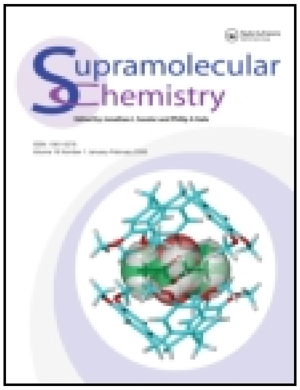

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Metallation of bipyridine derivatives substituted at meta position by alkyl chains: effects on the 2D structures

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Bipyridine derivatives (bpys) substituted by alkyl chains at meta position were observed by scanning tunnelling microscopy at a highly oriented pyrolytic graphite–1-phenyloctane interface. In those molecules, the alkyl chains were interdigitated, and the π-conjugated bipyridine core parts were aligned side by side. Metal coordination should induce 2D structural transformations due to the alteration of intermolecular interactions. The bpy platinum complexes were aligned in a straight fashion, in which the alkyl chains were interdigitated. The molecular arrangements were quite different from those of free bpy. In contrast, there was no structural change in the case of palladium complexes, suggesting the decoordination of the ligand from the metal. The equilibrium of metallation/demetallation affected the 2D structure, and should be taken into account for the nanoarchitecture design on the basis of the intermolecular interactions.

Keywords: scanning tunnelling microscopy; self-assembly; solid–liquid interfaces; bipyridine; HOPG; metal coordination

1. Introduction

Towards the production of molecule-based devices and circuits, self-assembly, which is the spontaneous organisation of molecules, is one of the main candidates for the controlled integrations and arrangements of functional molecules on a surface (*1–3*). Therefore, understanding the intermolecular as well as the molecule–substrate interactions is fundamental to control the positions of well-designed molecules (*4*, *5*). 2D structures have been visualised by using scanning tunnelling microscopy (STM) at solid–liquid interface to study and realise various 2D patterns formed via weak molecular interactions such as hydrogen bonds, van der Waals interactions, metal coordination and so on (*6–10*). Because of its importance in biological systems from both skeletal and functional viewpoints, metal coordination has attracted much attention in the field of supramolecular chemistry (*11*).

Equilibrium of metal coordination–decoordination is one of the important factors affecting the stability of the 2D structures. In our previous study (*12*), palladium complexes of bipyridine derivatives (bpys) substituted by different numbers of alkyl chains (1, 2 or 3) at various positions (ortho, meta, para) were prepared, and their 2D structures were studied by STM at a highly oriented pyrolytic graphite (HOPG)–1-phenyloctane interface. While different 2D structures were observed for palladated bpys with *p*-substituted single-, double- and triple alkyl chain units in comparison to the free ligand, they remained unchanged in the case of bpys with *m*-substituted single alkyl chains. To explain these experimental observations, it was proposed that decoordination of the *m*-substituted ligands occurs during the formation of 2D structure.

To investigate this phenomenon in more detail, herein, we focus on the 2D structure formation of bpys with *m*-substituted single alkyl chain units (**C$_n$*m*:** Chart 1). Platinum is known to form more stable metal–ligand bounds than palladium. For instance, cisplatin (cis-diamminedichloro-platinum(II)) is known as a platinum-based anti-cancer agent, which firmly coordinates to guanine and adenine in the DNA sequence, and the cross-linking of DNA results in the apoptosis of cancer cell (*13*). In this study, the high coordination ability of platinum metal centre will enable us to study the effect of metallation on the 2D structure changes of **C$_n$*m***.

2. Experimental

2.1 Materials

The bpys substituted at *m*-position (**C$_n$*ms***) were synthesised as reported previously (*12*). Every reagent was purchased from Kanto, Tokyo or Wako, Osaka, Japan, except $Pt(CH_3CN)_2Cl_2$ which was purchased from Aldrich, Milwaukee, WI, USA, and were used as received.

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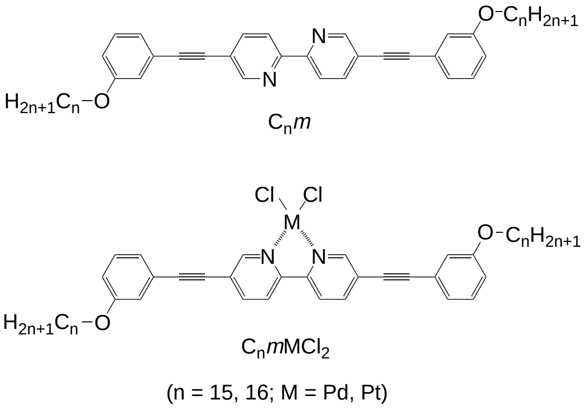

Chart 1. Chemical structures of bpys substituted at meta position by alkyl chains ($\mathbf{C_n}\boldsymbol{m}$) and metallated ones ($\mathbf{C_n}\boldsymbol{m}\mathbf{MCl_2}$).

Platinum complexes ($\mathbf{C_n}\boldsymbol{m}\mathbf{PtCl_2}$) were synthesised by stirring one equivalent of $\mathbf{C_n}\boldsymbol{m}$ with one equivalent of $Pt(CH_3CN)_2Cl_2$ in 1,4-dioxane at 110°C for 17 h. After evaporation of the solvents, the complexes were purified by washing with cold diethyl ether and methanol to yield yellow slightly orange solids. Nuclear magnetic resonance (NMR) spectra were recorded on a 500 MHz Bruker Avance 500 spectrometer using tetramethylsilane as an internal standard to check the formation of platinum complexes.

2.2 STM observation

The $\mathbf{C_n}\boldsymbol{ms}$ were dissolved in 1-phenyloctane at a concentration below 0.1 mM. The samples were placed on a freshly cleaved HOPG of ZYB grade (NT-MDT, Zelenograd, Russia), and STM (Nanoscope IIIa, Veeco Instruments, Santa Barbara, CA, USA) observation was performed in a constant current mode at solid–liquid interface. The STM tip was mechanically formed by cutting the Pt–Ir wire (90/10). All the STM images were analysed by the SPIP software (Image Metrology, Horsholm, Denmark). HOPG lattice was used as an internal standard to correct each of the STM images as well as to determine the molecular alignment of $\mathbf{C_n}\boldsymbol{ms}$ on the HOPG.

3. Results and discussion

Self-assembled monolayers of bpys with different alkyl chain length were prepared on HOPG, and the 2D structures were observed by STM at solid–liquid interface. Figure 1 shows the STM images of $\mathbf{C_{15}}\boldsymbol{m}$ and $\mathbf{C_{16}}\boldsymbol{m}$. In both cases, bright columns of π-conjugated bipyridine cores are intercepted by the dark troughs consisting of alkyl chains. The π-conjugated units are aligned side by side with intervals (*D*) of *ca.* 0.74 nm, which is almost identical to the molecular width occupied by the flatly oriented aromatic ring on a surface (0.75 nm) (*14*, *15*), indicating that the π-conjugated bipyridine cores are densely packed via the intermolecular interactions. The interdigitated alkyl chains are oriented along one of the underlying HOPG lattice directions, suggesting that both intermolecular and molecule–substrate interactions stabilise the 2D packing of bpys at the alkyl chain units. Molecular model is superimposed on the STM images. The unit cell parameters measured from STM images are listed in Table 1.

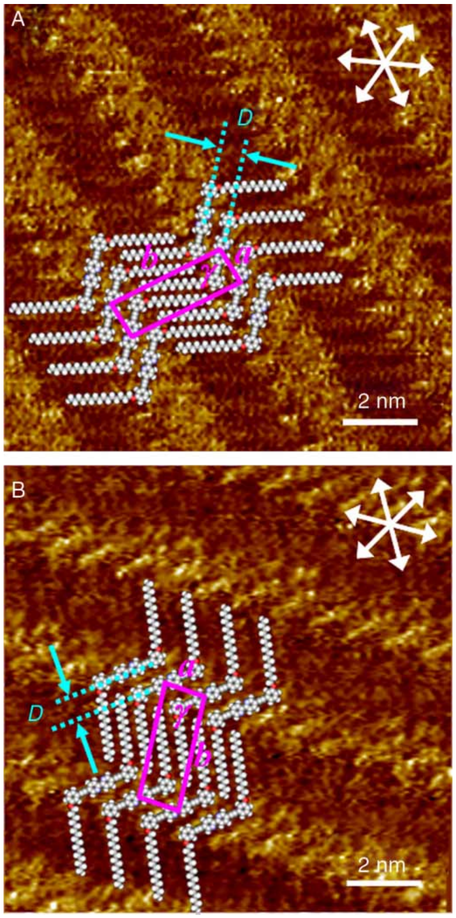

Figure 1. STM images of $\mathbf{C_{15}}\boldsymbol{m}$ (A) and $\mathbf{C_{16}}\boldsymbol{m}$ (B) at a HOPG–1-phenyloctane interface. Molecular model is superimposed on the STM images. A set of arrows indicates the underlying HOPG lattice direction. Tunnelling condition: (A) $I = 81$ pA, $V = -1000$ mV and (B) $I = 70$ pA, $V = -1000$ mV.

Intermolecular interactions are expected to vary upon metal coordination even on a surface. In our previous study (*12*), mixing the bpys and $Pd(CH_3CN)_2Cl_2$ resulted in the formation of bpys–palladium complexes, namely bipyridine core part was coordinated to the $PdCl_2$ unit. The reaction could be followed by the characteristic colour change of the reaction solution and the downfield shift of the α-proton on bipyridine core in ^{1}H NMR. However, STM observations of Pd-complexed bpys revealed the same 2D structures as those of free bpys. This result

Table 1. Unit cell parameters of the molecule and intermolecular distance (*D*) at the π-conjugated unit measured from STM images.

	a(nm)	*b*(nm)	γ(deg)	*D*(nm)
C$_{15}$*m*	1.09 ± 0.07	3.13 ± 0.07	92.2 ± 0.8	0.73 ± 0.06
C$_{16}$*m*	1.06 ± 0.01	3.22 ± 0.11	92.0 ± 1.2	0.74 ± 0.06
C$_{15}$*m*PtCl$_2$	1.04 ± 0.21	4.05 ± 0.19	92.9 ± 2.1	1.04 ± 0.21
C$_{16}$*m*PtCl$_2$	0.95 ± 0.11	4.21 ± 0.14	93.9 ± 2.7	0.95 ± 0.11

suggested that the 2D structure of **C$_n$*m*** is very dense, and that the metal decoordination of **C$_n$*m*PdCl$_2$** occurs because of the high stability of the crystalline packing structure of **C$_n$*m***.

It is well known that platinum complexes form persistent structures due to their thermodynamic stability, whereas the palladium ones are labile at room temperature (*16*). Therefore, we prepared platinum complexes in order to achieve the stable alignment of metallated **C$_n$*m*s**. The platinum complexes were synthesised and their generation could be confirmed in the ^{1}H NMR spectrum by the downfield shift of the α-proton, which is characteristic of metallation of the bipyridine unit. The δ value was shifted from 8.81 ppm (**C$_{15}$*m*, C$_{16}$*m***) to 9.16 ppm (**C$_{15}$*m*PtCl$_2$**) and 9.39 (**C$_{16}$*m*PtCl$_2$**), respectively. The monolayers of **C$_{15}$*m*PtCl$_2$** and **C$_{16}$*m*PtCl$_2$** were prepared on the HOPG, and their nanostructures were visualised by STM (Figure 2). The 2D structures are very different from those of the ligand (**C$_n$*m***) and of **C$_n$*m*PdCl$_2$**. The **C$_n$*m*PtCl$_2$** showed lamellar structures, in which the molecules adopt a linear conformation with interdigitated alkyl chains. Intermolecular distance of π-conjugated unit was $D = ca.$ 1 nm, which corresponds to the molecular width of metallated bipyridine unit (*14*, *17*). The alkyl chains were aligned along the HOPG lattice. These results indicate that the 2D structures of **C$_n$*m*PtCl$_2$** are stabilised by the alkyl chain unit–HOPG interaction as well as by the intermolecular interactions of alkyl–alkyl and metallated bipyridine cores. Thus, by platination, we could accomplish a change of 2D structure.

Therefore, it can be concluded that even though both palladium and platinum complexes of **C$_n$*m*** can exist in each solution, only **C$_n$*m*PtCl$_2$** can form the 2D molecular alignment on a surface. This confirms our previous hypothesis that **C$_n$*m*PdCl$_2$** decoordinates upon surface adsorption, and thereby display the same nanostructure as the free ligand (**C$_n$*m***). These are examples of how the balance between the original crystalline packing of ligand and equilibrium of metallation affects the 2D structure formation at solid–liquid interface.

4. Conclusion

Self-assembled 2D structures of bpys and metallated ones were investigated by STM at HOPG–1-phenyloctane interface. The **C$_n$*m*** displayed Z-shaped morphology with the interdigitated alkyl chains. The π-conjugated bipyridine core parts were aligned side by side. The formation of palladium complexes of **C$_n$*m*** could be confirmed in solution, whereas the 2D structures remained unchanged (same structure as the one of **C$_n$*m***). This result suggests that decoordination of **C$_n$*m*PdCl$_2$** occurs because of the close packed 2D structure of **C$_n$*m***. In contrast, persistent complexes of **C$_n$*m*PtCl$_2$** formed monolayers at solid–liquid interface. The molecules adopt a linear conformation and align to form lamellar structures. These

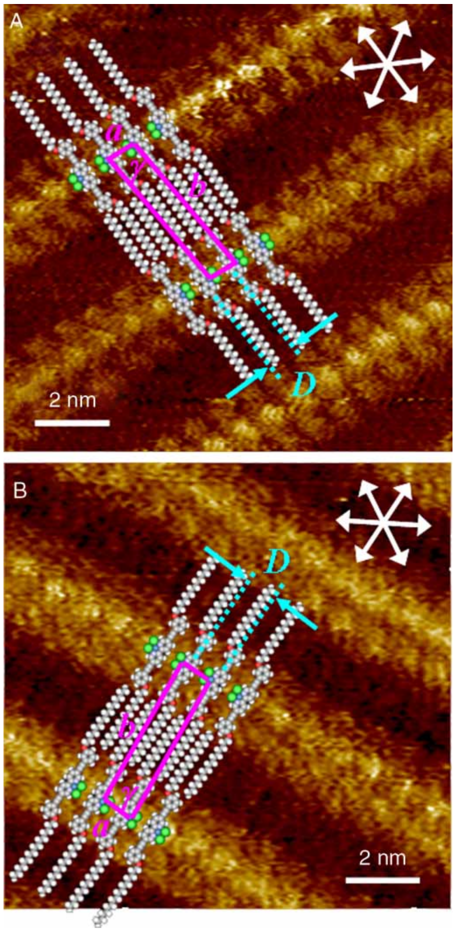

Figure 2. STM images of **C$_{15}$*m*PtCl$_2$** (A) and **C$_{16}$*m*PtCl$_2$** (B) physisorbed at a HOPG–1-phenyloctane interface. Molecular models are depicted on the basis of the STM images. A set of arrows indicates the underlying HOPG lattice direction. Tunnelling condition: (A) $I = 1.1$ pA, $V = -990$ mV and (B) $I = 1.7$ pA, $V = -622$ mV.

results indicate that metal decoordination occurs to keep the balance in the system if the crystalline packing of the original ligand is energetically more stable than the metallation of the ligand and the resultant 2D structure. Therefore, the equilibrium of the molecular packing and metallation should be taken into account to transform the 2D structures by metal coordination at solid–liquid interface.

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