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PAPER

## “Doping” Pentacene with $sp^2$ -phosphorus Atoms: Towards High Performance Ambipolar Semiconductors

Guankui Long,<sup>a,b</sup> Xuan Yang,<sup>b</sup> Wangqiao Chen,<sup>a</sup> Mingtao Zhang,<sup>c\*</sup> Yang Zhao,<sup>a\*</sup> Yongsheng Chen,<sup>b\*</sup> Qichun Zhang,<sup>a,d\*</sup>

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Recent research progress on black phosphorus sheets strongly encourage us to employ pentacene as a parent system to systematically investigate how the “doping” of  $sp^2$ -phosphorus atoms onto the backbone of pentacene to influence its optical and charge transport properties. Our theoretical investigations proved that increasing the contribution of the  $p_z$  atomic orbital of the  $sp^2$ -phosphorus in the frontier molecular orbital of the phosphapentacenes could significantly decrease both hole and electron reorganization energies and dramatically red-shift the absorption of pentacene. The recorded smallest hole and electron reorganization energies of 69.80 and 95.74 meV for heteropentacene derivatives were obtained. These results suggest that phosphapentacenes (or phosphacenes) could be potential promising candidates to achieve both higher and balanced mobilities in organic field effect transistors and realize better power conversion efficiency in organic photovoltaics.

### Introduction

Acenes are polycyclic aromatic hydrocarbons consisting of linearly fused benzene rings, which are the simplest zig-zag type graphene nanoribbon (GNR) with largest length/width ratio. In the past decades, these compounds have received wide interest from both theoretical<sup>1</sup> and experimental points.<sup>2</sup> Although acenes with different lengths can have different bandgaps or energy levels, which are very important for the applications in diverse devices like organic field effect transistors (OFETs) and organic photovoltaics (OPVs), further tuning their properties to approach better performance in these devices is still highly desirable. Generally, there are four ways to modify the properties of oligoacenes: (1) increasing the conjugated length to reduce the HOMO-LUMO energy gaps;<sup>2</sup> (2) introducing electron-withdrawn groups (e.g. F-, CN-) to switch the charge transport properties from p type to n type;<sup>3</sup> (3) optimizing the device fabrication conditions to enhance the crystallinity;<sup>4</sup> and (4) “doping” the framework of oligoacenes with heteroatoms (B, P, S, O, N).<sup>2f, 5</sup> In fact, doping strategy has been widely used in the silicon industry.

It is well-known that ion-implantation of silicon with heteroatoms (B, P, As, Sb) can enhance its charge-carrier mobility (p- or n-doped). These heteroatoms were also used to dope graphene and other carbon materials to achieve better performance in lithium batteries and supercapacitors.<sup>6</sup> Logically, introducing heteroatoms into the backbone of oligoacenes (so-called “doping”) will also influence their optical and charge transport properties. However, the concept of “doping” here is different from ion-implantation for silicon or chemically doping for conducting polymers: (1) the “doping” would be realized through step-by-step reactions with heteroatom-contained starting materials or intermediates; (2) the positions of all heteroatoms are well-defined; (3) the properties of as-prepared oligoheteroacenes are strongly dependent on the types/positions/numbers of heteroatoms; and (4) “doping” oligoacenes with more different types of heteroatoms is feasible. Among the above mentioned modifications, the introduction of nitrogen,<sup>5, 7</sup> boron atoms<sup>8</sup> and boron-nitrogen bonds<sup>5f, 9</sup> into aromatic compounds are proven to be very successful and electron mobility up to  $5.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was achieved by “doping” the backbone of pentacene with four nitrogen atoms.<sup>7a</sup>

However, the influence of phosphorus atoms on the charge transport and optical properties of acene is still missing due to synthetic difficulties and only several phosphorus “doped” aromatic compounds (Scheme 1) have been reported up to date.<sup>10</sup> On the other hand, black phosphorus nanomaterials have drawn great research interests recently. Few-layer black phosphorus sheets (phosphorene) like graphene has been successfully exfoliated and hole mobility as high as  $\sim 1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was achieved experimentally.<sup>11</sup> Given the emergence development of 2D phosphorus materials and their advantages, we are interested in theoretical investigation of phosphorus-atom-“doped” acenes because theoretical calculation could predict the advantages and dis-advantages of phosphacenes in advance of the synthetic works.<sup>12</sup> In this work, we used pentacene as

<sup>a</sup> School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore, E-mail: qczhang@ntu.edu.sg; yzhao@ntu.edu.sg

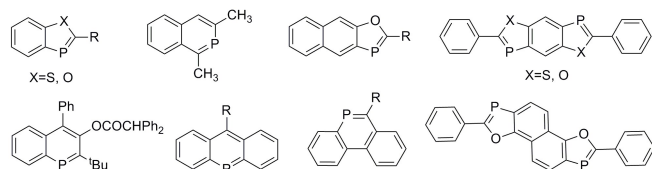
<sup>b</sup> State Key Laboratory and Institute of Elemento-Organic Chemistry, Synergetic Innovation of Chemical Science and Engineering (Tianjin), School of Materials Science and Engineering, Nankai University, Tianjin 300071, China, E-mail: yschen99@nankai.edu.cn

<sup>c</sup> Computational Center for Molecular Science, College of Chemistry, Nankai University, Tianjin, 300071, China, E-mail: zhangmt@nankai.edu.cn

<sup>d</sup> Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

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a model system and systematically investigated the influence of phosphorus atoms on its optical and charge transport properties. Our results proved that the replacement of C-H moieties in pentacene could effectively decrease the hole and electron reorganization energy and largely red-shift the absorption of pentacene. According to our results, we do believe that this type of materials should have potential promising applications in OFETs and OPVs to achieve higher mobilities and better photo-electric conversion efficiency.



**Scheme 1.** The representative structures of phosphorus “doped” aromatic compounds.

## Calculation Method

All the geometries of the ground states, radical cations, radical anions and triplet states for the phosphapentacenes were optimized by B3LYP functional combined with 6-311+G\*\* basis sets,<sup>13</sup> and the frequency analysis was followed to assure that the optimized structures were stable states. The reorganization energies were calculated using a standard four-point method.<sup>12b</sup> Time-dependent DFT (TDDFT) calculation for the  $S_0 \rightarrow S_n$  transitions using B3LYP/6-311+G\*\* were then performed based on the optimized structures at ground states. The intermolecular transfer integrals were obtained through a direct evaluation of the coupling element between frontier orbitals using the unperturbed density matrix of the dimer Fock operator.<sup>14</sup> All the calculations were carried out using Gaussian 09 package.<sup>15</sup> The normal-mode analysis and the Huang-Rhys factors were obtained through the DUSHIN program developed by Reimers.<sup>16</sup>

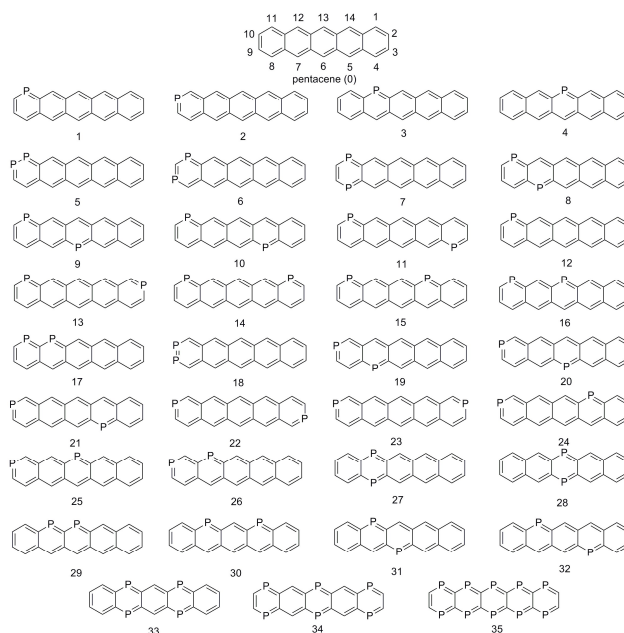
## Results and Discussion

### Chemical Structures of Phosphapentacenes

Due to the huge number of isomers resulting from varying the numbers and positions of phosphorus atoms on the backbone of pentacene, we mainly focus on the isomers containing one and two phosphorus atoms. In addition, the other three representative structures with four, six and ten phosphorus atoms modified pentacenes are also investigated for comparison. The chemical structures and nomenclatures of the phosphapentacenes in this study are shown in Scheme 2 and Table S1 (ESI<sup>†</sup>).

There are 4 isomerides after replacing only one C-H group in pentacene with phosphorus atom, and 28 isomerides in total when two C-H groups were replaced. The optimized structures of the ground states, radical cations and anions for the phosphapentacenes are shown in Fig. S1-S3 (ESI<sup>†</sup>), and only the anion state of 1,4,5,6,7,8,11,12,13,14-decaphosphapentacene (**35**) is highly twisted, others are planar geometry. The calculated C=P bond length is 1.709 Å, which is consistent with the reported C=P bond length (1.706 Å) in single crystals.<sup>10b</sup> The contribution of the  $p_z$  atomic orbital of the  $sp^2$ -phosphorus in the frontier molecular orbitals

(FMO) of the phosphapentacenes are calculated and summarized in Table S2 (ESI<sup>†</sup>), and pentacene is also calculated for comparison. As shown in Fig. S4 (ESI<sup>†</sup>), the influence of different positions on the optical and charge transport properties of pentacene derivative should be in the order of 6- (or 13-) > 5- (or 7-, 12-, 14-) > 1- (or 2-, 3-, 4-, 8-, 9, 10-, 11-) position.



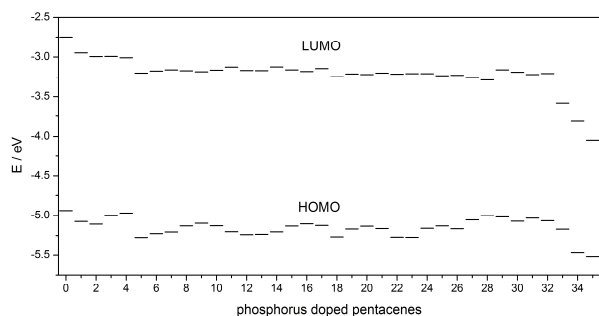
**Scheme 2.** The chemical structures of pentacene and phosphapentacene derivatives discussed in this work.

### Frontier Molecular Orbitals

Compared with pentacene, the LUMO energy level decreased *ca.* 0.2 eV after replacing with one phosphorus atom, and *ca.* 0.4 eV for two phosphorus atoms (Fig. 1). The HOMO energy levels of these phosphapentacene derivatives exhibit positive correlation with increasing the percentage of the  $p_z$  atomic orbital of phosphorus in the HOMO of phosphapentacenes (Fig. S5, ESI<sup>†</sup>). Thus, the HOMO-LUMO energy gap shows a large decrease from 2.19 eV for pentacene to 1.71 eV for 6,13-diphosphapentacene (**28**), 1.59 eV for 5,7,12,14-tetraphosphapentacene (**33**), and 1.47 eV for 1,4,5,6,7,8,11,12,13,14-decaphosphapentacene (**35**).

### Optical properties

The reduced HOMO-LUMO energy gap could be further confirmed by TDDFT calculation. The  $S_0 \rightarrow S_1$  excitation energies for these phosphapentacenes exhibit very large red-shift compared with pentacene itself after replacing with phosphorus atoms at different positions (Fig. S6, ESI<sup>†</sup>), which further confirm that P=C double bonds with lower lying  $\pi^*$  orbitals could efficiently decrease the HOMO-LUMO energy gaps.<sup>10d</sup> The simulated absorption peak shifts from 652.53 nm for pentacene to 714.95 nm for 6-phosphapentacene (**4**) and 808.50 nm for 6,13-diphosphapentacene. After more phosphorus atoms were added, the absorption peaks could further red-shift to 921.45 nm for compound **33** and 1027.56 nm for **35**. This further proves that the positions and numbers of phosphorus atoms could effectively control the optical properties of phosphapentacene derivatives as discussed above.



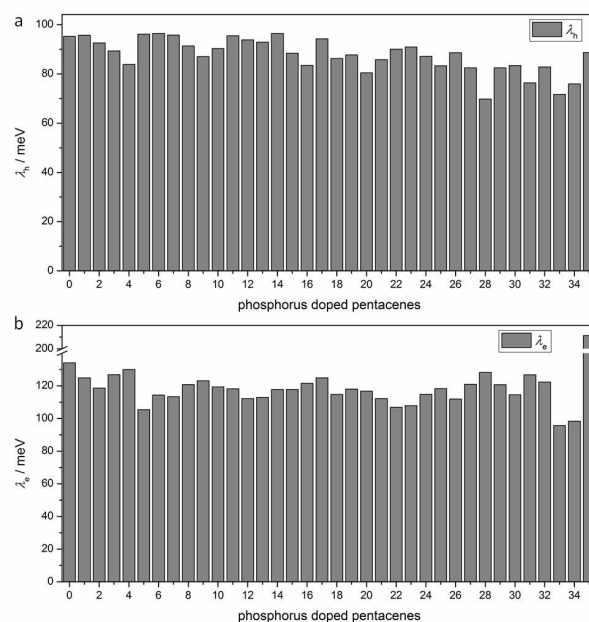
**Fig. 1** The calculated energy levels for the frontier molecular orbitals of the phosphapentacene derivatives compared with pentacene. The number is consistent with structures showed in Scheme 2.

### Charge transport properties

The most important impact is the “doping” of phosphorus atoms on the charge transport properties of pentacene derivatives. According to the Marcus electron transfer theory,<sup>17</sup> increasing the transfer integrals ( $V$ ) between neighbour molecules and decreasing the reorganization energies ( $\lambda$ ) could improve the charge transport mobility.<sup>12d-12f, 17</sup> In order to investigate the impact of phosphorus “doping” on the transfer integrals, we have calculated the transfer integrals at a fixed distance and orientation between the dimers of pentacene and 6,13-diphosphapentacene. As shown in Fig. S7 (ESI<sup>†</sup>), the calculated transfer integrals for hole (a, c, e) and electron transfer (b, d, f) in the dimer of 6,13-diphosphapentacene along the  $\pi$ - $\pi$  stacking direction (a, b), long axis (c, d) and short axis (e, f) directions are larger than that for pentacene, which evident that the introduction of phosphorus could increase both the hole and electron transfer integrals for pentacene. Then the reorganization energies for hole and electron transport of the phosphapentacenes are calculated and summarized in Fig. 2 and Table S3 (ESI<sup>†</sup>). The hole and electron reorganization energies are largely dependent on the positions of the phosphorus atoms. After replacing with one phosphorus atom, only the isomer with phosphorus at the 6- position shows a more decreased hole reorganization energy of 83.86 meV, while 1- or 2- position shows similar hole reorganization energies (larger than 90 meV) compared with pentacene. The electron reorganization energy also shows significant changes after replacing with only one phosphorus atom, and the smallest electron reorganization energy is 118.61 meV for 2-phosphapentacene (2), which is 15.5 meV lower than that of pentacene (134.11 meV).

Once the 6- and 13- positions are replaced by two phosphorus atoms, the hole reorganization energy could further decrease to 69.80 meV, which is the smallest hole reorganization energy reported for heteropentacene derivatives (Table S4, ESI<sup>†</sup>). It is reported that the active sites in pentacene are 6- and 13- positions, which could react with oxygen or acenes through *Diels-alder* reaction.<sup>2</sup> However, after replacing the C-H groups by phosphorus atoms at 6- and 13- positions, not only the hole reorganization energy is decreased, but also the stability is enhanced. The other interesting phenomenon is that the hole reorganization energies could be decreased with replacing one C-H group in the 6- or 13- position of pentacene by phosphorus atom, such as 76.36 meV for 5,13-diphosphapentacene (31). After replacing one C-H group at 5- position with phosphorus atom, the hole reorganization energies also

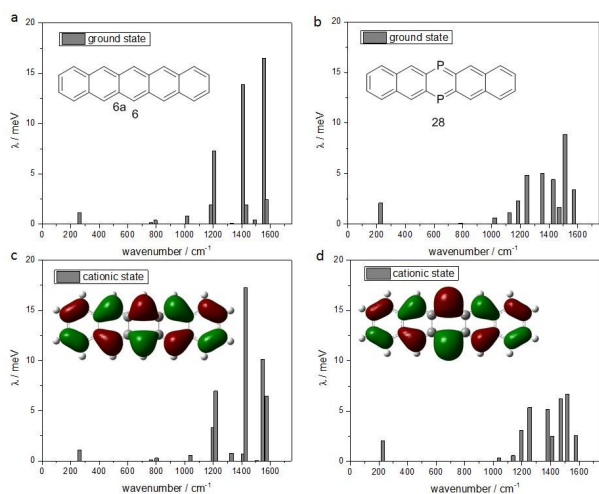
get significant reducing to 82.85 meV (5,12-diphosphapentacene, 32) and 82.49 meV (5,14-diphosphapentacene, 27), respectively. Among these two phosphorus containing pentacene derivatives, the electron reorganization energy could further decrease to 107.87 meV (2,10-diphosphapentacene, 23), 106.85 meV (2,9-diphosphapentacene, 22) and 105.40 meV (1,2-diphosphapentacene, 5) after replacing one C-H group at the 2-position, which are potentially good candidates toward the application in n-type OFET. Based on the above discussion, it is obvious that the charge transport properties of pentacene could be controlled effectively by the replacement of C-H moieties with phosphorus atoms at different positions.



**Fig. 2** The calculated hole (a) and electron (b) reorganization energies of the phosphapentacenes compared with pentacene.

After phosphorus atoms replaced more C-H groups in pentacene, both hole and electron reorganization energies could be further decreased significantly. The hole and electron reorganization energies would reduce to 71.68 meV and 95.74 meV after four phosphorus atoms were introduced into pentacene (33), similar values of 75.97 meV and 98.37 meV were achieved after six C-H groups were replaced with phosphorus atoms (1,4,6,8,11,13-hexaphosphapentacene, 34), respectively. On the contrary, compound 35 with ten phosphorus atoms shows very large electron reorganization energy of 211.32 meV, which is mainly ascribed to the highly twisted structure in the anionic states (Fig. S3, ESI<sup>†</sup>), and could not facilitate the electron transport. Thus, compounds 33 and 34 are potentially good candidates for ambipolar semiconductors.





**Fig. 3.** Contribution of the neutral and cationic state vibrational modes to the hole reorganization energy of pentacene (a, c) and 6,13-diphosphapentacene (b, d) calculated at the B3LYP level combined with the 6-311+G\*\* basis set. The inset shows the calculated HOMO electron density for pentacene and 6,13-diphosphapentacene.

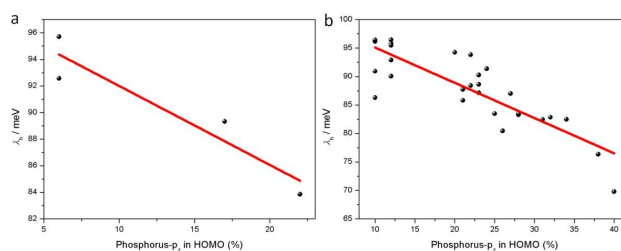
### The Origin of the Reduced Reorganization Energies

In order to investigate the origin of the decreased reorganization energy and the contributions of C=P bond vibration to the hole and electron reorganization energy, normal mode (NM) analysis methods are applied.<sup>16</sup> Within the harmonic approximation, the total reorganization energy was decomposed into the contributions of each vibrational mode according to Equation 1:

$$\lambda = \sum_i \lambda_i = \hbar \omega_i S_i \quad \text{Equation 1}$$

Here,  $\lambda_i$  denotes the reorganization energy from vibrational mode  $i$  with frequency  $\omega_i$ , and  $S_i$  is the dimensionless Huang-Rhys factor describing the coupling strength of charge and phonons. The reorganization energies for holes and electrons calculated by NM analysis method are in good agreement with that from the adiabatic potential (AP) energy surface method (Table S5, ESI†). Fig. 3 shows the decomposition of total reorganization energy for hole into the contributions of individual vibrational modes for pentacene and 6,13-diphosphapentacene. Based on the normal mode analysis, it is found that three high frequency modes with  $\lambda_i > 6.50$  meV in the region of 1200-1600  $\text{cm}^{-1}$  contribute to the majority of the hole reorganization energy for pentacene, which can be attributed to the stretching modes of C=C bond. After replacing the 6- and 13-positions with two phosphorus atoms, the contribution of vibrational modes to the hole reorganization energy decreases significantly. The largest contribution comes from the vibrational mode at 1511  $\text{cm}^{-1}$  with  $\lambda_i$  of 8.85 meV, which is almost half of that (16.53 meV) for pentacene at 1556  $\text{cm}^{-1}$ . Amazingly, the four major vibrational modes at 1248, 1355, 1429 and 1511  $\text{cm}^{-1}$  for 6,13-diphosphapentacene are mainly ascribed to the C=C bond stretching, and the only major contribution from phosphorus is the C-P-C angle bending mode (2.07 meV) at 227  $\text{cm}^{-1}$ . Based on this, we have compared the bond length changes for C=P bond from ground state to cationic state, which is only  $8.1 \times 10^{-4}$  Å, while the C=C bond (C<sub>6</sub>-

C<sub>6a</sub>) shows very large displacement of  $3.7 \times 10^{-3}$  Å in pentacene. The prominent reduction in the reorganization energies for these phosphapentacenes should therefore be ascribed to the smaller electronegativity and weaker binding energy to the valence electron of phosphorus atom, which makes the FMOs more “soft”. Thus contributes to less geometrical changes during donating or accepting electrons.<sup>12k</sup> In order to further confirm this, the hole reorganization energies were correlated with the contribution of the  $p_z$  atomic orbital of the  $sp^2$ -phosphorus in the HOMO of the phosphapentacenes, and positive correlation was obtained (Fig. 4), which further evident the importance of phosphorus components in FMO in determining the charge transport properties of phosphapentacenes.



**Fig. 4** Correlations between hole reorganization energies of phosphapentacene derivatives with the percentage of  $p_z$  atomic orbital of the  $sp^2$ -phosphorus in the HOMO of the monophosphapentacene (a) and diphosphapentacene (b) derivatives.

### Conclusion

In summary, based on the theoretical investigation of the optical and charge transport properties of phosphorus “doped” pentacene derivatives, we found that the optical and charge transport properties of pentacene could be tuned effectively through controlling the percentage of the  $p_z$  atomic orbital of the  $sp^2$ -phosphorus in the frontier molecular orbital of the phosphapentacenes. 6,13-diphosphapentacene is the simplest example exhibits the smallest hole transport reorganization energy reported for heteropentacene derivatives up to today, and this compound could be a potential promising candidate in high performance p-type OFET. 2,9-diphosphapentacene, 2,10-diphosphapentacene and 1,2-diphosphapentacene exhibit great potential towards the application in n-type OFET with very small electron reorganization energy of ca. 106 meV. With four or six phosphorus atoms are introduced into pentacene, both the hole and electron reorganization energies and HOMO-LUMO energy gaps of the phosphapentacene derivatives could be significantly reduced, which would be potentially used as ambipolar semiconductors in OFET.

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