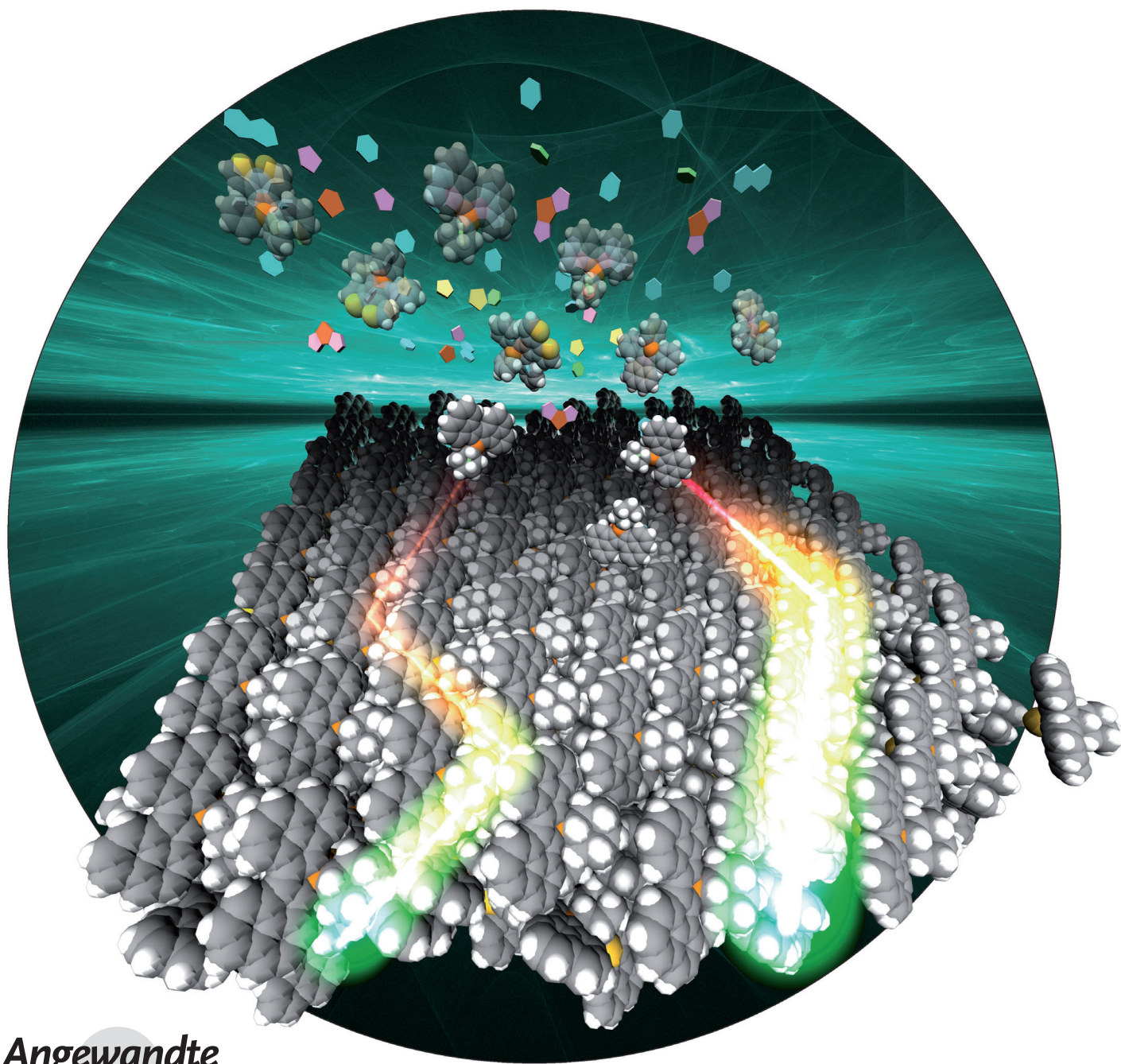


Fusion of Phosphole and 1,1'-Biacenaphthene: Phosphorus(V)-Containing Extended π -Systems with High Electron Affinity and Electron Mobility**

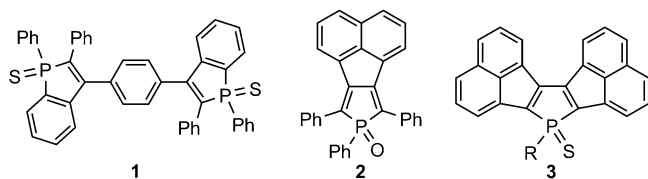
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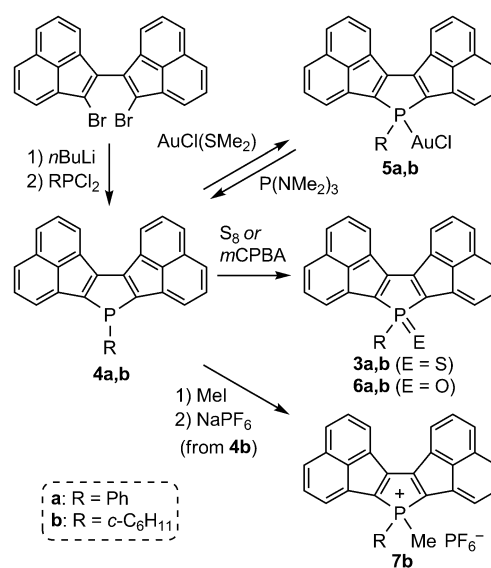
Recent developments in the chemistry of arene-fused phosphole π systems have shed light on their characteristic properties for use in optoelectronic applications.^[1] For example, many derivatives of benzo[*b*]phospholes,^[2] dibenzo[*b,d*]phospholes,^[3] dithieno[*b,d*]phospholes,^[4] and P,X-bridged 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 $\sigma^*-\pi^*$ 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) (Alq₃).^[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.

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 PhPCl₂ gave



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

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(NMe₂)₃ reproduced the σ^3 -P derivative **4a** quantitatively. The P-thiooxidation (with S₈) 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*-C₆H₁₁PCl₂ instead of PhPCl₂. The thermal stability of **6b** was found to be higher than that of **6a**. Methylation of the in-situ generated **4b** with excess iodo-methane, followed by treatment with an aqueous NaPF₆ solution produced phosphonium salt **7b**.

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

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whereas those of the P-cyclohexyl derivatives **3b**, **4b**, **5b**, and **6b** showed the corresponding peaks at more downfield ($\delta_P = 35.4$, -8.41 , 7.0 , and 35.0 ppm). The onium salt **7b** displayed ^{31}P and ^1H (methyl) peaks at δ_P 19.6 ppm and δ_H 2.46 ppm ($J_{\text{PH}} = 13.7$ 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).

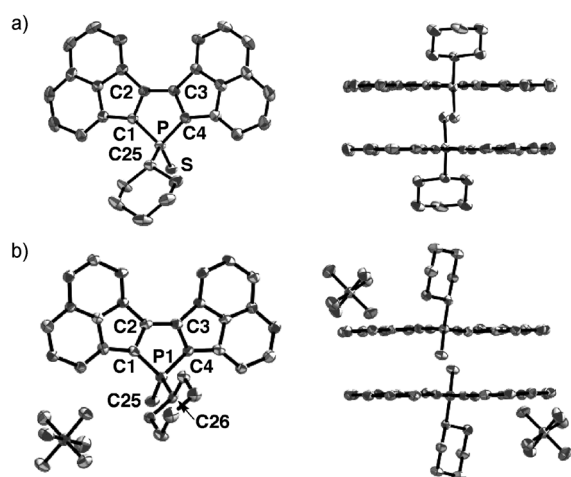


Figure 1. Top and side views of a) **3b** and b) **7b**. Hydrogen atoms and dichloromethane molecules are omitted for clarity. Selected bond lengths [Å]: **3b**: P–C1 1.801(2), P–C4 1.801(2), P–C25 1.833(2), P–S 1.9322(9), C2–C3 1.451(3), C3–C4 1.381(3). **7b**: P1–C1 1.787(7), P1–C4 1.783(6), P1–C25 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 ($\Delta\lambda_{\text{ab}}/\Delta\lambda_{\text{em}} = 18$ – $48/27$ – 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 $E_{\text{red}} = -1.36$, -1.40 , and -1.00 V (vs. Fc/Fc^+ ; $\text{Fc} = [(\text{C}_5\text{H}_5)_2\text{Fe}]$), 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

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] $\lambda_{\text{ex}} = 440$ nm (except for **6b**). $\lambda_{\text{ex}} = 580$ 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 $\text{Bu}_4\text{N}^+\text{PF}_6^-$; 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].

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.

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

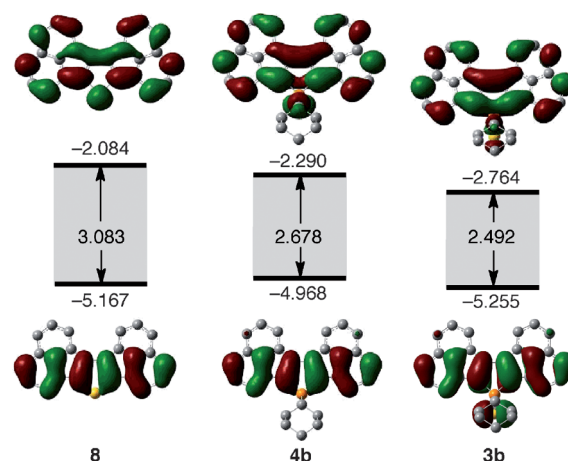


Figure 2. HOMOs (bottom) and LUMOs (top) of **3b**, **4b**, and **8** with their orbital energies and HOMO–LUMO gaps (in eV) calculated at the B3LYP/6-31G* level. Orange P, yellow S.

LUMO level due to the $\sigma^*(\text{P-C})-\pi^*$ orbital interaction. The P-thiooxidation (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 $n\text{Bu}_4\text{NPF}_6$ 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

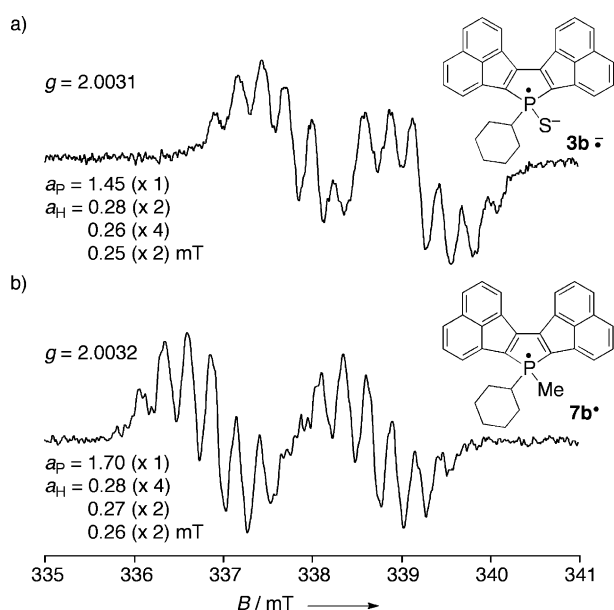


Figure 3. ESR spectra of a) **3b** $^{\bullet-}$ in THF and b) **7b** $^{\bullet}$ in CH_2Cl_2 at 183 K with g , a_p , and selected a_H values (>0.10 mT).

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 ^1H 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.

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_γ 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 $\text{Alq}_3/\text{Alq}_3^{\bullet-}$ (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** ($T_m = 283^\circ\text{C}$, $T_g = 135^\circ\text{C}$; 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 $2.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $E = 4.3 \times 10^5 \text{ V cm}^{-1}$. 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 ($\mu_E = 2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $E = 2.5 \times 10^5 \text{ V cm}^{-1}$ 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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Keywords: biacenaphthene · electron mobility · EPR spectroscopy · phosphole · radical ions

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- [12] CCDC 810806 (**3b**) and CCDC 818337 (**7b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif: **3b**: $\text{C}_{60}\text{H}_{46}\text{P}_2\text{S}_2 \cdot (\text{CH}_2\text{Cl}_2)$, $M_{\text{w}} = 977.97$, $0.25 \times 0.10 \times 0.04$ mm, monoclinic, $C2/c$, $a = 20.150(4)$, $b = 14.549(3)$, $c = 16.304(4)$ Å, $\beta = 93.259(3)^\circ$, $V = 4772.0(18)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.361$ g cm⁻³, $\mu = 3.33$ cm⁻¹, collected 18351, independent 5385, parameters 313, $R_{\text{w}} = 0.1421$, $R = 0.0556$ ($I > 2.00\sigma(I)$), GOF = 1.093. **7b**: $\text{C}_{31}\text{H}_{26}\text{F}_6\text{P}_2$, $M_{\text{w}} = 574.46$, $0.25 \times 0.10 \times 0.03$ mm, monoclinic, $P2_1/c$, $a = 13.126(9)$, $b = 14.700(10)$, $c = 13.886(10)$ Å, $\beta = 99.671(10)^\circ$, $V = 2641(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.445$ g cm⁻³, $\mu = 2.27$ cm⁻¹, collected 38812, independent 5983, parameters 352, $R_{\text{w}} = 0.2757$, $R = 0.1300$ ($I > 2.00\sigma(I)$), GOF = 1.635.
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- [17] The calculated λ_{in} value of **8/8**[•] (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.