SUPPORTING INFORMATION

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Strain-Sensitive On-Surface Ladderization via Non-Dehydrogenative Heterocyclization

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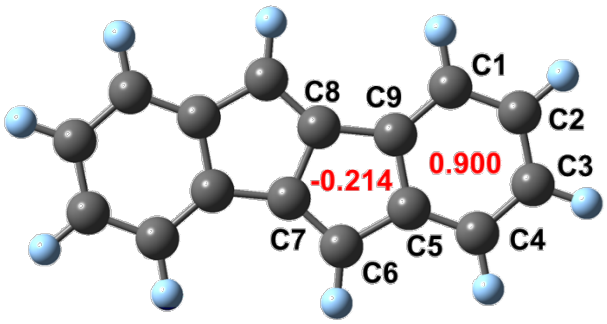
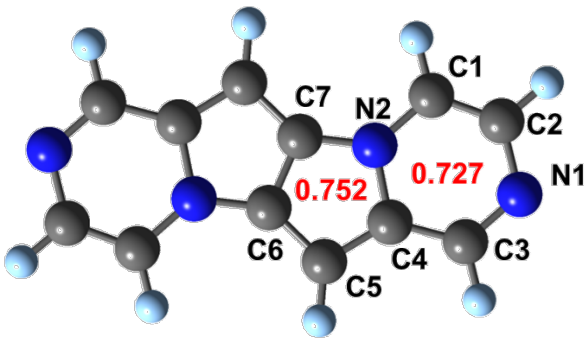
STM/AFM measurement: All the experiments were conducted with home-made scanning tunneling microscopy (STM) system, operating at 4.3 K under an ultra-high vacuum environment. Clean Ag(111) single crystal substrates were prepared by cyclic Ar^+ sputtering for 5 min and annealing at 420 °C for 10 min. 11,11,12,12-Tetrabromo-1,4,5,8,tetraaza-9,10-anthraquinodimethane and its derivative molecule were deposited on clean Ag(111) surfaces kept at different temperatures from crucibles of a Knudsen cell, heated at approximately 100 °C. For bond-resolved STM imaging, the apex of the chemically-etched tungsten tip was terminated with a CO molecule by picking up from the surface.[1] The DC sample bias voltage was set close to zero voltage. The modulation amplitude was 7 mV_{rms} and the frequency was 510 Hz.

(1) Bartels, L.; Meyer, G.; Rieder, K.-H. Appl. Phys. Lett. 1997, 71, 213−215.

(a)



(b)



(a) Dibenzopentalene		(b) Pyrazinopyrrolopyrrolopyrazine	
	Bond length [Å]		Bond length [Å]
C1-C2	1.406	C1-C2	1.361
C2-C3	1.394	C2-N1	1.377
C3-C4	1.405	N1-C3	1.311
C4-C5	1.388	C3-C4	1.420
C5-C6	1.477	C4-C5	1.396
C6-C7	1.357	C5-C6	1.410
C7-C8	1.472	C6-C7	1.414
C8-C9	1.465	C7-N2	1.372
C9-C1	1.387	N2-C1	1.377
C5-C9	1.429	C4-N2	1.426

Figure S1. Local aromatic character described by HOMA (harmonic oscillator model of aromaticity) values[2] for (a) dibenzopenthalene and (b) pyrazinopyrrolopyrrolopyrazine. Optimized structures calculated by DFT methods (B3LYP/6-31G(d)) were used to estimate the HOMA values.

(2) T. M. Krygowski, *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70-78.

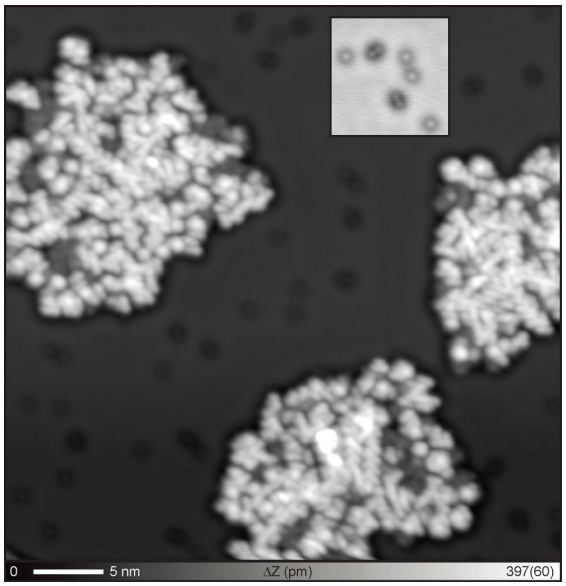


Figure S2. As deposited 1 on Ag(111) kept below -80 °C. No well-ordered molecular assembled structure was seen. Inset shows the same area with a narrow contrast, in which the dissociated bromine atoms are seen. Although the substrate temperature was kept below room temperature, the C-Br bond was cleaved on the surface. Measurement parameters: *V* = 300 mV and *I* = 10 pA.

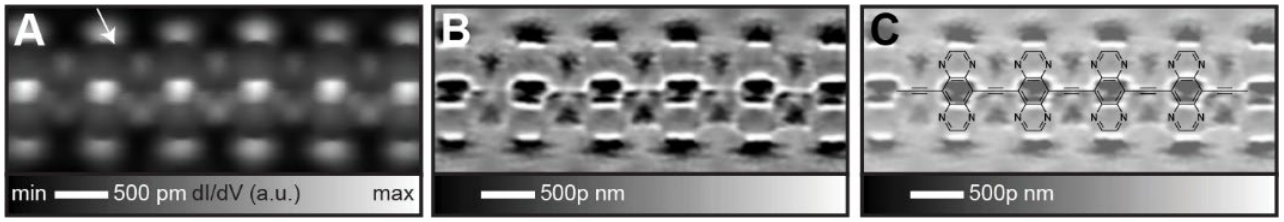


Figure S3. Bond-resolved STM image of the linear oligomer taken with a CO terminated tip. (a) dI/dV map, (b) the corresponding Laplace filtered image superimposed the chemical structure in (c).

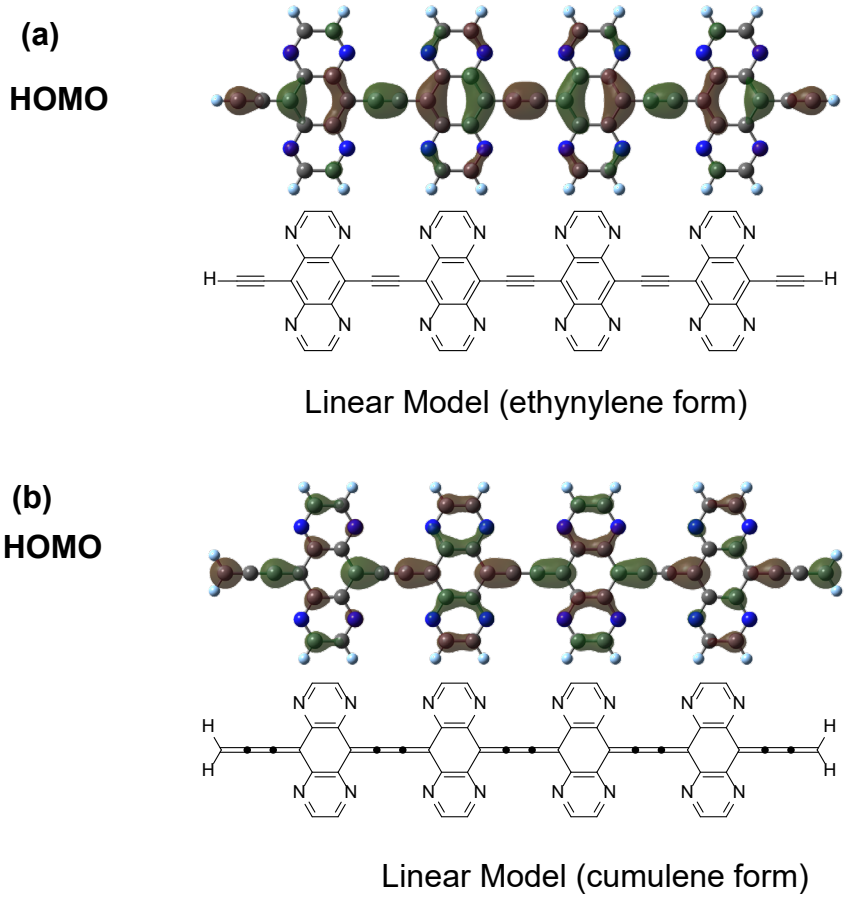


Figure S4. HOMO of tetramer models for the linear oligomer 2. (a) ethynylene form (b) cumulene form calculated by DFT method (B3LYP-6-31G(d)).

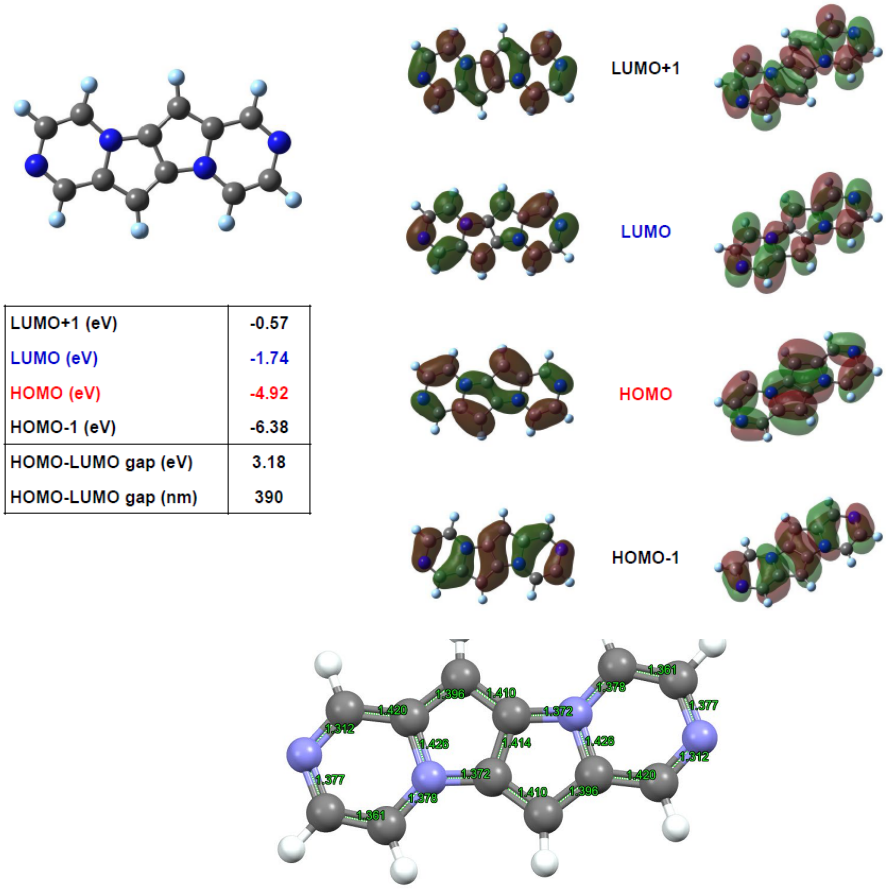


Figure S5. DFT calculation: Calculation of the new aromatic skeleton of pyrazino[1'',2'':1',5']pyrrolo[2',3':4,5]pyrrolo[1,2-a]pyrazine was conducted at B3LYP/6-31g(d) level[3].

(3) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li,H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi,J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi,C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 16 (Revision A.03), Gaussian, Inc., Wallingford CT, **2016**.

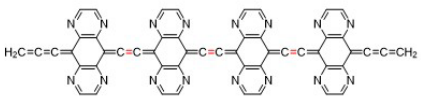
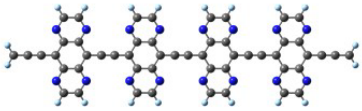
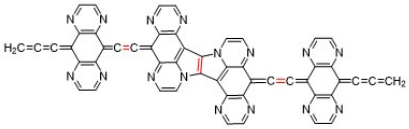
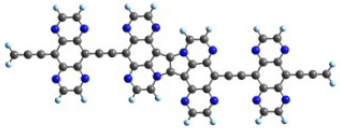
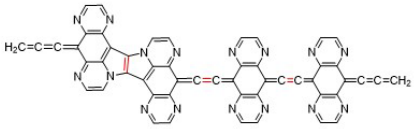
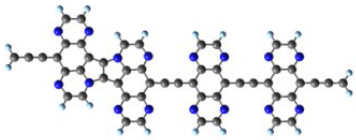
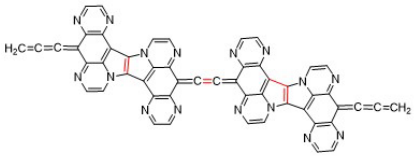
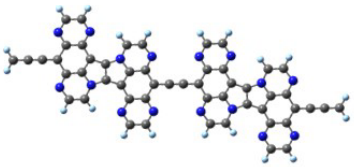
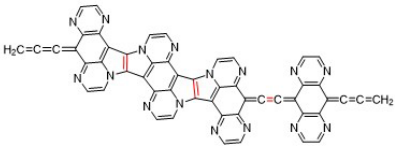
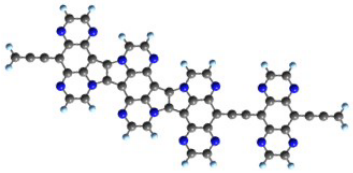
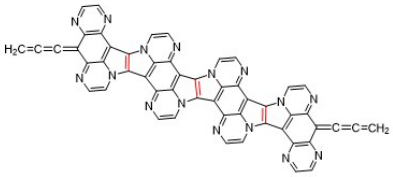
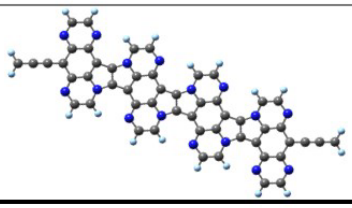
	Chemical structures	Optimized structures	Relative energy [kcal/mol]
I			0
II			-39.7
III			-40.2
IV			-80.5
V			-82.9
VI			-126.1

Figure S6. Comparisons of gas-phase energy for several model compounds including pyrazinepyrrolopyrrolopyrazine units as well as its condensed forms. Cyclization of (I) to generate one pyrazinepyrrolopyrrolopyrazine unit causes stabilization by ca. 40 kcal/mol as in (II) and (III). Further cyclization with forming two pyrazinepyrrolopyrrolopyrazine units is marginally favored for fusing the unit as in (V) than in the dimeric form (IV).

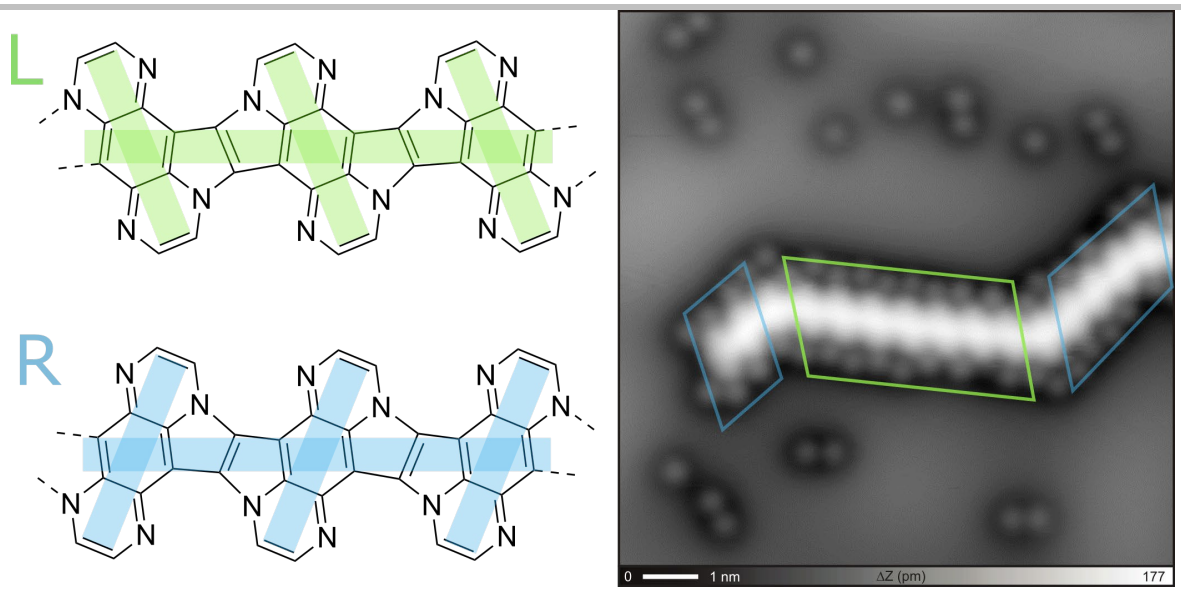


Figure S7. Structure and topography illustration of two chiral *trans* isomers. Left panel is showing the chemical structures, naming intuitively after their distinction where the central moieties can tilt left (L-type *trans* isomer, marked with green) or right (R-type *trans* isomer, marked with blue) with respect to the molecular backbone. Right panel is a STM topography of these *trans*-oligomers, having two kink sites. Measurement parameters: V = 10 mV and I = 500 pA.

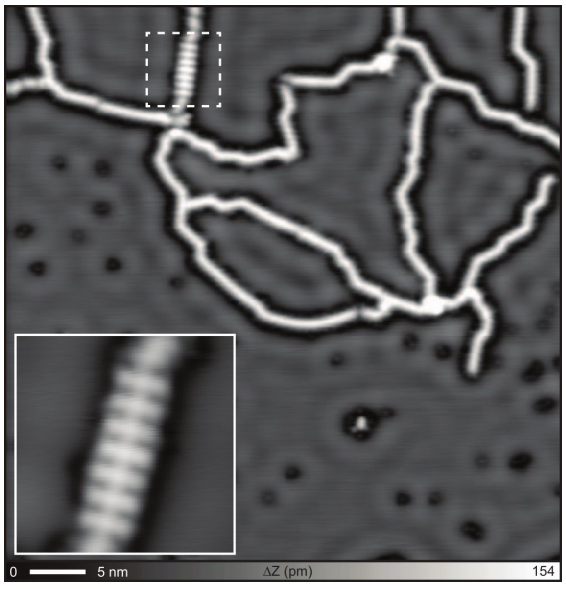


Figure S8. **Remaining linear oligomer after annealing at 200 °C**. Large scale STM topography taken after the precursor molecules deposition onto Ag (111) kept at RT and followed by post annealing to 200 °C. The surface still has remnants of linear oligomers **2**. Inset shows the close-up view of the area indicated by dotted square. Measurement parameters: V=100 mV and I= 100pA.

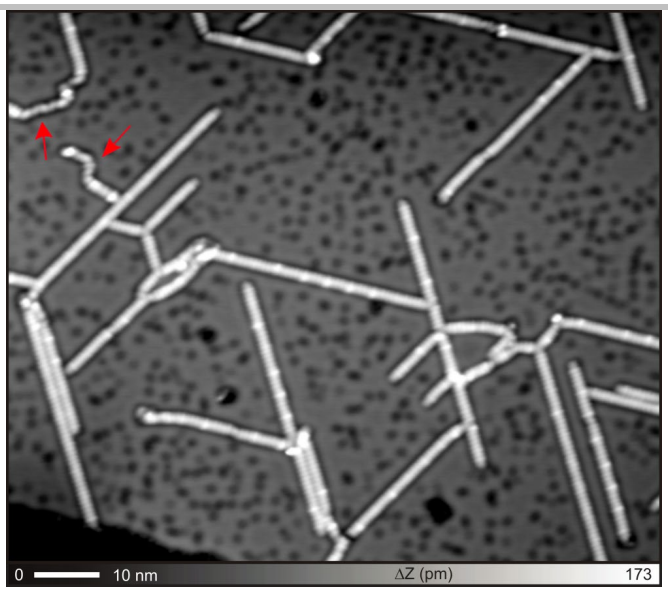


Figure S9. **Large-scale STM topography after deposition of precursor molecule 1 at Ag(111) kept at 40°C.** Red arrows indicates small portion of α oligomer which are co-existing with the prevailing linear oligomer **2**. Measurement parameters: V = 200 mV and I = 5 pA.

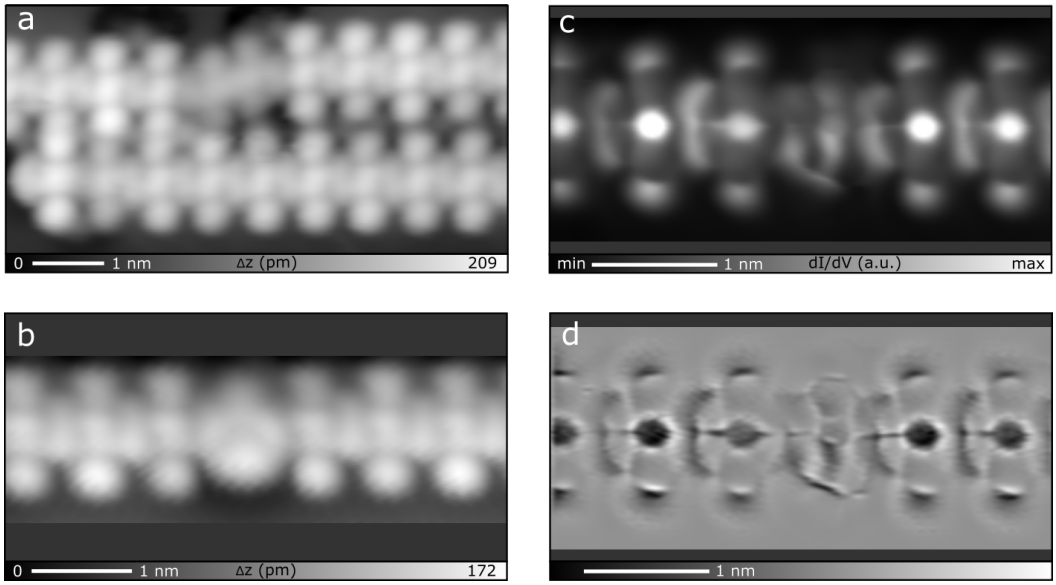


Figure S10. Initial transformation to the ladder oligomer by cyclization. (a) STM topography taken just after depositing **1** on Ag(111) kept at 80 °C. One dimer unit was formed in the upper oligomer. By this dimerization, longitudinal axes of the linear oligomer were shifted. (b-d) STM topography, corresponding constant height d*I*/d*V* image and the Laplace filtered image, showing the intermediate state in the dimerization in **2**. Measurement parameters: *V* = 100 mV and *I* = 80 pA in (a), and *V* = 100 mV and *I* = 60 pA in (b).

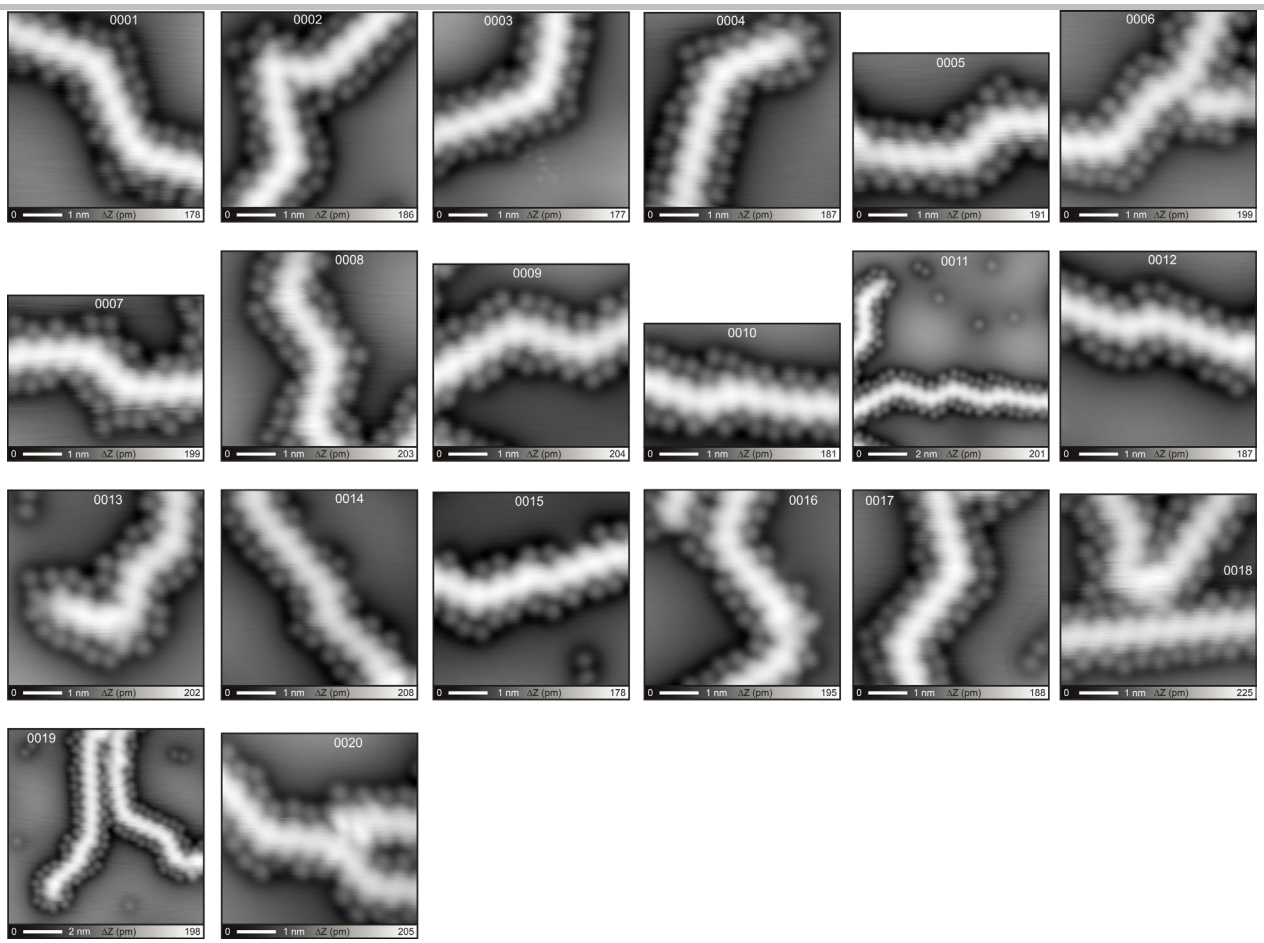


Figure S11. Close-up views of STM topographies around the kink site. Molecule **1** was deposited on substrate kept at 200 °C.

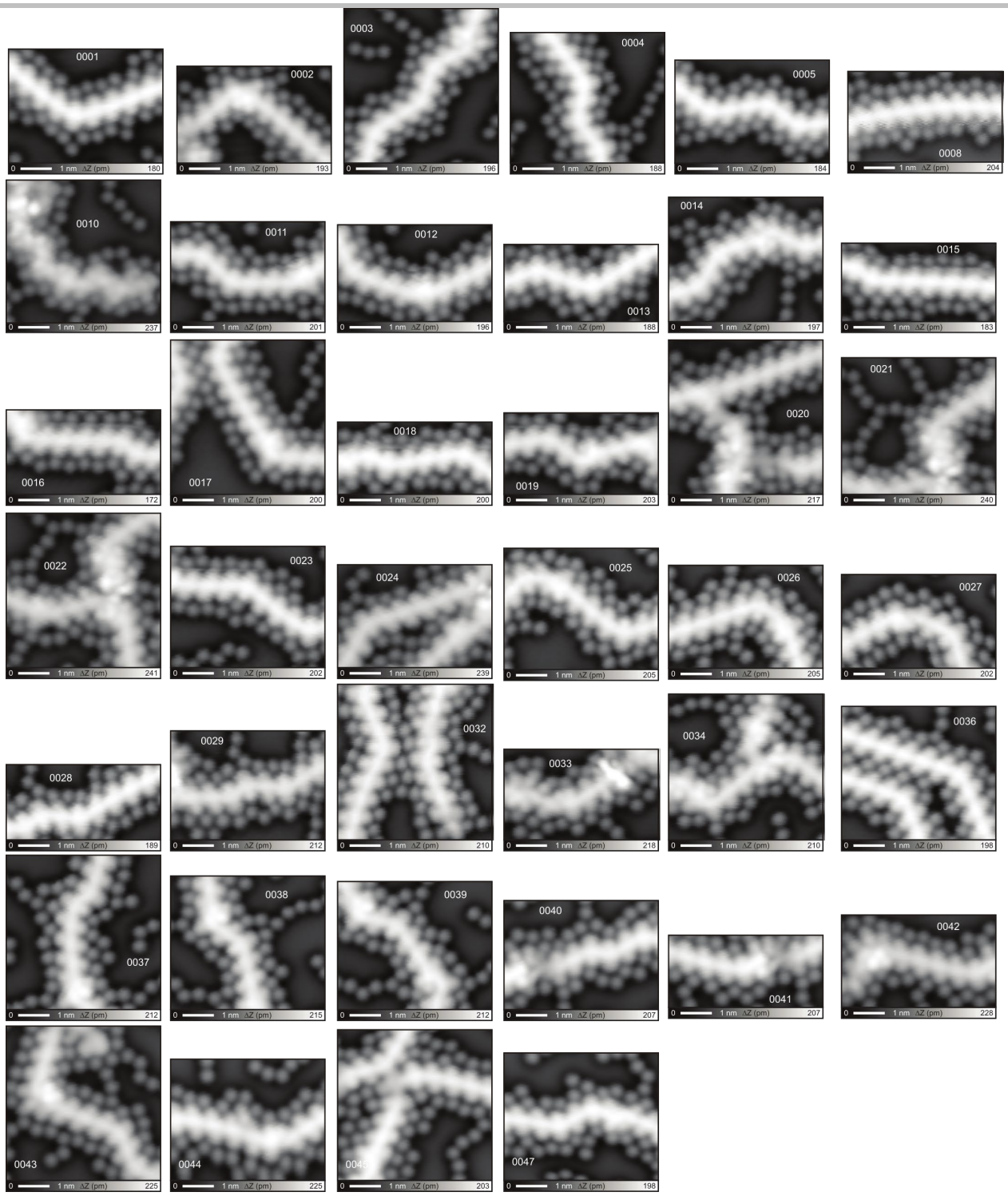


Figure S12. Close-up views of STM topographies around the kink site. Molecule **1** was deposited on substrate kept at 250 °C.

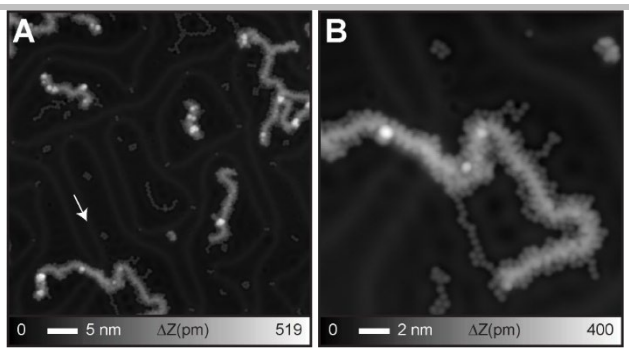


Figure S13. Formation of the ladder oligomers on Au(111). (a) Large-scale STM topography taken after annealing at 215 °C. (b) Close-up view around the area indicated by an arrow in (a). In contrast to the formation of the ladder oligomers on Ag(111), more kink sites were formed on Au(111). This result suggests that the monomer diffuses along the herringbone structure and consequently the linear oligomer (not shown here) would have formed along the herringbone structure, similar to the synthesis of polyfluorene observed by Lafferentz *et al*.[4] Measurement parameters: V = 200 mV and I = 10 pA in (a) and (b).

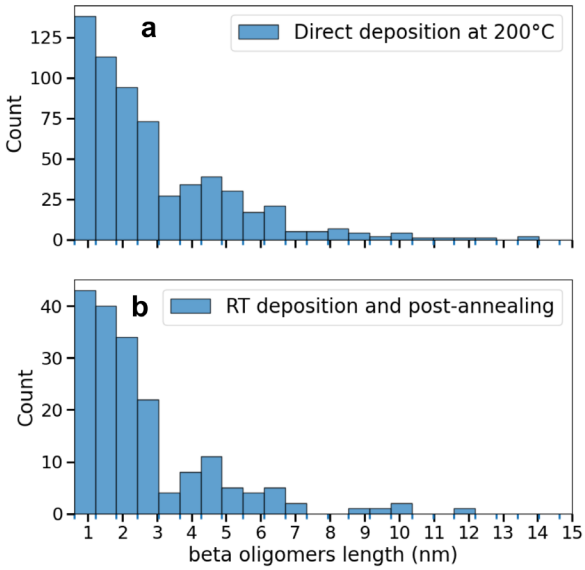


Figure S14. **Histogram of length distributions compared under different preparation conditions.** (a) Precursor molecule **1** deposition on hot substrate held directly at 200°C. The distribution spreads wide ranging up to 14nm. (b) Annealing at 200 °C after oligomer **2** was formed. This result in length concentrated more towards to shorter end as well as affecting a maximum length.

(4)L. Lafferentz, F. Ample, H. Yu, S. Hecht, C. Joachim, L. Grill1, Science **2009**, *323*, 1193−1197.

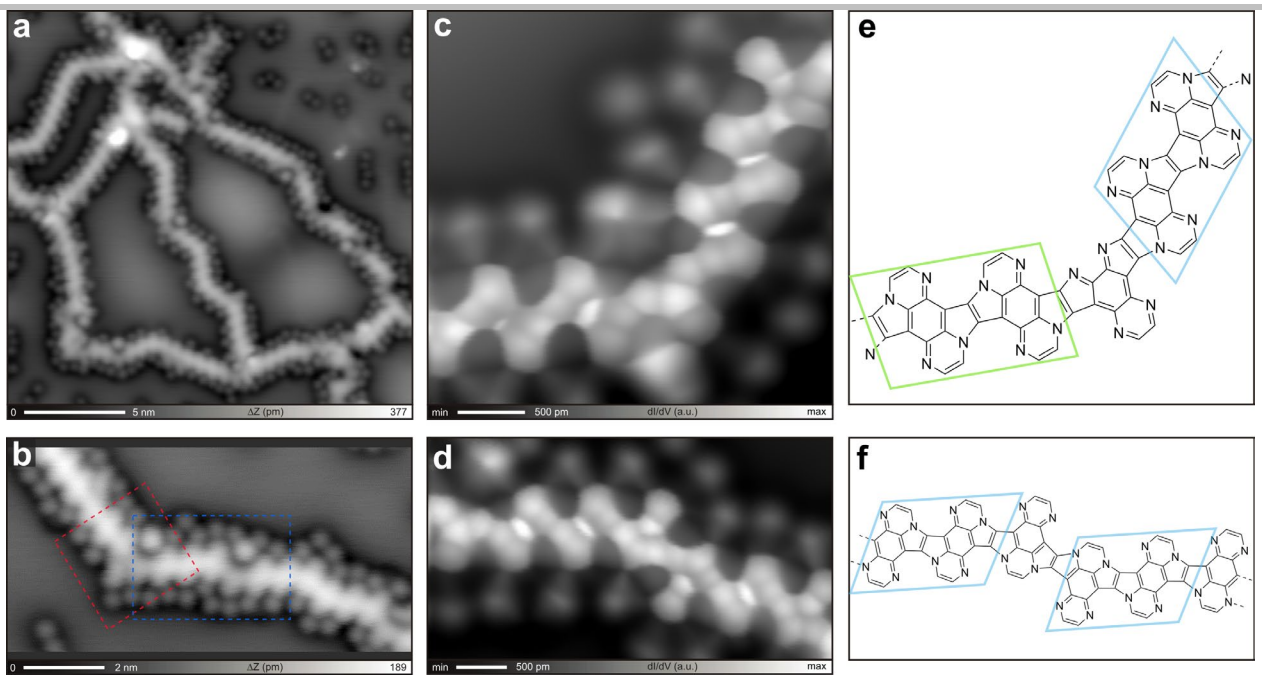


Figure S15. C-N bond cleavage after further annealing. (a) Large-scale STM topography of the Ag(111) surface after annealing at 400 °C. (b) Small-scale topography around a kink site.(c) Bond-resolved images taken around the kink sites, indicated by a red square and (c) a blue rectangle in (b). (e) Chemical structures of image (c). The kink site locates between L-type and R-type *trans* oligomers. The missing ring in the cis isomer moiety indicates the C-N bond cleavage. (f) Chemical structure of image (d). No C-N bond cleavage was seen in the cis unit between the *trans* oligomer with the same chirality. Measurement parameters: V = 10 mV and I = 100 pA in (a), and V = 180 mV and I = 20 pA in (b).

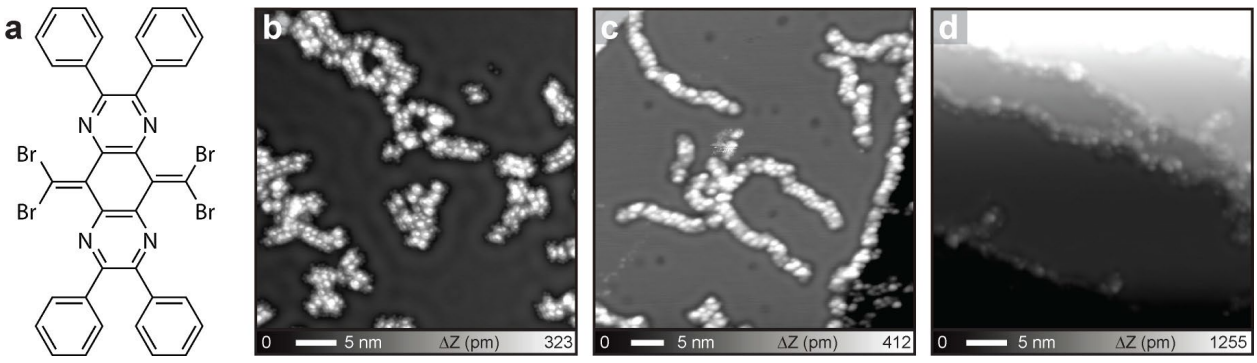


Figure S16. (a) Chemical structure of **1** derivative with the extra four phenyl groups **4**. (b) STM topography of as deposited of **4** on Ag(111) kept at RT. Scattered cluster formation was seen. (c) STM topographies taken after annealing at 130 °C and (d) at 220 °C. No well-structured polymer was synthesized. Measurement parameters: *V*= 100 mV and *I* = 10 pA in (b), and *V*= 200 mV and *I* = 10 pA in (c, d).