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Thermally Irreversible Photochromic Systems. Substituent Effect on the Absorption Wavelength of 11,12-Dicyano-5a,5b-dihydro-5a,5b-dimethylbenzo[1,2-*b*:6,5-*b*′]bis[1]benzothiophene

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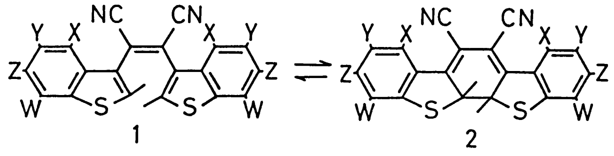
Cyano- and halogen-substituted 1,2-bis(1-benzothiophen-3-yl)ethene derivatives were synthesized in an attempt to obtain compounds with sensitivity at longer wavelengths. Under UV irradiation, the derivatives underwent ring closure reactions to form the substituted 11,12-dicyano-5a,5b-dihydro-5a,5b-dimethylbenzo[1,2-*b*:6,5-*b*′]bis[1]benzothiophenes. Among cyano-substituted compounds, the 3,8-dicyano derivative showed an absorption maximum at the longest wavelength, 530 nm, which is 23 nm longer than the maximum of the unsubstituted compound. The absorption maximum of the 3,8-difluoro derivative, on the other hand, was 28 nm shorter than the maximum of the 2,9-difluoro derivative. Although the absorption maximum shift of the calculated values (MO INDO/S) by cyano substitution agreed well with the observed maxima, the calculation hardly reproduced the shift by halogen substitution.

Although photochromic organic compounds have potential for use in rewritable optical memory media,[1,2] the compounds still await practical applications. The conditions indispensable for the applications are i) thermal stability of both isomers, ii) a fatigue-resistant property,[3,4] iii) non-destructive read-out capability and iv) high sensitivity at diode laser wavelengths. Recently, it has been shown that 1,2-bis(1-benzothiophen-3-yl)ethene derivatives undergo thermally irreversible photochromic reactions, and their coloration/decoloration cycles are able to be repeated more than 6000 times without any loss of performance.[5] In this study, we have investigated the substituent effect on the absorption wavelength of 11,12-dicyano-5a, 5b-dihydro-5a, 5b-dimethylbenzo[1,2-*b*: 6,5-*b*′]bis [1] benzothiophene (the closed-ring form of 1,2-dicyano-1,2-bis(2-methyl-1-benzothiophen-3-yl)ethene) in order to obtain compounds with sensitivity at longer wavelengths. Cyano and halogen groups were chosen as the substituents, because these groups are known to be effective in modifying organic colorants.[6]

Results and Discussion

Synthesis and Photochromic Character of Cyano-Substituted 1,2-Dicyano-1,2-bis(2-methyl-1-benzothiophen-3-yl)ethene Derivatives. 1,2-Dicyano-1,2-bis(4-cyano-2-methyl-1-benzothiophen-3-yl)ethene (**1a**) was prepared by the coupling reaction of two molecules of 4-cyano-3-(cyanomethyl)-2-methyl-1-benzothiophene.[5] The cis and trans isomers were separated by HPLC and recrystallized from hexane–benzene (1 : 1). 5,5′-, 6,6′-, and 7,7′-Dicyano-substituted compounds, **1b**, **1c**, and **1d**, were also prepared by the coupling reactions of appropriate 1-benzothiophenes and purified in a manner similar to **1a**.



a :X=CN, Y=Z=W=H
b :Y=CN, X=Z=W=H
c :Z=CN, X=Y=W=H
d :W=CN, X=Y=Z=H
e :X=F, Y=Z=W=H
f :Y=F, X=Z=W=H
g :Z=F, X=Y=W=H
h :Y=Cl, X=Z=W=H
i :Y=Br, X=Z=W=H
j :X=Y=Z=W=H

Figure 1a illustrates the absorption spectral change of a benzene solution of **1a** (λ_{max} 312 nm, ε 12000) by irradiation with 334 nm light. Irradiation of the benzene solution with the light led to a decrease of the

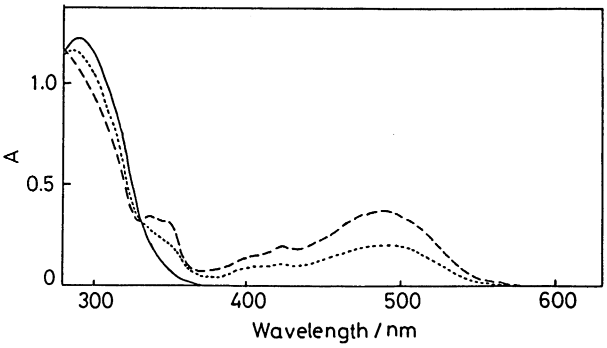


Fig. 1a. Absorption spectra of benzene solutions of **1a** (1×10^{-4} mol dm^{-3}) (——), **2a** (– – – –), and **2a** at the photostationary state (······) under irradiation with 334 nm light.

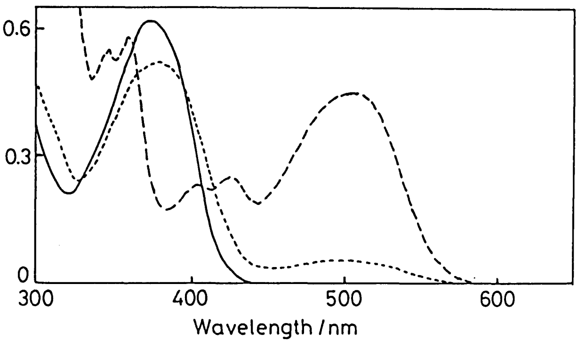


Fig. 1b. Absorption spectra of benzene solutions of **1b** (1×10^{-4} mol dm^{-3}) (——), **2b** (----), and **2b** at the photostationary state (······) under irradiation with 380 nm light.

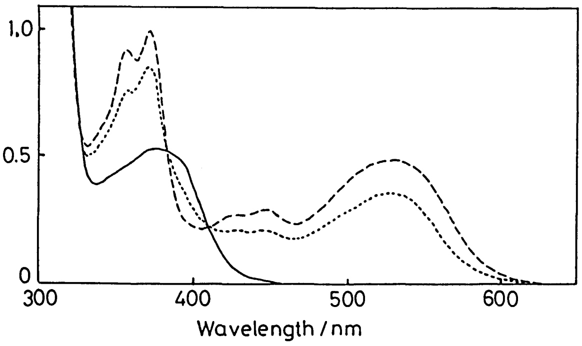


Fig. 1c. Absorption spectra of benzene solutions of **1c** (1×10^{-4} mol dm^{-3}) (——), **2c** (----), and **2c** at the photostationary state (······) under irradiation with 405 nm light.

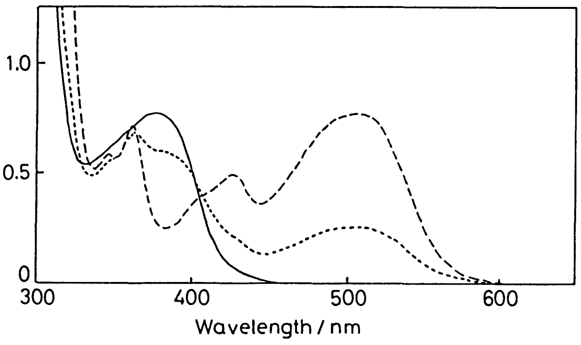


Fig. 1d. Absorption spectra of benzene solutions of **1d** (1×10^{-4} mol dm^{-3}) (——), **2d** (----), and **2d** at the photostationary state (······) under irradiation with 405 nm light.

absorption at 312 nm, and the formation of a red solution, in which a visible absorption at 486 nm (ε 4800) is observed. The absorption maximum of **2a** showed a 21 nm blue shift in comparison with that of the closed-ring form of the unsubstituted compound, 1,2-dicyano-1,2-bis(2-methyl-1-benzothiophen-3-yl)ethene (**2j**; $\lambda_{\max}$ 507 nm).

Figures 1b—1d illustrate the absorption spectral changes of benzene solutions of **1b** ($\lambda_{\max}$ 373 nm, ε 6200), **1c** ($\lambda_{\max}$ 380 nm, ε 4800), and **1d** ($\lambda_{\max}$ 378 nm, ε 7700) by irradiation with ultraviolet light. The absorption maxima of the photogenerated closed-ring forms, **2b**—**2d**, are 506 nm (**2b**, ε 4500), 530 nm (**2c**, ε 4800), and 505 nm (**2d**, ε 7700), respectively. The fractions of the closed-ring forms in the total isomers, (closed-ring form)/(closed-ring form+trans open-ring form+cis open-ring form), at the photostationary state under irradiation with ultraviolet light were 0.59 for **2a** (irradiation wavelength, 334 nm), 0.15 for **2b** (380 nm), 0.72 for **2c** (405 nm), and 0.33 for **2d** (405 nm). Substitutions at the 5,5′- and 7,7′-positions of the benzothiophene moieties with cyano groups showed little effect on the absorption wavelength of the closed-ring forms. On the other hand, substitutions at the 6,6′-positions brought about a spectral shift to longer wavelengths as much as 23 nm in comparison with the unsubstituted compound.

In the spectra of Fig. 1b and 1d, no isosbestic points were observed. This is due to the presence of cis to trans isomerization in addition to the ring closure reactions. At the photostationary state, the spectra include the closed-ring, the cis, and the trans forms.

Synthesis and Photochromic Character of Halogen-Substituted 1,2-Dicyano-1,2-bis(2-methyl-1-benzothiophen-3-yl)ethene Derivatives. 1,2-Dicyano-1,2-bis(2-methyl-1-benzothiophen-3-yl)ethenes that have halogen substituents on their aromatic rings were synthesized by a method similar to that used for cyano-substituted derivatives. 4,4′-, 5,5′-, and 6,6′- Difluoro-substituted compounds (**1e**, **1f**, and **1g**), 5,5′-dichloro-substituted compound **1h**, and 5,5′-dibromo-substituted compound **1i** were prepared.

Figure 2a illustrates the absorption spectral change of a benzene solution of **1e** ($\lambda_{\max}$ 375 nm, ε 4500) by irradiation with 385 nm light. The irradiation caused a decrease of the absorption at 375 nm and an increase in the visible absorption at 482 nm (ε 4800). The absence of an isosbestic point suggests the presence of cis to trans isomerization in the reaction. 1,10-Difluoro-

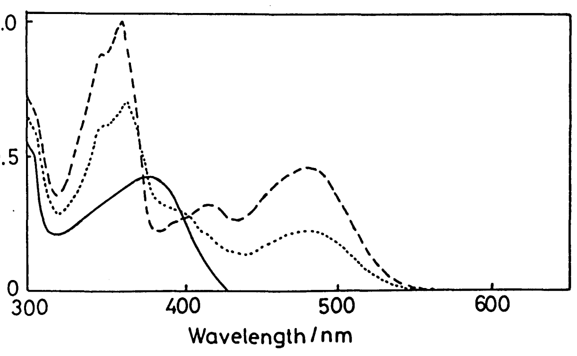


Fig. 2a. Absorption spectra of benzene solutions of **1e** (1×10^{-4} mol dm^{-3}) (——), **2e** (----), and **2e** at the photostationary state (······) under irradiation with 385 nm light.

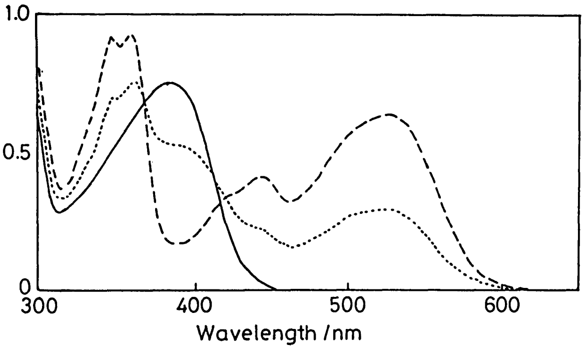


Fig. 2b. Absorption spectra of benzene solutions of **1f** $(1\times10^{-4}\ \mathrm{mol\,dm^{-3}})$ (——), **2f** (----), and **2f** at the photostationary state (······) under irradiation with 390 nm light.

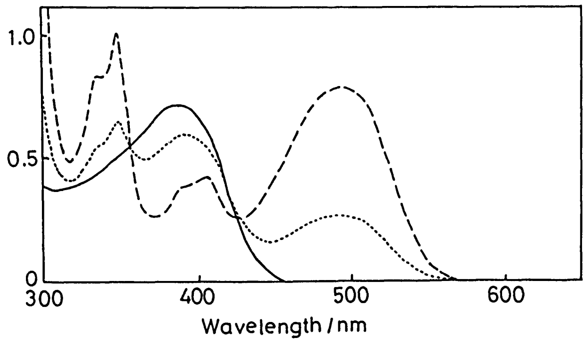


Fig. 2c. Absorption spectra of benzene solutions of **1g** $(1\times10^{-4}\ \mathrm{mol\,dm^{-3}})$ (——), **2g** (----), and **2g** at the photostationary state (······) under irradiation with 390 nm light.

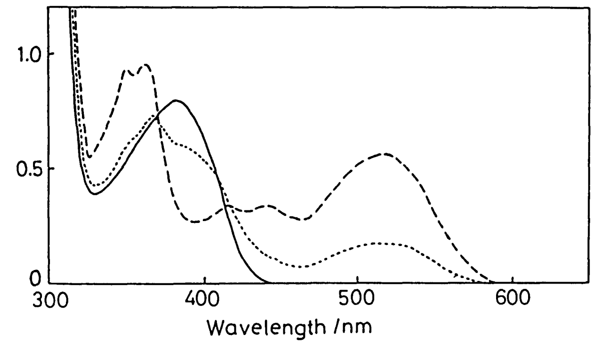


Fig. 2d. Absorption spectra of benzene solutions of **1h** $(1\times10^{-4}\ \mathrm{mol\,dm^{-3}})$ (——), **2h** (----), and **2h** at the photostationary state (······) under irradiation with 390 nm light.

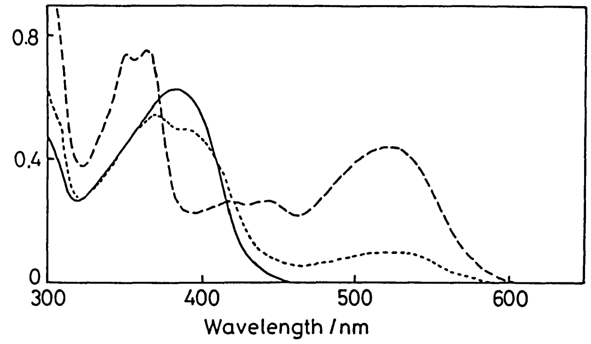


Fig. 2e. Absorption spectra of benzene solutions of **1i** $(1\times10^{-4}\ \mathrm{mol\,dm^{-3}})$ (——), **2i** (----), and **2i** at the photostationary state (······) under irradiation with 390 nm light.

substituted compound **2e** showed a 28 nm blue shift in comparison with **2j**. The blue shift was similar to that observed for 1,10-dicyano-substituted compound **2a**.

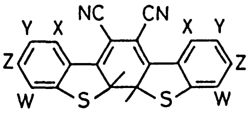
Figures 2b, 2c illustrate the absorption spectral changes of benzene solutions of **1f** ($\lambda_{\max}$ 385 nm, ε 9100) and **1g** ($\lambda_{\max}$ 386 nm, ε 7100) by irradiation with ultraviolet light. The absorption maxima of the photogenerated closed-ring forms of **1f** and **1g** are 527 nm (**2f**, ε, 7700) and 499 nm (**2g**, ε 7800), respectively. The fractions of the closed-ring form in the total isomers, (closed-ring form)/(closed-ring form+trans open-ring form+cis open-ring form), at the photostationary state under irradiation with ultraviolet light were 0.50 for **2e** (irradiation wavelength, 385 nm), 0.48 for **2f** (390 nm), and 0.32 for **2g** (390 nm). In the case of the fluoro-substituted derivatives, substitution at the 2,9-positions was the most effective for shifting the absorption band to longer wavelengths.

Substitutions at the 5,5′-positions of the benzothiophene moieties with chloro and bromo groups also brought about the spectral shifts of their closed-ring forms to longer wavelengths. Figures 2d and 2e illustrate the absorption spectral changes of the benzene solution of **1h** ($\lambda_{\max}$ 381 nm, ε 9600) and **1i**($\lambda_{\max}$ 383 nm ε7300) by irradiation with ultraviolet light. The absorption maxima of the photogenerated closed-ring forms of **1h** and **1i** are observed at 519 nm (**2h**, ε 6700), and 523 nm (**2i**, ε 5100), respectively. The fractions of the closed-ring form in the total isomers at the photostationary state were rather low (0.30 for **2h** and 0.23 for **2i** by irradiation with 390 nm light). The absorption maxima of the closed-ring forms shifted to longer wavelengths in the order of Cl<Br<F. On the other hand, the fraction of the closed-ring form at the photostationary state increased in the order of Br<Cl<F. The low yield of the closed-ring forms for bromo- and chloro-substituted compounds is possibly due to the heavy atom effect.

Theoretical Calculation of the Absorption Wavelengths. Table 1 summarizes the absorption maximum wavelengths of the closed-ring forms as determined experimentally and predicted by theoretical calculations. The absorption wavelengths and the oscillator strengths were calculated by the semiempirical MO INDO/S method. The excitation energy of this INDO/S method was calculated including all valence electrons; not only π-electrons but also σ-electrons. The method is appropriate for nonplanar molecules like our closed-ring forms.[7)]

The tendency of the shift of the calculated values by

Table 1. Experimental and Calculated λ_{max} Values of Closed-Ring Forms



	X	Y	Z	W	Calculated	Experimental
					λ_{max}/nm., (Oscillator strength)	λ_{max}/nm (ε)
2a	CN	H	H	H	489 (0.74), 342 (0.08), 321 (0.02), 269 (0.01), 234 (0.17)	486 (4800)
2b	H	CN	H	H	508 (0.75), 329 (0.04), 316 (0.02), 263 (0.27), 226 (0.59)	506 (4500)
2c	H	H	CN	H	531 (0.92), 326 (0.18), 308 (0.03), 284 (0.25), 237 (0.34)	530 (4800)
2d	H	H	H	CN	502 (0.75), 334 (0.05), 321 (0.005), 261 (0.14), 224 (0.45), 179 (0.24), 169 (0.13)	505 (7700)
2e	F	H	H	H	—	482 (4800)
2f	H	F	H	H	507 (0.72), 327 (0.12)	527 (7700)
2g	H	H	F	H	—	499 (7800)
2h	H	Cl	H	H	502 (0.73), 318 (0.09)	519 (6700)
2i	H	Br	H	H	501 (0.74)	523 (5100)
2j	H	H	H	H	502 (0.72), 310 (0.12), 297 (0.02), 266 (0.23), 224 (0.40)	507 (8200)

cyano-substitution qualitatively agreed well with the observed absorption maxima. The cyano-substitution at the 1,10-positions of the closed-ring form brought about an absorption spectral shift to shorter wavelengths, while substitution at the 3,8-positions caused a bathochromic shift. Substitution at the 2,9- and 4,7-positions scarcely affected the absorption maximum, and the maxima were similar to that of the unsubstituted compound.

The blue shift observed for the 1,10-substituted compound suggests that substitution at the 1,10-positions possibly destroyed the π-conjugation because of the steric hindrance between the substituted cyano groups and the cyano groups on the ethylenic double bond. This was confirmed by the MOPAC/AM1 calculation of the geometrical optimization of the closed-ring forms. The cyano groups of the 2,9-, 3,8-, and 4,7-substituted compounds lay in the plane of the 1-benzothiophene rings, while the cyano groups of the 1,10-substituted compound were situated out of the plane, the N atom of the cyano group being apart from the 1-benzothiophene plane as much as 0.225 Å. The calculated λ_{max} values for the 1,2-bis(2-methyl-1-benzothiophen-3-yl)ethene derivatives that had no cyano group on their ethylene moieties showed the longer wavelength for the 1,10-substituted compound (506 nm) in comparison with the 2,9-substituted (455 nm), 3,8-substituted (491 nm), and 4,7-substituted compounds (487 nm). The blue shift observed for 1,10-substituted **2a** is due to its steric hindrance.

Experimental

^{1}H NMR spectra were recorded in $CDCl_3$ with a 100 MHz NMR spectrometer (JEOL-FX100). Absorption spectra were measured with a spectrophotometer (Hitachi U-3410). A high pressure mercury lamp (Ushio, 1 kw) and a Xe lamp (Ushio, 500 W) were used as light sources. Mercury lines were isolated by passing the light through a monochrometer (Jobin Yvon H10-UV). Spectrophotometric grade benzene was used as the solvent.

Calculation Method. The geometry of each isomer was optimized by using the semiempirical MO AM1 method[8] without any symmetry constraints. The optimization process was continued until the norm of the gradient remained less than 1.0.

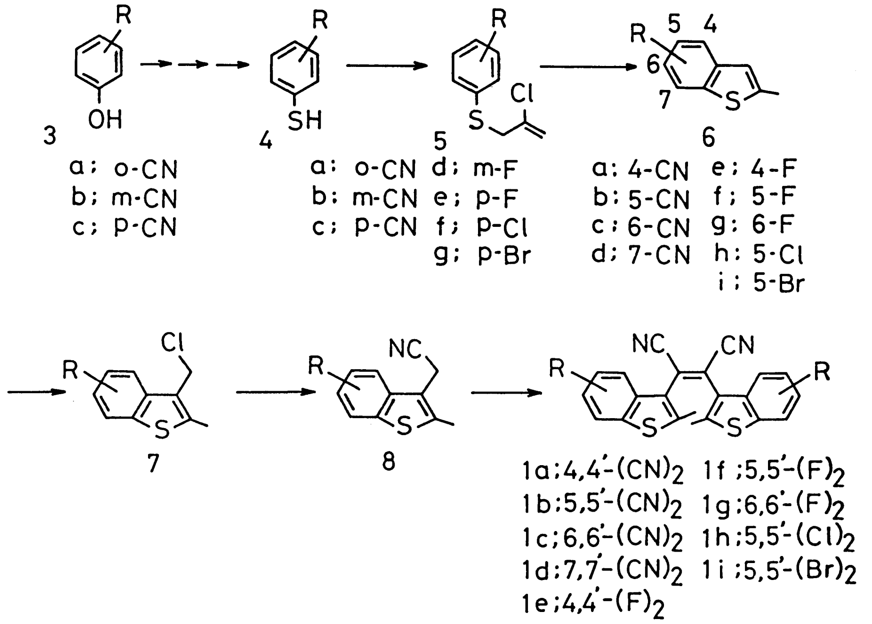
The absorption wavelengths and oscillator strengths were calculated by the semiempirical MO INDO/S method,[9] which is a modified version of the INDO/1 method for spectroscopic properties. The two-center electron repulsion integrals were evaluated by the Mataga-Nishimoto formula.[10] The configuration interaction (CI) up to 197 configurations generated through the single excitation was carried out by adopting the 13 highest occupied orbitals and 13 lowest unoccupied orbitals. The calculated values (λ^{calcd}) of λ_{max} listed in Table 1 were given by correction of originally calculated values (λ^{orig}) using the following equation.

$$\lambda^{calcd}=2.63\times\lambda^{orig}-481$$

The correction equation was determined by the least-squares method to fit the observed λ_{max} values.

Materials. 1,2-Dicyano-1,2-bis (2-methyl-1-benzothiophen-3-yl)ethenes were synthesized from cyanophenols as follows.

(2-Chloroallylthio)benzonitriles, **5a**—**c**, were prepared from 2,3-dichloropropene and mercaptobenzonitriles **4**, that were converted from appropriate phenols **3** via dimethylthiocarbamates by Newman's method[11] in good yields. *m*- or *p*-Halophenyl 2-chloroallyl sulfides **5d**—**g** were also prepared from 2,3-dichloropropene and commercial grade *m*- or *p*-halobenzenethiols **4d**—**g**.



Scheme 1.

Cyano-substituted 1-benzothiophenes **6a**—**d** and halogen-substituted 1-benzothiophenes **6e**—**i** were prepared by thio-Claisen rearrangement of appropriate sulfides **5**.[12] Benzothiophenes **6** were converted to 3-cyanomethyl-1-benzothiophenes **8** via chloromethylated derivatives **7**. Cyano-substituted 1,2-bis(1-benzothiophen-3-yl)-1,2-dicyanoethylenes **1a**—**1d** and halogen-substituted derivatives **1e**—**1i** were synthesized by a coupling reaction of appropriate benzothiophenes **8**. Experimental details were described in a previous paper.[5]

1,2-Dicyano-1,2-bis(4-cyano-2-methyl-1-benzothiophen-3-yl)ethene 1a: MS *m/z* 420(M$^+$). ^{1}H NMR (CDCl$_3$) δ=2.02 (3H, s, Me), 2.08 (3H, s, Me), and 7.0—8.0 (6H, m, aromatic protons). Found: C, 68.85; H, 3.01; N, 13.09%. Calcd for $C_{24}H_{12}N_4S_2$: C, 68.57; H, 2.86; N, 13.33%.

1,2-Dicyano-1,2-bis(5-cyano-2-methyl-1-benzothiophen-3-yl)ethene 1b: MS *m/z* 420(M$^+$). ^{1}H NMR (CDCl$_3$) δ=2.01 (3H, s, Me), 2.04 (3H, s, Me), and 7.0—8.0 (6H, m, aromatic protons). Found: C, 68.78; H, 2.57; N, 13.60%. Calcd for $C_{24}H_{12}N_4S_2$: C, 68.57; H, 2.86; N, 13.33%.

1,2-Dicyano-1,2-bis(6-cyano-2-methyl-1-benzothiophen-3-yl)ethene 1c: MS m/z 420 (M$^+$). ^{1}H NMR (CDCl$_3$) δ=2.12 (3H, s, Me), 2.41 (3H, s, Me), and 7.2—8.0 (6H, m, aromatic protons). Found: C, 68.49; H, 2.93; N, 13.42%. Calcd for $C_{24}H_{12}N_4S_2$: C, 68.57; H, 2.86; N, 13.33%.

1,2-Dicyano-1,2-bis(7-cyano-2-methyl-1-benzothiophen-3-yl)ethene 1d: MS *m/z* 420 (M$^+$). ^{1}H NMR (CDCl$_3$) δ=2.10 (3H, s, Me), 2.36 (3H, s, Me), and 7.2—8.0 (6H, m, aromatic protons). Found: C, 68.60; H, 2.92; N, 13.55%. Calcd for $C_{24}H_{12}N_4S_2$: C, 68.57; H, 2.86; N, 13.33%.

1,2-Dicyano-1,2-bis(4-fluoro-2-methyl-1-benzothiophen-3-yl)ethene 1e: MS *m/z* 406 (M$^+$). ^{1}H NMR (CDCl$_3$) δ=2.05 (6H, s, Me) and 7.1—7.6 (6H, m, aromatic protons). Found: C, 64.77; H, 3.22; N, 7.19%. Calcd for $C_{22}H_{12}N_2F_2S_2$: C, 65.01; H, 2.98; N, 6.89%.

1,2-Dicyano-1,2-bis(5-fluoro-2-methyl-1-benzothiophen-3-yl)ethene 1f: MS *m/z* 406 (M$^+$). ^{1}H NMR (CDCl$_3$) δ=2.11 (3H, s, Me), 2.33 (3H, s, Me), and 7.0—7.65 (6H, m, aromatic protons). Found: C, 64.87; H, 2.87; N, 7.06%. Calcd for $C_{22}H_{12}N_2F_2S_2$: C, 65.01; H, 2.98; N, 6.89%.

1,2-Dicyano-1,2-bis(6-fluoro-2-methyl-1-benzothiophen-3-yl)ethene 1g: MS *m/z* 406(M$^+$). ^{1}H NMR (CDCl$_3$) δ=2.12 (6H, brs, Me) and 6.8—7.8 (6H, m, aromatic protons). Found: C, 65.24; H, 2.92; N, 6.59%. Calcd for $C_{12}H_{12}N_2F_2S_2$: C, 65.01; H, 2.98; N, 6.89%.

1,2-Bis(5-chloro-2-methyl-1-benzothiophen-3-yl)-1,2-dicyanoethene 1h: MS *m/z* 438 (M$^+$). ^{1}H NMR (CDCl$_3$) δ=2.33 (6H, s, Me) and 7.2—8.0 (6H, m, aromatic protons). Found: C, 60.14; H, 2.73; N, 6.38%. Calcd for $C_{22}H_{12}N_2Cl_2S_2$: C, 60.01; H, 2.86; N, 6.15%.

1,2-Bis(5-bromo-2-methyl-1-benzothiophen-3-yl)-1,2-dicyanoethene 1i: MS *m/z* 526 (M$^+$). ^{1}H NMR (CDCl$_3$) δ=2.46 (6H , brs, Me) and 7.1—7.9 (6H, m, aromatic protons). Found: C, 50.16; H, 2.32; N, 5.51%. Calcd for $C_{22}H_{12}N_2Br_2S_2$: C,50.02; H, 2,29; N, 5,30%.

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