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Highly Fluorescent and Photochromic Diarylethene Oligomer Bridged by *p*-Phenylenevinylene

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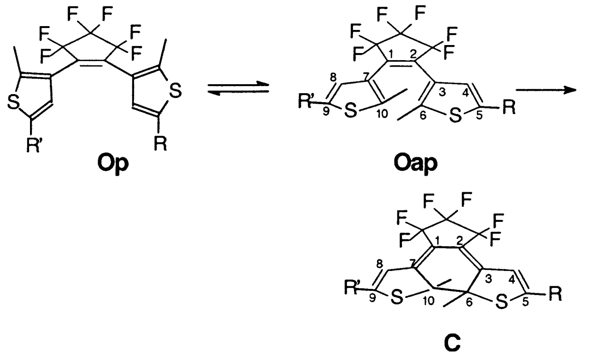
Introduction. Fluorescent photochromic materials collect strong interest for their possible application in optical memory as well as in fluorescent probe. In particular, fluorescent diarylethenes, which show reversible change in fluorescence intensity with photochromic reaction, are useful for the nondestructive optical readout system. Since diarylethene molecules do not show strong fluorescence, they are modified by substituting a fluorescent chromophore such as anthracene, 2,4,5-triphenylimidazole, diporphyrins, or tungsten complex.[1−3] These diarylethenes having a fluorescent group showed interesting fluorescent photochromic properties; however, the fluorescence quantum yields (Φ_F) of them are rather low (9.1% maximum). Furthermore, Φ_F of those diarylethenes decreased with increasing photocyclization quantum yields (Φ_{pc}). Such an interplay between photochromism and fluorescence are best understood by existence of two different conformations in the open state: the so-called antiparallel (O_{ap}) conformation and the parallel conformation (O_p).[4] In the previous fluorescent diarylethenes, the rotation between C2−C3 (and C1−C7, C5−R, C9−R′) in the open form (eq 1) is facile, and thus the population of O_{ap}:O_p in solution is about 1:1.

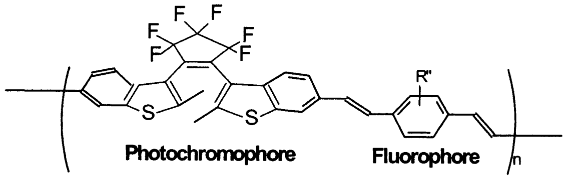


(1)

Photocyclization of diarylethene to a colored state (C) can proceed only from the O_{ap} conformation,[5] while the conformer O_p is involved in the fluorescence. Therefore, diarylethenes with high Φ_{pc} shows low Φ_F. Furthermore, rotation between C2−C3 (and C1−C7) in the open form is considered to increase radiationless transition to the ground state, resulting in low Φ_F. Thus, Φ_F of 0.4 in 2,4,5-triphenylimidazole was decreased to 0.091 when 2,4,5-triphenylimidazole was substituted to a diarylethene unit.[3] Therefore, the materials having both high photochromic conversion and fluorescence have to be designed in a way to overcome such interplay between photochromism and fluorescence, by controlling the population of conformation isomers, deterring rotation between C2−C3 (and C1−C7) in the open form, and introduction of an appropriate fluorophore.

To achieve high photochromic quantum yield (Φ_{pc}), it is crucial to increase population of O_{ap} in the ground state or photoexcited state.[2,6,7] Thus, polymers having dithienylethenes in the main chain showed a high cyclization quantum yield due to the enforced antiparallel conformation of the dithienylethene moieties.[6] Recently, Irie et al. reported increased Φ_{pc} from 0.21 to 0.40 by increasing the number of the dithienylethene moieties in the multidithienylethene arrays, in which two, three, or four 1,2-bis(2,4-dimethylthiophen-3-yl)-perfluorocyclopentenes are ethynylene-bridged.[8]

Highly fluorescent diarylethene could be prepared by linking the diarylethene unit to a fluorescent bis (phenylethynyl)anthracene; however, it shows poor photochromic color contrast due to large absorption at 400−500 nm in both O and C forms.[9] Thus, we designed new types of diarylethene oligomers having a fluorophore bridge between the diarylethene units. As a fluorophore bridge, we use *p*-phenylenevinylene (PPV) derivatives since they show strong fluorescence. Furthermore, PPV has a planar structure that may induce planarity (antiparallel) in a diarylethene unit and reduce the rotation between C2−C3 (and C1−C7). To minimize interaction between the fluorophores, we designed an alternating copolymer type of photochromophore and fluorophore, as described below:



BTF-PPV

Here we report the synthesis and novel dual functionality (photochromic and fluorescent property) of a *p*-phenylenevinylene (PPV)-linked diarylethene oligomer, BTF−PPV.

Experimental Section. a. Materials. Potassium *tert*-butoxide (1.0 M solution in THF) was purchased from Aldrich and used as received. Triphenylphosphine was purchased from Aldrich and recrystallized from hexane. Solvents were dried and purified by fractional distillation over sodium/benzophenone and handled in a moisture-free atmosphere. Column chromatography was performed using silica gel (Merck, 250−430 mesh). 1,2-Bis(2-methylbenzo[*b*]thiophene-3-yl)hexafluorocyclopentene (**4**),[10] 1,2-bis(6-formyl-2-methylbenzo[*b*]thiophene-3-yl)hexafluorocyclopentene (**1**),[11] 1-(6-(2-phenylethenyl)-2-methylbenzo[*b*]thiophene-3-yl), 2-(2-methylbenzo[*b*]thiophene-3-yl)hexafluorocyclopentene (**5**),[12] and 1,4-bis(triphenylphosphonionmethyl)benzene dibromide[13] were synthesized according to the literature.

b. Synthesis of 3 (BTF−PPV). Compound **1** (0.7 g, 1.3 mmol) and 1,4-bis(triphenylphosphonionmethyl)benzene dibromide (1.05 g, 1.3 mmol) were dissolved in $CHCl_3$ (10 mL) at room termperature. To the above solution was added dropwise a solution of potassium

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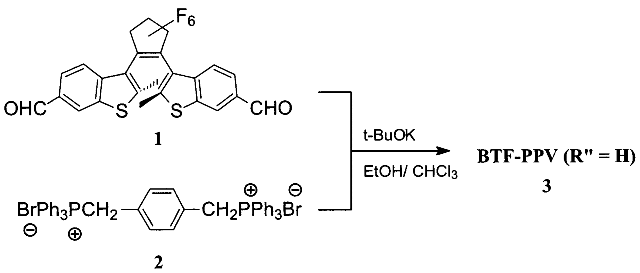
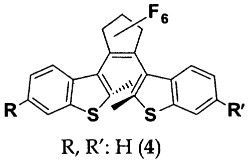
Scheme 1. Synthetic Route of BTF−PPV



tert-butoxide (0.75 g, 6.6 mmol) dissolved in 10 mL of EtOH. After stirring for 24 h, solvent was removed, to give yellow solids. Then, the product was redissolved in dichloromethane and precipitated in methanol. The product yield (BTF−PPV) was 62%. M_n, 2702; M_w, 3806 ($M_w/M_n = 1.40$). ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.22 (s, 3H), 2.50 (s, 3H), 6.16 (m, 4H), 7.06−7.19 (4H), 7.58−7.84 (m, 4H), 8.06−8.14 (m, 2H).

Results and Discussion. BTF−PPV was synthesized starting from 1,2-bis(2-methylbenzo[*b*]thiophene-3-yl)hexafluorocyclopentene derivative with a fluorescent builder. Scheme 1 describes the synthetic route of BTF−PPV (**3**) by the Wittig polycondensation reaction of a diarylethene derivative having aldehyde groups (**1**) and 1,4-bis(triphenylphosphoniomethyl)benzene dibromide (**2**). Thus, compound **1** was reacted with compound **2** under potassium *tert*-butoxide in a mixture of chloroform and ethanol, at room temperature. The oligomer was obtained as a pale yellow powder, which was soluble in common solvents such as dichloromethane and tetrahydrofuran. Weight-average molecular weight (M_w) of the resultant oligomer was ~3800 ($M_w/M_n = 1.4$), indicating that about five molecules of diarylethene and PPV unit are linked together. The ^{1}H NMR spectrum of **3** indicated that the oligomer consists of a diarylethene unit plus PPV unit. The peaks at 2.2−2.5 and 7.3−8 ppm are characteristic of the proton resonance of a methyl and an aromatic ring, respectively, in the diarylethene unit. The peaks at ~6.6 and 6.9−7.3 ppm are characteristic of the proton resonance of vinyl and phenylene ring, respectively, of the PPV unit. The rest of the proton resonance for phenylene ring of PPV is possibly overlapped with those of diarylethene at 7.6−8 ppm. Interestingly, the intensity of methyl peaks at 2.2 ppm, characteristic of antiparallel (ap) conformer, was 5 times higher than that of parallel (p) (2.5 ppm). This result indicates that the content of an ap isomer in BTF−PPV is ~5 times higher than the p conformer.

Figure 1 shows the absorption spectral change of **3** in CHCl$_3$ by photoirradiation, as compared to monomeric type **4** and **5**. Upon irradiation with 325 nm light, the colorless solution of the open form of oligomer **3** turned deep red, in which characteristic absorption maxima were observed at 381 and 555 nm. The red color indicates formation of the ring-closed isomer (C). Upon visible (λ > 540 nm) light irradiation, the red color disappeared, indicating the formation of initial open form (O).



R, R′: H (**4**)
R, R′ : CH=CH-C$_6$H$_5$ (**5**)

The λ_{max} of the open form of **3** was observed at 339 nm, which is shifted toward longer wavelength as compared with those of the monomeric type (**4** and **5**). Similarly, the λ_{max} at 555 nm for closed isomer at visible region was also shifted toward longer wavelength as compared with those of **4** and **5**. This result indicates that the structures of the singlet excited state for both C and O form of **3** were stabilized compared to the monomeric type, possibly due to increased π-delocalization.

Interestingly, photochromic conversion of BTF−PPV was high as determined from the slope of the absorbance increase with irradiation time.[14] The quantum yield of photocyclization (Φ_{pc}) for **3** was determined as 0.38, which was comparable to that of tetramer (0.40 in hexane) bridged by ethynylene group.[8]

Figure 2 shows fluorescence spectra for BTF−PPV (**3**), **4**, and **5** in CHCl$_3$ (1×10^{-5} M). Surprisingly strong emission with λ_{max} at 450 nm was observed from the open form of **3**, when excited with a UV light. The fluorescence intensity of **3** was much higher than those of monomeric diarylethenes (**4** and **5**) as compared in Figure 2a,b.

The fluorescence quantum yield (Φ_F) for the open form of **3** was determined as 0.53, which is quite high as compared to that of other photochromic diarylethenes. On the other hand, Φ_F for open form of **4** and **5** were 0.02 and 0.05, respectively. Thus, both the photochromic response and fluorescence quantum yields of the polymer **3** were increased by incorporating PPV unit, as compared to those of monomeric diarylethenes.

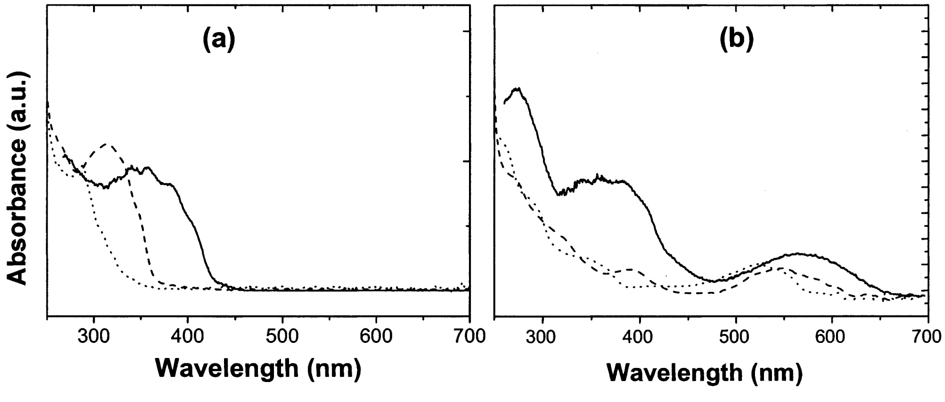


Figure 1. Absorption spectra of **3** (solid line), **4** (dot), and **5** (dash) in open form (a) and those in closed form (b) in chloroform (1×10^{-5} M).

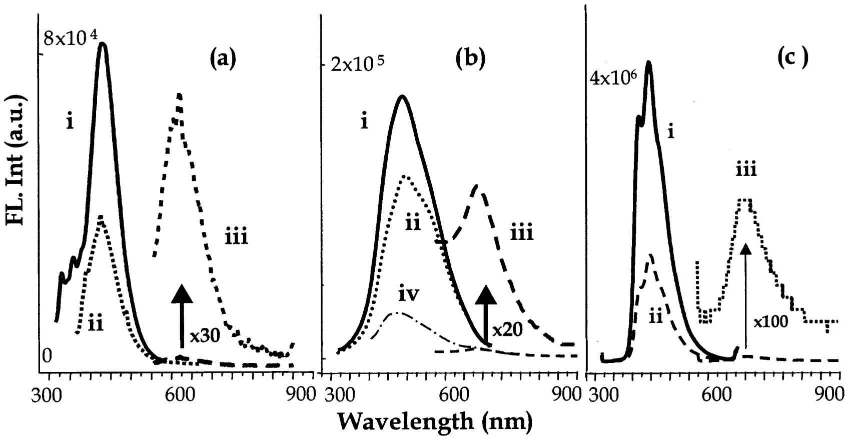


Figure 2. Emission spectra of **4** (a), **5** (b), and **3** (c) in open form (i, excited at λ_{max} of open form) and in closed form (ii ∼ iv) excited at λ_{max} of closed form in UV region (ii and iv) and that in visible region (iii).

Table 1. Fluorescence Property of BTF−PPV Oligomer (3) As Compared with That of Diarylethene Molecules (4 and 5) in CHCl$_3$

sample	state of diarylethene	λ_{ex},[a] nm	λ_{em},[b] nm	Φ_F[c]
3	open	339	450 (i)	0.16
	open	381	450	0.53
	closed	339	450 (ii)	0.07
	closed	555	673 (iii)	0.0019
4	open	297	432 (i)	0.02
	closed	297	432 (ii)	0.006
	closed	520	621 (iii)	0.0007
5	open	313	491 (i)	0.051
	closed	313	491 (ii)	0.036
	closed	545	664 (iii)	0.001
	closed	389	480 (iv)	0.008

[a] Excitation wavelength (λ_{max} in UV or visible region). [b] λ_{max} of emission band. Numbers i ∼ iv correspond to those in Figure 2. [c] Determined by using quinine sulfate solution as a reference.[15]

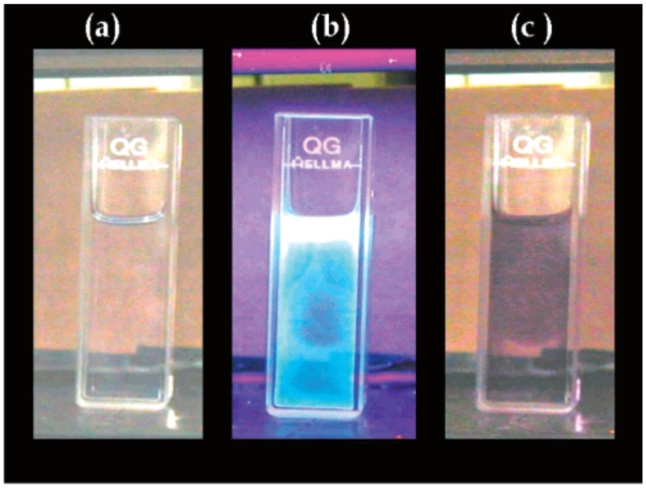


Figure 3. Photographs of a solution containing **3** in chloroform (1 × 10^{-4} M): (a) before UV irradiation under room light, (b) under UV irradiation in a dark room, and (c) after UV irradiation under room light.

The results of the steady-state fluorescence study are summarized in Table 1. Φ_F of the closed form of **3,** excited at 339 nm, was lower than that of the open form but much higher than those of the closed form of **4** and **5**. Importantly, the fluorescence quantum yield difference ($\Delta\Phi_F$**)** between the open vs closed form of **3**, excited both at 339 nm, was much larger than those of monomeric diarylethenes, as compared in Table 1. This result strongly indicates potential application of the polymer **3** in a nondestructive optical reading system, where the fluorescence difference between marked and unmarked area is important.

Φ_F for the closed isomer, excited in the visible region, was low in all three samples (Table 1). Such a result correlates well with the previous observation that the closed isomers do not emit significantly.[3,9,16] Figure 3 shows photographs of a solution containing **3** in chloroform in three different states: (a) before UV irradiation under room light (ring open form, O), (b) under UV irradiation in a dark room (ring opened excited state, O*), and (c) after UV irradiation under room light (ring closed form, C). The photographs show clearly the visible difference between the C and O forms. Further characterization and application of PPV bridged diarylethene oligomers are in progress and will be published later.

In conclusion, a new type of fluorescent diarylethene oligomer was synthesized by connecting diarylethene unit with PPV through Wittig polycondensation reaction. Such connections of PPV with diarylethene unit are an effective strategy for obtaining dual functionality of photochromism and fluorescence with high Φ_F.

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