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Supramolecular 2D monolayered nanosheets constructed by using synergy of non-covalent interactions†

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Here, a straightforward and rational approach to construct supramolecular assemblies with ordered nanostructures in a two-dimensional arrangement is reported. Taking advantage of the synergistic effect of multiple non-covalent interactions (hydrogen bonding and π–π interactions), the designed molecular monomer has a specific orientation in the self-assembly process, thus realizing two-dimensional control. Supramolecular two-dimensional nanosheets with single-layer thickness and controllable dimensions have been obtained, which can be clearly confirmed using TEM, SEM, AFM and XRD and by comparing with the self-assembled structures of the control system. The strategy of collaborative self-assembly proposed here using multiple non-covalent interactions is expected to be extended to the construction of various kinds of unique supramolecular 2D materials.

Two-dimensional (2D) nanomaterials are quite fascinating to the scientific community and have been the subject of intensive research in the last dozen-plus years, as a result of their unique physical, electronic optical, and chemical properties compared to zero-dimensional (0D), one-dimensional (1D) and three-dimensional (3D) nanomaterials as well as the promise of diverse potential applications arising from these properties.[1–7] By far, tens of thousands of academic articles on 2D nanomaterials have been published every year, suggesting that they are among the most popular research topics in the fields of chemistry, materials science, condensed matter physics and nanotechnology and have tremendous impacts on industry and our daily life.[8,9] This field has been in a state of explosive development since 2004, when graphene was successfully prepared from graphite for the first time by mechanical exfoliation with Scotch tape by Novoselov, Geim and co-workers.[10] The discovery of graphene as a 2D-structured material and its excellent physical and chemical properties has given rise to the research upsurge of a series of new and fascinating 2D materials.[11–18] Supramolecular 2D nanomaterials with sheet-like structures have attracted extensive attention in recent years because of their unique structural properties and potential applications in biomedicine, sensing and catalysis.[19]

Molecular self-assembly processes widely exist in nature. Generally, natural biomolecules (protein, polypeptide, DNA, *etc.*) involved in all fundamental processes in life fold into complex architectures through hierarchical self-assembly. The double helix structure of DNA is a typical example of self-assembly, and its stability is achieved by the coordination of multiple non-covalent interactions such as hydrophobic, hydrogen-bonding and π stacking. The information at the molecular level of peptides can be utilized to direct highly specific intramolecular and intermolecular interactions that promote the self-assembly of 2D assemblies with thermodynamic stability and defined structure.[20] Obviously, supramolecular self-assembly based on intermolecular noncovalent interactions is a promising and powerful approach for the preparation of highly ordered nanostructures with specific size and function due to the remarkable advantages such as facile construction, adjustable structure, easy functionalization and so on.[3,21–28] Many efforts have been made so far in the construction of sophisticated supramolecular architectures by precisely designing the molecular structures of building blocks and controlling the dimensions, sizes and manners of the further self-assembly to form diversified supramolecular materials displaying superiority and functionality. It is noteworthy that, from the unique structural characteristics and excellent properties brought by the good combination of 2D material and supramolecular assembly points of view, the design and fabrication of supramolecular 2D nanostructures by precisely controlling the self-assembly behavior of building blocks has become an appealing and significant research topic. At present, in 2D nanomaterials formed using non-covalent bonds, intensive research and considerable development have been carried

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out in the fabrication of 2D metal–organic frameworks.[29–31] However, the design and construction of 2D supramolecular assemblies containing hydrogen bonding interactions are still insufficient and in a fledgling stage.[26,32–35] On the other hand, it is a challenging and elusive task to achieve 2D supramolecular engineering by utilizing the cooperation of various intermolecular interactions.[36]

Here, we develop a rational and simple 2D supramolecular polymerization methodology based on the combination of multiple non-covalent interactions, which is a more general strategy to realize the 2D arrangement of supramolecular assemblies in a controllable manner, and opens up a significant perspective toward the construction and potential applications of various 2D nanomaterials. Having this in mind, we report the synthesis of molecule monomer **1**, which is designed to have a plethora of molecular interactions and can self-assemble directly into 2D supramolecular nanosheets with controllable architectures and single-layer thickness *via* directional complementary multiple hydrogen-bond-induced preorganization and the aromatic stacking of π–π interactions (Fig. 1a). We applied a previously reported single benzene-based compound 2,5-bis(amino)terephthalate as the precursor because the molecule has high crystallinity, and in a crystal, strong intramolecular hydrogen bonds are formed between the hydrogen atom of an amino group and the carbonyl oxygen atom, which makes the whole molecule present a rather planar structure.[37] Notably, based on the multiple intermolecular hydrogen bonds and negligible π–π interactions contributed by the mini π-system, one molecule is connected to other neighboring molecules and stacked in a layer-by-layer fashion in the crystal.[37] The building block **1** self-assembles to form one dimensional nanowires by means of intermolecular hydrogen bonding in the *x*-axial direction, with concomitant stacking in the *y*-axial direction *via* hydrogen-bonding interactions from the side chains at both ends and aromatic π–π interactions, with further lateral organization to form 2D nanosheets (Fig. 1a). In order to better understand the nature of molecular interactions and the growth mechanisms and establish the self-assembly principles for the formation of supramolecular 2D nanosheets, we also designed and synthesized another similar molecule **2**, which was obtained by replacing the amino group previously used as a hydrogen bond donor with an ether bond at the same position (Fig. 1b, left). Due to the lack of intermolecular hydrogen bonding interactions in the *x*-axis direction, it is more likely to form one-dimensional nanowires along the *y*-axis (Fig. 1b, right). A controlled 2D-to-1D morphological transition was achieved by simply and subtly adjusting the intermolecular forces. The chemical structures of monomers **1** and **2** were completely characterized (see ESI†).

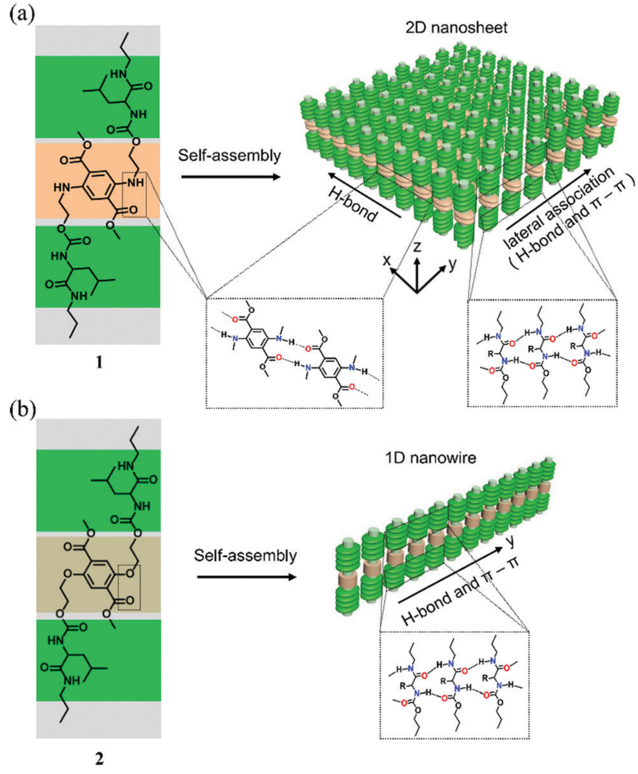

Fig. 1 (a) Molecular structure of **1** and schematic diagram of directional self-assembly into supramolecular 2D nanosheets *via* multiple noncovalent interactions. (b) Molecular structure of **2** and schematic diagram of self-assembly into 1D nanowires.

To elaborate the aggregation behavior in solution, various spectroscopic analyses were carried out. By increasing the concentration of control molecule **2**, a significant red shift occurred in the fluorescence (FL) emission spectra (from 380 nm to 400 nm) (Fig. 2a and b). The ultraviolet-visible (UV-Vis) spectra showed that the absorbance at 330 nm increased nonlinearly with increasing the concentration of **2**, and a deviated point at the concentration of approximately 20 μM was observed (Fig. S1, ESI†). These appearances demonstrate that in the case of intermolecular hydrogen bonding and π stacking, self-assembly of molecule **2** gave rise to the formation of aggregates in solution. However, no red shift and deviated point were observed in the same spectroscopic studies of **1**

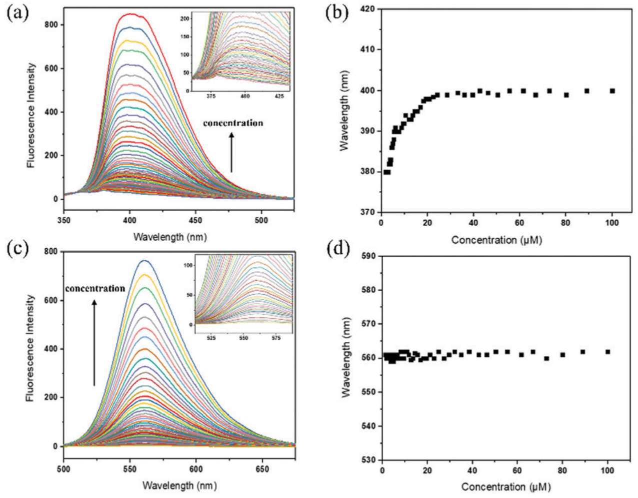

Fig. 2 (a) Fluorescence (FL) spectra (λ_{ex} = 336 nm) of **2** at 298 K at different concentrations (0–100 μM) in $CHCl_3$; (b) the maximum emission wavelength of **2** varied with the concentration. (c) Fluorescence emission spectra (λ_{ex} = 480 nm) of **1** at different concentrations (0–100 μM) in $CHCl_3$; (d) variation of the maximum emission wavelength of **1** *versus* concentration.

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(Fig. 2c, d and Fig. S2, ESI†). Compared with the study given in reference 2, molecule **1** was self-assembled into 2D nanosheets after the introduction of the hydrogen bonding interactions in the *x*-axis direction. Due to the stronger molecular interactions, self-assembly of **1** had taken place at a very low concentration, and consequently, the red shift and deviated point were not observed. In addition, the FT-IR spectrum of nanosheets formed by self-assembly of **1** exhibited a new absorption peak at 3300 cm^{-1}, which corresponded to the N–H group of amides on both side chains (Fig. S3, ESI†). Significantly, the vibrational frequency of C═O shifted to a lower wavenumber, and the vibration peak of amide I (1650 cm^{-1}) appeared, suggesting that hydrogen-bonding interactions play a critical role in the formation of the self-assembled nanosheets.

In order to characterize the self-assembly morphology of the two monomers in solution, we made an observation using transmission electron microscopy (TEM). TEM samples were prepared by adding several microliters of the sample solution dropwise on a fresh carbon support film copper surface, followed by removal of the excess solution by tilting the TEM support. The formation of the self-assembled nanosheets requires holding together a large number of individual building blocks **1** and ordered arrangement *via* the high directionality and cooperativity of H-bonding and aromatic interactions in a 2D space. We succeeded to obtain a TEM image of the stacked supramolecular nanosheets (Fig. 3a). Scanning electron microscopy (SEM; Fig. 3b and Fig. S4, ESI†) was further employed to image the structures of the assembly and unambiguously reveal the sheet-like morphology, which confirmed the proposed supramolecular polymerization method for constructing a two-dimensional topological structure. In the process of self-assembly, cooperative interactions of hydrogen bonding and π stacking play a crucial role in the construction of a highly ordered 2D nanosheet structure and its morphological control. The intermolecular hydrogen bonding interactions in the *x*-axis direction can be eliminated by simply replacing the amino group previously used as a hydrogen bond donor with an ether bond at the same position, and a controlled 2D-to-1D morphological transformation will be achieved (Fig. 1a and b). Therefore, monomer **2** can only self-assemble along the *y*-axis to form one-dimensional nanostructures due to the loss of the ability to self-assemble in the *x*-axis direction. Inevitably, the assembly behavior of **2** was observed using TEM and SEM under the same conditions, which was significantly different from that of **1**. The TEM result is consistent with the expectation that the monomer **2** self-assembled to form 1D nanowires rather than 2D nanosheets (Fig. 3c and Fig. S5, ESI†). Similarly, the self-assembled nanowires of **2** were also observed using SEM (Fig. 3d). Therefore, this reasonable design described here enables the successful construction of 2D supramolecular assemblies *via* a simple cooperative strategy of non-covalent interactions in supramolecular self-assembly.

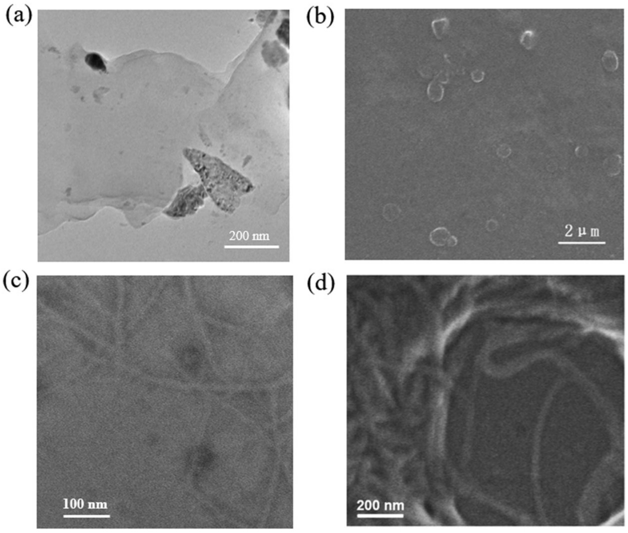

Fig. 3 (a) TEM and (b) SEM images of the self-assembled nanosheets. The sample was prepared by using a $CHCl_3$ solution of **1**. (c) TEM and (d) SEM images of nanowires formed by self-assembly of building block **2**.

To measure the topographical thickness of the 2D nanosheets, we applied a tapping mode atomic force microscopy (AFM) study. The self-assembled nanosheets with a flat and smooth surface can be clearly seen using AFM (Fig. 4a and b). The thickness of these sheets, based on AFM height profiles, reveals a relatively uniform thickness of around 2.1 nm, which is reasonable by calculating the single molecule height of the nanosheets in the minimum energy state (Fig. S6, ESI†). X-Ray diffraction (XRD) analysis was also conducted by using a solid powder sample of the nanosheets prepared by lyophilization of chloroform solution of **1**. A quantitative assessment of the thickness of the structures was accomplished by fitting the data as lamellar sheets and indicated a thickness of 2.03 nm, in agreement well with the height of the nanosheet determined using AFM (Fig. 4c). These results clearly

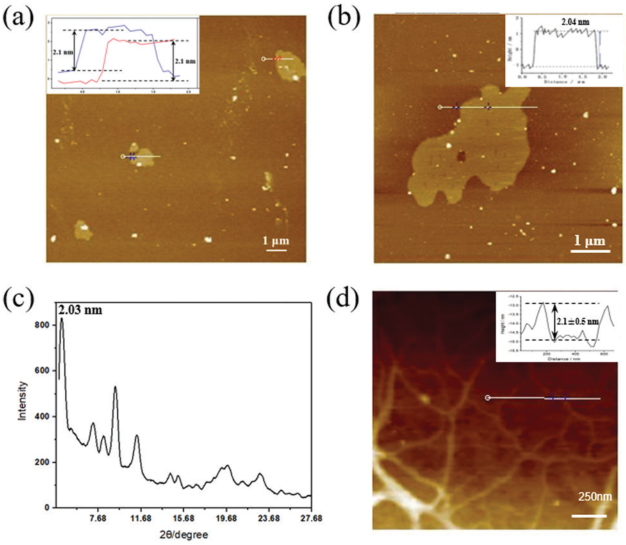

Fig. 4 (a and b) Tapping-mode AFM images of the self-assembled nanosheets of compound **1** on silicon wafer. The white line in the image represents the height profile across the ultrathin nanosheet indicating a thickness of 2.0–2.1 nm, consistent with the thickness of the expected monolayer framework. (c) X-Ray diffraction (XRD) pattern of a self-assembled **1** powder sample in the solid state. The *d* spacing values in nm are given next to the peaks, corresponding to lamellar sheets with a thickness of 2.03 nm. (d) Tapping-mode AFM image of the self-assembled nanowires of compound **2**.

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suggest that the self-assembled nanosheets maintain their lamellar structures not only in solution but also in powder samples. For a deeper understanding of the assembly mechanism, we also characterized the self-assembly behavior of **2** in solution. Under the same conditions, the designed control molecular **2** spontaneously self-assembled into one-dimensional nanowires along the *y*-axis due to the lack of supramolecular interactions in the *x*-axis direction, which are clearly visualized using AFM (Fig. 4d). Therefore, the synergistic effect of hydrogen bond preorganization and π–π interactions in two directions is the key strategy to the successful preparation of 2D supramolecular nanostructures, which provides important insight into the 2D supramolecular polymerization.

In conclusion, supramolecular 2D nanosheets with single layer thickness were successfully prepared using the precise design of the structure of monomers, the control of monomer properties and the regulation of the self-assembly behavior. Through the structural analysis obtained by various testing methods, we can evidently conclude that hydrogen bonding and π–π interactions play a synergistic role in the formation of 2D supramolecular nanostructures. By simply adjusting the molecular interactions, the morphological transformation from 2D nanosheets to 1D nanowires is realized, which also proves the assembly mechanism from this side. This synergy of multiple non-covalent interactions also widely appears in the self-assembly of proteins or polypeptides in biological systems. Such a cooperative self-assembly strategy through multiple non-covalent interactions is expected to be extended to the construction of diverse supramolecular two-dimensional materials with dynamic response and may hold promise for a wide range of potential applications in various areas, such as biochemistry and green chemistry. In addition, these self-assembled supramolecular nanosheets have a molecular-scale thickness (less than 5 nm) and lateral sizes ranging from several hundred nanometers to several micrometers, which provide ample scope for further chemical modification and functionalization.

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Conflicts of interest

The authors declare no competing financial interest.

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