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ARTICLE TYPE

Efficient Molecular Recognition Based on Nonspecific van der Waals Interaction at the Solid/Liquid Interface

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A highly efficient recognition phenomenon was observed between alkoxyated arylene-ethynylene macrocycles bearing identical side chains but different core size, which is based on van der Waals interactions between alkoxy chains. The ratio of both molecules and the environment of each molecule have been statistically analyzed to quantify the recognition efficiency.

Well-ordered supramolecular structures formed by molecular self-assembly through noncovalent interactions have wide applications in nanopatterning, surface templating^[1] and also in molecular and nanoelectronics.^[2] The formation of supramolecular architectures with long range ordering depends on efficient recognition between building blocks.^[3] Noncovalent intermolecular interactions, including van der Waals interactions, hydrogen bonding and metal coordination interactions, are the basis of molecular recognition.^[4-13] Among them, hydrogen and coordination bondings are more frequently exploited for the fabrication of complex architectures through cocrystallization because these interactions are relatively strong and directional. However, carefully designed molecular building blocks can also cocrystallize into architectures with large lattice constants based on complementary van der Waals interactions, for instance recognition between alkoxy chains of identical length, or shape complementary of build blocks.^[10a,15]

The recognition between molecules at the interface involves many simultaneous interactions, which depend on the reversibility of the weak noncovalent interactions sustaining these networks and enables to read out the structural and functional information installed in the building blocks.^[5-6] Better understanding of the phase behaviour of binary mixtures at the interface helps to design and fabricate pre-programmable supramolecular architectures.^[5,6] The recognition of molecules on surfaces can be used to fabricate highly complex hierarchical structures, and this strategy provides a basis for the formation and application of for instance nanoporous network structures.^[7-11] However, if we are to exploit the full potential of multi-component and hierarchical assembly on surfaces, there is a pressing need to address fundamental issues: what controls phase separation versus mixing, what is the effect of solution composition (concentration and molar ratio), and how to balance kinetics versus thermodynamics.

In this communication we report on the highly efficient heteromolecular recognition mainly based on van der Waals interactions between alkoxy chains. Instead of the length of alkyl

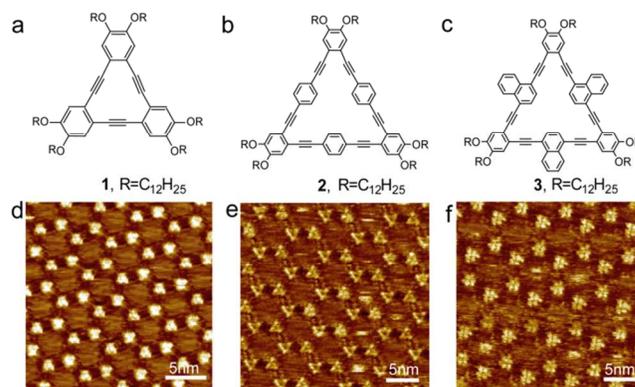


Figure 1. Chemical structures and STM images of self-assembled patterns formed at the interfaces between HOPG and 1,2,4-trichlorobenzene of (a, d) **1**, (b, e) **2** and (c, f) **3**. The bright features correspond to the triangular cores of these molecules. See also Figure S1.

chains, we make use of the selectivity of the interdigitation mode by manipulating the distance between neighbouring alkoxy chains on the same molecule. Alkoxyated arylene-ethynylene macrocycles bear identical alkoxy substituents (OC₁₂H₂₅ chains) while differ in core size and structure were chosen as a model system. They all formed honeycomb networks stabilized by van der Waals interactions between alkoxy chains (Figure 1 and Figure S1).^[15] The possible interaction modes between alkoxy chains are shown in Figure 2a and 2b. The favourable interdigitation mode of **1** is [2+2], while for **2** and **3**, the most favourable mode is [1+1] due to the larger core size,^[14,16] “[x+y]” being the interaction mode referring to the number of alkyl chains for each compound involved in intermolecular stabilization via van der Waals interactions. For the interaction between **1** and **2** or **3**, the most likely interaction mode is [2+1] because of the favourable distance between the two alkoxy chains on the same edge of **1** (0.9nm, perfect for alkoxy chain interdigitation). Due to the relative shift between neighbouring molecules imposed by the interaction of the alkoxy chains, the interdigitation can be either (+)-type or (-)-type,^[14b] and as a result, these molecules can form chiral 2D architectures at the interface (Figure 2c). When a binary mixture of **1** with **2** or **3** is applied on the surface, the outcome of

the self-assembly process depends on the competition of these different homo- and hetero-molecular interaction modes. Using STM we have studied the assembling behaviour of these binary mixtures on the surface of highly oriented pyrolytic graphite (HOPG). The effect of concentration, mole ratio and temperature were investigated.

Mixtures of **1** and **3** assemble into hybrid honeycomb networks at the interface between HOPG and 1,2,4-trichlorobenzene (TCB). Typical STM images of the hybrid network of **1/3** are shown in Figure 3 and Figure S2. In these quasi-constant current images, the image contrast reflects differences in tip trajectory, the brightest features corresponding to the largest displacement of the STM tip perpendicular to the surface. In the network, aromatic cores of **1** appear as smaller and with usually slightly brighter triangular features depending on the tunnelling bias compared to **3**. While **3** appear as larger and slightly dimmer triangles with small protrusions on the edges, similar to the observations made for pure **3**.^[16]Note that the pores appear to be filled, a feature that will be discussed later on. In the high resolution image in Figure 3b, the cores of **1** and **3** are marked by green and light yellow triangles, respectively. The white rhomboid marks out the unit cell and the parameters are $a = 5.2 \pm 0.1$ nm, $b = 5.2 \pm 0.1$ nm, $\alpha = 60 \pm 1^\circ$. The honeycomb lattice of this hybrid network is composed by two sublattices, each occupied by **1** or **3** respectively, thus each unit cell contains two molecules (ignoring what is trapped in the pore). Compounds **1** and **3** appear to recognize each other quite nicely, arranged alternately to form a hybrid honeycomb network. The white lines in Figure 3a mark out the domain boundaries. On these domain boundaries each hexagon is composed by two molecules of **1** and four molecules of **3**. In the domains on opposite sides of the boundary, the molecules of **1** and **3** exchange their position in the sublattice. However, the chirality of the assembly, with clockwise or counterclockwise pores, does not change (Figure 3c). Thus the domains on both sides of the boundary are rotational rather than mirror domains. A different kind of domain boundary, each hexagon composed by four molecules of **1** and two molecules of **3** can also be observed occasionally as indicated by the blue arrow in Figure 3a. An enlarged version of this image can be found in ESI.

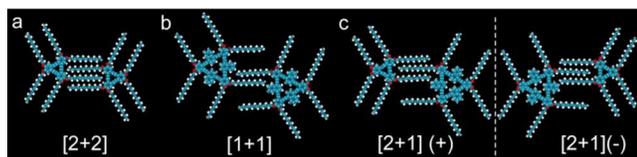


Figure 2. Interaction modes of alkoxy chains in homomolecular dimers of **1** and **3** and heteromolecular dimer between **1** and **3**. In the latter case, a racemic dimer is also shown.

In the hybrid network, almost every molecule of **1** is connected with three molecules of **3**. Homomolecular dimers of **1** connected via alkoxy chain interdigitation are rarely observed, which reflects the efficient recognition between **1** and **3**. This indicates that the [2+1] type interdigitation between **1** and **3** is the more favourable interdigitation mode in the binary assembly.

At the current mole ratio in solution (**1:3** = 1.32:1), the hybrid network covers most of the surface, while pure honeycomb

domains of **3** can only be observed occasionally (Figure S2). We have tested a series of binary mixtures with different mole ratios, and the results reveal that the mixtures have a strong tendency to form hybrid networks. Only when **3** is in great excess (**1:3** = 0.33:1) phase segregation becomes significant. On the contrary when **1** is in excess, the tendency to phase segregation is even weaker. Even with **1:3** = 5.29:1, honeycombs (and domains) formed by **1** are scarce, though honeycombs consisting of two molecules of **1** and **3** or five and one molecule(s) of **1** and **3** were more frequently observed (Figure S3), leading to a decrease in recognition efficiency.

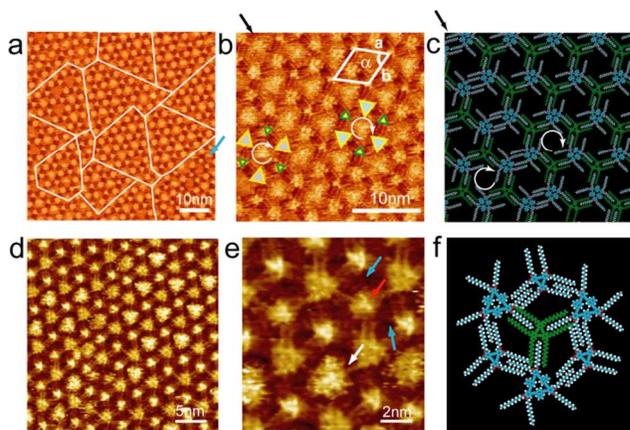


Figure 3. (a, d) Large-scale and (b, e) high-resolution STM images of the hybrid network formed by a binary mixture of **1** and **3** (**1:3** = 1.32:1) at the TCB-graphite and 1-octanoic acid-graphite interface, respectively. (c, f) Molecular models of the hybrid assembly. The white lines in (a) mark the domain boundaries. Similar domain boundaries are indicated by the black arrow in (b) and (c). Another different domain boundary is indicated by a blue arrow in (a). In (e) the white, red and blue arrows show the trapped **3**, **1** and 1-octanoic acid molecules in the hybrid network, respectively. (a) Concentration of **1**: 5.16×10^{-6} M, $V_{\text{bias}} = 0.80$ V, $I_{\text{set}} = 0.020$ nA, (b) concentration of **1**: 2.58×10^{-6} M, $V_{\text{bias}} = 1.10$ V, $I_{\text{set}} = 0.05$ nA. (d, e) Concentration of **1**: 3.25×10^{-6} M, $V_{\text{bias}} = 1.10$ V, $I_{\text{set}} = 0.05$ nA.

To quantitatively evaluate the efficiency in recognition, we have carried out a statistical analysis on the environment of each molecule of **1**. As shown in the high resolution STM image and molecular model of the hybrid network, in a perfect “recognition” hybrid network, each **1** molecule should be involved in [2+1] interdigitation with three molecules of **3**, and should be in no “direct” contact with same molecule. So we define the recognition efficiency as the ratio of **1** not in contact with same molecule against the total number of **1** on the surface.

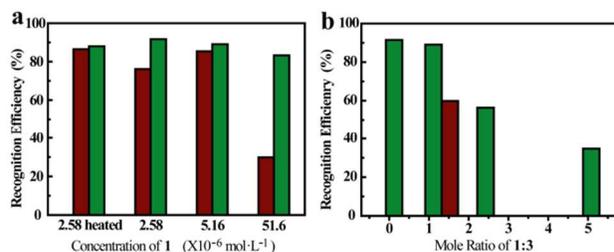


Figure 4. (a) The recognition efficiency of binary mixtures of **1/3** (green) and **1/2** (red) at the TCB/graphite interface at different concentrations for a constant ratio of both molecules in solution (**1:3** = 1.32 : 1, **1:2** = 1.22 : 1). (b)

The dependence of recognition efficiency of **1/3** on solution composition in both TCB (green) and 1-octanoic acid (red). The total mass concentration is 0.01 mg/g in both solutions.

When the mole ratio is kept at **1:3** = 1.32:1, at all concentrations the **1/3** binary mixtures show quite good recognition efficiency, in most cases above 80% (Figure 4a and Table S1). The recognition efficiency increases with decreasing solution concentration. To test the hybrid network is thermodynamically stable or kinetically trapped, we have carried out sample annealing at 40 °C for 10 minutes. After annealing, the recognition efficiency is not significantly changed. These results indicate that the intermolecular recognition behaviour is most likely ruled by thermodynamics, rather than being the result of kinetic trapping.

The recognition efficiency shows a clear decrease with increasing mole ratio of **1** (Figure 4b and Table S2). This is to be expected since a change in solution composition is also reflected in the monolayer composition (though the relationship is not linear, see below and in ESI). The higher the fraction of **1** adsorbed on the surface, the larger the possibility that a **1** molecule will be in direct contact with another molecule of **1**.

A statistical analysis on the surface composition indicates that both the solution composition and concentration has a significant influence on the composition of the adlayer (Figure S6, S7). At the TCB/graphite interface, for all mole ratios **3** shows a significant preferential adsorption against **1**: the mole ratio of **1** in the adlayer is significantly lower than that in the solution. As for the influence of concentration, the ratio of **1** against **3** in the adlayer is reduced upon decreasing the concentration, which means that **3** exhibits a higher adsorption preference compared to **1** (Table S1, S2 and Figure S6, S7). Previous reports have demonstrated that for multi-component mixtures, preferential adsorption may happen due to a difference in affinity to the substrate. The composition in the adlayer shows always nonlinear dependence on the solution composition.^[17]

All the observations demonstrate that the hybrid structure is thermodynamically stable, which means that the [2+1] type interdigitation is energetically favourable.^[14a] This preference cannot be understood simply by the different magnitudes of van der Waals interactions depending on the interdigitation modes.^[18] Co-adsorption of solvent molecules have been reported to stabilize the desired nanopatterns and also to induce homochirality to the supramolecular assembly.^[19] Thus the influence of solvent should be taken into account. We tested the assembly of the binary mixture in another solvent, 1-octanoic acid. Surprisingly, at the 1-octanoic acid/graphite interface, the molecules trapped in the pores of the hybrid network, which appear always fuzzy at the TCB/graphite interface, can now be clearly resolved, especially in the case when the trapped molecule is **1** (Figure 3d and 3e). If the trapped molecule is **3**, it can appear a bit fuzzy, though the triangular shape can be distinguished. As illustrated in the model, the molecule of **1** trapped in the hybrid network also forms [2+1] interdigitation with the three molecules of **3**. Though due to steric constraints the interdigitation between this trapped **1** molecule and **3** is not as perfect as the interdigitation between the molecules forming the hybrid network itself (Figure S4), it provides extra stability to the hybrid network. Also co-adsorption of 1-octanoic acid molecules can be identified as extra bright bars

around the trapped **1**. This also serves to stabilize the network. According to this observation we attributed the preference of [2+1] interdigitation to the co-adsorption of trapped “guest” **1** and solvent molecules.

As a comparison we have also investigated the recognition behaviour of **1** with **2**. Similar recognition was observed (Figure S2). The unit cell parameters of the hybrid network of **1** and **2** were measured to be $a = 5.4 \pm 0.1$ nm, $b = 5.3 \pm 0.1$ nm, $\alpha = 59 \pm 2^\circ$. Comparing **2** with **3**, we expected that the naphthalene groups in **3** would lead to some steric hindrance upon interdigitation of alkoxy chains, thus we expect **1/2** show better recognition efficiency than **1/3**. However, at all concentrations the combination **1/3** shows higher recognition efficiency than **1/2**. **1/2** also shows a stronger tendency of phase separation than **1/3**. Considering the symmetry of the supramolecular assemblies formed by **2** ($p2gg$ for linear pattern and $p6$ for honeycomb network) and **3** ($p6$ for both flower and filled-honeycomb pattern) (Figure S1), the above observations indicate that the small steric hindrance brought by the naphthalene groups is negligible, and that the symmetry of the intrinsic supramolecular assembly of the components may play a role in determining the recognition efficiency.

Efficient recognition based on van der Waals interactions has been reported exploiting the selectivity afforded by alkyl chain length^[10a,14b,14c] or alkadiyne side chain shape.^[20] In this communication we have demonstrated an efficient strategy for the design of a recognition system based on selectivity of alkoxy chain interdigitation modes. Two binary mixtures of alkoxyated arylene-ethynylene macrocycles bearing identical alkoxy substituents (OC₁₂H₂₅ chains) while differing in core size and structure, **1/3** and **1/2**, show very high recognition efficiency at the TCB/graphite interface, and the recognition efficiency increases with the reduction of solution concentration, and is not affected by sample annealing. Steric hindrance brought by the naphthalene group showed no obvious effect on the molecular recognition behaviour. The efficient recognition between with the AEMs proves that the design of the supramolecular assembly from its building blocks represents a highly promising and general strategy, and may open a way for the design of hierarchical assemblies based on recognition between alkoxy chains.

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Notes and references

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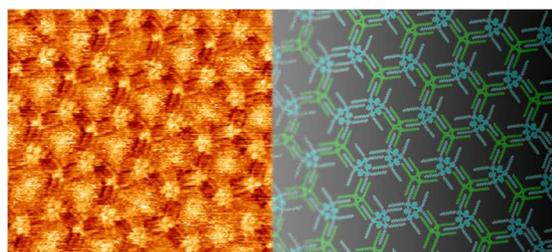
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† Electronic Supplementary Information (ESI) available: [Experimental and instrumentation details, synthesis and characterization of compounds and materials, extra STM results].

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TOC

**Efficient Molecular Recognition Based on Nonspecific van der Waals Interaction at the Solid/Liquid Interface**

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A surprising recognition phenomenon based on van der Waals interactions was observed, which proves that the design of the supramolecular assembly from its building blocks represents a highly promising and general strategy.