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Novel compounds producing a photochromic spiropyran on heating

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Abstract

The synthesis and properties of merocyanine–pyrrole adducts, which are irreversible and quantitatively reverted to the original photochromic spiropyran and pyrrole by a thermal reaction, are described. The merocyanine–pyrrole adducts were synthesized by the reaction of 1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] derivatives with 1-pyrrolylpotassium in THF at room temperature. Though, these compounds are amorphous solids and stable at room temperature, by partial heating at 130°C in a polymer matrix film, they quantitatively decomposed to the original spiropyran remaining in the matrix such as the polymer film and to pyrrole missing from the matrix due to the vaporization. Therefore, photochromic patterns will be formed in the polymer film. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Merocyanine–pyrrole adduct; Spiropyran; Pyrrole; Photochromic pattern

1. Introduction

1′,3′,3′-Trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] **1a** is the best known spiropyran with photochromic, thermochromic, and solvatochromic properties [1,2]. It is reversibly converted to the merocyanine dye **2a** upon irradiation with light of a suitable wavelength, heating, or with increasing polarity of the solvent. A number of studies have been made concerning ordinary spiropyrans; the colored forms are best regarded as zwitterionic species (Scheme 1). The thermal stability of a colored merocyanine is affected by solvent polarity. For the solvation structure of merocyanine in ethanol, colorless merocyanine–ethanol adducts **3a** have been reported [3].

Tomioka and Takahashi have studied the kinetics of the fading reaction of the merocyanine form in ethanol. They interpreted the two simultaneous first-order reactions as indicating that the initial fast-fading reaction takes place from the merocyanine directly formed from the excited spiropyran, but that the final slow-fading reaction may result from the merocyanine–ethanol adducts **3a**, which are formed by the reaction of the excited spiropyran with ethanol, and gradually decompose to give the colored merocyanine [4] (Scheme 2). However, the merocyanine–ethanol adducts have not been isolated.

In this paper, we now report the methodology that allows this chemistry to be accomplished by an addition reaction sequence, analogous to that already described in the literature using ethanol as the solvent. We report the first examples of merocyanine–pyrrole adducts that have been formed by the addition of a pyrrole to a spiropyran.

2. Experimental details

2.1. Synthesis of merocyanine–pyrrole adducts

2.1.1. General procedure for synthesis of merocyanine–pyrrole adducts

The spiropyrans were synthesized by methods previously reported in the literature [5–8]. The 3-phenyl and 3-propanoyl pyrroles were donated by Masuda and Kaeriyama [9]. The other pyrroles and reagents were of the highest commercial quality and used without further purification unless otherwise stated. The general procedure for the synthesis of the merocyanine–pyrrole adducts is described below (Scheme 3).

In a dry, 100 ml, three-necked flask equipped with a magnetic stirrer, a thermometer, a silicone rubber septum, and a reflux condenser with a three-way stopcock attached to an argon source are placed 20 ml of dry THF and 1.24 g (0.01 mol) of potassium *t*-butoxide. The solution is cooled in an ice bath, and 0.74 g (0.01 mol) of pyrrole in 20 ml of dry THF is slowly added with stirring. A 0.01 mol solution of the spiropyran, dissolved in 20 ml of dry THF, is added dropwise to the stirred solution. At the completion of the addition, the cooling bath is removed, the flask is allowed to

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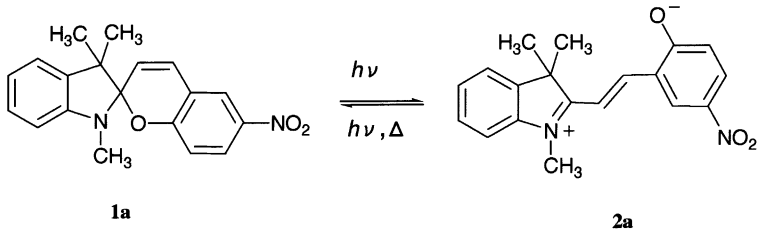
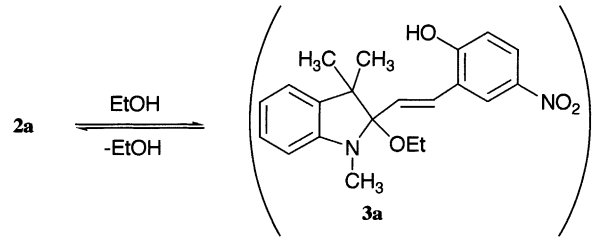


Scheme 1.



Scheme 2.

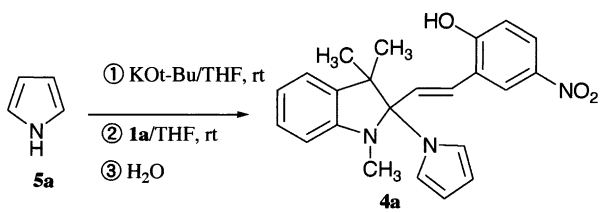
come to room temperature, and stirring is continued at room temperature for 2 h. The progress of the reaction is followed by TLC.

The reaction mixture is poured into a large amount of water and extracted with ether, and the organic layer is washed with saturated sodium chloride solution followed by water until neutral and then dried over anhydrous sodium sulfate. The solution is filtered and the solvent is evaporated under vacuum. The residue is purified by recrystallization as appropriate. The typical merocyanine–pyrrole adduct **4a** is a dark blown product (the isolated yield of **4a** is 45%).

Spectroscopic data for **4a** are as follows: IR (cm^{-1}, KBr) 3379, 2927, 1608, 1589, 1485, 1331, 1288, 1087, 748; ^{1}H NMR (90 MHz, $CDCl_3$) 0.94 (3H, s), 1.30 (3H, s), 2.67 (3H, s), 6.13 (2H, t, J = 2 Hz), 6.55 (1H, d, J = 8 Hz), 6.64 (1H, d, J = 16 Hz), 6.73 (2H, t, J = 2 Hz), 6.82 (1H, d, J = 16 Hz), 6.83 (1H, t, J = 8 Hz), 7.05 (1H, dd, J = 8 and 1 Hz), 7.18 (1H, dt, J = 1 and 8 Hz), 8.05 (1H, dd, J = 9 and 3 Hz), 8.29 (1H, d, J = 3 Hz). Analysis: Calc. for $C_{23}H_{23}N_3O_3$: C, 70.93; H, 5.95; N, 10.79%. Found: C, 70.63; H, 5.94; N, 10.64%.

2.1.2. In situ synthesis of merocyanine–pyrrole adducts in an NMR tube

Several merocyanine–pyrrole adducts were synthesized in situ in an NMR tube using THF-d_8 as the solvent. In these cases, the merocyanine–pyrrole adducts were not isolated but characterized by the ^{1}H NMR spectra of the reaction mixture solutions without treatment.



Scheme 3.

2.2. Spectroscopic and TG–DTA measurements

The 90 MHz ^{1}H NMR and UV–VIS absorption spectra were measured with a FT-NMR (Hitachi R-1900) and a spectrophotometer (Shimadzu UV-2100), respectively. The TG–DTA curves were measured with a Rigaku TAS-100.

3. Results and discussion

3.1. Preparation of merocyanine–pyrrole adducts

The merocyanine–pyrrole adduct **4a** was prepared by the reaction of **1a** and the reaction mixture of potassium *t*-butoxide and pyrrole in dry THF at room temperature. A similar adduct was also obtained for the reaction of **1a** with 1-pyrrolylpotassium, which was synthesized by the reaction of potassium and pyrrole. Therefore, it is suggested that the reaction path in the presence of 1-pyrrolylpotassium, formed by the reaction of pyrrole with potassium *t*-butoxide, will be applicable to the present system.

NMR monitoring of this reaction was performed by the following in situ synthesis in an NMR tube.

A THF-d_8 solution of pyrrole (10 mmol) was added to THF-d_8 solution of potassium *t*-butoxide (10 mmol) in an NMR tube; the ^{1}H NMR spectra were measured (Fig. 1(A)–(C)). To this solution, a THF-d_8 solution of **1a** was then added. Immediately after the addition, the signals of **1a** disappeared and new signals assigned to the potassium salt of the merocyanine–pyrrole adduct **4a** appeared (Fig. 1(D) and (E)). In all cases, when the merocyanine–pyrrole adducts were formed, the NMR spectra showed that these reactions proceeded almost quantitatively.

In Fig. 1(C), a new signal for the OH of *t*-butyl alcohol detected at 4.35 ppm and a shift change in the *t*-butyl substituent from 1.05 to 1.15 ppm suggest the formation of 1-pyrrolylpotassium. Fig. 2 shows the ^{1}H NMR spectrum of compound **4a** in THF-d_8. The difference in the chemical shifts between Figs. 1(E) and 2 shows that the structure of the product in Fig. 1(E) could be the potassium salt form.

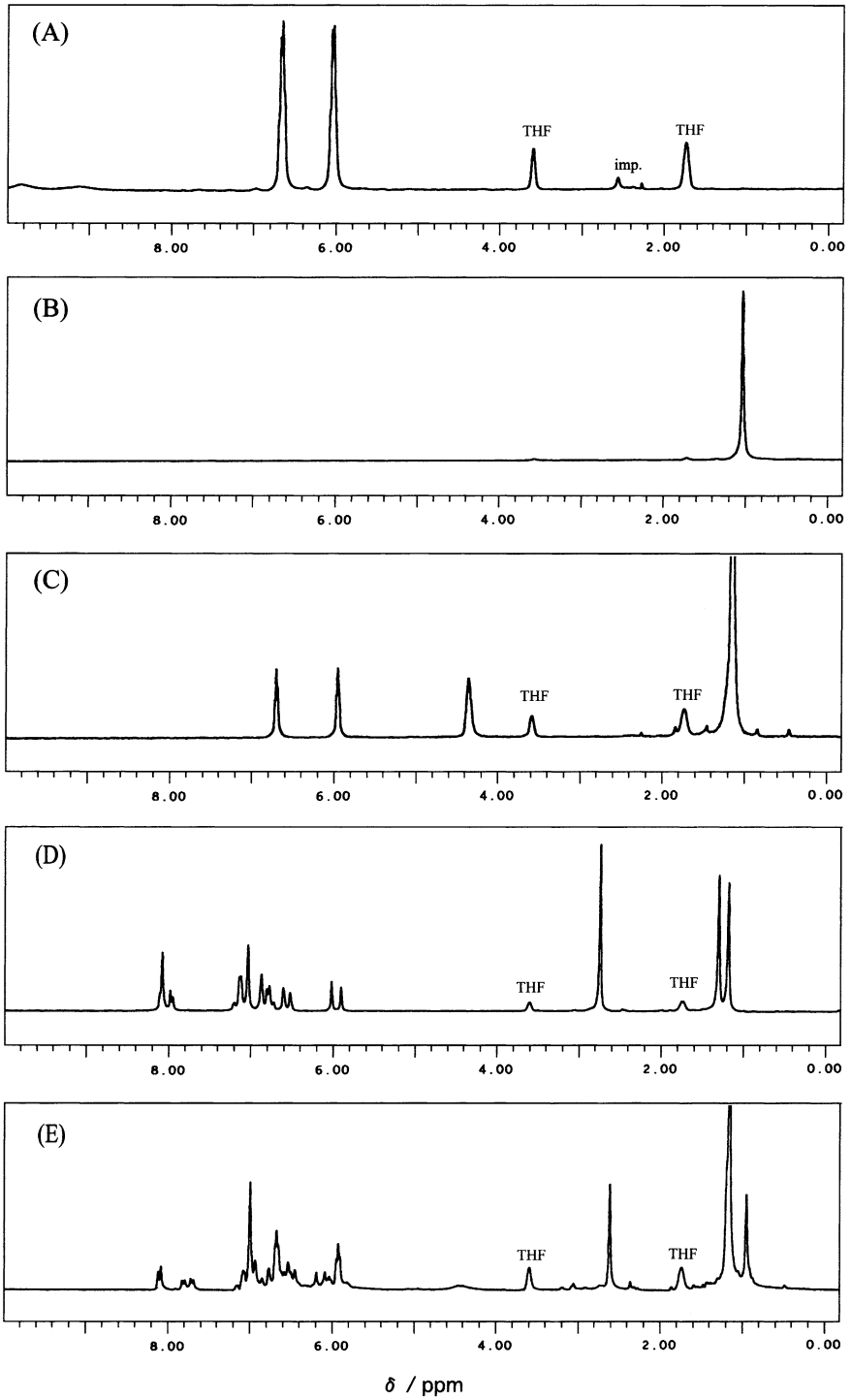


Fig. 1. The ^{1}H NMR spectra in THF-d_8: (A) pyrrole; (B) potassium *t*-butoxide; (C) after the addition of A to B; (D) spiropyran **1a**; (E) immediately after the addition of D to C.

Compound **4a** is a reddish brown or reddish purple solid and is stable at room temperature. The structure of **4a** was determined on the basis of ^{1}H NMR and ^{1}H–^{1}H COSY experiments in chloroform-d. The vicinal olefinic protons showed typical *trans*-coupling (J_{vic} H–H = 16 Hz), which was also proven by homo-nuclear decoupling techniques. It is very characteristic that the two methyl substituents at the 3′-position of **4a** show the two ^{1}H NMR resonances at $\delta = 0.94$ and 1.30. It can be presumed that steric crowding between two adjacent substituents, which are styryl and the pyrrolyl, at the 2-position is responsible for this nonequivalence.

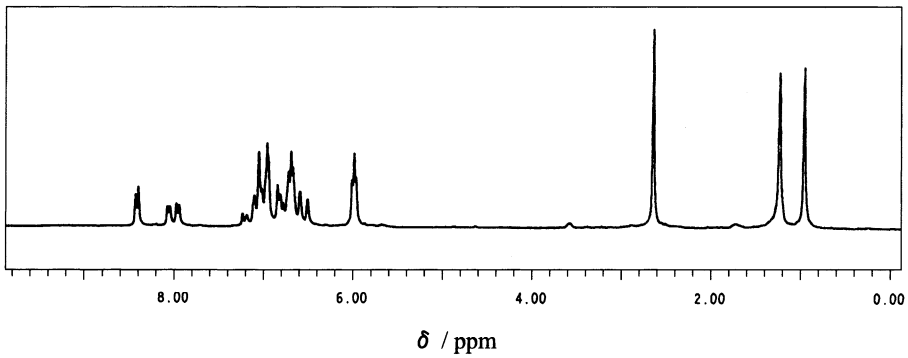
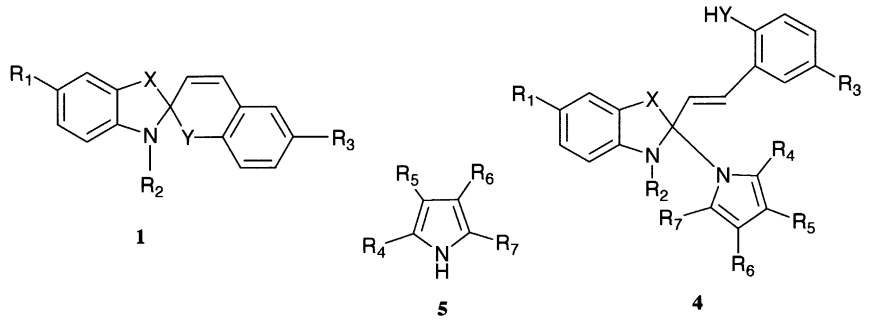


Fig. 2. ^{1}H NMR spectrum of **4a** in THF-d_8.



Scheme 4.

The effect of substituents in the starting materials on the formation of merocyanine–pyrrole adducts is shown in Scheme 4 and Table 1. Interestingly, spiropyrans having a Br or H substituent instead of a NO_2 substituent at the 6-position of **1** did not give merocyanine–pyrrole adducts. On the other hand, among spiropyrans having a NO_2 substituent at the 6-position of **1**, **1b** having a Br substituent at the 5′-position, and **1c** having a benzyl substituent at the 1′-position gave a merocyanine–pyrrole adduct, but spirothiopyran (**1f**) [7] and benzothiazolinic spiropyran (**1g**) [8], whose ring opening forms were thermally unstable, did not give them.

Table 1
The effect of substituents in starting materials on the formation of merocyanine–pyrrole adducts

Spiropyran **1**	Substituent					Pyrrole **5**	Substituent				Adduct **4**
	R_1	R_2	R_3	X	Y		R_4	R_5	R_6	R_7	
1a	H	CH_3	NO_2	$C(CH_3)_2$	O	**5a**	H	H	H	H	**4a**
1b	Br	CH_3	NO_2	$C(CH_3)_2$	O	**5a**	H	H	H	H	**4b**
1c	H	CH_2Ph	NO_2	$C(CH_3)_2$	O	**5a**	H	H	H	H	**4c**
1d	H	CH_3	H	$C(CH_3)_2$	O	**5a**	H	H	H	H	No reaction
1e	H	CH_3	Br	$C(CH_3)_2$	O	**5a**	H	H	H	H	No reaction
1f	H	CH_3	NO_2	$C(CH_3)_2$	S	**5a**	H	H	H	H	No reaction
1g	H	CH_3	NO_2	S	O	**5a**	H	H	H	H	No reaction
1h	H	CH_3	H	S	O	**5a**	H	H	H	H	No reaction
1I	H	CH_3	NO_2	S	S	**5a**	H	H	H	H	No reaction
1a	H	CH_3	NO_2	$C(CH_3)_2$	O	**5b**	CH_3	H	H	CH_3	Unknown products
1a	H	CH_3	NO_2	$C(CH_3)_2$	O	**5c**	C_2H_5	H	H	H	Unknown products
1a	H	CH_3	NO_2	$C(CH_3)_2$	O	**5d**	H	n-C_7H_{15}	H	H	**4d**
1a	H	CH_3	NO_2	$C(CH_3)_2$	O	**5e**	H	n-C_8H_{17}	H	H	**4e**
1a	H	CH_3	NO_2	$C(CH_3)_2$	O	**5f**	H	CH_3	H	H	**4f**
1a	H	CH_3	NO_2	$C(CH_3)_2$	O	**5g**	H	Ph	H	H	**4g**
1a	H	CH_3	NO_2	$C(CH_3)_2$	O	**5h**	H	COEt	H	H	**4h**
1a	H	CH_3	NO_2	$C(CH_3)_2$	O	**5i**	H	NO_2	H	H	**4I**

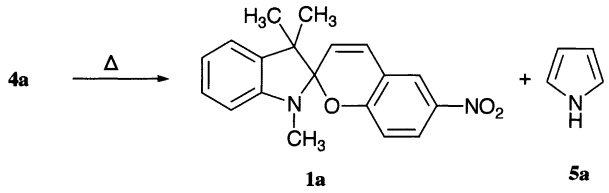
It is well known that the stability of the merocyanine form depends on the NO_2 substituent at the 6-position of **1** [6]. However, it is not considered that under alkaline conditions, such as in the presence of 1-pyrrolylpotassium as in this study, ring opening occurs prior to attack by pyrrole. This is manifested by the fact that the THF solution of the spiropyran is colorless and the mixture solution, after reaction with 1-pyrrolylpotassium, does not have the color of ring-opening products. Therefore, the formation mechanism of **4a** may be assumed to take place via an S_N2-type nucleophilic substitution reaction of the pyrrolyl anion at the C–O linkage of the spiropyran.

The electron-attracting nitro group on the 6-position of a spiropyran would accelerate the rupture of the C–O linkage and stabilize the structure of merocyanine–pyrrole adducts formed. With the use of 3-substituted pyrrole instead of pyrrole, analogous merocyanine–pyrrole adducts were formed. However, pyrroles having substituents at the 2- and/or 5-position (R_4 and/or R_7) did not give merocyanine–pyrrole adducts. This difference in reactivity can be explained using an argument based on steric hindrance.

3.2. Thermal stability

Fig. 3 is a TG–DTA curve of merocyanine–pyrrole adduct **4a**. It clearly shows that the peak at 125°C with weight loss is related to the boiling point of pyrrole, and the peak at 169°C without weight loss is related to the melting point of spiropyran **1a**. The decomposition of **4a** resulted in a weight loss of about 15%, in fair agreement with the value of pyrrole calculated on the basis of **4a**.

Thus, TG results show that decomposition of **4a** by heating gives spiropyran **1a** and pyrrole quantitatively (Scheme 5). This phenomenon, which is irreversible, could be accounted for by steric hindrance around 2′-carbon which must weaken the covalent bond between the 2′-carbon and the nitrogen of pyrrole.



Scheme 5.

3.3. Solvent effects

Merocyanine–pyrrole adduct **4a** immediately became deep purple by dissolving in acetone or chloroform; however, these colored solutions rapidly bleached to light purple. In this case, no difference of ^1H NMR spectra between the colored solution and the bleached solution was recognized. It was reported that the merocyanine structure of spiropyrans could take a number of stereoisometric configurations with respect to the three C–C partial double bonds [10]. Similarly, it is considered that merocyanine–pyrrole adduct **4a** can take some stereoisometric configurations around the double bond. The above phenomenon can be explained by a solvent effect; that is, in solution one of the isomers might be stabilized by association with the solvent. The absorption spectra of **4a** in chloroform are shown in Fig. 4.

By UV irradiation at a distance of 5 cm from a 100 W high-pressure mercury lamp in a quartz cell, **4a** gradually formed an unidentified product in acetone, while it decomposed to spiropyran and pyrrole in chloroform. The difference in these experimental results is considered to be attributed to hydrochloric acid, which was formed by the decomposition of chloroform upon UV irradiation. This finding becomes understable based on the observations below.

NMR monitoring showed that **4a** survived heating up to 80°C for 30 min in acetone-d_6, although it easily decomposed

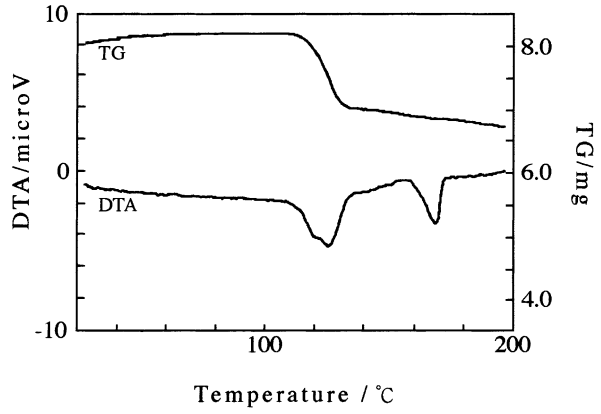


Fig. 3. TG–DTA curves of **4a** at the rate of 5°C/min under an atmosphere of N_2.

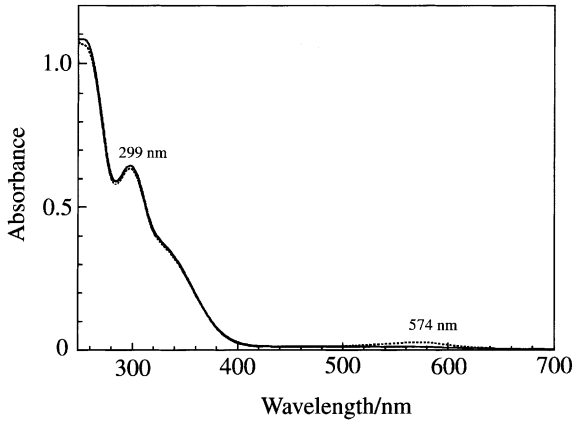


Fig. 4. Absorption spectra of **4a** in chloroform (5.1×10^{-4} mol/dm^3) — dotted line: immediately after the preparation of the solution; solid line: after 15 min. Optical path 1 mm.

to pyrrole and spiropyran at the same temperature in about 5 min when in chloroform-d. In addition, this decomposition proceeds even at 80°C in acetone-d_6 in the presence of small amounts of *p*-toluenesulfonic acid. These results suggest that in solutions, **4a** decomposes into spiropyran and pyrrole by an acid-catalyzed reaction at a lower temperature than that of thermal decomposition.

3.4. Formation of photochromic patterns

Merocyanine–pyrrole adducts are compounds with a protected spiropyran and can produce a spiropyran on heating, as required. It was found, furthermore, that their thermal properties could be applied to designing photochromic spiropyran patterns. For example, by partial heating at about 130°C for a few seconds of a polymer matrix film, such as polystyrene or polyvinylacetate, containing a merocyanine–pyrrole adduct **4a**, the photochromic patterns of spiropyran **1a** will be formed only in the heating block. Pyrrole formed at the same time is removed from the film by vaccum-drying at room temperature. This process is applicable also for thermal-recording and an optical-reading transducer system.

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