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Syntheses, Structures, and Properties of Biphosphinines Tethered Aromatic π-System

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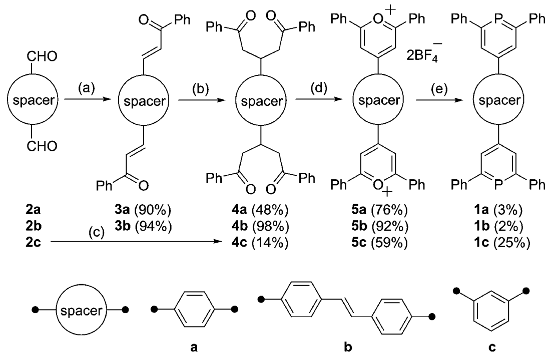
The syntheses of a series of biphosphinine derivatives inserted an aromatic π-spacer have been achieved. Their absorption, emission properties, and electrochemical behavior are also disclosed.

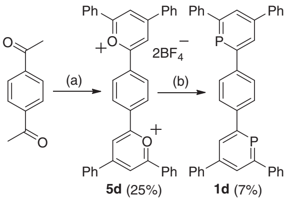
The chemistry of phosphinine, a heavier analogue of pyridine, has been studied extensively for a long time,[1] since Märkl and co-workers reported the synthesis of stable phosphinine by the reaction of the corresponding pyrylium salt with tris(trimethylsilyl)phosphine.[2] Up to now, many examples of phosphinines were synthesized, and their unique properties were revealed, most remarkably, their low-lying LUMO level as compared with the corresponding pyridine should be noted.[3]

Stable biphosphinines, which have two phosphinine moieties intramolecularly connected by an organic fragment, have also been synthesized by Märkl,[4,5] Mathey and Le Floch,[6] and Müller's group,[7] while some of them could have an important role in the development of organometallic chemistry as bidentate ligands. Although several biphosphinines were synthesized, reporting of their fundamental properties in photophysics and electrochemistry has been limited because attention has been focused on their structural properties and skeletal functions, and accordingly there has been less interest in their physical properties.[6b,6c,8] Thus, we would like to describe design and syntheses of revisited Märkl's 4,4′-biphosphinine **1a** having a *p*-phenylene and novel biphosphinines **1b**–**1d** bearing *p*-phenylene–vinylene–*p*-phenylene (*trans*-stilbene-4,4′-diyl), *m*-phenylene, and *p*-phenylene backbone, respectively, in order to investigate their structures and properties.

We have decided to use the methodology for the construction of a phosphinine framework by the reaction of an oxygen-containing six-membered ring heterocycle, pyrylium salt, with tris(trimethylsilyl)phosphine reported by Märkl.[1,2] The synthetic route for biphosphinines **1a**–**1d** is shown in Schemes 1 and 2. Aldol condensation reactions of benzaldehydes **2a** and **2b**[9] with barium or potassium enolate, generated by treatment of acetophenone with barium or potassium hydroxide, gave compounds **3a** and **3b** in 90% and 94% yields, respectively. Michael addition reactions of **3a** and **3b** with the sodium enolate in toluene or *o*-dichlorobenzene gave tetraones **4a** and **4b** in 48% and 98% yields, respectively. In the case of synthesis of **3c**, we found that the reaction of isophthalaldehyde (**2c**) of the barium or potassium enolate afforded a complicated mixture. Thus, one-pot operation of the synthesis of **4c** was performed, that is, the reaction of **2c** with acetophenone with sodium amide gave tetraone **4c** in 14% isolated yield. Treatment of tetraones **4a**–**4c** with tetrafluoroboric acid in the presence of triphenylmethanol in acetic anhydride afforded bipyrylium tetrafluoroborates **5a**–**5c** in 76%, 92%, and 59% yields, respectively.[10] The reaction of 1,4-diacetylbenzene with 1,3-diphenyl-2-propen-1-one in the presence of tetrafluoroboric acid afforded compound **5d** in 25% yield (Scheme 2). The molecular structure of **5a** was determined by X-ray crystallographic analysis, and we confirmed the formation of six-membered ring framework (Figure 1).[11]



Scheme 1. Syntheses of 4,4′-biphosphinines **1a**–**1c**. Reagents and conditions: (a) $PhCOCH_3$, $Ba(OH)_2 \cdot 8H_2O$, 2-PrOH, reflux, 4.5 h (for **3a**), $PhCOCH_3$, KOH, 2-PrOH, reflux, 2.5 h (for **3b**); (b) $PhCOCH_3$, $NaNH_2$, toluene, rt, 20 h (for **4a**), $PhCOCH_3$, $NaNH_2$, *o*-$Cl_2C_6H_4$, 100 °C, 4 h (for **4b**); (c) $PhCOCH_3$, $NaNH_2$, toluene, rt, 72 h; (d) HBF_4, Ph_3COH, Ac_2O, rt, 20 h (for **5a** and **5b**), HBF_4, Ph_3COH, 70 °C, rt, 16 h (for **5c**); (e) $P(SiMe_3)_3$, C_6H_6, CH_3CN, 60 °C, 5 h (for **1a**–**1c**).



Scheme 2. Synthesis of 2,2′-biphosphinine **1d**. Reagents and conditions: (a) PhCOCH=CHPh, HBF_4, 1,2-$Cl_2C_2H_4$, reflux, 18.5 h; (b) $P(SiMe_3)_3$, C_6H_6, CH_3CN, 60 °C, 5 h.

Syntheses of 4,4′-biphosphinines **1a**–**1c** inserting a *p*-phenylene, *trans*-stilbene-4,4′-diyl, or *m*-phenylene moiety, respectively, were performed by the reactions of bipyrylium tetrafluoroborates **5a**–**5c** with $P(SiMe_3)_3$ in benzene/acetonitrile solution at 60 °C for 5 h (Scheme 1). Similarly, 2,2′-biphosphinine **1d** bearing *p*-phenylene, a regioisomer of **1a**, was also synthesized by treatment of **5d** with $P(SiMe_3)_3$ in benzene/acetonitrile solution (Scheme 2). After chromatographic purification of the reaction mixture, biphosphinines **1a**–**1d** were obtained as pale yellow crystals in 3%, 2%, 25%, and 7% isolated yields, respectively. All compounds can be handled under air without any decomposition, and were thermally stable under inert atmosphere.

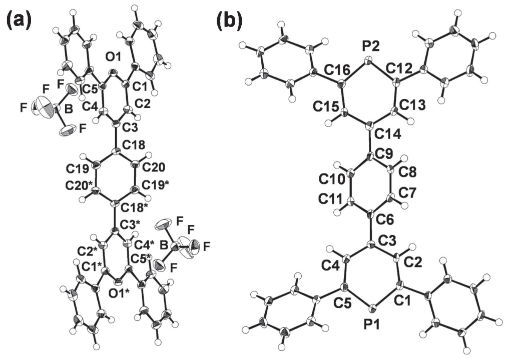


Figure 1. Molecular structures of (a) **5a** and (b) **1a** with thermal ellipsoid plot (30% probability). The solvated acetonitrile molecules of **5a** are omitted for clarity. Selected bond lengths [Å] and angles [°] of **5a**: O(1)–C(1) 1.356(3), O(1)–C(5) 1.352(3), C(5)–O(1)–C(1) 122.54(19). Selected bond lengths [Å] and angles [°] of **1a**: P(1)–C(1) 1.752(3), P(1)–C(5) 1.743(3), P(2)–C(12) 1.743(3), P(1)–C(16) 1.746(3), C(5)–P(1)–C(1) 101.84(14), C(12)–P(2)–C(16) 101.63(14).

Biphosphinines **1a**–**1d** showed a singlet signal at +186.2 (for **1a**), +185.2 (for **1b**), +185.3 (for **1c**), +183.5 ppm (for **1d**) in the ^{31}P NMR spectra, and a doublet signal at 8.25 ($^3J_{\mathrm{PH}} = 5.6$ Hz) (for **1a**), 8.22 ($^3J_{\mathrm{PH}} = 6.0$ Hz) (for **1b**), 8.23 ($^3J_{\mathrm{PH}} = 6.0$ Hz) (for **1c**), and 8.21/8.26 ($^3J_{\mathrm{PH}} = 5.2/5.6$ Hz) ppm (for **1d**), which can be assigned to protons at the 3-position for the phosphinine ring, in the ^{1}H NMR spectra. In the ^{13}C NMR spectra, biphosphinines **1b**–**1d** in $CDCl_3$ (CS_2:$CDCl_3$ = 9:1 was used for **1a**) showed characteristic doublet signals at 171.5 ($^1J_{\mathrm{PC}} = 56$ Hz) (for **1a**), 171.8 ($^1J_{\mathrm{PC}} = 52$ Hz) (for **1b**), 172.0 ($^1J_{\mathrm{PC}} = 53$ Hz) (for **1c**), and 171.0 ($^1J_{\mathrm{PC}} = 53$ Hz) (for **1d**), attributable to carbons at the 2-position for the phosphinine ring. These spectral features were comparable to those of 2,4,6-triphenylphosphinine (**6**),[12] indicating that phosphinine moieties of **1a**–**1d** did not display remarkable electronic perturbations when connecting the π-electron frameworks, such as *p*-, *m*-phenylene, and *trans*-stilbene-4,4′-diyl.

X-ray crystallographic analysis of the single crystals of **1a** revealed the solid-state structure, the molecular structure of which was depicted in Figure 1.[11] The P–C bond lengths of **1a** lie in a range of 1.743(3)–1.752(3) Å, being slightly longer than those of typical P=C double bonds (1.61–1.71 Å),[13] and are comparable to those of previously reported phosphinines (1.728–1.758 Å).[8a,14] The C–P–C bond angles of 101.84(14) and 101.63(14)° are similar to those of known phosphinines (98.38–105.10°).[8a,14] The torsion angles of **1a** showed C(4)–C(3)–C(6)–C(11) of −35.6(4)° and C(8)–C(9)–C(14)–C(13) of 30.1(4)°, the dihedral angles between the phosphinine and inserted phenylene rings were ca. 30–36° in the solid state.

The UV–vis absorption measurement of biphosphinines **1a**–**1d** together with monophosphinine **6** was performed (Figure 2), the data are shown in Table 1. They were shifted bathochromically in the order of **1b** > **1a** ≈ **1d** > **1c** ≈ **6**. These results indicate that *trans*-stilbene-4,4′-diyl moiety in **1b** can be effectively extension of the π-conjugation, whereas *m*-phenylene unit of **1c** cause not varying absorption wavelength but enhancing absorption coefficient as compared with **6**.

To gain insight into the electronic structure, the theoretical calculations were carried out.[15,16] The absorptions of **1a**–**1d** were estimated on the basis of the results of TD-DFT calculations, it was found that both the HOMO and LUMO of **1a**–**1d** dominantly delocalized on the phosphinines and inserted *p*-phenylene (**1a** and **1d**), *trans*-stilbene-4,4′-diyl (**1b**), and *m*-phenylene (**1c**) fragments, respectively, except for the phenyl substituents (Figures S1–S4 in Supporting Information). Assignment of the absorption was estimated based on TD-DFT calculations of **1a**–**1d**.[15,16] The absorption maxima of **1a**, **1b**, and **1d** at the lowest energy area ($\lambda = 339$ nm; $f = 0.728$ (for **1a**), $\lambda = 396$ nm; $f = 1.929$ (for **1b**), and $\lambda = 345$ nm; $f = 0.439$ (for **1d**)) are dominantly assignable to the symmetry-allowed π–π* (HOMO to LUMO) electron transitions for phosphinine chromophore and the connected fragment moieties. Meanwhile, in the case of *m*-phenylene derivative **1c**, λ_{abs} corresponds to combinations of the π–π* electron transitions from HOMO−2/HOMO−3 to LUMO/LUMO+1 ($\lambda = 331.81$ nm; $f = 0.0610$).

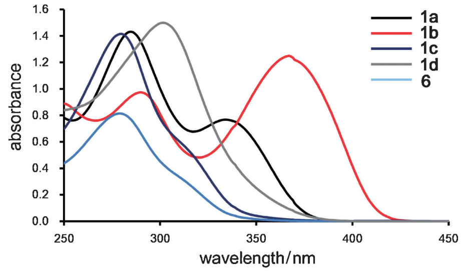


Figure 2. UV–vis absorption spectra of **1a**–**1d** and **6** in CH_2Cl_2 (concentration; 2.15×10^{-5} mol L^{-1} for **1a**, 1.95×10^{-5} mol L^{-1} for **1b**, 2.20×10^{-5} mol L^{-1} for **1c**, 2.15×10^{-5} mol L^{-1} for **1d**, and 2.05×10^{-5} mol L^{-1} for **6**).

Table 1. Photophysical properties of biphosphinines **1a**–**1d** and monophosphinine **6**

Compd.	Solvent	Absorption		Emission	Stokes shift
		λ/nm	ε/M^{-1} cm^{-1}	λ/nm	k/cm^{-1}
1a	hexane	282, 323(sh)	—[a]	465	9080
	CH_2Cl_2	335	36000	—[b]	—
1b	hexane	354	—[a]	464	6700
	CH_2Cl_2	368	64000	439	4400
1c	hexane	280, 311(sh)	—[a]	455	10200
	CH_2Cl_2	278, 321(sh)	61000, 12000	—[b]	—
1d	hexane	296, 326(sh)	—[a]	472	9490
	CH_2Cl_2	303, 337(sh)	63000, 13000	—[b]	—
6	hexane	277, 317(sh)	39000, 4900	352	3100
	CH_2Cl_2	277, 319(sh)	39000, 6000	—[b]	—

[a]The molar absorption coefficient could not be determined because of its low solubility. [b]The emission spectrum was not detected.

Moreover, in hexane solution, the emission spectra of **1a**–**1d** appeared emission maxima at 465, 464, 455, and 472 nm, respectively. The Stokes shifts of **1a**–**1d** were found to be 9080, 6700, 10200, and 9490 cm^{-1}, respectively. These values are larger than that of **6**, it is reasonable to assume that **1a**–**1d** do not have entirely flat π-system in the ground state but their geometry may become altered in the excited state.

The electrochemical behavior of **1a**–**1d** has been discovered by cyclic and differential pulse voltammetry. (Figures 3 and S5–S7 in Supporting Information) In dichloromethane solution, while an irreversible one-electron oxidation wave was observed at +1.09 V (for **1c**) and +0.94 V (for **1d**), an irreversible stepwise one-electron oxidation waves were displayed at +0.88/

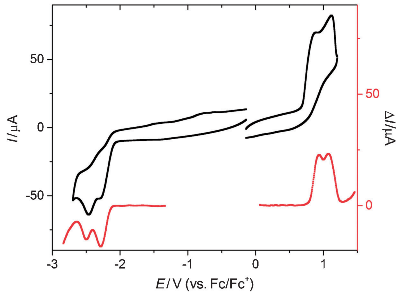


Figure 3. Cyclic (black lines) and differential pulse (red lines) voltammograms of **1a** in n-Bu$_4$NPF$_6$/CH$_2$Cl$_2$ at room temperature.

$+1.12$ V (for **1a**), and $+0.78/+0.94$ V (for **1b**) versus Fc/Fc$^+$, respectively (see Supporting Information). The first oxidation potentials of **1a** and **1b** were somewhat lower than those of **1c** and **1d** as well as monophosphinine **6** ($E_{\rm pa} = +0.91$ V versus Fc/Fc$^+$). Difference between the oxidation potentials of **1a** and **1b** are 0.24 and 0.16 V, respectively, which are somewhat smaller than that of 2,2′-biphosphinine (0.40 V),[6b] indicating electronic interaction between the phosphinine units.

On the other hand, irreversible one-electron reduction waves were found, and their reduction potentials were $-2.25/-2.46$ V (for **1a**), -2.34 V (for **1b**), -2.48 V (for **1c**), and $-2.27/-2.45$ V (for **1d**), which were higher than those of 2,2′-biphosphinine ($E_{1/2} = -1.78/-2.18$ V),[6b] and comparable to those the previously reported parent phosphinine (-2.10 V, $I_{\rm pa}/I_{\rm pc} = 0.56$ in n-Bu$_4$NClO$_4$/dimethoxyethane)[17] and **6** ($E_{\rm pc} = -2.25$ V). The results suggested that π-electrons of the phosphinine framework of **1a**–**1d** can be slightly perturbed by the peripherally connected aromatic π-systems. We found that biphosphinine **1a** showed novel and unique stepwise two-electron oxidation/reduction behavior.

Finally, we succeeded in the syntheses of a series of biphosphinines **1a**–**1d**, and their photophysical properties and electrochemical behavior have been disclosed. Due to expansion of the π-system consisting of phosphinines, biphosphinines **1a**, **1b**, and **1d** have absorption maxima at longer wavelength and luminesces with larger Stokes shift in comparison with monophosphinine **6**. Research of further properties of **1a**–**1d** is in progress.

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Supporting Information is available electronically on J-STAGE.

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11 Crystallographic data for **1a**; C$_{40}$H$_{28}$P$_2$, $M = 570.56$, monoclinic, $P2_1/c$ (#14), $a = 17.770(2)$ Å, $b = 7.2108(7)$ Å, $c = 23.780(3)$ Å, $\alpha = 90°$, $\beta = 110.031(4)°$, $\gamma = 90°$, $V = 2862.6(6)$ Å^3, $Z = 4$, $\rho_{\rm calcd} = 1.324$ g cm^{-3}, $2\theta_{\rm max} = 55.9°$, 30424/5170 measured/independent reflections, 379 refined parameters, R_1 ($_{\rm w}R_2$) = 0.0588 (0.1515) [$I > 2\sigma(I)$], R_1 ($_{\rm w}R_2$) = 0.0868 (0.1763) (for all data), $T = 93(2)$ K, GOF = 1.076. Crystallographic data for **5a**; C$_{40}$H$_{28}$B$_2$F$_8$O$_2$·2(CH$_3$CN), $M = 796.35$, triclinic, $P\bar{1}$ (#2), $a = 7.889(6)$ Å, $b = 9.663(8)$ Å, $c = 13.868(11)$ Å, $\alpha = 102.558(9)°$, $\beta = 103.216(9)°$, $\gamma = 106.519(11)°$, $V = 940.4(13)$ Å^3, $Z = 1$, $\rho_{\rm calcd} = 1.406$ g cm^{-3}, $2\theta_{\rm max} = 52.0°$, 9840/3653 measured/independent reflections, 263 refined parameters, R_1 ($_{\rm w}R_2$) = 0.0622 (0.1462) [$I > 2\sigma(I)$], R_1 ($_{\rm w}R_2$) = 0.1048 (0.1732) (for all data), $T = 113(2)$ K, GOF = 1.067. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. 1043686 (**1a**) and 1043685 (**5a**). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

12 NMR data of monophosphinine **6**; $\delta_{\rm H} = 8.22$ (d, $^3J_{\rm PH} = 5.6$ Hz), $\delta_{\rm C} = 171.4$ (d, $^1J_{\rm PC} = 52$ Hz), $\delta_{\rm P} = +185.8$.

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