

## Supporting Information

# Deep molecular orbital driven high-temperature hydrogen tautomerization switching

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## Bell-Limbach models

To provide more theoretical insight into the tautomerization process, we then introduce Bell-Limbach tunneling model<sup>1-2</sup> to give a qualitative discussion on the mechanisms of tautomerization in our adsorption system below.

Bell-Limbach (BL) tunneling model was developed to include the tunneling effect of nuclei when across an energy barrier. The solution of BL tunneling model involves solving the one-dimensional Schrodinger equation. To simplify the discussion (not influence our final conclusion), here based on WKB theory, the simplified BL formula for the transition rate can be expressed as:

$$k_{QM} = A \exp(-E_d/K_B T) \int_0^{\infty} \frac{G(W)}{RT} \exp((E_d - W)/RT) dW \quad (1)$$

Where  $k$  is hydrogen transition rate,  $E_d$  is the transition barrier height,  $K_B$  is Boltzmann constant,  $T$  is temperature,  $G(W)$  is probability for transition through the barrier, based on WKB theory, which can be deduced as:

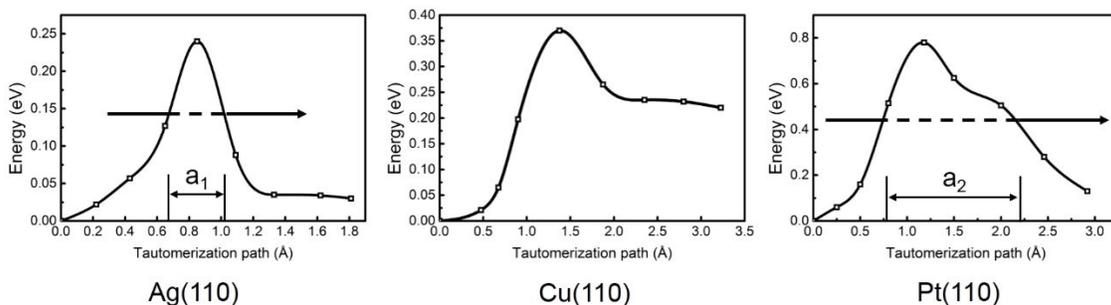
$$G(W) = [1 + \exp(E_d - W)/\hbar v_t]^{-1} \quad (2)$$

Where  $v_t$  called imaginary tunneling frequency with  $v_t \propto \sqrt{E_0/a}$  ( $a$  is width of the barrier and  $E_0$  is value of energy at half-width of the barrier).

Compared with Arrhenius formula  $k_{classic} = J_0 \exp(-E_d/k_B T)$ , we can obtain the ratio between quantum and classic contribution to the transition rate:

$$Q = \exp(E_d/k_B T) / (k_B T) \int_0^{\infty} \exp(-W/k_B T) G(W) dW \quad (3)$$

Based on above formula, the mechanisms of hydrogen transfer can be discussed with the following condition: a) at high temperature, the vibration energy of hydrogen is high enough to overcome the barrier, i.e.,  $G(W)=1$ , then we get  $Q \propto \exp(E_d/k_B T)$ . At high temperature limit ( $W > E_d$ ),  $Q$  reduces to unity, indicating thermally dominated transition rate; b) at intermediate temperature ( $W < E_d$ ), we obtain  $Q \propto \exp(E_d/k_B T) \exp[(E_d - W)a/\sqrt{E_d/2}]$ , which indicating that the contribution from tunneling effect decreases exponentially with the increase of barrier width and height.



Caption: Minimum energy paths (MEPs) of porphycene on Ag, Cu and Pt(110) surfaces.

$a_1$  and  $a_2$  is the width of the barrier for Ag(110) and Pt(110).

In figure, we calculated the transition barriers of porphycene on Ag(110), Cu(110) and Pt(110) along the transition paths. The barrier width and height is smallest on Ag(110), so the hydrogen can easily tunneling across the barrier with small size of decay. However, for the transfer process on Cu(110), since there is platform at trans side, the barrier width is significantly larger than that on Ag(110), the tautomerization process is mainly governed with thermal mechanism, as supported from experimental observation. In our system, because the barrier height and height are significantly larger than that on Ag(110), similar as Cu(110) system, it is safely concluded that for porphycene/Pt(110) the tautomerization is driven by thermally vibrations of the molecule.

In addition, experimental work also supports our deduction discussed above. For example, for porphycene/Cu(110) system, the tautomerization process can be induced via inelastic electron tunneling at 5 K. However, when the temperature is at 78K, the tautomerization is neither induced by the tunneling electrons nor the electric field in the STM junction, and thus only a thermal process is involved<sup>3</sup>. This phenomenon also occurs on the Cu(111) surface<sup>4</sup>. In the low temperature, it has the same tautomerization rate, but at high temperatures, which is consistent with the Arrhenius formula. For our system, we are considering hydrogen tautomerization switching at high temperature. Therefore, it is reasonable to use the Arrhenius equation to estimate the switching temperature.

Figure S1. Illustration of the high-symmetry adsorption sites for porphycene on the Cu(110) surface. There are four possible adsorption sites (top, bridge, fcc and hcp for porphycene on the Cu(110) surface. At each site, porphycene has two orientations, *i.e.*,  $0^\circ$  and  $90^\circ$ . The adsorption sites on other metal faces are the same as Cu(110) surface.

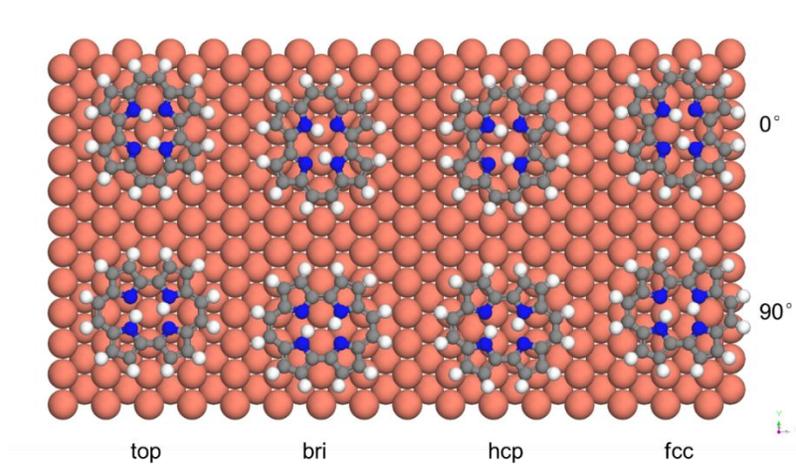


Figure S2. Optimized structures of porphycene on Ag, Cu, Pd, Pt(110) surfaces.

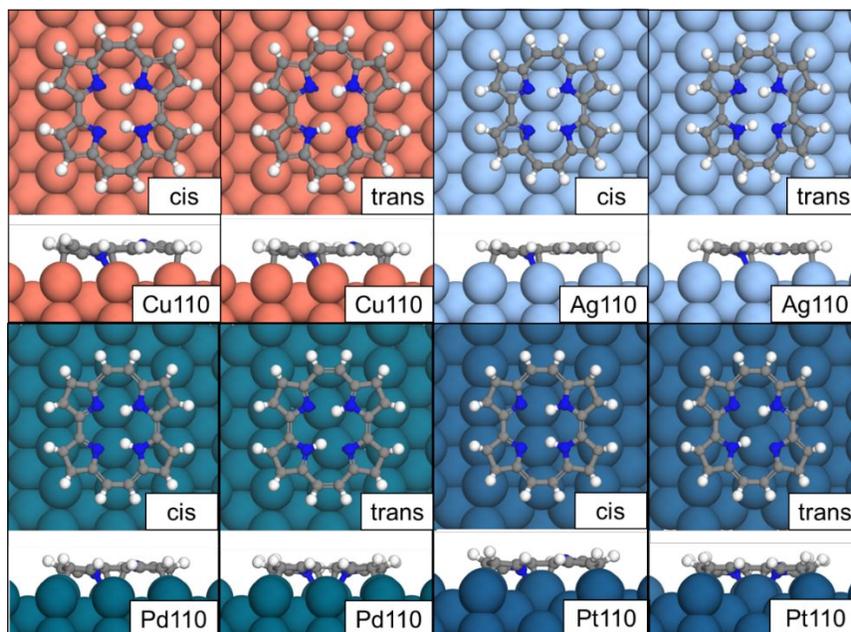


Table S1. Tautomerization barrier (in eV) of porphycene on the Pd(110) and Pt(110) surfaces. The transition structures for the stepwise and concerted are denoted by TS<sub>SP</sub> and TS<sub>CP</sub>, respectively.

	Pd(110)	Pt(110)
TS <sub>SP</sub>	0.63	0.78
TS <sub>CP</sub>	1.58	2.03

Table S2. Vibrational free energy difference between *cis* and transition states on Ag, Cu, Pd, Pt(110) surfaces as a function of temperature.

Surface	0 K	50 K	100 K	150 K	200 K	250 K	300 K
Ag(110)	-0.131	-0.133	-0.135	-0.138	-0.140	-0.141	-0.143
Cu(110)	-0.134	-0.135	-0.137	-0.139	-0.140	-0.142	-0.143
Pd(110)	-0.151	-0.152	-0.155	-0.159	-0.162	-0.165	-0.168
Pt(110)	-0.152	-0.152	-0.151	-0.149	-0.147	-0.144	-0.141

Figure S3. Molecular orbital density of states (MODOS) projected on the free porphycene HOMO-2, HOMO-1, HOMO, and LUMO orbitals for porphycene on the Ag, Cu, Pd(110) surfaces.

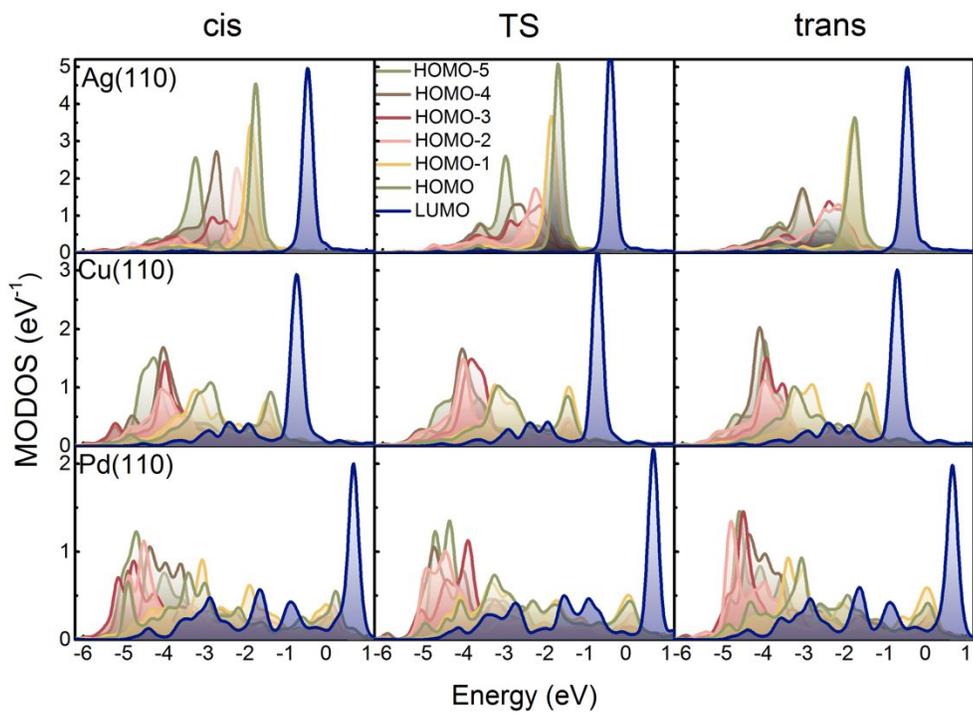


Figure S4. Plots of the barrier energy against the difference of the charge transfer between different states from (a) HOMO, (b) HOMO-1, (c) HOMO-2, (d) HOMO-3, (e) HOMO-4, and (f) HOMO-5 orbitals on Ag, Cu, Pd, Pt(110) surfaces.

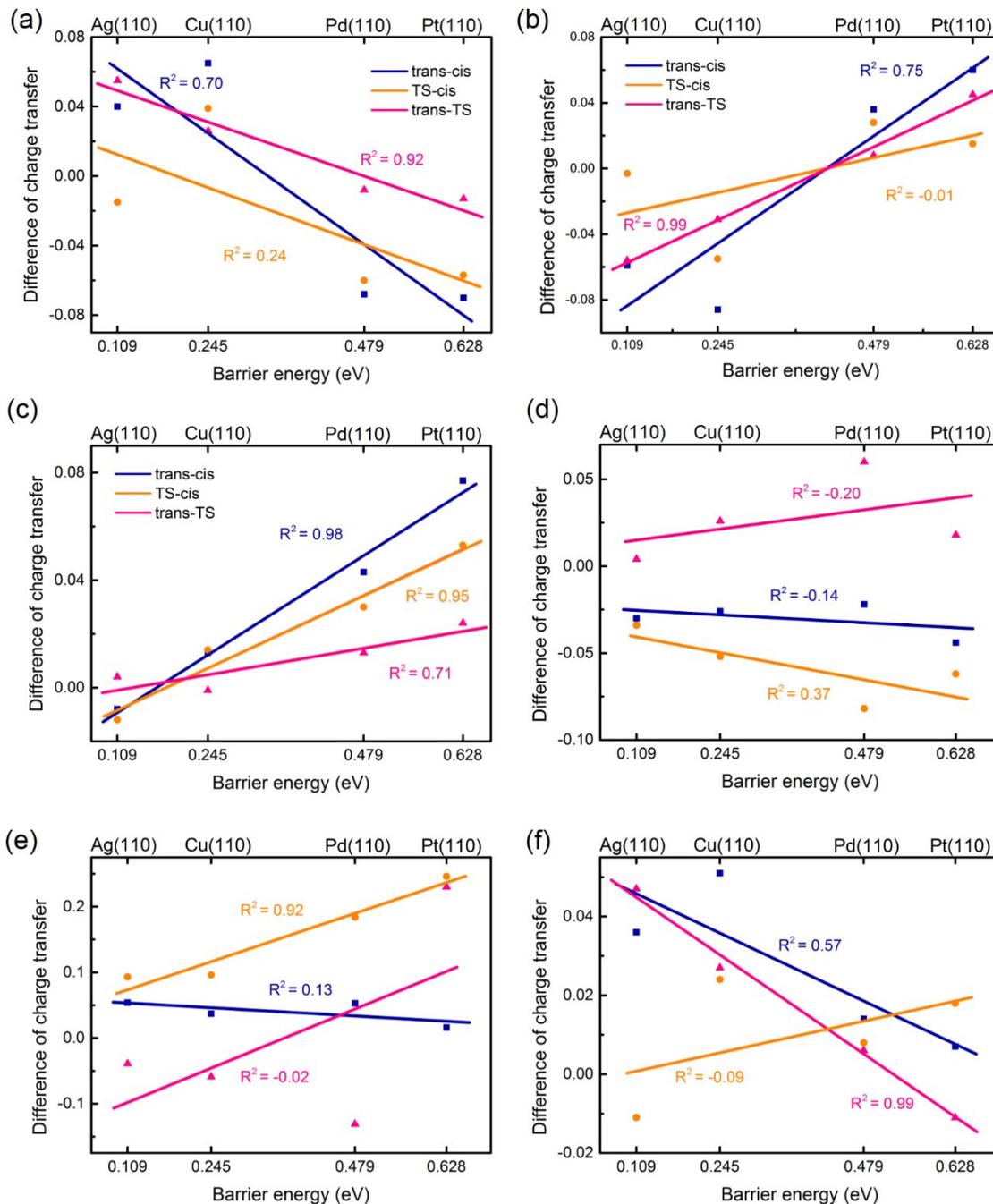


Figure S5. Calculated  $I$ - $V$  curves for *cis*-1-porphycene, *trans*-porphycene and *cis*-2-porphycene on the Pt(110) surface.

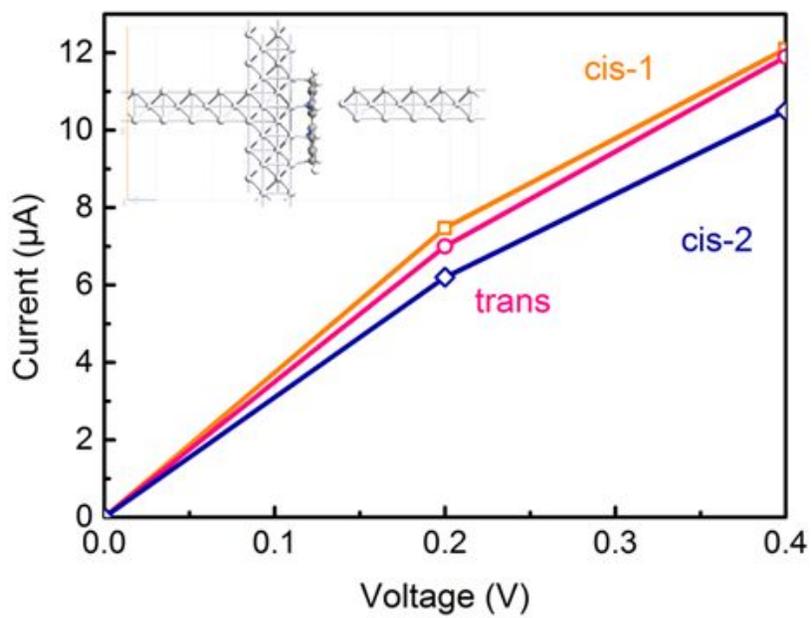


Table S3. Charge transfer of HOMO–5, HOMO–4, HOMO–3, HOMO–2, HOMO–1, HOMO and LUMO orbitals in of *cis*, TS and *trans* states on Ag, Cu, Pd, Pt(110) surfaces. The net charge of *cis*, TS and *trans* states on each surface are also in the table. A negative value means that the molecule gains electrons, and a positive value means that it loss electrons.

Surface	State	HOMO –5	HOMO –4	HOMO –3	HOMO –2	HOMO –1	HOMO	LUMO	net charge
Ag(110)	<i>cis</i>	–0.088	–0.059	–0.211	–0.199	–0.186	–0.109	+0.243	–0.138
	TS	–0.077	–0.152	–0.177	–0.187	–0.183	–0.094	+0.255	–0.200
	<i>trans</i>	–0.124	–0.113	–0.181	–0.191	–0.127	–0.149	+0.259	–0.174
Cu(110)	<i>cis</i>	–0.164	–0.118	–0.283	–0.263	–0.264	–0.180	+0.299	+0.412
	TS	–0.188	–0.214	–0.231	–0.277	–0.209	–0.219	+0.292	+0.392
	<i>trans</i>	–0.215	–0.155	–0.257	–0.276	–0.178	–0.245	+0.301	+0.376
Pd(110)	<i>cis</i>	–0.234	–0.173	–0.459	–0.429	–0.362	–0.447	+0.971	+1.802
	TS	–0.242	–0.357	–0.377	–0.499	–0.389	–0.387	+0.974	+1.689
	<i>trans</i>	–0.248	–0.226	–0.437	–0.472	–0.398	–0.379	+0.970	+1.792
Pt(110)	<i>cis</i>	–0.361	–0.278	–0.596	–0.530	–0.494	–0.589	+0.878	+1.906
	TS	–0.379	–0.524	–0.534	–0.583	–0.509	–0.532	+0.902	+1.830
	<i>trans</i>	–0.368	–0.294	–0.552	–0.607	–0.554	–0.519	+0.852	+1.998

#### References:

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