

HETEROCYCLES, Vol. 80, No. 2, 2010, pp 1227 - 1238. © The Japan Institute of Heterocyclic Chemistry
 Received, 11th August, 2009, Accepted, 18th September, 2009, Published online, 18th September, 2009
 DOI: 10.3987/COM-09-S(S)108

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

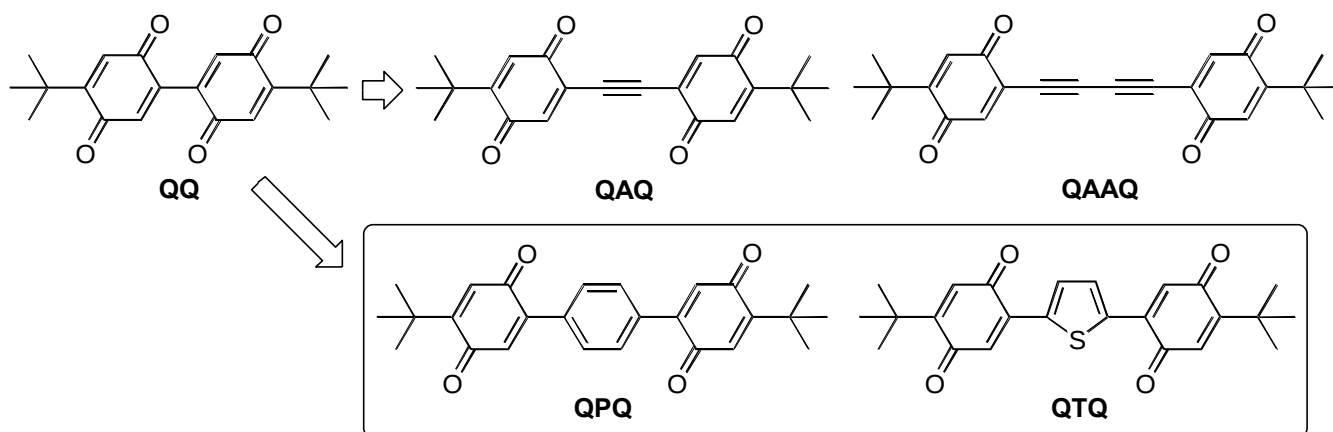
Naoto Hayashi,* Teru Sakakibara, Takahiro Ohnuma, Junro Yoshino, and
 Hiroyuki Higuchi

Graduate School of Science and Engineering, University of Toyama, Gofuku,
 Toyama 930-8555, Japan. Email: nhayashi@sci.u-toyama.ac.jp

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 quinone 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



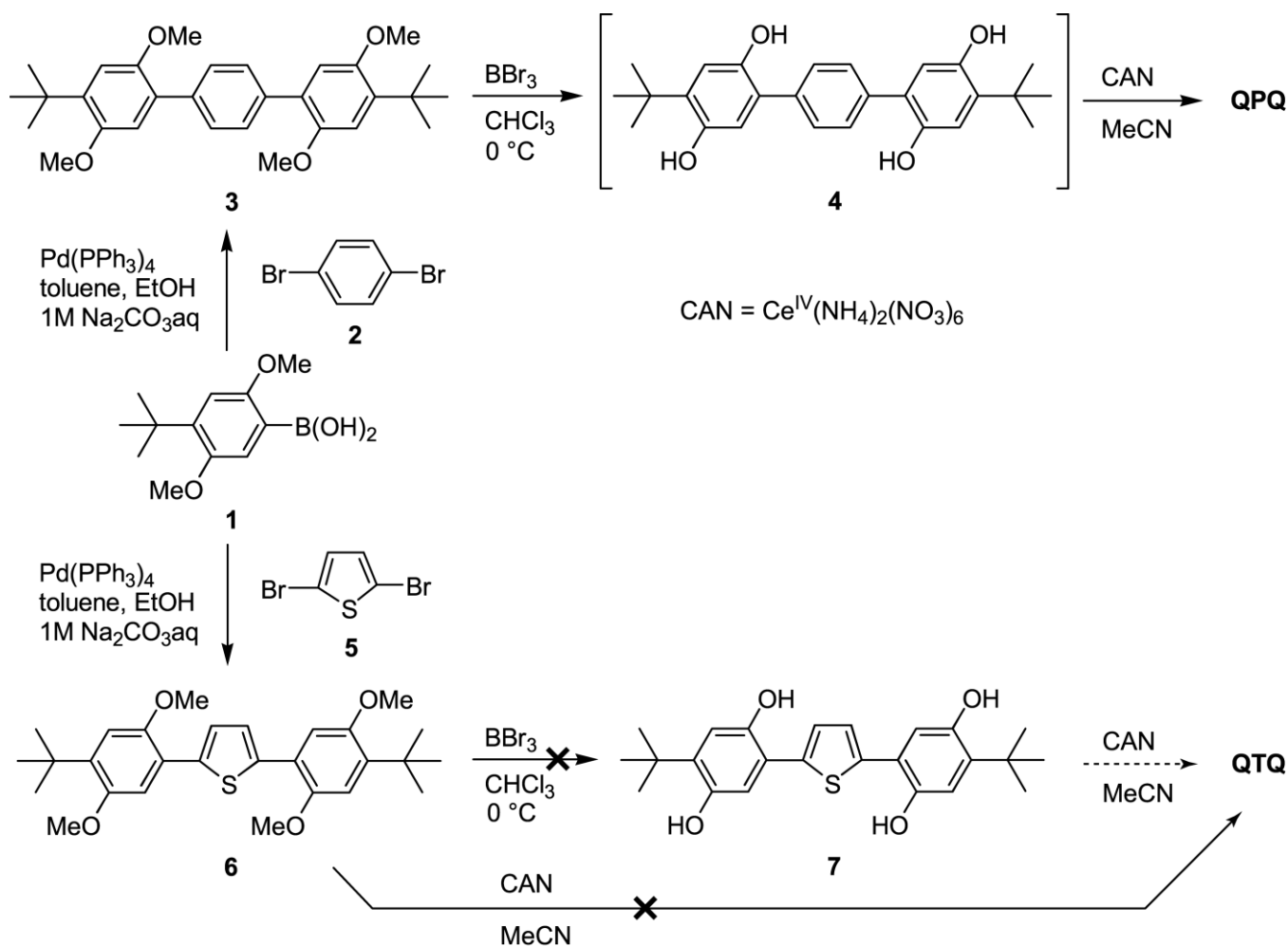


Figure 1. Synthesis of **QPQ** and attempt of synthesis of **QTQ**

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 quinone 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

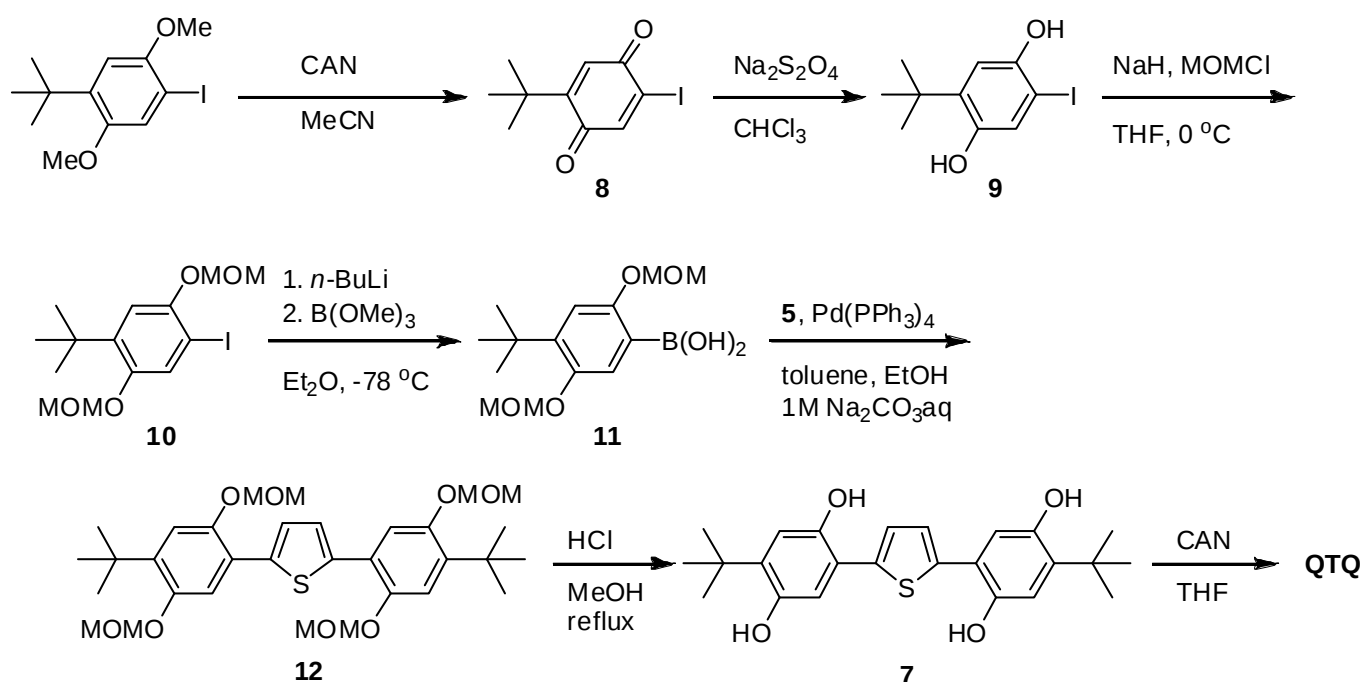


Figure 2. Synthesis of QTQ

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 BBr₃, 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 BBr₃ did not afford hydroquinone **7**. This was likely due to the formation of charge-transfer complex of **6** and BBr₃. Demethylation of **6** using either EtSNa or Me₃SiI 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.

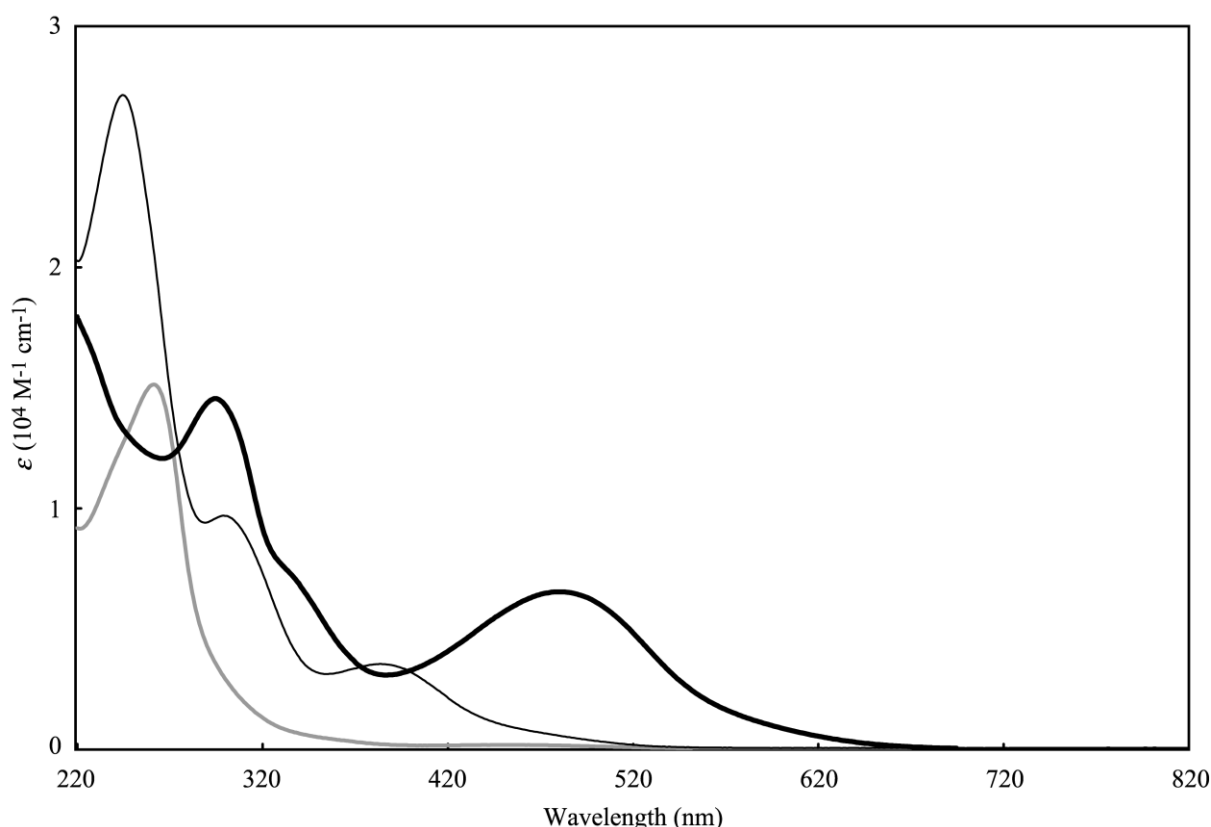


Figure 3. Electronic absorption spectra of **QQ** (gray), **QPQ** (thin), and **QTQ** (thick) in 1,4-dioxane

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 Na₂S₂O₄ 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.

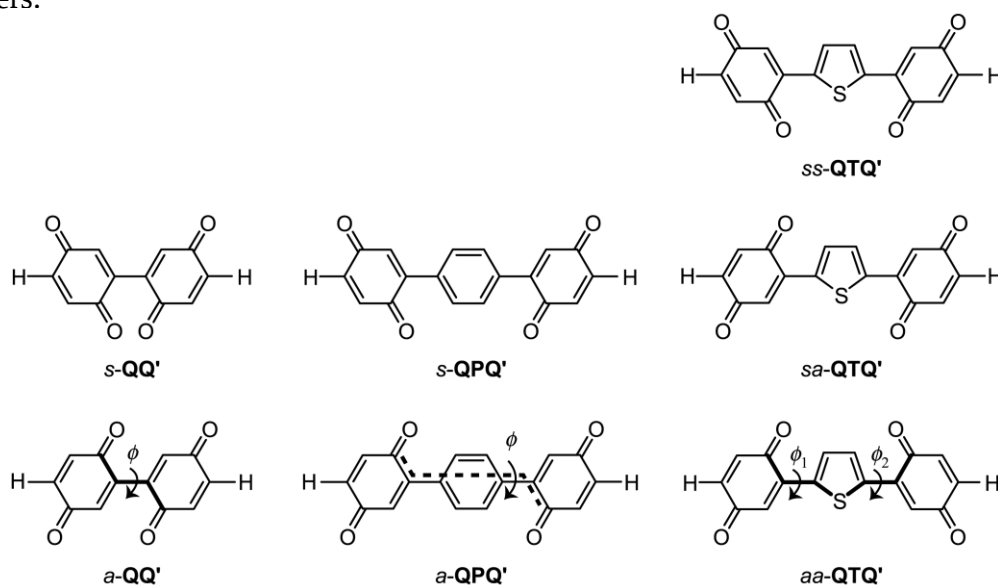
Electronic absorption spectra of **QPQ**, **QTQ**, and **QQ** are shown in Figure 3. The bathochromic shift of the longest wavelength absorption band (λ_{max}) was observed in **QPQ** compared to **QQ**. This is most likely to be attributed to the HOMO of **QPQ**, which is supposed to be located mainly 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 voltammetry of **QQ**, **QPQ**, and **QTQ** and minimum energy conformers of **QQ'**, **QPQ'**, and **QTQ'** in B3LYP/6-31G** calculations

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

^aElectrode; Pt (working), Pt (counter) and Ag/Ag⁺ (reference). Supporting electrolyte; *n*-Bu₄NClO₄. Scan rate; 0.1 V s⁻¹. In CH₂Cl₂. ^bReference 10. ^cEnergy 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 $\lambda_{\max}$ 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

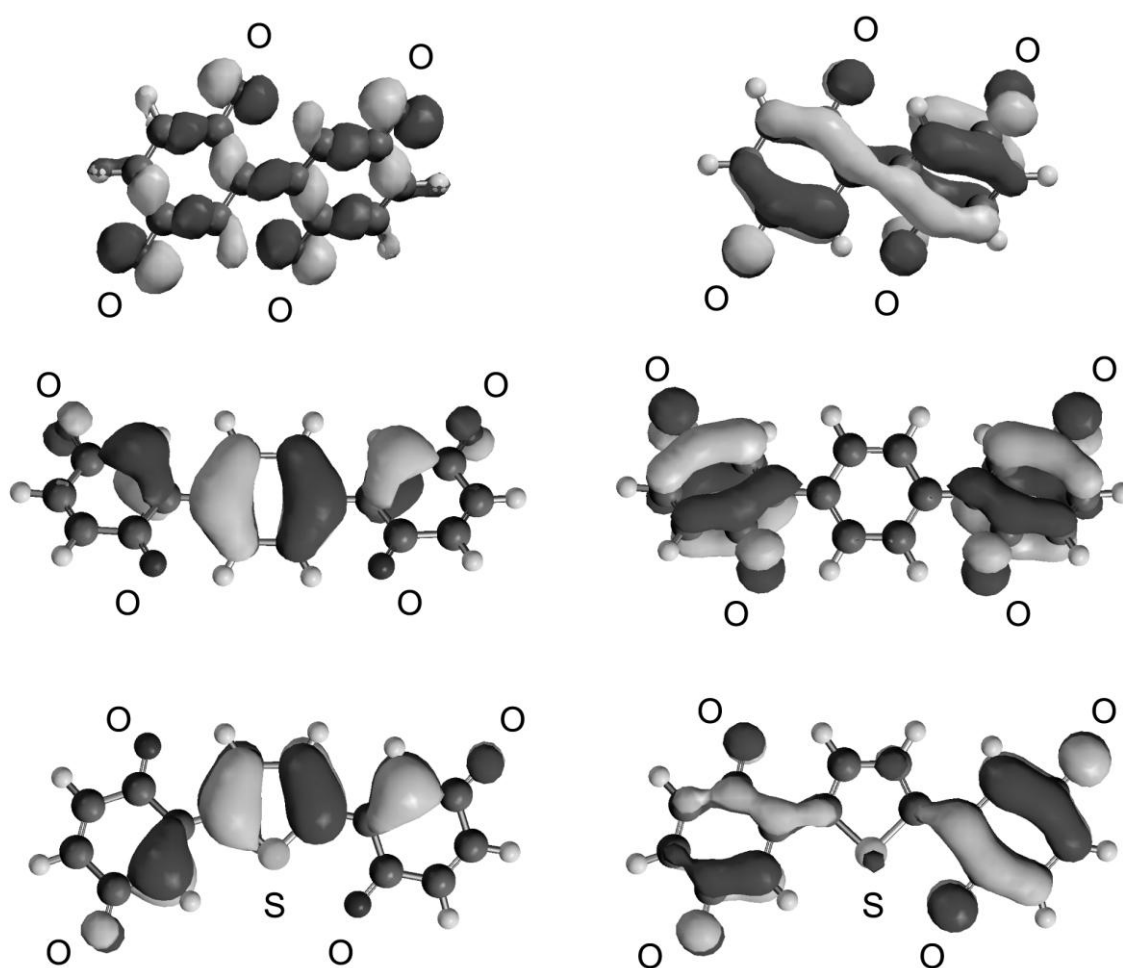


Figure 5. HOMO (left) and LUMO (right) orbitals of *a*-QQ' (top), *s*-QPQ' (middle), and *as*-QTQ' (bottom) calculated by B3LYP/6-31G** methods. Oxygen and sulfur atoms are noted

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 ($= \Delta E$) 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 $\lambda_{\max}$ 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 $\lambda_{\max}$ 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 Et₂O 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 ¹³C 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 ¹³C) 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 CH₂Cl₂ containing 0.1 M tetrabutylammonium perchlorate (*n*Bu₄NClO₄) 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 Et₂O. Combined organic phase was washed with brine, dried over Na₂SO₄, and evaporated to dryness. From the crude product, **3** (0.77 g, 71%) was isolated by preparative chromatography (SiO₂, *n*-hexane/EtOAc 9:1) as a white powder.

Mp 218-220 °C. ¹H NMR (600 MHz, CDCl₃): δ = 7.59 (s, 4H, Ar), 6.97 (s, 2H, Ar), 6.93 (s, 2H, Ar), 3.84 (s, 6H, OCH₃), 3.79 (s, 6H, OCH₃), 1.43 (s, 18H, *tert*-Bu). ¹³C NMR (75 MHz, CDCl₃): 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 C₃₀H₃₈O₄).

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 CHCl₃ (10 mL) was added BBr₃ (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 Et₂O. Combined organic phase was washed with brine, dried over Na₂SO₄, 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. ¹H NMR (600 MHz, CDCl₃): δ = 7.57 (s, 4H, Ar), 6.81 (s, 2H, CH), 6.70 (s, 2H, CH), 1.33 (s, 18H, *tert*-Bu). ¹³C NMR (75 MHz, CDCl₃): 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 C₂₆H₂₆O₄).

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 Et₂O. Combined organic phase was washed with brine, dried over Na₂SO₄, and evaporated to dryness. From the

crude product, **6** (1.60 g, 70%) was isolated by preparative chromatography (SiO₂, *n*-hexane/EtOAc 9:1) as a pale yellow solid.

Mp 155-157 °C. ¹H NMR (600 MHz, CDCl₃): δ = 7.43 (s, 2H, Ar), 7.15 (s, 2H, Ar), 6.96 (s, 2H, Ar), 3.89 (s, 6H, OCH₃), 3.88 (s, 6H, OCH₃), 1.40 (s, 18H, *tert*-Bu). ¹³C NMR (75 MHz, CDCl₃): 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 C₂₈H₃₆O₄S).

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. ¹H NMR (300 MHz, CDCl₃): δ = 7.55 (s, 1H, CH), 6.82 (s, 1H, CH), 1.28 (s, 9H, *tert*-Bu). ¹³C NMR (75 MHz, CDCl₃): 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 C₁₀H₁₁O₂I). IR (Nujol. cm⁻¹): 1649 (ν_{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), Na₂S₂O₄ (22.6 g, 130 mmol) in water (100 mL) and CHCl₃ (80 mL) was stirred for 2 h in the dark. The reaction mixture was acidified with dilute HCl, extracted with CHCl₃, dried over MgSO₄, and concentrated under vacuum to give analytically pure **9** as a brownish yellow solid (7.41g, 98%).

Mp 115-116 °C. ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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 C₁₀H₁₃O₂I). 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 MgSO₄, and concentrated under vacuum. From the crude product, **10** (2.56 g, 88%) was isolated by preparative chromatography (SiO₂, *n*-hexane/EtOAc 9:1) as pale yellow oil.

^1H NMR (300 MHz, CDCl_3): δ = 7.49 (s, 1H, Ar), 7.04 (s, 1H, Ar), 5.15 (s, 2H, CH_2OCH_3), 5.13 (s, 2H, CH_2OCH_3), 3.53 (s, 3H, CH_2OCH_3), 3.47 (s, 3H, CH_2OCH_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 $\text{C}_{14}\text{H}_{21}\text{O}_4\text{I}$).

Synthesis of 4-*tert*-butyl-2,5-bis(methoxymethoxy)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 $68\text{--}69^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 7.50 (s, 1H, Ar), 7.11 (s, 1H, Ar), 5.24 (s, 2H, CH_2OCH_3), 5.23 (s, 2H, CH_2OCH_3), 3.51 (s, 6H, CH_2OCH_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 $\text{C}_{14}\text{H}_{23}\text{O}_6\text{B}$).

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 $121\text{--}123^\circ\text{C}$. ^1H 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, CH_2OCH_3), 5.17 (s, 4H, CH_2OCH_3), 3.52 (s, 6H, CH_2OCH_3), 3.51 (s, 6H, CH_2OCH_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 $\text{C}_{32}\text{H}_{44}\text{O}_8\text{S}$).

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 NaHCO₃ and brine, dried over MgSO₄, and evaporated to dryness. From the crude product, **7** (0.124 g, 91%) was isolated by recrystallization from Et₂O and *n*-hexane as a slightly purple solid.

Mp 214-216 °C. ¹H NMR (300 MHz, CDCl₃): 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). ¹H NMR (300 MHz, (CD₃)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). ¹³C NMR (75 MHz, (CD₃)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 C₂₄H₂₈O₄S). 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. ¹H NMR (300 MHz, CDCl₃): δ = 7.71 (s, 2H, Ar), 6.98 (s, 2H, C=CH), 6.68 (s, 2H, C=CH), 1.32 (s, 18H, *tert*-Bu). ¹³C NMR (75 MHz, CDCl₃): 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 C₂₄H₂₄O₄S). IR (Nujol, cm⁻¹): 1653, 1635 (ν_{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.

ACKNOWLEDGMENTS

This work was financially supported by the Saneyoshi Scholarship Foundation, Japan. The authors appreciate the useful advice given by Dr. Yen Ting Chen (Scripps Florida).

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