Supporting Information

Chiral Recognition of PVBA on Pd(111) and Ag(111) Surfaces

Byung I. Kim

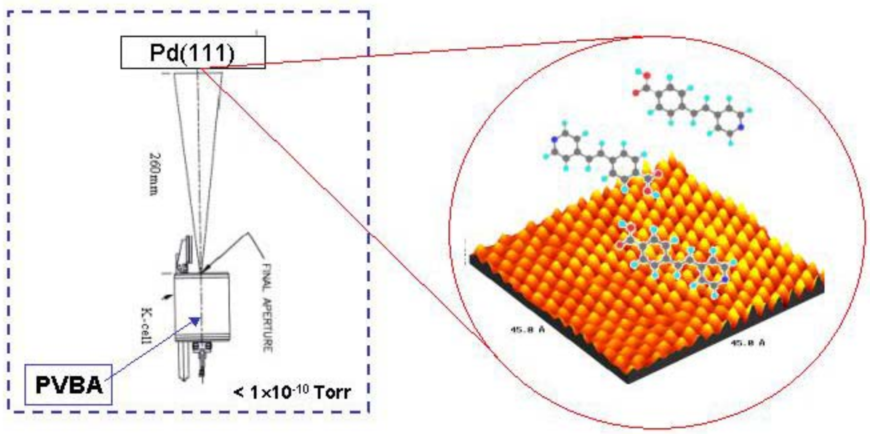

Figure S1. Organic molecular beam deposition system with Knudsen-type source to deposit organic molecules on single crystal with well-ordered surface Pd(111) substrates by thermal evaporation under UHV environment at the background pressures less than 1×10^{-10} Torr. Three dimensional STM image of Pd(111) clearly shows a well-ordered atomic structure.

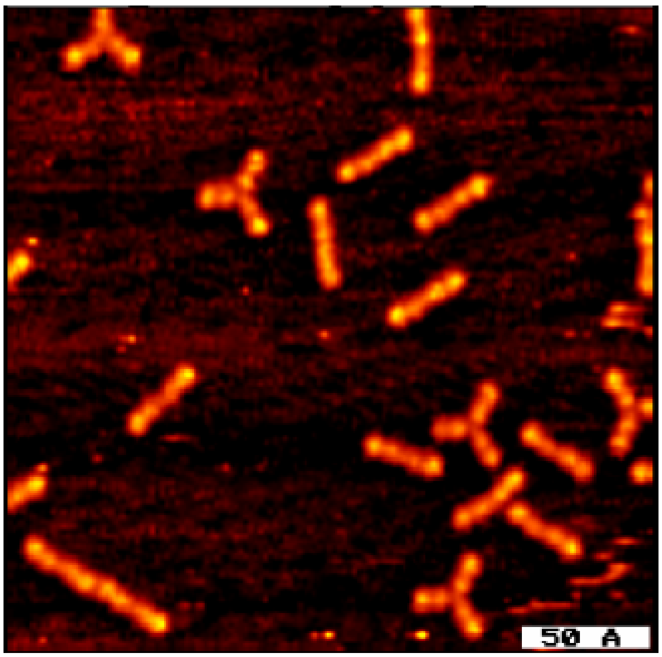

Figure S2. PVBA dimers and trimers on Pd(111) at ~0.1 ML coverage at room temperature (V_t = -1.0V, I_t =250pA) (scan size = 250 Å×250 Å)

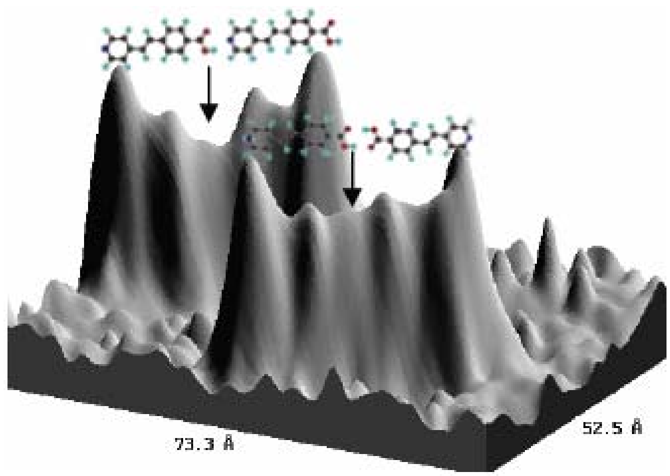

Figure S3. Three dimensional representation of two homochiral PVBA dimers with the corresponding model hydrogen bonds (**inset**). Each PVBA molecule of dimer has two peaks with different intensity with height ~1 Å. The STM image of intermolecular bond is a symmetric shape in the front dimer and may come from hydrogen bonding between two carboxyl groups. The back dimer, however, has an asymmetric shape that may come from hydrogen bonding between a carboxyl group and a pyridyl group.

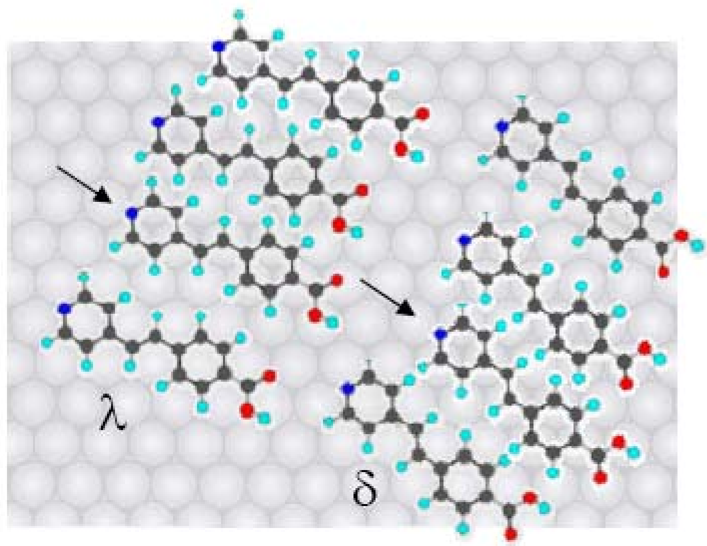

Figure S4. Four possible adsorption configurations for λ-PVBA and δ-PVBA on Pd(111). A on-top site, two hollow-sites, and a bridge site are sites with high symmetry in a unit cell for each PVBA molecules. Two arrows point the adsorption sites observed experimentally by STM, indicating the energetically favorable sites.

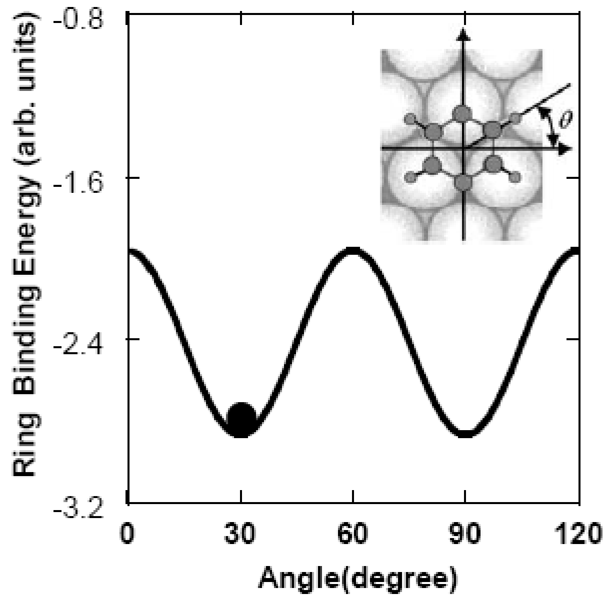

Figure S5. The minimum relative binding energy with $V_0(z) = +1$. The calculation reproduces the adsorption configuration of aromatic ring on Pd(111). (**inset**) The adsorption configuration of each aromatic ring on fcc(111). The configuration is obtained from the experimental adsorption configuration of PVBA on Pd(111)

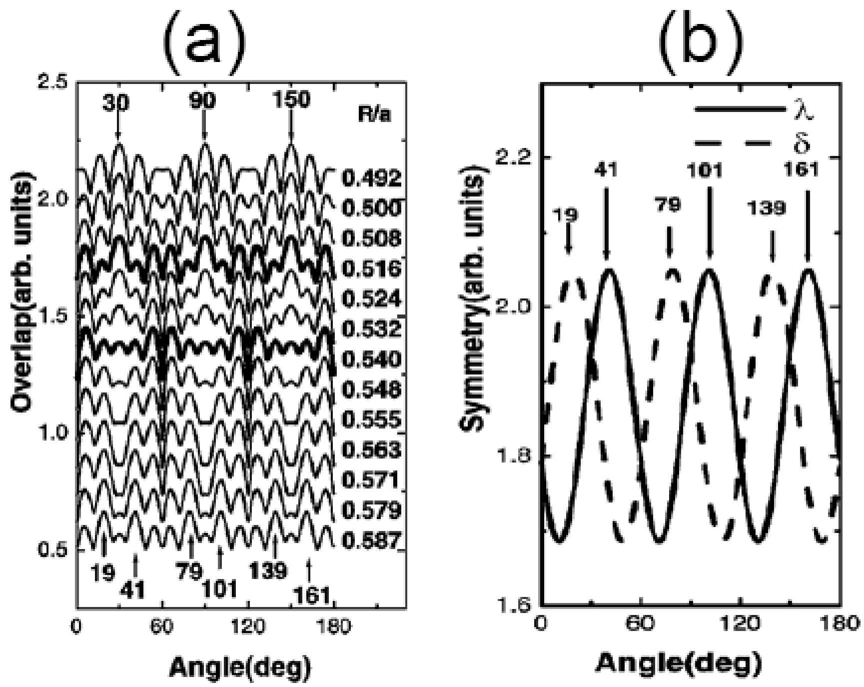

Figure S6. Two factors of the relative binding energy. (**a**) "Overlap" factor. The angle with maximum overlap changes from 30°, to 7° and 53°, to 19° and 41° , as lattice spacing decreases regardless of chirality. (**b**) "Symmetry" factor. The highest symmetry, C_{2v}, occurs at the angles 19° and 41° for δ and λ, respectively.

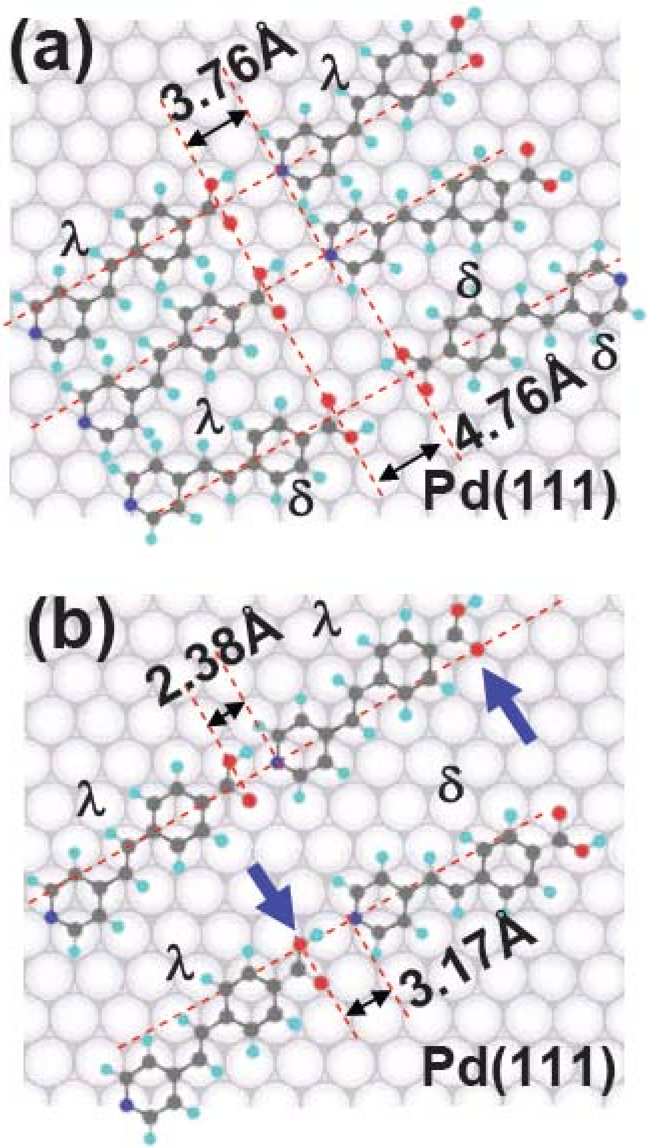

Figure S7. Hydrogen bonding of PVBA on Pd(111) (**a**) No chiral recognition between δ and λ on Pd(111). Chirality plays no role in dimer formation. (**b**)Energetically unfavorable adsorption sites of PVBA on Pd(111). Shorter bonding length, 2.38Å and 3.17Å, are possible only when the two oxygen atoms sits on hollow sites as pointed by two arrows. This result implies that the on-top sites of oxygen atoms with a longer length 3.76Å hydrogen bond is more energetically favorable than the hydrogen bonding with shorter distances 2.38Å and 3.17Å.

Appendix: Derivation of Equation (5)

Relative binding energy $\mathrm{E}_\chi(\vec{C}_B,\vec{P})$ was calculated by summing all potential energies for all carbons of two aromatic rings.

$$\mathrm{E}_\chi(\vec{C}_B,\vec{P}) = \sum_{\mathrm{j}} \mathrm{V}(\vec{\mathrm{r}}_{\mathrm{j}},\mathrm{z}) \qquad \text{(A1)}$$

where $\mathrm{V}(\vec{\mathrm{r}},\mathrm{z}) = \frac{2}{3} - \frac{2}{9}\sum_{n=0}^{2}\cos\vec{\omega}_n\cdot k\vec{r}$ with $\vec{\omega}_0 = (0,1)$, $\vec{\omega}_1 = (-\sqrt{3}/2,-1/2)$, $\vec{\omega}_1 = (\sqrt{3}/2,-1/2)$, and $k = 4\pi/\sqrt{3}a$ the length of a primitive reciprocal lattice vector with a lattice parameter of *a*. The relative binding energy $\mathrm{E}_\chi(\vec{C}_B,\vec{P})$ is

$$\begin{aligned}\mathrm{E}_\chi(\vec{C}_B,\vec{P}) &= \sum_{\mathrm{j}}\left[\frac{2}{3} - \frac{2}{9}\sum_{n=0}^{2}\cos\vec{\omega}_n\cdot k\vec{r}_j\right]\\ &= \frac{2}{3}\cdot 12 - \frac{2}{9}\sum_{\mathrm{j}}\sum_{n=0}^{2}\cos\vec{\omega}_n\cdot k\vec{r}_j \qquad \text{(A2)}\end{aligned}$$

Since $\cos\vec{\omega}_n\cdot k\vec{r}_j = \mathrm{Re}(\exp(i\vec{\omega}_n\cdot k\vec{r}_j))$, $\vec{\mathrm{r}}_{\mathrm{j}} = \vec{C}_B + \vec{\mathrm{R}}_{\mathrm{j},\chi}$ for benzoic ring, and $\vec{\mathrm{r}}_{\mathrm{j}} = \vec{C}_B + \vec{P} + \vec{\mathrm{R}}_{\mathrm{j},\chi}$ for pyridyl ring, the relative binding energy $\mathrm{E}_\chi(\vec{C}_B,\vec{P})$ is

$$\begin{aligned}\mathrm{E}_\chi(\vec{C}_B,\vec{P}) &= \frac{2}{3}\cdot 12 - \frac{2}{9}\mathrm{Re}\left[\sum_{n=0}^{2}\sum_{\mathrm{j}}\exp(i\vec{\omega}_n\cdot k\vec{r}_j)\right]\\ &= \frac{2}{3}\cdot 12 - \frac{2}{9}\mathrm{Re}\left[\sum_{n=0}^{2}\left(\sum_{\mathrm{j\ for\ benzoic\ ring}}\exp(i\vec{\omega}_n\cdot k\vec{r}_j) + \sum_{\mathrm{j}\ for\ \mathrm{pyridyl\ ring}}\exp(i\vec{\omega}_n\cdot k\vec{r}_j)\right)\right]\\ &= \frac{2}{3}\cdot 12 - \frac{2}{9}\mathrm{Re}\left[\sum_{n=0}^{2}\left(\sum_{\mathrm{j\ for\ benzoic\ ring}}\exp(i\vec{\omega}_n\cdot k(\vec{C}_B+\vec{R}_{j,\chi})) + \sum_{\mathrm{j}\ for\ \mathrm{pyridyl\ ring}}\exp(i\vec{\omega}_n\cdot k(\vec{C}_B+\vec{P}+\vec{R}_{j,\chi}))\right)\right]\\ &= \frac{2}{3}\cdot 12 - \frac{2}{9}\mathrm{Re}\left[\sum_{n=0}^{2}\left(\left(\exp(i\vec{\omega}_n\cdot k\vec{C}_B) + \exp(i\vec{\omega}_n\cdot k(\vec{C}_B+\vec{P})\right)\sum_{j=0}^{5}\exp(i\vec{\omega}_n\cdot k\vec{R}_{j,\chi})\right)\right]\end{aligned}$$

(A3)

With **Fig. 6(b),**

$$\vec{\mathrm{R}}_{\mathrm{j},\chi} = \mathrm{R}\left(\cos(\theta+\chi\zeta+\chi\frac{\pi}{3}j),\quad \sin(\theta+\chi\zeta+\chi\frac{\pi}{3}j)\right) \qquad \text{(A4)}$$

$$\vec{\omega}_n = \left(\sin(-\frac{2n\pi}{3}), \cos(-\frac{2n\pi}{3})\right) \qquad \text{(A5)}$$

Thus

$$\vec{\omega}_n \cdot k\vec{R}_{j,\chi} = \mathrm{kR}\left(\sin(-\frac{2\mathrm{n}\pi}{3})\cos(\theta + \chi\zeta + \chi\frac{\pi}{3}j) + \cos(-\frac{2\mathrm{n}\pi}{3})\sin(\theta + \chi\zeta + \chi\frac{\pi}{3}j) \right)$$

(A6)

$$\vec{\omega}_n \cdot k\vec{R}_{j,\chi} = k\mathrm{R}\sin(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta + \chi\frac{\pi}{3}j) \qquad \text{(A7)}$$

Now the summation $\sum_{j=0}^{5}\exp(i\vec{\omega}_n \cdot k\vec{R}_{j,\chi})$ becomes

$$\sum_{j=0}^{5}\exp(i\vec{\omega}_n \cdot k\vec{R}_{j,\chi}) = \sum_{j=0}^{5}\exp\left(ik\mathrm{R}\sin(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta + \chi\frac{\pi}{3}j) \right)$$

$$= \sum_{j=0}^{5}\left[\cos\left(k\mathrm{R}\sin(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta + \chi\frac{\pi}{3}j) + i\sin\left(k\mathrm{R}\sin(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta + \chi\frac{\pi}{3}j) \right) \right) \right]$$

(A8)

We expand the first term in **Eq. A8** with Bessel Functions of the First Kind, $J_n(x)$.

$$\sum_{j=0}^{5}\cos\left(k\mathrm{R}\sin(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta + \chi\frac{\pi}{3}j) \right) = \sum_{j=0}^{5}\left[J_0(kR) + 2\sum_{m=1}^{\infty} J_{2m}(kR)\cos\left(2m\left(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta + \chi\frac{\pi}{3}j \right) \right) \right]$$

(A9)

It is easy to show that the following relation:

$$\sum_{j=0}^{5}\cos\left(2m\left(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta + \chi\frac{\pi}{3}j \right) \right) = \sum_{j=0}^{5}\mathrm{Re}\left[\exp i\left(2m\left(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta + \chi\frac{\pi}{3}j \right) \right) \right]$$

$$= \mathrm{Re}\left[\exp i\left(2m\left(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta \right) \right) \sum_{j=0}^{5}\left(\exp i\left(\chi\frac{2\pi m}{3} \right) \right)^J \right]$$

(A10)

Since $\sum_{j=0}^{5}\left(\exp i\left(\chi\frac{2\pi m}{3} \right) \right)^J = 6\delta_{m,3l}$, the equation becomes

$$\sum_{j=0}^{5}\cos\left(2m\left(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta + \chi\frac{\pi}{3}j \right) \right) = 6\delta_{m,3l} \cdot \cos\left(2m\left(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta \right) \right).$$

(A11)

Again we expand the second term in **Eq. A8** with Bessel Functions of the First Kind, $J_n(x)$.

$$\sum_{j=0}^{5}\sin\left(k\mathrm{R}\sin(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta + \chi\frac{\pi}{3}j) \right) = \sum_{j=0}^{5}\left[2\sum_{m=1}^{\infty} J_{2m-1}(kR)\sin\left((2\mathrm{m}-1)\left(-\frac{2\mathrm{n}\pi}{3} + \theta + \chi\zeta + \chi\frac{\pi}{3}j \right) \right) \right]$$

(A12)

It is easy to show that the following relation:

$$\sum_{j=0}^{5}\sin\left((2\mathrm{m}-1)\left(-\frac{2\mathrm{n}\pi}{3}+\theta+\chi\zeta+\chi\frac{\pi}{3}j\right)\right)=\sum_{j=0}^{5}\mathrm{Im}\left[\exp i\left((2\mathrm{m}-1)\left(-\frac{2\mathrm{n}\pi}{3}+\theta+\chi\zeta+\chi\frac{\pi}{3}j\right)\right)\right]$$

$$=\mathrm{Im}\left[\sum_{j=0}^{5}\exp i\left((2\mathrm{m}-1)\left(-\frac{2\mathrm{n}\pi}{3}+\theta+\chi\zeta+\chi\frac{\pi}{3}j\right)\right)\right]$$

(A13)

Since $\sum_{j=0}^{5}\sin\left((2\mathrm{m}-1)\left(-\frac{2\mathrm{n}\pi}{3}+\theta+\chi\zeta+\chi\frac{\pi}{3}j\right)\right)=0$,

$$\sum_{j=0}^{5}\sin\left(k\mathrm{R}\sin(-\frac{2\mathrm{n}\pi}{3}+\theta+\chi\zeta+\chi\frac{\pi}{3}j)\right)=0 \qquad \text{(A14)}$$

Thus,

$$\sum_{j=0}^{5}\exp\left(ik\mathrm{R}\sin(-\frac{2\mathrm{n}\pi}{3}+\theta+\chi\zeta+\chi\frac{\pi}{3}j)\right)=6J_0(kR)+2\sum_{m=1}^{\infty}J_{2m}(kR)\cdot 6\delta_{m,3l}\cdot\cos\left(2m\left(-\frac{2\mathrm{n}\pi}{3}+\theta+\chi\zeta\right)\right)$$

(A15)

Now the summation $\sum_{j=0}^{5}\exp(i\vec{\omega}_n\cdot k\vec{R}_{j,\chi})$ becomes

$$\sum_{j=0}^{5}\exp(i\vec{\omega}_n\cdot k\vec{R}_{j,\chi})=6J_0(kR)+12\sum_{l=1}^{\infty}J_{6l}(kR)\cos\left(2\cdot 3l\left(-\frac{2\mathrm{n}\pi}{3}+\theta+\chi\zeta\right)\right)$$

$$=6J_0(kR)+12\sum_{l=1}^{\infty}J_{6l}(kR)\cos\left(6l\left(\theta+\chi\zeta\right)\right) \qquad \text{(A16)}$$

Since $\sum_{j=0}^{5}\exp(i\vec{\omega}_n\cdot k\vec{R}_{j,\chi})$ is real and does not have index n and is only function of angle depending on chirality χ,

$$\mathrm{E}_{\chi}(\vec{C}_B,\vec{P})=\frac{2}{3}\cdot 12-\frac{2}{9}\mathrm{Re}\left[\sum_{n=0}^{2}\left(\left(\exp(i\vec{\omega}_n\cdot k\vec{C}_B)+\exp(i\vec{\omega}_n\cdot k(\vec{C}_B+\vec{P})\right)\sum_{j=0}^{5}\exp(i\vec{\omega}_n\cdot k\vec{R}_{j,\chi})\right)\right]$$

$$=\frac{2}{3}\cdot 12-\frac{2}{9}\sum_{j=0}^{5}\exp(i\vec{\omega}_n\cdot k\vec{R}_{j,\chi})\cdot\mathrm{Re}\left[\sum_{n=0}^{2}\left(\exp(i\vec{\omega}_n\cdot k\vec{C}_B)+\exp(i\vec{\omega}_n\cdot k(\vec{C}_B+\vec{P})\right)\right]$$

$$=\frac{2}{3}\cdot 12-\frac{2}{9}\sum_{j=0}^{5}\exp(i\vec{\omega}_n\cdot k\vec{R}_{j,\chi})\cdot\left[\sum_{n=0}^{2}\cos(\vec{\omega}_n\cdot k\vec{C}_B)+\sum_{n=0}^{2}\cos(\vec{\omega}_n\cdot k(\vec{C}_B+\vec{P}))\right]$$

(A17)

From the following identity,

$$\begin{aligned}\sum_{j=0}^{5}\exp(i\vec{\omega}_n\cdot k\vec{R}_{j,\chi}) &= \frac{1}{3}\sum_{j=0}^{5}\sum_{n=0}^{2}\exp(i\vec{\omega}_n\cdot k\vec{R}_{j,\chi})\\ &= \frac{1}{3}\mathrm{Re}\sum_{j=0}^{5}\sum_{n=0}^{2}\exp(i\vec{\omega}_n\cdot k\vec{R}_{j,\chi})\\ &= \frac{1}{3}\sum_{j=0}^{5}(\sum_{n=0}^{2}\cos(\vec{\omega}_n\cdot k\vec{R}_{j,\chi}))\\ &= \frac{1}{3}\sum_{j=0}^{5}(3-\frac{9}{2}V(\vec{R}_{j,\chi}))\end{aligned} \tag{A18}$$

$$\begin{aligned}\mathrm{E}_\chi(\vec{C}_B,\vec{P}) &= 8-\frac{2}{9}\frac{1}{3}\sum_{j=0}^{5}\left(3-\frac{9}{2}\mathrm{V}(\vec{\mathrm{R}}_{\mathrm{j},\chi})\right)\cdot\left(3-\frac{9}{2}\mathrm{V}(\vec{\mathrm{C}}_\mathrm{B})+3-\frac{9}{2}\mathrm{V}(\vec{\mathrm{C}}_\mathrm{B}+\vec{\mathrm{P}})\right)\\ &= 8-\frac{1}{3}\sum_{j=0}^{5}\left(3-\frac{9}{2}\mathrm{V}(\vec{\mathrm{R}}_{\mathrm{j},\chi})\right)\cdot\left(\frac{2}{3}-\mathrm{V}(\vec{\mathrm{C}}_\mathrm{B})+\frac{2}{3}-\mathrm{V}(\vec{\mathrm{C}}_\mathrm{B}+\vec{\mathrm{P}})\right)\\ &= 8+\frac{3}{2}\cdot\left(4-\sum_{j=0}^{5}\mathrm{V}(\vec{\mathrm{R}}_{\mathrm{j},\chi})\right)\cdot\left(\mathrm{V}(\vec{\mathrm{C}}_\mathrm{B})+\mathrm{V}(\vec{\mathrm{C}}_\mathrm{B}+\vec{\mathrm{P}})-\frac{4}{3}\right)\end{aligned} \tag{A19}$$

Since $\vec{R}_{j,\chi}$ represents the locations of carbon atoms at a hollow site, finally we obtain

Equation 5

$$\mathrm{E}_\chi(\vec{C}_B,\vec{P}) = 8+\frac{3}{2}\cdot\left(4-\sum_{\textit{Ring at a hollow site}}\mathrm{V}(\vec{\mathrm{r}}_{\mathrm{j},\chi})\right)\cdot\left(\mathrm{V}(\vec{\mathrm{C}}_\mathrm{B})+\mathrm{V}(\vec{\mathrm{C}}_\mathrm{B}+\vec{\mathrm{P}})-\frac{4}{3}\right). \tag{A20}$$