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

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1. Synthetic procedure and spectroscopic characterization data of **bpy** samples

The **bpy** samples used in this study were synthesized by the previous method.[S1] Briefly, the 5,5'-dibromo-2,2'-bipyridine was prepared according to the reported method.[S2] Then, the compound was reacted with trimethylsilylacetylene to obtain the 5,5'-diethynyl-2,2'-bipyridine. 1,2-dialkyloxy-4-iodobenzene (n=11-18) was introduced to 5,5'-diethynyl-2,2'-bipyridine so as to prepare the **bpy** (n=11-18). NMR spectra were recorded on a 500 mHz Bruker Avance 500 spectrometer using tetramethylsilane as an internal standard as:

bpy (n=11): ^{1}H NMR (CDCl$_3$): δ 0.88 (t, J = 6.95 Hz, 12H, –C$\underline{H}_3$), 1.22-1.40 (br, 56H, –C$\underline{H}_2$–), 1.44-1.52 (m, 8H, O–(CH$_2$)$_2$–C$\underline{H}_2$–), 1.80-1.88 (m, 8H, O–CH$_2$–C$\underline{H}_2$–), 4.03 (t, J = 6.55 Hz, 8H, O–C$\underline{H}_2$–), 6.85 (d, J = 8.40 Hz, 2H, Ar), 7.07 (d, J = 1.55 Hz, 2H, Ar), 7.14 (dd, J_1 = 8.23 Hz, J_2 = 1.35 Hz, 2H, Ar), 7.92 (d, J = 4.30 Hz, 2H, Ar), 8.41 (brs, 2H, Ar), 8.79 (brs, 2H, Ar).

bpy (n=12): ^{1}H NMR (CDCl$_3$): δ 0.88 (t, J = 6.80 Hz, 12H, –C$\underline{H}_3$), 1.22-1.40 (br, 64H, –C$\underline{H}_2$–), 1.44-1.52 (m, 8H, O–(CH$_2$)$_2$–C$\underline{H}_2$–), 1.80-1.87 (m, 8H, O–CH$_2$–C$\underline{H}_2$–), 4.03 (t, J = 6.55 Hz, 8H, O–C$\underline{H}_2$–), 6.85 (d, J = 8.35 Hz, 2H, Ar), 7.07 (d, J = 1.85 Hz, 2H, Ar), 7.14 (dd, J_1 = 8.25 Hz, J_2 = 1.85 Hz, 2H, Ar), 7.91 (d, J = 8.10 Hz, 2H, Ar), 8.41 (d, J = 7.65 Hz, 2H, Ar), 8.79 (brs, 2H, Ar).

bpy (n=13): ^{1}H NMR (CDCl$_3$): δ 0.88 (t, J = 6.80 Hz, 12H, –C$\underline{H}$$_3$), 1.22-1.40 (br, 72H, –CH$_2$–), 1.44-1.52 (m, 8H, O–(CH$_2$)$_2$–C$\underline{H}$$_2$–), 1.80-1.87 (m, 8H, O–CH$_2$–C$\underline{H}$$_2$–), 4.03 (t, J = 6.55 Hz, 8H, O–C$\underline{H}$$_2$–), 6.85 (d, J = 8.40 Hz, 2H, Ar), 7.07 (d, J = 2.00 Hz, 2H, Ar), 7.14 (dd, J_1 = 8.25 Hz, J_2 = 1.85 Hz, 2H, Ar), 7.91 (dd, J_1 = 8.25 Hz, J_2 = 2.15 Hz, 2H, Ar), 8.41 (d, J = 8.25 Hz, 2H, Ar), 8.79 (s, 2H, Ar).

bpy (n=14): ^{1}H NMR (CDCl$_3$): δ 0.88 (t, J = 6.88 Hz, 12H, –C$\underline{H}$$_3$), 1.22-1.40 (br, 80H, –CH$_2$–), 1.44-1.52 (m, 8H, O–(CH$_2$)$_2$–C$\underline{H}$$_2$–), 1.80-1.87 (m, 8H, O–CH$_2$–C$\underline{H}$$_2$–), 4.03 (t, J = 6.70 Hz, 8H, O–C$\underline{H}$$_2$–), 6.85 (d, J = 8.40 Hz, 2H, Ar), 7.07 (d, J = 1.80 Hz, 2H, Ar), 7.14 (dd, J_1 = 8. 23 Hz, J_2 = 1.85 Hz, 2H, Ar), 7.91 (dd, J_1 = 8.23 Hz, J_2 = 2.15 Hz, 2H, Ar), 8.41 (d, J = 8.25 Hz, 2H, Ar), 8.79 (s, 2H, Ar).

bpy (n=15): ^{1}H NMR (CDCl$_3$): δ 0.88 (t, J = 6.80 Hz, 12H, –C$\underline{H}$$_3$), 1.23-1.42 (br, 88H, –CH$_2$–), 1.44-1.52 (m, 8H, O–(CH$_2$)$_2$–C$\underline{H}$$_2$–), 1.80-1.87 (m, 8H, O–CH$_2$–C$\underline{H}$$_2$–), 4.03 (t, J = 6.55 Hz, 8H, O–C$\underline{H}$$_2$–), 6.85 (d, J = 8.35 Hz, 2H, Ar), 7.07 (d, J = 1.85 Hz, 2H, Ar), 7.14 (dd, J_1 = 8.25 Hz, J_2 = 1.85 Hz, 2H, Ar), 7.91 (dd, J_1 = 8.25 Hz, J_2 = 2.00 Hz, 2H, Ar), 8.41 (d, J = 8.25 Hz, 2H, Ar), 8.79 (s, 2H, Ar).

bpy (n=16): ^{1}H NMR (CDCl$_3$): δ 0.88 (t, J = 6.78 Hz, 12H, –C$\underline{H}$$_3$), 1.23-1.42 (br, 96H, –CH$_2$–), 1.44-1.52 (m, 8H, O–(CH$_2$)$_2$–C$\underline{H}$$_2$–), 1.80-1.87 (m, 8H, O–CH$_2$–C$\underline{H}$$_2$–), 4.03 (t, J = 6.55 Hz, 8H, O–C$\underline{H}$$_2$–), 6.85 (d, J = 8.50 Hz, 2H, Ar), 7.07 (d, J = 1.85 Hz, 2H, Ar), 7.14 (dd, J_1 = 8.30 Hz, J_2 = 1.65 Hz, 2H, Ar), 7.92 (dd, J_1 = 8.25 Hz, J_2 = 2.00 Hz, 2H, Ar), 8.41 (brs, 2H, Ar), 8.79 (brs, 2H, Ar).

bpy (n=17): ^{1}H NMR (CDCl$_3$): δ 0.88 (t, J = 6.88 Hz, 12H, –C$\underline{H}$$_3$), 1.23-1.38 (br, 104H, –CH$_2$–), 1.44-1.52 (m, 8H, O–(CH$_2$)$_2$–C$\underline{H}$$_2$–), 1.78-1.87 (m, 8H, O–CH$_2$–C$\underline{H}$$_2$–), 4.03 (t, J = 6.55 Hz, 8H, O–C$\underline{H}$$_2$–), 6.85 (d, J = 8.40 Hz, 2H, Ar), 7.07 (d, J = 1.85 Hz, 2H, Ar), 7.14 (dd, J_1 = 8.08 Hz, J_2 = 1.85 Hz, 2H, Ar), 7.92 (d, J = 8.25 Hz, Hz, 2H, Ar), 8.41 (brs, 2H, Ar), 8.78 (brs, 2H, Ar).

bpy (n=18): ^{1}H NMR (CDCl$_3$): δ 0.88 (t, J = 6.88 Hz, 12H, –C$\underline{H}$$_3$), 1.21-1.38 (br, 112H, –CH$_2$–), 1.44-1.52 (m, 8H, O–(CH$_2$)$_2$–C$\underline{H}$$_2$–),1.78-1.87 (m, 8H, O–CH$_2$–C$\underline{H}$$_2$–), 4.03 (t, J = 6.55 Hz, 8H, O–C$\underline{H}$$_2$–), 6.85 (d, J = 8.55 Hz, 2H, Ar), 7.07 (d, J = 1.70 Hz, 2H, Ar), 7.14 (dd, J_1 = 8.30 Hz, J_2 = 1.80 Hz, 2H, Ar), 7.92 (d, J = 7.75 Hz, Hz, 2H, Ar), 8.41 (brs, 2H, Ar), 8.78 (brs, 2H, Ar).

S1 Y. Kikkawa, E. Koyama, S. Tsuzuki, K. Fujiwara, K. Miyake, H. Tokuhisa, M. Kanesato, *Langmuir*, 2006, **22**, 6910.

S2 S. Oae, T. Kawai, N. Furukawa, *Phosphorus Sulfur Relat. Elm.*, 1987, **34**, 123.

2. Thermal data

Melting temperature of bulk **bpy** samples was evaluated by DSC (EXSTAR6000, Seiko Instruments Inc.).   The bulk sample of ca. 2 mg was encapsulated in the aluminum pans and heated from 90 to 150 ˚C at a heating rate of 2 ˚C/min.   The onset melting temperatures were plotted as a function of the number of carbon atoms in the peripheral alkyl chains (Fig. S1).   The onset melting temperature of odd **bpy** (n=11, 13, 15) and even one (n=12, 14, 16) was linearly reduced, respectively, as the carbon numbers in the alkyl chains were increased.   The **bpy** (n=17) and **bpy** (n=18) were deviated from the above relations.   Therefore, it is conceivable that **bpy** (n=17) and **bpy** (n=18) have a different crystalline packing structure compared with **bpy** (n=11-16).   In addition, **bpy** (n=18) shows the two melting endothermic peaks, suggesting that **bpy** (n=18) has at least two crystalline states.
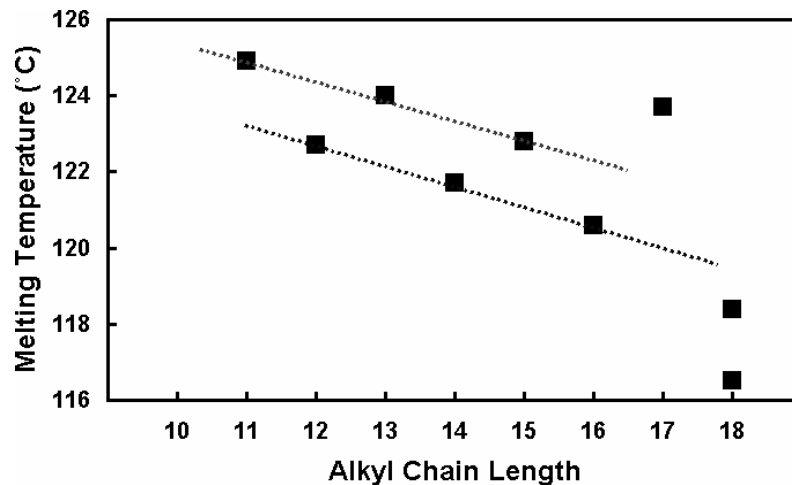

Fig. S1. Plots of onset melting temperature vs. the number of carbon atoms in the peripheral alkyl chains of **bpy**.

3. Additional STM images of **bpy** before and after metal coordination

The monolayers of **bpy** (n=12, 13, 15, 16) at HOPG/1-phenyloctane interface was observed by STM, and the images are shown in Fig. S2.   After metal coordination, STM observation was performed in the monolayers of **bpy** (n=11, 12, 13, 15, 16, 18), and the images are shown in Fig. S3.
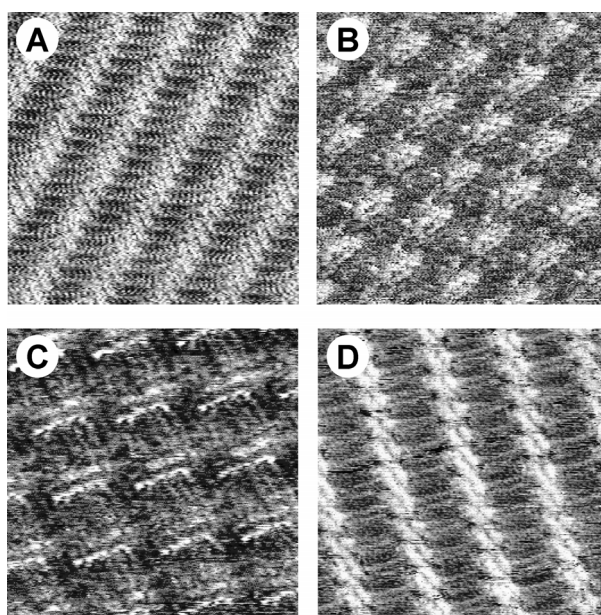

Fig. S2   STM images (15 nm × 15 nm) of **bpy** with odd and even number of carbon atoms in the alkyl chains.   (A) n = 12, (B) n=13, (C) n=15, (D) n=16.
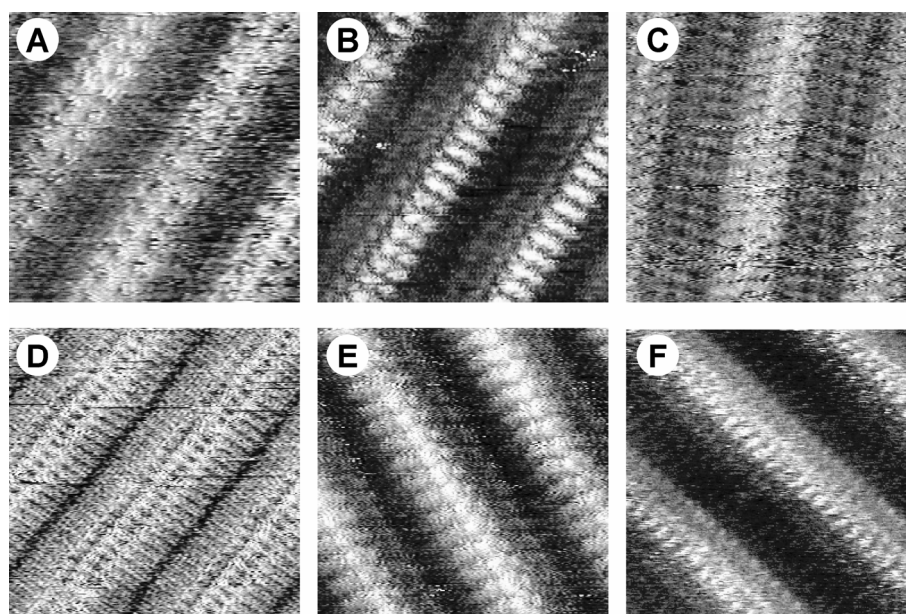

Fig. S3   STM images (15 nm × 15 nm) of **bpy** after metal coordination.   (A) n=11, (B) n=12, (C) n=13, (D) n=15, (E) n=16, (F) n=18.

4. Large area STM images of **bpy** (n=18)

Fig. S4 shows the large area STM images of **bpy** (n=18) at HOPG/1-phenyloctane interface.　Figs. 2B-2D were enlarged images of Fig. S4.
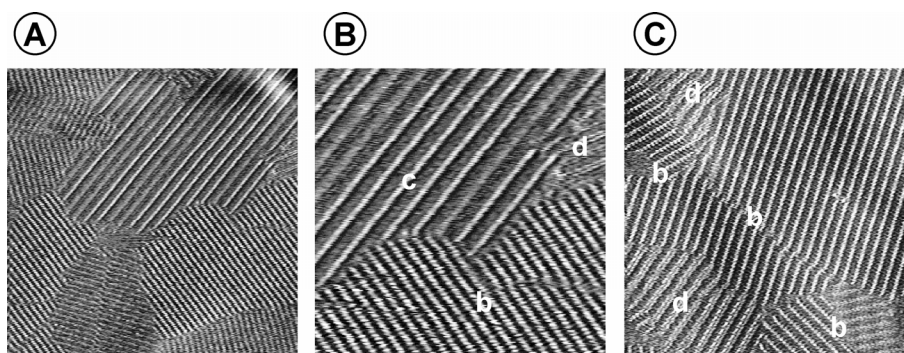

Fig. S4　STM images (A: 200 nm × 200 nm, B and C: 100 nm × 100 nm) of **bpy** (n=18). The white symbols (b-c) in the image indicate the two-dimensional patterns found in Figs. 2B-2D, respectively.

5. Intermolecular distance at the π-conjugated units

The periodical length between the π-conjugated units before (Figs. 1, 2 and S2) and after metal coordination (Figs. 3 and S3) was measured from STM images.　The data are listed in Table S1.　The distance between the neighboring π-conjugated units after metal coordination was larger than that of bare **bpy**.

Table S1.　Measured intermolecular distances between the π coordinated units.

bpy (n)	Intermolecular distance (Å)	
	bare **bpy**	metal coordinated **bpy**
11	7.5 ± 0.6	10.4 ± 0.6
12	8.0 ± 0.4	9.9 ± 0.4
13	7.8 ± 0.8	10.3 ± 0.5
14	7.5 ± 0.6	10.4 ± 0.3
15	7.8 ± 0.7	9.5 ± 0.3
16	7.9 ± 0.4	9.6 ± 0.5
17	7.6 ± 0.4	9.5 ± 0.3
18	7.7 ± 0.5	10.3 ± 0.5
Average	7.6 ± 0.6	10.0 ± 0.4