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QUINONE DIMERS CONNECTED BY 1,4-PHENYLENE AND 2,5-THIENYLENE MOIETIES AS A π-LINKER

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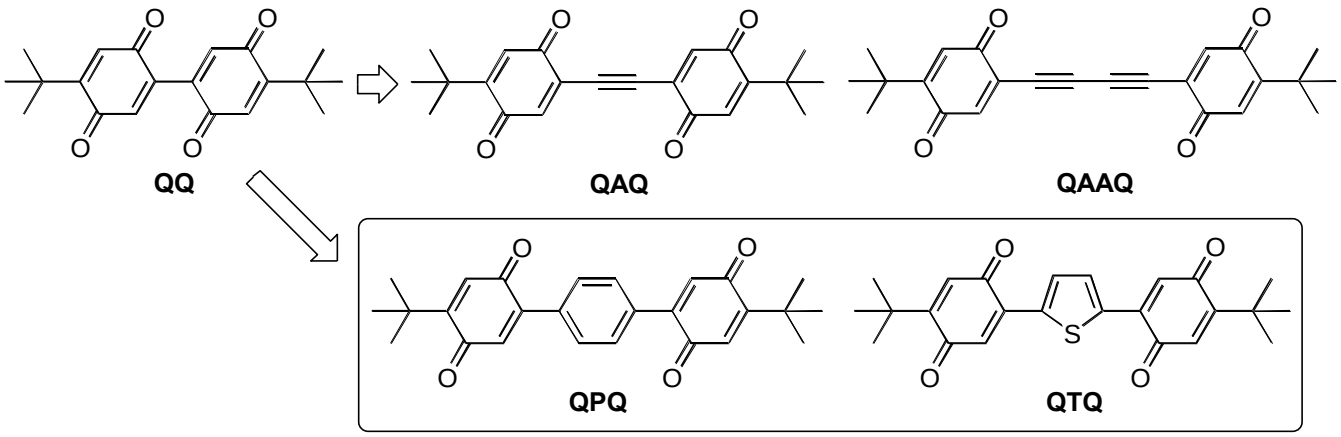
Abstract – The synthesis and characterization of quinone dimers connected by 1,4-phenylene (**QPQ**) and 2,5-thienylene (**QTQ**) linkers are described. **QPQ** and **QTQ** were synthesized by means of Suzuki coupling and subsequent oxidation. Significant bathochromic shifts were observed in the electronic absorption spectra of **QPQ** and **QTQ** as compared to that of the quinine dimers without a linker. In addition, cyclic voltammetry and DFT calculations demonstrated that **QTQ** was a stronger electron acceptor than **QPQ** due to its planar structure, even though **QTQ** contains an electron-rich thiophene ring.

INTRODUCTION

π-linkers are important tools to control the structure and properties of π-conjugated compounds.[1] In general, π-linkers are required to be stable and structurally rigid, in order for their p orbitals to overlap efficiently with the p orbitals of the π-moieties situated at both ends. In this regard, acetylene, diacetylene, arylene, and oligo(arylene) groups have been frequently employed as π-linkers.[2-9]



Dedicated to Professor Emeritus Akira Suzuki on the occasion of his 80th birthday

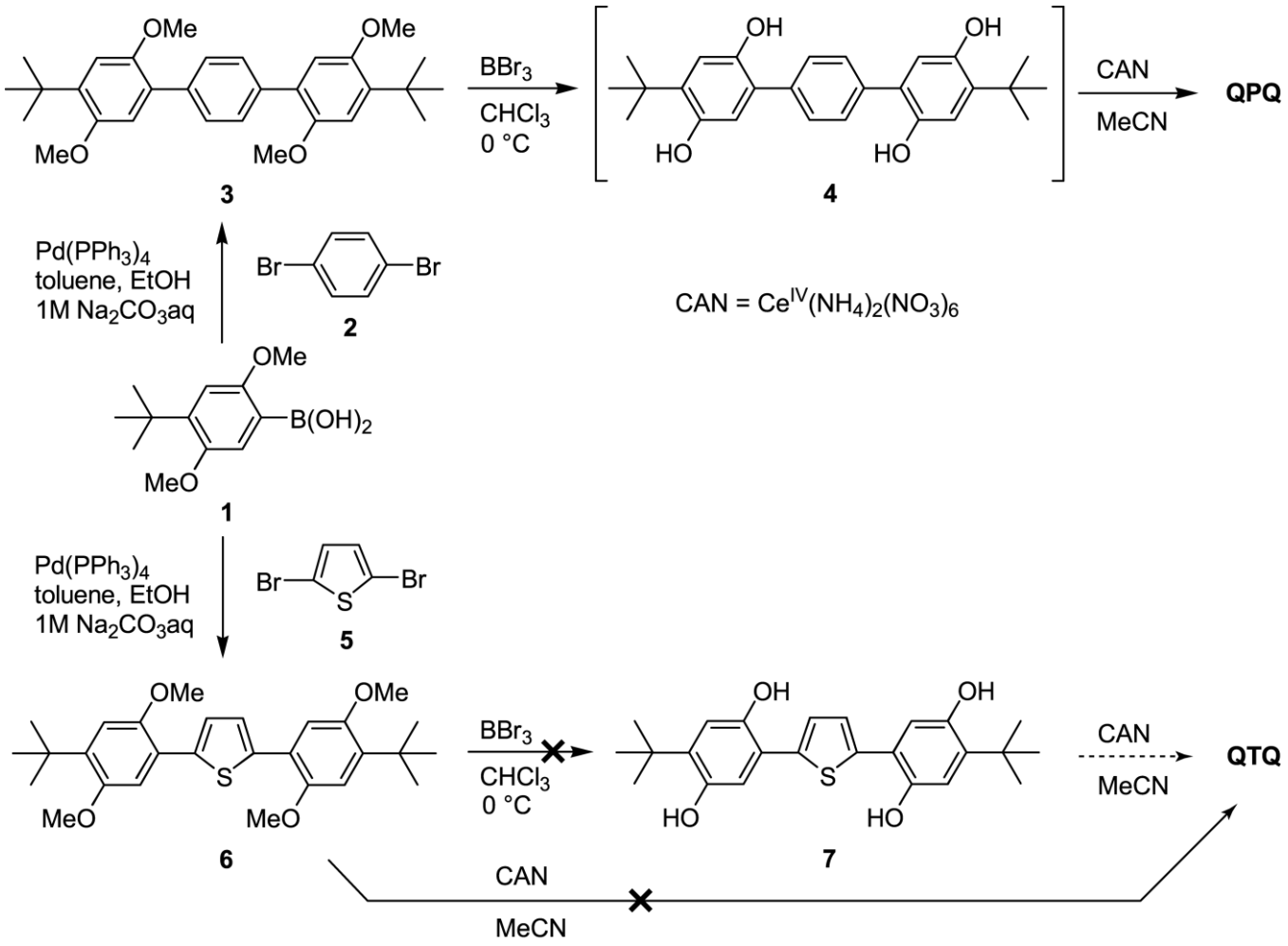


Figure 1. Synthesis of **QPQ** and attempt of synthesis of **QTQ**

Recently, we reported the synthesis and properties of quinone dimers bearing acetylene (**QAQ**) and diacetylene (**QAAQ**) moieties as a π-linker.[10] As compared to the quinine dimers without a linker (**QQ**),[11] **QAQ** and **QAAQ** showed significant bathochromic shifts and increases in their first reduction potentials. We proposed that this was due to the essentially planar π-conjugated systems of **QAQ** and **QAAQ** based on their X-ray diffraction analysis and molecular-orbital calculations. In contrast, the X-ray structure of **QQ** showed that the quinone moieties were tilted by 38°.

In the present study, we report the synthesis and characterization of quinone dimers linked by arylene moieties, **QPQ** and **QTQ**. As the π-linker, we selected 1,4-phenylene and 2,5-thienylene, since these functional groups are widely employed in oligomer and material chemistry. The 1,4-phenylene moiety is the simplest in structure and can be synthesized in a facile manner. However, the p orbital overlap with the adjacent π-moieties is generally inefficient because of a large dihedral angle between 1,4-phenylene and the adjacent π-moiety due to the steric repulsion between the *ortho*-hydrogen atoms. In contrast, π-systems constructed with a 2,5-thienylene linker usually adopt a planar conformation in order to give

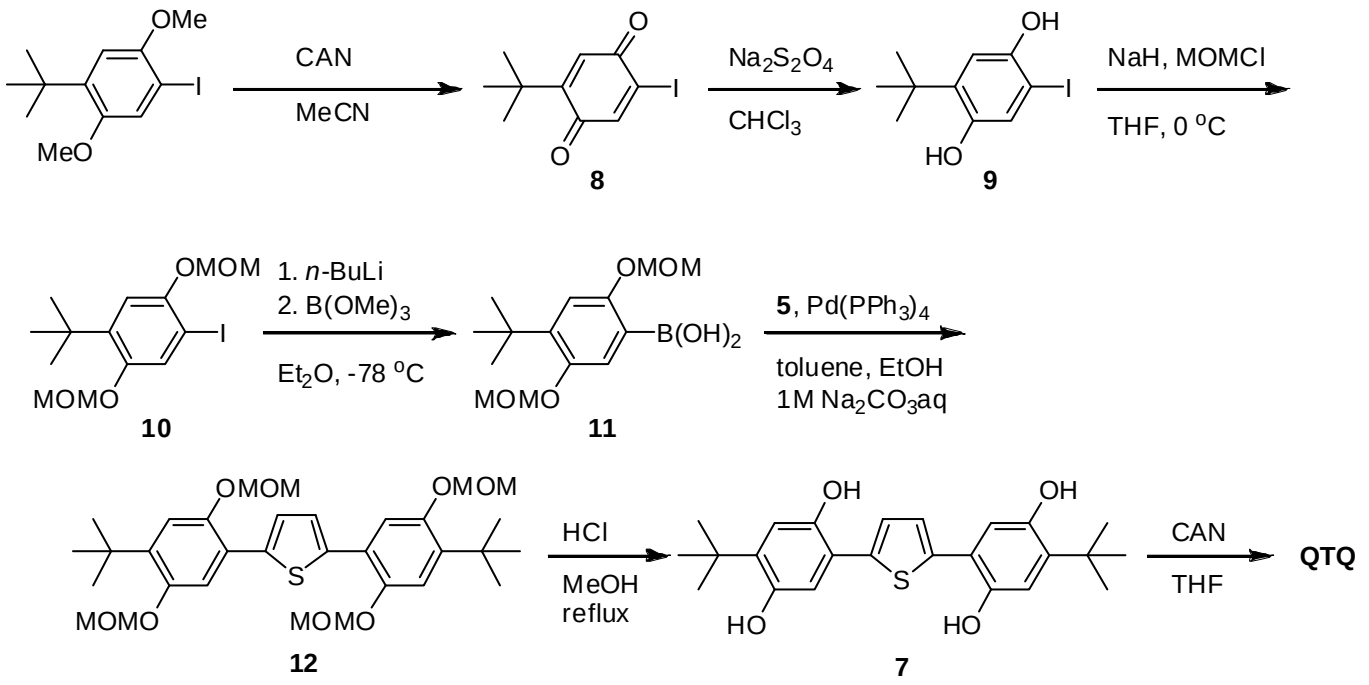


Figure 2. Synthesis of **QTQ**

fully conjugated π-system. Nevertheless, the 2,5-thienylene linker appeared to be disadvantageous in the present study because electron-rich character of thiophene could potentially impair the electron acceptor character of the quinone moiety. The target compounds were synthesized by means of Suzuki coupling of the quinone precursor and π-linker,[12] which has been quite widely employed in the synthesis of biaryls.[13] *tert*-Butyl groups were incorporated to increase the solubility and stability of the compounds. Properties of the π-conjugated system of **QPQ** and **QTQ** were investigated by electronic absorption spectroscopy, cyclic voltammetry, and DFT calculations. The experimental and theoretical results were then compared with those of **QQ**.

RESULTS AND DISCUSSION

The synthesis of **QPQ** is shown in Figure 1. 4-*tert*-Butyl-2,5-dimethoxyphenylboronic acid (**1**) and 1,4-dibromobenzene (**2**) were subjected to Suzuki coupling to give compound **3**. Deprotection by BBr_3, followed by oxidation using cerium(IV) ammonium nitrate (CAN) afforded **QPQ**. Synthesis of **QTQ** was initially attempted in a similar manner, but with unsatisfactory results. Suzuki coupling of **1** and 2,5-dibromothiophene (**5**) gave thiophene **6**. However, the reaction of **6** with BBr_3 did not afford hydroquinone **7**. This was likely due to the formation of charge-transfer complex of **6** and BBr_3. Demethylation of **6** using either EtSNa or Me_3SiI was also unsuccessful. The direct oxidation of thiophene **6** with CAN also gave a complex mixture, probably because the thiophene moiety was oxidized by CAN.

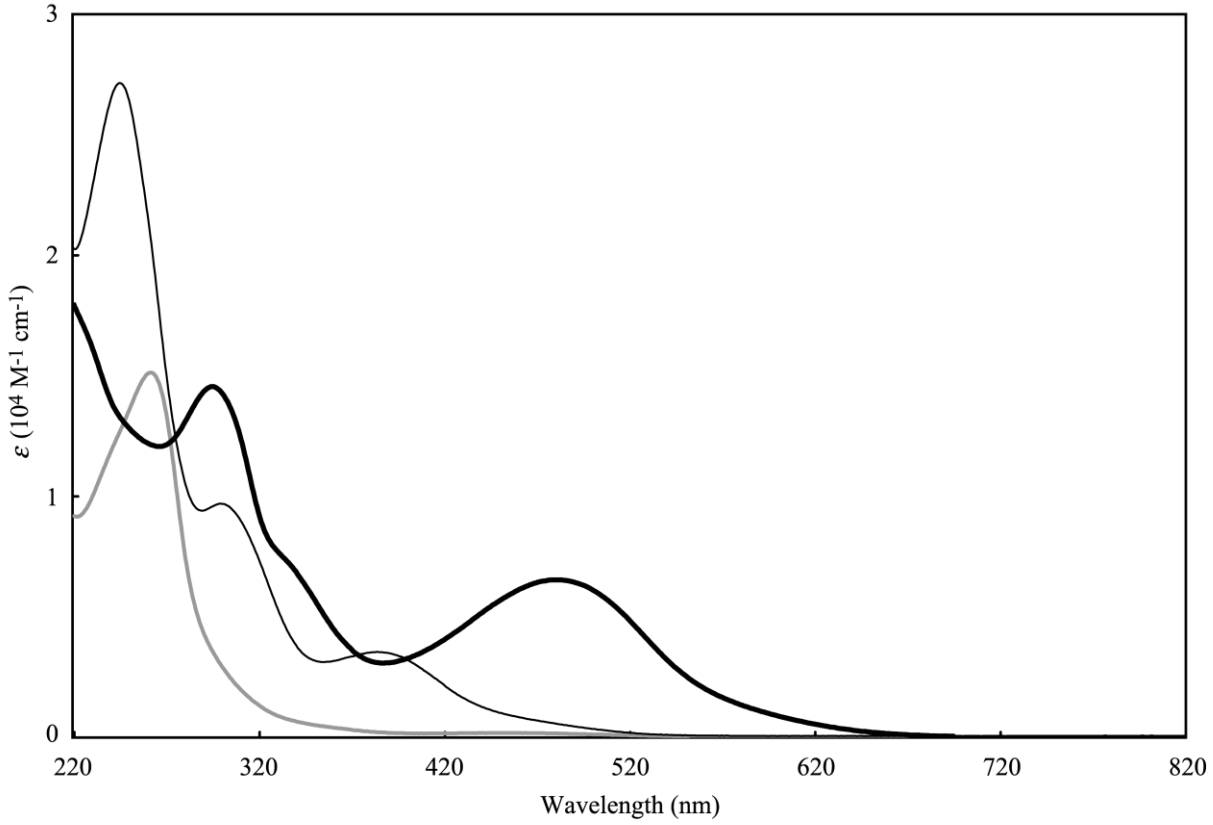


Figure 3. Electronic absoption spectra of **QQ** (gray), **QPQ** (thin), and **QTQ** (thick) in 1,4-dioxane

Hydroquinone **7** was successfully prepared by an alternative route. As shown in Figure 2, 2-*tert*-butyl-5-iodo-1,4-dimethoxybenzene was oxidized with CAN to give quinone **8**, which was then reduced by $Na_2S_2O_4$ to yield hydroquinone **9**. The hydroxy groups of **9** were protected with methoxymethyl (MOM) groups to provide iodide **10**, which was converted to arylboronic acid **11** by conventional methods.[14] Boronic acid **11** and **5** were subjected to Suzuki coupling to give **12**, which was then deprotected in the presence of acid, and oxidized by CAN to yield **QTQ**. Both **QPQ** and **QTQ** were stable in air, and highly soluble in halogenated solvents, such as chloroform and dichloromethane, and moderately soluble in ethereal solvents.

Electronic absorption spectra of **QPQ**, **QTQ**, and **QQ** are shown in Figure 3. The bathochromic shift of the longest wavelength absorption band (λ_{max}) was observed in **QPQ** compared to **QQ**. This is most likely to be attributed to the HOMO of **QPQ,** which is supposed to be located mainly on the phenylene linker, being higher in energy. The bathochromic shift of λ_{max} of **QTQ** could be explained in a similar manner. The larger bathochromic shift in **QTQ** should be due to either the electron-rich character of 2,5-thienylene linker or the highly planar structure of the π-conjugated system, or both.

In order to elucidate the origin of the bathochromic shifts in **QPQ** and **QTQ**, DFT calculations (B3LYP/6-31G** methods) were performed for model compounds, **QQ'**, **QPQ'**, and **QTQ'**, which have

Table 1. Summary of cyclic voltammety of **QQ**, **QPQ**, and **QTQ** and minimum energy conformers of **QQ'**, **QPQ'**, and **QTQ'** in B3LYP/6-31G** calculations

	CV[a]			DFT calculation					
	$E_1^{1/2}$ (V)	$E_2^{1/2}$ (V)	E_3^{pc} (V)		ΔE^c (kcal mol^{-1})	symmetry	$\phi_{(1,2)}$ (°)	HOMO (eV)	LUMO (eV)
QQ	–0.73[b]	–1.07[b]	–1.54[b]	*s*-**QQ'**	0.75	C_2	37.4	–7.39	–3.79
				a-**QQ'**	0.00	C_2	122.0	–7.29	–3.87
QPQ	–0.77	–0.85	–1.61	*s*-**QPQ'**	–2.94	C_s	37.5	–6.77	–3.66
				a-**QPQ'**	0.00	*Ci*	52.6	–6.89	–3.59
QTQ	–0.68	–0.85	–1.58	*sa*-**QTQ'**	–0.51	C_1	15.7, 178.2	–6.34	–3.85
				aa-**QTQ'**	0.00	C_s	9.8	–6.43	–3.86

[a]Electrode; Pt (working), Pt (counter) and Ag/Ag$^+$ (reference). Supporting electrolyte; *n*-Bu_4NClO_4. Scan rate; 0.1 V s^{-1}. In CH_2Cl_2. [b]Reference 10. [c]Energy differences relative to the energy of the *a* and *aa*-conformers.

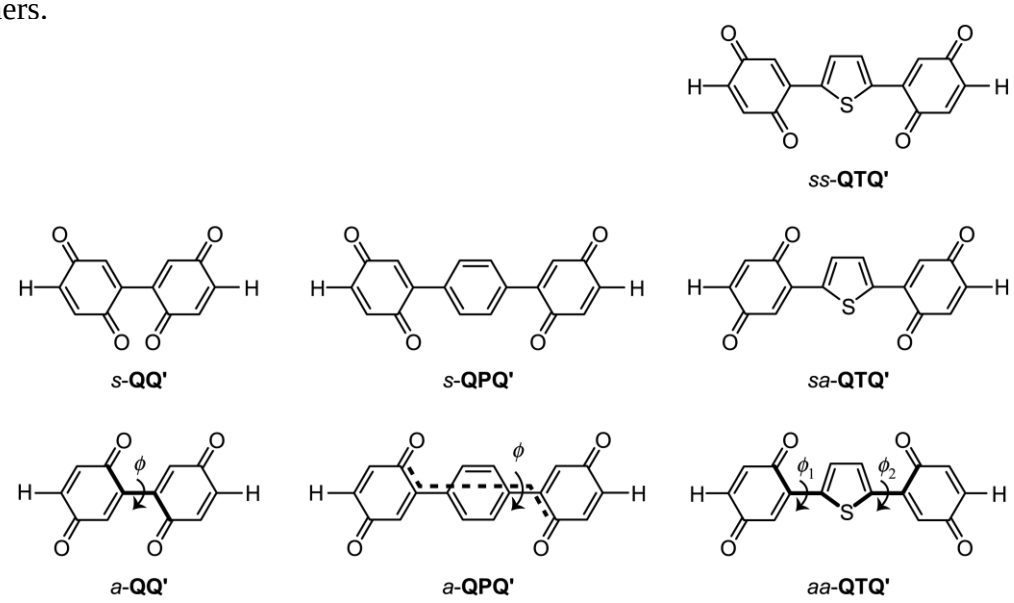


Figure 4. Conformers of **QQ'**, **QPQ'**, and **QTQ'**

no *tert*-butyl substituents for simplicity. For each compound, geometrical optimizations of a series of conformers shown in Figure 4 were conducted. In the global minimum energy structures for **QQ'** and **QPQ'** are the *a*-conformer and *s*-conformer, respectively. When the energy levels of *s*-**QPQ'** are compared to those of *a*-**QQ'**, the rise of HOMO (0.52 eV) is more significant than that of LUMO (0.21 eV). This observation, compounded by the fact that HOMO is mainly located on the phenylene moiety (Figure 5), supports our hypothesis that the HOMO located on the linker should be responsible for the bathochromic shift of λ_{max} of **QPQ** compared to **QQ**. In the case of **QTQ'**, the *sa*-conformer is the global minimum energy structure, followed by the *aa*-conformer, which virtually possesses the same energy. However, the *ss*-conformer is unstable, thus a minimum energy structure is unobtainable. The π-conjugated systems of the *sa*- and *aa*-conformers are highly planar and the HOMO levels are raised

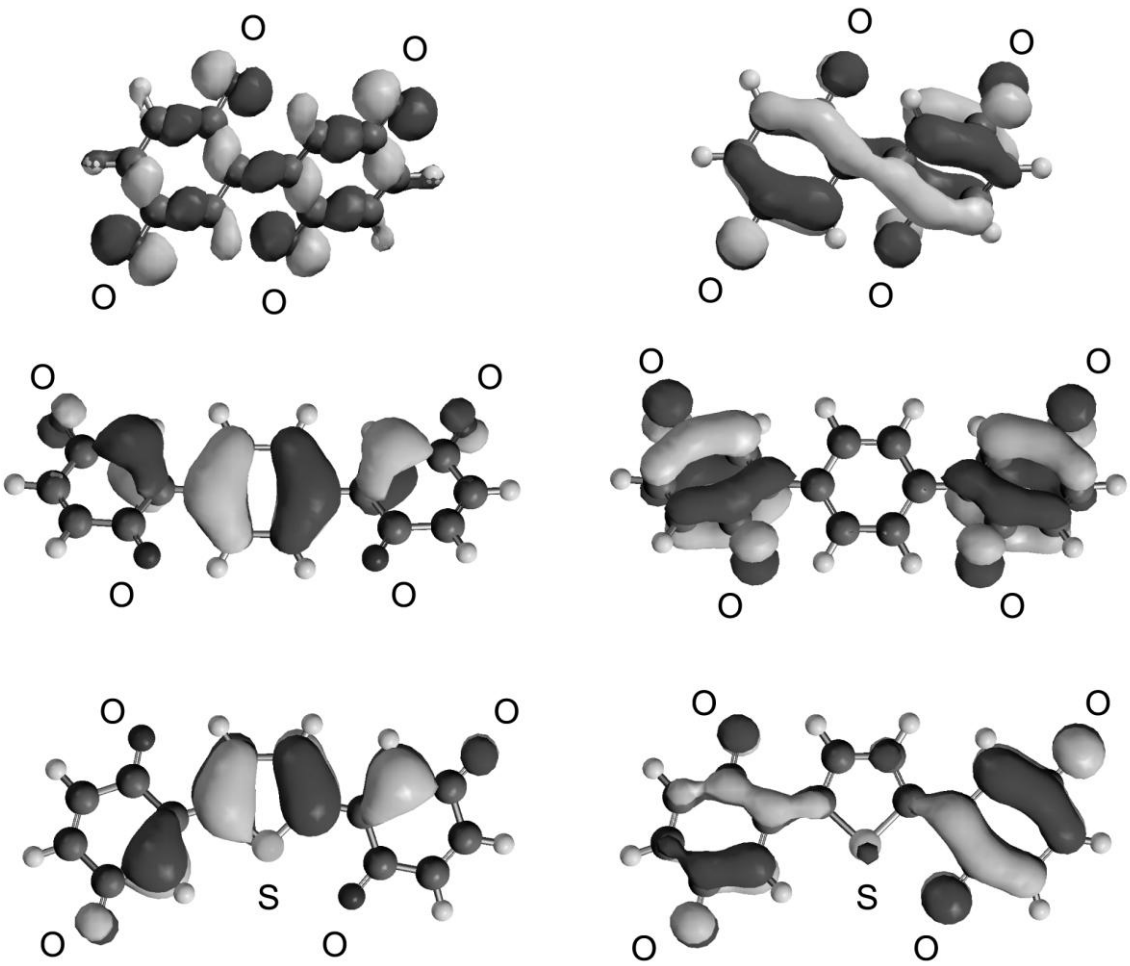


Figure 5. HOMO (left) and LUMO (right) orbitals of *a*-**QQ'** (top), *s*-**QPQ'** (middle), and *as*-**QTQ'** (bottom) calculated by B3LYP/6-31G** methods. Oxygen and sulfur atoms are noted

significantly (Table 1). Evidently, these are characteristics of the 2,5-thienylene linker, which should be responsible for the significant bathochromic shift in **QTQ**.

It is noteworthy that, even though the thienylene group is inherently electron-donating in nature, the LUMO level of **QTQ'** is considerably lower than that of *s*-**QPQ'** and comparable to that of *a*-**QQ'**. A similar tendency was observed in the reduction potentials of **QQ**,[10] **QPQ**, and **QTQ** as measured by cyclic voltammetry (Table 1). Both **QPQ** and **QTQ** showed the reversible first (E_1) and second (E_2) waves, which were both attributed to one-electron reductions, followed by the irreversible third (E_3) wave. As expected from the theoretical calculations, E_1 of **QTQ** was positively shifted by 0.09 V as compared to that of **QPQ**. The higher electron-acceptor character should be due to the extended LUMO of **QTQ**. In fact, as shown in Figure 5, the LUMO of **QTQ'** is efficiently delocalized between the quinone and thienylene moieties, while the LUMO of **QPQ'** is localized on the quinone groups. The difference between E_1 and E_2 (= ΔE) is larger in **QTQ** (0.17 V) than in **QPQ** (0.08 V). This is also indicative of

strong interaction between the two quinone moieties and the presence of efficiently delocalized LUMO in **QTQ** with the aid of 2,5-thienylene linker. In spite of a large dihedral angle (37°), a significantly higher ΔE was found in **QQ** (0.34 V), probably because of the large inductive (field) effects of the quinone moieties.[11]

In conclusion, two quinone dimers bearing arylene π linkers, **QPQ** and **QTQ**, have been synthesized, and their π-conjugated systems were characterized. In **QPQ**, a significant bathochromic shift of λ_{max} was observed as compared to **QQ**, which was mainly attributed to the rise of the HOMO level. The LUMO level of **QPQ** was also higher than that of **QQ**, which led to the negative shift of E_1. In **QTQ**, greater bathochromic shift of λ_{max} was observed, which was also due to the rise of the HOMO level. Despite the electron-rich character of the 2,5-thienylene moiety, E_1 of **QTQ** was positively shifted as compared to that of **QQ**. DFT calculations revealed that this should arise from the planar structure of **QTQ**, which results in a fully conjugated π-system. These studies suggest that even an electron-rich arylene moiety could serve as a viable linker to construct an efficiently conjugated π system without impairing the electron acceptor character, and therefore could provide insight to the design of higher quinine oligomers.

EXPERIMENTAL

General. All commercially available chemicals were used without further purification except Et_2O and THF, which were dried over sodium and distilled from sodium containing benzophenone to form the ketyl before use, respectively. Melting points were determined on microscopic thermometer without correction. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECP600 (600 MHz for ^1H) or a JEOL ECX-300/TRH (300 MHz for ^1H and 75 MHz for ^{13}C) with tetramethylsilane as internal reference. Mass spectra were conducted on a JEOL MStation JMS-700 (EI and HRMS/EI). Infrared spectra were measured on a JASCO FT/IR-6100. Cyclic voltammetry (CV) was performed on an ALS model 600A in 1.0 mM of substrate. All CV measurements were carried out in anhydrous CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate (nBu$_4$NClO$_4$) as a supporting electrolyte, purging with argon prior to conduct the experiment. Platinum electrode was used as a working electrode and a platinum wire as a counter electrode. All potentials were recorded versus Ag/Ag^+ electrode (in MeCN) as a reference electrode.

Synthesis of 4,4''-di-*tert*-butyl-2,2'',5,5''-tetramethoxyl-1,1':4',1''-terphenyl (3). A bi-layer solution of 4-*tert*-butyl-2,5-dimethoxyphenylboronic acid (**1**) (1.29 g, 5.4 mmol) and 1,4-dibromobenzene (**2**) (0.51 g, 2.2 mmol) in toluene (30 mL), EtOH (10 mL) and 1 mol L^{-1} aqueous sodium carbonate (20 mL) was degassed with argon. After tetrakis(triphenylphosphine)palladium (0.25 g, 0.22 mmol) was added, the

reaction mixture was refluxed overnight. After cooling, organic layer was separated, and aqueous layer was extracted with Et_2O. Combined organic phase was washed with brine, dried over Na_2SO_4, and evaporated to dryness. From the crude product, **3** (0.77 g, 71%) was isolated by preparative chromatography (SiO_2, *n*-hexane/EtOAc 9:1) as a white powder.

Mp 218-220 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.59 (s, 4H, Ar), 6.97 (s, 2H, Ar), 6.93 (s, 2H, Ar), 3.84 (s, 6H, OCH_3), 3.79 (s, 6H, OCH_3), 1.43 (s, 18H, *tert*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.77, 150.04, 138.36, 136.91, 129.02, 128.36, 114.71, 111.72, 56.61, 55.80, 35.01, 29.74. MS: *m*/*z* = 462 (M^+). HRMS (*m*/*z*): 462.2766 (M^+, calcd. 462.2771 for $C_{30}H_{38}O_4$).

Synthesis of 4,4''-di-*tert*-butyl-1,1':4',1''-terphenyl-2,2',5,5'-tetraol (4). To a solution of **3** (0.40 g, 0.86 mmol) in $CHCl_3$ (10 mL) was added BBr_3 (0.32 mL, 3.5 mmol) at 0 °C dropwisely under argon. After stirring 4 h, MeOH and water were added in this order. After removing methanol in vacuum, the organic layer was separated and the aqueous layer was extracted with Et_2O. Combined organic phase was washed with brine, dried over Na_2SO_4, and evaporated to dryness to leave **4** quantitatively as a white powder. The crude **4** was used in the following reaction without further purification.

Synthesis of 1,4-bis(5-*tert*-butyl-1,4-benzoquinon-2-yl)benzene (QPQ). To a solution of **4** (0.43 g, 1.1 mmol) in MeCN (40 mL) was added cerium ammonium nitrite (CAN, 2.36 g, 4.3 mmol) at ambient temperature in the dark. After stirring for 4 h, the reaction mixture was quenched with water, then subjected to supersonic treatment until the solid was precipitated. The precipitate was separated by suction filtration, washed with acetone/water (1:1 v/v), and dried to give analytically pure **QPQ** as a yellow powder (0.35 g, 85%).

Mp 291-294 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.57 (s, 4H, Ar), 6.81 (s, 2H, CH), 6.70 (s, 2H, CH), 1.33 (s, 18H, *tert*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.59, 187.40, 156.02, 143.42, 134.99, 133.82, 132.07, 129.29, 35.15, 29.14. MS: *m*/*z* = 402 (M^+). HRMS (*m*/*z*): 402.1832 (M^+, calcd. 402.1832 for $C_{26}H_{26}O_4$).

Synthesis of 2,5-bis(4-*tert*-butyl-2,5-dimethoxyphenyl)thiophene (6). A bi-layer solution of **1** (2.60 g, 10 mmol) and 2,5-dibromothiophene (**5**) (0.54 g, 4.9 mmol) in toluene (30 mL), EtOH (10 mL) and 1 mol L^{-1} aqueous sodium carbonate (20 mL) was degassed with argon. After tetrakis(triphenylphosphine)palladium (0.58 g, 0.50 mmol) was added, the reaction mixture was refluxed overnight. After cooling, organic layer was separated, and aqueous layer was extracted with Et_2O. Combined organic phase was washed with brine, dried over Na_2SO_4, and evaporated to dryness. From the

crude product, **6** (1.60 g, 70%) was isolated by preparative chromatography (SiO_2, *n*-hexane/EtOAc 9:1) as a pale yellow solid.

Mp 155-157 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43 (s, 2H, Ar), 7.15 (s, 2H, Ar), 6.96 (s, 2H, Ar), 3.89 (s, 6H, OCH_3), 3.88 (s, 6H, OCH_3), 1.40 (s, 18H, *tert*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.88, 149.50, 139.00, 138.57, 125.28, 121.72, 112.36, 111.87, 56.77, 55.79, 35.02, 29.69. MS: *m*/*z* = 468 (M^+). HRMS (*m*/*z*): 468.2333 (M^+, calcd. 468.2334 for $C_{28}H_{36}O_4S$).

Synthesis of 2-*tert*-butyl-5-iodo-1,4-benzoquinone (8). To a solution of 2-*tert*-butyl-5-iodo-1,4-dimethoxybenzene (4.39 g, 13.7 mmol) in MeCN (80 mL) was added CAN (22.9 g, 41.8 mmol) dissolved in a minimum amount of water. After stirring for 3.5 h in the dark, the reaction mixture was diluted by water, and then exposed to supersonic waves. The precipitation was collected by suction filtration, washed by water, and dried under vacuum to give analytically pure **8** as an orange powder (3.88g, 98%).

Mp 83-84 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (s, 1H, CH), 6.82 (s, 1H, CH), 1.28 (s, 9H, *tert*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.18, 181.34, 156.62, 147.92, 129.78, 117.48, 35.45, 29.02. MS: *m*/*z* = 290 (M^+). HRMS (*m*/*z*): 289.9818 (M^+, calcd. 289.9804 for $C_{10}H_{11}O_2I$). IR (Nujol. cm^{-1}): 1649 ($\nu_{C=O}$).

Synthesis of 2-*tert*-butyl-5-iodobenzen-1,4-diol (9). A bi-layer solution of **8** (7.54 g, 26.0 mmol), $Na_2S_2O_4$ (22.6 g, 130 mmol) in water (100 mL) and $CHCl_3$ (80 mL) was stirred for 2 h in the dark. The reaction mixture was acidified with dilute HCl, extracted with $CHCl_3$, dried over $MgSO_4$, and concentrated under vacuum to give analytically pure **9** as a brownish yellow solid (7.41g, 98%).

Mp 115-116 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.97 (s, 1H, CH), 6.92 (s, 1H, CH), 4.89 (s, 1H, OH), 4.86 (s, 1H, OH), 1.36 (s, 9H, *tert*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.74, 148.69, 139.17, 124.80, 113.58, 80.42, 34.59, 29.23. MS: *m*/*z* = 292 (M^+). HRMS (*m*/*z*): 291.9968 (M^+, calcd. 291.9960 for $C_{10}H_{13}O_2I$). IR (Nujol. cm^{-1}): 3494, 3408 (ν_{O-H}).

Synthesis of 1-*tert*-butyl-4-iodo-2,5-bis(methoxymethoxy)benzene (10). NaH (60% in mineral oil, 1.64g, 0.99 g as NaH, 41.0 mmol) was added to THF (60 mL) under argon. The mixture was cooled to 0 °C and a solution of **9** (2.00 g, 6.85 mmol) in THF (30 mL) was added portionwisely. After stirring for 30 min at 0 °C, chloromethyl methyl ether was added, and the mixture was stirred for additional 16 h at ambient temperature. After excess amount of aqueous 10% NaOH was added, the mixture was extracted with EtOAc, dried over $MgSO_4$, and concentrated under vacuum. From the crude product, **10** (2.56 g, 88%) was isolated by preparative chromatography (SiO_2, *n*-hexane/EtOAc 9:1) as pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (s, 1H, Ar), 7.04 (s, 1H, Ar), 5.15 (s, 2H, C$\underline{H_2}$OCH$_3$), 5.13 (s, 2H, C$\underline{H_2}$OCH$_3$), 3.53 (s, 3H, CH$_2$OC$\underline{H_3}$), 3.47 (s, 3H, CH$_2$OC$\underline{H_3}$), 1.36 (s, 9H, *tert*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.81, 150.88, 139.90, 124.55, 114.77, 96.00, 94.45, 83.91, 56.25, 55.85, 34.90, 29.39. MS: *m*/*z* = 380 (M^+). HRMS (*m*/*z*): 380.0495 (M^+, calcd. 380.0485 for $C_{14}H_{21}O_4I$).

Synthesis of 4-*tert*-butyl-2,5-bis(methoxylmethoxy)phenylboronic acid (11). To a solution of **10** (6.43 g, 16.9 mmol) in Et_2O (100 mL) was dropwised *n*-butyllithium (1.6 M in *n*-hexane, 17.0 mL, 27.2 mmol) at –78 °C under argon. After stirring for 1.5 h at –78 °C, trimethyl borate (5.70 mL, 51.3 mmol) was added slowly. The resulting mixture was stirred for additional 1 h, while the temperature was held at –78 °C, then the reaction mixture was allowed to warm to ambient temperature. After cooling to 0 °C, small amount of water was added to quench the reaction, then 25% acetic acid was added to keep pH of the solution to be 6.5.[14] The reaction mixture was extracted with Et_2O. Combined organic extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. The crude product was recrystallized from *n*-hexane to give **11** (2.45 g; 49%) as a white solid.

Mp 68-69 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (s, 1H, Ar), 7.11 (s, 1H, Ar), 5.24 (s, 2H, C$\underline{H_2}$OCH$_3$), 5.23 (s, 2H, C$\underline{H_2}$OCH$_3$), 3.51 (s, 6H, CH$_2$OC$\underline{H_3}$), 1.40 (s, 9H, *tert*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.07, 151.18, 143.48, 120.98, 113.11, 95.44, 94.33, 56.43, 56.13, 35.32, 29.55. MS: *m*/*z* = 298 (M^+). HRMS (*m*/*z*): 298.1579 (M^+, calcd. 298.1588 for $C_{14}H_{23}O_6B$).

Synthesis of 2,5-bis{4-*tert*-butyl-2,5-bis(methoxymethoxy)phenyl}thiophene (12). A b-layer solution of **11** (2.57 g, 8.62 mmol) and **5** (0.846 g, 3.50 mmol) in toluene (30 mL), EtOH (10 mL) and 1 mol L^{-1} aqueous sodium carbonate (20 mL) was degassed with argon. After tetrakis(triphenylphosphine)palladium (0.402 g, 0.348 mmol) was added, the reaction mixture was refluxed for 18 h. After cooling, organic layer was separated, and aqueous layer was extracted with Et_2O. Combined organic phase was washed with brine, dried over $MgSO_4$, and evaporated to dryness. From the crude product, **12** (1.42 g, 69%) was isolated by recrystallization from Et_2O and *n*-hexane as a yellow solid.

Mp 121-123 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40 (s, 2H, Ar), 7.39 (s, 2H, Ar), 7.14 (s, 2H, Ar), 5.24 (s, 4H, C$\underline{H_2}$OCH$_3$), 5.17 (s, 4H, C$\underline{H_2}$OCH$_3$), 3.52 (s, 6H, CH$_2$OC$\underline{H_3}$), 3.51 (s, 6H, CH$_2$OC$\underline{H_3}$), 1.41 (s, 18H, *tert*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.55, 147.60, 139.07, 138.86, 125.23, 123.04, 115.95, 114.25, 95.98, 94.74, 56.36, 56.00, 34.98, 29.75. MS: *m*/*z* = 588 (M^+). HRMS (*m*/*z*): 588.2736 (M^+, calcd. 588.2757 for $C_{32}H_{44}O_8S$).

Synthesis of 2,5-bis(4-*tert*-butyl-2,5-dihydroxyphenyl)thiophene (7). A solution of **12** (0.195 g, 0.331 mmol) and concentrated HCl (1 mL) in MeOH (30 mL) was refluxed for 20 h in the dark. After water was added, the mixture was extracted with ethyl acetate. Combined organic phase was washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated to dryness. From the crude product, **7** (0.124 g, 91%) was isolated by recrystallization from Et_2O and *n*-hexane as a slightly purple solid.

Mp 214-216 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (s, 2H, Ar), 6.88 (s, 2H, Ar), 6.79 (s, 2H, Ar), 5.16 (s, 2H, OH), 4.74 (s, 2H, OH), 1.41 (s, 18H, *tert*-Bu). ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ = 8.17 (s, 2H, OH), 7.90 (s, 2H, OH), 7.49 (s, 2H, Ar), 7.11 (s, 2H, Ar), 6.90 (s, 2H, Ar), 1.39 (s, 18H, *tert*-Bu). ^{13}C NMR (75 MHz, $(CD_3)_2CO$): δ = 149.62, 147.05, 139.59, 136.94, 125.87, 119.94, 115.92, 115.39, 35.06, 29.75. MS: *m*/*z* = 412 (M^+). HRMS (*m*/*z*): 412.1717 (M^+, calcd. 412.1708 for $C_{24}H_{28}O_4S$). IR (Nujol, cm^{-1}): 3626, 3497, 3341, 3182 (ν_{O-H}).

Synthesis of 2,5-bis(5-*tert*-butyl-1,4-benzoquinon–2–yl)thiophene (QTQ). To a solution of **7** (0.680 g, 1.65 mmol) in MeCN (40 mL) was added CAN (2.75 g, 5.02 mmol) at ambient temperature in the dark. After stirring for 4 h, the reaction mixture was quenched with water, and subjected to supersonic treatment until the solid was precipitated. The precipitate was separated by suction filtration, washed with water, and dried to give analytically pure **QTQ** as a reddish purple powder (0.606 g, 90%).

Mp 265-267 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (s, 2H, Ar), 6.98 (s, 2H, C=CH), 6.68 (s, 2H, C=CH), 1.32 (s, 18H, *tert*–Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.15, 186.79, 156.35, 138.92, 136.40, 131.51, 130.19, 130.02, 35.22, 29.15. MS: *m*/*z* = 408 (M^+). HRMS (*m*/*z*): 408.1395 (M^+, calcd. 408.1395 for $C_{24}H_{24}O_4S$). IR (Nujol. cm^{-1}): 1653, 1635 ($\nu_{C=O}$).

Theoretical calculations. Geometry optimizations were conducted with Spartan PC '04 software package on Microsoft Window XP. In all calculations, B3LYP/6-31G** levels were employed and the symmetry of the conformers of **QQ'**, **QPQ'**, and **QTQ'** were assumed as shown in Table 1.

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