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Supplementary Information

A Topological Model for Predicting Adsorption Energies of Polycyclic Aromatic Hydrocarbons on Late-Transition Metal Surfaces

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1. Geometry of the supercells used for adsorption energy calculations

Table S1 the dimension of the supercells used for adsorption energy calculations. Detailed cell parameters of the supercells are listed in Table S2. All the supercells are in the hexagonal shape because of the geometric nature of (111) facet of the face-centered cubic metals.

Table S1 Supercell dimension for adsorption energy calculations described by a×b unit cells.

	Dimension
Benzene	
hcp0	3×3
bri30	3×3
Naphthalene	
di-bridge[6]	3×4
di-bridge[7]	3×4
Tetracene	
bridge[10]	6×3
bridge[13]	6×3
Phenanthrene	
bridge[8]	4×4
bridge[9]	4×4
Pyrene	
bridge[10]	4×4
hollow[8]	5×4
bridge[11]	4×4

Table S2 Size of the supercells used for calculating PAH adsorption. The cell dimension is described by (*a,b,c*) of the hexagonal cell. All units are in Å. The lattice constant of c axis has been converged so that the distance between slabs in the neighboring cell are separated by a vacuum that is greater than 10 Å.

	Ni	**Rh**	**Pd**	**Pt**
Benzene				
hcp0	7.47, 7.47, 18.28	8.18,8.18,21.20	8.37,8.37,27.34	8.47,8.47,20.74
bri30	7.47, 7.47, 18.28	8.18,8.18,21.20	8.37,8.37,27.34	8.47,8.47,20.74
Naphthalene				
di-bridge[6]	7.47, 9.96, 18.28	8.18,10.91,20.68	8.37,11,16,20.34	8.47,11.30,20.74
di-bridge[7]	7.47, 9.96, 18.28	8.18,10.91,20.68	8.37,11,16,20.34	8.47,11.30,20.74
Tetracene				
bridge[10]	14.94, 7.47, 18.28	16.37,8.18,21.20	16.74,8.37,27.34	16.95,8.47,20.74
bridge[13]	14.94, 7.47, 18.28	16.37,8.18,21.20	16.74,8.37,27.34	16.95,8.47,20.74
Phenanthrene				
bridge[8]	9.96, 9.96, 18.28	10.91,10.91,21.20	11.16,11.16,20.34	11.30,11.30,20.74
bridge[9]	9.96, 9.96, 18.28	10.91,10.91,21.20	11.16,11.16,20.34	11.30,11.30,20.74
Pyrene				
bridge[10]	9.96, 9.96, 18.28	10.91,10.91,21.20	11.16,11.16,20.34	11.30,11.30,20.74
hollow[8]	12.44, 9.96, 18.28	13.64,10.91,21.20	13.95,11.16,27.34	14.12,11.30,20.74
bridge[11]	9.96, 9.96, 18.28	10.91,10.91,21.20	11.16,11.16,20.34	11.30,11.30,20.74

2. Adsorption energies of polycyclic aromatic hydrocarbons (PAHs) on M(111) surfaces (M=Ni, Rh, Pd, Pt)

Table S3 provides the detail values of the adsorption energies of PAHs on Ni(111), Rh(111), Pd(111) and Pt(111) surfaces. The adsorption energies are calculated using the equation (S1):

$$E_{binding} = - (E_{total} - E_{slab} - E_{PAH}) \tag{S1}$$

where "total" denotes the PAH adsorbed on the slab, "slab" is the bare slab, and the "PAH" is the free PAH molecule. In such definition, a more positive value indicates a stronger binding of PAH.

Table S3 Adsorption energies of PAHs listed in Figure 1 in the text on Ni(111), Rh(111), Pd(111) and Pt(111) surfaces. The binding energies are calculated with equation (S1). All units are in eV.

	Ni	**Rh**	**Pd**	**Pt**
Benzene				
hcp0	2.28	3.19	2.66	3.07
bri30	2.31	3.19	2.76	3.22
Naphthalene				
di-bridge[6]	3.62	5.01	4.16	4.57
di-bridge[7]	3.62	5.03	4.29	4.87
Tetracene				
bridge[10]	6.43	8.57	6.80	7.10
bridge[10] (buckled)	-------	------	------	6.94
bridge[13]	6.46	8.71	7.07	7.73
Phenanthrene				
bridge[8]	4.90	6.66	5.43	5.86
bridge[9]	4.84	6.64	5.43	5.96
Pyrene				
bridge[10]	5.24	7.24	5.78	6.16
hollow[8]	------	6.39	4.86	5.65
bridge[11]	5.23	7.25	5.79	6.14

3. Analysis of interactions between the bands on metal surfaces and the orbitals on PAHs

In this section, we investigate the detail interactions between metal bands and orbitals on PAH through the change of projected density of states (PDOS) on the surface Rh atoms and the carbons of the PAH. We take naphthalene-bridge[7] on Rh(111) surface as an example. The PDOS of naphthalene shown in Figure S1 indicates that the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO), which are all the conjugated π-orbitals, are all formed by the p_z orbitals. After adsorption, Figure S1 shows that the PDOS on p_z orbitals are broadened, while the orbitals formed by p_x, p_y and s orbitals barely change. On Rh atoms, only the PDOS on s orbitals and d_{z2} orbitals change. It indicates that the adsorption bonds are mainly formed by hybridising the conjugated π-orbitals, metal s-orbitals and metal d_{z2}-orbitals, which results in the electron transferring from both the metal atoms and the conjugated π-bonds to the adsorption bonds. This interpretation is supported by the geometric expansion of the PAH molecule structures upon adsorption. For example, our results show 6% increase of the area of naphthalene upon adsorption on Rh(111) surfaces. The mechanism of the PAH adsorption agrees to previous analysis of the adsorption of both benzene and naphthalene[1–3]. The resulting net charge transfer between metal surfaces and PAHs represented by Bader charge are also listed in Table S4 for an indication of the PAH-M chemical bond formation.

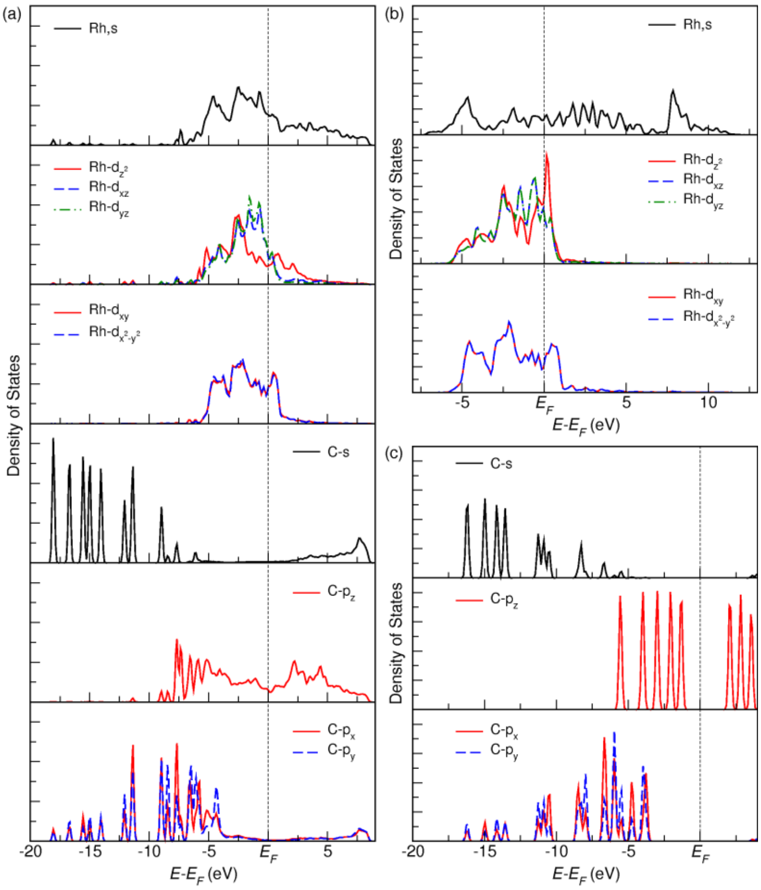


Figure S1 Projected density of states (PDOS) on a) C of the naphthalene-di-bridge[7] on Rh(111) and Rh that directly bind with naphthalene; b) surface Rh atoms on bare Rh(111) and c) C of the free naphthalene molecule.

Table S4 Net charge on PAH calculated with Bader charge analysis[4]. Negative values indicate electron gaining.

	Ni	**Rh**	**Pd**	**Pt**
Benzene				
hcp-0	-0.31	-0.15	0.04	0.20
bri-30	-0.30	-0.18	0.01	0.15
Naphthalene				
di-bridge[6]	-0.56	-0.33	-0.02	0.14
di-bridge[7]	-0.58	-0.40	-0.08	0.06
Tetracene				
bridge[10]	-1.10	-0.70	-0.22	0.09
bridge[10](buckled)	-------	------	------	0.21
bridge[13]	-1.13	-0.88	-0.34	-0.13
Phenanthrene				
bridge[8]	-0.80	-0.51	-0.08	0.14
bridge[9]	-0.82	-0.56	-0.11	0.08
Pyrene				
bridge[10]	-0.93	-0.65	-0.18	0.02
hollow[8]	-------	-0.46	-0.08	0.17
bridge[11]	-0.92	-0.59	-0.14	0.08

4. Summary of the coefficients of the adsorption energy model

Table S5 summarises the parameters of the model proposed in the text:

$$E_{bind} = E_{Ph}n_{Ph} + E_{M-C}n_1 + gE_{M-C}n_2 \tag{S2}$$

Where the coefficients, E_{Ph}, and E_{M-C}, are respectively the energy contribution of the non-chemical bonding interactions and the formation of η_1-coordinations. The energy contributions of η_2-coordinations are represented by the $gE_{M\text{-}C}$ with a g factor represents the ratio between the contribution from each M-C bonds involved in η_2-cooordination and that from the M-C bonds of the η_1-coordinations. The n_{ph} equals to the number of rings contacting the surface. The linearity, measured by linear correlation coefficient and maximum absolute error, are also listed in Table S5 to show that our model is general for different PAHs on different M(111) surfaces. The correlation between the g factor and the lattice mismatch is depicted on Figure S2.

Table S5 Summary of the coefficients of equation (S2) on all M(111) surfaces we considered in this work. They include the contributions from non-bonding interactions between each ring and the metal surface (E_{ph}), each η^1-coordination ($E_{\text{M-C}}$) and each η^2-coordination ($gE_{\text{M-C}}$). The linear correlation coefficient squares, R^2, and the maximum absolute error (MaxAE) are also listed. The lattice mismatch measured by $2a$(GR)/d(M-M) where a(GR) is the size of aromatic rings represented by the lattice constant of graphene and d(M-M) is the distance between two neighbouring M atoms on the surface.

	E_{ph}(eV)	E_{M-C} (eV)	R^2	MaxAE	g	a(GR)/d(M-M)
Ni(111)	-0.66	0.51	1.00	0.17	1.92	0.99
Rh(111)	-0.29	0.59	1.00	0.46	1.80	0.90
Pd(111)	-0.24	0.50	1.00	0.43	1.70	0.88
Pt(111)	-0.60	0.71	0.99	1.13	1.48	0.87

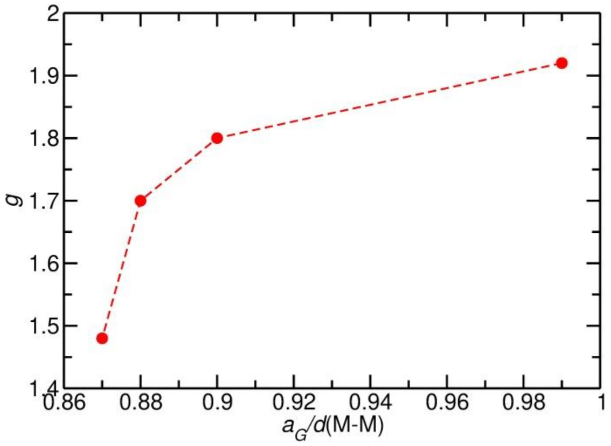
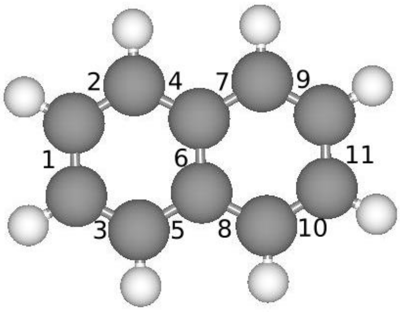


Figure S2 Correlation between g factor and the lattice mismatch defined by $2a$(GR)/d(M-M) where a(GR) is the size of aromatic rings represented by the lattice constant of graphene and d(M-M) is the distance between two neighbouring M atoms on the surface.

5 The geometries of the free and the adsorbed naphthalene and phenanthrene molecules.

In Table S6 and Table S7, we summarised the geometries of the free and the adsorbed naphthalene and phenanthrene molecules. The results indicate that the bond length of the bonds in the free molecule and those in the adsorbed molecule are not correlated. Table S8 and Table S9 summarised the average and the standard deviation of the bond lengths of the η^2-CC bonds and the non η^2-CC bonds of naphthalene and phenanthrene in different adsorption configurations. They demonstrate the stiffness of the η^2-CC bonds and the flexibility of the other CC bonds.

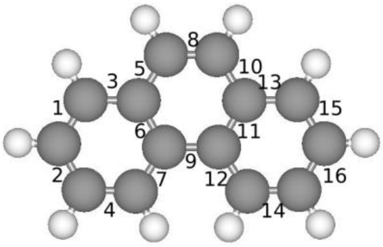
Table S6 C-C Bond lengths of the free and the adsorbed naphthalene. See the image for the numbering of the bonds. The η^2-CC bonds are labelled out after the values.



	Mol	**Ni-br6**	**Ni-br7**	**Pt-br6**	**Pt-br7**
1	1.41	1.45	1.43(η^2)	1.47	1.43(η^2)
2	1.38	1.42(η^2)	1.44	1.43(η^2)	1.47
3	1.38	1.44	1.44	1.47	1.47
4	1.42	1.45	1.45	1.47	1.48
5	1.42	1.44(η^2)	1.45	1.44(η^2)	1.48
6	1.43	1.46	1.46(η^2)	1.47	1.46(η^2)
7	1.42	1.44(η^2)	1.45	1.44(η^2)	1.48
8	1.42	1.45	1.45	1.47	1.48
9	1.38	1.44	1.44	1.47	1.47
10	1.38	1.42(η^2)	1.44	1.43(η^2)	1.47
11	1.41	1.45	1.43(η^2)	1.47	1.43(η^2)

	Mol	**Rh-br6**	**Rh-br7**	**Pd-br6**	**Pd-br7**
1	1.41	1.46	1.43(η^2)	1.45	1.43(η^2)
2	1.38	1.43(η^2)	1.46	1.42(η^2)	1.45
3	1.38	1.46	1.46	1.45	1.45
4	1.42	1.46	1.47	1.46	1.46
5	1.42	1.44(η^2)	1.47	1.44(η^2)	1.46
6	1.43	1.47	1.46(η^2)	1.46	1.46(η^2)
7	1.42	1.44(η^2)	1.47	1.44(η^2)	1.46
8	1.42	1.47	1.47	1.46	1.46
9	1.38	1.46	1.46	1.45	1.45
10	1.38	1.43(η^2)	1.46	1.42(η^2)	1.45
11	1.41	1.46	1.43(η^2)	1.45	1.43(η^2)

Table S7 C-C Bond lengths of the free and the adsorbed naphthalene. See the figure below for the numbering of the bonds. The η^2-CC bonds are labelled out after the values.



	Mol	Ni-br8	Ni-br9	Pt-br8	Pt-br9
1	1.38	1.44	1.42(η^2)	1.47	1.42(η^2)
2	1.41	1.45	1.44	1.47	1.47
3	1.41	1.43(η^2)	1.45	1.44(η^2)	1.47
4	1.38	1.42(η^2)	1.44	1.43(η^2)	1.48
5	1.43	1.45	1.43(η^2)	1.46	1.44(η^2)
6	1.43	1.46	1.46	1.47	1.47
7	1.42	1.45	1.44(η^2)	1.47	1.45(η^2)
8	1.36	1.41(η^2)	1.44	1.42(η^2)	1.47
9	1.45	1.45(η^2)	1.47	1.47(η^2)	1.49
10	1.43	1.45	1.45	1.46	1.48
11	1.43	1.46	1.45(η^2)	1.47	1.47(η^2)
12	1.42	1.45	1.46	1.47	1.49
13	1.41	1.43(η^2)	1.46	1.44(η^2)	1.49
14	1.38	1.42(η^2)	1.44	1.43(η^2)	1.47
15	1.38	1.44	1.44	1.47	1.46
16	1.41	1.45	1.43(η^2)	1.47	1.43(η^2)

	Mol	Rh-br8	Rh-br9	Pd-br8	Pd-br9
1	1.38	1.46	1.42(η^2)	1.44	1.42(η^2)
2	1.41	1.46	1.46	1.45	1.45
3	1.41	1.44(η^2)	1.47	1.44(η^2)	1.46
4	1.38	1.43(η^2)	1.46	1.43(η^2)	1.45
5	1.43	1.46	1.43(η^2)	1.45	1.44(η^2)
6	1.43	1.47	1.47	1.46	1.46
7	1.42	1.47	1.44(η^2)	1.46	1.44(η^2)
8	1.36	1.42(η^2)	1.46	1.42(η^2)	1.44
9	1.45	1.46(η^2)	1.48	1.46(η^2)	1.48
10	1.43	1.46	1.47	1.45	1.46
11	1.43	1.47	1.46(η^2)	1.46	1.46(η^2)
12	1.42	1.47	1.47	1.46	1.47
13	1.41	1.44(η^2)	1.47	1.44(η^2)	1.47
14	1.38	1.43(η^2)	1.46	1.43(η^2)	1.45
15	1.38	1.46	1.46	1.45	1.44
16	1.41	1.46	1.43(η^2)	1.45	1.42(η^2)

Table S8 Average bond lengths of the η^2-coordinated C-C bonds and the non-η^2-coordinated C-C bonds of naphthalene and phenanthrene. All the units are in Å.

	Nap-di-bridge[6]		**Nap-di-bridge[7]**		**Phen-bridge[8]**		**Phen-bridge[9]**	
	η^2	Non- η^2	η^2	Non-η^2	η^2	Non- η^2	η^2	Non-η^2
Ni	1.43	1.45	1.44	1.45	1.43	1.45	1.43	1.45
Rh	1.44	1.46	1.44	1.47	1.44	1.46	1.44	1.47
Pd	1.43	1.45	1.44	1.46	1.44	1.45	1.44	1.46
Pt	1.44	1.47	1.44	1.48	1.44	1.47	1.44	1.48

Table S9 Standard deviation of the bond lengths of the η^2-coordinated C-C bonds and the non-η^2-coordinated C-C bonds of naphthalene and phenanthrene. All the units are in Å.

	Nap-di-bridge[6]		**Nap-di-bridge[7]**		**Phen-bridge[8]**		**Phen-bridge[9]**	
	η^2	Non-η^2	η^2	Non-η^2	η^2	Non-η^2	η^2	Non-η^2
Ni	0.03	0.04	0.02	0.06	0.03	0.04	0.02	0.04
Rh	0.04	0.06	0.02	0.08	0.02	0.06	0.04	0.05
Pd	0.03	0.05	0.02	0.07	0.04	0.04	0.02	0.05
Pt	0.04	0.06	0.02	0.09	0.04	0.05	0.03	0.07

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