV for a, $I_{\text{set}} = 52$ pA and $V_{\text{set}} = -550$ mV for b). Unit cell parameters of the honeycomb structure of **DBA-C10** are $a = b = 5.0 \pm 0.1$ nm, $\gamma = 60 \pm 1^\circ$. White lines indicate the domain boundaries between the monolayers of **DBA-C10** and **PEM-TEG**. White dotted lines and arrows indicate the domain boundaries of the honeycomb structure of **DBA-C10** and the directions of the main symmetry axes of underlying graphite, respectively. (c) The same STM images as (b), in which red, yellow, and white hexagons indicate *filled pores*, *fuzzy pores*, and *open pores*, respectively.

STM observations of monolayers formed by a mixture of DBA-C10 and PEM-C6 at the TCB/graphite interface. Finally, we investigated the self-assembly of a 1 : 1 mixture of **DBA-C10** (1.0×10^{-5} M) and **PEM-C6** (1.0×10^{-5} M). Similar to the case of the mixture of **DBA-TeEG** and **PEM-C6**, the phase segregation between domains of the honeycomb structures formed by **DBA-C10** and **PEM-C6** was observed (Figure 8a) with an area ratio of approximately 9:1 before annealing (9 images of a 100×100 nm² area and 3 images of a 200×200 nm² area). Figure S11 shows an STM image of the honeycomb structures of **DBA-C10** and **PEM-C6**. Analysis of the pores showed no *filled pores* or *partly filled pores*; 98% of *open pores* (Table 1). In contrast, annealing treatment changed the phase distribution significantly and the honeycomb structure of **PEM-C6** was observed preferentially (Figures 8b and S12) with the surface coverage of more than 95% (5 images of a 100×100 nm² area and 5 images of a 200×200 nm² area).

Figure 8. STM images of monolayers formed by a mixture of **DBA-C10** (1.0×10^{-5} M) and **PEM-C6** (1.0×10^{-5} M) before annealing (a) and after annealing (b) at the TCB/graphite interface (tunneling parameters: $I_{\text{set}} = 72$ pA and $V_{\text{set}} = -100$ mV for a, $I_{\text{set}} = 72$ pA and $V_{\text{set}} = -160$ mV for b).

White solid and dotted lines indicate the domain boundaries between the monolayers of **DBA-C10** and **PEM-C6** and the domain boundaries of the honeycomb structure of **DBA-C10**, respectively.

Table 1. Distributions of *Filled Pores*, *Partly Filled Pores*, *Fuzzy Pores*, and *Open Pores*, and Phase Behavior for Monolayers Formed by Combinations of **DBA-TeEG/PEM-TEG**, **DBA-TeEG/PEM-C6**, **DBA-H/PEM-TEG**, and **DBA-H/PEM-C6**

compound	mixing ratio (DBA : PEM)	annealing ^a	total number of pores ^b	number of pores counted and its fraction (%)				phase behavior
				filled pores	partly filled pores	fuzzy pores	open pores	
DBA- TeEG/PEM -TEG	1 : 1	–	640 (8)	271 (42 ± 5%)	45 (7 ± 3%)	13 (2 ± 1%)	311 (49 ± 5%)	preferential adsorption (DBA) incorporating guest
		+	1120 (11)	443 (40 ± 7%)	56 (5 ± 3%)	41 (4 ± 2%)	580 (51 ± 6%)	preferential adsorption (DBA) incorporating guest
	1 : 2.6	–	712 (13)	338 (47 ± 7%)	149 (21 ± 6%)	12 (2 ± 3%)	213 (30 ± 5%)	phase segregation (DBA/PEM = 1/1)
		+	396 (5)	239 (60 ± 3%)	25 (6 ± 3%)	5 (1 ± 1%)	127 (32 ± 5%)	phase segregation (DBA/PEM = 3/7)
DBA- TeEG/PEM -C6	1 : 1	–	291 (4)	26 (9 ± 2%)	10 (3 ± 2%)	11 (3 ± 3%)	244 (85 ± 3%)	phase segregation (DBA/PEM = 7/3)
		+	–	–	–	–	–	preferential adsorption (PEM)
DBA-C10/ PEM-TEG	1 : 1	–	496 (6)	4 (<1%)	3 (<1%)	7 (1 ± 2%)	482 (97 ± 2%)	preferential adsorption (DBA)
		+	1103 (11)	9 (1 ± 1%)	2 (<1%)	18 (2 ± 1%)	1074 (97 ± 1%)	preferential adsorption (DBA)
	1 : 2.6	–	353 (9)	4 (1 ± 1%)	12 (3 ± 3%)	14 (4 ± 4%)	323 (92 ± 5%)	phase segregation (DBA/PEM = 7/3)
		+	750 (14)	15 (2 ± 3%)	13 (2 ± 2%)	32 (4 ± 4%)	690 (92 ± 4%)	phase segregation (DBA/PEM = 3/7)
DBA-C10/ PEM-C6	1 : 1	–	350 (5)	0 (0%)	0 (0%)	7 (2 ± 2%)	343 (98 ± 2%)	phase segregation (DBA/PEM = 9/1)
		+	–	–	–	–	–	preferential adsorption (PEM)

^aThe + and – signs mean the conditions with or without annealing at 70 °C for 1 h. ^bThe numbers of STM images analyzed are shown in parentheses.

Guest occupancy in the porous space by electrostatic host-guest interaction. The results of STM observations are summarized in Table 1. Firstly, we discuss the different guest occupancies observed among the host-guest combinations. Because **DBA-C10** did not exhibit marked guest immobilization toward either guest **PEM-TEG** or **PEM-C6**, we focus mainly on the effect of the peripheral functional group of the guest molecules **PEM-TEG** and **PEM-C6** for co-adsorption in polar pores created by self-assembly of **DBA-TeEG**. In the **DBA-TeEG/PEM-TEG** host-guest combination, the co-adsorption rate of *filled pores* was 42%, whereas that of the **DBA-TeEG/PEM-C6** combination was reduced to 9%. To elucidate the driving force for the favorable co-adsorption of **PEM-TEG**, host-guest interaction energies of the DBA/PEM combinations were estimated by MM simulations on a graphene bilayer under the periodic boundary conditions ($a = b = 4.97$ nm, $\gamma = 60.0^\circ$).

The orientation of the TeEG units of **DBA-TeEG** and the TEG units or alkyl chains of **PEM-TEG** or **PEM-C6** could not be determined experimentally from the STM images due to limited resolution. Therefore, MM simulations were performed for the four initial structures which are different with respect to two geometrical elements: (1) which of the terminal chains, either the host matrix (the TeEG units of **DBA-TeEG**) or the guest (the TEG units of **PEM-TEG** or C₆ chains of **PEM-C6**), are adsorbed on the surface and (2) the relative orientation (clockwise (CW) or anticlockwise (ACW)) of the TEG units or C₆ chains of the guest with respect to that of the TeEG units of **DBA-TeEG** which is tentatively fixed to adopt the ACW orientation (Figures 9 for the **DBA-TeEG/PEM-TEG**

combination and S14 for the **DBA-TeEG/PEM-C6** combination).

Calculated intermolecular interactions are summarized in Table 2. E_{total} stands for the noncovalent interaction energies of the entire system consisting of the molecular network of DBA, guest molecules, and the graphene bilayer including all internal, intermolecular, and molecule-substrate interactions. E_{host} consists of two kinds of the noncovalent interaction energies, one for the molecular network of DBA without the graphene bilayer including internal and host-host, and the other for host-substrate interactions. E_{guest} refers to the sum of the internal interaction of the guest molecule in itself without substrate and the interactions between the guest and substrate. From these values, the interaction energies between the host matrix and guest molecule, $E_{\text{host-guest}} = E_{\text{total}} - E_{\text{host}} - E_{\text{guest}}$, were calculated as shown in Table 2. The lower energy in Table 2 indicates stronger interactions. For the **DBA-TeEG/PEM-TEG** combination, the host-guest interaction energies are estimated to be in a range of -85.8 to -100.3 kcal/mol, while for the **DBA-TeEG/PEM-C6** combination they range from -48.5 to -64.6 kcal/mol. Therefore, on the basis of MM simulations, even the energetically most unfavorable **DBA-TeEG/PEM-TEG** combination has host-guest interactions which are stronger by 20 kcal/mol than the most favorable geometry of the **DBA-TeEG/PEM-C6** combination. It is considered that this difference of energetic stabilities is driven from dipole-dipole interactions between the ethylene glycol units of host and guest.^{63,64} Additionally, hydrogen bonds between the terminal OH group of the TeEG units of **DBA-TeEG** and the carbonyl or ether oxygen atoms of **PEM-TEG**^{65,66} would also

contribute to the intermolecular interactions (indicated by yellow arrows in Figure 9a, 9b, and 9d), although the TeEG and TEG units are highly flexible when they are exposed to the solution phase. Moreover, to take into account the effect of solvent molecules adsorbed in the pores of different polarity, we estimated interaction energies between the host matrix and solvent molecules, $E_{\text{host-TCB}}$, by MM simulations for models of the honeycomb networks of **DBA-TeEG** and **DBA-C10** containing seven molecules of TCB in the pores. The geometries of the solvent molecules were optimized as shown in Figure S14 and the $E_{\text{host-TCB}}$ values are listed in Table S1. The interaction energies between the host matrix and TCB molecules are -28.0 and -26.1 kcal/mol for the monolayers of **DBA-TeEG** and **DBA-C10**, respectively. This indicates that (i) the host-solvent interactions are much smaller than the host-guest interactions ($E_{\text{host-guest}} = -85.8$ to -100.3 kcal/mol for **DBA-TeEG/PEM-TEG** and -48.5 to -64.6 kcal/mol for **DBA-TeEG/PEM-C6** (Table 2)) and (ii) the solvent molecules are slightly more stabilized in the matrix of **DBA-TeEG** than **DBA-C10**. However, in view of the significantly larger difference in the host-guest interaction energies between the two host-guest systems, the effect of competitive adsorption of solvent molecules can be neglected. Consequently, the higher guest occupancy for the **DBA-TeEG/PEM-TEG** combination compared to the **DBA-TeEG/PEM-C6** combination is ascribed to electrostatic interactions, such as dipole-dipole and hydrogen bonding interactions, between the polar tails of the host and guest molecules.

Figure 9. Molecular models optimized by COMPASS force field under periodic boundary conditions ($a = b = 4.97$ nm, $\gamma = 60^\circ$) on a bilayer graphene for monolayers formed by a mixture of **DBA-TeEG** and **PEM-TEG**. (a) The TeEG units of **DBA-TeEG** being adsorbed and the TEG units of **PEM-TEG** adopting the same (ACW) orientation with respect to the TeEG units of **DBA-TeEG**. (b) The TeEG units of **DBA-TeEG** being adsorbed and the TEG units of **PEM-TEG** adopting the opposite (CW) orientation with respect to the TeEG units of **DBA-TeEG**. (c) The TeEG units of **DBA-TeEG** being desorbed and the TEG units of **PEM-TEG** adopting the same (ACW) orientation with respect to the TeEG units of **DBA-TeEG**. (d) The TeEG units of **DBA-TeEG** being desorbed and the TEG units of **PEM-TEG** adopting the opposite (CW) orientation with respect to the TeEG units of **DBA-TeEG**. The yellow arrows indicate one of hydrogen bonding sites between the terminal OH group of **DBA-TeEG** and the carbonyl oxygen of **PEM-TEG**.

Table 2. Intermolecular Energies for Host-Guest Systems on Bilayered Graphene Sheet Calculated by MM Simulations Using COMPASS Force Field under Periodic Boundary Condition ($a = b = 4.97$ nm, $\gamma = 60.0^\circ$)

system	geometry		intermolecular energy ^c (kcal/mol)					$E_{\text{host-guest}}^f$ (kcal/mol)
	TeEG unit of DBA-TeEG	TEG or C ₆ unit of PEM-TEG or PEM-C6	E_{total}	E_{host}^d		E_{guest}^e		
				nonbonding interactions without substrate	host-substrate interaction	nonbonding interactions without substrate	guest- substrate interaction	
DBA- TeEG/PEM- TEG	adsorbed ^a	same ^b	−623.5	117.8	−615.6	96.2	−125.5	−96.4
		opposite ^b	−629.5	128.9	−615.7	113.2	−159.6	−96.3
	desorbed ^a	same ^b	−568.8	115.3	−529.5	102.3	−171.1	−85.8
		opposite ^b	−556.5	104.1	−496.3	141.3	−205.3	−100.3
DBA- TeEG/PEM- C6	adsorbed ^a	same ^b	−667.2	119.9	−616.9	20.9	−126.5	−64.6
		opposite ^b	−662.3	119.8	−616.3	21.2	−138.5	−48.5
	desorbed ^a	same ^b	−582.3	134.6	−527.3	19.2	−155.1	−53.7
		opposite ^b	−639.7	135.2	−583.8	20.6	−149.7	−62.0

^aThe TeEG units of **DBA-TeEG** are adsorbed on graphite or desorbed from it. ^bThe relative orientation (“same” for ACW or “opposite” for CW) of the TEG or C₆ units of the guest with respect to that of the TeEG units of **DBA-TeEG** which adopt tentatively the ACW orientation. ^cSum of the intermolecular and molecule-substrate interaction energies. ^d E_{host} was obtained by single point energy calculations for the host-guest systems in their optimized geometries which do not contain the guest molecules. ^e E_{guest} was obtained by single point energy calculations for the host-guest systems in their optimized geometries which do not contain the host networks. ^fCalculated by the following equation,

$$E_{\text{host-guest}} = E_{\text{total}} - E_{\text{host}} - E_{\text{guest}}.$$

In contrast to the host-guest events with the host network of **DBA-TeEG** described above, the non-polar host matrix formed by **DBA-C10** did not exhibit binding ability towards **PEM-TEG** and **PEM-C6**. Even for the anticipated favorable **DBA-C10/PEM-C6** combination in view of polarity matching, only phase separation and preferential adsorption were observed. This result is ascribed to the strong affinity between the guest molecules which form by themselves densely packed van der Waals networks on the surface as described in the following section.

Phase behavior of bicomponent systems. Next, phase behavior of the mixtures of DBAs and PEMs is discussed. On the basis of previously reported results of self-assembly at the liquid/solid interfaces, it is reasonable to assume that a kinetically trapped structure is observed before annealing treatment, whereas after annealing a thermodynamically stable phase is favored in the present system.⁵⁷ We note that, in general, the honeycomb structures of DBAs with co-adsorbed TCB molecules are formed preferentially before annealing, whereas after annealing they are replaced by domains consisting of PEMs. Most typically, in the combination of **DBA-C10/PEM-C6**, most of the surface originally covered by **DBA-C10** before annealing turned to be dominated by **PEM-C6** after annealing. This result is probably due to co-adsorbed solvent (TCB) molecules in the honeycomb networks of DBAs;^{67,68} adsorption kinetics of the solvent molecules must be much faster than that of the solute molecules because of the large excess amount of the solvent, favoring the porous structure

kinetically.

Consequently, in the following discussion, we focus on STM observations after annealing. Although the formation of 2D co-crystal networks of DBAs and PEMs is possible in view of the presence of the phenylene-ethynylene units as a common structural unit,^{45,49} no such complementary networks were observed. This is due to mismatch of alkyl chain lengths between the building blocks.⁴⁵ As a result, either preferential adsorption or phase segregation was observed. In the case of the mixture of **DBA-TeEG** and **PEM-TEG**, preferential adsorption of **DBA-TeEG** was observed at equimolar solution, while phase segregation took place only at higher molar ratio of **PEM-TEG**. The thermodynamic stability of the network of **DBA-TeEG** probably arises from favorable van der Waals interactions between the alkyl chains and the HOPG surface as well as intermolecular interactions between the interdigitated alkyl chains. To further estimate the relative stability, we calculated surface densities of the honeycomb structure of **DBA-TeEG** (without co-adsorbed solvent molecules) and the dense hexagonal and zigzag structures of **PEM-TEG** by dividing the number of adsorbed heavy atoms (non-hydrogen atoms) by the unit cell area used for molecular mechanics simulations. As a result, the surface density of the former was calculated to be 15.1 nm^{-2} , whereas those of the latter were 18.3 and 15.3 nm^{-2} for the dense hexagonal and zigzag structures, respectively. Though the density of the hexagonal network of **PEM-TEG** is larger than that of **DBA-TeEG**, the alkyl chains in the latter building block contribute significantly to adsorption on the graphite surface. In contrast,

in the network of **PEM-TEG**, the TEG side chains orient to the solution phase and do not participate in the network formation.³³ On the other hand, using the mixture of **DBA-TeEG** and **PEM-C6**, preferential adsorption of **PEM-C6** was observed, which is due to the higher density of the honeycomb structure of **PEM-C6** (16.2 nm^{-2}) compared to that of **DBA-TeEG** (15.1 nm^{-2}). For the **DBA-C10/PEM-TEG** combination, **DBA-C10** was adsorbed on the surface more preferentially compared to **DBA-TeEG** because all alkyl chains including the terminal C₁₀ alkyl chains of **DBA-C10** contributed to adsorption, in spite of the lower density of the honeycomb structure of **DBA-C10** (14.6 nm^{-2}) than the monolayers of **PEM-TEG** (18.3 and 15.3 nm^{-2}). Finally, in the case of the **DBA-C10/PEM-C6** combination, the latter was adsorbed preferentially due to the higher density network of **PEM-C6** (16.2 nm^{-2}) compared to that of **DBA-C10** (14.6 nm^{-2}). The dense van der Waals packing in the network of **PEM-C6** is apparently more favorable than that of **DBA-C10**.

SUMMARY AND CONCLUSIONS

We have investigated the guest binding ability in highly polar pores created by self-assembly of **DBA-TeEG** bearing tetraethylene glycol units at the liquid/solid interface. Their self-assembled porous patterns act as host matrix toward the adsorption of hexagonal macrocyclic guests, i.e. **PEM-TEG** and **PEM-C6**, with functional groups of different polarity, i.e. triethylene glycol units and hexyl chains, respectively. STM observations revealed that **PEM-TEG** was immobilized in the pores at

higher probability due to electrostatic interactions such as dipole-dipole and hydrogen bonding interactions between oligoether units of the host and guest in comparison to **PEM-C6** with non-polar groups. In addition, self-assembling behavior of opposite combination of polarity using a non-polar host matrix formed by **DBA-C10** with the same guests, **PEM-TEG** and **PEM-C6**, was also investigated. However, only phase separation and preferential adsorption were observed; virtually no host-guest complexation was discernible even for the favorable polarity-matched combination of **DBA-C10/PEM-C6**. This is ascribed to the strong affinity between the guest molecules which form by themselves densely packed van der Waals networks on the surface. The present results provide useful insight toward the control of the 2D self-assembly of multicomponent mixtures.

SUPPORTING INFORMATION

Additional STM images and models, and synthetic details, ^1H and ^{13}C NMR spectra of **DBA-TeEG**.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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