V-Shape Molecular Self-Adaption Triggered 2D Self-Assembled Polymorphism by Coadsorption of *n*-Tetradecane Solvent

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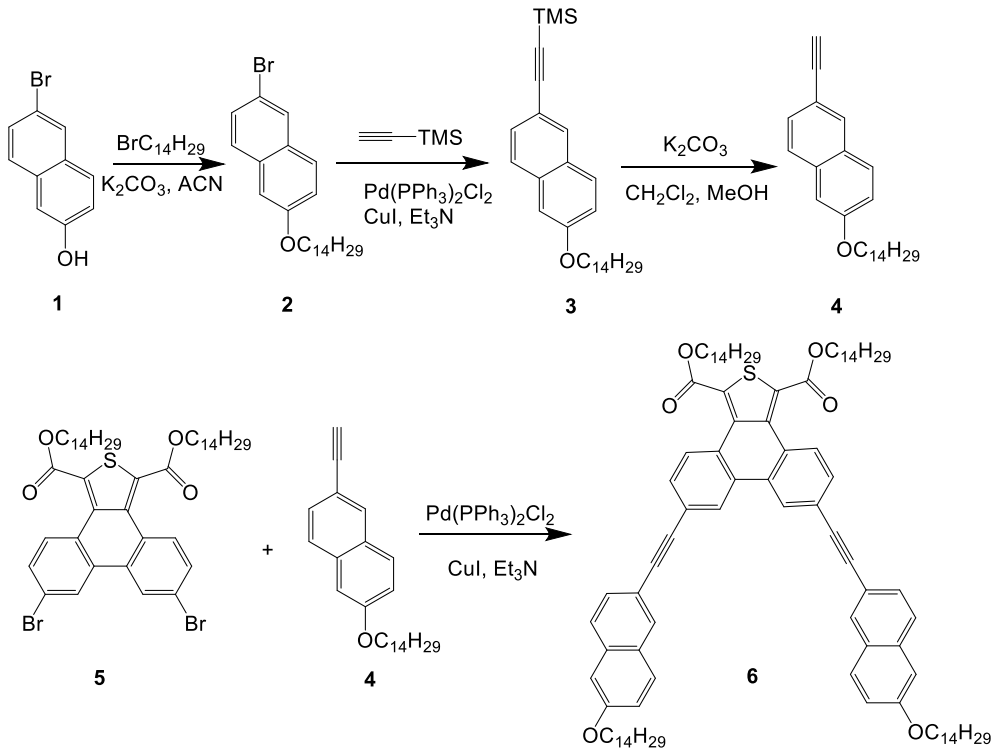
Synthesis and Characterization of TPTD-Nap

Scheme S1 for the synthesis of TPTD-Nap



2-Bromo-6-tetradecyloxy-naphthalene (compound 2)

A mixture of 6-bromo-2-naphthol (6.00 g, 26.9 mmol), 1-bromotetradecane (13.25 g, 48 mmol), potassium carbonate (6.60 g, 48 mmol) and acetonitrile (100 ml), and then, this was stirred at 85 °C overnight. The solvent was removed under reduced pressure, and the obtained residue was poured into water and extracted with dichloromethane, washed with water and dried over $MgSO_4$. After removing the solvent under reduced pressure and purifying by column chromatography eluted using hexane to yield compound 2 (9.94g, 88%).

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.93 (1H, m), 7.65 (1H, m), 7.60 (1H, m), 7.50 (1H, m), 7.17 (1H, m), 7.11 (1H, m), 4.08 (2H, m), 1.86 (2H, m), 1.51 (2H, m), 1.28 (20H, m), 0.90 (3H, m).

2-[2-(trimethylsilyl)ethynyl]- 6-hexadecyloxy-naphthalene (compound 3)

A mixture of 2-Bromo-6-tetradecyloxy-naphthalene (5.35 g, 12.8 mmol), trimethylsilylacetylene (2.2 ml, 16 mmol), $Pd(PPh_3)_2Cl_2$ (0.12 g, 0.16 mmol), triethylamine (33 ml), and CuI (0.03 g, 0.48 mmol) was stirred and at 80 °C for 24 h. After removal of the reaction solvent at reduced pressure, petroleum ether was added (100 mL) and the organic layer washed with aq. HCl 5% (50 mL). The organic phase was dried by $MgSO_4$, and petroleum ether was evaporated. The crude product (viscous liquid) was purified by column chromatography eluted using hexane to yield compound 3 (4.75 g, 85%).

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.74 (1H, m), 7.49 (1H, m), 7.44 (1H, m), 7.28 (1H, m), 6.96 (1H, m), 6.90 (1H, m), 3.89 (2H, m), 1.67 (2H, m), 1.32 (2H, m), 1.08 (20H, m), 0.72 (3H, m), 0.10 (9H, m).

2-ethynyl-6-tetradecyloxy-naphthalene (compound 4)

A mixture of 2-[2-(trimethylsilyl)ethynyl]- 6-hexadecyloxy-naphthalene (2.4 g 5.5 mmol), potassium carbonate (3.9 g, 28 mmol), THF (20 ml), and MeOH (20 ml) was stirred at room temperature for 3 h. The solvent was removed under reduced pressure, and the obtained residue was extracted with ether, washed with water and dried over $MgSO_4$. The solvent was removed to yield compound 4 (1.38 g, 69%).

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.74 (1H, m), 7.49 (1H, m), 7.44 (1H, m), 7.28 (1H, m), 6.96 (1H, m), 6.90 (1H, m), 3.89 (2H, m), 1.67 (2H, m), 1.32 (2H, m), 1.08 (20H, m), 0.72 (3H, m), 0.10 (9H, m).

Ditetradecyl 6,9-bis((6-(tetradecyloxy)naphthalen-2-yl)ethynyl)phenanthro[9,10-c]thiophene-1,3 dicar-boxylate (TPTD-Nap compound 6)

A mixture of 6,9-TPTD (**compound 5**)[1] 8.35 g (9.6 mmol), 2-ethynyl-6-hexadecyloxy-naphthalene (**compound 4**) 7.0 g (19.2 mmol), $Pd(PPh_3)_2Cl_2$ (0.35 g, 0.48 mmol), triethylamine (33 ml), and CuI (91 mg, 0.48 mmol) was stirred and at 80 °C for 24 h. After removal of the reaction solvent at reduced pressure, petroleum ether was added (100 mL) and the organic layer washed with aq. HCl 5% (50 mL). The organic phase was dried by $MgSO_4$, and petroleum ether was evaporated. The crude product was purified by column chromatography eluted using hexane to yield compound 6 (7.32 g, 53%).

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 8.81 (2H, m), 8.61 (2H, m), 8.01 (2H, m), 7.67 (2H, m), 7.64 (2H, m), 7.62 (2H, m), 7.57 (2H, m), 7.12 (2H, m), 7.06 (2H, m), 4.39 (4H, m), 4.02 (4H, m), 1.78 (8H, m), 1.43 (8H, m), 1.19 (80H, m), 0.81 (12H, m).

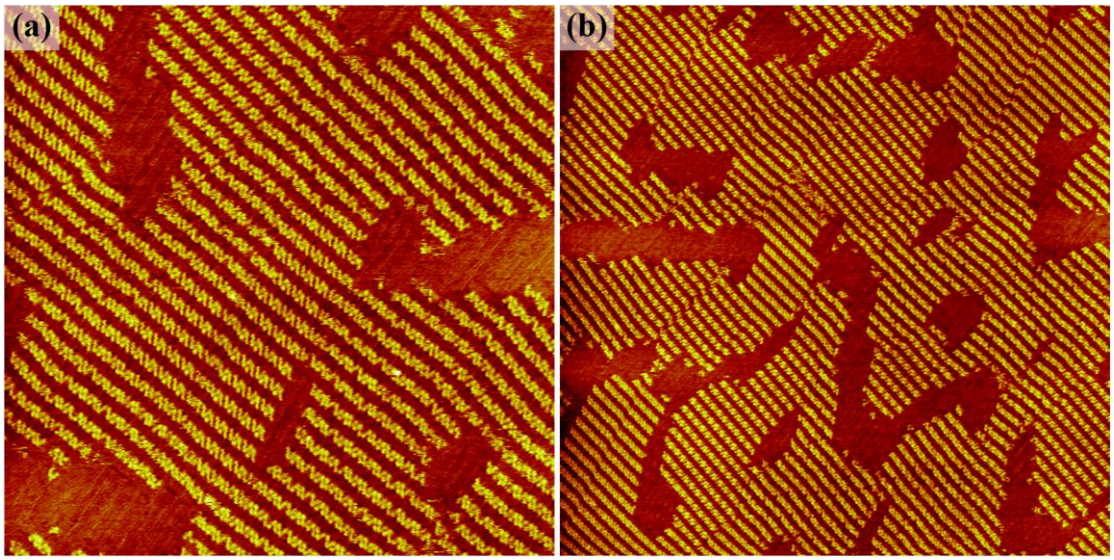


Figure S1. Large-scale STM images (a) (100 × 100 nm^2) and (b) (200 × 200 nm^2) of TPTD-Nap self-assembly at the tridecane/HOPG interface (c = 6.2 × 10^{-5} M). Scanning parameters: V_{bias} = 592 mV and I_t = 458 pA.

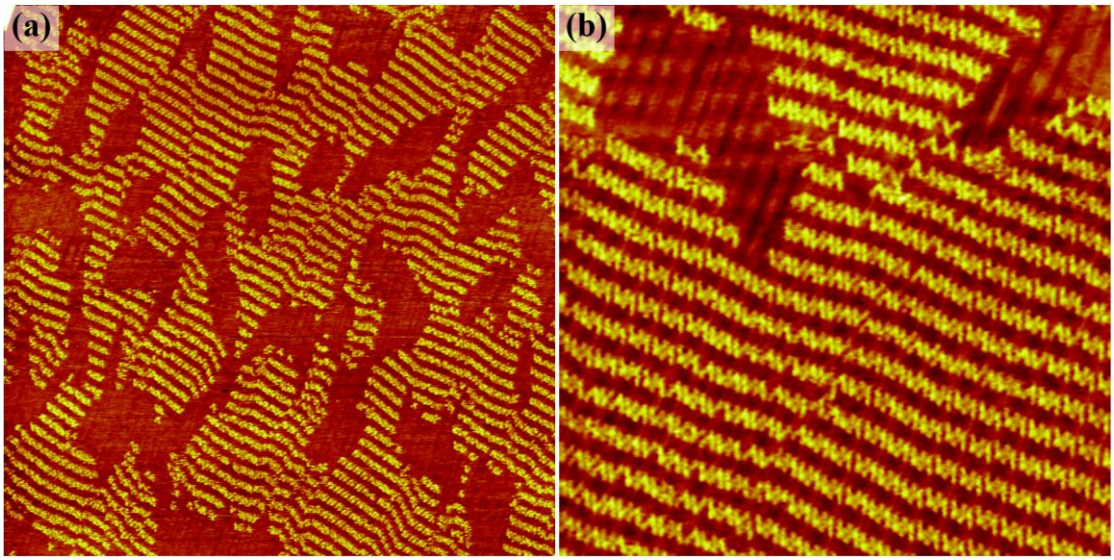


Figure S2. Large-scale STM images (a) (200 × 200 nm^2) and (b) (60 × 60 nm^2) of TPTD-Nap self-assembly at the hexadecane/HOPG interface (c = 3.6 × 10^{-5} M). Scanning parameters: V_{bias} = 585 mV and I_t = 490 pA.

Reference

1. Zha, B.; Miao, X.; Liu, P.; Wu, Y.; Deng, W. Concentration Dependent Halogen-Bond Density in the 2D Self-Assembly of a Thienophenanthrene Derivative at the Aliphatic Acid/Graphite Interface. *Chem. Commun.* **2014**, *50*, 9003-9006.