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Square Tiling by Square Macrocycles at Liquid/Solid Interface: Co-Crystallization with One-Dimensional or Two-Dimensional Order

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Abstract: We systematically investigated the self-assembled monolayers of seven bimolecular mixtures of square-shaped pyridinophanes and cyclophanes having alkoxy or carbalkoxy substituents in the presence of tropylium ion as a marker of pyridinophanes at the liquid/graphite interfaces by means of scanning tunneling microscopy (STM). The purpose of this work is to elucidate the mixing behaviour of these macrocycles highlighting the formation of one- or two-dimensionally ordered square tilings consisting of alternating alignments of different macrocycles through attractive dipole-dipole or hydrogen bonding interactions. As a result, four co-crystals that differ in the dimensionality of the ordering of pyridinophane and cyclophane were observed. The different interaction modes between the functional groups (ether or carbonyl group) in the side chains of pyridinophane and cyclophane led to the formation of co-crystals with dimensionally different orderings of two macrocycles. These observations revealed that a slight modification of the molecular structure may dramatically change the mixing behaviour and the structure of the co-crystals.

Introduction

Surface organization of functional organic molecules by self-assembly is a subject of intense interest in connection with the perspective of various applications, such as fabrication of molecular scale devices and machines for realization of molecular electronics¹ as well as construction of thin film organic devices.² A rich library of physisorbed two-dimensional (2D) molecular self-assemblies has been scrutinized both at

liquid/solid interfaces and under ultrahigh vacuum (UHV) conditions employing various molecular building blocks for understanding of their self-assembling behaviours on solid surfaces.³ Through elucidation of guiding principles of the self-assembly process, it would become possible to tailor the 2D patterns together with specific functionalities. Scanning tunneling microscopy (STM) is a useful tool to investigate these 2D nano-architectures revealing submolecular resolution.

Among various 2D molecular self-assemblies, those consisting of multiple components have raised special interest because of the challenges to control the formation of ordered multicomponent structures based on the following recognition criteria: (1) the molecular size and shape of each component, (2) the nature of chemical functionalities of each component, (3) the plane group symmetry and (4) the unit cell area of the typical pattern formed by the individual components.⁴ In general, bringing more than two molecular components on solid surfaces leads to four different outcomes, *phase segregation*,⁵ *preferential adsorption*,⁶ *random mixing*,⁷ or *co-crystallization*. To achieve co-crystallization of multiple components, each component should cooperatively participate in the 2D co-crystal formation by favourable inter-component interactions.⁸⁻¹⁷ A peculiar example of co-crystallization is the co-adsorption of one or several guest molecules at network pores through recognition via size and shape complementarity between guest molecule(s) and the network pore.⁸ There are several examples of two- and three-component co-crystals but four-component co-crystals are still scarce.^{8g,17} Moreover, control of ordering of each component such as dimensionality (1D or 2D) in 2D co-crystals is an unexplored challenging topic.

For the construction of multi-component surface-confined patterns, hydrogen bonding is probably the most frequently employed interaction as seen, for example, in the combinations of alkoxylated isophthalic acids and pyrazine,⁹ trimesic acid and straight chain alkanols,¹⁰ melamine and perylenetetra-carboxylic diimide,¹¹ and others.¹² Dipole-dipole interactions between ether groups¹³ as well as CF₂ or carbonyl groups¹⁴ were also employed for control of multiple-component self-assembly. In multi-component two-dimensional molecular networks formed by van der Waals interaction, shape recognition sometimes play a significant role.¹⁵ Similarly, the kinked shape of the diacetylene units flanked by alkyl chains were used for the formation of bimolecular networks between different components¹⁶ and even a four-component pattern.¹⁷

Previously, we reported that butadiyne-bridged pyridino and benzo square macrocycles **1a** and **2c** (Scheme 1) form a molecular network in which **1a** and **2c** aligned alternately in one-

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dimension (1D alternating pattern) via attractive dipole-dipole interactions between the ester groups of **1a** and the ether groups of **2c**.¹⁸ Note that this alternating network structure is different from the pattern formed by each single component (**1a** or **2c**). Tropylium ion selectively binds **1a** forming a 1 to 1 complex on the graphite surface. The tropylium guest is stabilized in the cavity of **1a** via ion-dipole interactions with the nitrogen atoms in the cavity of **1a**.¹⁹ This leads to a change in the STM image contrast of the complex from that of **1a** thereby making it possible to discriminate **1a** from **2c**. Thus the tropylium salt acts as a marker of **1a** in the monolayer. On the basis of the preceding results, we expect that square macrocycles having alkyl ether substituents with the oxygen atom at an appropriate position would form 2D co-crystals consisting of square bimolecular tilings in vertical, horizontal and diagonal directions (2D alternating pattern), if attractive dipole-dipole interactions between the substituents work in two-dimensional manner.

Three possible alternating square tilings (types I–III) are shown in Figure 1. In type I, dark and light gray tiles align in an alternating fashion along the vertical and horizontal directions (black dotted lines in type I tiling, Figure 1), whereas the tiles of the same colour align along the diagonal directions (white dotted lines in type I tiling, Figure 1). In type II, the tiles align alternatingly along the horizontal and diagonal directions. Therefore the tiles of the same colour align vertically. For type III, the tiles align in an alternating mode only along the horizontal direction; they align randomly along the vertical and diagonal directions. Thus, types I and II are 2D crystals with alternating alignment, whereas type III tiling is regarded random, i.e. solid solution. It should be noted that square tilings consisting of alternating bimolecular components were reported previously for those consisting of phthalocyanine metal complexes (or their hexadecafluoro derivatives) and porphyrin derivatives formed via inter-component van der Waals (or H···F hydrogen bonding) interactions.²⁰ However, the alternating alignments in these examples were formed by shape-complementarity between the components that maximized intermolecular interactions. In contrast, in the present study, because the molecular building blocks have identical square shape and size, alternating alignments are formed mainly via intermolecular dipole-dipole interactions between the polar groups in the substituents and hydrogen bonding between the polar groups and the aromatic hydrogen.

In this connection, we designed and synthesized macrocycles **1c** and **2b–d** having alkyl chains containing an ether group at different positions of the chain (Scheme 1). Self-assemblies of seven bimolecular mixtures of pyridinophanes **1a** and **1c** with cyclophanes **2b–d** were systematically investigated at the liquid/graphite interface by means of STM. Among the seven pairs, four of them produced co-crystals with different alternating alignments of a pyridinophane and a cyclophane. We deduce that the major driving force for the formation of the alternating networks is the favourable dipole-dipole interaction between the polar groups in the alkyl chains. In addition, hydrogen bonding interactions including the macrocyclic cores also participate in the formation of alternating patterns. The present study offers new insight into controlling the

dimensionality of 2D co-crystals. This is important for the construction of multi-component self-assemblies on surfaces in general.

Figure 1. Ideal alternating square tilings (types I–III) and those including open squares between tiles. Dark and light gray square tiles correspond to the square macrocycles having either pyridine or benzene rings. Open squares in the bottom patterns represent vacant spaces between the square tiles, which are occupied by substituents or solvent molecules. Black and white dotted lines in type I tiling indicate the directions parallel and diagonal to the square edges, respectively. (Left) A 2D alternating molecular network, type I. The dark and light gray tiles align alternately along the parallel directions. (Centre) A 2D alternating molecular network, type II. The dark and light gray tiles align alternately along only one of the directions (horizontally in this case), whereas the same tiles align along the other direction (vertically). (Right) A 1D alternating molecular network, type III. The alternating pattern of the dark and light gray tiles appears along only one direction (horizontally), while they align randomly along the other direction (vertically).

Scheme 1. Chemical Structures of Butadiyne-Bridged Pyridinophanes **1a** and **1c**, Cyclophanes **2a–d**, and Tropylium Salt **3**.

Results and Discussion

Syntheses of Butadiyne-Bridged Macrocycles

The syntheses of square-shaped macrocycles **1c** and **2b–d** were conducted based on the previously reported methods^{18,19} starting from bis(trimethylsilyl)ethynylbenzene or bis(trimethylsilyl)ethynylpyridine derivatives as outlined in Scheme 2 (See also Supporting Information).

Scheme 2. Syntheses of Macrocycles **1c** and **2b–d**.

STM Observations of Self-Assembled Monolayers Formed by Macrocycles at the Liquid/Graphite Interface

All STM observations were performed at the interface between an organic solvent and graphite at room temperature. A macrocycle was dissolved in 1,2,4-trichlorobenzene (TCB) at a concentration of ca. 1×10^{-3} M and tropylium tetrafluoroborate (**3**) was dissolved in a mixture of chloroform (CHCl₃) and acetonitrile (CH₃CN, a volumetric ratio of 1/9) at a concentration of ca. 2×10^{-2} M. The sample concentrations are described in the Figure captions. After dropping the sample solution, STM observations of the pristine macrocycles were performed at the TCB/graphite interface, while those using pyridinophane complexes with tropylium ion were performed using a mixture of

TCB, CH₃CN and CHCl₃ (10/9/1) as solvent to ensure solubility of salt **3**. For binary mixtures, the mixing ratios between two macrocycles were optimized to find conditions at which both components were observed on the surface. All images were recorded within ca. 2 h after bringing a drop of the solution (less than 10 μ L) on top of the graphite substrate. The images are recorded in the quasi constant-current mode. Differences in brightness reflect the STM tip–sample distance: the brighter, the larger the tip–sample distance.

Molecular Networks Formed by Single-Component Macrocycles at the TCB/Graphite Interface

For the monolayers of macrocycles **1a**, **1c**, **2a–c** and complexes of **1a,b** with tropylium cation **3**, we observed three network patterns: porous, non-porous A, and non-porous B. Figure 2 shows representative STM images of these patterns observed for **2b**, **1a**, and **1c**·**3**, respectively, together with the corresponding network models constructed based on the experimentally obtained unit cell parameters. We were unable to observe a self-assembled monolayer of **2d** in spite of many attempts under various experimental conditions. The results are schematically summarized in Table 1, together with those of mixing experiments described later. The experimental unit cell parameters and the network densities ($d_{\text{structure}}$), which were estimated by dividing the number of molecules in a unit cell (Z) by the unit cell area (area), are summarized in Table S1.

In Table 1, signs P, A, and B in each panel stand for the network patterns, porous, non-porous type A, and non-porous type B, respectively. Italicized lower case characters (*b* and *p*) and plus sign on an orange background placed in each square indicate that the macrocycles are cyclophanes **2a–d**, pyridinophanes **1a,c**, and their tropylium ion complexes **1a**·**3** and **1c**·**3**, respectively. Since the on-surface geometries of the macrocycles defined by the number of the adsorbed alkyl chains and their directions with respect to the square macrocyclic core are closely related to the network patterns, the structures of the macrocycles are drawn by simplified models. In the porous pattern, macrocycles adopt a C_{4h} symmetric conformation like a pinwheel, whereas in the non-porous B pattern they adopt an approximate D_{2h} conformation as if holding their two hands up and two legs down. Conversely, in the non-porous A pattern, because only two alkyl groups are adsorbed on the surface, it has only one 'hand' and 'leg'. As shown in Table 1, the network patterns depend critically on the substituents of the macrocycles. Both ester substituted pyridinophane **1a** and its complex **1a**·**3** form the non-porous A pattern. On the other hand, **1c** forms a porous pattern by itself, whereas for its tropylium complex **1c**·**3** the non-porous B pattern is observed. Similar to **1a**, ester group-bearing **2a** forms the non-porous A pattern, whereas both ether-substituted macrocycles **2b** and **2c** form a porous pattern. To summarize, macrocycles with ester groups tend to form the non-porous A pattern, while those with ether groups tend to self-assemble into a porous pattern with an exception for complex **1c**·**3**. More details for the respective network pattern are described below.

Table 1. Monolayer Structures of Pristine Macrocycles **1a**, **1c**, and **2b–2d**, Complexes between Pyridinophanes and Tropylium Salt **1a+3** and **1c+3**, and Mixtures of Cyclophane and Complex.

		2a CO ₂ C ₈ H ₁₇	2b OC ₈ H ₁₉	2c CH ₂ OC ₈ H ₁₇	2d CH ₂ CH ₂ OC ₇ H ₁₅	
	Single Component Network Pattern	A	P	P	None	P = Porous Structure
1a CO ₂ C ₈ H ₁₇	without C ₇ H ₇ ⁺	random mixing A	preferential adsorption A	1D mixing (Type III) B	2D mixing (Type II) A	A = Non-porous A Structure
	with C ₇ H ₇ ⁺	A	A	B	A

1c CH ₂ OC ₈ H ₁₇	without C ₇ H ₇ ⁺		2D mixing (Type II) P	phase segregation P	2D mixing (Type I) P	B = Non-porous B Structure
	with C ₇ H ₇ ⁺	not investigated	P	B	P

Macrocycles **1c**, **2b**, and **2c** exhibit porous patterns. Figure 2a displays an STM image of the porous network of **2b**. In the STM image, the bright features correspond to the π -conjugated part of **2b** attributed to a high tunneling efficiency compared to the other parts.²¹ The darker lines with dim small dots running along the bright π -conjugated core are ascribed to the adsorbed alkyl chains. All alkyl chains of **2b** are adsorbed on surface and two of them align parallel to one of the three equivalent graphite main axes (the $\langle 1, -2, 1, 0 \rangle$ directions). The angle between the other two alkyl chains and the graphite main axis is $15 \pm 3^\circ$. The size of the pores formed between the adsorbed molecules of **2b** is ca. 1.9 nm (corner-to-corner) and ca. 1.2 nm (edge-to-edge), which is large enough to accommodate one TCB molecule. Indeed, the pores were sometimes imaged as the species with the brightest contrast (Figure S1e), indicating the co-adsorption of TCB molecules. A tentative network model is shown in Figure 2b. In this case, a **2b** molecule adopts pseudo C_{4h} geometry. The molecular density of the porous pattern is relatively low ($d_{\text{porous}} = 0.18\text{--}0.19$ molecule/nm²).

The porous patterns formed by the other macrocycles **1c** and **2c** are shown in Supporting Information (Figure S1). The small difference between the porous networks of **2b** and **1c** is the orientation of alkyl chains with respect to the main symmetric axes of graphite. In both cases, two alkyl chains are parallel to the main symmetric axes of graphite. On the other hand, the

angles between the other two alkyl chains and the axes of graphite is $21 \pm 4^\circ$ for **1c** (cf. $15 \pm 3^\circ$ for **2b**).

Figure 2c shows an STM image of a non-porous pattern, classified as non-porous A pattern, of octyl ester substituted pyridinophane **1a** at the TCB/graphite interface. The square bright features correspond to the rim of the π -conjugated system of the macrocycle. Though the alkyl chains are not observed, we assume that two of them are adsorbed on graphite preferentially along one of the three equivalent directions of graphite (the $\langle 1, -2, 1, 0 \rangle$ directions) whereas the other two chains are free to move in a supernatant phase because of the limited space on the surface. The network density of this structure is high (0.22 molecule/nm²) compared with those of the porous patterns due to the close packing (Table S1). On the basis of the network model generated using the unit cell parameters and the orientation of π -core in the image, we estimate that the distance between the oxygen atom of carbonyl group and the hydrogen atom of the aromatic ring of the neighbouring molecule is very close (ca. 2 Å), indicating hydrogen bonding interactions between them (highlighted by the yellow circle in Figure 2d).²² While originally we reported that cyclophane **2c** formed the non-porous A pattern,¹⁸ careful re-examination revealed that this pattern appears as a minor structure. The majority of the domains of **2c** consist of the porous pattern (vide supra).

Complexation with Tropylium Ion: Effect of Guest on Network Structure

Square-shaped pyridinophane **1a** binds tropylium salt **3** via ion-dipole interactions in solution.¹⁹ The complexation is observed at the liquid/solid interface too. As reported previously, the complex between **1a** and tropylium salt **3** (**1a-3**) forms the non-porous A pattern at the TCB/CH₃CN/CHCl₃ (10/9/1)/graphite interface,

similar to **1a** itself.¹⁸

As described in the previous section, macrocycle **1c** forms a porous pattern in the absence of the guest ion. On the other hand, a non-porous pattern, classified as non-porous B pattern, was observed when **1c** was mixed with the guest, as shown in Figure 2e for a mixture of **1c** and **3** (1:23 molar ratio) at TCB/CH₃CN/CHCl₃ (10/9/1)/graphite interface. All square cores of the macrocycle adopt the same orientation and align close to each other in a side-by-side fashion. In this case, the complex adopts a *D*_{2h} symmetric conformation. In the macrocycle cavities of **1c**, bright spots were observed, which correspond to the trapped tropylium ion showing relatively high conductivity.²³ Moreover, all alkyl chains of **1c** align parallel to one of the three equivalent graphite main axes (the <1,−2,1,0> directions). Counter anion PF₆[−] of the tropylium cation could not be detected in the image. The network density (*d*_{porous}) of this pattern is 0.19 molecule/nm². A tentative network model is shown in Figure 2f.

Figure 2. (a) An STM image of the porous pattern of **2b** at the TCB/graphite interface (9.8×10^{-3} M, $I_{\text{set}} = 0.45$ nA, $V_{\text{set}} = -0.69$ V). (b) A tentative network

model of the porous structure of **2b**. Unit cell parameters of the model are $a = 2.39$ nm, $b = 24.0$ nm, and $\gamma = 89.3^\circ$. (c) An STM image of the non-porous A pattern of **1a** at the TCB/graphite interface (8.9×10^{-4} M, $I_{\text{set}} = 0.22$ nA, $V_{\text{set}} = -0.70$ V). (d) A tentative network model of the non-porous A pattern of **1a**. The yellow circle indicates a hydrogen bonding site between the oxygen atom of the carbonyl group and the hydrogen atoms of the aromatic ring. Unit cell parameters of the model are $a = 1.96$ nm, $b = 2.41$ nm and $\gamma = 81.0^\circ$. (e) An STM image of the non-porous B structure of the complex **1c** at the TCB/graphite interface (2.5×10^{-4} M for **1c** and 1.1×10^{-2} M for **3**, $I_{\text{set}} = 0.15$

nA, $V_{\text{set}} = -0.49$ V). (f) A tentative network model of the non-porous B pattern

of **1c**. Unit cell parameters of the model are $a = 1.88$ nm, $b = 2.91$ nm and $\gamma = 71.6^\circ$. A high resolution image of the non-porous B pattern formed by **1c** and **3** was taken during the observation of monolayer formed by a mixture of **1c**, **2b**, and **3** (Figure S2).

Molecular Networks Formed by Bimolecular Mixtures of Pyridinophane and Cyclophane

We systematically investigated seven bimolecular mixtures of pyridinophanes and cyclophanes to study whether regularly mixed patterns would be formed. Because of the higher adsorption affinity of the pyridinophane-tropylium ion complexes, the cyclophanes were used in excess with molar ratios of ca. 1:1 to 1:100 (pyridinophane:cyclophane) to avoid preferential absorption of the complex and optimize mixing of the two components on the surface. The results obtained at the optimal concentrations and mixing ratios are described in Figure captions. As summarized in Table 1, all four possible outcomes—phase segregation, preferential absorption, random mixing, and co-crystallization—were observed.

Preferential absorption was observed for a mixture of **1a-3** and **2b** despite attempts to optimize mixing ratio (Figure S3); the non-porous A pattern of complex **1a-3** was observed exclusively.

Random mixing was observed in two cases. Complex **1a-3** and cyclophane **2a** randomly mixed on the surface forming the non-porous A pattern,¹⁸ which is not surprising in view of the same substituents in these macrocycles. Occasionally, randomly mixed domains were observed in the case of a mixture of **1c-3** and cyclophane **2c** (on an average 17%, Figure S4b), in addition to segregated domains of each component. The positional randomness of the components in the mixed domains was confirmed by the alternation analysis described in the next section.

A mixture of **1c-3** and **2c** exhibited phase segregation mainly, i.e., both domains of the porous pattern of **2c** and the non-porous B pattern of **1c-3** were observed (Figure S4a). The populations of the domains are as follows (analysed from 15 large area images: total area: 54000 nm²)—the porous pattern of **2c**, 44%, the non-porous B pattern of **1c-3**, 39%, and the porous pattern consisting of the both components, 17%.

Co-crystallization was observed for the other four combinations, **1a-3+2c**, **1a-3+2d**, **1c-3+2b**, and **1c-3+2d**. The degree of ordering of each system was examined by the analytical method described in the following section. Structural parameters of co-crystals are summarized in Table S2. As shown in Table 1, in the co-crystal of **1a-3+2c**, both components adopt a *D*_{2h} symmetric conformation, which they don't adopt in their own networks, to form the non-porous pattern B. On the other hand, in the co-crystal of **1c-3+2b**, both components adopt the same *C*_{4h} symmetry conformation as in their own networks,

forming the porous pattern. Note that macrocycle **2d** forms mixed networks of the non-porous A and the porous patterns when mixed with **1a-3** and **1c-3**, respectively, though **2d** itself did not form a self-assembled monolayer. The details of the network patterns are shown in Figure 4 and are discussed in the latter section.

Alternation Analysis: Correlation Factor and Monte Carlo Simulations

To analyse the positional relationships between different macrocycles, we introduce the correlation factor (CF) which is defined as the value obtained by dividing the number of neighbouring heteromacrocycle pairs along a molecular row by the total number of neighbouring macrocycle pairs (See Supporting Information for detail).¹⁸ For ideal random and perfect alternating orderings formed by equal number of two macrocycles, the CF values should become 0.5 and 1, respectively. Moreover, a CF value of 0 indicates perfect domain separation. Indeed, a 1000 times random generation of "0" or "1", afforded 490 times "1" and 510 times "0", collected in a row by the Monte Carlo simulations. In this case, the correlation factor is 0.51, as expected for a random sequence of "1" and "0". Moreover, to evaluate alternating alignments formed by unequal numbers of pyridinophane and cyclophane, we performed similar analyses by changing the number of "0" and "1". Figure 3 summarizes the ratio (0/1)-dependent change of the CF values. The blue and red lines correspond to the ideal CF values for perfect alternating alignment and random ordering, respectively, at given ratios of the components on the surface. To determine the experimental CF values from the STM images, the alternation of neighbouring molecules were analysed in several domains from more than three large area images (60 nm × 60 nm or 80 nm × 80 nm) for each mixed system.

For random mixing systems, the CF values experimentally determined in each domain are close to the theoretical random CF value. For instance, in the case of mixtures of **1a-3+2a** and **1c-3a+2c**, all experimental CF values are located close to the red line (Figure 3a), confirming the randomness of their relative positions.

Figure 3. CF values of random networks (a) and alternating alignments (b) for mixtures of two macrocycles. The blue and red lines indicate the ideal alternating alignments and random patterns derived from the Monte Carlo simulations at the different molecular ratios. Black, green, and magenta dots in (a) correspond to the CF values of the random domains of **1a-3+2c** (along the yellow line in Figure 4a), **1c-3+2c**, and **1a-3+2a**, respectively. Black dots, green dots and triangles, orange dots and triangles, and magenta dots and triangles in (b) correspond to the CF values of mixed domains formed by mixtures of **1a-3+2c** (along the white line in Figure 4a), **1a-3+2d**, **1c-3+2b**, and **1c-3+2d**, respectively. The dots and triangles for the latter three cases indicate the CF values in the different directions (white and yellow lines, respectively) in a domain.

1D Alternating Network: Mixture of Pyridinophane **1a** and Cyclophane **2c**

A mixture of **1a**, **2c**, and **3** in a 1:1:85 molar ratio in TCB/CH₃CN/CHCl₃ (20/9/1) formed the non-porous B pattern containing both **1a-3** and **2c** together with the non-porous A domains formed only by the complex **1a-3**. Figure 4a shows the non-porous B pattern of the mixed molecular network. The brighter and darker square features correspond to the complex **1a-3** and cyclophane **2c**, respectively. The appearance of each macrocycle is ordered in an alternating fashion along unit cell vector a (the white line in Figure 4a). In fact, the CF values experimentally obtained from several domains distribute between the blue and red lines (Figure 3b, black dots). Though correlations between the black dots and blue line (perfect alternating alignment) is not excellent, these data indicate the existence of alternating tendency along this direction. On the other hand, similar treatment along unit cell vector b (the yellow line in Figure 4a) affords the CF values shown by black dots in Figure 3a which are located close to the red line (ideal random values), indicating a random sequence of location of the different

macrocycles along this direction. Therefore the monolayer composed of a mixture of **1a**·**3** complex and **2b** is regarded as a 1D alternating molecular network (type III, Figure 1).

2D Alternating Network: Mixtures of Pyridinophane **1a** and Cyclophane **2d**, Pyridinophane **1c** and Cyclophane **2b**, and Pyridinophane **1c** and Cyclophane **2d**

Figure 4c shows an STM image of a monolayer formed by a mixture of **1a**, **2d**, and **3** in a 1:97:2200 molar ratio at the TCB/CH₃CN/CHCl₃ (20/9/1)/graphite interface. The domains composed of squares with and without bright features at the intrinsic voids exclusively covered the whole surface. The bright squares of the **1a**·**3** complex are typically surrounded by less bright ones, attributed to cyclophane **2d**. A network model based on the image and the unit cell parameters indicates the formation of the non-porous A pattern (Figure 4d). As observed in the non-porous A pattern of **1a** itself, hydrogen bonding interactions between the ester carbonyl group and the aromatic hydrogen of the neighbouring molecule seem to play a role in the network stabilization.^{18,22} Indeed, the distance between carbonyl groups and adjacent aromatic hydrogen atoms in the network model are estimated to be ca. 2 Å. Because the alternation analyses along both the white and yellow lines afford high CF values in both directions (green dots and triangles for each direction in Figure 3b), this system is regarded as a nearly perfect 2D alternating molecular network (type II, Figure 1).

In the case of a mixture of **1c**, **2b**, and **3** (1:67:2200 molar ratio), a porous pattern consisting of **1c**·**3** and **2b** together with small areas of the non-porous B pattern of the complex **1c**·**3** were formed at the TCB/CH₃CN/CHCl₃ (20/9/1)/graphite interface. The surface coverage of the mixed domains was 97% (analysed from 12 images; 30000 nm²). Figure 4e displays an STM image of the mixed porous domain consisting of bright features, i.e. complex **1c**·**3**, and less bright squares, i.e. cyclophane **2b**. The network parameters of the mixed phase are identical to those of the network formed by the individual components (Figure 4f). The macrocycles aligned in an alternating fashion along both the white and yellow lines in the image. The CF values obtained from both directions are nearly identical (orange dots and triangles in Figure 3b) and approach the value expected for a perfect alternating alignment. The above analysis indicates the formation of a nearly perfect 2D alternating molecular network (type II, Figure 1) in the majority domain.

A porous molecular network consisting of **1c**·**3** and **2d** was exclusively observed for the mixture of **1c**, **2d**, and **3** (1:97:2200) at the TCB/CH₃CN/CHCl₃ (20/9/1)/graphite interface (Figure 4g). In the image, 1D rows of bright features and dim square features appear alternately. Though the unit cell parameters indicate the formation of the porous pattern, the core orientations of the

complex **1c**·**3** and cyclophane **2d** are slightly different. Unlike the

case of the mixture of **1c**·**3** and **2b**, the edges of the neighbouring molecules are not parallel; the angle between their nearest edges of **1c**·**3** and **2d** is $15 \pm 3^\circ$. A network model which was constructed taking into account the image contrast and the unit cell parameters is shown in Figure 4h. The CF values along both the white and yellow lines are nearly identical (magenta

dots and triangles in Figure 3b) and close to the theoretical perfect alternating alignment. Therefore, this system is regarded as a 2D alternating molecular network (type I, Figure 1).

Figure 4. (a, b) An STM image and the corresponding network model of the non-porous B pattern formed by **1a**·**3** and **2c** (concentration; 3.3×10^{-4} M, 3.3

$\times 10^{-4}$ M, and 6.7×10^{-3} M for **1a**, **2c**, and **3**, tunneling parameters; $I_{\text{set}} = 0.30$ nA, $V_{\text{set}} = -0.33$ V). Unit cell parameters of the model (b) are $a = 1.78$ nm, $b = 2.85$ nm and $\gamma = 72.0^\circ$. (c, d) An STM image and the corresponding network model of the non-porous B pattern formed by **1a**·**3** and **2d** (concentration; 3.4×10^{-6} M, 3.3×10^{-4} M, and 7.4×10^{-3} M for **1a**, **2d**, and **3**, tunneling parameters; $I_{\text{set}} = 0.20$ nA, $V_{\text{set}} = -0.31$ V). The red circles in (d) highlight hydrogen bonding sites between the carbonyl groups of **1a** and aromatic hydrogen of **2d**. Unit cell parameters of the model (d) are $a = 2.65$ nm, $b = 2.80$ nm and $\gamma = 86.9^\circ$. (e, f) An STM image and the corresponding network

model of the porous pattern formed by **1c-3** and **2b** (concentration; 3.3×10^{-6} M, 6.4×10^{-5} M, and 7.5×10^{-3} M for **1c**, **2b**, and **3**, tunneling parameters; $I_{\text{set}} = 0.40$ nA, $V_{\text{set}} = -0.49$ V). Unit cell parameters of the model (f) are $a = 3.25$ nm, $b = 33.3$ nm and $\gamma = 89.1^\circ$. (g, h) An STM image and the corresponding network model of the porous pattern formed by **1c-3** and **2d** (concentration; 1.6×10^{-5} M, 3.3×10^{-4} M, and 7.4×10^{-3} M for **1c**, **2d**, and **3**, tunneling parameters; $I_{\text{set}} = 0.85$ nA, $V_{\text{set}} = -0.90$ V). Unit cell parameters of the model (h) are $a = 2.55$ nm, $b = 4.89$ nm and $\gamma = 88.5^\circ$. All measurements were performed at the TCB/CH₃CN/CHCl₃ (20/9/1)/graphite interface. The pink arrows in the images are main symmetric axes of graphite. Unit cell is imposed on the image by red lines. The white and yellow lines indicate two directions used for the alternation analysis.

Network Patterns Formed by Single-Component Macrocycles and Pyridinophane-Tropylium Ion Complexes

The macrocycles adopt either a C_{4h} or D_{2h} conformation with all four alkyl chains adsorbed on the surface, or with only two alkyl chains adsorbed and the other two dissolved in the solution phase. To evaluate the intrinsic geometries of the macrocycles, we performed DFT calculations using the B3LYP/6-31g(d) level of theory. Both C_{4h} and D_{2h} symmetric geometries were optimized (Figure 5, see Supporting Information for details). The energy difference between two geometries is small (Figure S6), suggesting that the macrocycles can adopt either conformation depending on other factors such as intermolecular interactions. It should be pointed out that in both structures, the alkyl chain orientation with respect to the side of the π -core is nearly perpendicular in **1a**, **1c**, **2a**, and **2c**, while the orientation angles in **2b** and **2d** are ca. 113° . Moreover, complexation with the tropylium cation does not influence the alkyl chain orientations. Therefore, in the case of ester-substituted macrocycles **1a** and **2a**, the hydrogen bond between the oxygen atom of the ester group and the hydrogen atom attached to the aromatic ring leads to the formation of the non-porous A pattern. The ether-substituted macrocycles form porous patterns probably to minimize the dipole-dipole repulsive energies between the ether groups. In addition, co-adsorption of the solvent molecule could stabilize this pattern.

While pristine **1c** forms the porous pattern, the non-porous B pattern is formed by complex **1c-3**. No structural change was detected in a control experiment for **1c** by using a mixture of TCB/CH₃CN/CHCl₃ (20/9/1) as solvent (5.1×10^{-4} M), excluding the solvent effect. A plausible reason for this structural change is enthalpically favourable increased electrostatic interactions between the positive charge of the complex and induced dipole of the graphite substrate.²⁴

Self-Assembling Behaviour of Bimolecular Mixtures

When one of the components has a relatively large affinity to the surface compared to the other, preferential adsorption of a single component occurs. Indeed, preferential adsorption of the pyridinophane-tropylium complexes was generally observed from equimolar mixtures of the complex and cyclophane, except in the cases of **1a-3+2a** and **1a-3+2c** where both components appeared 1 to 1 ratio on the surface. For example, preferential adsorption of **1a-3** was observed for a mixture of **1a-3** and **2b** even at a molar ratio of 1 to 100 (Figures S3), indicating a significant larger adsorption affinity of **1a-3**. The higher

adsorption probability of positively charged molecules is ascribed on the one hand to electrostatic interaction between the positively charged ion and graphite to which the negative substrate bias is applied,²⁵ and on the other hand to ion-dipole interaction due to the induced dipole generated on the graphite surface by the positive charge as described above.²⁴

When there is no favourable inter-component interaction, each component assembles into individual domains resulting in phase segregation (Table 1). For example, a mixture of complex **1c-3** and cyclophane **2c** form distinct domains because each component favours a different pattern, the non-porous B pattern for **1c-3** (D_{2h} symmetry) and the porous pattern for **2c** (C_{4h} symmetry, Figure S4), despite both molecules have the same substituent ($R = \text{CH}_2\text{OC}_8\text{H}_{17}$).

In contrast, random mixing occurs when molecular structures of the components in monolayers preserve resemblance. For instance, random mixing was observed for a mixture of **1a-3** and **2a** because both components form the same non-porous A pattern. In a small number of cases, random mixing of **1c-3** into domains of the porous pattern of **2c** (C_{4h} symmetry) was also observed, because **1c-3** can adopt a C_{4h} symmetric geometry as well (vide supra).

Co-crystallization occurs when a co-crystal is more stabilized by favourable inter-component interactions compared to the networks of each component. In the case of the mixture of **1c-3** and **2b**, both components adopt C_{4h} symmetric geometries forming the porous pattern. While cyclophane **2b** keeps its intrinsic network structure, the network pattern of complex **1c-3** is altered from the non-porous B pattern. In the alternating network, the ether groups of **1c-3** and **2b** are located close to each other (Figure 4f), generating attractive dipole-dipole interactions due to the favourable orientation of the ether dipoles (Figure 6a). Therefore, the main driving force for the formation of this *2D alternating molecular network of type II* (Figure 1) with the porous network pattern is attributed to the attractive dipole-dipole interactions between the side chain ether groups with all adjacent molecules. This result contrasts that of **1c-3+2c** where phase separation and random mixing were observed, because favourable inter-component interaction don't occur.

Though macrocycle **2d** does not form a stable monolayer, a mixture of complex **1c-3** and cyclophane **2d** would acquire similar dipole-dipole interactions between the side chain ether groups because of the similar relationship in their positions and orientations. Indeed, the mixture forms the alternating porous pattern. Again the network structure for complex **1c-3** is changed from its original form (the non-porous B pattern). While both components adopt C_{4h} symmetric geometries, the favourable inter-component interaction operates only in one direction with two adjacent molecules (Figure 4h), leading to the formation of the *2D alternating molecular network of type I* (Figure 1) with the porous network pattern. Some unidentified driving force which overrules the above-mentioned dipole-dipole interaction rotates the orientation of one component with respect to the other.

In the case of **1a-3+2c** system, the formation of the non-porous B pattern was observed which was entirely different from those patterns formed by each component (the non-porous A pattern for **1a-3** and the porous pattern for **2c**). As discussed

above, both components can adopt optimal geometries for the formation of the non-porous B (D_{2h}) pattern. The main driving force for the structural change and co-crystal formation is again the attractive dipole-dipole interactions between the carbonyl groups of **1a** and the ether groups of **2c** (Figure 6b).²⁶ The attractive dipole-dipole interactions between **1a-3** and **2c** along the molecular row leads to the formation of 1D alternating molecular network, type III (Figure 1).

Contrary to the above three examples, no attractive dipole-dipole interaction is expected between the side chains of **1a-3** and **2d**, though the mixture formed the 2D alternating molecular network of type II with the non-porous A network pattern. In this case, the complex **1a-3** retains its intrinsic network pattern. On the basis of the inter-molecular distances estimated by the network model (Figure 4d), we assume that hydrogen bonding interactions between the oxygen atom of the carbonyl groups and the hydrogen atoms of the neighbouring molecules facilitate the co-crystallization.²² Indeed, four hydrogen bonds per unit cell can be formed in co-crystal of **1a-3** and **2d** (Figures 4d and 6c), whereas only two such interactions can be formed for the monolayer of **1a-3** (Figure 2d).

It should be mentioned that 2D molecular self-assembly are known to be subject to kinetic effects exhibiting different outcomes after annealing treatments.²⁷ For the 2D co-crystals reported here, the observed patterns are most likely thermodynamic, because they did not change after annealing at 50 °C for 10 min. However, for those mixtures exhibiting preferential adsorption, phase separation, or random mixing, although no significant structural transitions were observed during the STM observations at ambient conditions, we could not exclude the possibility of kinetic effects.

Figure 5. C_{4h} (a) and D_{2h} (b) symmetric molecular models of pyridinophane **1a**.

Figure 6. Structures of 2D alternating network with the porous pattern formed by **1c-3** and **2b** (a), 1D alternating network with the non-porous B pattern formed by **1a-3** and **2c** (b), and 2D alternating network with the porous pattern formed by **1a-3** and **2d** (c). The arrows in (a) and (b) indicate dipole-dipole interactions between the side chain polar groups. The oxygen atoms of the carbonyl groups of **1a** in (c) are involved in the hydrogen bonds.

Conclusions

We investigated self-assembling behaviour of pyridinophanes and cyclophanes and their bimolecular mixtures using STM focusing on the formation of alternating networks by attractive dipole-dipole interactions. In addition to the previously reported macrocycles **1a**, **2a**, and **2c**, we synthesized two cyclophanes **2b** and **2d** and pyridinophane **1c** having ether groups at different

positions in the chains. Two different patterns, porous and non-porous A structures, were observed for the macrocycles depending on their substituents. Pyridinophanes **1a** and its complex with tropylium salt **3** formed the non-porous A structure. On the other hand, the non-porous B structure was observed for pyridinophane **1c** after complexation with **3** although **1c** by itself forms only the porous structure. The self-assembled monolayers formed from bimolecular mixtures of pyridinophanes **1a,c** and cyclophanes **2a–d** were investigated in the presence of **3** which served as a marker of the pyridinophanes. All possible alternating square tilings were observed depending on the combination of the pyridinophane and cyclophane: the 2D alternating molecular network, type I for **1c·3** and **2d**, 2D alternating molecular network, type II for **1c·3+2b** and **1a·3+2d**, and 1D alternating molecular network, type III for **1a·3** and **2c**. The different inter-component interaction modes between the pyridinophane and cyclophane induced by the functional groups in the side chains led to the formation of all three alternating networks of the bimolecular square tiling. The main driving forces for the formation of alternating networks are the attractive dipole-dipole interactions between the side chain polar groups as we designed. However, in certain cases, hydrogen bonding interactions between the side chain polar group and the aromatic hydrogen play a major role. Though we could not exclude a kinetic factor, the present study reveals that a slight modification of the molecular structures influences thermodynamic equilibrium in 2D molecular self-assembly of the bimolecular mixtures leading to unique mixing behaviours such as the formation of the 2D crystals with the different orderings of each component. This knowledge is useful not only for control of dimensionality of co-crystals but also 2D crystal engineering in general.

Experimental Section

Synthesis of Macrocycles

The details of the syntheses of square-shaped macrocycles **1c** and **2b–d** are described in Supporting Information.

Details of STM Observation

All experiments were performed at 20–26 °C using a Nanoscope IIIa (Digital Instruments Inc.) with an external pulse/function generator (model HP 8111a or Agilent 33220A) or PicoSTM (Agilent) with negative sample bias. Tips were mechanically cut from Pt/Ir wire (80%/20%, diameter 0.2 mm). Prior to imaging, a compound under investigation was dissolved in commercially available anhydrous 1,2,4-trichlorobenzene (TCB, Aldrich) at a concentration of ca. 1×10^{-3} M and tropylium tetrafluoroborate (**3**) was dissolved in a mixture of chloroform (CHCl₃) and acetonitrile (CH₃CN, the volumetric ratio is 1/9) at a concentration of ca. 2×10^{-2} M. Mixing experiments were performed by dropping a solution of a mixture of cyclophane, pyridinophane and tropylium cation in a mixture of TCB, CH₃CN and CHCl₃ (10/9/1). Various mixing ratio between two macrocycles were investigated in order to prompt the mixing of both components on the surface. A drop of this solution was applied on a freshly cleaved surface of HOPG (grade ZYB, Momen Performance

Material Quartz Inc., Strongsville, OH). All STM observations were performed at the organic solvents/graphite interface at room temperature. All images were taken within 2 h after applying a drop of the solution on the graphite substrate. By changing the tunneling parameters during the STM imaging, namely, the voltage applied to the substrate and the average tunneling current, it was possible to switch from the visualization of the adsorbate layer to that of the underlying HOPG substrate. This enabled us to correct for drift effects by the use of SPIP software (Image Metrology A/S). The pink coloured axes shown in Figures indicate the direction of main symmetry axes of graphite underneath the molecular layers. The unit cell parameters are determined from more than 30 experimental values of at least two calibrated STM images. The network coverage (θ_{network}) of each structure was calculated by analysing more than 10 large area images.

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