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Synthesis of Blue-Luminescent Seven-Membered Phosphorus Heterocycles

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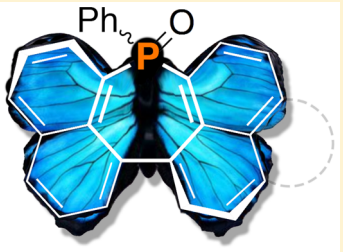
Supporting Information

ABSTRACT: A facile synthetic procedure to prepare π-extended seven-membered phosphorus heterocycles, both symmetric and asymmetric, is reported. The prepared molecules present a persistent nonplanar framework and are soluble in a wide variety of solvents. The seven-membered phosphorus heterocycles can be electrochemically reduced and oxidized, and photoluminesce with a blue color.



Seven-membered heterocycles are possibly the least explored type of systems. The first records on π-extended "epines"; i.e., cycloheptatrienes, date from 1939. After failed attempts to build up unsaturated seven-membered rings by ring closure, Kohler et al. prepared the first cycloheptatriene, starting from the reaction between ketones and diazomethane.[1] As for five- and six-membered π-conjugated rings, the phosphorus-containing cycloheptatrienes, phosphepines, have been relatively much less developed compared with their relative heteroles. As a matter of fact, the number of molecular motifs based on conjugated seven-membered phosphorus heterocycles (7MPHs) is fairly limited. Winter prepared, in 1976, fused phosphepines with, among others, benzenes, cyclopropadienes, and azulene.[2,3] Since then, excepting the dithieno-[3,2-*c*:2′,3′-*e*]-2,7-dithienophosphepins,[4] fused phosphepines have been largely based on the molecular patterns **a**−**c** (Figure 1).[5−11] Fused five- and six-membered phosphorus heterocycles have led to extraordinary properties, which have found applications as photo-[12−18] and electroluminescent[19−24] materials, liquid crystals,[25−27] photoelectrochemical[28] and solar cells,[29−32] biomarkers,[33−37] and sensors,[34,38] just to name a few. However, reports on the optoelectronic properties of π-extended phosphepines are rather scarce to date.[4,5] This is in stark contrast to the saturated 7MPHs analogues, whose properties have been widely investigated in the context of catalysis. Gladiali et al.[39] prepared, in 1994, the first binapthalene-annulated phosphepines, binepines, which triggered the investigations of their application in enantioselective catalysis. Soon, binepines,[40,41] took over the place of bidentate diphosphines, which previously aroused a great interest as catalysts in asymmetric synthesis.

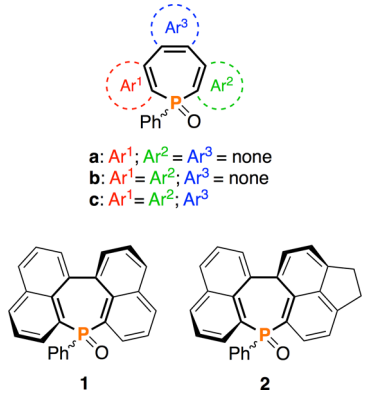


Figure 1. Structures **a**−**c** and compounds **1** and **2**.

Thus, to further explore the chemistry of conjugated 7MPHs, we targeted the investigation of preparative methods to access π-extended phosphepines. In this article, we present a new and facile synthetic procedure to prepare symmetric and nonsymmetric π-extended phosphepines (compounds **1** and **2**, Figure 1) and the study of their properties.

The synthesis we designed for the preparation of **1** and **2** involved two synthetic steps with a final cyclization reaction based on a double nucleophilic substitution to dichlorophenylphosphane (Scheme 1). Precursors **5** and **7** were prepared by the Suzuki−Miyaura cross-coupling reaction between **3** and the 1-bromo-8-iodonaphthalene **4** or the 5,6-dibromo-1,2-dihydroacenaphthylene **6**, respectively. The control of the thermodynamic conditions (see Supporting Information) allowed us to obtain reaction conversions over 60%, even though the formation of the corresponding perylene derivatives was also detected as minor side products (<10%). The X-ray structures of precursors **3** and **5** are shown in Figure S1. Finally, the cyclization reaction of **5** or **7** by the lithium-halogen exchange with 2 equiv of *tert*-butyllithium, followed by

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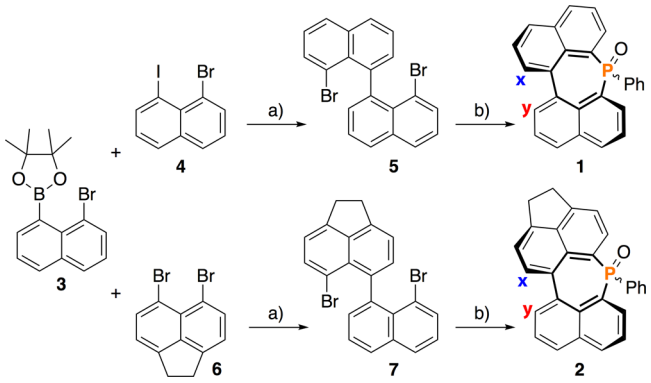
Scheme 1. Synthesis of 1 and 2[a]



[a](a) $Pd(PPh_3)_4$, K_3PO_4; (b) (1) ^tBuLi, −78°C; (2) $PhPCl_2$, −78 °C; (3) H_2O_2, 25 °C. Here, x and y indicate the positions responsible for the torsion of the molecule.

the reaction with dichlorophenylphosphane at low temperature and the in situ oxidation of the phosphorus atoms led to the 7MPHs **1** and **2**, respectively (see Supporting Information for details). Thus, our synthetic approach demonstrated to be applicable for the preparation of both, symmetric and asymmetric 7MPHs.

Both phosphepines were soluble in a wide range of organic solvents, i.e., acetone, chloroform, dichloromethane, ethyl acetate, tetrahydrofuran, and toluene. By ^{31}P NMR, compounds **1** and **2** showed only one singlet around 24 ppm, which remarkably differs from the singlet at around 5−10 ppm found for the phosphaphenalene analogues,[42a] and the one from the somewhat corresponding open structure, the 1-naphthalenyldiphenylphosphine oxide at 33.12 ppm.[42b]

Insights on the structural features of both phosphepines came from DFT calculations at the B3LYP/6-31G* level of theory (Figure 2). Molecules **1** and **2** are not planar; the main scaffold appears distorted (Figure 2). It is worth noting that the endocyclic P−C bonds are relatively shorter (1.82 and 1.812 Å for **1** and **2**) than the exocyclic ones (1.837 and 1.839 Å for **1** and **2**) as a result of the contribution from the phosphorus moiety into the π-system; a feature that is in sharp contrast to the acyclic triaryl phosphines, in which all bond distances are typically in the same range. On the other hand, the interaction between hydrogen atoms from carbons x and y, (Scheme 1) induces a distortion angle of 37.7° and 34.3° for **1** and **2**, respectively (Figures S2 and S3). Thus, both phosphepines appear as atropoisomers. The latter distortion, in combination with the non-inversion of the phosphorus atoms due to their well-documented high inversion barrier,[43−45] (ca. 30−35 kcal mol^{-1})[13] is therefore expected to lead to four isomers for **1**, a mixture that is anticipated to be more complex for the asymmetric compound **2**. Unfortunately, attempts to separate the isomers from both compounds by chromatography and a variety of crystallization techniques were unsuccessful. Notwithstanding, we further investigated the structural features by means of temperature-variable ^1H NMR and ^{31}P NMR seeking for the any coalescence that could shed light into the dynamics/rigidity of the phosphepins' scaffold (Figures S4 and S5). Thus, the variation of the temperature from 70 °C to −40 °C led to comparative results for **1** and **2**. Reducing the temperature mainly gives rise to an upfield shift of the proton at the β-position of the phosphorus atom from both the main scaffold and the exocyclic phenyl ring

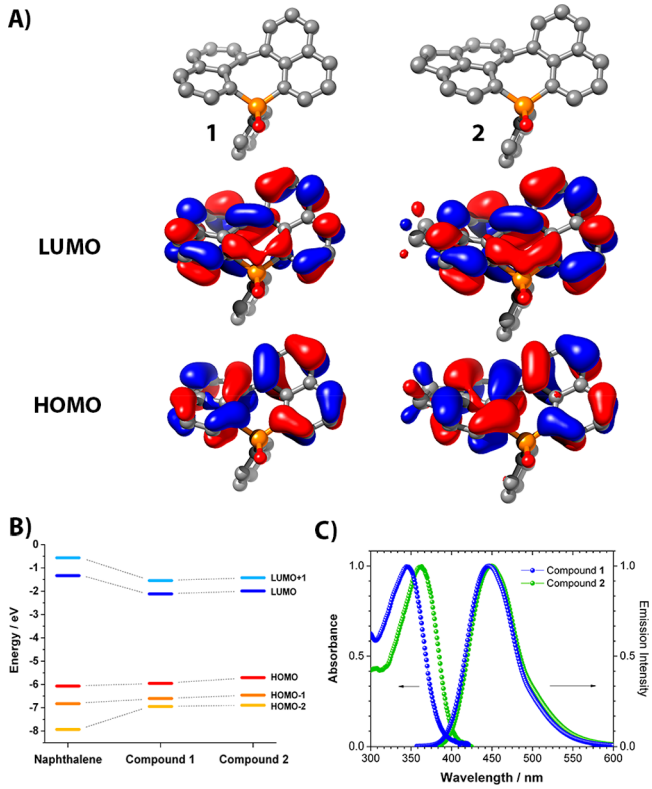


Figure 2. (A) Optimized molecular structure, HOMO and LUMO of **1** and **2** computed at the B3LYP/6-31G* level of theory. (B) Energetic level distribution of naphthalene, compounds **1** and **2**. (C) Absorption and emission spectra of **1** (in blue) and **2** (in green) from DCM solutions.

(see Figures S4 and S5 for details). This is indicative of changes in the angle/rotation of the phenyl substituent with respect to the phosphepins scaffold. The latter comes hand-in-hand with a downfield shift of the phosphorus singlet of **1** and **2** (Figures S4 and S5). Thus, our experiments appear to point to a persistent rigidity of the main framework within the employed experimental conditions; no experimental evidence was found to indicate any equilibrium involving dynamic structural changes at the phosphepins scaffold. In comparison with plausible acyclic triarylphosphine analogues, we hypothesize the presence of a 7MPH between the binaphthalene fragments to further contribute to the rigidity of the systems in combination with the repulsion from the hydrogen atoms of carbons x and y (Scheme 1).

Regarding the energetic levels of the phosphepins **1** and **2**, examination of the frontier molecular orbitals revealed, as often observed in π-extended five- and six-membered phosphorus heterocycles, that, while the HOMO does not involve the phosphorus atom, the LUMO possesses a significant contribution of the latter heteroatom (Figure 2). As a result, compared with the unfunctionalized naphthalene, the LUMO of both 7MPHs is significantly reduced from −1.329 eV to −2.114 and −1.991 eV for **1** and **2**, respectively (Figure 2, Table S2). It is worth noting that the HOMO of **2** is relatively higher in energy, presumably due to the electron-donating bridge of the acenaphthene moiety (Table 1).

To corroborate the latter energetic levels experimentally, we performed electrochemical measurements through different techniques (Figure S6). Both 7MPHs present an oxidation process and two reduction processes, all of them irreversible

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Table 1. Properties of Phosphepines 1 and 2

Comp.	Abs λ_{max} [nm][a]	Em λ_{max} [nm][b]	$\Delta\lambda$ [cm^{-1}][c]	log ε[d]	τ1 [ns][e]	Φ[f]	HOMO [eV][g]	LUMO [eV][h]	Eg[eV][i]	Red.2 $E_{1/2}$[V][j]	Red.1 $E_{1/2}$[V][k]	Ox.1 $E_{1/2}$[V][l]
1	347	446	6400	4.06	2.9	0.43	−5.953	−2.114	3.839	−1.82	−1.59	1.63
2	363	449	5200	4.11	3.0	0.51	−5.708	−1.991	3.717	−1.95	−1.65	1.44

[a]Absorption maxima recorded from DCM solutions. [b]Emission maxima recorded from DCM solutions. [c]Stokes shifts. [d]Molar extinction coefficient. [e]Fluorescence lifetimes. [f]Fluorescence quantum yields relative to quinine sulfate in 0.1 M H_2SO_4, Φ = 0.54. [g]Calculated highest occupied molecular orbital energy. [h]Calculated lowest occupied molecular orbital energy. [i]Energy band gap. [j]Second reduction potentials. [k]First reduction potentials. [l]Oxidation potentials. See Supporting Information for details.

(Table 1). In accordance to the theoretical calculations, the lowest reduction potential belongs to compound **1** (Red.1 $E_{1/2}$ = −1.59 V), while the lowest oxidation potential corresponds to compound **2** (Ox.1 $E_{1/2}$ = +1.44 V). These values fall within the range of the electrochemical properties of π-extended six-membered phosphorus heterocycles, phosphaphenalene derivatives.[28] To provide insights into the optical properties, we turned to the steady-state spectroscopy measurements. Both phosphepines are photostable; no decomposition was observed after repetitive cycles of illumination. Compound **1** exhibits absorption and emission maxima at 347 and 446 nm, respectively. In turn, phosphepine **2** reveals a relative red-shifted absorption and emission maxima lying at 363 and 449 nm, respectively (Figure 2). Both derivatives possess monoexponential fluorescence decays with lifetimes of 2.9 and 3.0 ns for **1** and **2** (Table 1). The emission color corresponds to the blue color with coordinates x = 0.15, y = 0.085 and x = 0.15, y = 0.1 for **1** and **2**, respectively. In terms of fluorescence quantum yield (Φ), the asymmetric phosphepine shows a Φ = 0.51, while the corresponding symmetric phosphepine **1** Φ = 0.43, which are in sharp contrast with the π-extended dithienophosphepines (Φ = 0.06)[5] with a **b**-type structure (Figure 1).

All in all, we report a facile synthetic procedure that allows access to π-extended phosphepines, both symmetric and asymmetric. Compounds **1** and **2** are air- and photostable and dissolve in a wide range of organic solvents. They are not planar, and variable-temperature NMR measurements point to a persistent rigidity of the main scaffold. In line with observations obtained from fused six-membered phosphorus heterocycles, compounds **1** and **2** possess an ambipolar redox behavior and emit in the blue region of the visible spectrum with rather good fluorescence quantum yields, i.e., 0.43 and 0.51. In views of the stability, persistent chiral structure, and optical properties of these π-extended phosphepines, we envisage their use for the construction of luminescent, chiral self-assembled architectures and their application as chiral photocatalysts. Investigations targeting the separation of the different isomers is currently underway in our laboratories.

EXPERIMENTAL SECTION

General Experimental Procedures. Reactions were carried out in dry glassware and under an inert atmosphere of purified argon or nitrogen using Schlenk techniques. Et_2O, THF, and toluene were used directly from a solvent purification system, MB SPS-800. 1-Bromo-8-iodonaphthalene was prepared according to our reported protocol.[42] ^1H, ^{13}C, ^{31}P, and ^{11}B NMR as well as COSY spectra were recorded on a Bruker Avance III, Bruker Avance 400, Bruker Avance-III-300, Bruker Avance DRX-300, Bruker Avance 500, or Bruker Avance 600. Chemical shifts are expressed as parts per million (ppm, δ) and referenced to 85% H_3PO_4 (^{31}P) or $CDCl_3$ (^1H: 7.27 ppm/^{13}C: 77.16 ppm) as internal standards. Signal descriptions include the following: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet. All coupling constants (J) values are absolute and are expressed in hertz (Hz).

Mass Spectrometry. MS and HRMS spectra were measured at the Institute of Organic Chemistry of the University Heidelberg. A Bruker ApexQe FT-ICR was used for ESI spectra and a JEOL JMS-700 MS for EI. GC−MS was performed in a GC system 7890a from Agilent Technologies.

X-ray Crystallography. X-ray crystal structure analyses were measured on Bruker Smart CCD or Bruker Smart APEX instrument using Mo Kα radiation. Diffraction intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using SADABS[46] based on the Laue symmetry of reciprocal space. Hydrogen atoms were either isotropically refined or calculated. The structures were solved and refined using the SHELXTL[47] software package. Crystal structures of **3** and **5** were obtained by crystallization from DCM. CCDC 1958094 (**3**) and 1958095 (**5**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Theoretical Calculations. Theoretical calculations have been carried out at the B3LYP/6-31G* level of theory by using the Gaussian 09 suite of programs.[48]

Steady-State Spectroscopy. Absorption and emission spectra were recorded from DCM solutions using a Jasco V660 and Jasco FP6500 spectrometer, respectively. Fluorescence quantum yields (Φ) were measured using quinine sulfate in 0.1 N sulfuric acid as a reference (Φ = 0.54) according to the literature.[49] Fluorescence quantum yields are average values from at least two independent measurements.

Fluorescence Lifetimes τ. The fluorescence decays were recorded with a HORIBA Scientific Fluorocube single photon counting system operated with HORIBA Scientific DataStation, version 2.2. Fluorescence lifetimes were acquired by an exponential fit according to the least mean square with commercially available software, HORIBA Scientific Decay Data Analyses 6 (DAS6), version 6.4.4.

Electrochemistry. Voltammograms (cyclic voltammetry, differential pulse voltammetry, and square wave voltammetry) were recorded using a Metrohm Autolab PGSTAT101 potentiostat/galvanostat from acetonitrile solutions using tetrabutylammonium hexafluorophosphate as electrolyte, glassy carbon as a working electrode, Pt wire as a counter electrode, and Ag wire as a pseudoreference electrode. The scan rate was 100 mV s^{-1}. The curves were calibrated vs SCE ($E_{1/2}$Fc/Fc+ = 0.54 V vs SCE).

Synthetic Procedures. *Synthesis of 2-(8-Bromonaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**).* In a 250 mL Schlenk flask, 1,8-dibromonaphthalene (1.0 equiv, 3.5 mmol, 1 g) was dissolved in 20 mL of dry THF. The reaction mixture was cooled to −78 °C, and *n*-BuLi (1.05 equiv, 3.6 mmol, 2.3 mL, 1.6 M in hexane) was added dropwise. The reaction mixture was stirred vigorously for 1 min, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.05 equiv, 3.6 mmol, 0.79 mL, 98 wt %) was added dropwise. The cooling bath was removed, and the reaction mixture was stirred for 1 h and quenched with 70 mL of brine. The organic phase was separated, and the aqueous layer was extracted with DCM three times. The combined organic layers were washed three times with water and dried over $MgSO_4$. The solvent was removed under a vacuum. The yellowish solid crude was washed with small amounts of

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heptane and pentane and recrystallized from a saturated DCM solution overlaid with hexane at room temperature. Then, 880 mg of a crystalline yellowish solid was obtained (2.64 mmol, 75% yield). ^{1}H NMR (301 MHz, in $CDCl_3$): δ 7.83 (ddd, J = 9.8, 7.8, 1.3 Hz, 3H), 7.77−7.68 (m, 1H), 7.49 (dd, J = 8.0, 7.0 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 1.47 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, in $CDCl_3$): δ 135.3 (C), 134.5 (C), 133.4 (CH), 130.8 (CH), 130.2 (CH), 128.8 (CH), 126.2 (CH), 125.8 (CH), 123.7 (C), 84.3 (C), 25.2 (CH_3). ^{11}B{^{1}H} NMR (128 MHz, in $CDCl_3$): δ 31.8 (B). HRMS (EI) m/z: [$M^{+\bullet}$] calcd for $[C_{16}H_{18}BO_2Br]^{+\bullet}$, 332.0583; found, 332.0571.

*Synthesis of 8,8′-Dibromo-1,1′-binaphthalene (**5**).* In a 250 mL three-neck round-bottom flask equipped with a condenser, 2-(8-bromonaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**) (1.0 equiv, 1.5 mmol, 500 mg), 1-bromo-8-iodonaphthalene[42] (**4**) (1.0 equiv, 1.5 mmol, 500 mg), and $Pd(PPh_3)_4$ (3 mol %, 45 μmol, 52 mg) were dissolved in 140 mL of dry toluene. K_3PO_4 (3.0 equiv, 4.5 mmol, 953 mg) was added, and the reaction mixture was stirred at 140 °C for 4 weeks. The reaction was quenched with 80 mL of water, and the aqueous layer was extracted with 100 mL of DCM for three times. The combined organic layers were dried over $MgSO_4$, and the solvent was removed under a vacuum. After purification by column chromatography using alumina and a gradient mixture of hexane and toluene as an eluent (0.95:0.05 to 0.7:0.3), 50 mg (0.12 mmol) of a colorless solid was obtained (40% yield). ^{1}H NMR (400 MHz, in $CDCl_3$): δ 7.96−7.90 (ddd, J = 12.2, J = 8.2 Hz, 4H), 7.78−7.75 (dd, J = 7.4 Hz, 2H), 7.50−7.46 (t, J = 8.1 Hz, 2H), 7.34−7.32 (dd, J = 7.1, 1.3 Hz, 2H), 7.31−7.29 (d, J = 7.9 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, in $CDCl_3$): δ 140.3 (C), 135.9 (C), 133.5 (CH), 131.8 (CH), 131.4 (C), 129.2 (CH), 129.1 (CH), 126.0 (CH), 125.1 (CH), 121.1 (C). HRMS (EI) m/z: [$M^{+\bullet}$] calcd for $[C_{20}H_{12}Br_2]^{+\bullet}$, 409.9306; found, 409.9299.

*Synthesis of 5,6-Dibromo-1,2-dihydroacenaphthylene (**6**).* This compound was synthesized according to a modified protocol described elsewhere.[50] In a 250 mL flame-dried round-bottom flask equipped with a Schlenk adapter, 1,2-dihydroacenaphthylene (1.0 equiv, 129.7 mmol, 20 g) was dissolved in 25 mL of dry DMF. The reaction solution was cooled to 10 °C, and an NBS suspension (2.15 equiv, 278.9 mmol, 50.09 g, in 80 mL of dry THF) was added dropwise via a dropping funnel over a time of 20 min. The solution was stirred at 10 °C for 18 h, protected from light, and was warmed up to room temperature. A beige solid precipitate was filtered from the reaction solution and washed three times with 125 mL of EtOH. After drying under a vacuum at 40 °C, the product was obtained as a beige solid, which was further crystallized from a mixture of DCM and $CHCl_3$ and upon cooling in the fridge. Yield: 25% (10.24 g, 32.82 mmol). ^{1}H NMR (301 MHz, in $CDCl_3$): δ 7.81−7.78 (d, J = 7.4 Hz, 2H), 7.11−7.08 (d, J = 7.4 Hz, 2H), 3.31 (s, 4H). ^{13}C{^{1}H} NMR (101 MHz, in $CDCl_3$): δ 147.1 (C), 142.0 (C), 135.9 (CH), 127.9 (C), 121.0 (CH), 114.4 (C), 30.1 (CH_2). MS (EI) m/z: [$M^{+\bullet}$] calcd for $[C_{12}H_8Br_2]^{+\bullet}$, 309.8993; found, 310.

*Synthesis of 5-Bromo-6-(8-bromonaphthalen-1-yl)-1,2-dihydroacenaphthylene (**7**).* In a 100 mL two-neck round-bottom flask equipped with a condenser, 2-(8-bromonaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**) (1.0 equiv, 1.50 mmol, 170 mg), 5,6-dibromo-1,2-dihydroacenaphthylene (**6**) (1.0 equiv, 0.51 mmol, 159 mg), and $Pd(PPh_3)_4$ (3 mol %, 15 μmol, 18 mg) were dissolved in 48 mL of dry toluene. K_3PO_4 (3 equiv, 1.53 mmol, 223 mg) was added, and the reaction mixture was stirred at 115 °C for 2 weeks and 4 days. The reaction was quenched with 30 mL of water, and the aqueous layer was extracted with 60 mL of DCM three times. The combined organic layers were dried over $MgSO_4$, and the solvent was removed under a vacuum. After purification by column chromatography using silica and a gradient mixture of hexane and toluene as an eluent (0.90:0.1 to 0.70:0.3), 54 mg (0.12 mmol) of a pale beige solid was isolated (24% yield). ^{1}H NMR (301 MHz, in $CDCl_3$): δ 7.95−7.89 (ddd, J = 14.8, 8.2, 1.1 Hz, 2H), 7.76−7.74 (dd, J = 7.4, 1.2 Hz, 1H), 7.64−7.63 (d, J = 7.3 Hz, 1H), 7.51−7.47 (t, J = 7.1 Hz, 1H), 7.39−7.37 (dd, J = 7.1, 1.4 Hz, 1H), 7.31−7.27 (m, 3H), 7.14−7.12 (d, J = 7.3 Hz, 1H), 3.50−3.41 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, in $CDCl_3$): δ 146.4 (C), 146.3 (C), 140.7 (C), 139.3 (C), 136.0 (C), 135.7 (C), 133.7 (CH), 133.3 (CH), 132.6 (CH), 132.1 (CH), 131.7 (C), 130.2 (C), 129.0 (CH), 128.9 (CH), 125.8 (CH), 124.9 (CH), 121.0 (C), 120.1 (CH), 119.1 (CH), 115.8 (C), 30.4 (CH_2), 30.1 (CH_2). HRMS (EI) m/z: [$M^{+\bullet}$] calcd for $[C_{22}H_{14}Br_2]^{+\bullet}$, 435.9462; found, 435.9462.

*Synthesis of 7-Phenyldinaphtho[1,8-bc:1′,8′-ef]phosphepine 7-Oxide (**1**).* In a 10 mL Schlenk tube, 8,8′-dibromo-1,1′-binaphthalene (**5**) (1.0 equiv, 68 μmol, 28 mg) was dissolved in 3.4 mL of dry Et_2O and cooled to −78 °C. Then, ^{t}BuLi (2.0 equiv, 136 μmol, 0.08 mL, 1.7 M in pentane) was added dropwise for 5 min. The lithiated intermediate was reacted with $PhPCl_2$ (1.0 equiv, 68 μmol, 9.5 μL, 97%) and warmed up to room temperature. After the mixture was stirred for 3 h, the solvent was removed under a vacuum. The intermediate product was dissolved in 2 mL of DCM and 1 mL of water and cooled to 0 °C. Two drops of an aqueous H_2O_2 solution (34.5−36.5%) were added, and the reaction solution was stirred for 25 min. The solvent was removed, and the crude was subsequently washed with hexane and pentane to obtain 17 mg (45 μmol) of a yellowish solid (66% yield). ^{1}H NMR (301 MHz, in $CDCl_3$): δ 8.84−8.77 (dd, J = 14.4, 6.6 Hz, 2H), 8.15−8.12 (d, J = 8.1 Hz, 2H), 7.94−7.91 (d, J = 7.3 Hz, 2H), 7.78−7.73 (t, J = 7.0 Hz, 2H), 7.52−7.46 (m, 4H), 7.12−7.09 (t, J = 7.2 Hz, 1H), 6.98−6.94 (t, J = 6.0 Hz, 2H), 6.83−6.76 (dd, J = 12.2, 7.4 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, in CD_2Cl_2): δ 140.2 (C), 136.1 (CH), 134.8 (d, J = 4.7 Hz, CH), 134.0 (d, J = 3.2 Hz, CH), 133.8 (CH), 132.0 (C), 131.1 (CH), 130.2 (d, J = 2.3 Hz, CH), 130.1 (CH), 128.9 (d, J = 12.4 Hz, C), 128.6 (C), 128.1 (CH), 128.0 (CH), 126.8 (C), 126.4 (C), 125.7 (CH), 125.6 (d, J = 12.3 Hz, CH). ^{31}P{^{1}H} NMR (162 MHz, in $CDCl_3$): δ 24.10 (P). HRMS (EI) m/z: [$M^{+\bullet}$] calcd for $[C_{26}H_{17}OP]^{+\bullet}$, 376.1017; found, 376.1024.

*Synthesis of 5-Phenyl-1,2-dihydroacenaphtho[5,6-bc]naphtho[1,8-ef]phosphepine 5-Oxide (**2**).* In a 10 mL Schlenk tube, 5-bromo-6-(8-bromonaphthalen-1-yl)-1,2-dihydroacenaphthylene (**7**) (1.0 equiv, 80 μmol, 35 mg) was dissolved in 4 mL of dry Et_2O and cooled to −78 °C. Then, ^{t}BuLi (2.0 equiv, 0.16 mmol, 0.09 mL, 1.7 M in pentane) was added dropwise. The lithiated intermediate was reacted with $PhPCl_2$ (1.0 equiv, 80 μmol, 11 μL, 97%), and the reaction warmed up to room temperature. After the mixture was stirred for 3 h, the solvent was removed under a vacuum. The intermediate product was dissolved in 2 mL of DCM and 1 mL of water and cooled to 0 °C. Two drops of an aqueous H_2O_2 solution (34.5−36.5%) were added, and the reaction solution was stirred for 10 min. The solvent was removed, and the crude was purified by column chromatography using silica and the mixture of DCM/MeOH/NH_3 (aq) = 100:4:0.5 (v/v/v) to isolate 7 mg (17 μmol) of a pale yellow solid (22% yield). ^{1}H NMR (600 MHz, in $CDCl_3$): δ 8.84−8.67 (ddd, J = 84.9, 14.3, 6.9 Hz, 2H), 8.02−8.01 (d, J = 8.0 Hz, 1H), 7.81−7.80 (d, J = 7.6 Hz, 1H), 7.76−7.75 (d, J = 7.1 Hz, 1H), 7.70−7.67 (t, J = 7.3 Hz, 1H), 7.64−7.63 (d, J = 6.7 Hz, 1H), 7.46−7.42 (dd, J = 14.5, 7.3 Hz, 2H), 7.36−7.35 (d, J = 7.5 Hz, 1H), 7.12−7.10 (t, J = 7.4 Hz, 1H), 7.00−6.96 (t, J = 5.2 Hz, 2H), 6.83−6.79 (dd, J = 12.1, 7.7 Hz, 2H), 3.57−3.43 (m, 4H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 152.9 (C), 148.1 (C), 140.1 (C), 139.9 (CH), 136.7 (C), 136.5 (CH), 135.0 (C), 133.9 (CH), 133.1 (C), 133.0 (CH), 132.7 (C), 131.7 (CH), 130.9 (CH), 130.2 (d, J = 10.6 Hz, CH), 129.1 (CH), 128.8 (C), 127.9 (d, J = 12.4 Hz, CH), 126.5 (CH), 125.4 (d, J = 12.5 Hz, CH), 123.6 (C), 122.9 (C), 121.3 (CH), 120.1 (d, J = 12.1 Hz, CH), 31.1 (CH_2), 29.9 (CH_2). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 23.97 (P). HRMS (EI) m/z: [$M^{+\bullet}$] calcd for $[C_{28}H_{19}OP]^{+\bullet}$, 402.1173; found, 402.1166.

■ ASSOCIATED CONTENT

Supporting Information

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Crystallographic data; DFT calculations; temperature-variable NMR; electrochemical measurements and NMR data (PDF)

Crystal data (CIF)

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Notes

The authors declare no competing financial interest.

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