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Photochromism and Electrical Transport Characteristics of a Dyad and a Polymer with Diarylethene and Quinoline Units

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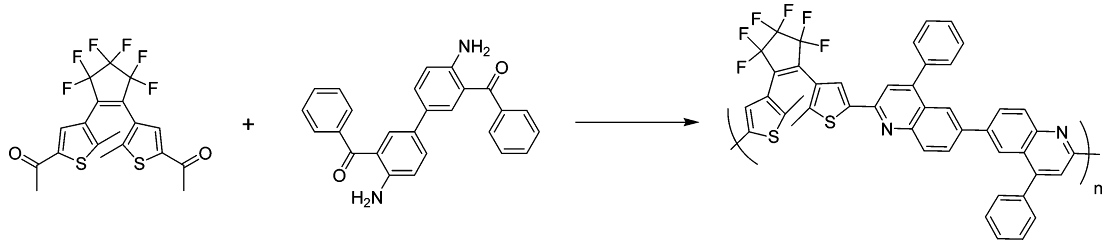
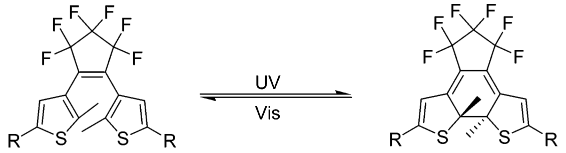


The synthesis of a series of photochromic compounds incorporating a phenylquinoline unit and the photophysical and electric transport properties are described. The dyad and polymer with a quinoline unit show a high quantum yield due to the enforced antiparallel conformation of the dithienylethene moieties. High carrier conductivity was observed in the closed form of the diarylethene with a phenylquinoline unit.

Introduction

Photochromic compounds undergo reversible transformation between two distinct chemical isomers by different colors of light.[1] Switching between the two isomers of 1,2-dithienylalkene derivatives can be accompanied by changing physical properties such as luminescence,[2] refractive index,[3] electronic conductivity,[4] optical rotation,[5] and viscosity.[6] Some of the most promising candidates for photochromic materials are 1,2-diarylethene derivatives due to their remarkable thermal stability and fatigue resistance[7] (Scheme 1).

SCHEME 1



The functionalization of the photochromic unit is a major issue for reasons such as tuning the absorption properties to excite the molecule at a desired wavelength[8] or creating the electrical changes upon the photochromic reactions. The Tsujioka[9] and Taniguchi[10] groups reported

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(1) (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (b) Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777. (c) Morimoto, M.; Kobatake, S.; Irie, M. *J. Am. Chem. Soc.* **2003**, *125*, 11080. (d) Kaieda, T.; Kobatake, S.; Miyasaka, H.; Murakami, M.; Iwai, N.; Nagata, Y.; Itaya, A.; Irie, M. *J. Am. Chem. Soc.* **2002**, *124*, 2015. (e) Higashiguchi, K.; Matsuda, K.; Tanifuji, N.; Irie, M. *J. Am. Chem. Soc.* **2005**, *127*, 8922.

(2) (a) Norsten, T. B.; Branda, N. R. *J. Am. Chem. Soc.* **2001**, *123*, 1784. (b) Tsivgoulis, G.; Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1119. (c) Norsten, T. B.; Branda, N. R. *Adv. Mater.* **2001**, *13*, 347. (d) Yam, V. W.-W.; Ko, C.-C.; Zhu, N. *J. Am. Chem. Soc.* **2004**, *126*, 12734.

(3) (a) Kim, E.; Choi, Y.-K.; Lee, M.-H. *Macromolecules* **1999**, *32*, 4855. (b) Kim, M.-S.; Maruyama, H.; Kawai, T.; Irie, M. *Chem. Mater.* **2003**, *15*, 4539.

(4) Kawai, T.; Kunitake, T.; Irie, M. *Chem. Lett.* **1999**, 905.

(5) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789.

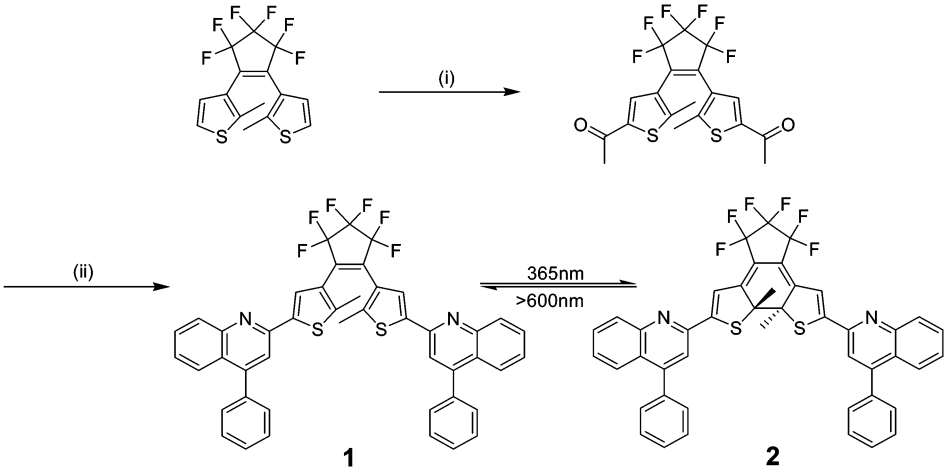
(6) Lucas, L. N.; van Esch, J.; Kellog, R. M.; Feringa, B. L. *Chem. Commun.* **2001**, 759.

(7) Hanazawa, M.; Sumiya, R.; Horikawa, Y.; Irie, M. *J. Chem. Soc., Chem. Commun.* **1992**, 206

(8) (a) Peters, A.; McDonald, R.; Branda, N. R. *Chem. Commun.* **2002**, 2274. (b) Kawai, T.; Iseda, T.; Irie, M. *Chem. Commun.* **2004**, 72. (c) Frigoli, M.; Mehl, G. H. *Chem. Commun.* **2004**, 818.

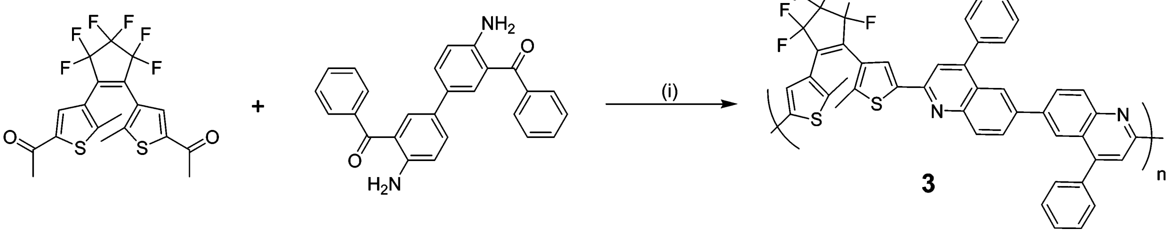
10.1021/jo050710t CCC: $30.25

SCHEME 2[a]



[a] Reagents and conditions: (i) acetic anhydride, $SnCl_4$, CH_2Cl_2, reflux (82%); (ii) 2-aminobenzophenone, diphenyl phosphate, toluene, 120 °C (76%).

SCHEME 3[a]



[a] Reagents and conditions: (i) diphenyl phosphate, *m*-cresol, 135 °C (74%).

that the diarylethenes with triphenylamine groups showed good hole-transport characteristics. One can thus envision that the incorporation of 1,2-diarylethene with molecules and polymers containing oxadiazole,[11] benzobisazole,[12] quinoxaline,[13] and quinoline[14] offer highly efficient electron-transport material. Recently, Jenekhe and co-workers[15] reported that a new n-type conjugated copolymer containing 3,3′-dialkylthiophene and bis(phenylquinoline) moieties was shown to be a good electron-transport material for polymer LEDs. One challenge of particular focus here is the development of more efficient and robust electron-transport photochromic compounds which can be utilized as a nondestructive readout method of photomode optical memory using a photocurrent detection[16] and organic semiconductor memory device.[17] Accordingly, we attempted to synthesize such compounds by incorporating the diarylethene with quinoline unit because the polyquinolines are characterized by high thermal and good film forming properties.[18] Here, we report the photoswitching of a dyad **1** and polymer **3** containing diarylethene and quinoline units and their electron-transport property.

Results and Discussion

Molecular Design and Synthesis. Schemes 2 and 3 describe the synthetic routes of monomer **1** and polymer **3** by the Friedländer condensation reaction. Compound **1** was made in two steps from the 1,2-bis(2-methyl-3-thienyl)perfluorocyclopentene according to the previous procedures.[15] The acetylation of the dithienyl perfluorocyclopentene in the presence of acetic anhydride and $SnCl_4$ catalysts gave the diacetyl monomer. Phenyl quinolinylation of diacetyl monomer with 2-aminobenzophenone resulted in formation of dyad **1** in 74% yield after column chromatography. The diacetyl monomer was copolymerized with 3,3-dibenzoylbenzidine to yield the copolymer **3** that contained the diarylethene. The dyad **1** was obtained as a colorless powder, which was soluble in dichloromethane and tetrahydrofuran. The closed-ring dyad **2** was prepared by irradiating a dichloromethane solution of **1** with UV light ($\lambda = 365$ nm) and isolated from the blue solution by HPLC. The dyads (**1** and **2**) and polymer **3** were identified by NMR, IR, and elemental analysis. In the ^{1}H NMR spectrum of **1**, one methyl

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(9) Tsujioka, T.; Masuda, K. *Appl. Phys. Lett.* **2003**, *83*, 4978.
(10) Taniguchi, A.; Tsujioka, T.; Hamada, Y.; Shibata, k.; Fuyuki, T. *Jpn. J. Appl. Phys.* **2001**, *40*, 7029.
(11) Peng, Z. H.; Bao, Z. N.; Galvin, M. E. *Adv. Mater.* **1998**, *10*, 680.
(12) Alam, M. M.; Jenekhe, S. A. *Chem. Mater.* **2002**, *14*, 4775.
(13) Cui, Y.; Zhang, X.; Jenekhe, S. A. *Macromolecules* **1999**, *32*, 3824.
(14) (a) Zhang, X.; Jenekhe, S. A. *Macromolecules* **2000**, *33*, 2069. (b) Zhang, X.; Kale, D. M.; Jenekhe, S. A. *Macromolecules* **2002**, *35*, 382.
(15) (a) Tonzola, C. J.; Alam, M. M.; Bean, B. A.; Jenekhe, S. A. *Macromolecules* **2004**, *37*, 3554. (b) Tonzola, C. J.; Alam, M. M.; Jenekhe, S. A. *Adv. Mater.* **2002**, *14*, 1086.
(16) Tsujioka, T.; Hamada, Y.; Shibata, A.; Taniguchi, A.; Fuyuki, T. *Appl. Phys. Lett.* **2001**, *78*, 2282.
(17) Tsujioka, T.; Irie, M. *J. Opt. Soc. Am. B* **2002**, *19*, 297.
(18) (a) Alam, M. M.; Jenekhe, S. A. *J. Phys. Chem. B* **2001**, *105*, 2479. (b) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1996**, *8*, 579.

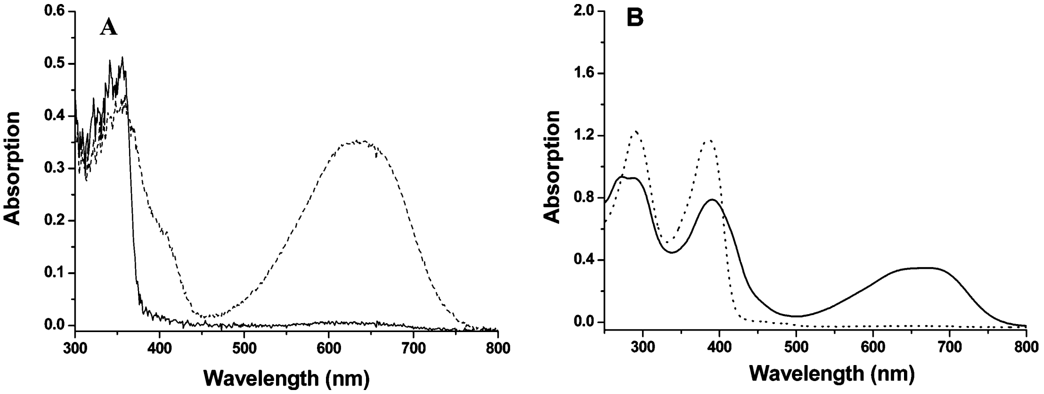

FIGURE 1. (A) UV−vis spectra of compound **1** (—) and a solution of **1/2** in the photostationary state (· · ·) in dichloromethane after irradiation with 365 nm light for 5 min. (B) UV−vis spectra of compound **3** (· · ·) and a solution of **3o/3c** in the photostationary state (—) in dichloromethane after irradiation with 365 nm light for 5 min.

TABLE 1. Quantum Yields and Conversions of Photochromic Reaction of 1−3 in CH_2Cl_2

diarylethene	Φ (%)	conversion (%)
1 → **2**	64[a]	7
2 → **1**	0.3[b]	100
3o → **3c**	68[a]	
3c → **3o**	0.5[b]	100

[a] Measured at 365 nm. [b] Measured at 532 nm.

resonance was observed at δ 2.03. In the blue isomer **2** and copolymer **3**, distinct new resonance peaks appeared at δ 2.31 and 2.25, respectively. IR spectroscopy of compound **1** and copolymer **3** showed the complete disappearance of the carbonyl group (1712 cm^{-1}) of the starting materials and the appearance of strong new bands between 1400 and 1600 cm^{-1}, which are characteristic of the quinoline uint. The structure of **1** and **2** was established by single-crystal X-ray analysis. The dyad **1** in CH_2Cl_2 is colorless. Irradiation of dichloromethane solution **1** at 365 nm light resulted in an immediate increase in the absorption intensity at 608 nm (Figure 1A). In the photostationary state, 88% of **1** was converted into the closed form **2**. The photostationary state was analyzed with ^1H NMR spectroscopy by comparing the relative intensities of methyl proton signals. After visible light irradiation ($\lambda > 600$ nm) for 15 min, the colored solution of **2** was completely bleached, indicating the formation of initial open form. Figure 1B shows the absorption spectral change of **3** in CH_2Cl_2 by photoirradiation. Upon irradiation with 365 nm light, the colorless solution of the open form of polymer **3** turned deep green, in which a characteristic absorption maximum was observed at 672 nm. This color disappeared upon irradiation with visible light ($\lambda > 600$ nm). A bathochromic shift of 64 nm is observed when compared with the maximum absorption value of dyad **2** and closed-ring polymer **3**, possibly due to increased π-delocalization. Similar results have been observed for structurally related dithienylethene derivatives.[19] The copolymer is also soluble in organic solvents such as dichloromethane and tetrahydrofuran. The molecular weight M_w, based on polystyrene standards, was 24200, and the polydispersity was 2.72. Thermogravimetric analysis under nitrogen shows that the decomposition temperature of the copolymer was in the range 420−440 °C. A glass transition (T_g) was determined by differential scanning calorimetry (DSC). The T_g was 221 °C. The value is comparable to those observed for the poly(phenylquinoline)s.[20]

Molecular Structure of 1 and 2. The single crystals of **1** and **2** were obtained from the recrystallization in the absence and presence of UV light in MeOH/THF. Figure 2 shows ORTEP drawings of the open-ring isomer **1** and the closed-ring isomer **2**. The dihedral angle between thiophene ring and perfluorocyclopentene ring in **1** was 40.15°, suggesting the presence of some π-conjugation between the thienyl ring and the ethene unit. The distance between the two reactive carbons C6−C29 in **1** was 3.496 Å, which is short enough for the reaction to take place.[21] The two molecules **1** and **2** were identical except for the dihedral angle between the perfluorocyclopentene ring and the thiophene ring. The dihedral angle between the thiophene ring and perfluorocyclopentene ring in **2** was 6.97°, suggesting that π-electrons were delocalized through the molecule. The bond distances of C18−C19 and C27−C28 in **2** are 1.357 and 1.54 Å, respectively. There data clearly indicate that the C18−C19 bond is a double bond, being significantly shorter than the other carbon−carbon single bond.[22]

Cyclization Quantum Yields. Table 1 summarizes the photochemical quantum yield of cyclization and cycloreversion reactions of the compounds. The most interesting property we found is the cyclization quantum yield, which was measured as 64% in **1**. This is the highest quantum yield measured in diarylethene molecules except for a few diarylethene backbone polymers.[23] The opening quantum yield in **2** → **1** turns out to be 0.3%. The polymer **3** also showed high quantum yield in cyclization (68%). The reason that compound **1** has the high cyclization quantum yield can be interpreted as the conformational orientation of crystal **1**. It is generally accepted that diarylethene molecules in the open form

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(19) Cho, H.; Kim, E. *Macromolecules* **2002**, *35*, 8654.

(20) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 895.

(21) (a) Ramamuthy, V.; Venkateson, K. *Chem. Rev.* **1987**, *87*, 433. (b) Higashiguchi, K.; Matsuda, K.; Matsuo, M.; Yamada, T.; Irie, M. *J. Photochem. Photobiol. A: Chem.* **2002**, *152*, 141.

(22) Pu, S.; Xu, J.; Shen, L.; Xiao, Q.; Yang, T.; Liu, G. *Tetrahedron Lett.* **2005**, *46*, 871.

(23) Stellacci, F.; Bertarelli, C.; Toscano, F.; Gallazzi, M. C.; Zolti, G.; Zerbi, G. *Adv. Mater.* **1999**, *11*, 292.

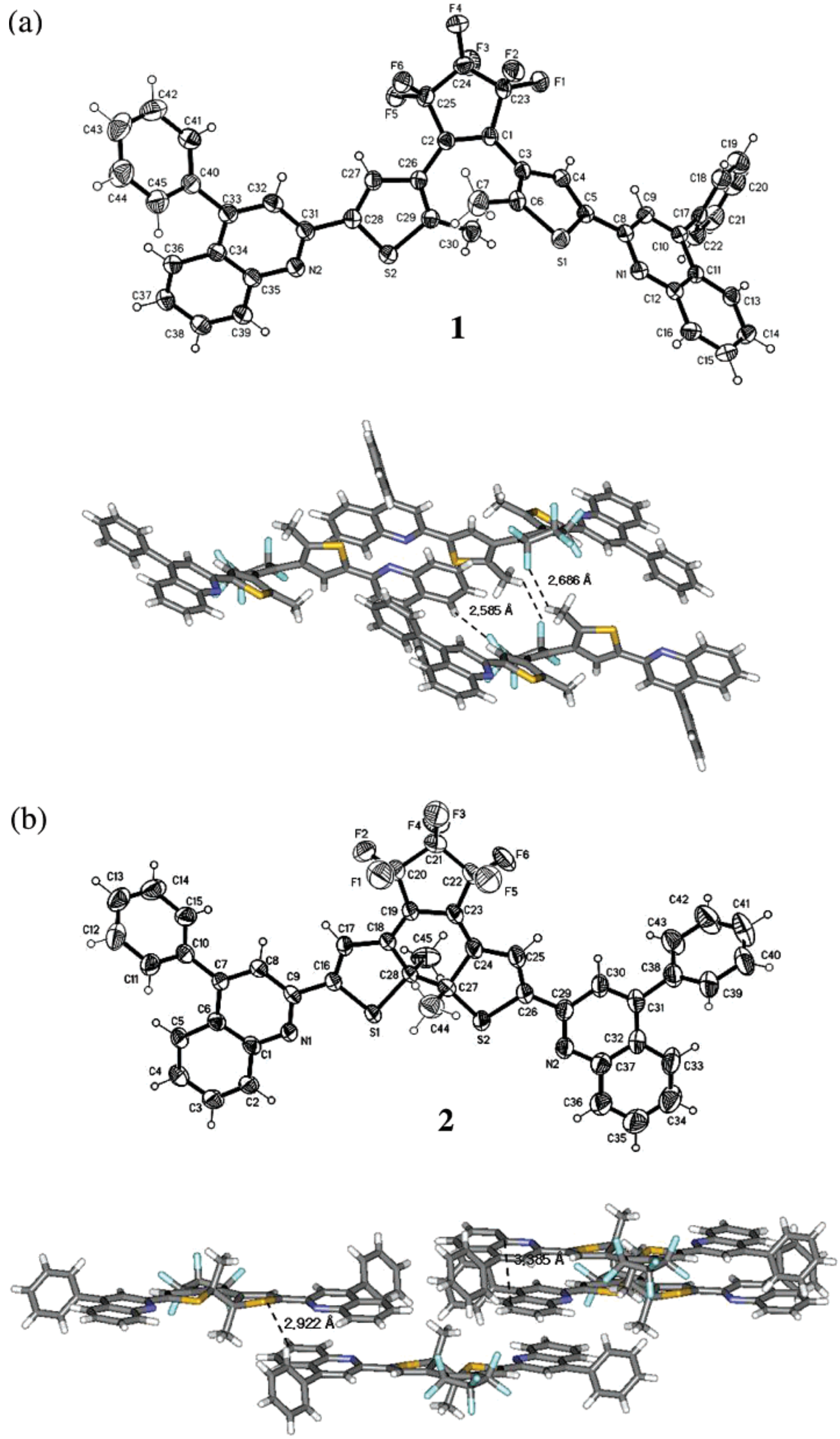

FIGURE 2. (a) Crystal structure of open-ring isomer **1** (top) and a diagram showing intermolecular interactions between two adjacent molecules in **1** (bottom). (b) Crystal structure of close-ring isomer **2** (top) and diagram showing intermolecular interactions between two adjacent molecules in **2** (bottom) along with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Disordered C44′ and C45′ and solvent in **2** are omitted for clarity.

may exist as two conformational isomers labeled C_2 and C_s.[24] To achieve high quantum yield, it is crucial to increase the population of the antiparallel conformation in the ground state.[25] As shown in the crystal structure of **1**, the distortion angle between thiophene ring and perfluorocyclopenten ring is relatively small. Thus, compound **1** showed a high cyclization quantum yield due to the enforced antiparallel conformation of the dithi-

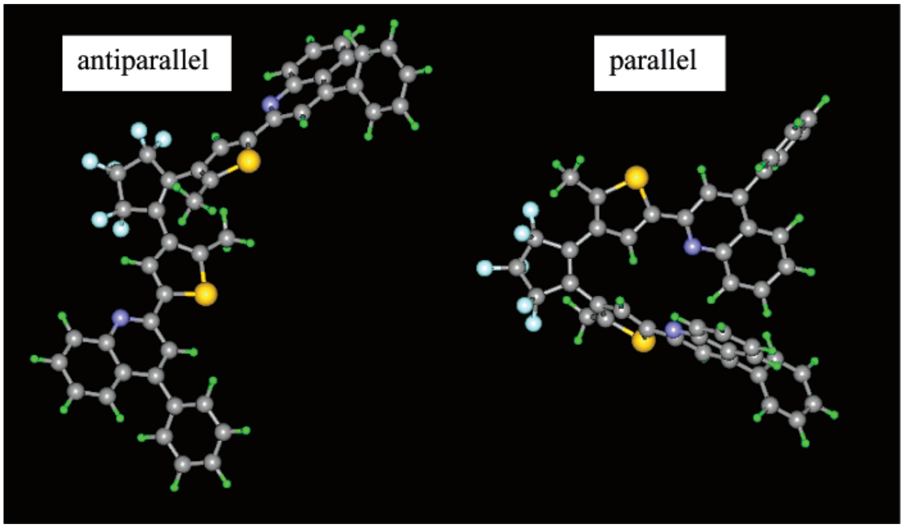

FIGURE 3. B3LYP/3-21G-optimized structures of **1**.

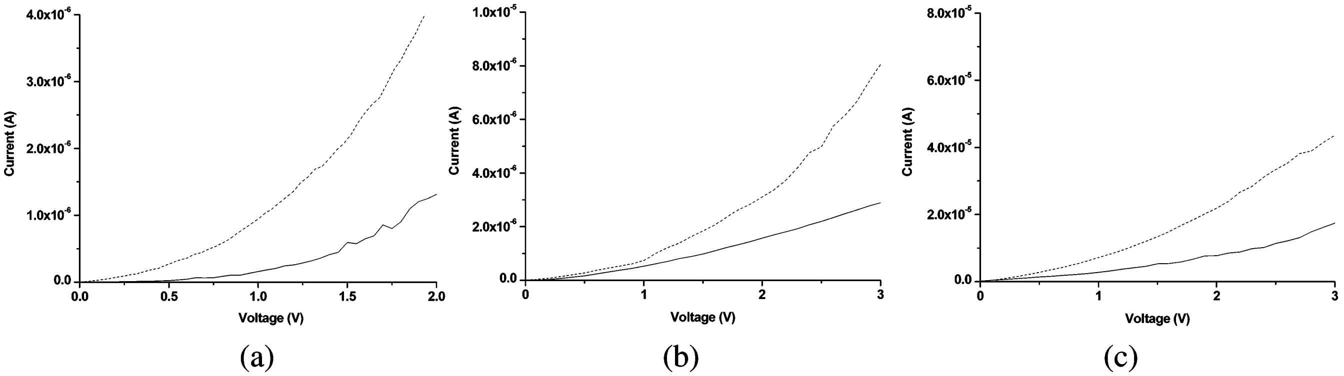

FIGURE 4. Applied voltage dependence of the current for a photocell containing polystyrene (90 wt %) and (a) **1** (10 wt %) or (b) **3** (10 wt %) and (c) the pure polymer film of **3** upon irradiation with 365 nm light (colored, dotted line) and 532 nm (bleached, solid line).

enylethene moieties.[23] Although the crystal structure of **1** provided a partial explanation for the high cyclization quantum yield, the photochromic reaction was carried out in solution. Thus, further information about the conformation of **1** in solution is important. Therefore, we have carried out ab initio calculations to investigate the relative stability of antiparallel and parallel conformers of **1** (Figure 3). The density functional theory with exchange correlation functionals of B3LYP was employed with 3-21G for the geometry optimization, and B3LYP/6-31G* calculations were carried out to obtain the relative energy at the B3LYP/3-21G-optimized geometries. All of the calculations were carried out using a suite of Gaussian 98 programs.[26] The relative stability in solution (solvent is dichloromethane, MC, and its dielectric constant is 8.93) was compared by the self-consistent reaction field (SCRF) calculations using the Onsager model,[27] which places the solute in a spherical cavity within the solvent reaction field. For Onsager model calculations, the radii of solute molecules of parallel and antiparallel structures were estimated to be 6.71 and 6.60 Å, respectively, from the volume calculations. On the basis of the B3LYP/6-31G* results in the gas phase, the antiparallel conformer is lower in energy than parallel one by 1.30 kcal/mol, and in MC solution, it is lower by 1.50 kcal/mol. The relative stability is almost the same in both the gas and solution phase. These calculation results support our discussion.

Electric Characteristics. We have examined the redox potentials of **1** and **3** by CV. The CV of the solution containing open form of compound **1** (1×10^{-3} mol/L) in dichloromethane showed an irreversible current increase beyond 1.5 V (vs Ag/AgCl). Upon excitation with UV light, the colored solution showed an irreversible oxidation peak at ~1.6 V, indicating that the oxidation potential of the closed form becomes lower than that of the open isomer. In the case of polymer **3**, the open form showed an irreversible oxidation peak at 1.1 V, which was shifted to ~1.2 V upon excitation with a UV light (365 nm) (see the Surporting Information). To examine the photoinduced electric property change, current−voltage (I−V)

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(24) Irie, M.; Mohri, M. *J. Org. Chem.* **1988**, *53*, 803.

(25) Lammi, R. K.; Ambroise, A.; Balasubramanian, T.; Wagner, R. W.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 7579.

(26) Frisch, M. J. et al. *Gaussian 98*, revision A6; Gaussian Inc.: Pittsburgh, PA, 1999.

(27) (a) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486. (b) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776. (c) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 523. (d) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1645.

characteristics were measured on a photocell containing a **1** and **3** dispersed polymer layer. Figure 4 shows the applied voltage dependence of the current for the photocells containing **1** and **3** polymer layer. The cell fabricated from closed form of **1** showed a sharp current increase by the potential rise. The current at 2 V was 3.6 times larger than that of the cell prepared from the open isomer **1** (bleached cell). The current increase by the potential rise was also observed for the open isomer **1**, but the slope of I against V of the cell fabricated from the open form of **1** was much smaller than that of the closed form. It demonstrates that the extension of π-conjugation between the thienyl rings and the ethene unit in the closed form leads higher current response in the potential than in the open form where such π-conjugation is limited. In the photocell containing **3**, the current increases 2 times larger than that of the open form at 2 V. It may be attributable to the geometrical characteristics due to the enforced configuration of the dithienylethene moieties in the polymeric form, where dithienylethene moieties are chemically bound. The electric-current characteristics depends on the carrier conductivity (σ) of the layer, and the slope of I−V curve relates to resistance ($1/\sigma$). Compounds with phenylquinoline groups show high electrical transport characteristics;[15] thus, the diarylethenes with such groups are also regarded as having electrical conductivity. Importantly, having a photochromic diarylethenes unit, the electrical properties can be modulated by UV and visible light, which can increase and decrease, respectively, the electrical conductivity. Indeed the electrical conductivity, estimated typically from the slope of a linear region in an I−V plot, is much enhanced in the closed form and reduced in the open form, as shown in Figure 4. The electrical modulation was possible by optically by using UV and visible light sources. The I−V plot for the pure film of 3 is shown in Figure 4C, indicating large increase in conductivity when it is excited by UV light.

In summary, we have synthesized a series of photochromic compounds incorporating bis(phenylquinoline)-unit and investigated the photophysical and electric transport properties. Compounds **1** and **3** show a high quantum yield due to the enforced antiparallel conformation of the dithienylethene moieties. Good transport characteristics were observed in the colored form of the diarylethenes with phenylquinoline group.

Experimental Section

All reactions were carried out under an argon atmosphere. 1,2-Bis(2-methyl-3-thienyl)perfluorocyclopentene,[2] 3,3-dibenzoylbenzidine,[28] and 1,2-bis(5-acetyl-2-methyl-3-thienyl)perfluorocyclopentene[15] were synthesized using a modified procedure from previous references. For general experimental details and instrumentation, see our previous publication.[29]

X-ray Crystallography. Suitable crystals of **1** and **2** were obtained from the recrystallization in the presence or absence of UV light in MeOH/THF. The crystals of **1** and **2** were attached to glass fibers and mounted on a diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, operating at 50 kV and 30 mA and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. All data collections were performed at 223 K. The data collection 2θ ranges are 3.24−56.88° for **1**, 3.06−49.42 for **2**, respectively. No significant decay was observed during the data collection. The raw data were processed to give structure factors using the SAINT program. Each structure was solved by direction methods and refined by full matrix least squares against F^2 for all data using SHELXTL software (version 5.10).[30] All non-hydrogen atoms in compounds **1** and **2** were anisotropically refined. All other hydrogen atoms were included in the calculated positions and were refined by using a riding model. The crystal system in compound **1** is triclinic and has a $P\bar{1}$ space group. The compounds **2** cocrystallize with methanol, and crystal system is the triclinic space groups and $P\bar{1}$. There are one and a half solvent (methanol) molecules disordered in the asymmetric unit. The disordered solvent molecules were modeled successfully and their contribution was also included in the structure factor. One of oxygen atom in methanol was heavily disordered. Therefore, the oxygen atom was divided into two parts, O50 and O50′, with an occupancy of 0.20(2) and 0.30(2), respectively. However, hydrogen atoms in methanol were not included in the calculated positions.

Determination of Quantum Yields. The quantum yield of the photochromic ring-cyclization of **1** was determined from the absorption changes at $\lambda_{\max}$ in UV spectra upon excitation with UV light for the ring-closure reaction and visible light for the ring- opening reaction. The molar extinction coefficients of **1** and **2** are 4.6×10^4 M^{-1} cm^{-1} and 4.1×10^4 M^{-1} cm^{-1} at 365 nm, respectively. The quantum yield of the photochromic ring-cyclization of **3** was determined from the ^{1}H NMR signal changes of methyl resonance peak at δ 2.05. Conversion and the number of absorbed photons were determined at a given radiation power and absorbance of the sample. Then, quantum yield was determined according to the method described in ref 31.

Electric Characteristics. A photocell was fabricated by spin coating of the solution of polystyrene (90 wt %) and compound **1** or **3** (10 wt %) and **3** (100 wt %) onto a precleaned ITO electrode coated glass and then dried at 70 °C for 24 h. The thickness of the polymer film was determined by an α-step (α-step Model-500) and was about 200 nm. Au strip (purity >99.9%, Aldrich) was vacuum deposited to a thickness of 40 nm onto the polymer film, using a mask to form devices of Au/polymer/ITO with an active area of 0.02 cm^2 per device. During the film formation and device fabrication, the color of the film was maintained. The current−voltage (I−V) characteristics were measured on a photocell at the room temperature. Each device was analyzed at least five times. The relative error of the analysis was about 5%. The I−V characteristics of the device were measured in colored state by UV excitation and then under photostationary conditions (irradiating the device with 532 nm laser for 2 h) to convert the diarylethene unit in an open form. The potential change from 0 to 2 V and 2 to 0 V was repeated for at least 10 cycles but there was no detectable decomposition during the cycles.

1,2-Bis[5-(4-phenylquinolinyl)-2-methyl-3-thienyl]perfluorocyclopentene (1). A mixture of 1,2-bis(5,5'-diacetyl-2-methyl-3-thienyl)perfluorocyclopentene (1 g, 2.21 mmol), 2-aminobenzophenone (0.959 g, 4.86 mmol), and diphenyl phosphate (11 g) in toluene (10 mL) was purged with argon for 20 min. The mixture was refluxed at 120 °C overnight. The mixture was precipitated into 10% triethylamine/ethanol. The product was purified on silica gel column (eluent 1:1 CH_2Cl_2/hexane) to give **1** in 70% yield: mp 204 °C; ^{1}H NMR ($CDCl_3$) δ 8.12 (d, J = 8.10 Hz, 2H), 7.85 (d, J = 8.10 Hz, 2H), 7.73 (s,

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(28) Pelter, M. W.; Stille, J. K. *Macromolecules* **1990**, *23*, 2418.

(29) (a) Kim, S.; Kim, J. S.; Kim, S. K.; Suh, I.-H.; Kang, S. O.; Ko, J. *Inorg. Chem.* **2005**, *44*, 1846. (b) Lee, T.; Jung, I.; Song, K. H.; Lee, H.; Choi, J.; Lee, K.; Lee, B. J.; Pak, J. Y.; Lee, C.; Kang, S. O.; Ko, J. *Organometallics* **2004**, *23*, 5280.

(30) SHELXTL NT Crystal Structure Analysis Package, Version 5.14; Bruker AXS, Analytical X-ray System, Madison, WI, 1999.

(31) Mejiritski, A., Polykarpov, A. Y., Sarker, A. M., Neckkers, D. C., J. *Photochem. Photobiol.* **1997**, *108*, 289.

2H), 7.68 (d, J = 5.70 Hz, 4H), 7.52 (m, 6H), 7.48 (m, 4H), 7.42 (s, 2H), 2.03 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 150.8, 149.5, 148.5, 145.5, 143.6, 138.0, 130.5, 129.7, 129.2, 128.7, 128.1, 127.1, 126.7, 126.0, 125.1, 117.3, 116.2, 115.2, 114.2, 15.2 Anal. Calcd for $C_{45}H_{28}F_6N_2S_2$: C, 69.75; H, 3.64. Found: C, 69.42; H, 3.51.

Closed-Ring Isomer of 1 (2). Compound **2** was isolated by chromatographing a photostationary solution containing **1** and **2** through HPLC (silica gel column) with hexane as the eluent to yield a blue powder: ^1H NMR ($CDCl_3$) δ 8.14 (d, J = 9.00 Hz, 2H), 7.83 (d, J = 8.70 Hz, 2H), 7.74 (s, 2H), 7.71 (d, J = 6.60 Hz, 4H), 7.55 (m, 6H), 7.45 (m, 4H), 7.08 (s, 2H), 2.31 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 150.4, 149.2, 147.5, 144.5, 143.3, 137.8, 131.5, 129.2, 128.2, 127.3, 127.1, 126.4, 126.2, 126.0, 125.4, 118.3, 117.2, 115.2, 113.2, 15.7 Anal. Calcd for $C_{45}H_{28}F_6N_2S_2$: C, 69.75; H, 3.64. Found: C, 69.32; H, 3.41.

Poly(2,2'-(1,2-bis(2-methyl-3-thienyl)perfluorocyclopentenylene-6,6'-bis(4-phenylquinoline))) (3). 1,2-Bis(5,5'-diacetyl-2-methyl-3-thienyl)perfluorocyclopentene (0.30 g, 0.66 mmol), 3,3'-dibenzoylbenzidine (0.26 g, 0.66 mmol), diphenyl phosphate (4.83 g), and *m*-cresol (5 g) were placed to a Schlenk tube. The tube was purged with argon. The reaction temperature was raised to 130−135 °C. The polymerization mixture was stirred at this temperature for 60 h and then precipitated into 10% triethylamine/ethanol. The green solid was isolated, and the polymer was extracted with 20% triethylamine/ethanol. The polymer was dissolved in $CHCl_3$ and precipitated into ethanol. The resulting polymer **3** was dried under vacuum for 12 h: yield 0.37 g (70%); ^1H NMR ($CDCl_3$) δ 8.15 (d, 2H), 8.09 (s, 2H), 8.00 (d, 2H), 7.71 (s, 2H), 7.54 (br, 10H), 7.42 (s, 2H), 2.05 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 151.0, 149.5, 148.2, 145.6, 143.7, 138.2, 137.9, 136.2, 129.8, 129.4, 129.0, 128.7, 127.7, 126.3, 126.0, 125.5, 123.9, 117.9, 117.4, 116.3, 15.0. Anal. Calcd for $C_{45}H_{26}F_6N_2S_2$: C, 69.94; H, 3.39. Found: C, 69.56; H, 3.28.

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Supporting Information Available: Tables listing crystallographic information, atomic coordinates and U(eq) values, and intramolecular bond distances and angle and crystallographic data (CIF) for **1** and **2** and cyclic voltammogram data for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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