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Synthesis, structure, and properties of extended π-conjugated systems bearing sterically crowded triarylphosphines

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ABSTRACT

The sterically crowded triarylphosphines bearing formyl and benzoyl groups were synthesized and characterized by X-ray crystallography. The benzoyl derivative was converted to the *p*-quinomethane conjugated with the triarylphosphine. The McMurry coupling of the formyl derivative afforded the diarylethene bearing the two sterically-crowded-triarylphosphine moieties. The cyclic voltammograms of these compounds show reversible redox waves corresponding to the oxidation to the radical cations of the triarylphosphines and irreversible or quasi-reversible waves corresponding to the reduction of the acceptor moieties. The electronic and the fluorescence spectra of these π-conjugated systems, especially push-pull substituted derivatives, exhibit bathochromic shift typical of the extended π-conjugated systems especially in the polar solvent, and the large Stokes shift typical of the crowded triarylphosphines is enhanced by conjugation with the acceptor moiety.

1. Introduction

The sterically crowded triarylphosphines such as tris(2,4,6-triisopropylphenyl)phosphine (**1**) [1] have large bond angles around the phosphorus and some of them are reversibly oxidized at low potential to the stable radical cations because of the synergistic effect of high HOMO arising from the structural change around the phosphorus and the steric protection by the bulky aryl groups (Chart 1) [2]. Because such a good donor molecule is expected to be substructure of the functional materials, we synthesized crowded triarylphosphines similar to **1** bearing donors [3], acceptors [4], and radicals [5], and revealed their redox properties. The triarylphosphine moieties generally work as reversible redox sites even if bound to other redox sites and construct the multistep redox systems. Among the compounds we surveyed, the sterically crowded triarylphosphines bearing naphthoquinone moieties such as **2** are worth mentioning [4b]. They exhibit purple to blue color arising from intramolecular charge transfer from the phosphine to the naphthoquinone moieties and are expected to be the potential candidates for the functional dyes. Being encouraged by these results, we continued to explore the synthesis of the chromophores bearing the triarylphosphine moieties applicable to the functional dyes. As a fundamental strategy toward colored molecules, the captodative or push-pull π-electronic system has long been known [6] and widely applied to the functional materials such as nonlinear optics [7] and fluorescent emitting materials [8]. They exhibit deeper color than the parent π-conjugated systems because the push-pull substitution enhances delocalization of the π-electrons to make the HOMO-LUMO gap narrower, as conventionally expressed by the neutral and twitterionic resonance structures (Scheme 1). Herein we report synthesis, structure and properties of the formyl and the benzoyl substituted sterically crowded triarylphosphines **3** and **4**, and the related compounds **5** and **6**. The formyl and the benzoyl derivatives can be regarded as typical examples of the push-pull substituted benzenes bearing the sterically crowded phosphinyl group as a donor. They also serve as the key synthetic intermediates to the extended π-conjugated systems. Further extended push-pull π-conjugated system **5** was synthesized from **4** with the use of the *p*-quinomethane structure. The diarylethene **6** bearing the two sterically-crowded-triarylphosphine moieties was synthesized by the McMurry coupling of the aldehyde **3**.

2. Results and discussion

2.1. Synthesis and characterization

We reported the sterically crowded triarylphosphine **7** bearing a bromo group as a key intermediate for the synthesis of the triarylphosphines bound to various functional sites [4,5]. The

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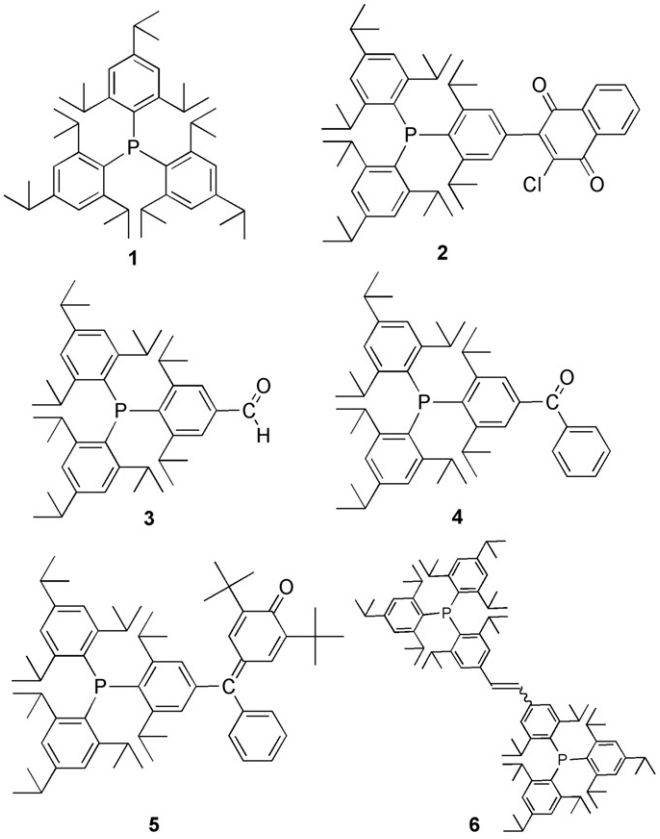
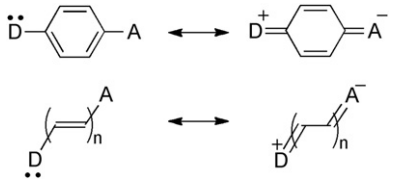


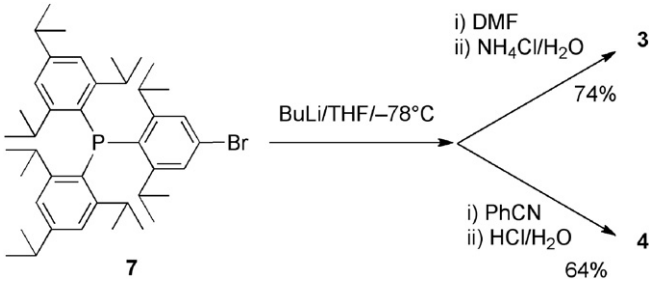
Chart 1. Sterically crowded triarylphosphines.

bromoaryl derivative **7** was found to serve as a starting material for the construction of the extended π-conjugated systems (Scheme 2). The (bromoaryl)phosphine **7** was lithiated with butyllithium, reacted with DMF [9] and benzonitrile [10], and hydrolyzed to afford the formyl derivative **3** and the benzoyl derivative **4**, respectively. The addition of the highly nucleophilic 4-oxide-aryllithium [11], prepared by the dilithiation of 2,6-di-*tert*-butyl-4-iodophenol [12], to **4** followed by hydrolysis gave the carbinol **8** (Scheme 3). The dehydration of **8** in the presence of trifluoroacetic acid afforded the *p*-quinomethane **5**. The McMurry coupling of **3** in the presence of the low valent titanium generated from $TiCl_3$ and $LiAlH_4$ [13] afforded an *E*/*Z* mixture (1/0.3) of the diarylethene **6**. The *E*/*Z* ratio was reversed to 0.2/1 by the irradiation with a Xe lamp ($\lambda > 300$ nm) in benzene, but the irradiation in the polar solvents such as dichloromethane lead to the formation of the radical cation as evidenced by the purple color of the solution and the broadening of the NMR spectra. The *E*/*Z* ratio was not changed by heating (70 °C, 15 min in C_6D_6), but attempted chromatographic purification of the *Z* isomer lead to isomerization to give the *E*-rich mixture.

The newly synthesized extended π-conjugated compounds were characterized by conventional spectroscopy. The triarylphosphines **3**, **4**, **5**, **6**, and **8** show up-fielded ^{31}P NMR (162 MHz, $CDCl_3$, 296 K) chemical shifts typical of the sterically crowded triarylphosphines (δ −48.5 (**3**), −49.5 (**4**), −50.6 (**5**), −50.7, −50.9 ((*Z*)-**6**), −50.9 ((*E*)-**6**), −51.5, −51.7(**8**), −51.9 (**1**) [1]). The electron withdrawing formyl and benzoyl groups have deshielding effect as compared with the alkenyl and alkyl groups. The diarylethene **6** bearing the two sterically-crowded-triarylphosphine moieties exhibits two singlets with the ratio of 1/1 for the *Z* isomer, because of the diastereomers arising from the helicity of the propellers composed of the three aromatic rings on the phosphorus [2,4]. The *E* form exhibits a single peak because the two triarylphosphine moieties are separated without the intervening substituents. The peak separation of the diastereomers was enhanced by the measurement in C_6D_6 (δ −50.04, −50.25 ((*Z*)-**6**), −50.33, −50.38 ((*E*)-**6**)). The carbinol **8** has two stereocenters, the helicity of the propeller of the triarylphosphine moiety and the quaternary carbon, and also exhibits two ^{31}P chemical shifts with 1/1 ratio. The ^{1}H and ^{13}C NMR spectra of the substituents on the phosphorus exhibit the inversion-averaged patterns typical of the triarylphosphines such as **1**. The two 2,4,6-triisopropylphenyl groups gave one *o*-methine, one *m*-aromatic, and four *o*-methyl ^{1}H signals as a result of the averaging. The remaining aryl group gave one *o*-methine, one *m*-aromatic, and two *o*-methyl signals. The structures of **3** and **4** were further studied by X-ray crystallography (Figs. 1 and 2). The average bond angles and lengths around the phosphorus of **3** (111.9°, 1.835 Å) and **4** (111.6°, 1.845 Å and 111.2°, 1.851 Å for independent molecules) are similar to those of **1** (111.5°, 1.845 Å) [1]. The dihedral angle of the least squares planes defined by the formyl group and the aromatic ring of **3** is 1.585°, while the benzoyl group of **4** deviates from co-planarity with the dihedral angles as 24.28° and 29.42°.



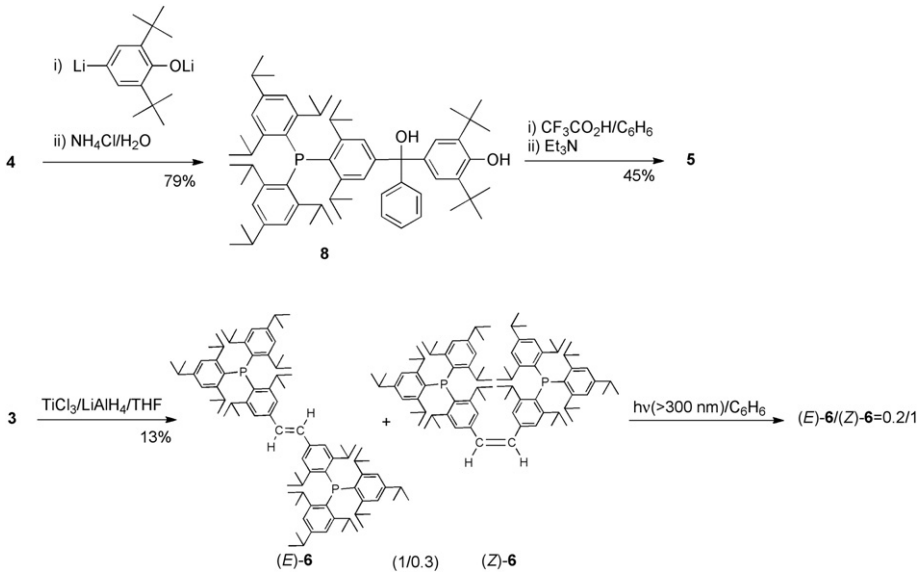
Scheme 1. Push-pull π-conjugated systems.



Scheme 2. Synthesis of the sterically crowded triarylphosphines bearing formyl and benzoyl groups.

2.2. Redox properties and UV–Vis and fluorescence spectra

The redox properties of the newly synthesized triarylphosphines were studied by cyclic voltammetry in dichloromethane and tetrahydrofuran. The redox and spectral properties are summarized in Table 1. The triarylphosphines **3**, **4**, **5** (Fig. 3) **8**, and **6** (Fig. 4) show the first reversible redox waves corresponding to the oxidation of the triarylphosphines to the corresponding radical cations. The triarylphosphines **3** and **4** show irreversible waves corresponding to the reduction of the carbonyl moiety and **5** shows quasi-reversible redox waves corresponding to the two step reduction of the *p*-quinomethane moiety. The first oxidation potentials depend on the substituents in the order of $^{1}E^{ox}_{1/2} = 0.34$ (formyl (**3**)) > 0.31 (benzoyl (**4**)) > 0.27 (*p*-quinomethane (**5**)) > 0.22 (alkenyl (**6**)) > 0.19 (diarylhydroxymethyl (**8**)) > 0.13 (isopropyl (**1**)) V vs Ag/Ag^{+} in dichloromethane) groups. The electron withdrawing substituent raises the oxidation potential. The diarylethene **6**, a mixture of the *E*/*Z* isomers as well as having two triarylphosphine moieties, exhibits a single unresolved redox wave with wider peak-to-peak separation.



Scheme 3. Synthesis of the extended π-conjugated systems bearing the sterically-crowded-triarylphosphine moieties.

The UV–Vis and the fluorescence spectra were measured in *n*-hexane and dichloromethane, and shown in Fig. 5 (**1**, **3**, **4** and **6** in dichloromethane) and Fig. 6 (**5** and **8** in *n*-hexane), and summarized in Table 1. The UV–Vis and the fluorescence spectra of the triarylphosphines reflect the extension and the push-pull substitution of the π-conjugated systems. The crowded triarylphosphines **1** and **8**, which do not have conjugated substituents, show ππ* absorption at aound $^{abs}\lambda_{max}$ = 330 nm and weak fluorescence upon excitation by $^{abs}\lambda_{max}$ at around $^{em}\lambda_{max}$ = 510 nm. The absorption shows little solvent effect, while the fluorescence in dichloromethane shows small bathochromic shift as compared with that in *n*-hexane. The formal Stokes shifts of these triarylphosphines [1c] are smaller than more pyramidalized triarylphosphines such as triphenylphosphine ($^{abs}\lambda_{max}$ = 262, $^{em}\lambda_{max}$ = 465 nm) [14] but still substantial. Similar ππ* absorptions insensitive to the solvents are also observed at around $^{abs}\lambda_{max}$ = 315 nm for **3**, **4**, and **6**. The formyl and the benzoyl derivatives **3** and **4** show the red-shifted ππ* transition responsible to the orange color ($^{abs}\lambda_{max}$ = 407 (**3**), 401(**4**) nm in dichloromethane), and the weak fluorescence in complementary color ($^{em}\lambda_{max}$ = 712 (**3**), 710 (**4**) nm in dichloromethane) (Fig. 5). Introduction of the formyl and the benzoyl groups leads to considerable increase of the formal Stokes shift especially in dichloromethane. Both the absorption and the fluorescence show bathochromic shift in dichloromethane, especially more than 70 nm of bathochromic shift of the fluorescence contributes large Stokes shift in dichloromethane. The *p*-quinomethane **5** shows the absorption at $^{abs}\lambda_{max}$ = 433 nm in *n*-hexane with the solvent effect similar to **3** and **4** and the fluorescence at $^{em}\lambda_{max}$ = 713 nm in *n*-hexane, but nonfluorescent in dichloromethane (Fig. 6). The change of the UV–Vis and the fluorescence spectra from the precursor **8** to **5** indicated the formation of the π-conjugated system. The parent compounds **9** and **10a** (λ < 300 nm (**9**), λ_{max} = 366 (25700) nm (**10a**) in *n*-hexane) also show similar spectral change (Chart 2) [15]. The most red-shifted absorption and emission of **5** among the compounds studied in this work reflect the smallest difference of the oxidation potential of the triarylphosphine moiety and the reduction potential of the acceptor moiety. The $^{abs}\lambda_{max}$ of **5** is intermediate between **10a** and the push-pull *p*-quinomethane **10b** ($^{abs}\lambda_{max}$ = 419 (28200), 479 (35500) nm in toluene, 495 nm in dichloromethane), although the intensity is weaker [16]. The diarylethene **6** shows the UV–Vis absorption ($^{abs}\lambda_{max}$ = 309, 391 nm in dichloromethane) and the fluorescence ($^{em}\lambda_{max}$ = 653 nm in dichloromethane) in shorter wavelength with weaker solvent effect as compared with **3** and **4** (Fig. 5).

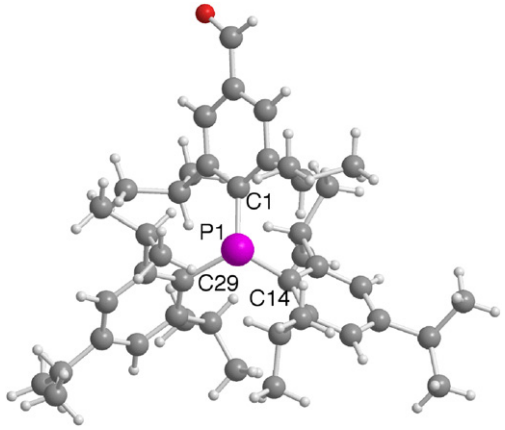


Fig. 1. Molecular structure of **3**. Selected bond lengths (Å) and angles (°): P1–C1 1.830(4), P1–C14 1.833(4), P1–C29 1.843(4), C1–P1–C14 110.2(2), C1–P1–C29 113.5(2), C14–P1–C29 111.9(2).

The wavelength and the molar extinction coefficient, and the solvent effect of the UV–Vis spectra suggest that the visible absorptions of **3**, **4**, **5** and **6** have ππ* character with the polar excited state. The solvent effect of the fluorescence, the emission in longer wavelength with lower quantum yield in the polar solvent, suggests further enhanced polarity of the excited state or geometrical change to more polar structure after excitation. The large Stokes shift of the fluorescence typical of the triarylphosphines is enhanced by the conjugation with the electron withdrawing groups. The push-pull π-conjugated systems such as **3**, **4**, and **5** can be interpreted as a merocyanine dye and the twitterionic resonance structure in the excited state could contribute to the red-shifted UV–Vis spectra and the solvent effect (Scheme 4). In addition, taking inherently ineffective π-conjugation and the crowded environment of the phosphorus into consideration, the π-conjugated systems bearing the crowded triarylphosphine would prefer the twisted intramolecular charge transfer state [17] with increased dipole rather than delocalized quinoid contribution.

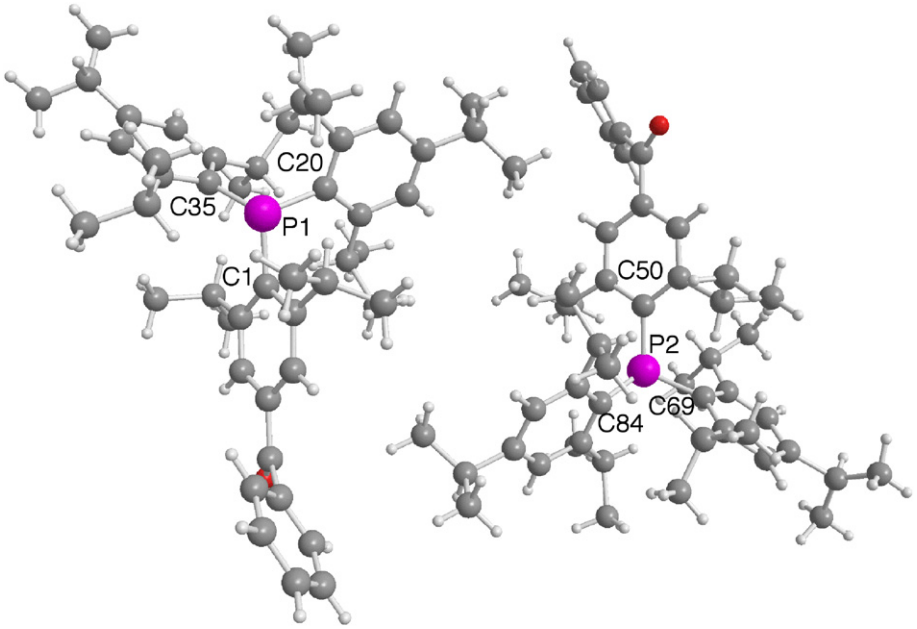


Fig. 2. Molecular structure of **4**. Selected bond lengths (Å) and angles (°): P1–C1 1.852(5), P1–C20 1.841(6), P1–C35 1.842(7), C1–P1–C20 108.1(3), C1–P1–C35 115.6(3), C20–P1–C35 111.2(3), P2–C50 1.848(5), P2–C69 1.853(7), P2–C84 1.851(5), C50–P2–C69 111.3(3), C50–P2–C84 109.9(2), C69–P2–C84 112.3(3).

Magnitude of the red shift of the ππ* absorption by the substitution of the electron withdrawing group is larger than that observed in triphenylamine (λ_{max} = 301 (26000) nm) [18] and (4-formylphenyl) diphenylamine (λ_{max} = 230 (37000), 289 (29700), 347(39800) nm) [19], while the enhancement of the intensity is smaller. The effect of the π-conjugation is intermediate between the nitrogen counterparts and the quinone-substituted crowded triarylphosphines such as **2** (λ_{max} = 557 (1700) nm in dichloromethane) where the π-conjugated systems are separated by the twisted aromatic-ring quinone linkage. The spectral properties of the crowded triarylphosphine, the ππ* absorption in longer wavelength and the fluorescence with the large Stokes shift and low quantum yield, are succeeded by the push-pull substituted π-conjugated systems, in addition, the stability of the radical cation of the crowded triarylphosphine and the ineffective conjugation of the phosphorus contributed formation of the very polar excited state to result in the large bathochromic shift in the polar solvent.

3. Conclusion

The extended π-conjugated systems bearing the sterically crowded triarylphosphine moieties were synthesized by using the crowded (bromoaryl)phosphine as a key intermediate. The crowded triarylphosphine moieties still work as reversible redox sites even connected to the π-conjugated systems. The electronic spectra of the triarylphosphines demonstrated that the sterically-crowded-triarylphosphine moiety in the π-conjugated systems works as a good donor and the push-pull substitution enhances bathochromic effect rather than hyperchromic effect. The large Stokes shift of the fluorescence characteristic of the

Table 1
Redox and spectral properties of the crowded triarylphosphines.

	1	**3**	**4**	**5**	**6**	**8**
Redox potentials in dichloromethane						
$^{1}E^{ox}_{1/2}$/V[a]	0.13	0.34	0.31	0.27	0.22	0.19
Redox potentials in tetrahydrofuran						
$^{1}E^{ox}_{1/2}$/V[b]	0.33	0.47	0.47	0.44	–[e]	–[e]
$^{1}E^{red}_{p}$/V[b]		−2.42	−2.43	−1.85		
$^{2}E^{red}_{p}$/V[b]			−2.87	−2.41		
UV–Vis absorption and fluorescence in *n*-hexane						
$^{abs}\lambda_{max}(\varepsilon)$/nm	326 (14300)	318 (7900)	319 (8400)	361 (22600)	312 (20700)	329 (13200)
		388 (7900)	384 (8100)	433 (12200)	380 (16200)	
$^{em}\lambda_{max}(\phi)$/nm[c]	502 (0.0002)	635 (0.017)	639 (0.014)	713 (0.0057)	604 (0.14)	515 (0.0029)
UV–Vis absorption and fluorescence in dichloromethane						
$^{abs}\lambda_{max}(\varepsilon)$/nm	327 (13500)	318 (8600)	318 (8700)	375 (24800)	309 (27000)	329 (14400)
		407 (7800)	401 (7200)	447 (13100)	391 (23000)	
$^{em}\lambda_{max}(\phi)$/nm[c]	516 (0.0004)	712 (0.0001)	710 (0.0002)	–[d]	653 (0.03)	535 (0.0028)

[a] V vs Ag/Ag^{+}. Conditions: *ca* 10^{-3} mol L^{-1} in dichloromethane with 0.1 mol L^{-1} *n*-Bu_4NClO_4; working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/0.01 mol L^{-1} $AgNO_3$ in acetonitrile with 0.1 mol L^{-1} *n*-Bu_4NClO_4; $E_{1/2}$(ferrocene/ferrocenium) = 0.17 V; scan rate: 30 mV s^{-1}; 293 K.

[b] V vs Ag/Ag^{+}. Conditions: *ca* 10^{-3} mol L^{-1} in tetrahydrofuran with 0.1 mol L^{-1} *n*-Bu_4NClO_4; working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/0.01 mol L^{-1} $AgNO_3$ in acetonitrile with 0.1 mol L^{-1} *n*-Bu_4NClO_4; $E_{1/2}$(ferrocene/ferrocenium) = 0.15 V; scan rate: 30 mV s^{-1}; 293 K.

[c] Excited at $^{abs}\lambda_{max}$. Quantum yields were estimated by comparison with the reference compounds.

[d] No fluorescence.

[e] Not measured.

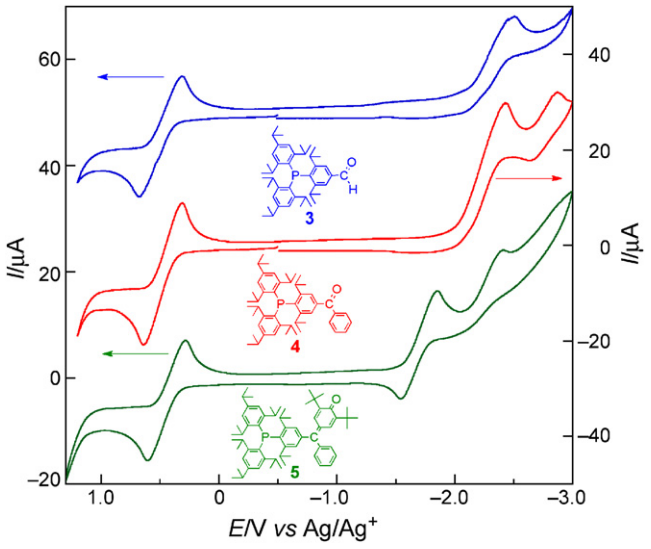


Fig. 3. Cyclic voltammograms of **3**, **4** and **5** in tetrahydrofuran with 0.1 mol L^{-1} *n*-Bu_4NClO_4. Conditions: See Table 1.

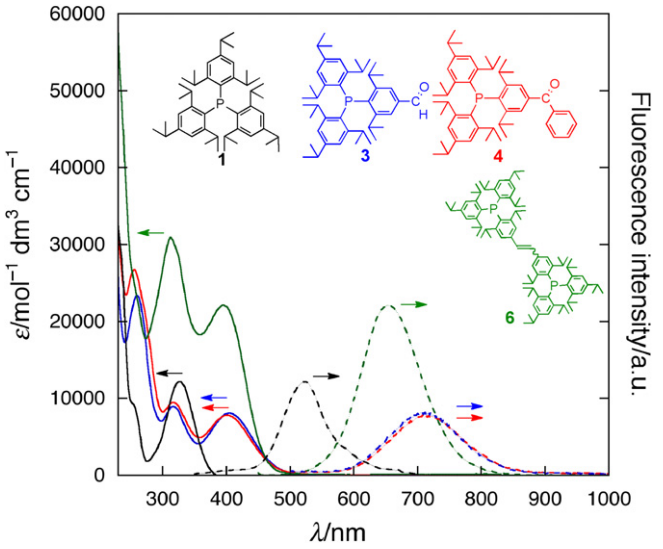


Fig. 5. UV–Vis and fluorescence spectra of the triarylphosphines **1**, **3**, **4**, and **6** in dichloromethane. Conditions: See Table 1.

triarylphosphines is enhanced by the conjugation with the electron withdrawing substituents and the solvent effect of the fluorescence as well as the UV–Vis absorption suggests formation of the very polar excited state. The conventional molecular design of the functional dyes composed of π-conjugated systems can be applied to these newly developed triarylphosphines and it should be mentioned that the crowded triarylphosphines not only work as good donors, but also exhibit characteristics distinct from the second-row π-conjugated systems such as formation of the very polar excited state.

4. Experimental

4.1. General

The ^1H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker AV400 spectrometer. ^1H and ^{13}C NMR chemical shifts are expressed as δ downfield from external tetramethylsilane and calibrated to the residual proton of the deuterated solvent (δ 7.25 for chloroform-*d*) or the carbon of the deuterated solvent (δ 77.0 for chloroform-*d*). ^{31}P NMR chemical shifts are expressed as δ downfield from external 85% H_3PO_4. FT-ICR mass spectra were measured on a Bruker APEX III with electrospray ionization (ESI). Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. UV–Vis spectra were measured on a Hitachi U-3210 or a Shimadzu UV-3600 spectrometer. Fluorescence spectra were measured on a Jasco FP-6600 spectrometer and the quantum yields were estimated by comparison with the standard (4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) in methanol as 0.43 [20] or quinine sulfate dihydrate in 0.1 mol L^{-1} H_2SO_4 as 0.577 [21]). Infrared spectra were measured on a Horiba FT-300 spectrometer. Microanalyses were performed at Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University. Sumitomo basic alumina (KCG-30) was used for

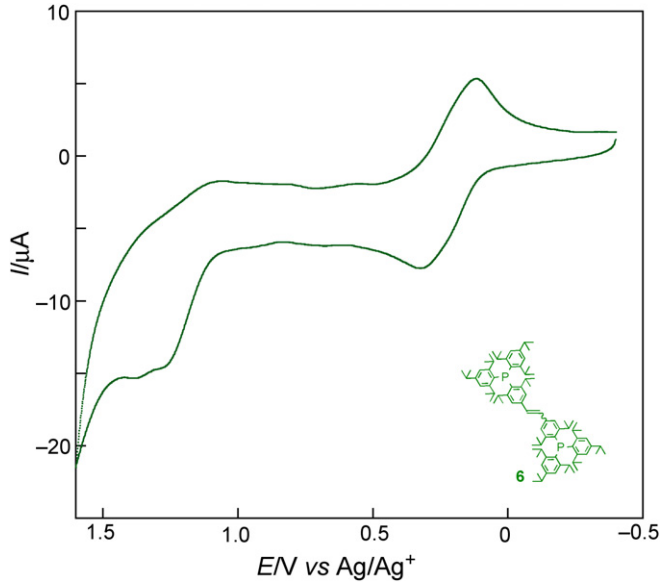


Fig. 4. Cyclic voltammogram of **6** in dichloromethane with 0.1 mol L^{-1} *n*-Bu_4NClO_4. Conditions: See Table 1.

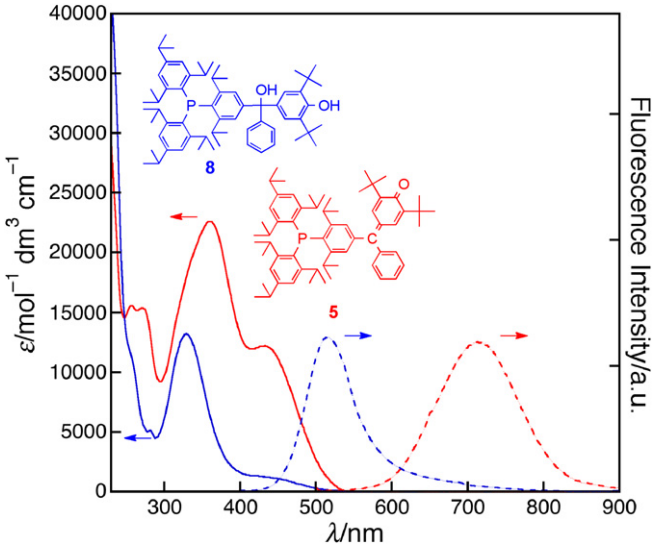


Fig. 6. UV–Vis and fluorescence spectra of the triarylphosphines **5** and **8** in *n*-hexane. Conditions: See Table 1.

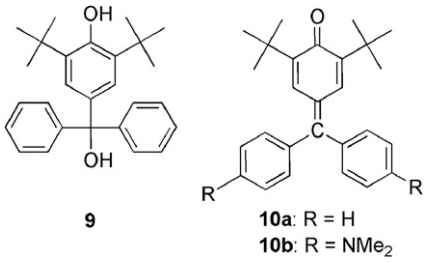


Chart 2. Related *p*-quinomethanes.

the column chromatography. Recycling preparative HPLC system Japan Analytical Industry LC-908 with JAIGEL 1H+2H column was used for gel permeation chromatography (GPC). All reactions were carried out under argon unless otherwise specified. Anhydrous tetrahydrofuran (Kanto Chemical Co., Inc.) was used for reactions. Cyclic voltammetry was performed on a BAS CV-50W controller with a glassy carbon, Pt wire, and Ag/0.01 mol L^{-1} $AgNO_3$/0.1 mol L^{-1} n-Bu_4NClO_4/CH_3CN as a working, counter, and reference electrode, respectively (ferrocene/ferrocenium = 0.17 V in dichloromethane, 0.15 V in tetrahydrofuran). A substrate (*ca.* 10^{-3} mol L^{-1}) was dissolved in dichloromethane or tetrahydrofuran with 0.1 mol L^{-1} n-Bu_4NClO_4 as a supporting electrolyte and the solution was degassed by bubbling with nitrogen gas.

4.2. Synthesis

4.2.1. (4-Formyl-2,6-diisopropylphenyl)bis(2,4,6-triisopropylphenyl) phosphine (**3**)

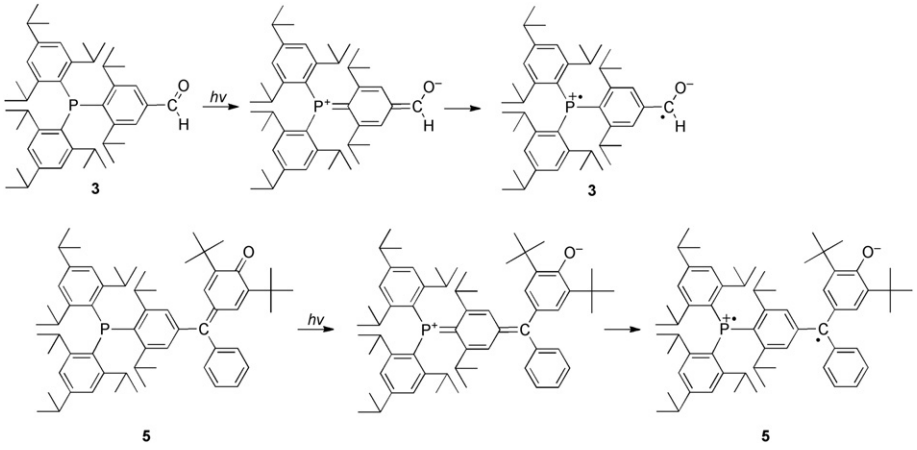
To a solution of (4-bromo-2,6-diisopropylphenyl)bis(2,4,6-triisopropylphenyl)phosphine (**7**) (380 mg, 0.561 mmol) in tetrahydrofuran (5 mL) was added butyllithium (1.58 mol L^{-1} in n-hexane, 0.55 mL, 0.87 mmol) at −78 °C. The solution was stirred for 30 min, and then *N*,*N*-dimethyl formamide (0.09 mL, 1.14 mmol) was added. The resultant mixture was stirred for 10 min, gradually warmed to room temperature, stirred for 16 h, cooled to 0 °C, and then saturated ammonium chloride solution was added. The organic layer was extracted with ether, washed with saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography (Al_2O_3/n-hexane, n-hexane/ethyl acetate = 9/1) to give **3** (260 mg, 0.415 mmol, 74%).

3: orange crystals; mp 144.0–145.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 9.93 (1H, s, CHO), 7.54 (2H, d, J = 2.80 Hz, arom.(Ar)), 6.91 (4H, d, J = 3.20 Hz, arom.(Tip)), 3.52–3.32 (6H, m, *o*-CH), 2.83 (2H, sept, J = 6.80 Hz, *p*-CH), 1.20 (12H, d, J = 6.80 Hz, *p*-CH_3), 1.17 (6H, d, J = 6.80 Hz, *o*-CH_3), 1.14 (6H, d, J = 6.80 Hz, *o*-CH_3), 1.136 (6H, d, J = 6.80 Hz, *o*-CH_3), 0.73 (6H, d, J = 6.80 Hz, *o*-CH_3), 0.68 (6H, d, J = 6.80 Hz, *o*-CH_3), 0.64 (6H, d, J = 6.80 Hz, *o*-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, 296 K) δ 192.76 (s, CHO), 153.95 (d, J_{PC} = 18.3 Hz, *o*-arom.(Ar)), 153.22 (d, J_{PC} = 18.7 Hz, *o*-arom.(Tip)), 153.16 (d, J_{PC} = 17.9 Hz, *o*-arom.(Tip)), 150.00 (s, *p*-arom.(Tip)), 145.29 (d, J_{PC} = 32.2 Hz, *ipso*-arom.(Ar)), 136.15 (s, *p*-arom.(Ar)), 130.67 (d, J_{PC} = 21.0 Hz, *ipso*-arom.(Tip)), 125.05 (d, J_{PC} = 3.8 Hz, *m*-arom.(Ar)), 122.33 (d, J_{PC} = 5.1 Hz, *m*-arom.(Tip)), 122.28 (d, J_{PC} = 4.5 Hz, *m*-arom.(Tip)), 34.10 (s, *p*-CH), 32.31 (d, J_{PC} = 18.1 Hz, *o*-CH), 32.24 (d, J_{PC} = 18.2 Hz, *o*-CH), 31.96 (d, J_{PC} = 16.0 Hz, *o*-CH), 24.53 (s, *o*-CH_3), 23.87 (s, *p*-CH_3), 23.18 (s, *o*-CH_3), 23.02 (s, *o*-CH_3), 22.52 (s, *o*-CH_3); ^{31}P NMR (162 MHz, $CDCl_3$, 296 K) δ −48.5 (s); UV–Vis (CH_2Cl_2, c = 1.68 × 10^{-5} mol L^{-1}) λ_{max} (ε)/nm 318 (8600), 407 (7800); (n-hexane, c = 6.73 × 10^{-5} mol L^{-1}) λ_{max} (ε)/nm 318 (7900), 388 (7900); IR (KBr) 3043, 2956, 2931, 2867, 2723, 1697 ($\nu_{C=O}$), 1676, 1592, 1556, 1461, 1419, 1361, 1309, 1253, 1242, 1173, 1126, 1101, 1066, 962, 933, 879, 715, 650, 586, 525 and 455 cm^{-1}; FT-ICR-MS (ESI) Calcd. for $[C_{43}H_{63}OP + H]^+$: 627.4689, Found: 627.4693; Anal. Calcd for $C_{43}H_{63}OP$: C, 82.38; H, 10.13; Found: C, 82.07; H, 10.18.

4.2.2. (4-Benzoyl-2,6-diisopropylphenyl)bis(2,4,6-triisopropylphenyl) phosphine (**4**)

To a solution of (4-bromo-2,6-diisopropylphenyl)bis(2,4,6-triisopropylphenyl)phosphine (**7**) (166 mg, 0.245 mmol) in tetrahydrofuran (2 mL) was added butyllithium (1.56 mol L^{-1} in n-hexane, 0.24 mL, 0.374 mmol) at −78 °C. The solution was stirred for 30 min, and then benzonitrile (0.05 mL, 0.49 mmol) was added. The resultant mixture was stirred for 30 min, gradually warmed to room temperature, stirred for 3.5 h, then hydrochloric acid solution (1.2 mol L^{-1}, 1 mL) was added, and the mixture was stirred for 18 h. The organic layer was extracted with ether, washed with saturated sodium hydrogen carbonate solution, saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography (Al_2O_3/n-hexane, n-hexane/ethyl acetate = 9/1) to give **4** (110 mg, 0.156 mmol, 64%).

4: orange crystals; mp 149.5–151.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 7.75 (2H, d, J = 7.40 Hz, *o*-arom.(Ph)), 7.56 (1H, t, J = 7.40 Hz, *p*-arom.(Ph)), 7.48 (2H, d, J = 3.20 Hz, arom.(Ar)), 7.46



Scheme 4. Formation of the polar excited state.

(2H, t, J = 7.40 Hz, *m*-arom.(Ph)), 6.93 (4H, d, J = 2.40 Hz, arom. (Tip)), 3.57–3.41 (6H, m, *o*-CH), 2.84 (2H, sept, J = 6.80 Hz, *p*-CH), 1.21 (12H, d, J = 6.80 Hz, *p*-CH_3), 1.17 (6H, d, J = 6.80 Hz, *o*-CH_3), 1.15 (6H, d, J = 7.20 Hz, *o*-CH_3), 1.15 (6H, d, J = 7.20 Hz, *o*-CH_3), 0.75 (6H, d, J = 6.80 Hz, *o*-CH_3), 0.70 (6H, d, J = 6.40 Hz, *o*-CH_3), 0.67 (6H, d, J = 6.40 Hz, *o*-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, 296 K) δ 197.04 (s, COPh), 153.20 (d, J_{PC} = 18.4 Hz, *o*-arom.(Ar)), 153.14 (d, J_{PC} = 18.1 Hz, *o*-arom.(Tip)), 153.11 (d, J_{PC} = 17.8 Hz, *o*-arom.(Tip)), 149.84 (s, *p*-arom.(Tip)), 142.36 (d, J_{PC} = 30.3 Hz, *ipso*-arom.(Ar)), 138.15 (s, *ipso*-arom.(Ph)), 136.98 (s, *p*-arom.(Ar)), 132.16 (s, *p*-arom.(Ph)), 130.97 (d, J_{PC} = 21.5 Hz, *ipso*-arom.(Tip)), 130.06 (s, *o*-arom.(Ph)), 128.13 (s, *m*-arom.(Ph)), 125.68 (d, J_{PC} = 3.8 Hz, *m*-arom.(Ar)), 122.25 (d, J_{PC} = 5.2 Hz, *m*-arom.(Tip)), 122.20 (d, J_{PC} = 5.0 Hz, *m*-arom.(Tip)), 34.10 (s, *p*-CH), 32.27 (d, J_{PC} = 18.0 Hz, *o*-CH), 32.19 (d, J_{PC} = 20.0 Hz, *o*-CH), 32.01 (d, J_{PC} = 16.8 Hz, *o*-CH), 24.57 (s, *o*-CH_3), 24.51 (s, *o*-CH_3), 24.47 (s, *o*-CH_3), 23.89 (s, *p*-CH_3), 23.21 (s, *o*-CH_3), 23.07 (s, *o*-CH_3), 22.56 (s, *o*-CH_3); ^{31}P NMR (162 MHz, $CDCl_3$, 296 K) δ −49.5 (s); UV–Vis (CH_2Cl_2, $c = 3.00 \times 10^{-5}$ mol L^{-1}) : λ_{max} (ε)/nm 318 (8700), 401 (7200); (*n*-hexane, $c = 1.46 \times 10^{-4}$ mol L^{-1}) : λ_{max} (ε)/nm 319 (8400), 384 (8100); IR (KBr) 2960, 2931, 2906, 2867, 1658 ($\nu_{C=O}$), 1599, 1593, 1545, 1462, 1383, 1362, 1331, 1274, 1223, 1178, 1163, 1103, 1068, 989, 935, 879, 808, 729, 698, 667, 650, 525 and 492 cm^{-1}; FT-ICR-MS (ESI) Calcd. for $[C_{49}H_{67}OP + H]^+$: 703.5002, Found: 703.5004; Anal. Calcd for $C_{49}H_{67}OP$: C, 83.71; H, 9.61; Found: C, 83.78; H, 9.61.

4.2.3. *[4-{Bis(2,4,6-triisopropylphenyl)phosphino}-3,5-diisopropylphenyl](3,5-di-tert-butyl-4-hydroxyphenyl)phenylmethanol (**8**)*

To a solution of 2,6-di-*tert*-butyl-4-iodophenol (502 mg, 1.51 mmol) in ether (12 mL) was added butyllithium (1.58 mol L^{-1} in *n*-hexane, 1.92 mL, 3.03 mmol) at −78 °C. The solution was warmed to 20 °C, cooled to −78 °C, and then a solution of the phosphine **4** (355 mg, 0.504 mmol) in ether (3 mL) was added. The resultant mixture was gradually warmed to room temperature, then saturated ammonium chloride solution (5 mL) was added. The mixture was stirred for 10 min, poured onto ice-water, extracted with ether, washed with saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography (Al_2O_3/*n*-hexane, *n*-hexane/ethyl acetate = 24/1, 5/1) to give **8** (360 mg, 0.396 mmol, 79%).

8: orange crystals; mp 66.0–68.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 7.25–7.13 (5H, m, arom.(Ph)), 7.02 (2H, d, J = 2.00 Hz, arom.(Ar)), 6.91 (1H, d, J = 3.60 Hz, arom.(phenol)), 6.90 (1H, d, J = 3.60 Hz, arom.(phenol)), 6.88 (4H, d, J = 3.20 Hz, arom.(Tip)), 5.171 (0.5H, s, ArOH, *dl* or *meso*), 5.165 (0.5H, s, ArOH, *dl* or *meso*), 3.55–3.37 (6H, m, *o*-CH), 2.81 (2H, sept, J = 6.90 Hz, *p*-CH), 2.65 (1H, s, OH), 1.33 (9H, s, *t*-Bu), 1.32 (9H, s, *t*-Bu), 1.19 (12H, d, J = 6.80 Hz, *p*-CH_3), 1.13 (6H, d, J = 6.80 Hz, *o*-CH_3), 1.12 (6H, d, J = 6.40 Hz, *o*-CH_3), 1.02 (6H, d, J = 6.00 Hz, *o*-CH_3), 0.68 (6H, d, J = 5.60 Hz, *o*-CH_3), 0.67 (6H, d, J = 6.00 Hz, *o*-CH_3), 0.54 (6H, d, J = 5.20 Hz, *o*-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, 296 K) δ 153.04 (d, J_{PC} = 18.1 Hz, *o*-arom.), 152.87 (d, J_{PC} = 16.0 Hz, *o*-arom.), 152.44 (d, J_{PC} = 18.2 Hz, *o*-arom.), 152.40 (d, J_{PC} = 18.2 Hz, *o*-arom.), 149.24 (s, *p*-arom.(Tip)), 147.53 (s, C–OH.(phenol)), 147.50 (s, *ipso*-arom.(Ph)), 137.51 (s, *p*-arom.(Ar)), 137.45 (s, *p*-arom.(Ar)), 134.91 (s, *C*C(CH$_3$)$_3$), 134.11 (d, J_{PC} = 22.3 Hz, *ipso*-arom.(Ar)), 131.76 (d, J_{PC} = 23.6 Hz, *ipso*-arom.(Tip)), 127.82 (s, *m*-arom.(Ph)), 127.80 (s, *m*-arom.(Ph)), 127.46 (s, *o*-arom.(Ph)), 126.70 (s, *p*-arom.(Ph)), 125.17 (s, arom.(phenol)), 123.86 (d, J_{PC} = 4.5 Hz, *m*-arom.(Ar)), 123.81 (d, J_{PC} = 5.0 Hz, *m*-arom.(Ar)), 121.95 (d, J_{PC} = 4.1 Hz, *m*-arom.(Tip)), 82.54 (s, CPh), 82.52 (s, CPh), 34.39 (s, *C*(CH$_3$)$_3$), 34.07 (s, *p*-CH), 32.03 (d, J_{PC} = 17.0 Hz, *o*-CH), 31.99 (d, J_{PC} = 17.8 Hz, *o*-CH), 31.94 (d, J_{PC} = 18.1 Hz, *o*-CH), 31.90 (d, J_{PC} = 17.9 Hz, *o*-CH), 30.28 (s, C(*C*H$_3$)$_3$), 24.57 (s, *o*-CH_3), 24.48 (s, *o*-CH_3), 24.42 (s, *o*-CH_3), 23.92 (s, *p*-CH_3), 23.13 (s, *o*-CH_3), 23.08 (s, *o*-CH_3), 22.75 (s, *o*-CH_3), 22.68 (s, *o*-CH_3); ^{31}P NMR (162 MHz, $CDCl_3$, 296 K) δ −51.5 (s), −51.7 (s); IR (KBr) 3647, 2964, 2956, 2933, 2868, 1601, 1550, 1462, 1437, 1419, 1382, 1362, 1313, 1259, 1236, 1161, 1099, 1032, 933, 889, 877, 806, 702, 686, 673, 650, 525 and 494 cm^{-1}; UV–Vis (CH_2Cl_2, $c = 3.00 \times 10^{-5}$ mol L^{-1}) : λ_{max} (ε)/nm 329 (14400); (*n*-hexane, $c = 1.79 \times 10^{-5}$ mol L^{-1}) : λ_{max} (ε)/nm 329 (13200); FT-ICR-MS (ESI) Calcd. for $[C_{63}H_{89}O_2P + H]^+$: 909.6673, Found: 909.6676.

4.2.4. *4-[[4-{Bis(2,4,6-triisopropylphenyl)phosphino}-3,5-diisopropylphenyl](phenyl)methylene]- 2,6-di-tert-butyl-2,5-cyclohexadiene-1-one (**5**)*

To a solution of **8** (360 mg, 0.396 mmol) in dehydrated benzene (5 mL) was added one drop of trifluoroacetic acid and the solution was stirred for 5 min. To a resultant yellow solution was added triethylamine (0.2 mL) and the mixture was stirred for 5 min. The reddish purple mixture was poured onto ice-water, extracted with ether, washed with saturated ammonium chloride solution, saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography (Al_2O_3/*n*-hexane, *n*-hexane/ethyl acetate = 24/1) to give **5** (160 mg, 0.180 mmol, 45%).

5: brown red solid; mp 117.0–118.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 7.42–7.33 (3H, m, *m,p*-arom.(Ph)), 7.22 (1H, d, J = 2.40 Hz, C=CH), 7.19 (1H, d, J = 2.40 Hz, C=CH), 7.17 (2H, dd, J = 7.60, 1.80 Hz *o*-arom.(Ph)), 6.92 (4H, d, J = 3.20 Hz, arom.(Tip)), 6.87 (2H, d, J = 2.80 Hz, arom.(Ar)), 3.60–3.39 (6H, m, *o*-CH), 2.83 (2H, m, *p*-CH), 1.24 (9H, s, C(CH$_3$)$_3$), 1.23 (9H, s, C(CH$_3$)$_3$), 1.21 (12H, d, J = 6.80 Hz, *p*-CH_3), 1.16 (6H, d, J = 6.80 Hz, *o*-CH_3), 1.15 (6H, d, J = 6.80 Hz, *o*-CH_3), 1.09 (6H, d, J = 6.80 Hz, *o*-CH_3), 0.76 (6H, d, J = 6.80 Hz, *o*-CH_3), 0.71 (6H, d, J = 6.80 Hz, *o*-CH_3), 0.60 (6H, d, J = 6.80 Hz, *o*-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, 296 K) δ 186.22 (s, CO), 157.31 (s, PhC =), 153.14 (d, J_{PC} = 18.8 Hz, *o*-arom.), 152.80 (d, J_{PC} = 17.6 Hz, *o*-arom.), 152.76 (d, J_{PC} = 17.8 Hz, *o*-arom.), 149.65 (s, *p*-arom.(Tip)), 147.12 (s, C-*t*-Bu), 147.03 (s, C-*t*-Bu), 140.89 (d, J_{PC} = 27.4 Hz, *ipso*-arom.(Ar)), 138.46 (s, *p*-arom.(Ar) or *i*-arom.(Ph)), 138.19 (s, *p*-arom.(Ar) or *i*-arom.(Ph)), 132.52 (s, *p*-arom.(Ph)), 132.30 (s, *o*-arom.(Ph)), 132.10 (s, PhC = C), 131.08 (d, J_{PC} = 22.5 Hz, *ipso*-arom.(Tip)), 129.24 (s, = CH), 129.22 (s, = CH), 128.21 (d, J_{PC} = 4.0 Hz, *m*-arom.(Ar)), 127.71 (s, *m*-arom.(Ph)), 122.12 (d, J_{PC} = 4.7 Hz, *m*-arom.(Tip)), 35.25 (s, *C*(CH$_3$)$_3$), 35.23 (s, *C*(CH$_3$)$_3$), 34.08 (s, *p*-CH), 32.12 (d, J_{PC} = 17.7 Hz, *o*-CH), 32.08 (d, J_{PC} = 18.1 Hz, *o*-CH), 32.01 (d, J_{PC} = 17.0 Hz, *o*-CH), 29.52 (s, C(*C*H$_3$)$_3$), 24.60 (s, *o*-CH_3), 24.52 (s, *o*-CH_3), 24.41 (s, *o*-CH_3), 23.91 (s, *p*-CH_3), 23.15 (s, *o*-CH_3), 23.05 (s, *o*-CH_3), 22.52 (s, *o*-CH_3); ^{31}P NMR (162 MHz, $CDCl_3$, 296 K) δ −50.6 (s); UV–Vis (CH_2Cl_2, $c = 3.00 \times 10^{-5}$ mol L^{-1}): λ_{max} (ε)/nm 320sh (18000), 375 (24800), 447sh (13100); (*n*-hexane, $c = 1.53 \times 10^{-5}$ mol L^{-1}): λ_{max} (ε)/nm 361 (22600), 433 (12200); IR (KBr) 2960, 2933, 2970, 1610 ($\nu_{C=O}$), 1462, 1384, 1362, 1257, 1099, 1032, 1024, 962, 933, 918, 893, 877, 768, 700, 525 and 496 cm^{-1}; FT-ICR-MS (ESI) Calcd. for $[C_{63}H_{87}OP + H]^+$: 891.6567, Found: 891.6566; Anal. Calcd for $C_{63}H_{87}OP$: C, 84.89; H, 9.84; Found: C, 84.73; H, 9.82.

4.2.5. *1,2-Bis[4-{bis(2,4,6-triisopropylphenyl)phosphino}-3,5-diisopropylphenyl]ethene (**6**)*

To a suspension of titanium (III) chloride (150 mg, 0.973 mmol) in tetrahydrofuran (9 mL) was added lithium aluminum hydride (18.9 mg, 0.498 mmol) at 0 °C and the resultant mixture was refluxed for 15 min. A solution of (4-formyl-2,6-diisopropylphenyl) bis(2,4,6-triisopropylphenyl)phosphine (**3**) (230 mg, 0.367 mmol) in tetrahydrofuran (3 mL) was added at 0 °C and the mixture was refluxed for 5 h. Water (20 mL) was added at 0 °C and the mixture was stirred for 5 min, poured onto ice-water, extracted with ether,

washed with saturated sodium hydrogen carbonate solution, saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography (Al_2O_3/*n*-hexane) and GPC (Jaigel 1H+2H, toluene) to give **6** (30.0 mg, 0.0246 mmol, 13%) as an *E*/*Z* mixture (1/0.3).

6: yellow solid; mp 274.0–276.0 °C; (*E*)-**6**:^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 7.23 (4H, d, J = 3.20 Hz, arom.(Ar)), 7.09 (2H, s, CH═CH), 6.89 (8H, d, J = 3.20 Hz, arom.(Tip)), 3.58–3.38 (12H, m, *o*-CH), 2.82 (4H, sept, J = 6.90 Hz, *p*-CH), 1.20 (24H, d, J = 6.80 Hz, *p*-CH_3), 1.19 (12H, d, J = 6.80 Hz, *o*-CH_3), 1.14 (24H, d, J = 6.40 Hz, *o*-CH_3), 0.72 (12H, d, J = 6.80 Hz, *o*-CH_3), 0.70 (12H, d, J = 6.80 Hz, *o*-CH_3), 0.66 (12H, d, J = 6.40 Hz, *o*-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, 296 K) δ 153.37 (d, J_{PC} = 18.4 Hz, *o*-arom.), 153.04 (d, J_{PC} = 18.2 Hz, *o*-arom.), 153.03 (d, J_{PC} = 17.6 Hz, *o*-arom.), 149.31 (s, *p*-arom.(Tip)), 137.20 (s, *p*-arom.(Ar)), 135.52 (d, J_{PC} = 26.1 Hz, *ipso*-arom.(Ar)), 131.77 (d, J_{PC} = 22.8 Hz, *ipso*-arom.(Tip)), 128.27 (s, CH═CH), 122.23 (d, J_{PC} = 4.2 Hz, *m*-arom. (Ar)), 122.00 (d, J_{PC} = 4.2 Hz, *m*-arom. (Tip)), 34.08 (s, *p*-CH), 32.04 (d, J_{PC} = 18.2 Hz, *o*-CH), 32.02 (d, J_{PC} = 18.3 Hz, *o*-CH), 31.95 (d, J_{PC} = 17.0 Hz, *o*-CH), 24.60 (s, *o*-CH_3), 24.56 (s, *o*-CH_3), 24.54 (s, *o*-CH_3), 23.93 (s, *p*-CH_3), 23.26 (s, *o*-CH_3), 23.03 (s, *o*-CH_3), 22.87 (s, *o*-CH_3); ^{31}P NMR (162 MHz, $CDCl_3$, 296 K) δ −50.9 (s); (*Z*)-**6**:^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ7.03 (2H, d, J = 3.60 Hz, arom.(Ar, *dl* or *meso*)), 7.02 (2H, d, J = 4.00 Hz, arom.(Ar, *dl* or *meso*)), 6.88 (8H, d, J = 2.40 Hz, arom.(Tip, *dl* or *meso*)), 6.87 (8H, d, J = 2.80 Hz, arom.(Tip, *dl* or *meso*)), 6.46 (2H, s, CH═CH, *dl* or *meso*), 6.45 (2H, s, CH═CH, *dl* or *meso*), 3.58–3.38 (12H + 12H, m, *o*-CH), 2.82 (4H + 4H, sept, J = 6.90 Hz, *p*-CH), 1.19 (24H + 24H, d, J = 6.60 Hz, *p*-CH_3), 1.15–1.04 (36H + 36H, *o*-CH_3), 0.62 (12H + 12H, d, J = 6.53 Hz, *o*-CH_3), 0.61 (12H + 12H, d, J = 6.75 Hz, *o*-CH_3), 0.59 (12H + 12H, d, J = 6.88 Hz, *o*-CH_3); ^{31}P NMR (162 MHz, $CDCl_3$, 296 K) δ −50.7 (s, *dl* or *meso*), −50.9 (s, *dl* or *meso*); UV–Vis (CH_2Cl_2, $c = 5.10 \times 10^{-6}$ mol L^{-1}): λ_{max} (ε)/nm 309 (27000), 391 (23000); (*n*-hexane, $c = 7.82 \times 10^{-6}$ mol L^{-1}): λ_{max} (ε)/nm 312 (20700), 380 (16200); IR (KBr) 3045, 2964, 2929, 2868, 1599, 1549, 1462, 1417, 1383, 1362, 1308, 1261, 1238, 1186, 1161, 1126, 1101, 1063, 958, 935, 879, 804 and 652 cm^{-1}; FT-ICR-MS (ESI) Calcd. for $[C_{86}H_{126}P_2 + H]^+$: 1221.9408, Found: 1221.9414; Anal. Calcd for $C_{86}H_{126}P_2 \bullet CHCl_3$: C, 77.91; H, 9.54; Found: C, 77.68; H, 9.94.

4.3. X-ray crystallography

The single crystal data were collected using a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-K_α radiation (λ = 0.71069 Å). The structure was solved by direct methods (SIR92) [22], expanded using Fourier techniques (DIRDIF94) [23], and refined by full matrix least squares on *F*. The non-hydrogen atoms were anisotropically refined. The hydrogen atoms were included but not refined. The structure solution, refinement, and graphical representation were carried out using the teXsan package [24].

Crystal data of **3**: $C_{43}H_{63}OP$, M = 626.94, orange block, crystal dimensions 0.50 × 0.50 × 0.30 mm^3, monoclinic, space group $P2_1/c$ (no.14), a = 10.361(1), b = 36.114(2), c = 10.662(1) Å, β = 100.211(2)°, V = 3926.3(6) Å^3, D_c = 1.061 gcm^{-3}, μ = 0.099 mm^{-1}, T = 140 K, Z = 4, $F(000)$ = 1376.00. Of 29150 reflections measured ($2\theta_{max}$ = 51.0°), 7166 were observed [$I > 0.0\sigma(I)$] (R_{int} = 0.048). Variable parameters 407. Goodness of fit S = 3.69 for observed reflections, and R_1 = 0.082 for $I > 2.0\sigma(I)$, R = 0.092 R_w = 0.160 for all reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.92 and −0.62 eÅ^{-3}, respectively. CCDC 801473.

Crystal data of **4**: $C_{49}H_{67}OP$, M = 703.74, orange block, crystal dimensions 0.50 × 0.50 × 0.50 mm^3, orthorhombic, space group $Pca2_1$ (no. 29), a = 24.2449(6), b = 10.7761(4), c = 34.899(1) Å, V = 9117(1) Å^3, D_c = 1.02 gcm^{-3}, μ = 0.092 mm^{-1}, T = 140 K, Z = 8, $F(000)$ = 3072.00. Of 44046 reflections measured ($2\theta_{max}$ = 51.0°), 7422 were observed [$I > 0.0\sigma(I)$] (R_{int} = 0.051). Variable parameters 920. Goodness of fit S = 1.96 for observed reflections, and R_1 = 0.067 for $I > 2.0\sigma(I)$, R = 0.077 R_w = 0.086 for all reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.42 and −0.45 eÅ^{-3}, respectively. CCDC 801474.

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Appendix. Supplementary material

CCDC 801473 and 801474 contain the supplementary crystallographic data for **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.07.013.

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