JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2007; **20:** 894–899
Published online 31 May 2007 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/poc.1204

Photochromism of dithiazolylethenes having pyridyl and *N*-methylpyridinium groups

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Received 29 December 2006; revised 20 March 2007; accepted 27 March 2007

ABSTRACT: Dithiazolylethenes **1a** and **2a** having 4- or 3-pyridyl groups and **3a** having *N*-methylpyridinium groups at thiazole rings were prepared and their photochromic performance was examined. Upon irradiation with 313 nm light the colorless acetonitrile solutions of **1a** and **2a** turned violet, which show the absorption maxima at 538 and 530 nm, respectively. The violet color is due to the closed-ring isomers **1b** and **2b**. The violet color disappeared upon irradiation with visible light ($\lambda > 480$ nm). When the pyridine rings were converted to *N*-methylpyridinium ions, the colorless acetonitrile solution of **3a** turned blue ($\lambda_{max} = 596$ nm) upon irradiation with 365 nm light. The absorption maximum of the closed-ring isomer **3b** showed a bathochromic shift as much as 58 nm relative to the maximum of **1b**. In methanol **3a** changed to green ($\lambda_{max} = 750$ nm) upon irradiation with 365 nm light. It was suggested *J*-aggregates of **3b** are formed in methanol. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: photochromism; diarylethene; pyridyl group; *N*-methylpyridinium group

INTRODUCTION

Photochromic compounds have attracted much attention because of their potential applications to optical memory media and photo-optical switching devices.[1] Among various types of photochromic compounds diarylethenes with heterocyclic aryl groups, such as thiophene or benzothiophene groups, are the most promising candidates for the applications because of their fatigue-resistant and thermally irreversible photochromic performance.[2] Several attempts have been reported to provide water-soluble property to diarylethenes.[3–7] When sulfonyl substituents are introduced to the aryl groups, they show photochromic performance even in aqueous solution.[3] 1,2-Bis(5-phenyl-2-methyl-3-thienyl)perfluorocyclopentene having *N*-methylpyridinium groups at the *para*-positions of the phenyl rings exhibits a photochromic reaction in acetonitrile and methanol.[4,8] Dithiazolylethene[9,10] has an isoelectronic structure as dithienylethene and also exhibits the thermally irreversible and fatigue-resistant photochromic reaction. Recently, a dithiazolyl-ethene **10a** having 2-pyridyl group at 2-position of both thiazole rings has been synthesized.[11] In this paper, we have prepared dithiazolylethene derivatives **1a** and **2a** having 4- or 3-pyridyl groups and examined their photochromic performance. We have also synthesized dithiazolylethene **3a** having *N*-methylpyridinium groups and examined the photochromic reaction (Scheme 1).

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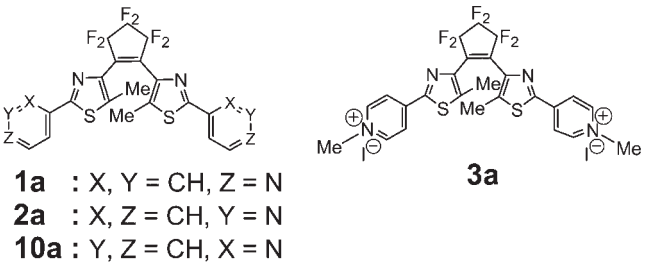
RESULTS AND DISCUSSION

5-Methyl-2-(4′-pyridyl)thiazole **4** and 5-methyl-2-(3′-pyridyl)thiazole **7** were prepared by palladium-catalyzed tandem C—H substitution.[12] Bromination of **4** and **7** was performed with bromine in a mixed solvent of acetonitrile and chloroform according to the reported method.[11] Synthesis of 1,2-bis[5-methyl-2-(4′-pyridyl)-4-thiazolyl] perfluorocyclopentene **1a** was carried out by the reaction of 4-bromo-5-methyl-2-(4′-pyridyl)thiazole **5** with monosubstituted perfluorocyclopentene **6** at $-100\,^{\circ}C$ in a mixed solvent of THF and ether according to the procedure for dipyrrolylperfluorocyclopentene.[13] 1,2-Bis-[5-methyl-2-(3′-pyridyl)-4-thiazolyl]perfluorocyclopentene **2a** was also synthesized by the similar method.[13] Compounds **1a** and **2a** were purified by GPC and HPLC. These structures were confirmed by ^1H NMR, mass spectra, and elemental analysis (Scheme 2). The hexane solutions of **1a** and **2a** were irradiated with UV light and the photoproducts were isolated using HPLC.

The absorption spectral changes of **1** (1.02×10^{-5} mol) and **2** (7.80×10^{-6} mol) in acetonitrile are shown in

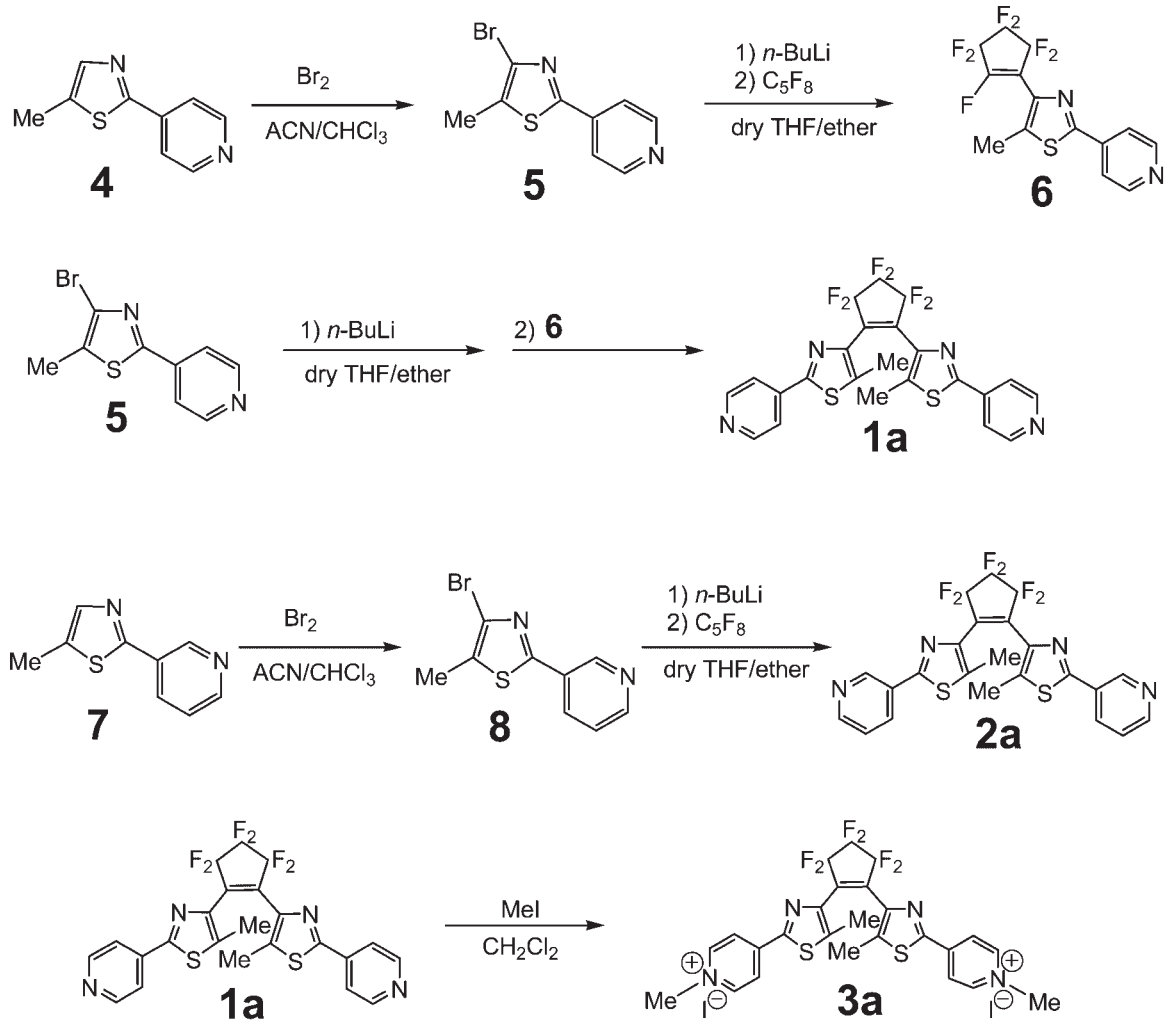


Scheme 1

Figs 1a and 1b. Upon irradiation with 313 nm light, the colorless solutions of **1a** and **2a** turned violet, in which visible absorption bands were observed at 538 nm ($\varepsilon = 10\,100\,M^{-1}\,cm^{-1}$) and 530 nm ($\varepsilon = 11600\,M^{-1}\,cm^{-1}$), respectively. The violet color is due to the closed-ring isomers **1b** and **2b**. When the violet solutions were irradiated with visible light ($\lambda > 480$ nm), the spectra readily returned back to the original ones. The conversions in the photostationary state were 94 and 90%, respectively.

The photocyclization and cycloreversion quantum yields were measured in acetonitrile using 1,2- bis[5-methyl-2-(2′-pyridyl)-4-thiazolyl]perfluorocyclopentene **10a** as a reference.[11] The photocyclization quantum yields (313 nm) of both **1a** and **2a** were determined to be 0.20 and 0.19, which are similar to that of **10a** (0.17).[11] The photocycloreversion quantum yields of **1b** and **2b** were determined to be 0.039 and 0.037, respectively. These values are also similar to that of **10b** (0.035).[11] Table 1 summarizes the quantum yields, the absorption maxima, and absorption coefficients of the open- and closed-ring isomers **1**, **2**, and **10** in acetonitrile. It was found the absorption maximum of **10b** having 2-pyridyl groups is slightly red-shifted in comparison with that of **1b** and **2b** having 4- or 3-pyridyl groups.

Methylation of the pyridine ring was easily performed for **1a** by treating with methyl iodide in dichloromethane (Scheme 2). Methylation for **2a** and **10a** was failed. Figure 2 shows the orbital profiles of HOMO based on PM3 calculation.[14] Electron density on *N*-position of 5-methyl-2-(4′-pyridyl)thiazole **4** is significantly larger



Scheme 2

DOI: 10.1002/poc

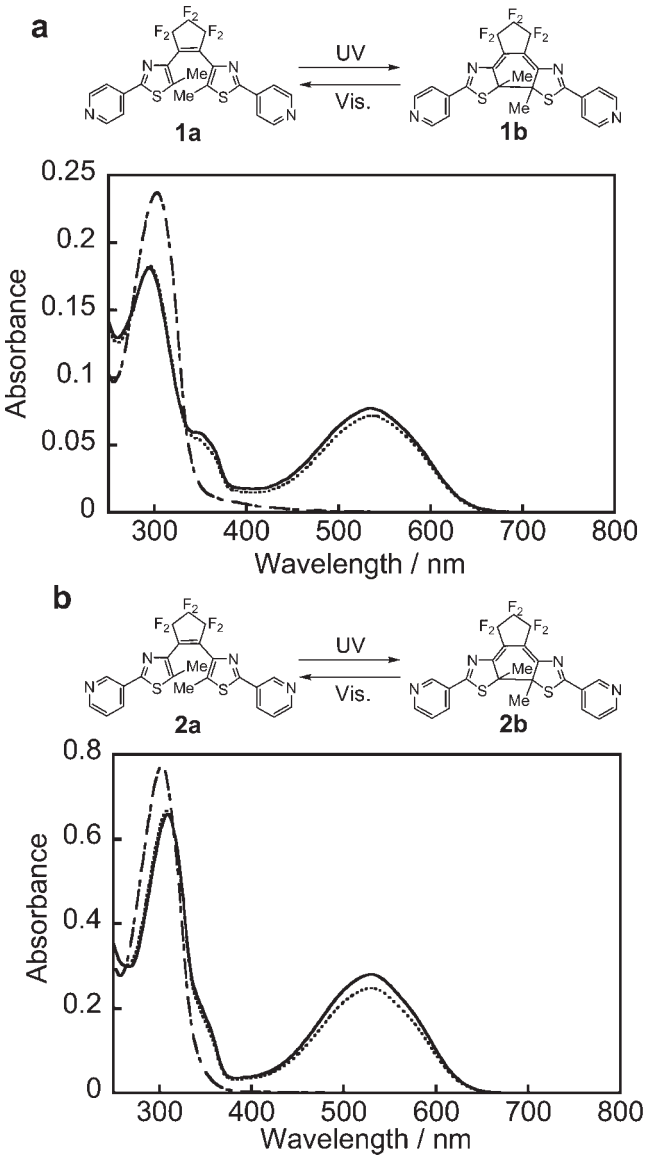


Figure 1. Absorption spectral changes of **1** (1.02×10^{-5} mol) (a) and **2** (7.80×10^{-6} mol) (b) in acetonitrile by photoirradiation: (dashed line) open-ring isomer, (solid line) closed-ring isomer, and (dotted line) in the photostationary state under irradiation with 313 nm light

than that of 5-methyl-2-(2′-pyridyl)thiazole or 5-methyl-2-(3′-pyridyl)thiazole **7**. This indicates that electron density of *N*-positions of **1a** is larger than that in **2a** or **10a**. The electron density difference on the *N*-positions can explain the difference in reactivity for these compounds.

Figure 3a shows the absorption spectral changes of **3a** in acetonitrile. Upon irradiation with 365 nm light, the colorless solution of **3a** turned blue, showing an absorption maximum at 596 nm. The blue color is due to the closed-ring isomer **3b**. The absorption maximum of **3b** showed a bathochromic shift as much as 58 nm relative to the maximum of **1b**. Similar absorption spectrum ($\lambda_{max} = 590$ nm) was also observed in aqueous solution. As can be seen in Fig. 3b, the methanol solution of **3a** changed from colorless to green upon irradiation with 365 nm light and a new band appeared at 750 nm. The absorption maximum exhibits a dramatically large red-shift in comparison with that observed in acetonitrile and water. Although the intensity of the green or blue color decreased by irradiation with visible light ($\lambda > 480$ nm), the absorption spectra did not return back to the original one. This suggests that some side-reactions take place in the reverse process.

When the blue-color photoproduct obtained in acetonitrile was added to methanol, the color changed to green. This indicates that the photogenerated products in both solutions are the same. The extremely red-shifted and narrow absorption band suggested formation of *J*-aggregates of **3b** in methanol. The absorption at 750 nm gradually decreased and a new absorption appeared at 600 nm in 24 h. This suggests that the *J*-aggregates of **3b** are thermodynamically unstable and convert to stable products.

CONCLUSION

Dithiazolylethenes **1a**, **2a**, and **3a** were synthesized. Upon irradiation with 313 nm light, the colorless acetonitrile solutions of **1a** ($\lambda_{max} = 538$ nm) and **2a** ($\lambda_{max} = 530$ nm) turned violet. Photochromic properties of **1a** and **2a** having 4- or 3-pyridyl groups are similar to that of **10a** having 2-pyridyl groups. Upon irradiation with 365 nm light, the colorless acetonitrile solution of **3a** turned blue ($\lambda_{max} = 596$ nm). On the other hand, the methanol solution of **3a** changed to green ($\lambda_{max} = 750$ nm) upon irradiation with 365 nm light. The red-shifted narrow visible absorption band suggested formation of *J*-aggregates of **3b** in methanol.

Table 1. Absorption maxima and coefficients of the open- and closed-ring isomers of dithiazolylethenes **1**, **2**, and **10** and the quantum yields in acetonitrile

	λ_{max}/nm (ε /$M^{-1}\,cm^{-1}$)	$\Phi_{a\rightarrow b}$		λ_{max}/nm (ε/$M^{-1}\,cm^{-1}$)	$\Phi_{b\rightarrow a}$	Conversion (313 nm)
1a	303 (31 300)	0.20 (313 nm)	**1b**	538 (10 100)	0.039 (538 nm)	0.94
2a	301 (31 600)	0.19 (313 nm)	**2b**	530 (11 600)	0.037 (530 nm)	0.90
10a	310 (40 000)[a]	0.17 (313 nm)[a]	**10b**	545 (12 700)[a]	0.035 (545 nm)[a]	0.90[a]

[a] Ref. [11].

DOI: 10.1002/poc

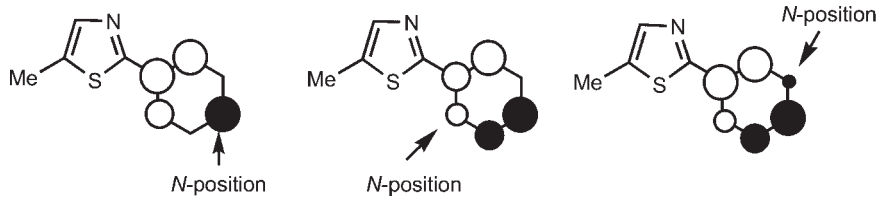
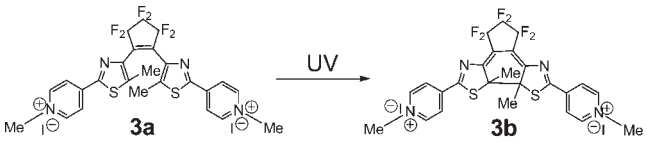


Figure 2. PM3 calculation of HOMO for 5-methyl-2-(4′-pyridyl)thiazole **4** (left), 5-methyl-2-(2′-pyridyl)thiazole (middle), and 5-methyl-2-(3′-pyridyl)thiazole **7** (right)

EXPERIMENTAL

General remarks

^{1}H NMR spectra were recorded on a Varian Gemini 200 instrument. Mass spectra were taken with a Shimadzu GCMS-QP5050A gas chromatography-mass spectrometer. Absorption spectra were measured with a Hitachi U-3500 absorption spectrophotometer. Photoirradiation was carried out using USHIO 500-W super high-pressure mercury lamp or an USHIO 500-W xenon lamp. Monochromatic light was obtained by passing the light through a combination of a Toshiba band-pass filter (UV-D33S) or sharp cut filter (Y-48) and monochromator (Ritsu MC-10N). Melting points were not corrected.



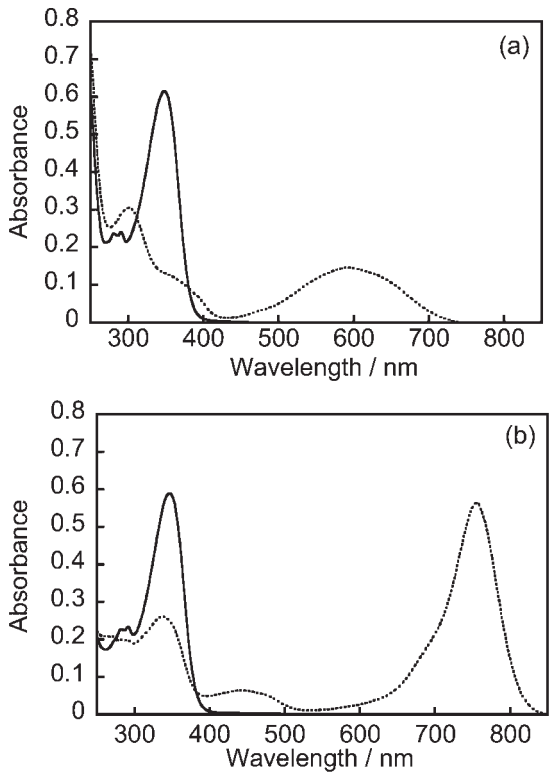


Figure 3. Absorption spectral changes of **3a** in acetonitrile (a) and methanol (b) solutions by photoirradiation: (solid line) open-ring isomer **3a**, and (dotted line) closed-ring isomer **3b** under irradiation with 365 nm light for 10 s

Materials

1,2-Bis[5-methyl-2-(2′-pyridyl)-4-thiazolyl]perfluorocyclopentene **10a** was prepared according to method reported previously.[11] Solvents of spectroscopic grade were purified by distillation before use. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Merck, 70–230 mesh).

5-Methyl-2-(4′-pyridyl)thiazole (4)[15]

To a solution of 5-methylthiazole (10 g, 99 mmol), 4-iodopyridine (10 g, 50 mmol), $PdCl_2(PPh_3)_2$ (4 g, 4.7 mmol), and CuI (500 mg, 2.63 mmol) in dry DMSO (250 ml) 100 ml of TBAF (1 M THF solution, 100 mmol) was added under an argon atmosphere. The resulting solution was degassed via five freeze-pumo-thaw cycles and heated in an oil bath (65 °C). The solution was stirred at that temperature for 4 days and then distilled water was added. The product was extracted with diethyl ether, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane = 1:1) to afford to 1.8 g (20%) of **4** as a colorless solid: ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 8.67$ (d, $J = 4.8$ Hz, 2H), 7.74 (d, $J = 4.8$ Hz, 2H), 7.59 (s, 1H), 2.55 (s, 3H) MS $m/z = 176$ ($M^+ - 1$).

4-Bromo-5-methyl-2-(4′-pyridyl)thiazole (5)

To a solution of 3 g (17 mmol) of **4** in 40 ml of $CHCl_3$ and 40 ml of MeCN, 3.0 ml (51 mmol) of Br_2 was slowly added. After refluxing for 48 h the solvents were removed under vacuum and extracted with ethyl acetate. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The reduced layer was purified by column chromatography (ethyl acetate/hexane = 1:1)

DOI: 10.1002/poc

to afford 1 g (30%) of **5** as colorless solid: m.p. 94–95 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 8.69$ (d, $J = 6.0$ Hz, 2H), 7.73 (d, $J = 6.0$ Hz, 2H), 2.48 (s, 3H), MS $m/z = 255$ (M^+), Anal. Found: C, 42.09; H, 2.83; N, 11.05%. Calcd for $C_9H_7BrN_2S$: C, 42.37; H, 2.77; N, 10.98%.

1-[5-Methyl-2-(4′-pyridyl)-4-thiazolyl] perfluorocyclopentene (6)

To a stirring solution of **5** (500 mg, 1.96 mmol) in 35 ml THF and 23 ml ether, 1.6 M *n*-BuLi in hexane (1.1 ml, 2.06 mmol) was slowly added dropwise under an atmosphere of argon at −80 °C . After the mixture had been stirred for 15 min at −80 °C, perfluorocyclopentene (0.3 ml, 2.10 mmol) in dry Et_2O (0.5 ml) was slowly added at −100 °C. The reaction mixture was stirred at −100 °C for 30 min and at −80 °C for 2 h, and then distilled water was added. The product was extracted with diethyl ether, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane = 1:1) to afford to 400 mg (48%) of **6** as a colorless solid: ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 8.73$ (d, $J = 6.0$ Hz, 2H), 7.77 (d, $J = 6.0$ Hz, 2H), 2.58 (d, $J = 3.0$ Hz, 3H), MS $m/z =$ 368 (M^+).

1,2-Bis[5-methyl-2-(4′-pyridyl)-4-thiazolyl] perfluorocyclopentene (1a)

To a stirring solution of **5** (100 mg, 0.39 mmol) in 7 ml THF and 4.5 ml Et_2O, 1.6 M *n*-BuLi in hexane (0.27 ml, 0.41 mmol) was slowly added dropwise under an atmosphere of argon at −80 °C. After the mixture had been stirred for 15 min at −80 °C, **6** (100 mg, 0.27 mmol) in dry THF (2 ml) was slowly added at −100 °C. The reaction mixture was stirred at −100 °C for 30 min and at −80 °C for 2 h, and then distilled water was added. The product was extracted with diethyl ether, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (THF/ethyl acetate/hexane = 2:1:1) and GPC and HPLC (THF/ethyl acetate/hexane = 2:1:1) to afford to 50 mg (30%) of **1a** as a colorless solid: m.p. 179–180 °C. ^{1}H NMR (CD_3OD, 200 MHz): $\delta = 8.65$ (d, $J = 6.4$ Hz, 2H), 7.89 (d, $J = 6.4$ Hz, 2H), 2.17 (s, 3H), MS (FAB) $m/z = 524$ (M^+), Anal. Found: C, 52.61; H, 2.83; N, 10.83%. Calcd for $C_{23}H_{14}F_6N_4S_2$: C, 52.67; H, 2.69; N, 10.68%.

1,2-Bis[5-methyl-2-(*N*-methyl-4′-pyridyl)-4-thiazolyl]perfluorocyclopentene (I^{2+}) (3a)

To a stirring solution of **1a** (100 mg, 0.39 mmol) in 7 ml dry CH_2Cl_2, 0.24 ml of methyl iodide (3.9 mmol, 10 eq. for **1a**) was slowly added. The reaction was stirred at ambient temperature under a nitrogen atmosphere. After 24 h, the resulting suspension was filtered, the solid washed repeatedly with dichloromethane, and then dried *in vacuo*. **3a** was obtained as a yellow powder; ^{1}H NMR (CD_3OD, 200 MHz): $\delta = 8.98$ (d, $J = 6.4$ Hz, 2H), 8.48 (d, $J = 6.4$ Hz, 2H), 4.42 (s, 3H), 2.28 (s, 3H), Anal. Found: C, 36.85; H, 2.51; N, 7.25%. Calcd for $C_{25}H_{20}F_6I_2N_4S_2$: C, 37.14; H, 2.49; N, 6.93%.

5-Methyl-2-(3′-pyridyl)thiazole (7)

Compound **7** was synthesized under the similar conditions as for the synthesis of **4**. Four grams (46%) of **7** was obtained as a colorless solid: m.p. 88–89 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 9.09$ (s, 1H), 8.61 (br d, $J = 3.8$ Hz, 1H), 8.18 (br d, $J = 7.6$ Hz, 1H), 7.55 (s, 1H), 7.4–7.3 (m, 1H), 2.53 (s, 3H), MS $m/z = 176$ (M^+), Anal. Found: C, 61.20; H, 4.60; N, 16.04%. Calcd for $C_9H_8N_2S$: C, 61.34; H, 4.58; N, 15.90%.

4-Bromo-5-methyl-2-(3′-pyridyl)thiazole (8)

Compound **8** was also synthesized under the similar conditions as for the synthesis of **5**. **8** (2.3 g, 39%) was obtained as colorless solid: m.p. 84–85 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 9.07$ (dd, $J = 2.2$, 0.6 Hz, 1H), 8.64 (dd, $J = 5$, 1.8 Hz, 1H), 8.24–8.15 (m, 1H), 7.41–7.34 (m, 1H), 2.47 (s, 3H), MS $m/z = 255$ (M^+), Anal. Found: C, 42.33; H, 2.80; N, 11.00%. Calcd for $C_9H_7BrN_2S$: C, 42.37; H, 2.77; N, 10.98%.

1,2-Bis[5-methyl-2-(3′-pyridyl)-4-thiazolyl] perfluorocyclopentene (2a)

To a stirring solution of **8** (2.0 g, 7.84 mmol) in 120 ml Et_2O, 1.6 M *n*-BuLi in hexane (5.4 ml, 8.62 mmol) was slowly added dropwise under an atmosphere of argon at −80 °C. After the mixture had been stirred for 15 min at −80 °C, perfluorocyclopentene (0.6 ml, 4.10 mmol) in Et_2O (1 ml) was slowly added at −100 °C. The reaction mixture was stirred at −100 °C for 30 min and at −80 °C for 2 h, and then distilled water was added. The product was extracted with diethyl ether, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (THF/ethyl acetate/hexane = 2:1:1) and GPC and HPLC (THF/ethyl acetate/hexane = 2:1:1) to afford to 100 mg (5%) of **2a** as a colorless solid: m.p. 127–128 °C. ^{1}H NMR (CD_3OD, 200 MHz): $\delta = 9.05$ (s, 1H), 8.7–8.6 (m, 1H), 8.4–8.3 (m, 1H), 7.6–7.5 (m, 1H), 2.17 (s, 3H), MS $m/z =$ 524 (M^+), Anal. Found: C, 52.81; H, 2.88; N, 10.48%. Calcd for $C_{23}H_{14}F_6N_4S_2$: C, 52.67; H, 2.69; N, 10.68%.

DOI: 10.1002/poc

Acknowledgements

This work was partly supported by 'Nanotechnology Support Project' and a Grant-in-Aid for Scientific Research (S) (No. 15105006) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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