# Supporting Information

# Cold Crystallization in Mixed System of Adenine and Thymine Dodecyl Derivatives

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#### **Experimental Section**

#### **Materials and Sample Preparation**

All chemicals including adenine and thymine were purchased from Tokyo Chemical Industry (Tokyo, Japan) and used without further purification. <sup>1</sup>H-NMR spectra were measured with a JEOL JNM-ECS 300 or Bruker AVANCE DPX-400 spectrometer using chloroform-d for A-C12 and methanol-d<sub>4</sub> for T-C12 as the solvent. The chemical shifts ( $\delta$ ) were measured in ppm relative to trimethylsilane. Elemental analyses were performed on a Perkin-Elmer 2400II CHN Analyzer.

#### Synthesis of A-C12

Adenine (0.41 g, 3.0 mmol) and potassium carbonate (0.55 g, 4.0 mmol) were gradually added to 150 mL of N, N-dimethylformamide and stirred at room temperature for about 10 minutes. 1-Bromododecane (0.98 g, 3.9 mmol) was added to the suspension and the mixture was heated at 85°C for 48 hours, then poured into ice water (300 mL). The precipitate was filtered off, dried and purified by silica gel column chromatography (eluent, chloroform and methanol, 4:1). A-C12 was obtained as white powder. Yield: 0.25 g (28%); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  8.38 (s, 1H),  $\delta$  7.80 (s, 1H),  $\delta$  5.60 (br, 2H),  $\delta$  4.19 (t, J = 7.2 Hz, 2H),  $\delta$  1.89 (quin, J = 7.8 Hz, 2H),  $\delta$  1.33-1.19 (m, 19H),  $\delta$  0.88 (t, J = 6.3 Hz, 3H), elemental analysis for C<sub>17</sub>H<sub>29</sub>N<sub>5</sub>, Calcd: C, 67.29; H, 9.63; N, 23.08%, Found: C, 67.61; H, 9.77; N, 22.84%;

### Synthesis of T-C12<sup>1</sup>

Thymine (0.38 g, 3.0 mmol) and potassium carbonate (0.47 g, 3.4 mmol) were gradually added to 10 mL of N, N-dimethylformamide and stirred at room temperature for about 10 minutes. 1-Bromododecane (0.83 g, 3.3 mmol) was added to the suspension and the mixture was heated at 45°C for 48 hours. Water (15 mL) was added to the solution, and the resulting mixture was extracted with diethyl ether (200 mL). Organic layer was washed with brine (300 mL), dehydrated by MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by recrystallization (3:1 v/v hexane-ethyl acetate). Yield: 0.11 g (13%); <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 400 MHz):  $\delta$  7.40 (s, 1H),  $\delta$  3.69 (t, J = 7.6 Hz, 2H),  $\delta$  1.86 (s, 3H),  $\delta$  1.66 (quin, 2H),  $\delta$  1.32-1.28 (m, 18H),  $\delta$  0.89 (t, J = 6.4 Hz, 3H), elemental analysis for C<sub>17</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>, Calcd: C, 69.35; H, 10.27; N, 9.51%, Found: C, 69.31; H, 10.65; N, 9.61%;

#### **Thermal and Structural Analysis**

Thermal behavior was investigated by differential scanning calorimetry (DSC) using NETZSCH DSC Sirius 3500 under N<sub>2</sub> atmosphere. Samples were prepared in an aluminum pan with the following weight: A-C12, 4.801 mg; T-C12, 4.516 mg; AT-C12, 4.998 mg (2.525 mg of A-C12 and 2.473 mg of T-C12). Heating and cooling rate were 5°C min-1 and 10°C min-1, respectively. DSC measurements were carried out in the temperature range from 10 to 145°C for A-C12 and T-C12 (Fig. S1) and from -20 to 160°C for the mixed system (AT-C12, Fig. 2). The dry nitrogen gas flow rate was 40 mL min<sup>-1</sup>. In the discussion of the DSC diagrams, the starting points of the peaks were used to describe the melting points, and the temperature range of the peaks were used for the broader peaks. Polarized optical images were recorded on Nikon, ECLIPSE LV 100 POL using crossed Nicols. AT-C12 powder after the 6<sup>th</sup> cooling process on DSC measurement was sandwiched between thin glass plates and placed on a temperature controlled stage (Linkam, THMS 600). Then, polarized optical microscopic images were captured using a CCD camera (Nikon, DS-Fi 1) under temperature control (heating rate: 5°C min<sup>-1</sup>, cooling rate: 10°C min<sup>-1</sup>). Purified A-C12 and T-C12 were dissolved in a 1:4 mixture of chloroform and methanol, and a co-crystal of AT-C12 was obtained by solvent evaporation method. Bruker APEX II diffractometer using MoKa radiation was used to analyze the crystal structure. Structural change of the crystal depending on the temperature was investigated on Rigaku Mini Flex 600 powder X-ray diffractometer using CuKa radiation with temperature control stage. A-C12 and T-C12 were weighed on a metal plate at a 1:1 molar ratio, and then, melted and mixed by heating to 145°C on a temperature controlled stage. In order to investigate the powder XRD pattern before appearance of the cold crystallization, the sample was cooled to 0°C and immediately placed in the XRD stage, then, the pattern at about 0°C was measured. To keep the constant temperature was difficult because the XRD apparatus did not have cooling function, therefore, a small amount of crystals might be present. The sample was heated on a heating stage equipped with Mini Flex 600, and the pattern after cold crystallization was measured at about 40°C. IR spectra were measured with a JASCO FT / IR-4200 spectrometer using a KBr plate.



**Fig. S1** DSC thermograms of (a) A-C12 and (b) T-C12 on  $2^{nd}$  heating process at scan rate of 5°C min<sup>-1</sup> and cooling process at scan rate of 10°C min<sup>-1</sup>. The measurement was carried out in the temperature range from 10 to 145°C.



**Fig. S2-1** Crossed Nicols POM images of A-C12 at (a, b) heating process and (c, d) cooling process. On heating process, a melting transition from (a) solid to (b) isotropic state was observed. On cooling process, a crystallization from (c) to (d) was observed.



**Fig. S2-2** Crossed Nicols POM images of T-C12 at (a, b) heating process and (c, d) cooling process. The phase transitions were similar to A-C12: melting and crystallization were observed.



**Fig. S3** Powder X-ray diffraction diagrams of at (a) ca. 0°C and (b) 40°C of AT-C12. (c) X-ray diffraction diagrams model calculated from single crystal structure.



**Fig. S4** ORTEP drawings of single co-crystal. Thermal ellipsoids are drawn at 50% probability level.

Table S1	Distances	and ar	ngles c	of the	hydrogen	bonds	in the	single	crystal

<b>D-H···</b> A	D····A (Å)	D-H•••A (°)
N5-H···O1	2.923	163.98
N7-H•••N3	2.867	175.03



(a) Watson-Crick base pair



(c) Hoogsteen base pair



(b) Reverse Watson-Crick base pair



(d) Reverse Hoogsteen base pair

**Fig. S5** Schematic images of the complementary hydrogen bonds: (a) Watson-Crick base pair, (b) Reverse Watson-Crick base pair, (c) Hoogsteen base pair, and (d) Reverse Hoogsteen base pair.

## Reference

1 Y. Tao, K. Satoh and M. Kamigaito, Macromol. Rapid Commun., 2011, 32, 226-232.