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Synthesis and properties of sterically crowded triarylphosphines bearing anthra- and naphtho-quinones, and their oligomers

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ABSTRACT

Sterically crowded triarylphosphines bearing anthraquinones were synthesized by Suzuki–Miyaura coupling of arylboronic acids derived from (bromoaryl)phosphines with haloanthraquinones. The anthraquinone bearing the two triarylphosphine moieties at the 2,6-positions shows the smaller difference between the oxidation potential of the triarylphosphine moieties and the reduction potential of the anthraquinone moiety, and the more red-shifted visible absorption responsible for the reddish brown color as compared with the 1,5-derivative. A sterically crowded triarylphosphine–naphthoquinone oligomer composed of alternately aligned three triarylphosphine and four naphthoquinone moieties were also synthesized by repeated Suzuki–Miyaura coupling using arylboronic acids derived from (bromoaryl)phosphines and chloronaphthoquinone derivatives. The ^{31}P NMR spectrum of the oligomer consists of several peaks in a narrow range reflecting distribution of the diastereomers arising from the helicity of the propellers composed of the three aromatic rings on the phosphorus atom. The oligomer exhibits a purple color resulting from the intramolecular charge transfer from the triarylphosphine moiety to the neighboring naphthoquinone moiety, and the wavelength and the intensity of the charge transfer band have a demonstrable correlation with the redox potentials and the number of the neighboring triarylphosphine–naphthoquinone pairs, respectively.

1. Introduction

The sterically crowded triarylphosphines have attracted considerable attention in this 50 years because of their unique structure, properties, and reactivities. Especially, some of them have large bond angles around the phosphorus and are reversibly oxidized at low potentials to the stable radical cations because of the synergistic effect of the high HOMO arising from the structural change around the phosphorus and the steric protection by the bulky aryl groups [1]. Trimesitylphosphine, known as one of the most typical compounds from this standpoint for a long time, was isolated by Mislow et al., in 1967 [2] and synthesized by using Grignard reagent by Stepanov et al., in 1969 [3], and the X-ray crystallography [4] and the redox studies [5] revealed their unique structure and properties (Chart 1). We have been involved in this area in this decade. Our first attempt was construction of the redox systems bearing trimesitylphosphine as a redox site [6], but the triarylphosphine moieties similar to trimesitylphosphine were not stable enough to construct reversible multistep redox systems. In order to improve the redox instability of trimesitylphosphine, we synthesized tris(2,4,6-triisopropylphenyl)phosphine (**1**) [7]. Triarylphosphine **1** as well as the arsenic and antimony derivatives have more crowded structures and better redox stabilities as compared with the corresponding trimesityl derivatives. Tris(2,6-diisopropylphenyl)phosphine has been reported by Boeré et al. around the same time and the structure and the properties have been studied in detail [8]. The X-ray crystallographic analyses of radical cations of **1** [9a] and trimesitylphosphine [9b] have been reported very recently. Because **1** is expected to be a better candidate for the substructure of the functional materials, we have synthesized crowded triarylphosphines similar to **1** bearing donors [10], acceptors [11], and radicals [12], and revealed their redox properties. The triarylphosphine moieties generally work as reversible redox sites even if bound to other redox sites and can construct the multistep redox systems. Recently, we have synthesized sterically crowded triarylphosphines bearing naphthoquinone moieties **2a**, **2b**, and **2c**, which can be extended to oligomer **3** [11b]. They show a characteristic purple color resulting from the intramolecular charge transfer from the triarylphosphine

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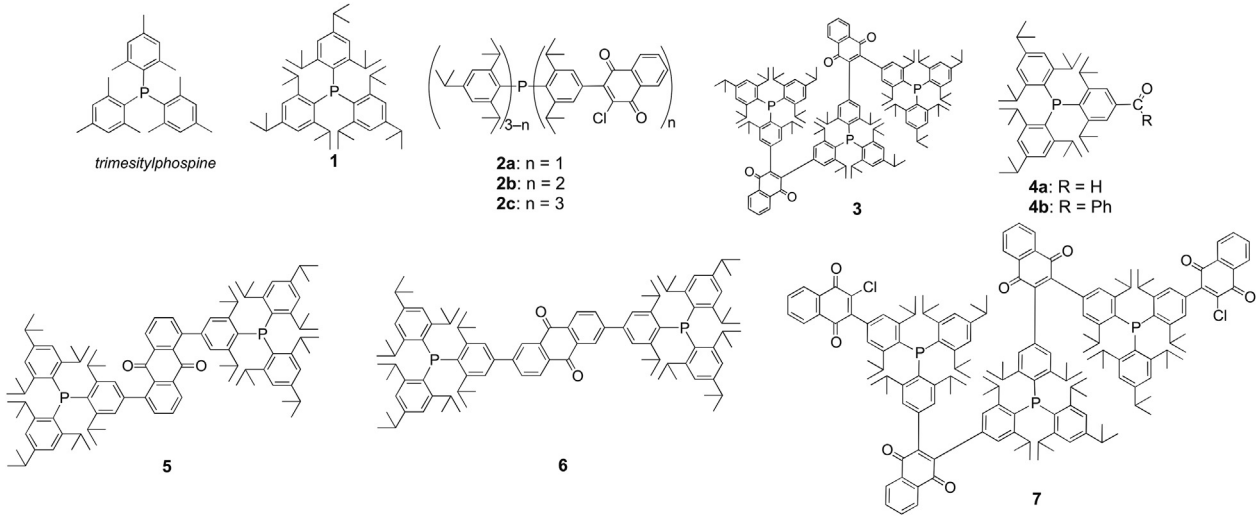


Chart 1. Sterically crowded triarylphosphines.

to the naphthoquinone moieties, and we revealed a correlation between the charge transfer band and the redox properties. On the other hand, we synthesized sterically crowded triarylphosphines simply conjugated with electron acceptors such as **4a** and **4b**, which exhibit an orange color of the red shifted $\pi \rightarrow \pi^*$ transition [11c]. In this paper, we report our recent exploration on the construction of the repeated donor–acceptor diads bearing the sterically crowded triarylphosphines as donor units. Anthraquinones are rather weaker acceptor as compared with 1,4-benzoquinones and 1,4-naphthoquinones, and various halogenated derivatives, which are expected to serve as substrates for Suzuki–Miyaura coupling, are readily available. The intramolecular interaction of the sterically crowded triarylphosphine and the acceptor moieties different from the previously investigated systems in terms of the π-conjugation as well as the through-space interaction can be expected. Herein, we describe the synthesis, the redox properties, and the electronic spectra of the sterically crowded triarylphosphines connected to anthraquinone moieties, 1,4-anthraquinonylene derivative **5** and its oligomer, and 2,5-derivative **6**. In addition, the extension of the linear triarylphosphine–naphthoquinone oligomer **3**, the synthesis, redox properties, and electronic spectra of **7** composed of alternately aligned three triarylphosphine and four naphthoquinone moieties, is also presented.

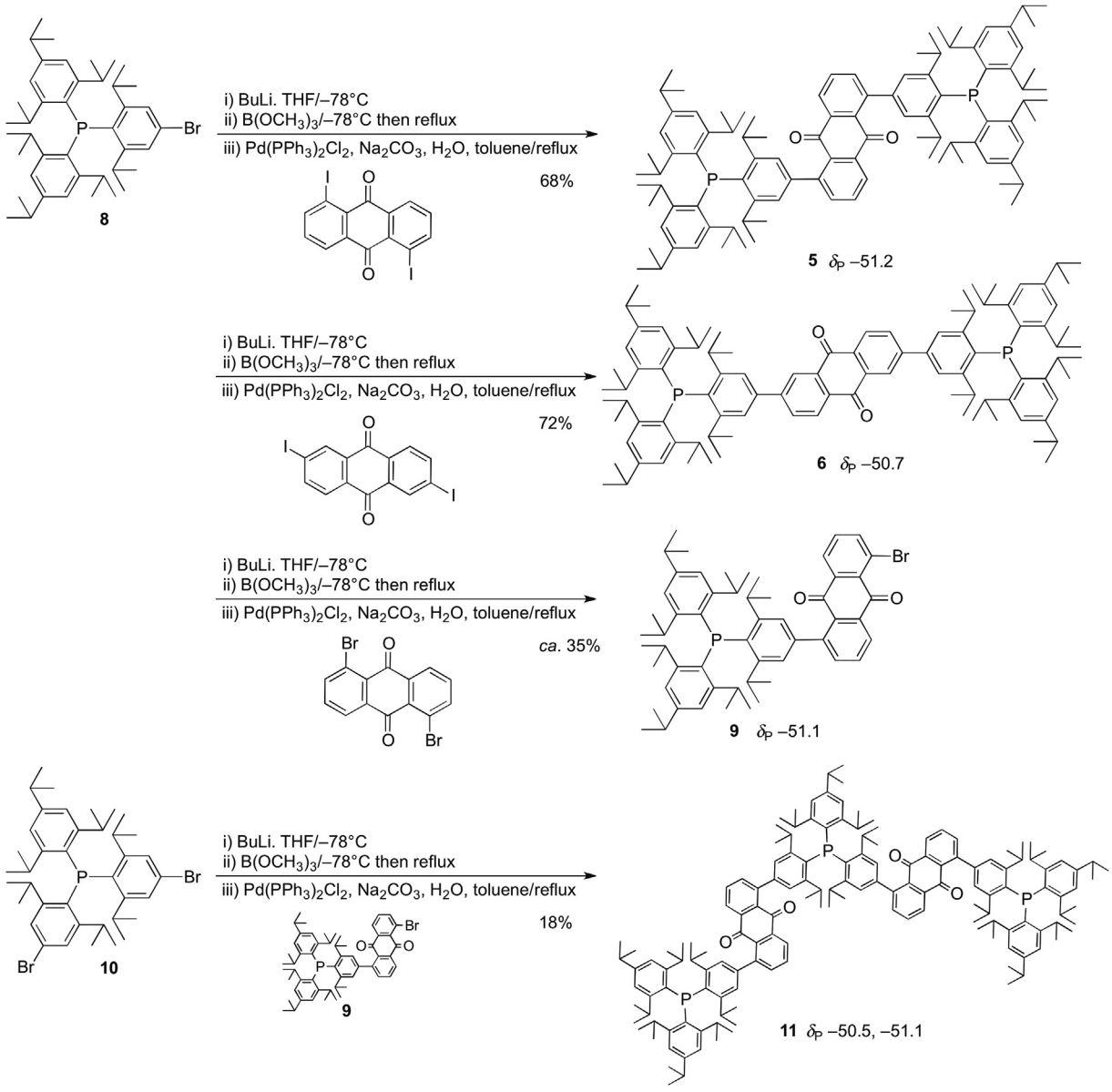
2. Results and discussion

2.1. Synthesis and characterization

We have previously synthesized various sterically crowded triarylphosphines bearing quinone moieties by using Suzuki–Miyaura coupling as a key-reaction [11b]. Haloanthraquinones were found to work as substrates for the Suzuki–Miyaura coupling, and were employed to the synthesis of the sterically crowded triarylphosphines bearing anthraquinone moieties (Scheme 1). The Suzuki–Miyaura coupling of the arylboronic acid derived from (bromoaryl)phosphine **8** with a half equivalent of 1,5- and 2,6-diiodoanthraquinones afforded anthraquinones bearing two triarylphosphine moieties **5** and **6**, respectively. The employment of 1,5-dibromoanthraquinone in place of the diiodoanthraquinone allowed a preparation of 5-bromo-1-anthraquinonyl derivative **9**, although the product was contaminated with **5** and the 1-anthraquinonyl derivative. The Suzuki–Miyaura coupling of the arylboronic acid derived from bis(bromoaryl)phosphine **10** with **9** gave triarylphosphine–anthraquinone oligomer **11**. The sterically crowded triarylphosphines bearing anthraquinones were obtained as brown or reddish brown solids.

We have previously reported the synthesis of sterically crowded triarylphosphine–naphthoquinone oligomer **3** by Suzuki–Miyaura coupling of the arylboronic acid derived from **10** and triarylphosphine bearing chloronaphthoquinone moiety **2a** [11b]. However, the attempted synthesis of the dendritic triarylphosphine–naphthoquinone oligomer by the coupling of the arylboronic acid derivative prepared from tris(4-bromo-2,6-diisopropylphenyl)phosphine with **2a** was unsuccessful. We have previously experienced a drop of the yield in this manner of multiple substitution (*e.g.* **2a**: 58, **2b**: 35, **2c**: 14%) [11b], thus, side reactions such as reduction to C–H bond in addition to a failure of lithiation severely affected the coupling with **2a**. Whereas, linear triarylphosphine–naphthoquinone oligomer **7** was synthesized by the cross-coupling of the arylboronic acid derivative prepared from **10** with chloronaphthoquinone derivative **2b**, and the fraction mainly composed of **7** was obtained as air-stable purple solids after column chromatography (Al_2O_3) followed by GPC (Scheme 2).

Newly synthesized triarylphosphines **5**, **6**, **9**, **11**, and **7** were characterized by conventional spectroscopies. The formations of large oligomers **11** and **7** were confirmed by FT-ICR mass spectroscopy with electron spray ionization, where the $[M + Na]^+$ ions were observed. Triarylphosphines **5**, **6**, **9**, **11**, and **7** show the ^{31}P NMR signals in a high field typical of such sterically crowded triarylphosphines (*e.g.* **1**: δ −51.9). Although some of the compounds composed of the multiple sterically crowded triarylphosphine moieties similar to **1** are known to exhibit characteristic spectral patterns resulting from the statistical distribution of the diastereomers arising from helicity of the propellers composed of the three aromatic rings on the phosphorus [11b], diphosphines **5** and **6** show a single peak, and triphosphine **11** shows two singlets (δ −50.5, −51.1 in 1/2 ratio). The triarylphosphine moieties are too far to sense the helicity of other sites. On the other hand, the ^{31}P NMR spectrum of the triarylphosphine–naphthoquinone oligomer **7** is more complex (Fig. 1). The ^{31}P NMR spectra of previously reported triarylphosphines bearing naphthoquinones such as **3** reflect statistical distribution of the diastereomers [11b]. The three propellers of triphosphine **3** can make 2^3 permutations, which means 6 enantiomers or 3 diastereomers. Because the ^{31}P chemical shifts are

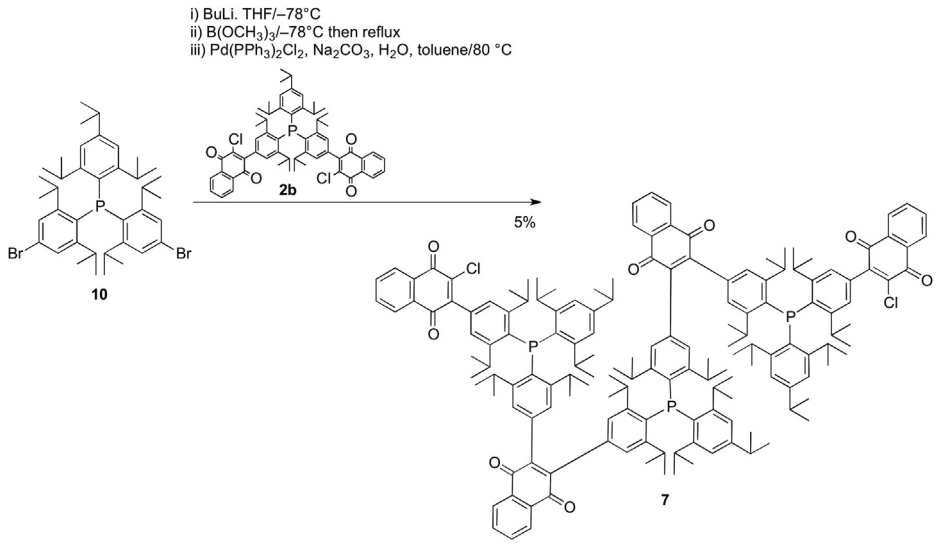


Scheme 1. Synthesis of sterically crowded triarylphosphines bearing anthraquinone moieties.

mainly influenced by the deshielding effect of the naphthoquinonyl groups at *para* positions and additionally perturbed by the closely located triarylphosphine moieties, **3** shows four lines for the outer phosphine moieties bearing one naphthoquinonyl group in a higher field in the ratio of 4/4/4/4 (δ −49.7, −50.0, −50.6, −50.7) and three lines for the central phosphine moiety bearing two naphthoquinonyl groups in a lower filed in the ratio of 2/4/2 (δ −47.7, −47.8, −48.5). The ^{31}P NMR spectrum of triphosphine **7** (Fig. 1), which consists of seven peaks (δ −47.31, −47.60, −47.91, −48.00, −48.52, −48.58, −48.62), can be similarly interpreted as a distribution of the diastereomers. However, the assignment of the spectrum is more difficult than that of **3** because all the triarylphosphine moieties have two naphthoquinone moieties and the peaks are observed in a narrower range than **3**. Thus, it is not sure if the spectrum of the congested oligomer **7** really reflects a statistical distribution, but we can predict that the ^{31}P NMR spectra of the longer oligomers consist of peaks in a narrower range around δ −48.

2.2. Redox properties and UV–Vis spectra

The cyclic voltammograms of sterically crowded triarylphosphines bearing anthraquinones **5**, **6**, and **11** exhibit the first reversible and the second irreversible oxidation of the triarylphosphine moieties and the quasi-reversible reduction of the anthraquinone moieties (Fig. 2). The introduction of anthraquinone moieties leads to a slight shift of the oxidation potential of the triarylphosphine moieties in positive direction as compared with **1** ($^{ox}E_{1/2} = 0.18$ V *vs* Ag/Ag$^+$). The effect is smaller for the 1,5-derivatives and comparable for the 2,6-derivative as compared with that of quinones and naphthoquinones ($^{ox}E_{1/2} = 0.28$ (**2a**), 0.25 (2,3-bis[3,5-diisopropyl-4-{bis(2,4,6-triisopropylphenyl)phosphino}phenyl]-1,4-naphthoquinone (**12**)), 0.29 ([2,6-diisopropyl-4-(1,4-benzoquinon-2-yl)phenyl]bis(2,4,6-triisopropylphenyl)phosphine (**13**)) V) [11b]. The two or three triarylphosphine moieties are oxidized to the corresponding radical cations in one step reflecting the distance of the phosphine moieties. The anthraquinone moieties of **11** are also



Scheme 2. Synthesis of sterically crowded triarylphosphine–naphthoquinone oligomer **7**.

reduced in one step. 2,6-Derivative **6** shows positive shifts of both the oxidation potential of the triarylphosphine and the reduction potential of the anthraquinone moieties as compared with 1,5-derivatives **5** and **11**. The difference of the oxidation and the reduction potentials is smaller for **6** mainly because of the significantly lower reduction potential of the anthraquinone moiety. The more effective conjugation of 2,6-derivative **6** resulting from the less hindered triarylphosphine–anthraquinone bond and the larger coefficient of the LUMO of anthraquinone at the 2,3,6,7-positions raise the oxidation potential and lower the reduction potential.

The three triarylphosphine moieties of **7** are oxidized in two steps because of the larger electron withdrawing effect of the chloronaphthoquinonyl group, which raises the oxidation potential of the two outer triarylphosphine moieties, and the positive charge repulsion of the triarylphosphine moieties in the 2,3-positions (Fig. 2, Scheme 3). The second irreversible oxidation of the triarylphosphine moiety often observed around 1.3 V was not observed probably because of the introduction of two naphthoquinones in one triarylphosphine moiety and the formation of the triply

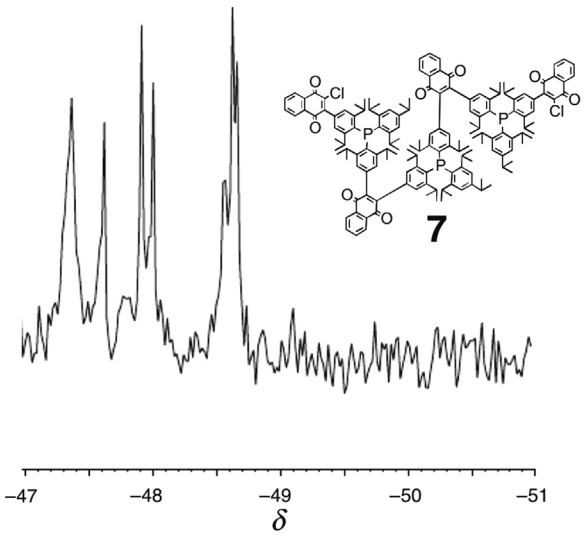


Fig. 1. ^{31}P NMR (162.06 MHz, $CDCl_3$, 293 K) spectrum of **7**.

charged species. On the other hand, the two outer chloronaphthoquinone moieties are reduced in the first step and the inner naphthoquinone moieties in the second step because of the electron withdrawing effect of the chloro group. The assignment is consistent with the previously reported reduction potentials of the related compounds (*e.g.* $^{red}E_{1/2} = -0.89$ (**2b**), -1.14 (**3**)) [11b].

The UV–visible spectra of triarylphosphines **5**, **6** and **11** in dichloromethane exhibit strong absorptions around 300–400 nm and weak tailing absorptions around 400–600 nm (Fig. 3). The former is mainly contributed by the HOMO → π* transitions of the triarylphosphine moieties and additionally by the π → π* transition of the anthraquinone moiety, and the latter is the intramolecular charge transfer form the triarylphosphine to the anthraquinone moieties responsible to the reddish brown color of these compounds. 1,5-Derivatives **5** and **11** show λ_{max} (ε) similar to **1** (327 (13,500) [7]) suggesting loss of the effective conjugation, while that of 2,6-derivative **6** at *ca.* 20 nm longer wavelength means contribution of the π-conjugation. 1,5-Derivatives **5** and **11** show only tailing without a maximum in a visible region, while the 2,6-derivative shows a rather strong peak (λ_{max} (ε) = 464 (7800)). We have previously reported that the crowded triarylphosphines bearing quinones show the intramolecular charge transfer, which depends on the difference of the redox potentials of the interacting phosphine and quinone moieties and the number of the interacting pairs (*e.g.* **2a**: λ_{max} (ε) = 557 (1700) nm, $\Delta E = 1.15$ V) [11b]. The λ_{max} of the visible absorptions of anthraquinone derivatives **5**, **6**, and **11** shorter than the previously reported triarylphosphines bearing quinone or naphthoquinone moieties reflects the larger differences of the oxidation potentials of the triarylphosphine moieties and the reduction potentials of the anthraquinone moieties ($\Delta E = 1.62$ (**5**), 1.43 (**6**), 1.63 (**11**)) and the considerably intense visible absorption of **6** suggests a more effective overlap of the molecular orbitals responsible for the charge transfer. The comparison of **5** and **11** clearly shows an additive property of the repeating units.

Triarylphosphine–naphthoquinone oligomer **7** exhibits the intramolecular charge transfer band responsible for the purple color around 400–700 nm (λ_{max} (ε) = 531 (11,800) nm) in dichloromethane (Fig. 3). The comparison with the previously reported triarylphosphines bearing quinones and naphthoquinones [11b] reveals a good correlation between the differences of the redox potentials of the interacting triarylphosphine and

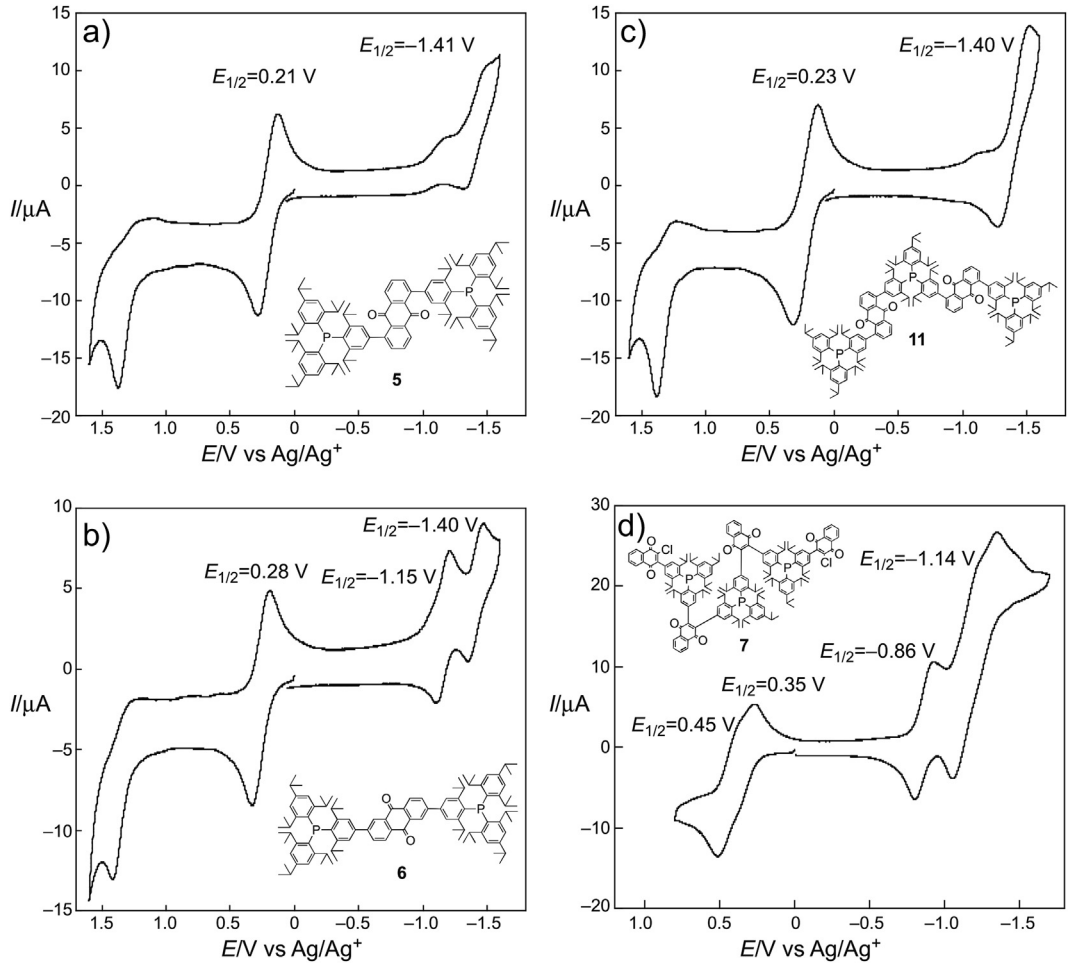
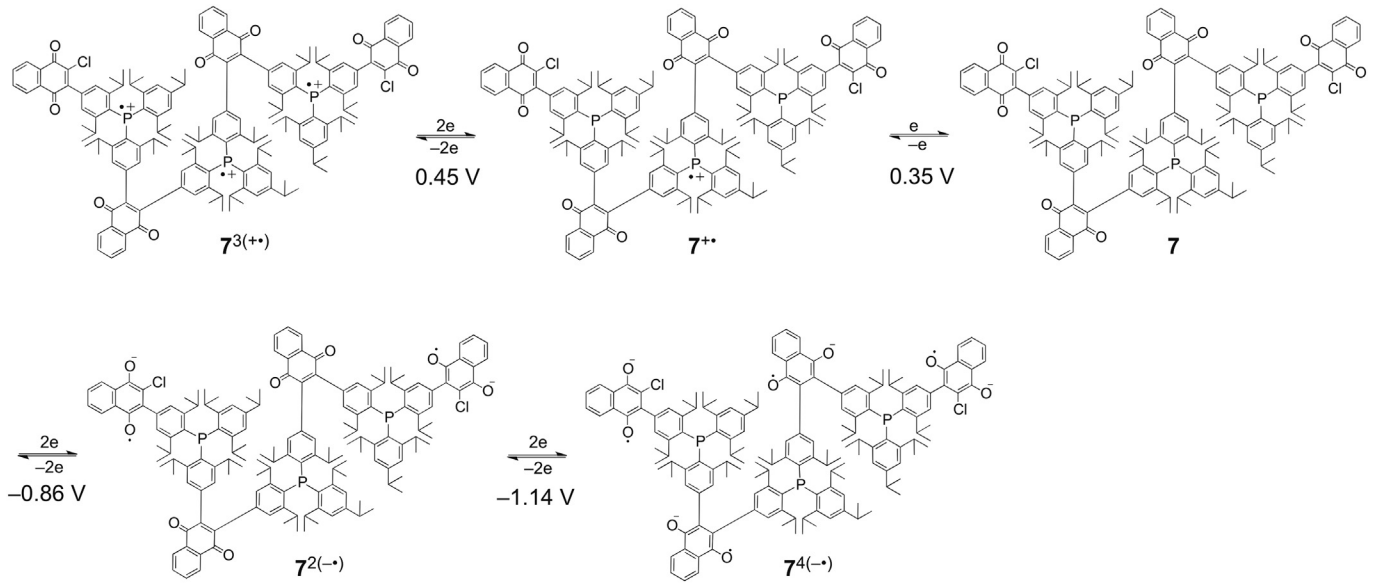


Fig. 2. Cyclic voltammograms of sterically crowded triarylphosphines bearing anthraquinone moieties a) **5**, b) **6**, c) **11**, and d) triarylphosphine–naphthoquinone oligomer **7**. Conditions: *ca.* 10^{-3} mol L^{-1} in dichloromethane with 0.1 mol L^{-1} *n*-Bu_4NClO_4 as a support electrolyte; 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/Ferricinium) = 0.21 V); scan rate: 30 mV s^{-1}; temperature: 293 K.



Scheme 3. Redox process of triarylphosphine–naphthoquinone oligomer **7**.

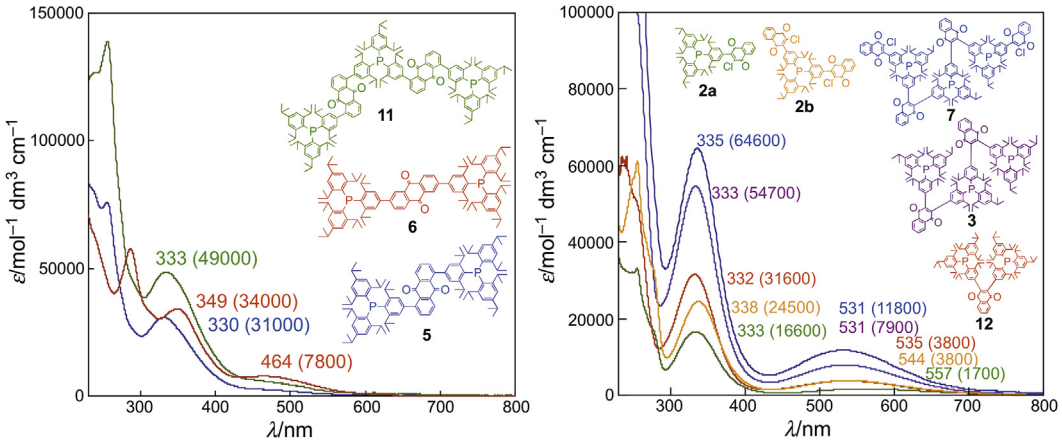
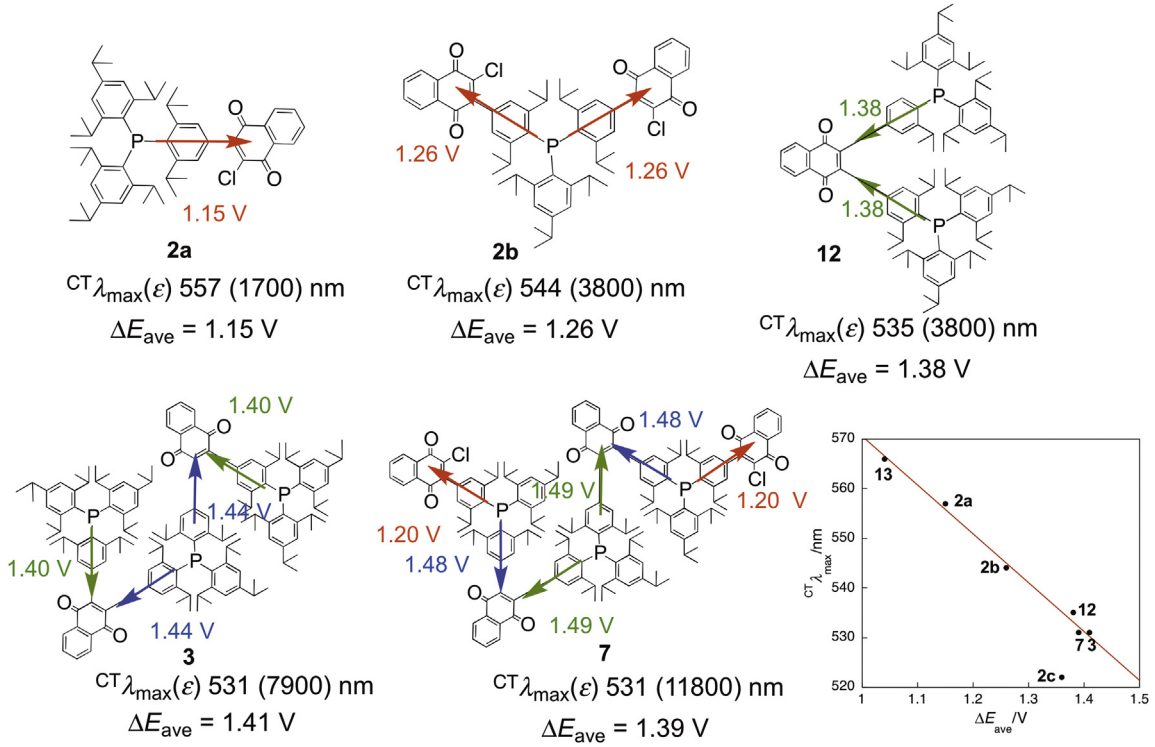


Fig. 3. UV–Vis spectra of left) sterically crowded triarylphosphines bearing anthraquinone moieties **5**, **6**, and **11**, and right) triarylphosphine–naphthoquinone oligomer **7** and the related compounds in dichloromethane.

naphthoquinone moieties (ΔE_{ave}) and the wavelengths of the intramolecular charge transfer band ($^{CT}\lambda_{max}$) (Scheme 4). A plot of ΔE_{ave} *vs* $^{CT}\lambda_{max}$ except for **2c** shows a good linear correlation. The oxidation and the reduction potentials are closely related to the energy levels of the occupied orbital on the phosphine moieties and the unoccupied orbital on the quinone moieties responsible for the particular charge transfer transition, respectively. The deviation of **2c** from the linearity suggests the stabilization of the charge transfer excited state by the electron donating 2,4,6-triisopropylphenyl group taking the linear correlation between the number of the naphthoquinone moieties and the difference of the oxidation and the reduction potentials among **2a**, **2b**, and **2c** into consideration [11b]. On the other hand, the intensity or ε of the intramolecular charge transfer depends on the number of the interacting units. Although the cyclic voltammogram and the UV–Vis spectrum of triarylphosphine–naphthoquinone oligomer **7** still reflect the detailed structure, the redox properties and the UV–Vis spectra of the longer oligomer or polymer can be estimated from the comparison of the properties of the oligomers shown in Fig. 3 and Scheme 4. The difference of the redox potentials and the wavelength of the intramolecular charge transfer band will converged to 1.45–1.50 V *vs* Ag/Ag^+ and *ca.* 530 nm with the intensity (ε) as 1900 times the number of the interacting units, respectively.



Scheme 4. The differences between the oxidation potential of the triarylphosphine moiety and the reduction potential of the naphthoquinone moiety for the interacting pairs shown by arrows, the average of the differences (ΔE_{ave}), $^{CT}\lambda_{max}(\varepsilon)$, and a plot of ΔE_{ave} *vs* $^{CT}\lambda_{max}$ with a linear fitting excluding **2c** ($R = 0.99607$). The oxidation potentials of the triarylphosphine moieties observed as the second oxidation are evaluated by taking positive charge repulsion into consideration (0.11 V per one adjacent radical cation). **13**: [2,6-diisopropyl-4-(1,4-benzoquinon-2-yl)phenyl]bis(2,4,6-triisopropylphenyl)phosphine.

3. Conclusion

Redox properties and UV–Vis spectra of the sterically crowded triarylphosphines bearing anthraquinone moieties depend on the position of the triarylphosphine moieties. The 2,6-derivative exhibits the smaller difference between the oxidation potential of the triarylphosphine moieties and the reduction potential of the anthraquinone moiety, and the considerably intense intramolecular charge transfer band at long wavelength due to the effective conjugation. On the other hand, the 1,5-derivatives show the larger difference of the redox potentials and the weaker intramolecular charge transfer at short wavelength because of the loss of conjugation.

The triarylphosphine–naphthoquinone oligomer composed of the three triarylphosphine and the four naphthoquinone moieties was synthesized and purified. Although the ^{31}P NMR spectra, the redox properties, and the UV–Vis spectra still reflect the detailed structure, the comparison with the oligomers synthesized so far enables prediction of the properties of the longer oligomers or polymers.

4. Experimental

4.1. General

^{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 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 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–visible spectra were measured on a Hitachi U-3210 or a Shimadzu UV-3600 spectrometer. 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 the column chromatography. A 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. *n*-Butyllithium was purchased from Kanto Chemical Co., Inc. and used as it was. Triarylphosphines **8** [12], **10** [11b], 1,5- and 2,6-diiodoanthraquinones [13], and 1,5-dibromoanthraquinone [13] were prepared by the literature methods. Cyclic voltammetry was performed on a BAS CV-50W controller with a glassy carbon, a 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, a counter, and a reference electrode, respectively (Ferrocene/Ferricinium = 0.21 V in dichloromethane). A substrate (*ca.* 10^{-3} 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.

4.2. Synthesis

4.2.1. 1,5-Bis[3,5-diisopropyl-4-{bis(2,4,6-triisopropylphenyl) phosphino}phenyl]anthraquinone (**5**)

To a solution of **8** (342 mg, 0.501 mmol) in tetrahydrofuran (5 mL) was added butyllithium (1.56 M in *n*-hexane, 0.39 mL, 0.608 mmol) at −78 °C. The resultant mixture was stirred for 30 min, and trimethyl borate (0.10 mL, 0.890 mmol) was added. The mixture was warmed, refluxed for 2 h, and concentrated under reduced pressure. To the residue was added 1,5-diiodoanthraquinone (117 mg, 0.254 mmol), dichlorobis(triphenylphosphine) palladium(II) (33.0 mg, 0.0470 mmol), sodium carbonate (312 mg, 2.94 mmol), toluene (5 mL), and degassed water (2 mL). The mixture was refluxed for 14 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 **5** (234 mg, 0.167 mmol, 68%).

5: Reddish brown solid; mp 164–167 °C; ^{1}H NMR (400.33 MHz, $CDCl_3$, 293 K) δ 8.06 (2H, d, J_{HH} = 7.60 Hz, arom), 7.62–7.72 (4H, m, arom), 7.09 (4H, d, J_{PH} = 3.20 Hz, arom), 6.95–7.05 (8H, brm, arom), 3.56–3.73 (12H, m, CH-*o*), 2.89 (4H, sept, J_{HH} = 7.20 Hz, CH-*p*), 1.27 (24H, d, J_{HH} = 6.80 Hz, $CH(C\underline{H}_3)_2$-*p*), 1.24 (18H, d, J_{HH} = 6.00 Hz, $CH(C\underline{H}_3)_2$-*o*), 1.23 (18H, d, J_{HH} = 6.40 Hz, $CH(C\underline{H}_3)_2$-*o*), 0.96 (12H, d, J_{HH} = 6.40 Hz, $CH(C\underline{H}_3)_2$-*o*), 0.76 (12H, d, J_{HH} = 6.40 Hz, $CH(C\underline{H}_3)_2$-*o*), 0.75 (12H, d, J_{HH} = 6.40 Hz, $CH(C\underline{H}_3)_2$-*o*); ^{13}C NMR (100.67 MHz, $CDCl_3$, 293 K) δ 184.90 (s, C=O), 153.69 (d, J_{PC} = 17.1 Hz, *o*-arom), 153.07 (d, J_{PC} = 18.3 Hz, *o*-Tip), 153.52 (d, J_{PC} = 17.8 Hz, *o*-Tip), 149.78 (s, *p*-Tip), 144.25 (s, quinone), 141.47 (s, quinone), 137.22 (s, quinone), 136.75 (s, quinone), 135.29 (d, J_{PC} = 26.0 Hz, *ipso*-arom), 132.98 (s, *p*-arom), 132.29 (d, J_{PC} = 23.1 Hz, *ipso*-Tip), 132.29 (s, quinone), 126.47 (s, quinone), 125.08 (d, J_{PC} = 3.9 Hz, *m*-arom), 122.54 (d, J_{PC} = 4.5 Hz, *m*-Tip), 122.49 (d, J_{PC} = 6.9 Hz, *m*-Tip), 34.61 (s, CH-*p*), 32.62 (d, J_{PC} = 17.8 Hz, CH-*o*), 32.57 (d, J_{PC} = 18.0 Hz, CH-*o*), 25.15 (s, $CH(\underline{C}H_3)_2$-*o*), 25.09 (s, $CH(\underline{C}H_3)_2$-*o*), 24.48 (s, $CH(\underline{C}H_3)_2$-*o*), 23.88 (s, $CH(\underline{C}H_3)_2$-*o*), 23.58 (s, $CH(\underline{C}H_3)_2$-*p*-Tip), 23.34 (s, $CH(\underline{C}H_3)_2$-*o*); ^{31}P NMR (162.06 MHz, $CDCl_3$, 293 K) δ −51.2 (s); IR (KBr) 1679 ν(C=O) cm^{-1}; UV–Vis (CH_2Cl_2, $c = 3.91 \times 10^{-6}$ mol L^{-1}) λ_{max} (ε) 330 (31,000), 255 (76,000) nm; FT-ICR–MS (ESI) Calcd For: $[C_{98}H_{130}O_2P_2]^+$: 1400.9541. Found: 1400.9552; Calcd For: $[C_{98}H_{130}O_2P_2 + Na]^+$: 1423.9438. Found: 1423.9442; Anal. Calcd for $C_{98}H_{130}O_2P_2 \cdot 0.25CHCl_3$: C, 82.41; H, 9.17%, Found: C, 82.46; H, 8.98%.

4.2.2. 2,6-Bis[3,5-diisoprpyl-4-{bis(2,4,6-triisopropylphenyl) phosphino}phenyl]anthraquinone (**6**)

To a solution of **8** (340 mg, 0.500 mmol) in tetrahydrofuran (5 mL) was added butyllithium (1.56 M in *n*-hexane, 0.39 mL, 0.608 mmol) at −78 °C. The resultant mixture was stirred for 30 min, and trimethyl borate (0.10 mL, 0.890 mmol) was added. The mixture was warmed, refluxed for 3 h, and concentrated under reduced pressure. To the residue was added 2,6-diiodoanthraquinone (110 mg, 0.239 mmol), dichlorobis(-triphenylphosphine)palladium(II) (34.0 mg, 0.0484 mmol), sodium carbonate (320 mg, 3.02 mmol), toluene (5 mL), and degassed water (2 mL). The mixture was refluxed for 14 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 **6** (260 mg, 0.186 mmol, 77%).

6: Reddish brown solid; mp 244–247 °C; ^{1}H NMR (400.33 MHz, $CDCl_3$, 293 K) δ 8.57 (2H, d, J_{HH} = 1.20 Hz, arom), 8.40 (2H, d, J_{HH} = 8.40 Hz, arom), 8.05 (2H, dd, J_{HH} = 8.00 Hz, J_{HH} = 1.60 Hz, arom), 7.43 (4H, d, J_{PH} = 2.80 Hz, arom), 6.93 (8H, d, J_{PH} = 3.20 Hz, arom), 3.45–3.60 (12H, m, CH-*o*), 2.85 (4H, sept, J_{HH} = 6.80 Hz, CH-*p*), 1.24 (12H, d, J_{HH} = 7.60 Hz, $CH(C\underline{H}_3)_2$-*o*), 1.22 (24H, d, J_{HH} = 7.20 Hz, $CH(C\underline{H}_3)_2$-*p*), 1.19 (12H, d, J_{HH} = 6.00 Hz, $CH(C\underline{H}_3)_2$-*o*), 1.17 (12H, d, J_{HH} = 5.20 Hz, $CH(C\underline{H}_3)_2$-*o*), 0.80 (12H, d, J_{HH} = 6.80 Hz, $CH(C\underline{H}_3)_2$-*o*), 0.76 (12H, d, J_{HH} = 6.40 Hz, $CH(C\underline{H}_3)_2$-*o*), 0.68 (12H, d, J_{HH} = 6.40 Hz, $CH(C\underline{H}_3)_2$-*o*); ^{13}C NMR (100.67 MHz, $CDCl_3$, 293 K) δ 183.23 (s, C=O), 154.02 (d, J_{PC} = 18.2 Hz, *o*-arom), 153.07 (d, J_{PC} = 18.3 Hz, *o*-Tip), 153.04 (d, J_{PC} = 18.2 Hz, *o*-Tip), 149.56 (s, *p*-Tip), 147.41 (s, quinone), 138.63 (s, quinone), 137.54 (d, J_{PC} = 28.6 Hz, *ipso*-arom), 134.00 (s, *p*-arom), 132.17 (s, quinone), 132.02 (s, quinone), 131.32 (d, J_{PC} = 22.1 Hz, *ipso*-Tip), 127.98 (s, quinone), 125.23 (s, quinone), 122.71 (d, J_{PC} = 3.2 Hz, *m*-arom), 122.13 (d,

J_{PC} = 4.7 Hz, *m*-Tip), 122.08 (d, J_{PC} = 4.6 Hz, *m*-Tip), 34.08 (s, CH-*p*), 32.17 (d, J_{PC} = 17.9 Hz, CH-*o*), 32.11 (d, J_{PC} = 17.8 Hz, CH-*o*), 24.64 (s, CH($\underline{C}H_3$)$_2$-*o*), 24.55 (s, CH($\underline{C}H_3$)$_2$-*o*), 23.92 (s, CH($\underline{C}H_3$)$_2$-*o*), 23.26 (s, CH($\underline{C}H_3$)$_2$-*o*), 23.01 (s, CH($\underline{C}H_3$)$_2$-*p*-Tip), 22.87 (s, CH($\underline{C}H_3$)$_2$-*o*); ^{31}P NMR (162.06 MHz, $CDCl_3$, 293 K) δ −50.7 (s); IR (KBr) 1675 ν(C═O) cm^{-1}; UV–Vis (CH_2Cl_2, $c = 5.62 \times 10^{-6}$ mol L^{-1}) λ_{max} (ε) 464 (7800), 349 (34,000), 286 (58,000) nm; FT-ICR–MS (ESI) Calcd For: $[C_{98}H_{130}O_2P_2 + H]^+$: 1401.9619. Found: 1401.9629; Anal. Calcd for $C_{98}H_{130}O_2P_2 \cdot 0.35CHCl_3$: C, 81.81; H, 9.10%, Found: C, 81.79; H, 8.95%.

4.2.3. [2,6-Diisopropyl-4-(5-bromoanthraquinon-1-yl)phenyl] bis(2,4,6-triisopropylphenyl)phosphine (**9**)

To a solution of **8** (1.01 g, 1.49 mmol) in tetrahydrofuran (15 mL) was added butyllithium (1.58 M in *n*-hexane, 1.13 mL, 1.79 mmol) at −78 °C. The resultant mixture was stirred for 30 min, and trimethyl borate (0.25 mL, 2.23 mmol) was added. The mixture was warmed, refluxed for 3 h, and concentrated under reduced pressure. To the residue was added 1,5-dibromoanthraquinone (1.42 g, 3.88 mmol), dichlorobis(triphenylphosphine)palladium(II) (93.0 mg, 0.133 mmol), sodium carbonate (606 mg, 5.72 mmol), toluene (15 mL), and degassed water (4 mL). The mixture was refluxed for 14 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 crude **9** (460 mg, 0.520 mmol, 35%). The product was contaminated with **5** and the debrominated anthraquinon-1-yl derivative, but was used in the next step without further purification.

9: Reddish brown solid; mp 182–194 °C; ^{1}H NMR (400.33 MHz, $CDCl_3$, 293 K) δ 8.31 (1H, dd, J_{HH} = 8.00 Hz, J_{HH} = 1.20 Hz, arom), 8.04 (1H, dd, J_{HH} = 7.60 Hz, J_{HH} = 1.20 Hz, arom), 7.97 (1H, dd, J_{HH} = 8.00 Hz, J_{HH} = 1.20 Hz, arom), 7.75 (1H, t, J_{HH} = 8.00 Hz, arom), 7.64 (1H, dd, J_{HH} = 7.60 Hz, J_{HH} = 1.20 Hz, arom), 7.51 (1H, t, J_{HH} = 8.00 Hz, arom), 7.00 (2H, d, J_{PH} = 3.20 Hz, arom), 6.96–6.97 (2H, bm, arom), 6.90–6.92 (2H, bm, arom), 3.52–3.68 (6H, m, CH-*o*), 2.86 (2H, sept, J_{HH} = 6.80 Hz, CH-*p*), 1.24 (12H, d, J_{HH} = 7.20 Hz, CH($C\underline{H}_3$)$_2$-*p*), 1.24 (18H, d, J_{HH} = 7.20 Hz, CH($C\underline{H}_3$)$_2$-*p, o*), 0.91 (6H, d, J_{HH} = 6.80 Hz, CH($C\underline{H}_3$)$_2$-*o*), 0.71 (6H, d, J_{HH} = 6.40 Hz, CH($C\underline{H}_3$)$_2$-*o*); ^{31}P NMR (162.06 MHz, $CDCl_3$, 293 K) δ −51.1 (s); IR (KBr) 1680 (C═O) cm^{-1}; FT-ICR–MS (ESI) Calcd For: $[C_{56}H_{68}BrO_2P]^+$: 882.4135. Found: 882.4116; Calcd For: $[C_{56}H_{68}BrO_2P + Na]^+$: 905.4033. Found: 905.4039.

4.2.4. Bis[2,6-diisopropyl-4-[5-[3,5-diisopropyl-4-bis{(2,4,6-triisopropylphenyl)phosphino}phenyl]-anthraquinon-1-yl] phenyl](2,4,6-triisopropylphenyl)phosphine (**11**)

To a solution of **10** (98.0 mg, 0.137 mmol) in tetrahydrofuran (5 mL) was added butyllithium (1.58 M in *n*-hexane, 0.21 mL, 0.332 mmol) at −78 °C. The resultant mixture was stirred for 30 min, and trimethyl borate (0.06 mL, 0.537 mmol) was added. The mixture was warmed, refluxed for 3 h, and concentrated under reduced pressure. To the residue was added dichlorobis(triphenylphosphine)palladium(II) (21.0 mg, 0.0299 mmol), sodium carbonate (155 mg, 1.46 mmol), and **9** (250 mg, 0.283 mmol) in toluene (5 mL), and degassed water (2 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) and GPC to give **11** (50 mg, 0.0231 mmol, 18%).

11: Reddish brown solid; mp 228–234 °C; ^{1}H NMR (400.33 MHz, $CDCl_3$, 293 K) δ 8.03 (4H, dd, J_{HH} = 7.60 Hz, J_{HH} = 1.20 Hz, arom), 7.50–7.80 (8H, m, arom), 7.07–7.13 (4H, m, arom), 7.05 (4H, d, J_{PH} = 3.20 Hz, arom), 7.00 (2H, d, J_{PH} = 3.60 Hz, arom), 6.92–9.98 (8H, m, arom), 3.50–3.77 (18H, m, CH-*o*), 2.80–2.94 (5H, m, CH-*p*), 1.26 (9H, d, J_{HH} = 7.20 Hz, CH($C\underline{H}_3$)$_2$-*o*), 1.24 (12H, d, J_{HH} = 6.40 Hz, CH($C\underline{H}_3$)$_2$-*o*), 1.23 (30H, d, J_{HH} = 6.80 Hz, CH($C\underline{H}_3$)$_2$-*p*), 1.22 (12H, d, J_{HH} = 6.80 Hz, CH($C\underline{H}_3$)$_2$-*o*), 0.96 (6H, d, J_{HH} = 6.00 Hz, CH($C\underline{H}_3$)$_2$-*o*), 0.95 (6H, d, J_{HH} = 6.40 Hz, CH($C\underline{H}_3$)$_2$-*o*), 0.91 (12H, d, J_{HH} = 6.80 Hz, CH($C\underline{H}_3$)$_2$-*o*), 0.76 (3H, d, J_{HH} = 6.40 Hz, CH($C\underline{H}_3$)$_2$-*o*), 0.72 (12H, d, J_{HH} = 6.40 Hz, CH($C\underline{H}_3$)$_2$-*o*), 0.71 (12H, d, J_{HH} = 6.40 Hz, CH($C\underline{H}_3$)$_2$-*o*); ^{13}C NMR (100.67 MHz, $CDCl_3$, 293 K) δ 184.90 (s, C═O), 184.87 (s, C═O), 153.72 (d, J_{PC} = 18.2 Hz, *o*-arom), 153.62 (d, J_{PC} = 16.6 Hz, *o*-Tip), 153.45 (d, J_{PC} = 18.1 Hz, *o*-Tip), 153.26 (d, J_{PC} = 19.2 Hz, *o*-Tip), 153.16 (d, J_{PC} = 18.3 Hz, *o*-Tip), 149.95 (s, *p*-Tip), 149.70 (s, *p*-Tip), 144.20 (s, quinone), 144.13 (s, quinone), 141.62 (s, quinone), 141.36 (s, quinone), 137.17 (s, quinone), 137.15 (s, quinone), 136.71 (s, quinone), 135.24 (d, J_{PC} = 26.2 Hz, *ipso*-arom), 134.78 (d, J_{PC} = 25.4 Hz, *ipso*-arom), 132.93 (s, quinone), 132.32 (s, *p*-arom), 132.25 (s, quinone), 132.24 (s, quinone), 132.09 (s, *p*-arom), 131.77 (d, J_{PC} = 22.7 Hz, *ipso*-Tip), 126.45 (s, quinone), 126.40 (s, quinone), 125.11 (br, *m*-arom), 125.00 (d, J_{PC} = 3.9 Hz, *m*-arom), 122.47 (d, J_{PC} = 4.5 Hz, *m*-Tip), 122.42 (d, J_{PC} = 6.9 Hz, *m*-Tip), 34.53 (s, CH-*p*), 32.30–32.80 (m, CH-*o*), 25.16 (s, CH($\underline{C}H_3$)$_2$-*o*), 25.07 (s, CH($\underline{C}H_3$)$_2$-*o*), 25.00 (s, CH($\underline{C}H_3$)$_2$-*o*), 24.41 (s, CH($\underline{C}H_3$)$_2$-*o*), 23.85 (s, CH($\underline{C}H_3$)$_2$-*o*), 23.80 (s, CH($\underline{C}H_3$)$_2$-*o*), 23.60 (s, CH($\underline{C}H_3$)$_2$-*p*-Tip), 23.50 (s, CH($\underline{C}H_3$)$_2$-*p*-Tip), 23.30 (s, CH($\underline{C}H_3$)$_2$-*o*), 23.26 (s, CH($\underline{C}H_3$)$_2$-*o*); ^{31}P NMR (162 MHz, $CDCl_3$, 293 K) δ −50.5 (s), −51.1(s); IR (KBr) 1681 ν(C═O) cm^{-1}; UV–Vis (CH_2Cl_2, $c = 1.76 \times 10^{-5}$ mol L^{-1}) λ_{max} (ε) 333 (49,000), 256 (140,000) nm; FT-ICR–MS (ESI) Calcd for $[C_{151}H_{191}O_4P]^+$: 2161.3950. Found: 2161.3941, Calcd for $[C_{151}H_{191}O_4P_3 + H]^+$: 2162.4028. Found: 2162.4009, Calcd for $[C_{151}H_{191}O_4P_3 + Na]^+$: 2184.3847. Found: 2184.3862; Anal. Calcd for $C_{151}H_{191}O_4P_3 \cdot 0.5CHCl_3$: C, 81.86; H, 8.68%, Found: C, 81.73; H, 8.66%.

4.2.5. Triarylphosphine–naphthoquinone oligomer **7**

To a solution of **10** (356 mg, 0.500 mmol) in tetrahydrofuran (10 mL) was added butyllithium (1.59 M in *n*-hexane, 0.70 mL, 1.11 mmol) at −78 °C. The resultant mixture was stirred for 30 min, and trimethyl borate (0.17 mL, 1.50 mmol) was added. The mixture was warmed, refluxed for 3 h, cooled to 20 °C, and concentrated under reduced pressure. To the residue was added **2b** (1.13 g, 1.20 mmol), dichlorobis(triphenylphosphine)palladium(II) (40.0 mg, 0.06 mmol), sodium carbonate (342 g, 3.28 mmol), toluene (20 mL), and degassed water (10 mL). The mixture was heated at 80 °C for 12 h, cooled to 20 °C, extracted with ether, dried over anhydrous magnesium sulfate, concentrated under reduced pressure, and purified by column chromatography (Al_2O_3/*n*-hexane, *n*-hexane/ethyl acetate = 20/1) and GPC ($CHCl_3$) to give **7** (57.0 mg, 0.016 mmol, 5%).

7: purple solid; mp 284–285 °C; ^{1}H NMR (400.33 MHz, $CDCl_3$) δ 8.25–8.06 (8H, m, quinone), 7.81–7.68 (8H, m, quinone), 7.10–6.80 (18H, m, *m*-arom), 3.74–3.24 (18H, m, C$\underline{H}$(CH$_3$)$_2$-*o*), 2.90–2.72 (3H, m, C$\underline{H}$(CH$_3$)$_2$-*p*), 1.33–0.90 (72H, m, CH(C$\underline{H}_3$)$_2$), 0.86–0.40 (54H, m, CH(C$\underline{H}_3$)$_2$); ^{13}C NMR (100.67 MHz, $CDCl_3$, 293 K) δ 184.72 (C═O), 184.68 (C═O), 182.04 (C═O), 182.03 (C═O), 178.43 (C═O), 153.8–152.0 (m, *o*-Tip), 149.86 (s, *p*-Tip), 146.28 (naphthoquinone), 144.82 (s, *p*-arom), 144.64 (s, *p*-arom), 142.49 (s, *p*-arom), 137.69 (dm, *J* = 26.0 Hz, *ipso*), 134.27 (brs), 134.00–133.75 (m), 133.35 (brs), 132.30 (brs), 132.05 (brs), 131.81 (s), 131.38 (s), 131.10 (d, *J* = 21.3 Hz, *ipso*), 128.02 (brs), 127.52 (brs), 127.75 (brs), 127.19 (s) 127.07 (s), 126.95 (s), 126.91–126.64 (m), 126.42 (brs, *m*-arom), 125.7–125.9 (m, *m*-arom), 122.5–122.0 (m, *m*-Tip)), 34.05 (s, CH-*p*), 32.7–31.3 (m, CH-*o*), 25.1–22.3 (m, CH($\underline{C}H_3$)$_2$); ^{31}P NMR (162.06 MHz, $CDCl_3$) δ −47.31 (s), −47.60 (s), −47.91 (s), −48.00 (s), −48.52 (s), −48.58 (s), −48.62 (s); UV–Vis (CH_2Cl_2) λ_{max} (ε) nm 531 (11,800), 335 (64,600); FT-ICR-MS (ESI) Calcd for $[C_{157}H_{181}O_8P_3Cl_2 + Na]^+$: 2380.2239. Found: 2380.2262; Anal.

Calcd for $C_{157}H_{181}O_8P_3Cl_2$: C, 79.90; H, 7.73%. Found: C, 79.64; H, 7.51%.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.10.055.

References

[1] S. Sasaki, M. Yoshifuji, Curr. Org. Chem. 11 (2007) 17.
[2] E.J. Halpern, K. Mislow, J. Am. Chem. Soc. 89 (1967) 5224.
[3] B.I. Stepanov, E.N. Karpova, A.I. Bokanov, Zh. Obshch. Khim. (J. Gen. Chem. USSR) 39 (1969) 1544.
[4] J.F. Blount, C.A. Maryanoff, K. Mislow, Tetrahedron Lett. 48 (1975) 913.
[5] (a) M. Culcasi, Y. Berchadsky, G. Gronchi, P. Tordo, J. Org. Chem. 56 (1991) 3537;
(b) C. Palau, Y. Berchadsky, F. Chalier, J.-P. Finet, G. Gronchi, P. Tordo, J. Phys. Chem. 99 (1995) 158;
(c) A.V. Il'yasov, Yu M. Kargin, A.A. Vafina, Russ. J. Gen. Chem. 63 (1994) 1833.
[6] (a) S. Sasaki, F. Murakami, M. Yoshifuji, Tetrahedron Lett. 38 (1997) 7095;
(b) S. Sasaki, F. Murakami, M. Yoshifuji, Organometallics 25 (2006) 140.
[7] S. Sasaki, K. Sutoh, F. Murakami, M. Yoshifuji, J. Am. Chem. Soc. 124 (2002) 14830.
[8] (a) R.T. Boeré, Y. Zhang, J. Organomet. Chem. 690 (2005) 2651;
(b) R.T. Boeré, A.M. Bond, S. Cronin, N.W. Duffy, P. Hazendonk, J.D. Masuda, K. Pollard, T.L. Roemmele, P. Tran, Y. Zhang, New J. Chem. 32 (2008) 214.
[9] (a) X. Pan, X. Chen, T. Li, Y. Li, X. Wang, J. Am. Chem. Soc. 135 (2013) 3414;
(b) G. Menard, J.A. Hatnean, H.J. Cowley, A.J. Lough, J.M. Rawson, D.W. Stephan, J. Am. Chem. Soc. 135 (2013) 6446.
[10] (a) K. Sutoh, S. Sasaki, M. Yoshifuji, Inorg. Chem. 45 (2006) 992;
(b) S. Sasaki, K. Sasaki, M. Yoshifuji, Phosphorus Sulfur Silicon Relat. Elem. 183 (2008) 410;
(c) S. Sasaki, M. Murakami, F. Murakami, M. Yoshifuji, Heteroat. Chem. 22 (2011) 506.
[11] (a) S. Sasaki, F. Murakami, M. Murakami, M. Watanabe, K. Kato, K. Sutoh, M. Yoshifuji, J. Organomet. Chem. 690 (2005) 2664;
(b) S. Sasaki, K. Ogawa, M. Watanabe, M. Yoshifuji, Organometallics 29 (2010) 757;
(c) S. Sasaki, K. Sasaki, M. Yoshifuji, J. Organomet. Chem. 696 (2011) 3307.
[12] S. Sasaki, K. Kato, M. Yoshifuji, Bull. Chem. Soc. Jpn. 80 (2007) 1791.
[13] J.K. Kendall, H. Shechter, J. Org. Chem. 66 (2001) 6643.