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Synthesis and Properties of Sterically Crowded Triarylphosphines Bearing Naphthoquinone Moieties

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Sterically crowded triarylphosphines bearing naphthoquinone moieties were synthesized by the Suzuki−Miyaura coupling of the corresponding (phosphinoaryl)boronic acid derivatives with 2,3-dichloro-1,4-naphthoquinone. The triarylphosphine−naphthoquinone unit can be extended by employing a triarylphosphine bearing a chloronaphthoquinone moiety as a substrate. As an example, an oligomer bearing three triarylphosphine and two naphthoquinone moieties was synthesized. The triarylphosphines bearing naphthoquinone moieties exhibited purple to blue colors arising from intramolecular charge transfer. A systematic study of various derivatives showed that the corresponding absorption shifted toward longer wavelengths as the difference between the oxidation potential of the triarylphosphine moieties and the reduction potential of the naphthoquinone moieties becomes smaller. On the other hand, the intensity of the charge transfer absorption depends on the number of interacting triarylphosphine−naphthoquinone units. The purple color of the charge transfer turned to pale yellow after protonation of the phosphorus atom with trifluoroacetic acid, while deprotonation by addition of triethylamine regenerated the color as well as the phosphine. The intramolecular charge transfer is sensitive to structural changes, as insertion of a 1,4-phenylene spacer between the triarylphosphine and naphthoquinone moieties leads to a loss of the purple color.

Introduction

Sterically crowded triarylphosphines have attracted considerable attention because of their unique structure, properties, and reactivity. Some of them have large C−P−C bond angles around phosphorus and are reversibly oxidized to stable radical cations because of their high HOMOs arising from structural changes around the phosphorus and the steric protection by the bulky substituents.[1] Trimesitylphosphine (**1**)[2] has long been known as a representative compound (Chart 1). Tris(9-anthryl)phosphine has been reported to have a crowded structure as well as unique photophysical properties arising from the anthryl groups.[3] Recently, more hindered triarylphosphines such as tris(2,4,6-triisopropylphenyl)phosphine (**2**)[4] and tris(2,6-diisopropylphenyl)phosphine[5] have been synthesized and shown to have improved redox properties and enhanced stability of the corresponding radical cations. We also synthesized crowded triarylphosphines bearing donors (e.g., **3a**),[6] phosphines bearing neutral radicals (e.g., **3b**),[7] phosphines bearing acceptors,[8] and crowded diphosphines such as **3c**.[7,8] Some of them, especially those having triarylphosphine moieties similar to **2**, have been shown to be reversible multistep redox systems. The redox process was rationalized by taking the charge repulsion between cationic centers into consideration. Herein, we report the synthesis and properties of crowded triarylphosphines bearing naphthoquinone moieties. Amines such as

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Chart 1. Crowded Triarylphosphines

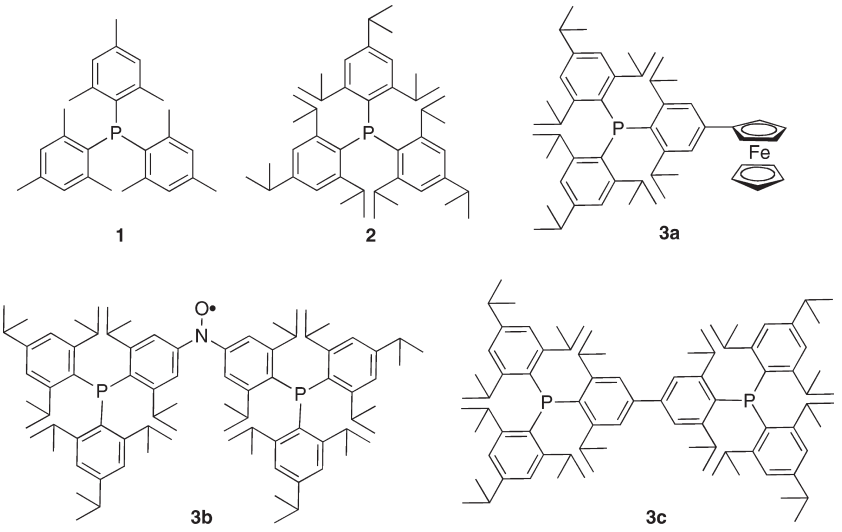
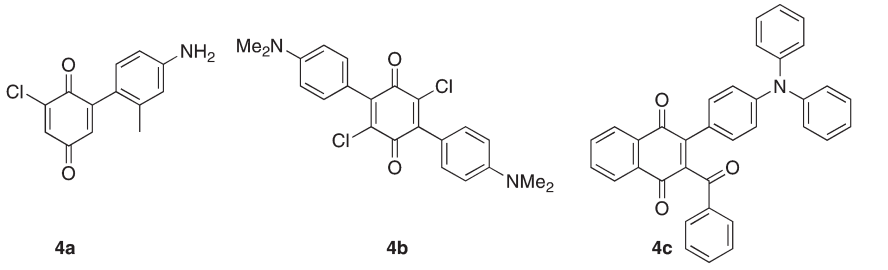
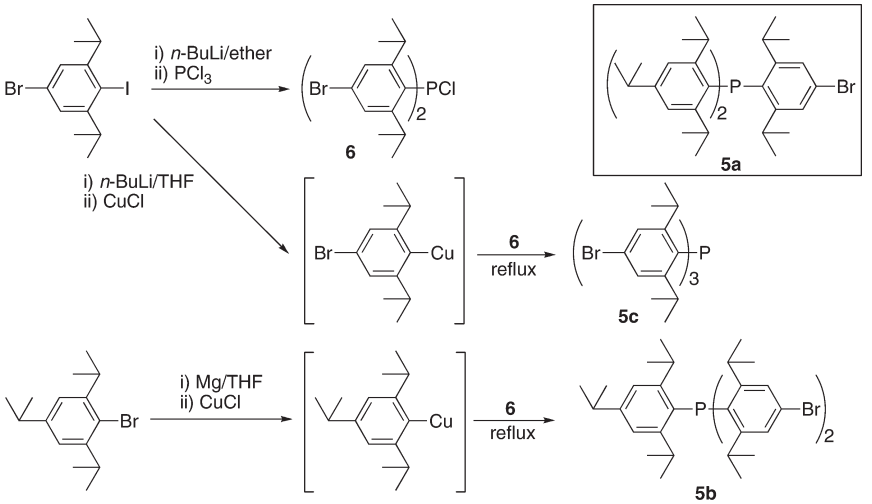


Chart 2. Amines Bearing Quinones



Scheme 1. Synthesis of Crowded (Bromoaryl)phosphines



4a−**c** that incorporate quinone moieties are reported to show visible absorption due to intramolecular charge transfer,[9] and **4c** and related compounds were studied as candidates for functional molecules such as photoconductors for electrophotography (Chart 2).[10] On the other hand, trivalent phosphorus compounds have long been known to react with quinones to form a P−C or P−O bond.[11] Because crowded triarylphosphines such as **2** are good electron donors comparable to triarylamines and the

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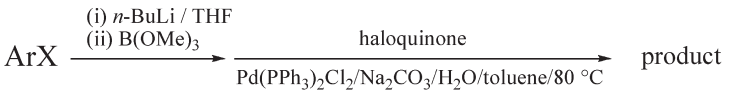
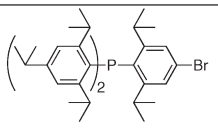
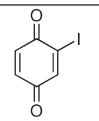
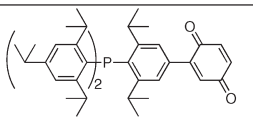
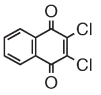
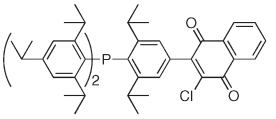
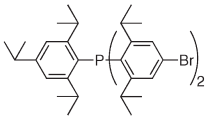
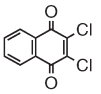
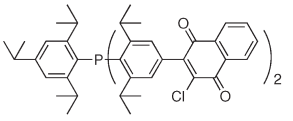
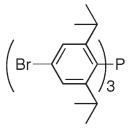
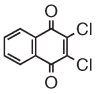
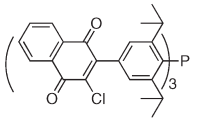
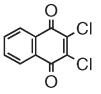
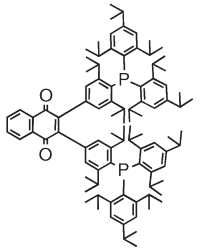
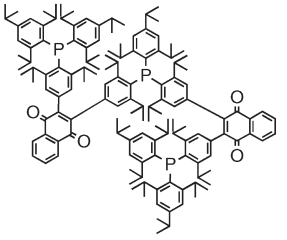
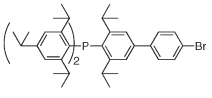
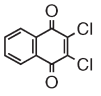
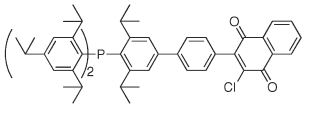
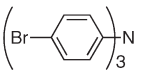
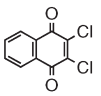
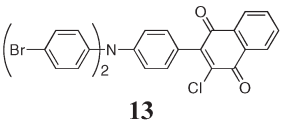
Table 1. Synthesis of Crowded Triarylphosphines Bearing Naphthoquinones and Related Compounds by Suzuki−Miyaura Coupling



entry	ArX	haloquinone	ratio[a]	product	yield/%
1	 **5a**		1.00	 **7**	5[b]
2	**5a**		2.35	 **8a**	58
3	 **5b**		4.00	 **8b**	35
4	 **5c**		4.90	 **8c**	14
5	**5a**		0.34	 **9**	43
6	**5b**	**8a**	2.53	 **10**	26
7	 **11**		3.02	 **12**	23
8			2.54	 **13**	44

[a] Ratio of haloquinone to ArX. [b] $Pd(PPh_3)_4$ was used.

phosphorus atom is sterically protected by bulky substituents to prevent new bond formation, crowded triarylphosphines bearing quinone moieties are expected to be intramolecular charge transfer as well as multistep redox systems that can be candidates for novel functional materials.

Results and Discussion

Synthesis. The crowded (bromoaryl)phosphine **5a** has been employed as a key synthetic intermediate for the synthesis of crowded triarylphosphines bearing functional groups such as nitroxyl radicals (Scheme 1).[7] We planned the synthesis of crowded triarylphosphines bearing quinone moieties by transition-metal-catalyzed cross-coupling of organometallic reagents derived from **5a** and haloquinones. In addition to **5a**, crowded (bromoaryl)phosphines bearing two and three bromoaryl groups, **5b**,**c**, which allow the introduction of two and three functional sites, respectively, were synthesized. The diarylchlorophosphine **6** was synthesized analogously to chlorobis(2,4,6-triisopropylphenyl)phosphine[12] and was coupled with arylcopper(I) reagents to give **5b**,**c**. These (bromoaryl)phosphines were converted to arylboronic acid esters and employed for Suzuki−Miyaura coupling with haloquinones. The synthesis of crowded triarylphosphines bearing quinone moieties by Suzuki−Miyaura coupling is summarized in Table 1. The coupling of an arylboronic acid derivative prepared from **5a** with 2-iodo-1,4-benzoquinone afforded the desired coupling product **7**, only in low yield (entry 1). In contrast, 2,3-dichloro-1,4-naphthoquinone is reported to be a good substrate for Suzuki−Miyaura coupling with an arylboronic acid.[13] Suzuki−Miyaura coupling of 2,3-dichloro-1,4-naphthoquinone with arylboronic acid derivatives prepared from **5a**−**c** afforded crowded triarylphosphines bearing one, two, and three chloronaphthoquinone moieties (**8a**−**c**, respectively) in moderate yields (entries 2−4). The use of excess arylboronic acid derivatives gave naphthoquinone **9** bearing two triarylphosphine moieties in the 2- and 3-positions (entry 5). The triarylphosphine−naphthoquinone unit can be extended by employing **8a** as a substrate (entry 6). The Suzuki−Miyaura coupling of bis(arylboronic acid) prepared from **5b** with **8a** gave the linear oligomer **10**, possessing three triarylphosphine and two naphthoquinone moieties. The crowded triarylphosphine **12** with a 1,4-phenylene spacer between the triarylphosphine and naphthoquinone moieties of **8a** (entry 7) and triarylamine **13** bearing a naphthoquinone (entry 8) were synthesized for comparison using similar methods. These compounds were purified by column chromatography on Al_2O_3, and **8b**,**c**, **9**, **10**, and **12** were further purified by GPC. Triarylphosphine−quinones **7**, **8a**−**c**, **9**, and **10** and the triarylamine−quinone **13** were isolated as blue to purple stable solids. Compounds bearing multiple crowded triarylphosphine moieties, such as **3c**, are unstable in air. Introduction of quinone moieties improved the stability of crowded triarylphosphines toward aerobic oxidation and enabled the isolation of triphosphine **10**.

Structure and Properties. The ^{31}P NMR signals of triarylphosphines bearing naphthoquinones are observed around δ −50, as is typical of crowded triarylphosphines similar to **2**.[4] Introduction of 3-chloro-1,4-naphthoquinonyl groups in place of isopropyl groups leads to downfield shifts (δ −52.4 (**2**),[4] −50.2 (**8a**), −48.8 (**8b**), −47.5 (**8c**)). Diphosphine **9** shows two singlets with a 1:1 ratio (δ −50.1, −50.6, Figure 1a) because of the formation of (*P**, *P**) and (*P**, *M**) diastereomers arising from the helicity of the two propellers composed of three aryl groups on the phosphorus.[1,4,5] A similar situation is observed with crowded diphosphines such as **3c**.[7,8] Triphosphine **10** shows a group of signals reflecting the diastereomers arising from the helicity of the three propellers and the congested structure (Figure 1b). The three propellers composed of crowded triarylphosphine moieties give six stereoisomers. A random formation of the stereoisomers gives the ratio of diastereomers (*P**,*P**,*P**):(*P**,*M**,*P**):(*P**,*P**,*M**) as 2:2:4. If the ^{31}P chemical shifts depend on the relative helicity of the three propellers, the central phosphorus gives three signals with a ratio of 2:4:2, and the outer phosphorus atoms give four signals with a ratio of 4:4:4:4. The ^{31}P NMR spectrum of **10** displays three singlets (δ −47.7, −47.8, −48.5) in the downfield region, which can be assigned as the central phosphorus, taking the substituent effect of the naphthoquinonyl groups into consideration (see above). The spectrum also includes four singlets for the outer phosphorus atoms (δ −49.7, −50.0, −50.6, −50.7) in the upfield region, with the signal intensity ratio close to the expected value. The satisfactory agreement between the experiment and prediction strongly supports the formation and structure of **10**. The ^{1}H NMR spectra of the triarylphosphines bearing naphthoquinones show averaged signals of the substituents on the phosphorus, suggesting rapid inversion of the phosphorus, as is common for structures such as **2**.[1,4,5] The structures of the crowded triarylphosphines bearing naphthoquinones were further confirmed by FT-ICR MS analysis with ESI ionization. In all cases, the corresponding parent or related peaks were observed.

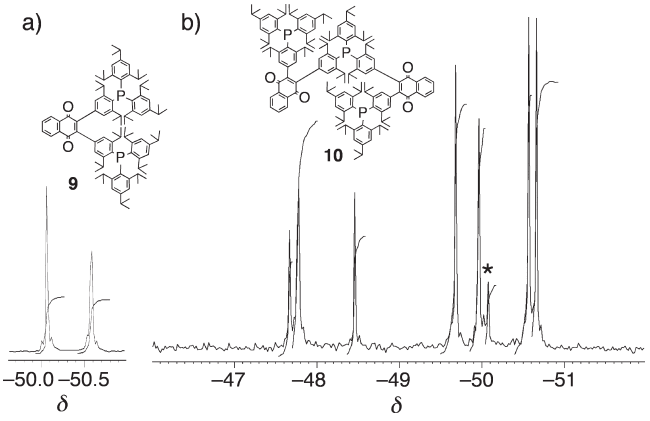


Figure 1. ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) spectra of (a) **9** and (b) **10**. The asterisk denotes an impurity.

The redox properties of the triarylphosphines bearing naphthoquinones were studied by cyclic voltammetry. The cyclic voltammograms of **8a**−**c**, **12**, **9**, and **10** are shown in Figure 2, and the redox properties and UV−vis absorptions are summarized in Table 2. The triarylphosphines bearing naphthoquinones exhibit reversible oxidation of the triarylphosphine moieties at 0.2−0.5 V and reversible first and quasi-reversible second reduction of the naphthoquinone moieties at −0.7 to −1.3 V, with the intensity reflecting the ratio of the phosphine to the naphthoquinone moieties. For example, triarylphosphine−naphthoquinone **8a** is oxidized to the radical cation **8a**$^{\bullet+}$ at 0.26 V and reduced to semiquinone radical anion **8a**$^{\bullet-}$ at −0.89 V, and it is further reduced to the dianion **8a**$^{2-}$ at −1.28 V (Figure 2a, Scheme 2). Comparison of the redox potentials of **8a**−**c** clearly shows that replacement of the *p*-isopropyl groups with 3-chloro-1,4-naphthoquinonyl groups raises the oxidation potential

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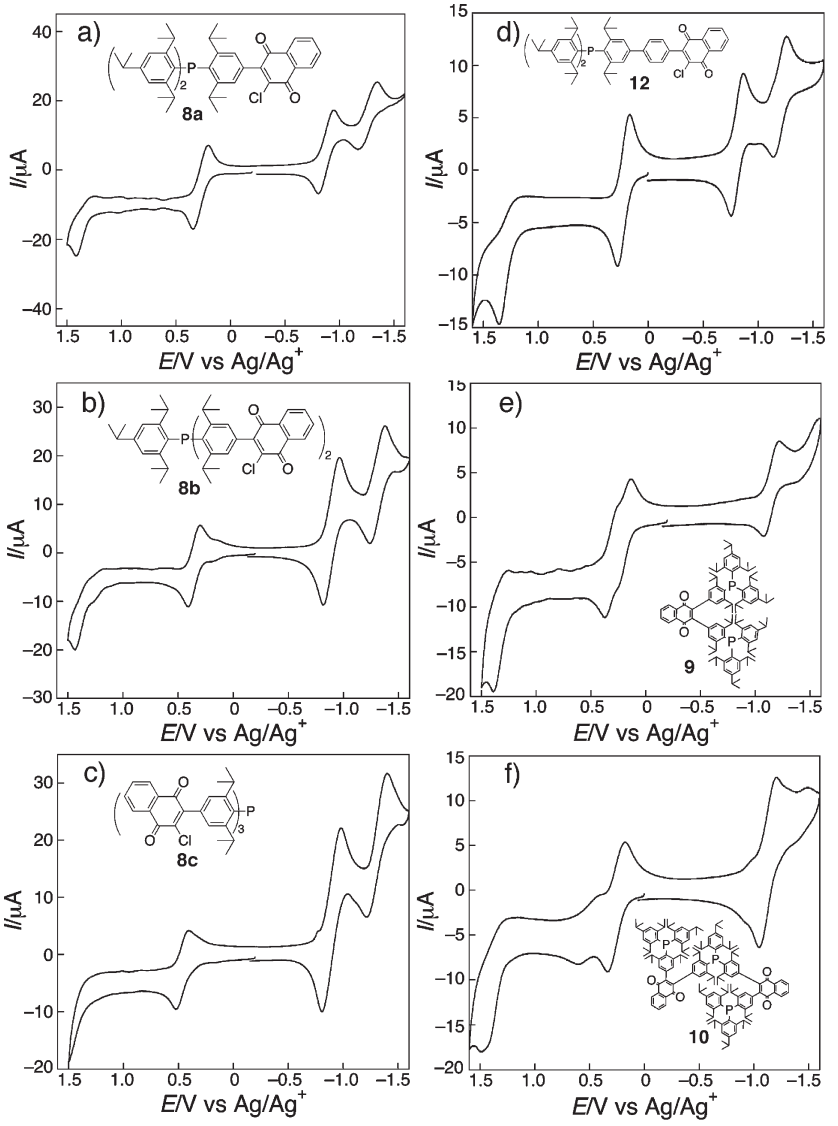


Figure 2. Cyclic voltammograms of (a) **8a**, (b) **8b**, (c) **8c**, (d) **12**, (e) **9**, and (f) **10** in dichloromethane with 0.1 mol L^{-1} *n*-Bu_4NClO_4. Conditions: working electrode, glassy carbon; counter electrode, Pt wire; reference electrode, Ag/0.01 mol L^{-1} $AgNO_3$ in acetonitrile with 0.1 mol L^{-1} *n*-Bu_4NClO_4; ferrocene/ferrocenium at 0.19 V; scan rate, 30 mV s^{-1}; temperature, 293 K.

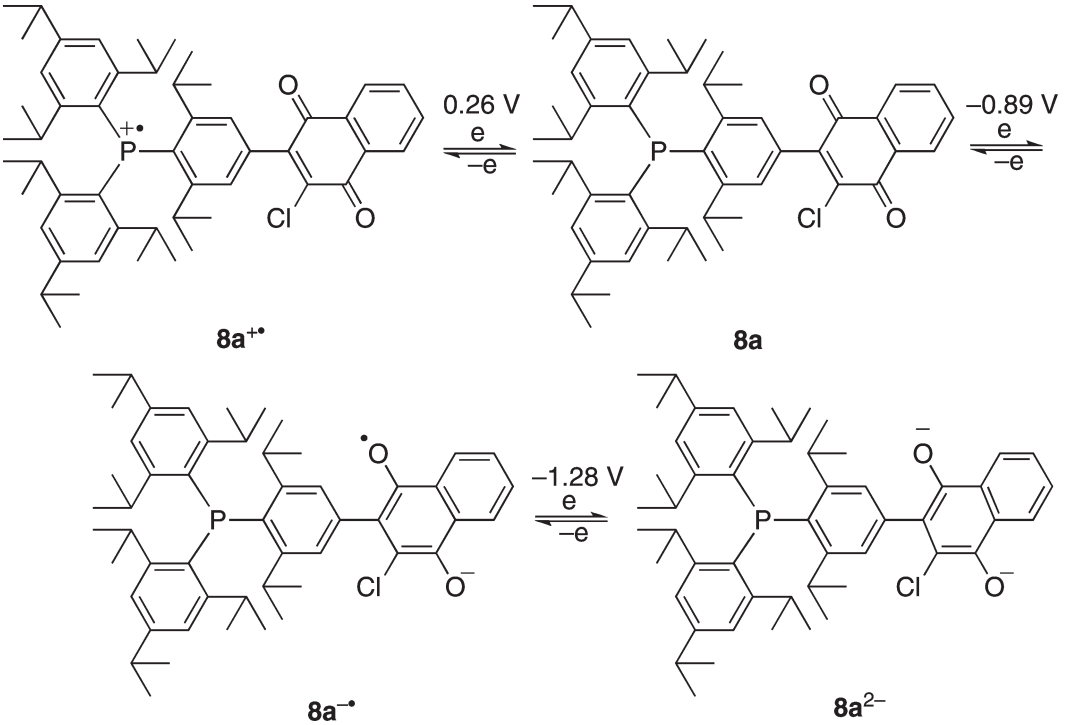
Table 2. Redox Properties and UV−Vis Absorptions of Triarylphosphines Bearing Naphthoquinones and Related Compounds

compd	$^1E_{1/2}{}^{ox}/V^a$	$^2E_{1/2}{}^{ox}/V^a$	$^1E_{1/2}{}^{red}/V^a$	$^2E_{1/2}{}^{red}/V^a$	$\Delta E/V^b$	λ_{max}/nm (ε)^c	$^{CT}\lambda_{max}$/nm (ε)^c
7	0.27		−0.77	−1.13	1.04	334 (13 500)	566 (2 500)
8a	0.26		−0.89	−1.28	1.15	333 (16 600)	557 (1 700)
8b	0.37		−0.89	−1.30	1.26	338 (24 500)	544 (3 800)
8c	0.47		−0.89	−1.34	1.36	338 (30 600)	522 (5 700)
9	0.23	0.34	−1.15		1.38/1.49^d	332 (31 600)	535 (3 800)
10	0.26	0.52	−1.14		1.40/1.66^d	333 (54 700)	531 (7 900)
12	0.24		−0.81	−1.20	1.05	344 (18 100)	
13	0.91		−0.82	−1.20	1.73	313 (35 700)	525 (4 600)
2	0.16					327 (13 600)	
2,3-dichloro-1,4-naphthoquinone			−0.67	−1.11		343 (3 200)	

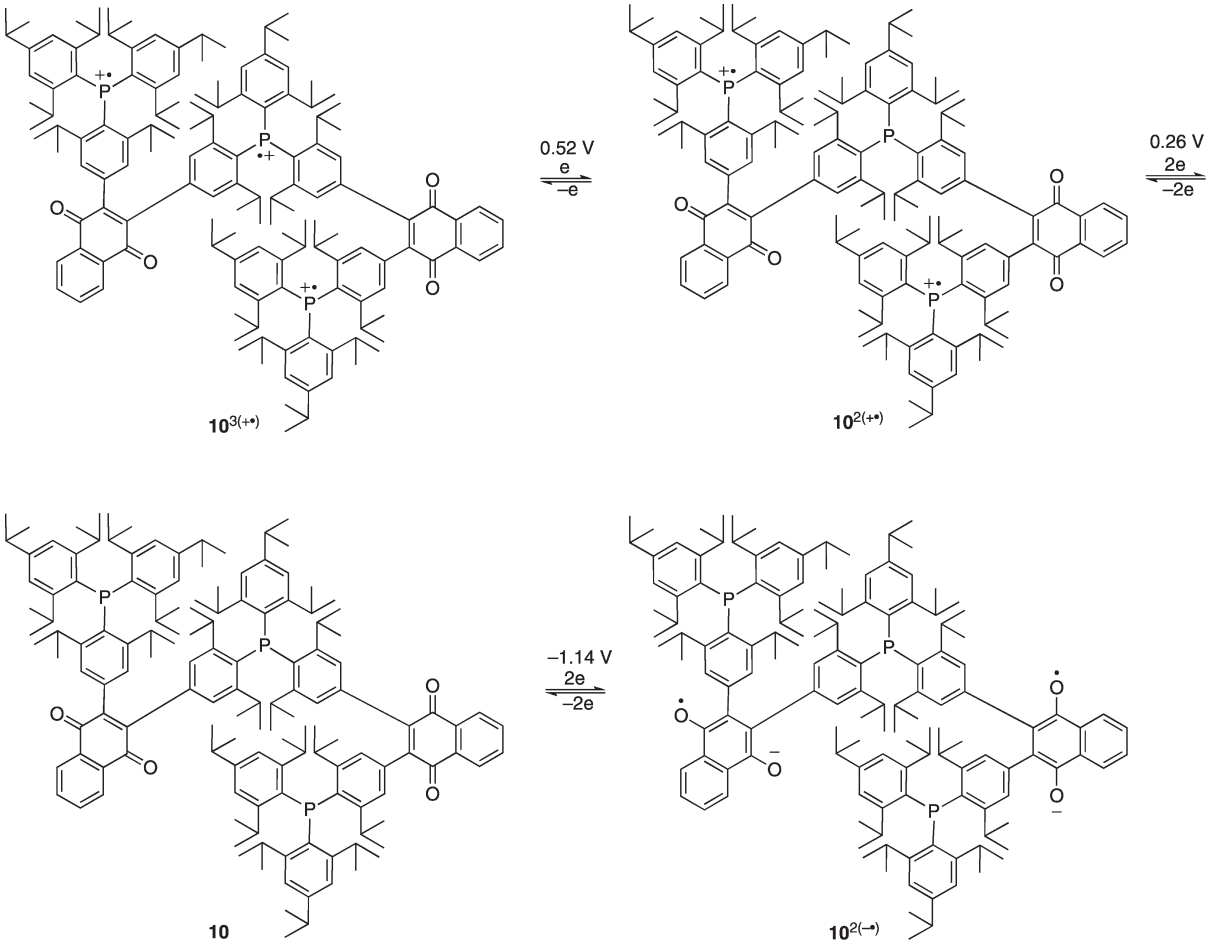
^{a} In V vs Ag/Ag^+ measured by cyclic voltammetry. Conditions: ca. 10^{-4} mol L^{-1} in dichloromethane with 0.1 mol L^{-1} *n*-Bu_4NClO_4 as a support electrolyte; working electrode, glassy carbon; counter electrode, Pt wire; reference electrode, Ag/0.01 mol L^{-1} $AgNO_3$ in acetonitrile with 0.1 mol L^{-1} *n*-Bu_4NClO_4 ($E_{1/2}$(ferrocene/ferrocenium) = 0.19 V); scan rate, 30 mV s^{-1}; temperature, 293 K. ^{b} $\Delta E = {}^1E_{1/2}{}^{ox} - {}^1E_{1/2}{}^{red}$. ^{c} Measured in dichloromethane. ^{d} ${}^2E_{1/2}{}^{ox} - {}^1E_{1/2}{}^{red}$.

without affecting the reduction potentials of the naphthoquinone moieties. No intramolecular Coulombic interaction is observed among the naphthoquinone moieties of **8b**,**c** and **10**. The naphthoquinone moieties are reduced at the same potential. On the other hand, the two-step oxidation of the triarylphosphine moieties of **9** suggests Coulombic repulsion between adjacent phosphorus radical cation centers at the 2- and 3-positions of the naphthoquinone during anodic oxidation (Figure 2e). The cyclic voltammogram of **10** reflects the course of oxidation, where the first two-electron

Scheme 2. Redox Process of Triarylphosphine−Naphthoquinone 8a



Scheme 3. Redox Process of Triarylphosphine−Naphthoquinone 10



oxidation takes place on the outer phosphine moieties at 0.26 V and the second one-electron oxidation occurs on the inner phosphine moiety at 0.52 V as a result of the substituent effect of the naphthoquinone moieties and/or Coulombic repulsion between the three radical cation centers (Figure 2f, Scheme 3).

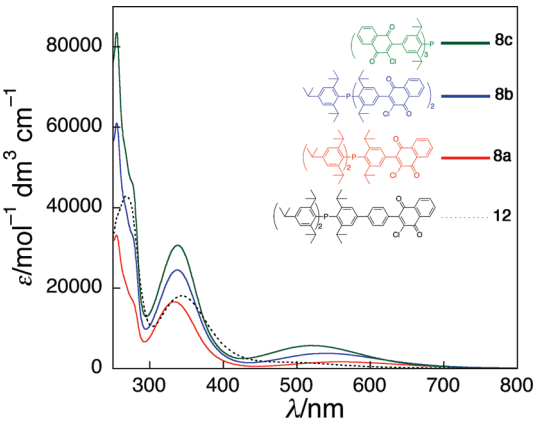


Figure 3. UV−vis spectra of **8a**−**c** and **12** in dichloromethane.

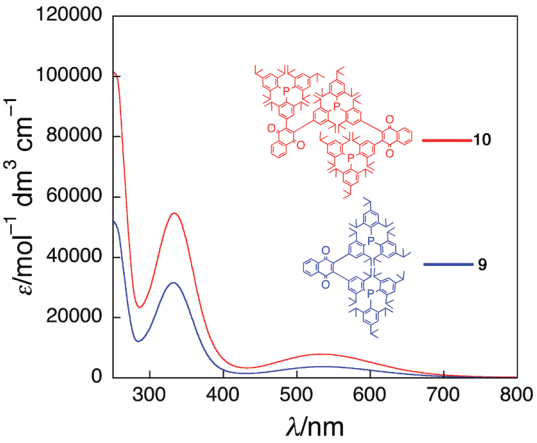
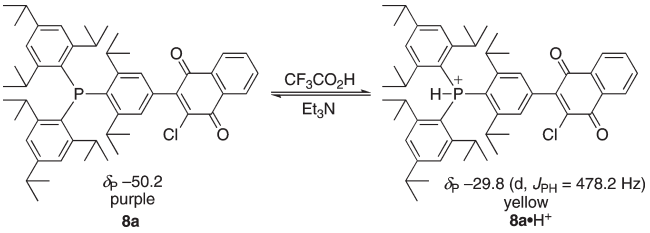


Figure 4. UV−vis spectra of **9** and **10** in dichloromethane.

The UV−vis spectra of the crowded triarylphosphines **8a**−**c** (Figure 3), **9**, and **10** (Figure 4) in dichloromethane exhibit intramolecular charge transfer bands around 500−600 nm responsible for the blue to violet colors. The intense absorptions around λ_{max} 330−340 nm are attributable to the sum of the $\pi\pi^*$ transitions similar to those of **2** (327 nm) and 2,3-dichloro-1,4-naphthoquinone (343 nm). The charge transfer absorption is more sensitive to the solvent than the $\pi\pi^*$ transition (**8a**: λ_{max} (ε) 557 (1700), 333 (16 600) nm (dichloromethane); 534 (2100), 332 (17 400) nm (hexanes)). A comparison of the maximum absorption wavelengths of intramolecular charge transfer ($^{CT}\lambda_{max}$) with the redox potentials of **8a**−**c** shows that a smaller difference between the oxidation potential of the triarylphosphine moieties and the reduction potential of the quinone moieties ($\Delta E = {}^{ox}E_{1/2} - {}^{red}E_{1/2}$: **8a**, 1.15 V; **8b**, 1.26 V; **8c**, 1.36 V) gives $^{CT}\lambda_{max}$ at a longer wavelength (**8a**, 557 nm; **8b**, 544 nm; **8c**, 522 nm). On the other hand, the intensity of the intramolecular charge transfer band, or ε at $^{CT}\lambda_{max}$, of **8a**−**c**, **9**, and **10** is approximately dependent on the number of interacting triarylphosphine−naphthoquinone pairs. Triarylphosphine−naphthoquinones **8a** (ε 1700), **8b** (ε 3800), **8c** (ε 5700), **9** (ε 3800), and **10** (ε 7900) have 1, 2, 3, 2, and 4 interacting triarylphosphine−naphthoquinone pairs, respectively. Triarylphosphine−naphthoquinone **12**, which has a 1,4-phenylene spacer between the chloronaphthoquinone and the triarylphosphine moieties of **8a**, is not purple but red-brown, and it does not show an apparent $^{CT}\lambda_{max}$ in spite of the small difference (ΔE = 1.05 V) between the oxidation and the reduction potentials

Scheme 4. Protonation of 8a



(Figures 2d and 3). This result shows that the naphthoquinones have to be connected directly to the 4-position of the triarylphosphine for the construction of effective intramolecular charge transfer systems. A longer distance between the phosphorus and the naphthoquinone seems to prevent effective intramolecular charge transfer, possibly due to ineffective π-conjugation of the phosphorus 3p and carbon 2p orbitals. Triarylphosphine **2** can be reversibly protonated by trifluoroacetic acid to give the phosphonium salt **2**·H$^+$ (δ −30.1, d, J_{PH} = 480.1 Hz). Addition of trifluoroacetic acid to **8a** in dichloromethane also gives the phosphonium salt **8a**·H$^+$ (δ −29.8, d, J_{PH} = 478.2 Hz), accompanied by a fading of the purple color. Subsequent deprotonation with triethylamine regenerates **8a** as well as the purple color (Scheme 4). Although the color change cycle of **8a** is not completely reversible and lacks long-term stability, further improvement of the phosphorus redox center could lead to construction of molecular switching systems based on a redox cycle coupled with protonation. Naphthoquinone-substituted triarylamine **13** exhibits a purple color and shows a cyclic voltammogram and UV−vis spectrum similar to those of its phosphorus counterpart **8a**. The more intense charge transfer absorption of **13** relative to **8a** reflects the more delocalized HOMO of the triarylamine.

Conclusion

Crowded triarylphosphines bearing naphthoquinone moieties have been synthesized by using Suzuki−Miyaura coupling as a key reaction. They have been demonstrated to be unique functional units that are intramolecular charge transfer systems as well as reversible multistep redox systems. Furthermore, the inherent properties of the crowded triarylphosphines, such as the helicity of the propellers and the formation of phosphonium salts, could provide additional functions for advanced materials. Introduction of naphthoquinone moieties improves the stability of crowded triarylphosphines toward aerobic oxidation and allows extension to triarylphosphine−naphthoquinone oligomers. The crowded triarylphosphine−naphthoquinone unit is expected to be a new key structure of functional polymers bearing heavier main-group elements in the main chain. Further improvement of crowded triarylphosphine units oriented toward advanced materials and extension to larger crowded triarylphosphine−quinone oligomers is in progress.

Experimental Section

General Procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker AV400 spectrometer. ^{1}H 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). Mass spectra were measured on a Hitachi M-2500S with electron impact (EI) ionization at 70 eV. Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. Infrared and UV−vis spectra were measured on a Horiba FT-300 and a Hitachi U-3210 or a Shimadzu UV3600 spectrometer, respectively. Microanalyses were performed at Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University. Merck silica gel 60 and Sumitomo basic alumina (KCG-30) were used for 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 and ether (Kanto Chemical Co., Inc.) were used for reactions. Cyclic voltammetry was performed on a BAS CV-50W controller with glassy carbon, Pt wire, and Ag/0.01 mol L^{-1} $AgNO_3$/0.1 mol L^{-1} *n*-$BuNClO_4$/CH_3CN as working, counter, and reference electrodes, respectively (ferrocene/ferrocenium 0.19 V). A substrate (ca. 10^{-4} mol L^{-1}) was dissolved in dichloromethane with 0.1 mol L^{-1} *n*-Bu_4NClO_4 as a supporting electrolyte, and the solution was degassed by bubbling with nitrogen gas.

Bis(4-bromo-2,6-diisopropylphenyl)chlorophosphine (6). To a solution of 5-bromo-2-iodo-1,3-diisopropylbenzene (10.0 g, 27.2 mmol) in ether (60 mL) was added butyllithium (1.54 mol L^{-1} in *n*-hexane, 17.0 mL, 26.7 mmol) at −78 °C. The solution was stirred for 30 min, and then phosphorus trichloride (1.15 mL, 13.2 mmol) was added. The resultant mixture was stirred for 30 min, warmed to room temperature, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2/*n*-hexane) to give **6** (6.10 g, 11.2 mmol, 85%). **6**: colorless prisms; mp 109−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 7.22 (4H, d, J_{PH} = 2.85 Hz, arom), 3.70−3.57 (4H, m, CH-*o*), 1.02 (12H, d, J_{HH} = 6.62 Hz, CH(CH_3)$_2$-*o*), 1.01 (12H, d, J_{HH} = 6.54 Hz, CH(CH_3)$_2$-*o*); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) δ 153.87 (d, J_{PC} = 16.56 Hz, *o*-arom), 135.23 (d, J_{PC} = 52.34 Hz, *ipso*-arom), 127.80 (s, *m*-arom), 125.16 (s, *p*-arom), 31.40 (d, J_{PC} = 18.23 Hz, *C*H(CH$_3$)$_2$), 24.38 (s, CH(*C*H$_3$)$_2$), 23.70 (s, CH-(*C*H$_3$)$_2$); ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) δ 84.3 (s); LRMS (EI, 70 eV) *m*/*z* (intensity) 548 (25, $M^+ + 4$), 546 (35, $M^+ + 2$), 544 (15, M^+), 505 (70, $M^+ + 4 - i$-Pr), 503 (100, $M^+ + 2 - i$-Pr), 501 (42, $M^+ - i$-Pr)). Anal. Calcd for $C_{24}H_{32}Br_2ClP$: C, 52.72; H, 5.90. Found: C, 52.70; H, 6.02.

Bis(4-bromo-2,6-diisopropylphenyl)(2,4,6-triisopropylphenyl)-phosphine (5b). To a solution of (2,4,6-triisopropylphenyl)-magnesium bromide, prepared from 2-bromo-1,3,5-triisopropylbenzene (2.90 g, 10.00 mmol), magnesium (243 mg, 10.00 mmol), and tetrahydrofuran (10 mL), was added copper(I) chloride (1.15 g, 11.6 mmol) at −78 °C. The mixture was warmed to room temperature and stirred for 3 h. The resultant mixture was cooled to −78 °C, and a solution of **6** (3.70 g, 5.20 mmol) in tetrahydrofuran (15 mL) was added. The mixture was warmed and refluxed for 15 h, concentrated under reduced pressure, and purified by column chromatography (Al_2O_3/*n*-hexane) to give crude **5b**. The crude product was washed with methanol to give **5b** (950 mg, 1.30 mmol, 26%). **5b**: colorless prisms; mp 166−168 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 7.23−7.17 (4H, br m, arom), 6.94 (2H, d, J_{PH} = 3.35 Hz, arom), 3.49−3.31 (6H, m, CH-*o*), 2.85 (1H, sept, J_{HH} = 6.88 Hz, CH-*p*), 1.22 (6H, d, J_{HH} = 6.91 Hz, CH(CH_3)$_2$-*p*), 1.17 (6H, d, J_{HH} = 6.72 Hz, CH(CH_3)$_2$-*o*), 1.16 (6H, d, J_{HH} = 6.22 Hz, CH(CH_3)$_2$-*o*), 1.14 (6H, d, J_{HH} = 6.26 Hz, CH(CH_3)$_2$-*o*), 0.75 (6H, J_{HH} = 6.41 Hz, CH(CH_3)$_2$-*o*), 0.74 (6H, J_{HH} = 6.40 Hz, CH(CH_3)$_2$-*o*), 0.67 (6H, J_{HH} = 6.61 Hz, CH(CH_3)$_2$-*o*); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) δ 155.37 (d, J_{PC} = 19.01 Hz, *o*-arom), 155.26 (d, J_{PC} = 18.73 Hz, *o*-arom), 153.07 (d, J_{PC} = 18.43 Hz, *o*-Tip), 150.11 (s, *p*-Tip), 134.78 (d, J_{PC} = 27.23 Hz, *ipso*-arom), 129.91 (d, J_{PC} = 21.69 Hz, *ipso*-Tip), 127.40 (d, J_{PC} = 4.43 Hz, *m*-arom), 127.32 (d, J_{PC} = 4.27 Hz, *m*-arom), 124.02 (s, *p*-arom), 122.30 (d, J_{PC} = 4.86 Hz, *m*-Tip), 34.08 (s, CH-*p*), 32.16 (d, J_{PC} = 18.09 Hz, CH-*o*), 32.12 (d, J_{PC} = 16.95 Hz, CH-*o*), 32.06 (d, J_{PC} = 17.38 Hz, CH-*o*), 24.50 (s, CH(*C*H$_3$)$_2$-*o*-Tip), 24.36 (s, CH(*C*H$_3$)$_2$-*p*-arom), 23.90 (s, CH(*C*H$_3$)$_2$-*o*-arom), 23.88 (s, CH(*C*H$_3$)$_2$-*o*-arom), 23.22 (s, CH-(*C*H$_3$)$_2$-*o*-Tip), 22.91 (s, CH(*C*H$_3$)$_2$-*o*-arom), 22.65 (s, CH-(*C*H$_3$)$_2$-*o*-arom); ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) δ −50.0 (s); FT-ICR-MS (ESI) *m*/*z* calcd for $[C_{39}H_{55}Br_2P]^+$ 712.2403, found 712.2404. Anal. Calcd for $C_{39}H_{55}Br_2P$: C, 65.54; H, 7.76. Found: C, 65.51; H, 7.91.

Tris(4-bromo-2,6-diisopropylphenyl)phosphine (5c). To a solution of 5-bromo-2-iodo-1,3-diisopropylbenzene (2.90 g, 8.00 mmol) in tetrahydrofuran (30 mL) was added butyllithium (1.50 mol L^{-1} in *n*-hexane, 5.00 mL, 8.00 mmol) at −78 °C. The solution was stirred for 30 min, and copper(I) chloride (890 mg, 9.00 mmol) was added. The resultant mixture was warmed to 20 °C, stirred for 3 h, and cooled to −78 °C. A solution of **6** (4.70 g, 10.00 mmol) in tetrahydrofuran (15 mL) was added, and the mixture was warmed and refluxed for 18 h, concentrated under reduced pressure, and purified by column chromatography (Al_2O_3/*n*-hexane) to give crude **5c**. The crude product was washed with methanol to give **5c** (713 mg, 0.90 mmol, 11%). **5c**: colorless prisms; mp 147−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 7.19 (6H, d, J_{PH} = 2.98 Hz, arom), 3.80−3.40 (6H, m, CH-*o*), 1.13 (18H, d, J_{HH} = 6.70 Hz, CH(CH_3)$_2$-*o*), 0.72 (18H, d, J_{HH} = 6.65 Hz, CH(CH_3)$_2$-*o*); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) δ 155.44 (d, J_{PC} = 19.01 Hz, *o*-arom), 133.72 (d, J_{PC} = 25.95 Hz, *ipso*-arom), 127.61 (d, J_{PC} = 4.50 Hz, *m*-arom), 124.52 (s, *p*-arom), 32.23 (d, J_{PC} = 17.22 Hz, CH-*o*), 24.33 (s, CH(*C*H$_3$)$_2$-*o*), 22.89 (s, CH(*C*H$_3$)$_2$-*o*); ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) δ −49.2 (s); FT-ICR-MS (ESI) *m*/*z* calcd for $[C_{36}H_{48}Br_3P]^+$ 748.1038, found 748.1038. Anal. Calcd for $C_{36}H_{48}Br_3P$: C, 57.54; H, 6.44. Found: C, 57.48; H, 6.59.

Typical Suzuki−Miyaura Coupling of an Arylboronic Acid Derivative with a Chloronaphthoquinone: [4-(3-Chloro-1,4-naphthoquinon-2-yl)-2,6-diisopropylphenyl]bis(2,4,6-triisopropylphenyl)-phosphine (8a). To a solution of **5a** (1.02 g, 1.50 mmol) in tetrahydrofuran (10 mL) was added butyllithium (1.54 mol L^{-1} in *n*-hexane, 1.10 mL, 1.69 mmol) at −78 °C. The resultant mixture was stirred for 30 min, and then trimethyl borate (0.20 mL, 1.79 mmol) was added. The mixture was warmed, refluxed for 3 h, and concentrated under reduced pressure. To the residue was added 2,3-dichloronaphthoquinone (799 mg, 3.52 mmol), dichlorobis(triphenylphosphine)palladium(II) (100 mg, 0.140 mmol), sodium carbonate (400 mg, 3.77 mmol), toluene (10 mL), and degassed water (3 mL). The mixture was refluxed for 13 h, extracted with toluene, dried over anhydrous magnesium sulfate, concentrated under reduced pressure, and purified by column chromatography (Al_2O_3/*n*-hexane, chloroform) to give **8a** (605 mg, 0.770 mmol, 51%). **8a**: purple solid; mp 69−71 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 8.40−8.18 (1H, m, naphthoquinone), 8.18−8.12 (1H, m, naphthoquinone), 7.81−7.72 (2H, m, naphthoquinone), 7.06 (2H, d, J_{PH} = 3.04 Hz, arom), 6.95−6.90 (4H, m, arom), 3.60−3.43 (6H, m, CH-*o*), 2.84 (2H, sept, J_{HH} = 6.88 Hz, CH-*p*), 1.21 (12H, d, J_{HH} = 6.91 Hz, CH(CH_3)$_2$-*p*), 1.18 (12H, d, J_{HH} = 6.11 Hz, CH-(CH_3)$_2$-*o*), 1.16 (6H, d, J_{HH} = 6.65 Hz, CH(CH_3)$_2$-*o*), 0.77 (6H, d, J_{HH} = 6.65 Hz, CH(CH_3)$_2$-*o*), 0.70 (6H, d, J_{HH} = 6.55 Hz, CH(CH_3)$_2$-*o*), 0.69 (6H, d, J_{HH} = 6.54 Hz, CH-(CH_3)$_2$-*o*); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) δ 182.13 (s, *C*=O), 178.47 (s, *C*=O), 153.09 (d, J_{PC} = 18.04 Hz, *o*-arom), 152.47 (d, J_{PC} = 18.32 Hz, *o*-arom), 149.53 (s, *p*-Tip), 146.36 (s, naphthoquinone), 142.44 (s, *p*-arom), 138.06 (d, J_{PC} = 27.95 Hz, *ipso*-arom), 134.27 (s, naphthoquinone), 133.90 (s, naphthoquinone), 131.83 (s, naphthoquinone), 131.72 (s, naphthoquinone), 131.39 (s, naphthoquinone), 131.31 (d, J_{PC} = 22.42 Hz, *ipso*-arom), 127.20 (s, naphthoquinone), 127.07 (s, naphthoquinone), 125.73 (d, J_{PC} = 4.04 Hz, *m*-arom), 122.12 (d, J_{PC} = 5.12 Hz, *m*-Tip), 122.06 (d, J_{PC} = 5.38 Hz, *m*-Tip), 34.08 (s, CH-*p*), 32.16 (d, J_{PC} = 17.36 Hz, CH-*o*), 32.09

(d, J_{PC} = 17.93 Hz, CH-*o*), 31.99 (d, J_{PC} = 16.27 Hz, CH-*o*), 24.57 (s, CH(CH_3)$_2$-*o*-Tip), 24.49 (s × 2, CH(CH_3)$_2$-*o*-arom), 23.92 (s, CH(CH_3)$_2$-*p*-Tip), 23.90 (s, CH(CH_3)$_2$-*p*-arom), 23.16 (s, CH(CH_3)$_2$-*o*-arom), 23.09 (s, CH(CH_3)$_2$-*o*-arom), 22.67 (s, CH(CH_3)$_2$-*o*-arom); ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) δ −50.2 (s); FT-ICR-MS (ESI) calcd for $[C_{52}H_{66}O_2PCl]^+$ 788.4483, found 788.4486; IR (KBr) 1676 ν(C=O) cm^{-1}; UV−vis (CH_2Cl_2, $c = 2.06 \times 10^{-5}$ mol L^{-1}) λ_{max}/nm (log ε) 557 (3.23), 333 (4.22). Anal. Calcd for $C_{52}H_{66}O_2PCl \cdot 0.15CHCl_3$: C, 77.58; H, 8.26. Found: C, 77.48; H, 8.44.

[4-Benzoquinonyl-2,6-diisopropylphenyl]bis(2,4,6-triisopropylphenyl)phosphine (7). 7 (31.1 mg, 0.044 mg, 5%) was synthesized from **5a** (601 mg, 0.89 mmol) and 2-iodo-1,4-benzoquinone (208 mg, 0.89 mmol) in a similar manner to that for **8a**. **7**: purple solid; mp 189−191 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 7.20 (2H, d, J_{PH} = 3.08 Hz, arom), 6.91 (4H, J_{PH} = 3.22 Hz, Tip-arom), 6.87 (1H, d, J = 2.14 Hz, quinone), 6.82 (1H, d, J = 10.04 Hz, quinone), 6.79 (1H, dd, J = 10.04, 2.14 Hz, quinone), 3.55−3.39 (6H, m, CH-*o*), 2.83 (2H, sept, J_{HH} = 6.87 Hz, CH-*p*), 1.20 (12H, d, J_{HH} = 6.68 Hz, CH(CH_3)$_2$-*p*), 1.17 (6H, d, J_{HH} = 6.48 Hz, CH(CH_3)$_2$-*o*), 1.15 (6H, d, J_{HH} = 6.27 Hz, CH(CH_3)$_2$-*o*), 1.14 (6H, d, J_{HH} = 6.53 Hz, CH(CH_3)$_2$-*o*), 0.71 (12H, d, J_{HH} = 6.59 Hz, CH(CH_3)$_2$-*o*), 0.65 (6H, d, J_{HH} = 6.63 Hz, CH(CH_3)$_2$-*o*); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) δ 187.91 (s, *C*=O), 186.91 (s, *C*=O), 153.26 (d, J_{PC} = 17.95 Hz, *o*-arom), 153.86 (d, J_{PC} = 16.37 Hz, *o*-arom × 2), 149.67(s, *p*-Tip), 145.90 (s, quinone), 139.52 (d, J_{PC} = 29.24 Hz, *ipso*-arom), 137.26 (s, quinone), 136.02 (s, quinone), 132.47 (s, quinone or *p*-arom), 131.42 (d, J_{PC} = 32.79 Hz, *ipso*-arom × 2), 131.04 (s, quinone or *p*-arom), 124.88 (d, J_{PC} = 3.73 Hz, *m*-arom), 122.16 (d, J_{PC} = 4.25 Hz, *m*-arom), 122.12 (d, J_{PC} = 4.37 Hz, *m*-arom), 34.07 (s, CH-*p*), 32.21 (d, J_{PC} = 17.92 Hz, CH-*o*), 32.12 (d, J_{PC} = 18.66 Hz, CH-*o*), 32.20 (d, J_{PC} = 17.43 Hz, CH-*o*), 24.52 (s, CH(CH_3)$_2$-*p*-Tip), 23.89 (s, CH(CH_3)$_2$-*o*-Tip), 23.16 (s, CH(CH_3)$_2$-*o*-Tip), 23.00 (s, CH(CH_3)$_2$-*o*-Tip), 22.72 (s, CH(CH_3)$_2$-*o*-Tip); ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) δ −50.1 (s); FT-ICR-MS (ESI) *m*/*z* calcd for $[C_{48}H_{65}O_2P]^+$ 704.4717, found 704.4718; IR (KBr) 1657, 1633 ν(C=O) cm^{-1}; UV−vis (CH_2Cl_2, $c = 1.63 \times 10^{-5}$ mol L^{-1}) λ_{max}/nm (log ε) 566 (3.40), 334 (4.13). Anal. Calcd for $C_{48}H_{65}O_2P \cdot 0.1CHCl_3$: C, 80.58; H, 9.15. Found: C, 80.72; H, 9.34.

Bis[4-(3-chloro-1,4-naphthoquinon-2-yl)-2,6-diisopropylphenyl](2,4,6-triisopropylphenyl)phosphine (8b). 8b (130 mg, 0.139 mg, 33%) was synthesized from **5b** (301 mg, 0.420 mmol) and 2,3-dichloronaphthoquinone (382 mg, 1.68 mmol) in a manner similar to that for **8a** and purified by column chromatography (Al_2O_3/*n*-hexane, chloroform) and GPC (JAIGEL 1H+2H/toluene). **8b**: purple solid; mp 289−291 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 8.24−8.18 (2H, m, naphthoquinone), 8.18−8.13 (2H, m, naphthoquinone), 7.81−7.70 (4H, m, naphthoquinone), 7.12−7.07 (4H, m, *m*-arom), 6.96 (2H, d, J_{PH} = 3.34 Hz, *m*-Tip), 3.61−3.48 (6H, m, CH-*o*), 2.86 (1H, sept, J_{HH} = 6.87 Hz, CH-*p*), 1.22 (6H, d, J_{HH} = 7.16 Hz, CH(CH_3)$_2$-*o*), 1.22 (6H, d, J_{HH} = 6.75 Hz, CH(CH_3)$_2$-*p*), 1.20 (12H, d, J_{HH} = 6.86 Hz, CH(CH_3)$_2$-*p*), 0.81 (6H, d, J_{HH} = 6.25 Hz, CH(CH_3)$_2$-*o*), 0.79 (6H, d, J_{HH} = 6.29 Hz, CH(CH_3)$_2$-*o*), 0.73 (6H, d, J_{HH} = 6.62 Hz, CH(CH_3)$_2$-*o*); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) δ 182.09 (s, *C*=O), 178.43 (s, *C*=O), 153.29 (d, J_{PC} = 18.30 Hz, *o*-arom), 152.70 (d, J_{PC} = 18.23 Hz, *o*-arom), 152.68 (d, J_{PC} = 18.74 Hz, *o*-Tip), 150.07 (s, *p*-Tip), 146.26 (s, naphthoquinone), 142.60 (s, *p*-arom), 137.05 (d, J_{PC} = 26.57 Hz, *ipso*-arom), 134.32 (s, naphthoquinone), 133.95 (s, naphthoquinone), 132.23 (s, naphthoquinone), 131.83 (s, naphthoquinone), 131.41 (s, naphthoquinone), 130.47 (d, J_{PC} = 21.40 Hz, *ipso*-Tip), 127.22 (s, naphthoquinone), 127.11 (s, naphthoquinone), 125.93 (d, J_{PC} = 4.67 Hz, *m*-arom), 125.88 (d, J_{PC} = 4.54 Hz, *m*-arom), 122.34 (d, J_{PC} = 4.92 Hz, *m*-Tip), 34.12 (s, CH-*p*), 32.33 (d, J_{PC} = 17.81 Hz, CH-*o*), 32.24 (d, J_{PC} = 17.13 Hz, CH-*o*), 32.16 (d, J_{PC} = 16.73 Hz, CH-*o*), 24.54 (s, CH(CH_3)$_2$-*o*-Tip), 24.44 (s, CH(CH_3)$_2$-*o*-arom), 23.89 (s, CH(CH_3)$_2$-*p*-arom), 23.24 (s, CH(CH_3)$_2$-*o*-arom), 22.85 (s, CH(CH_3)$_2$-*o*-Tip), 22.75 (s, CH(CH_3)$_2$-*o*-arom); ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) δ −48.8 (s); FT-ICR-MS (ESI) *m*/*z* calcd for $[C_{59}H_{63}Cl_2O_4P]^+$ 936.3836, found 936.3838; IR (KBr) 1678 ν(C=O) cm^{-1}; UV−vis (CH_2Cl_2, $c = 2.84 \times 10^{-5}$ mol L^{-1}) λ_{max}/nm (log ε) 544 (3.58), 338 (4.39). Anal. Calcd for $C_{59}H_{63}Cl_2O_4P$: C, 75.55; H, 6.77. Found: C, 75.14; H, 6.85.

Tris[4-(3-chloro-1,4-naphthoquinon-2-yl)-2,6-diisopropylphenyl]phosphine (8c). 8c (65.0 mg, 0.0598 mg, 14%) was synthesized from **5c** (305 mg, 0.406 mmol) and 2,3-dichloronaphthoquinone (454 mg, 2.00 mmol) in a manner similar to that for **8a** and purified by column chromatography (Al_2O_3/*n*-hexane, chloroform) and GPC (JAIGEL 1H+2H/toluene). **8c**: purple solid; mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 8.24−8.18 (3H, m, naphthoquinone), 8.18−8.12 (3H, m, naphthoquinone), 7.81−7.70 (6H, m, naphthoquinone), 7.14 (6H, d, J_{PH} = 3.10 Hz, arom), 3.66−3.52 (6H, m, CH-*o*), 1.25 (18H, d, J_{HH} = 6.59 Hz, CH(CH_3)$_2$-*o*), 0.84 (18H, d, J_{HH} = 6.56 Hz, CH(CH_3)$_2$-*o*); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) δ 182.02 (s, *C*=O), 178.35 (s, *C*=O), 152.86 (d, J_{PC} = 18.45 Hz, *o*-arom), 146.13 (s, naphthoquinone), 142.72 (s, *p*-arom), 136.08 (d, J_{PC} = 25.52 Hz, *ipso*-arom), 134.36 (s, naphthoquinone), 133.99 (s, naphthoquinone), 132.68 (s, naphthoquinone), 131.80 (s, naphthoquinone), 131.39 (s, naphthoquinone), 127.22 (s, naphthoquinone), 127.13 (s, naphthoquinone), 126.08 (d, J_{PC} = 4.41 Hz, *m*-arom), 32.40 (d, J_{PC} = 17.21 Hz, CH-*o*), 24.49 (s, CH(CH_3)$_2$-*o*), 22.91 (s, CH(CH_3)$_2$-*o*); ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) δ −47.5 (s); FT-ICR-MS (ESI) *m*/*z* calcd for $[C_{66}H_{60}Cl_3O_6P]^+$ 1084.3188, found 1084.3200; IR (KBr) 1676 cm^{-1} ν(C=O); UV−vis (CH_2Cl_2, $c = 3.76 \times 10^{-5}$ mol L^{-1}) λ_{max}/nm (log ε) 522 (3.76), 338 (4.49). Anal. Calcd for $C_{66}H_{60}Cl_3O_6P$: C, 72.96; H, 5.57. Found: C, 72.96; H, 5.57.

2,3-Bis[4-bis(2,4,6-triisopropylphenyl)phosphino-3,5-diisopropylphenyl]-1,4-naphthoquinone (9). 9 (100 mg, 0.0740 mg, 43%) was synthesized from **5a** (339 mg, 0.500 mmol) and 2,3-dichloronaphthoquinone (39.0 mg, 0.172 mmol) in a manner similar to that for **8a** and purified by column chromatography (Al_2O_3/*n*-hexane, chloroform) and GPC (JAIGEL 1H+2H/toluene). **9**: purple solid; mp 195−198 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 8.21−8.16 (2H, m, naphthoquinone), 7.75−7.70 (2H, m, naphthoquinone), 7.02−6.99 (4H, m, arom), 6.97−6.93 (4H, m, arom), 6.91 (4H, br s, arom), 3.71−3.56 (4H, m, CH-*o*), 3.56−3.38 (8H, m, CH-*o*), 2.85 (4H, sept, J_{HH} = 6.90 Hz, CH-*p*), 1.23 (24H, d, J_{HH} = 6.99 Hz, CH(CH_3)$_2$-*p*), 1.21 (12H, d, J_{HH} = 6.70 Hz, CH(CH_3)$_2$-*o*), 1.16 (12H, d, J_{HH} = 6.70 Hz, CH(CH_3)$_2$-*o*), 1.13 (6H, d, J_{HH} = 6.83 Hz, CH(CH_3)$_2$-*p*), 1.11 (6H, d, J_{HH} = 6.69 Hz, CH(CH_3)$_2$-*o*), 0.80 (12H, d, J_{HH} = 6.67 Hz, CH(CH_3)$_2$-*o*), 0.68 (6H, d, J_{HH} = 6.67 Hz, CH(CH_3)$_2$-*o*), 0.65 (6H, d, J_{HH} = 6.63 Hz, CH(CH_3)$_2$-*o*), 0.59 (12H, d, J_{HH} = 6.55 Hz, CH(CH_3)$_2$-*o*); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) δ 184.82 (s, *C*=O), 184.71 (s, *C*=O), 153.48 (d, J_{PC} = 18.25 Hz, *o*-arom), 153.45 (d, J_{PC} = 18.29 Hz, *o*-arom), 152.98 (d, J_{PC} = 18.24 Hz, *o*-arom), 152.93 (d, J_{PC} = 18.34 Hz, *o*-arom), 152.33 (d, J_{PC} = 16.30 Hz, *o*-Tip), 152.15 (d, J_{PC} = 16.25 Hz, *o*-Tip), 149.36 (s, *p*-Tip), 149.34 (s, *p*-Tip), 144.91 (s, *p*-arom), 144.67 (s, *p*-arom), 135.85 (d, J_{PC} = 31.27 Hz, *ipso*-arom), 135.77 (d, J_{PC} = 30.91 Hz, *ipso*-arom), 133.80 (s, naphthoquinone), 133.69 (s, naphthoquinone), 133.28 (s, naphthoquinone), 132.35 (s, naphthoquinone), 132.32 (s, naphthoquinone), 132.03 (d, J_{PC} = 22.46 Hz, *ipso*-Tip), 132.00 (d, J_{PC} = 22.48 Hz, *ipso*-Tip), 126.72 (br s, *m*-arom), 126.41 (s, naphthoquinone), 122.06 (br s, *m*-Tip), 34.06 (s, CH-*p*), 32.41 (d, J_{PC} = 17.37 Hz, CH-*o*), 32.03 (d, J_{PC} = 18.43 Hz, CH-*o*), 31.50 (d, J_{PC} = 17.62 Hz, CH-*o*), 31.45 (d, J_{PC} = 18.35 Hz, CH-*o*), 24.75 (s, CH(CH_3)$_2$-*o*-Tip), 24.70 (s, CH(CH_3)$_2$-*o*-Tip), 24.59 (s, CH(CH_3)$_2$-*o*-Tip), 24.45 (s, CH(CH_3)$_2$-*o*-Tip), 24.39 (s, CH(CH_3)$_2$-*o*-Tip), 23.97 (s, CH(CH_3)$_2$-*o*-arom), 23.90 (s, CH-(CH_3)$_2$-*o*-arom), 23.62 (s, CH(CH_3)$_2$-*p*-Tip), 23.57 (s, CH(CH_3)$_2$-*p*-Tip), 23.46 (s, CH(CH_3)$_2$-*o*-Tip), 23.30 (s, CH(CH_3)$_2$-*o*-Tip), 22.86 (s, CH(CH_3)$_2$-*o*-Tip), 22.78 (s, CH(CH_3)$_2$-*o*-Tip), 22.66 (s, CH(CH_3)$_2$-*o*-Tip); ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) δ −50.1 (s), −50.6 (s); FT-ICR-MS (ESI) *m*/*z* calcd for $[C_{94}H_{128}O_2P_2 + H]^+$

1351.9462, found 1351.9471; IR (KBr) 1666 ν(C═O); UV−vis (CH_2Cl_2, $c = 6.28 \times 10^{-5}$ mol L^{-1}) λ_{max}/nm (log ε) 535 (3.58), 332 (4.50). Anal. Calcd for $C_{94}H_{128}O_2P_2 \cdot 0.7CHCl_3$: C, 79.23; H, 9.04. Found: C, 79.49; H, 8.99.

Bis[2,6-diisopropyl-4-[3-[4-bis(2,4,6-triisopropylphenyl)phosphino-3,5-diisopropylphenyl]-1,4-naphthoquinon-2-yl]phenyl](2,4,6-triisopropylphenyl)phosphine (10). 10 (270 mg, 0.131 mmol, 26%) was synthesized from **5b** (358 mg, 0.501 mmol) and **8a** (1.00 g, 1.27 mmol) in a manner similar to that for **8a** and purified by column chromatography (Al_2O_3/*n*-hexane, chloroform) and GPC (JAIGEL 1H+2H/toluene). **10**: purple solid; mp 243−247 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 8.21−8.12 (4H, m, naphthoquinone), 7.77−7.70 (4H, m, naphthoquinone), 6.97−6.91 (6H, br m, arom), 6.91−6.87 (6H, m, arom), 6.87−6.83 (6H, m, arom), 3.67−3.29 (18H, m, CH-*o*), 2.80 (5H, sept, J_{HH} = 6.61 Hz, CH-*p*), 1.23−1.12 (30H, m, CH-(CH_3)$_2$-*o*), 1.18 (30H, d, J_{HH} = 6.82 Hz, CH(CH_3)$_2$-*p*), 1.10 (12H, d, J_{HH} = 6.53 Hz, CH(CH_3)$_2$-*o*), 1.06 (12H, d, J_{HH} = 6.48 Hz, CH(CH_3)$_2$-*o*), 0.78−0.69 (12H, br m, CH(CH_3)$_2$-*o*), 0.70 (6H, d, J_{HH} = 6.69 Hz, CH(CH_3)$_2$-*o*), 0.63 (12H, d, J_{HH} = 5.01 Hz, CH(CH_3)$_2$-*o*), 0.59 (6H, d, J_{HH} = 5.75 Hz, CH(CH_3)$_2$-*o*), 0.53 (12H, d, J_{HH} = 6.31 Hz, CH(CH_3)$_2$-*o*), 0.48 (3H, d, J_{HH} = 6.94 Hz, CH(CH_3)$_2$-*o*), 0.45 (3H, d, J_{HH} = 6.42 Hz, CH(CH_3)$_2$-*o*); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) δ 184.88 (s, *C*═O), 184.78 (s, *C*═O), 184.72 (s, *C*═O), 153.77−151.99 (m, *o*-arom), 149.64 (s, *p*-Tip), 149.34 (s, *p*-Tip), 145.00 (s, quinone), 144.76 (br s, *p*-arom), 144.53 (s, *p*-arom), 136.09−135.59 (m, *ipso*-arom), 134.27−133.65 (m, quinone), 133.31 (s, quinone), 132.34 (s, quinone), 131.97 (d, J_{PC} = 22.20 Hz, *ipso*-Tip), 127.20−126.41 (m, quinone), 126.41 (br s, *m*-arom), 122.34−121.87 (m, *m*-Tip), 34.03 (s, CH-*p*), 32.66-31.20 (m, CH-*o*), 24.82−22.59 (m, CH-(*C*H$_3$)$_2$-*o*-Tip), 23.92 (br s, CH(*C*H$_3$)$_2$-*p*-Tip), 23.89 (brs, CH-(*C*H$_3$)$_2$-*p*-Tip); ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) δ −47.7 (s), −47.8 (s), −48.5 (s), −49.7 (s), −50.0 (s), −50.6 (s), −50.7 (s); FT-ICR-MS (ESI) *m*/*z* calcd for $[C_{143}H_{187}O_4P_3]^+$ 2062.3715, found 2062.3772; IR (KBr) 1666 cm^{-1} ν(C═O); UV−vis (CH_2Cl_2, $c = 7.68 \times 10^{-6}$ mol L^{-1}) λ_{max}/nm (log ε) 531 (3.90), 333 (4.74). Anal. Calcd for $C_{143}H_{187}O_4P_3 \cdot 0.2CHCl_3$: C, 82.42; H, 9.04. Found: C, 82.39; H, 9.14.

[4-(4-Bromophenyl)-2,6-diisopropylphenyl]bis(2,4,6-triisopropylphenyl)phosphine (11). 11 (500 mg, 0.663 mg, 44%) was synthesized from **5a** (1.02 g, 1.50 mmol) and 1,4-dibromobenzene (511 mg, 2.17 mmol) in a manner similar to that for **8a** and purified by column chromatography (Al_2O_3/*n*-hexane, chloroform) and GPC (JAIGEL 1H+2H/toluene). **11**: pale yellow solid; mp 289−291 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 7.53 (2H, d, J_{HH} = 8.54 Hz, arom), 7.47 (2H, d, J_{HH} = 8.54 Hz, arom), 7.23 (2H, d, J_{PH} = 3.06 Hz, arom), 6.90 (4H, d, J_{PH} = 3.19 Hz, Tip-*m*), 3.58−3.43 (6H, m, CH-*o*), 2.83 (2H, sept, J_{HH} = 6.91 Hz, CH-*p*), 1.20 (12H, d, J_{HH} = 7.10 Hz, CH(CH_3)$_2$-*p*), 1.19 (6H, d, J_{HH} = 7.64 Hz, CH(CH_3)$_2$-*o*), 1.15 (6H, d, J_{HH} = 6.65 Hz, CH(CH_3)$_2$-*o*), 1.14 (6H, d, J_{HH} = 6.66 Hz, CH(CH_3)$_2$-*o*), 0.73 (6H, d, J_{HH} = 7.22 Hz, CH(CH_3)$_2$-*o*), 0.71 (6H, d, J_{HH} = 7.26 Hz, CH(CH_3)$_2$-*o*), 0.66 (6H, d, J_{HH} = 6.62 Hz, CH(CH_3)$_2$-*o*); ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) δ −51.2 (s).

[4-{4-(2-Chloro-1,4-naphthoquinon-2-yl)phenyl}-2,6-diisopropylphenyl]bis(2,4,6-triisopropylphenyl)phosphine (12). 12 (80.0 mg, 0.924 mg, 23%) was synthesized from **11** (300 mg, 0.398 mmol) and 2,3-dichloronaphthoquinone (272 mg, 1.20 mmol) in a manner similar to that for **8a** and purified by column chromatography (Al_2O_3/*n*-hexane, chloroform) and GPC (JAIGEL 1H+2H/toluene). **12**: red-brown solid; mp 122−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 8.26−8.21 (1H, m, naphthoquinone), 8.21−8.16 (1H, m, naphthoquinone), 7.83−7.76 (2H, m, naphthoquinone), 7.77 (2H, d, J_{HH} = 8.31 Hz, arom), 7.46 (2H, d, J_{HH} = 8.31 Hz, arom), 7.38 (2H, d, J_{PH} = 3.07 Hz, arom), 6.93 (4H, d, J_{PH} = 3.22 Hz, Tip-*m*), 3.61−3.45 (6H, m, CH-*o*), 2.85 (2H, sept, J_{HH} = 6.87 Hz, CH-*p*), 1.23 (18H, d, J_{HH} = 6.88 Hz, CH (CH_3)$_2$-*p*, *o*), 1.18 (6H, d, J_{HH} = 6.64 Hz, CH (CH_3)$_2$-*o*), 1.18 (6H, d, J_{HH} = 6.67 Hz, CH (CH_3)$_2$-*o*), 0.77 (6H, d, J_{HH} = 6.67 Hz, CH(CH_3)$_2$-*o*), 0.74 (6H, d, J_{HH} = 6.67 Hz, CH(CH_3)$_2$-*o*), 0.69 (6H, d, J_{HH} = 6.61 Hz, CH(CH_3)$_2$-*o*); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) δ 182.14 (s, *C*═O), 178.24 (s, *C*═O), 153.64 (d, J_{PC} = 18.27 Hz, *o*-arom), 153.03 (d, J_{PC} = 18.32 Hz, *o*-Tip), 153.01 (d, J_{PC} = 18.17 Hz, *o*-Tip), 149.37 (s, *p*-Tip), 145.73 (s, naphthoquinone), 142.83 (s, C_6H_4), 142.67 (s, C_6H_4), 139.80 (s, *p*-arom), 135.78 (d, J_{PC} = 26.77 Hz, *ipso*-arom), 134.41 (s, naphthoquinone), 134.09 (s, naphthoquinone), 131.72 (s, naphthoquinone), 131.48 (s, naphthoquinone), 131.36 (s, naphthoquinone), 130.24 (d, J_{PC} = 24.69 Hz, *ipso*-Tip), 130.12 (s, C_6H_4), 127.37 (s, naphthoquinone), 127.18 (s, naphthoquinone), 126.48 (s, C_6H_4), 122.66 (d, J_{PC} = 4.06 Hz, *m*-arom), 122.02 (d, J_{PC} = 3.74 Hz, *m*-Tip), 34.08 (s, CH-*p*), 32.06 (d, J_{PC} = 16.73 Hz, CH-*o*), 24.62 (s, CH(*C*H$_3$)$_2$-*o*-arom), 24.55 (s, CH(*C*H$_3$)$_2$-*o*-arom), 23.92 (s, CH(*C*H$_3$)$_2$-*p*-arom), 23.19 (s, CH(*C*H$_3$)$_2$-*o*-Tip), 23.03 (s, CH-(*C*H$_3$)$_2$-*o*-arom), 22.91 (s, CH(*C*H$_3$)$_2$-*o*-arom); ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) δ −51.1 (s); IR (KBr) 1678 cm^{-1} ν(C═O); UV−vis (CH_2Cl_2, $c = 1.69 \times 10^{-5}$ mol L^{-1}) λ_{max}/nm (log ε) 344 (4.26); FT-ICR-MS (ESI) *m*/*z* calcd for $[C_{58}H_{70}ClO_2P]^+$ 864.4796, found 864.4793. Anal. Calcd for $C_{58}H_{70}ClO_2P \cdot 0.15CHCl_3$: C, 79.05; H, 8.00. Found: C, 79.15; H, 8.13.

Bis(4-bromophenyl)[4-(3-chloro-1,4-naphthoquinon-2-yl)phenyl]-amine (13). 13 (160 mg, 0.270 mg, 44%) was synthesized from tris(4-bromophenyl)amine (300 mg, 0.620 mmol) and 2,3-dichloronaphthoquinone (358 mg, 1.58 mmol) in a manner similar to that for **8a**. **13**: blue solid; mp 213−216 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 8.24−8.19 (1H, m, quinone), 8.18−8.12 (1H, m, quinone), 7.82−7.76 (2H, m, quinone), 7.40 (4H, d, J = 8.86 Hz, arom), 7.27 (2H, d, J = 8.80 Hz, arom), 7.08 (2H, d, J = 8.80 Hz, arom), 7.03 (4H, d, J = 8.86 Hz, arom); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) δ 182.27 (s, *C*═O), 178.18 (s, *C*═O), 147.96 (s, arom), 145.76 (s, arom), 145.05 (s, naphthoquinone), 142.22 (s, naphthoquinone), 134.35 (s, naphthoquinone), 134.10 (s, naphthoquinone), 132.61 (s, arom), 131.68 (s, naphthoquinone), 131.45 (s, arom), 131.35 (s, naphthoquinone), 127.30 (s, naphthoquinone), 127.13 (s, naphthoquinone), 126.59 (s, arom), 125.39 (s, arom), 121.41 (s, arom), 116.74 (s, arom); UV−vis (CH_2Cl_2, $c = 1.76 \times 10^{-5}$ mol L^{-1}) λ_{max}/nm (log ε) 525 (3.66), 313 (4.55); FT-ICR-MS (ESI) *m*/*z* calcd for $[C_{28}H_{16}Br_2ClNO_2 + Na]^+$ 613.9129. found 613.9129. Anal. Calcd for $C_{28}H_{16}Br_2ClNO_2$; C, 56.65; H, 2.72; N, 2.36. Found: C, 56.44; H, 2.96; N, 2.43.

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Supporting Information Available: Text and figures giving detailed experimental procedures, analytical data, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.