Supplementary Information

Revealing the high-resolution structures and electronic properties of ZnTPP and its derivatives formed by thermally induced cyclodehydrogenation on Au(111)

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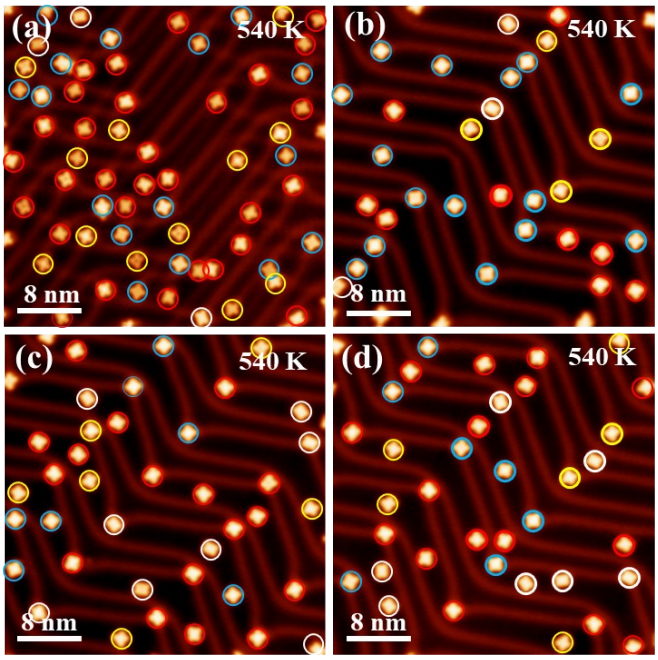

Fig. S1 (a-d) Large-scale STM images of four cyclodehydrogenation products of ZnTPP molecules on Au(111) surface after annealing at 540 K, which are used for quantity statistics of four products. Four products are marked by circles with different colour: **2** (red); **3** (blue); **4** (yellow); **5** (white). Tunnelling parameters: (a-e) V_b = -1 V, and I_t = 20 pA.

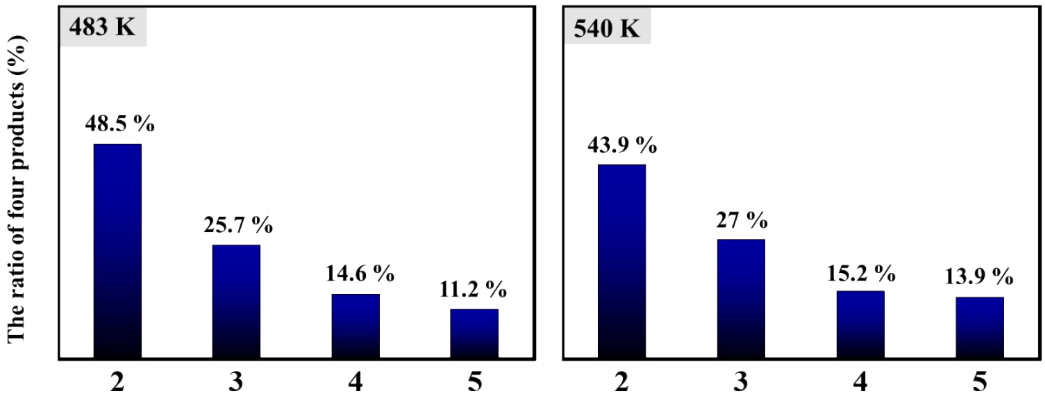

Fig. S2 The ratios of four cyclodehydrogenation products at two different annealing temperatures (483 K, 540 K).

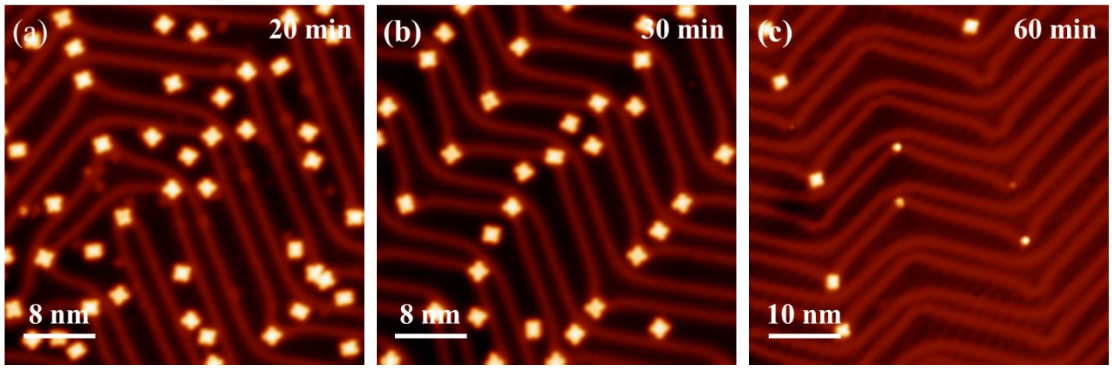

Fig. S3 (a-c) Large-scale STM images of four cyclodehydrogenation products of ZnTPP molecules on Au(111) surface after annealing for different times for 540 K , Tunnelling parameters: (a-c) V_b = -0.5 V, and I_t = 100 pA.

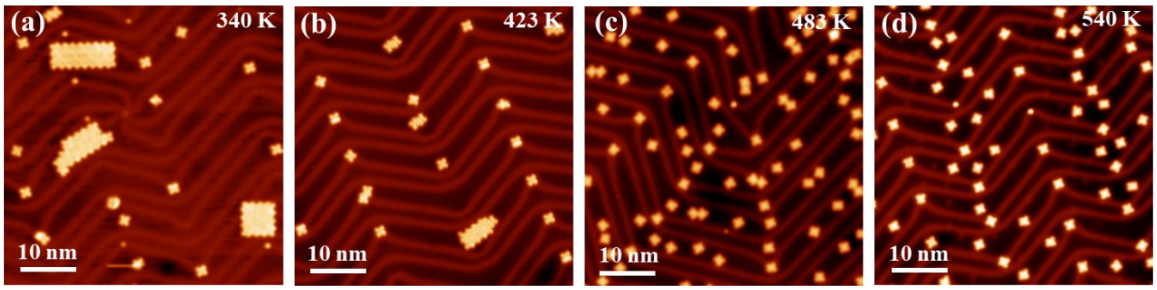

Fig. S4 (a-e) STM images of ZnTPP and four dehydrogenated products existing on Au(111) surface after annealing at varied temperatures (340 K, 423 K, 483 K, 540 K). Tunnelling parameters: (a-e) V_b = -1 V, and I_t = 20 pA.

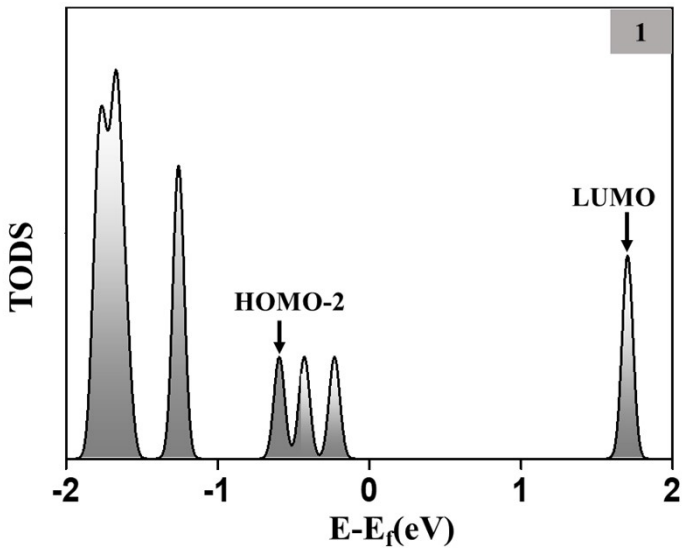

Fig. S5 DFT calculated total density of state of ZnTPP monomer, the peaks at the similar energy in d*I*/d*V* spectra (**Fig. 5a**) are marked by the corresponding molecular frontier orbitals (HOMO-2 and LUMO).

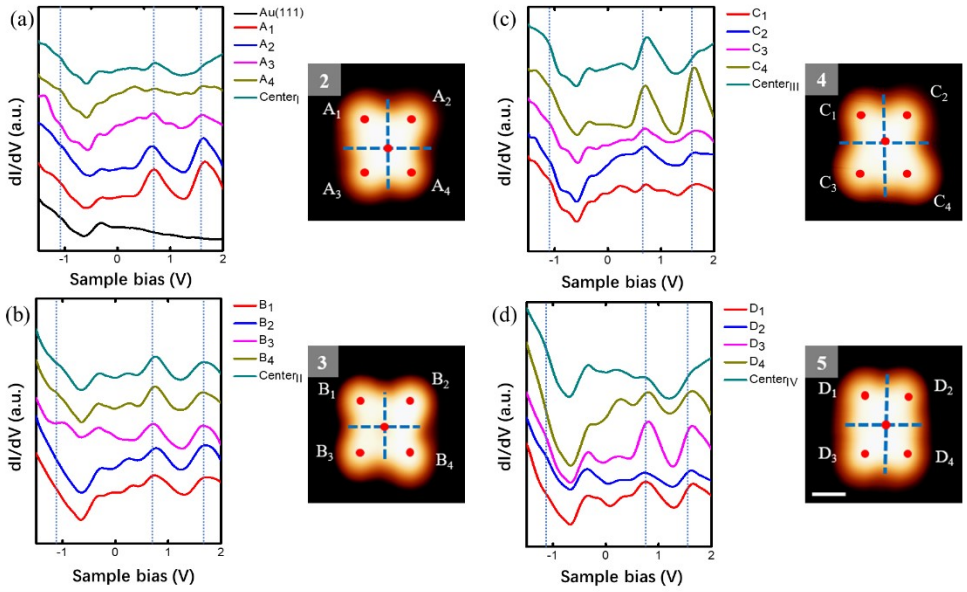

Fig. S6 (a-d) d*I*/d*V* spectra obtained on four planarized ZnTPP cyclodehydrogenation derivatives at the positions indicated by the red dots, and a reference spectrum acquired on the atomic clean Au(111) surface (grey line). The vertical blue dashed lines mark the energy positions of molecular frontier orbitals of four products. Tunneling parameters for STM image: V_b = 0.1 V, and I_t = 200 pA. All scale bars correspond to 6 Å.

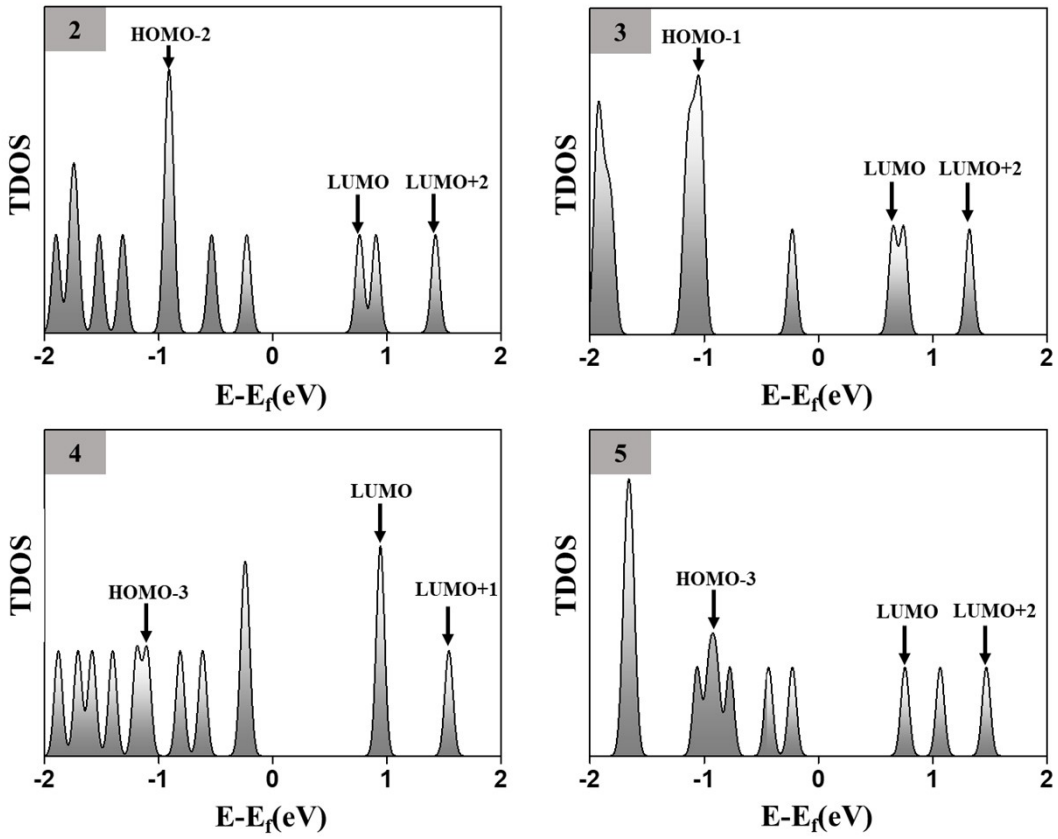

Fig. S7 DFT calculated total density of states of four cyclodehydrogenation derivatives. The peaks observing at the similar energy of the peaks in STS (**Fig. S6**) are marked by the corresponding molecular frontier orbitals.