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One-touch Nanofabrication of Regular-sized Disks through Interfacial Dewetting and Weak Molecular Interaction

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Nanodisks with uniform height and tunable diameter on the nanometer scale were constructed without any lithographic processes. The disks consisting of an amphiphilic triimide module were formed at the air–water interface in the presence of cyclen as an aqueous shackle and transferred onto substrates by the surface-touching (Langmuir–Schaefer) technique. The 3 nm height of the disks was maintained, whereas the diameter was tunable from 45 to 74 nm by varying surface pressures.

Practical and theoretical studies on nanoscience and nanotechnology are dominated by nanomaterials with controlled sizes and morphologies.[1] In particular, nanodisks can be regarded as restricted quantum wells within a two-dimensional plane.[2] Quantum effects can be expected orthogonal to the object plane, whose thickness is a few nm, with confined in-plane effects for nanodisk widths between 10 and 100 nm. Lithographic processes for regular-sized nanodisks of the required sizes or shapes are still limited owing to high costs and low energy efficiency. Alternative approaches might involve self-assembly of soft materials into two-dimensional structures and subsequent transcription of those into the desired materials.[3] However, most self-assembly processes using block copolymers,[4] oxidized organogelators,[5] or salt-free surfactant mixtures[6] provide disk-like objects of excessive thicknesses (>10 nm) and polydispersity. In contrast, molecular assemblies confined at interfaces such as Langmuir monolayers, lipid bilayers, and bicelles have thicknesses of only 1–5 nm, although they usually possess extended lateral dimensions (i.e., micrometer scale or more) even after phase-separation[7] or other processes.[8]

Here we report a novel methodology for creation of monodisperse regular-sized disks of several nanometer thickness and with diameters less than 100 nm (Figure 1) by combining two concepts, (i) relatively weak intermolecular interactions within an interfacial medium and (ii) two-dimensional quick dewetting. Use of weak interactions should provide greater control over domain size across two dimensions compared to the stronger and more specific molecular recognition events.[9] Dewetting processes are widely known to be useful for formation of regular patterns.[10] Chi and co-workers proposed a method to create regularly aligned and one-dimensionally extended nanoscopic channels through anisotropic dewetting using the Langmuir–Blodgett (LB) process.[11] Continuous shifts of one-dimensional interfacial lines during vertical lifting of a solid substrate through a Langmuir monolayer results in regular one-dimensional nanostructures. If the process is similarly conducted in two dimensions by horizontal-touching transfer of the Langmuir monolayer, regular-shaped two-dimensional nanostructures such as nanodisks could be formed.

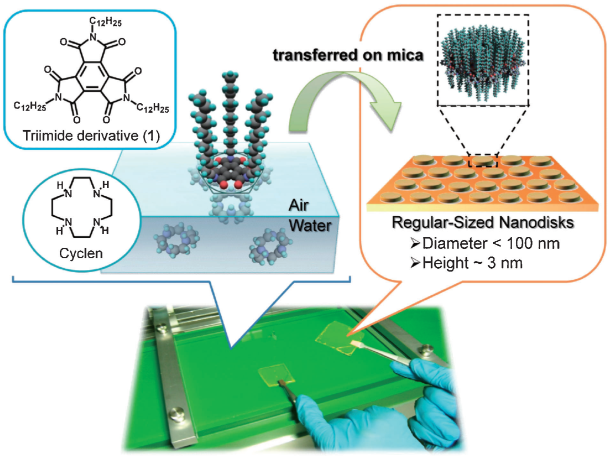


Figure 1. Schematic representation of the formation of regular-sized nanodisks at the air–water interface.

In order to establish a novel methodology for synthesis of regular-sized nanodisks through a nonlithographic interfacial process based on the strategy described above (Figure 1), an amphiphilic triimide, tri-*n*-dodecylmellitic triimide (**1**, ca. 0.98 nm in diameter),[12] and a water-soluble macrocyclic oligoamine, 1,4,7,10-tetraazacyclododecane (cyclen, ca. 0.76 nm in diameter) were applied. The imide moieties of **1** act as hydrogen-bonding acceptors and can interact weakly with the secondary amine moieties of cyclen as hydrogen-bonding donors. The Langmuir monolayer formed was transferred onto freshly cleaved mica by the surface-touching (i.e., Langmuir–Schaefer) method.

Surface pressure (π)–molecular area (A) isotherms (Figure 2A) of **1** on pure water exhibit a plateau region at a surface pressure of about 17 mN m^{-1} characteristic of a phase transition. Molecular area at the transition (1.15 nm^2) corresponds to an intermolecular distance of 1.18 nm of a two-dimensional hexagonal model structure.[13] Presence of cyclen (1.0 mM) in the subphase led to a decrease in the molecular area and an increase in the transition-point pressure to 28 mN m^{-1}. Excessively close molecular packing with an intermolecular distance of 1.06 nm was estimated from the molecular area at the transition pressure of **1** on 1.0 mM cyclen (0.95 nm^2).[13] In

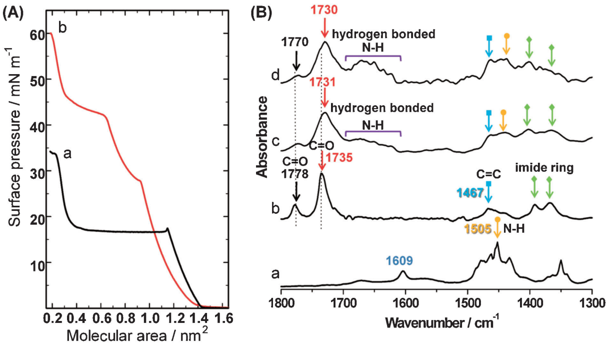
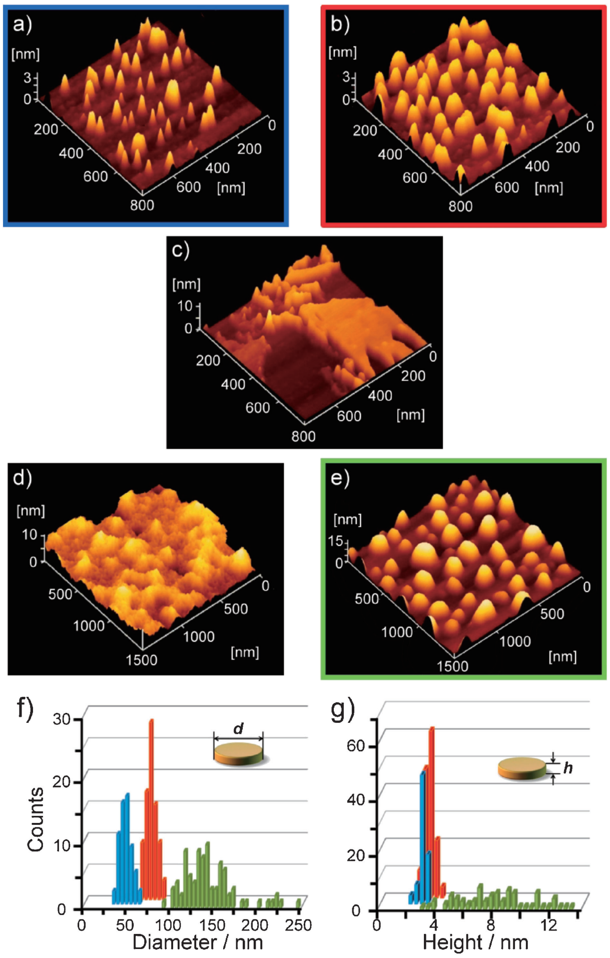


Figure 2. (A) π–A isotherms for **1** in the absence (a) and presence (b) of 1.0 mM cyclen at 20.0 ± 0.2 °C. (B) FT-IR-RAS spectra of (a) cyclen on KBr plate, (b) LB monolayer film of **1** prepared on pure water at 30 mN m^{-1}; LB monolayer film of **1** prepared on aqueous solution of cyclen (1.0 mM) at a surface pressure of (c) 15 and (d) 30 mN m^{-1}. Gold-coated glass was used as substrate for samples (b–d).

addition to appearance of bands of bound cyclen molecules in the IR spectrum (Figure 2B), interactions between **1** and cyclen in the subphase are indicated by a shift to lower frequency of ν(C=O) band and broadening of the δ(N–H) bands.

AFM investigation on the samples prepared by the surface-touching method onto mica surfaces revealed well-dispersed nanostructures whose sizes depended on the surface pressure applied (Figure 3a at 15 mN m^{-1} and Figure 3b at 30 mN m^{-1}). Diameters of these objects on mica are narrowly distributed at 46 ± 7 and 73 ± 6 nm for samples prepared at 15 and 30 mN m^{-1}, respectively (Figure 3f). Similarly, their thicknesses have well-defined values, 2.6 ± 0.3 and 2.9 ± 0.4 nm at 15 and 30 mN m^{-1}, respectively (Figure 3g). These observations strikingly reveal the successful formation of monodisperse regular-sized nanodisks of controlled size obtained simply by touching a solid substrate on a Langmuir monolayer. The necessity of interaction between triimide and cyclen was clearly revealed by comparing AFM images of a film of **1** transferred from the surface of pure water (no cyclen). Films formed without cyclen only produce continuous and irregular films (Figures 3c and 3d). However, AFM images of cast films of both **1** and the cyclen clearly show that interaction is not sufficient to form monodisperse nanodisks (Figure 3e). Some structures were observed, but the diameters and heights (Figures 3f and 3g) are not regular and monodisperse like the nanodisks from surface touching.

Here, a question arises as to why the disks maintain a height of ca. 3 nm. If dodecyl chains of **1** stand perpendicular to the triimide core while retaining an all-trans conformation, the thickness of the monolayer should be approximately 1.5 nm (C–C distance = 0.154 nm, C–C–C angle = 109.28°, thickness of graphene = 0.34 nm). This leads us to hypothesize that the nanodisks consist of a bilayer structure (reverse bicelle) where cyclen is trapped between two triimide molecules with their planar aromatic rings positioned facing each other following transfer onto the mica substrate. This situation is reasonable since the deposition technique (i.e., the surface-touching method) used in this study often yields bilayer structures through layer overturning.[14] The presence of cyclen should strongly enhance association of the head groups of **1** in forming a bilayer structure.



	🟦 15 mN m^{-1}	🟥 30 mN m^{-1}	🟩 cast film
Diameter / nm	46 ± 7	73 ± 6	140 ± 28
Height / nm	2.6 ± 0.3nm	2.9 ± 0.4	7.9 ± 2.5

Figure 3. AFM images of LB films of **1** transferred using the surface-touching mode from an aqueous solution of cyclen (1.0 mM) at surface pressures of 15 (a) and 30 mN m^{-1} (b), from pure water at a surface pressure of 8 mN m^{-1} (c); and cast films of **1** (d), prepared from a mixed solution of **1** and cyclen (e). Histograms showing diameter (f) and height (g) distribution of corresponding regular-sized nanodisks.

In summary, we have developed a new strategy for manufacturing regular-sized disks using an interface-assisted self-assembly technique: the amphiphilic triimide–cyclen system at air–water interface. The proposed method can provide size-defined two-dimensional objects, because horizontal dewetting is advantageous for two-dimensional regular structures and layer overturning confers defined thickness. The disk diameter is tunable through mechanical motion of the monolayer, whereas the height remains constant at the molecular level. Distributions of these size parameters are quite small. Controlled formation of defined nanostructures through easy macroscopic processes (surface touching in this case) should lead to unique approaches for economical and energy efficient nanofabrication.

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13 We assume hexagonal packing of two-dimensional circles of **1**. Intermolecular distance was estimated from averaged molecular area at given surface pressure.

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