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# Role of Hydrogen Bonding on the Self-Organization of Phenyleneethynylenes on Surfaces

Pratap Zalake and K. George Thomas\*

School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram (IISER-TVM), CET Campus, Thiruvananthapuram, 695 016, India

# **Supporting Information**

**ABSTRACT:** A series of carboxylic acid substituted phenyleneethynylenes, having a rigid backbone of  $2.7 \pm 0.1$  nm, were synthesized by following the Heck-Cassar-Sonagashira-Hagihara cross-coupling reaction. Hydrogen bonding, through the formation of cyclic dimers of carboxylic acid, is more preferred over catemeric structures in all the molecular systems under investigation. The formation of extended two-dimensional patterns on highly oriented pyrolitic graphite (HOPG) surface is dictated by the position as well as number of the carboxylic acid groups on the phenyleneethynylenes. Highly ordered extended arrangements, in the linear and stepwise fashion, were observed when the carboxylic acid groups are attached in



the para and meta positions of phenyleneethynylenes. The vital role of the number of carboxylic acid on the organization of molecules is evident in the case of tetracarboxylic acid derivative wherein a Kagome-type structure was observed. Further, the coassembly of two types of phenyleneethynylenes was achieved on HOPG surface through acid base interaction.

# 1. INTRODUCTION

Among various noncovalent interactions, hydrogen bonding remains a topic of great interest due to its continuing relevance in chemical and biological research.<sup>1</sup> Carboxylic acid derivatives, in principle, can form two types of hydrogen bonding interactions: cyclic dimers and open catemers. Cyclic dimer formed through the interaction of equivalent hydrogen bonds of two carboxylic acid groups are of particular interest, since they are relatively strong and directional.<sup>1,2</sup> For example, the enthalpy of association  $(\Delta H)$  of twofold O—H···O=C bond in cyclic dimers of benzoic acids is estimated as  $-88.7 \text{ kJmol}^{-1.3}$ In contrast, the typical energies of van der Waals interactions are 10- to 15-fold lower than hydrogen bond interactions in cyclic dimers.<sup>1-4</sup> Often, van der Waals interactions collectively compete with hydrogen bond interactions; however, the former one cannot provide any directionality.<sup>4</sup> The obvious advantage of the directionality of hydrogen bonds has been utilized for the design and effective control of various supramolecular structures having functional properties.<sup>5,6</sup> The hydrogen bond interactions of carboxylic acids have also been utilized to create host network, having cavities, which can accommodate guest molecules such as coronene<sup>7–9</sup> and  $C_{60}$ .<sup>10</sup> It has been also demonstrated that molecules bearing carboxylic acids can interact with proton accepting groups to form self-assembled structures on surfaces.  $^{11-13}$ 

One of the factors that dictate the efficiency of optoelectronic devices is the way in which photo- as well as electroactive molecules are organized on surfaces.<sup>14,15</sup> An understanding on the organization of molecules on surfaces, with atomic resolution, is essential for designing various devices, and scanning tunneling microscopy is an excellent tool for probing these aspects.<sup>6,16–22</sup> The organization of such molecules on surfaces can be effectively modulated through hydrogen bond interactions of cyclic dimers of carboxylic acids. Investigations on the self-assembled monolayers of various molecular systems bearing carboxylic acid groups include (i) mono-, di-, and trisubstituted benzoic acids and alkoxy-substituted benzoic acids;<sup>23–26</sup> (ii) larger ones such as porphyrins;<sup>27</sup> and (iii) rigid molecular systems such as oligothiophenes<sup>28–30</sup> and phenylene ethynylenenes.<sup>31–35</sup>

Phenyleneethynylene-based rigid rod molecular systems do not involve any possibility of isomerization and maintains  $\pi$ electron conjugation at any degree of rotation.<sup>36–38</sup> This unique property has been utilized to understand the organization of molecules on the surface by our group<sup>35,39,40</sup> and others.<sup>31–34,41–46</sup> We have previously demonstrated that phenyleneethynylenes, even in the absence of any functional group, can self-organize into wire-like structures in a skewed 1D fashion on highly oriented pyrolytic graphite (HOPG) surface, and various modes of alkyl CH– $\pi$  interaction drive the organization.<sup>39</sup> This organization can be further modulated by introducing hydroxyl as well as aldehyde groups at the terminal positions of phenyleneethynylenes.<sup>40</sup> More interestingly, the position of carboxylic acids on phenyleneethynylenes has a

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Scheme 1



(i) CuCl, diazabicyclo[5.4.0]undec-7-ene; *N*,*N*,*N'*,*N'*-tetramethylethylenediamine; (ii) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, PPh<sub>3</sub>, disopropyl amine; (iii) KOH, MeOH.

significant influence on their self-organization: from linear assembly to rectangular network having periodic cavities<sup>35</sup> and Kagome network.<sup>34</sup> These studies clearly indicate that the directionality of carboxylic acid moiety and the rigid rod structure of phenyleneethynylenes makes this class of molecules an ideal candidate for designing programmable monolayers. Herein, we report the role of hydrogen bonding of carboxylic acid groups on the organization of phenyleneethynylenes by systematically varying the position and number of the

carboxylic groups. Further, we report the preliminary results on the coassembly of two molecules of phenyleneethynylenes, one bearing carboxylic acids at the terminal position and the other one bearing proton accepting groups.

# 2. RESULTS AND DISCUSSION

We have previously investigated the self-organization of phenyleneethynylenes having three phenyl groups linked together by acetylenic bridging units as rigid aromatic backbone having a dimension of  $1.8 \pm 0.1$  nm (for example, compound 6 in Chart 1 and its derivatives).<sup>35,39,40</sup> The rigid aromatic backbone of these molecular systems can be easily distinguished in STM as bright rod-like structures due to high tunneling current. In contrast, the alkyl chain of phenyleneethynylene derivatives appeared as dark regions due to the large energy difference between the electronic states of the aliphatic chain and the Fermi level of the substrate. Various patterns can be viewed with more clarity if the length of aromatic rigid backbone is longer. With this objective, we have further increased the length of the rigid backbone to  $2.7 \pm 0.1$  nm by introducing additional phenyl group and acetylenic bridging units (1-5; Chart 1).

Synthesis of 1-5 was carried out by following the Heck-Cassar-Sonagashira-Hagihara cross-coupling reaction, using Pd(II) as catalyst,<sup>36,47,48</sup> as shown in Scheme 1. The intermediate compound 8 was prepared through the dimerization of acetylene by following Glaser reaction, catalyzed by CuCl.49 Further, on reacting 8 with 2 equiv of respective phenylacetylene derivative, using Pd(II) as catalyst, yielded 1 and 9a-c. The reaction of 8 with 1 equiv of methyl-4ethynylbenzoate give the compound 10, which on further reaction with 1 equiv of methyl-3-ethynyl-benzoate yielded product 11. The compound 1 and the precursor of carboxylic acid derivatives (9a-c, and 11) were purified using recycling HPLC to maintain high purity of the final products. The purified products (9a-c and 11) were hydrolyzed using KOH to yield the corresponding acid derivatives (2-5). The final products were further characterized through analytical and spectroscopic techniques and the details are presented as Supporting Information.

To obtain good STM images, uniform organization of molecules on HOPG surface is necessary and various attempts have been made in this direction. Samples for STM investigations were prepared by dissolving the respective molecules in a mixture (1:9) of THF and 1,2,4-trichlorobenzene, and the final concentration of the solution is maintained at ~5  $\mu$ M in all the cases. Attempts to drop-cast the solution on HOPG surface and drying the solvent by slow evaporation were not successful. This may be due to the precipitation of the compound while drying. In the present study, the imaging was carried out at the liquid-solid interface immediately after dropcasting the solution on the HOPG surface. Images were acquired in the constant-height mode, under ambient conditions, using a multimode scanning probe microscope. Electrochemically etched Pt/Ir wire (80:20) was used as the STM tip. The molecules were physically adsorbed on HOPG surface, and their stability was confirmed by recording the STM images after a few days. The HOPG surfaces having the selfassembled molecules were dried and wetted using a mixture (1:9) of THF and 1,2,4-trichlorobenzene before imaging. STM images are reproducible, indicating that the molecular systems are stable on HOPG surface at normal atmospheric condition.

STM images of model compound 1, which does not possess any functional groups, are presented as Figure 1B,C. Large area scan showed the presence of well-organized arrangements of molecules at various locations with clear domain boundaries (Figure 1B). Organization of 1 on HOPG showed a skewed 1D wire-like structure similar to that of compound 6. The unit cell parameters were estimated as  $a = 1.2 \pm 0.1$  nm,  $b = 2.5 \pm 0.1$ nm, and  $\alpha = 85 \pm 5^{\circ}$ .

The main objective of the present investigation is to understand the role of hydrogen bonding of carboxylic acid



**Figure 1.** (A) Molecular structure of **1**. (B) STM image of **1** on HOPG showing skew one-dimensional arrangement: scan size  $50 \times 50$  nm<sup>2</sup>;  $V_{\text{bias}} = -852$  mV;  $I_t = 200$  pA; and (C) corresponding high-resolution image: scan size  $8 \times 8$  nm<sup>2</sup>;  $V_{\text{bias}} = -1354$  mV;  $I_t = 80$  pA. (D) Schematic representation of the organization of **1** on surface.

groups on the organization of phenyleneethynylenes by varying the (i) position and (ii) number of the carboxylic groups. Position-dependent organization was investigated by introducing carboxylic acid at the terminal phenyl rings of phenyleneethynylenes which include para-disubstituted carboxylic acid derivative (2), meta-disubstituted carboxylic acid derivative (3), and one having carboxylic acid groups at the para and meta positions (4). In the case of 2, intermolecular hydrogen bonding of the carboxylic groups at the para positions leads to the formation of well-ordered linear arrangement whereas stepwise arrangement was observed for 3 having carboxylic acids in the meta positions (Figure 2).

Schematic representation of the various interactions in compounds 2 and 3 leading to the formation of linear and stepwise organization are presented in Figure 3. Both molecules possess four hexyloxy groups which can undergo interaction with the acetylenic  $\pi$ -bond of the adjacent molecules, leading to the formation of molecular strips (xy and x'y' in Figure 2C,F). A close analysis of STM images further showed that the adjacent molecules in a strip possess a constant spacing of 1.3  $\pm$ 0.1 nm. These results clearly indicate that the interdigitation of hexyloxy groups which undergo  $CH-\pi$  interaction with adjacent molecules results in the formation of molecular strips. Similar molecular packing was observed earlier by our group for molecule 6 and related compounds having three phenyl group and two acetylenic bridging units.<sup>35,39,40</sup> In these systems, the alkoxy chain of the adjacent molecules interacts with the acetylenic moiety, from either the ortho or meta position, leading to two types of arrangements with an angle of orientation of  $65 \pm 5^{\circ}$  and  $85 \pm 5^{\circ}$ , respectively. However, only one type of arrangement was observed in the present case, having an angle >85  $\pm$  5°, favoring meta interaction. The angle of orientation ( $\alpha$ ) of phenyleneethynylene core for compounds 1–3 was estimated from the high-resolution STM images as 85  $\pm$  5° (1), 99  $\pm$  5° (2), and 103  $\pm$  5° (3).



**Figure 2.** (A,D) Molecular structure of **2** and **3**, respectively. (B) STM image of **2** showing linear arrangement: scan size  $20 \times 20 \text{ nm}^2$ ;  $V_{\text{bias}} = -1732 \text{ mV}$ ;  $I_t = 60 \text{ pA}$ ; and (C) corresponding high-resolution image: scan size  $10 \times 10 \text{ nm}^2$ ;  $V_{\text{bias}} = -1925 \text{ mV}$ ;  $I_t = 58 \text{ pA}$ . (E) STM image of **3** showing stepwise arrangement: scan size  $50 \times 50 \text{ nm}^2$ ;  $V_{\text{bias}} = -753 \text{ mV}$ ;  $I_t = 610 \text{ pA}$ ; and (F) corresponding high resolution image scan size:  $10 \times 10 \text{ nm}^2$ ;  $V_{\text{bias}} = -841 \text{ mV}$ ;  $I_t = 100 \text{ pA}$ .



**Figure 3.** Schematic representation of parallel stacks (PS) of **2** and **3** formed through CH $-\pi$  interaction and extended organization (EO) through hydrogen bonding (note: the phenyl ring of the phenyleneethynylenes can freely rotate along the alkyne-aryl single bonds leading to the formation of two types of rotamers on surface having carboxylic acids located in the opposite side **PS-b** or in the same side **PS-c**).

It is also clear from the STM images that the formation of the extended organization (EO) is dictated by the functional groups present on the terminal phenyl rings in the case of 2-4. In the absence of any functional group, the parallel stacks of phenyleneethynylenes interlock through aromatic CH-aromatic  $\pi$ -interaction leading to the formation of a skewed 1D arrangement. However, the presence of carboxylic acid groups at the terminal positions has a significant influence in

modulating their organization. For example, 2 having both carboxylic groups at the para positions form intermolecular hydrogen bonding in an end-to-end fashion leading to the formation of parallel stacks (PS-a; Figure 3). Interestingly, an extended 2D organization, in a stepwise fashion (Figure 2F), was observed in the case of 3 wherein both carboxylic groups are at the meta positions. The phenyl group can freely rotate, along the alkyne-aryl single bonds leading to the formation of two types of rotamers on surface having carboxylic acids located in the opposite side PS-b or in the same side PS-c. Thus, the alkyl CH–acetylenic  $\pi$ -interaction can lead to the formation of two types of molecular strips as shown in Figure 3 (PS-b and PS-c). These molecular strips can further interlock through intermolecular hydrogen bonding of carboxylic acids leading to the formation of extended organization (EO-b and EO-c). However, it is difficult to distinguish the way in which phenyleneethynylenes undergo hydrogen bonding in 3 using STM. A recent report on the crystal structure of biphenyl-3,3'dicaboxylic acid showed the formation of zigzag arrangements wherein one-dimensional chains of molecules are formed through intermolecular hydrogen bonding. In this case, it was found that the carboxylic acid groups are located in the opposite sides.<sup>50</sup> In the present case, a similar arrangement having carboxylic acid on the opposite sides (EO-b) may be more preferred. The unit cell parameters were further calculated from STM images: for 2,  $a = 1.3 \pm 0.1$  nm; b = $3.2 \pm 0.1$  nm;  $\alpha = 99 \pm 5^{\circ}$ ; and for 3,  $a = 1.2 \pm 0.1$  nm;  $b = 3 \pm 0.1$ 0.1 nm;  $\alpha = 103 \pm 5^{\circ}$ .

Various possibilities of hydrogen bonding exist in the case of phenyleneethynylene **4** having carboxylic acid groups at the para and meta positions. For example, it can be seen from the STM images that the carboxylic groups at the para position underwent intermolecular hydrogen bonding leading to the formation of linear assembly, while the carboxylic acid groups at the meta positions result in a stepwise organization. Irregularity in the STM image of **4** arises from the existence of various modes of hydrogen bonding (Figure 4). Thus, the positions of carboxylic acid groups play a significant role in the organization phenyleneethynylenes on surfaces.

The organization of phenyleneethynylenes on surfaces was further investigated systematically by increasing the number of carboxylic acid groups. Compound 3, which possesses two



**Figure 4.** (A) Molecular structure of 4. (B) STM image of 4: scan size  $50 \times 50 \text{ nm}^2$ ;  $V_{\text{bias}} = -500 \text{ mV}$ ;  $I_t = 653 \text{ pA}$  and (C) corresponding high-resolution image: scan size  $10 \times 10 \text{ nm}^2$ ;  $V_{\text{bias}} = -1653 \text{ mV}$ ;  $I_t = 150 \text{ pA}$ .

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carboxylic groups in the meta positions of phenyleneethynylene, forms beautiful a stepwise arrangement on the surface (Figure 2F). It is interesting to investigate the organization of phenyleneethynylenes by attaching two more carboxylic acid groups at the meta positions. With this objective, a phenyleneethynylene derivative 5 which possess four carboxylic acid groups at the meta positions was synthesized. Surprisingly, STM images showed network-like organization (Figure 5B,C),



**Figure 5.** (A) Molecular structure of **5.** (B) STM image of **5** showing Kagome arrangement: scan size  $30 \times 30 \text{ nm}^2$ ;  $V_{\text{bias}} = -850 \text{ mV}$ ;  $I_t = 50 \text{ pA}$ ; and (C) corresponding high-resolution image: scan size  $12 \times 12 \text{ nm}^2$ ;  $V_{\text{bias}} = -1400 \text{ mV}$ ;  $I_t = 140 \text{ pA}$ . (D) Schematic representation of the organization of **5** on surface.

with a regular pattern on the surface. The unit cell parameters were estimated from STM images for 5:  $a = b = 4.2 \pm 0.1$  nm and  $\alpha = 64 \pm 5^{\circ}$ . Close analysis of the image (Figure 5C) showed that six phenyleneethynylene molecules interact through intermolecular hydrogen bonding leading to Kagome-type structure. Schematic representation of the hydrogen bonding interactions in compound 5 leading to the formation of Kagome-type structure is presented in Figure 5D. Thus, compound 3 which possess two carboxylic acids at the meta positions forms a stepwise arrangement, which transforms to a Kagome-type structure by incorporating two additional carboxylic acid groups in the meta positions. These results clearly indicate that, in the absence any functional groups, CH $-\pi$  interaction is the main driving force for the organization of phenyleneethynylenes. However, as the number of carboxylic group increases, intermolecular hydrogen bonding between carboxylic acids dominates, leading to the formation of various types of organization.

Further, we have investigated the coassembly between two phenyleneethynylene molecules: para-disubstituted carboxylic acid derivative **2** and a phenyleneethynylene having pyridine groups at the terminal position 7.<sup>51</sup> Equimolar concentrations (5  $\mu$ M) of **2** and 7 were dissolved in a mixture (1:9) of THF and 1,2,4-trichlorobenzene. The solution was drop-cast onto HOPG and the STM investigations were carried out at the liquid–solid interface. The images of the coassembly are presented in Figure 6C,D. A linear assembly of molecules with alternate regions of low and high tunneling currents was



**Figure 6.** (A,B) Molecular structures of 2 and 7, respectively. (C) STM image showing coassembly of 2 and 7: scan size  $20 \times 20$  nm<sup>2</sup>;  $V_{\text{bias}} = -900$  mV;  $I_t = 150$  pA and (D) corresponding high-resolution image: scan size  $15 \times 15$  nm<sup>2</sup>;  $V_{\text{bias}} = -800$  mV;  $I_t = 170$  pA. (E) Schematic representation of the formation coassembly on surface.

observed throughout. The difference in tunneling current leads to regions of varying contrast having dimensions of 1.8  $\pm$  0.1 nm and 2.7  $\pm$  0.1 nm. The dimensions of these strips match well with the molecular lengths of 2 (2.7  $\pm$  0.1 nm) and 7 (1.8  $\pm$  0.1 nm). Compound 2 has an extended aromatic backbone compared to 7 and possesses higher tunneling current, resulting in regions of higher contrast. The lone pair of electrons on the nitrogen atom of the pyridine moieties in compound 7 can undergo strong interaction with the carboxylic acid group at the terminal positions of 2 through intermolecular N····H-O-C(O)-type hydrogen bonds leading to the formation of coassembled linear structures.<sup>52–54</sup> From the STM image, it is clear that two coassembled linear structures maintain a constant distance of 1.3  $\pm$  0.1 nm throughout, further indicating the role of CH $-\pi$  acetylene interaction in forming 2D assembly.

On the basis of the present investigations and earlier reports,  $^{35,39,40}$  some important generalizations can be made on the self-organization of rigid rod molecular systems such as phenyleneethynylenes. Schematic representation of the role of hydrogen bonding in the organization of compounds 2, 3 and 5 is illustrated in Figure 7. As mentioned earlier, carboxylic groups can, in principle, form cyclic dimeric as well as extended structures (catamers).<sup>1,2</sup> However cyclic dimeric arrangement of carboxylic acids, formed through twofold O—H…O==C bonding, is favored due to their higher enthalpy of association compared to that of catamers.<sup>3</sup> In the case of monosubstituted carboxylic acid derivatives, independent of whether the substitution is at the para or meta position of phenyl ring,

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Figure 7. Schematic representation of basic hydrogen bonding interactions leading to various types of self-organization of molecules on HOPG surface as shown in Figures 2, 3 and 5: (a) 2 forming linear assembly, (b) 3 forming stepwise arrangement, (c) 5 forming hexagonal pattern and Kagome-type arrangement, and (d) coassembly of 2 and 7.

dimerization of molecules is preferred. These structures can be further extended into periodic patterns by proper substitution at the other end of the molecule. For example, well-organized linear and stepwise arrangements over a large area were observed for 2 and 3, respectively (Figure 2). Earlier, we demonstrated that the self-organization of a meta-substituted phenyleneethynylene derivative having short rigid aromatic backbone (1.8  $\pm$  0.1 nm) yielded a rectangular network through multiple hydrogen bonding. Stepwise arrangement was observed in the case of 3 on increasing the length of the rigid backbone to 2.7  $\pm$  0.1 nm, further indicating the role of the phenyleneethynylene core on the self-organization. In contrast, compound 5 having four carboxylic acid groups results in the formation of highly stable hexagonal arrangement through twofold O—H…O=C bonds.

# 3. CONCLUSION

Engineering of two-dimensional supramolecular structures on surfaces was achieved by the design of molecular systems having two important structural motifs: (i) phenyleneethynylene core providing rigidity and (ii) carboxylic acid moiety providing directionality. In the present case, two types of noncovalent forces, namely,  $CH-\pi$  and hydrogen bonding interactions are mainly operative. In the absence of functional groups, collective CH $-\pi$  interactions drive the self-organization of phenyleneethynylene. However, incorporation of carboxylic acid moieties significantly influences their organization from linear assembly to stepwise arrangement by varying the position of carboxylic acid group. As the number of carboxylic groups increases, intermolecular hydrogen bonding between the phenyleneethynylenes becomes more dominant and stable Kagome-type structures were observed. Strong enthalpy of association of twofold O-H···O=C bond in cyclic dimers, compared to that of open catemers, may be responsible for the formation of periodic patterns. Coassembly of donor-acceptor molecules, in an ordered fashion, was achieved on surface, and such systems can show interesting charge transfer properties. Investigations of the optical and electrical properties of these well-organized molecular assemblies on surfaces are in progress. These studies may pave the way toward the design of nextgeneration optoelectronic devices with tunable functional properties.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Details on the synthesis and characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: kgt@iisertvm.ac.in.

## **Present Address**

School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram (IISER-TVM), CET Campus, Thiruvananthapuram, 695 016, India.

#### Notes

The authors declare no competing financial interest.

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