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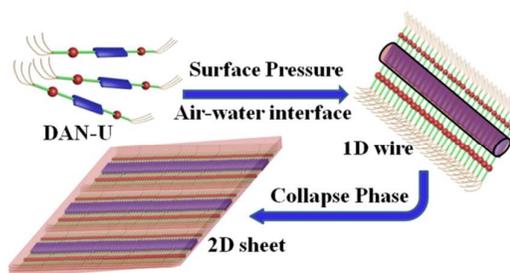
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TOC:

Micrometer long oriented one-dimensional wires and two-dimensional sheets from a bis-urea functionalized dialkoxy-naphthalene organogelator

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Fabrication of 1D wires and 2D sheets of organogelator DAN-U at air-water interface below critical gelation concentration is reported here.



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ARTICLE TYPE

Micrometer long oriented one-dimensional wires and two-dimensional sheets from a bis-urea functionalized dialkoxy-naphthalene organogelator

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Unidirectionally aligned 1D wires of an organogelator ranging over twenty five square microns are fabricated at air-water interface at a significantly lower critical gelation concentration, which merges into 2D sheets with the aid of surface pressure.

One-dimensional (1D) nanostructures have gained considerable attention in the recent past owing to their possible applications in opto-electronics. However, most of the reports are based on the inorganic materials,¹ while the analogous research on organic molecules has not been fully explored yet except for few well-known organic dye molecules, although there remain enormous potential of such 1D organic wires in existing optoelectronics.² Chromophoric building blocks spontaneously self-assemble to form aggregates by various non-covalent forces such as π - π interactions, hydrogen bonding, van der Waals or electrostatic interactions and other forces operating in multiple directions.³ This is particularly true for π -gelators, which spontaneously self-assemble into entangled network fibers.⁴ Thus, designing 1D ordered wires of organic chromophoric building blocks is not only fundamentally challenging but also may help in modulation of inter-chromophoric interactions and consequently the photo-physical properties by precisely tailoring molecular orientations within an aggregated assembly.⁵ Tuning such molecular-level interactions may lead to fabrication of macroscopic ordered assemblies by “bottom-up” approach that can be exploited for versatile optoelectronic applications.⁶ Langmuir-Blodgett (LB) technique is well-known for tailoring the molecular level interactions at the air-water interface by controlling packing, orientation and spatial arrangement of molecules with precise control.⁷ Earlier report on dialkoxy-naphthalene-based gelator (DAN-U, Figure 1a) revealed a strong solvent dependent aggregation and gelation properties leading to entangled network fibers.⁸ At the air-water interface, due to the confined geometry and possibility of hydrogen-bonding network formation with water subphase, the molecular interaction can be manipulated to organize the gelators in an ordered fashion with the aid of surface pressure. Here we report on the fabrication of micrometers long 1D ordered wires of π -gelator, DAN-U, in a controllable and efficient way at the air-water interface using LB technique. We show that the critical gelation concentration (CGC) for DAN-U

can be lowered significantly at the air-water interface with the aid of 2D surface pressure to reinforce gelation into uniform 1D ordered wires. A further increase in the surface pressure uniquely merges the ordered wires in side-by-side fashion forming 2D molecular sheets.

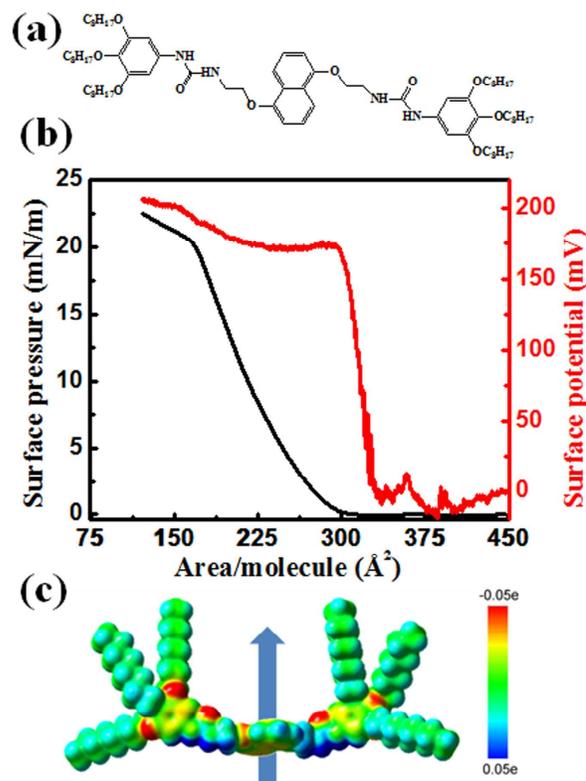


Figure 1. (a) Molecular structure of DAN-U π -System. (b) Surface pressure-Area isotherm of DAN-U π -System on milli-Q water subphase at 22^o C. (c) Charge density distribution plot of DAN-U. The red color depicts the negative charge density, while the blue color depicts the positive charge density. The arrow indicates the direction of dipole moment.

Urea functionalised DAN-U π -system contains six alkyl chains which are hydrophobic in nature (Figure 1a). Although DAN-U contains polar urea groups, it is not amphiphilic in nature.

Nevertheless, it can still form monolayer due to hydrophobicity required at air-water interface. The surface pressure (π) versus area per molecule (A) isotherm shows a liquid-condensed phase until a collapse pressure of ~ 20 mN/m (Figure 1b). A limiting molecular area of $265 \text{ \AA}^2/\text{molecule}$ is extracted from the π - A isotherm curve which is larger than the geometric area of a single **DAN-U** molecule suggesting formation of aggregates at the air-water interface upon spreading.

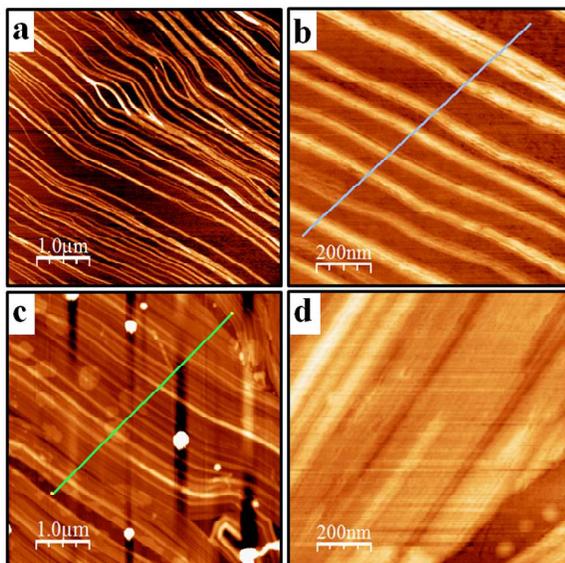


Figure 2. (a) AFM topography image of aligned molecular wires of **DAN-U** π -system spanning over $5 \times 5 \mu\text{m}^2$ area lifted on freshly cleaved mica at surface pressure 14 mN/m. (b) High resolution AFM image showing aligned molecular wires (c) AFM image of close packed wires lifted at 18 mN/m. (d) AFM topography image lifted after collapse pressure shows formation of 2D molecular sheets.

Interestingly, uniaxial compression at the air-water interface of a Langmuir trough leads to the formation of well aligned **DAN-U** supramolecular wires. Tapping mode atomic force microscopy (AFM) images of monolayer LB film shows well aligned **DAN-U** wires spanning over an area of $25 \mu\text{m}^2$ (Figure 2a). The optimum alignment of the wires can be achieved in the surface pressure range spanning from 10 to 18 mN/m. Higher magnification AFM image and the cross-sectional analysis (Figure 2b and Figure S2, ESI \dagger) indicate uniform height (4 ± 0.5 nm) and width (40 ± 5 nm) of the wires. The observed ~ 4 nm height of the wires is consistent with the drop cast entangled fibres as reported earlier.⁸ While the morphology of the individual wires is not affected by the applied surface pressure below the collapse pressure, the increase in surface pressure effectively fill voids in the monolayer film bringing the wires into closer proximity retaining the 1D alignment (Figure 2c). Since we have used the conventional LB deposition technique, the angle between the direction of compression and the mica substrate is exactly perpendicular. The direction of compression in LB trough is fixed, which results in ordering of **DAN-U** wires parallel to the barrier of LB trough. The change in dipping direction of the mica substrate obviously does not affect this ordering or direction of alignment on mica substrate. Interestingly, some of these wires are observed to fuse in the side-by-side fashion at this surface pressure. Further

increase in surface pressure above the collapse pressure leads to the formation of 2D sheets (Figure 2d). Cross-sectional analysis of the 2D sheets (Figure S3, ESI \dagger) reveal a height of $\sim 8 \pm 0.5$ nm, which is the double of the wires suggesting a bi-layer formation of **DAN-U** molecules within the sheets. Thus, the 2D surface pressure prevalent in the Langmuir monolayer uniquely merges 1D wires into 2D sheets. The formation of aligned 1D wires and 2D sheets of **DAN-U** gelators is surprising since cross-linked entangled network of fibers are commonly found in drop cast films from solution phase.

We have carried out surface potential measurements (Figure 1b) at the air-water interface during uniaxial compression process, (see the ESI \dagger).⁹ An optimal dipole moment is expected for parallel arrangement of **DAN-U** molecules where the direction of the effective molecular dipole moment is perpendicular to the air-water interface. The surface potential (ΔV) versus area (A) isotherm does not show change in ΔV at the initial stage of compression. Expectedly, the **DAN-U** molecules form random aggregates at large separation distances at lower surface pressure. The surface potential starts rising at mean molecular area of 330 \AA^2 , which is higher than the limiting area per molecule of **DAN-U** observed in the π - A isotherm curve. The π - A isotherm reflects van der Waals interactions between the hydrocarbon chains and π - π interactions of the **DAN-U** molecules, while the ΔV - A isotherm is dominated by the dipole-dipole interactions between the polar parts of **DAN-U** molecules. Evidently, the dipolar interaction operates at larger intermolecular distances whereas the van der Waals interactions are short range. The dipole moment calculation and conformational analysis reveal that **DAN-U** molecule can remain flat at air-water interface when the urea functional groups remain in *cis* position (Figure 1c and Figure S1, ESI \dagger). In such configuration, the dipole moment remains perpendicular to the plane of **DAN-U** molecules with maximum value 5.6 D (Figure 1c and Figure S1, ESI \dagger).

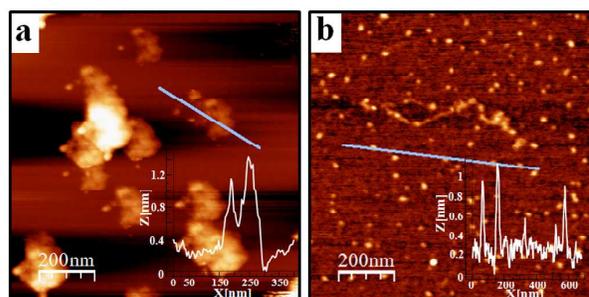


Figure 3. (a) AFM topography image of small droplet like aggregate structure **DAN-U** π -system of chloroform solution drop-cast film. (b) AFM topography image of small droplet like aggregate structure formed at air-water interface at low surface pressure of 4mN/m.

In order to investigate the formation mechanism of 1D wires, we first verified the gel formation possibility in the starting solution phase. AFM images of solution drop-cast **DAN-U** molecules reveal droplet like aggregated structures of $\sim 40 \pm 10$ nm form large aggregates of $\sim 250 \pm 50$ nm sizes (Figure 3a). Additionally, a monolayer LB film lifted at a low surface pressure of 4 mN/m on mica also reveals small droplet like structures with sizes of 35 ± 5 nm (Figure 3b). The differences in the droplet sizes may arise due to different mode of interactions of **DAN-U** molecules at the

air-water interface in comparison to bulk solution phase. The formation of platelets instead of fibers can be explained by considering significantly less concentration of the working solution compared to the critical gelation concentration (CGC) of **DAN-U** molecules, below which formation of fibers is prevented.^{4, 8} The CGC of **DAN-U** in the same solvent is 0.30 gm/100 ml, while the solution concentration used for drop-cast film or for LB measurements is 0.05 gm/100 ml, which is six-fold lower than the CGC for **DAN-U** molecule. These observations univocally suggest the molecular wires do not exist in the solution phase or at the air-water interface at low surface pressure. Hence the

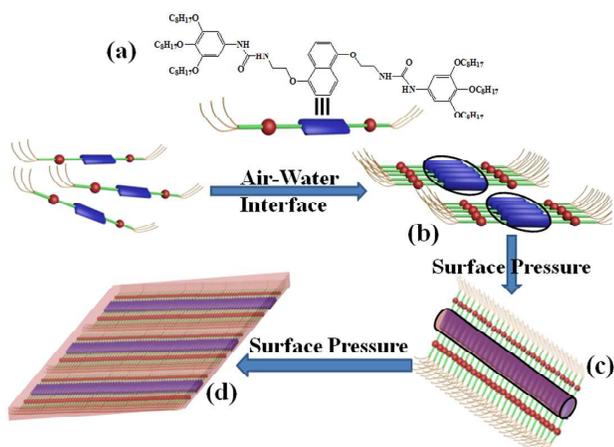


Figure 4. (a) Cartoon of **DAN-U** π -system at air-water interface. (b) A schematic model showing formation of droplet structure at low surface pressure (c) molecular wire at high surface pressure (d) molecular sheet at collapse pressure.

ordered molecular wires are formed with the aid of uniaxial surface pressure which brings the platelets in the closer proximity reaching CGC of **DAN-U** molecules at 2D air-water interface facilitating wire formation. Notably, the ΔV versus A isotherm (Figure 1b) revealed a flat conformation of **DAN-U** molecules at air-water interface with the alkyl tails are supposedly extending outwards. Such a confirmation enhances the π - π interaction between the adjacent **DAN-U** molecules at the air-water interface. Urea functional group is well known for highly directional hydrogen bonding motif for long range molecular interactions.¹⁰ The **DAN-U** molecule contains two symmetrical urea functional groups at the two sides of the naphthalene chromophore π -portion. Hence, **DAN-U** molecules can stack into 1D wires easily through π - π stacking and hydrogen bonding interactions under the directionality offered by the surface pressure.

Based on AFM observation and surface potential isotherm evidences, we modelled the 1D ordering of **DAN-U** molecules in the form of molecular wires and 2D sheets (Figure 4). The urea functional groups are supposed to be in contact with water subphase, while the hydrophobic chains are facing outwards. Implicit here is the strong π - π electronic interactions and hydrogen bond formation by the urea groups and hydrophobic interactions between the alkyl groups leading to the supramolecular 1D wires (Figure 4c). Increasing surface pressure brings the platelets observed at the low surface pressure (Figure 4b) into closer proximity. When the concentration of **DAN-U**

molecules at 2D air-water interface reaches CGC, gelation into 1D structure takes place. Owing to the directional nature of hydrogen bonds between **DAN-U** molecules and the π - π interactions facilitated by the well-known orientational ordering in Langmuir monolayer, micrometers 1D wires are generated. Increasing the surface pressure brings these 1D wires into closer proximity at which some of these wires are fused in side-by-side fashion (Figure 2c). Increasing the surface pressure beyond the collapse pressure completely fills the voids in the monolayer and brings the 1D wires into closely packed conditions resulting in 2D sheets (Figure 4d).

In summary, at the air-water interface, organogelator **DAN-U** molecules assemble to form 1D wires in contrast to the usual entangled gel network fibers. The wire assembly spans over twenty five square microns retaining tight spatial registry and alignment, which can be further tuned by applied surface pressure. Importantly, the CGC of **DAN-U** gelator is significantly reduced at the air-water interface with the aid of 2D surface pressure leading into ordered wires. The wires are merged into 2D sheets simply by increasing the surface pressure above the collapse phase. Our method is quite flexible since the wire assembly can be precisely controlled by varying the applied surface pressure. Both the ordered wires and sheets can be lifted-up onto a variety of solid substrates offering optoelectronic device fabrication possibilities.

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Notes and references

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- [†] Electronic Supplementary Information (ESI) available: Surface potential measurement, charge density calculation and AFM analysis. See DOI: 10.1039/b000000x/
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