Extended π-Systems

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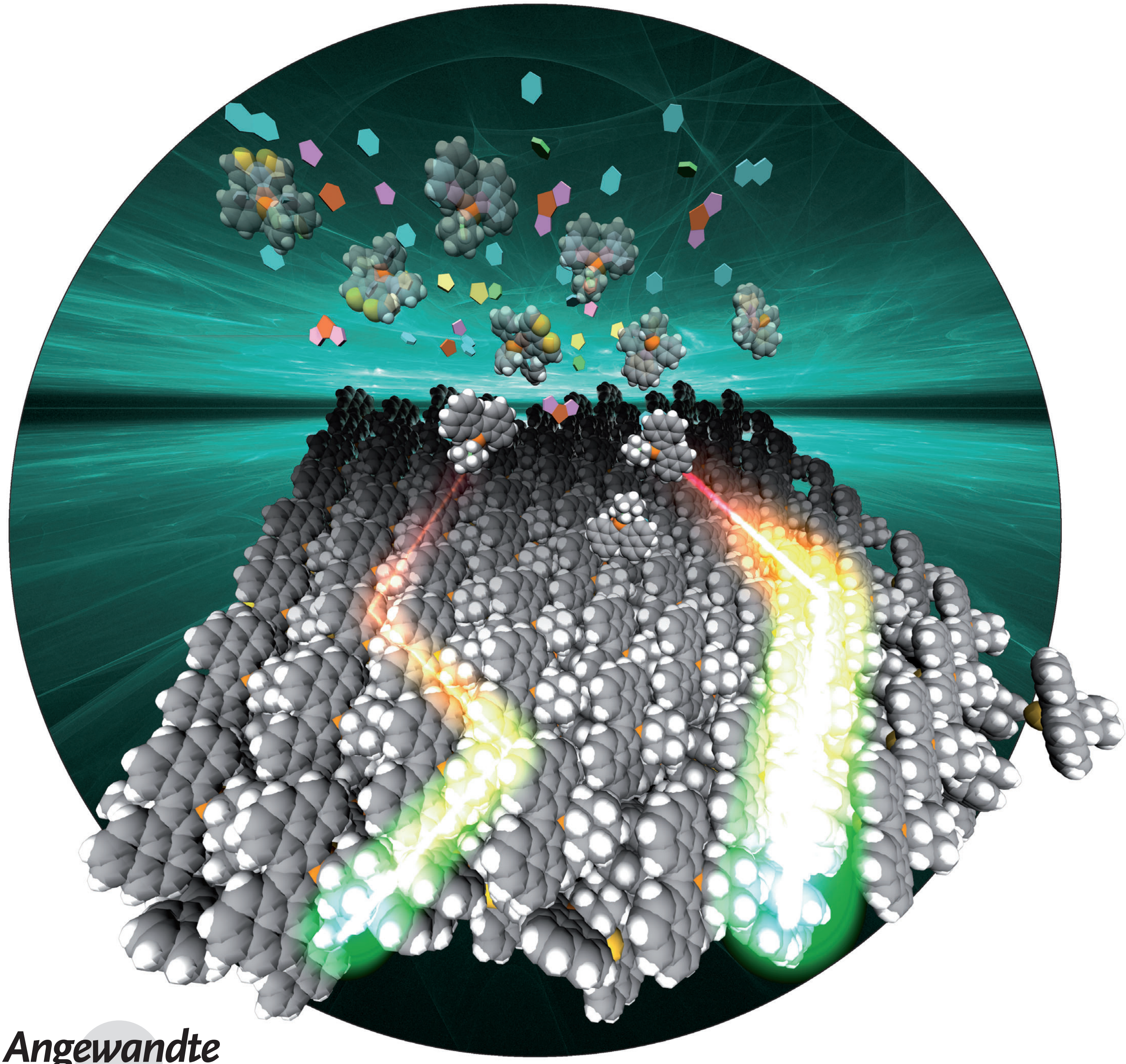
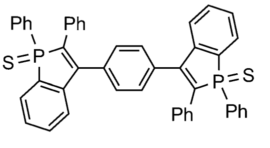
Fusion of Phosphole and 1,1′-Biacenaphthene: Phosphorus(V)-Containing Extended π-Systems with High Electron Affinity and Electron Mobility**

Yoshihiro Matano, Arihiro Saito, Tatsuya Fukushima, Yasuaki Tokudome, Furitsu Suzuki, Daisuke Sakamaki, Hironori Kaji, Akihiro Ito, Kazuyoshi Tanaka, and Hiroshi Imahori*



Recent developments in the chemistry of arene-fused phosphole π systems have shed light on their characteristic properties for use in optoelectronic applications.[1] For example, many derivatives of benzo[*b*]phospholes,[2] dibenzo-[*b*,*d*]phospholes,[3] dithieno[*b*,*d*]phospholes,[4] and P,X-bridged stilbenes (X = P, B, S)[5] have been reported to possess highly fluorescent nature partly due to their rigid π skeletons. It is well established that phosphole has a low-lying LUMO derived from the effective σ*–π* orbital interaction.[1d] This implies that arene-fused phosphole π-systems, especially those having the phosphorus(V) center, are also potential candidates as n-type semiconducting materials. Indeed, several research groups have designed and synthesized their own phosphole derivatives with high electron affinity.[2a,c,6–9] Furthermore, Tsuji, Nakamura, and co-workers reported very high electron drift mobility for *para*-phenylene-linked benzo[*b*]phosphole P-sulfide **1** and demonstrated its utility in organic devices such as light emitting diode and photovoltaic cell.[6] We independently reported a few phosphole-based n-type materials,[9] among which acenaphtho[1,2-*c*]phosphole P-oxide **2** exhibited one-order higher electron mobility than did tris(8-hydroxyquinoline)aluminum(III) (Alq$_3$).[9b] Despite these intriguing results, however, the semiconducting ability of arene-fused phosphole derivatives has not been fully explored due to the limited number of promising candidates.

Herein, we report the first examples of diacenaphtho[1,2-*b*:1′,2′-*d*]phospholes including **3**, which were designed as a new class of n-type phosphole derivatives based on the following concepts: 1) the intrinsically electron-accepting nature of phosphole would be enhanced by the fusion with a 1,1′-biacenaphthene moiety, 2) the electron affinity of the π-system would be tunable by P-functionalizations, and 3) the extended π-plane would be beneficial to π–π stacking and electron-spin delocalization. In this study, we aimed to reveal the effects of P-substituents as well as P-oxidation states on the structural and electrochemical properties of the diacenaphtho[*b*,*d*]phosphole π-systems. A high electron drift mobility of **3b** (R = cyclohexyl) in a vacuum-deposited film is also reported.



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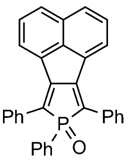

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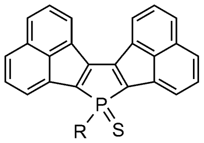

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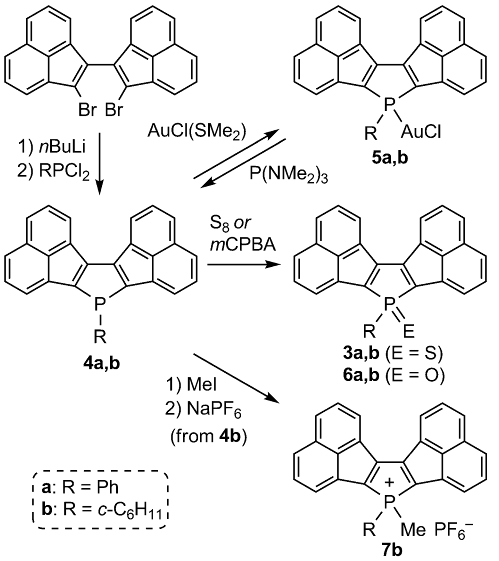
Scheme 1 depicts the synthesis of target compounds. Treatment of 2,2′-dibromo-1,1′-biacenaphthene[10] with two equiv of *n*BuLi followed by the addition of PhPCl$_2$ gave diacenaphtho[1,2-*b*:1′,2′-*d*]phosphole **4a**. As **4a** was rather difficult to isolate from the reaction mixture, crude **4a** was subsequently converted into gold(I) complex **5a**, which was then purified by column chromatography. The yield of isolated **5a** was 77% based on the dibromide. Demetallation of **5a** with P(NMe$_2$)$_3$ reproduced the σ^3-P derivative **4a** quantitatively. The P-thioxidation (with S$_8$) and the P-oxidation (with *m*CPBA) of **4a** afforded P-sulfide **3a** and P-oxide **6a**, respectively; however, **6a** slowly decomposed in solution at room temperature.[11] According to similar procedures, another series of diacenaphtho[*b*,*d*]phosphole derivatives **3b**, **4b**, **5b**, and **6b** bearing a P-cyclohexyl group were prepared by using *c*-C$_6$H$_{11}$PCl$_2$ instead of PhPCl$_2$. The thermal stability of **6b** was found to be higher than that of **6a**. Methylation of the in-situ generated **4b** with excess iodomethane, followed by treatment with an aqueous NaPF$_6$ solution produced phosphonium salt **7b**.



Scheme 1. Synthesis of diacenaphtho[1,2-*b*:1′,2′-*d*]phospholes. *m*CPBA = *m*-chloroperoxybenzoic acid.

Compounds **3**–**7** were characterized by conventional spectroscopic methods. The ^{31}P NMR spectra of the P-phenyl derivatives **3a**, **4a**, **5a**, and **6a** showed a sharp singlet peak at $\delta_P = 19.2$, -27.7, -4.4, and 18.5 ppm, respectively,

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[*] Prof. Dr. Y. Matano, A. Saito, D. Sakamaki, Prof. Dr. A. Ito,
Prof. Dr. K. Tanaka, Prof. Dr. H. Imahori
Department of Molecular Engineering
Graduate School of Engineering
Kyoto University, Nishikyo-ku, Kyoto 615-8510 (Japan)
E-mail: matano@scl.kyoto-u.ac.jp
T. Fukushima, Y. Tokudome, F. Suzuki, Prof. Dr. H. Kaji
Institute for Chemical Research
Kyoto University, Uji, Kyoto 611-0011 (Japan)
Prof. Dr. H. Imahori
Institute for Integrated Cell-Material Sciences (iCeMS)
Kyoto University, Nishikyo-ku, Kyoto 615-8510 (Japan)
Prof. Dr. K. Tanaka, Prof. Dr. H. Imahori
Fukui Institute for Fundamental Chemistry
Kyoto University, Sakyo-ku, Kyoto 606-8103 (Japan)

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whereas those of the P-cyclohexyl derivatives **3b**, **4b**, **5b**, and **6b** showed the corresponding peaks at more downfield (δ_P = 35.4, −8.41, 7.0, and 35.0 ppm). The onium salt **7b** displayed ^{31}P and ^{1}H (methyl) peaks at δ_P 19.6 ppm and δ_H 2.46 ppm (J_{PH} = 13.7 Hz), respectively. The structures of **3b** and **7b** were further elucidated by X-ray crystallography.[12] As shown in Figure 1, the phosphorus-linked π-systems are almost flat, and two biacenaphthene planes are stacked in parallel and in head-to-tail orientation with π–π distances of 3.32–3.47 Å. In both **3b** and **7b**, the phosphorus center adopts a distorted tetrahedral geometry with the cyclohexyl group in chair conformation. On the other hand, the whole packing arrangement of **7b** differs from that of **3b** (Figure S1 in the Supporting Information).

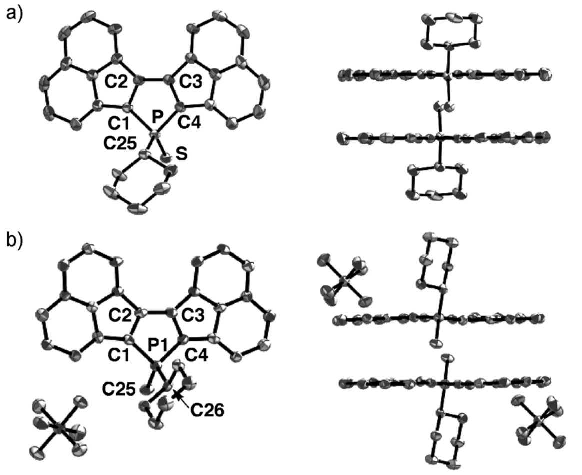

Figure 1. Top and side views of a) **3b** and b) **7b**. Hydrogen atoms and dichloromethane molecules are omitted for clarity. Selected bond lengths [Å]: **3b**: P–C1 1.801(2), P–C4 1.801(2), P–C25 1.833(2), P–S 1.9322(9), C2–C3 1.451(3), C3–C4 1.381(3). **7b**: P1–C1 1.787(7), P1–C4 1.783(6), P1–C25 1.790(6), P1–C26 1.801(6), C1–C2 1.383(8), C2–C3 1.470(9), C3–C4 1.380(8).

To reveal the optical and electrochemical properties of the present π-systems, UV/Vis absorption/fluorescence spectra and redox potentials of **3**–**7** and thiophene analogue **8**[13] were measured in CH_2Cl_2 (Table 1, Figure S2 and S3 in the Supporting Information). The lowest π–π* transitions of **4a**,**b** appeared at longer wavelengths than the corresponding transition of **8**. The P-functionalizations from **4a**,**b** to **3a**,**b**/**5a**,**b**/**6b**/**7b** caused noticeable red shifts of absorption/emission maxima ($\Delta\lambda_{ab}/\Delta\lambda_{em}$ = 18–48/27–58 nm), which is a typical trend observed for the π-conjugated phospholes.[1] All the diacenaphtho[*b*,*d*]phospholes were found to be weakly fluorescent ($\Phi_F < 0.01$).

As expected, the P-functionalizations induced anodic shifts for both oxidation and reduction potentials (E_{ox} and E_{red}). In cyclic voltammetry (CV) measurements, **3a**, **3b**, and **7b** showed reversible reduction processes at E_{red} = −1.36, −1.40, and −1.00 V (vs. Fc/Fc$^+$; Fc = [$(C_5H_5)_2Fe$]), respectively. These values are less negative than E_{red} values of Tsuji–Nakamura's benzo[*b*]phosphole **1** (−2.08 V),[6] our acenaphtho[*c*]phosphole **2** (−1.82 V),[9b] and the thiophene analog **8** (−2.02 V), indicating that the electron-accepting ability of **3a**,**b** and **7b** is considerably higher than that of **1**, **2**, and **8**. The reversible voltammograms observed for **3a**,**b** and **7b** exhibit their high stability in the electrochemical reduction processes. In each pair of **3a**,**b** and **4a**,**b**, there are very small differences in E_{ox} values between the P-phenyl and P-cyclohexyl derivatives. On the other hand, E_{red} of the P-phenyl derivatives are anodically shifted by 0.04–0.12 V relative to E_{red} of the P-cyclohexyl derivatives, which probably reflects the slight difference in the inductive effects of these two organyl (R) substituents on the LUMO energies.

Table 1: Optical and electrochemical data for **2**–**8**.[a]

Compd	λ_{ab} (log ε)	λ_{em}[b]	E_{ox}[c]	E_{red}[c]
3a	587 (3.54)	678	+0.66 (ir)	−1.36 (r)
3b	579 (3.57)	670	+0.64 (ir)	−1.40 (r)
4a	539 (3.72)	622	+0.28 (ir)	−1.76 (r)
4b	537 (3.68)	626	+0.30 (ir)	−1.88 (r)
5a	561 (3.62)	655	N.d.	−1.36 (qr)
5b	555 (3.68)	653	N.d.	−1.44 (ir)
6b	582 (3.53)	680	N.d.	−1.44 (ir)
7b	583 (3.71)	684	N.d.	−1.00 (r)
8	457 (3.76)	561	+0.59 (ir)	−2.02 (r)
2[d]	439 (3.62)	552	+0.94 (ir)	−1.82 (r)

[a] Measured in CH_2Cl_2; N.d. = Not determined. [b] λ_{ex} = 440 nm (except for **6b**). λ_{ex} = 580 nm for **6b**. Fluorescence quantum yields (Φ_F): < 0.01 for **3**–**7** and 0.01 for **8**. [c] Determined by differential pulse voltammetry (0.1 M $Bu_4N^+PF_6^-$; Ag/Ag$^+$); First oxidation (E_{ox}) and reduction (E_{red}) potentials vs. ferrocene/ferrocenium. r: reversible; qr: quasi-reversible; ir: irreversible. [d] Data from Ref. [9b].

To know the nature of frontier orbitals of the present π-systems, we carried out density functional theory (DFT) calculations of **3b**, **4b**, and **8** at the B3LYP/6-31G* level. The P-cyclohexyl group in **3b** and **4b** was found to adopt a chair conformation at their optimized structures. The calculated bond parameters of **3b** are almost identical to the observed ones (by X-ray). As depicted in Figure 2, HOMOs possess the heteroacene character to a large extent, whereas LUMOs consist of the heterole- and biacenaphthene-derived orbitals and are spread over the whole π-planes. The replacement of the sulfur bridge with the P-R bridge (from **8** to **4b**) stabilizes

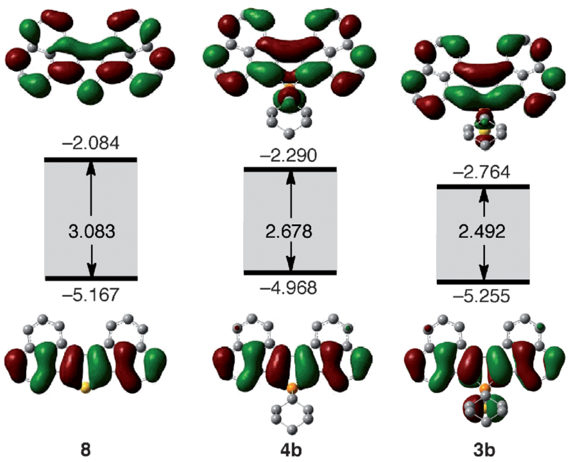

Figure 2. HOMOs (bottom) and LUMOs (top) of **3b**, **4b**, and **8** with their orbital energies and HOMO–LUMO gaps (in eV) calculated at the B3LYP/6-31G* level. Orange P, yellow S.

LUMO level due to the σ*(P-C)-π* orbital interaction. The P-thioxidation (from **4b** to **3b**) enhances this interaction, resulting in a further stabilization of LUMO level. Judging from the orbital diagrams and energies, the electronic effect of the P=S linker on LUMO is more significant than that on HOMO, and as a consequence, the HOMO–LUMO gap decreases in the order: **8** > **4b** > **3b**. These theoretical results are in good qualitative agreement with the above-mentioned experimental results.

To reveal a role of phosphorus(V) linkages in electron-spin delocalization of two kinds of π-radical species derived from **3b** and **7b**, we performed electrochemical ESR measurements. The electrochemical single-electron reductions of **3b** and **7b** were conducted in an electrode-equipped ESR cell with THF (for **3b**) or CH_2Cl_2 (for **7b**) as a solvent and nBu$_4$NPF$_6$ as an electrolyte. The ESR spectra recorded at 183 K showed well-resolved hyperfine structure, centered at $g = 2.0031$–2.0032 (Figure 3). The generated species were assigned to anion radical **3b**$^{-\bullet}$ and neutral radical **7b**$^{\bullet}$ by comparison with their simulated spectra (Figure S4 in the Supporting Information). In each radical species, the major contributions to the hyperfine splitting stem from the bridging ^{31}P nucleus ($a_P = 1.45$ or 1.70 mT) and eight of the peripheral ^{1}H nuclei ($a_H = 0.25$–0.28 mT) in the biacenaphthene moiety.[14] The observed difference in a_P values between **3b**$^{-\bullet}$ and **7b**$^{\bullet}$ represents that the interaction of the unpaired electron with the ^{31}P nucleus varies depending on the charge and the substituents of phosphorus. More importantly, it has become evident that an unpaired electron delocalizes into the phosphorus(V)-linked whole π-systems efficiently.

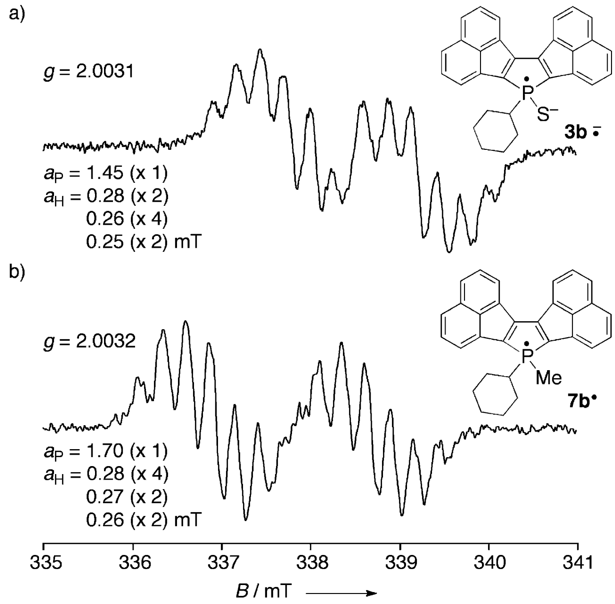

Figure 3. ESR spectra of a) **3b**$^{-\bullet}$ in THF and b) **7b**$^{\bullet}$ in CH_2Cl_2 at 183 K with g, a_P, and selected a_H values (> 0.10 mT).

To evaluate the electron-transporting property of the P-sulfide **3b** in a solid state, we first calculated its internal reorganization energy (λ_{in}), which is one of the key parameters to determine the charge-transfer rate constant given by Marcus theory.[15] The λ_{in} value was quantified using the DFT method[16] by considering energy differences between neutral and charged geometries for two (neutral and radical anion) states. As shown in Table S1 in the Supporting Information, the electron injection into **3b** reduces the C−C bond alternation of the fused phosphole ring ($\Delta l = 0.069$ Å for **3b** and $\Delta l = 0.008$ Å for **3b**$^{-\bullet}$; Δl is a difference of C_α−C_β and C_β−C_β bond lengths), reflecting the enhanced π-conjugation between the two acenaphthylene subunits. The spin density distributions of **3b**$^{-\bullet}$ obtained by the DFT calculations (Figure S5 in the Supporting Information) support the hyperfine coupling constants of **3b**$^{-\bullet}$ obtained by the ESR measurements (see above). The calculated λ_{in} value of **3b**/**3b**$^{-\bullet}$ (0.198 eV) was significantly smaller than that of meridional Alq$_3$/Alq$_3^{-\bullet}$ (0.270 eV at the B3LYP/6-31G* level), which suggested that **3b** would be a potential candidate as an electron-transporting material in terms of the reorganization energy.[17] With this in mind, we finally measured electron drift mobility of a vacuum-deposited film of **3b** ($T_m = 283$ °C, $T_g = 135$ °C; determined by differential scanning calorimetry measurements) by a time-of-flight (TOF) method.[18] Figure S6 in the Supporting Information shows the field dependency of the logarithmic electron mobility (μ_E) of **3b** and **2**.[9b] The μ_E value of **3b** slightly increased with decreasing the electric field (E) and reached 2.4×10^{-3} cm^{2}V^{-1}s^{-1} at $E = 4.3 \times 10^{5}$ V cm^{-1}. It should be emphasized here that the observed electron drift mobility of **3b** is 1–2 orders of magnitude larger than that of **2**[9b] and is comparable to the highest value ($\mu_E = 2 \times 10^{-3}$ cm^{2}V^{-1}s^{-1} at $E = 2.5 \times 10^{5}$ V cm^{-1} for **1**; determined by the TOF method)[6a] ever reported for the π-conjugated phosphole derivatives.

In summary, we successfully prepared diacenaphtho[1,2-*b*:1′,2′-*d*]phospholes as a new class of arene-fused phosphole π-systems with high electron affinity. The electrochemically reduced states of the phosphorus(V)-linked derivatives were stabilized by the effective delocalization of the unpaired electron over the whole π-systems. Most importantly, the cyclohexylphosphine–sulfide derivative exhibited a high electron-transporting ability in the vacuum-deposited film. The present results unambiguously corroborate that the fusion of phosphole and planar arene rings based on the rational design concept is a promising strategy for the development of phosphorus(V)-containing organic n-type semiconductors.

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[17] The calculated λ_{in} value of **8**/**8**$^{-\bullet}$ (0.167 eV) is also small (Table S1 in the Supporting Information), implying that the diacenaphtho-[*b*,*d*]heteroles are promising building blocks for the design of organic semiconductors.

[18] We have not measured the electron mobility of **3a** and **7b** because of their thermal instability for device fabrication.