Thermally Irreversible Photochromic Systems. Photoreaction of Diarylethene Derivatives with Imidazo[1,2-*a*]pyridine Rings

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(Received September 13, 1990)

A non-symmetrical diarylethene with imidazo[1,2-*a*]pyridine ring on one end and thiophene ring on the other end, 1,2-dicyano-1-(2-methylimidazo[1,2-*a*]pyridin-3-yl)-2-(2,4,5-trimetyl-3-thienyl)ethene **2Z** underwent a hexatriene-cyclohexadiene type reversible ring-closure reaction by photoirradiation, while an only *Z*–*E* isomerization was observed for a symmetrical diarylenthene with two imidazo[1,2-*a*]pyridine rings, 1,2-dicyano-1,2-bis(2-methylimidazo[1,2-*a*]pyridin-3-yl)ethene **1Z**. The ring-closure reaction was not discerned. The photogenerated closed-ring form **2C** had the absorption band at 535 nm, which is 23 nm longer wavelengths than that of the corresponding dithienylethene, and kept the absorption intensity constant for more than 24 h at 80 °C. The quantum yield close to unity was observed for the photochemical ring-opening reaction of **2C** with 546 nm light.

Recently, a new type of thermally stable photochromic systems, diarylethene derivatives with heterocyclic rings, has been developed, such as 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene and 2,3-bis-(2,4,5-trimethyl-3-thienyl)maleic anhydride.[1] The compounds have no thermochromic property even at 300 °C and the closed-ring forms are stable for more than 3 months at 80 °C.[2,3] In addition, no appreciable fatigue was observed for the diarylethenes with benzothiophene rings even after 8×10^3 ring closure/opening cycles.[2]

Although these compounds have promising properties for optical data storage media,[4–6] they still lack several indispensable conditions, such as diode laser sensitivity and non-destructive read out capability. The absorption edges of the closed-ring forms are less than 700 nm. Replacement of the thiophene rings with indole ones, which have high electron-donating ability, shifted the absorption maximum of the closed-ring form as much as 60 nm, and the absorption edge of the acid anhydride derivative reached 800 nm.[7] Although the compound has the sensitivity at the diode laser wavelength ($780<\lambda<830$ nm), the conversion of the open-ring to the closed-ring form in the photostationary state under irradiation with 474 nm light is less than a few percent, and the thermal stability of the closed-ring form is insufficient.

In the present study, we synthesized a symmetrical diarylethene derivative with two imidazo[1,2-*a*]pyridine rings, which have higher electron-donating ability than indole ring, and a non-symmetrical one with imidazo[1,2-*a*]pyridine ring on one end and thiophene ring on the other end in attempting to shift the absorption bands to longer wavelengths.

Results and Discussion

A Symmetrical Diarylethene Derivative with Two Imidazo[1,2-*a*]pyridine Rings. A diarylethene derivative with two imidazo[1,2-*a*]pyridine rings was prepared by a self-coupling reaction[1] of two 3-(cyanomethyl)-2-methylimidazo[1,2-*a*]pyridine. The mixture of *Z* and *E* forms was dissolved in benzene and exposed to 490 nm light to convert the *E* form to the *Z* form. The *Z* form was separated from the mixture of *Z* and *E* forms by HPLC and purified by crystallization from a hexane–ether mixture.

The *Z* form, **1Z**, was irradiated in benzene (6.8×10^{-5} mol dm^{-3}) in the presence of air with 475 nm light, and the reaction was followed by absorption and HPLC measurements (silica-gel column, 1:1 chloroform–acetone). Figure 1 shows the spectra of **1Z** before and after photoirradiation with 475 nm light in the

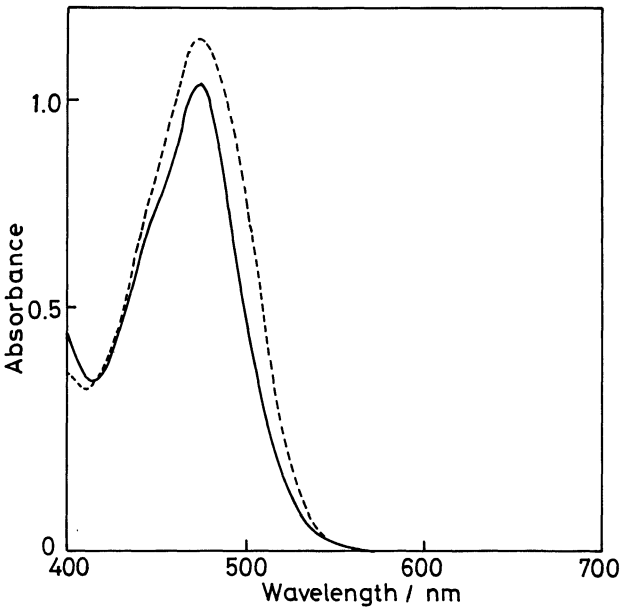
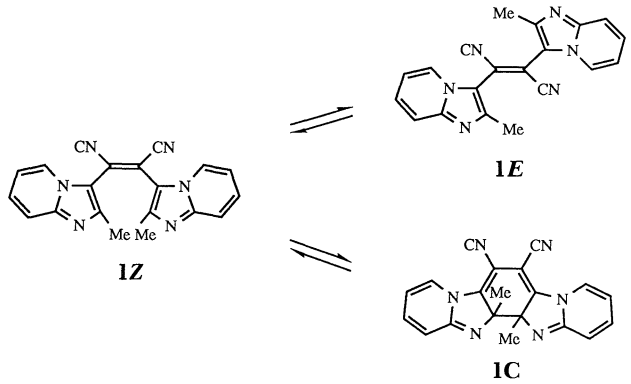


Fig. 1. Absorption spectra of **1Z** (6.8×10^{-5} mol dm^{-3}) (—) before photoirradiation and (---) in the photostationary state under irradiation with 475 nm light.

dilute benzene solution. The absorption maximum of **1Z** was observed at 475 nm and the molar absorption coefficient was 15,000 $dm^3\ mol^{-1}\ cm^{-1}$. The absorption maximum shifts to a longer wavelength as much as 40 nm in comparison with *Z* form of 1,2-dicyano-1,2-bis(1,2-dimethyl-3-indolyl)ethene.[7] Upon irradiation with 475 nm light, the intensity of the absorption in 420—550 nm region increases. Any new absorption was not observed at longer wavelengths. It was inferred from the NMR measurement that the absorption intensity change is due to the *Z*–*E* isomerization from **1Z** to **1E** (see below). Under the photostationary state, the *Z* to *E* ratio was estimated by HPLC to be **1E**/**1Z**=33/67. A ring-closure reaction was not discerned even after prolonged irradiation with lights of 420—550 nm wavelengths.



Scheme 1.

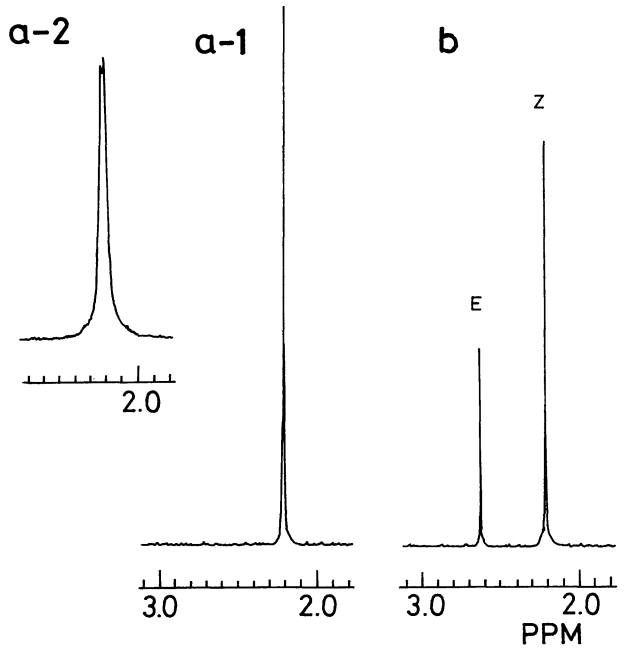
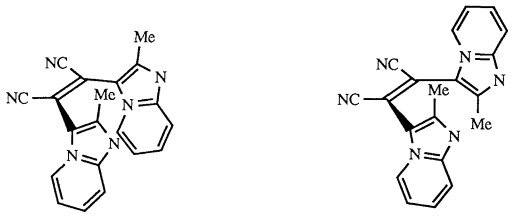


Fig. 2. ^1H NMR spectra (270-MHz) of **1E** in $CDCl_3$: (a-1) before irradiation at room temperature; (a-2) at −25 °C; (b) after irradiation with 475 nm light.

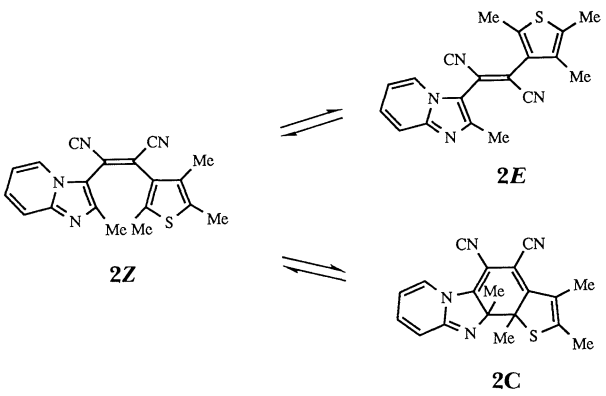
Figure 2 a-1 and b show the 270-MHz ^1H NMR spectra of methyl protons of **1Z** in $CDCl_3$ before and after photoirradiation with 475 nm light in benzene solution, respectively. Figure 2 a-2 shows the signals of methyl protons of **1Z** in $CDCl_3$ at −25 °C. At this temperature, the sharp singlet splits into two peaks at 2.19 and 2.21 ppm. The two methyl protons indicate the existence of two atropisomers in the compound **1Z**. A similar line-shape change was reported for dibenzothiophene derivatives.[8] One conformer has two imidazo[1,2-*a*]pyridine rings in mirror symmetry (in parallel orientation) and the other C_2 symmetry (in anti-parallel orientation).

After photoirradiation a new signal appeared at 2.63 ppm (Fig. 2). The absence of other signals except the one line indicates that the signal is ascribable to the *E* form and the ring-closure reaction is negligible. The assignment was further confirmed by the ^{13}C NMR measurement. Any signal ascribable to sp^3 carbons was not discerned after photoirradiation.

A Non-symmetrical Diarylethene Derivative with Imidazo[1,2-*a*]pyridine and Thiophene Rings. A diarylethene derivative with imidazo[1,2-*a*]pyridine ring on one end and thiophene ring on the other end was prepared by a cross-coupling reaction[2] of 3-(cyanomethyl)-2-methylimidazo[1,2-*a*]pyridine[9] and 4-(cyanomethyl)-2,3,5-trimethylthiophene.[1] The mixture of *E* and *Z* forms was dissolved in benzene and exposed to the light longer than 450 nm. The



Scheme 2.



Scheme 3.

irradiation is expected to convert the *E* form to the *Z* form. The *Z* form was separated by HPLC and purified by crystallization from a hexane–ether mixture.

The *Z* form, **2Z**, was irradiated in benzene (1.25×10^{-4} mol dm^{-3}) in the presence of air with 450 nm light, and the reaction was followed by absorption and HPLC measurement (silica-gel column, chloroform). Figure 3 shows the spectra of **2Z** before and after photoirradiation with 450 nm light. Irradiation of the yellow benzene solution with 450 nm light led to the formation of a red solution, in which a visible absorption was observed at 535 nm and a shoulder at 580 nm. The visible absorption was ascribed to the closed-ring form, **2C**, from the NMR measurement (see below).

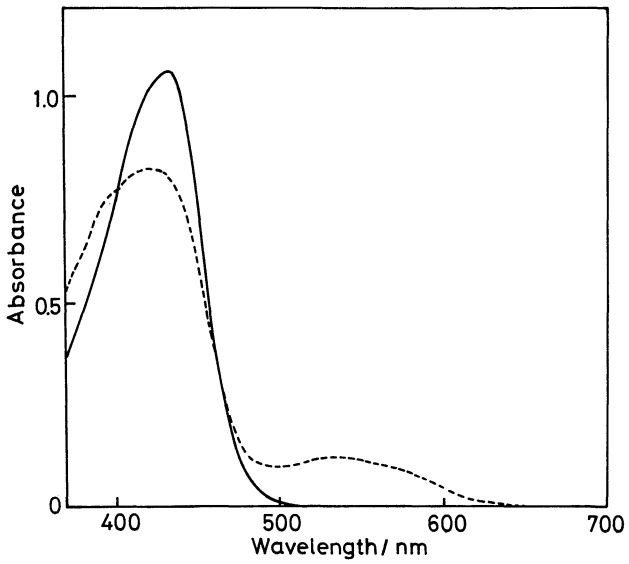


Fig. 3. Absorption spectra of **2*E*** (1.25×10^{-4} mol dm^{-3}) (——) before photoirradiation and (---) in the photostationary state under irradiation with 450 nm light.

The replacement of one of imidazo[1,2-*a*]pyridine rings with a thiophene ring enables the diarylethene to undergo the ring-closure reaction. The absorption maximum wavelength is 23 nm longer than that of the dithienylethene derivative.[1] The conversion from **2Z** to **2C** in the photostationary state under irradiation with 450 nm light was estimated to be 30% by HPLC analysis.

The irradiation was also accompanied with a *Z*–*E* isomerization from **2Z** to **2*E***. In the photostationary state, the contents of each isomer were estimated by HPLC as **2Z** (40%), **2C** (30%), and **2*E*** (30%). The yield of the closed-ring form depended on the irradiation wavelength. When the solution was irradiated with 425 nm light, the conversion was decreased to less than 15%.

The ^{1}H NMR spectra (360-MHz) of **2Z** in C_6D_6 before photoirradiation and after irradiation with 450 nm light are shown in Fig. 4 a and b. Before photoirradiation, 4 lines were observed at 1.41, 1.50, 1.62, and 1.96 ppm, which are assigned to the **2Z** form.

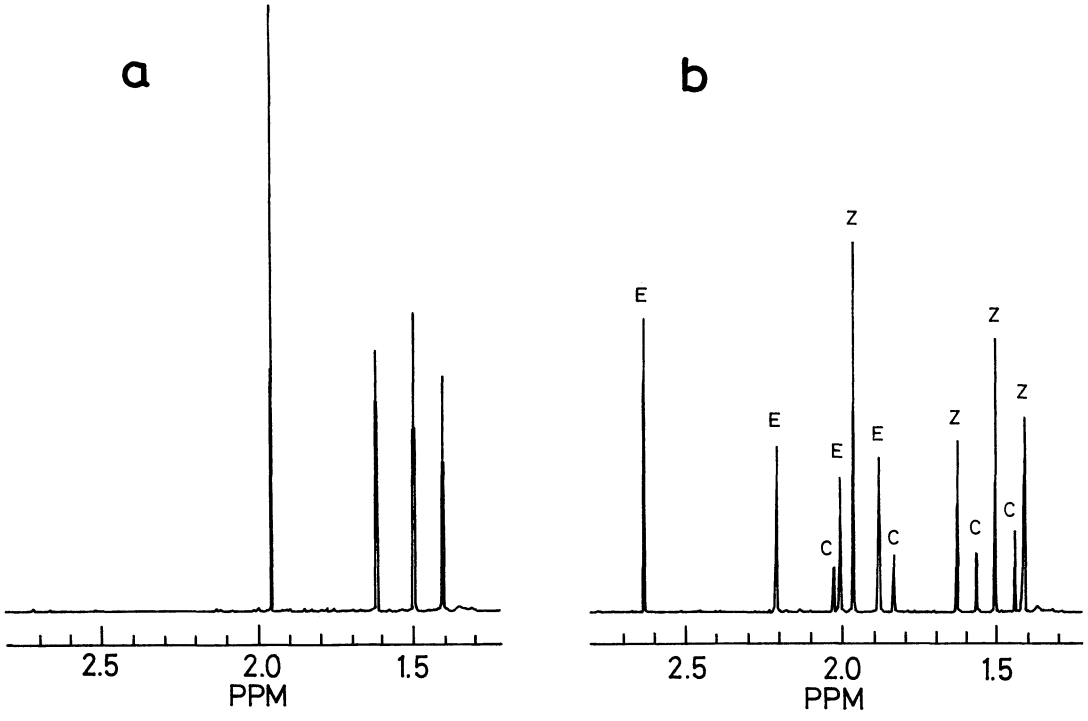


Fig. 4. ^{1}H NMR spectra (360-MHz) of **2Z** in C_6D_6: (a) before irradiation (b) after irradiation with 450 nm light.

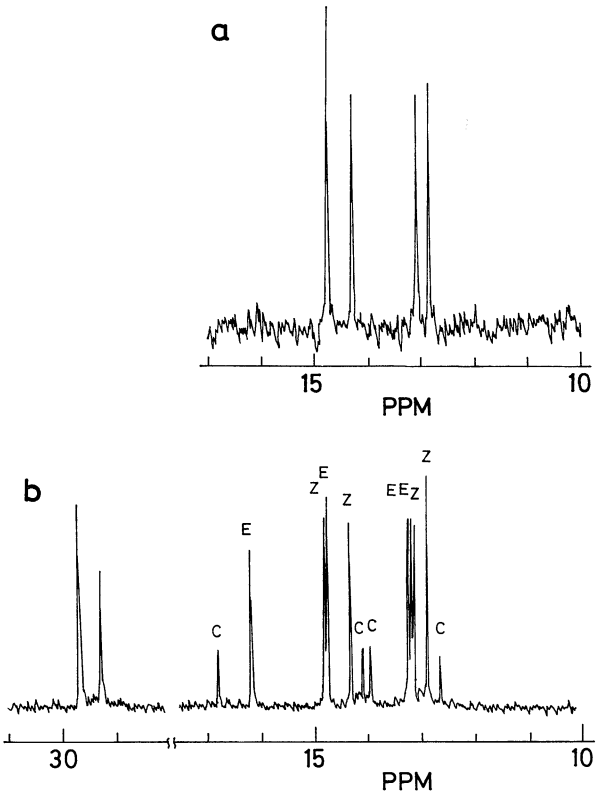


Fig. 5. ^{13}C NMR spectra (68-MHz) of **2Z** in $CDCl_3$: (a) before irradiation (b) after irradiation with 450 nm light.

Upon irradiation with 450 nm light, new 8 lines appeared at 1.43, 1.56, 1.83, 1.87, 2.00, 2.02, 2.20, and 2.62 ppm along with a decrease of the intensity of the 4 lines. The eight lines observed after photoirradiation indicate the co-existence of three isomers, **2Z**, **2C**, and **2*E***. The assignments are shown in the figure.

Figure 5 a and b show the 68-MHz ^{13}C NMR spectra of methyl carbon of **2** in $CDCl_3$ before photoirradiation and after irradiation with 450 nm light, respectively. Before photoirradiation, 4 lines were observed at 12.86, 13.09, 14.32, and 14.77 ppm, which are due to **2Z** form. Upon irradiation, new 8 lines appeared at 12.57, 13.12, 13.19, 13.92, 14.11, 14.74, 16.17, and 17.01. These 8 lines may be classified into two groups (13.12, 13.19, 14.74, and 16.17 ppm) and (12.57, 13.92, 14.11, and 17.01 ppm). The former is assigned to the *E* form, **2*E***, and the latter to the closed-ring form, **2C**. The other two lines at 29.29 and 29.69 ppm observed after photoirradiation indicate the existence of sp^3 carbon after photoirradiation. This result confirms that closed-ring form, **2C**, was formed by photoirradiation.

The photogenerated closed-ring form, **2C** was thermally stable. Any changes of the absorption intensity at 535 nm was not observed even at 80 °C. The absorption intensity remained constant for more than 24 h, at 80 °C.

Table 1. Quantum Yields for Ring-Closure and Ring-Opening Reactions in Benzene Solution

Reaction	Excitation wavelength / nm	Quantum yield
2Z→**2C**	405	0.06
2C→**2Z**	546	1.00

Quantum yields for the cyclization and the ring-opening reactions of **2** were determined in benzene solution in the presence of air at 25 °C. Table 1 summarized the results. The cyclization quantum yield of the imidazo[1,2-*a*]pyridine-thiophene derivative **2Z** at 405 nm was 0.06, which is similar value observed for 1,2-dicyano-1,2-bis(1,2-dimethyl-3-indolyl)-ethene[7] and 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride.[1] The quantum yield of the ring-opening reaction at 546 nm was obtained to be close to unity. The value is 8 times larger than that observed for dithienylethene derivative.[1] The large value is possibly due to the steric strain of the closed-ring form, especially the strain of the imidazo[1,2-*a*]pyridine ring.[7,8]

Summary

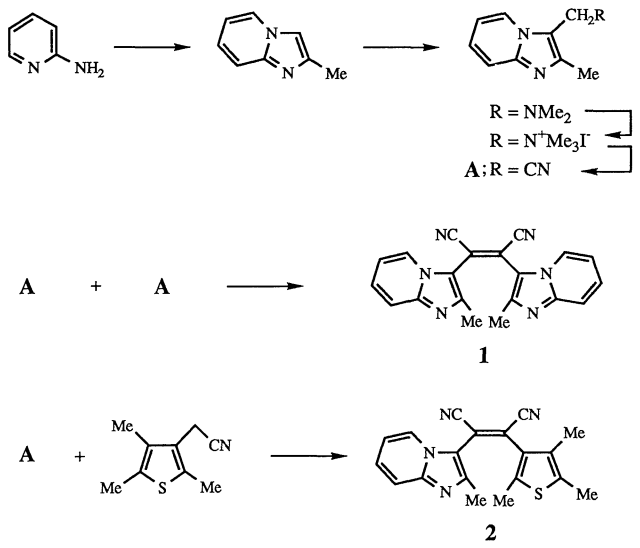
Diarylethene derivatives with imidazo[1,2-*a*]pyridine rings were synthesized. The symmetric diarylethene derivative with two imidazo[1,2-*a*]pyridine rings underwent only the *Z*–*E* photoisomerization. The ring-closure reaction was not observed. On the other hand, the non-symmetrical diarylethene derivative with imidazo[1,2-*a*]pyridine ring on one end and thiophene ring on the other end underwent both the *Z*–*E* isomerization and the ring-closure reaction. The absorption maximum showed a bathochromic shift as much as 23 nm in comparison with that of dithienylethene derivative. A quantum yield close to unity was observed for the ring-opening reaction of **2C**.

Experimental

General Method. IR spectra were measured with a Perkin Elmer Model 1618 spectrophotometer using KBr disks. ^1H NMR spectra (360 MHz) were recorded with a Bruker WN-360 spectrometer. Samples were measured in C_6D_6 or $CDCl_3$ using the tetramethylsilane (0 ppm) as an internal standard. ^{13}C NMR spectra (68 MHz) were recorded on JOEL JNM-GSX-270 spectrometer using $CDCl_3$ as the solvent with tetramethylsilane as an internal standard. Mass spectra and elemental analyses were performed in the Material Analysis Center of Osaka University. Melting points were determined by using a Gallenkamp melting point apparatus (MP-41). HPLC analysis was carried out on a JASCO 800 system. Stainless-steel columns (length, 250 mm; i.d., 4.6 mm, for analytical purposes, length, 250 mm; i.d., 10.0 mm, for preparative purposes) were slurry packed using silica gel (Fine SIL-5). Absorption spectra were measured with a Shimadzu MPS-200 instrument.

Photoirradiation was carried out with a EWIG XC-500 Xenon lamp. The wavelength of light was selected by passing the light through a monochrometer (Jobin Yvon H10-UV). Quantum yields were determined by measuring the rate of isomerization in the initial stage of the reaction at low concentration (absorbance at the irradiation wavelength <0.2) and the light intensity was measured with a photometer (International Light IL1700).

Materials. 1,2-Dicyano-1,2-bis(2-methylimidazo[1,2-*a*]-pyridin-3-yl)ethene and 1,2-dicyano-1-(2-methylimidazo[1,2-*a*]pyridin-3-yl)-2-(2,4,5-trimethyl-3-thienyl)ethene were synthesized as follows.



2-Methylimidazo[1,2-*a*]pyridine.[9] A mixture of 11.3 g (0.12 mol) of 2-aminopyridine and 11.1 g (0.12 mol) of chloroacetone in 120 mL of ethanol was heated under reflux for 20 h. The ethanol was removed by evaporation, and the residual material was dissolved in 100 mL of water. The aqueous solution was extracted with dichloromethane (4×20 mL). The dichloromethane extracts were washed with water (20 mL). The aqueous solutions were combined, and adjusted to pH 11.5—12 by the addition of 50% sodium hydroxide (ca. 12 mL). The basic aqueous solution was extracted with dichloromethane (3×20 mL). The dichloromethane extracts were combined and washed with water (20 mL). The aqueous solution was cooled with ice and was adjusted to pH 7 by the addition of 6 M hydrochloric acid (ca. 20 mL, M=mol dm^{-3}). After the solution was allowed to stand overnight, the solid that precipitated was isolated by filtration, washed with water and dried. Recrystallization from dichloromethane–methanol gave 5.6 g (0.042 mol) (35%) of 2-methylimidazo[1,2-*a*]pyridine. bp 120 °C/0.35 mmHg (1 mmHg=133.322 Pa). ^{1}H NMR ($CDCl_3$), δ=2.45 (s, 3H), 7.00 (dt, J=1.1 and 6.8 Hz, 1H), 7.09 (ddd, J=1.4, 6.8, and 9.4 Hz, 1H), 7.32 (s, 1H), 7.49 (d, J=9.4 Hz, 1H), 8.01 (dt, J=6.5 and 1.1 Hz, 1H).

3-[(Dimethylamino)methyl]-2-methylimidazo[1,2-*a*]pyridine.[9] A mixture of 5.6 g (0.042 mol) of 2-methylimidazo-[1,2-*a*]pyridine, 4.45 g (0.055 mol) of dimethylamine hydrochloride and 1.64 g (0.055 mol) of paraformaldehyde in 40 mL of methanol was heated under reflux for 1.5 h with stirring. Thereafter, the mixture was evaporated. Upon cooling to ambient temperature, the reaction mixture was acidified by the addition of concentrated hydrochloric acid (ca. 4 mL) and stirred for 18 h. The solid was isolated by filtration and washed with methanol and finally ether. After drying the solid was dissolved in 52 mL of hot water. The aqueous solution was adjusted to pH 11—12 by adding 50% sodium hydroxide. The mixture was cooled to 0 °C and extracted with dichloromethane (3×20 mL). The extracts were combined and washed with aqueous NaCl solution (20 mL). The dichloromethane was removed under reduced pressure to give an oil 3-[(dimethylamino)methyl]-2-methylimidazo[1,2-*a*]pyridine 7.9 g (0.042 mol) (100%). This material was used without further purification. ^{1}H NMR ($CDCl_3$), δ=2.22 (s, 6H), 2.44 (s, 3H), 3.65 (s, 2H), 6.75 (td, J=7.0 and 1.1 Hz, 1H), 7.13 (ddd, J=1.1, 6.8, and 9.0 Hz, 1H), 7.49 (d, J=9.0 Hz, 1H), 8.17 (d, J=7.2 Hz, 1H).

2-Methyl-3-[(trimethylammonio)methyl]imidazo[1,2-*a*]pyridine Iodide.[9] 3-[(Dimethylamino)methyl]-2-methylimidazo-[1,2-*a*]pyridine 7.9 g (0.042 mol) was dissolved in 58 mL of ethanol. To the ethanol solution at 0 °C was added dropwise with stirring 6.6 g (0.047 mol) of methyl iodide. The reaction mixture was stirred at ambient temperature overnight. The solid that formed was isolated by filtration and washed with ethanol (10 mL) and finally ether (35 mL). After drying, 14.0 g (0.042 mol) (100%) of 2-methyl-3-[(trimethylammonio)methyl]imidazo[1,2-*a*]pyridine iodide was obtained.

3-(Cyanomethyl)-2-methylimidazo[1,2-*a*]pyridine.[9] A mixture of 14.0 g (0.042 mol) of 2-methyl-3-[(trimethylammonio)-methyl]imidazo[1,2-*a*]pyridine iodide and 2.16 g (0.044 mol) of sodium cyanide in 120 mL of *N*,*N*-dimethylformamide was heated on a steam bath for 1 h with stirring. The mixture was poured into ice/water (360 mL) and stirred for 1 h. The solid was isolated by filtration, washed with water, and dried. Recrystallization from acetonitrile gave 2.4 g (0.014 mol) (33%) of 3-(cyanomethyl)-2-methylimidazo[1,2-*a*]pyridine. IR(KBr) 2246 cm^{-1}; MS (EI) *m/z* (rel intensity), 171 (M^+, 100), 156 (M^+—Me, 29), 145 (M^+—CN, 37); ^{1}H NMR ($CDCl_3$), δ=2.47 (s, 3H), 3.98 (s, 2H), 6.91 (t, J=6.8 Hz, 1H), 7.24 (t, J=7.9 Hz, 1H), 7.57 (d, J=9.0 Hz, 1H), 7.94 (d, J=6.8 Hz, 1H); mp 157—9 °C; Found: C, 70.31; H, 5.23; N, 24.46%. Calcd for $C_{10}H_9N_3$: C, 70.16; H, 5.30; N, 24.54%.

1,2-Dicyano-1,2-bis(2-methylimidazo[1,2-*a*]pyridin-3-yl)-ethene 1*Z*. This was prepared by a self-coupling reaction of 3-(cyanomethyl)-2-methylimidazo[1,2-*a*]pyridines by the method of Irie et al.[1] To 1.1 mL of 50% NaOH aqueous solution containing tetrabutylammonium bromide (0.07 g, 0.2 mmol) was added over a period 0.5 h a mixture of 3-(cyanomethyl)-2-methylimidazo[1,2-*a*]pyridine (462 mg, 2.7 mmol) and carbon tetrachloride (0.79 mL, 8 mmol), benzene 0.79 mL and acetone 1.0 mL at 40 °C. The solution was stirred for 3 h at 45 °C. Then the reaction mixture was poured into water. The aqueous solution was extracted with $CHCl_3$ and the organic phase was dried over $MgSO_4$. After the solvent was removed, the mixture of *Z* and *E* form was obtained in 79% yield by column chromatography on silica gel. The mixture of *Z* and *E* forms was dissolved in benzene and then exposed to 490 nm light. The *Z* form was separated from the solution by HPLC and then purified by recrystallization from a hexane–ether mixture. Mp 250—2 °C; IR(KBr) 2211 cm^{-1}; ^{1}H NMR[10] ($CDCl_3$), δ=2.21 (s, 6H), 6.75

(td, J=6.8 and 1.3 Hz, 2H), 7.27 (ddd, J=1.4, 6.5, and 8.3 Hz, 2H), 7.53 (d, J=9.7 Hz, 2H), 7.54 (d, J=6.8 Hz, 2H); ^{1}H NMR (C_6D_6), δ=2.02 (s, 6H), 5.77 (td, J=6.8 and 1.4 Hz, 2H), 6.31 (ddd, J=8.6, 7.2, and 1.4 Hz, 2H), 6.71 (d, J=6.8 Hz, 2H), 7.07 (d, J=8.6 Hz, 2H); MS (EI) m/z (rel intensity) 338 (M^+, 100) 323 (M^+—Me, 8); Found: C, 70.93; H, 3.98; N, 24.83%. Calcd for $C_{20}H_{14}N_6$: C, 70.99; H, 4.17; N, 24.84%.

1,2-Dicyano-1-(2-methylimidazo[1,2-*a*]pyridin-3-yl)-2-(2,3,5-trimethyl-3-thienyl)ethene 2Z.[2] This was prepared by a cross-coupling reaction of 3-(cyanomethyl)-2-methylimidazo-[1,2-*a*]pyridine and 4-(cyanomethyl)-2,3,5-trimethylthiophene[1] and isolated in 18% yield, mp>300 °C; IR(KBr) 2215 cm^{-1}; ^{1}H NMR[11] ($CDCl_3$), δ=1.79 (s, 6H), 2.00 (s, 6H), 2.12 (s, 6H), 2.18 (s, 6H), 6.88 (td, J=6.8 and 1.4 Hz, 2H), 7.39 (ddd, J=1.4, 6.8, and 9.0 Hz, 2H), 7.58 (d, J=8.6 Hz, 2H), 7.87 (td, J=6.8 and 1.1 Hz, 2H); ^{1}H NMR (C_6D_6) δ=1.41 (s, 6H), 1.50 (s, 6H), 1.62 (s, 6H), 1.96 (s, 6H), 6.05 (td, J=6.8 and 1.1 Hz, 2H), 6.49 (ddd, J=7.6, 6.8, and 1.1 Hz, 2H), 7.22 (d, J=7.6 Hz, 2H), 7.33 (d, J=6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$), δ=12.86, 13.09, 14.32, 14.77, 113.00, 113.75, 114.383, 114.529, 116.01, 117.38, 119.59, 124.08, 127.15, 128.85, 130.26, 132.55, 137.69, 146.88, 147.95; MS (EI) m/z (rel intensity), 332 (M^+, 100), 317 (M^+—Me, 63); Found: C, 68.58; H, 4.96; N, 16.71%. Calcd for $C_{19}H_{16}N_4S_1$: C, 68.65; H, 4.85; N, 16.85%.

We thank Mr. Masato Sekiguchi (Osaka Univ.) for his helps in NMR measurements.

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10) **1*E*** form: ^{1}H NMR ($CDCl_3$) δ=2.63 (s, 6H), 7.07 (td, J=6.8 and 1.1 Hz, 2H), 7.46 (ddd, J=1.4, 6.8, and 9.0 Hz, 2H), 7.72 (d, J=9.0 Hz, 2H), 8.30 (d, J=6.5 Hz, 2H); ^{1}H NMR (C_6D_6) δ=2.56 (s, 6H), 6.10 (td, J=1.4 and 6.8 Hz, 2H), 6.55 (ddd, J=1.4, 7.0, and 8.8 Hz, 2H), 7.33 (d, J=8.6 Hz, 2H), 7.79 (d, J=7.2 Hz, 2H).
11) **2*E*** form: ^{1}H NMR ($CDCl_3$) δ=2.21 (s, 3H), 2.35 (s, 3H), 2.52 (s, 3H), 7.05 (td, J=6.8 and 1.1 Hz, 1H), 7.43 (ddd, J=10.1, 6.8 and 1.1 Hz, 1H), 7.69 (d, J=10.1 Hz, 1H), 8.20 (d, J=6.8 Hz, 1H); ^{1}H NMR (C_6D_6) δ=1.87 (s, 3H), 2.00 (s, 2H), 2.20 (s, 2H), 2.62 (s, 2H), 6.08 (td, J=7.2 and 1.4 Hz, 2H), 6.54 (ddd, J=7.9, 7.2, and 1.4 Hz, 2H), 7.33 (d, J=7.2 Hz, 2H), 7.71 (d, J=7.9 Hz, 2H).