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In-plane Van der Waals interactions of molecular self-assembly monolayer

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We demonstrate that the Van der Waals interactions in plane are important to control molecular self-assembly structure as well their phase transition. Using precise chemical modification to mediate such in-plane cohesive interactions, we observed the spontaneous formations of 2D order or disorder molecular self-assembly structures, as well their order-disorder phase transitions by annealing. Interestingly, we identified that the side alkyl chains stand up at surfaces and form the ‘locked’ pairs/windmill structures. Moreover, we realized the covalent coupling based on ethynyl functionality before molecular desorption from metal surfaces, by enhancing the in-plane interactions. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4907777>]

It is well known that adsorption of organic molecules at surfaces will spontaneously form self-assembled structures.^{1–3} Considering the Van der Waals interactions to confine such structure, a balanced molecule-substrate interaction is required.² Meanwhile, the Van der Waals interaction in-plane, especially the attractive force, is expected as the stronger—the better for potential applications. Along this line, it should be possible to add some specific functionality to molecules, enhancing the Van der Waals in-plane interactions. Indeed, the hydrogen bonding functionalities^{4–6} were successfully applied to control molecular self-assembly nanostructures, as well their physical and chemical properties such as the thermal desorption^{7,8} and coordinated bonding.⁹ On the other side, it is also possible to realize the above self-assembly control via varying the substrates, which determines different molecule-substrate interactions.^{8,10,11}

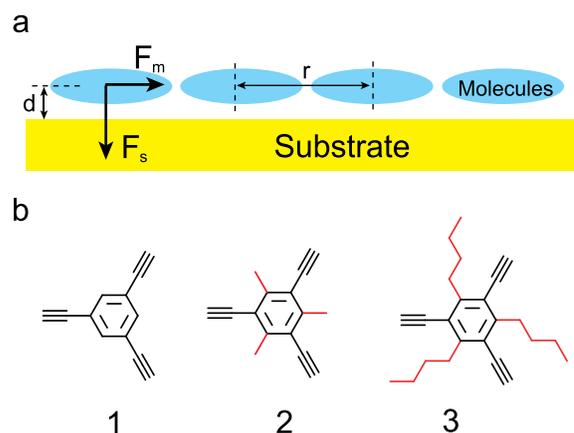
Based on these results, we proposed here a simple model that the long-range interactions to confine self-assembly structure at surfaces can be assigned into two components: F_s , the molecule-substrate adsorption force and F_m , the molecule-molecule attraction interaction (Scheme 1(a)). Here, the molecule-to-molecule distance r and molecule-to-substrate distance d depend on the size of molecule, as well the strength of forces F_s and F_m . By adding the specific chemical groups to enhance the molecule-molecule in-plane interactions, the molecular self-assembly structure, as well their properties (for example phase transition), will be influenced.

In this paper, we employed the flexible alkyl chains for the obtaining enhanced in-plane molecule-molecule adhesion forces F_m .^{12–14} We investigated the roles of alkyl chains in

molecular self-assembly structures, for molecules from **1** (1,3,5-triethynylbenzene) to **2** (1,3,5-triethynyl-2,4,6-trimethylbenzene) and further to **3** (1,3,5-tributyl-2,4,6-triethynylbenzene) (Scheme 1(b)).

Experiments were performed with a UHV LT-STM (Omicron) at a base pressure of 1×10^{-10} millibar, which was operated at 78 K. The bias is the sample voltage with respect to the STM tip. Atomically clean metal surfaces (Au(111) and Ag(111)) were obtained by several ion-sputtering and annealing cycles. Molecules (**1**, **2**, and **3**) were deposited onto the metal surfaces by free diffusion using a custom-designed funnel in an isolated chamber. An IR thermometer was applied to monitor the sample annealing process (30 min).

Molecule **1** was deposited onto an Au(111) surface. Clockwise- and anti-clockwise SAM structures were observed (Figure 1(a)), which agrees with previous works.^{15,16} We found that the Ag(111) shows a weaker substrate-molecule



SCHEME 1. (a) A simple model for molecule-substrate and molecule-molecule interactions to confine self-assembly structure. (b) Molecular structures for investigation.

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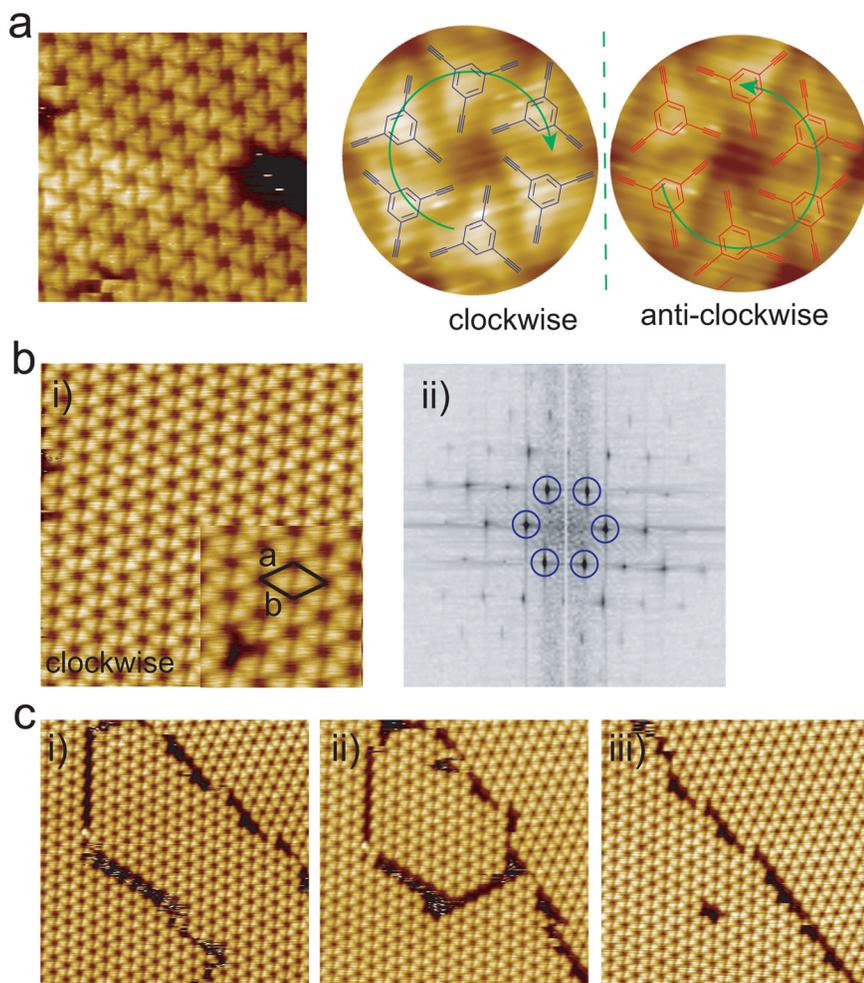


FIG. 1. (a) STM images of molecule **1** on Au(111) surface (1 V, 200 pA, 10×10 nm) as well its stacking in clockwise (blue) and anti-clockwise (red). (b) STM images (i), 1 V, 10 pA, 17×17 nm with an inset 6×6 nm) of molecule **1** in clockwise assembly on Ag(111) with its geometrical FFT image (ii), 7.0×7.0 nm $^{-1}$). (c) The diffusion of molecule **1** at Ag(111) surface proved by the continuous images on the same area (i) beginning, (ii) middle, and (iii) final (1 V, 10 pA, 25×25 nm).

interaction (F_s) to molecules than the Au(111) surface, the latter exhibiting a herringbone $22 \times \sqrt{3}$ reconstruction. The clockwise structure on Ag(111) can be treated as a 2D crystal with a hexagonal Bravais lattice (Figures 1(bi) and 1(bii)). The periodicity parameters were measured as: $\mathbf{a} = 1.30 \pm 0.02$ nm; $\mathbf{b} = 1.30 \pm 0.02$ nm; angle $\mathbf{a}, \mathbf{b} = 60 \pm 0.5^\circ$. Interestingly, we found that molecule **1** could diffuse freely to leave and join the self-assembly structure, which indicates the weak Van der Waals in-plane interactions between ethynyl groups (Figure 3(c)).¹⁶

Next we tested 1,3,5-triethynyl-2,4,6-trimethylbenzene (molecule **2**), which should have a stronger in-plane Van der Waals interaction, because of the stronger interactions between methyl and ethynyl groups (methyl cannot reach methyl due to steric reason). Indeed, we identified that molecule **2** formed a closely stacking self-assembly structure as a result of stronger in-plane forces (Figure 2(ai)). Surprisingly, we found molecule **2** has two local orientations in the self-assembly structure (as indicated by the black and red chemical structures in Figure 2(aii)). In spite of the small triangular orientational-domains at some area, it belongs to a 2D orientation disordered structure (Figures 2(aii) and 2(aiii)). It is very interesting that if we ignore the orientation disorder (marked by the blue hexagon), the structure can be treated as an ordered crystal with a hexagon FFT pattern as marked by red circles.

It is well known that varying the temperature could trigger a self-assembly phase transition.^{17–20} This may include also an orientation phase transition. To verify this point, annealing of the sample was applied. Figures 2(bi) and 2(bii), the STM image and its FFT pattern (the rhombic Bravais lattice), clearly show that molecule **2** eventually forms a self-assembly structure with their orientations kept in long range order. Molecular stacking model was illustrated with a periodic parameters: $\mathbf{a} = 5.05 \pm 0.05$ nm; $\mathbf{b} = 5.36 \pm 0.05$ nm, angle $\mathbf{a}, \mathbf{b} = 56.8 \pm 0.5$. The difference between lattice vectors \mathbf{a} and \mathbf{b} is deduced to molecular orientation difference along \mathbf{a} and \mathbf{b} axes in Figure 2(biii). Moreover, the desorption temperature of molecule **2** was found higher than molecule **1** (roughly, 120°C VS 90°C).

Encouraged by the obtained results, we finally investigated the self-assembly of molecule **3**. Because of the interactions between alkyl chains (alkyl chains are long enough to reach each other for the adhesion interactions), the in-plane Van der Waals interactions for this molecule were expected to be strongest. We first tested the Au(111) substrate and found the disordered self-assembly structure, because the molecule-substrate interaction F_s is rather strong (Figure 3(a)). To our surprise, we found that the alkyl chains stood up normal to the surface (illustrated as Figure 3(aiii)) and part of them formed the ‘locked’ pairs (marked by the black circles). Here, an interesting aspect is that we obtained

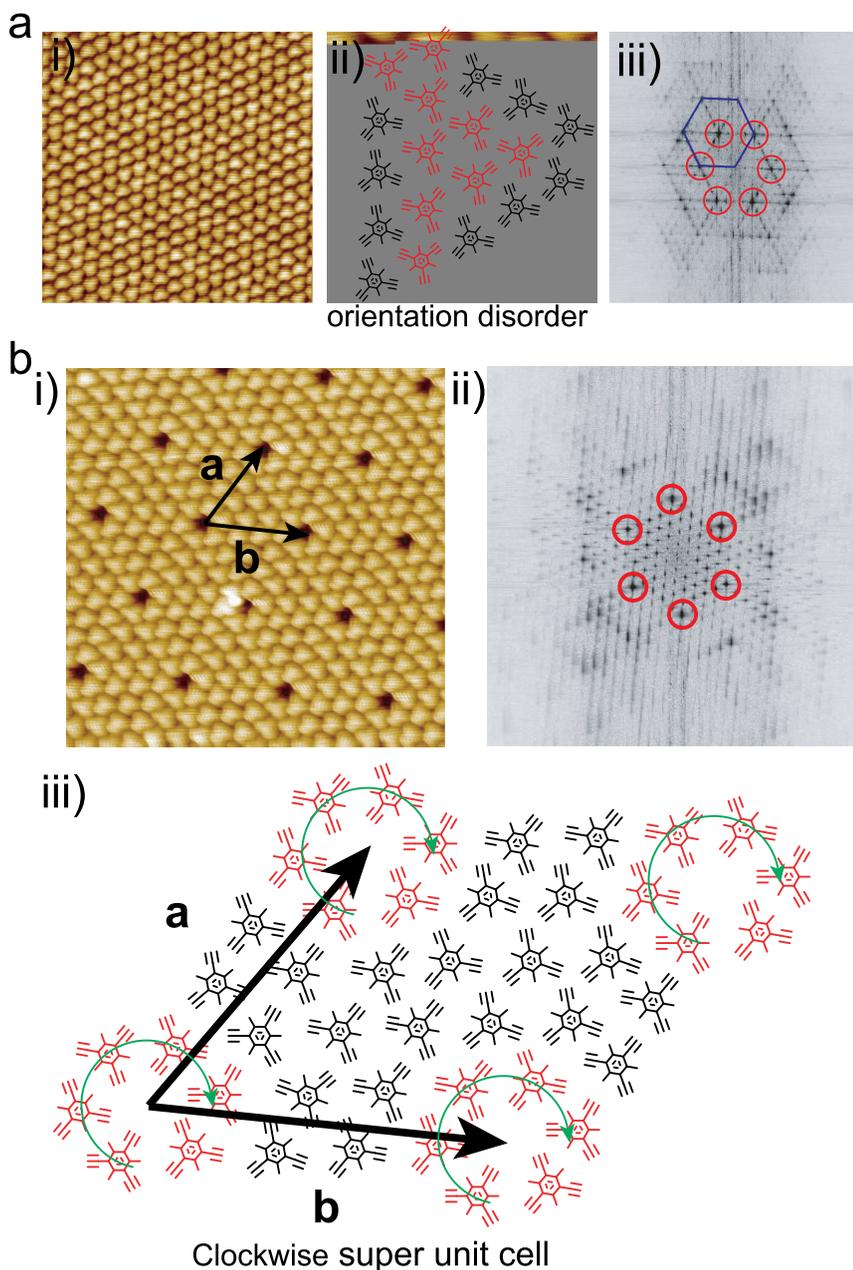


FIG. 2. (a) STM image (i), 17×17 nm, and high resolution image (ii), 5×5 nm, of the 2D orientation disordered phase formed by molecule **2** on Ag(111) with its geometrical FFT image (iii), $8.0 \times 8.0 \text{ nm}^{-1}$. (b) High resolution STM image (i), 20×20 nm, as well its FFT image (ii), $8.0 \times 8.0 \text{ nm}^{-1}$ and crystal stacking model (iii), of molecule **2** 2D crystal phase on Ag(111) surface, after annealing to 125°C . All STM images were acquired at -1 V, 100 pA.

different molecular images at different tunneling distances. When the tunneling distance is close, the STM image dominantly shows a molecular “bottom template,” containing one benzene ring, three carbon-triple bond arms, and three bottom carbons (C1) of alkyl groups (Figure 3(ai)). However, when it is far, STM image provide the standing carbons of alkyl groups (Figure 3(aii)).

Then, we used Ag(111) substrate for the proper substrate-molecule interaction (Because Ag(111) has no surface reconstruction, which is easier for molecule to diffuse and form the self-assembly structure). Indeed, we found an ordered self-assembly structure with periodic parameters: $\mathbf{a} = 3.20 \pm 0.02$ nm; $\mathbf{b} = 3.20 \pm 0.02$ nm; angle $\mathbf{a}, \mathbf{b} = 120 \pm 0.5^\circ$ (as shown in Figure 3(b)). Similar with it on gold surface, when the tip is far, only alkyl groups (standing carbons) are visible and they form the windmill-like structure (by the ‘locked’ alkyl pairs) with clockwise/

anti-clockwise property. The corresponding FFT pattern shows a hexagon symmetric of alkyl groups. Very interesting, if the distance is far further, STM image could provide the top-C4 movements of alkyl groups.²¹ The molecule in the center of each windmill looks unstable, as displayed by the stripes within in the STM image. Going closer to the molecule with the STM probe, the STM image provides more information of alkyl bottom carbons (C2/C3), and looks like balls attached to a benzene ring (Figure 3(bii)). Going even closer with the STM tip, the benzene ring with three carbon-triple bond arms and three bottom carbons (C1) show up in the images (Figure 3(biii)). The FFT patterns of Figures 3(bii) and 3(biii) show more information about the Bravais lattices of molecular “bottom templates.”

Here, the “locked” alkyl pairs definitely enhanced the adhesion forces (in-plane Van der Waals interaction) among molecule **3**, which will induce molecular thermal phase

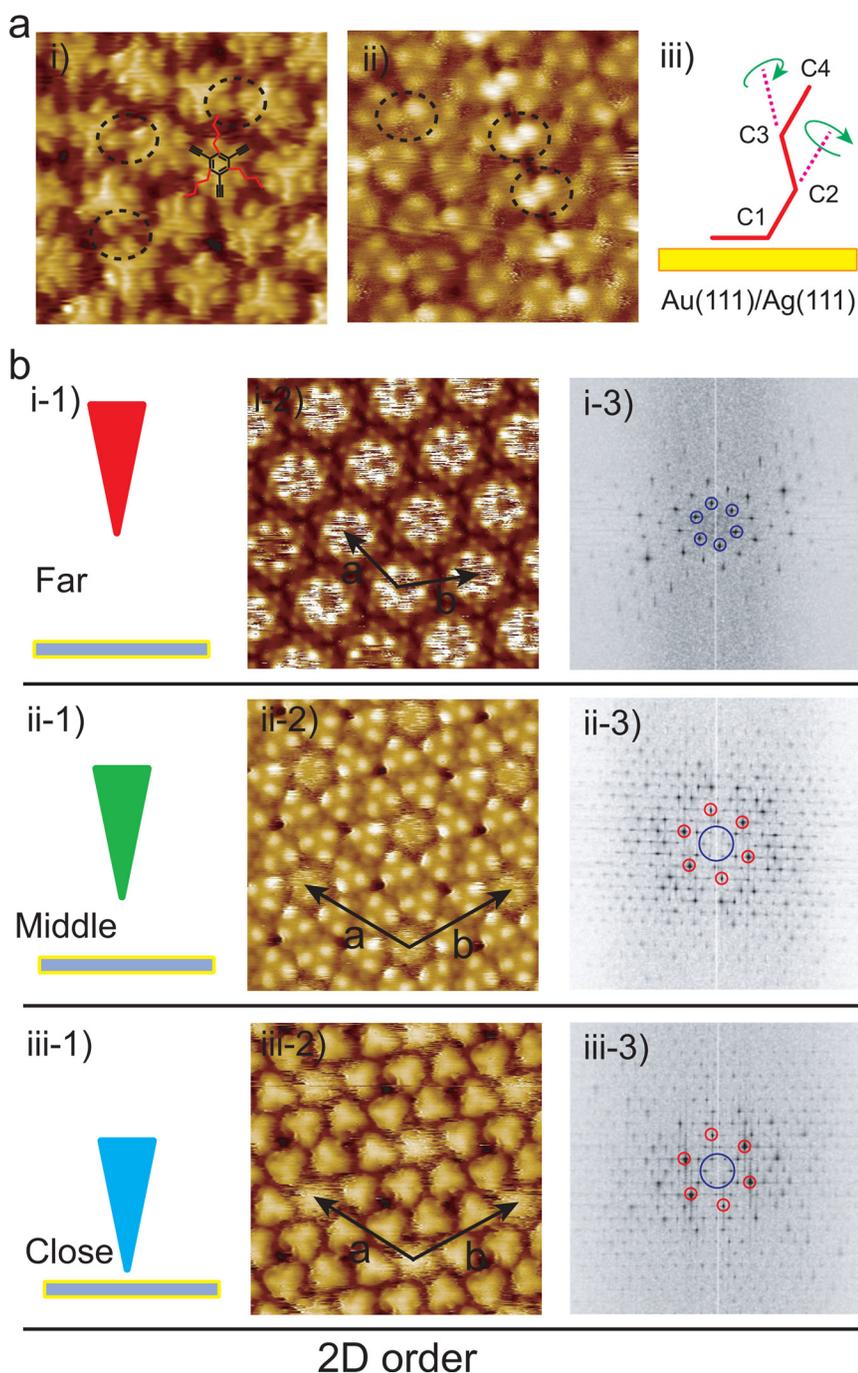


FIG. 3. (a) STM high resolution images of molecule **3** at different tunneling distances ((i), 1 V, 50 pA, 5×5 nm and (ii), 2 V, 50 pA, 6×6 nm), with an illustration of the standing C4 chain on Au(111) surface. (b) High resolution STM images of molecule **3** on Ag(111) surface at different tunneling distances ((i), far, 2 V, 10 pA, 12×12 nm; (ii), middle, 2 V, 50 pA, 8×8 nm; (iii), close, 1 V, 50 pA, 8×8 nm), as well their corresponding FFT images ((i-3), 5×5 nm⁻¹), ((ii-3), 8×8 nm⁻¹) and ((iii-3), 8×8 nm⁻¹) show their hexagonal Bravais lattice in symmetry.

transition acts differently. For the annealing up to 125 °C, a lot of the windmills of ‘locked’ alkyls were converted to be disordered ‘locked’ pairs (Figure 4(ai)); as a result, its FFT image of alkyls shows a cloudy pattern (Figure 4(aii)). However, as the tip is closer to molecule, the molecular “bottom templates” were still in the semi-order structure (Figure 4(aii) and 4(aiii)), which were supported by their FFT patterns. Further annealing to 137 °C, most of the windmill structures disappeared and more disorder was formed (Figure 4(bi) and 4(bii)). Even the stacking of molecular “bottom templates” also shows more disorder properties, supported by its FFT image with much larger dispersed points (Figure 4(biii)). Additionally, by the strong in-plane Van der Waals interactions of alkyl chains, we realized the

covalent coupling based on the ethynyl functionality before molecular desorption from metal surfaces.

In summary, we have shown a simple model for molecule-substrate and in-plane molecule-molecule interactions to confine molecular self-assembly structure. It was demonstrated that the in-plane Van der Waals interaction is important to control molecular self-assembly structure, as well its properties. Using tailored chemical modifications to mediate such in-plane cohesive interactions, we observed the spontaneous formations of order (molecule **1** and **3**) and disorder (molecule **2**) molecular self-assembly structures, as well their order-disorder phase transitions triggered by thermal annealing. Moreover, it was identified that the flexible alkane chains stand up at surfaces with the terminal carbons

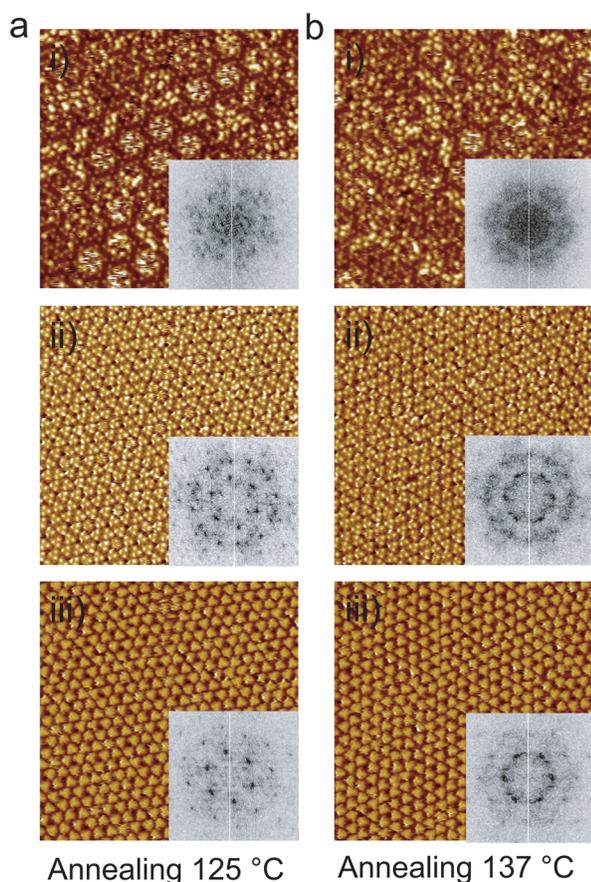


FIG. 4. (a) and (b) STM images ((i), 2 V, 5 pA; (ii), 2 V, 50 pA; (iii), 1 V, 50 pA) of molecule **3** in the same area (25×25 nm) on Ag(111) after annealing up to 125 °C (a) and 137 °C (b); Their corresponding FFT images were in size of 5.0×5.0 nm⁻¹.

moving. Interestingly, the alkyl chains formed 'locked' pair/windmill structures, and their strong in-plane adhesion forces were helpful for on-surface covalent coupling occurrence.

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- ²¹See supplementary material at <http://dx.doi.org/10.1063/1.4907777> for the dynamical movements of terminal carbons of C4 groups.