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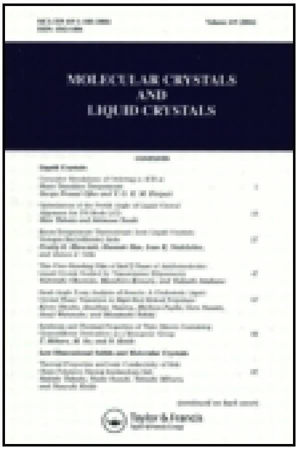

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Photochromism of Fulgides and Related Compounds

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PHOTOCHROMISM OF FULGIDES AND RELATED COMPOUNDS

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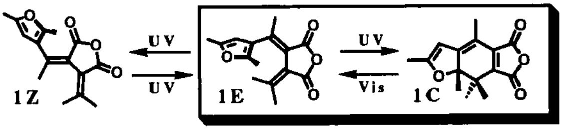
Abstract Steric effect and electronic effect on photochromic properties of fulgides are discussed. A non-destructive readout method using 5-dimethylaminoindolylfulgide is presented. Photochromism of fulgenates and fulgenolides, new classes of thermally irreversible photochromic compounds related to fulgides, are described.

INTRODUCTION

Fulgides have been known as the representative organic photochromic compounds since the beginning of this century.[1] A mesitylmethylene fulgide, the first thermally irreversible photochromic compound of 6π-electrocyclic reaction mode, was synthesized by Heller *et al.* in 1974.[2] The major defect of this compound was the low conversion ratio of the colored form upon irradiation of UV light. This was improved by the same group[3] by replacing the mesityl group with 2,5-dimethyl-3-furyl group. As the result, the furylfulgide **1** has the characters of (1) thermal irreversibility, and (2) complete conversion between colorless and colored forms.



SUBSTITUENT EFFECT ON PHOTOCHROMISM OF FULGIDES

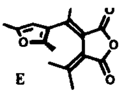
When we started the research on photochromism, we first aimed to remove the *E*-*Z* isomerization from **1**, since it is an energy-wasting process, and retards the coloration rate. We simply enlarged the alkyl substituents on the furylmethylidene group of **1E**, for the steric repulsion between the alkyl substituent and the *E*-methyl group (inside methyl) of the isopropylidene group would prevent the *E*-to-*Z* isomerization.

Thus, furylfulgides **2**, **3**, and **4**, with alkyl substituents of different sizes were synthesized and their photochromic properties were examined.[4] The results are shown in Tables 1 and 2. Although the bulkiness of alkyl substituents did not affect the absorption maximum and absorption coefficient of *E*, *Z*, and *C* forms for **2** and **3**, molar absorption coefficients of

4E and **4Z** decreased substantially. We assume that the most stable conformation of these compounds might be different from others.

Table 1. Spectroscopic data of furylfulgides in $CHCl_3$

	E	Z	C
	λ_{max}/nm(ε_{max})	λ_{max}/nm(ε_{max})	λ_{max}/nm(ε_{max})
1	347 (6780)	358 (8900)	510 (9690)
2	349 (6690)	358 (8480)	510 (10270)
3	348 (6210)	358 (7460)	510 (9590)
4	347 (4080)	360 (4700)	510 (9320)



E

1 R=Me
2 R=Et
3 R=*n*-Pr
4 R=*i*-Pr

Table 2. Quantum yields of photoreactions of furylfulgides in $CHCl_3$

	Φ_{EC}[a)]	Φ_{EZ}[a)]	Φ_{ZE}[a)]	Φ_{CE}[b)]
1	0.19	0.13	0.11	0.035
2	0.34	0.06	0.12	0.027
3	0.45	0.04	0.10	0.044
4	0.62	0.00	0.06	0.040

a) 366 nm light irradiation. b) 492 nm light irradiation.

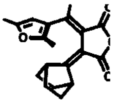
The cyclization quantum yield Φ_{EC} increased and the *E*-to-*Z* isomerization quantum yield Φ_{EZ} decreased as the size of the alkyl substituent increased. For fulgide **4**, with an isopropyl group as the alkyl group, showed 0.62 as the cyclization quantum yield Φ_{EC}, and 0.00 as the *E*-to-*Z* isomerization quantum yield Φ_{EZ}. The bleaching quantum yield Φ_{CE} and the *Z*-to-*E* isomerization quantum yield Φ_{ZE}, however, were hardly affected.

In 1983, Heller commented that introduction of an adamantylidene group greatly increased the bleaching quantum yield Φ_{CE}.[5)] We next tried to synthesize a furylfulgide with large Φ_{EC} and Φ_{CE}. Thus, fulgides **5** - **8** were synthesized.[6)] Contrary to our expectations, the 7-norbornylidene group of fulgides **5** and **6** did not give any notable effects. Fulgides **7** and **8**, with an adamantylidene group, however, increased the bleaching quantum yield significantly. The fulgide **8**, with an isopropyl group and an adamantylidene group in one molecule, showed the monumental quantum yields, *i. e.*, 0.51 for Φ_{EC}, and 0.26 for Φ_{CE}, which are about three times and five times of the values of **1**, respectively.

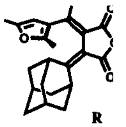
Table 3. Quantum yields of furylfulgides in toluene

	Φ_{EC}[a)]	Φ_{EZ}[a)]	Φ_{ZE}[a)]	Φ_{CE}[a)]	Φ_{CE}[b)]
1	0.18	0.13	0.11	0.00	0.048
4	0.58	0.00	-----	0.00	0.043
5	0.20	0.30	0.42	0.01	0.057
6	0.56	0.01	0.01	0.00	0.049
7	0.12	0.10	0.10	0.06	0.21
8	0.51	0.02	0.05	0.28	0.26

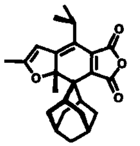
a) 366 nm light. b) 492 nm light.



	R
5E	Me
6E	*i*-Pr



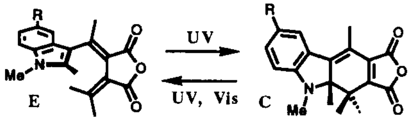
	R
7E	Me
8E	*i*-Pr



8C

ELECTRONIC EFFECT ON PHOTOCHROMISM OF FULGIDES

If an organic photochromic compound such as fulgide would be applied to the photon-mode rewritable optical memory, the light source to be used must be a diode laser. We therefore tried next to lengthen the absorption maximum of the colored form of fulgides, toward 780 nm, at which the AlGaAs diode laser emits the light. We chose the indolylfulgide **9** as the lead compound, because its *C*-form has the absorption maximum longer than furylfulgides, and much stronger than furylfulgides against fatigue and thermal degradation.[7] According to the PPP calculation, an electron-donating substituent on the C-5 of the indole ring would increase the absorption maximum wavelength value. We therefore synthesized **10**, **11**, and **12**, with a methylthio, a methoxy, and a dimethylamino group, respectively.[8] As shown in Table 4, the absorption band of the *C*-forms reached 780 nm. For **12**, with dimethylamino group on it, has λ_{max} of 673 nm, and the absorption coefficient at 780 nm is 2780. Thus, our expectation seemed to be satisfied.



9 R=H
10 R=SMe
11 R=OMe
12 R=NMe$_2$

Table 4. Absorption spectral data of indolylfulgides in toluene

	E	C		
	λ_{max}/nm(ε_{max})	λ_{max}/nm(ε_{max})	λ_{max}/nm(by PPP)	ε_{780}(C)
9	385 (8150)	584 (6810)	614	0
10	387 (8750)	600 (7090)	650	80
11	393 (9530)	625 (7060)	625	230
12	404 (8040)	673 (6200)	703	2780

That was not the case! All the quantum yields of the photoreactions became smaller as the absorption maximum of the colored form lengthened, and for **12**, the bleaching quantum yield Φ_{CE} was practically zero. This means that **12** is no longer photochromic.

Table 5. Quantum yields of photoreactions of indolylfulgides in toluene[a)]

	Φ_{EC}(403)	Φ_{CE}(403)	E/C(403-PSS)[b)]	Φ_{CE}(608)
9	0.040	0.067	40/60	0.051
10	0.028	0.027	32/68	0.011
11	0.024	0.024	30/70	0.012
12	0.015	0.001	3/97	0.00004

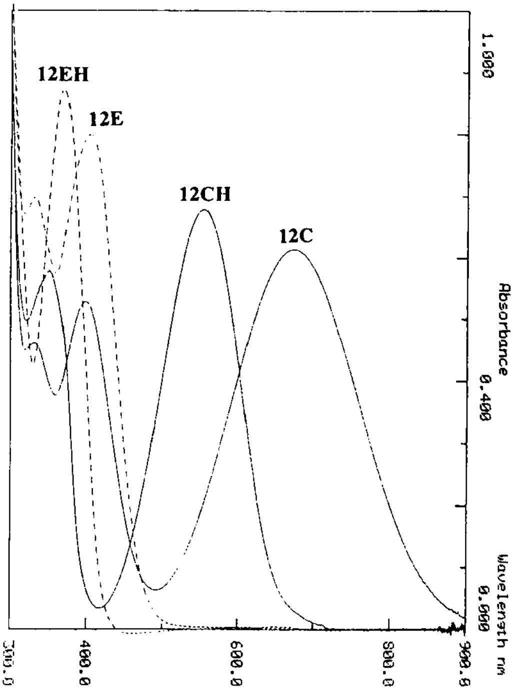
a) 403 and 608 nm light irradiation. b) Photostationary state at 403 nm light irradiation.

NON-DESTRUCTIVE READOUT METHOD

Although discouraged by the above result, we tried to find the way to take advantage of this peculiar property of **12**. As indolylfulgide **9** is photochromic, the irreversibility of **12C** might be caused by the existence of the dimethylamino group, or more precisely, a lone pair of electrons on the nitrogen atom of dimethylamino group. We therefore added various kinds of acids to the toluene solution of **12C**.[9]

When a large excess of trichloroacetic acid was added to the toluene solution of **12C**, the absorption maximum moved to the shorter wavelength. Furthermore, the species in the solution was bleached upon irradiation of visible light, and colored again with UV light (Fig. 1). That the species in the solution was **12CH**, the protonated species on the nitrogen of dimethylamino group, was confirmed by ^{1}H NMR measurement.

Fig. 1 Absorption spectra of 12C, 12CH, 12E, and 12EH



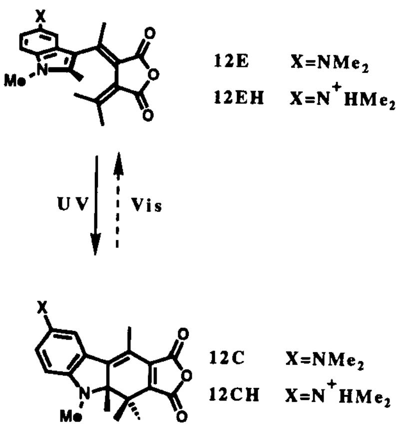


Fig. 2 Absorption spectral change of bleaching of 12C/12CH mixture in toluene

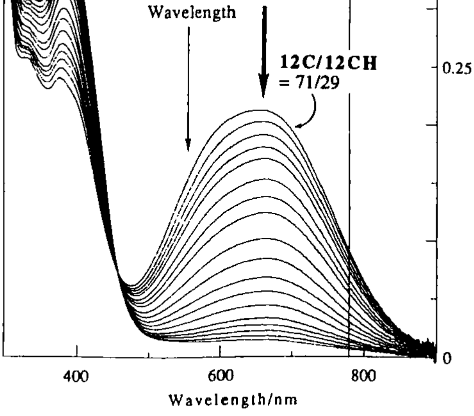
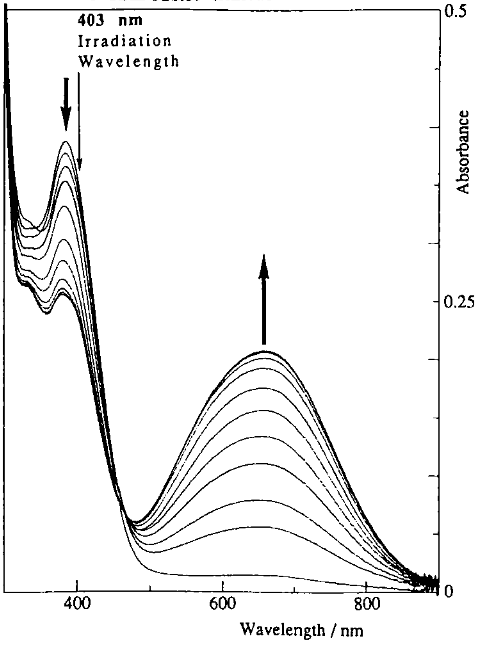


Fig. 3 Absorption spectral change of coloring of 12E/12EH mixture in toluene



One of the most remarkable features of this protonated species **12CH** is that it does not have absorption at 780 nm. We next examined what would happen if a controlled amount of acid was added to the solution of **12C**.

Addition of 1.4 equivalent of trichloroacetic acid to the toluene solution of **12C** afforded a 71:29 mixture of **12C** and **12CH**. While irradiation of 780 nm light for a substantial period did not cause any spectral change, irradiation of 554 nm light brought about gradual decrease in the absorption of the visible light region to generate a mixture of **12E** and **12EH** together with small amount of **12C** and **12CH** (**12C**:**12CH**:**12E**:**12EH** = 5:3:75:17). This result implies that a proton exchange equilibrium exists between these four species. Irradiation of 403 nm light to the mixture obtained above again generated the **12C**/**12CH**-rich mixture (**12C**:**12CH**:(**12E**+**12EH**) = 67:23:10) (Figs. 2 and 3).

If an organic photochromic compound is applied to the photon-mode rewritable optical memory, the readout process might be problematic. For, the simplest way to detect the signal is to know if the light of a specific wavelength is absorbed by the memory unit or not. This procedure, however, may cause destruction of the record by the photochromic reaction. Thus, the system of dimethylaminoindolylfulgide - trichloroacetic acid can be regarded as the four-species - three-state non-destructive readout method of photon-mode rewritable optical memory. Namely, the write procedure can be achieved by 403 nm irradiation to the **12E**/**12EH** mixture, the readout procedure can be attained by 780 nm light irradiation, and the erase procedure can be carried out by 554 nm light irradiation.

Fig. 4 Absorption spectral change of bleaching of 12C/12CH mixture in PMMA

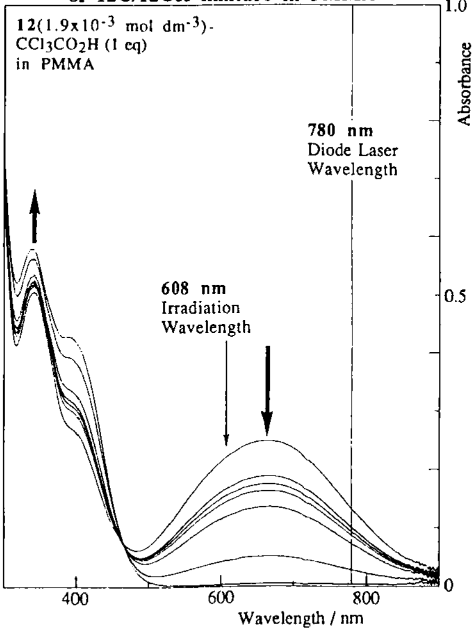
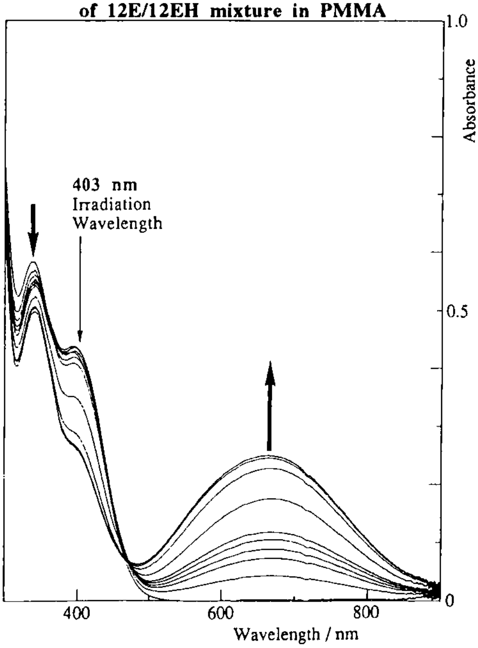


Fig. 5 Absorption spectral change of coloring of 12E/12EH mixture in PMMA



Because the optical memory media might take the figure of a polymer disc in which the photochromic compound is dispersed, we next tried to realize this phenomena in a polymer film. That this system worked well was shown in Figs. 4 and 5. While irradiation of 780 nm light to the colored film did not cause any change in absorption spectra, it was bleached with 608 nm light. The colorless film again turned blue-green upon irradiation of 403 nm light. Thus, we now have a simple non-destructive readout method for photon-mode rewritable optical memory in hand. Further efforts of improvement are now under way.

FULGENATES

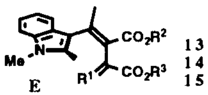
One drawback of fulgides is that the acid anhydride moiety is labile to protic chemical species such as water, alcohols, and amines. If this part of a fulgide molecule becomes stronger, then the durability of fulgides would be highly increased. In connection with our interest to substitute the acid anhydride moiety with other functional groups, we intended to modify the anhydride group.

We prepared diesters and a monoester with a mixed anhydride functionality. Because Stobbe named the corresponding diacid "Fulgensäure"[1] and its translation into English might be "fulgenic acid," we would like to call the esters "fulgenates." The results were shown in Tables 6 and 7. In short, all the properties important for photochromic reactions, *i. e.*, quantum yields of photoreactions and absorption maximum wavelength of the colored form, moved toward the less favorable direction with regard to the diesters, compared with the fulgide **9**. However, the diesters are intact when the photoreaction was carried out in an alcoholic media, in which fulgides turned to half acids. Furthermore, the diester moiety would be useful to introduce some functional groups.

Table 6. Absorption spectral data of indolylfulgenates in hexane

	E	Z	C
	λ_{max}/nm(ε_{max})	λ_{max}/nm(ε_{max})	λ_{max}/nm(ε_{max})
9[a]	385 (8150)	———	584 (6810)
13	293(11500)	285 (9300)	438 (7300)
14	293(11500)	286 (9000)	436 (7500)
15	b)	b)	469 (3010)

a) In toluene. b) No absorption maximaum is observed above 300 nm.



	R^1	R^2	R^3
13	IPD	Me	Me
14	IPD	Et	Me
15	ADD	Et	Ac

IPD: isopropylidene ADD: adamantylidene

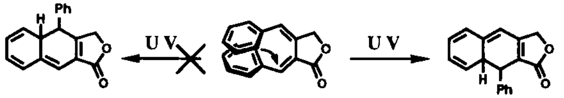
Table 7. Quantum yields of photoreactions of fulgenates

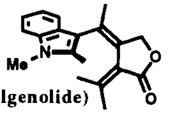
	Φ_{EC}(UV)	Φ_{CE}(UV)	Φ_{EZ}(UV)	Φ_{ZE}(UV)	E/Z/C(UV-PSS)	Φ_{CE}(Vis)
9[a]	0.040	0.067	———	———	40/0/60	0.051
13[b]	0.061	0.39	0.054	0.10	39/51/10	0.27
14[b]	0.058	0.31	0.044	0.10	40/49/11	0.31
15[c]	0.21	0.67	0.041	0.11	67/13/20	0.83

a) 403 and 608 nm light irradiation in toluene. b) 313 and 446 nm light irradiation in hexane.
c) 366 and 497 nm light irradiation in toluene.

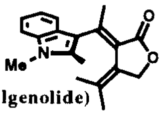
FULGENOLIDES

Our next interest was to change the acid anhydride moiety to a lactone, to be called "fulgenolide". In 1974,[10] Heller *et al.* reported that only one of two possible regioisomers was obtained upon UV-irradiation of 2,3-bisbenzylidene-1,4-butanolide. When this concept is applied to the two regioisomers of indolylfulgenolides (L-fulgenolide **17E** and U-fulgenolide **18E**), the cyclizable isomer is L-fulgenolide. Thus, we synthesized **17E** and **18E**. As shown in Figs. 6 and 7, L-fulgenolide **17** showed remarkable photochromic properties, whereas U-fulgenolide did not. The quantum yields of photoreactions of **17** was excellent compared with those of fulgide **9**, although the absorption maximum wavelength of the colored form was more than 120 nm shorter than that of indolylfulgide **9**.





17E (L-Fulgenolide)



18E (U-Fulgenolide)

Fig. 6 Absorption spectral change of coloring of 17E in hexane

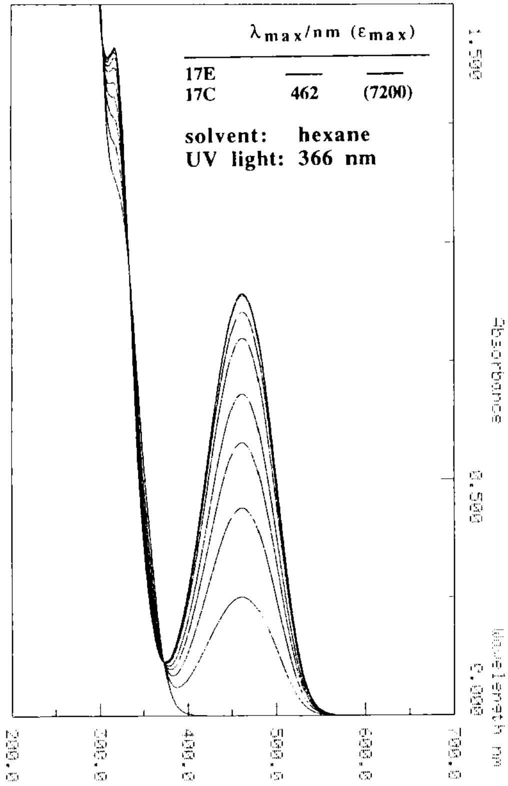


Fig. 7 Absorption spectral change of coloring of 18E in hexane

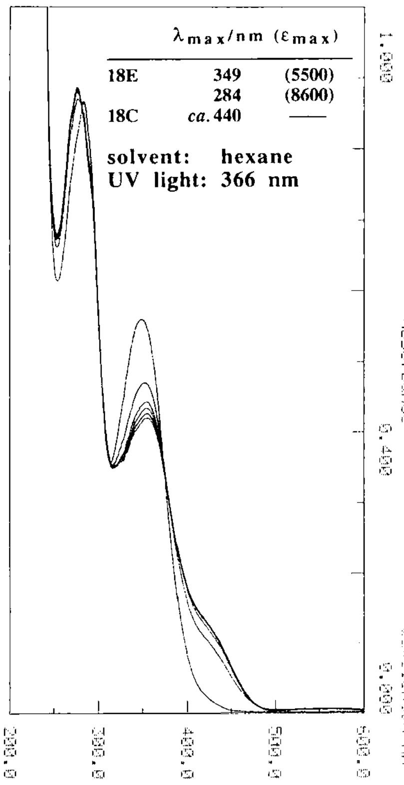


Table 8. Quantum yields of fulgide and L-fulgenolide

	UV light irradiation1)					Visible light irradiation2)		
	Φ_{EC}	Φ_{CE}	Φ_{EZ}	Φ_{ZE}	E/Z/C3)	λ_{max}(C)	ε_{max}(C)	Φ_{CE}
9	0.040	0.067	——	——	40/0/60	584	6810	0.051
17	0.48	0.64	0.021	0.076	27/27/46	462	7200	0.17

1) 403 nm light for 9, 366 nm light for 17. 2) 608 nm light for 9, 492 nm light for 17. 3) Isomer ratio at the photostationary state of UV light irradiation.

CONCLUDING REMARKS

We have described our efforts of development of chemistry of fulgides and related compounds. Although thermally irreversible organic photochromic compounds have been regarded as the potential candidate applicable to photon mode rewritable optical memory media, we feel that the structural change of a molecule associated with photochromic reactions should be more emphasized. The structural change is controllable by light, therefore change in function of appended functional groups might be controllable by light. This kind of photochromic molecules will play important roles in the upcoming "Era of Photonics".

REFERENCES

1 H. Stobbe, *Chem. Ber.*, **1904**, *37*, 2232; **1905**, *38*, 3673.
2 H. G. Heller and R. M. Megit, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 923.
3 P. J. Darcy, H. G. Heller, P. J. Strydom, and J. Whittall, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 202.
4 Y. Yokoyama, T. Goto, T. Inoue, M. Yokoyama, and Y. Kurita, *Chem. Lett.*, **1988**, 1049.
5 H. G. Heller, *IEE Proc.*, Part I, **1983**, *130*, 209.
6 Y. Yokoyama, T. Iwai, N. Kera, I. Hitomi, and Y. Kurita, *Chem. Lett.*, **1990**, 263.
7 A. Kaneko, A. Tomoda, M. Ishizuka, H. Suzuki, and R. Matsushima, *Bull. Chem. Soc. Jpn.*, **1988**, *61*, 3569.
8 Y. Yokoyama, T. Tanaka, T. Yamane, and Y. Kurita, *Chem. Lett.*, **1991**, 1125.
9 Y. Yokoyama, T. Yamane, and Y. Kurita, *J. Chem. Soc., Chem. Commun.*, **1991**, 1722.
10 H. G. Heller and M. Szewczyk, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1487.