Geometrical and electronic structures of tripotassium-doped hydrocarbon superconductors: Density functional calculations

Guohua Zhong\textsuperscript{1}, Zhongbing Huang\textsuperscript{2,3}, Chao Zhang\textsuperscript{3,4}, Xunwang Yan\textsuperscript{3}, Xiaojia Chen\textsuperscript{5}, and Haiqing Lin\textsuperscript{1,†}

\textsuperscript{1}Center for Photovoltaics and Solar Energy, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences and The Chinese University of Hong Kong, Shenzhen, 518055, China
\textsuperscript{2}Faculty of Physics and Electronic Technology, Hubei University, Wuhan, 430062, China
\textsuperscript{3}Beijing Computational Science Research Center, Beijing, 100089, China
\textsuperscript{4}Department of Physics, Yantai University, Yantai 264005, China
\textsuperscript{5}Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China

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A systematically theoretical study has been presented to explored the crystal structures and electronic characteristics of polycyclic aromatic hydrocarbons (PAHs), such as solid phenanthrene, picene, 1,2;8,9-dibenzopentacene, and 7-phenacenes, since these PAHs exhibited the superconductivity when potassium doping into. For tripotassium-doped phenanthrene and picene, we demonstrate the K atomic positions to fit the experimental lattice parameters, and analyze the distinction between the stablest configuration and the fitted experimental one. Based on the first-principles calculations, for the first time, we predict the possible crystal configurations of pristine and tripotassium-doped 1,2;8,9-dibenzopentacene and 7-phenacenes, respectively. For these four PAHs, the electronic structures after doping are investigated in details. The results show that the electronic characters near the Fermi level are high sensitive to structure. Because of the change of the benzene rings arrangement, the 1,2;8,9-dibenzopentacene exhibits visibly different band structures from other three PAHs. In these metallic PAHs, two bands cross the Fermi level which results in the complicated multiband feature of Fermi surfaces. Fascinatingly, we find that the electronic states of potassium contribute to the Fermi surfaces especially for K-3d electrons, which improves a way to understand this superconductivity. As a result, we suggest that the rigid-band picture is invalidated due to the hybridization between K atoms and PAH molecules as well as the rearrangement and distortion of PAH molecules.

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I. INTRODUCTION

The discovery of superconductivity in potassium-doped picene (C\textsubscript{22}H\textsubscript{14}) with a critical temperature $T_c = 7 \sim 18$ K for the doping level $x \sim 3$ has renewed the interest in organic superconductors.\textsuperscript{2} Subsequently, the superconductivity has been also observed in other doped polycyclic aromatic hydrocarbons (PAHs), such as phenanthrene (C\textsubscript{14}H\textsubscript{10}), coronene, and, very recently, 1,2;8,9-dibenzopentacene (C\textsubscript{30}H\textsubscript{18})\textsuperscript{3}, with $T_c$ of about 5, 15, and 33 K, respectively.\textsuperscript{4} In contrast to the previous organic superconductors, such as tetraphiafulvalene (TTF)\textsuperscript{5}, bis-ethylenedithrio-TTF(BEDT-TTF)\textsuperscript{6} and tetramethyltetraselenafvalene (TMTSF)\textsuperscript{7} derivatives, hydrocarbon superconductors are novel superconducting materials with intriguing properties. The feature of armchair edge type, which is regarded as a key factor of superconductivity in such a system, is shared in the hydrocarbon superconductors in contrast to the zigzag edge type.\textsuperscript{8} A new avenue in the quest for organic superconductors has been opened, since the $T_c$ changes with the number and arrangement of benzene rings.\textsuperscript{9} The highest $T_c$ of 33 K in hydrocarbon superconductors is comparable to the carbon based superconductor metal-doped fullerides ($T_c = 38$ K) under pressure. Besides, hydrocarbon superconductors are a low-dimensional system with strong electron-electron and electron-phonon interactions, and both of which may be involved in superconductivity as suggested by some theoretical works.\textsuperscript{10–15} Therefore, the kind of aromatic compounds provides a way to reveal the origin of the superconductivity.

To unveil these superconductors, it is in great need of investigations of the crystal and electronic structures, which is also fundamental to understand these superconducting PAHs. For K-doped phenanthrene and picene, K\textsubscript{3}C\textsubscript{14}H\textsubscript{10} and K\textsubscript{3}C\textsubscript{22}H\textsubscript{14} ($x \sim 3$), we have known their roughly geometrical configurations from experimental measurements.\textsuperscript{12} The solid system with the $P2_1$ symmetry is comprised of two phenanthrene or picene molecules in unit cell, forming the herringbone structure. But the experiment did not provide more details of crystal structure due to the difficulty of sample fabrication and measurements, such as the K atomic positions. For K\textsubscript{3}C\textsubscript{14}H\textsubscript{10}, the previous first-principles calculation\textsuperscript{16} has figured out its geometrical structure in which K atoms are intercalated into the herringbone structure, with some of them tending to the interlayer region. Comparing with experimental lattice parameters, however, there are obviously expansions of the unit cell in the $b$ and $c$ directions, a contraction in the $a$ direction, and a small increase in the angle $\beta$ for the optimized configuration. The lattice constants predicted by the theory deviates from the experimental values, which results in the different electronic structures such as Fermi surface topography.\textsuperscript{16} For K\textsubscript{3}C\textsubscript{22}H\textsubscript{14} ($x \sim 3$), with the increase of molecular length, K atomic positions in K\textsubscript{3}C\textsubscript{22}H\textsubscript{14} are more complicated...
than those in $K_3C_{14}H_{10}$. Numerous studies on crystal and electronic structures have been reported.\textsuperscript{14,15,17,26} In a optimized structure with the $P2_1$ symmetry, three $K$ atoms forming a line are inserted into the herringbone-arranged picene layer, and all of $K$ atoms are staying in intralayer region (This kind of configuration is called as K3 type).\textsuperscript{13,14,17,24} Consequentially, similar to $K_3C_{14}H_{10}$, the optimized unit cell of $K_3C_{22}H_{14}$ appears the expansions in the $b$ and $c$ directions, the contraction in the $a$ direction, and the increase in the angle $\beta$, comparing with the lattice parameters measured by experiment.\textsuperscript{14}

In order to explain the optimized lattice parameters not matching the experimental ones, the influence of van der Waals (vdW) forces in the low-dimensional systems was evaluated. Our previous study on pristine and La-doped phenanthrene showed that it was important for the dispersion interactions to predict the lattice constants of pristine phenanthrene.\textsuperscript{22} At the same time, Naghavi \textit{et al.}\textsuperscript{28} also gave the similar results from researching pristine and La-doped phenanthrene. How about in K-doped phenanthrene, picene, and other PAHs? It is worth searching. Moreover, the $K_3C_{22}H_{14}$ sample prepared by the solution method with annealing\textsuperscript{22} exhibited the larger lattice constants in $b$ and $c$ directions than that prepared by the solid reaction method,\textsuperscript{14} which indicated that some $K$ atoms might be intercalated into the interlayer region. The previous theoretical calculation on $K_3C_{22}H_{14}$ has predicted thus structure in which four of six $K$ atoms are in intralayer region and the other two $K$ atoms are intercalated in the interlayer regions, called as K2K1 type.\textsuperscript{22} From the lattice constants, the K2K1 configuration seems to be nearer the experimental case than K3 type, though the K3 is more stable configuration. Thus, the difference of $K$ atomic positions leads to the variousness of geometrical configuration. Examining the $K$ atomic positions presents another way to avoid the contrast between experiment and theoretical prediction. As a result, more investigations on crystal structure are needed.

With regard to the electronic structures, the $K$ doping results in the transition from insulator to metal with two bands crossing the Fermi level. The Fermi surface sheets showed the low-dimensional\textsuperscript{16} or the complicated three-dimensional characteristics.\textsuperscript{17,22} Both first-principles calculation\textsuperscript{22} and photoemission spectroscopy measurement\textsuperscript{18} suggested that the rigid-band model should be suitable for K-doped PAHs. The doping makes electrons transport from $K$ atoms to hydrocarbons, which is related to superconductivity.\textsuperscript{14,17,23,29} However, the investigations from the fluorescence-yield X-ray absorption spectroscopy and the X-ray emission spectroscopy implied a hybridization of electronic states between $C$ and $K$ atoms at Fermi level.\textsuperscript{22} Contrarily, the absence of metallic features has been also reported in the $K_3C_{22}H_{14}$ or the volume enhanced case due to the electronic correlations.\textsuperscript{13,15}

Given all that, the discussion on crystal and electronic structure are still opened questions. On one hand, the crystal and electronic structures are still lack for the potassium-doped 1,2,8,9-dibenzopentacene ($K_2C_{30}H_{18}$ ($x \sim 3$)) which has the highest $T_c$ among these doped PAHs. Due to the same arrangement of zigzag type, phenanthrene and picene also called as 3-phenacenes and 5-phenacenes, respectively. Similarly, 7-phenacenes (Here, marked as $C_{30}H_{18}$(II)), an allotropes of 1,2,8,9-dibenzopentacene, has the same arrangement of benzene rings as phenanthrene or picene. Then, the crystal and electronic structures of pristine and doped 7-phenacenes are fascinating though its superconductivity has not yet been observed. On the other hand, from phenanthrene to picene and then to 1,2,8,9-dibenzopentacene, the variations of molecular size in materials result in the different $T_c$. Moreover, the different arrangement orderings of benzene rings exist between 1,2,8,9-dibenzopentacene and 7-phenacenes, which will lead to the change of crystal and electronic properties. Hence, phenanthrene, picene, 1,2,8,9-dibenzopentacene and 7-phenacenes are four representative PAHs. In this work, therefore, we have studied the geometrical and electronic structures of these four PAHs, investigating the $K$ atomic positions, the intermolecular interactions, the interactions between $K$ atoms and molecular layers, and the variations of electronic characters at Fermi level induced by the different crystal configuration. It is useful for understanding the superconductivity in these PAHs.

The paper is structured as follows. In the second section, we present the Computational Details. In the third section, we analyze and discuss the calculated results in detail, including the geometrical and electronic structures of pristine and K-doped phenanthrene, picene, and 1,2,8,9-dibenzopentacene as well as 7-phenacenes, respectively. Finally, the fourth section is devoted to Conclusions.

II. COMPUTATIONAL DETAILS

Within the framework of the density functional theory (DFT), the Vienna \textit{ab initio} simulation package (VASP)\textsuperscript{30} was employed to carry out the full optimization calculations of these PAHs. Inner electrons were replaced by the projector augmented wave (PAW) method, while the monoelectronic valence electrons were expanded in plane waves with an cutoff energy of 600 eV. For the optimization, a conjugate-gradient algorithm was used to relax the ions into their instantaneous ground state. The Monkhorst-Pack $k$-point grids were generated according to the specified $k$-point separation 0.04 Å\textsuperscript{-1}. And the convergence thresholds were set as $10^{-5}$ eV in energy and 0.005 eV/Å in force. In the standard DFT, the local density approximation (LDA)\textsuperscript{31} and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof version\textsuperscript{32} were adopted to describe the electronic exchange-correlation interactions, respectively. As a comparison, the vdW density functional (vdW-DF\textsuperscript{33}), the second version of vdW-DF (vdW-DF2\textsuperscript{34}), and the semi-empirical DFT method of Grimme (DFT-D2)\textsuperscript{35} were used.
were adopted to investigate the influence of the dispersion interactions to the optimization of crystal structures.

To calculate self-consistent properties such as charge density, density of states (DOS), band structures, and Fermi surface features, we employed the highly precise full-potential linearized augmented plane wave (FLAPW) method\textsuperscript{26-34} which treats all electrons and has no shape approximations for the potential and the charge density, as implemented in the WIEN2k simulation package.\textsuperscript{34} The selections of crystal structures and exchange-correlation functionals are based on the optimization calculations above. The separate energy of −6.0 Ry was used between valence and core states. The muffin-tin radii were set to 1.3, 0.72, and 2.5 a.u. for C, H, and K atoms, respectively. Integrations in the first Brillouin zone (FBZ) were performed using double \textit{k}-points in the optimization, while tenfold \textit{k}-points were used in the Fermi surface calculations. Self-consistency calculation of electronic structures was achieved when the total-energy variation from iteration to iteration converged to a 0.01 mRy accuracy or better.

\section{RESULTS AND DISCUSSION}

\subsection{Crystal structures of the pristine PAHs}

Starting from the experimental values of crystal parameters,\textsuperscript{39,40} we firstly optimized the geometrical structure of pristine phenanthrene and relaxed the inner atomic coordinates with the different functional forms. The results are summarized in Table I, comparing with experimental and previous theoretical results. Our data based on LDA/GGA is consistent with previous LDA/GGA calculations.\textsuperscript{16,28} However, the GGA leads to the enlargements of all of crystal parameters comparing with experiment. In particular, the expansions of lattice constant in the \textit{b} direction and volume of unit cell reach ~9\% and ~15\%, respectively. On the contrary, the optimized crystal parameters based on LDA are correspondingly smaller than the experimental ones. The contraction of cell volume reaches 10.8\% or over this. As a result, both LDA and GGA functionals are unsuited to obtain the reasonable crystal parameters. Based on the considering vdW interactions, the calculation results listed in Table I imply the importance of the dispersion interactions in this molecular crystal. Differing from previous theoretical studies\textsuperscript{22} in which the vdW-DF was the optimal approach, the crystal parameters optimized with the help of vdW-DF2 in our calculations are in perfect agreement with experimental values. The biggest errors in lattice constants and cell volume in Table I are only 0.7\% and 1.3\%, respectively. However, the vdW-DF (DFT-D2) overestimates (underestimates) the lattice constants and cell volume. The geometrical configuration obtained by vdW-DF2 form is shown in Fig. 1(a) where the molecular arrangements are viewed from different directions (top panel and low panel).

The optimized lattice parameters of pristine picene also exhibits the similar behavior to phenanthrene, as shown in Table I. Although the previous LDA calculation\textsuperscript{21} has led to the lattice constants near the experimental ones,\textsuperscript{29} the smaller cell volume of picene was obtained from LDA. The GGA still overestimates the crystal parameters. Comparing with other functionals, the vdW-DF2 is still an effective functional in the optimization of pristine picene. The theoretically obtained lattice constants and cell volume are in good agreement with the experimental ones under considering the correction of vdW forces in the scheme of vdW-DF2. The biggest error in all of the crystal parameters in Table I is only 0.7\%. Figure 1(b) depicts the geometries of pristine picene based on the vdW-DF2 functional. Thus, combining pristine phenanthrene with picene cases, we conclude that the vdW forces can not be ignored in the investigations on crystal structures of undoped PAHs. Especially, the vdW-DF2 functional gives key contributions to obtain the crystal parameters according with experiment.

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline
Symbol & \textit{a} & \textit{b} & \textit{c} & \text{Volume} & \text{\% Error} \\
\hline
\text{LDA} & 6.745 & 7.613 & 18.495 & 98.1 & 6.5 & 6.5 \\
\text{GGA} & 7.815 & 8.659 & 20.035 & 105.3 & 9.8 & 9.8 \\
\text{vdW-DF2} & 6.587 & 7.473 & 17.956 & 94.2 & 7.8 & 7.8 \\
\hline
\end{tabular}
\caption{The optimized lattice parameters of pristine picene.}
\end{table}
B. Crystal structures of the K-doped PAHs

1. $K_3C_{14}H_{10}$

As mentioned above, the vdW-DF2 functional successfully predicts the crystal structures of pristine PAHs. However, how about in the K-doped cases? Which configurations induced by the doping is perfect? We have searched for many doped configurations of phenanthrene and picene based on the concentration of $x = 3$ to answer these questions. Changing K atomic positions and intermolecular distance, dozens of configurations have been tested for $K_3C_{14}H_{10}$. Comparing the different functionals, we find that all of the geometrical structures predicted by GGA and vdW functionals including vdW-DF, vdW-DF2, and DFT-D2 forms obviously deviate from the experimental values. The result indicates that the vdW interactions become weak when K atoms are intercalated into phenanthrene. LDA is competent to the optimization of $K_3C_{14}H_{10}$. From the search of structures, the initial positions of K atoms pay an key role during the optimization. Two optimal structures of $K_3C_{14}H_{10}$ are picked out from all of checked configurations to compare with previous studies. One is the geometrical structure fitted experiment, called as $C_{14}$-K2K1 configuration, the other one is the stablistest configuration, called as $C_{14}$-K3 type. Table III presents the optimized results of these two structural types using different functionals. With the help of LDA, the crystal structure with of $C_{14}$-K2K1 configuration is close to the experimental data, though there is an expansion in the $c$ direction which causes a small increase of cell volume. The predicted lattice constants of $C_{14}$-K2K1 configuration are $a = 8.440 \text{ Å}$, $b = 6.195 \text{ Å}$, and $c = 10.124 \text{ Å}$, and the angle $\beta = 98.32^\circ$ between $a$ and $c$ axes. This result is nearer the experiment than previous theoretical predictions. For $C_{14}$-K3 configuration, the optimized lattice constants are $a = 7.796 \text{ Å}$, $b = 6.834 \text{ Å}$, and $c = 10.028 \text{ Å}$, and the angle $\beta = 111.10^\circ$ between $a$ and $c$ axes. Its total energy is 0.28 eV/f.u. lower than that of $C_{14}$-K2K1. However, there are the expansions in the $b$ and $c$ directions, a contraction in the $a$ direction, and a big increase in the angle $\beta$, compared with the experimental ones.

Figure 2 shows these two geometrical configurations of K-doped phenanthrene. The K atoms are intercalated into the herringbone structure consisted of two phenanthrene molecular layer. The angle $\theta$ formed by two molecular layers in herringbone structure becomes smaller than that in undoped case. For the $C_{14}$-K2K1 type, the inner coordinates of three K atoms are $K_1(0.1734,0.2295,0.6693)$, $K_2(0.3989,0.2153,0.3484)$, and $K_3(0.2415,0.2530,0.0384)$, respectively. Examining the geometry along the $b$ direction, as the top panel shown in Fig. 2(a), two of three K atoms ($K_2$ and $K_3$) stay in the intralayer region (molecular layer) and occupy a benzene ring near the C atom. The other K atom ($K_1$) moves into the interlayer region. It is just the reason of the definition of $C_{14}$-K2K1 type. In the intralayer region, the atomic distances are 3.235 Å between $K_2$ and $K_3$ and 3.700 Å between $K_1$ (equivalent position of $K_1$) and $K_3$, respectively. In the interlayer region, the atomic distance is 3.997 Å between $K_1$ and $K_2$. The expansion in the $c$ direction in $C_{14}$-K2K1 configuration possibly originates from the big distance of 3.997 Å between $K_1$ and $K_2$. For the $C_{14}$-K3 type, the inner coordinates of three K atoms are $K_1(0.2082,0.2269,0.6740)$, $K_2(0.3641,0.2319,0.3305)$, and $K_3(0.2185,0.1909,0.9921)$, respectively. In the interlayer region, the atomic distances shorten to 3.172 Å between $K_1$ and $K_3$ and 3.179 Å between $K_2$ (equivalent position of $K_2$) and $K_3$, respectively. In the interlayer region, the atomic distance increases to 4.045 Å between $K_1$ and $K_2$. Different from $C_{14}$-K2K1, as shown in Fig. 2(b), all of three K atoms are in the intralayer region in $C_{14}$-K3 configuration due to the $K_1$ atom shifting toward phenanthrene molecule, which is also the reason of the definition of $C_{14}$-K3 type. Additionally, the distance between two phenanthrene molecules along $c$ direction becomes bigger in $C_{14}$-K3 than that in $C_{14}$-K2K1. It is one of causes of different geometries between these two configurations.

2. $K_3C_{22}H_{14}$

For tripotassium-doped picene, the geometrical structure of $K_3C_{22}H_{14}$ has also been optimized with several different functionals. Table IV presents the optimization calculation results for several types of configurations. Similar to the phenomena in $K_3C_{14}H_{10}$, the LDA functional can be used to obtain reasonable crystal parameters of $K_3C_{22}H_{14}$, while the vdW functional does not bring expectable effects in the optimization. With regard to crystal structure, the different configurations and stability were observed because of the variations of K atomic positions. The experiment by Kambe et al. has also established it. Hence, three special configurations of $C_{22}$-K2K1, $C_{22}$-K3-A, and $C_{22}$-K3-B types are selected. Based on the optimizations with LDA, the geometries of three special configurations of $K_3C_{22}H_{14}$ are shown in Fig. 3. For $C_{22}$-K2K1 configuration shown in Fig. 3(a), the inner coordinates of three K atoms are $K_1(0.3254,0.2426,0.6315)$, $K_2(0.1792,0.2403,0.3240)$, and $K_3(0.1906,0.2116,0.0342)$, respectively. Observed along $b$ direction, two of three K atoms ($K_1$ and $K_2$) are in the intralayer region with occupying the second and fourth benzene rings, while the third K atom ($K_3$) enters the interlayer region. Thus, the structure close to experiment presentation is obtained. The optimized lattice constants of $C_{22}$-K2K1 are $a = 8.773 \text{ Å}$, $b = 6.433 \text{ Å}$, and $c = 13.310 \text{ Å}$, and the angle $\beta = 93.76^\circ$, which are in good agreement with previous theoretical results. The atomic distances are 4.207 Å between $K_1$ and $K_2$ and 3.870 Å between $K_2$ and $K_3$, respectively, larger than those in $K_3C_{14}H_{10}$.

For $C_{22}$-K3-A and $C_{22}$-K3-B configurations shown in Fig. 3(b) and 3(c), seen along the $b$ direc-
tion, all of three K atoms are in the intralayer region with occupying the first, third, and fifth benzene rings. Three K atoms almost form a line along the c direction. In C_{22}-K3-A, the inner coordinates of three K atoms are K_1(0.4312,0.2592,0.7423), K_2(0.2070,0.2638,0.4515), and K_3(0.9896,0.2211,0.1617), respectively. The atomic distances are 4.000 Å between K_1 and K_2 and 3.986 Å between K_2 and K_3, respectively. In C_{22}-K3-B, the inner coordinates of three K atoms are K_1(0.3412,0.1535,0.8224), K_2(0.2301,0.1732,0.5033), and K_3(0.1133,0.1549,0.1819), respectively. Thus the atomic distances are 4.345 Å between K_1 and K_2 and 4.373 Å between K_2 and K_3, respectively, correspondingly larger than those in C_{22}-K3-A. The crystal parameters of C_{22}-K3-A and C_{22}-K3-B from LDA are listed in Table IV. The expansions of lattice constants in b and c directions and the contraction in a direction visibly exist, compared with experiments.\(^{22}\) The C_{22}-K3-B of K_{3}C_{22}H_{14} also reported by Kosugi et al.\(^{22}\) However, in this study, we present a more stable configuration, C_{22}-K3-A. The total energy of C_{22}-K3-A is 0.52 and 0.07 eV/f.u. lower than those of C_{22}-K2K1 and C_{22}-K2K3-B, respectively.

3. K_{3}C_{30}H_{18} and K_{3}C_{30}H_{18}II

Analyzing these two cases of K-doped phenanthrene and picene, we have confirmed that the LDA is more effective in predicting crystal structures of K-doped PAHs than vdW functionals, which is different from the pristine PAHs. One reason is that the intercalation of K atoms into herringbone structure strengthens the intermolecular interactions by the hybridization between K atom and molecules (Subsequent electronic structures in the text will be evidence.). With the help of LDA functional, we could predict the crystal structures of tripotassium-doped 1,2:8,9-dibenzo- pentacene (K_{3}C_{30}H_{18}). For K_{x}C_{30}H_{18} (x \sim 3), the high superconducting transition temperature of 33 K in PAHs has been observed.\(^{14}\) But the information on crystal structure is still lack. We assumed that the P2\(_1\) symmetry should be kept in K_{3}C_{30}H_{18} with two 1,2:8,9-dibenzo- pentacene molecules per unit cell. The structure was optimized and the K atomic positions were checked carefully. Two kinds of stable configurations were found for K_{3}C_{30}H_{18}, defined as C_{30}-K3-A and C_{30}-K3-B types. The crystal parameters and geometries of K_{3}C_{30}H_{18} are listed in Table V and shown in Fig. 4, respectively. The optimized lattice constants of C_{30}-K3-A type are a = 7.741 Å, b = 7.043, and c = 17.693 Å, and the angle \(\beta = 100.97^\circ\), respectively. For C_{30}-K3-B type, a = 7.880, b = 6.993, and c = 17.918 Å, and \(\beta = 101.05^\circ\), respectively. The intercalations of K atoms make lattice constants expand in a direction and contract in b and c directions comparing with the pristine 1,2:8,9-dibenzo-pentacene, respectively. And the volume of unit cell slightly increases. In K_{3}C_{30}H_{18}, the K atoms have difficulty in moving into the interlayer region due to the longer molecular chain. Hence, all of three K atoms are in the intralayer region and approximately on a line along c direction, as shown in Fig. 4. The distinction between C_{30}-K3-A and C_{30}-K3-B is the difference of the space of interlayer region. As a result, three K atoms are localized at the 2, 4, and 6 benzene rings in C_{30}-K3-A, while three K atoms lie at the joints of 1/2, 3/4, and 5/6 benzene rings in C_{30}-K3-B configuration, respectively. In C_{30}-K3-A, the inner coordinates of three K atoms are K_1(0.52456,0.5969,0.2450), K_2(0.2502,0.5705,0.0002), and K_3(0.9756,0.5447,0.7555), respectively. In C_{30}-K3-B, the inner coordinates of three K atoms are K_1(0.5643,0.5588,0.3465), K_2(0.3121,0.5834,0.0385), and K_3(0.9856,0.5515,0.7802), respectively. In the intralayer region of C_{30}-K3-A, the distance between K_1 and K_2 or between K_2 (equivalent position of K_2) and K_3 atoms shortens to 4.451 Å. However, the distances among K atoms in K_{3}C_{30}H_{18} are distinctly larger than those in K_{3}C_{4}H_{10} and K_{3}C_{22}H_{14}. In the intralayer region of C_{30}-K3-B, these two distances become very large, both are 5.499 Å. In addition, although C_{30}-K3-A is slightly stabler than C_{30}-K3-B, the total energy difference is only 2.9 meV/f.u.\(_{II}\).
C. Electronic structures

1. $C_{14}H_{10}$ and $K_3C_{14}H_{10}$

The possible crystal structures of pristine and doped PAHs have been figured out by the investigations and analysis above. Besides crystal structure, however, the electronic properties of doped PAHs are very important to understand the superconductivity. Starting from the optimized crystal structures above, therefore, the electronic structures of pristine and tripotassium-doped PAHs have been also investigated based on the FLAPW method employing WIEN2k package. The exchange-correlation functional adopts LDA which is competent to describe the electronic properties. For pristine and doped phenanthrene, the electronic structures have been reported in the previous theoretical study. As mentioned above, however, we examined and presented more crystal configurations in this work. The crystal configuration nearer the experiment and the more stable one are obtained by performing the full optimization calculations, $C_{14}$-K2K1 and $C_{14}$-K3, respectively. In this paper, therefore, we focus on the difference of electronic structures induced by the structural change. For $C_{14}H_{10}$, a direct band-gap of 2.77 eV is observed, which is in good agreement with previous theory and to be compared with an experimental one of 3.16 eV. Both valence band maximum (VBM) and conduction band minimum (CBM) are at $Z$ k-point in F2BZ. As shown in Fig. 6(a), the band dispersions along some k-path directions are doubly degenerate. Four bands form the first group of conduction bands in the range of 2.67 $\sim$ 3.22 eV, marked as CB1, CB2, CB3, and CB4, respectively. After doping K atoms, the Fermi level is shifted toward higher energy. Two bands of CB3 and CB4 cross the Fermi level with the widths of 0.26 eV for $C_{14}$-K2K1 and 0.27 eV for $C_{14}$-K3. As shown in Fig. 6, the width of the first group of conduction bands changes from 0.55 eV for $C_{14}H_{10}$ to 0.67 eV for $C_{14}$-K2K1 and 0.64 eV for $C_{14}$-K3. The dopant reduces the band degeneracy, and strengthens the coupling between the first and second group of conduction bands. The intercalated K atoms lead to increase the intermolecular interactions, which is a possible reason that the contribution of vdW functionals to the optimizations of the doped PAHs is weakened.

As shown in Fig. 6, the doping brings the big variations of band width and morphology near Fermi level. The band structures of doped system can not simply obtained from the shift of Fermi level relative to pure material. This mainly results from the rearrangement and deformation of molecules and the accompanied charge redistribution between the molecules and dopants. Different from some previous theoretical and experimental studies, our result affirms that the rigid-band model is not suitable for the doped PAHs systems. Comparing $C_{14}$-K2K1 with $C_{14}$-K3, we find a energy gap of 0.3 eV between the first and second group of conduction bands in $C_{14}$-K2K1 while 0.47 eV in $C_{14}$-K3 configuration. The DOS at the Fermi level in $C_{14}$-K2K1 (9.57 states/eV/f.u.) is somewhat larger than that in $C_{14}$-K3 configuration (8.76 states/eV/f.u.). The structural difference between $C_{14}$-K2K1 and $C_{14}$-K3 induces the variations of electronic characteristics near the Fermi level. For $C_{14}$-K2K1 shown in Fig. 6(b), the CB3 band generates the hole-like Fermi sheets around A and D k-points as well as along $E - C$ direction, while the CB4 band builds the electron-like Fermi surface along $\Gamma - Y - A$ direction. For $C_{14}$-K3 shown in Fig. 6(c), the CB3 band shapes the hole-like Fermi surfaces around $\Gamma$ k-point and along $E - C$ direction, while the CB4 band forms the electron-like Fermi sheets around Y, B, and D k-point. The Fermi surfaces in K-doped phenanthrene are complicated three-dimensional features and visibly differing from the previous study. The calculated results indicate that the Fermi surface topography is highly sensitive to crystal structures.

In order to explore the conformation of Fermi surfaces, we have also investigated the fine electronic structures. The electronic states near the Fermi level mainly result from C-2p electrons, with forming the $\pi$ state by $p_x$ and $p_y$. The $C-p_z$ states distribute in the lower energy region. The charge transfers from K atoms to C atoms (or phenanthrene molecule). However, the hybridization between K and near neighbor C atoms can not be ignored. Figure 7 shows the projected density of states (PDOS) on one C and three K atomic orbitals. We find that the electronic states of C atoms mix with those of K atoms near the Fermi level. The hybridization character is visibly observed, which is consistent with the experimental investigation. This is just an explanation of that the vdW interactions become weak after the K atoms intercalating. In $C_{14}$-K2K1 and $C_{14}$-K3 configurations, the K-sp$d$ electrons significantly contribute to the electronic states near the Fermi level, though the electronic states at Fermi level mainly result from C-2p states. In particular, the K-3$d$ electrons is important for the formation of Fermi surfaces. The d-electronic feature of Fermi surfaces was observed in the La-doped phenanthrene. It is interested in understanding the superconductivity in the doped phenanthrene.

2. $C_{22}H_{14}$ and $K_3C_{22}H_{14}$

For electronic structures of pristine and tripotassium-doped picene, numerus studies have been reported. In this paper, we present a more stable doped configuration and reproduce their electronic structures to make a comparison. Similar to $C_{14}H_{10}$, $C_{22}H_{14}$ is also a direct band gap semiconductor. The band gap of 2.28 eV based on LDA is less than the experimental 3.3 eV. Both VBM and CBM are at $Z$ k-point. As shown in Fig. 8(a), the first group of conduction bands covers the range of 2.28 $\sim$ 2.73 eV, composed of two doubly degenerate bands marked as CB1, CB2, CB3, and CB4, respectively. The electron-doping results in the shift of Fermi
level. Figure 8(b)-8(d) show that two bands of CB3 and CB4 cross the Fermi level in C_{22}-K2K1 and C_{22}-K3-A configurations, while three bands of CB2, CB3, and CB4 cross the Fermi level in C_{22}-K3-B configuration. The intercalation of K atoms reduces the band degeneracy due to the enhancement of intermolecular interactions, especially for C_{22}-K2K1 and C_{22}-K3-A configurations shown in Fig. 8(b) and 8(c). The width of these four bands of CB1-CB4 becomes from 0.45 eV to 0.49 eV for C_{22}-K2K1, 0.48 eV for C_{22}-K3-A, and 0.62 eV for C_{22}-K3-B, respectively. Similar to the phenanthrene and picene, our calculation shows that the pristine 1,2,8,9-dibenzopentacene is an indirect semiconductor with the band gap of 1.03 eV. The VBM and CBM are at \( B \) and \( Z \) \( k \)-point, respectively. The origin is mainly the different arrangement ordering of benzene rings in 1,2,8,9-dibenzopentacene, compared with phenantherene and picene. For C_{30}H_{18}, the first group of conduction bands is in the range of 1.03 \( \sim \) 1.44 eV, comprised of two bands marked as CB1 and CB2, respectively. As shown in Fig. 10(a), five bands make up of the second group of conduction bands covering the range of 2.04 \( \sim \) 2.83 eV, marked as CB3, CB4, CB5, CB6, CB7, and CB8, respectively. The K-doping results in these two bands of CB3 and CB4 crossing the Fermi level. As shown in Fig. 10(b) and 10(c), two bands of CB3 and CB4 are almost completely degenerate. Furthermore, we find that the CB1 and CB2 are also almost completely degenerate under the Fermi level, localized in the ranges of \(-1.25 \sim -1.01\) eV for C_{30}-K3-A and \(-1.01 \sim 0.96\) eV for C_{30}-K3-B configuration, respectively. This is an abnormal phenomenon of that the K atomic intercalation enhances the band degeneracy. Besides the difference of arrangement ordering of benzene rings, we examine the K atomic distances in all observed doped PAHs. In the 1,2,8,9-dibenzopentacene, the K atomic distance is the biggest such as 4.451 or 5.499 Å. However, the increase of band degeneracy in the K-doped 1,2,8,9-dibenzopentacene is still opened issue. More future efforts are required. For C_{30}-K3-A configuration shown in Fig. 10(b), go back to the electronic characteristics, the CB3 and CB4 mainly form the electron-like Fermi surfaces along \( Y - A \) and \( D - E - C \) directions, while form small hole-like Fermi surface sheets along \( B - D \) direction. For C_{30}-K3-B configuration shown in Fig. 10(c), the CB3 mainly builds the hole-like Fermi surfaces around \( Y \) \( k \)-point and along \( B - D \) direction, while the CB4 mainly shapes the electron-like Fermi surface sheets along \( D - E - C \) direction.

Comparing C_{30}-K3-A with C_{30}-K3-B, the electronic structures exhibit a large difference though these crystal structures are similar. The DOS peaks are more sharp in C_{30}-K3-B configuration. The DOS at Fermi level of C_{30}-K3-A and C_{30}-K3-B configuration are 17.67 and 20.02 states/eV/f.u., respectively. This further illustrates that the electronic features near the Fermi level is highly sensitive to crystal structures. It is one reason that the superconductivity is difficulty in being observed in this type materials. The slight variation of experimental conditions can cause the change of electronic states near the Fermi level so that the superconductivity weakens or disappears. The PDOSs shown in Fig. 11 still indicate that the K atoms contribute to the formation of Fermi surfaces, especially for K-3d electrons. Combining with the calculated results shown in Fig. 10 and 11, the introduction of K atoms not only provides the electrons for hydrocarbon molecules but also affects the electronic characteristics of materials by the interaction between K atoms and molecules.

3. \( C_{30}H_{18} \) and \( K_3C_{30}H_{18} \)

With regard to pristine and tripotassium-doped 1,2,8,9-dibenzopentacene, the information of electronic structures is still lack. So the band structures, DOS, and Fermi surfaces based on our predicted crystal structures are presented for the first time in this paper. Differing from phenantherene and picene, our calculation shows
4. \( \text{C}_{30}\text{H}_{18}\text{II} \) and \( \text{K}_{3}\text{C}_{30}\text{H}_{18}\text{II} \)

7-phenacenes has the similar arrangement ordering of benzene rings to phenanthrene and picene, and is an allotrope of 1,2,8,9-dibenzopentacene. Although the superconductivity has not yet been observed in the doped 7-phenacenes, the electronic structures is still interested. As a comparison, we show the band structures, DOS, and Fermi surface characteristics in Fig. 12. The pristine 7-phenacenes is also a direct band gap semiconductor similar to phenanthrene and picene. Both VBM and CBM are at \( z \) \( k \)-point. The band gap of 2.09 eV based on LDA is underestimated relative to the experimental value of 3.2 eV\(^2\). Two doubly degenerate bands form the first group of conduction bands, also marked as CB1, CB2, CB3, and CB4, respectively. The band evolutions induced by doping in 7-phenacenes are the same as to those in phenanthrene and picene. In \( \text{C}_{30}\text{II-K3-A} \) and \( \text{C}_{30}\text{II-K3-B} \) configurations of the doped 7-phenacenes, CB3 and CB4 cross the Fermi level where the electronic features are slightly different. In \( \text{C}_{30}\text{II-K3-A} \) configuration, the CB3 forms the hole-like Fermi surfaces along \( D - E - C \) direction in FBZ, while the CB4 shapes the electron-like Fermi surfaces along \( Y - A - B \) direction. In \( \text{C}_{30}\text{II-K3-B} \) configuration, the CB3 builds a hole-like Fermi shell around \( B \) and \( D \) \( k \)-point in FBZ, while the CB4 forms the electron-like Fermi ribbon along \( Y - A \) and \( E - C \) directions. The DOS at the Fermi level are 14.54 and 14.29 states/eV/f.u. in these two configurations, respectively, which less than those in doped 1,2,8,9-dibenzopentacene but larger than those in phenanthrene and picene. In addition, the PDOS results shown in Fig. 13 also suggest that the K-3d electrons contribute to the electronic states at the Fermi level. The electronic characteristics of pristine and tripotassium-doped 7-phenacenes indicate that a high superconductivity possibly exist, since the similar electronic properties to doped phenanthrene and picene.

D. Discussion

Look back to the crystal structures of these four PAHs, we find that the lowest-energy structure shown above contains the dopants in the intralayer region, such as \( \text{C}_{14}\text{K3} \), \( \text{C}_{22}\text{-K3-A} \), \( \text{C}_{30}\text{K3-A} \), and \( \text{C}_{30}\text{II-K3-A} \) configurations of doped PAHs. Unfortunately, the lattice constants in \( a, b, \) and \( c \) directions greatly deviate from experimental ones for tripotassium-doped phenanthrene and picene. However, the determination of crystal structure is sensitive to the K atomic positions. When one of three K atoms moves into the interlayer region, the lattice constants in \( a \) and \( b \) directions are close to the experimental values\(^{1,2,23} \), such as \( \text{C}_{14}\text{K2K1} \) and \( \text{C}_{22}\text{K2K1} \) configurations. Moreover, the experimental observations also indicate that the some of K atoms can be intercalated into in the interlayer region, and show that the shrink or expansion of lattice constant in \( c \) direction is obviously dependent on the preparation methods of samples. For tripotassium-doped phenanthrene and picene, therefore, the \( \text{C}_{14}\text{K2K1} \) and \( \text{C}_{22}\text{K2K1} \) configurations may respectively reflect their experimental structures, though the behavior of K atom moving into the interlayer region will raise the systematic energy. Additionally, in our more recent study on Ba doped phenanthrene\(^{44} \), we have found that the Ba content obviously changes the crystal lattice constants. Hence, from the viewpoint of fitting experimental crystal structure, the doping concentrations of potassium is also one of factors considered. With the increase of the number of benzene rings, the intercalating K atoms into interlayer region need more energy. So the metastable state of that some K atoms stay in the interlayer region is not existent in doped 1,2,8,9-dibenzopentacene and 7-phenacenes. More experimental observations are needed to clear the structural characteristics. The pristine 7-phenacenes is more stable than 1,2,8,9-dibenzopentacene. On the contrary, the latter is more stable after doping. As a result, the superconductivity was first observed in tripotassium-doped 1,2,8,9-dibenzopentacene. However, the superconductivity in doped 7-phenacenes is also expected.

From the electronic features, these are strongly affected by the crystal structure. Our predicted results and previous theoretical calculations reflect this point. But there are the common characters in these PAHs due to the same arrangement ordering of benzene rings. From phenanthrene to picene and then to 7-phenacenes, the K-doping causes the similar shift of the Fermi level and the arrangement of band ordering. However, the doped 1,2,8,9-dibenzopentacene exhibits the different electronic structures and abnormal phenomena such as the variations of band ordering and degeneracy. In addition, the rigid-band picture is invalid for doped PAHs. The reasons are mainly the rearrangement and distortion of molecules, as well as the hybridization between K-\( s, p, d \) orbitals and molecular orbitals of PAHs. As a consequence, the resultant Fermi surface exhibits a variety of multiband structures. This obviously provides an intriguing starting point for exploring mechanisms of superconductivity as a future work.

In addition, the calculated widths of bands crossing the Fermi level are often small. The values are about 0.26, 0.25, 0.21 eV for 3-, 5-, and 7-ring systems, respectively. It was reported that the experimental electronic correlation energy \( U \approx 0.85 \text{ eV} \)\(^{44} \) for doped picene indicating that the material is a strongly correlated electronic system. Further investigations for clarifying the material properties and the mechanism of superconductivity in doped PAHs should thus take into account the magnetic instability and the strong Coulomb interaction, as pointed out by previous theoretical reports\(^{13, 15, 45, 46} \). The detailed studies on electronic correlations in these PAHs will be presented in the future work.
IV. SUMMARY

We have systematically studied the crystal and electronic structures of pristine and tripotassium-doped PAHs based on the DFT first-principles calculations, covering these four materials of phenanthrene, picene, 1,2;8,9-dibenzopentacene, and 7-phenacenes. The full optimizations for pristine phenanthrene and picene suggest that the vDW-DF2 functional is important to obtain the crystal parameters according to experiments. Instead, the LDA functional is more favorable to fully optimizing the tripotassium-doped phenanthrene and picene. The possible reason is that the intercalation of K atoms reduces the nonlocal interactions by the hybridization with molecules. Based on the conclusion above, we found out the crystal structures similar to experimental ones and the more stable doped configurations for phenanthrene and picene. Most importantly, we have predicted for the first time the crystal structures of pristine and tripotassium-doped 1,2;8,9-dibenzopentacene and 7-phenacenes, respectively. The crystal symmetry of pristine PAHs of $P2_1$ was found to be preserved in all the optimized structures despite the deformation and rearrangements of the molecules upon doping. The doped structures are regarded to the K atomic positions. For phenanthrene and picene with the short molecular chain, one of three K atoms moves into the interlayer region, which makes the lattice constants fit the experiments. All of three K atoms localizing the intralayer region may decrease the systemic energy, but thus make the lattice parameters greatly deviate from the experimental values. With the increase of the number of benzene rings, such as 1,2;8,9-dibenzopentacene and 7-phenacenes, the K atoms have the difficulty in moving into the interlayer region. Many configurations have investigated with the difference K atomic positions. Observing along $b$ direction, three intercalated K atoms are easily localized at the second, fourth, and sixth benzene rings for both doped 1,2;8,9-dibenzopentacene and 7-phenacenes.

For the phenanthrene, picene, and 7-phenacenes with the same arrangement ordering of benzene rings, the electronic structures have the common characters. The first group of conduction bands comprises of four bands where two bands with the higher energy cross the Fermi level after doping. These three materials transform from direct band gap semiconductor to metal. The electronic structures near Fermi level exhibit the multiband feature. Generally, the bands are doubly degenerate and the degeneracy reduces after doping. However, the different electronic characters were observed in the superconducting 1,2;8,9-dibenzopentacene due to the variations of arrangement ordering of benzene rings. The pristine 1,2;8,9-dibenzopentacene is an indirect band gap semiconductor. The first group of conduction bands contains two bands, while the second group of conduction bands is made up of six bands. Although two with lowest energy of these six bands cross the Fermi level, the double degeneracy of bands increases with the doping. Note that the DOS at Fermi level is further increased with the number of benzene rings. It is useful for understanding the higher superconductivity in doped 1,2;8,9-dibenzopentacene and 7-phenacenes. Comparing the electronic structures, we find that the rigid-band picture is invalid for multiple reasons, i.e., through the rearrangement and distortion of molecules, but also via hybridization of the K-$s,p,d$ orbitals with the molecular orbitals of PAHs. In particular, the Fermi surfaces have the clear K-3$d$ feature which is interested for exploring the superconducting mechanism. In addition, the narrow bands crossing the Fermi level do not exceed 0.4 eV, which implies strong electronic correlations effects in these PAHs.

V. ACKNOWLEDGMENTS

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TABLE I. Optimized lattice constants $a$, $b$, $c$ (in Å), angle $\beta$ between $a$ and $c$ axes, and volume $V$ of a unit cell for the pristine phenanthrene ($C_{14}H_{10}$) and picene ($C_{22}H_{14}$) molecular crystals, with the $P_{2_1}$ symmetry and two molecules per cell, obtained with different approximations, compared with experimental results and previous theoretical results.

| System          | Source              | $a$   | $b$   | $c$   | $\beta$ | $V$    |
|-----------------|---------------------|-------|-------|-------|---------|--------|
| $C_{14}H_{10}$  | Expt. (Ref. 38)     | 8.46  | 6.16  | 9.47  | 97.7    | 489.1  |
|                 | LDA (Ref. 16)       | 8.05  | 5.96  | 9.16  | 96.8    | 436.4  |
|                 | GGA (Ref. 27)       | 9.25  | 6.31  | 9.71  | 100.6   | 557.4  |
|                 | vdW-DF (Ref. 27)    | 8.51  | 6.19  | 9.49  | 98.2    | 494.8  |
|                 | vdW-DF2 (Ref. 27)   | 8.27  | 6.09  | 9.34  | 97.7    | 466.5  |
|                 | DFT-D2 (Ref. 27)    | 7.87  | 5.95  | 9.19  | 96.5    | 427.7  |
|                 | Expt. (Ref. 39)     | 8.51  | 6.19  | 9.49  | 98.2    | 494.8  |
|                 | LDA (Ref. 21)       | 8.137 | 5.810 | 9.091 | 96.82   | 426.75 |
|                 | GGA                 | 9.241 | 6.454 | 9.753 | 99.37   | 573.92 |
|                 | vdW-DF              | 8.684 | 6.220 | 9.542 | 98.25   | 510.06 |
|                 | vdW-DF2             | **8.472** | **6.121** | **9.402** | **97.92** | **494.8** |
|                 | DFT-D2              | 8.101 | 5.900 | 9.220 | 96.37   | 437.95 |

TABLE II. Optimized lattice constants $a$, $b$, $c$ (in Å), angle $\beta$ between $a$ and $c$ axes, and volume $V$ of a unit cell for the pristine 1,2;8,9-dibenzo-pentacene ($C_{30}H_{18}$) and 7-phenacenes ($C_{30}H_{18}$II), with the $P_{2_1}$ symmetry and two molecules per cell, obtained by the vdW-DF2 scheme, compared with the results from other functionals.

| System          | Source              | $a$   | $b$   | $c$   | $\beta$ | $V$    |
|-----------------|---------------------|-------|-------|-------|---------|--------|
| $C_{30}H_{18}$  | LDA                 | 6.302 | 7.433 | 18.006| 93.58   | 841.90 |
|                 | GGA                 | 6.991 | 8.636 | 18.660| 96.03   | 1120.25|
|                 | vdW-DF              | 6.868 | 7.792 | 18.638| 97.07   | 989.80 |
|                 | vdW-DF2             | **6.745** | **7.613** | **18.495** | **97.13** | **942.47** |
|                 | DFT-D2              | 6.400 | 7.353 | 18.229| 94.13   | 853.46 |
| $C_{30}H_{18}$II| LDA                 | 8.237 | 5.844 | 17.295| 85.72   | 830.19 |
|                 | GGA                 | 9.378 | 6.482 | 17.933| 88.37   | 1089.76|
|                 | vdW-DF              | 8.781 | 6.257 | 17.793| 86.81   | 976.06 |
|                 | vdW-DF2             | **8.613** | **6.144** | **17.644** | **86.32** | **931.80** |
|                 | DFT-D2              | 8.191 | 5.908 | 17.507| 85.46   | 844.57 |

TABLE III. Optimized lattice constants $a$, $b$, $c$ (in Å), angle $\beta$ between $a$ and $c$ axes, and volume $V$ of a unit cell for the tripotassium-doped phenanthrene ($K_3C_{14}H_{10}$) with the $P_{2_1}$ symmetry, obtained with different approximations, compared with experimental results and previous theoretical results. The interest is in two special configurations of $C_{14}K_2K_1$ and $C_{14}K_3$ which are the nearest to experimental structure and the stablist case, respectively.

| Configuration   | Source              | $a$   | $b$   | $c$   | $\beta$ | $V$    |
|-----------------|---------------------|-------|-------|-------|---------|--------|
| $C_{14}K_2K_1$  | Expt. (Ref. 2)      | 8.430 | 6.134 | 9.417 | 98.18   | 482.0  |
|                 | LDA (Ref. 16)       | 8.04  | 6.54  | 10.09 | 102.6   | 517.77 |
|                 | LDA                 | **8.440** | **6.195** | **10.124** | **98.32** | **523.78** |
|                 | GGA                 | 9.458 | 6.485 | 10.928| 92.52   | 669.67 |
|                 | vdW-DF              | 9.191 | 6.495 | 10.782| 92.33   | 643.11 |
|                 | vdW-DF2             | 9.079 | 6.504 | 10.669| 92.40   | 629.39 |
|                 | DFT-D2              | 8.745 | 6.918 | 10.229| 90.13   | 618.83 |
|                 | LDA                 | 7.796 | 6.834 | 10.028| 111.10  | 498.45 |
|                 | GGA                 | 8.849 | 7.083 | 10.917| 119.11  | 597.81 |
|                 | vdW-DF              | 8.697 | 7.122 | 10.773| 116.76  | 595.76 |
|                 | vdW-DF2             | 8.519 | 7.125 | 10.664| 115.91  | 582.26 |
|                 | DFT-D2              | 8.105 | 6.825 | 10.153| 111.81  | 521.41 |
TABLE IV. Optimized lattice constants \(a, b, c\) (in Å), angle \(\beta\) between \(a\) and \(c\) axes, and volume \(V\) of a unit cell for the tripotassium-doped picene \((K_3C_{22}H_{14})\) with the \(P2_1\) symmetry, obtained with different approximations, compared with experiment and previous theoretical results. The interest focuses on three special configurations of \(K_3C_{22}H_{14}\), \(C_{22}-K2K_1\), \(C_{22}-K3-A\), and \(C_{22}-K3-B\), respectively. \(C_{22}-K2K1\) means that one of three \(K\) atoms is in the interlayer region, while \(C_{22}-K3\) means that all of three \(K\) atoms are in the intralayer region.

| Configuration | Source | \(a\)  | \(b\)  | \(c\)  | \(\beta\) | \(V\)  |
|---------------|--------|--------|--------|--------|-----------|--------|
| Expt. (Ref. 1) | 8.707  | 5.912  | 12.970 | 92.77  | 666.86    |
| Expt. (Ref. 23)| 8.571  | 6.270  | 14.001 | 91.68  | 752.09    |
| LDA (Ref. 21) | 7.359  | 7.361  | 14.018 | 105.71 | 730.98    |
| LDA (Ref. 22) | 7.421  | 7.213  | 14.028 | 104.53 | 726.85    |
| LDA           | 8.776  | 6.394  | 13.346 | 94.20  | 747.07    |
| LDA           | 8.773  | 6.433  | 13.310 | 93.76  | 749.62    |
| GGA           | 9.105  | 6.980  | 13.986 | 96.30  | 883.53    |
| vdw-DF        | 9.283  | 6.834  | 13.843 | 95.11  | 874.69    |
| vdw-DF2       | 9.102  | 6.839  | 13.694 | 93.83  | 850.52    |
| DFT-D2        | 9.065  | 6.445  | 13.448 | 93.21  | 784.52    |
| LDA           | 7.248  | 7.507  | 13.340 | 97.72  | 719.34    |
| GGA           | 7.613  | 8.044  | 14.186 | 99.08  | 857.85    |
| vdw-DF        | 7.694  | 7.991  | 13.938 | 99.20  | 845.96    |
| vdw-DF2       | 7.657  | 7.893  | 13.850 | 99.29  | 826.01    |
| DFT-D2        | 7.375  | 7.598  | 13.543 | 98.23  | 751.09    |
| LDA           | 7.374  | 7.283  | 13.986 | 103.74 | 729.58    |
| GGA           | 7.779  | 7.742  | 14.693 | 102.39 | 864.20    |
| vdw-DF        | 7.859  | 7.719  | 14.506 | 104.62 | 851.56    |
| vdw-DF2       | 7.805  | 7.624  | 14.374 | 104.43 | 828.44    |
| DFT-D2        | 7.534  | 7.323  | 14.114 | 103.62 | 763.02    |

TABLE V. Optimized lattice constants \(a, b, c\) (in Å), angle \(\beta\) between \(a\) and \(c\) axes, and volume \(V\) of a unit cell for the tripotassium-doped 1,2;8,9-dibenzopentacene \((K_3C_{30}H_{18})\) and 7-phenacenes \((K_3C_{30}H_{18}II)\), with the \(P2_1\) symmetry and two molecules per cell, based on LDA.

| System          | configuration | \(a\)  | \(b\)  | \(c\)  | \(\beta\) | \(V\)  |
|-----------------|---------------|--------|--------|--------|-----------|--------|
| \(K_3C_{30}H_{18}\) | C_{30}-K3-A  | 7.741  | 7.043  | 17.693 | 100.97    | 946.99 |
|                 | C_{30}-K3-B  | 7.880  | 6.993  | 17.918 | 101.05    | 969.08 |
| \(K_3C_{30}H_{18}II\) | C_{30}II-K3-A | 7.269  | 7.550  | 16.682 | 88.75     | 915.38 |
|                 | C_{30}II-K3-B | 7.162  | 7.462  | 18.889 | 107.13    | 964.79 |
FIGURE CAPTIONS

**Fig.1:** (Color online) Optimized crystal structures of undoped PAHs with the $P_{21}$ symmetry and two molecules per cell, based on the vdW-DF2 scheme. The unit cell size is marked by the blue line. Brown and grey balls represent C and H atoms, respectively. (a)-(d) correspond to phenanthrene (C$_{14}$H$_{10}$), picene (C$_{22}$H$_{14}$), 1,2;8,9-dibenzopentacene (C$_{30}$H$_{18}$), and 7-phenacenes (C$_{30}$H$_{18}$II) crystals, respectively.

**Fig.2:** (Color online) Two special crystal configurations of tripotassium-doped phenanthrene obtained with LDA. (a) C$_{14}$-K2K1 is a configuration of the nearest to experiment. (b) C$_{14}$-K3 is the stablest case. Brown, grey and purple balls represent C, H, and K atoms, respectively.

**Fig.3:** (Color online) Three special crystal configurations of tripotassium-doped picene obtained with LDA. (a) C$_{22}$-K2K1 is the nearest to experimental structure. (b) C$_{22}$-K3-A is the stablest case. (c) C$_{22}$-K3-B is the next stabest. Brown, grey and purple balls represent C, H, and K atoms, respectively.

**Fig.4:** (Color online) Predicted crystal structures of tripotassium-doped 1,2;8,9-dibenzopentacene (K$_3$C$_{30}$H$_{18}$) based on LDA. Brown, grey and purple balls represent C, H, and K atoms, respectively. (a) K3-A type; (b) K3-B types.

**Fig.5:** (Color online) Predicted crystal structures of tripotassium-doped 7-phenacenes (K$_3$C$_{30}$H$_{18}$II) based on LDA. Brown, grey and purple balls represent C, H, and K atoms, respectively. (a) C$_{30}$II-K3-A type; (b) C$_{30}$II-K3-B types.

**Fig.6:** (Color online) Calculated band structures along high symmetrical k-point directions in the FBZ, total density of states (DOS), and Fermi surface sheets. (a) Pristine phenanthrene: band structure and typical FBZ marked by high symmetrical k-points. (b) and (c) correspond to the tripotassium-doped phenanthrene in C$_{14}$-K2K1 and C$_{14}$-K3 configurations, respectively, presenting band structures, DOSs, and Fermi surface sheets. The Fermi level is set to zero energy point.

**Fig.7:** (Color online) Calculated the projected density of states (PDOS) on orbitals of one C atom and three K atoms for tripotassium-doped phenanthrene. (a) and (b) correspond to C$_{14}$-K2K1 and C$_{14}$-K3 configurations, respectively. The Fermi level is set to zero energy point.

**Fig.8:** (Color online) Calculated band structures along high symmetrical k-point directions in the FBZ, total density of states (DOS), and Fermi surface sheets. (a) Pristine picene: band structure and typical FBZ marked by high symmetrical k-points. (b) and (d) correspond to the tripotassium-doped picene in C$_{22}$-K2K1, C$_{22}$-K3-A, and C$_{22}$-K3-B configurations, respectively, presenting band structures, DOSs, and Fermi surface sheets. The Fermi level is set to zero energy point.

**Fig.9:** (Color online) Calculated the projected density of states (PDOS) on orbitals of one C atom and three K atoms for tripotassium-doped picene. (a)-(c) correspond to C$_{22}$-K2K1, C$_{22}$-K3-A, and C$_{22}$-K3-B configurations, respectively. The Fermi level is set to zero energy point.

**Fig.10:** (Color online) Calculated band structures along high symmetrical k-point directions in the FBZ, total density of states (DOS), and Fermi surface sheets. (a) Pristine 1,2;8,9-dibenzopentacene (C$_{30}$H$_{18}$): band structure and typical FBZ marked by high symmetrical k-points. (b) and (c) correspond to the tripotassium-doped 1,2;8,9-dibenzopentacene (K$_3$C$_{30}$H$_{18}$) in C$_{30}$-K3-A and C$_{30}$-K3-B configurations, respectively, presenting band structures, DOSs, and Fermi surface sheets. The Fermi level is set to zero energy point.

**Fig.11:** (Color online) Calculated the projected density of states (PDOS) on orbitals of one C atom and three K atoms for tripotassium-doped 1,2;8,9-dibenzopentacene (K$_3$C$_{30}$H$_{18}$). (a) and (b) correspond to C$_{30}$-K3-A and C$_{30}$-K3-B configurations, respectively. The Fermi level is set to zero energy point.

**Fig.12:** (Color online) Calculated band structures along high symmetrical k-point directions in the FBZ, total density of states (DOS), and Fermi surface sheets. (a) Pristine 7-phenacenes (C$_{30}$H$_{18}$II): band structure and typical FBZ marked by high symmetrical k-points. (b) and (c) correspond to the tripotassium-doped 7-phenacenes (K$_3$C$_{30}$H$_{18}$II) in C$_{30}$II-K3-A and C$_{30}$II-K3-B configurations, respectively, presenting band structures, DOSs, and Fermi surface sheets. The Fermi level is set to zero energy point.
to zero energy point.

**Fig.13:** (Color online) Calculated the projected density of states (PDOS) on orbitals of one C atom and three K atoms for tripotassium-doped 7-phenacenes ($K_3C_{30}H_{18}$II). (a) and (b) correspond to $C_{30}$II-K3-A and $C_{30}$II-K3-B configurations, respectively. The Fermi level is set to zero energy point.
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