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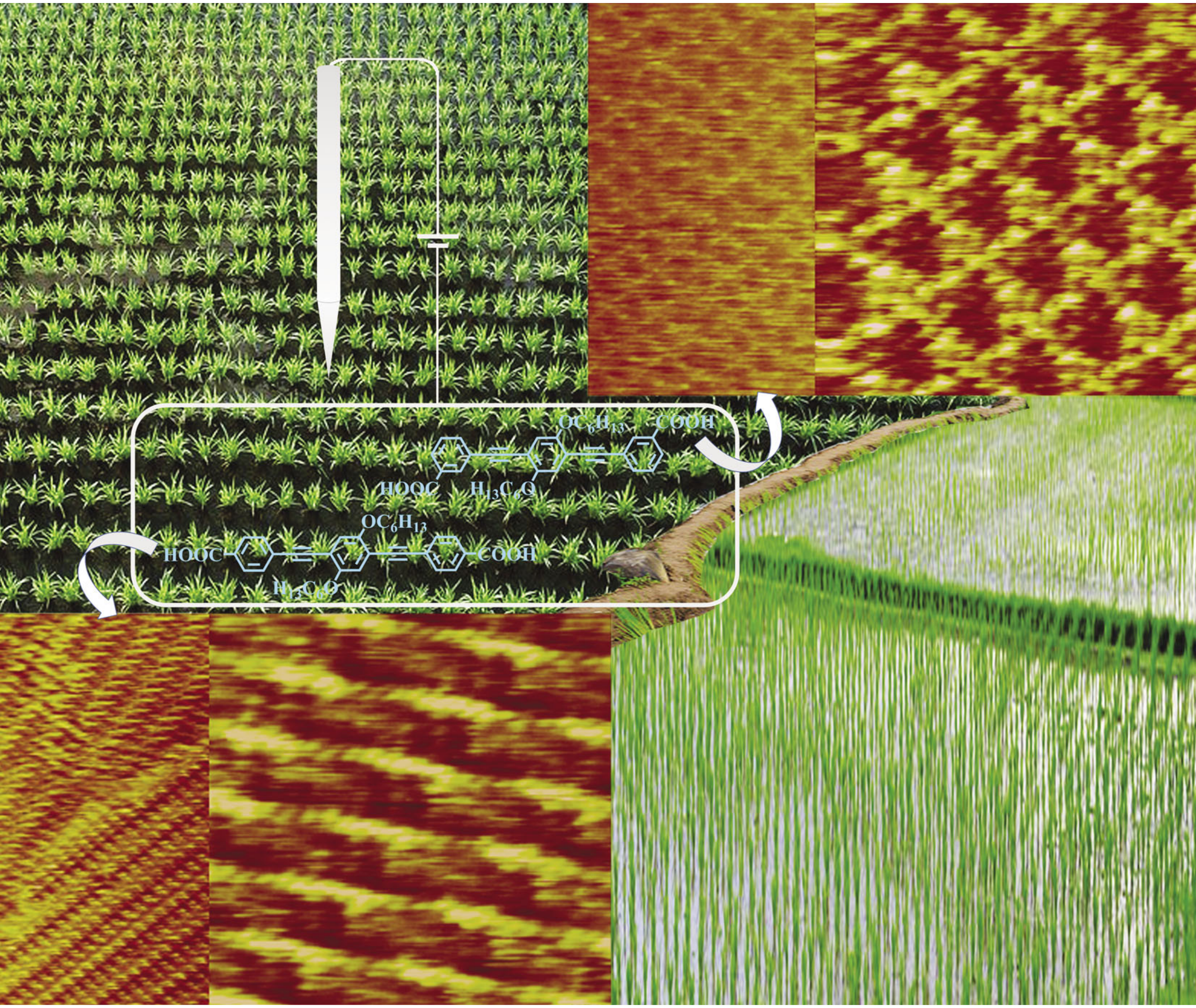

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Directional hydrogen bonding controlled 2D self-organization of phenyleneethynylenes: from linear assembly to rectangular network†

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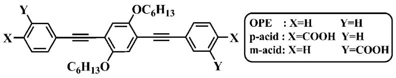
The effect of the carboxylic acid substituent position of phenyleneethynylene systems on the 2D self-organization is revealed by scanning tunneling microscopy.

Nature has utilized various noncovalent interactions for the fabrication of nanostructures which can perform specific biofunctions that maintain life on earth.[1] Inspired by the remarkable functions of natural nanostructured systems, efforts have been focused in recent years on the construction of molecular materials having potential applications as components in optoelectronic devices.[2] However, the design of molecular materials with predictable composition, structure, and function still remains a major challenge. An in depth understanding of the arrangements of molecules, with atomic resolution can provide valuable information on various noncovalent interactions[3] that control and direct their self-organization to materials.[4] Herein we report the role of directionality of hydrogen bonding in the 2D self-organization of phenyleneethynylenes possessing carboxylic acid groups at the terminal positions (Scheme 1) by using scanning tunneling microscopy (STM).

Phenyleneethynylenes are an interesting class of rigid rod molecular systems which maintains π-electron conjugation at any degree of rotation of phenyl rings and is proposed as linker for electronic communication in molecular electronic devices.[5,6] Phenyleneethynylenes possess tunable optical properties both in solution and in the solid state.[5] They are proposed as components in optoelectronic devices; for example, efficient blue electroluminescence was achieved in a single layer OLED using a phenyleneethynylene based polymer system.[7] For solid state device applications, it is extremely important to understand the self-organization of phenyleneethynylenes,[8] since the interchromophoric interactions significantly influence their optoelectronic properties.[9] Recent studies on the self-organization of phenyleneethynylenes, by our group[10] and others,[11] have revealed that these systems can be well organized on surfaces. Based on our studies, it is concluded that the organization of phenyleneethynylenes on 2D surfaces is mainly driven by alkyl CH···acetylenic π interactions (CH···π), which can be further modulated by (i) varying the alkyl chain length and (ii) by introducing hydroxyl and aldehyde groups at the terminal positions.[10] Intermolecular hydrogen bonding between carboxylic acids is highly selective and directional.[12] This type of hydrogen bonding is effectively utilized in various molecular systems for self-organization.[13] Two phenyleneethynylene derivatives possessing carboxylic acid groups at the *para* and *meta* positions (**p-acid** and **m-acid**) were synthesized using a Heck–Cassar–Sonagashira–Hagihara cross coupling reaction (ESI†).

STM investigations of **p-acid** and **m-acid** were carried out by drop casting 0.1 mM solution in a 9 : 1 mixture of 1,2,4-trichlorobenzene and THF on to a freshly cleaved HOPG surface, followed by drying in air. A well organized linear wire like arrangement was observed for **p-acid** at various locations with clear domain boundaries (Fig. 1A). High resolution STM current images recorded at two different domains, at a scan size of 6 × 6 nm^2 are presented in Fig. 1B,C. Due to the high electron density, phenyleneethynylene core units are observed as bright rod like structures, with an average length of 1.8 ± 0.1 nm. The alkyl chain regions of phenyleneethynylene derivatives appeared as dark due to the large energy difference between the electronic states of the aliphatic chain and the Fermi level of the substrate.[10] In contrast to the skewed type arrangement observed for unsubstituted phenyleneethynylenes, **p-acid** showed a linear arrangement which arises from two types of basic arrangement of molecules: (i) a parallel strip-like arrangement of phenyleneethynylenes along the '*a*' axis (*a-strip*) and (ii) a linear arrangement of phenyleneethynylenes resulting from an end to end interaction along the '*b*' axis (*b-strip*).

Based on our earlier studies it is well understood that the parallel arrangement of phenyleneethynylenes along the *a-strip* arises through the alkyl CH···acetylenic π interactions (CH···π; CH from the terminal –CH_3 of the hexyloxy moiety) and interdigitation of the hexyloxy chain.[10] The average distance between identical points on the '*a*' axis is 1.3 ± 0.1 nm which suggests that there is enough room for accommodating hexyloxy chains (~0.89 nm in the extended conformation). With respect to the alkyloxy groups, two modes of CH···π interactions are possible: either from the *ortho* or *meta* positions with an angle of orientation of 65 ± 5° and 85 ± 5°, respectively.[10] Images of **p-acid** presented in Fig. 1B and 1C



Scheme 1 Chemical structure of **p-acid** and **m-acid** under investigation.

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† Electronic supplementary information (ESI) available: Details of synthesis, and crystal data for **p-acid**. CCDC 758463. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b927281j

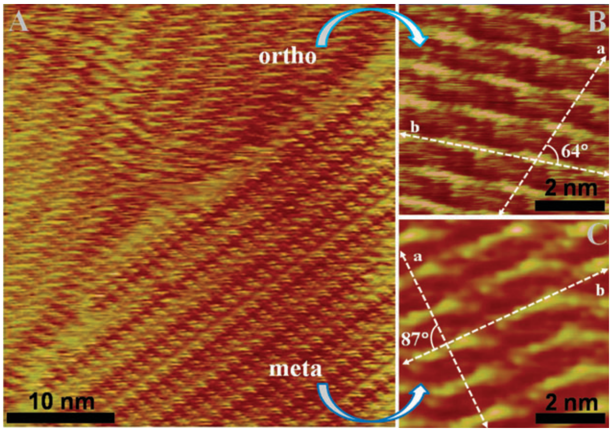
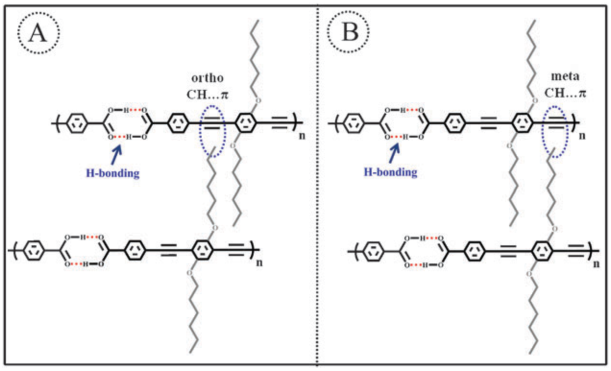


Fig. 1 (A) STM current image of **p-acid** on HOPG showing linear 1D organization with clear domain boundary, scan size 40 × 40 nm^2; $V_{bias} = -500$ mV; $I_t = 653$ pA. High resolution STM current image of (B) *ortho* arrangement: scan size 6 × 6 nm^2; $V_{bias} = -570$ mV; $I_t = 405$ pA. and (C) *meta* arrangement: scan size 6 × 6 nm^2; $V_{bias} = -500$ mV; $I_t = 653$ pA.

show an orientation angle of 64° and 87° along the '*a*' axis indicating that the interactions do occur through the *ortho* and *meta* positions, respectively. The strong intermolecular hydrogen bonding interactions between the carboxylic acids along the '*b*' axis result in the formation of a linear 2D organization of **p-acid** (Scheme 2).

Attempts were made to crystallize **p-acid** from various solvents to obtain a correlation between their organizations on surface and crystal. Single crystals of **p-acid** were obtained from DMSO. The ORTEP structure and packing diagram along a plane are presented in Fig. 2. The shortest intermolecular contact distance $C(1)H\cdots C'(11)$ of 3.23 Å and the intermolecular distance between identical points of 1.3 nm indicate that the $CH\cdots\pi$ interactions assist the strip formation. An earlier report on the crystal structure of unsubstituted phenyleneethynylene (**OPE**) showed that there are two major interactions: (i) $CH\cdots\pi$ interactions and (ii) interdigitation of alkyl chains.[5] In the present case, the *meta* $CH\cdots\pi$ interactions with an orientation angle of 89° assist the strip formation of the **p-acid**. However, we have observed that the DMSO solvent molecules are entrapped during the crystallization of **p-acid** which prevents the intermolecular hydrogen bonding between the carboxylic acid groups. The terminal carboxylic acid groups of **p-acid** are solvated with the DMSO molecules through strong hydrogen bonding between the $O(2)H\cdots O'(4)$ in which the distance between the H and O(4) atoms is 1.77 Å. Interaction between a carboxylic acid group and DMSO was reported earlier for a dehydrobenzo[12]annulene based molecular system.[14] In the present case, DMSO acts like a cap for the **p-acid** at both ends and the **p-acid.2DMSO** assemblies were further interlocked to a skewed arrangement as presented in Fig. 2B. The capped DMSO molecules further act as the glue for the construction of the 3D structure through two weak hydrogen bonding interactions: (i) $C''(19)H\cdots O(3)$ and (ii) $C'''(14)H\cdots O'(4)$. Trapping of the solvent molecules is difficult in a monolayer of **p-acid** on the HOPG surface and the linear arrangement of molecules was observed in an STM image resulting from the dimerization of carboxylic acid groups.



Scheme 2 Schematic representation of the 2D organization of **p-acid** into linear wires through (A) *ortho* and (B) *meta* interaction.

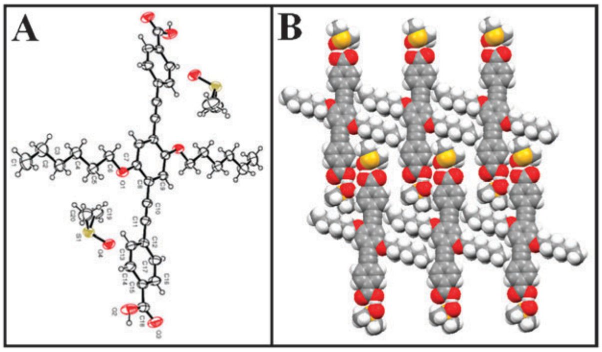


Fig. 2 (A) ORTEP view of the single crystal structure of the **p-acid** obtained from DMSO solvent. (B) Sliced packing diagram of the crystal structure of the **p-acid** along a plane showing a skewed organization due to the capping of DMSO molecules on to the carboxylic acid.

STM imaging of phenyleneethynylene possessing carboxylic acids at the *meta* positions (**m-acid**) was carried out under similar conditions in order to understand the role of the directionality of hydrogen bonding. In contrast to the regular linear arrangement for **p-acid**, a distinctly different organization was observed for **m-acid** over a large area with a rectangular network having periodic cavities (Fig. 3A). High resolution imaging was carried out at lower scan size (13 × 13 nm^2) to understand the molecular arrangement in the network. A periodic rectangular network having cavity dimensions of ~(2.3 × 2.5) nm^2 was observed in the high resolution images (Fig. 3B) which are aesthetically appealing. One of the noticeable points is that the **m-acid** possesses the same functionality as that of **p-acid**, however directionality of the carboxylic acid group played a significant role in their 2D organization. The shortest intermolecular distance between two parallel molecules in the image is 2.3 nm, which rules out the possibility of $CH\cdots\pi$ interactions and alkyl chain interdigitation. In the absence of these interactions, hydrogen bonding directed by the carboxylic acid at the *meta* position is the main driving force. The phenyleneethynylene core appeared as bright rods on the four sides of the rectangle and multiple hydrogen bonding between the terminal carboxylic acid units at the *meta* position holds the molecules as a

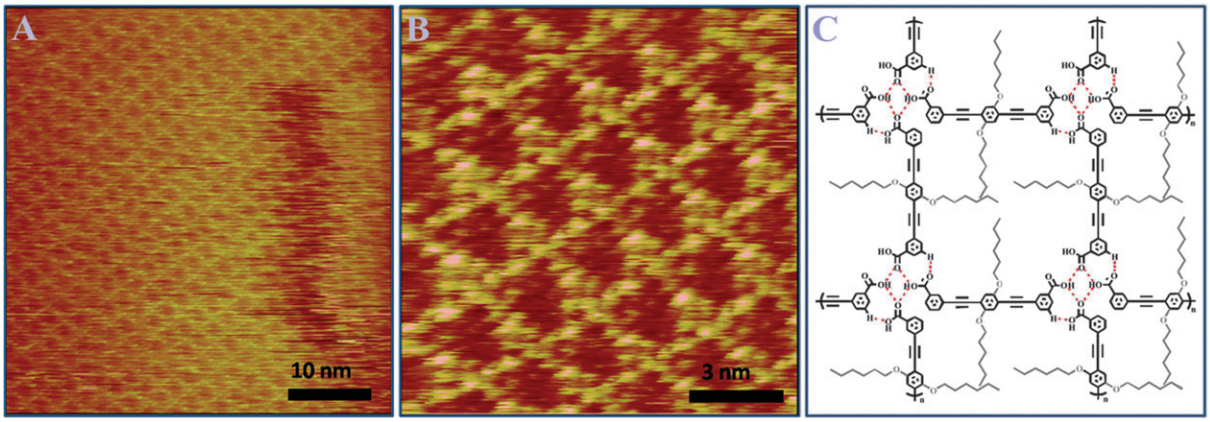


Fig. 3 STM current images of **m-acid** showing rectangular network type organization: (A) scan size: 45 × 45 nm^2; V_{bias} = −663 mV; I_t = 672 pA; (B) scan size: 13 × 13 nm^2; V_{bias} = −730 mV; I_t = 544 pA. (C) Schematic representation of the 2D molecular arrangement for **m-acid** into a rectangular network.

rectangular network having periodic cavities. Multiple hydrogen bonding can occur at the corners of the rectangle in several ways and a possible arrangement is presented in Fig. 3C. It is interesting to note that the alkyl chains do not play a significant role in the organization of **m-acid** as in the case of **OPE** and **p-acid**. The crystal structure of **m-acid** can provide more information on the 3D organizations, however our attempt to crystallize the molecule was not successful. The rectangular porous network on the surface is regular and the cavities having dimensions of ~(2.3 × 2.5) nm^2 are an excellent template for host molecules such as fullerenes.

In summary, we have demonstrated that the position of carboxylic acid plays a crucial role in the self-organization of phenyleneethynylenes on a surface. Two point hydrogen bonding interactions between the carboxylic acid groups lead to a linear wire type arrangement for **p-acids** and a periodic rectangular network having cavity dimensions of ~(2.3 × 2.5) nm^2 for **m-acids**. Multiple hydrogen bonding between the terminal carboxylic acid units at the *meta* position holds phenyleneethynylenes as a rectangular network having periodic cavities. Thus, the organization of the phenyleneethynylene building block is greatly influenced by the position of the functional group and an understanding of the optical and electronic properties of these assemblies is essential for designing next generation molecular devices.

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