

# Odd–even effect and metal induced structural convergence in self-assembled monolayers of bipyridine derivatives†

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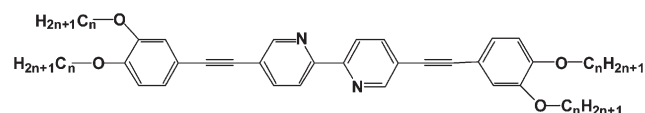
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Scanning tunneling microscopy (STM) observations reveal that bipyridine derivatives which exhibit various two-dimensional structures due to the odd–even chain length effect are converged into a lamellar structure upon metal coordination.

Self-assembly has been studied due to the promising and efficient approach to construct molecular devices based on nanoscience and nanotechnology.<sup>1</sup> Self-assembled monolayers at the solid/liquid interface have been studied by STM, which displays the detailed surface features. Controlling the self-assembled patterns at interfaces has been attempted by changing the molecular shapes including the chain length and functional groups,<sup>2</sup> and by inducing non-covalent interactions such as hydrogen bonding<sup>3</sup> and metal coordination.<sup>4</sup> An odd–even effect of molecular chains on two-dimensional structure formation has been studied in liquid crystals, fatty acids and so on.<sup>5</sup> The number of carbon atoms in the molecular chains has a strong influence on the resultant morphologies. Metal coordination has been used for the formation of ordered nanostructures, and the combination of molecules and coordinated metals produces a variety of packing patterns.<sup>4</sup>

In this contribution, we focus on the odd–even effect of peripheral alkyl chains in bipyridine derivatives (**bpy**, Scheme) as well as cooperative metal coordination. Combination of a systematic odd–even effect and metal coordination has not yet been attempted. Therefore, we have selected **bpy** molecules which have the ability to coordinate a metal, and tuned the carbon numbers in the peripheral alkyl chains.‡ The two-dimensional structures of **bpy** were studied by using STM at a highly oriented pyrolytic graphite (HOPG)/1-phenyloctane interface. In terms of the odd–even effect, much attention has been paid towards the



Scheme 1 Structure of bipyridine derivatives (**bpy**),  $n = 11$ –18.

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two-dimensional structures of molecules exhibiting dipolar interaction or hydrogen bonding.<sup>5</sup> The relations between dipolar units or functional groups affect the resultant packing patterns. However, we demonstrate here that a “pure” odd–even effect of alkyl chain length can be used to generate systematic two-dimensional structures and that unique structures can be generated in the monolayers of **bpy** with alkyl chain lengths over certain numbers of carbon atoms ( $n \geq 17$ ). Moreover, all the structures can be converged into the same lamellar structure after metal coordination, regardless of the interlamellar distances.

Fig. 1 shows typical STM images of **bpy** with different alkyl chain length observed at the HOPG/1-phenyloctane interface. The  $\pi$ -conjugated units appeared as bright parts in the images, whereas the alkyl chain units are dark.<sup>6</sup> As shown in Fig. 1(A), a pair of **bpy** ( $n = 11$ ) was aligned in a columnar manner accommodating the alkyl chains in between the columns. From the STM image, one side of the peripheral alkyl chains were bent against the  $\pi$ -conjugated unit, and the other side was straight. In the case of **bpy** ( $n = 14$ ), the molecules also exhibited a row structure, but the  $\pi$ -conjugated units aligned continuously along the row direction (Fig. 1(B)). The columns of  $\pi$ -conjugated units and interdigitated alkyl chains aligned alternately. The **bpy** with odd ( $n = 11, 13, 15$ ) and even ( $n = 12, 14, 16$ ) numbers of carbon atoms in the alkyl side

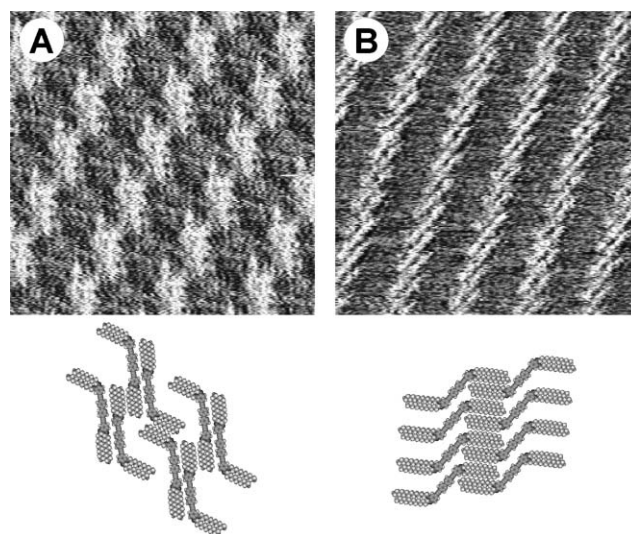


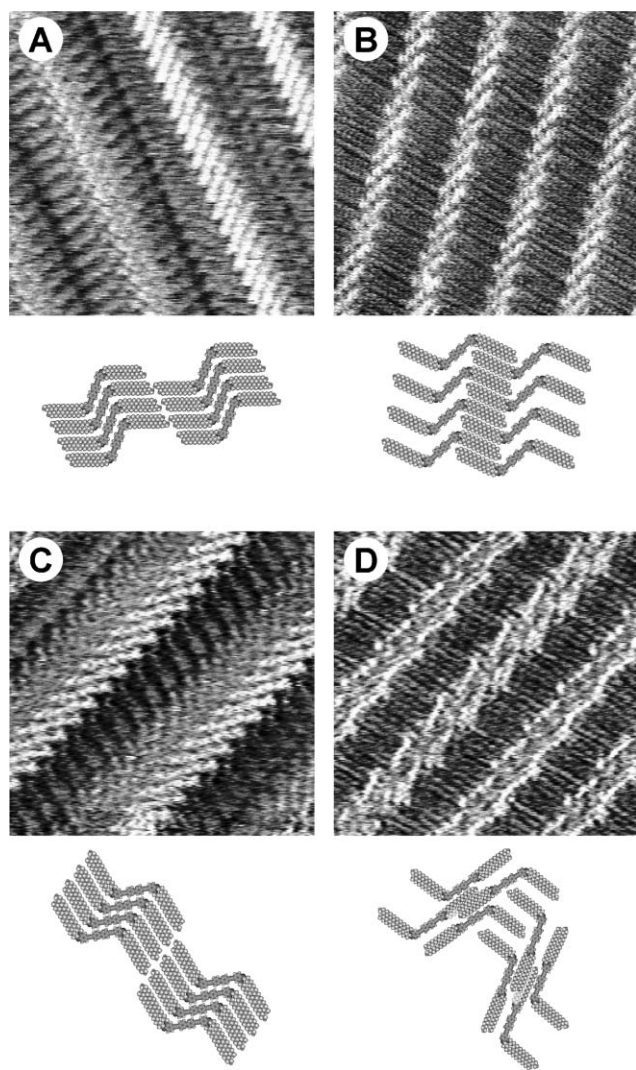
Fig. 1 Typical STM images (15 nm  $\times$  15 nm) of **bpy** with odd and even numbers of carbon atoms in the alkyl chains. (A)  $n = 11$ ,  $I = 1.8$  pA,  $V = -299$  mV; (B)  $n = 14$ ,  $I = 1.7$  pA,  $V = -262$  mV. Tentative molecular models are depicted on the basis of the STM images, and shown under each image.

chains showed similar two-dimensional structures as shown in Fig. 1(A) and (B), respectively, excepting the distances between the neighboring rows (see ESI†).

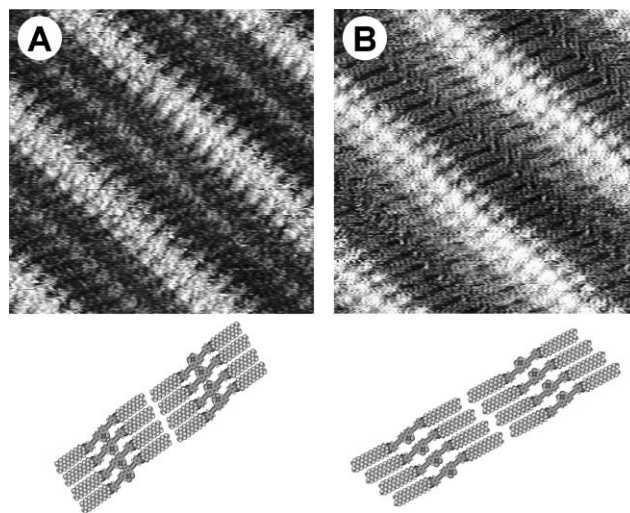
**bpy** ( $n = 17$ ) exhibited a different two-dimensional structure compared with the other **bpy** ( $n = 11, 13, 15$ ) despite the odd number of carbon atoms in the peripheral alkyl chains as shown in Fig. 2(A). The bent molecules formed a lamellar structure defined by dark troughs, suggesting non-interdigitated alkyl chains. **bpy** ( $n = 18$ ) showed polymorphism, and three types of structures were found in the monolayer (Fig. 2(B)–(D)). The structure shown in Fig. 2(B) is similar to that in Fig. 1(B) in which bent molecules were interdigitated at the alkyl chain units. The structure in Fig. 2(C) was a bent form with non-interdigitated alkyl chains similar to **bpy** ( $n = 17$ ) in Fig. 2(A). The structure in Fig. 2(D) exhibited  $pg$  plane group symmetry where a pair of separated molecules forms the columnar structure.† Differential scanning calorimetry analysis of bulk **bpy** samples (see ESI†) indicates that **bpy** ( $n = 11$ – $17$ ) shows a single endothermic peak, whereas **bpy**

( $n = 18$ ) exhibits two endothermic peaks. This result suggests that **bpy** ( $n = 18$ ) has at least two crystalline states, which is determined by the molecular interactions in the bulk. In the case of a **bpy** ( $n = 18$ ) monolayer on HOPG, the crystalline structure is affected by not only adsorbate–adsorbate interactions but also surface–adsorbate ones.<sup>1–6</sup> Therefore, more than two polymorphic crystals could be formed at the HOPG/solvent interface, as shown in Fig. 2(B)–(D). These results indicate that the two-dimensional structures of **bpy** are strongly dependent on the (odd or even) carbon numbers of peripheral alkyl chains. In addition, upon elongating the alkyl chain length (typically 17 in the present case), intermolecular interactions at the alkyl chain part increase enough to change the stable molecular packing state, resulting in the formation of different two-dimensional structures compared with **bpy** ( $n = 11$ – $16$ ).

Metal coordination of **bpy** is anticipated to change the two-dimensional arrangement in the monolayer due to an increase in the intermolecular distance at the  $\pi$ -conjugated unit ( $D_i$ ).<sup>6</sup> Therefore, the analysis of  $D_i$  would provide information as to whether metal coordination occurs or not. Fig. 3 shows typical STM images of **bpy** ( $n = 14, 17$ ) after metal coordination treatment. As shown in Fig. 3, in spite of the odd or even numbers of carbon atoms in the peripheral alkyl chains, the molecules formed a lamellar structure, which was composed of almost straight shaped molecules with non-interdigitated alkyl chains. Indeed, all the **bpy** samples ( $n = 11$ – $18$ ) in this study exhibited a similar structure as Fig. 3, after metal coordination treatment. Quantitative analysis of STM images revealed that  $D_i$  for bare **bpy** was  $7.6 \pm 0.6$  Å on average for the series of **bpy** ( $n = 11$ – $18$ ), whereas  $D_i$  for **bpy** after metal coordination treatment increased to  $10.0 \pm 0.4$  Å, suggesting that metal coordination actually occurs at the bipyridine unit. In addition, considering the  $D_i$  values show only small deviation after metal coordination, it is clear that the lamellar structure is preserved in all the **bpy** monolayers even if the alkyl chain length is different (see ESI†). Our previous study has revealed that bare **bpy** has a different molecular width between the  $\pi$ -conjugate and alkyl chain units.<sup>6</sup> Such a heterogeneity makes the



**Fig. 2** Typical STM images ( $15 \text{ nm} \times 15 \text{ nm}$ ) of **bpy** with different alkyl chain lengths. (A)  $n = 17$ ,  $I = 2.2 \text{ pA}$ ,  $V = -273 \text{ mV}$ ; (B–D)  $n = 18$ ,  $I = 1.3 \text{ pA}$ ,  $V = -275 \text{ mV}$ . Tentative molecular models estimated from the STM images are shown under each image.†



**Fig. 3** Typical STM images ( $15 \text{ nm} \times 15 \text{ nm}$ ) of bipyridine derivatives after metal coordination. (A)  $n = 14$ ,  $I = 2.8 \text{ pA}$ ,  $V = -667 \text{ mV}$ ; (B)  $n = 17$ ,  $I = 1.4 \text{ pA}$ ,  $V = -630 \text{ mV}$ . Tentative molecular models are depicted on the basis of STM images, and shown under each image.

**bpy** bent so as to maximize the molecular packing density. Metal coordination increases the molecular width occupied by the  $\pi$ -conjugated unit, which becomes almost identical to that of the alkyl chain unit. As a result, metal coordinated **bpy** forms a lamellar structure, that is, the odd–even effect of alkyl chains is quenched by the molecular width variation. This result indicates that a variety of two-dimensional structures of **bpy** with different alkyl chain length can be converged into lamellar structures by metal coordination, and that molecular width control is one of the strategies to control the two-dimensional structures.

## Notes and references

‡ The **bpy** samples were synthesized by a previous method<sup>6</sup> besides the alkyl chain part, for which appropriate compounds were selected to prepare the samples with various alkyl chain lengths. Prior to STM imaging, **bpy** was dissolved in 1-phenyloctane with a concentration below 0.1 mM. For the metal coordination experiment, **bpy** and excess Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> were separately dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and the solutions were mixed together to disperse in 1-phenyloctane. A drop of the solution was placed on HOPG to obtain a self-assembled monolayer. Low-current STM (Veeco, Nanoscope IIIa) was operated in the constant current mode at the HOPG/1-phenyloctane interface using a mechanically cut Pt/Ir wire (80/20).

§ In Fig. 2(D), the shaded alkyl chain is thought to dangle into the solvent. The vacancy seen between the alkyl chain rows may be filled with coadsorbed solvent molecules.

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